CRC

FENAROLI'S
HANDBOOK of FLAVOR INGREDIENTS

Volume I

2ND EDITION

CRC PRESS

~~D. F. Rugge~~

CRC

FENAROLI'S HANDBOOK *of* FLAVOR INGREDIENTS

Second Edition

Volume 1

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EDITORIAL FOREWORD, FIRST EDITION

The subject of flavor and flavor ingredients, much like its close allies fragrance and perfumery, is still viewed by many through a veil of mystery. To contemporary practitioners of the "pure sciences," the subject of flavors is grossly misunderstood, suggestive of alchemy, and at times subject to condescending criticism. No such indictments are further from reality; few areas of research are more serious or embellished more by sound, scientific thought, and sophisticated techniques. The giants of chemistry have often resorted to problems in flavors and fragrances as a platform for hallmark contributions. It is true that the final assessment of flavor is subjective in character, but, prior to reaching that level of development, most, if not all, of.the more objective measuring parameters are *fully* utilized. TLC, GLC, Mass Spec, NMR, UV, and IR, to mention a few, are *routinely* employed not only for resolving flavor components and elucidating structures but also as product control measures. The interdisciplinary nature of the flavor and fragrance industry is characterized by numerous scientific specialties, including analytical, organic, physical, and natural products, chemistry, agronomy, botany, genetics, and taxonomy; food technology; engineering; and finally the artistic efforts of the *flavorist*.

The chemical armament of the flavor industry contains the most numerous constituents of all food ingredients. In the United States it consists of no less than 1,200 ingredients of which approximately 200 are well characterized products of natural origin, while approximately 1,000 are precisely defined synthetics. The task of selecting and blending those ingredients capable of imparting a desired flavor characteristic to complex substrates (often having flavor backgrounds of their own) and at the same time being mindful of toxicological, regulatory, and economic considerations is indeed formidable.

While detailed treatises on various aspects of flavor technology have appeared from time to time, first-source reference texts on the subject as a whole are not readily available in the English language. Those seriously interested in flavor technology have had to wade through numerous journals to locate pertinent information, while the novice or cursory inquirer had only one or two general sources. The scope of this volume is therefore to present a current, authoritative, first-source description of natural and synthetic flavor ingredients, their detailed characteristics, and their application in food. It is primarily intended for those using flavors rather than for the accomplished *flavorist*. Furthermore, it is our intent to revise and up-date this handbook periodically in order to keep pace with advancing technology.

We especially wish to thank Prof. Dr. Giovanni Fenaroli, who arranged to be with us late in 1968 for editorial sessions, and Ulrico Hoepli and L. di G. Pirola, publishers of Prof. Dr. Fenaroli's Italian language books (*Sostanze Aromatiche*, Vols. I, II, and III, and *Aromatizzazione*), for their kind permission to translate and adapt the information for this work. We are grateful to those members of the flavor and fragrance industry who supplied valuable information; outstanding among these is Mr. Frank Fischetti, Jr., of Fritzsche Dodge & Olcott, Inc. We also wish to thank Naarden, Inc., for their permission to reproduce the fold-out schematic flow sheet (Figure 1) in Part I, Volume 1.

Ardsley, New York
November, 1970

T.E.F./N.B.

PREFACE, FIRST EDITION

Flavor is undoubtedly a basic characteristic stimulating the desirability of food; together with color, texture, and nutrition, it forms the cornerstone of contemporary food industries throughout the world. The economic importance of flavor ingredients (essential oils, synthetics, compounded formulations, etc.) is evident from current estimates placing their value at about two-thirds the total sales of all products offered by the flavor and fragrance industry. It is widespread opinion that within a few years an even greater shift in the value of flavors as opposed to fragrances will occur not only from normal increases in productivity but mainly as the result of demands for new food products by both affluent societies and those now in the process of increasing their living standards. Within the decade, however, sharpest increases in the demand for flavor ingredients will arise from new requirements for finished foods geared toward solving the critical starvation problem in most underdeveloped nations. It is therefore evident that while present achievements in flavor technology are indeed remarkable, considering the wide range of products currently offered by the food industry, the tempo will increase sharply. New techniques and more sophisticated flavor formulations designed to respond more precisely to the exacting specifications of future food manufacturers will be required. An example of the quickening pace and exacting specifications that we speak of is the problem of countering flavor modification and alteration in high-protein foods ("protein breakthrough").

With these basic thoughts in mind, it is my primary goal to summarize for the reader my personal experiences lived in this climate of continuing evolution and to rapidly update current efforts in flavor technology. I am convinced that the present state of the art furnishes a sufficiently broad and dynamic base to permit subsequent advances; it is therefore appropriate to describe and examine it in some detail. Certain flavor secrets employed by nature and their exact function are not as yet disclosed, but the investigational means are at our disposal; this makes us confident of the future success in identifying extremely complex systems. The more difficult problems concerning biological factors linked in the formation of naturally occurring flavors, as well as the assessment of the physiological reactions connected with their perception and assimilation by humans and animals, will also be resolved in due course. In the present work I wish to define flavor ingredients as to what they are, how they are manufactured, and how they are used.

In attempting to organize this handbook into a logical sequence capable of future expansion, my primary concern was to present as broad an information base as possible. This was accomplished by presenting the information in four interrelated parts. Part I treats definitions, nomenclature, assessment, and general methods of preparing flavor ingredients; in this section the viewpoint is generalized. (Those who argue that flavor manufacturing methods deserve detailed attention are probably correct, and we shall endeavor to do so in subsequent editions.) Parts II and III consist of detailed descriptions of the natural and synthetic flavor ingredients including the FDA regulatory status and FEMA proposals. Part IV deals exclusively with formulation technology and the uses of compounded flavors of natural and synthetic origin to achieve the most effective flavoring of foods and kindred products. From a technical viewpoint this section presents the greatest challenge, since I felt obliged to discuss not only the organoleptic effects of flavor ingredients and their combined effects in certain food substrates but also auxiliary flavor components, such as non-nutritive sweeteners and flavor potentiators. The flavor formulations presented in Part IV under various substrate categories are typical; while faithfully reproduced and tested, they are intended as guidelines only. In this sense I have attempted to explain the study and evolution of a formulation by stressing those general concepts that must be kept in focus (together with personal taste and experience) during the compounding of a flavor complex or flavoring a finished food product. While of paramount importance, the examples must be considered in light of current regulatory statutes, since it is nearly impossible to predict future restrictions aimed toward safeguarding public health. No doubt, future editions of the handbook will reflect significant changes of this section to keep pace with the application of flavors to food manufacturing problems.

The information presented in this text is partially derived from other works that I have written. Thanks to the Italian publishers Ulrico Hoepli (Milano) and L. di G. Pirola, I was able to summarize and enlarge herein the more basic parts concerning flavor ingredients appearing in *Sostanze Aromatiche Isolate e Sintetiche*, Vol. II, Tomo II, U. Hoepli, Milano, 1968, and *Aromatizzazione*, L. di G. Pirola, Milano, 1969. A personal note of thanks to Dr. U. Hoepli and Messrs. L. A. Bosisio and D. Caremoli of Curt Georgi Imes for their kind cooperation and assistance.

Finally, if I am at all successful in fulfilling my goal, it will be through the invaluable cooperative efforts of T. Furia and N. Bellanca, who not only translated and edited the original manuscript but also interpreted it in its present fashion so as to stress those areas of importance, especially with regard to U.S. regulatory statutes.

Longmeadow, Massachusetts
December 15, 1968

GIOVANNI FENAROLI

PREFACE TO THE SECOND EDITION

The scientific and technological progress which has characterized numerous sectors of industry during the latter half of the 20th century has likewise been extremely apparent in the area of flavor ingredients. Since the publication of the first edition in 1971 (certainly since its inception in 1968), the flavor industry has traveled a rather precipitous road at what must often appear to peripheral observers as hurtling speeds. However, during this period several bench marks have been established:

1. The need for flavors has been recognized at all levels of food processing.
2. The concept that flavor ingredients should be considered food ingredients rather than isolated components of the flavor subunit has been accepted as rational from a technological viewpoint and punctuated by regulatory agencies concerned with safety.
3. Possibly most important, a more valid scientific notion of "flavoring" has been formulated with respect to the preparation of flavors and their uses.

In addition, the food industry is constantly presenting flavor manufacturers with new and increasingly difficult problems. To meet such needs, the number of new flavor ingredients has been expanded, and many await review by regulatory agencies.

Towards this end, the preparation of a revised and expanded second edition, rather than a second printing, was initiated.

As in the first edition, the same four-part format has been maintained, with corrections, additions, and the contributions of specific authors inserted in what was felt to be appropriate sections. The new material presented includes the following:

1. Data on new synthetic flavor ingredients appearing in FEMA lists 4 through 8 (1970–74).
2. Updating of the natural occurrence of flavor ingredients.
3. Addition of references, augmenting many of the topics already discussed while inserting new ones.
4. Through the cooperation of CRC Press, utilization of new, comprehensive reviews on significant flavor topics.

In expressing my thanks to all those who have contributed to the publication of this edition, I would like to highlight the efforts of Thomas E. Furia and Nicolo Bellanca of Dynapol (Palo Alto, California), who edited, translated, and revised the overall publication. Further, during the intervening years since publication of the first edition, they have maintained a close watch on developments in the flavor industry, reminding us, among other things of regulatory issues and gathering new material for review.

Milano
April 1, 1975

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PART I

General Considerations

DEFINITIONS

In most technical disciplines the elucidation of concepts by some common ground symbolism, such as mathematics, serves as a prelude to establishing definitions. Lacking certain elements of objectivity, flavor concepts are discussed in terms of a frequently non-specific vocabulary, the description of which appears useful if not absolutely necessary.

In common usage the word *flavor* is often intended to mean flavor ingredient; there is, however, a very basic difference. Flavor is the effect perceived by the senses as the resulting action of flavor ingredients. As such, flavor is the product of a physiological reaction that to date defies objective measurement. This rather oversimplified working definition is further complicated by the misuse of related words and terms, such as aroma, aromatic, odor, odoriferous, fragrance, and perfume.

The problem of non-specific terminology is not, however, unique to English. Modern French and Italian also display uncertainties, since they too have inherited and modified (with all due shortcomings) a vocabulary stemming from other root languages. For example, Italian dictionaries do not attribute to the word *aroma* the same meaning of flavor as defined above. Referring instead to the Greek origin, they conveyed to the word *aroma* the meaning "any odoriferous substance, spice, perfume" and, to make things worse, "strong and at the same time delicate odor." Similarly, the differentiation between flavor and fragrance was not made clear at the origins of the language, since both words were clearly connected to the odor sensation. Hence, the word *aroma* in Italian (and English) defines a product capable of conferring odor and to some extent flavor. One therefore speaks of *il profumo* (odor, not perfume) of a soap to mean fragrance and *l'aroma* of coffee to mean the combined effect of flavor and odor. With advancing technology the verb *aromatizzare* developed meaning "to flavor"; the adjective *aromatico* (aromatic) is not at all clear, since it is also used as a chemical description (*e.g.*, aromatic molecules, benzene). The French word *aromate* did not fare better. The proposal to introduce a new term *flarome* to define the combined effect of flavor/fragrance remains unsuccessful, while *flaveur*, which more closely resembles the English meaning of the word *flavor*, is rarely employed.

When certain molecules in the vapor or liquid phase impinge on the inner lining of the nose covered with epithelial cells, and the brain responds by identifying the stimulus conveyed to it by the olfactory nerve, we say that the sensory apparatus has sensed an odor. The olfactory system in fact is stimulated only if the stimuli concentration (the number of molecules impinging on the olfactory region of the nasal fossa) is above a minimum value. This "threshold" value varies for any given substance in individuals and from one animal species to another. Dogs, wild animals, and even fish are interesting examples of how threshold values can reach limits of extreme dilution. The olfactory system is therefore capable of measuring odor intensity with a certain degree of accuracy.

Selectivity is another very important characteristic of the olfactory system of humans. The very existence and function of fragrances is strictly related to the selectivity of the olfactory system. Flavor sensations are further complicated when one considers that the olfactory region, located above the turbinate bones and sharing a common opening in the rear of the mouth, is directly influenced by the papillae of different selectivity strategically placed over the entire surface of the tongue. By eliminating the overlapping odor sensations, we are left with the four pure flavor responses: sweet, bitter, salty, and sour. The distribution and selectivity of the papillae are exploited by flavorists who have established specific techniques (sometimes modified by personal experience) for evaluating product flavor.

In addition to the four basic flavor sensations, others called accessory responses are capable of altering, modifying, or in certain cases completely masking basic flavor responses. Some of these include astringent, pungent, chalky, warm, and cool. The cooling sensation is caused when a substance varies the thermal sensitivity of the papillae. This is instantaneously perceived from absorption of heat of solution upon inhaling air. Most flavor ingredients exhibiting a cooling sensation do so secondary to some other distinct flavor sensation (*e.g.*, menthol). Analogous examples are the warming sensation of cassia, the bite of pepper, and the metallic off-flavors of considerable importance to the canning and edible oil industries.

If it is easy to identify and classify a flavor ingredient in one of the basic groups, it becomes increasingly difficult to establish its characteristic intensity and specific type. While it is possible to establish an intensity scale for pure substances by comparative tasting experiments, the problem becomes extremely complex in the case of mixtures; not only are the results subjective but they also lack universally accepted methods of evaluation. The ultimate possible determination of the classification of the type of sweet, bitter, salty, or sour flavor represents a problem for which the solution still appears to be remote. Attempts to determine the flavor class of any one substance even by the simplest expression of judgment (*i.e.*, palatable, unpalatable) is difficult, since the reactions of the taster are always subjective. The sensory scale of the taster is not fixed and can be affected by either a temporary or preset physiological imbalance. With certain flavor ingredients, such as *l*-quinine sulfate, the taste threshold in humans has been associated with sex, age, food preferences, hunger, smoking habits, phases of the menstrual cycle, and even with variations in personality-test scales and pharmacological effects.[1-11] While statistically designed panel tests conducted with a large number of subjects may lead to more reliable results, it is still advisable to recognize the limitations of such tests, since they provide an acceptance index relative to the majority of the panel but are in no way absolute.

It appears evident that numerous difficulties can interfere in the assessment of a given flavor. This assessment can be strongly influenced not only by the characteristics of certain flavor ingredients but also by the olfactory sensation inducing (1) primary attractive or repulsive reactions and (2) secondary reactions influencing the psyche with memories and recollections of positive or negative events. The task of the flavorist is to recognize the components and levels comprising a flavor blend in such a way that his judgment and formulating decisions are generally in line with good tastes. Good tastes are to flavors much as color and form ratios are to aesthetics.

Mention should be made of other factors influencing the judgment of any given flavor, such as shape, color, and texture of the finished food product. The textural quality of a food (viscosity, hardness, tenacity, crispness, etc.) has a very distinct effect on the flavor sensation. Similarly, the chemical nature of the substrate has a significant influence on the perception of flavor shades and on the sensory intensity. As an example, the presence of fats and oils influences the velocity of flavor diffusion toward the sensory organs.

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HISTORY AND EVOLUTION

The widespread introduction and study of flavor ingredients in food technology are the result of an evolutionary process directly connected with the growth of the food industry and man's quest to render food more flavorful. Early man was indeed aware of the flavor conveyed by basic foods such as meat, fish, animal and vegetable fats and oils, sugars, dairy products, fermented beverages, fresh and dried fruits and vegetables, baked goods, and other such products. Although flavor varieties became known and appreciated at different stages in man's development, potentially they have always been at his disposal. In an effort to defeat hunger, man evolved from hunter to fisherman, subsequently to farmer, and finally to industrialist; the present living standards of primitive tribes are testimony of the evolutionary process.

It is said that hunger sharpens ingenuity. After the discovery of fire, which permitted the cooking of food, primitive peoples also discovered techniques of smoking and seasoning necessary for survival during those periods when fresh game, fish, and other natural food resources were in shortage. The preserving of food stemmed from necessity; new and exciting flavors were a bonus for man's efforts. At the start only a few crude spices and herbs were added to food during cooking. The added flavor ingredients burned during the smoking process or were macerated during salting and fermentation.

In addition to the limited number of known herbs and spices, the list included a basic sweetener, such as honey, salt, and a few flowers, such as the highly regarded rose. This evolution took place with the introduction of spices in countries surrounding the Mediterranean; it also occurred in other regions, except that tastes and combinations of aromatic substances were subordinated to local availability. It was only after the introduction of alcohol and distillation techniques that a more functional use of aromatic substances was realized. Infusions, tinctures, distillates, and the first few essential oils came into use as novel ingredients for food flavoring. With the development of extraction techniques based on the use of volatile solvents and fractional distillation, the problem of concentrating aromatic substances for more specific end-uses was solved. Originally, the preparation of compounded flavors was oriented toward combining existing flavor ingredients with new ones as soon as they became available. This development occurred almost exclusively in the sector of alcoholic beverages (elixirs, spirits, etc.). When the number of natural flavor ingredients was extended and chemists were able to isolate or synthesize other interesting varieties, the study of the imitation of fruital aromas began. This second stage is of particular importance. The first approach to the formulation of new flavors would have continued to use traditionally available raw materials relying on the artistry of the formulator for updating; the second approach required the development of new formulation criteria and availability of more functional raw materials. An analysis of this situation has been presented, and a summary of the issues follows.[1]

The manufacture of effective flavor ingredients can no longer be separated from research; in the field of aromatic substances research today is livelier than ever. While this observation was discussed by Naves from the viewpoint of factors inspiring the creation of synthetic perfumes, a similar research orientation exists for flavor ingredients, *i.e.*, although man retains a preference for familiar products and is conservative in regard to new materials, he also accepts quite a few novelties.[2]

Every flavor ingredient confers a characteristic flavor, but products capable of conferring an odor-flavor complex to food substrates are balanced combinations of several ingredients. Nature follows the same pattern; in the flavoring of fruits, the aroma is in almost all cases a complex of chemically defined ingredients. The flavor ingredients obtained from natural sources, such as the essential oils, are in turn complex entities. Compounded flavor ingredients (equivalent to the finished, formulated perfumes) are new, non-traditional formulations, capable of creating new flavor sensations. An example is the flavor of cola beverages obtained from a combination of flavor ingredients known for a long time but never associated in quite that fashion prior to the turn of the century. Going one step further, complex flavor ingredients can be defined as substances already existing in nature or rebuilt according to their natural composition. Compounded flavor ingredients are those formulated through the imagination of the flavorist by properly combining simple and complex flavor ingredients.

Analyzing the purposes and goals of a modern flavor ingredient manufacturing industry, we find the following:

1. Research is inspired toward synthesis of naturally occurring flavor ingredients subsequent to their identification but also strives to search for the creation of new molecules.
2. The finished flavor formulations presented to consumers can exhibit not only traditional but also non-conventional flavors, which also find acceptance.
3. Since a large number of food products exhibit a characteristic flavor caused by the modification of precursors or components occurring during the preparation of food (boiling, frying, baking, toasting, smoking, etc.), the food industry may have a need for this final flavor ingredient to be added to ready-to-use foods when it is otherwise impossible to duplicate these conditions.

Let us examine these three goals separately. The reason for the identification and preparation of naturally occurring flavor ingredients is twofold: the first is economic, the second technical but stemming from man's preference for flavor ingredients of natural origin. The economic advantages are various and obvious—reduction of costs, standard quality, and independence from speculative factors such as availability of raw materials at stable costs independent of harvest and season. The technical advantages are (1) the possibility of having at one's disposal all the basic constituents of a given flavor, and (2) dosage forms permitting additions to a food product in a way otherwise impossible to prepare by the direct use of flavor ingredients obtained from the natural source. In addition, the knowledge and availability of the primary constituents of a given flavor permit, as in the case of drug flavors, the use of only those functional principles responsible for flavoring while eliminating those interfering with the activity or stability of the substrate. An intimate knowledge of primary ingredients also affords the possibility of reconstituting a natural flavor with those small quantities of volatile compounds usually lost during the manufacturing process. While a continuous research program may also lead to the creation of new molecules, the use of these is dependent on their compatibility with existing varieties (*e.g.*, ethyl vanillin couples well with vanilla). Frequently, however, flavor substances believed to be new have been subsequently discovered among the trace constituents of naturals. For example, nonalactone was identified in the peach flavor several years after its synthesis and use in flavor formulations. Although the synthesis of new flavor molecules is difficult, years of work have amassed a good number of synthetic products with flavor characteristics blending very well with those of simple or compounded naturals. It is not possible, however, to give an accurate estimate of exactly how many such products are available (several hundreds for sure), since those who have such research capabilities are usually unwilling to share their proprietary knowledge. The chemical structure of many products is in the public domain, but all of those very interesting notes that enrich or extend the armament of the flavorist are not. The use of some of these interesting notes may also be restricted by government regulations. A paradox exists when the use of a given flavor ingredient conforming to the regulations of one country is outlawed by another. Hopefully, this unfortunate situation will be resolved in the near future.

Parallel to the efforts of the chemist to identify and synthesize individual constituents of a natural flavor ingredient are the efforts of the flavorist. The responsibilities of the flavorist are twofold: (1) the reconstruction of natural complex flavors and (2) the creation of new flavors. The formulation of natural flavors has undergone a similar evolution and today follows two basic orientations: the construction of fruital aromas and the study of flavor precursors. Recent trends indicate that formulations with entirely new flavors find widespread acceptance in alcoholic and non-alcoholic beverages, especially bitters.

An additional segment of research on flavor ingredients is that of application. The use of a flavor ingredient in food products is a function of its safety and functionality. The latter characteristic is dependent in turn on its intrinsic characteristics, such as compatibility with other flavor substances, with the food substrate, and with the specific food manufacturing process. Finally, use is controlled by the government regulations of a nation. In this respect, the major criteria of applicability are concerned with product safety. Toxicological considerations have had a great influence in past years and are expected to continue at an accelerated pace. The field of investigation is vast, however, and toxicological studies are lengthy, laborious, and costly. Considerable efforts are still required to accrue complete safety information on all the known flavor substances. Based on today's available information, it is certain that flavor ingredients approved for use in highly developed countries may be considered safe; those in doubt or not sufficiently investigated have been judiciously set aside.

The flavorist with the cooperation of the analyst is responsible for yet another type of application research on flavor ingredients. First, the investigation of "purity" determines the presence of certain impurities that may interfere with the final performance of a formulation and therefore may restrict use in a specific food. Second, compatibility must be examined under both physical and chemical profiles. The compatibility most important in formulating a flavor complex is solubility or miscibility; generally it is advisable to avoid partially soluble or insoluble ingredients. In liquid products all components must be soluble or at least miscible in a common solvent base (alcohol, carbitols, etc.). Emulsions may be employed to formulate pastes and dispersions for conversion to powders. In the preparation of spray-dried flavors, it is advisable to start with a feed consisting of a solution of the flavor ingredients and the neutral carrier in order to obtain a product with uniform yield. The flavor ingredients in the feed solution should display equivalent volatilities for the finished product to retain full flavor value. Equivalent volatility, already difficult to achieve in the formulation of perfumes to which the addition of various regulators and fixatives is permitted, becomes even more difficult in flavors where certain effective additives may not be employed. An example of such a problem is the higher volatility of trace amounts of acetaldehyde in the presence of large quantities of vanillin. Fortunately, other factors tend to stabilize the above system allowing the full development of the flavor. Processing at room temperature usually circumvents dissimilar volatility problems. The presence of alcohol, sugar, and water aid in producing soluble components, while aging contributes to a better distribution of the flavor ingredients in the bulk formulation and stabilizes the flavor against evaporation losses on repeated uncorkings.

The flavoring of any product will be "on target" only when odor and flavor sensations are stimulated in a coordinate fashion. Flavor ingredients interacting with one another or with the substrate may cause the resulting flavor to alter or degrade on aging. When components of a flavor ingredient are altered or lost during food processing, formulation modifications are necessary. Sometimes modification is impossible, since the desired notes do not have stable alternates. In certain cases, however, an upgrading of flavor may occur as a result of interactions (*e.g.*, the aging of wine and distilled liquors). In addition to being nonreactive, the components must display stability in storage conditions, such as the presence of air, light, heat. Citrus flavors, which are notoriously unstable, often cause stability problems even when present in small concentrations in compounded flavor ingredients. The flavorist must therefore be mindful of the physical-chemical compatibility between the flavor ingredients and the food substrate.

The evolution of the flavor ingredients can be summarized as follows:

1. The direct addition of dried herbs and spices to food
2. The extraction and concentration of active ingredients of dried herbs and spices and the blending of these to imitate natural flavors
3. The formulation of compounded flavorings
4. The combining of extracts and synthetic products to imitate additional natural flavor ingredients and to formulate non-existing types
5. The rebuilding of natural flavor ingredients and precursors through the identification and synthesis of the components.

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SENSORY MECHANISMS AND CHEMICAL STRUCTURE

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In order to discuss this actively studied, controversial, unresolved subject, it is important to understand the underlying physiology of odor and taste. While taste and odor will be discussed separately, the reader is reminded that these sensations are intimately interrelated with respect to food; the scientific community has accepted the mandate to clarify the issue.

It is beyond doubt that material contact between particles of a substance and the taste sensors is necessary to produce the taste sensation. Early investigators theorized that the papillae (taste buds) covering the entire surface of the tongue could be classified according to their predisposition for specific taste sensations, *i.e.*, for any one of the four basic flavors. However, according to more contemporary views based on electrophysiological studies, human sensors, including papillae, are not very specific and can respond to a great variety of chemical stimuli, although certain areas of the tongue are particularly sensitive to well defined tastes.[1-5] While the classification of tastes in four basic groups (sweet, bitter, salty, and sour) is supported on a physiological basis, the exact mechanism generating the sensation is still quite elusive. An important contribution to the mechanism of taste is that the final sensation is in part dependent on the sensors' response to tactile sensations as well as the complicating role of olfaction. Once the early theories attributing olfaction to a pressure wave were set aside, it was ascertained that material contact between particles of a substance and the sensor organs is necessary to initiate the taste-odor sensation. To the objections raised by some investigators that an odoriferous substance may continue to lose weight until it disappears, it is agreed that weight is quite negligible even after a prolonged contact time because of the very small number of molecules needed to initiate an odor sensation (threshold value).

Theories of Olfaction

The mechanisms taking place when odoriferous molecules impinge on the olfactory sensors are perhaps more controversial than those dealing with taste. Various theories of olfaction have been proposed; presently active ones can be grouped as follows:

1. The Vibrational Theory[6-12]
2. The Stereochemical Theory[13-24]
3. The Theory of Interfacial Adsorption[25-31]
4. The Profile Functional Group Theory[32-34]

Basically all four active theories are concerned with the size and shape of odorant molecules; each, however, augments the underlying concept by making allowances for functional groups, election donor-acceptor characteristics, and the sorptive nature of odorants on sensor sites. While the Vibrational Theory considers the far-infrared and Raman spectral characteristics of odoriferous substances, the other three are concerned with structural characteristics and/or the behavior of odorant molecules in direct interaction with the physical, chemical, and biological makeup of sensor systems.

According to the Vibrational Theory odor-relevant attributes are associated with certain far-infrared or Raman frequencies (termed *osmic* frequencies by Wright). Odor qualities arise when molecular vibrations at osmic frequencies increase by resonance vibrations in the sensory organs. Evidence that osmic frequencies exist is still elusive. Molecules with similar odorant qualities often display significantly different spectra. Although the Vibrational Theory needs much more supporting evidence, it contains salient features not to be discarded. For example, since far-infrared and Raman spectra reflect in part the structural characteristics of a molecule, there is good reason to suspect a relevant relationship exists between vibrations and odor qualities. Dravnieks observes that spectra are codes describing molecular structures and shapes with emphasis on the distribution of atomic masses, distances, and bond polarities; questions regarding corresponding intramolecular vibrations as direct factors in odor discrimination are independent of the validity of the spectral code.[35]

The Stereochemical Theory as developed by Amoore emphasizes the shape and size of molecules to odor-relevant events and is augmented by considering chemical factors as well. These include electrophilic-nucleophilic characteristics, rotational moment, and the presence of functional groups. In small molecules odor-relevant events are particularly associated with the presence of functional groups; in large, bulky molecules the presence of functional groups plays a less important role. Similarities in size and shape are measured by superimposing silhouettes fashioned from three-dimensional molecular models.

Two main objections to the Stereochemical Theory have been raised. The first points out that the theory postulates the presence of receptors in the sensor organs generally sensitive to shape and size. As noted previously, electrophysiological data do not entirely support this view. The theory also gives equal weight to positive and negative differences in odor-relevant molecules. The second major objection to the theory is based on cases of *anosmia* (odor blindness) and experiments with selective olfactory fatiguing. For example, some people are incapable of perceiving the odor of one category of musk while clearly discerning others. The condition can be experimentally reproduced for musk odors by fatiguing the olfactory sensors. From these experiments it is apparent that the musk odor, defined by the theory as one of the primary odor sensations, is probably compounded by several odor-relevant parameters; whether these lie principally at the chemical or physiological levels is currently under intense investigation. Nonetheless there is little doubt that molecular size and shape together with reactive character are odor-relevant.

The Profile Functional Group Theory (PFG), as elegantly devised by Beets, calls attention to the peripheral functional group of a molecule together with its size and shape as odor-relevant characteristics. The theory as developed by various investigators is based on the following mechanism: (1) the ability of a molecule to interact with the sensor site is dependent on the nature and reactivity of the functional groups in the odorant, and (2) the reactivity of the peripheral functional groups then determines the orientation of the rest of the odorant molecule, which forms the final odor-relevant profile. Thus similarity in profile at the sensor leads to similarity of odor. This occurs independently of the nature of the functional group as long as the orientation of the molecule is governed in the same way. When odorant mixtures are introduced, the final profile will be governed by the odorant reacting more strongly with the receptor; this changes the entire orientation of the molecule, and corresponding changes in the odor sensation are noted. Functional groups hindered by other segments of a molecule probably lack orienting characteristics, but it is important to note that the theory provides for the entire aromatic or heterocyclic ring to act as an orienting moiety. The theory serves to explain how molecular modification alters odors and urges careful placement of functional groups to guide molecular orientation for comparisons of shape and size.

The Interfacial Adsorption Theory is quite similar to PFG. However, the theory also postulates that the olfactory sensation is stimulated by interactions occurring at the hydrophilic-hydrophobic interface of the mucosa and the adjacent olfactory membrane. According to Davies, the odor-relevant characteristics of a substance are the molecular cross sections and the free energy of adsorption at the interface. The orientation of odorant molecules within the boundary of the two-dimensional field represented by cross section and free energy of adsorption determines odor quality. Molecules with similar odors are oriented similarly in the field; the odor quality changes gradually as the orientation moves over the field. Lack of odor occurs when a molecule's orientation falls beyond the field boundary because of too small or large a size or too weak or strong an adsorption. Reduced to its basic precept, the theory attributes the orientation of odorant molecules to their behavior at the hydrophilic-hydrophobic interface, while the PFG theory considers orientation apart from the physical nature of the receptor system.

The main criticism of the Interfacial Adsorption Theory is the scant use of psychophysical measurements. Demonstrating that molecules lying within the same field area always have similar odor-relevant attributes is difficult to quantitate, especially since pungent or other sharp odors have not as yet been investigated. These characteristics are present in many odorants and significantly influence odor-relevant attributes. The two-dimensional field presented by the theory appears crowded to encompass the vast number of discernible odorants.

None of the theories thus far proposed are entirely satisfactory. It would be necessary to take into account almost all the molecular characteristics examined by the individual theories to find a satisfactory general relationship between olfaction and chemical structure.

Chemical Structure and Flavor

Although much experimental data are available on the relationship of chemical structure to flavor, they are scarcely useful to draw generally valid conclusions. Among the four basic flavors only those having sour and salty characteristics show a somewhat rigid correlation with the presence of a specific functional group in the molecule. In sour tastes the sensation is associated with acids, but the intensity can vary in a manner quite independent of acid strength. Non-acid compounds with a sour taste are unknown. Similarly, the salty taste typical of sodium chloride is more or less common to both organic and inorganic salts. The ability of sodium chloride to enhance other flavors (exhibited to a greater extent by monosodium glutamate) is probably caused by a particular physiological action; however, this is in no way related to the chemical character of a salt, since flavor potentiation is also exhibited by some nucleotides, a very dissimilar class of compounds from a chemical point of view.

The bitter taste is characteristic of various groups of substances, the most important of which are the alkaloids and glucosides, followed by coumarins, terpene hydrocarbons, and terpenoids.

Sweet taste would appear on cursory analysis to be related in a rather direct fashion to chemical structure, since saccharides and polyvalent alcohols exhibit a more or less pronounced sweet taste. There are exceptions, however, such as gentiobiose, which is bitter. Other compounds with divergent chemical structures, representing amides, oximes, sulfoimides, benzenoids, and heterocyclic compounds, often exhibit a sweet taste at times more intense than sugars themselves. As a consequence, "glucophore theories" have been proposed where sweetness was attributed to groups such as $—CHOH—CH_2OH$; $—CO—CH_2OH$; $—CHNH_2—COOH$; and CH_2ONO_2. For the most part such theories have only limited validity, since they have been inferred and are generally applicable only to saccharides and polyvalent alcohols.

The relationship between odors and chemical structure is probably even more vague. The musk odor, for example, is generally related to compounds with high molecular weights and compact structures, whereas the presence of various functional groups does not appear relevant. Although many esters exhibit floral aromas, numerous non-ester compounds also exhibit floral fragrances. Sulfur-containing compounds generally exhibit strong and often unpleasant odors, but these differ widely from one another. The low-molecular-weight aldehydes in the aliphatic series are of little commercial value because they exhibit highly pungent odors; high-molecular-weight aliphatic and terpenic aldehydes are quite appealing and have widespread commercial use.

In acids odors range from pungent for formic and acetic acids to rancid for high-molecular-weight fatty acids; cyclic benzoic acid is odorless. The persistence of odors is related to lower volatility, whereas odor intensity is not related to this characteristic.

Odor is related to the overall physical-chemical properties of molecules, whereas flavor appears to be influenced to a large extent by the presence of specific functional groups and therefore by the chemical properties of the compound.

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HUMAN TASTE PERCEPTION

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INTRODUCTION

Overview

Recent research in human taste perception is critically and selectively reviewed. Special attention is given to the basis of quality judgments in taste. Detailed discussions of this topic include the research methods and phenomena of single taste bud (papilla) stimulation, cross-adaptation, and taste modifiers, as well as a critical discussion of research methods in this area. Discussion of human judgments of taste intensity emphasizes the relatively more recent contributions from scaling approaches. The distinction between two basically different approaches, searching for the psychophysical invariant vs. the investigation of psychophysical differences, is highlighted. Consideration is given to the broad topic of taste research procedures, an area which has received little formal attention compared to research in other senses. Topics discussed include choice of experimental subjects, choice and calibration of stimuli, stimulus delivery systems, and the real-life relevance of the taste research procedures to issues of food ingestion. A discussion of the effects of continued stimulus presentation (adaptation) focuses on the the description of the process of adaptation, and the effects of adaptation. Last, a discussion of taste mixtures highlights what is known about how tastes interact. The emphases in the review are on the research methods employed and the problems of doing research in a sensory system whose physics (stimulus), anatomy (receptor), and physiology (neural mechanisms) are not completely understood.

History of Taste Research

The history of the study of human taste perception is not impressive from the viewpoint of scientific accomplishment. The research has not shown the resolution of any major problem in taste psychophysics: the specification of the stimulus, the specification of the taste qualities, the specification of the psychophysical function(s) for taste, or the nature of taste reception. A large amount of literature exists from early European researchers, largely German. These papers deal with many of the same issues dealt with in contemporary work, although they often suffer from insufficient experimental control and primitive methodology. Nevertheless, in some instances the early workers arrived at the same conclusions as we do today.

Taste research in America increased in the 1940's. Psychophysical scaling of taste received much attention from researchers at Harvard. The electrophysiological approach which began with the work of Pfaffmann[98] continues to the present day. Behavioral work in animals and humans was under way in large research projects with the work of P. T. Young, C. Richter, and others. However, in the period from 1940 to 1965, when there was a sizable increase in both electrophysiological and behavioral animal research, there was no concomitant increase in human work. Certainly, the absolute number of papers devoted to human work did increase, but they were not parts of a literature devoted to specific issues as were the animal papers. Within this context, the increase in human taste research since 1965 is perhaps surprising. Much of the work has been devoted to phenomena previously researched, e.g., cross-adaptation. Other work has focused on variables hitherto not investigated in humans (water taste, stimulus flow rate). A sizeable literature has grown on the mathematical properties of psychophysical functions. In many instances, the human taste research has tried to find a comfortable relationship with the animal data (e.g., quality coding).

Scope of Present Article

The task of this writer is made much easier because of the number of excellent reviews which have appeared, especially within the last ten years. The *Annual Review of Psychology* has reviewed the *Chemical*

Senses in 1965[12] and in 1969.[124] Much relevant material can be found in the three volumes of *Olfaction and Taste*.[50,101,130] The early human literature is covered in Pfaffmann's chapter for the *Handbook of Physiology*,[101] and in Moncrieff's *Chemical Senses*,[85] and the early work plus more recent work is detailed by Bartoshuk in the revised Woodworth and Schlosberg,[5] and by Pfaffmann, McBurney, and Bartoshuk.[103]

With these reviews and others, the reader might question the need for yet another review. The present review is designed to be nonexhaustive and critical in nature. The present paper is oriented towards human taste perception. The literature pertaining to taste anatomy will not be reviewed, and will not be mentioned except in the context of the human work. Similarly the physiological (especially electrophysiological) literature will not be reviewed, but will be used to provide a context for some of the human material and to broaden discussions of human receptor mechanisms in several places. The chemical constitution of the stimulus and the biochemical constitution of the receptor will also be used only in support of the human material.

The purpose of the present article is to present a selective, critical review of the recent literature. The preceding paragraph detailed what related areas of taste research will not be covered. In addition, the coverage of the human taste research will not be exhaustive. Research and theoretical papers will be covered insofar as they relate to the phenomena, theoretical issues, and procedural points being discussed. Further, the material will be largely limited to the more recent literature in English. Classical papers which do not relate to current issues will not be reviewed. Thus, inclusion in the present paper is not intended to be a measure of merit but simply a matter of relevance to the topics under discussion.

The topics for discussion were chosen as those occupying current interest in human taste research. Some have occupied taste researchers for a long time, e.g., adaptation and quality categories, while others are relatively new, e.g., procedural considerations and ratio scaling. In a critical review such as the present article, the bias of the writer does interfere with the choice of topics, the choice of material, and the arguments presented. Where possible, I will try to make my bias clear. The reader should be aware that a nonexhaustive critical review will stimulate some dissatisfaction from certain readers and researchers. Hopefully this dissatisfaction will be the stimulus for resolution of some of the issues raised.

TASTE QUALITIES

The issue of what qualities exist in the gustatory sense has been a perplexing one in taste research, even more so in recent years. Taste researchers have accepted a relative ignorance of the stimuli for taste. Their lack of certainty of what qualities should comprise the taste repertoire has been less visible but no less there. Most basic reference works in psychology used in the past 25 years present sour, salty, sweet, and bitter as the *four* qualities with only minor hesitation if any.[15,85,99,100,127] More recent reviews and discussions have presented the question of taste qualities as a question, an unsolved issue in taste research.[5,28,102]

The literature which has produced this reassessment of the taste quality question is the electrophysiological literature of the last 30 years. Pfaffmann[98] found, seemingly to his own surprise, that when the neural signals passing along single units of the mammalian chorda tympani nerve (which innervates the anterior region of the tongue) were electrically monitored, they were not specific to one of the four classical taste qualities of sour, salty, bitter, and sweet. In other words, one taste neuron (or unit) might respond to several stimuli thought to represent different taste qualities (acid, quinine, etc.). The previously held notion of four distinct taste qualities had led investigators to believe that they would find four distinct receptor types and/or four distinct neural transmission routes. In the past 30 years, Pfaffmann's original demonstration of little or no specificity in mammalian taste systems has been repeated in many different species. In fact, the replication of this basic finding has occupied a large percentage of the overall effort in taste research.

The results of these efforts have been many: the large body of evidence amassed in several laboratories has permitted several investigators to develop sophisticated models of the data.[35,107] Such model-building is impossible with small amounts of data or with pilot-experiment data. Secondly, these findings have forced all taste researchers to reexamine their position on taste qualities. The physiological literature no longer supported a specificity view, i.e., a view that specific qualities exist and that a neural apparatus exists to transmit them. What was suggested in place of a specificity view by the physiologically oriented workers was some form of a neural patterning view which held that the higher brain centers decoded a neural pattern which contained the information about taste quality. Most taste nerve fibers respond to many stimuli but to varying degrees. The higher centers decode these patterns of responding. Erickson[34] suggested that a single dimension could be used to describe the taste stimulus (as in audition). Pfaffmann[102] noted how the specificity and pattern views could become almost imperceptibly different.

Single Papilla Stimulation

The effect of all this on human taste research was not overwhelming. Recall that most of the taste research effort was going into the physiological research outlined above. Still, several experimenters began to deal with new phenomena or approach older phenomena in a new light. Some of the work centered around the work of Bekesy, the Nobel Prize winner in audition research, who did a series of taste experiments in the mid 1960's. What Bekesy did was to try to stimulate single taste papillae to determine the range of stimuli to which they would respond, i.e., how specific they were. The stimulation of individual papillae had been attempted many times,[5,15] but earlier techniques were often unclear or left much to be desired from the standpoint of methodological sophistication.

Bekesy reported two investigations of individual papilla stimulation, one using electrical stimulation[9] and one using chemical stimulation.[11] Bekesy[9] stimulated single human fungiform papilla with 0.5 msec anodal pulses produced from a gold-tip electrode 0.5 mm in diameter. Stimulation of individual papillae produced reports of only one quality, except in several instances where more than one papilla appeared to have fused.

Bekesy further reported that visual inspection of the papillae under 30 to 60 power magnification permitted discrimination between 4 different papilla types.

Bekesy[11] confirmed the above findings with chemical stimulation of individual papillae. He gently elevated a papilla using slight suction, and applied a drop of stimulus solution to the side of a papilla. Again, with the few exceptions mentioned above, papillae responded to one quality only. The same papilla would elicit the same quality whether stimulated electrically or chemically. From two observers, the papillae responded as shown in Table 1.

Reviewers and critics of Bekesy's experiments have brought up several technical issues. First, the two articles[9,11] which set forth Bekesy's work did not specify details of procedure to the degree where an exact replication of his work was possible. The specification of timing intervals and durations, the specification of various stimulus parameters, and other methodological details were omitted. This situation always leaves an investigator open to criticism, and makes attempted replication of the work difficult.

TABLE 1

Number and Percentage of Papillae Responding to Different Chemical Stimuli in Two Observers. (Data from Bekesy.[11])

	Observer			
	1		2	
	No.	%	No.	%
Hydrochloric acid	10	14	44	37
Sodium chloride	5	7	17	14
Quinine sulfate	11	16	29	25
Sugar	9	13	13	11
Total sensitive	35	50	103	87
Insensitive	35	50	15	13
Total	70	100	118	100

Second, the existence of the "demand characteristics" in a situation such as described by Bekesy is possible. Did his observers really know what the experiment was all about, and did they know what biases, if any, the investigator had? Naturally, such questions can be asked of any experiment with humans. Some experiments do control for these factors by using so-called blind procedures. If controls existed in Bekesy's research the reader is not so informed.

Third, several reviewers have questioned the possibility of obtaining a human response to one drop of chemical stimulus on one papilla, especially when the chemical stimulus is of approximately the same concentration as would be used in near threshold whole mouth stimulation.[5,124] Indeed, Bekesy[11] reports that thresholds determined for single papillae were of the same order of magnitude as for the whole mouth.

Fourth, one theoretical point with regard to Bekesy's work should be mentioned in the context of the physiological work mentioned above. Bekesy is talking about specificity of papillae. Note that a papilla contains more than one taste bud, and that each taste bud contains more than one taste cell. Further, each taste cell can be innervated by more than one nerve fiber, and each nerve fiber innervates more than one cell. With these facts in mind, the correspondence between the electrophysiological evidence against specific taste fibers or cells and the observations of Bekesy with respect to specific papillae is difficult.

The challenge posed by Bekesy's work stimulated work by researchers generally involved in animal behavioral and physiological research. Harper, Jay, and Erickson[48] attempted to "reinvestigate" the single papilla stimulation issue, making clear their bias that Bekesy's findings did not fit with current taste theory based on animal physiology and that certain deficiencies in his procedures were thought sufficiently serious to cast doubt on his results. They used suction to hold a stimulator on the tongue, and to draw fungiform papillae into a chamber for stimulation of their dorsal surface. A double blind procedure was used to deliver several replications of the treatments of each of 23 papillae in 4 observers. Most papillae tested were insensitive (13/23), some responded to more than one compound (6/23), and some responded to only one compound (4/23). The stimuli used were several relatively high concentrations of sodium chloride, sucrose and dulcin, quinine, and citric acid. Two of the observers showed only one sensitive papilla each. Therefore, almost all of the data comes from two observers. Keeping in mind that the concentrations used by Harper et al. were many times more concentrated than those used by Bekesy, the general lack of response is surprising.

Harper et al. state that the relatively small amount of data does not permit statements about numbers and kinds of gustatory primaries (or qualities). In fact they feel that such an approach to taste research is "misleading" because simultaneous stimulation of several papillae is the probable basis for sensory discriminations. The fact remains that Harper et al. found a far smaller proportion of sensitive papillae than either Bekesy or the earlier studies of Oehrwall[94] or Kiesow.[61] They recognized this and state several methodological issues which might be responsible. However, they conclude that the data support a patterning model rather than a specificity model. It is unclear to the present author how such a conclusion follows from the work reported above. Most papillae tested were insensitive. Of the 10 which showed responses, 6 were nonspecific (more than one quality) and 4 were specific. A more likely conclusion would be that some papillae are specific and some are not. Recall that Bekesy did find papillae (which he claimed were fusions of several smaller ones) which were not specific, although not in very large numbers. The experiment by Harper et al. did not resolve the question of papilla specificity.

A study of McCutcheon and Saunders[75] has attempted to resolve the issue. Two subjects were chosen on their ability to correctly label five presentations of each of the following: 0.04 M sucrose (sweet), 0.001 M citric acid (sour), 0.04 M sodium chloride (salty), and 3×10^{-4} M quinine sulfate (bitter). Each subject was given 30 training trials in which the experimenter presented a stimulus and then identified it chemically. Two papillae were tested in each subject once a week for several weeks. Each test session consisted of three presentations of each of five stimuli, plus five presentations of a control stimulus near the papilla. A double blind procedure was used so that neither the investigator nor the subject knew what stimulus was being given.

While the results contain many interesting points, let us focus on what significant effects were observed. Both observers reliably reported sweet in response to sucrose. One subject reliably reported sour for citric acid for both papillae, the other subject for only one papilla. There was some tendency for citric acid to evoke salty in both subjects. Quinine evoked sour, bitter, or no taste to some degree in both subjects. The

TABLE 2

Quality Responses from the Ten Sensitive Papillae Reported by Harper et al.[48] The Papilla Numbers Identify the Papillae within the Harper et al. Report.

Qualities	Papilla number(s)
Sweet	22
Bitter	6
Sour	3, 14, 15
Sweet, sour	1, 2
Sour, salt, bitter, sweet	13, 16, 17

control stimulus reliably produced reports of no taste in one subject, and in one papilla in the other subject.

The authors concluded that the single fungiform papilla is capable of eliciting appropriate response to both sucrose and citric acid. They suggest that saltiness response may be dependent on simultaneous stimulation of several papillae. The results are viewed as supporting the findings of Harper, Jay, and Erickson[48] and as adding further doubt to the findings of Bekesy.[9,11] Unfortunately, the large differences observed by Harper et al. in what compounds single papillae respond to, make the present result of McCutcheon and Saunders difficult to interpret. The latter authors are reporting on only four papillae. Harper et al. found papillae with the following sensitivities (Table 2). Had McCutcheon and Saunders used more papillae they might have found the same distribution of sensitivities or a different one. Both sweet and sour are represented much more often than would be expected from chance. Salty is absent except in cases where subjects responded to all four tastes. The similarity between the data of Harper et al. and those of McCutcheon and Saunders is striking; there were relatively good reports for sweet and/or sour either by themselves or with other taste qualities. Perhaps future research will uncover why the method of single papilla stimulation elicits these qualities.

It certainly cannot be assumed that single papillae are specific for quality; on the other hand it probably should not be assumed that multiple specificity is the rule.

Cross-adaptation

When any sensory system is exposed to a constant stimulus, there are changes in that system, most notably a decrease in sensitivity sometimes to the point of no response. The types of changes encountered, the form of these changes, and other considerations will be treated in a later chapter devoted to the topic of adaptation. At present, we are concerned with the relevance of adaptation to the issue of qualities. The relevance is the phenomenon or technique of cross-adaptation. If presentation of one stimulus compound leads to decreased responsiveness to other compounds, then we have the phenomenon of cross-adaptation. As a technique, the term refers to the prolonged presentation of one compound followed by presentation of another.

The relevance of this technique and phenomenon to issues of receptor specificity has received some attention. The argument goes that adaptation involves depression or deactivation of a "system." If the following test compound also shows decreased response then the same "system" is involved; if no effect is observed then a different system or systems are involved. This position has been taken by Pfaffmann,[100,102] Meiselman,[77] McBurney,[70] Smith and McBurney,[116] and McBurney and Lucas.[73]

The cross-adaptation procedure has been used by McBurney and a series of collaborators to specify the number of qualities (defined by cross- adaptation) which exist within three of the four classically considered taste qualities (sour, salty, bitter). The work has been conveniently summarized in a recent paper.[70] The general technique was as follows: the procedure of direct magnitude estimation has been used in which the observer estimates the strength of a stimulus in proportion to the strength of other stimuli. If one stimulus is twice as strong as another, it is assigned a number twice as large. For each classical taste quality, a representative solution was chosen as the adapting compound in the test for cross-adaption: sodium chloride for salty, citric acid for sour, and quinine hydrochloride (and urea) for bitter. Test compounds representing each taste quality were then chosen: these included compounds having tastes similar to and different from the adapting compound. The procedure used was a profile procedure, in which the observer first gave a magnitude estimate of the total intensity of the taste and then divided it into the four qualities. In other words, if the total taste were two times the previous stimulus (for example, 10) it was assigned a number twice as large (for example, 20). If the taste of this second sample was an equal mix of the four tastes the profile would read: sour 5, salty 5, bitter 5, sweet, 5. If the sample was approximately half sweet and half bitter, then the profile would read: sour 0, salty 0, bitter 10, sweet 10.

The necessity of using a profile procedure is shown by the results for salty cross-adaptation. When overall intensity is used as the measure, sodium chloride adaptation does reduce total intensity response to other salts. However, the cross-adaptation effect is even more striking if the saltiness response is used. The decrease in saltiness is offset in some cases, e.g., potassium bromide bitter, by increase in other qualities, thus reducing the total intensity rating.

Sour adaptation led to reduced sourness of all test compounds, confirming the findings for saltiness. The findings for bitterness were not as clear. Adaptation with quinine hydrochloride reduced the bitterness of quinine hydrochloride, quinine sulfate, caffeine, and sucrose octaacetate, but *not* KNO_3, PTC, or $MgSO_4$. Surprisingly, urea adaptation produced reduction in bitterness in all compounds except caffeine. Perhaps there are two bitter systems. Further replication of these data, with controls for sour-bitter confusions, is probably in order. The results to date suggest that saltiness and sourness each represent a unitary dimension.

The findings from cross-adaptation experiments in which adaptation with a compound of one quality has been tested on compounds of other qualities have been much more puzzling. The general result here has been a cross-enhancement, that is, the test compound following the adapting compound is increased in intensity.[25,60,71,76] If any pronounced depression of one taste quality was achieved by another, then the results would have suggested a lack of independence of the two qualities. The problem of what to do with the observed enhancement was unclear until McBurney and Bartoshuk[71] offered the water taste mechanism.

The water taste mechanism proposed by McBurney and Bartoshuk[71] not only provides us with a model for explaining cross-enhancement, it also helps to specify the role of water (distilled) in taste research and taste models. In their treatment of cross-enhancement, which McBurney and Bartoshuk call *successive potentiation*, the argument is based on the observation that water is not tasteless as has been often assumed, but rather that its taste is contingent on the adaptation state of the tongue. Given appropriate adaptation, the taste of water can be any of the four qualities (see section on Adaptation). In cross-enhancement, the water taste of the first compound is added to the taste of the second compound, producing a greater perceived intensity for the latter.

To test this hypothesis, the authors tested the effects of adaptation with 0.1 *M* caffeine, 0.004 *M* citric acid, 0.18 *M* sucrose and 0.82 *M* urea, and 0.1 *M* NaCl on each other and on two weaker concentrations of each compound and on water. A profile magnitude estimation procedure was used. Results supported the hypothesis that when a stimulus is tasted after adaptation to another stimulus, the taste of the second stimulus is the sum of the water taste produced by the first stimulus, plus the usual taste of the second, minus any effect of the first stimulus on the second due to cross-adaptation.

Taste Quality Modifiers

Several compounds have been discovered which have rather dramatic effects on the qualities of taste. The relevance of these compounds in this discussion is to the question of quality identification. The compounds themselves are of interest for several reasons, ranging from their basic chemistry to their practical use in the food industry. The discussion will consider the most well-known taste modifiers which have qualitative effects, both of which are natural plant materials. The topic of flavor enhancers will not be discussed. This large topic with an impressive, if somewhat confusing, literature is too large an area to be dealt with within the scope of this paper.

The taste effects of the plant *Gymnema sylvestre* have stimulated interest for over 100 years, and its importance in understanding taste qualities was clearly recognized by early investigators.[112] The plant is native to India, tropical Africa, and Australia. The chemistry of the active component of *Gymnema sylvestre* is a glycoside called gymnemic acid, which has received extensive chemical investigation.[4] It appears to be separable into several components.

The interest in gymnemic acid for the taste researcher has been mainly aimed at specification of its qualitative effects. The suppression of sweetness by gymnemic acid is the most reliable effect. Sweet suppression has been reported for every sapid compound except chloroform: raw leaves with sugar;[54] aqueous extract with sucrose;[59,82] aqueous extract or potassium gymnemate with sucrose or sodium saccharin;[125,126,128] gymnemate salts with sucrose;[6,82] potassium gymnemate with sucrose, cyclamate, D-tryptophan, D-leucine, beryllium, and chloride lead acetate.[65] Suppression of other qualities has also been reported. Bitter suppression was reported for raw leaves with quinine sulfate[59] and for aqueous extract or soluim gymnemate and quinine sulfate.[65] Saltiness suppression was reported for sodium chloride with both aqueous extract and sodium gymnemate[112] and gymnemic acid in alcohol.[59]

This rather puzzling picture of the qualitative effects of gymnemic acid was clarified somewhat by Bartoshuk et al.,[6] who suggested that previously reported effects other than sweet suppression were due to cross-adaptation between a taste in the *Gymnema sylvestre* preparation and the test compound which followed it. They demonstrated that when a 40-second rinse followed gymnemic acid presentation, the only effect to be observed was sweet suppression. The previously reported bitter suppression, they argued, was due to the bitterness of the *Gymnema sylvestre* preparations, and the saltiness suppression was from preparations containing salts.

However, Meiselman and Halpern[83] used an experimental paradigm which avoided cross-adaptation problems and observed qualitative effects other than on sweetness. They presented an aqueous decoction of *Gymnema sylvestre* only once at the beginning of a session lasting almost a full hour. No test stimuli were presented for five minutes after the decoction. The effects over the next 55 minutes were stable and included the following: suppression of sweetness of sucrose, glycine, and dl-alanine; suppression of the sourness of sucrose and the saltiness of dl-alanine; enhancement of the sourness of glycine, the bitterness of sucrose and dl-alanine, and the saltiness of sucrose. These results were obtained using a profile procedure. Subjects were asked for responses after *Gymnema sylvestre* treatment and, in a different session, after treatment with a control tea tasting similar to the decoction.[82]

The authors suggested three possible explanations for reported qualitative effects of *Gymnema sylvestre*. The first is that various experiments have used chemically different *Gymnema sylvestre* preparations. Various components of these preparations might have qualitatively different effects. Second, removal of sweetness by gymnemic acid might be similar to a taste mixture effect. For example, removal of sweetness from coffee leads to increased bitterness. The bitter effect would be an indirect effect of the sweet suppression. Third, some procedural differences among the various studies could account for the differences. For example, Meiselman and Halpern noted that they used only one presentation of gymnemic acid whereas Bartoshuk et al. used a presentation before each stimulus. If qualitative effects of the material change over time, then a possible mechanism could be found.

The second natural plant with well-known taste modifying properties is *Synsepalum dulcificum* berries. This plant has been known as miracle fruit for many years. It is native to tropical west Africa, where it is used by the local natives as a sweetener. Miracle fruit has been the subject of less formal research than gymnemic acid, although references to it have been increasing, especially in the popular press.[4] The chemistry of the active principle of miracle fruit, called miraculin, has been identified as a high molecular weight protein.

Bartoshuk[4,6] has demonstrated that the effect of miracle fruit is basically the addition of sweetness to normally sour substances. Its effects on stimuli representative of sweet, salty, and bitter are not significant. The apparent suppression of sourness is another example of mixture suppression. This sweetness is suppressed by gymnemic acid.

Several models have been formulated to deal with the miracle fruit effects.[4,26,66] The details of these models are not important to the present topic. Suffice it to say that they demonstrate the importance of this type of research in identifying and explaining taste qualities.

Stimulus Classes

In spite of the many problems discussed throughout this paper, there have been some generalizations about gustatory stimuli which seem to justifiably group stimuli according to their quality. This evidence is exhaustively reviewed by Moncrieff[85] and will be only briefly reviewed and slightly updated here.

The quality of sour has been linked to hydrogen ion concentration for some time. For inorganic acids, e.g., hydrochloric, the relationship is apparently satisfactory: the greater the hydrogen ion concentration the greater the sourness. For organic acids, e.g., acetic, tartaric, citric, the sourness appears to be greater than what their hydrogen ion concentrations would dictate. Moskowitz[89] has used direct scaling techniques (see section on psychophysics) to better quantify the relationships between sourness and various physical dimensions. He observed that different psychophysical functions resulted when the measure of physical concentration was changed from molarity on percentage to pH.

The basis for the salty quality is more complicated than sourness but has received much attention.[30,85] In a particularly detailed analysis of the salty taste, Kionka and Stratz[62] demonstrated that the quality was generally attributable to the anion (vs. cation) in the 18 alkali halides tested. The cation appeared more related to intensity. Dzendolet and Meiselman[30] asked observers to assign qualitative labels to solutions of the chloride and sulfate of lithium and potassium. Analysis of the results (Figure 1) led the authors to agree with Kionka and Stratz that chlorides and sulfates (to a lesser degree) are responsible for the salty quality. The authors related anions to other qualities of the stimuli, suggesting that the potassium ion is responsible for bitterness and the lithium ion for sourness.

The mechanism for sweet has been the subject of much discussion,[85] but until recently no models of sweetness had received much attention. Two such models now exist. Since the models both involve rather advanced chemistry they will only be briefly reviewed. Shallenberger and Acree[111] have suggested that sweet-tasting compounds possess *AH* and *B* units where *H* is an acidic proton and *B* is an electronegative atom or center. The distance between the proton and *B* is specified at about 3A. The responsible elements for several stimuli are specified. Dzendolet[27]. has proposed that sweet-tasting compounds are proton acceptors. His model accounts for the sweetness of dilute salts, which are not considered in the former model.

Work on the bitter taste is much more limited than for any other quality,[85] and to date no mechanism for bitterness has been widely discussed.

Methodological Considerations in Quality Research

Several methodological issues have contributed to the problems in research on what qualities are appropriate in taste and what mechanisms underlie these qualities. The first issue concerns the lack of a no-stimulus condition. Visual or auditory research, as we know them, would be difficult to conceive if the same condition existed there as in taste, namely, the virtual impossibility of producing an extended no-stimulus condition. The work of McBurney, Bartoshuk, and colleagues on water taste and adaptation should have established that water is a stimulus. It has a reliable taste, depending on conditions. To use it as rinse is no more supportable than using any weak moving stimulus to remove what is on the tongue. Sometimes this is called for, especially when relatively concentrated stimuli are to be removed.

Rather than a rinse condition, some investigators simply wait a period of time which they feel is sufficient to undo the effects of adaptation and permit the solution on the tongue to disappear.[11,77,82] The advantage is obviously one of avoiding problems associated with water and other rinses. The problem is one of saliva. Since saliva changes qualitatively and quantitatively in reponse to stimuli, then the salivary state of the mouth might change over the course of an experimental session. Even this can probably be avoided by using very long interstimulus rest periods. Bekesy[11] used 10 minutes.

In qualitative taste research, the classical four-quality scheme, although unpopular with most investigators, has contributed much to the choice of stimuli. Most experiments, behavioral and physiological, human and animal, have used compounds which the investigators feel represent the *four* qualities. These have usually been

salty . . . . . . sodium chloride
sour . . . . . . tartaric, hydrochloric, or citric acid
bitter . . . . . quinine hydrochloride or sulfate, or caffeine
sweet . . . . . sucrose (to a lesser degree saccharine).

At least two separate issues can be raised: should any given stimulus be defined by a single quality? and does qualitative description change with concentration?

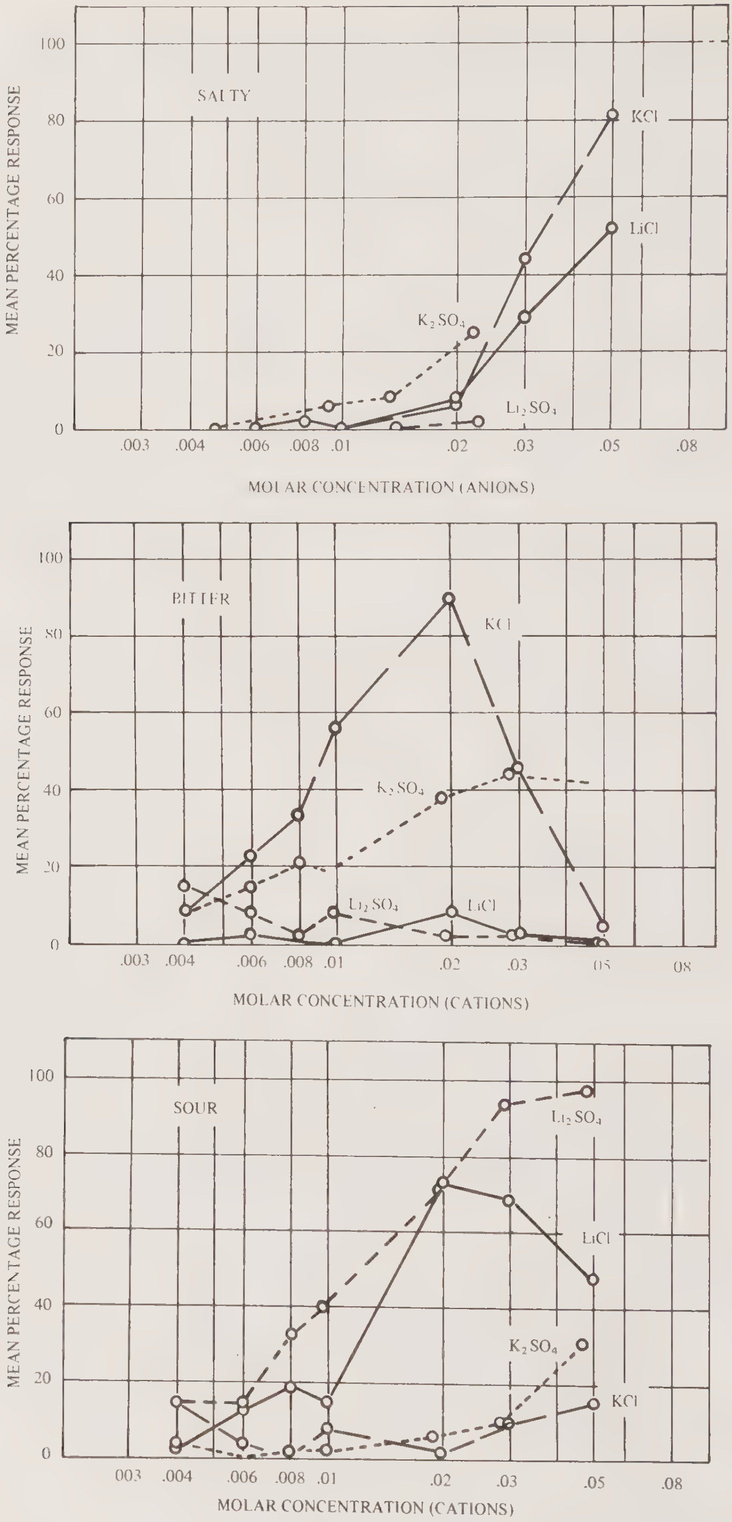

FIGURE 1. Mean percentage response as a function of molar concentration of anion or cation. Each point represents three repeated measurements from four screened female subjects. (Adapted from Dzendolet and Meiselman.[30])

Description of taste stimuli with simple, single qualitative labels is the practiced rule rather than the exception. Citric acid is widely used as a stimulus for sour when it is widely recognized that it contains a sizable sweet taste as well. Saccharine is widely used as a sweet stimulus, but most agree that its taste is not only sweet. Since the search for pure and/or simple stimuli is difficult if not impossible, then the answer to this problem probably lies in changing the typical way in which we measure response. The profile technique, used recently in several papers by McBurney[70] and Meiselman and Halpern,[82,83] requires the observer to specify the contribution of each of the four qualities to every stimulus. The limitation of the system to four qualitative categories is not necessary, and experience might show that fewer or more categories are appropriate.

The other observation standing in the way of specific quality labels for stimulus compounds is the reported quality change with concentration change. This long-known phenomenon was recently investigated by Dzendolet and Meiselman,[29] who asked screened observers to label sipped stimuli as sour, salty, bitter, or sweet. For each compound (lithium chloride and potassium chloride) the modal quality response changed progressively from one quality to another with increasing or decreasing concentration. All four classical qualities could be reliably obtained from stimuli normally considered "simply salty." These data illustrate further why it is misleading to assign a specific quality label to a compound. The further changes which can be elicted by adapting conditions and other special conditions strengthen the argument against the use of specific quality labels.

Other Approaches

At least three other approaches to specification of gustatory qualities appear worthy of note, although space and other considerations do not permit any more than a brief mention.

The technique of multidimensional scaling has been used successfully in a wide range of problems to specify what variables contribute significantly to a given system, i.e., what variables account for the variability in a system. This technique has been applied to taste research.[44,45,106,109,129] At least to this author, the results have not yet provided any clear mandates for making decisions about appropriateness of quality labels in taste. Nevertheless, the techniques have great promise in this problem area.

Second, the use of anesthetics and other means of changing response is a possible way of demonstrating the separateness of taste qualities. The ingenious work of Skramlik[114] in this area has never been widely discussed or replicated. His report of differential response to anesthetics on stimuli representing the four classical tastes is worthy of replication and further study.

Third, the use of clinical material has been helpful in developing understanding in vision (e.g., color blindness) and audition (e.g., recruitment). Such approaches have never caught on widely within taste research, with the striking exception of Henkin, who has presented much interesting and challenging data from the clinical realm.[51] This type of work should be brought more within the mainstream of human taste research so that its value can be better realized.

BASIC TASTE PSYCHOPHYSICS

Psychophysics is the study of the relationship between what exists in the real world (the stimulus or stimuli) and the human experience of these events. Psychophysics was the first discipline within modern experimental psychology, beginning in 1860 with Fechner.[15] Psychophysics has contributed to science not only a large body of literature about the form which our percepts take, but also a large body of literature on appropriate procedures for investigating the senses. These psychophysical methods have been reviewed in many sources.[33,118,127] An arbitrary distinction can be made between the psychophysics of detection (thresholds) and the psychophysics of scaling. The discussion of taste psychophysics will follow this distinction.

Taste Thresholds

The literature on taste thresholds consists of many unrelated topics. The threshold procedure has been used to study phenomena both within and outside of taste, and the material is not as easily assembled as it is in scaling psychophysics. A large portion of the taste threshold work has been devoted to threshold determinations of bitter phenylthiourea (PTC) type compounds. The aim of this work has been an understanding of genetics and physiological mechanisms through a taste phenomenon. Roland Fischer and his colleagues have pursued this approach for a number of years, and the results of their work have been organized in several publications.[39,40]

It appears that the classical concern of genetic PTC blindness has brought with it a classical procedure for investigation. When an increasing proportion of sensory research has been using the direct and indirect scaling techniques, the threshold technique has persisted in PTC studies. While this makes current work more directly comparable with previous research, and also permits the assembing of sufficient data to lead to models such as Fischer's, it can also stand in the way of a new view of an area generated by new procedures. The threshold technique focuses attention on one point of the psychophysical function, the point at which the subject just reports the presence of a stimulus (detection threshold), or recognizes some quality of the stimulus (recognition threshold). When scaling techniques can yield the entire psychophysical function including the threshold with about the same input of work, it appears somewhat uneconomical to pursue the threshold approach. Also, perhaps some new insights into the PTC issue, and other issues, could be generated by new psychophysical techniques.

Summaries of reported taste thresholds were compiled by Pfaffmann.[100] The American Society for Testing and Materials is now preparing a thorough compilation of all reported taste thresholds. This should prove helpful for future work using threshold procedures. These procedures, while receiving less attention in recent years in favor of the taste scales discussed below, are nevertheless relevant to issues such as pollution (detection of threshold off-tastes in food) and other real life problems concerned with maintaining the absence of certain tastes.

Taste Scales

Scaling of gustatory intensity had a slow start. As with many other research areas in gustation, this can probably be attributed to the greater importance placed on vision and audition research, and also to the problems inherent in investigating a sensory system in which the stimulus is unknown and the physiology relatively uncertain. Virtually no work has been done on indirect scales of taste. These are the so-called *confusion scales,*[33] in which one directly determines ordinal scales of taste (i.e., scales where only order is important) or indirectly determines equal interval scales (i.e., scales where order and interval are important). Schutz and Pilgrim[110] used a nine-point category scale with verbal keys at alternate scale points (none, slight, moderate, strong, extreme) to develop scales of 16 sweet-tasting substances. They determined that the relationship between the category rating of sweetness and the physical concentration was logarithmic, in keeping with previous findings of category scaling of many other dimensions.[33] This logarithmic relationship is attributed to the observer's inability to discriminate constant physical differences equally well along the scale.[33]

The direct scales are of two types, partition scales (judgment of intervals) and magnitude scales (judgment of ratios). A further distinction within direct scaling methods separates those methods in which the subject controls the stimulus (production) and those methods in which the experimenter controls the stimulus (estimation).

Early direct scaling of taste intensity used a fractionation procedure in which the observer selects a physical stimulus concentration which is some fraction (e.g., one half) of another.[8,67,68] Lewis[67] obtained negatively accelerated functions for sodium chloride, sucrose, quinine sulfate, and tartaric acid, and MacLeod[68] obtained similarly shaped functions for sucrose and glucose. Beebe-Center and Waddell[8] reported linear relationships. These early studies laid the groundwork for later work in direct scaling of taste, and suggested that ratio scales of taste conforming to Stevens' power law (see below) should have exponents equal to or greater than one.

The early direct taste scales never caught on, and taste research was slow to pick up the next movement in sensory scaling, the magnitude estimation technique. This technique consists of matching numbers to physical magnitudes in correct proportion to their strengths. A stimulus which is perceived as twice as strong as another stimulus is assigned a number twice as large. This technique has certain advantages over fractionation.[86]

Many investigations using the magnitude estimation technique and various "validating" procedures

TABLE 3

Exponents for Taste Functions. Exponents Are Listed in Order of Decreasing Size for Each Compound.

Exponent	Source
	Sodium Chloride
1.59	Ekman, 1961
1.58	Ekman and Akesson, 1965
1.43	Meiselman, 1968
1.40	Moskowitz, 1968
1.40	Stevens, 1969
1.35	Meiselman, 1971
1.30	Stevens, 1960
1.05	Jones and Marcus, 1961
1.00	Lewis, 1948
1.00	Borg et al., 1967
0.97	Moskowitz, 1972
0.92	Bruvold and Gaffey, 1965
0.80	Meiselman, 1971
0.78	Meiselman, 1971
0.73	Faull, Meiselman, and Halpern, 1971
0.54	Kocher and Fisher, 1969
0.49	Smith, 1969
0.44	Feallock, 1965
0.42	Bartoshuk, 1968
0.41	McBurney, 1966
	Quinine (Hydrochloride and Sulfate)
1.00	Stevens, 1969
1.00	Moskowitz, 1968
0.98	Meiselman, 1968
0.86	Ernits, 1967 (Unpublished)
0.65	Moskowitz, 1972
0.54	Meiselman, 1971
0.54	Ernits, 1967
	Quinine (Hydrochloride and Sulfate)
0.52	Meiselman, 1971
0.49	Moskowitz and Arabie, 1971
0.49	Kocher and Fisher, 1970
0.36	Feallock, 1965
0.32	Bartoshuk, 1968
0.31	Meiselman, 1971
0.30	Smith, 1969
	Sucrose
1.80	Meiselman and Halpern, 1970
1.60	Moskowitz, 1970
1.47	Ekman and Akesson, 1965
1.40	Moskowitz, 1968
1.40	Moskowitz, 1970
1.30	Stevens, 1960
1.30	Stevens, 1969
1.10	Stone and Oliver, 1969
0.98	Meiselman and Halpern, 1970
0.79	Kocher and Fisher, 1969
0.70	Meiselman, 1968
0.67	Bartoshuk, 1968
0.62	Gregson and Russell, 1965
0.46	Feallock, 1965
	Hydrochloric Acid
1.48	Bartoshuk, 1968
0.87	Meiselman, 1968
0.84	Feallock, 1965

(cross-modality matching, etc.) have led to the conclusion that the relationship (the psychophysical function) between perceived stimulus intensity (S) and physical intensity (I) is best described by a power function of the form, $S = kI^n$. When plotted on log-log coordinates, a power function is a straight line with slope n. The arguments against and in favor of Stevens' power law are outside the interest of and beyond the scope of this paper. Suffice it to say that the reliable form of the data obtained from particular techniques provides a convenient tool for taste research.

Table 3 presents exponents of power functions for sodium chloride, sucrose quinine (hydrochloride and sulfate), and acid. At least two things are clear. First, the exponents for each taste quality (keeping in mind the above comments about pure tasting stimuli) are in overlapping distributions with different measures of central tendency. In other words, a different exponent appears to describe each quality. Second, the variability in published exponents is very large, the ratio of the greatest to the smallest being 3.9 for sodium chloride, 3.9 for sucrose, 3.3 for quinine, and 1.8 for acid. The finding of large variability among reported exponents is not typical of findings for other sensory modalities. In fact, the stability of the exponent from laboratory to laboratory and within laboratories across experiments has led to its being regarded as the *invariant* around which research can work.[118]

This search for invariance has motivated some current taste research. In a series of papers, Moskowitz[86-89] has attempted to show the stability of the exponent within taste quality categories. Specification of the invariant exponent within a quality permits the experimenter to develop mathematical models of various psychophysical relationships, for example, mixtures, equal taste intensities, relative sweetness, etc. Moskowitz argues that the exponent for each of the four qualities can be fixed at one value, e.g., 1.3 for sweetness. These and other papers then make use of these invariants for model building.

Several comments can be made about this approach to taste intensity scaling. First, the search for invariant(s) in taste scaling is intimately connected with the argument that direct magnitude scaling directly reflects biological processes.[86,119] In other words, the statement that 1.3 is the exponent for sugar sweetness function is strongly arguing that the mathematical relationship:

$$\text{sugar sweetness} = kX(\text{sugar concentration})^{1,3}$$

is not only a convenient description of the data but a true reflection of *the* operating characteristic of the system. If such a strong argument is being made, then what evidence is presented?

Moskowitz has presented the largest amount of data for sweetness. He claims that an exponent of about 1.3 describes the sugar sweetness psychophysical function.[87] It should be noted that no statistical curve-fitting analysis is used to determine whether or not the functions under examination are power functions. This is assumed. Again, when one is using direct scaling psychophysics as a tool to answer questions of methodology or receptor mechanisms, this assumption might appear to be part of the game. When one is trying to best describe the psychophysical function, this assumption is unwarranted. After assuming power functions, a least-squares analysis is performed to determine the slope of the straight line (which is the same as the power of the power function). For 15 sugars, the functions plotted against a molarity measure of physical concentration yield the distribution of exponents shown in Table 4. The median exponent (out of 15) is 1.22. On the basis of these data, it is unclear why 1.3 was chosen as *the* best estimate of exponent. Moskowitz claims that this value was suggested by earlier work.[86] However, that study reported a value of 1.43 for sucrose and a later study[87] obtained 1.4 for total intensity and 1.6 for sweetness.

Moskowitz[88] presents an impressive amount of data on scaling of 42 sugars. Glucose was used in each of the nine experiments as a control. Earlier, Moskowitz[87] had reported 1.18 as the exponent for glucose. The distribution of glucose exponents in the nine experiments is shown in Table 5. Exponents ranged from 0.90 to 1.73, with a median exponent of 1.31. For glucose, 1.3 appears to represent a good approximation of the average exponent. Since publications from other laboratories have not scaled glucose with the frequency with which they have scaled sucrose, comparative data are not available.

A distribution of all exponents reported for the 32 sugars appears to center at or around 1.3 as well

TABLE 4

Frequency Distribution of Psychophysical Function Exponents for Fifteen Sugars. (Data from Moskowitz.[87])

Range of exponents	Number
0.20 – 0.29	1
0.60 – 0.69	1
0.70 – 0.79	0
0.80 – 0.89	1
0.90 – 0.99	0
1.00 – 1.09	1
1.10 – 1.19	3
1.20 – 1.29	4
1.30 – 1.39	4

TABLE 5

Frequency Distribution of Psychophysical Function Exponents for Glucose in Nine Experiments. (Data from Moskowitz.[88])

Range of exponents	Number
0.90 – 0.99	1
1.00 – 1.09	2
1.10 – 1.19	0
1.20 – 1.29	1
1.30 – 1.39	3
1.70 – 1.79	2

TABLE 6

Frequency Distribution of Psychophysical Function Exponents for 32 Sugars. (Data from Moskowitz.[88])

Range of exponents	Number
0.40 – 0.49	1
0.50 – 0.59	0
0.60 – 0.69	1
0.70 – 0.79	0
0.80 – 0.89	1
0.90 – 0.99	2
1.00 – 1.09	5
1.10 – 1.19	3
1.20 – 1.29	7
1.30 – 1.39	11
1.40 – 1.49	3
1.50 – 1.59	3
1.60 – 1.69	4
1.70 – 1.79	3
1.80 – 1.89	2
1.90 – 1.99	0
2.00 – 2.09	0
2.10 – 2.19	1
2.20 – 2.29	0
2.30 – 2.39	2
2.40 – 2.49	0
2.50 – 2.59	0
2.60 – 2.69	1

(Table 6). Stevens[120] has presented loudness data in support of the notion that the exponent is distributed according to a bell-shaped curve. The above data appear to be in the right direction although a larger sample would be needed to smooth out the curve.

The question of distributions of exponents is involved with that of individual differences in exponents. Is the power law an artifact of group data or is it demonstrable for individuals? While the broader question is left to its proper domain of psychophysical investigation, one published paper has dealt with this issue in taste. Ekman and Akesson[32] obtained individual saltiness (sodium chloride) and sweetness (sucrose) psychophysical functions from eight and seven observers, respectively. All functions were satisfactorily fit by power functions. Exponents varied from 1.11 to 1.97 for saltiness, and from 1.33 to 1.98 for sweetness. Group data showed exponents of 1.58 and 1.47 for saltiness and sweetness, respectively. More observers would have to be tested to have sufficient data to make distributions of exponents.

Another approach to invariance of exponent within taste quality categories has come from direct scaling (magnitude estimation) of taste intensity of qualities within complex stimuli. This technique has been used by McBurney[70] and by Meiselman and Halpern.[82,83] Meiselman and Halpern asked observers to first rate the total taste intensity of the sample and then to break down the portion attributable to each of the four taste qualities, thus producing a quadrifid taste profile for each stimulus. Sucrose and two amino acids (glycine and dl-alanine) were used. Sucrose is the most commonly used "pure taste stimulus" for sweet and is generally assumed to have a simple taste. The two amino acids are known complex stimuli with large contributions of both sweetness and sourness. The authors concluded that the psychophysical equation (power function) describing many of the qualities of the complex tastes was similar to those previously reported for simple stimuli. For example, previously reported exponents for acids ranged between 0.7 to 0.9 (citing sip experiments only); the sourness of dl-alanine produced a 1.1 and that of glycine a 0.8. While these data were only suggestive, it was thought possible that the psychophysical relationships within

TABLE 7

The Magnitude Estimation Exponent and the Magnitude Production Exponent for Sodium Chloride (NaCl), Quinine Hydrochloride (QHCl), Sucrose, and Hydrochloric Acid (HCl). (Adapted from Table 1 in Meiselman, Bose, and Nykvist.[80])

	NaCl	QHCl	Sucrose	HCl
Magnitude estimation exponent	0.91	0.85	0.93	0.99
Magnitude production exponent	2.09	1.28	2.93	0.70

complex stimuli and mixtures might demonstrate that each taste quality has a representative descriptive function. This is another way of looking for invariance.

Thus, the search for invariance of the taste psychophysical function can take different forms and be approached at different levels. More data are needed, especially functions for individual observers, to resolve this issue. There is the possibility that each taste quality is best represented by a different function with a characteristic exponent.

It should be kept in mind that the reported values for most stimuli (Table 3) show broad variation. It appears, to this author at least, more instructive to examine the differences between exponents rather than study their sameness. The approach of trying to investigate differences is largely dealt with in the section of this article on procedure.

So far, we have been talking about direct psychophysical scaling using magnitude estimation. Other techniques exist for producing ratio scales. Magnitude production involves giving control of the stimulus dimension to the observer. In magnitude estimation, the experimenter presents discrete stimulus physical magnitudes to the observer who estimates their magnitudes using numbers in proportion to their perceived strength. In magnitude production, the experimenter presents numbers to the observer who chooses a stimulus which represents the number. If the second number is twice as strong as the first, the observer selects a stimulus which appears twice as strong. Until recently, the technique of magnitude production had not been applied to taste, probably because of the difficulty of stimulus control. Magnitude production is ideally done by giving the observer a continuously variable stimulus control.

Recently, Meiselman, Bose, and Nykvist[80] have produced such a piece of apparatus by using a three-way valve with two inputs and one output. One of the two inputs contains distilled water and the other contains a highly concentrated stimulus solution (e.g., 1.0 *M* sodium chloride). Turning the valve by using a set of reduction gears can produce varying proportions of the two inputs, thereby producing a continuously variable stimulus dimension from 0.0 *M* (distilled water) to 1.0 *M* sodium chloride. Using this apparatus, magnitude productions of taste intensity were obtained along with magnitude estimations for four stimuli representing the four taste qualities. Table 7 presents the exponents for each stimulus for the two procedures. Except for the acid, the exponent generated by magnitude production is greater than the exponent generated by magnitude estimation. This finding is in agreement with the findings of magnitude production of sensory intensity in other modalities.[121] Stevens and Greenbaum related the magnitude estimation-magnitude production difference to a so-called regression effect, wherein an observer tends to constrict the range of the variable dimension. They suggest that the geometric mean of the two exponents (estimation, production) might represent an unbiased estimate of the exponent.

The presentation of exponents (Table 3) can be adjusted to represent the findings for magnitude production (Table 8). The geometric mean of estimation and production is also included. The relatively large size of the production exponents for sodium chloride, sucrose, and quinine is even more apparent in this format. Clearly, the results of further magnitude production work must be included into specifications of psychophysical functions.

Moskowitz[88] argues against both the practical problems of magnitude production in taste and against Stevens' suggestions for averaging estimation and production. First, his suggestion is valid that sensory

TABLE 8

Exponents for Taste Functions Showing the Relative Size of Exponents for Magnitude Production. The Geometric Mean of the Magnitude Estimation and Magnitude Production Exponent Reported by Meiselman, Bose, and Nykvist (1972) Is Included. (Adapted from Meiselman, Bose, and Nykvist.[80])

	Sodium chloride
2.09	PRODUCTION
1.59	Ekman, 1961
1.58	Ekman and Akesson, 1965
1.43	Meiselman, 1968
1.40	Moskowitz, 1968
1.40	Stevens, 1969
1.37	GEOMETRIC MEAN
1.35	Meiselman, 1971
1.30	Stevens, 1960
1.05	Jones and Marcus, 1961
1.00	Lewis, 1948
1.00	Borg et al., 1967
0.97	Moskowitz, 1972
0.92	Bruvold and Gaffey, 1965
0.91	ESTIMATION
0.80	Meiselman, 1971
0.78	Meiselman, 1971
0.54	Kocher and Fisher, 1969
0.49	Smith, 1969
0.44	Feallock, 1965
0.42	Bartoshuk, 1968
0.41	McBurney, 1966

	Quinine (Hydrochloride and Sulfate)
1.28	PRODUCTION
1.04	GEOMETRIC MEAN
1.00	Stevens, 1969
1.00	Moskowitz, 1968
0.98	Meiselman, 1968
0.86	Ernits, 1967 (Unpublished)
0.85	ESTIMATION
0.73	Faull, Meiselman and Halpern, 1971
0.65	Moskowitz, 1972
0.54	Meiselman, 1971
0.54	Ernits, 1967
0.52	Meiselman, 1971
0.49	Moskowitz and Arabie, 1971
0.49	Kocher and Fisher, 1970
0.36	Feallock, 1965
0.32	Bartoshuk, 1968
0.31	Meiselman, 1971
0.30	Smith, 1969

	Sucrose
2.93	PRODUCTION
1.80	Meiselman and Halpern, 1970
1.62	GEOMETRIC MEAN
1.60	Moskowitz, 1970
1.47	Ekman and Akesson, 1965
1.40	Moskowitz, 1968
1.40	Moskowitz, 1970
1.30	Stevens, 1960
1.30	Stevens, 1969
1.10	Stone and Oliver, 1969
0.98	Meiselman and Halpern, 1970
0.93	ESTIMATION
0.79	Kocher and Fisher, 1969
0.70	Meiselman, 1968
0.67	Bartoshuk, 1968
0.62	Gregson and Russell, 1965
0.46	Feallock, 1965

	Hydrochloride Acid
1.48	Bartoshuk, 1968
0.99	ESTIMATION
0.87	Meiselman, 1968
0.84	Feallock, 1965
0.83	GEOMETRIC MEAN
0.70	PRODUCTION

adaptation problems would become critical in a production task in which continued presentation of a changing stimulus was used. The technique of Meiselman, Bose, and Nykvist[80] tries to avoid this problem with discrete presentations of the stimulus. In place of averaging of estimation and production, Moskowitz suggests the use of a third continuum (in addition to number and taste intensity) against which each is matched. This technique is basically cross-modality matching.

Another technique which has been recently applied to ratio scaling of taste intensity has been cross-modality matching. In this procedure the estimates of sensory intensity are made by adjustment of a

TABLE 9

Exponents for Taste Functions Calculated from Loudness Matches and Number Matches. (Data from Moskowitz.[86])

	Exponent	
	Magnitude estimate	0.64 X noise match
NaCl	1.22	1.09
sucrose	1.49	1.36
quinine	0.98	0.95
acid	1.04	0.95

second sensory stimulus. For example, if the observer perceives a second taste stimulus as being twice as strong as the first, he would adjust the intensity of a noise or tone to be twice as loud. It can be shown that the resulting matching function should produce a straight line on log-log coordinates with a slope equal to the ratio of the slopes of the two dimensions (here, taste and loudness). Whether this procedure validates other procedures is not an issue here. Our concern is with another approach to ratio scaling. Of course the argument can be and has been made that cross-modality matching is just another form of matching as is magnitude estimation; in one case the observer matches with numbers, in the other case he matches with sound intensity or another dimension.

Moskowitz[86] asked subjects for number matches (magnitude estimation) and loudness matches (cross-modality matching) for sodium chloride, sucrose, quinine sulfate, and tartaric acid. The loudness matches were multiplied by 0.64 to give estimates of the psychophysical functions for taste intensity. The two estimates can be directly compared (Table 9).

While the two figures for each stimulus are similar, in every case the loudness match exponent is less than the magnitude estimation exponent. The basis for this is unclear. It provided yet another example of the differences in psychophysical scaling of taste intensity which deserve further attention.

HUMAN TASTE RESEARCH PROCEDURES

Sensory research in vision and audition has been much more widespread than in gustation. Similarly, in these two "higher" senses the stimulus has been well defined. Over the years, rather definite and accepted procedures have developed for running human visual and auditory experiments. For example, choice of experimental subjects is determined by much more than their availability. No one would consider doing visual research without some consideration of the potential subject's sight. Persons with glasses, with uncorrected visual problems, with color blindness (objectively determined), or with a host of other problems would be either eliminated or would be intentionally chosen. Similarly in a visual experiment, the choice and presentation of stimuli would involve generally careful calibration of equipment. When periods of no stimulation were desired, the experimental room would be capable of blackout (zero stimulus) conditions. The effects of a large number of variables in vision are known, and in a well executed experiment, these would be carefully controlled. If relevance to a real life situation were desired, then the testing stimuli might be reading materials or pictures.

The comparable situation in human taste research is the following: 1) research procedures in taste are poorly, if at all, standardized; 2) the effects of many variables in taste research are unknown and/or poorly controlled; 3) little concern is given to the choice of experimental subjects; and 4) the relevance of taste research procedures to realistic situations involving taste (food ingestion, etc.) is questionable.

Taste research has one relatively unique problem compared to other senses: the constant presence of an adapting condition within the mouth. Complete drying of the tongue is not advisable and the value of rinses is questionable.

Choice of Subjects in Human Taste Research

In most taste research the criteria in choosing experimental subjects appear to be the availability of the

TABLE 10

Screening Test No. 1 from Meiselman and Dzendolet.[81] Percentages of Quality Responses to Four Screening Solutions. Forty Females and Forty Males Were Used.

		Qualities				
Subjects	Solutions	sour	salty	bitter	sweet	no taste
Females	HCl	57.5	5.4	28.2	7.8	1.1
	NaCl	3.9	86.4	5.0	2.9	1.8
	KCl	15.0	5.4	62.8	4.3	12.5
	Sucrose	11.4	2.9	14.6	45.4	25.7
Males	HCl	42.9	10.0	28.6	13.2	5.3
	NaCl	7.9	82.1	8.6	0.3	1.1
	KCl	19.6	3.7	49.6	10.0	17.1
	Sucrose	9.3	4.3	10.7	52.1	23.6

subjects and the experimenter's "feeling" that they are unbiased. In some cases, subjects are limited to one sex, more often males because of the potential problems with the female menstrual cycle. In some cases, smokers are avoided, and an age range is sometimes established.

Meiselman and Dzendolet[81] tested a total of 120 males and females on two different screening tasks based on correct responding near threshold. The first test asked for quality responses from subjects to 10 ml of sipped liquid. Stimuli were 2 m*M* hydrochloric acid, 50 m*M* sodium chloride, 20 m*M* potassium chloride, and 15 m*M* sucrose representing sour, salty, bitter, and sweet, respectively. Each of the four stimuli was presented seven times in random order with the exception that no stimulus was presented twice in succession. No rinses were used. A pause of 90 to 120 sec was used between stimuli. The percentages of quality responses to the four screening stimuli are given in Table 10. For both males and females, the quality label used most reliably was salty with NaCl. For both hydrochloric acid and potassium chloride, there was a tendency to use both sour and bitter, with one being used about half as much as the other. Weak sucrose elicited reports of sour and bitter and to a lesser degree salty as well as sweet.

In order to test the effect of a criterion on subject selection, Meiselman and Dzendolet chose the arbitrary criterion of four "correct" quality responses out of seven presentations for each stimulus. Nine males (22.5%) and fifteen females (37.5%) reached or exceeded this criterion for all four stimuli.

A second screening task was devised based on these data. In the new test the stimuli were 2 m*M* hydrochloric acid, 40 m*M* sodium chloride, 0.008 m*M* quinine sulfate, and 25 m*M* sucrose. Half of the subjects were run according to the procedure used above, except only six replications were used. The other subjects were run in a correction procedure, in which the first four stimuli (one of each quality) were presented with the added information of how the average subject would respond. Each subject was encouraged to give his own opinion. After the first four stimuli, no corrections were supplied.

Table 11 presents percentages of quality responses for the second test. The percentage data were subjected to an analysis of variance, and the instruction variable (correction vs. noncorrection) was not significant. Subjects continued to make the sour-bitter confusion, especially with weak acid. Disregarding the correction procedure, 10% of the females and 28% of the males in both tests (n = 120) made the confusion. A criterion of correct responding was arbitrarily set at 4/6 presentations. This yielded one male and three females in the noncorrection groups, and two males and five females in the correction groups. The totals therefore are three males (15%) and eight females (40%). Thus, both tests show females slightly more sensitive than males to quality responses to near threshold solutions.

These data are not sufficiently broad in either subject population or stimulus population to be definitive. They do suggest the need for further work to develop screening procedures for human taste research. Many of the phenomena dealt with in this review involve situations in which observers are asked to respond to relatively weak stimuli. A task such as that described by Meiselman and Dzendolet might be appropriate.

In a series of investigations related to studies of heredity, Fischer and colleagues have uncovered a pattern of responding based on threshold measurements. This work is reviewed elsewhere in this paper. Its

TABLE 11

Screening Task No. 2 from Meiselman and Dzendolet.[81] Percentages of Quality Responses to Four Screening Solutions. Ten Males and Ten Females Each Received Either a Correction or Noncorrection Procedure.

			Qualities				
Subjects	Procedure	Solutions	sour	salty	bitter	sweet	no taste
Females	Noncorrection	HCl	56.7	8.3	33.3	0	1.7
		NaCl	5.0	76.7	6.6	0	11.7
		Quinine	5.0	0	63.3	5.0	26.7
		Sucrose	5.0	0	11.7	75.0	8.3
Females	Correction	HCl	66.7	1.7	28.3	3.3	0
		NaCl	1.7	83.3	5.0	3.3	6.7
		Quinine	18.3	0	55.0	5.0	21.7
		Sucrose	3.4	0	8.3	88.3	0
	Noncorrection	HCl	43.4	5.0	36.7	15.0	0
		NaCl	6.7	65.0	16.7	1.6	10.0
		Quinine	10.0	10.0	43.3	1.7	35.0
		Sucrose	5.0	0	1.7	80.0	13.3
Males	Correction	HCl	60.0	1.6	36.7	1.7	0
		NaCl	10.0	76.7	6.7	5.0	1.6
		Quinine	23.3	0	35.0	13.4	28.3
		Sucrose	1.7	1.7	1.7	93.2	1.7

relevance here is to suggest another avenue for development of a screening task. Fischer has determined that low thresholds for some compounds are associated with low thresholds for other compounds. This type of approach can lead to a more thorough specification of the interrelationships between thresholds for various substances.

Two variables in human subject choice deserve attention: age and smoking. Many experiments have assessed the role of age on quantitative and qualitative taste responses. Increasing age has no significant effect on the ability to name taste solutions representing one or more of the four "basic" tastes or of PTC or related compounds. Increasing age does have an effect in threshold tasks for solutions representing one or more of the four basic tastes or PTC type compounds. This is clear in Table 12, which summarizes this literature. Interestingly, the effect of age might be strongly related to the effect of another variable, cigarette smoking.

Several studies had shown that cigarette smoking does affect taste responses.[2,97,113] Kaplan, Glanville, and Fischer[58] concluded that age is related to increased taste threshold only for smokers. Glanville, Kaplan, and Fischer[43] were able to find a deterioration in thresholds with age using the same age groups when smokers were not separated from nonsmokers.

Choice and Calibration of Stimuli

Criteria for selection of chemical grade (reagent, USP, etc.) are not standard in taste research. Criteria for distilled water are not standard. Criteria for maintenance of stimuli and periodic calibration of stimuli are not standard. Most of those doing taste research are forced to use chemistry. The equipment and procedures for much of the standardization needed in taste research are available in any chemistry laboratory.

Much of the need for control in taste research is related to the same ignorance of taste which stimulates the lack of control. Until we know what the stimuli for taste are, until we understand the taste receptor mechanisms, and until we specify the taste psychophysical relations, taste research must be better controlled so that we have confidence in what the results demonstrate. An experiment using tap water as a solvent is generally giving a mild salt solution (among many other things). The experiment cannot assume

TABLE 12

Effect of Age on Taste Responses. The Experiments Are Divided According to What the Task Was: Quality Response or Threshold.

Response Required	Authors	Effect
Experiments on one or more of four "basic tastes."		
Quality Response	Byrd and Gertman (1959)	no effect
	Byrd (1958)	no effect
	Cohen and Gitman (1959)	no effect
Thresholds	Cooper, Bilash and Zubek (1959)	significant effect
	Glanville, Kaplan and Fischer (64)	significant effect
	Kaplan, Glanville and Fischer (65)	significant effect
	Richter and Campbell (1940)	significant effect
	Hinchcliffe (1958)	significant effect
	Hinchcliffe (1962)	significant effect
Experiments on PTC type compounds:		
Quality Response	Fox (1932)	no effect
	Synder (1931)	no effect
	Cohen and Ogden (1949)	no effect
	Rikimaru (1936)	no effect
Thresholds	Blakeslee and Salmon (1931)	significant effect
	Harris and Kalmus (1949)	significant effect
	Mohr (1951)	significant effect
	Kalmus and Trotter (1962)	significant effect
	Glanville, Kaplan and Fischer (64)	significant effect
	Kaplan, Glanville and Fischer (65)	significant effect

that responses to table sugar in tap water are necessarily the same as responses to reagent grade sucrose in distilled water.

Wherever possible from the viewpoints of cost, etc., reagent grade chemicals should be used. In any case the grade of chemical used should always be specified in a report of research. Solutions should be made with the reagent grade chemical and distilled water. The latter is defined, not by the equipment which produced it but by the physicochemical properties of the water. These can be determined by several pieces of equipment, available in most chemistry laboratories: a conductivity meter, a refractometer, and a fluorometer. These three instruments should be used to check the purity of the distilled water, to check the proper levels of the solutions made up for stimuli, and to calibrate the stimuli from time to time. When stimuli are properly checked and rechecked from time to time, then errors of preparation and errors from spoilage cannot affect results.

It should be unnecessary to mention that the precautions outlined above are a waste of effort unless all laboratory glassware and equipment are kept clean. Here clean does not mean clean to the eye, but chemically clean.

Stimulus Delivery

Many means have been used to deliver the taste stimulus liquid to the tongue. Research has not yet elucidated the properties of each procedure, and therefore the choice of experimental procedures is still a decision subjectively determined. Briefly, let us define the various delivery systems and note some of their more obvious advantages and faults.

(1) Brushing of stimulus onto the tongue. In this procedure, the stimulus is mechanically applied to the tongue. This procedure can be gross, involving a large tongue area,[22] or can be as refined as delivery of one

TABLE 13

Exponents for Taste Functions of Sodium Chloride Showing Effect of Procedure. Exponents are Listed in Order of Decreasing Size.*

	Sodium Chloride	
	2.09	PRODUCTION
Ekman, 1961	1.59	
Ekman and Akesson, 1965	1.58	
Meiselman, 1968	1.43	
Moskowitz, 1968	1.40	
Stevens, 1969	1.40	
	1.37	GEOMETRIC MEAN
Meiselman, 1971	1.35	
Stevens, 1960	1.30	
Jones and Marcus, 1961	1.05	
Lewis, 1948	1.00	
Borg et al., 1967	1.00	
Moskowitz, 1972	0.97	
Bruvold and Gaffey, 1965	0.92	
	0.91	ESTIMATION
	0.80	Meiselman, 1971 (W)
	0.78	Meiselman, 1971 (D)
	0.54	Kocher and Fisher, 1969 (D)
	0.49	Smith, 1969 (D)
	0.44	Feallock, 1965 (d)
	0.42	Bartoshuk, 1968 (D)
	0.41	McBurney, 1966 (D)

*Experiments cited to the left of the exponent used a sip procedure; those cited to the right used a flow procedure. Flow experiments are distinguished as follows: D, dorsal flow; W, whole mouth flow; d, dorsal flow to small area.

drop to one papilla.[11] In the more gross instances, the taste sensation is intermingled with the sensations resulting from tactile senses of the tongue. With very weak stimuli this could present a problem. Control over the effects of saliva is possible if the tongue is extended from the mouth with the lips closed on it. Control of the movement of stimulus onto the tongue (flow rate, etc.) is impossible.

(2) Sipping. In this procedure, the subject brings a glass or other container to his lips and either sucks in the liquid or pours the liquid over his tongue. This probably represents the stimulation condition most generally comparable to real life ingestion situations. However, control of the situation is minimal. Saliva mixes with the stimulus and dilutes it. The effects of this in adaptation situations can be somewhat reduced by repeated sips of solutions. Control of stimulus entry is impossible.

(3) Restricted dorsal flow procedures. These procedures involve delivery of a flow of stimulus to a portion of the tongue, usually a section of the anterior dorsal surface. This can be accomplished with a pipette or medicine dropper, or with the use of a tongue chamber which routes the flowing solution to a small tongue area.[38] These procedures have the advantage of using a flowing stimulus and thus maintaining stimulus constancy. In most instances the effects of saliva can be minimized. For studying small tongue areas these procedures are advisable, but for generalizing to how the entire taste system works they are potentially misleading because of the differential sensitivity of the tongue. Also with the various chambers, one has to contend with the mechanical influence. Control over stimulus movement is possible.

(4) Anterior dorsal flow. This procedure has been widely used (see Table 13 for references). The subject extends his tongue and closes his lips on it, insuring no saliva. Solution is flowed over the outstretched tongue. This position can become uncomfortable if prolonged. Control of stimulus delivery (flow, etc.) is possible, although not as well as with tongue chambers.

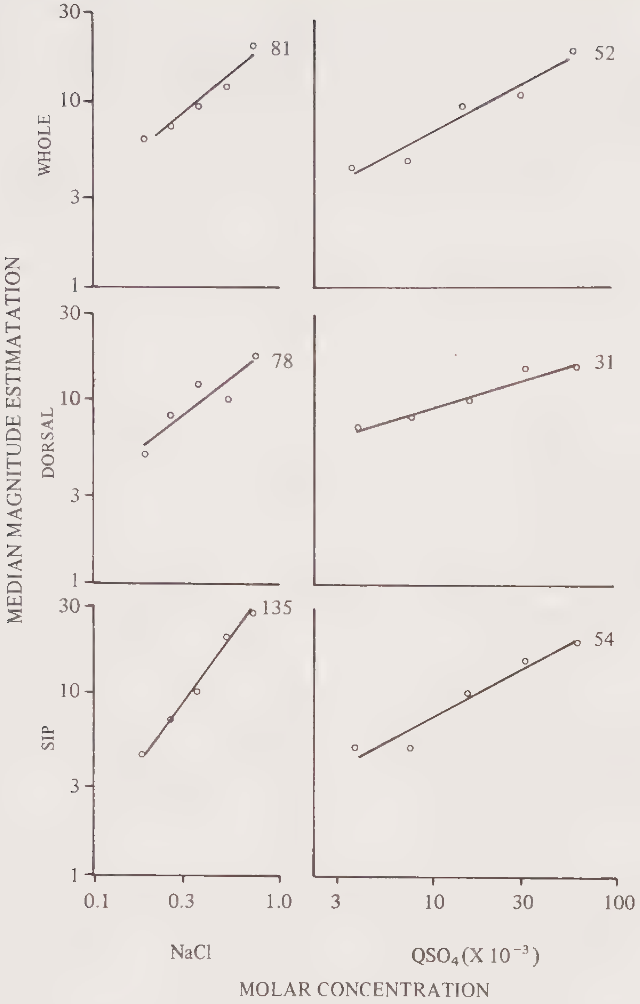

FIGURE 2. Effect of presentation procedure on taste power functions. Each point represents two replications on each of six subjects. The slopes of the best-fitting straight lines are shown next to each function. (Adapted from Meiselman.[78])

(5) Whole mouth flow. This procedure was introduced with a mechanism called the Cornell gustometer.[1] The device used a dental impression compound dam and inflow and outflow tubes to deliver a constant flow of liquid to the entire mouth cavity, and then remove the material by siphoning. Bujas, Majer, and Ostojcic[17] used a similar procedure, and more recently Meiselman[78] has revived the procedure. Control over saliva is exercised by constant removal of the saliva as it enters the mouth. Control over stimulus flow is possible. The entire mouth is used as in normal eating or drinking.

Clearly, one procedure is not appropriate for every kind of experiment. Single papilla stimulation requires accurate delivery of small volumes, whereas whole mouth adaptation involves delivery of large volumes with rapid replacement. Procedures utilizing only the anterior portion of the tongue yield data which are comparable to electrophysiological recordings from animal chorda tympani nerve. Meiselman[78] investigated the effects of three different stimulus presentation systems on magnitude estimation functions of sodium chloride and quinine sulfate, an anterior and posterior tongue stimulus, respectively. Figure 2 shows the results. Dorsal flow and whole mouth flow produced similar psychophysical functions for sodium chloride, whereas the sipping task produced a significantly steeper function. For the bitter quinine stimulus,

TABLE 14

Exponents for Taste Functions of Quinine Showing Effect of Procedure. Exponents are Listed in Order of Decreasing Size.*

Quinine (Hydrochloride and Sulfate)

	1.28	PRODUCTION
	1.04	GEOMETRIC MEAN
Stevens, 1969	1.00	
Moskowitz, 1968	1.00	
Meiselman, 1968	0.98	
Ernits, 1967 (Unpublished)	0.86	
	0.85	ESTIMATION
Moskowitz, 1972	0.65	
Meiselman, 1971	0.54	
	0.54	Ernits, 1967 (D)
	0.52	Meiselman, 1971 (W)
Moskowitz and Arabie, 1971	0.49	
	0.49	Kocher and Fisher, 1970 (D)
	0.36	Feallock, 1965 (d)
	0.32	Bartoshuk, 1968 (D)
	0.31	Meiselman, 1971 (D)
	0.30	Smith, 1969 (D)

*Experiments cited to the left of the exponent used a sip procedure; those cited to the right used a flow procedure. Flow experiments are distinguished as follows: D, dorsal flow; W, whole mouth flow; d, dorsal flow to small area.

both whole mouth procedures (sipping or whole mouth flow) produced similar functions, whereas the dorsal flow produced a flatter function. These results indicate that for different stimuli, different variables can be effective. For salt, the effect of a sipping vs. a flowing task is quite clear-cut as shown in Table 13, which is a regrouping of Table 8. When experiments are divided by stimulus presentation procedure a clear break results. The results for quinine are almost as clear (Table 14).

What these findings mean is that for salt, sipping the stimulus will give more discrimination between stimuli. With a steeper psychophysical function, there is a greater perceptual difference between adjoining stimuli. For quinine, this effect holds up but not as clearly. There, an additional problem is whether the entire mouth is used: the rear of the mouth is usually considered most sensitive to bitter.

Meiselman, Bose, and Nykvist[79] suggested that one uncontrolled variable among the different procedures was flow rate of the stimulus. This variable has received little attention in previous research, either animal or human. Using a specially constructed tongue chamber which exposed the sensitive borders of the tongue, they presented 1 *M* sodium chloride at flow rates of 2, 5, and 8 cc/sec rate of flow. Results indicated that subjects perceived the intensities of saltiness to increase significantly with increased flow rate. In other words, the same strength stimulus tastes stronger when it is moving faster. A more complete investigation is needed to account for other methodological findings in terms of flow rate.

Another variable in stimulus delivery is temperature. While there has been general agreement that temperature is critical in any biological system, the effect of temperature on taste is as yet unclear.[92,96,107] Even recent studies have not reported consistent effects. Pangborn et al. report decreased taste intensity at temperatures significantly different from body temperature, Moskowitz reports maximum response at body temperature, but Stone et al.[123] report no temperature effect.

In practice most experimenters use one of two temperatures, room temperature of about 22°C or tongue temperature of about 34°C. Whichever is used, it is probably most important that a constant temperature be used throughout an experiment, or across experiments if comparisons will be made. Presentation of stimuli at tongue temperature is often used to allow the subject to focus on the taste rather than on any temperature difference.

Many investigators routinely use rinses in their experimental procedures to rid the mouth of any stimulus from the previous trial and to try to begin each trial at the baseline. The almost universal rinse is water, usually distilled. Several investigators have cautioned on the use of water rinses.[11,74,81] The problem lies in the fact that water is not a zero point. As pointed out elsewhere in this paper, the taste of water appears to depend on the prior adaptation of the tongue. To use such a variable stimulus as a rinse appears very questionable. The procedure used instead of a water rinse is waiting. This is essentially a saliva rinse, i.e., allowing time for saliva to wash away previous stimuli. These rest periods last up to 10 minutes.[11] Obviously, a water rinse can be combined with a rest period. The water rinse can serve to mechanically remove much material, and a lengthy pause can then allow any small effect of water taste to dissipate.

Relevance of Human Taste Research Procedures

In their zeal to overcome the difficulties of investigating a sensory system in which the stimulus is unknown, the appropriate quality distinctions are arguable, and the underlying biology is not settled, taste researchers seem to have lost sight of the place of taste in the real world. Taste is studied primarily because of its role in food ingestion, yet many of the procedures used in taste research have little or no relationship to food intake.

For example, the choice of stimuli in taste research is mainly limited to sodium chloride, sugar, hydrochloric, tartaric or citric acid, quinine, or caffeine. These stimuli occur rarely in nature in their pure form. While use of pure stimuli might help to uncover how the taste system works, the exclusive use of pure or simple stimuli is questionable. Some exceptions to this rule exist, most notably those who have mixed these stimuli into real foods.

The choice of stimulus delivery systems is also questionable. This topic was covered above. In the real world stimuli are rarely flowed over the tongue or discretely presented to small tongue areas. I am not suggesting that these procedures have no place in taste research. However, the effects of using these procedures must be researched so that we know the effects of the procedures used. The procedures should be compared to modes of stimulus intake more typical of eating and drinking.

SENSORY ADAPTATION

Sensory adaptation of taste has been a topic of research and discussion for over 100 years, and represents one of the most favored of taste research topics, not only in human psychophysical approaches but also in animal physiological research as well. The continuing interest in the phenomena related to prolonged stimulation probably results from the variety of these phenomena. This has led to confusion in the use of the term "adaptation." As recently discussed by Bartoshuk,[5] it is unclear whether adaptation refers to any or all of the following: (1) the procedure of prolonged stimulation itself without considering its effects; (2) the decrement in sensation observed with prolonged stimulation; (3) the disappearance in sensation with prolonged stimulation; (4) the physiological mechanism underlying the decrement and/or disappearance of sensation; (5) the qualitative changes in stimuli with prolonged stimulation; (6) threshold changes with prolonged stimulation. Probably others could be added to this list. This section will deal with those topics related to adaptation. Research which uses adaptation as a research tool to study a phenomenon other than adaptation will be treated elsewhere, e.g., see cross-adaptation.

Course of Gustatory Adaptation

Traditionally, the course of gustatory adaptation has been measured by threshold changes. This work, largely done by Hahn[47] and his colleagues, has been reported widely in reviews of the last 25 years.[5,42,99,100] Because of the repeated presentations of these data, and hence their relative familiarity and availability, they will not be treated here except in capsule form.

Generally, prolonged stimulation leads to an elevation of threshold to a level slightly higher than that of the adapting solution. This elevation is proportional to stimulus concentration, and adaptation time is longer with higher concentrations. Adaptation functions within and across modalities may vary in shape, although the form of recovery from adaptation is usually similar.

TABLE 15

Adaptation Times for Four Stimuli Using Whole Mouth Flow Procedure. (Adapted from Abrahams, Krakauer and Dallenbach,[1] Table I, and Krakauer and Dallenbach,[64] Tables I and II.)

	Range of Concentration (*M*)	Range of adaptation time (sec)
Sodium chloride	0.84–3.11	16.2–115.6
Sugar	0.066–1.260	46.5–326.0
Tartaric acid	0.0022–0.013	78.6–194.8
Quinine hydrochloride	0.000013–0.000083	74.7–115.6

TABLE 16

Adaptation Times for Sodium Chloride Using Whole Mouth Flow Procedure. (Adapted from Bujas, Majer, and Ostojcic,[17] Tables 3, 4.)

		Subject	
		A	B
Sodium chloride	0.06	78.51	82.75
Concentration (*M*)	0.12	106.42	–

TABLE 17

Number of Complete Adaptations after Two Minutes of Continuous Stimulation Using One of Four Procedures. Each Condition Was Run Twice on Each of Five Observers, Making the Highest Total Possible Per Cell 10.

Procedure	NaCl (mM)					QSO (mM)				
	180	255	360	510	720	.0375	.076	.155	.315	.600
Sip	5	4	2	0	0	2	0	0	0	0
Resips	3	2	1	1	0	4	2	0	0	0
Dorsal flow	6	5	4	5	3	2	2	2	2	2
Whole mouth flow (Cornell)	4	3	2	0	0	5	2	2	2	2

The time required to arrive at some measure of adaptation has been investigated in several laboratories. A device called the Cornell gustometer (see Procedure section), which presents a constantly moving stimulus to the whole mouth, has been used in several investigations. Dallenbach and his associates measured the times for complete adaptation (Table 15). Bujas, Majer, and Ostojcic[17] obtained many replications of adaptation time measurements from two subjects using a simpler modification of the Cornell gustometer, and found much longer adaptation times (Table 16). Considering the relatively weak stimuli used by Bujas et al., the adaptation times are high relative to Table 15.

The time required for complete adaptation has not been the only issue. Recent investigators have reported some difficulty in obtaining complete adaptation in all subjects, i.e., adaptation to the point of no sensation.[3,69,76] This is surprising since both McBurney and Bartoshuk used a dorsal tongue flow technique which maximizes stimulus constancy and hence should aid in reaching complete adaptation. Meiselman (unpublished data) asked subjects for direct magnitude estimates of sodium chloride and quinine sulfate solutions at intervals over a two-minute period. He noted the number of complete adaptations, report of zero magnitude, at the end of the two-minute period using three different procedures (Table 17).

TABLE 18

Number of Complete Adaptations out of 40 Possible in Two Minutes Using Four Procedures Arranged by Observer.

Observer	NaCl	QSO_4
1	0	1
2	2	1
3	8	0
4	28	25
5	11	4

These data suggest that the sipping and whole mouth procedures are equivalent for adaptation of sodium chloride and that the dorsal flow procedure is superior to sip procedures.

The breakdown of these data by subject is of interest (Table 18). Thus, some observers adapt more readily than others, and some adapt to certain compounds more readily than to others. The role of individual differences in adaptation and the mechanisms responsible for them (saliva, etc.) is an unsolved issue. Whether or not a particular subject will show complete adaptation to a particular compound cannot be specified as yet, nor can the time for this event be specified.

An important variable in obtaining adaptation recognized by many investigators has been tongue movements. Moving the tongue brings previously unexposed receptors into contact with the stimulus, bringing about an increase in sensation. Krakauer and Dallenbach[64] argued that tongue movements and the resulting rise in sensation were responsible for the relatively long adaptation times for one of their subjects. Bekesy[10] used graphical outputs from his automatic gustometer to demonstrate the effects of tongue movement during adaptation. The typical smooth adaptation function is jolted and made jagged by tongue movements.

The problem with tongue movements and adaptation is not the agreement on its importance but the means of controlling it and the meaning of this for relating taste experiments to real life tasting situations. Clearly, in the latter, the tongue is very active. Halpern (unpublished) has suggested a means of stabilizing the tongue in experiments using the dorsal tongue flow procedure outlined elsewhere in this paper. The subject is asked to extend his tongue through two parallel bars (plastic) and make contact between the tip of his tongue and a small rough area on a plastic disc. Maintaining this contact keeps the tongue in a relatively stable position.

Recent data have shed some light on the shape of the adaptation process itself. Meiselman[76] asked subjects to give magnitude estimations of the strength of a solution either held in the mouth for 5 minutes or refreshed with fresh solution every minute. The results indicate that the strength of each solution fell from a beginning rating of 10 to a rating of 1 in 5 minutes. When repeated sips of fresh solution were used to offset the changes from salivary dilution, the final adaptation level was closer to 3. Interestingly, the shapes of these functions for sucrose, sodium chloride, and quinine sulfate were all similar in contrast to the findings of Hahn,[47] who observed differences in the shapes of adaptation functions based on thresholds for sodium chloride, sugar, and glycocol. This is another instance where threshold data and direct scaling data yield different results.

Meiselman (unpublished) has also examined the changes in the psychophysical function during adaptation. In other sensory modalities there is general tendency toward increased slope (exponent) and increased threshold with increased adaptation level. Meiselman presented two-minute stimulations of sodium chloride or quinine sulfate to observers using four procedures: sipping, repeated sipping, dorsal flow, or whole mouth flow (Cornell gustometer). Observers gave magnitude estimations at 10-sec intervals following the procedure of Meiselman[76] to map out the course of adaptation and at the same time yield psychophysical functions when the data for different concentrations are combined. Meiselman concluded from the data that for both salt and quinine the Y-intercept decreases in value with increasing adaptation time, with the dorsal flow procedure producing consistently lower Y-intercept values. The change in exponents shows a distinction between the two compounds: exponents for salt generally increase with increasing adaptation, whereas exponents for quinine are stable over time.

Effects of Taste Adaptation

Traditional studies of adaptation effects concentrated on measuring decreased responsiveness through measures of threshold, as outlined briefly above. Recently, both the subject and technique of gustatory adaptation research have changed. The subject has shifted to what new or increased information is produced during prolonged adaptation, and the technique often used is direct scaling.

McBurney, Kasschau, and Bogart[72] did use the traditional method of constant stimuli to determine taste jnds (the just noticeable difference between two stimuli). The obtained difference threshold was 0.09 *M* after adaptation to 0.1 *M* sodium chloride and 0.18 *M* after adaptation to water. These values agree with the summary of previous research provided by Pfaffman.[100] In other words, the ability to discriminate change is better after adaptation to salt than after adaptation to water. In this way, adaptation increases information rather than simply decrementing it.

It is sometimes thought that concentrations below the level of adaptation. i.e., subadapting concentrations, are not tasted. In a series of papers, Bartoshuk and McBurney have shown that not only are subadapting stimuli tasted but also that their quality is altered.[3,7,69] This was first demonstrated qualitatively for sodium chloride concentrations between 0.1 *M* and 0.001 *M* plus water.[7] Subjects were asked for qualitative labeling (sour, salty, bitter, sweet, or tasteless) of stimuli preceded by either 0.003 *M* or 0.03 *M* salt adaptation. Supra-adapting level stimuli were predominantly called salty; stimuli at the adaptation level were called tasteless; and subadapting stimuli were labeled bitter, sour, or tasteless.

McBurney[69] asked observers to give magnitude estimates of sodium chloride stimuli between 1.0 *M* and 0.001 *M* plus water after adaptation to 0.1, 0.01, or 0.001 *M* salt. Qualitative descriptions were not obtained. For each adapting level, perceived magnitude reached a minimum at the adapting level, rising in magnitude at both supra-adapting and subadapting levels.

Bartoshuk[3] obtained both magnitude estimates and quality reports from observers who received subadapting and supra-adapting solutions of sodium chloride, quinine hydrochloride, sucrose, or hydrochloric acid. Subadapting tastes increased in intensity with decreasing concentration (with a maximum at water), and the quality varied with the stimulus: bitter for salt, sweet for quinine, bitter for sucrose, and probably sweet for the acid. The subadapting tastes did not depend on complete adaptation, although this was obtained in most instances.

One problem with examining subadapting quality shifts is that the quality dimension of most stimuli is not unitary, as mentioned previously. This has been well documented for sodium chloride.[100] Since sodium chloride concentrations below 0.03 or 0.04 *M* are often called sweet, their quality shift from salty to sour-bitter might actually be a shift from sweet to sour-bitter. The resting sodium level in the mouth is near this value (0.04 *M*), and perhaps a subadapting situation always exists. When a water adaptation condition is imposed, the sweet reports persist.[3] It appears legitimate to question whether subadapting salt would be called sour-bitter if the adapting level and subadapting levels were well above the range usually used, i.e., the range which is already multidimensional.

Meiselman (unpublished) has recently studied different aspects of the subadapting experiments with salt. He compared the dorsal tongue flow procedure used in the research of Bartoshuk and McBurney with the whole mouth flow of the Cornell gustometer. This appeared advisable because of the prevalence of bitter responses and the knowledge that the back of the tongue, unavailable with dorsal flow, is especially sensitive to bitter. The stimuli used were 0.001, 0.01, 0.1, and 1.0 *M* sodium chloride and the adapting level was 0.1 *M*. Subjects gave both magnitude estimates of all four qualities (profiles). The estimation of bitterness was significantly greater with whole mouth flow than dorsal flow for 0.001 and 0.01 *M* salt subadapting stimuli. Thus, the use of whole mouth procedures is probably advisable in adaptation research.

Meiselman further tested the role of the normal sweetness of low concentration salt stimuli in eliciting quality shifts with adaptation. Observers were given a treatment with either gymnemic acid aqueous decoction, a known sweet suppressant, or a control substance of similar bitter taste.[82] After a 10-minute wait to avoid any cross-adaptation effects, the adaptation with 0.1 *M* NaCl was again tested on the four stimuli as described above. No significant differences in magnitude estimates of subadapting tastes were observed. Since the gymnemic acid suppressed sweetness, it can be argued that the mechanism for subadapting sour-bitterness does not depend on sweetness. Further research should directly attempt to elicit sour-bitterness from subadapted sodium chloride at relatively high concentrations.

In the course of these studies, Meiselman observed repeatedly that subjects do describe the subadapted taste of NaCl as a mixture of sour and bitter. This is in agreement with the original observations of Bartoshuk et al.[7] Bartoshuk[3] has suggested that bitter alone might better represent the subadapted taste of salt.

TASTE MIXTURES

A specification of the effects of mixing tastes and an understanding of taste mixture mechanisms are essential to our understanding of how taste functions in the real world. With few exceptions, pure tastes rarely occur in isolation. As noted in the last section, tastes generally occur in one sequence or another, necessitating the consideration of adaptation and cross-adaptation. Also, tastes usually occur in mixtures. As with adaptation, taste mixtures have been studied for some time,[103] but the basic phenomena and mechanisms are still not established.

Mixtures of the Same Taste

Most of the research in mixtures of substances with the same tastes has been done with sweet-tasting compounds, probably because of their greater commercial interest. Recent work by Moskowitz[91] has helped to refocus attention in this area to the mathematical form of sweetness mixtures.

The basic question in the mathematical models is what is added in taste mixtures, physical units, or subjective units. Earlier work[20,24] suggested that a mixture of *a* and *b* was equivalent to the physical concentrations of each (C_a, C_b) expressed as the fraction of glucose sweetness which it represented (k_1, k_2, etc.). In other words,

$$C_{a,b(mix)} = k_1 C_a + k_2 C_b$$

An alternate presentation of this model takes the form of the power function of taste intensity growth with physical concentration. As Moskowitz[91] notes, this assumes that the taste system responds to the mixture as it would to a single stimulus since the response occurs after addition of physical concentrations. In mathematical form this would be

$$T_{a,b(mix)} = k_3 (C_{a,b})^n = k_3 (k_1 C_a + k_2 C_b)^n$$

The argument could be made, however, that the taste system sums psychological units and not physical concentrations as above. This can be represented as follows:

$$T_{a,b} = k_1 C_a^n + k_2 C_b^m$$

Here *m* and *n* may be different. While supporting this model of psychological summation, recent authors[57,122,123] have often noted synergistic effects, that is, a resultant mixture sweetness greater than the sum of the individual component sweetnesses.

Moskowitz[91] directly tested the different mathematical relationships for sweetness mixture of sugars (glucose, fructose) and artificial sweetners (saccharin,cyclamate). His results showed no clear superiority of the model in which physical concentrations are summed when compared to the model in which subjective sweetnesses are summed. Moskowitz goes on to reanalyze the data of previous experimenters in order to resolve this dilemma, but the result is never clear cut. While this work has not specified the results of sweetness mixtures, it has perhaps pointed the direction of future research in this area.

Mixtures of Different Tastes

The work on mixtures of different tastes has naturally been varied because of the variety of compounds and possible combinations. Several recent reviews of this area[5,90,95,103] have concluded the same thing, namely, that within mixtures of different tastes, the tastes usually suppress each other except with some very weak tastes which produce enhancement.

Since the detailing of what results can be expected from various mixtures has been presented in several sources,[103] what is needed is a more standardized procedure for doing mixture experiments to avoid the methodological jumble of the past 25 years. A standardized experiment might consist of the following:

Use of certain compounds to represent taste qualities, perhaps sodium chloride for salty, sucrose for sweet, quinine hydrochloride for bitter, and hydrochloric acid for sour. Other compounds could be added in any particular study, but consistent use of these four would permit more comparison between studies.

Use of subthreshold concentrations or suprathreshold concentrations or both. The inclusion of at least one subthreshold concentration might be a good idea.

Standardized stimulus presentation procedure. Naturally this involves consideration of a large number of variables, as discussed above. Until we learn differently, it would be best to use a whole mouth procedure (either sipping or whole mouth flow). The whole mouth flow technique offers more stimulus control, but is somewhat more complicated and cumbersome. Use of the whole mouth is advisable so that the results will be more applicable to real life situations. Differential sensitivity of different mouth areas might present a problem in presentation to smaller areas.

Control of adaptation level by use of an appropriate interval between presentations and by consistent use of rinses. In keeping with previous discussions on procedures, a rinse is probably acceptable if followed by a sufficiently long interval.

Use of magnitude estimation method of subjective response. If this is done with a standard, this will permit precise determination of enhancement or suppression within the mixture.

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BIOGENESIS

Biogenesis is the natural process by which flavor develops with progressive ripening, reaches an optimum value corresponding to the perfect ripening stage, and subsequently exhibits a generalized rapid decay.[1-3] The most relevant studies of the biogenesis of fruital aromas are those regarding banana and avocado. In the first stage of the ripening of banana, there is a strong and continuous increase in carbon dioxide production; subsequently carbon dioxide levels reach a maximum and finally decrease. During ripening the total acids in the pulp also increase; this is due primarily to formation of malic and citric acids, whereas the original oxalic acid content decreases during ripening to about 60%. Among the amino acids, valine and leucine appear to be precursors (at least in part) to the banana flavor, as their decrease during ripening is accompanied by the formation of isobutyl and isoamyl alcohols and the corresponding acetates. Even oleic acid appears to be a banana flavor precursor leading to the formation of 2-hexanal.

While data on flavor biogenesis is scarce and fragmentary, it appears that flavor formation during ripening takes place via the degradation mechanism rather than synthesis with enzymes playing a key role.

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IDENTIFICATION AND EVALUATION OF FLAVORS

Identification

A fundamental problem challenging the creativity of the flavor chemist is the identification of active principles of natural flavors with the view of removing irrelevant constituents, reproducing the flavor synthetically or at least specifying generally relevant characteristics, and insuring their functionality in the finished food substrate. For a successful identification it usually is necessary to (1) *isolate* the flavor complex, (2) *fractionate* the complex into basic constituents, and (3) *characterize* the constituents. These investigational criteria apply not only to the identification of natural flavor complexes but also to those flavors that are formed during the preparation of certain products (*e.g.*, cocoa before and after fermentation, coffee before and after roasting, etc.).

Isolation

Operating techniques for isolating flavors are numerous and must be adapted to the particular problem. The simplest but also the most complex techniques are all based on distillation and extraction processes. The final flavor sensation is often based on the presence of trace quantities of several components (as low as 0.1 ppm) that can act as flavor synergists; therefore, during isolation nothing must be lost or altered. Laboratory techniques usually employed for the isolation of flavor ingredients include the following:

1. Vacuum distillation
2. Steam distillation
3. Solvent extraction
4. Concentration

In the first two methods, condensation is effected on a cold surface using special coolants (solid carbon dioxide, liquid air, etc.) capable of decreasing the condenser temperature to very low limits. In technical jargon these special condensers are called "traps," and the word well describes their capability of entrapping flavor ingredients.

Solvent and even water extraction are used either in one step for particularly easy and straightforward cases or subsequent to distillation for the recovery of non-distillable products from residues. Extraction techniques can also include the use of inert gases as extractants. The extracting gases are recycled over the material and become enriched in volatile flavor ingredients. The enriched gases undergo subsequent separation. Percentage-wise, the yield of relevant flavor ingredients from natural products is usually very low. Sometimes it is necessary to extract several hundred pounds of product to isolate the minimum quantity of flavor ingredient necessary for further investigation. In such cases the raw material undergoes a concentration process to enrich the flavor ingredient content. Once a flavor complex is isolated, it is subsequently processed into fractions.

Fractionation

Fractionation can be accomplished by physical and/or chemical means. Physical methods include fractional distillation, fractional crystallization, molecular distillation, sublimation, and chromatography. Chemical means include the preparation of addition compounds such as phenylhydrazones, oximes, bisulfites, etc. In employing chemical methods, the reaction products often permit the immediate characterization of a component.

Characterization

Mass spectroscopy, IR, UV, NMR, melting point, boiling point, refractive index, optical rotation, etc. are the basic tools for the positive characterization of flavor ingredients. Gas chromatographic techniques are presently considered indispensable for the characterization of flavor ingredients, since they can be applied directly to the isolated flavor complex as well as to the fractionated components. Thin-layer chromatography and electrophoresis share the dual potential of GLC, but they have limited application in the fractionation and characterization of flavor ingredients because of reduced sensitivity to volatile components.

Evaluation

Flavor ingredients are evaluated on the basis of yield criteria, *i.e.*, the lowest percentage ratio between the flavor ingredient and the food substrate necessary to achieve the desired flavoring goal. Flavor yield is defined in terms of the finished product and is expressed in per cent, *i.e.*, 1:25 = 4:100. Flavor accuracy is easily attained with products of low yield (*e.g.*, 1:10 to 1:100); in very high yields (1:10,000 or greater) data are only indicative. A complicating factor is that the correct flavoring sensation or flavor intensity is highly subjective. Therefore, minimum-maximum levels should be established by the flavorist. In practice the flavorist works at intermediate levels that can be readily increased or reduced within limits to accommodate for personal taste.

The flavorist, in recommending flavor doses, must take into account not only the quantities of finished product but other factors, such as product texture (solid, liquid, viscosity, water and fats content, etc.), color, substrate composition (alcohol, carbon dioxide, acids, etc.), manufacturing process, and the temperature at which the product is to be consumed.

PYRAZINES IN FOODS

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INTRODUCTION

Desirable food flavor is one of the key factors governing food consumption. Since prehistoric times man has chosen and prepared foods in such a manner as to give pleasing flavor. Thus, it is not suprising that the food scientist has devoted much of his energies to the area of food flavor research. With the recent introduction of sophisticated analytical aids the food scientist has been able to report on the isolation and identification of numerous classes of compounds and in some cases specific compounds which contribute directly to characteristic food flavors. Therefore, it is the primary purpose of this review to report on one of these specific classes of food flavor related compounds, namely pyrazines.

Structurally, pyrazines are heterocyclic nitrogen containing compounds. The organic chemist has had a long association with pyrazine compounds but their occurrence in foods was not widely reported until the mid 1960s. Since then pyrazines have been characterized as significantly contributing to the unique flavor and aroma associated with the roasting or toasting of numerous foods. However, naturally occurring pyrazines have also been isolated from food systems that have not undergone heat treatment, thus demonstrating that various biological pathways for pyrazine formation exist. Interestingly, pyrazines are one of the few classes of compounds that have the distinction among food scientists as being associated with desirable food flavor properties. Realizing the potential of pyrazines and related compounds as flavoring agents, the flavor chemist has synthesized numerous nonnaturally occurring pyrazine compounds with the hope of obtaining flavoring agents possessing unique and potent characteristic flavor and aroma notes.

Other food chemists have attempted to better understand the occurrence and formation of pyrazines in foods by studying reaction mechanisms in model systems. In doing so they have developed isolation, identification, and quantitation techniques that have been useful in the search for pyrazines in numerous complex food systems.

PYRAZINE OCCURRENCES IN FOOD SYSTEMS

Introduction

Due to the wide variety of food systems (Table 1) from which pyrazines have been reported to be isolated (Maga and Sizer, 1973) the authors, where possible, will discuss these findings on an individual food product basis.

Bakery Products

A total of 12 pyrazines were isolated and identified by von Sydow and Anjou (1969) from rye crispbread. The presence of pyrazines in this type of product is not surprising since the product is only 8 to 9 mm thick and the internal temperature rises above 100°C during its 7 min baking period. In addition, they reported at least 6 pyrazines of unspecified structure. The authors postulated that the compounds found in the pyrazine fraction are important in bread aroma.

Numerous volatile flavor compounds have been identified in conventional white bread and recently Sizer et al. (1973) reported on the formation of the major pyrazines in the crust of American-type white wheat bread as influenced by baking time. The one pound loaves were baked at 218°C for 10, 15, 20, 25, and 30 min with the standard loaf being baked for 20 min. Approximate quantitation through the use of an internal standard of the major pyrazines, showed that production of pyrazines increased from 0.1 ppm for 10 min baking to 6 ppm in the breads baked for 30 min. Thus, from threshold values reported in the

TABLE 1

Foods from Which Pyrazines Have Been Isolated

American white bread
rye crispbread
roasted barley
cocoa products
coffee products
milk protein (casein)
whey powder
stale skim milk powder

galbanum oil
heated beef fat
fried lean veal meat
roast beef drippings
boiled beef
roasted peanuts
roasted pecans
roasted fiberts
pressure-cooked beef

popcorn
potato chips
explosion puffed dehydrated potatoes
Jamaican rum
scotch whisky
molasses fusel oil
potato fusel oil
fermented soybeans (Natto)

deep fat-fried soybeans
hydrolyzed soy protein
green bell peppers
green peas
tomatoes
sesame oil
chicken broth
dried mushrooms
pressure-cooked pork liver

TABLE 2

Pyrazines Reported in Bakery Products

pyrazine
methylpyrazine
2,3-dimethylpyrazine
2,5-dimethylpyrazine
ethylpyrazine
trimethylpyrazine
2-ethyl-3-methylpyrazine
2-ethyl-6-methylpyrazine
propylpyrazine
2-methyl-5-propylpyrazine
3-methyl-2,5-dimethylpyrazine
vinylpyrazine
2-vinyl-6-methylpyrazine

TABLE 3

Pyrazines Reported in Roasted Barley

pyrazine
methylpyrazine
2,3-dimethylpyrazine
2,5-dimethylpyrazine
trimethylpyrazine
2-ethyl-3-methylpyrazine
2-ethyl-5-methylpyrazine
2,5-dimethyl-3-ethylpyrazine
3,5-dimethyl-2-ethylpyrazine

literature the authors also concluded that pyrazines significantly contribute to the aroma of bread. Pyrazines were also found in the crumb or noncrust portion of the breads but at comparatively low levels and these probably resulted from the inclusion of a dry milk product to the formulation. See pyrazine occurrence in dairy products section for additional clarification. A summary of pyrazines reported in bakery products is presented in Table 2.

Roasted Barley

While investigating roasted barley flavor Wang et al. (1969) reported the presence of five pyrazine compounds in the isolated basic fraction. Later, Collins (1971) identified four additional pyrazines in roasted barley. The specific pyrazines found in both of these studies are listed in Table 3. Interestingly, Collins (1971) used a roasting temperature of 225°C whereas Wang et al. (1969) used a roasting temperature of only 180°C. Wang et al. (1969) postulated that pyrazines play an important role in roasted barley flavor since their removal resulted in a loss of the typical desirable roasted aroma. Pathways for the formation of pyrazines found by Wang et al. (1969) were postualted and will be discussed elsewhere. Neither study reported relative or absolute concentrations found. It was also postulated (Wang et al., 1969) that if dihydropyrazines were present, which have been reported to give a roasted odor (Bondarovich et al., 1967), the isolation procedure used promoted their destruction.

Cocoa Products

Cocoa products have been a favorite food source for the isolation and identification of pyrazine compounds. To date, numerous pyrazine compounds have been identified in cocoa products. These are summarized in Table 4. The first such report appeared in 1964 when tetramethylpyrazine and 2,6-dimethylpyrazine were among the 29 new compounds found in chocolate liquor (Dietrich et al., 1964).

Rizzi (1967) used the volatile basic fraction from cocoa butter in reporting the presence of seven alkyl pyrazines. He calculated that this fraction represented 0.05% by weight of the original cocoa butter and concluded that pyrazines contributed significantly to the basic odor in cocoa butter volatiles.

At approximately the same time Marion et al. (1967) reported the presence of 8 pyrazine compounds among the 126 they identified in cocoa aroma.

Also in 1967 Flament et al. reported on the occurrence of pyrazines in cocoa aroma. Of the 62 compounds they isolated, 15 were reported to be pyrazines and included several propyl, isopropyl, and isoamyl pyrazine derivatives. The most predominant pyrazines found included trimethyl and tetramethylpyrazine.

van Praag et al. (1968) added ethyl- and 2,3-dimethyl-6-ethylpyrazine to the list of pyrazines identified in cocoa products. They used the steam distillate from roasted cocoa bean nibs and found a total of 15 pyrazine compounds among the 56 they reported and also concluded that the basic fraction has a nut-like odor which was specifically attributed to the presence of pyrazines. Aside from the contribution of pyrazines the authors concluded that a portion of cocoa aroma was present in the neutral fraction and that the acidic fraction contributed more to cocoa taste than to aroma.

Five additional pyrazines were added to the cocoa list by van der Wal et al. in 1968. van der Wal et al. (1971), in turn, reported the presence of seven additional pyrazine compounds.

A report appeared in 1972 (Reineccius et al.) whereby various factors affecting the formation of pyrazines in cocoa beans were investigated. They found no qualitative pyrazine differences by cocoa bean variety. However, quantitative differences were quite evident. These differences were attributed to the degree of fermentation that the varieties traditionally undergo even though they were roasted under the same conditions. Thus the greater the fermentation, the higher the total pyrazine level in the roasted

TABLE 4

Pyrazines Reported in Cocoa Products

methylpyrazine
2,3-dimethylpyrazine
2,5-dimethylpyrazine
2,6-dimethylpyrazine
trimethylpyrazine

tetramethylpyrazine
ethylpyrazine
2-ethyl-5-methylpyrazine
2-ethyl-6-methylpyrazine
2-ethyl-3,6-dimethylpyrazine

2-ethyl-5,6-dimethylpyrazine
2-ethyl-3,5,6-trimethylpyrazine
2,5-dimethyl-3-propylpyrazine
2,5-dimethyl-3-isoamylpyrazine
2,3-dimethyl-5-isoamylpyrazine

2,3-dimethyl-5-(2-methylbutyl)pyrazine
2-isoamyl-3,5,6-trimethylpyrazine
2-(2-methylbutyl)-3,5,6-trimethylpyrazine
2-methyl-6-isoamylpyrazine
2-methyl-6-(2-methylbutyl)pyrazine

2-methyl-6-(3-methylbutyl)pyrazine
2,5-dimethyl-3,6-diethylpyrazine
2,6-dimethyl-3,5-diethylpyrazine
2,6-dimethyl-3-isoamylpyrazine
isopropylpyrazine

2,5-diethylpyrazine
2,5-dimethyl-3-isobutylpyrazine
2,5-dimethyl-3-(2-methylbutyl)pyrazine
2,5-dimethyl-3-(3-methylbutyl)pyrazine
2,6-dimethyl-3-(3-methylbutyl)pyrazine

product. Especially susceptible to these quantitative changes were dimethyl-, trimethyl- and tetramethylpyrazine. Thus total pyrazine content was found to vary from 142 to 698 μg/100 g of beans. A portion of this study dealt with the influence of roasting time at 150°C on pyrazine formation. In light of the above data on varietal differences, it would have been interesting to follow pyrazine formation as a function of time using several varieties. However, with the one variety evaluated, they found pyrazine formation to be fairly rapid and linear during the first 30 min of roasting at 150°C. The authors cited three possible explanations as to why total pyrazine concentration did not increase beyond 30 min. It could have been due to the depletion of precursors. However, in a later section the authors stated that only approximately 0.2% of the amino acids and sugars consumed during roasting resulted in pyrazines. Other explanations listed included the possibility of pyrazines being consumed in other reactions or volatilization occurring which was equal to their formation rate. The influence of roasting temperature on pyrazine formation for one cocoa bean variety was also investigated. They found a linear relationship of increased pyrazine formation as temperature of roasting was increased up to 150°C. Also, tetramethylpyrazine formation was unique in that it was found in heavily fermented but unroasted beans but was not found in lightly or unfermented unroasted beans. Its presence in highly fermented beans was postulated to arise from either thermal reactions during fermentation, since in the heating portion of this study tetramethylpyrazine was the most predominant pyrazine at the lower temperature used, or it may have formed through microbial synthesis. Sugar analyses also revealed that ketoses, which are highly reactive in the formation of volatiles, were present at a level three times as high in well fermented beans as compared to nonfermented beans. Thus the authors concluded that the degree of fermentation influenced both the rate of formation and final pyrazine concentration mainly by altering the amount of free sugars present.

Coffee

A summarization of pyrazine compounds reported in coffee can be found in Table 5. Viani et al. (1965) were the first to report the presence of pyrazine compounds in coffee. Among the 38 compounds reported they identified pyrazine, methyl-, and 2,5-dimethylpyrazine. An additional pyrazine (2,3-dimethylpyrazine) was added to the list by Reymond et al. (1966). The third isomeric form of dimethylpyrazine (2,6-dimethylpyrazine) was reported to be present in coffee by Gianturco et al. (1966).

Two reports appearing in 1967 added substantially to the list of pyrazines occurring in coffee. Twenty such compounds were reported by Goldman et al. (1967). A total of 22 pyrazine compounds were reported by Bondarovich et al. (1967). This later study also mentioned that, during the syntheses of certain pyrazines, odors characteristic of roasted peanuts or popcorn resulted from some of the dihydropyrazine intermediates. However, these intermediates were reported to be quite unstable.

TABLE 5

Pyrazines Reported in Coffee

pyrazine
methylpyrazine
2,3-dimethylpyrazine
2,5-dimethylpyrazine
2,6-dimethylpyrazine
ethylpyrazine
2-ethyl-3-methylpyrazine

2-ethyl-5-methylpyrazine
2-ethyl-6-methylpyrazine
trimethylpyrazine
2,5-diethylpyrazine
2,6-diethylpyrazine
3-ethyl-2,5-dimethylpyrazine
3-ethyl-2,6-dimethylpyrazine
2-ethyl-3,5,6-trimethylpyrazine
tetramethylpyrazine
2,3-diethyl-5-methylpyrazine

2,6-diethyl-3-methylpyrazine
propylpyrazine
2-methyl-5-propylpyrazine
2-methyl-6-propylpyrazine
2-methyl-5-isopropylpyrazine
2-ethyl-6-propylpyrazine
2-isobutyl-3-methylpyrazine

vinylpyrazine
2-methyl-5-vinylpyrazine
2-methyl-6-vinylpyrazine
2-ethyl-6-vinylpyrazine
2-isobutyl-3-methoxypyrazine
2,5-dimethyl-3-isobutylpyrazine
2-(2′-furyl)pyrazine
2-(trans-1-propenyl)pyrazine
2-methyl-5-(trans-1-propenyl)pyrazine
2-methyl-6-(trans-1-propenyl)pyrazine

The following year Stoffelsma et al. (1968) reported 14 pyrazines in coffee, most of which had been previously reported.

In 1971 Friedel et al. added eight pyrazines isolated from coffee aroma. One of these was 2-isobutyl-3-methoxypyrazine which has an extremely low odor threshold.

Dairy Products

Ferretti et al. (1970) reported on the volatile reaction products formed during the nonenzymatic browning of a casein-lactose model system that was maintained at 75% relative humidity at 80°C for 8 days. Among the resulting 40 compounds identified were five pyrazines. An additional five pyrazines were reported by Ferretti and Flanagan (1971a), again involving the volatiles associated with a casein-lactose browning system.

Also in 1971 Ferretti and Flanagan (1971b) reported on the occurrence of seven pyrazine compounds isolated from the steam distillate of spray-dried whey powder which had been stored at 4°C for three years. In this latter study the authors reported that the alkylpyrazines were among the major volatile components found in spray-dried whey and postulated that processing conditions were more important to their formation than was nonenzymatic browning.

Ferretti and Flanagan (1972) also characterized the steam volatile components of stale skim milk powder which had been stored for 28 months, presumably at room temperature. They found five pyrazines similar to the ones they reported earlier in casein-lactose and whey systems. Preliminary studies indicated that of the 44 compounds found in stale skim milk powder, no single compound was specifically associated with typical stale milk flavor. However, based on flavor thresholds, they concluded that when considered in combination with other compounds found, perhaps trimethylpyrazine could contribute to stale flavor. The authors disproved this assumption when a mixture was formulated to include trimethylpyrazine. When added at a level of 2 ppm to fresh skim milk, no stale flavor was detected.

Kato et al. (1972a) investigated the major volatile components formed when casein was roasted at 250°C for 1 hr. Among the reaction products found were 2-methyl- and 2-ethyl-6-methylpyrazine which the authors postulated came from amino acid thermal decomposition.

Table 6 represents a summation of the pyrazines found to date in dairy related products.

Galbanum Oil

Galbanum oil is a yellowish to green or brown aromatic bitter gum resin derived from several Asiatic plants that has found use in medicinal, incense, and food flavoring preparations. The characteristic odor of galbanum oil has been attributed to an isomeric form of undecatriene. However, several investigative groups have reported that galbanum oil also contains numerous pyrazine compounds and these are listed in Table 7.

TABLE 6

Pyrazines Reported in Dairy Products

pyrazine
methylpyrazine
2,3-dimethylpyrazine
2,5-dimethylpyrazine
2,6-dimethylpyrazine
trimethylpyrazine
tetramethylpyrazine
2-ethyl-5-methylpyrazine
2-ethyl-6-methylpyrazine
2-vinyl-5-methylpyrazine
2-vinyl-6-methylpyrazine

TABLE 7

Pyrazines Reported in Galbanum Oil

tetramethylpyrazine
2,6-diethyl-3-methylpyrazine
2,3-dimethyl-5-ethylpyrazine
2-butyl-3-methoxypyrazine
2-isobutyl-3-methoxypyrazine
2-isopropyl-3-methoxypyrazine
2-methoxy-3-isopropyl-5-methylpyrazine
2,6-dimethoxy-3-isopropyl-5-methylpyrazine

For example, Bramwell et al. (1969) identified 2-methoxy-3-sec-butylpyrazine at a concentration estimated to be less than 0.05% of the total volatiles present. They also reported that other pyrazines were present and tentatively identified 2-isobutyl-3-methoxypyrazine.

Burrell et al. (1970) reported finding three alkylpyrazines and five alkoxyprazines in galbanum oil. Interestingly, Burrell et al. (1970) found the alkylpyrazines to be present in only trace amounts whereas the alkoxypyrazines were present in greater concentrations. Types of alkoxypyrazines found included methoxy butyl and isobutyl, methoxyisopropyls, and a dimethoxyisopropylmethyl-pyrazine. Thus, due to their extremely low odor thresholds, alkoxypyrazines can contribute to the characteristic odor associated with galbanum oil.

Meat Products

Watanabe and Sato (1971a) isolated the nonacidic flavor fraction from heated beef fats and concluded that at a proper dilution the basic fraction had a flavor resembling that of the original heated fats. The basic portion was further fractioned using silicic acid column- and gas chromatography. Two of the five resulting fractions contained pyrazines. One such fraction was described as having a potato-chip-like flavor and was found to contain ethyl-, 2-ethyl-5-methyl-, and 3-ethyl-2,5-dimethylpyrazine in approximately the same ratios. The other pyrazine fraction contained 2,5-dimethyl- and trimethylpyrazine again in relatively equal ratios and this fraction was described as possessing a roasted and burnt-like flavor. However, the authors felt that another fraction, which contained no pyrazines, and which was described as having a greenish and tallowish flavor contributed most to total heated beef fat flavor.

Having previously investigated the contribution of basic compounds found in heated beef fat to flavor (Watanabe and Sato, 1971a), the authors (1971b) also isolated the basic flavor fraction containing pyrazines from fried lean veal meat. The pyrazine fraction isolated essentially contained the same types of pyrazines reported from the heat treatment of beef fat. Major pyrazines found in fried lean veal meat included trimethyl- and 2,5-dimethyl pyrazine. In this latter study the authors stated that the basic pyrazine fraction isolated from fried lean veal meat contributed to a characteristic roasted flavor.

In another study dealing with flavor in meats Liebich et al. (1972) analyzed the total flavor extract from roast beef and its drippings. No attempt was made to fractionate the extract into acidic and basic portions. However, dimethylpyrazine was tentatively identified as being present in the roast beef drippings. This same study briefly mentioned the evaluation of volatiles in boiled beef but gave no experimental details. Pyrazines mentioned to be present in boiled beef included dimethyl-, trimethyl-, and dimethylethyl-pyrazine.

Mussinan et al. (1973) cooked 40 pounds of lean ground beef with 5 gallons of distilled water to 162°C for 15 minutes at 90 PSI. This was followed by a 2-day distillation-extraction process. A total of 33 pyrazines were identified, 19 for the first time in beef. Due to their fundamental roasted aroma, the authors concluded that pyrazines contribute to the characteristic aroma of cooked beef.

A later study by Mussinan and Waldradt (1974) investigated the volatiles associated with pressure-cooked pork liver. Similar excessive conditions as described above were employed to obtain a flavor concentrate. It should also be noted that raw liver was comminutated which would result in an active enzymatic state suitable for formation of pyrazine precursors. The product was then heated to 325°F for 15 minutes at 98 PSI. Over 40% of the 179 compounds identified were pyrazines. The authors stated that none of the compounds identified had a typical liver character.

A listing of pyrazines found in meat products is included in Table 8.

Dried Mushroom

Thomas (1973) reported on the volatiles obtained from the dried mushroom, *Boletus Edulis.* An aqueous extract was further extracted with pentane for 1 week. Gas chromatographic analysis resulted in the separation of over 130 compounds, with 70 being identified. Among these 70 were the 10 pyrazines shown in Table 8A.

Nut Products

Mason et al. (1966) were the first to report the presence of pyrazines in roasted peanuts. They isolated

TABLE 8

Pyrazines Reported in Meat Products

pyrazine
methylpyrazine
ethylpyrazine
2,3-dimethylpyrazine
2,5-dimethylpyrazine
2,6-dimethylpyrazine
2-ethyl-5-methylpyrazine
2-ethyl-6-methylpyrazine
2,5-diethylpyrazine
2,6-diethylpyrazine

trimethylpyrazine
2-ethyl-3,5-dimethylpyrazine
2-ethyl-3,6-dimethylpyrazine
5-ethyl-2,3-dimethylpyrazine
2,3-diethyl-5-methylpyrazine
2,5-diethyl-3-methylpyrazine
3,5-diethyl-2-methylpyrazine
3,6-diethyl-2,5-dimethylpyrazine
triethylpyrazine
tetramethylpyrazine
methylpropylpyrazine

vinylpyrazine
2-methyl-3-vinylpyrazine
2-methyl-5-vinylpyrazine
2-methyl-6-vinylpyrazine
isopropenylpyrazine
acetylpyrazine
2-methyl-5(or 6)-acetylpyrazine
2-ethyl-3-acetylpyrazine
2-ethyl-5(or 6)-acetylpyrazine
6,7-dihydro-5H-cyclopentapyrazine

2-methyl-6,7-dihydro-5H-cyclopentapyrazine
5-methyl-6,7-dihydro-5H-cyclopentapyrazine
2(or 3),5-dimethyl-6,7-dihydro-5H-cyclopentapyrazine
quinoxaline
2-methylquinoxaline
6-methylquinoxaline
5,6,7,8-tetrahydroquinoxaline
2-methyl-5,6,7,8-tetrahydroquinoxaline
(2-furyl) pyrazine
2-(2-furyl-5(or 6)-methylpyrazine
1-pyrazinyl-2-propanone

TABLE 8A

Pyrazines Reported in Dried Mushrooms (*Bolethus Edulis*)

methylpyrazine
2,3-dimethylpyrazine
2,5-dimethylpyrazine
2,6-dimethylpyrazine
2-ethyl-5-methylpyrazine

2,3,6-trimethylpyrazine
3-ethyl-2,5-dimethylpyrazine
tetramethylpyrazine
2-ethyl-3,5,6-trimethylpyrazine
2-methylquinoxaline

and identified five pyrazine compounds and stated that all possessed a roasted aroma but that specifically a fraction containing both trimethyl- and 2-ethyl-5-methylpyrazine had a potent and pleasing nutty aroma similar to the original roasted peanuts. No quantitative data were presented and the roasting temperature was 160°C.

An additional 19 alkylpyrazines were reported by Johnson et al. in 1971. Whereas the previous study had used whole roasted peanuts, the latter study reported on the isolation of pyrazines from the oil fraction of freshly roasted peanuts. None of the additional compounds had a specific roasted peanut aroma; however, the group of pyrazines isolated significantly contributed to the nutty character of roasted peanuts. No roasting temperature was reported.

Pyrazines isolated from roasted peanuts are reported in Table 9.

Shu and Waller (1971) also isolated pyrazines from the oil fraction of roasted peanuts. Essentially this study reported finding the same pyrazines as Johnson et al. (1971) except in this latter study unsubstituted pyrazine was also found. The Shu and Waller (1971) study was primarily concerned with comparative analyses of pyrazines isolated from different peanut varieties which were planted, fertilized, harvested, and stored under varying conditions. Although Shu and Waller (1971) did mention that all samples were roasted in a rotisserie oven preheated to 450°F, roasting was not reported to be uniform in time for all variables since time of roasting was judged by the color and aroma of the product during roasting.

The authors did demonstrate quantitative pyrazine differences as influenced by variety. Both peanut varieties evaluated contained all 19 pyrazines; however, one variety was higher in 2-ethyl-3-methyl- and trimethylpyrazine mixture, 3-ethyl-2,5-dimethylpyrazine, 2-isopropenylpyrazine and methylisopropenyl-

TABLE 9

Pyrazines Reported in Peanut Products

pyrazine
2-methylpyrazine
2,3-dimethylpyrazine
2,5-dimethylpyrazine
2,6-dimethylpyrazine
ethylpyrazine

2-ethyl-3-methylpyrazine
2-ethyl-5-methylpyrazine
2-ethyl-6-methylpyrazine
trimethylpyrazine
2-ethyl-3,5-dimethylpyrazine

2-ethyl-3,6-dimethylpyrazine
diethylpyrazine
2,5-diethyl-3-methylpyrazine
2,6-diethyl-3-methylpyrazine
diethyldimethylpyrazine

2-ethyl-3,5,6-trimethylpyrazine
tetramethylpyrazine
propylpyrazine
isopropylpyrazine

methylpropylpyrazine
methylisopropylpyrazine
methylpropenylpyrazine
2-isopropenylpyrazine
methylisopropenylpyrazine
vinylpyrazine

2-methyl-5-vinylpyrazine
2-methyl-6-vinylpyrazine
ethylvinylpyrazine
acetylpyrazine
5-acetyl-2-methylpyrazine

6-acetyl-2-methylpyrazine
6-acetyl-2-ethylpyrazine
6,7-dihydro-5H-cyclopentapyrazine
2-methyl-6,7-dihydro-5H-cyclopentapyrazine
5-methyl-6,7-dihydro-5H-cyclopentapyrazine

dimethyl-6,7-dihydro-5H-cyclopentapyrazine
5,6,7,8-tetrahydroquinoxaline
quinoxaline

pyrazine. This would perhaps suggest that pyrazine formation may be influenced by varietal differences. However, it should be remembered that in this study the two peanut varieties evaluated were not grown at the same location, nor did the authors mention if they were even grown in the same year.

A boron fertilization of deficiency produced some interesting results. Of the six pyrazine compounds that were significantly different in concentration as influenced by the addition or lack of boron to the soil, five pyrazines were actually at a significantly higher level in the boron deficient samples. Since this portion of the study was done with the same variety grown under the same conditions except for the boron variable, it may suggest that certain mineral deficiencies actually result in the formation of additional pyrazine precursors.

Length of growing time (120 vs 160 days) had little if any effect on relative pyrazine concentrations. The only significant concentration difference was with the mixture of 2-ethyl-3-methyl- and trimethylpyrazine which decreased with increased growing time.

The storage of peanuts before roasting under five different atmospheric conditions resulted in no significant pyrazine concentration differences for four of the atmospheres. However, an atmosphere consisting of sulfur dioxide and nitrogen showed some relative pyrazine concentration differences but these were mainly due to a dramatic change in the concentration of pyridine found with this specific atmospheric variable.

Walradt et al. (1971) conducted an extensive study on the volatiles from roasted peanuts. They were able to identify 187 compounds of which 36 were pyrazine derivatives. Some of the pyrazines of unique structure found included the saturated six-membered bicyclic pyrazine 5,6,7,8-tetrahydroquinoxaline and several oxygenated pyrazines such as methyl and ethylacetylpyrazines.

Wang and Odell (1972) isolated and identified eight different pyrazine compounds from the basic fraction of raw pecans that were dry roasted at 170°C. The authors stressed that these compounds only represented the major compounds and that no specific compound was identified as having a characteristic roasted pecan aroma although the pyrazine fraction provided a roasted or nutty "backbone" for roasted pecans. Specific pyrazines found in pecans are listed in Table 10.

Filbert nuts were dry roasted for 18 min at 177°C, the oil extracted, and the volatiles from the oil analyzed (Sheldon et al., 1972). Of the resulting 32 compounds found, 9 were reported to be pyrazines.

TABLE 10

Pyrazines Reported in Roasted Pecans

methylpyrazine
2,3-dimethylpyrazine
2,5-dimethylpyrazine
2,6-dimethylpyrazine
trimethylpyrazine
2-ethyl-5-methylpyrazine
2-ethyl-6-methylpyrazine
3-ethyl-2,5-dimethylpyrazine

TABLE 11

Pyrazines Reported in Roasted Filberts

pyrazine
methylpyrazine
2,3-dimethylpyrazine
2,5-dimethylpyrazine
2,6-dimethylpyrazine

ethylpyrazine
2-ethyl-3-methylpyrazine
2-ethyl-5-methylpyrazine
2-ethyl-6-methylpyrazine
2,3-diethylpyrazine

2,5-diethylpyrazine
2,6-diethylpyrazine
2-ethyl-3,5-dimethylpyrazine
2-ethyl-3,6-dimethylpyrazine
2,3-diethyl-5-methylpyrazine

2,5-diethyl-3-methylpyrazine
2,6-diethyl-3-methylpyrazine
trimethylpyrazine
triethylpyrazine
tetramethylpyrazine
diethyldimethylpyrazine

propylpyrazine
isopropylpyrazine
2-methyl-5-pentylpyrazine
dimethylisobutylpyrazine
vinylpyrazine

2-methyl-5-vinylpyrazine
2-methyl-6-vinylpyrazine
acetylpyrazine
2-methyl-5-acetylpyrazine
ethylacetylpyrazine

6,7-dihydro-5H-cyclopentapyrazine
2-methyl-6,7-dihydro-5H-cyclopentapyrazine
5-methyl-6,7-dihydro-5H-cyclopentapyrazine
2-ethyl-6,7-dihydro-5H-cyclopentapyrazine
2,5-dimethyl-6,7-dihydro-5H-cyclopentapyrazine

3,5-dimethyl-6,7-dihydro-5H-cyclopentapyrazine
2,3-dimethyl-6,7-dihydro-5H-cyclopentapyrazine
quinoxaline
5,6,7,8-tetrahydroquinoxaline
2-methyl-5,6,7,8-tetrahydroquinoxaline
(2′-furyl)pyrazine

They reported that although the pyrazine fraction contributed greatly to the character of roasted filberts, other classes of compounds such as aldehydes and furans also demonstrated burnt and nutty notes.

Another portion of this study dealt with following the formation and/or decomposition of certain volatiles as influenced by roasting time. However, pyrazines were not evaluated in this phase.

An extensive study of the volatile components of roasted filberts was reported by Kinlin et al. (1972). They found 228 compounds of which 42 were pyrazines. Thus, this represents the largest number of pyrazines reported from one food source. The filberts were dry roasted in the shell at 200°C for 5 min and then submitted to various extraction and concentation methods. Due to the magnitude of the study, no effort was made to characterize aromas or quantitate the findings. Several cyclic and condensation pyrazine forms were reported. Aside from the efficiency of the detection system employed, the elevated roasting temperature (200°C) of the product in the shell may be a possible explanation for the vast number of pyrazines reported in this study.

A listing of pyrazines found in filberts is presented in Table 11.

Popcorn

One report has appeared in the literature implicating alkyl substituted pyrazines as the primary contributors to the characteristic nutty flavor of popcorn (Walradt et al., 1970). The 8 pyrazines out of the 56 compounds reported are listed in Table 12. Of the eight, 2,3,5-trimethyl-and 2-acetylpyrazine were only tentatively identified. The fact that 2-acetylpyrazine was only tentatively identified is interesting since the

TABLE 12

Pyrazines Reported in Popcorn

pyrazine
methylpyrazine
2,3-dimethylpyrazine
2,5-dimethylpyrazine
2-ethyl-5-methylpyrazine
trimethylpyrazine
2-ethyl-3,6-dimethylpyrazine
acetylpyrazine

TABLE 13

Pyrazines Reported in Potato Products

methylpyrazine
2,3-dimethylpyrazine
2,5-dimethylpyrazine
2,6-dimethylpyrazine
ethylpyrazine
2-ethyl-3-methylpyrazine
2-ethyl-3,6-dimethylpyrazine
2,5-diethylpyrazine
2,6-diethylpyrazine
2,5-dimethyl-3-vinylpyrazine
2-isobutyl-3-methylpyrazine
2,3-diethyl-5-methylpyrazine

2-ethyl-5-methylpyrazine
2-ethyl-6-methylpyrazine
trimethylpyrazine
2-methyl-5-vinylpyrazine
2-methyl-6-vinylpyrazine
2-ethyl-3,5-dimethylpyrazine
2,5-dimethyl-6-isopropylpyrazine
2-isobutyl-3,6-dimethylpyrazine
2-isoamyl-5-methylpyrazine
methylethylisobutylpyrazine
2-isobutenyl-3-methylpyrazine
2-isoamyl-3,6-dimethylpyrazine
isobutenyldimethylpyrazine

2-methoxy-3-isopropylpyrazine
2,6-diethyl-5-methylpyrazine
2,5-diethyl-3-methylpyrazine
2-isobutyl-5-methylpyrazine
diethylpropylpyrazines
isoamyldimethylpyrazines
alkylalkenylpyrazines
dimethylpropylpyrazine
isoamylpyrazine
ethylvinylpyrazine
amylmethylpyrazines
ethyldimethylvinylpyrazine
alkylpyrazines

authors reported a characteristic popcorn-like aroma between two other major nonpyrazine gas chromatography peaks. The retention time of this popcorn aroma compound corresponded to authentic 2-acetylpyrazine which according to Roberts (1968) possesses a popcorn-like aroma in low concentrations. However, no attempt was made to further purify the mixture to obtain a sufficient quantity to verify it to actually be acetylpyrazine. Pathways for the presence of other important flavor compounds were discussed but mechanisms for the occurrence of pyrazines, and especially acetylpyrazine in popcorn, were not reported. No quantities were reported, but using the gas chromatography scan as a guide, it would appear that unsubstituted pyrazine and methylpyrazine were the most prevalent pyrazines in popcorn.

Potato Products

In 1965 Deck and Chang reported on the isolation and identification of 2,5-dimethylpyrazine from potato chips. At a concentration of 10 ppm in oil they reported that this compound has a characteristic raw, earthy potato flavor. Later Deck (1968) reported on the occurrence of seven additional pyrazine compounds from potato chips.

An additional 23 pyrazine compounds were found in the steam volatile oil of potato chips by Buttery et al. (1971b). They stated that the formation of pyrazines is one of the major changes that occurs during the frying of potato chips. Based on their study, Buttery et al. (1971b) concluded that the pyrazine 3-ethyl-2,5-dimethylpyrazine, due to its relative concentration and low threshold, was the primary contributor to the aroma of the isolated basic volatile fraction in potato chips.

A detailed listing of pyrazines found in potato products can be seen in Table 13.

A recent study by Sizer and Maga (1973) was designed to evaluate the roles of frying time, temperature, and pH on the major pyrazines in potato chips. Pyrazine formation was found to occur late in the frying process since it took approximately 4 min at 150°C before appreciable amounts of pyrazines appeared. With temperature as the variable, total pyrazine content was found to increase approximately 2.5 times for every 15°C increase in frying oil temperature. Total pyrazine formation reached maximum levels at 180°C. Since pyrazine formation is theoretically base catalyzed, the study included evaluation of leaching solutions at various pH levels. However, changes in the pH of the leaching solution did not significantly affect pyrazine formation rates, probably due to the fact that the potato slices actually did not change much during the half hour leaching period.

In this study, 3-ethyl-2,5-dimethylpyrazine was also thought to contribute significantly to overall potato chip flavor since it was found at levels 120 times its odor threshold level.

Taste panel studies revealed that potato chips containing the highest levels of pyrazines in the temperature series studied were described as tasting burnt. However, when time of frying was the variable at a constant temperature of 150°C, the chips highest in pyrazines were chosen as the most desirable. Thus, it would appear that optimum pyrazine levels from a flavor standpoint exist for each food product.

A toasted flavor is not always desirable in all foods. For example, in certain dehydrated potato products an off-flavor which has been described as toasted may be detected. Explosion puffing (heating potato cubes containing approximately 27% moisture with superheated steam for 1 min at 65 psi and then suddenly releasing the pressure) results in the formation of an objectionable toasted off-flavor.

Thus Sapers et al. (1971) demonstrated that steam distillates obtained from explosion puffed dehydrated potato that had been adjusted to pH 9 had a characteristic toasted aroma whereas conventionally dried potatoes had a sulfur odor. Gas chromatography scans of the volatiles from explosion puffed and conventionally dried potatoes were qualitatively similar. However, relative compound quantities, as determined by peak areas, were significantly different for the two products. They found that the peak areas of ten components, many of which were pyrazines, could be directly correlated to the degree of toasted off-flavor. Specific pyrazine compounds that were found to increase with a corresponding increase in toasted off-flavor included methyl-, 2,5-dimethyl-, 2,3 and/or 2,6-dimethyl-, ethyl-, trimethyl- and ethyldimethylpyrazine. Other compounds isolated in the same fraction also exhibited pyrazine-like aromas; however, their identity was not established. Thus the authors concluded that alkylpyrazines along with products of proline and Strecker degradation are responsible for the toasted off-flavor associated with explosion puffed dehydrated potatoes since only trace or low concentrations of these products were found in conventionally dehydrated potatoes.

A recent study by Deck et al. (1973) verified the presence of seven pyrazine compounds from the steam distillate of potato chips.

Buttery and Ling (1973) characterized an earthy aroma associated with potatoes to be 2-methoxy-3-isopropylpyrazine. They reported that it was found at a level of 1 part in 10^{10} parts of potato which is approximately 50 times its odor threshold in water. Another methoxypyrazine, 2-ethyl-3-methoxypyrazine, is also thought to contribute to an earthy potato aroma but its presence was not confirmed. If present, it would be at a concentration of less than 1 part in 10^{12} which is significantly lower than its odor threshold. Buttery and Ling (1973) postulated that 2-methoxy-3-isopropylpyrazine could either result through plant synthesis or by absorption from microbial production in the soil or on the potato tuber surface.

Buttery et al. (1973) also reported on the volatiles associated with baked potatoes. A total of 42 compounds were identified with over half being pyrazines. The ratio of pyrazines to aldehydes between the skins and the potato insides indicated that a greater amount of pyrazines were present in the skins, thus leading the authors to conclude that pyrazines are formed in the skins. Moisture levels inside the potato maintain the temperature near 100°C whereas skin temperature would be higher and thus favor pyrazine formation. Based on the amount found and on its odor threshold, the authors concluded that 2-ethyl-3,6-dimethylpyrazine is a major contributor to baked potato aroma.

A recent study by Pareles and Chang (1974) also reported on the volatiles associated with baked potato. They agreed with Buttery et al. (1973) on the importance of 2-ethyl-3,6-dimethylpyrazine but also pointed out that the naturally occurring potato pyrazine mixture of 2-isobutyl-3-methylpyrazine, 2,3-diethyl-5-methylpyrazine and 3,5-diethyl-2-methylpyrazine has an odor closer in character to baked potato than the above mentioned single pyrazine. However, the relative proportions of the mixture mentioned by Pareles and Chang (1974) were not reported.

Rum and Whisky

Wobben et al. (1971) isolated the basic flavor fraction from a Jamaican rum and a Scotch blended whisky. The pyrazines isolated are summarized in Table 14. Of the pyrazine compounds positively identified all except 2-methyl-6-vinylpyrazine were common to both products with 2-methyl-6-vinylpyrazine only being found in the rum. No possible explanation for this discrepancy was given. The authors also reported that an amylpyrazine was present in both products but the exact structure was not determined. Judging from gas chromatography scans presented for both products, the tentatively reported amylpyrazine is one of the most predominant pyrazines present, especially in the whisky sample evaluated. Other predominant pyrazines in the two products included methyl-, 2,5 and 2,6-dimethyl-, and trimethylpyrazine in the rum sample and 3-ethyl-2,5-dimethylpyrazine in the Scotch. No interpretation of the role of these specific pyrazines on product flavor was discussed.

An earlier review by Kahn (1969) reported that whisky contained trimethyl-, tetramethyl-, and 2,5-dimethylpyrazine. Interestingly, Wobben et al. (1971) did not report the presence of tetramethylpyrazine in their whisky sample.

Several other scattered reports on the presence of pyrazines in fusel oils appear in the literature. For example, Morin (1888) reported trimethylpyrazine to be present in molasses fusel oil. Later Chapman and Hatch (1929) reported that fusel oil from molasses contained trimethyl-, tetramethyl-, and probably 2,5-dimethylpyrazine. Trimethyl-, tetramethyl-, diethyl-, and triethylmethylpyrazine were also reported in potato fusel oil (Shoruigin et al., 1933). Taira (1936) reported 2,5-diethylpyrazine to be present in beet molasses fusel oil.

Soy Products

Kosuge et al. (1962) found tetramethylpyrazine in the fermented soy product Natto and reported that this pyrazine had the same odor as Natto. The fact that tetramethypyrazine was found in a fermented product led Kosuge and Kamaiya (1962) to report on the isolation of tetramethylpyrazine from cultures of a strain of *Bacillus subtilis* grown on a sucrose and asparagine medium. They also reported that the isolated pyrazine had a characteristic odor of fermented soybeans.

Toasting or oil roasting of raw soybeans greatly alters their flavor from a green, or beany, character to a roasted nut flavor. Therefore, Wilkens and Lin (1970) investigated the types of flavor compounds formed during the deep fat frying of soybeans. Of the approximately 60 compounds observed from such a system, 7 were identified as pyrazines. Due to the relatively large amounts found, especially of ethyl-, 3,6-dimethyl-, and trimethylpyrazine, the authors suggested that pyrazines were responsible for the nut-like or peanut butter-like aroma associated with deep fat fried soybeans. They also stated that the occurrence of pyrazines in the product they evaluated was directly related to the heat treatment involved since no pyrazines were found in raw soybeans or in soymilk prepared under 100°C.

The basic flavor fraction from a laboratory prepared spray-dried hydrolyzed soy protein was found to contain 11 different pyrazines (Manley and Fagerson, 1970). The major pyrazines found in this product were 2-ethyl-3-methyl-, 2,6-dimethyl-, and 2,5-dimethylpyrazine. It is interesting to note that in viewing the gas chromatography scan of the basic fraction from which the pyrazines were identified in hydrolyzed soy protein, a series of major size peaks appears downrange from the pyrazine area. However, the authors did not report on the identity of these compounds.

Manley and Fagerson (1970) made some interesting observations on the influence of pH on pyrazine odor. They reported that hydrolyzed soy protein which was at an acid pH did not possess a characteristic nut-like odor. However, when the pH of the product was adjusted to the alkaline side, typical nutty odor was evident. They reported that a panel described the odor of both a water solution of 2,5-dimethylpyrazine and alkaline treated hydrolyzed soy protein to be nut-like. These observations can be explained by the fact that as the pH is lowered, the non-volatile pyrazine salts are formed, which are converted back to the volatile pyrazines when the pH is increased. Thus it would appear that the desirable flavor associated with most pyrazines could be intensified by adjusting the pH of the food system upward where feasible.

TABLE 14

Pyrazines Reported in Rum and Whisky

methylpyrazine
2,3-dimethylpyrazine
2,5-dimethylpyrazine
2,6-dimethylpyrazine
2-methyl-5-ethylpyrazine
2-methyl-6-ethylpyrazine
trimethylpyrazine
3-ethyl-2,5-dimethylpyrazine
2-methyl-6-vinylpyrazine
tetramethylpyrazine
amylpyrazine (tentative)

TABLE 15

Pyrazines Reported in Soy Products

pyrazine
methylpyrazine
2,3-dimethylpyrazine
2,5-dimethylpyrazine
2,6-dimethylpyrazine
2-ethyl-3-methylpyrazine
2-ethyl-5-methylpyrazine
trimethylpyrazine
tetramethylpyrazine
2-ethyl-3,5-dimethylpyrazine
2-ethyl-3,6-dimethylpyrazine
2-ethyl-3,5,6-trimethylpyrazine

Although no reports have appeared in the literature on formation of pyrazine compounds during the common practice of toasting defatted soy flours, it would be a logical assumption that pyrazines could contribute significantly to the typical nutty-toasted flavor associated with these products.

A listing of pyrazines reported to date in soy products can be found in Table 15.

Vegetables

Several reports have appeared in which pyrazines were found in vegetables. For example, Buttery et al. (1969a,b) reported that 2-isobutyl-3-methoxypyrazine was the characteristic odorant of green bell peppers. They also reported (1969a) that 2-isobutyl-3-methoxypyrazine was found in the steam volatile oil of chili peppers at approximately the same relative concentration as found in green bell peppers.

Several alkoxypyrazines have also been found in green peas (Murray et al., 1970). The specific compounds found include 2-butyl-3-methoxypyrazine, 2-isobutyl-3-methoxypyrazine, and 2-isopropyl-3-methoxypyrazine. The authors suggested that alkoxypyrazines could be widely distributed in the plant kingdom. They also suggested a pathway for their biosynthesis. Thus, from the above studies it is apparent that not all pyrazines result from heat treatments but some, especially the potent alkoxypyrazines, may be present in the raw products.

Ryder (1966) reportedly found methyl- and 2,6-dimethylpyrazine in tomatoes. However, no details of the isolation procedure are given and thus it is not known if pyrazines reported in this product are artifacts or not.

Miscellaneous Food Products

Two other isolated reports of pyrazines in foods have appeared. Takei et al. (1969) reported finding pyrazine compounds in sesame oil and Wilson and Katz (1972) tentatively identified methylpyrazine in chicken broth.

To better aquaint the reader with the structural similarities of pyrazines found in foods and in some cases with the unique structures involved, Figure 1 has been included.

PYRAZINE ISOLATION TECHNIQUE

Various methods for the isolation of pyrazines from food systems appear in the literature. Essentially most of the methods reported involve at least three separate steps, namely, some form of distillation which is usually followed by concentration and then fractionation to recover the pyrazine portion. Thus, in this portion of the review the authors will discuss each of the methods using one literature reference typical of the specific technique discussed. As a further aid to the reader, advantages and disadvantages for each technique are summarized in Table 16.

Atmospheric Steam Distillation

This represents the most common type of initial pyrazine isolation technique. A typical literature citation would be Wang and Odell (1972). Essentially the food product is blended with water and the temperature of the mixture raised to the boiling point either through the use of direct steam injection or outside heating of the reaction vessel. The emitted volatiles are then usually condensed through the use of a water condenser.

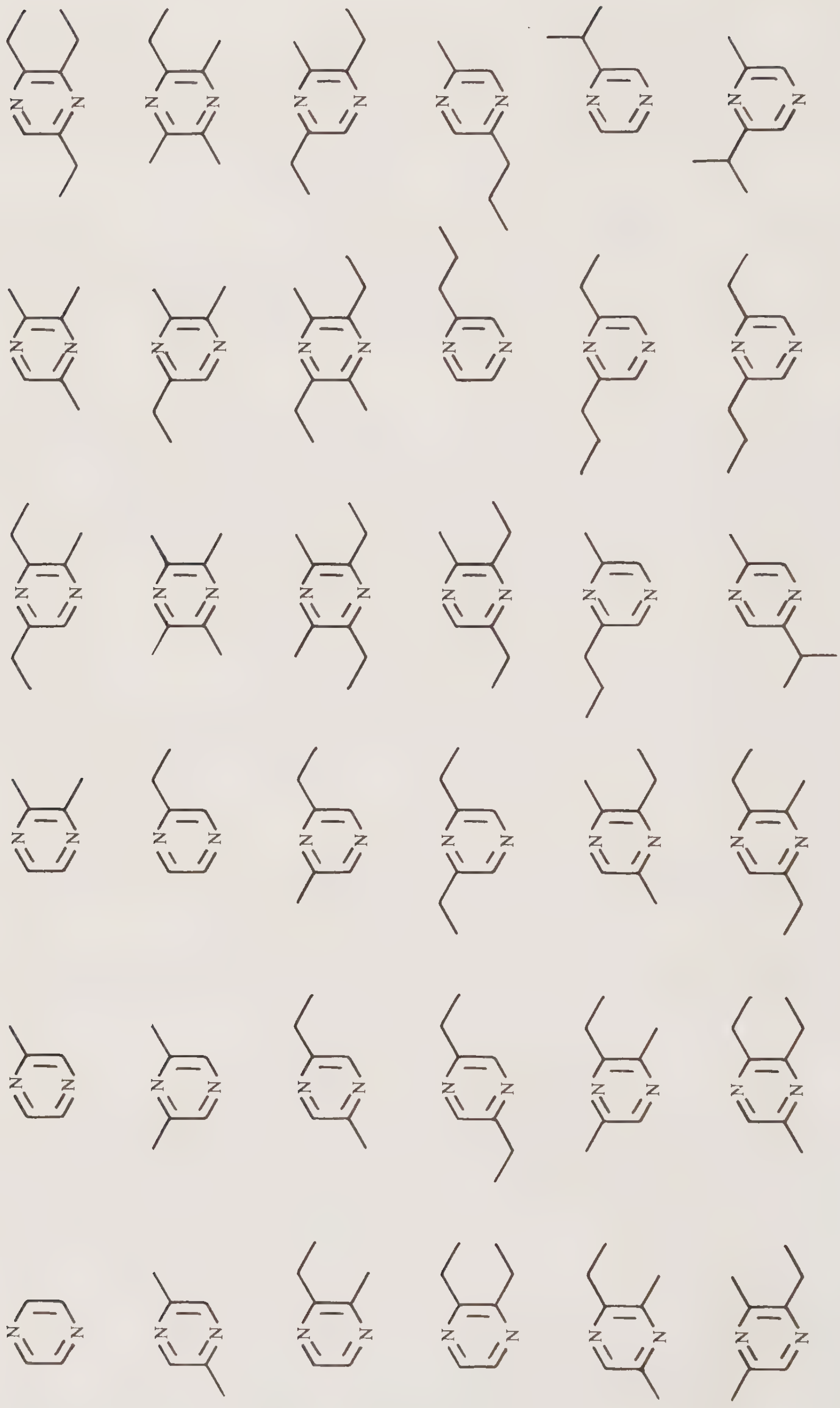

FIGURE 1. Structural relationships of certain naturally occurring pyrazines in foods.

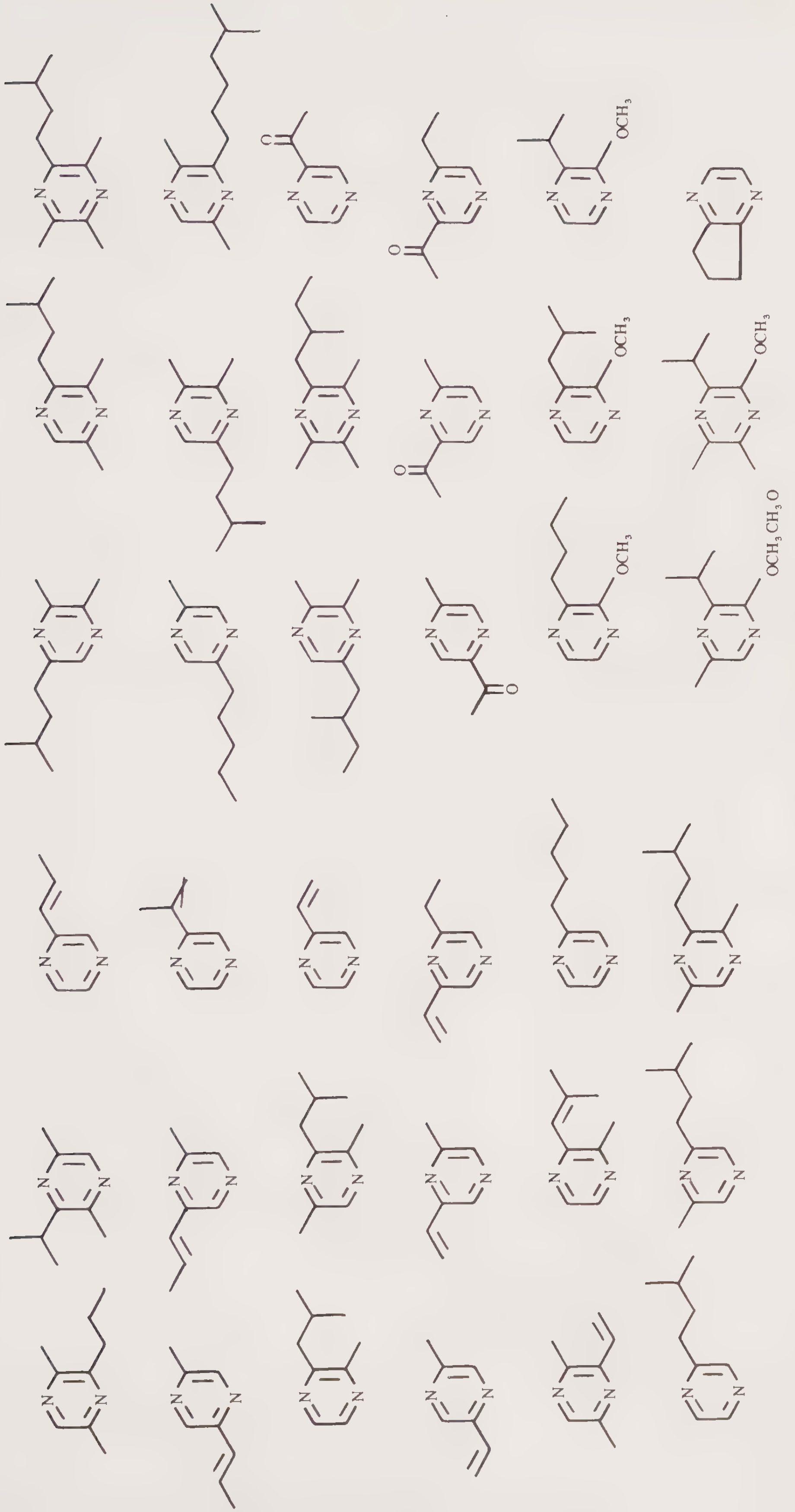

FIGURE 1. (continued)

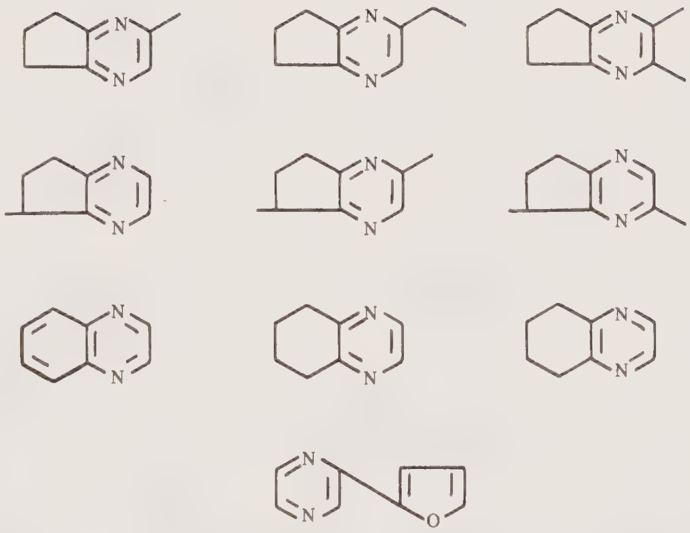

FIGURE 1. (continued)

TABLE 16

Summary of Pyrazine Isolation Techniques from Food Systems

Method	Advantages	Disadvantages
Atmospheric steam distillation	Ease of operation Water as solvent	Time consuming Possibility of burn-on Heat artifact formation Not typical process for some foods
Vacuum steam distillation	Same as above Less chance of burn-on	Same as above Volatile loss through cold trap Product may foam
Vacuum stripping	No direct solvent contact Good for small, concentrated sample	Flowrate critical Possibility of burn-on Incomplete recovery
Soaking-steam distillation	Less chance of burn-on	Pyrazine formation precursors also removed Incomplete recovery
Atmospheric solvent distillation	Less chance of burn-on	Time consuming Product denaturation
Vacuum solvent distillation	Reduces distillation temperature	Same as above
Room temperature solvent	Rapid No heat artifact formation	Incomplete recovery Product denaturation
Rotary evaporation	Reduces artifact formation	Time consuming Volatile loss through cold trap
Headspace-inert gas-cold trap	Fairly rapid No solvent required Little artifact formation	Volatile loss through cold trap Incomplete recovery
Headspace vapor condensation	No solvent required Ideal to follow pyrazine formation rates	Same as above
Headspace collection on precolumn	Least artifact formation of all above Combines isolation and concentration steps	Incomplete recovery

Several problems can be associated with this procedure. For example, the ratio of product to water is critical due mainly to the possible formation of pyrazines resulting from the burning on of food product. Thus, for foods which have not been exposed to a severe roasting or heating process previously, the distillation procedure can actually result in pyrazine formation. Also, although pyrazines are quite volatile, they are also quite water soluble; thus the researcher has to decide as to the amount of distillate to collect in order to insure complete pyrazine removal from the product. Some investigators dislike this procedure since they argue that it may represent an unnatural step in the normal processing or preparation of the product; thus although pyrazines may be found, they are not truly representative of the product. The method can be fairly time consuming since depending on the distillation equipment available, it may take hours to heat and collect distillate from a large sample. Advantages of the method include its ease of operation and no need for solvents other than water.

Vacuum Steam Distillation

Essentially this method is the same as that discussed above except that a vacuum is applied to the system (Mason et al., 1966). However, for quantitative results or even in some cases for qualitative results, especially of highly volatile pyrazine compounds, care must be excercised by providing a series of cold traps for distillate collection. Otherwise, some pyrazines may be stripped from the distillate. Another possible difficulty in using this method with certain food systems is the problem of excessive product foaming. However, this can be overcome by degassing the system under positive vacuum at room temperature, or by the addition of commercial antifoaming agents. However, it should be noted that commercial antifoaming agents frequently contain substantial amounts of volatiles which may interfere in subsequent GLC analysis.

The primary advantage of this system is that since distillation of a water system proceeds at a lower temperature under partial vacuum, less possibility exists of burn-on and subsequent pyrazine formation at or near the boiling point of water. Normally vacuum distillation is performed at 40 to 60°C. However, through the use of an efficient vacuum distillation system, distillate can be collected at room temperature operation. Thus, for food systems that do not undergo heating before consumption (raw vegetables) this provides an effective initial pyrazine recovery method.

Vacuum Stripping or Molecular Distillation

The work reported by Shu and Waller (1971) can be cited as an example of the use of vacuum stripping. This technique works especially well where concentrated sources such as oils of food volatiles are present. For example, in the above study the oil extract from roasted peanuts was used. Aside from the advantage listed under vacuum steam distillation, this method has the additional advantage that no solvent comes into contact with the flavor concentrate. The reaction can take place in a condenser equipped with expansion bellows with steam serving as the heating medium or in a falling film evaporator assembly. However, flowrate is critical since if too much product is admitted into the system at once, complete volatile removal is not achieved and if not enough sample is introduced, burn-on may result.

Soaking Followed by Atmospheric Steam Distillation

Collins (1971) assumed that since pyrazines are readily soluble in water, there was no need to steam distill the entire food system. Thus, he leached the pyrazines out of ground roasted barley by permitting the barley to stand in water for 1 hr at 66°C and then filtering. This was then followed by atmospheric steam distillation of the filtrate. By using this technique, chances for burn-on are minimized since no major food particles were present in the heating flask. However, the soaking procedure may not have been efficient in removing all pyrazines from the food system. Also, pyrazine precursors such as free amino acids and sugars are also water soluble and thus could have resulted in pyrazine formation, especially with the use of atmospheric steam distillation.

Rotary Evaporation

A water suspension of product was evaporated under reduced pressure using a rotary evaporator (Reymond et al., 1966) which was operating at 45°C. Cold traps were connected in line between the evaporator and vacuum pump to collect the clear distillate. Distillation took approximately 1 hr.

Atmospheric Solvent Distillation

As an alternative to a water-based extraction, various organic solvents have been used. These include diethyl ether (Sapers et al., 1971), dichloromethane (Manley and Fagerson, 1970), hexane (Buttery et al., 1969a,b), pentane (Flament et al., 1967), carbon disulfide (Wilkens and Lin, 1970), and ethanol (van der Wal et al., 1971).

The primary advantage of using a solvent extraction distillation technique is that the temperature of distillation is lower than a water distillation; thus less chance of heat induced artifact formation exists. Extraction time may be up to 20 hr (Liebich et al., 1972). However, some researchers feel that since solvent distillation may result in alteration of all or part of the food system, the data obtained are not completely valid.

An example of the degree of involvement that some research groups devote to pyrazine isolation is typified by the study of van der Wal et al. (1971). They used 92% aqueous ethanol as the primary extracting solvent. A total of 2500 kg of cocoa powder was extracted and this resulted in the collection of 650 l of distillate. The ethanol distillate was further extracted with 1200 l of pentane.

Vacuum Steam Solvent Distillation

Buttery et al. (1969a) have theoretically increased the effectiveness and decreased the possibility of artifact formation by applying vacuum to a water-solvent distillation procedure through the use of a Likens-Nickerson continuous steam distillation apparatus. Distillation using this procedure took approximately 3 hr.

Room Temperature Column Solvent Extraction

A pyrazine isolation process has been described by Reineccius et al. (1972) whereby a coarsely ground food product is placed in a glass liquid chromatography tube and solvent passed through the column at room temperature. Thus, no possibility of heat induced artifact formation exists. The method is also one of the most rapid isolation techniques available. However, one must wonder as to the efficiency of complete pyrazine removal from the product especially if it is coarsely ground.

Headspace-Inert Gas-Cold Trap Technique

The volatiles from an 80°C water suspension of product were flushed into cold traps using nitrogen (Reymond et al., 1966). Time required was approximately 30 min. Most headspace techniques have the advantage that they not only act as isolation steps, but in most cases they also serve as concentration techniques. However, a primary disadvantage of most headspace techniques is that complete removal of all volatile material is hardly ever attained. Wang et al. (1969) described a similar headspace flushing technique except that air was used to purge the system which, from a flavor stability standpoint, is not recommended.

Headspace Vapor Condensation

Kinlin et al. (1972) used a negative pressure gradient and a series of cold traps to condense the vapors emitted during the roasting of pecans. A primary advantage of this technique it that no additional solvents including water are required. This technique would be especially useful in studying the formation rates of specific pyrazines as influenced by processing variables such as time and temperature. For example, the pyrazine composition collected during the first minute of roasting could be compared to the compositional pyrazine ratios as influenced by additional time intervals of roasting by simply having various sets of cold traps ready to receive the vapors by switching a valving system at the appropriate time.

Headspace Collection on Precolumn

Perhaps the most theoretically acceptable volatile isolation procedure was that applied by Kinlin et al. (1972) for analyses of pyrazines in roasted filberts. The technique originally suggested flushing of the volatiles with nitrogen onto a packed gas chromatography column containing a packing which would permit the passage of water vapor yet entrap the volatiles and thus serve as a means of volatile concentration. Then the precolumn was attached to a gas chromatography unit and by the application of heat and a switching valve the volatiles were swept onto another gas chromatography column for separation.

Kinlin et al. (1972) used the same general concept, but they attached the precolumn to the end of a steam distillation apparatus to collect the volatiles emitted from the 20-min steam distillation of roasted filberts in water. Thus, the possibility of heat induced artifact formation existed. An ideal situation would have been to use a combination of a nitrogen flush and room temperature vacuum application, resulting in the concentration of volatiles onto the precolumn. The use of the precolumn technique has the added advantage in that its capacity to retain volatiles can be evaluated by simply sniffing the effluent. Also, flushing with nitrogen at room temperature provides the mildest isolation procedure reported and thus represents the truest picture of pyrazine composition in foods due to the lack of artifact formation in the isolation process.

Another on-column trapping technique that would be applicable for pyrazine compound isolation is the charcoal adsorption of volatiles as described by Carson and Wong (1961). Activated charcoal has a strong affinity for adsorbing volatiles while permitting water vapor to pass. Thus, the volatiles from a product could be flushed or permitted to naturally pass through an activated charcoal filter. Then the filter can be flushed with solvent to remove the volatiles for further analysis.

PYRAZINE CONCENTRATION TECHNIQUES

As discussed previously, several of the headspace isolation techniques also serve as a means of concentrating pyrazines. However, most of the steam distillation isolation techniques outlined above result in a dilute distillate which in turn is normally concentrated in volume and/or extracted as such. Also, some methods exist for both extracting and fractionating the pyrazine components directly from the distillate.

All of the concentration procedures reported in the literature rely on solvents for extraction. The solvent extract can then easily be concentrated by rotary evaporation, by fractional solvent distillation, or by the use of nitrogen. Typical examples of these procedures will now be discussed.

Diethylether Extraction

Diethylether as an extracting solvent is the most commonly used. A typical literature reference would be that of Walradt et al. (1970). Naturally, when using organic solvents their degree of purity is important and in all cases freshly redistilled solvent is a necessity. Also with the use of extracting solvents the number of extractions performed can be critical, especially if the results are to be quantitative. Some investigators have extracted two to eight times. The number of extractions required for complete volatile removal depends somewhat on the food system, but the extraction efficiency can easily be checked by permitting a drop of the ether extract to evaporate from a finger. If any residual characteristic odor other than that of the ether remains, it would be advisable to continue the extraction process.

To better insure stability against oxidation of the ether extract, Buttery et al. (1971b) have suggested the use of the nonvolatile antioxidant Ionox®-330. However, some researchers may object to this technique since the antioxidant may not be originally present in the food system.

Dichloromethane Extraction

Numerous researchers prefer to use dichloromethane as the extraction solvent. A typical example would be the work of Ferretti and Flanagan (1971b). The primary advantage of using dichloromethane is that lipids are not completely soluble in this solvent. Thus, if a product or extract has an appreciable lipid content, the majority of it will not be extracted with dichloromethane. This extraction technique can then be used as a direct treatment for the isolation and concentration of volatiles from fatty foods.

Dual Solvent Extractions

Recently Kinlin et al. (1972) have reported that a dual solvent extraction technique was found to be more efficient than either of the solvents used alone. Thus, they first extracted with trichloromonofluoromethane and then diethylether.

Miscellaneous Solvents

Citing no apparent advantages or disadvantages, other investigators have reported using hexane (Buttery et al., 1969a), pentane (Buttery et al., 1969a), and carbon disulfide (Wilkens and Lin, 1970).

FRACTIONATION OF SPECIFIC PYRAZINE PORTIONS

Essentially two methods exist for the final fractionation of pyrazines from the other volatile materials that may be present in the distillate obtained from a food system.

Gas Chromatography Separation

The first procedure to be discussed relies on gas chromatography to perform the separation of a complex volatile mixture. Quite simply, the concentrated solvent extract from the distillate is injected as such into the gas chromatograph. Generally the mixture is composed of acidic and basic compounds and therefore some difficulty may be encountered in the interpretation of the complex scan. However, when compared to the second procedure described below, it represents a relatively mild fractionation technique. An advantage of direct gas chromatography injection is that a relative idea of pyrazine concentration in relation to the other detectable volatile compounds can easily be obtained. A typical example of this technique was reported by Wilkens and Lin (1970). Specific gas chromatography conditions which can make the compound identification task easier will be discussed in a later section.

Acidic-Basic Fractionation

The second process involves the chemical separation of the complex volatile mixture into acidic and basic fractions before injection into the gas chromatograph of only the basic fraction which contains the pyrazines. An example of this technique would be the study of Manley and Fagerson (1970). This process first involves the adjustment of the pH of the extract to approximately 1 or lower with hydrochloric acid. The acidified mixture is then multi-extracted with solvent to remove acidic and neutral compounds. This is followed by readjustment of the pH to between 8 and 9 and again extracted with solvent to remove the desired basic fraction. The basic solvent extract fraction can then be concentrated and this concentrate injected into the gas chromatography unit. The injection of only the basic fraction usually results in a more "uncluttered" scan representing mainly pyrazine compounds. However, it should be noted that compounds such as pyridines and furfural may also be present in the basic fraction. Thus, care must be used in the interpretation of these scans. Another problem that may be encountered is that pyrazine recovery is affected by the final basic pH used. Thus, a pH of 8 will result in a lower pyrazine concentration than a pH of 9.

One of the major reservations using the pH adjustment technique for pyrazine fractionation is the fact that the dramatic changes in pH normally associated with this procedure represent a prime situation for artifact formation. For example, the acidic treatment can result in protein denaturation which could expose reactive nitrogen groups while pH adjustment to the basic side could influence carbohydrate fragmentation. Therefore, through the manipulation of pH, pyrazine formation could actually be encouraged.

FLAVOR PROPERTIES

Although it is generally agreed that pyrazines found in foods contribute to characteristic flavor, surprisingly few reports have appeared dealing specifically with the taste and odor properties of individual pyrazines or with their approximate concentration found in foods. Also, little consideration has been given to the overall significance of pyrazine type and concentration to specific food flavors. However, the above deficiencies can be defended in light of the fact that the occurrence of pyrazines in most foods has only recently been recognized and thus research into their flavor properties may be forthcoming.

Pyrazine Odor Descriptions

There are various factors that dictate whether a compound can contribute significantly to the flavor of a food. First, the compound must possess a characteristic odor or taste associated with a specific food. For example, the detection of ethanol in some foods may not necessarily mean that ethanol contributes to the unique and characteristic flavor of that food, whereas the presence of ethanol in other foods and beverages is important to the flavor characteristics of the product. The flavor properties of most foods are highly complex. However, the flavor chemist has been fortunate in that some single specific compounds have been found to contribute a major portion to the flavor properties of certain foods. Examples would be ethyl-2-methylbutyrate, nona-2-*trans*-6-*cis*-dienal and nootkatone typical of apple, cucumber, and grapefruit, respectively.

With respect to pyrazines, some characteristic odor descriptions have been reported. These are summarized in Table 17.

Looking through this list it is quite apparent that some investigators have primarily concerned

TABLE 17

Odor Descriptions Reported for Various Pyrazine Compounds

Compound	Odor description	Reference
2,5-dimethylpyrazine	Earthy raw potato	Deck and Chang (1965)
5-ethyl-2,3-dimethylpyrazine	Chocolaty sweet	Polak's Frutal Works (1972)
Tetramethylpyrazine	Fermented soybeans	Kosuge and Kamiya (1962)
Acetylpyrazine	Popcorn	Roberts (1968)
2-acetyl-3-methylpyrazine	Cereal, roast grain	Polak's Frutal Works (1972)
Hydroxyalkylpyrazines	Odorless	Seifert et al. (1970)
Pyrazinones	Odorless	Seifert et al. (1970)
Methylisoamylpyrazine	Green, cocoa note	Polak's Frutal Works (1972)
Ethylisoamylpyrazine	Green, cocoa note	Polak's Frutal Works (1972)
Methoxypyrazine	Not characteristic	Seifert et al. (1970, 1972)
2-methyl-3-methoxy-pyrazine	Roasted peanuts	Seifert et al. (1970, 1972)
2-methyl-3-methoxy-pyrazine	Nutty, earthy	Parliment and Epstein (1973)
2-ethyl-3-methyl-pyrazine	Raw potato	Buttery et al. (1970)
2-ethyl-3-methoxy-pyrazine	Raw potato	Seifert et al. (1970, 1972)
2-ethyl-3-methoxy-pyrazine	Earthy, bell pepper	Parliment and Epstein (1973)
2-propyl-3-methoxy-pyrazine	Bell pepper	Seifert et al. (1970, 1972)
2-propyl-3-methoxy-pyrazine	Bell pepper	Parliment and Epstein (1973)
2-isopropyl-3-methoxy-pyrazine	Earthy, bell pepper	Parliment and Epstein (1973)
2-isopropyl-3-methoxy-pyrazine	Bell pepper, raw potato	Seifert et al. (1970, 1972)
2-butyl-3-methoxypyrazine	Bell pepper	Parliment and Epstein (1973)
2-isobutyl-3-methoxy-pyrazine	Green bell pepper	Buttery et al. (1969a)
2-isobutyl-3-methoxy pyrazine	Bell pepper	Seifert et al. (1970, 1972)
2-isobutyl-3-methoxy-pyrazine	Bell pepper	Parliment and Epstein (1973)
2-isobutyl-6-methoxy-pyrazine	Bell pepper	Parliment and Epstein (1973)
2-isopentyl-3-methoxy-pyrazine	Bell pepper	Parliment and Epstein (1973)

TABLE 17 (continued)

Odor Descriptions Reported for Various Pyrazine Compounds

Compound	Odor description	Reference
2-hexyl-3-methoxypyrazine	Bell pepper	Seifert et al. (1970, 1972)
2-hexyl-3-methoxypyrazine	Bell pepper	Parliment and Epstein (1973)
2-methoxy-3-(1-methylpropyl)pyrazine	Bell pepper	Parliment and Epstein (1973)
2-methoxy-3-(1-methylbutyl)pyrazine	Bell pepper	Parliment and Epstein (1973)
2-methoxy-3-(2-methyloctyl)pyrazine	Earthy, bell pepper	Parliment and Epstein (1973)
2-methoxy-3-isononylpyrazine	Bell pepper	Parliment and Epstein (1973)
2-methoxy-3-isobutyl-5-methylpyrazine	Minty, camphoraceous	Seifert et al. (1970, 1972)
2-methoxy-3-isobutyl-6-methylpyrazine	Bell pepper, mint	Seifert et al. (1970, 1972)
2-methoxy-3-isobutyl-5,6-dimethylpyrazine	Minty, camphoraceous	Seifert et al. (1970, 1972)
2-methoxy-3,6-dimethylpyrazine	Medicinal, earthy	Parliment and Epstein (1973)
2-methoxy-3,6-diisobutylpyrazine	Earthy, bell pepper	Parliment and Epstein (1973)
3-ethoxy-3-methylpyrazine	Earthy, nutty	Parliment and Epstein (1973)
2-ethoxy-3-ethylpyrazine	Raw potato	Seifert et al. (1970, 1972)
2-ethoxy-3-iobutylpyrazine	Earthy, bell pepper	Parliment and Epstein (1973)
2-butoxy-3-methylpyrazine	Floral, medicinal	Parliment and Epstein (1973)
2-butoxy-3-propylpyrazine	Medicinal, earthy	Parliment and Epstein (1973)
2-methylthio-3-methylpyrazine	Nutty, cracker	Parliment and Epstein (1973)
2-methylthio-3-isobutylpyrazine	Bell pepper	Parliment and Epstein (1973)
2-methylthio-6-isobutylpyrazine	Bell pepper	Parliment and Epstein (1973)
5H-6,7-dihydrocyclopentapyrazine	Green, phenolic	Polak's Frutal Works (1972)
2-methyl-5H-6,7-dihydrocyclopentapyrazine	Chocolaty	Polak's Frutal Works (1972)
5-methyl-5H-6,7-dihydrocyclopentapyrazine	Peanut	Polak's Frutal Works (1972)
5-methyl-2H-3,4,6,7-tetrahydrocyclopentapyrazine	Roasted nut, burnt	Pittet et al. (1972)
5,7,7-trimethyl-2,3,4,6,7,8-hexahydroquinoxaline	Sweet, tobacco-like	Pittet et al. (1972)
2,3-dimethyl-4a,5,6,7,8,8a-hexahydroquinoxaline	Tobacco-like, buttery	Pittet et al. (1972)
2,3,5,6,7,8,9,10,11,12-decahydrocyclodecapyrazine	Nut-like, fatty	Pittet et al. (1972)

themselves with describing the odor properties of numerous synthetic pyrazines but the specific odor properties of fewer than five naturally occurring pyrazines have been reported. Also, some of the published odor descriptions are quite vague. For example, terms like nutty, toasted, medicinal, floral, and earthy have been used.

Recently Guadagni et al. (1972) emphasized the importance of pyrazines in potato chip aroma. They formulated three different mixtures containing flavor compounds found in potato chips and asked their panel to rate these mixtures as to their similarity to fresh potato chips. Of the 3 mixtures the one with the largest proportion of pyrazines (4 out of 9 compounds in the mixture, totaling 56 ppm) was rated closest to fresh potato chip aroma. The mixture containing an intermediate number of pyrazine types (2 out of the 8 compounds, totaling 28 ppm) was second and that with the least number of pyrazine compounds present (2-ethyl-3-methoxypyrazine at a level of 66 ppm) was rated last. This study also points out the synergistic effect of pyrazines since the best product had the greatest number of pyrazine compounds but not the greatest pyrazine concentration. Thus, it can be seen that a definite need exists for a critical evaluation of the specific odor properties of both naturally occurring and synthesized pyrazines. This would help tremendously in relating to the overall contribution of pyrazines to food flavor.

Pyrazine Thresholds

Another factor to consider is the odor and/or taste threshold of the compound. Numerous factors can influence the threshold properties of compounds. For example, isomeric forms of a compound possessing the same mass will possess different threshold values. Also, within a homologous series, chain length can influence the partition coefficient. This is clearly demonstrated in Figure 2. Another factor to consider is

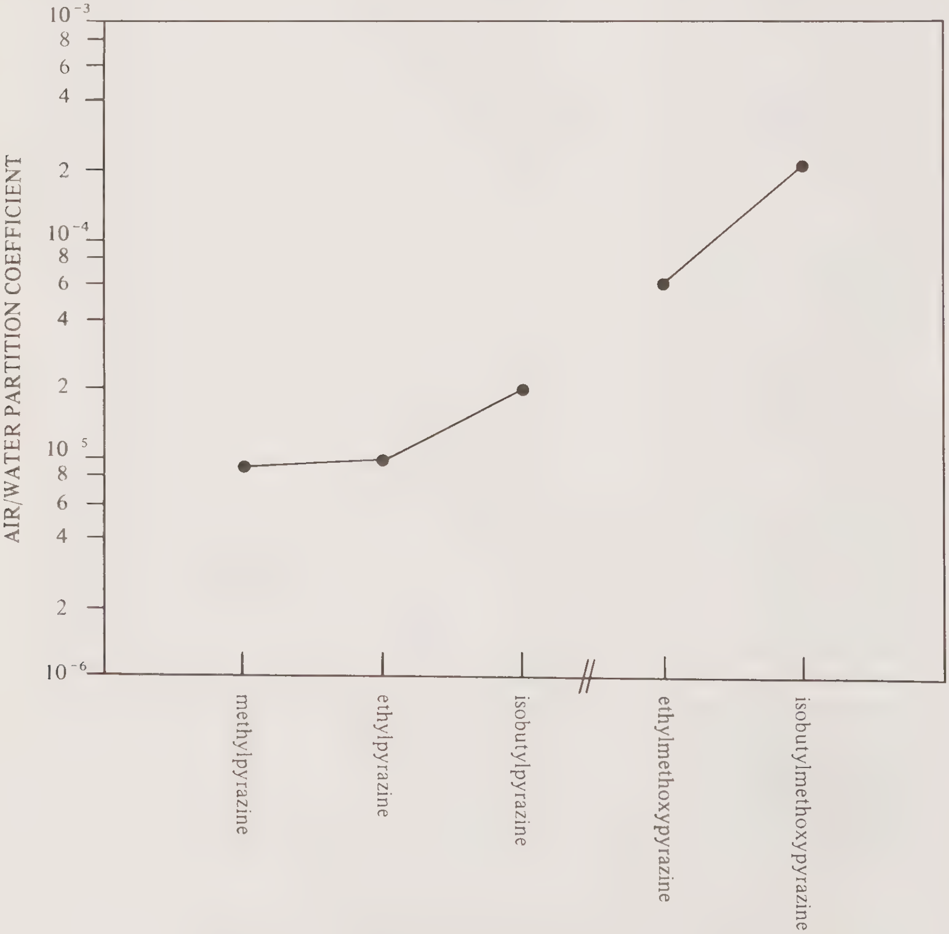

FIGURE 2. Influence of chain length on pyrazine volatility.

the partition coefficient between the types of media in which the compound is present. Thus the odor threshold for a compound normally will be different in water than in oil. In the case of pyrazines this is especially important since pyrazines have been found in both fat-based foods (nut products, potato chips) and essentially waterbased foods (coffee, vegetables). Table 18 is included not only to demonstrate the differences in odor thresholds that may occur with pyrazines in different media (water and oil), but also to dramatically illustrate the vast differences in odor thresholds as influenced by type of pyrazine, isomeric forms of pyrazines, and investigative techniques. The majority of thresholds listed in Table 18 are for naturally occurring pyrazines. An appreciation for the odor potency of these compounds is quite apparent.

TABLE 18

Typical Pyrazine Compound Odor Thresholds

Compound	PPB threshold in water	PPB threshold in oil
Methylpyrazine[a]	105,000	27,000
Methylpyrazine[b]	60,000	–
2,3-dimethylpyrazine[b]	2,500	–
2,5-dimethylpyrazine[a]	35,000	17,000
2,5-dimethylpyrazine[b]	1,800	2,600
2,5-dimethylpyrazine[d]	1,000	2,000
2,6-dimethylpyrazine[a]	54,000	8,000
2,6-dimethylpyrazine[b]	1,500	–
Trimethylpyrazine[a]	9,000	27,000
Tetramethylpyrazine[a]	10,000	38,000
Ethylpyrazine[a]	22,000	17,000
Ethylpyrazine[b]	6,000	–
Ethylmethylpyrazine[a]	500	900
2-ethyl-3-methylpyrazine[b]	130	–
2-ethyl-5-methylpyrazine[b]	100	320
2-ethyl-3,5-dimethylpyrazine[a]	15,000	24,000
2-ethyl-3,6-dimethylpyrazine[a]	43,000	24,000
2-ethyl-3,6-dimethylpyrazine[b]	0.4	24
2,5-diethylpyrazine[b]	20	270
2,6-diethylpyrazine[b]	6	–
Pentylpyrazine[a]	1,000	9,000
2-isobutyl-3-methylpyrazine[b]	35	–
Methoxypyrazine[c]	700	–
2-methyl-3-methoxypyrazine[c]	4	–
2-ethyl-3-methoxypyrazine[c]	0.4	–
2-propyl-3-methoxypyrazine[c]	0.006	–
2-isopropyl-3-methoxypyrazine[c]	0.002	–
2-isobutyl-3-methoxypyrazine[c]	0.002	–
2-hexyl-3-methoxypyrazine[c]	0.001	–
2-isobutyl-3-methoxy-5-methylpyrazine[c]	0.3	–
2-isobutyl-3-methoxy-6-methylpyrazine[c]	2.6	–
2-isobutyl-3-methoxy-5,6-dimethylpyrazine[c]	315	–
2-ethyl-3-ethoxypyrazine[c]	11	–

[a] Koehler et al. (1971).
[b] Guadagni et al. (1972).
[c] Seifert et al. (1970, 1972).
[d] Deck and Chang (1965).

The obvious discrepancies among threshold values between the work of Koehler et al. (1971) and Guadagni et al. (1972) can be explained partly on the basis of the odor evaluation techniques used by the two groups. Koehler et al. (1971) determined odor thresholds by having their panel sniff water and oil solutions containing pyrazines; whereas, Guadagni et al. (1972) actually induced the sample vapor containing pyrazine compounds into the nose cavity through the use of teflon tubing and squeeze bottles partly filled with sample. Thus, one would expect lower threshold values using the Guadagni et al. (1972) technique. However, some may argue that the technique used by Koehler et al. (1971) would be more realistic from a consumer standpoint.

Another major discrepancy exists with the data presented in Table 18. In all cases, where measured, Guadagni et al. (1972) reported the odor threshold of pyrazines to be higher in oil than water. Odor threshold values decreased as little as 1.5 times (2,5-dimethylpyrazine) to as much as 60 times (3-ethyl-2,5-dimethylpyrazine) when compared in water and then in oil. However, Koehler et al. (1971) reported both increases and decreases in odor thresholds as influenced by the sampling medium. Assuming that the study reported by Guadagni et al. (1972) was conducted under more controlled conditions, the authors are in general agreement with the trends as reported by this group. At any rate, it can be stated that the odor thresholds of pyrazines will vary depending on the type of liquid phase present.

Another interesting pyrazine threshold study has appeared in the literature (Collins, 1971). This study dealt with the pyrazines found in roasted barley and their possible contribution to the flavor of dark Irish beer. He stated that one would not normally find many pyrazines present in the final dark beer since they would be lost during a common boil-off step used in processing. However, if the compounds normally lost during this boil-off were trapped, and refluxed back into the product, the beer developed strong pyrazine-like flavor which was found to be objectionable. In conjunction with this observation, Collins (1971) determined the flavor thresholds of 13 pyrazines added to dark Irish beer. These data are presented in Table 19. As can be seen, the reported flavor thresholds range from greater than 100 ppm for unsubstituted pyrazine and tetramethylpyrazine to as low as 0.005 ppm for 3-ethyl-2,5-dimethylpyrazine. However, it should be remembered that these compounds were added to a product that already had a unique flavor base (beer) and that no effort was made to actually detect pyrazines in the beer. Thus the actual level of certain pyrazines may actually have been higher than the amount added. Also, although the results were reported as flavor thresholds, no doubt odor was the primary means by which judgments were made.

TABLE 19

Flavor Thresholds of Various Pyrazines Added to Dark Irish Beer

Compound	Flavor threshold (ppm)
unsubstituted	>100
tetramethylpyrazine	>100
methylpyrazine	100
2,5-diethyl-3,6-dimethylpyrazine	100
2,3-dimethylpyrazine	50
2,5-dimethylpyrazine	25
ethylpyrazine	10
2,6-dimethylpyrazine	3
2-ethyl-3-methylpyrazine	2
2-ethyl-5-methylpyrazine	1
trimethylpyrazine	1
3-ethyl-2,6-dimethlypyrazine	0.025
2-ethyl-3,6-dimethylpyrazine	0.005

From Collins (1971).

Both the absolute and relative concentrations of a flavor compound in a food system should also be considered. If a compound is found at an absolute concentration below its reported threshold value, most researchers will dismiss it as not significantly contributing to the characteristic flavor of a product. However, a greater number of researchers are now realizing that this assumption may not be valid since combinations of compounds, each present at individual subthreshold amounts, can result in a possible synergistic situation whereby the mixture is detectable.

The relative concentration present is important from several aspects. For example, if it is present in very small amounts relative to the concentration of other flavor compounds present and possesses an average threshold value, chances are its contribution to overall flavor is insignificant. However, if it is present in larger amounts, even though it may have an average threshold value, its overall importance will naturally be greater.

Odor Unit Concept

Aside from relative concentration, the threshold value is also critical in the assessment of overall flavor contribution. For example, compounds with extremely low thresholds (3-ethyl-2,5-dimethyl-, 2,6-dimethyl-, and most methoxy pyrazines) do not have to be present in a very high concentration before they can significantly affect product odor. However, due to their higher thresholds, compounds such as methyl- and 2,6-dimethylpyrazine will need to form a larger relative proportion of the flavor mixture before they can be considered as contributing significantly. This fact has resulted in the introduction of the odor unit concept (Guadagni et al., 1966) which is a value obtained by dividing the component concentration found in a food system by the threshold concentration of the product. The value obtained, when considered in relation to the values for all compounds found in a system, can serve as a qualitative tool in the identification of compounds which make major flavor contributions.

Recently, Guadagni et al. (1972) applied this odor unit concept to the evaluation of volatiles obtained from potato chip oil. Of the 26 compounds reported, 11 were pyrazines. Since potato chips are essentially an oil-based food (30 to 40% lipid and only approximately 2% moisture), they used threshold values based on an oil medium and the relative percent of each volatile in the potato chip oil extract as the basis for calculating respective odor units. From the values calculated, they concluded that the only pyrazines that could significantly contribute to potato chip aroma were 3-ethyl-2,5-dimethylpyrazine and 2,6-diethylpyrazine. In this same study they concluded that on the odor unit values calculated, the compound methional was the most important contributor to the potato chip aroma.

Naturally, the use of the odor unit concept involves the application of several assumptions. For example, it is assumed that the different components in the mixture have additive threshold values. Other assumptions include the use of reliable threshold data for the approximate medium and that the relative concentration data obtained are truly representative of the product. Thus, problems such as separation efficiency and accurate identification are critical.

Pyrazine Quantitation

Another problem that faces the researcher in the evaluation of the flavor contribution of pyrazines in specific foods is in the area of accurate and consistent quantitation. Most investigators have been satisfied with detection of pyrazines in foods and have not reported on concentrations found. Other reports have appeared in which terms such as small, medium, and large have been used to describe relative pyrazine concentrations (Wang and Odell, 1972).

Koehler et al. (1971) attempted to quantitate several pyrazines in coffee, roasted peanuts, and potato chips by comparing gas chromatography peak areas of the isolated pyrazines with those areas of known concentrations of pyrazine standards. Specific pyrazine compounds measured were pyrazine, methylpyrazine, and dimethylpyrazine. Due to their isolation and quantitation techniques they were only able to quantitate dimethylpyrazine in potato chips and due to the small amount (0.2 mg/kg) found, they concluded that it contributed little to characteristic potato chip flavor. However, they were able to quantitate larger amounts of pyrazines in roasted peanuts (methylpyrazine at 6 mg/kg and dimethylpyrazine at 11 mg/kg) and in coffee (pyrazine at 5 mg/kg, methylpyrazine at 65 mg/kg, and dimethylpyrazine at 19 mg/kg).

Reiniccius et al. (1972) used an internal standard technique in an attempt to quantitate pyrazines isolated from cocoa beans. Since pyrazine itself had never been reported as present in cocoa products, it was used as the internal standard. Even when using a mild extraction procedure (diethylether extraction in a liquid chromatography column at room temperature) factors such as concentration, drying, and transfer resulted in an overall loss of 30% of pyrazine internal standard, 20% of a methylpyrazine standard, and approximately 15% of dimethyl- and tetramethylpyrazine standards. The precision of the procedure was such that if 20 μg standards were used, data varied ± 15%, whereas if 100 μg standards were used, the values only varied ± 6%. Thus, they reported that different varieties of cocoa beans roasted at 150° for 30 min had total pyrazine contents ranging from 142 to 698 μg/100 g. A portion of their data is summarized in Table 20.

Recently Sizer and Maga (1973) also used an internal standard technique to quantitate pyrazine formation in potato chips processed under varying conditions. They stated that by using steam distillation, complete volatile recovery was not achieved and that the higher boiling pyrazines, due to their higher activity coefficients, were recovered at a higher level than the lower boiling pyrazines. Thus, in their study, correction factors were used in quantitation based on a calibration curve. Typical pyrazine recoverability calibration curves can be seen in Figure 3. Correction factors were calculated by determining the recoverability of typical C_2, C_3, and C_4 substituted pyrazines as compared to the 2-methyl-pyridine internal standard. Their pyrazine quantitation results for potato chips are summarized in Table 21.

Thus from the above studies where quantitation was attempted, it can be seen that numerous difficulites can be encountered. However, quantitation data are needed to make more definite predictions of pyrazine flavor contribution to specific product and in the formulation of synthetic pyrazine based flavoring mixtures.

PYRAZINE FORMATION PATHWAYS

Pyrazine Nitrogen Sources

The nitrogen atoms in a pyrazine molecule can be incorporated into the compound by two possible pathways. Essentially, free ammonia can combine with reducing sugars to form pyrazines, or nitrogen not in the free state (nitrogen attached to amino acids) can also react. If free ammonia were the primary intermediate, one would expect the same pattern of pyrazine product formation regardless of the amino

TABLE 20

Pyrazine Quantitation of Cocoa Bean Varieties

	Variety					
Compound	1	2	3	4	5	6
methylpyrazine	49.6[a]	31.7[a]	26.9[a]	24.0[a]	24.0[a]	51.1[a]
2,5- and 2,6-dimethylpyrazine + ethylpyrazine	155.7	85.1	68.0	60.0	82.0	51.1
2,3-dimethylpyrazine	37.0	28.8	24.0	2.09	14.0	9.9
2-ethyl-5-methylpyrazine	30.7	15.3	14.0	9.0	7.0	3.0
2-ethyl-6-methylpyrazine	24.4	11.7	14.0	9.0	7.0	3.0
trimethylpyrazine	99.1	99.8	50.8	34.0	38.0	7.0
3-ethyl-2,3-dimethylpyrazine	54.4	25.8	26.9	16.9	17.0	9.9
6-ethyl-2,3-dimethylpyrazine	16.8	18.8	6.8	5.0	3.0	0.0
tetramethylpyrazine	228.9	268.8	126.0	59.0	41.0	7.0
Total	698	587	358	238	233	142

[a] μg/100 g

From Reiniccius et al. (1972).

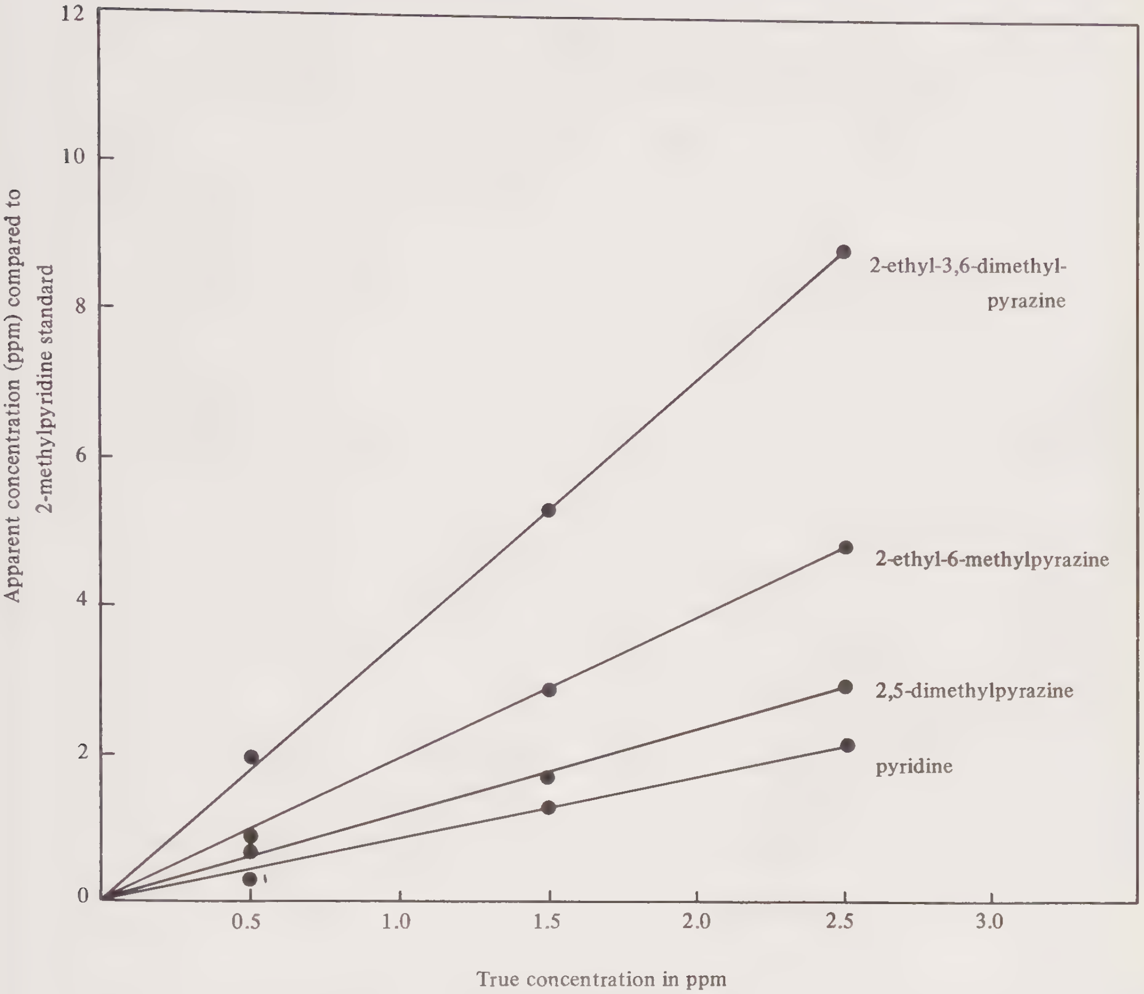

FIGURE 3. Pyrazine recoverability calibration curve.

acid present; whereas if the latter were the case, the types of pyrazines found would be dependent upon the amino acid present.

Early investigators had demonstrated the formation of pyrazines through the interaction of aldoses and ammonia (Brandes and Stoehr, 1896; Irvine et al., 1913; Hough et al., 1952; Wiggins and Wise, 1955). In conjunction with studies on the high temperature ammoniation of molasses, Davison and Wiggins (1956) ammoniated invert sugar at 120°C for two hr and pyrolyzed the solvent extract at 600°C. Within the residue they were able to identify 2,6-dimethylpyrazine. Krems and Spoerri (1947) demonstrated the formation of 2,5-dimethylpyrazine by reacting the 2-enal acrolein with ammonia.

In working with model glucose-amino acid systems, Newell et al. (1967) reported that essentially the same volatile pyrazine compounds were observed regardless of the nitrogen amino acid source employed. van Praag et al. (1968) also concluded that free ammonia was the primary intermediate and stated that the composition of the resulting pyrazine mixture was not dependent upon the amino acid source. They reacted the amino acids glycine, serine, leucine, isoleucine, valine, and alanine with D-fructose and found a similar series of pyrazines for all amino acids. Their conclusions were fortified by the fact that the use of fructose, glucose, or free ammonia in reaction with amino acids resulted in the same pyrazine series being formed. Examples of the types of pyrazines found by just refluxing sugars and ammonia are presented in Table 22.

A mechanism was proposed by van Praag et al. (1968) for the formation of pyrazines from glucose and ammonia based on the pathways of the Maillard reaction. Essentially, a glucosylamine is formed through

TABLE 21

Effect of Time and Temperature of Frying on Pyrazine Formation (ppm) in Potato Chips

	Minutes of frying					
Compound	2	3	4	5	6	7
2,3-dimethylpyrazine	0.21	0.18	0.55	0.42	0.64	0.71
2-ethyl-5-methylpyrazine	TR.	TR.	0.46	0.43	1.26	1.25
2-ethyl-6-methylpyrazine	0.14	0.17	0.42	0.22	1.63	1.92
ethyl- + 2,5 and 2,6-dimethylpyrazine	0.11	0.48	1.75	1.61	3.86	4.50
2-ethyl-3-methyl- and trimethylpyrazine	TR.	0.15	0.96	0.46	2.39	2.66
2-ethyl-3,5-dimethylpyrazine	TR.	TR.	0.27	0.16	0.83	0.85
2-ethyl-3,6-dimethylpyrazine	TR.	0.16	0.68	0.51	2.49	2.59

	Temperature of frying (°C)				
	120	135	150	165	180
2,3-dimethylpyrazine	0.15	0.18	0.43	0.67	1.67
2-ethyl-5-methylpyrazine	0.10	0.14	0.43	1.46	2.45
2-ethyl-6-methylpyrazine	TR.	0.19	0.22	1.60	2.25
ethyl- + 2,5 and 2,6-dimethylpyrazine	0.29	0.57	1.61	3.84	8.43
2-ethyl-3-methyl- and trimethylpyrazine	0.10	0.22	0.46	2.60	4.54
2-ethyl-3,5-dimethylpyrazine	TR.	0.10	0.16	1.03	1.41
2-ethyl-3,6-dimethylpyrazine	TR.	0.25	0.51	3.08	3.48

From Sizer and Maga (1973).

the loss of water during the glucose and ammonia reaction. Then, through an Amadori rearrangement, the product 1-amino-1- deoxy-2-fructose is formed which, with the loss of the amino group through progressive 2,3-enolization, results in a methyl-α-dicarbonyl intermediate. Resulting hydrolytic cleavage products could then directly condense with free ammonia to form a methyl substituted pyrazine. Interestingly, when one of these predicted glucose cleavage products (3-hydroxy-2-butanone) was reacted with free ammonia, a good yield of tetramethylpyrazine was obtained. However, as can be seen in Table 22, van Praag et al. (1968) did not report the presence of tetramethylpyrazine.

Wilkens and Lin (1970) had also assumed that free ammonia was necessary for pyrazine formation. They postulated that temperatures approximating 190°C were required to form pyrazines in heated soy products since it is the temperature at which ammonia is evolved from degradation of soy protein. However, as will be discussed below, free ammonia is not required; thus pyrazine formation in soy products can occur at a much lower temperature by relying on the free amino acids present in the system for a nitrogen source.

However, the work of Koehler et al. (1969) disputed the earlier studies of Newell et al. (1967) and van Praag et al. (1968) in that they reported that free ammonia was not the primary intermediate through which nitrogen was incorporated into the pyrazine ring. They found that in a low moisture model system different pyrazine distributions were obtained as influenced by the amino acid present. Their data are summarized in Tables 23 and 24. Thus, their study clearly demonstrated that the reactive ammonia unit was still attached to the amino acid and that the different pyrazine product profiles were the result of the differences in the ease of the nucleophilic attack of the amino acid molecules on the sugar. Thus, it would appear that in a food system where both sugars and amino acids are present, bound amino acid nitrogen is the primary contributor to the nitrogen found in the ring structure of pyrazines.

TABLE 22

Pyrazines Formed by Refluxing Sugars and Ammonia

Compound	Glucose + ammonia[a]	Rhamnose + ammonia[a]
pyrazine	5[b]	7[b]
methylpyrazine	1	1
2,3-dimethylpyrazine	3	3
2,5-dimethylpyrazine	2	2
2,6-dimethylpyrazine	4	0
trimethlypyrazine	5	0
ethylpyrazine	0	5
2-ethyl-3-methylpyrazine	0	6
2-ethyl-5-methylpyrazine	0	4
2-ethyl-3,5-dimethylpyrazine	0	9
2-ethyl-3,6-dimethylpyrazine	0	8
2-ethyl-3,5,6-trimethylpyrazine	0	10

[a] 100 g sugar + 40 ml, 28% ammonium hydroxide + 100 g water, refluxed for 2 hr.
[b] 1–largest quantity, 10–smallest quantity, 0–not present.

From van Praag et al. (1968).

TABLE 23

Influence of Ammonia Source on Pyrazine Formation Products

Compound	Glucose + asparagine	Glutamine	Glutamic	Aspartic	Ammonium chloride
pyrazine	3[a]	3[a]	3[a]	7[a]	1[a]
methylpyrazine	1	1	2	1	2
3,6-dimethylpyrazine	2	2	4	2	6
ethylpyrazine	4	5	5	6	6
2-ethyl-6-methylpyrazine	5	6	8	4	4
trimethylpyrazine	6	7	6	3	6
3-ethyl-2,5-dimethylpyrazine	7	8	1	5	5
3-ethyl-2,6-dimethylpyrazine	8	4	7	8	3

[a] 1–most abundant, 8–least abundant.

From Koehler et al. (1969).

TABLE 24

Influence of Ammonia and Carbohydrate Source on Total Pyrazine Formation

Reactants	Total yield (μmoles)
asparagine – glucose	411
asparagine – sucrose	268
glutamine – glucose	205
aspartic acid – glucose	198
ammonium chloride – fructose	195
glutamic acid – glucose	114
ammonium chloride – glucose	59

From Koehler et al. (1969).

Pyrazine Carbon Sources

Koehler et al. (1969) have clearly demonstrated that the primary carbon source for pyrazine formation comes from sugars. Through the use of a ^{14}C radioisotope technique, they labeled the sugar molecule and left the amino acid unlabeled in one study; in another, the amino acid was labeled while the sugar was not. In each of the resulting mixtures the formation of labeled pyrazine was almost nonexistent when the ^{14}C label was on the amino acid. However, a vast majority of the pyrazine produced from the labeled sugar contained ^{14}C.

The study by Koehler et al. (1969) also reported on the probable pathway of carbon atom incorporation from hexose degradation into pyrazine molecules. They assumed two possible pathways. The first involved the breakdown into only one two-carbon fragments per hexose unit, whereas the other pathway assumed that three equivalent two-carbon units would result from each hexose molecule. Their ^{14}C labeling data indicated that the first pathway was predominant and suggested an unsymmetrical intermediate. Koehler et al. (1969) pointed out that information such as whether the carbon fragments are positioned exocyclinically or endocyclinically in the pyrazine molecule and whether the intermediate is split by hydrolysis, aminolysis, or retroaldolization had not been determined. However, since hexose degradation can also result in three-carbon fragments, they postulated that the variable pyrazine distribution patterns they observed may have been due to the differing rates at which various amines would react with these variable hexose fragments.

The formation of 2,5-dimethylpyrazine from the reaction of either L-leucine or L-isoleucine with pyruvaldehyde was noted by Wang et al. (1969). Thus they postulated that α-dicarbonyls could induce Strecker degradation of any amino acid to form aminoreductones which through subsequent selfcondensation and oxidation lead to pyrazines.

An interesting study by Koehler and Odell (1970) demonstrated that numerous compounds can serve as carbon source intermediates in pyrazine formation. Typical data obtained are presented in Table 25. The most interesting conclusion that can be drawn from data in Table 25 is that many types of products, and thus not only sugars, can react with amines (asparagine in this case) to form pyrazines. Some of these products may arise from lipid degradation. Interestingly, all or most of the carbon sources evaluated are commonly present in most food systems. The two-carbon unit glyoxal gave the highest yield of unsubstituted pyrazine. However, some methylpyrazine was also found, thus indicating that some three-carbon units must also have been formed. The other two-carbon unit evaluated (acetaldehyde) was predicted to only yield unsubstituted pyrazine. However, the acetaldehyde-asparagine mixture yielded a pyrazine mixture with dimethylpyrazine being formed in the largest amount. Thus, the formation of a pyrazine mixture indicated that acetaldehyde is capable of reacting with itself for forming the required three-carbon units needed for the formation of methyl- and dimethylpyrazines. Two of the other three-carbon units evaluated were not very reactive carbon sources. Glycerol only gave small amounts of the

TABLE 25

Effect of Carbon Source on Pyrazine Yields

Reactive mixture	Carbon length	Pyrazine	Methyl-pyrazine	Dimethyl-pyrazine	Tetramethyl-pyrazine
glyoxal-asparagine	2	527[a]	91[a]	ND[b]	ND[b]
acetaldehyde-asparagine	2	29	51	291	ND
glycerol-asparagine	3	2	7	2	ND
propionaldehyde-asparagine	3	ND	ND	ND	ND
hydroxyacetone-asparagine	3	ND	ND	9725	ND
2,3-butanedione-asparagine	4	ND	ND	ND	2662
glucosamine	6	107	252	27	ND

[a] mol
[b] not detected

From Koehler and Odell (1970).

unsubstituted, mono-, and disubstituted pyrazines, whereas propionaldehyde and asparagine produced no detectable pyrazines. In an earlier study Lento et al. (1960) had predicted that the three-carbon unit hydroxyacetone could be an important browning intermediate especially under basic conditions. Thus, when Koehler and Odell (1970) reacted hydroxyacetone with asparagine, a high yield of the predicted compound dimethylpyrazine was found. This would indicate that hydroxyacetone can be an efficient and highly specific carbon source intermediate in pyrazine formation. Another highly specific carbon source intermediate found was 2,3-butanedione (diacetyl). It produced a high level of only tetramethylpyrazine. The last compound listed in Table 25 was included to demonstrate that there are compounds that are capable of supplying both the carbon and nitrogen through fragmentations and recombinations for pyrazine formation.

Rizzi (1972) demonstrated that the compound aminoacetone could be treated to produce polyalkylpyrazines. Specifically, he reported finding 50% 2,5-dimethylpyrazine, 33% trimethylpyrazine, and 17% 3-ethyl-2,5 dimethylpyrazine. As a result of this observation, Rizzi (1972) proposed a hypothetical pathway for the formation of the numerous polyalkylpyrazines reported in foods. He proposed a two-step procedure whereby aminoacetone formed a dimethyldihydropyrazine. Step one involves the formation of the acyclic imino-ketone through the condensation of two molecules of aminoacetone. This is followed by an additional loss of water via intramolecular condensation to yield the dihydropyrazine. Isomerization of the acyclic imino-ketone to its more stable conjugated isomer can then undergo retro-Mannich condensation to yield *N*-ethylideneamino-acetone as one of the by-products. Through realdolization of this product with formaldehyde and dehydration of the intermediate carbinol, a new four-carbon imino-ketone would form. A four-carbon amino-ketone and acetaldehyde could result from hydrolysis of the imino-ketone. Finally, condensation of the amino-ketone with aminoacetone could form trimethylpyrazine. Also, if realdolization of *N*-ethylidiene amino acetone were done with acetaldehyde instead of formaldehyde, a homologous amino-ketone would form which can condense with aminoacetone to yield 2,5-dimethyl-3-ethylpyrazine. Thus, by using the above reasoning, Rizzi (1972) has explained a nonoxidative pathway whereby complex branched chain pyrazines can be formed by reversible aldol condensations followed by the thermal rearrangement of the hydropyrazine intermediate. Rizzi (1972) expanded this concept to include the numerous aldehydes formed during Strecker degradation of α-amino acids.

Wang and Odell (1972) also demonstrated that the three-carbon fragment glycerol could react with several amino acids to form pyrazines. Their work is summarized in Table 26. The authors stated that when alanine or glycine were heated alone, no pyrazines were formed.

Carbohydrate-Amine Interactions

The influence of the interaction of amino acids and carbohydrates on the formation of flavor compounds has been well theorized (Hodge, 1953; Hodge et al., 1972). Decreases in amino acid and sugar contents as influenced by heating have been reported (Rohan and Stewart, 1966a,b; Fitzpatrick et al., 1965; Reineccius et al., 1972) for various food systems.

TABLE 26

Pyrazine Reaction Products of Glycerol and Amino Acids

Compound	Glycerol + alanine	Glycerol + glycine
methylpyrazine	+++	++++
2,3-dimethylpyrazine	+	++
2,5 + 2,6-dimethylpyrazine	++++	+++++
2-ethyl-5-methylpyrazine	++	–
trimethylpyrazine	+++	+++++
3-ethyl-2,5-dimethylpyrazine	+++++	++

+++++: Very large; ++++: large; +++: medium; ++: small; +: very small.

From Wang and Odell (1972).

Through the use of model systems Dawes and Edwards (1966) suggested that simple pyrazines could be formed in heated foods through condensation reactions of sugars and amino acids. They reported finding trimethylpyrazine from a refluxed mixture of fructose and glycine and the presence of 2,5-dimethylpyrazine in fructose-glycine and fructose-phenylalanine mixtures. Thus, they were among the first to postulate a pyrazine formation theory in a food system. Basically they believed that the aldose-amine reaction product pyruvaldehyde, by means of its action in Strecker degradation of the amino acid, resulted in the formation of an α-aminocarbonyl. Self-condensation of this resulting α-aminocarbonyl could form a dihydropyrazine which in turn easily could be oxidized to the corresponding dimethylpyrazine.

In 1967 Newell et al. published a pathway for the conversion of amino acids and sugars into pyrazines. In this theory an amino acid combined at the anomeric end of an aldose to form a glycosylamine. Then the 1,2-eneaminol was formed by dehydration of the glycosylamine with the resulting elimination of hydroxyl ion forming a Schiff base cation. This cation in turn could decarboxylate to form the imine which could then hydrolyze to form an aldehyde and a dienamine. Through enolization of the 1,2 double bond and migration of the 3,4 double bond in the dienamine, an unsaturated ketoamine can form which in turn can undergo retro-aldol condensation to produce glyceraldehyde and aminoacetone. Finally, condensation of two molecules of aminoacetone would form dimethylpyrazine.

The study by Koehler et al. (1969) involving sugar-amino acid model systems was previously discussed in the pyrazine nitrogen source portion of this review. In a later study, Koehler and Odell (1970) investigated various factors affecting the formation rates of pyrazines in sugar-amine model systems. When the ratio of sugar (glucose) to amine (asparagine) was changed from the normal 1:1 to 3:1, 2-methylpyrazine formation decreased tenfold and that of dimethylpyrazine approximately 125-fold. However, tripling the amount of asparagine did not affect dimethylpyrazine yield but decreased methylpyrazine yield by approximately 25%. Thus, they were able to demonstrate that optimum pyrazine formation was dependent upon proper sugar-amine reaction ratios. They also presented data demonstrating that pyrazine formation was influenced by the amine source. These data are summarized in Table 27. As can be seen from Table 27, asparagine was the most reactive amino acid and glycine the least active in pyrazine formation. These data also demonstrate that pyrazine formation is base catalyzed since the addition of sodium hydroxide to aspartate increased pyrazine yield as compared to aspartate without added sodium hydroxide.

Pyrazine formation rates as influenced by sugar sources were also investigated by Koehler and Odell (1970). The data are shown in Table 28. As can be seen, fructose was by far the most reactive sugar source. The higher yields for fructose are explained by the authors who cited the works of Stadtman et al. (1952), who found that fructose fragmented more easily than glucose, and Erickson (1953), who indicated that ketoses were more readily reactive with amines than aldoses, especially in aqueous alcoholic systems. As can be seen in Table 28, the pentose arabinose when reacted with asparagine also produced pyrazines. However,

TABLE 27

Influence of Nitrogen Source on Pyrazine Formation in Model Glucose-amine Systems

Nitrogen source	Methylpyrazine	Dimethylpyrazine
asparagine	110[a]	402[a]
ammonium hydroxide	1415	56
aspartate + sodium + hydroxide	92	282
alanine	23	82
aspartate	16	81
lysine	11	20
glycine	ND[b]	14
ammonium chloride	ND	ND

[a] mol
[b] not detected

From Koehler and Odell (1970).

TABLE 28

Effect of Sugar Source on Pyrazine Yield in Asparagine-sugar Model Systems

Sugar source	Methylpyrazine	Dimethylpyrazine
fructose	137[a]	1142[a]
glucose	110	402
sucrose	85	166
arabinose	94	48

[a] mol

From Koehler and Odell (1970).

due to the differences in fragmentation patterns between hexoses and pentoses, a larger proportion of methylpyrazine resulted from the pentose and more dimethylpyrazine from the hexoses.

Koehler and Odell (1970) postulated that pyrazine formation from sugar-amine reactions could result from two pathways primarily dependent upon the temperature involved. At low temperatures they postulated that the slow formation of pyrazines could result through the formation of a glucosylamine which could then condense to form a di-tetrahydroxybutylpyrazine intermediate as discussed by Hough et al. (1952). Pyrazines would then form through the rearrangement and cleavage of this intermediate. However, at high temperatures, sugars would directly rearrange and cleave to form smaller hydroxy- and dicarbonyl fragments which could then combine with amine nitrogen to form pyrazines.

With regard to the role of temperature on pyrazine formation in a sugar-amine model system Koehler and Odell (1970) found that few if any pyrazines were formed at temperatures below 100°C. Measurable pyrazine formation started to occur at 100°C and increased rapidly up to 150°C. After 150°C most pyrazine yields declined, probably due to either pyrazine destruction or losses from the system due to their volatility. At a constant temperature (120°C) pyrazine formation was found to rapidly increase the first 24 hr and then demonstrated little additional increase during the remainder of the 72 hr heating study.

Several other reports have appeared on pyrazine formation from sugar-amine interactions. Fujimaki et al. (1972) found pyrazine, methyl-, 2,3-dimethyl-, 2,5-dimethyl-, 2-ethyl-5-methyl-, trimethyl-, and a mixture of 2-methyl-3,5-diethyl- and 2-methyl-5,6-diethylpyrazine when D-glucose and L-alanine were heated. Several of the same pyrazines were found by Shigematsu et al. (1972) in a heated DL-α-alanine and glucose mixture. However, Kato et al. (1972b) were not able to detect any pyrazine compounds from a heated mixture of L-rhamnose and ethylamine.

In another study Kato et al. (1973) demonstrated that the sulfur containing amino acids L-cysteine and L-cystine would thermally react with either glucose or pyruvaldehyde to form pyrazines. Data of this nature are summarized in Table 29A. As seen, cysteine was more reactive than cystine and glucose more favorable than pyruvaldehyde in forming pyrazines.

TABLE 29A

Pyrazines Formed from Sulfur-amino Acids and Glucose or Pyruvaldehyde

Pyrazines Formed	Cysteine + Glucose	Cystine + Glucose	Cysteine + Pyruvaldehyde	Cystine + Pyruvaldehyde
Methylpyrazine	+	+	–	
2,5-dimethylpyrazine	+	–	+	+
2-methyl-3-ethylpyrazine	+	–	–	–
Trimethylpyrazine	–	–	+	–
2,5-dimethyl-3-ethylpyrazine	+	–	+	+

From Kato et al. (1973)

Amino-Hydroxy Compound Decompositions

Kato et al. (1970) demonstrated that pyrazines can result from the heating of β-hydroxy amino acids. The three specific amino acids investigated were L-serine, L-threonine and L-alanine. The amino acids were heated at 280 to 360°C and the resulting volatiles driven off with nitrogen. The basic volatile fraction was isolated and the pyrazines found are reported in Table 29. Since no dicarbonyl compounds were found among the volatile reaction products, the authors suggested that pyrazines could form directly from β-hydroxy amino acids with the aid of dicarbonyl compounds.

A recent study by Wand and Odell (1973) also reported that pyrazines can result from the heating of numerous amino-hydroxy compounds. A portion of their data is summarized in Table 30. In this same study the authors did not detect pyrazines by heating under the same conditions the compounds glycine, alanine, phenylalanine, leucine, isoleucine, valine, methionine, cystine, tyrosine, histidine, proline, hydroxyproline, tryptophan, lysine, hydroxylysine, aspartic acid, asparagine, glutamic acid, glutamine, adenine, and adenosine. Also, no pyrazines were detected by heating egg albumin and bovine albumin. Thus, this study demonstrated that pyrazines can be formed from certain amino-hydroxy compounds, especially those having amino and hydroxy groups in adjacent carbon positions.

TABLE 29

Pyrazines Found in Prolyzed α-Hydroxy Amino Acids

Compound	Serine	Threonine	Alanine
pyrazine	+	–	–
methylpyrazine	+	–	–
ethylpyrazine	+	–	–
2-ethyl-6-methylpyrazine	+	–	–
2-6-diethylpyrazine	+	–	–
2,6-diethyl-3-methylpyrazine	+	–	–
2,5-dimethylpyrazine	–	+	–
trimethylpyrazine	–	+	
3-ethyl-2,5-dimethylpyrazine	–	+	

From Kato et al. (1970).

TABLE 30

Pyrazines Found from Heated Amino-hydroxy Compounds

Compound	Serine	Threonine	Ethanolamine	Glucosamine	4-Amino-3-hydroxy butyric acid	Alanyl-serine
pyrazine	+++	–	++++	+	–	++
methylpyrazine	++	+	+++	++++	–	++
2,3-dimethylpyrazine	+	–	–	+	–	–
2,5-dimethylpyrazine	–	++++	+	+++	+++	–
ethylpyrazine	++++	–	++	–	–	+++
2-ethyl-5-methylpyrazine	–	–	–	+	–	–
2-ethyl-6-methylpyrazine	+	–	–	–	–	++
2,6-dimethylpyrazine	++	–	–	–	–	+++
3-ethyl-2,5-dimethylpyrazine	+	+++	++	–	++	–
trimethylpyrazine	–	+++	–	++	+	–

++++: very large; +++: large; ++: medium; +: small; –: not detected.

From Wang and Odell (1973).

With reference to heating protein sources, Kato et al. (1972a) did report finding methyl- and 2-ethyl-6-methylpyrazine from heated casein. Ferretti et al. (1970) also reported finding pyrazines from a heated protein source (casein) and lactose. The specific pyrazines they reported were pyrazine, methyl-, 2,3-, 2,5-, and 2,6-dimethylpyrazine. In a later similar study Ferretti and Flanagan (1971a) also found methylethyl-, tri-, and tetramethylpyrazine.

In an earlier study Deck (1968) has postulated that 2,5-dimethylpyrazine could arise from the cyclization of the amino acid threonine under the conditions of deep fat frying potato chips.

Biological Pathways

Since methoxypyrazines have been found in foods that have not undergone excessive heat treatment, one must assume that they can be synthesized in plants naturally. Murray et al. (1970) have postulated that naturally occurring methoxypyrazines can be derived through the amidation and condensation of α-amino acids with α, β dicarbonyls found in plant tissues with the resulting products being easily methylated.

Several reports have appeared implicating microbial metabolism as a means of pyrazine production. As discussed previously in the soy products occurrence section, Kosuge and Kamiya (1962) isolated tetramethylpyrazine from a strain of *Bacillus subtilis.* Demain et al. (1967) also isolated tetramethylpyrazine from a mutant strain of *Corynebacterium glutamicum.* Although no exact pathways were reported in the above two studies, the condensation of acetoin with ammonia was thought to be the pathway involved. As also discussed previously, a portion of the study reported by Reineccius et al. (1972) implicated microbial fermentation of certain cocoa bean varieties in the formation of tetramethylpyrazine.

It should also be remembered that the vitamin riboflavin is a condensed pyrazine derivative; thus in its synthesis and degradation pyrazine derivatives may appear. Also, thermal decomposition of riboflavin during roasting in a complex food system may also be a source of pyrazine compounds.

Miscellaneous Pathways

Walradt et al. (1971) stated that it would seem impossible that the appropriate α-dicarbonyl precursors are readily available from carbohydrate breakdown for the formation of complex alkyl and alkenyl substituted pyrazines. In the case of alkenyl substituted pyrazines they cited the study of Grimmett (1965) whereby these could be formed through dehydration of the corresponding hydroxypyrazines. They also postulated that acetyl and methylacetylpyrazines could result from the condensation of the browning reaction product *cis*-methylreductone with either glyoxal or pyruvaldehyde and amino acids. The formation pathway for pyrazine products such as cyclopentapyrazine may be due to the reaction of the carbohydrate degradation product 2-hydroxy-3-methyl-2-cyclopentane-1-one with amino acid, glyoxal, and pyruvaldehyde (Walradt et al., 1971).

For the convenience of the reader, pyrazine formation pathways are summarized in Figure 4.

PYRAZINE FLAVOR APPLICATIONS

Introduction

Since most pyrazine compounds possess unique flavor characteristics at extremely low concentrations, they are becoming more prevalent as flavoring compounds. For example, in 1965 Hall and Oser reported no pyrazine compounds to be present on the GRAS list among the more than 1,100 flavor compounds reviewed. However, by 1970 (Hall and Oser), 17 pyrazines used as flavoring agents were on the GRAS list. An additional 12 such compounds were reported by Oser and Hall in 1972. The most recent GRAS flavor compound list included three more pyrazine compounds (Oser and Ford, 1973). Presently slightly over 30 pyrazine compounds are on the list of close to 1,400 GRAS approved flavoring agents. The specific pyrazine compounds currently having GRAS approval along with the usage levels normally encountered in such food products as beverages, cereals, candy, ice cream, baked goods, gelatins, puddings, chewing gum, meat products, milk products, and condiments are listed in Table 31.

As can be seen from Table 31, none of the pyrazines listed is routinely used at levels higher than 10 ppm; thus any possible concern from a toxicity standpoint should be minimal.

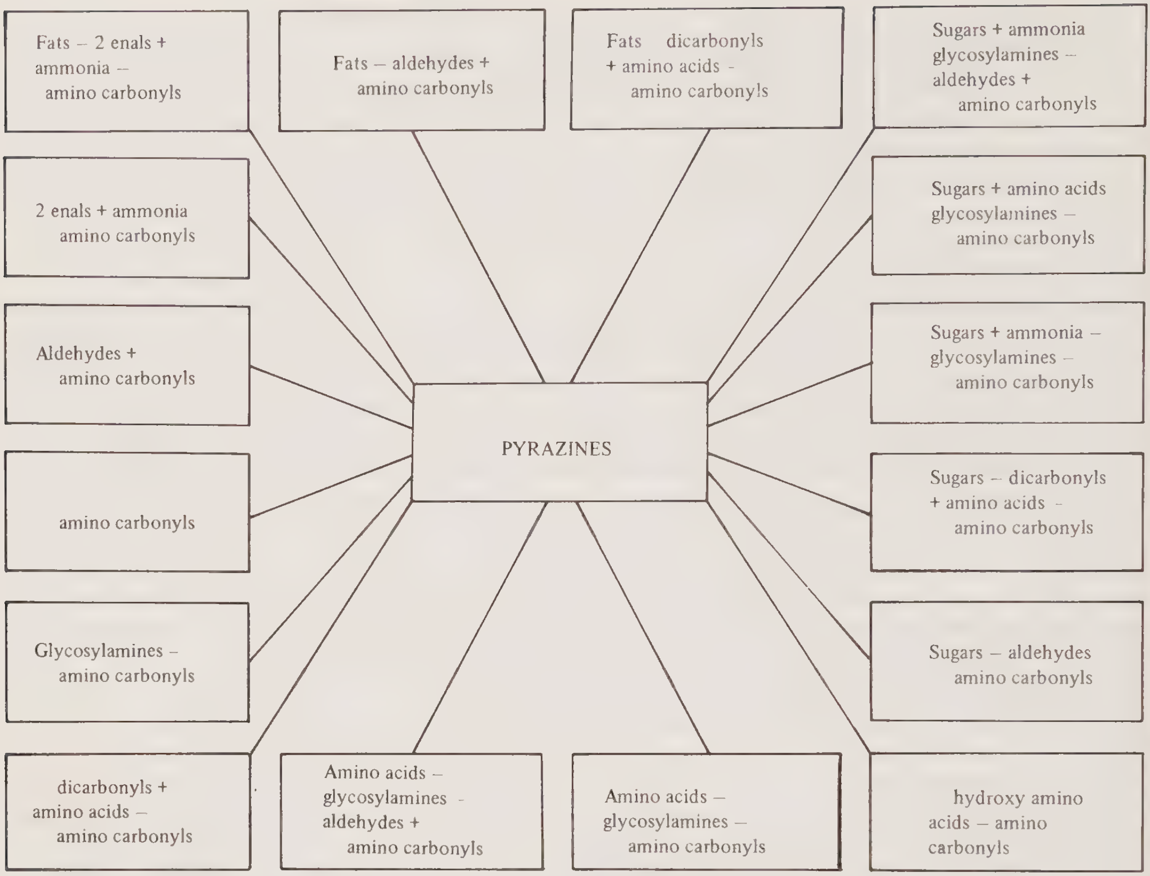

FIGURE 4. Summary of pyrazine formation pathways.

TABLE 31

Average Usage Levels of "GRAS" Approved Pyrazines as Food Flavorings

Compound	"FEMA" No.[a]	Average usage level (ppm)
methylpyrazine[c]	3,309	10
ethylpyrazine[c]	3,281	10
2,3-dimethylpyrazine[c]	3,271	10
2,5-dimethylpyrazine[c]	3,272	10
2,6-dimethylpyrazine[c]	3,273	10
2,3-diethylpyrazine[b]	3,136	1
3-ethyl-2-methylpyrazine[b]	3,155	3
2-ethyl-5-methylpyrazine[b]	3,154	2–5
2-ethyl-3,5- or 6-dimethylpyrazine[b]	3,149	2–5
3-ethyl-2,6-dimethylpyrazine[b]	3,150	5

[a] Flavor and Extract Manufacturers Association
[b] Hall and Oser (1970)
[c] Oser and Hall (1972)
[d] Oser and Ford (1973)

TABLE 31 (continued)

Average Usage Levels of "GRAS" Approved Pyrazines as Food Flavorings

Compound	"FEMA" No.[a]	Average usage level (ppm)
2,3-diethyl-5-methylpyrazine[d]	3,336	0.1–1
trimethylpyrazine[b]	3,244	5
tetramethylpyrazine[b]	3,237	5
2-methyl-5-vinylpyrazine[b]	3,211	10
5,6,7,8-tetrahydroquinoxaline[c]	3,321	1–5
5-methylquinoxaline[b]	3,203	10
acetylpyrazine[b]	3,126	5
2-acetyl-3-ethylpyrazine[c]	3,250	10
2-acetyl-3,5(and 6)-dimethylpyrazine[d]	3,327	1–5
isopropenylpyrazine[c]	3,296	10
methoxypyrazine[c]	3,302	10
2-methoxy-3(5 and 6)isopropylpyrazine[d]	3,358	0.05–2
2-isobutyl-3-methylpyrazine[b]	3,133	5
2-isobutyl-3-methoxypyrazine[b]	3,132	0.05
2,5 or 6-methoxy-3-methylpyrazine[b]	3,183	2–4
2-ethyl-(3,5 and 6)-methoxypyrazine (85%) plus 2-methyl-(3,5 and 6)-methoxypyrazine (13%)[c]	3,280	5
2-mercaptomethylpyrazine[c]	3,299	10
2-methyl-3,5 or 6-methylthiopyrazine[b]	3,208	2–4
2-methyl-3,5 or 6-furfurylthiopyrazine[b]	3,189	1
pyrazine ethanethiol[b]	3,230	10
pyrazine methyl sulfide[b]	3,231	1
5H-5-methyl-6,7-dihydrocyclopentapyrazine[c]	3,306	0.045–1

[a] Flavor and Extract Manufacturers Association
[b] Hall and Oser (1970)
[c] Oser and Hall (1972)
[d] Oser and Ford (1973)

General Applications

The observation by Seifert et al. (1970) that certain methoxypyrazines possessed unique flavor properties led Guadagni et al. (1971) to investigate the role of such compounds in the flavor enhancement of potato products. The specific pyrazines investigated included 2-methyl-3-methoxy-, 2-isopropyl-3-methoxy-, and 2-ethyl-3-methoxypyrazine. They found that 2-ethyl-3-methoxypyrazine, in some cases at levels as low as 0.03 ppm, was effective in enhancing the flavor of dehydrated mashed potatoes, potato salad, cream of potato soup, and scalloped potatoes. In the case of potato salad, 0.1 ppm of 2-ethyl-3-methoxypyrazine was required to significantly enhance the flavor and a level of 0.2 ppm was deemed necessary for sustained flavor improvement as influenced by storage at 3°C for one week.

The above observations have been commercially applied by the R. T. French Company in the marketing of potato and green bell pepper flavor concentrates.

The importance of the role of pyrazines in flavor applications can be appreciated best by reviewing some of the numerous patents issued in this area. Some of the flavor application examples listed in these patents are summarized in Table 32.

As can be seen from Table 32, numerous pyrazine compounds have been added to various food systems at levels of from less than 1 to over 700 ppm to produce desirable flavors or enhance existing flavors. However, some discrepancies do exist as to the descriptions of the flavors produced. For example, in the

TABLE 32

Pyrazine Patent Flavor Applications Summary

Pyrazine compound(s)	Food product incorporated in	Concentration (ppm)	Resulting flavor	Reference
methylpyrazine	peanut butter	200	musty, nutty	Nakel and Dirks (1971)
methylpyrazine	instant coffee	50	fruity, etheral	Nakel and Dirks (1971)
methylpyrazine	cocoa mix	400	richer cocoa	van Praag and Bidmead (1971)
2,3-dimethylpyrazine	shortening-bread	100	NSS[a]	Nakel and Dirks (1971)
2,3-dimethylpyrazine	instant coffee	50	roasted meat	Nakel and Dirks (1971)
2,3-dimethylpyrazine	water-wheat flour	20	vanilla-like	Nakel and Dirks (1971)
2,3-dimethylpyrazine	sugar syrup	20	caramel	Winter et al. (1972)
2,5-dimethylpyrazine	peanut butter	200	nutty, roasted	Nakel and Dirks (1971)
2,5-dimethylpyrazine	instant coffee	50	heavy roasted	Nakel and Dirks (1971)
2,6-dimethylpyrazine	vanilla flavored cake	15	richer vanilla	Nakel and Dirks (1971)
2,6-dimethylpyrazine	chocolate flavored cake	4–15	NSS	Nakel and Dirks (1971)
ethylpyrazine	cereal flakes	50	NSS	Nakel and Dirks (1971)
2-ethylpyrazine	sugar syrup	40	burnt	Winter et al. (1972)
2,3-diethylpyrazine	tea	10	NSS	Nakel and Dirks (1971)
2,3-diethylpyrazine	sugar syrup	10	earthy	Winter et al. (1972)
2,3-diethylpyrazine	instant coffee	0.15	earthy	Winter et al. (1972)

[a] Not specifically specified

TABLE 32 (continued)

Pyrazine Patent Flavor Applications Summary

Pyrazine compound(s)	Food product incorporated in	Concentration (ppm)	Resulting flavor	Reference
2,5-diethylpyrazine	oil-pie crust	25	NSS	Nakel and Dirks (1971)
2,5-diethylpyrazine	sugar syrup	10	hazelnut	Winter et al. (1972)
2,6-diethylpyrazine	ice cream	25	NSS	Nakel and Dirks (1971)
2,6-diethylpyrazine	sugar syrup	50	hazelnut	Winter et al. (1972)
trimethylpyrazine	caramel cake mix	10	NSS	Nakel and Dirks (1972)
trimethylpyrazine	sugar syrup	30	coffee	Winter et al. (1972)
tetramethylpyrazine	vanilla flavored cake	8	fuller vanilla	Nakel and Dirks (1971)
2-ethyl-3-methylpyrazine	sugar syrup	3	burnt, hardnut	Winter et al. (1972)
2-ethyl-3-methylpyrazine	instant coffee	4	woody	Winter et al. (1972)
2-ethyl-6-methylpyrazine	sugar syrup	20	roasted, hazelnut	Winter et al. (1972)
2-propyl-6-methylpyrazine	sugar syrup	10	burnt, hazelnut	Winter et al. (1972)
2-propyl-6-methylpyrazine	instant coffee	10	NSS	Winter et al. (1972)
2-propyl-6-methylpyrazine	chocolate frosting	10	NSS	Nakel and Dirks (1971)
2-propyl-5-methylpyrazine	cocoa	25	NSS	Nakel and Dirks (1971)
2-propyl-3-methylpyrazine	shortening-rolls	100	NSS	Nakel and Dirks (1971)
2-propyl-3-methylpyrazine	sugar syrup	5	earthy	Winter et al. (1972)
2-propyl-3-methylpyrazine	instant coffee	2	green	Winter et al. (1972)

TABLE 32 (continued)

Pyrazine Patent Flavor Applications Summary

Pyrazine compound(s)	Food product incorporated in	Concentration (ppm)	Resulting flavor	Reference
2-isopropyl-3-methylpyrazine	sugar syrup	5	earthy	Winter et al. (1972)
2-isopropyl-3-methylpyrazine	instant coffee	2	green	Winter et al. (1972)
2-butyl-3-methylpyrazine	sugar syrup	2.5	anise	Winter et al. (1972)
2-isobutyl-3-methylpyrazine	sugar syrup	5	green	Winter et al. (1972)
2-isobutyl-3-methylpyrazine	instant coffee	1.7	earthy	Winter et al. (1972)
2-amyl-3-methylpyrazine	sugar syrup	10	hazelnut	Winter et al. (1972)
2-hexyl-3-methylpyrazine	sugar syrup	5	anise	Winter et al. (1972)
2-vinyl-3-methylpyrazine	sugar syrup	30	hazelnut	Winter et al. (1972)
2-vinyl-3-methylpyrazine	instant coffee	7	earthy, green	Winter et al. (1972)
2-vinyl-5-methylpyrazine	sugar syrup	10	coffee	Winter et al. (1972)
2-vinyl-6-methylpyrazine	sugar syrup	40	hazelnut	Winter et al. (1972)
2-ethyl-3-methylpyrazine	oil-popcorn	100	NSS	Nakel and Dirks (1971)
2-ethyl-3-methylpyrazine	peanut butter	200	camphoraceous	Nakel and Dirks (1971)
2-ethyl-3-methylpyrazine	cocoa flavoring	NSS	fuller cocoa	van Praag and Bidmead (1971)
2-ethyl-3-methylpyrazine	instant coffee	50	burnt	Nakel and Dirks (1971)
2-ethyl-5-methylpyrazine	oil-meat	50	NSS	Nakel and Dirks (1971)
2-ethyl-5-methylpyrazine	sugar syrup	20	coffee	Winter et al. (1972)

TABLE 32 (continued)

Pyrazine Patent Flavor Applications Summary

Pyrazine compound(s)	Food product incorporated in	Concentration (ppm)	Resulting flavor	Reference
2-ethyl-6-methylpyrazine	oil-potatoes	25	NSS	Nakel and Dirks (1971)
2-ethyl-3-vinylpyrazine	instant coffee	6	earthy	Winter et al. (1972)
2-ethyl-3,5-dimethylpyrazine	cereal flakes	50	NSS	Nakel and Dirks (1971)
2-ethyl-3,5-dimethylpyrazine	sugar syrup	50	burnt almond	Winter et al. (1972)
2-ethyl-3,5-dimethylpyrazine	instant coffee	30	woody	Winter et al. (1972)
2-ethyl-3,6-dimethylpyrazine	potato chips	725	NSS	Nakel and Dirks (1971)
2-ethyl-3,6-dimethylpyrazine	sugar syrup	20	hazelnut	Winter et al. (1972)
2-ethyl-5,6-dimethylpyrazine	chocolate chip cookies	10	NSS	Nakel and Dirks (1971)
propylpyrazine	peanut butter	200	fruity, green	Nakel and Dirks (1971)
propylpyrazine	sugar syrup	10	green, burnt	Winter et al. (1972)
isopropylpyrazine	sugar syrup	40	caramel	Winter et al. (1972)
isopropylpyrazine	saltine crackers	100	NSS	Nakel and Dirks (1971)
2-isopropyl-3-methylpyrazine	fudge	10	NSS	Nakel and Dirks (1971)
2-isopropyl-5-methylpyrazine	sugar syrup	50	green	Winter et al. (1972)
isopropenylpyrazine	sugar syrup	20	burnt	Winter et al. (1972)
butylpyrazine	peanut butter	200	caraway	Nakel and Dirks (1971)
tert-butylpyrazine	margarine	25	NSS	Nakel and Dirks (1971)
isobutylpyrazine	muffins	75	NSS	Nakel and Dirks (1971)

TABLE 32 (continued)

Pyrazine Patent Flavor Applications Summary

Pyrazine compound(s)	Food product incorporated in	Concentration (ppm)	Resulting flavor	Reference
acetylpyrazine	pound cake	NSS	popcorn	Roberts (1968)
acetylpyrazine	mashed potatoes	NSS	popcorn	Roberts (1968)
acetylpyrazine	corn chips	NSS	popcorn	Roberts (1968)
acetylpyrazine	instant coffee	25	hazelnut	Winter et al. (1972)
acetonylpyrazine	sugar syrup	50	hazelnut	Winter et al. (1972)
2-acetyl-5-methylpyrazine	margarine	100	popcorn	Roberts (1968)
2-acetyl-6-methylpyrazine	margarine	100	popcorn	Roberts (1968)
pyrazine mixture	–	NSS	cereal, corny	Nakel and Dirks (1971)
pyrazine mixture		NSS	cocoa flavor	van Praag and Bidmead (1971)
pyrazine mixture	instant coffee	NSS	NSS	Polak's (1971)
vinylpyrazine	sugar syrup	40	green, burnt	Winter et al. (1972)
trimethylbutylpyrazine	sugar syrup	15	caramel	Winter et al. (1972)
trimethylisoamylpyrazine	sugar syrup	15	anise	Winter et al. (1972)
trimethylhexylpyrazine	sugar syrup	50	fatty	Winter et al. (1972)
formylpyrazine	sugar syrup	50	bread	Winter et al. (1972)
formylpyrazine	instant coffee	12.5	roasted	Winter et al. (1972)
2-hydroxymethylpyrazine	instant coffee	150	sweet	Winter et al. (1972)
2-methyoxymethylpyrazine	instant coffee	4	astringent	Winter et al. (1972)
2-isobutyl-3-methoxypyrazine		0.001–1	green bell peppers	Buttery et al. (1971)
2-ethoxymethylpyrazine	instant coffee	7.5	bitter	Winter et al. (1972)

TABLE 32 (continued)

Pyrazine Patent Flavor Applications Summary

Pyrazine compound(s)	Food product incorporated in	Concentration (ppm)	Resulting flavor	Reference
2-ethoxy-3-methylpyrazine	ice cream	NSS	roasted nut	Winter (1971)
2-ethoxy-3-methylpyrazine	fondant	NSS	roasted nut	Winter (1971)
2-ethoxy-3-methylpyrazine	milk pudding	NSS	roasted nut	Winter (1971)
2,5-dimethyl-3-propylpyrazine	sugar syrup	40	hazelnut	Winter et al. (1972)
2,5-dimethyl-3-butylpyrazine	sugar syrup	25	caramel	Winter et al. (1972)
2,3-dimethyl-5-isoamylpyrazine	sugar syrup	5	green	Winter et al. (1972)
2,5-dimethyl-3-isoamylpyrazine	sugar syrup	10	anise	Winter et al. (1972)
2,5-dimethyl-3,6-diethylpyrazine	sugar syrup	10	coffee	Winter et al. (1972)
2,5-dimethyl-3,6-dipropylpyrazine	sugar syrup	30	hazelnut	Winter et al. (1972)
2,5-dimethyl-3,6-diisopropylpyrazine	sugar syrup	30	burnt	Winter et al. (1972)
2,5-dimethyl-3,6-dibutylpyrazine	sugar syrup	40	fatty	Winter et al. (1972)
2,5-dimethyl-3,6-diisobutylpyrazine	sugar syrup	30	maple	Winter et al. (1972)
2,5-dimethyl-3,6-diamylpyrazine	sugar syrup	10	fatty	Winter et al. (1972)
2,5-dimethyl-3,6-dihexylpyrazine	sugar syrup	10	green	Winter et al. (1972)
2,6-diethyl-3-methylpyrazine	sugar syrup	10	coffee	Winter et al. (1972)
2,6-diethyl-3-methylpyrazine	instant coffee	10	NSS	Winter et al. (1972)
2,5-diethyl-3-methylpyrazine	sugar syrup	30	hazelnut	Winter et al. (1972)
2,3-diethyl-5-methylpyrazine	sugar syrup	5	hazelnut	Winter et al. (1972)

TABLE 32 (continued)

Pyrazine Patent Flavor Applications Summary

Pyrazine compound(s)	Food product incorporated in	Concentration (ppm)	Resulting flavor	Reference
2-methoxylquinoxaline	sugar syrup	40	phenolic	Winter et al. (1972)
5-methylquinoxaline	sugar syrup	10	burnt	Winter et al. (1972)
5-methylquinoxaline	instant coffee	2.7	toasted	Winter et al. (1972)
6-methylquinoxaline	sugar syrup	40	burnt	Winter et al. (1972)
2-methyl-3-ethylquinoxaline	instant coffee	7	hazelnut	Winter et al. (1972)
2-methyl-3-propylquinoxaline	instant coffee	25	bitter	Winter et al. (1972)
2-methyl-3-isopropylquinoxaline	instant coffee	12	bitter	Winter et al. (1972)
2-methyl-3-butylquinoxaline	instant coffee	25	bitter	Winter et al. (1972)
2-methyl-3-isobutylquinoxaline	instant coffee	12	bitter	Winter et al. (1972)
2-methyl-3-amylquinoxaline	instant coffee	12	bitter	Winter et al. (1972)
2,3-dimethylquinoxaline	instant coffee	25	astringent	Winter et al. (1972)
2-ethylquinoxaline	instant coffee	20	green	Winter et al. (1972)
2,3-diethylquinoxaline	instant coffee	6	bitter	Winter et al. (1972)
2-methyl-3(5,6)-(prolyl-1)-pyrazine	instant coffee	4.5	sweet	Winter et al. (1972)
2-methyl-3-(thienyl-2)-pyrazine	sugar syrup	20	earthy	Winter et al. (1972)
2-methyl-5,7-dihydrothieno(3,4-b)-pyrazine	–	NSS	roasted nut	Evers et al. (1972)
2-methyl-5,7-dihydrothieno(3,4-b)-pyrazine	cheese flavoring	NSS	cheddar	Evers et al. (1972)
(2-methylpyrazinyl-3,5 and 6) furfuryl sulfide	sugar syrup	1	roasted	Winter et al. (1972)
(2-methylpyrazinyl-3,5 and 6) furfuryl sulfide	instant coffee	1	roasted	Winter et al. (1972)

TABLE 32 (continued)

Pyrazine Patent Flavor Applications Summary

Pyrazine compound(s)	Food product incorporated in	Concentration (ppm)	Resulting flavor	Reference
pyrazinylmethylmercaptan	sugar syrup	20	roasted	Winter et al. (1972)
pyrazinylmethyl methyl sulfide	sugar syrup	1	cabbage	Winter et al. (1972)
pyrazinylmethyl methyl sulfide	instant coffee	0.15	strawy	Winter et al. (1972)
pyrazinylmethyl ethyl sulfide	sugar syrup	25	cabbage	Winter et al. (1972)
pyrazinylmethyl furfuryl sulfide	sugar syrup	20	coffee	Winter et al. (1972)
pyrazinylmethyl furfuryl sulfide	instant coffee	13.5	sulfury	Winter et al. (1972)
2,5-dimethyl-3-mercaptopyrazine	sugar syrup	10	coffee	Winter et al. (1972)
2,5-dimethyl-3-mercaptopyrazine	instant coffee	1.4	burnt	Winter et al. (1972)
2,5-dimethyl-3-methylthiopyrazine	instant coffee	5	turnip	Winter et al. (1972)
2,5-dimethyl-3-ethylthiopyrazine	sugar syrup	30	burnt	Winter et al. (1972)
2,5-dimethyl-3-furfurylthiopyrazine	sugar syrup	10	coffee	Winter et al. (1972)
2,5-dimethyl-3-acetylthiopyrazine	sugar syrup	50	sulfur	Winter et al. (1972)
5,7-dihydro-5,7-dimethylfuro(3,4-b)-pyrazine	–	NSS	nut	Evers et al. (1972)
5,7-dihydro-5,7-dimethylfuro(3,4-b)-pyrazine	chicken broth	3	NSS	Evers et al. (1972)
5,7-dihydro-5,7-dimethylfuro(3,4-b)-pyrazine	beef broth	10	baked potato	Evers et al. (1972)
5-methyl-3,4,6,7-tetrahydro-2(H)-cyclopentapyrazine	cream cheese	NSS	cheddar cheese	Pittet et al. (1972)
5-methyl-3,4,6,7-tetrahydro-2(H)-cyclopentapyrazine	beef soup base	10	NSS	Pittet et al. (1972)
5-methyl-3,4,6,7-tetrahydro-2(H)-cyclopentapyrazine	confection center	5	NSS	Pittet et al. (1972)

TABLE 32 (continued)

Pyrazine Patent Flavor Applications Summary

Pyrazine compound(s)	Food product incorporated in	Concentration (ppm)	Resulting flavor	Reference
5,7,7-trimethyl-2,3,4,6,7,8-hexahydroquinoxaline	bacon flavor	10	nut-like	Pittet et al. (1972)
2,3-dimethyl-4a,5,6,7,8,8a hexahydroquinoxaline	–	NSS	buttery	Pittet et al. (1972)
75% 2-methyl-3-methoxypyrazine + 25% 2-methyl-5-and-6-methoxypyrazine	fondant	NSS	almonds	Firmenich et al. (1967)
70% 2-methyl-3-methylmercaptopyrazine + 30% 2-methyl-5-and-6-methylmercaptopyrazine	fondant	NSS	almonds	Firmenich et al. (1967)
75% 2-methyl-3-methoxypyrazine + 25% 2-methyl-5-and-6-methoxypyrazine	ice cream	NSS	hazelnuts	Firmenich et al. (1967)
70% 2-methyl-3-methylmercaptopyrazine + 30% 2-methyl-5-and-6-methylmercaptopyrazine	ice cream	NSS	hazelnuts	Firmenich et al. (1967)
75% 2-methyl-3-methoxypyrazine + 25% 2-methyl-5-and-6-methoxypyrazine	milk pudding	NSS	hazelnuts	Firmenich et al. (1967)

case of acetylpyrazine, Roberts (1968) described it as possessing a distinctive popcorn flavor whereas Winter et al. (1972) described 2-acetylpyrazine as having the flavor of hazelnuts. A possible explanation for these differences could be the function of pyrazine concentration and the medium in which the evaluations were performed. This can best be appreciated by viewing the data summarized in Table 33.

For example, for the compound 5,7-dihydrothieno (3,4,6)-pyrazine, Evers et al. (1972) have described its organoleptic properties as ranging from roasted nuts to baked goods to fresh milk depending on concentration and evaluation medium. Thus, it would seem logical that the full potential in using pyrazine compounds as flavoring agents has by no means been fully realized due to the numerous possible combinations of pyrazine compounds, concentrations, and food media available.

Perhaps at this point a discussion of several specific patents relating to pyrazine flavor applications would be helpful. Roberts (1968) patented the application of acetylpyrazines as flavoring agents imparting a popcorn-like flavor to food systems. Final acetylpyrazine levels in foods were in the range of 0.0005 to 0.005% by weight. Some of the food systems in which he incorporated acetylpyrazines included an imitation butter-popcorn flavor concentrate containing 0.05% acetylpyrazine, popcorn flavored margarine, flavored mashed potatoes, and flavored corn chips.

A French patent granted to Firmenich et Cie (1965) on pyrazine derivatives was the basis for a British patent granted to Firmenich et al. (1967). This employed certain isomeric mixtures of oxygen and sulfur containing pyrazines as flavoring agents and possessed typical roasted hazelnut, peanut, and almond properties. Their effectiveness as flavoring agents was demonstrated in fondant, ice cream, and milk pudding. A United States patent number has been assigned to Winter (1971) for the use of pyrazines possessing typical nut flavors.

The use of over two dozen naturally occurring alkyl-substituted pyrazines as flavor additives was patented by Nakel and Dirks (1971). They based their patent claim on the fact that although naturally present, additional amounts of alkyl-substituted pyrazines in the range of 0.15 to 10,000 ppm resulted in improved or new organoleptic properties. Only alkyl methyl and ethyl groups ranging from one to four

TABLE 33

Influence of Pyrazine Compound Concentration and Media on Organoleptic Properties

Compound – concentration (ppm)		Medium	Organoleptic property	Reference
5-methyl-3,4,6,7-tetrahydro-2(H)-cyclopentapyrazine	5	water	sweet, roasted	Pittet et al. (1971)
	20	water	melted butter	
	50	sugar-water	corn flakes	
	50	salt-water	pretzels	
5,7-dihydro-5,7-dimethylfuro-(3,4-b)-pyrazine	3	water	popcorn	Evers et al. (1972)
	10	water	roasted nut	
	10	sugar-water	strong roasted nut	
	3	salt-water	yeasty, roasted	
	10	salt-water	salty, roasted	
5,7-dihydrothieno(3,4-b)-pyrazine	0.02	water	roasted peanut bread crust fresh milk	Evers et al. (1972)
	0.2	water	baked goods bread crust roasted nut	
	2.0	water	sweet, nut	
	4.0	sucrose-water	baked goods	
	3.0	salt-water	fried corn chip salted peanut	

carbons were considered. Three types of flavor reactions are claimed by this patent. First, certain alkylpyrazines added to foods are claimed to *improve* flavor. Also, certain alkylpyrazines result in *characteristic* flavors. The third claim suggests that flavor *potentiation* can result whereby the alkylpyrazines impart no flavor of their own but enhance existing flavors. Since most alkylpyrazines are highly potent flavoring agents, one must assume that sub-threshold amounts must be incorporated to achieve the latter flavor potentiation claim. Some of the food systems to which alkylpyrazines were added included peanut butter, cooking oil, baked doughs, potato chips, instant coffee, and cakes. By blending alkylpyrazines they formulated a cereal-corn-cracker flavor concentrate which was claimed to impart a characteristic cereal flavor to bland products and to mask the undesirable beany note of soy flour.

Alkyl-substituted pyrazines were also the basis for a Canadian patent granted to van Praag and Bidmead (1971) in the formulation of chocolate flavorings that imparted a flavor to, or enhanced, existing flavor in foods. Methyl and ethyl groups of from 1 to 5 carbons and consisting of mixtures of mono-, di-, tri-, and tetra-alkylpyrazines at levels of from 1 to 2,000 ppm were considered. Examples were given whereby weak flavored cocoa beans from certain areas of the world were fortified with pyrazine mixtures to more closely approximate the fuller flavor of higher quality cocoa beans.

A patent was granted to Buttery et al. (1971c) and assigned to the United States government whereby 2-isobutyl-3-methoxypyrazine was manufactured and promoted as a flavoring agent resembling freshly chopped green bell peppers.

Improved instant coffee flavor described as an earthy roasted nut, obtained through the incorporation of a pyrazine mixture, was the basis for a British patent granted to Polak's Frutal Works (1971). The pyrazine mixture was added at the rate of approximately 11 ppm.

Several pyrazines containing oxygen and sulfur and possessing unique organoleptic properties were patented by Evers et al. (1972) to be used at levels of from 0.05 to 50 ppm. By combining a dihydrothienopyrazine and other flavor compounds Evers et al. (1972) formulated a cheddar flavor concentrate. The use of certain bicyclic pyrazine based compounds as flavoring agents was also patented by Pittet et al. (1972).

By far the most extensive pyrazine flavor related patents were granted to Winter et al. (1968, 1972). A total of 38 classes of flavoring compounds including 4 classes of pyrazines (pyrazine hydrocarbons, pyrazine ethers and alcohols, pyrazine carbonyls, and pyrazine sulfur compounds) was patented. Approximately 80 different pyrazines are covered by these patents. Blends of pyrazines and other compounds resulted in flavor concentrate which enhanced the flavor of instant coffee to more closely approximate roasted coffee.

PYRAZINE SYNTHESIS TECHNIQUES

Introduction

Pyrazine synthesis has become quite sophisticated over the past 20 to 30 years, due mainly to the interest in pyrazine derivatives as chemotherapeutic agents. Thus, the flavor chemist has had this information as a starting point in synthesizing naturally and nonnaturally occurring pyrazine compounds. As a result cyclopenta-, oxygen, and sulfur containing pyrazines are now finding applications as flavoring agents. In the following section the authors will discuss some of the synthesis techniques which can lead to the formation of food related pyrazines.

Reduction of Oximino Ketones

Usually the proper oximino ketone has to be prepared from the corresponding ketone. This can most easily be accomplished by the action of free nitrous acid on the ketone (Krems and Spoerri, 1947). The resulting oximino ketone can then be reduced in an acid medium using stannous chloride or zinc to yield pyrazines. Thus, this method provides a relatively easy means for synthesizing several specific pyrazines. Typical examples are shown in Table 34.

Halocarbonyl-amino Reactions

Usually ammonia is reacted at elevated temperatures in sealed tubes with a halocarbonyl. In the process,

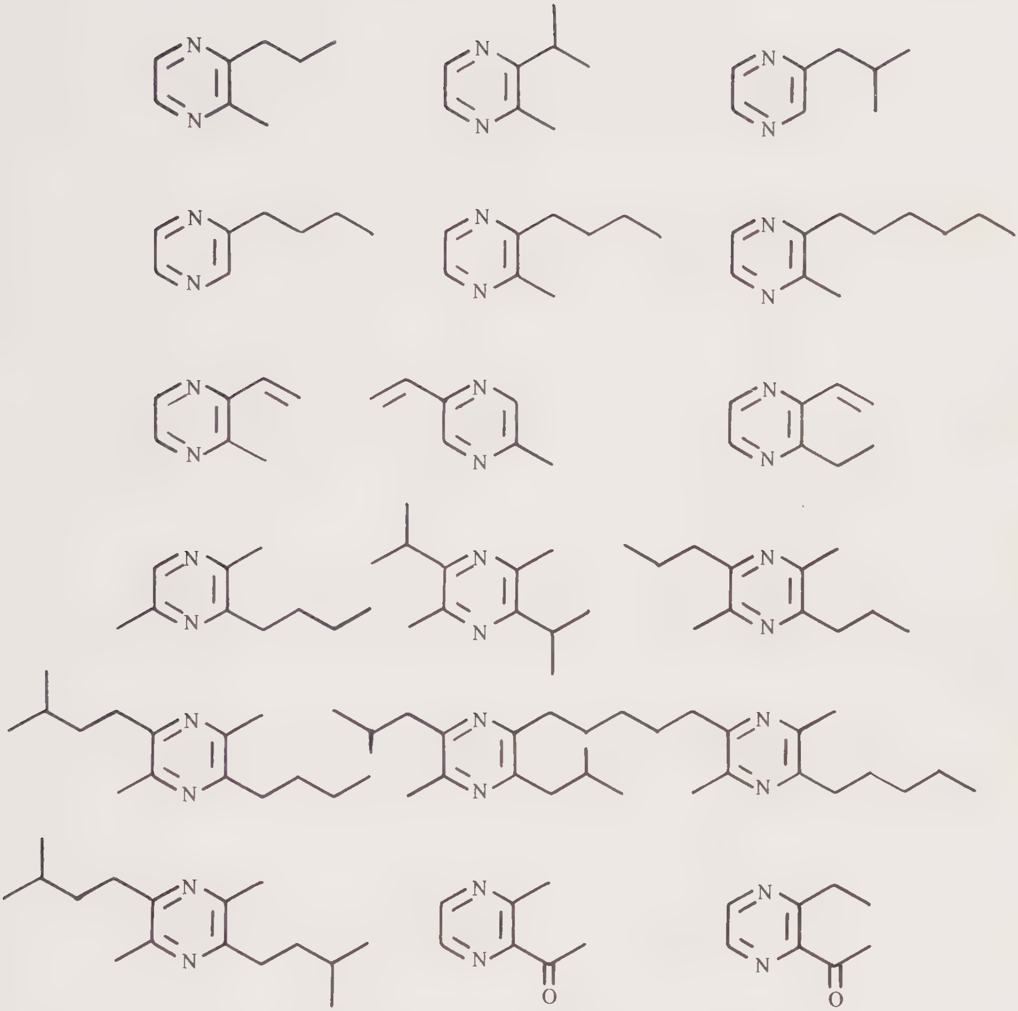

FIGURE 5. Structural relationships of certain synthesized pyrazines possessing characteristic food odors.

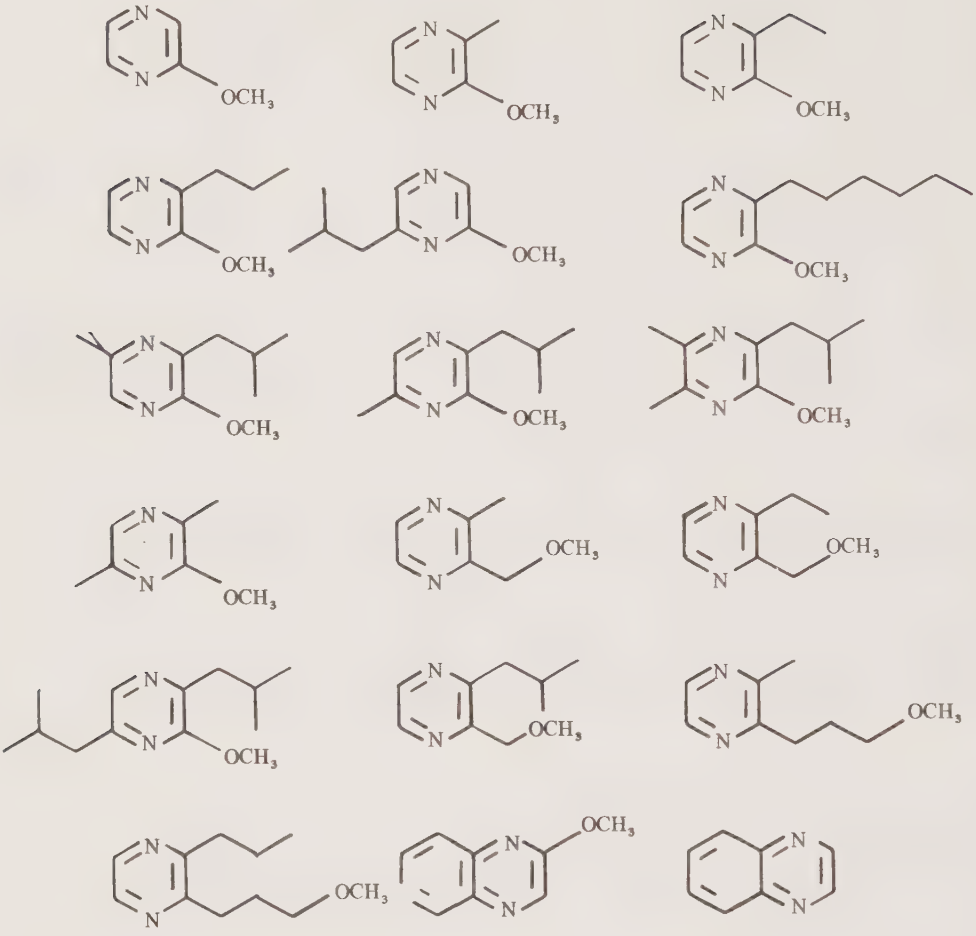

FIGURE 5. (continued)

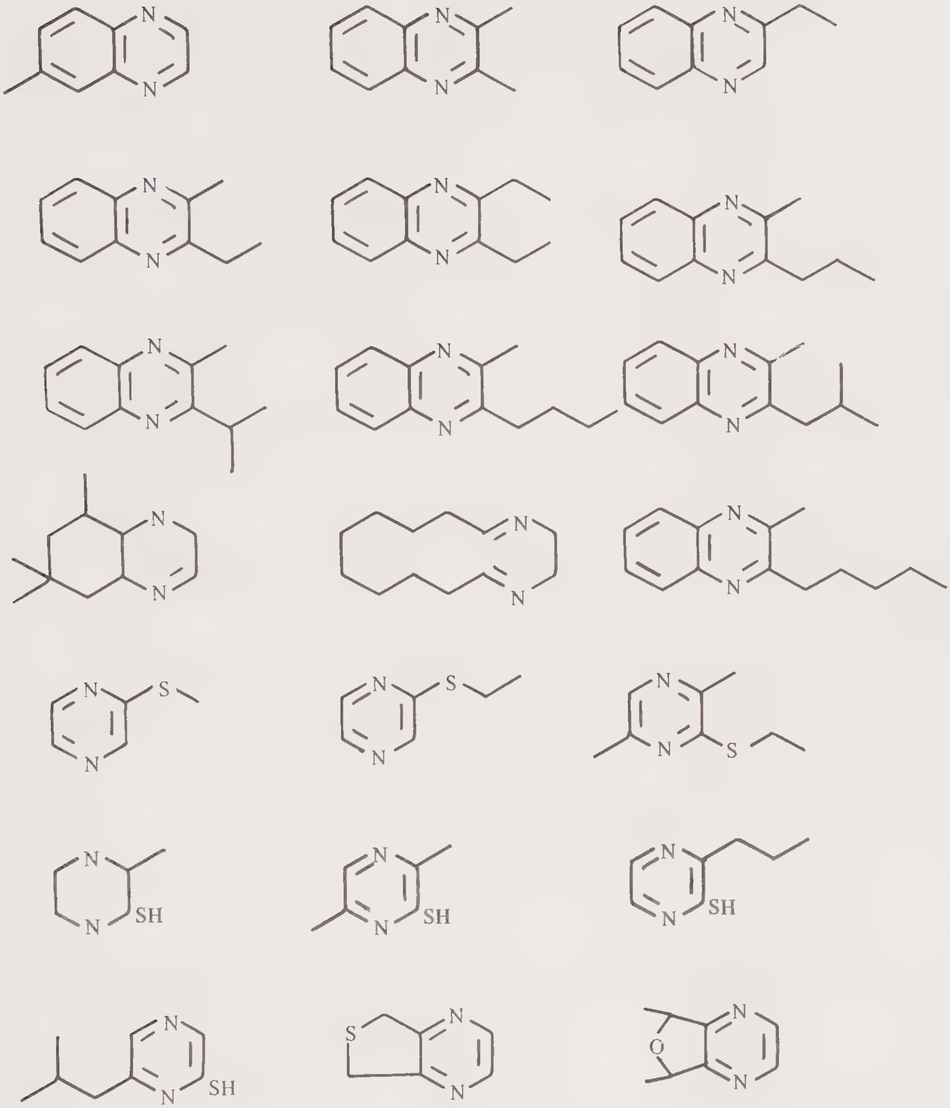

FIGURE 5. (continued)

TABLE 34

Oximino Ketone Reduction Pyrazine Formation Products

Oximino ketone reacted	Pyrazine derivative formed
oximinoacetone[a]	2,5-dimethylpyrazine
oximinoethylmethylketone[a]	tetramethylpvrazine
dimethylglyoxime[a]	tetramethylpyrazine
β-hydroxy-γ-oximino-*n*-valeric acid[a]	tetramethylpyrazine
oximinomethylpropylketone[a]	2,5-diethyl-3,6-dimethylpyrazine
oximinomethylbutylketone[a]	
oximinomethylbutylketone[a]	2,5-dimethyl-3,6-dipropylpyrazine
oximinoisoamylmethylketone[a]	2,5-dimethyl-3,6-diisobutylpyrazine
oximino-*n*-hexylmethylketone[a]	2,5-dimethyl-3,6-diamylpyrazine
oximinoacetylacetone[a]	2,5-dimethyl-3,6-diacetylpyrazine
3-oximino-2-hexanone[b]	2,5-dimethyl-3,6-dipropylpyrazine
4-methyl-3-oximino-2-pentanone[b]	2,5-dimethyl-3,6-diisopropylpyrazine
3-oximino-2-heptanone[b]	2,5-dimethyl-3,6-dibutylpyrazine
5-methyl-3-oximino-2-hexanone[b]	2,5-dimethyl-3,6-diisobutylpyrazine
3-oximino-2-octanone[b]	2,5-dimethyl-3,6-diamylpyrazine
3-oximino-2-nonanone[b]	2,5-dimethyl-3,6-dihexylpyrazine

[a] Krems and Spoerri (1974).
[b] Winter et al. (1972).

TABLE 35

Pyrazines Formed by the Ammonia Substitution of Halocarbonyls

Halocarbonyl reacted	Pyrazine derivative formed
β-bromolevulinic acid	tetramethylpyrazine
methyl α-chloroethylketone	tetramethylpyrazine
methyl α-chloropropylketone	2,5-dimethyl-3,6-diethylpyrazine
α-chlorodiethylketone	2,5-dimethyl-3,6-diethylpyrazine
α-chloromethylethylketone	2,5-diethylpyrazine

From Krems and Spoerri (1947).

the ammonia replaces the halogen portion and through subsequent oxidation the product is converted to a pyrazine derivative. However, if the reaction does not proceed rapidly enough, poor yields and other derivatives from secondary reactions result. Pyrazines formed from several halocarbonyls are reported in Table 35.

Reduction of Amino Acids

The formation of pyrazines via thermal reduction of amino acids was discussed in the pathway section of this review. Acid reduction of the amino acids glycine and alanine was shown by Neuberg (1910) to result in the formation of unsubstituted and 2,5-dimethylpyrazine.

A related system was reported whereby an amino acid (valine) was refluxed in the presence of diacetyl. Approximately 9% tetramethylpyrazine was recovered from the reaction (Rizzi, 1969).

Oxidation of Amino Alcohols

Aston (1934) reported that unsubstituted pyrazine can be formed by passing ethanolamine over a copper catalyst at 300°C. The dehydrogenated reaction product, aminoacetaldehyde, was converted to the corresponding dihydropyrazine which was oxidized to pyrazine. However, the yield of pyrazine was reported to be less than 6%.

Bimolecular cycloamination of amino alcohols has been employed by Deck et al. (1973) to synthesize pyrazines. For example, 2-amino-1-propanol was converted to 2,5-dimethylpyrazine and 2-amino-1-butanol to 2,5-diethylpyrazine. A mixture of 2-amino-1-propanol and 2-amino-1-butanol formed 2,5-dimethyl-, 2,5-diethyl-, and 2-ethyl-5-methylpyrazine. Trimethyl- and tetramethylpyrazine were formed by reacting a mixture of 2-amino-1-propanol and 3-amino-2-butanol.

Amino Acid-Acetic Anhydride-Pyridine Interactions

The formation of an acetylaminoacetone can result if an α-amino acid containing an unsubstituted hydrogen on the α carbon is reacted with acetic anhydride and pyridine (Dakin and West, 1928). By hydrolyzing this acetylaminoacetone and then treating with mercuric chloride in excess alkali, pyrazines such as those shown in Table 36 can be formed.

Ammonia and Polyhydroxy Compound Interactions

This technique would correspond to the ammonia-carbohydrate studies reported in a previous section of this review. For example, if glycerol is heated with an ammonia source, the predominant pyrazine formed would be dimethylpyrazine formed probably by the reaction of two molecules of the intermediate acrolein with two molecules of ammonia.

The formation of pyrazine compounds using this technique has been used extensively probably due to its simplicity. All that is required is a polyhydroxy compound source (glucose, rhamnose), ammonium hydroxide, and water. After refluxing for several hours, solvent extraction yields a pyrazine fraction (van Praag et al., 1968). However, the major disadvantage of using this technique is that complex pyrazine mixtures can form. For example, from a rhamnose-ammonia system, van Praag et al. (1968) isolated unsubstituted pyrazine, methyl-, dimethyls-, ethyl-, ethylmethyls-, ethyldimethyls-, and ethyltrimethylpyrazine. Thus, difficulty may be encountered in efficiently separating such mixtures into individual pyrazines. However, in certain applications, separation may not be desired. For example, pyrazines, with special preference for 2,6-dimethylpyrazine, are included in a chocolate flavoring composition (Nakel and Hiler, 1971). Formation of pyrazines including 2,6-dimethylpyrazine is suggested in this article by simply heating glucose and ammonia.

Oxidation of Piperazines

The compound piperazine can be converted to unsubstituted pyrazine by simply passing piperazine diluted in solvent in a vapor phase over copper chromate at elevated temperatures (Dixon, 1946).

Diaminothiophane-Pyruvic Aldehyde-Alkali Metal Reaction

Evers et al. (1972) reported on the formation of dihydrothienopyrazines from the action of mono or dialkyl-3-4-diaminothiophane with pyruvic aldehyde and an alkali metal hydroxide. Specifically, they formed 2-methyl-5,7-dihydrothieno (3,4-b)pyrazine by reacting 3,4-diaminothiophane in 95% ethanol with pyruvic aldehyde and sodium hydroxide. Exact yield was not reported.

TABLE 36

Pyrazine Formation Products Through Amino Acid-Acetic Anhydride – Pyradine Interactions

Amino acid reacted	Pyrazine derivative formed
glycine	2,5-dimethylpyrazine
hippuric acid	2,5-dimethylpyrazine
aspartic acid	Tetramethylpyrazine

From Krems and Spoerri (1947).

Pyrazinamide Reaction

Certain acetylpyrazines can easily be synthesized, but not in high yields, as outlined by Roberts (1968). Commercially available pyrazinamide was dehydrated with phosphorus oxychloride for 1.5 hr in a water bath. Vacuum distillation was used to remove the excess phosphorus oxychloride. A yield of 91% 2-cyanopyrazine was recovered. The resulting 2-cyanopyrazine was reacted with methyl magnesium bromide to yield 5.5% acetylpyrazine.

Several acetylmethylpyrazines have also been synthesized in the same manner by first opening the corresponding methylpyrazinamides through methylation of the methylpyrazinoic acids obtained from the permanganate oxidation of 2-methylquinoxaline.

Monohaloalkylpyrazine-sodium-2-propanenitronate Reaction

Synthesis of acetylpyrazines by a two-step procedure has been reported by Mookherjee and Klaiber (1972). The process essentially involves the oxidation of a monohaloalkylpyrazine to its corresponding ketone through the use of either sodium-2-propanenitronate or pyridine 1-oxide. For example, bromination of 2-ethyl-3-methylpyrazine with *N*-bromosuccinimide resulted in the formation of approximately 100% yield of 2-(1-bromoethyl)-3-methylpyrazine. This compound was then reacted with sodium-2-propanenitronate to form a 60% yield of 3-methyl-2-pyrazinyl methyl ketone. Reaction with pyridine 1-oxide instead of 2-propanenitronate formed the same acetylpyrazine in 25% yield. When 2,3-diethylpyrazine was used, 3-ethyl-2-pyrazinyl methyl ketone was formed in a similar fashion.

Diaminocycloalkane-Dicarbonyl Reaction

Numerous bicyclic pyrazine derivatives have been synthesized by Pittet et al. (1972) by reacting diamino cycloalkanes with dicarbonyls. Examples would be the formation of 4a,5,6,7,8 8a-hexahydroquinoxaline by the reaction of 1 2-diaminocyclohexane with glyoxal and the formation of 2,3-dimethyl-4a,5,6,7,8,8a,-hexahydroquinoxaline by reacting 1,2-diaminocyclohexane with diacetyl. The authors stated that logically other 2,3-dialkylhexahydroquinoxalines or 2-alkyl substituted hexahydroquinoxalines can be formed by reacting other 1,2-dialkyl glyoxals or 1-alkyl glyoxals. Some of the specific diaminocycloalkanes that can be utilized in this type of reaction are summarized in Table 37.

Cycloalkadione-Diamine Reaction

Pittet et al. (1972) also demonstrated that bicyclic pyrazine derivatives can also be formed by the interaction of numerous cycloalkadiones, such as those listed in Table 38, with diamines such as ethylenediamine.

For example, they formed 5-methyl-3,4,6,7-tetrahydro-2(H)-cyclopentapyrazine by reacting 3-methyl-2-hydroxy-2-cyclopentene-10 one with ethylenediamine. By using 1,2-cyclodecadione and ethylenediamine, decahydroxycyclodecapyrazine was formed.

TABLE 37

Typical Diaminocycloalkanes Useful in Forming Bicyclic Pyrazine Derivatives

1,2-diaminocyclohexane
1,2-diamino-4,5-dimethylcyclohexane
1,2-diamino-3,4,5,5-tetramethylcyclohexane
1,2-diamino-3,4,4-triethylcyclohexane
1,2-diamino-3,3-dimethyl-5,5-diethylcyclohexane

1,2-diamino-3-methylcyclooctane
1,2-diaminocyclodecane
1,2-diaminocyclopentane
1,2-diamino-5-methylcycloheptane
1,2-diamino-4,4,5,6-tetramethylcyclohexane
1,2-diamino-3,3-dimethyl-4,4-diethylcycloheptane

From Pittett et al. (1972).

TABLE 38

Typical Cycloalkadiones Useful in Forming Bicyclic Pyrazine Derivatives

3-methyl-1,2-cycloheptadione
1,2-cycloheptadione
3-methyl-1,2-cyclohexadione
1,2-cyclohexadione
3-methyl-1,2-cyclopentadione

1,2-cyclopentadione
1,2-cyclodecadione
4,5-dimethyl-1,2-cyclopentadione
3-ethyl-1,2-cyclopentadione
3-ethyl-1,2-cyclohexadione

3-propyl-1,2-cyclohexadione
3-ethyl-4-propyl-1,2-cyclohexadione
4-methyl-1,2-cyclooctadione
4-methyl-1,2-cyclodecadione
4-methyl-1,2-cyclononadione
5-propyl-1,2-cyclodecadione

From Pittet et al. (1972).

Ketone-Nitrogen Iodide Reaction

Fellman et al. (1956) demonstrated that symmetrical substituted pyrazines can be obtained by reacting certain ketones with iodine in aqueous ammonia. For example, 2,5-diethyl-3,6-dimethylpyrazine was formed from 3-pentanone and 2,5-dimethylpyrazine. Yields were reported to be substantial but no exact figures were given.

Amino Acid Amide-Glyoxal Reaction

The methoxypyrazine 2-isobutyl-3-methoxypyrazine was synthesized by first forming the 2-hydroxy-3-isobutylpyrazine by reacting the amide of the amino acid leucine with glyoxal and then methylating with diazomethane (Buttery et al., 1969a). The synthesis and uses of 2-isobutyl-3-methoxypyrazine are outlined in a patent based on the above study (Buttery et al., 1971a). In a later study Buttery et al. (1969b) reported the yield of 2-isobutyl-3-methoxypyrazine synthesized by the above procedure to be 25%. A major by-product of this reaction is pyrazinones.

Based on the above studies, Seifert et al. (1970) synthesized additional methoxyalkylpyrazines. They compared the use of the amino acid, amide hydrochloride, with that of the free amino acid amide, and found the latter to give higher yields.

In a later study, Seifert et al. (1972) reported on the synthesis of other methoxyalkylpyrazines. For example, a yield of approximately 3% 2-isobutyl-3-methoxy-5-methylpyrazine and 6% of the -6-methylpyrazine was obtained by methylating the hydroxypyrazines formed from the condensation of leucine amide with pyruvic aldehyde. The compound 2-isobutyl-3-methoxy-5,6-dimethylpyrazine at a 10% yield was formed by reacting leucine amide with butan-2,3-dione and methylating with diazomethane.

Halopyrazine-Alkali Metal Mercaptide and/or Methoxide Reaction

As can be seen from Table 39, a great variety of pyrazine derivatives have been synthesized using a halopyrazine-alkali metal type reaction. The method relies on the ability of first forming a halogenated pyrazine. Most investigators have preferred to form chloropyrazine derivatives. This can easily be accomplished by chlorination of the appropriate pyrazine with sulphuryl chloride as reported by Burrell et al. (1970). However, a drawback of forming halopyrazines is the fact that isomeric forms result, when reacted with sodium methoxide, for example, in pyrazine mixtures which then have to be separated. The

TABLE 39

Halopyrazine-Alkali Metal Mercaptide and/or Methoxide Pyrazine Formation Products

Reactants	Product(s)
2-methyl-3-,5-and 6-chloropyrazine + sodium furfurylmercaptide[a]	2-methylpyrazyl-3-, 5-and 6-furfuryl sulfide
chloromethylpyrazine + sodium hydrogensulfide[a]	pyrazinylmethylmercaptan
chloromethylpyrazine + sodium methylmercaptide[a]	pyrazinylmethyl methyl sulfide
chloromethylpyrazine + sodium ethylmercaptide[a]	pyrazinylmethyl ethyl sulfide
chloromethylpyrazine + sodium furfurylmercaptide[a]	pyrazinylmethyl furfuryl sulfide
2,5-dimethyl-3-iodopyrazine + sodium hydrogensulfide[a]	2,3-dimethyl-3-mercaptopyrazine
2,5-dimethyl-3-chloropyrazine + methylmercaptan[a]	2,5-dimethyl-3-methylthiopyrazine
2,5-dimethyl-3-chloropyrazine + ethylmercaptan[a]	2,5-dimethyl-3-ethylthiopyrazine
2,5-dimethyl-3-chloropyrazine + furfurylmercaptan[a]	2,5-dimethyl-3-furfurylthiopyrazine
2-methyl-chloropyrazine + sodium methoxide[b]	75% 2-methyl-3-methoxypyrazine + 25% 2-methyl-5- and 6-methoxypyrazines
2-methyl-chloropyrazine + methylmercaptan + sodium ethoxide[b]	70% 2-methyl-3-methylmercaptopyrazine + 30% 2-methyl 5-and 6-methylmercaptopyrazines
2-chloro-3-methylpyrazine + sodium + ethanol[b]	2-ethoxy-3-methylpyrazine
2,3-dichloromethylpyrazine + sodium hydrosulfide[c]	5,7-dihydrothieno (3,4-b)pyrazine
2-isopropyl-6-chloropyrazine + sodium methoxide[d]	2-methoxy-3-isopropyl-5-methylpyrazine
2-methoxy-3-isopropyl-5-chloropyrazine + sodium methoxide[d]	2,6-dimethoxy-3-isopropyl-5-methylpyrazine

[a] Winter et al. (1972).
[b] Winter (1971).
[c] Evers et al. (1972).
[d] Burrell et al. (1970).

number of pyrazine isomers formed by this technique has been questioned in the literature. Firmenich et al. (1967) reportedly found 2,3-, 2,5-, and 2,6-methoxymethylpyrazines using the above procedure. However, Nakel and Haynes (1972) only found the 2,3- and 2,6- varieties. Differences in ratios of starting materials probably account for these discrepancies.

Methylpyrazine Oxide-Phosphorus Oxychloride-Sodium Methoxide Reaction

Firmenich et al. (1967) and Nakel and Haynes (1972) also reported on the formation of methoxypyrazines by the interaction of methylpyrazine oxides with phosphorus oxychloride and sodium methoxide. For example, Nakel and Haynes (1972) found both 2-methoxy-3- and 6-methylpyrazines when 2-methylpyrazine-1-oxide was used and 2-methyl-3-methoxypyrazine forming from 2-methylpyrazine-4-oxide.

Dicarbonyl-Diamine Condensation

As can be seen from Table 40 the reaction of dicarbonyls with diamines has also proved to be a popular method for pyrazine derivative synthesis.

For example, a diamine such as ethylenediamine can condense with diketones such as diacetyl to yield 2,3-dialkyl-5,6-dihydropyrazines which can in turn be oxidized to the corresponding dialkylpyrazine. Using this technique, Nakel and Dirks (1971) reported a yield of 28% 2,3-dimethylpyrazine. If an unsymmetrical diketone such as 2,3-pentanedione is combined with ethylenediamine, the corresponding 2,3-dialkylpyrazine, namely 2-ethyl-3-methylpyrazine, can be formed. Thus, if the appropriate dicarbonyl can be purchased or synthesized, a wide variety of pyrazine derivatives can be synthesized using this technique.

Pittet et al. (1974) used this basic technique to synthesize the five- and six-membered alicyclic pyrazines listed in Table 40A.

TABLE 40

Pyrazine Formation Products by Condensation of Dicarbonyls and Diamines

Reactants	Pyrazine derivative formed
diacetyl + ethylenediamine[a,b,c]	2,3-dimethylpyrazine
methylethylketone + ethylenediamine[a]	2-methyl-3-propylpyrazine
anisil + ethylenediamine[a]	2,3-dimethoxyphenylpyrazine
2,3-pentanedione + ethylenediamine[b]	2-ethyl-3-methylpyrazine
3,4-hexanedione + ethylenediamine[b]	2,3-diethylpyrazine
2,3-hexanedione + ethylenediamine[b]	2-propyl-3-methylpyrazine
4-methyl-2,3-pentanedione + ethylenediamine[b]	2-isopropyl-3-methylpyrazine
2,3-pentanedione + propylenediamine[c]	2-ethyl-3,5-dimethylpyrazine
diacetyl + 1,2-butylenediamine[d]	5-ethyl-2,3-dimethylpyrazine
ethylmethyldiketone + ethylenediamine[e]	2-ethyl-3-methylpyrazine
isobutylmethyldiketone + ethylenediamine[e]	2-isobutyl-3-methylpyrazine
methylpropyldiketone + ethylenediamine[e]	2-propyl-3-methylpyrazine
methylisopropyldiketone + ethylenediamine[e]	2-isopropyl-3-methylpyrazine
butylmethyldiketone + ethylenediamine[e]	2-butyl-3-methylpyrazine
amylmethyldiketone + ethylenediamine[e]	2-amyl-3-methylpyrazine
hexylmethyldiketone + ethylenediamine[e]	2-hexyl-3-methylpyrazine
thienyl-2-methyldiketone + ethylenediamine[b]	2-(thienyl-2)-3-methylpyrazine
dipropionyl + 1,2-diaminopropane[b]	2,3-diethyl-5-methylpyrazine
2,5-dibromo-3,4-hexanedione + 1,2-diaminoethane[f]	5,7-dihydro-5,7-dimethylfuro(3,4-b)pyrazine
isopropylglyoxal + 1,2-diaminopropane[g]	2-isopropyl-5 and 6-methylpyrazine

[a] Krems and Spoerri (1947).
[b] Nakel and Dirks (1971).
[c] van Praag and Bidmead (1971).
[d] Polak's Frutal Works (1971).
[e] Winter et al. (1972).
[f] Evers et al. (1972).
[g] Peer and van der Heijden (1969).

TABLE 40A

Pyrazines Formed Through Condensation of an Alicyclic α, β-Diamine with an α, β-Dicarbonyl or α, β-Diketone.

5,7-Dihydro-5H-Cyclopentapyrazine
2-Methyl-5,7-Dihydro-5H-Cyclopentapyrazine
5-Methyl-5,7-Dihydro-5H-Cyclopentapyrazine
5-Ethyl-5,7-Dihydro-5H-Cyclopentapyrazine
2, 3-Dimethyl-5,7-Dihydro-5H-Cyclopentapyrazine
2(or 3), 5-Dimethyl-5,7-Dihydro-5H-Cyclopentapyrazine
3(or 2), 5-Dimethyl-5,7-Dihydro-5H-Cyclopentapyrazine
2, 3,5-Trimethyl-5,7-Dihydro-5H-Cyclopentapyrazine
5, 6,7,8-Tetrahydroquinoxaline
2-Methyl-5,6,7,8-Tetrahydroquinoxaline
2, 3-Dimethyl-5,6,7,8-Tetrahydroquinoxaline
5,7-Dimethyl-5,6,7,8-Tetrahydroquinoxaline
5, 7,7-Trimethyl-5,6,7,8-Tetrahydroquinoxaline

From Pittet et al. (1974).

Sodamide-Alkylpyrazine Reaction

Nakel and Dirks (1971) have summarized this important synthesis procedure by stating that an alkylpyrazine and sodamine can react by first replacing a hydrogen atom on an α-carbon from a substituted group with sodium. By then reacting the sodium substituted pyrazine with an appropriate alkyl halide, a more highly substituted pyrazine derivative can result. A few of the typical reactions of this nature are shown in Table 41.

This method is usually an efficient means of synthesizing pyrazine derivatives, and yields are normally in excess of 50%. Extensive earlier studies by Behum and Levine (1961) and Kamal and Levine (1962) on the mechanisms of this reaction served as the basis for the popularity of this method. Chakrabartty and Levine (1966) also demonstrated that pyrazine compounds such as tetramethylpyrazine and sodamide can be reacted to obtain mixtures of amyltrimethylpyrazine and 2,5-dialkyl-3,6-dimethylpyrazines.

Reactant ratios are important considerations with this synthesis procedure. This can be appreciated by viewing the data summarized in Table 42.

As can be seen, yield of the pyrazine derivative of interest can be maximized by varying the moles of reactants employed.

A recent study by Bramwell et al. (1971) demonstrated that if no catalyst is used in converting sodium into sodamide, pyrazine nuclear alkylation occurs preferentially at the six then three and finally five carbon position. Other metals besides sodium were investigated and it was found that potassium was even more effective than sodium in forming derivatives. Media other than liquid ammonia were also evaluated and it

TABLE 41

Pyrazine Formation Products from Sodamide-Alkylpyrazine Reactions

Reactants	Pyrazine derivative(s) formed
sodamide + methylpyrazine + ethyliodide[a,b]	propylpyrazine
sodamide + methylpyrazine + methyliodide[a,b]	ethyl-, methyl-, isopropylpyrazine
sodamide + methylpyrazine + propyliodide[a]	butylpyrazine
sodamide + 2,5-dimethylpyrazine – methyliodide[a,c]	2-ethyl-5-methylpyrazine
sodamide + 2,6-dimethylpyrazine + methyliodide[a]	2-ethyl-6-methylpyrazine
2-sodamide + 2,5-dimethylpyrazine + 2 methyl iodide[a]	2,5-diethylpyrazine
2 sodamide + 2,6-dimethylpyrazine + 2 methyl iodide[a]	2,6-diethylpyrazine
sodamide + 2,5-dimethylpyrazine + ethyl iodide[a]	2-propyl-5-methylpyrazine
sodamide + 2,6-dimethylpyrazine + ethyl iodide[a]	2-propyl-6-methylpyrazine
sodamide + methylpyrazine + isopropyl iodide[a]	isobutylpyrazine
sodamide + methylpyrazine + 2-bromopropane[d]	isobutylpyrazine

[a] Nakel and Dirks (1971).
[b] Walradt et al. (1971).
[c] Rizzi (1967).
[d] Seifert et al. (1970).

TABLE 42

Influence of Reactant Mixtures on Pyrazine Formation Products

	% Pyrazine products formed			
Moles of reactants	Methyl-	Ethyl-	Isopropyl-	Tert-butyl-
1 sodamide + 1 methylpyrazine + 1 methyl iodide	5	78	2	trace
2 sodamide + 1 methylpyrazine + 2 methyl iodide	4	32	42	4
4 sodamide + 1 methylpyrazine + 4 methyl iodide	0.5	24	10	25

From Nakel and Dirks (1971).

was found that derivative formation proceeded in a satisfactory manner in all solvents tested, including the presence of no solvent. With the use of any system, care must be exercised in the use of anhydrous materials since residual water can result in unexpected derivatives.

Alkenylpyrazine Synthesis

The method described by Kamal et al. (1962) has been used by later investigators for the synthesis of alkenylpyrazines. It essentially involves treatment of an alkylpyrazine with formaldehyde and dimethylamine to form a mannich base. The product is then methylated to give the quaternary amine which in turn is converted to a vinylpyrazine.

Kamal et al. (1962) also described the formation of numerous substituted vinylpyrazines through the dehydration of various alcohols resulting from adol condensation of alkylpyrazines with carbonyls.

Organolithium-Alkylpyrazine Reaction

The last popular synthesis method to be discussed involves the action of organolithium compounds on alkylpyrazines. Some of the typical reactants and products are listed in Table 43.

The procedure is relatively simple. However, the yields are generally below 40%. Again, elimination of residual water is critical if normal yields of predicted products are to be obtained.

TABLE 43

Organolithium-Alkylpyrazine Pyrazine Formation Products

Reactants	Product(s)
N-pyrrolyllithium + 3(5,6)-chloro-2-methylpyrazine[a]	2-methyl-3(5,6)-pyrrolyl-1-pyrazine
methyllithium + 2,5-dimethylpyrazine[b,e]	trimethylpyrazine
methyllithium + 2,5-dimethylpyrazine[d]	tri- and tetramethylpyrazine
butyllithium + unsubstituted pyrazine[c]	butylpyrazine
ethyllithium + 2,5-dimethylpyrazine[b]	2,5-dimethyl-6-ethylpyrazine
butyllithium + 2,5-dimethylpyrazine[b]	2,5-dimethyl-6-butylpyrazine
pentyllithium + 2,5-dimethylpyrazine[b]	2,5-dimethyl-6-pentylpyrazine
hexyllithium + 2,5-dimethylpyrazine[b]	2,5-dimethyl-6-hexylpyrazine
ethyllithium + 2,3-dimethylpyrazine[d]	5,6-dimethyl-3-ethylpyrazine
ethyllithium + 2,5-dimethylpyrazine[a,d,e,b]	2,5-dimethyl-3-ethylpyrazine
ethyllithium + 2,6-dimethylpyrazine[a,d,e,f]	2,6-dimethyl-3-ethylpyrazine
propyllithium + 2,5-dimethylpyrazine[a]	2,5-dimethyl-3-propylpyrazine
methyllithium + 2,6-diethylpyrazine[a]	2,6-diethyl-3-methylpyrazine
methyllithium + 2,5-diethylpyrazine[a]	2,5-diethyl-3-methylpyrazine
butyllithium + 2,5-dimethylpyrazine[a]	2,5-dimethyl-3-butylpyrazine
isoamyllithium + 2,3-dimethylpyrazine[a]	2,3-dimethyl-5-isoamylpyrazine
isoamyllithium + 2,5-dimethylpyrazine[a]	2,5-dimethyl-3-isoamylpyrazine
butyllithium + 2,3,5-trimethylpyrazine[a]	trimethyl-6-butylpyrazine
isoamyllithium + 2,3,5-trimethylpyrazine[a]	trimethyl-6-isoamylpyrazine
hexyllithium + 2,3,5-trimethylpyrazine[a]	trimethyl-6-hexylpyrazine
ethyllithium + 2,5-dimethyl-3-ethylpyrazine[a]	2,5-dimethyl-3,6-diethylpyrazine

[a] Winter et al. (1972).
[b] Klein and Spoerri (1950).
[c] Klein and Spoerri (1951).
[d] Nakel and Dirks (1971).
[e] Rizzi (1967).
[f] Deck et al. (1973).

PYRAZINE SEPARATION AND IDENTIFICATION TECHNIQUES

Introduction

Early investigators used optical rotation, elemental analysis, conversion to picrate derivatives, melting points, and fractional distillations to separate and identify pyrazines. With recent developments in instrumentation, the modern flavor chemist can potentially use gas-liquid chromatography, mass spectrometry, ultraviolet spectrometry, infrared spectrometry, nuclear magnetic resonance, and raman spectrometry to determine the composition of complex mixtures containing only trace amounts of each pyrazine.

Gas-Liquid Chromatography

A wide variety of compounds have been isolated in the basic fraction of flavor concentrates. Some polar, nonbasic compounds such as acetoin, furfuryl, and phenylacetaldehyde cannot be completely removed using solvent extractions. Other classes of nitrogen compounds which have been found in the basic fraction in addition to the pyrazines are the thiazoles and pyridines. The first task of the flavor chemist has been to separate this complex mixture into the individual components. Traditional separation methods such as fractional distillation or column chromatography have not been extensively employed since the advent of gas-liquid chromatography (glc). Gas-liquid chromatography has been the predominant tool in the separation and in some cases the identification of pyrazines (Table 44). It has afforded the researcher a convenient tool by which pyrazines can be quantitated, fractionated, and identified. Despite recent improvements in column efficiency, some positional isomers having the same molecular weight cannot be resolved by glc.

Prior to chromatographing the basic fraction, it is desirable to dry the basic fraction with a suitable desiccant. Pyrazines are hygroscopic and are infinitely soluble in water (Handbook of Chemistry and Physics, 1972). The inclusion of water in the sample interferes with mass spectral analysis and can also change the retention times of various peaks in the sample (Mon et al., 1967). A number of researchers have found that dry Na_2SO_4 was suitable for drying in that it is inert and commonly available. Also important is the choice of solvent. Highly polar diethylether is an excellent solvent for pyrazines, and has a low boiling point, but ether also has an affinity for water, thus requiring a considerable amount of drying. Other solvents such as dichloromethane chloroform or hexane are good solvents for pyrazines and have the advantage that they absorb little moisture.

The most prevalent type of glc column in pyrazine research has been the packed column (Table 45). Packed columns offer many advantages in that they are inexpensive, dependable, will tolerate large sample loads, and are easily prepared. When large samples are used, sufficient material can usually be trapped to allow further analysis by other means. The major limitation of most packed columns is their poor resolution. Short, packed columns of the type generally used in pyrazine research have a resolution of only a few thousand plates. Long columns packed with a low percentage of stationary phase are capable of getting 25,000 to 50,000 theoretical plates (Mon et al., 1967), but these columns are not as rugged as the normal column and require a smaller sample size. Pyrazines of the same molecular weight are difficult to separate using short packed columns. This situation may be further complicated by nonbasic compounds also present within a peak. However, this can be partially overcome by using multiple columns. For instance, if a mixture of compounds elutes from a column as a single peak, it may be possible to effect a separation of this same mixture merely by switching to a different column. Indeed, Reineccius et al. (1972) could not resolve acetoin from methylpyrazine on an 8 ft × 1/16 in. i.d., 10% DEGA column, but they found that this mixture was separable on a 10 ft × 1/16 in. i.d., 15% Carbowax® 20M column. This technique lends itself particularly well to trapping a peak and rechromatographing it on a different column.

The use of a packed column containing two stationary phases was employed by Johnson et al. (1971) to reduce the amount of column bleed. The first 23 ft of the column was packed with 15% Carbowax 20M on Gas-Chrom Q while the last foot of the column, packed with 5% OV-17 on Gas-Chrom Q, absorbed the volatiles from the Carbowax in the preceding portion of the column. This technique diminished the extraneous peaks in the mass spectra which were due to the stationary phase.

TABLE 44

Techniques Used by Researchers for the Separation and Identification of Pyrazine Compounds

Researcher	GLC	MS	IR	NMR	Traps	Glass columns	Capillary	UV
C. Shu and G. Waller, 1971	X	X						
B. Johnson et al., 1971	X	X	X		X		X	X
Mason et al., 1966	X	X		X	X			X
Buttery et al., 1969a,b; 1971b	X	X	X	X	X		X	X
Murray et al., 1970	X	X			X			
H. Kato et al., 1972	X	X	X	X				
Flanagan et al., 1972; 1971a,b; 1970	X	X	X		X		X	
Wobben et al., 1971	X	X						
Bramwell et al., 1969	X	X	X	X	X			
von Sydow and Anjou, 1969	X	X			X			
Wilkens and Lin, 1970	X	X			X			
Kosuge et al., 1962			X					
Bondorovich et al., 1967, 1970	X	X	X		X			X
Friedel et al., 1971	X	X	X		X			
Viani et al., 1965	X	X			X		X	
Stoffelsma et al., 1968	X	X	X		X			
Deck and Chang, 1965	X	X	X		X			
Walradt et al., 1970, 1971	X	X	X	X	X		X	
Kinlin et al., 1970	X	X			X		X	
Wang and Odell, 1972	X	X					X	
Sheldon et al., 1972	X	X						
Watanabe and Sato, 1971	X	X						
Leibich et al., 1972	X	X					X	
P. Wang et al., 1972, 1969	X	X				X		
Reineccius et al., 1972	X	X					X	
Flament et al., 1967	X	X	X		X			
van Praag et al., 1968	X	X						
Marion et al., 1967	X	X	X		X			
Deck et al., 1973	X	X	X		X			
Rizzi, 1967	X	X	X		X			
Collins, 1971	X							
Manley and Fagerson, 1970	X	X						
Koehler et al., 1969	X	X				X		X
van der Wal, 1971	X	X	X		X			
S. Kato et al., 1970	X	X						
Sapers et al., 1971	X	X						
Koehler and Odell, 1970	X							
Koehler et al., 1971	X							
Rizzi, 1972	X	X	X	X	X			X
Davison and Wiggins, 1956	X	X	X		X			
Dawes and Edwards, 1966								
Shigematsu et al., 1972	X	X	X					
Fujimaki et al., 1972	X	X						
Kosuge and Kamiya, 1962			X					
Burrell et al., 1970	X	X		X				

TABLE 45

Representative Packed GLC Columns

Stationary phase		Length	Support mesh	Reference
Carbowax 20M	10%	(3 m x 3 mm i.d.)	Diasolid L 60–80	S. Kato et al., 1970
Carbowax 20M	15%	(20 ft x 1/4 in.)	Gas-Chrom Q	Koehler et al., 1969
Carbowax 20M	20%	(3 m x 3 mm i.d.)	Chromosorb W 60–80	H. Kato et al., 1972
Carbowax 20M	15%	(20 ft x 1/4 in.)	Gas-Chrom Q 100–120	Koehler and Odell, 1970
Carbowax 20M	15%	(10 ft x 1/16 in. i.d.)	Gas-Chrom Z 80–100	Reineccius et al., 1972
Carbowax 20M	5%	(21 ft x 1/4 in.)	Gas-Chrom Q	Shu and Waller, 1971
Carbowax 20M	5%	(21 ft x 1/4 in.)	Gas-Chrom Q 100–120	Johnson et al., 1971
Carbowax 20M	1.5%	(60 ft x 1/4 in.)	Chromosorb G 60–80	Murray et al., 1970
Carbowax 20M	25%	(13 ft x 1/4 in.)	Diatoport 60–80	Friedel et al., 1971
Carbowax 20M	20%	(6 ft x 1/4 in.)	Chromosorb W 60–80	Deck and Chang, 1965
Carbowax 20M	20%	(9 ft x 1/8 in.)	Chromosorb W 60–80	Buttery et al., 1971b
Carbowax 20M	10%	(20 ft x 1/4 in.)	Gas-Chrom Q	Wang and Odell, 1972
Carbowax 20M	20%	(2 m x 1/8 in.)	Embacel 60–80	Wobben et al., 1971
Carbowax 20M	5–25%		Chrom AW or NAW	Flament et al.
Carbowax 20M	15%	(12 ft x 3/8 in.)	Gas-Chrom Q	Mason et al., 1966
Carbowax 20M	20%	(9 ft x 1/8 in.)	Chromosorb W 60–80	Sapers et al., 1971
Carbowax 20M	10%	(12 ft x 1/8 in.)		Walradt et al., 1971
Carbowax 20M	15%	(20 ft x 1/4 in.)	Gas Chrom Q 100–120	Koehler et al., 1971
Carbowax 20M	20%	(1 m x 3 mm)	Chromosorb W 60–80	H. Kato et al., 1972
Carbowax 20M	5% and Versamid 900 1%	(6 ft x 1/8 in.)	Chromosorb W 100–120	Ferretti and Flanagan, 1972
Carbowax 20M	5% + KOH 1%	(6 ft x 1/8 in.)	Gas Chrom P 80–100	Collins, 1971
SE-30	5%	(3 m x 3 mm i.d.)	Chromosorb W 60–80	S. Kato et al., 1970
SE-30	20%	(10 ft x 1/8 in.)	Chromosorb W AW-DMCS 60–80	Ferretti et al., 1970
SE-30	25%	(8 ft x 1/4 in.)	Chromosorb W 60–80	Friedel et al., 1971
SE-30	30%	(6 m)	Chromosorb P 60–80	Viani et al., 1965
SE-30	15%	(4 ft x 1/4 in.)	Chromosorb W 60–80	Deck and Chang, 1965
SE-30	20%	(6 m x 8 mm)	Chromosorb W 45–60	Marion et al., 1967
SE-30	15%	(10 ft x 3/8 in.)	Anakrom ABS 70–80	Deck et al., 1973
SE-52	5%	(6 ft x 1/4 in.)	Gas-Chrom Q	Mason et al., 1966
DEGS	10%	(3 m x 3 mm i.d.)	Diasolid L	Fujimaki et al., 1971
DEGS	30%	(3 m)	Chromosorb P 60–80	Viani et al., 1965
DEGS	5%	(12 ft x 1/8 in.)	Chromosorb G AW-DMCS 100–120	Walradt et al., 1970
DEGS	15%	(10 ft x 1/8 in.)	Chromosorb G AW-DMCS	Sheldon et al., 1972
DEGS	20%	(3 m x 8 mm)	Chromosorb W 45–60	Marion et al., 1967
DEGS	15%	(12 ft x 1/4 in.)	Anakrom ABS 80–90	Ryder et al., 1966
DEGS	18%	(610 x .635 cm)	Chromosorb W 60–80	Rizzi, 1967
SF 96–50 Igepal	12% 0.6%	(5.6 m x 3/8 in.)	Chromosorb W 45–60	van Sydow and Anjou, 1969
SF 96 Igepal	12% + 0.6%	(18 ft x 3/8 in.)	Gloss Chromosorb W AW-DMCS 60–80	Walradt et al., 1971
SF 96 (Fluorinated)	15%	(305 x .635 cm)	Silanized Chromosorb W 60–80	Rizzi, 1967
FFAB	3%	(3.6 m x 1/8 in.)	Chromosorb G AW-DMCS 80–100	van Sydow and Anjou, 1969
UCON-LB-550X	20%	(5 m)	Embacel 60–80	Viani et al., 1965
UCON-50-HB-280X	15%	(8 ft x 1/4 in.)	Anakrom ABS 70–80	Deck et al., 1973
BDS	2.5%	(12 ft x 1/8 in.)	Chromosorb G AW-DMCS 100–120	Walradt et al., 1970
Tris	20%	(12 ft x 1/8 in.)	Celite 545 80–100	Sheldon et al., 1972
PEG 20M	10%	(2 m x 3 mm i.d.)	Celite 545 80–100	Watanabe and Sato, 1971

TABLE 45 (continued)

Representative Packed GLC Columns

Stationary phase		Length	Support mesh	Reference
Tricresylphosphate	10%	(3.75 m x 3 mm i.d.)	Diasolid M 40–60	P. S. Wang et al., 1969
Triton X 100	10%	(3 m x 3 mm i.d.)	Diasolid L 60–80	P. S. Wang et al., 1969
Triton X 305	15%			
Phosphoric Acid	2%	(8 ft x 1/8 in.)	Chromosorb W AW-DMCS 100–120	Ferretti and Flanagan, 1972
Lac IR 296	25%	(5480 x 4 mm i.d.)	Gas-Chrom AW 60–70	Stoffelsma et al., 1968
Lac IR 296	20%	(7200 x 18 mm i.d.)	Chromosorb W 40–60	Stoffelsma et al., 1968
Reoplex 400	26%	(3600 x 8 mm i.d.)	Chromosorb W 50–60	Stoffelsma et al., 1968
Reoplex 400	20%	(5400 x 9 mm i.d.)	Gas-Chrom AW 60–70	Stoffelsma et al., 1968
Carbowax 600 + 10% Na Stearate	25%	(2,000–10,000 x 9 mm i.d.)	Sil-O-Cel 50–60	Stoffelsma et al., 1968
Squalane	25%	(5400 x 8 mm i.d.)	Chromosorb AW 50–60	Stoffelsma et al., 1968
Silicone Oil MS550 + Na Stearate	25%	(2,000–10,000 x 9 mm i.d.)	Sil-O-Cel 50–60	Stoffelsma et al., 1968
Silicone Oil Embaphase	20%	(7200 x 18 mm i.d.)	Chromosorb W 50–80	Stoffelsma et al., 1968
XF-1150	10%	(5 ft x 1/8 in.)	Celite 100–120	Collins, 1971
Carbowax 20M	.1%			
Dow Corning 550	30%	(2 m x 8 mm o.d.)	Chromosorb P 100–120	Goldman et al., 1967
Dow Corning 710	20%	(2 m x 8 mm o.d.)	Chromosorb P 80–100	Goldman et al., 1967
Polyethylene glycol photalate	20%	(2 m x 8 mm o.d.)	Chromosorb P 50–100	Goldman et al., 1967
Reoplex 400	20%	(5400 x 9 mm i.d.)	Gas-Chrom AW 60–70	van der Wal et al., 1971
Lac IR 296	25%	(7200 x 18 mm i.d.)	Chromosorb W 40–60	van der Wal et al., 1971
Embaphase	20%	(5400 x 9 mm i.d.)	Chromosorb AW 60–70	van der Wal et al., 1971
MS 550 L	25%	(2,000–10,000 x 9 mm i.d.)	Sil-O-Cel 50–60	van der Wal et al., 1971
+ Na Stearate	25%			

Many techniques for trapping pyrazines have been employed. Buttery et al. (1969a) utilized a 150 × 3 mm borosilicate glass capillary to condense the volatiles eluting from the column. One end of the capillary was heated by the exit port while the other end was at ambient temperature. This temperature gradient minimized fog formation and allowed good recovery. After the compound had condensed, one end of the capillary was sealed with a torch. The sample was then centrifuged and the other end sealed. Deck et al. (1973) used a U-shaped, dry-ice-cooled capillary that had constrictions every centimeter to reduce aerosol formation. Mason et al. (1966) added a small bit of stainless steel wool to the inside of the glass capillary trap to reduce vapor losses. Liquid air was used by von Sydow and Anjou (1969) to condense the volatiles on the walls of the glass capillary.

The use of long, capillary glc columns in the separation of pyrazine isomers is becoming more widespread. Capillary columns offer the advantage of being better able to resolve pyrazines but suffer in that they are expensive, difficult to prepare, require a smaller sample, and consume more time in analysis. Predicting the identity of a compound from only the retention time is more accurate with capillaries than with packed columns. In the authors' lab, retention times of pyrazines which eluted 15 min after injection seldom varied over ± 5 sec.

Three sizes of capillaries have been used: 0.01 in., 0.02 in., and 0.03 in. The 0.01 in. are high efficiency columns and do not require as much length to attain good separations. These columns are not durable and can handle sample loads of only a few tenths of a microliter. They also require the use of inlet splitters. This small sample size restricts the use of 0.01 in. columns primarily to surveying samples and they are not good for use with a mass spectrometer. The medium sized 0.02 in. columns also cannot tolerate large peak loads, but they have been used successfully in conjunction with mass spectrometry and have up to 400,000 plates in a 500 ft column. The large bore 0.03 in. columns require more length to attain resolution comparable to the 0.02 in. columns but are capable of handling larger samples. With a maximum sample size of 3 μl, it is even possible to trap major peaks as they elute from the column. Even though a 500 ft × 0.03 in. column may have 100,000 to 200,000 plates, some pyrazine isomers still may not be resolved (example: 2,5-dimethylpyrazine, 2,6-dimethylpyrazine, and ethylpyrazine).

Capillary columns require time and effort to make consistently good columns. One of the most critical steps in the preparation of capillary columns is the cleaning of the column prior to coating. The authors' lab uses a modification of the technique of Mon (1971) for the cleaning of columns prior to coating. One liter of each of the following is sequentially flushed through the column at 800 psi: chloroform, acetone, H_2O, concentrated nitric acid, H_2O, 10% KOH in 1:1 methane and H_2O, H_2O, concentrated NH_4OH, H_2O, acetone, and chloroform. This sequence leaves the interior of the column basic and allows a better coating of the wall with Amine-220. Three 10-ml aliquots of 9.5 g of Amine-220 and 5 g of Igepal-880 in 90 g of chloroform-acetone (1:1) are slowly pushed through the column at 30 psi. Following a slow conditioning period, the column is ready to use.

Polar stationary phases have been predominant in the capillary glc analysis of pyrazines (see Table 46). Their wide use is due to their ability to separate pyrazines and a variety of other polar compounds. One of these stationary phases, Amine-200, is highly specific for nitrogenous compounds, while not retaining other polar compounds (Figure 6 for typical scan). This considerably simplifies later analysis of the effluent by eliminating some interfering nonnitrogenous compounds.

Mass Spectrometry

Mass spectrometry is the most widely used spectral instrument for the identification of pyrazines. It has the advantage that it requires only 1 μg of sample (Teranishi et al., 1971), thus making it ideal to use in conjunction with glc. Often, glc-MS data alone are sufficient to confirm the presence of a pyrazine in a mixture. Some difficulty in interpretation may arise when two or more compounds are present in the same peak. For example, 2-ethyl-5-methylpyrazine, 2-ethyl-6-methylpyrazine, and 2-ethyl-3-methylpyrazine eluted close succession from a 10 ft × 1/8 in. amine-220 column. The spectra obtained then were complicated in that there was some overlapping, and all three have similar spectra with a molecular weight of 122. Closer examination of the spectra revealed that only 2-ethyl-3-methylpyrazine has a large peak at

TABLE 46

GLC Capillary Columns Employed

Capillary column used	Dimensions	Reference
SF 96–50 (95%) + Igepal (5%)	(1000 ft × .03 in.)	Buttery et al., 1969b
SF 96–50	(500 ft × .03 in.)	Ferretti and Flanagan, 1971a,b
SF 96	(500 ft × .03 in.)	Kinlin et al., 1972
Carbowax 20M	(100 ft × .02 in.)	Ferretti and Flanagan, 1972
Carbowax 20M	(50 ft × .02 in.)	van Praag, 1968
Carbowax 20M	(500 ft × .03 in.)	Walradt et al., 1970
Carbowax 1540	(500 ft × .02 in.)	Johnson et al., 1971
Carbowax 1540	(250 ft × .01 in.)	Wang and Odell, 1972
BDS	(300 ft × .01 in.)	Walradt et al., 1970
Dowfax 9N15	(500 ft × .02 in.)	Liebich et al., 1972
Dowfax 9N15	(700 ft × .03 in.)	Liebich et al., 1972
Amine 220 (95%) Igepal (5%)	(500 ft × .03 in.)	Sizer and Maga, 1972
UCON-LB-550-X	(50 m)	Viani et al., 1965
UCON-HB-2000	not specified	Viani et al., 1965
OV-101	(500 ft × .03 in.)	Murray et al., 1970
Polyglycol 1000	(170 ft × .02 in.)	Collins, 1971
Dinonyl Sebacate	(150 ft × .02 in.)	Collins, 1971
DEGS and H_3PO_4 (2%)	(200 ft × .02 in.)	Manley and Fagerson, 1970
Carbowax 20M	(50 ft × .02 in. SCOT)	Manley and Fagerson, 1970

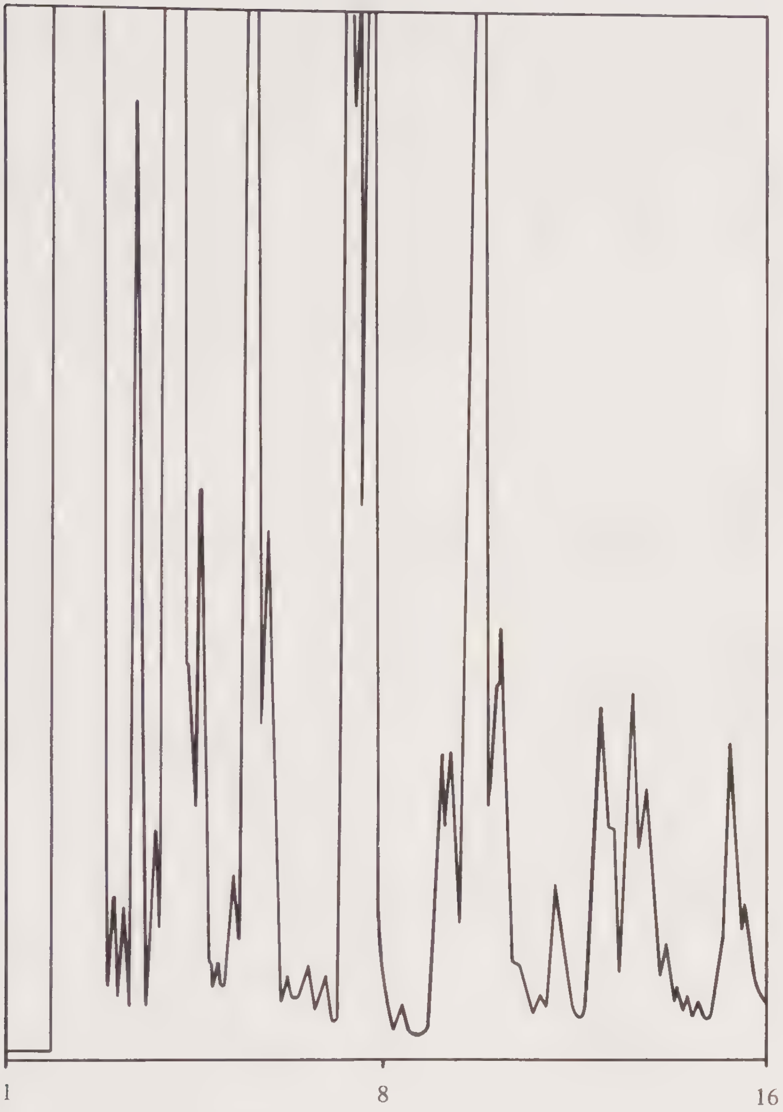

FIGURE 6. Basic pyrazine fraction GLC capillary column separation.

m/e 81. Thus, the amount of this compound in the mass spectrometer will be related to the size of this peak. In Figure 7, the intensity of m/e 81 was accorded in 20 sec intervals and superimposed in this was the inlet pressure of the mass spectrometer. The 2-ethyl-3-methylpyrazine is the third consecutive compound of m/e 122 but its presence can be followed by the intensity of m/e 81.

The spectra of pyrazines can be identified by certain characteristic peaks. A P-27 or P-41 peak corresponds to the loss of HCN and acetonitrile, respectively. The presence of an ethyl group anywhere on the ring will cause an intense P-1 peak from the loss of a H from the d-C. Pyrazines substituted with an alkyl side chain length of three or more carbons undergo a McClafferty type rearrangement cleaving the bond between the C_1 and C_2 carbons. In a normal propyl pyrazine this results in a large P-28 peak. This characteristic is also prominent in the methoxy pyrazines with alkyl side chains longer than three carbons. The spectra of a compound thought to be a pyrazine should be compared to spectra of authentic synthesized compounds or to spectra published in the literature. Table 47 lists all the published MS data of pyrazines to date.

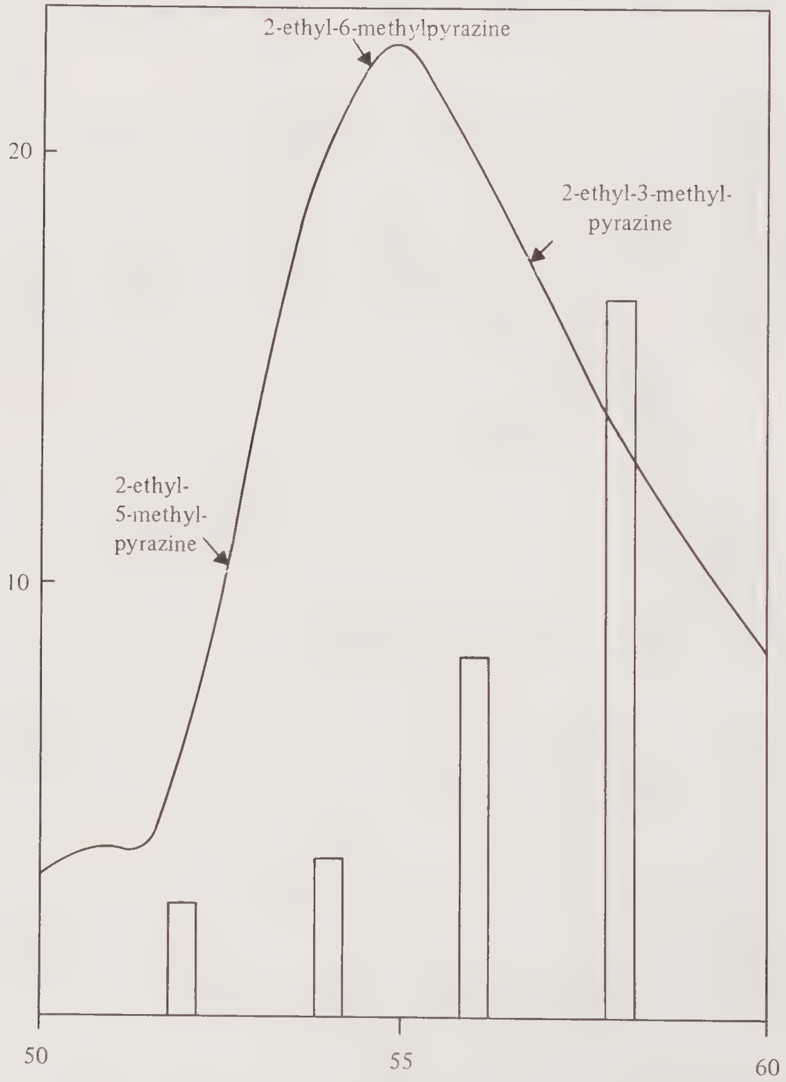

FIGURE 7. Interpretation of mass spectral data involving pyrazine mixture.

TABLE 47 Part I

Pyrazine Spectral Data of Alkyl and Methoxy Pyrazines

1. Pyrazine 80
MS 38(4), 39(2), 52(13), 53(46), 80(100), 81(4).
IR* S(3.3, 7.1, 8.7, 9.4, 9.8).
M(3.4, 5.1, 8.8, 9.1, 12.1).
W(5.3, 5.7, 5.8, 7.5).
UV (261.0, 255.5, 267.5, mμ).
Bondorovich et al., 1967. MS. IR. UV.

2. Methylpyrazine 94
MS 39(21), 40(18), 52(7), 53(17), 66(3), 67(55), 79(1), 94(100), 95(5).
IR S(6.8, 6.9, 7.1, 8.6, 9.5, 9.8, 12.0).
M(3.3, 6.3, 6.5, 7.7, 8.0, 8.5, 10.2).
W(5.2, 5.7).
UV (266.0, 272.0, mμ).
Bondorovich et al., 1967. MS. IR. UV.

3. Vinylpyrazine 106
MS 38(4), 39(6), 52(44), 53(35), 63(1), 64(1), 79(38), 80(15), 105(13), 106(100).
IR S(7.05, 8.1, 9.7, 9.9, 10.1, 10.6, 11.7).
M(3.3, 6.7, 7.2, 7.7, 8.1, 9.4).
W(5.2, 5.3, 6.1, 6.3, 6.6).
UV (229.5, 285.5, 294.0, mμ).
Bondorovich et al., 1967. MS. IR. UV.

4. 2,3-dimethylpyrazine 108
MS 40(20), 42(23), 51(6), 52(11), 67(100), 68(6), 93(4), 94(1), 108(97), 109(6).
IR S(6.9, 7.0, 7.1, 8.5, 10.1, 10.5, 11.8).
M(3.3, 3.4, 7.3, 9.8, 11.3).
W(5.2, 5.5, 6.5, 8.0, 8.3).
UV (273.0, 269.5, mμ).
Bondorovich et al., 1967. MS. IR. UV.

5. 2,5-dimethylpyrazine 108
MS 39(35), 42(87), 51(4), 52(6), 64(1), 66(2), 80(3), 81(18), 93(1), 108(100), 109(6).
IR S(6.7, 7.2, 7.5, 8.6, 9.6).
M(3.2, 3.3, 3.4, 6.4, 10.4, 11.4).
W(3.5, 3.6, 5.1, 5.5, 7.9, 9.2, 12.0).
UV (277.0, 272.0, mμ).
Bondorovich et al., 1967. MS. IR. UV.

6. 2,6-dimethylpyrazine 108
MS 40(43), 42(74), 52(4), 54(2), 66(7), 67(8), 80(1), 81(7), 92(3), 93(1), 108(100), 109(7).
IR S(6.8, 7.1, 7.2, 8.0, 8.6, 9.8, 11.6).
M(3.3, 3.4, 6.5, 7.8, 8.4, 10.7).
W(5.1, 5.3, 5.6, 5.8, 7.6, 10.2).
UV (275.6, 271.0, mμ).
Bondorovich et al., 1967. MS. IR. UV.

7. Ethylpyrazine 108
MS 39(16), 40(4), 52(18), 53(18), 64(1), 66(3), 80(23), 81(14), 92(1), 93(2), 107(100), 108(82).
IR S(3.4, 6.8, 7.1, 8.6, 9.4, 9.8, 11.8).
M(3.3, 3.5, 6.3, 6.5, 6.9, 7.7, 8.1, 10.3).
W(5.2, 5.4, 5.6, 5.7, 7.5, 10.7).
UV (266.2, 272.2, mμ).
Bonodorovich et al., 1967. MS. IR. UV.

8. Isopropenylpyrazine 120
MS 39(35), 41(18), 52(23), 67(24), 94(11), 119(100), 120(84).
Walradt et al., 1970. MS

9. 6,7-dihydro-5H-cyclopentapyrazine 120
MS 39(27), 41(22), 65(18), 66(19), 93(11), 119(87), 120(100).
NMR ($CDCl_3$) δ 7.8 (S,2,Ring-H), 2.5 (t,4,$\underline{CH_2}$,-$\underline{CH_2}$-$\underline{CH_2}$), 1.7(M,2,(CH_2-$\underline{CH_2}$-CH_2).
Walradt et al., 1971. MS. NMR.

TABLE 47 Part I (Continued)

Pyrazine Spectral Data of Alkyl and Methoxy Pyrazines

10. (2(*trans*-1-propenyl) pyrazine 120
MS 39(17), 41(12), 51(7), 52(5), 65(9), 67(18), 78(5), 80(3), 92(2), 94(4), 106(4), 119(100), 120(53).
IR S(6.0, 6.8, 6.9, 7.1, 8.7, 9.5, 9.9, 10.3, 11.7).
M(3.3, 3.4, 6.6, 7.2, 7.7, 8.5, 9.2, 10.6).
W(5.0, 5.2, 5.5, 6.3, 7.5, 8.1).
UV (239.5, 297.0, 292.0, mμ).
Bondorovich et al., 1967. MS. IR. UV.
NMR ($CDCl_3$) δ 7.9, 8.0, 8.4 (S,1-each, Ring-H)
5.4, 4.9, (s,1 each – $\underline{CH_2}$)
1.9 (S,3 – $\underline{CH_3}$).
Walradt et al., 1971.

11. 2-methyl-6-vinylpyrazine 120
MS 39(20), 40(13), 52(52), 54(18), 64(2), 66(5), 78(1), 79(2), 93(4), 94(15), 106(3), 120(100), 121(8).
IR S(7.0, 8.5, 8.6, 9.8, 10.1, 10.7, 11.4).
M(3.3, 3.4, 6.5, 6.9, 7.2, 7.3, 7.8, 8.0).
W(5.3, 5.5, 6.1, 7.7, 7.8, 8.3).
UV (229.5, 289.2, 295.3, mμ).
Bondorovich et al., 1967. MS. IR. UV.

12. 2-methyl-5-vinylpyrazine 120
MS 39(16), 40(7), 52(60), 54(29), 66(3), 67(2), 79(10), 80(1), 93(12), 94(9), 119(17), 120(100).
IR S(6.7, 8.6, 9.7, 10.1, 10.7).
M(3.3, 7.1, 7.2, 7.4, 7.6, 10.8, 11.1).
W(5.3, 6.1, 6.5, 7.8, 7.9, 8.2, 9.2, 11.4).
UV (233.3, 290.5, 297.0, mμ).
Bondorovich et al., 1967. MS. IR. UV.

13. Acetylpyrazine 122
MS 43(100), 52(44), 53(34), 79(27), 80(45), 122(37).
IR (1683, 1570, 1282, 1163, 1102, 1043, 1020, 950, 858 cm^{-1}).
UV λ_{max}^{ETOH} 269 mμ.
NMR T = .82 (1,db, Ring-H), 1.28 (1,db, Ring-H), 1.37 (1,qd, Ring-H), 7.28 (3,S, – $\underline{CH_3}$).
Walradt et al., 1970. MS.
Roberts et al., 1968. IR. UV. NMR.

14. Isopropylpyrazine 122
IR (1011, 1402, 1468, 1130, 1040, 841, 1151, 1519, cm^{-1}).
van der Wal et al., 1971. IR.

15. n-propylpyrazine 122
MS 39(16), 41(7), 52(9), 53(7), 66(5), 67(7), 79(2), 80(3), 94(100), 95(6), 107(23), 108(3), 121(11), 122(20).
IR S(3.4, 6.8, 7.1, 8.7, 9.5, 9.8).
M(3.3, 6.5, 6.9, 7.2, 7.7, 8.1, 8.5, 9.1, 9.7, 11.7, 12.1).
W(5.2, 6.3, 6.5, 7.5, 7.7, 7.9, 10.7, 11.5).
UV (266.2, 272.0, mμ).
Bondorovich et al., 1967. MS. IR. UV.

16. Trimethylpyrazine 122
MS 39(27), 42(100), 53(8), 54(12), 66(1), 67(2), 80(5), 81(22), 108(2), 122(81), 123(8).
IR S(3.4, 6.8, 7.2, 7.3, 8.6, 10.6).
M(7.8, 7.9, 9.8, 10.0, 11.2).
W(5.6, 6.5, 9.2, 10.2, 12.0).
UV (277.5 mμ).
Bondorovich et al., 1967. MS. IR. UV.

17. 2-ethyl-3-methylpyrazine 122
MS 39(18), 43(16), 52(7), 53(13), 65(6), 67(30), 80(14), 81(16), 93(9), 94(19), 107(7), 121(100), 122(92).
IR S(3.4, 6.8, 7.1, 8.6, 8.8, 9.7, 11.7).
M(3.3, 3.5, 7.3, 7.5, 9.4, 10.2).
W(5.2, 5.5, 6.5, 8.1, 9.2, 11.5, 12.1).
UV (273.0, 269.2, mμ).
Bondorovich et al., 1967. MS. IR. UV.

TABLE 47 Part I (Continued)

Pyrazine Spectral Data of Alkyl and Methoxy Pyrazines

18. 2-ethyl-5-methylpyrazine 122
MS 39(24), 42(10), 54(8), 56(16), 66(2), 67(2), 79(1), 80(3), 93(2), 94(13), 107(4), 121(100), 122(68).
IR S(3.4, 6.7, 8.6, 9.6).
M(3.2, 3.5, 6.8, 7.2, 7.4, 8.4, 9.3, 11.2).
W(5.5, 8.0, 8.2, 11.4, 11.7, 12.1).
UV (276.7, 272.0, mμ).
Bondorovich et al., 1967. MS. IR. UV.
NMR (CCl_4) δ 8.18 (S, 2, ring-H) 2.74 (q, 2,-$\underline{CH_2}$-CH_3) 2.45 (S, 3, ring-$\underline{CH_3}$) 128(t, J = 8, 3, CH_2-$\underline{CH_3}$).
Rizzi, 1967. NMR.

19. 2-ethyl-6-methylpyrazine 122
MS 39(27), 40(9), 54(6), 56(14), 66(5), 67(2), 94(17), 95(5), 121(100), 122(70).
IR S(3.4, 6.8, 7.0, 7.9, 8.6, 9.8, 11.5).
M(6.5, 7.2, 8.1, 9.5, 9.9, 10.3).
W(5.3, 5.5, 7.5, 11.7, 11.9).
UV (275.5, 271.0, mμ).
Bondorovich et al., 1967. MS. IR. UV.

20. Quinoxaline 130
MS 130, 76, 103, 50, 75, 51.
Kinlin et al., 1972. MS.

21. 2-methyl-5-(*trans*-1-propenyl)pyrazine 134
MS 39(20), 40(13), 51(4), 52(3), 65(13), 66(15), 78(2), 79(1), 92(3), 94(2), 106(1), 108(6), 118(2), 119(5), 133(100), 134(50).
IR S(6.7, 6.9, 7.5, 8.6, 9.7, 10.3).
M(3.3, 3.4, 6.0, 7.1, 7.2, 7.6, 9.1, 10.6, 11.1).
W(5.0, 5.5, 6.3, 6.5, 7.9, 8.0, 8.2, 11.4).
UV (240.5, 302.0, 293.0, mμ).
Friedel et al., 1972. MS.
Bondorovich et al., 1967. IR. UV.

22. 2-methyl-6-propenylpyrazine 134
MS 39(20), 40(9), 51(4), 52(3), 66(13), 68(11), 78(2), 80(1), 92(2), 93(3), 106(3), 108(5), 118(2), 119(4), 133(100), 134(48).
IR S(6.5, 6.9, 7.1, 8.5, 8.6, 9.8, 10.3).
M(3.3, 3.4, 6.0, 7.2, 7.7, 7.9, 8.2, 9.1, 10.9, 11.4).
W(3.1, 5.4, 5.5, 7.5, 9.6, 12.3).
UV (238.5, 300.5, 292.0, mμ).
Bondorovich et al., 1967. MS. IR. UV.

23. 2,5-dimethyl-3-vinylpyrazine 134
MS 133, 134, 42, 54, 91, 66, 108.
Buttery et al., 1971. MS.

24. 2-ethyl-6-vinylpyrazine 134
MS 38(7), 39(22), 51(25), 52(46), 66(5), 75(2), 78(5), 79(4), 91(3), 105(6), 106(16), 133(100), 134(81).
IR (7.02, 8.52, 8.61, 9.87, 11.29, 10.13, 10.67).
Friedel et al., 1972. MS.
Friedel et al., 1971. IR.

25. 2-methyl-6,7-dihydro-5H-cyclopentapyrazine 134
MS 39(46), 40(17), 65(14), 66(31), 107(16), 133(69), 134(100).
NMR ($CDCl_3$) δ 7.6 (S,1,Ring-H) 2.50 (t,4,$\underline{CH_2}$-CH_2-$\underline{CH_2}$), 2.0 (S,3,2-$\underline{CH_3}$) 1.7 (t,2,CH_2-$\underline{CH_2}$-CH_2).

26. 5-methyl-6,7-dihydro-5H-cyclopentapyrazine 134
MS 39(21), 41(12), 52(16), 78(12), 119(100), 133(25), 134(48).
NMR ($CDCl_3$) δ 9.7 (S,2,pyrazinyl-H), 2.7 (m,1,5-H) 2.4 (m,2,7-H) 2.0 & 1.30 (m,2,6-H) .80 (d,3,-CH_3).
Walradt et al., 1971. MS. NMR.

27. 5,6,7,8-tetrahydroquinoxaline 134
MS 39(37), 41(28), 51(25), 52(42), 106(33), 133(56), 134(100).
NMR ($CDCl_3$) δ 7.6 (S,2,pyrazinyl-H) 2.4 (t,4, $\underline{CH_2}$ – CH_2 – CH_2 – $\underline{CH_2}$) 1.4 (4, – CH_2 – $\underline{CH_2}$ – $\underline{CH_2}$ – CH_2).
Walradt et al., 1971. MS. NMR.

TABLE 47 Part I (Continued)

Pyrazine Spectral Data of Alkyl and Methoxy Pyrazines

28. Tetramethyl 136
MS 39(20), 42(37), 53(23), 54(100), 66(2), 68(2), 80(3), 94(3), 95(6), 121(3), 135(7), 136(85).
IR 7.06, 6.91, 10.08, 8.17, 3.42, 8.46, 8.32, μ.
Friedel et al., 1972. MS.
Friedel et al., 1971. IR.

29. 2-acetyl-3-methylpyrazine 136
MS 136, 43, 94, 93, 42.
IR 3.3, 3.4, 3.45, 5.92, 6.48, 6.55, 6.95, 7.09, 7.19, 7.3, 7.41, 7.82, 8.05, 8.42, 8.6, 9.23, 9.45, 9.7, 9.9, 10.2, 10.6, 11.7, μ.
NMR ($CDCl_3$) δ 2.7 (S, 3,-CO-CH_3) 2.8 (S,3,methyl H) 8.5 (d,1, Ring-H) 8.6 (d,1, Ring-H).
Mookherjee and Klaiber, 1972.

30. 2,3-diethylpyrazine 136
MS 39(16), 41(12), 54(12), 56(13), 65(4), 66(3), 80(22), 81(18), 93(3), 94(2), 107(17), 108(11), 119(7), 121(83), 135(46), 136(100).
IR 7.07, 3.36, 11.71, 6.82, 8.59, 9.67, 3.28, μ.
Friedel et al., 1972. MS.
Friedel et al., 1971. IR.

31. 2-methyl-3-i-propylpyrazine 136
MS 39(17), 42(19), 52(9), 53(14), 66(7), 67(18), 79(2), 80(8), 92(14), 93(12), 108(74), 109(7), 121(100), 122(9), 135(18), 136(36).
IR 7.11, 9.09, 3.38, 9.00, 8.58, 11.74, 6.81, μ.
Friedel et al., 1972. MS.
Friedel et al., 1971. IR.

32. 2-acetyl-5-methylpyrazine 136
MS 136-94-39.
Kinlin et al., 1972. MS.

33. 2-isopropyl-5-methylpyrazine 136
MS 39(18), 41(7), 52(8), 53(9), 66(6), 67(7), 79(1), 80(1), 93(5), 94(7), 107(2), 108(34), 121(100), 122(8), 135(23), 136(42).
IR S(3.4, 6.7, 6.8, 7.2, 8.6, 9.7).
M(3.2, 3.5, 7.3, 7.4, 7.6, 8.7, 9.3, 11.2).
W(5.5, 8.0, 8.2, 9.1, 10.2, 10.8).
UV (277.0, 272.0, mμ).
Bondorovich et al., 1967. MS. IR. UV.

34. 2-methyl-5-n-propylpyrazine 136
MS 39(28), 42(9), 107(9), 108(100), 121(25), 136(24).
IR 6.73, 9.68, 3.38, 7.23, 8.62, 6.86, 7.50, μ.
Friedel et al., 1971. MS. IR.

35. 2,5-diethylpyrazine 136
MS 39(63), 41(8), 53(38), 56(32), 65(3), 67(7), 80(6), 81(3), 93(4), 94(5), 106(6), 107(14), 121(92), 122(8), 135(96), 136(100).
IR 1490, 1036, 1160, 1463, 1371, 904, 1067, 1249 (cm^{-1}).
Friedel et al., 1972. MS.
van der Wal et al., 1971. IR.

36. 2-ethyl-6-propylpyrazine 150
MS 39(16), 122(100), 123(9), 135(22), 149(11), 150(18).
IR 3.38, 7.05, 9.87, 8.61, 6.52, 6.83, 3.28, μ.
Friedel et al., 1971. MS. IR.

37. 2-methyl-6-isopropylpyrazine 136
MS 39(19), 53(9), 67(6), 80(2), 94(8), 108(34), 121(100), 135(22), 136(39).
Goldman et al., 1967. MS.

TABLE 47 Part I (Continued)

Pyrazine Spectral Data of Alkyl and Methoxy Pyrazines

38. 2,6-diethyplyrazine 136
MS 39(20), 41(3), 53(16), 56(9), 66(2), 67(4), 79(1), 80(2), 93(1), 94(1), 107(4), 108(16), 120(5), 121(3), 135(100), 136(72).
IR S(3.4, 6.8, 7.0, 8.6, 9.8, 11.3).
M(6.5, 7.3, 7.8, 8.1, 9.5).
W(5.3, 5.5, 7.5, 10.3, 11.1, 12.1).
UV (276.0, 271.0, mμ).
Bondorovich et al., 1967. MS. IR. UV.

39. 2,3-dimethyl-5-ethylpyrazine 136
MS 39(27), 42(46), 53(35), 54(48), 66(3), 67(3), 79(2), 80(7), 94(3), 95(2), 107(4), 108(18), 121(4), 135(100), 136(67).
IR 7.18, 6.82, 3.37, 8.54, 8.61, 7.08, 7.34, μ.
Friedel et al., 1972. MS.
Friedel et al., 1971. IR.

40. 2,5-dimethyl-3-ethyl 136
MS 39(37), 42(42), 53(9), 56(22), 66(4), 67(6), 94(2), 107(13), 108(19), 121(8), 135(100), 136(86).
IR S(3.3, 6.9, 7.2, 7.3, 8.0, 8.1, 9.5, 9.9.).
M(7.5, 7.8, 8.8, 9.7, 10.4, 11.1).
W(5.5, 6.3, 6.5, 8.0, 12.1).
UV 278.0, mμ.
Bondorovich et al., 1967. MS. IR. UV.

41. 3,5-dimethyl-2-ethylpyrazine 136
MS 39(72), 42(53), 53(18), 56(63), 65(8), 66(13), 80(7), 81(3), 94(6), 95(4), 108(11), 109(20), 119(2), 120(10), 135(100), 136(15).
IR 6.80, 7.17, 3.37, 8.52, 7.33, 9.78, 7.83, μ.
Friedel et al., 1972. MS.
Friedel et al., 1971. IR.
NMR (CCl_4) δ 8.05 (S,1,Ring-H).
2.70 (q, J = 8,2, $\underline{CH}_2 - CH_3$) 2.42 (S,3, Ring-$\underline{CH}_3$) 2.38 (S,3, Ring – $\underline{CH}_3$) 1.24 (t, J = 8, 3, $CH_2 - \underline{CH}_3$).
Rizzi, 1967. NMR.

42. Dihydrothienopyrazine 138
MS 138, 137, 57, 41, 29, 39.
UV λmax at 211 and 255, mμ.
PMR ($CDCl_3$) δ 8.36 (S,2, pyrazinyl-H) 4.26 (S, 4, C-$\underline{CH}_2$-S-$\underline{CH}_2$-C).
Evers et al., 1972. MS. UV. PMR.

43. 2-(2′-furyl)pyrazine 146
MS 38(18), 39(18), 63(28), 64(20), 92(16), 93(55), 146(100).
IR 8.72, 9.84, 9.13, 9.91, 10.98, 6.23, 7.16, μ.
Friedel et al., 1971. MS. IR.

44. 2-isobutenyl-3-methylpyrazine 148
MS 148, 119, 133, 52, 55, 66, 67.
Buttery et al., 1971. MS.

45. 2-ethyl-6,7-dihydro-5H-cyclopentapyrazine 148
MS 147, 148, 39, 120, 65, 66.
Kinlin et al., 1972. MS.

46. 2,3-dimethyl-6,7-dihydro-5H-cyclopentapyrazine 148
MS 148, 43, 147, 66, 107.
Kinlin et al., 1972. MS.

47. 2,5-dimethyl-6,7-dihydro-5H-cyclopentapyrazine 148
MS 133, 148, 39, 147.
Kinlin et al., 1972. MS.

48. 3,5-dimethyl-6,7-dihydro-5H-cyclopentapyrazine 148
MS 133, 148, 39, 147.
Kinlin et al., 1972. MS.

49. 2-methyl-5,6,7,8-tetrahydroquinoxaline 148
MS 148, 147, 52, 39, 120, 79, 133.
Kinlin et al., 1972. MS.

TABLE 47 Part I (Continued)

Pyrazine Spectral Data of Alkyl and Methoxy Pyrazines

50. 2-acetyl-3-ethylpyrazine 150
MS 150, 43, 107, 52, 79, 27.
IR 3.3, 3.39, 3.41, 5.5, 5.9, 6.05, 6.45, 6.55, 6.85, 7.09, 7.14, 7.4, 7.6, 7.85, 8.02, 8.45, 8.6, 8.7, 9.2, 9.3, 9.45, 9.72, 10.3, 10.5, 11.65, μ.
NMR (CDCl$_3$) δ 1.28 (t, 3,-CH$_2$-$\underline{CH_3}$), 2.69 (s, 3, – C(=0)-$\underline{CH_3}$), 3.15 (q,2,–$\underline{CH_2}$ –CH$_3$) 8.44 (d,1, Ring-H), 8.61 (d,1, Ring-H).
Mookherjee and Klaiber, 1972.

51. 2-isobutyl-3-methylpyrazine 150
MS 41(17), 42(13), 53(5), 60(1), 67(12), 82(1), 93(4), 94(3), 108(100), 135(10), 150(5).
Buttery et al., 1971. MS.

52. 2-n-butyl-3-methylpyrazine 150
MS 39(7), 41(7), 66(3), 67(7), 80(3), 82(2), 93(3), 94(1), 108(100), 109(8), 121(13), 122(4), 133(2), 135(8), 149(2), 150(1).
IR 7.10, 3.38, 8.55, 6.82, 6.96, 11.77, 7.24, μ.
Friedel et al., 1972. MS.
Friedel et al., 1971. IR.

53. 2-ethyl-6-n-propylpyrazine 150
MS 39(16), 66(6), 122(100), 123(9), 135(22), 149(11), 150(18).
IR 3.38, 7.05, 9.87, 8.61, 6.52, 6.83, 3.28, μ.
Friedel et al., 1971. MS. IR.

54. 2,3-diethyl-5-methylpyrazine 150
MS 39(37), 41(14), 54(10), 55(51), 66(9), 67(8), 79(4), 80(3), 93(3), 94(7), 106(1), 107(2), 121(23), 122(9), 135(62), 136(7), 149(64), 150(100).
IR S(3.4, 6.9, 8.5, 9.5).
M(7.6, 7.9, 8.8, 9.9, 10.2, 10.3, 11.1).
W(5.6, 6.4, 6.5, 8.1, 10.8, 11.6, 11.8, 11.9).
UV 278.5
Bondorovich et al., 1967. MS. IR. UV.

55. 2,5-dimethyl-3-isopropylpyrazine 150
MS 122, 150, 149, 135, 42, 53, 67.
Buttery et al., 1971. MS.

56. 2.5-diethyl-3-methylpyrazine 150
MS 39(21), 54(17), 56(20), 135(91), 149(80), 150(100).
IR 7.15, 6.81, 3.37, 8.53, 7.29, 8.80, 9.63, μ.
Friedel et al., 1971. MS. IR.

57. 2,5-dimethyl-3-n-propylpyrazine 150
MS 39(17), 42(16), 52(6), 53(9), 67(3), 70(3), 107(6), 108(3), 122(100), 123(9), 135(21), 136(2), 149(7), 150(13).
IR 6.87, 3.38, 7.26, 8.54, 8.61, 8.72, 9.38, μ.
Friedel et al., 1972. MS.
Friedel et al., 1971. IR.

58. 3,5-dimethyl-2-n-propylpyrazine 150
MS 39(23), 42(17), 53(11), 122(100), 135(21), 150(11).
IR 6.83, 3.37, 7.19, 8.51, 7.33, 10.36, 9.77, μ.
Friedel et al., 1971. MS. IR.

59. 3,5-diethyl-2-methylpyrazine 150
MS 39(18), 42(12), 53(14), 54(12), 65(2), 67(5), 79(2), 80(4), 94(2), 95(1), 107(7), 108(1), 121(3), 122(15), 134(2), 135(13), 149(100), 150(77).
IR S(3.4, 6.8, 7.2, 8.5, 8.8, 10.3).
M(7.6, 7.9, 8.1, 9.4, 9.6, 9.9, 11.0).
W(5.5, 6.4, 6.5, 12.1).
UV 278.5, mμ.
Bondorovich et al., 1967. MS. IR. UV.

TABLE 47 Part I (Continued)

Pyrazine Spectral Data of Alkyl and Methoxy Pyrazines

60. 2-ethyl-3,5,6-trimethyl 150
MS 39(16), 42(23), 53(25), 54(19), 62(10), 63(11), 80(4), 81(1), 94(4), 107(2), 109(1), 121(9), 122(17), 135(9), 149(100), 150(81).
IR 7.04, 6.89, 3.37, 8.48, 8.28, 7.35, 10.47, μ.
Friedel et al., 1972. MS.
Friedel et al., 1971. IR.

61. 2-(2′-furyl)-3-methylpyrazine 160
MS 39(21), 42(13), 51(17), 52(12), 64(12), 67(48), 76(6), 77(8), 92(6), 93(47), 104(5), 106(7), 131(34), 132(8), 159(13), 160(100).
Friedel et al., 1972, MS.
Friedel et al., 1971. IR.

62. Triethylpyrazine 164
MS 104, 149, 163, 39, 56, 136.
Kinlin et al., 1972. MS.

63. 2-i-pentyl-3-methylpyrazine 164
MS 39(8), 41(8), 52(4), 53(5), 66(3), 67(7), 80(3), 81(2), 93(3), 94(2), 107(9), 108(100), 121(15), 122(4), 149(11), 150(3), 103(2), 164(1).
IR 7.09, 3.40, 8.54, 6.81, 7.20, 6.95, 7.29, μ.
Friedel et al., 1972. MS.
Friedel et al., 1972. IR.

64. 2-(2′-methylbutyl)-3-methyl 164
MS 41(5), 42(4), 52(2), 53(3), 66(2), 67(6), 80(2), 82(2), 93(2), 94(1), 108(100), 109(8), 119(1), 121(2), 133(1), 135(6), 149(8), 150(2), 163(1), 164(1).
IR 7.10, 3.38, 6.84, 8.56, 7.23, 6.96, 3.28, μ.
Friedel et al., 1972. MS.
Friedel et al., 1971. IR.

65. 2-methyl-3-n-pentylpyrazine 164
MS 39(8), 41(7), 52(4), 53(4), 66(3), 67(7), 80(2), 81(1), 93(3), 94(2), 108(100), 109(8), 121(14), 122(5), 135(9), 136(3), 149(4), 163(2), 164(2).
IR 7.08, 3.40, 6.83, 8.54, 6.95, 3.27, 7.22, μ.
Friedel et al., 1972. MS.
Friedel et al., 1971. IR.

66. 2-isoamyl-5-methylpyrazine 164
MS 108, 122, 42, 149, 67, 53, 164.
Buttery et al., 1971. MS.

67. 2-methyl-5-n-pentylpyrazine 164
MS 39(11), 41(5), 51(2), 52(3), 64(3), 80(5), 81(1), 107(7), 108(100), 121(17), 122(5), 135(15), 136(2), 163(2), 164(7).
IR 6.73, 3.41, 9.66, 7.23, 6.82, 7.47, 8.63, μ.
Friedel et al., 1972. MS.
Friedel et al., 1971. IR.

68. 2,3-dimethyl-5-butylpyrazine 164
MS 39(19), 42(12), 52(6), 53(10), 66(1), 67(2), 80(8), 81(2), 94(2), 95(1), 107(1), 108(1), 122(100), 123(18), 136(13), 137(5), 147(1), 149(6), 163(2), 164(3).
NIH 1973

69. 2,3-dimethyl-5-s-butylpyrazine 164
MS 39(14), 42(21), 52(13), 53(27), 66(6), 67(6), 79(2), 80(5), 93(1), 94(1), 108(5), 109(3), 122(28), 123(5), 135(52), 136(100), 149(48), 150(5), 163(4), 164(14).
NIH 1973

70. 2,5-dimethyl-3-butylpyrazine 164
MS 39(17), 42(15), 52(3), 53(8), 65(1), 66(2), 79(1), 80(3), 95(1), 96(1), 107(2), 108(1), 122(100), 123(9), 135(11), 136(3), 149(7), 150(1), 163(1), 164(1).
NIH 1973

TABLE 47 Part I (Continued)

Pyrazine Spectral Data of Alkyl and Methoxy Pyrazines

71. 2,5-dimethyl-3-isobutylpyrazine 164
MS 39(12), 42(13), 52(4), 53(7), 80(4), 81(2), 107(3), 108(2), 122(100), 123(9), 149(13), 150(2), 163(5), 164,(8).
IR 1445, 1365, 1162, 1069, 1282, 1329, 998, 1029 (cm^{-1}).
Friedel et al., 1972. MS.
van der Wal et al., 1971. IR.

72. 3,5-dimethyl-2-isobutylpyrazine 164
MS 42(36), 41(17), 53(12), 67(3), 80(4), 108(8), 122(100), 149(10), 164(6).
Buttery et al., 1971. MS.

73. 2,6-dimethyl-3-n-butylpyrazine 164
MS 39(18), 42(12), 53(8), 54(4), 66(3), 67(2), 80(3), 81(1), 93(1), 94(1), 107(2), 108(1), 122(100), 123(8), 135(11), 136(3), 149(7), 150(1), 163(1), 164(1).
NIH 1973

74. 3-isoamyl-2,5-dimethylpyrazine 178
MS 39(9), 42(11), 52(4), 53(7), 65(1), 66(2), 80(5), 81(1), 107(2), 108(2), 122(100), 123(9), 135(14), 136(3), 163(11), 178(2).
IR 3.39, 6.88, 7.26, 7.19, 8.53, 9.24, 8.17, μ.
Friedel et al., 1972, MS.
Friedel et al., 1971. IR.

TABLE 47 Part II

Methoxy Pyrazines

1. 2-methoxy-3-methylpyrazine 124
MS 40(3), 42(4), 52(4), 53(3), 67(3), 68(12), 80(8), 81(2), 94(15), 95(23), 106(33), 108(36), 123(28), 124(100).
Friedel et al., 1972. MS.

2. 2-ethyl-3-methoxypyrazine 138
MS 41(27), 42(18), 52(23), 53(19), 54(20), 56(23), 68(25), 107(22), 123(65), 137(35), 138(100).
IR* S(6.5, 6.85, 6.9, 7.16, 7.2, 7.5, 8.6, 8.9, 9.9).
M(7.7, 7.9, 8.4; 9.1, 9.2, 11.9).
W(6.3, 9.4, 11.2, 13.7).
VW(5.3, 5.6, 10.5, 10.8, 12.5).
Seifert et al., 1971. MS. IR.

3. 2-methoxy-3,6-dimethylpyrazine 138
MS 39(43), 42(57), 54(66), 107(37), 109(51), 123(57), 138(100).
IR S(3.4, 6.9, 7.3, 8.6).
M(6.5, 7.7, 9.7, 10.2).
W(3.4, 6.3, 9.2, 11.5).
Kolor et al., 1973. MS. IR.

4. 2-methyl-3-ethoxypyrazine 138
MS 81(36), 82(60), 93(20), 94(37), 110(71), 123(53), 138(100).
IR (8.55, 7.02, 7.22, 8.39, 7.41, 9.67, 7.61).
Friedel et al., 1971. MS. IR.

5. 2-methyl-3-methylthiopyrazine 140
MS 84(14), 93(14), 94(10), 106(18), 107(31), 125(27), 140(100).
IR (9.15, 7.37, 7.26, 9.07, 8.53, 9.40, 11.88 μ).
Friedel et al., 1971. MS. IR.

6. 2-ethoxy-3-ethylpyrazine 152
MS 41(60), 56(25), 57(32), 68(30), 81(42), 95(71), 107(27), 108(25), 123(94), 125(100), 152(60).
IR S(6.5, 6.8, 7.0, 7.3, 7.4, 7.5, 7.6, 8.5, 8.6, 8.7, 9.6, 9.7).
M(7.9, 11.9).
W(6.3, 9.1, 10.3, 10.8).
Buttery et al., 1972. MS. IR.

TABLE 47 Part II (Continued)

Methoxy Pyrazines

7. 2-isopropyl-3-methoxypyrazine 152
MS 41(25), 43(14), 52(12), 53(9), 54(10), 68(12), 95(11), 105(13), 124(21), 137(100), 152(38).
IR S(6.5, 6.85, 6.9, 7.16, 7.2, 8.6, 8.9, 9.9).
M(7.7, 7.9, 8.4, 9.1, 9.2, 11.9).
W(6.3, 9.4, 9.6, 11.2, 13.7).
VW(5.3, 5.6, 10.5, 10.8, 12.5).
Seifert et al., 1970. MS. IR.

8. 2-methoxy-3-n-propylpyrazine 152
MS 38(2), 39(2), 52(1), 53(3), 94(14), 95(8), 105(2), 109(3), 124(100), 125(9), 137(26), 138(3), 151(5), 152(12).
IR S(6.5, 6.8, 6.9, 7.2, 8.5, 9.7).
M(7.4, 7.8, 8.4, 8.7, 11.9).
W(6.3, 7.9, 9.2, 9.3, 11.3, 13.8).
VW(5.3, 5.6, 6.0, 6.2, 7.7, 12.6, 13.1).
Friedel et al., 1971. MS.
Seifert et al., 1970. IR.

9. 2-methyl-3-ethylthiopyrazine 154
MS 42(11), 45(4), 52(5), 57(10), 67(7), 68(4), 82(30), 84(26), 93(32), 94(19), 119(15), 121(83), 126(54), 139(25), 140(3), 153(6), 154(100).
IR (9.15, 7.40, 7.26, 8.53, 9.40, 11.87, 10.26).
Friedel et al., 1972(1). MS. IR.

10. 2-butoxy-3-methylpyrazine 166
MS 40(13), 41(15), 42(12), 82(75), 110(100), 111(18), 166(9).
IR S(3.4, 7.0, 7.3, 7.6, 8.5).
M(3.5, 6.5, 8.0, 8.4, 10.2, 11.9).
W(3.3, 6.3, 9.4).
Kolor et al., 1973. MS. IR.

11. 2-methoxy-3-i-butylpyrazine 166
MS 40(3), 41(2), 52(1), 53(3), 66(1), 68(3), 80(2), 81(6), 94(15), 95(9), 106(2), 109(3), 124(100), 125(8), 151(22), 152(2), 165(4), 166(9).
IR S(3.39, 3.43, 3.50, 6.49, 6.85, 6.9, 7.2, 7.7, 8.6, 9.9).
M(3.28, 3.46, 7.4, 8.4, 9.4, 11.8).
W(3.33, 6.34, 7.9, 8.1, 9.2, 10.5, 10.8, 11.2, 13.3).
Friedel et al., 1972. MS.
Buttery et al., 1969. IR.

12. 2-methoxy-3-(1-methylpropyl)-pyrazine 166
MS 105(14), 123(12), 124(100), 137(50), 138(90), 151(46), 152(12).
IR S(3.4, 6.9, 7.2, 7.4, 8.6).
M(3.5, 6.5, 7.7, 8.4, 8.9, 9.9, 11.9).
W(3.3, 6.4, 7.9, 9.0, 11.5).
Kolor et al., 1973. MS. IR.

13. 2-methoxy-6-isobutylpyrazine 166
MS 39(18), 41(16), 43(13), 81(13), 124(100), 151(13), 166(10).
IR S(6.5, 7.1, 7.6, 7.8).
M(3.5, 6.9, 7.0, 7.4, 8.0, 8.5, 9.6, 9.9).
W(3.3, 6.3, 7.4, 8.7, 11.6).
Kolor et al., 1973. MS. IR.

14. 2-methyl-3-(2′-thienyl)pyrazine 176
MS 39(8), 45(9), 51(4), 58(6), 64(5), 67(31), 77(5), 88(7), 93(2), 94(2), 109(55), 110(7), 120(4), 121(1), 175(72), 176(100).
Friedel et al., 1972. MS.

15. 2-ethoxy-3-isobutylpyrazine 180
MS 41(17), 81(22), 94(20), 95(14), 109(44), 138(100), 165(14), 180(6).
IR S(3.4, 7.1, 7.2, 7.5, 7.6, 8.6).
M(3.5, 6.6, 6.9, 7.7, 9.2, 9.4, 9.7, 11.9).
W(3.3, 6.4, 7.9, 8.3 8.9 10.8, 11.6).
Kolor et al., 1973. MS. IR.

TABLE 47 Part II (Continued)

Methoxy Pyrazines

16. 2-isoamyl-3-methoxypyrazine 180
MS 40(1), 53(1), 54(1), 65(1), 67(2), 79(2), 80(3), 94(10), 95(4), 107(2), 109(2), 124(100), 125(8), 137(17), 138(2), 149(2), 151(3), 165(7), 179(2), 180(1).
Friedel et al., 1972. MS.

17. 2-methoxy-3-n-pentylpyrazine 180
MS 40(5), 41(3), 53(3), 54(2), 80(2), 81(4), 94(13), 95(6), 109(2), 111(2), 124(100), 125(7), 137(18), 138(4), 149(2), 151(5), 165(2), 179(2), 180(4).
Friedel et al., 1972. MS.

18. 2-methoxy-3-(1-methylbutyl)-pyrazine 180
MS 94(20), 123(21), 124(100), 137(47), 139(16), 151(30), 180(1).
IR S(3.4, 6.9, 7.2, 7.4, 8.6).
M(3.5, 6.5, 7.7, 8.4, 8.9, 9.8, 11.9).
W(3.3, 6.3, 7.9, 9.2, 9.4).
Kolor et al., 1973. MS. IR.

19. 2-isobutyl-3-methoxy-5-methylpyrazine 180
MS 41(21), 53(12), 54(14), 56(14), 95(7), 107(15), 108(21), 109(19), 138(100), 180(5).
IR S(6.9, 7.3, 8.5, 9.6).
M(6.3, 6.5, 7.7, 9.2, 9.9).
W(7.9, 9.01, 10.3, 11.3).
Buttery et al., 1972. MS. IR.

20. 2-methoxy-3-isobutyl-4-methylpyrazine 180
MS 41(24), 42(19), 43(10), 54(15), 107(11), 108(20), 109(13), 138(100), 139(12), 165(15), 180(4).
IR S(6.8, 7.2, 7.7, 8.5, 9.8).
M(6.5, 7.4, 7.0, 9.2, 10.2).
W(6.3, 7.9, 8.1, 11.1, 12.0, 13.0, 13.9).
Buttery et al., 1972. MS. IR.

21. 2-methylthio-3-isobutylpyrazine 182
MS 93(10), 94(14), 107(14), 140(100), 141(10), 167(40), 182(36).
IR S(3.4, 7.3, 9.0).
M(3.4, 3.5, 6.6, 6.8, 6.9, 7.1, 8.6, 9.5, 11.9).
W(3.3, 7.5, 8.3, 8.8, 10.0, 10.5).
Kolor et al., 1973. MS. IR.

22. 2-methylthio-6-isobutylpyrazine 182
MS 39(32), 41(22), 92(13), 106(6), 140(100), 167(17), 182(23).
IR S(3.4, 6.6, 7.1, 8.5).
M(3.4, 3.5, 7.2, 8.8, 9.9).
W(3.3, 6.8, 6.9, 8.0, 9.2, 10.5).
Kolor et al., 1973. MS. IR.

23. 2-butoxy-3-propylpyrazine 194
MS 67(15), 95(100), 110(33), 137(24), 138(27), 166(63), 194(21).
IR S(3.4, 7.1, 7.4).
M(3.5, 6.5, 6.8, 7.3, 7.7, 8.6).
W(3.3, 6.4, 8.0, 9.4, 10.0, 10.4, 11.9).
Kolor et al., 1973. MS. IR.

24. 2-isobutyl-3-methoxy-5,6-dimethylpyrazine 194
MS 41(25), 42(23), 53(17), 54(10), 121(10), 122(18), 123(13), 151(15), 153(13), 179(13), 194(6).
IR S(6.9, 7.2, 7.6, 8.3, 8.5, 9.8).
M(6.4, 7.8, 8.0, 8.8, 10.1).
W(5.7, 6.4, 9.2, 14.4).
Buttery et al., 1972. MS. IR.

25. 2-methoxy-3,6-diisobutylpyrazine 222
MS 137(68), 138(8), 179(5), 180(100), 181(14), 222(6).
IR S(3.4, 6.9, 7.3, 8.6).
M(3.5, 6.5, 7.4, 7.7, 9.7).
W(6.4, 9.4, 10.2, 11.2).
Kolor et al., 1973. MS. IR.

TABLE 47 Part II (Continued)

Methoxy Pyrazines

26. 2-methoxy-3-isononylpropylpyrazine 236
    MS 41(12), 43(10), 94(9), 95(5), 123(8), 124(100), 137(15), 236(2).
    IR S(3.4, 6.9, 7.2).
    M(3.5, 6.5, 7.4, 7.7, 8.5, 9.9, 11.9).
    W(3.9, 6.3).
    Kolor et al., 1973. MS. IR.
27. 2-methoxy-3-2-methoxy-3-(methyloctyl)-pyrazine 236
    MS 41(3), 81(3), 94(6), 124(100), 125(9), 137(3), 151(11), 236(1).
    IR S(3.4, 6.9, 7.2).
    M(3.5, 6.5, 7.4, 7.7, 8.5, 8.6, 9.9).
    W(3.3, 6.3, 9.1, 11.9).
    Kolor et al., 1973. MS. IR.

*IR reported in microns:

The use of directly coupled glc-mass spectrometers has predominated in pyrazine identification. Direct coupling eliminates losses from trapping and requires a smaller sample size to obtain good spectra. It is the most direct method for getting the sample into the mass spectrometer and the system is more convenient to use. Trapping a sample and introducing it directly into the mass spectrometer is slow, inefficient, and requires larger samples.

Ultraviolet (UV) Spectrometry

A number of researchers have used UV-spectrometry to aid in the identification of pyrazines. Alkyl pyrazines have two UV-absorption bands. One band, at ~ 310 mμ is due to a n $\rightarrow \pi^*$ transition of the nonbonded electrons of the ring nitrogens. The second band, an intense, benzoid band, has a λ max at ~ 260 with an extinction coefficient in the range of from 5,000 to 10,000. Good spectra can be achieved with samples of less than 0.1 mg.

UV is useful in determining the position of alkyl groups substituted on the ring. Unsubstituted pyrazine has a broad, benzoid type absorption band with a λ max at 261.0 mμ. This band is thought to arise from a $\pi \rightarrow \pi^*$ transition and has vibrational sublevels superimposed upon it which cause the multiple peaks in this region. The introduction of one alkyl side chain produces a bathochromic shift of λ max 266.0 to 268.0 mμ. An even larger shift is produced by the addition of a second alkyl group to the ring. The second alkyl group will produce the greatest red shift if it is substituted on the 5-position while the weakest shift will occur when the substitution is at the 3-position (2,5-dimethylpyrazine (277.0 mμ) 2,6-dimethylpyrazine (275.6 mμ), 2,3-dimethylpyrazine (273.0 mμ)). Thus, the UV-spectra can be used to determine the position of substitution on the pyrazinyl ring.

Substitution of l-alkene on the pyrazine was marked by the appearance of an intense band at ~ 230 mμ corresponding to a $\pi \rightarrow \pi^*$ transition of the conjugated double bond. Accompanying this was a shift to longer wavelength of the benzoid band to ~ 290 mμ. This bathochromic shift distinctly marks the substitution of the l-alkenyl side chain on the pyrazine ring.

Nuclear Magnetic Resonance

Few researchers have used nuclear magnetic resonance (NMR) to identify pyrazines isolated from foods. Requiring a sample size of 1.5 mg, NMR is the least sensitive analytical instrument. Computer averaging of multiple scans reduces the amount of sample required, but unfortunately this technique is not widely used. The principal use of NMR has been to confirm the identity of synthesized pyrazines. When sufficient quantities are available, NMR can provide invaluable information to help determine the exact structure of the pyrazine. Table 47 contains some reported NMR data.

Raman Spectrometry

Raman spectra, obtained from pyrazine samples as small as 0.5 nanoliters have been used to determine the exact ring substitution patterns of pyrazines (Oertel and Myhre, 1972). Utilizing new sample manipulation techniques, Oertel and Myhre were able to correlate ring substitution with various bands in the spectrum. This technique offers a nondestructive method for analyzing minute quantities of pyrazines.

Thin-Layer Chromatography

Some pyrazine isomers having the same molecular weight have been difficult to separate by glc. This, in turn, has made subsequent analysis by MS, IR, and UV more difficult to interpret. Thin-layer chromatography (TLC) has been demonstrated as a means for separating some of these mixtures (Sizer, 1973). Figure 8 shows a TLC separation of 2,3-dimethylpyrazine, 2,5-dimethylpyrazine, 2,6-dimethylpyrazine, and ethylpyrazine. TLC is ideally suited for use in flavor research in that small samples can be used (<10 nl) and the sample can be scraped off the plate to be further analyzed.

Infrared Spectrometry

Infrared spectrometry (IR) has become an increasingly important tool in the identification of pyrazines. Refinement of micro-sampling techniques has enabled the researcher to obtain good IR spectra on samples of less than 0.1 μl. IR spectra in combination with mass-spectra and glc retention times provide a high degree of certainty in the identification of a pyrazine. Comparison of an unknown's spectra to the spectra of the authentic compound should be made before definite assignments are made. Table 47 includes the IR spectra of some pyrazines.

FIGURE 8. Typical thin-layer chromatography pyrazine separation.

Pyrazine has a C – H stretch absorption band in the 3075–3000 cm^{-1} region. With the addition of alkyl side groups, this band decreases in intensity with the concurrent rise in absorption of the aliphatic C – H stretch in the 3000–2850 region. Ring stretching vibrations in the area from 1600–1300 provide a good indication as to the pattern of substitution of the ring. The identity of the pyrazine can usually be established after comparison of the "fingerpoint region" (1300 cm^{-1} – 800 cm^{-1}) to that of authentic compounds.

Ultra-microcavity cells that can be used to obtain neat, liquid spectra from samples as small as 0.07 μl have been developed (van Wyk et al., 1967) and are now commercially available (Beckman Instruments). These cells have been used in conjunction with reflecting beam condensers and have windows of only 4 to 8 mm^2. The sample is introduced into the cell with a μl syringe and the liquid is held in place by capillary action. Numerous investigators have employed these cells to identify pyrazines. The sample size necessary for good spectra is in the range often encountered in the basic fraction.

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PRECURSORS OF SULFUR-CONTAINING FLAVOR COMPOUNDS

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I. INTRODUCTION

The flavor characteristics of a food are derived mainly from its volatile components. Although the nonvolatiles also play an important role in the flavor of the foodstuff, this role is generally restricted to taste sensations like sweet, sour, salt, and bitter. Of course, not all volatile compounds present in a food are equally important as flavor compounds. The degree to which they contribute to the flavor is dependent on their potency and on their concentration. The potency of a flavor compound is generally expressed as its *threshold value,* i.e., the concentration at which it is just perceived. The relative importance or *odor value* of a flavor volatile in a food may be expressed as the ratio between its *concentration* in the food and its *threshold value.*[104]

Most studies in the field of flavor chemistry are qualitative. Flavor compounds isolated and identified in a particular foodstuff are listed, but little information is given about their relative importance. This is almost inevitable, as the determination of the exact concentration and of the threshold value is extremely laborious. In a more intuitive approach, the importance of the compounds to the overall flavor can be evaluated by smelling. In addition, the experienced flavor chemist can tell from the chemical formula of a compound whether it may be expected to have a strong odor. Odoriferous compounds should be rather volatile, should be soluble in a polar phase in order to be able to penetrate through the mucus layer in the nose, and should possess at least one osmophoric group, e.g., a carbonyl group, a heterocyclic moiety, or a sulfur atom.

Volatile compounds, with the exception of water and carbon dioxide, are seldom bulk ingredients of the living organisms from which food is derived. Nor are they, in general, essential intermediates in the biochemistry of such an organism, like vitamins or hormones. They may be considered as being derived from the basic bulk ingredients of the living organism, i.e., carbohydrates, proteins, and fats (triglycerides).

Volatile compounds responsible for the flavor of a foodstuff may be formed in the living species, for example, in fruits during ripening (this is referred to as bioformation) or during the process that is required to make the food edible.[142] In the latter case, several methods of formation can be distinguished. First, the volatile flavor compounds may be formed enzymically; this can occur, for instance, during the chopping of vegetables, whereby flavor enzymes and precursors, originally separated from each other, are brought in close contact. The flavor enzymes may also be formed by microorganisms; the enzymes then react with the flavor precursors in the food in a fermentation process. Examples of this are the ripening of cheese and the fermentation of alcoholic beverages. Finally, flavors may be produced nonenzymically during the heating of the food, as in the roasting of coffee, cooking or frying of meat, baking of bread, and boiling of potatoes. In all cases mentioned above, the volatile flavor compounds are formed from the three basic food ingredients: carbohydrates, particularly the monosaccharides and disaccharides, proteins, particularly the free amino acids, and triglycerides or their derivatives. The most important classes of flavor compounds in various foodstuffs and the mode of their formation from precursors are summarized in Table 1. As can be seen, the main types of food with sulfur-containing flavor volatiles are vegetables, meat, and roasted products such as coffee, cocoa, and peanuts.

TABLE 1

Major Classes of Flavor Compounds in Various Foods and Their Mode of Formation from Precursors

Food	Precursors	Main mode of formation	Flavor compounds
Fruit	Sugars	Bioformation	Terpenes, terpenoids, acids, furans, pyrans, esters
	Fats	Bioformation	Aldehydes, ketones, esters, lactones
Vegetables, Spices, Herbs	Sugars	Bioformation	Terpenes, terpenoids, isoprenoids, phenols
	Fats	Bioformation	Lactones, aldehydes
	Amino acids, sugars	Bioformation (?)	Pyrazines
	Amino acids, sugars	Enzymes	Sulfur compounds, aldehydes
	Amino acids	Heat	Sulfur compounds, cyanides
Wine, beer	Sugars	Fermentation	Esters, acetals
	Amino acids	Fermentation	Lactones, amines
Dairy products	Fats	Enzymes, heat	Ketones, lactones, aldehydes
	Amino acids	Fermentation	Acids, amines
Meat	Amino acids, sugars	Heat	Acids, aldehydes, ketones, furans, pyrazines, phenols, sulfur compounds
Fish	Amino acids	Enzymes, heat	Amines, sulfur compounds
	Fats	Enzymes	Aldehydes, ketones
Coffee, cocoa	Amino acids, sugars	Heat	Heterocycles, aldehydes, ketones, phenols, sulfur compounds
Bread	Amino acids, sugars	Heat	Pyrroles, pyrazines, pyridines
Roasted nuts	Amino acids, sugars	Heat	Pyrazines, aldehydes, ketones, sulfur compounds

Sulfur-containing flavor compounds usually make a dominant contribution to the overall flavor impression of foods in which they are present because of their strong, often characteristic, odor and their very low threshold values (in the order of a few μg per kg food). Flavor threshold values of some sulfur-containing volatiles are given in Table 2.

The high volatility and reactivity of the sulfur-containing flavor compounds impairs their application as such in the flavoring of foodstuffs. Knowledge of the mode of formation of these compounds from natural precursors is therefore of more than academic interest. Application of precursors is often the only way of providing a more or less continuous release of balanced flavor. As the formation of the volatile sulfur-containing flavor compounds is the ultimate goal of the use of precursors, a discussion of these flavor compounds themselves is imperative in a treatment of their precursors. These compounds have recently also been reviewed by Shankaranarayana et al.[135a]

The present review appeared before in *CRC Critical Reviews in Food Technology.* The literature that has appeared since has been screened and briefly included in the present article.

TABLE 2

Flavor Threshold Values* of Some Sulfur-containing Flavor Compounds in Water

Compound	Flavor threshold value (μg/l)	Reference
Thiols, sulfides		
Hydrogen sulfide	5	Palamand et al.[116]
	10	Pippen et al.[123]
	0.5	Persson and von Sydow[121]
Methanethiol	0.02	Guadagni et al.[49]
	2	Patton et al.[119]
	2.1	Persson and von Sydow[121]
Ethanethiol	1.0	Persson and von Sydow[121]
	10	Palamand et al.[116]
Benzyl mercaptan	1.0	Walker and Grey[154]
2-Mercaptoethanol	120	Buttery et al.[21]
1-Methylthioethanethiol	5	Schutte data
Dimethyl sulfide	0.33	Guadagni et al.[49]
	1.0	Persson and von Sydow[121]
	1	Mulders[104]
	12	Patton et al.[119]
Benzyl methyl sulfide	10	Walker and Grey[154]
Dimethyl disulfide	30	Schutte data
	21	Patton[118]
	7.6	Persson and von Sydow[121]
	0.16	Mulders[104]
Diethyl disulfide	30	Schutte data
Dipropyl disulfide	3.2	Boelens et al.[10]
Methyl propenyl disulfide	6.3	Boelens et al.[10]
Propyl propenyl disulfide	2.2	Boelens et al.[10]
Dimethyl trisulfide	3	Schutte data
Methylthio-acetone	50	Schutte data
Methional	0.20	Buttery et al.[21]
	5	Patton[118]
	10	Schutte data
2-Methylthioethanal	16	Buttery et al.[21]
Heterocycles		
2-acetylthiazole	10	Schutte data
2-isobutylthiazole	2	Kazeniac and Hall[77]
	3	Schutte data
	3.5	Buttery et al.[21]
4-Methyl-2-acetylthiazole	300	Schutte data
2-Acetyl-2-thiazoline	3	Schutte data
3,4-Dimethylthiophene	1.3	Boelens et al.[10]
5-Methyl-2-formylthiophene	1	Schutte data
3,5-Dimethyl-1,2,4-trithiolane	10	Schutte data
Lenthionine	400	Wada et al.[151]
Others		
Benzyl isothiocyanate	100	Walker and Grey[154]
Benzyl thiocyanate	100	Walker and Grey[154]
Methyl propyl thiosulfonate	1.7	Boelens et al.[10]
Dipropyl thiosulfonate	1.5	Boelens et al.[10]
Thiamine	39	Kurkela and Uutela[86]

*The value of the threshold is highly dependent on the method of its determination as is indicated by the different values found by various authors for the same compound.[49]

II.OCCURRENCE AND PRECURSORS OF SULFUR-CONTAINING VOLATILES

Vegetables

General

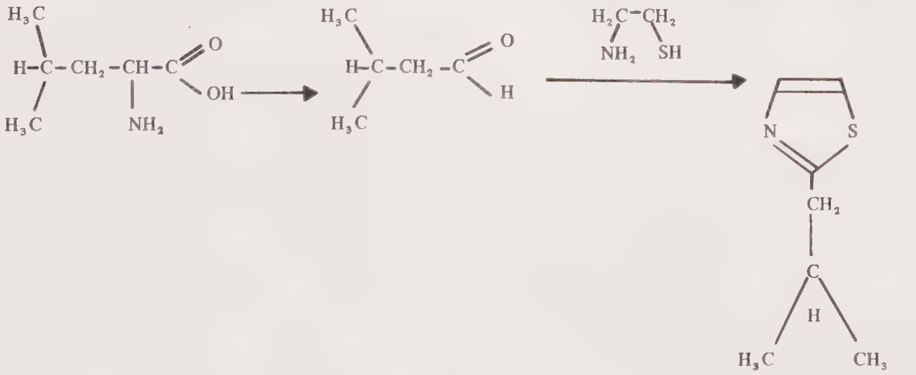
Volatile sulfur compounds play a predominant role in the flavor of vegetables. In a recent survey covering the volatile components of 23 types of vegetables[68] there were only two (parsley and cucumber) in which no volatile sulfur compounds have as yet been identified. The other vegetables share a large number of fairly common compounds, e.g., dimethyl monosulfide, dimethyl disulfide, methanethiol, and hydrogen sulfide; other sulfur compounds are more or less specific for the type of vegetable in question (see Table 3).

The formation of these flavor compounds[138] may follow enzymic or nonenzymic pathways or both. A recent review of MacLeod[90] deals with the formation of vegetable flavor. Many vegetables are cut, chopped, or crushed before or during consumption. Enzymes and flavor precursors, that are separated as long as the cells of the vegetables remain intact, are combined in these processes, and flavor compounds can then be formed. Most vegetables are then cooked. Also, during the heating-up period, enzymes do their job. This enzymic formation of flavors is summarized by Underkofler.[147]*

Vegetable flavors are also formed nonenzymically, and it is this mode of formation which predominates during cooking. Both the enzymic and the nonenzymic processes contribute to the overall flavor development.

The formation of sulfur-containing flavor compounds in the various types of vegetables will be dealt with in some detail in this chapter. Separate sections are devoted to the *Cruciferae,* in which isothiocyanates prevail, and to the *Allium* species, in which mono-, di-, and trisulfides are dominant flavor compounds. Finally, attention will be paid to vegetables which owe their characteristic flavor to the heating process. This treatment naturally involves a degree of overlap, as most vegetables are heated before consumption.

First, though, a few sulfur-containing flavor compounds which fall outside these categories will be dealt with. 2-Isobutylthiazole has been identified in fresh tomatoes.[77] The amounts of isobutylthiazole formed are not dependent on crushing nor on the presence of oxygen but highly dependent on the tomato variety. These findings indicate that isobutylthiazole is an exceptional case of a sulfur-containing flavor compound formed biologically in the intact plant. All other volatile thiazoles reported in foodstuffs (e.g., coffee and cooked beef) are formed by heat in nonenzymic browning reactions. Kazeniac[77] suggests that thiamine may be the precursor of 2-isobutylthiazole. This seems implausible, as thiazoles derived from thiamine are usually substituted at the 4- or 5-position and not at the 2-position. According to the abstracts of papers for the 162nd meeting of the American Chemical Society in September 1971, Kazeniac and his co-workers have evidence for the biosynthesis of 2-isobutylthiazole from methionine in tomatoes. Another possibility is that 2-isobutylthiazole is formed from cysteamine and isovaleraldehyde. This aldehyde, which can be



(leucine) (isovaleraldehyde) (2-isobutylthiazole)

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*It is interesting to note that these sulfurous flavor compounds generally possess some kind of physiological activity, e.g., microbial or antithyroid activity.[149]

TABLE 3

Sulfur-containing Flavor Compounds Identified in Vegetables

Compound	Vegetable
Hydrogen sulfide	leek, pea, bean, cabbage, cauliflower, rutabaga, parsnip, potato, celery,[68] onion,[10,68] tomato,[21,68] corn[32b]
Thiols	
Methane–	onion, leek, garlic, pea, bean, cauliflower, cabbage, carrot, potato, sprouts, parsnip,[68] corn[326]
Ethane–	onion, leek, pea, cauliflower, carrot, potato, parsnip,[68] corn[326]
Propane–	onion, leek, pea, cauliflower, potato, bean[68]
Isopropane–	potato[68]
t-Butane–	potato[68]
Allyl–	onion[10]
2-Hydroxypropane–	onion[68]
3,3′-Dimercaptoisobutyric acid	asparagus[169]
3-Thioacetoxy-3′-mercaptoisobutyric acid	asparagus[169]
Sulfides	
Carbonyl	cabbage[68]
Dimethyl	onion, leek, garlic, pea, bean, cabbage, cauliflower, rutabaga, carrot, sprouts, potato, celery, parsnip,[68] tomato,[21,68] corn[326]
Methyl ethyl	potato[68]
Diethyl	cabbage, potato[68]
Methyl propyl	potato[68]
Dipropyl	bean[68]
Dipropenyl	onion[10]
Methyl allyl	garlic,[68] onion[10]
Methyl propenyl	onion[10]
Propyl propenyl	onion[10]
Diallyl	onion, leek, garlic[68]
Allyl propyl	onion[10]
Dibutyl	cabbage[68]
Disulfides	
Carbon	pea, cabbage[68]
Dimethyl	onion, garlic, pea, cabbage, rutabaga, potato, sprouts, cauliflower,[68] tomato[21,68]
Methyl ethyl	cabbage, potato[68]
Diethyl	cabbage[68]
Methyl propyl	onion, leek, garlic, cabbage, sprouts, cauliflower,[68]
Methyl isopropyl	potato[107a]
Methyl allyl	onion, leek,[68] garlic[18,68]
Methyl propenyl	onion[68]
Ethyl propyl	cabbage[68]
Dipropyl	onion, leek, garlic, cabbage[68]
Diallyl	onion, leek,[68] garlic,[18,68] cabbage[3a]
Isopropyl propyl	onion[10]
Propyl allyl	onion, leek, garlic,[68] cabbage[3a]
Propyl propenyl	onion[10]
Allyl propenyl	onion[10]
Dipropenyl	onion[10]
Propyl butyl	cabbage[68]

derived from leucine, occurs in relatively large amounts in fresh tomatoes. These hypotheses should preferably be corroborated by investigations with ^{14}C-labeled precursors.

TABLE 3 (Continued)

Sulfur-containing Flavor Compounds Identified in Vegetables

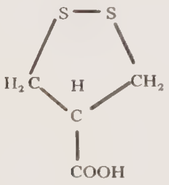
Compound	Vegetables
Trisulfides	
Dimethyl	onion, garlic, pea, cabbage[68]
Diethyl	cabbage[68]
Methyl propyl	onion, garlic[68]
Methyl allyl	garlic,[18,68] onion[10]
Methyl propenyl	onion[68]
Dipropyl	onion[68]
Di-isopropyl	onion[10]
Propyl isopropyl	onion[10]
Propyl allyl	onion[10]
Propyl propenyl	onion[68]
Diallyl	onion,[10,68] garlic[18,68]
Tetrasulfides	
Dimethyl	onion[10]
Diallyl	onion[68]
Thiosulfinates	
Dimethyl	onion, leek[68]
Methyl propyl	leek[68]
Methyl allyl	leek[68]
Dipropyl	onion, leek[68]
Diallyl	garlic[18]
Thiosulfonates	
Dimethyl	onion[10]
Methyl propyl	onion[10]
Dipropyl	onion[10]
Isothiocyanates	
Methyl	cabbage, sprouts, cauliflower[68]
Allyl	cabbage, sprouts, cauliflower,[68] horseradish,[46] mustard[135]
n-Butyl	cabbage, sprouts, cauliflower[68]
sec-Butyl	horseradish[46]
3-Butenyl	cabbage[68]
4-Pentenyl	horseradish[46]
2-Phenethyl	rutabaga, watercress,[68] horseradish[46]
p-Hydroxybenzyl	mustard[135]
Methylthiomethyl	cabbage[68]
3-Methylthiopropyl	cabbage[68]
4-Methylthiobutyl	cabbage[68]
4-Methylthio-3-butenyl	radish[68]
4-Butylthio-3-butenyl	radish[68]
3-Methylsulfinylpropyl	cabbage[68]
4-Methylsulfinylbutyl	radish[68]
Thiocyanates	
Hydrogen	bean[68]
Allyl	onion,[68] horseradish[46]
Heterocycles	
3,4-Dimethylthiophene	onion[10]
2,4-Dimethylthiophene	onion[10]
2,5-Dimethylthiophene	onion[10]
1,2-Diethiolane-4-carboxylic acid	asparagus[169]

TABLE 3 (Continued)

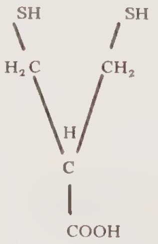
Sulfur-containing Flavor Compounds Identified in Vegetables

Compound	Vegetables
2-Isobutylthiazole	tomato[21]
Benzothiazole	potato[20]
2,4,5-Trimethylthiazole	potato[22a]
2-Isopropyl-4,5-dimethylthiazole	potato[22a]
2-Isopropyl-4-methyl-5-ethylthiazole	potato[22a]
2-Isobutyl-4,5-dimethylthiazole	potato[22a]
2-Acetylthiazole	potato[22a]
Dipropylthiazole (tent.)	potato[22a]
Ethyldimethylthiazole (tent.)	potato[22a]
3,5-Dimethyl-1,2,4-trithiolane	potato[20]
Miscellaneous	
Propanethial S-oxide	onion[16]
2-Methylthioacetaldehyde	tomato[21,68]
Methional	potato,[50] tomato[21,68]
2-Methylthioethanol	tomato[21]
3-Methylthio-1-propanol	tomato[21]

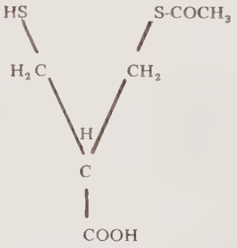
Jansen[67] isolated 3,3′-dimercaptoisobutyric acid from the juice of asparagus by reduction with sodium in liquid ammonia. He suggested that this compound, which has a weak smell, stems from a disulfide. Yanagawa et al.[169] recently isolated from asparagus 1,2-dithiolane-4-carboxylic acid, as well as the reduced forms 3,3′-dimercaptoisobutyric acid and 3-thioacetoxy-3′-mercaptoisobutyric acid. They called the cyclic compound "asparagusic acid." No mention is made of the flavor characteristics of these compounds, only that all three act as growth inhibitors. Jansen fed 10 mg of 3,3′-dimercaptoisobutyric acid to two individuals to investigate whether this compound is responsible for the characteristic methanethiol smell of the urine of some people who have eaten asparagus. The result was negative, but this is hardly conclusive considering the small scale of the experiment.



(asparagusic acid)



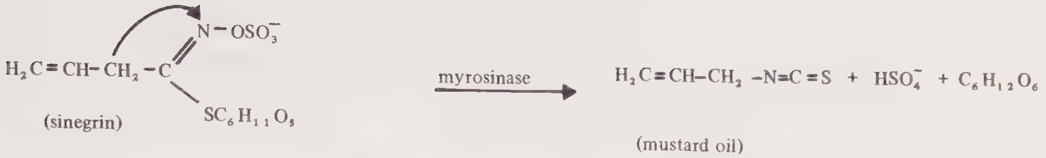
(dihydroasparagusic acid)



(S-acetyldihydroasparagusic acid)

Cruciferous Vegetables

A common characteristic of the *Cruciferae,* which include the *Brassicas* and related vegetables, is the pungent note originating from the isothiocyanates. The most notable example is mustard, but the characteristic flavor is readily noted in other vegetables, e.g., radish, watercress, and horseradish. In *Brassicas* like cabbage, cauliflower, sprouts, and rutabaga, we can also detect this pungent principle, though it is disguised in the cooked vegetable by other flavor notes formed during heating. The isothiocyanates give a pungent, strong taste sensation and have very low threshold values. Many of them are also odoriferous with an appetizing aroma at low concentrations.[149] Their precursors are glucosinolates, the mechanism of formation being well established. For example, sinegrin, a glucosinolate, is decomposed by the enzyme myrosinase to form allyl isothiocyanate, also known as mustard oil, glucose, and sulfate. The mechanism is a Lossen rearrangement:


(sinegrin)

(mustard oil)

$$H_2C{=}CH{-}CH_2{-}C(=N{-}OSO_3^-)(SC_6H_{11}O_5) \xrightarrow{\text{myrosinase}} H_2C{=}CH{-}CH_2{-}N{=}C{=}S + HSO_4^- + C_6H_{12}O_6$$

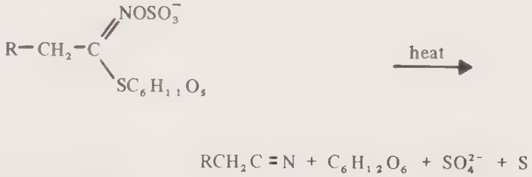
Sinegrin, or allyl glucosinolate, in black mustard and sinalbin, or *p*-hydroxybenzyl glucosinolate, in white mustard are among the most important precursors of isothiocyanates,[135] but benzyl, phenethyl, butyl, butenyl and 4-methylthiobutenyl glucosinolates also contribute to flavor development. The latter compound affords the pungent principle of radish, 4-methylthiobutenyl isothiocyanate.[39] The isothiocyanates may be partially converted to thiocyanates by enzymes (isomerase). The same can happen during heating, as an equilibrium then exists between the two isomers:[46]

$$R{-}CH_2{-}N{=}C{=}S \quad \underset{\text{heat}}{\overset{\text{isomerase}}{\longrightarrow}} \quad R{-}CH_2{-}S{-}C{\equiv}N$$

$$\underset{\rightleftarrows}{\text{heat}}$$

The thiocyanates occur less frequently and are less important for the flavor of vegetables.

During heating, the glucosinolate precursors can be decomposed in a different way to that outlined above. In this case, no rearrangement takes place; glucose, sulfur, and sulfate are split off and an alkyl cyanide is formed:



$$R{-}CH_2{-}C(=NOSO_3^-)(SC_6H_{11}O_5) \xrightarrow{\text{heat}} RCH_2C{\equiv}N + C_6H_{12}O_6 + SO_4^{2-} + S$$

Consequences of this change in the reaction course have been illustrated by McLeod and McLeod[91-93] in a series of articles.

The ratio between the flavor volatiles in some vegetables, e.g., cabbage, sprouts, cauliflower, and runner beans, is greatly dependent on the method of preservation and on the cooking time. This is illustrated in Table 4. It appears that the amount of isothiocyanate in cabbage decreases markedly as the cooking is increased from 20 to 90 min, or when the vegetable is stored in the dehydrated form. This decrease is caused by inactivation of the enzyme. The allyl cyanide and the dimethyl sulfide concentrations rise, indicating that these flavor compounds are formed in nonenzymic processes. In sprouts, the enzymes that release allyl isothiocyanate are clearly activated by chopping, but inactivated by freezing or rather by the blanching step that precedes freezing. With the frozen sprouts, the lower isothiocyanate formation is accompanied by a correspondingly higher level of allyl cyanide. The outer leaves of cauliflower release similar amounts of the sulfur volatiles as does cabbage. In the whole vegetable, though, more allyl cyanide is formed; perhaps, less enzyme is available in the center of cauliflower.

Not unexpectedly, runner beans behave differently from the *Brassica* vegetables. A precursor other than glucosinolate is probably responsible for the formation of allyl cyanide in this case. The formation of dimethyl sulfide is most probably a nonenzymic process, as the formation increases with cooking times, and its presence is unaffected by methods of processing. As dimethyl sulfide occurs in almost all cooked vegetables (see Table 3), its formation will be dealt with later, when heat-induced flavors are discussed.

Allinaceous Vegetables

The *Allium* family, comprising vegetables like onion, garlic, and leek, possess flavors that are characterized by disulfides, trisulfides, and related compounds. Of these, the allyl compounds are most associated with garlic and the propyl and propenyl compounds with onion. It has been established that S-alkylcysteine sulfoxides, which are activated by the enzyme alliinase, are the precursors of *Allium* flavor

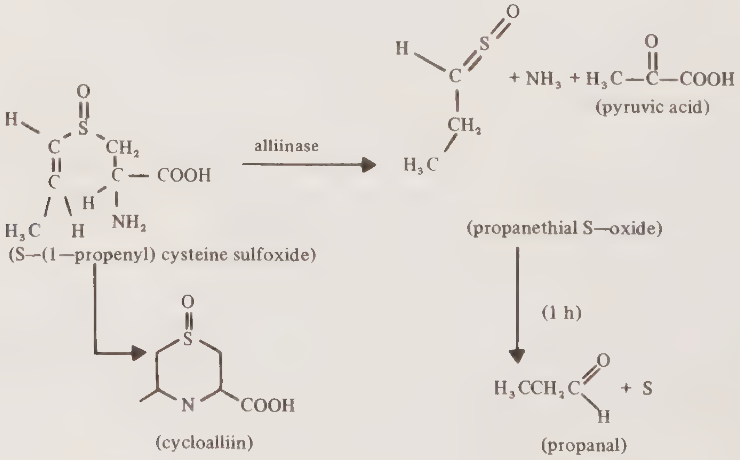
TABLE 4

Relative Abundance of Allyl Isothiocyanate, Allyl Cyanide, and Dimethyl Sulfide in the Volatiles of Vegetables Preserved in Different Ways and Cooked.[91,93] Cooking Time is 10 min Unless Stated Otherwise.

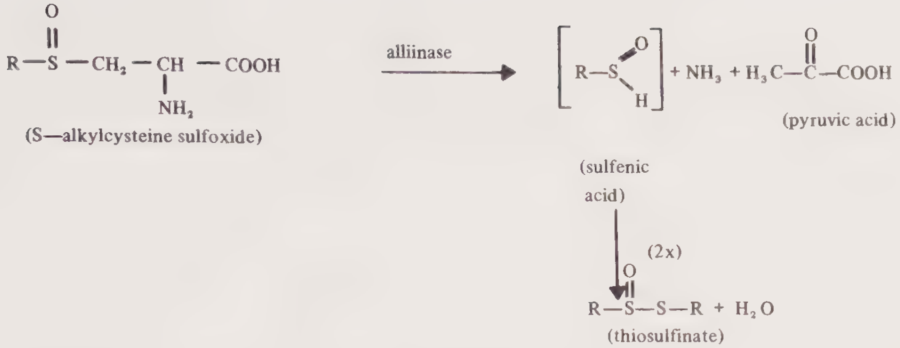
	Relative abundance (%)		
	Allyl isothiocyanate	Allyl cyanide	Dimethyl sulfide
Cabbage			
Fresh	6.5	3.0	26.5
Fresh, cooked for 20 min	15.5	4.5	28.0
Fresh, cooked for 90 min	3.0	8.5	38.5
Dehydrated	2.0	30.0	12.0
Brussels sprouts			
Fresh, whole	2.0	7.0	11.5
Fresh, chopped	4.0	15.0	9.0
Frozen, chopped	0.1	22.5	14.5
Cauliflower			
Fresh, whole	4.5	24.5	26.5
Fresh, outer leaves	10.0	9.5	16.5
Runner beans			
Fresh	–	6.5	4.5
Frozen	–	0.1	5.0

compounds.[148] As with the *Cruciferae*, the precursors and the enzyme are brought into contact with each other when the cell tissue of the plant is ruptured, e.g., by cutting or chopping.

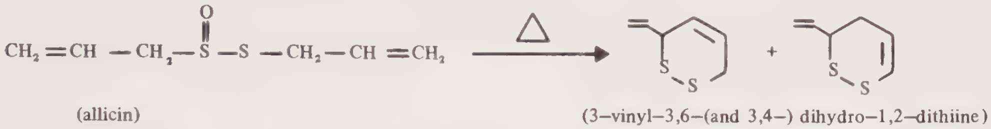
This enzymic reaction is also responsible for the formation of propanethial S-oxide, which has recently been identified as the compound responsible for the familiar lachrymatory activity of freshly chopped onions.[16] The precursor of this compound is S-(1-propenyl)cysteine sulfoxide, an onion constituent that is also responsible for the formation of the stable, cyclic amino acid, cycloalliin. Propanethial S-oxide is unstable at room temperature, decomposing within an hour to propanal and sulfur:



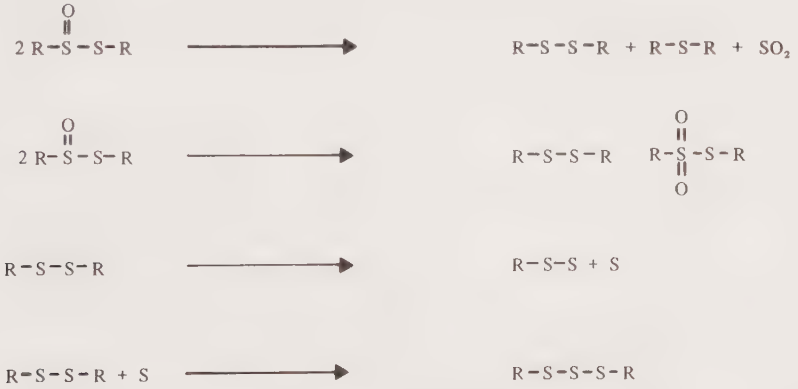
The formation of disulfides from S-alkylcysteine sulfoxides may be explained by the intermediate formation of sulfenic acids, which in turn condense to thiosulfinates. Indeed, thiosulfinates have been isolated from fresh *Allium* vegetables (see Table 1):



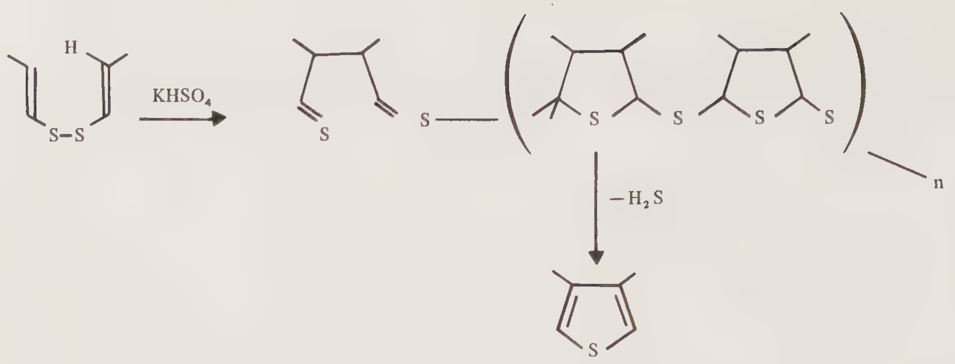
Thiosulfinates are often difficult to identify as they may rearrange upon gas chromatography. The presence of diallyl thiosulfinate (allicin) in fresh garlic extract, for instance, could only be established indirectly by identification of its 3-vinyldihydro-1,2-dithiine rearrangement products.[18]



Diallylthiosulfinate was found to decompose within 20 hr at room temperature to diallyl disulfide (66%), diallyl sulfide (14%), diallyl trisulfide (9%), and sulfur dioxide. This finding is in contrast to previous assumptions that thiosulfinates are disproportionate to disulfides and thiosulfonates. Brodnitz et al.[18] were unable to detect any thiosulfonate at all, though these compounds would be expected to be sufficiently stable. On the other hand, Boelens et al.[10] identified, in addition to disulfides, three thiosulfonates in fresh onion extract, though in lower amounts (0.5 mg/kg) than would be expected if disproportioning were the major decomposition reaction. These authors held the thiosulfonates most responsible for the odor of freshly cut onions, while the unsaturated disulfides, particularly propenyl disulfides, which are formed after 2 hr, make a dominant contribution to the odor of boiled onions. Generalization of these observations gives the following tentative scheme for the decomposition of thiosulfinates:



It is probable that free-radical reactions are involved in this scheme. In the volatile reaction products of fried onions 3,4-dimethylthiophene and 2,3-dimethylthiophene have been isolated in a ratio of 9 to 1.[10] The authors conclude that the typical flavor of fried onions must be largely attributed to these compounds. In a subsequent paper, Boelens and Brandsma[11] propose a mechanism for the formation of 3,4-dimethylthiophene from dipropenyl disulfide: in an experiment in which a model system was heated at 150 to 200°C with $KHSO_4$ as a catalyst, the thiophene was formed in 60% yield. The intermediate polymer is postulated; it has not been isolated.

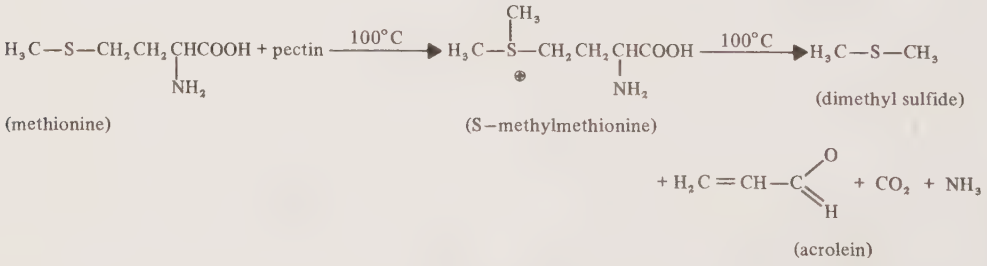


Some interesting disulfides related to those characteristic in onion and garlic have been isolated from asafoetida.[107] This is an oriental spice known as hing, an oleoresin obtained from Ferula plants belonging to the *Umbelliferae* family. The volatile disulfides are 2-butyl-1-propenyl disulfide, 1-(1-methyl-thiopropyl)-1-propenyl disulfide and 2-butyl-(3-methylthioallyl) disulfide in both their *cis* and *trans* configurations. The first and the last compounds have odors that are described as garlic-like, whereas the second compound has an odor characteristic of asafoetida.

Heat-induced Vegetable Flavors

The discussion of heat-induced vegetable flavors has already been touched upon in the discussion of fried onion flavor. Other heat-induced vegetable flavors will be dealt with below.

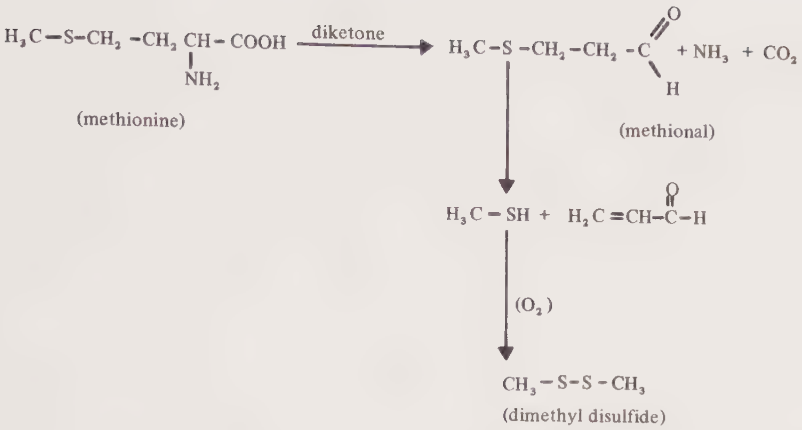
As summarized in Table 2, dimethyl sulfide is present in almost all types of vegetables. It has already been noted that dimethyl sulfide is formed in cabbage during heating (see Table 4). Freytag and Ney[38] compared the rate of formation of dimethyl sulfide during the cooking of asparagus and upon boiling a model solution of S-methylmethionine (or more correctly, S-methylmethionine sulfonium salt). From the striking similarity, they concluded that S-methylmethionine most probably acts as the precursor of dimethyl sulfide. S-methylmethionine is known to be present in uncooked asparagus, tomato,[167] and milk.[78] Casey et al.[23] showed that dimethyl sulfide is formed during the heating of methionine with pectin. The latter react to give S-methylmethionine, which in turn decomposes to afford dimethyl sulfide together with dimethyl disulfide, methanethiol, acrolein, and methanol. This may explain why dimethyl sulfide is formed when pectin-containing foodstuffs such as strawberries,[137] black currants,[73] potatoes,[51] sweet corn,[9] and roasted barley[158] are heated.



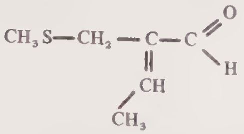
$$\underset{\text{(methionine)}}{H_3C{-}S{-}CH_2CH_2\underset{\substack{|\\NH_2}}{C}HCOOH} + \text{pectin} \xrightarrow{100°C} \underset{\text{(S-methylmethionine)}}{H_3C{-}\overset{\substack{CH_3\\|}}{\underset{\oplus}{S}}{-}CH_2CH_2\underset{\substack{|\\NH_2}}{C}HCOOH} \xrightarrow{100°C} \underset{\text{(dimethyl sulfide)}}{H_3C{-}S{-}CH_3}$$

$$+ \underset{\text{(acrolein)}}{H_2C{=}CH{-}CHO} + CO_2 + NH_3$$

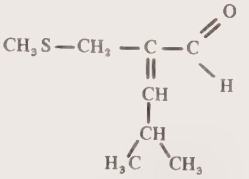
Various volatile sulfur compounds have been identified in boiled and fried potatoes. Methanethiol and dimethyl disulfide are liberated in large amounts upon the cooking of potatoes. Hydrogen sulfide is also evolved in quantities of about 400 µg/kg.[51] The most characteristic flavor compound in potatoes is methional,[50] which on its own has a flavor reminiscent of boiled potatoes. Methional has been identified in other foodstuffs such as tomato,[21] chocolate[124] and beef.[163] Strecker degradation of methionine is the generally accepted mechanism of formation:[4]



Buttery[22] recently reported some unusual volatile carbonyl compounds in potato chips. These compounds were aldol-type condensation products of aldehydes, such as 2-methylthiomethyl-2-butenal and 2-methylthiomethyl-4-methyl-2-pentenal, which stem from the reaction of methional with acetaldehyde and isobutyraldehyde, respectively. These components are reported to have interesting aroma properties.

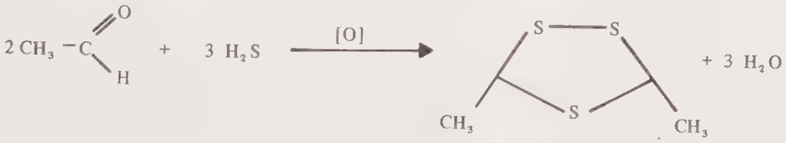


(2—methylthiomethyl—2—butenal)



(2—methylthiomethyl—4—methyl—2—pentenal)

Two other sulfur-containing flavor compounds isolated from boiled potatoes are benzothiazole and 3,4-dimethyl-1,2,4-trithiolane.[20] The first compound has also been isolated from other heated food products, such as popcorn,[155] peanuts,[156] and boiled beef.[163] The second compound is formed from acetaldehyde and hydrogen sulfide. It has also been found in boiled beef.[24]



cis and *trans*
(3,5-dimethyl-1,2,4-trithiolane)

Recently Buttery and Ling[22a] identified 2,4,5-trimethylthiazole and 2-isopropyl-4,5-dimethylthiazole in potato chips. These compounds and five more thiazoles were characterized in boiled potatoes.

Gumbmann and Burr[51] presume that not only sulfur-containing amino acids, but also thiamine, biotin, coenzyme A, and glutathione, contribute to the formation of sulfur-containing volatiles in potatoes and other foodstuffs. They also stress the role of transient sulfide ions, which, due to their high nucleophilicity, readily displace hydroxy and similar functional groups to form thiols and sulfides.

Meat

Chicken, Beef, Pork, and Lamb

The aroma of meat[47,57] is developed during cooking or frying. Various authors investigated what fractions in the raw meat are responsible for the volatiles.[6,7,63,85,89,94,159,160] They usually prepared a cold, aqueous extract of raw meat in which they separated the high- and low-molecular materials by dialysis. Upon heating of these fractions, the low-molecular diffusate afforded meat-like aroma. This fraction contained free amino acids and monosaccharides.

Reactions induced by heating amino acids and sugars are known as "nonenzymic browning" or "Maillard reactions." Meat flavors are generated in reactions of this type. Further separation of the diffusate revealed its amino acid composition. It is not surprising that the data reported by various authors vary, as the substrate is hardly standardized. It is striking that, initially, methionine was the only sulfur-containing amino acid identified; more recent studies, however, revealed the presence of cysteine, cystine, or cysteic acid, an indication of the importance of cysteine as a meat-flavor precursor. Taurine (2-aminoethanesulfonic acid) was also a component of the diffusate.[94] Glucose was the main sugar present, but ribose, fructose, deoxyribose and ribose-5-phosphate, fragments of 5′-nucleotides, were also identified.

No great differences were found between the amino acid patterns of the diffusates of beef, pork, and lamb.[94,161] The meaty aromas released are also similar, provided the fat has been removed before the extraction with cold water. This stresses the important function of the fat in determining the characteristic flavor, i.e., whether the flavor is typically beef, chicken, pork, or lamb, etc. It should be noted that chicken fat itself has a chicken-like odor. This is not unexpected as unsaturated aldehydes contribute to the typical chicken flavor, and these compounds are unmistakenly derived from polyunsaturated fatty acid residues in the chicken fat. Although less is known about pork and lamb flavor, a similar contribution of the fat may be expected.[63] In beef, this function of the fat seems to be less important.

Another role of the fat phase in meat is its capability to dissolve the nonpolar volatile compounds, thus providing a reservoir of flavor compounds.[122] Of course, reactions can take place between those compounds in the fat. In the meantime, the release of those flavor compounds is affected by this nonpolar phase acting similarly to a "fixative" in perfumery.

Various types of compounds, e.g., carbonyls, substitued heterocyclics such as furans and pyrazines, and sulfur compounds, have been identified in meat flavor concentrates (see Table 1). The various sulfur-containing flavor compounds identified in meat are summarized in Table 5. This table also covers other heat processed foods in which the flavors are formed from similar ingredients by nonenzymic browning. These foods will be discussed later.

TABLE 5

Sulfur-containing Flavor Compounds Formed by Maillard Reactions in Heat-processed Foods

Compound	Food
Thiols, sulfides	
Hydrogen sulfide	coffee,[157] chicken,[123] beef,[57,61] eggs,[42] fish,[71] bread[94a]
Methanethiol	coffee,[157] chicken,[166] filberts,[83] beef,[57,61,66a] fish,[71] pork liver,[106a], bread[94a]
Ethanethiol	chicken,[166] beef[57,61]
Propanethiol	chicken,[166] beef[57,61]
Butanethiol	beef[57]
Hexanethiol	chicken[166]
2-Methylpropanethiol	beef[166a]
2-Methylbutanethiol	beef[166a]
3-Methyl-2-butanethiol	beef[166a]
Naphthalenethiol	beef[166a]
1,2-Ethanedithiol	chicken[166]
Carbonyl sulfide	chicken,[166] beef[121]
Carbon disulfide	chicken,[166] coffee,[157] beef[121]
Dimethyl sulfide	bread,[143] chocolate,[127] coffee,[157] chicken,[166] beef,[57,61] fish,[71] pork liver [106a]
Dimethyl disulfide	bread,[143] chocolate,[127] coffee,[157] peanuts,[156] filberts,[83] chicken,[166] beef,[121,166a] pork liver[106a]
Dimethyl trisulfide	bread,[143] chocolate,[127] filberts,[83] chicken,[166] beef[121]
Diethyl sulfide	chicken,[166] beef[166a]
Diethyl disulfide	chicken,[166] coffee,[157] filberts[83]

TABLE 5 (Continued)

Sulfur-containing Flavor Compounds Formed by Maillard Reactions in Heat-processed Foods

Compound	Food
Methyl ethyl sulfide	chocolate,[153] coffee,[157] chicken,[166] beef[121,166a]
Methyl ethyl disulfide	coffee[157]
Methyl propyl sulfide	beef[57,61,166a]
Dipropyl sulfide	chicken[166]
Dipropyl disulfide	peanuts[158]
Dipropyl trisulfide	chocolate[127]
Methyl isopropyl sulfide	chicken[166]
Methyl isopropyl disulfide	chocolate[153]
Methyl isopropyl trisulfide	chocolate[127]
Methyl propyl sulfide	chocolate[153]
Ethyl propyl sulfide	chicken[166]
Methyl benzyl disulfide	chocolate,[127] peanuts[158]
Methyl allyl sulfide	beef[57,61]
Diallyl sulfide	beef[57,61]
Methyl ethylene sulfide	beef[166a]
Benzyl methyl sulfide	pork liver[106a]
1,1-Dimethylthioethane	beef[166a]
1-Methylthioethanethiol	beef[12]
bis(Methylthio)methane	beef[121]
Thioanisole	coffee[157]
o-Hydroxythioanisole	coffee[157]
Aldehydes, ketones	
Methional	chocolate,[124] peanuts,[158] beef,[12,57,61,163] filberts[83]
2-Methylthioisobutyraldehyde	chocolate[127]
1-Methylthio-2-butanone	coffee[157]
Furans	
Furfuryl mercaptan	coffee[157]
Furfuryl methyl sulfide	coffee[157]
Furfuryl methyl disulfide	pork liver[106a]
5-Methyl-2-furfuryl methyl sulfide	chocolate,[127] coffee[157]
Difurfuryl sulfide	coffee[157]
Methyl thiofuroate	coffee[157]
Furfuryl thioacetate	coffee[157]
5-Methyl-2-furyl methyl sulfide	coffee[157]
5-Methylthiofurfural	beef[57,61]
Thiophenes	
Thiophene	coffee,[157] beef[121,166a]
2-Methylthiophene	coffee,[157] chicken,[166] beef,[121,166a] pork liver[106a]
3-Methylthiophene	beef[121]
2-Methyl-4-ethylthiophene	coffee[157]
3-Ethylthiophene	beef[166a]
2-Butylthiophene	beef[166a]
2-Pentylthiophene	popcorn,[155] beef[121,166a]
Octylthiophene	beef[166a]
Tetradecylthiophene	beef[166a]
3-Vinylthiophene	coffee[157]

TABLE 5 (Continued)

Sulfur-containing Flavor Compounds Formed by Maillard Reactions in Heat-processed Foods

Compound	Food
2-Hydroxythiophene	coffee[157]
2,5- and 2,3-Dimethylthiophene	beef[121]
2-Ethyl-5-butylthiophene	popcorn[155]
2-Formylthiophene	bread,[143] coffee,[157] filberts,[83] beef,[57,61,121,166a] pork liver[106a]
3-Formylthiophene	pork liver[106a]
2-Acetylthiophene	coffee,[157] peanuts,[158] pork liver,[106a] beef[166a]
3-Acetylthiophene	bread,[104] coffee,[135] pork liver,[106a] beef[166a]
3-Methyl-2-formylthiophene	pork liver,[106a]
5-Methyl-2-formylthiophene	coffee,[157] peanuts,[158] popcorn,[155] pork liver,[106a] beef[166a]
2,5-Dimethyl-3-formylthiophene	pork liver,[106a] beef[166a]
5-Methyl-2-acetylthiophene	pork liver,[106a] beef[166a]
Dithiophene	coffee[157]
Thenyl formate	coffee[157]
Thenyl acetate	coffee[157]
Thenylalcohol	beef[166a]
Thiopheneacrolein	pork liver,[106a] beef[166a]
Dihydro-3(2H)thiophenone	coffee,[157] peanuts,[158] filberts[83]
2-Methyldihydro-3(2H)thiophenone	coffee,[157] peanuts[158]
1-(2-Thienyl)-1-propanone	beef[166a]
1-(5-Methyl-2-thienyl)-1-propanone	beef[166a]
1-(2′- or 3′Thienyl)propane-1,2-dione	coffee[157]
Methyl thienoate	coffee[157]
Thiolan-2-one	coffee[135]
Tetrahydrothiophene-3-one	beef[166a]
Benzothiophene	coffee[157]
Thiazole	peanuts,[158] popcorn,[155] coffee,[149a] pork liver,[106a] beef[166a]
4-Methylthiazole	peanuts,[158] pork liver[106a]
2-Methylthiazole	coffee,[149a] beef[166a]
5-Methylthiazole	coffee[149a]
2,4-Dimethylthiazole	coffee,[149a] beef[166a]
4,5-Dimethylthiazole	coffee[149a]
2-Ethylthiazole	coffee[149a]
4-Ethylthiazole	coffee[149a]
5-Ethylthiazole	coffee[149a]
5-Ethyl-4-methylthiazole	coffee,[149a] beef[166a]
2-Ethyl-4-methylthiazole	coffee[149a]
4-Ethyl-5-methylthiazole	coffee[149a]
4-Ethyl-2-methylthiazole	beef[166a]
2,4,5-Trimethylthiazole	coffee,[149a] beef[166a]
2,4-Diethylthiazole	coffee[149a]
2,5-Diethylthiazole	coffee[149a]
2,4-Dimethyl-5-ethylthiazole	coffee[149a]
2,5-Dimethyl-4-ethylthiazole	coffee[149a]
4,5-Dimethyl-2-ethylthiazole	coffee[149a]
4-*n*-Butylthiazole	coffee[149a]
2-Acetyl-4-methylthiazole	coffee[149a]
2-Acetylthiazole	beef[166a]
5-Methyl-4-vinylthiazole	filberts[83]
2,4-Dimethyl-5-vinylthiazole	beef[166a]

TABLE 5 (Continued)

Sulfur-containing Flavor Compounds Formed by Maillard Reactions in Heat-processed Foods

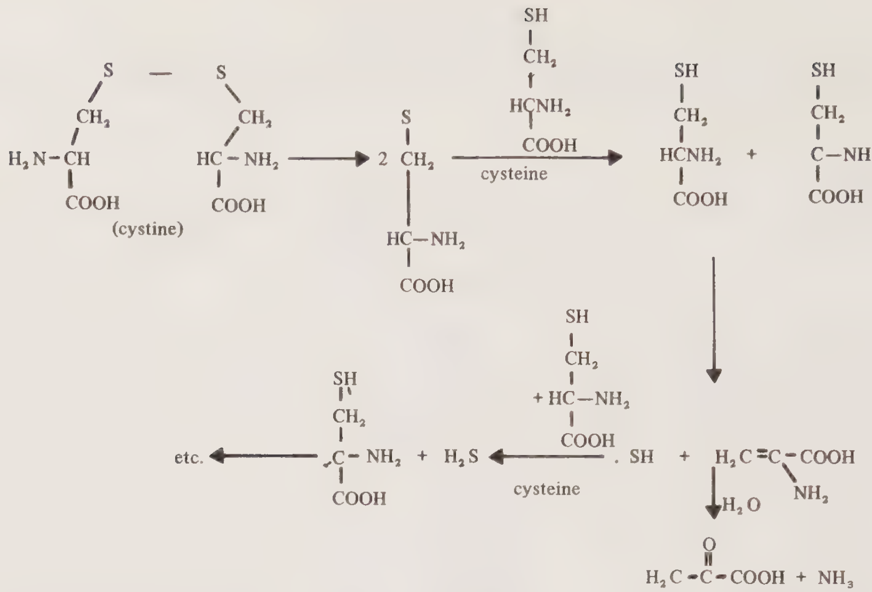
Compound	Food
Benzothiazole	chocolate,[153] peanuts,[158] filberts,[83] beef,[163,166a] popcorn,[155] coffee[149a]
2-Acetyl-2-thiazoline	beef[146]
Miscellaneous	
Ethylene sulfide	beef[121]
Propylene sulfide	beef[121]
3,5-Dimethyl-1,2,4-trithiolane	filberts,[83] beef,[12,57,61,121,166a]
1,3,5-Trithiane	chicken[166]
2,4,6-Trimethyl-*s*-trithiane	beef[166a]
2,2,4,4,6,6-Hexamethyl-*s*-trithiane	beef[166a]
Thialdine	beef[12,166a]
Isobutyl thiocyanate	chocolate[127]
Dimethyl sulfone	pork liver[106a]
Dimethylsulfoxide	pork liver[196a]
Methyl thioacetate	pork liver,[106a] beef[166a]
Methyl thiopropionate	pork liver[106a]

None of the compounds identified in meat flavor concentrates has, on its own, a distinct meaty aroma. It is, therefore, probable that a critically balanced mixture of several volatiles is responsible for meat flavor as we know it. The volatility and instability or reactivity of some of those compounds make it very difficult to compound a meat flavor mixture that maintains its character for some time without making use of precursors. In this respect, meat flavor is not unique; the same is true for coffee flavor.

An example of a highly volatile, reactive, and odoriferous meat flavor compound is hydrogen sulfide. It is known to be present in cooked meat far beyond its threshold value;[123] hence, it contributes to the characteristic flavor of meat. On the other hand, it easily gives rise to egg-like off-flavors when it is present in too high a concentration. This illustrates the narrow borderline between flavor and off-flavor.

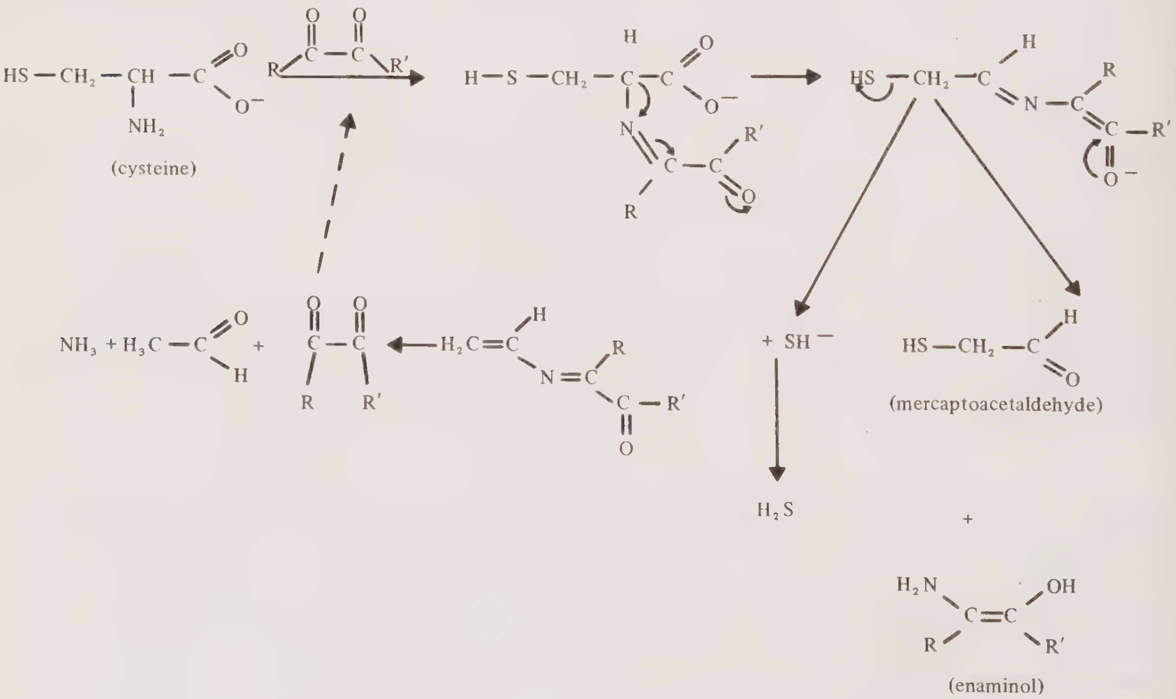
Hydrogen sulfide is formed in amounts of 0.2 to 1.0 mg/kg amounts in cooked chicken meat,[117] or about 20 to 100 times its threshold value. Model experiments with sulfur-containing peptides (glutathione = α-glutamylcysteinylglycine) and amino acids (cystine, cysteine, methionine) that are known to be present in chicken showed that only glutathione and cysteine yield hydrogen sulfide much faster and during a shorter period of time than chicken muscle.[99] It is assumed, therefore, that cysteine residues in the chicken protein act as the hydrogen sulfide precursor rather than the free amino acid or lower peptides.

The rate of hydrogen sulfide formation in meat[69] and in eggs[42] increases with increasing temperature and increasing pH (up to pH 11.2, after which occurrence of hydrogen sulfide in the ionized forms HS^- and S^{2-} prevents its release). This knowledge is of importance for meat processing. For instance, canned meat develops off-flavors due to the presence of up to 1 mg/kg hydrogen sulfide when it has been sterilized under extreme conditions; moreover, black spots may form on the can as a result of the reaction of hydrogen sulfide with the metal of the can.[48,69] It was found that in eggs, hydrogen sulfide production was not caused by enzymes, and that it was increased by the presence of oxygen or, when oxygen was absent, by the addition of small amounts of cystine. In the presence of 12% cystine, based on the concentration of cysteine, in a heated aqueous solution at pH 9.0, the rate of hydrogen sulfide formation was doubled.[42] It is postulated that an ionic mechanism is involved in the hydrogen sulfide elimination. This seems unlikely; a free-radical chain reaction as shown below seems more probable.



This might also explain the function of oxygen as an initiator in a reaction that, overall, is not an oxidation. The increased production of hydrogen sulfide at higher pH values may also be explained by this mechanism, since cysteine produces cystine under these conditions.

Hydrogen sulfide is also formed during the Strecker degradation of cysteine with a diketone.[84] Diketones present in food include glucosamine, dehydroascorbic acid, and pyruvaldehyde. In model systems, the highly reactive ninhydrin is often employed. The reaction may be represented as follows:

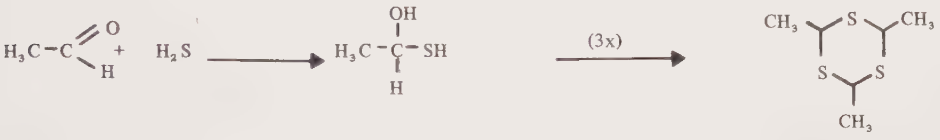


Hydrogen sulfide can also be formed in meat from thiamine; this will be discussed later.

Methanethiol and dimethyl disulfide are also present in relatively high concentrations in cooked beef. Like hydrogen sulfide, these compounds are also formed in excess under extreme sterilization conditions (up to 200 and 100 μg/kg, respectively) and thus give rise to off-flavors.[173] The major route by which methanethiol and dimethyl disulfide are formed is the Strecker degradation of methionine, which has already been discussed with respect to boiled potato flavor.[50] Methional would also be expected, and this compound has indeed been identified in cooked beef.[12,163] Dimethyl sulfide and dimethyl trisulfide are derived directly from dimethyl disulfide, as shown in the treatment of vegetable flavors.

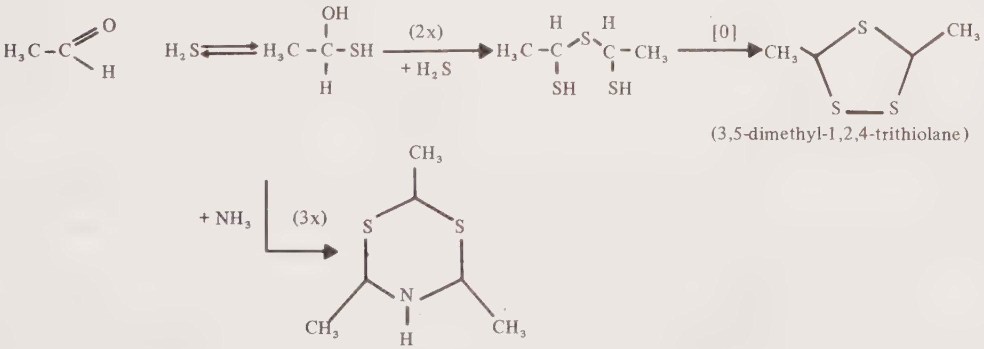
Homologs of methanethiol and of the (di)sulfides have also been detected in meat, though in smaller amounts. Recently, the dithiomethylacetal of formaldehyde, bis-(methylthio)methane, was found in canned beef.[121]

Pippen and Mecchi[123] have speculated about the indirect contribution of hydrogen sulfide to cooked chicken aroma.[30] They found that hydrogen sulfide was bound in the fat phase if aldehydes, e.g., acetaldehyde, were present. As the hydrogen sulfide was only partly recovered from the fat, the remainder must have reacted with the aldehydes. A homolog of one of the products they propose, i.e., trimethyl-*s*-trithiane, has indeed been identified in cooked chicken.[166]



(trimethyl-s-trithiane)

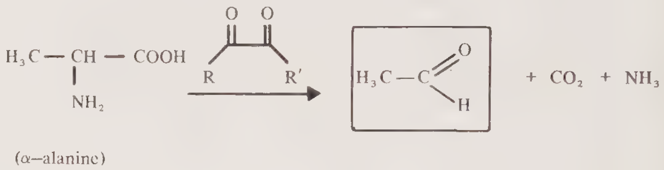
Indeed, as will be shown later, reactions of hydrogen sulfide with carbonyls and furans are very important in the formation of sulfur-containing meat odor compounds. This can at once be seen in the studies of Brinkman et al.[12] into the components in the headspace of beef broth. The vapor above a beef broth was led with a nitrogen stream through some cooled traps in which the components were condensed. In the −196°C trap, four sulfur compounds were identified as methional, l-methylthioethanethiol, 3,5-dimethyl-1,2,4-trithiolane[24] (*cis* and *trans* isomers), and thialdine (2,4,6-trimethylperhydro-1,3,5-dithiazine). As the relatively high-boiling thialdine would not be expected in this trap, it is probably an artifact formed from the far more volatile compounds acetaldehyde, hydrogen sulfide, and ammonia during thawing of the condensate. As the amounts of dimethyltrithiolane increased during storage of the condensate, it was assumed that the presence of this compound in the trap was at least partly caused by similar reactions.

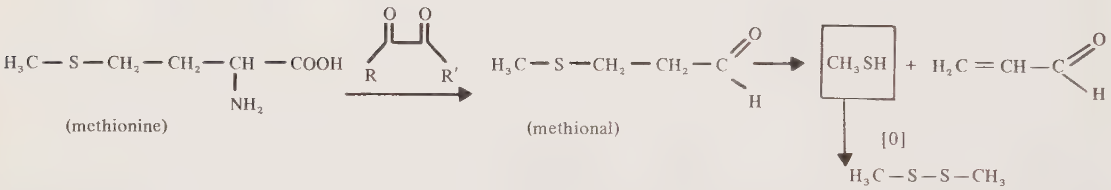


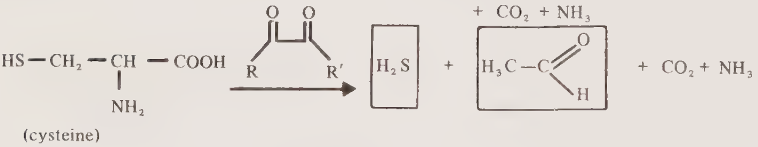
(3,5-dimethyl-1,2,4-trithiolane)

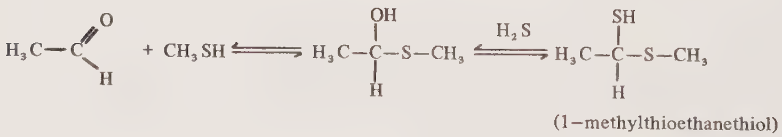
(thialdine)

In a similar reaction set-up to that of Brinkman et al.[12] but with a model system instead of the broth,[25] Schutte and Koenders[130] went at some length to prove that 1-methylthioethanethiol could not be formed in the condensate like the other two compounds. They showed that 1-methylthioethanethiol is formed in high yields upon heating an aqueous phase containing acetaldehyde, methanethiol, and hydrogen sulfide, and a nonpolar organic phase, *viz.*, dichloromethane, which simulated the fat. In addition, dimethyltrithiolane was formed in some cases, depending on the pH. Both 1-methylthioethanethiol and dimethyltrithiolane were also formed from a similar system in which the aqueous phase contained alanine, methionine, cysteine, and a diketone (ninhydrin). Acetaldehyde, methanethiol, and hydrogen sulfide are first released in Strecker degradation reactions from these amino acids and then recombine to the sulfur-containing flavor compounds. The organic phase in the system serves to keep the initial volatile products together until they are able to react. In the same system, dimethyl disulfide was also detected.





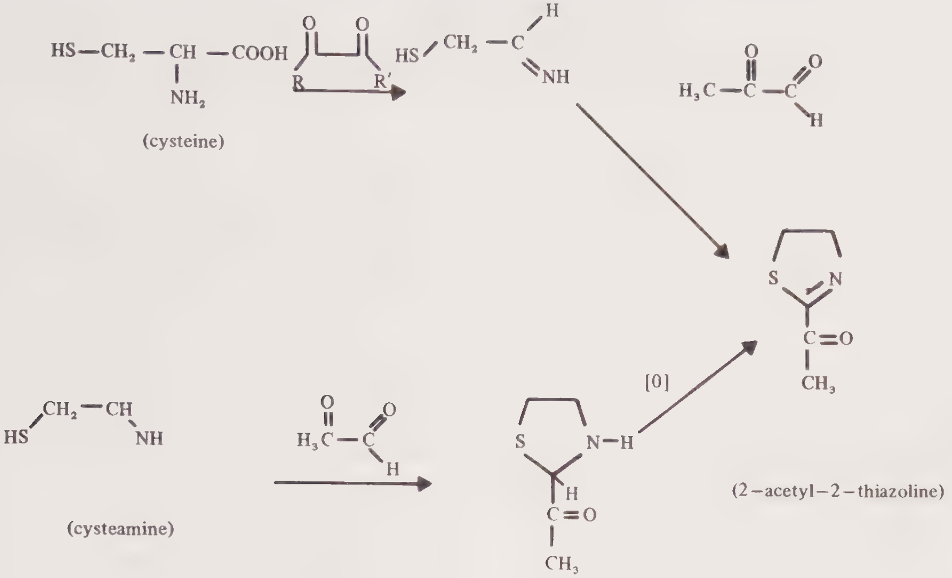




Tonsbeek et al.[146] isolated 2-acetyl-2-thiazoline from beef broth. Although the mechanism of formation was not elucidated, possible pathways are Strecker degradation of cysteine and subsequent addition to pyruvaldehyde, or addition of pyruvaldehyde to cysteamine and subsequent oxidation.[105]

Recently Mussinan and Walradt[106a] identified 179 volatile constituents of pressure cooked pork liver. Pyrazins were the major class of compounds found, representing almost 41% of the total gas chromatograph peak area. Sulfur compounds, 24 in number, amounted to 2% of the total peak area.

Wilson et al.[166a] identified 46 sulfur compounds including many new thiophenes and thiazoles in pressure cooked beef.



Model Meat-flavor Systems

The previous paragraphs demonstrate that, although many flavor compounds have been isolated from cooked meat, more information can often be obtained from studies on model systems. In such systems, flavor precursors are allowed to react in a more concentrated form and under more extreme conditions in order to afford the flavor compounds in amounts sufficient for them to be isolated and identified. In this way, the mechanism of formation in meat of sulfur-containing flavor compounds like methional, methanethiol, dimethyl disulfide, hydrogen sulfide, mercaptoethanal, 1-methylthioethanethiol and 3,5-dimethyl-1,2,4-trithiolane has been made plausible.[130] In similar model systems, a variety of sulfur-containing volatiles have been identified (see Table 6). These compounds have not as yet been isolated from cooked or fried meat, but it is probable that they contribute to the flavor of meat products, as many of them possess an odor reminiscent of cooked or roasted meat. It is understandable that isolation and identification of these odoriferous compounds from meat products is a very difficult task, as most of them are unstable, and hence, if there at all, they will be present in very low concentrations. In the next paragraphs, the analysis of heated model systems comprising precursors known to be present in raw meat will be dealt with.

Fujimaki et al.[40] studied the pyrolysis of the sulfur-containing amino acids cysteine, cystine, and methionine. Although the conditions of the reactions are hardly representative for those during the heating of natural products (the amino acids are heated in pure form at 270 to 300°C), some interesting volatiles are formed. Important products in the pyrolysis of methionine are methanethiol and methional, whereas cysteine and cystine yield hydrogen sulfide, sulfur, cysteamine, and 2-methylthiazolidine. The last compound is presumably formed by the addition of acetaldehyde to cysteamine. In a recent investigation, Severin and Ledl[134] heated cysteine in tributyrine, which served as a model triglyceride, at 200°C. In addition to 2-methylthiazolidine, they identified 2-methyl-thiazoline, 2-propylthiazoline, 2-propylthiazolidine, and *N-N'*-dibutyrylcysteamine as volatile sulfur-containing reaction products. The formation of these compounds can be represented schematically as follows:

TABLE 6

Sulfur-containing Flavor Compounds Isolated from Meat-simulating Model Systems after Heating

Compound	Model system
Thiols, sulfides	
Hydrogen sulfide	cysteine (P),[40] glutathione,[42] cysteine/cystine,[42] glucose/cysteine,[3] cysteine/cystine/ribose,[105] thiamine,[28] cysteine/xylose[88a]
Methanethiol	methionine (P),[40] methionine/glucose,[3] cysteine/cystine/ribose,[105] cysteine/glucose,[3] cystine/glucose,[3] methionine/diketone[130]
Ethanethiol	methionine/glucose,[3] cystine/glucose,[3] cysteine/cystine/ribose[105]
Propanethiol	methionine/glucose,[3] cysteine/glucose,[3] cystine/glucose,[3] cysteine/cystine/ribose[105]
Pentanethiol	cysteine/glucose[3]
Cyclopentanethiol	cysteine/xylose[106]
Dimethyl sulfide	methionine/glucose[3]
Dimethyl disulfide	methionine/glucose[3]
Dimethyl trisulfide	cysteine/xylose/HVP[106]
Methyl ethyl sulfide	cysteine/xylose/HVP[106]
Methyl ethyl disulfide	cysteine/xylose/HVP[106]
Diethyl disulfide	cysteine/xylose/HVP[106]
Methyl isopropyl disulfide	cysteine/xylose/HVP[106]
Ethyl isobutyl disulfide	cysteine/xylose/HVP[106]
Di-isobutyl disulfide	cysteine/xylose/HVP[106]
Methyl benzyl sulfide	cysteine/xylose/HVP[106]
Methyl benzyl disulfide	cysteine/xylose/HVP[106]
2-Aminoethanethiol	cystine (P)[40]
3-Methylthiopropylamine	methionine (P)[40]
1-Methylthioethanethiol	alanine/methionine/cysteine/diketone[130]
2-Mercaptoacetaldehyde	cysteine/diketone[84]
Methional	methionine (P),[40] methionine/diketone,[130] cysteine/xylose/(HVP)[106, 88a]
3-mercapto-4-oxo-1-pentanol	thiamine[28]
Furfuryl mercaptan	cysteine/xylose[106,88a]
Furfuryl methyl sulfide	cysteine/xylose/HVP[106]
2-methyl-5-thiomethylfuran	cysteine/xylose/HVP,[106] thiamine[28]
Thiophenes	
Thiophene	cystine/xylose/(HVP),[106,88a] cysteine/glucose,[74] cysteine/pyruvaldehyde[74]
2-Methylthiophene	cysteine/xylose/(HVP),[106] thiamine,[28] cysteine/glucose[129]
3-Methylthiophene	cysteine/xylose/(HVP),[106] cysteine/pyruvaldehydes[74]
2,3-Dimethylthiophene	cysteine/glucose[129] cysteine/xylose[88a]
2,5-Dimethylthiophene	cysteine/xylose/(HVP),[106] cysteine/glucose,[129] cysteine/pyruvaldehyde[74]
2,3,5-Trimethylthiophene	cysteine/xylose[106]
2-Ethylthiophene	cysteine/xylose,[106,88a] cysteine/glucose,[129] cysteine/pyruvaldehyde[74]
2-Hydroxythiophene	cysteine/glucose[74]
2-Formylthiophene	cysteine/xylose/(HVP),[106,88a] cysteine/glucose,[134] cysteine/cystine/ribose[105]
5-Methyl-2-formylthiophene	cysteine/xylose/(HVP),[106,88a] cysteine/glucose,[134] cysteine/cystine/ribose[105]
2-Methyl-3-formylthiophene	cysteine/glucose,[129] cysteine/cystine/ribose[105]
2-Acetylthiophene	cysteine/xylose/HVP,[106] cysteine/glucose,[134] cysteine/cystine/ribose[105]
2-Methyl-5-acetylthiophene	cysteine/cystine/ribose[105]

TABLE 6 (Continued)

Sulfur-containing Flavor Compounds Isolated from Meat-simulating Model Systems after Heating

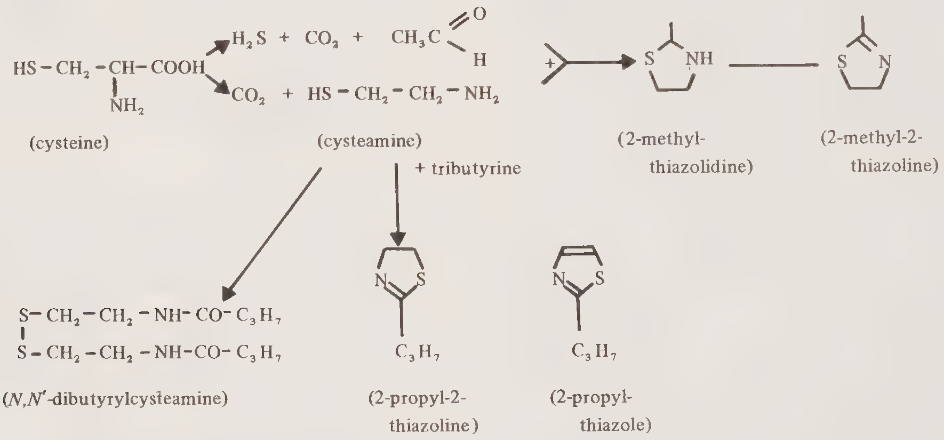
Compound	Model system
2-Propionylthiophene	cysteine/glucose[129]
1-(Thienyl)-1-propanone	cysteine/xylose[106]
1-(Thienyl)-1-propanone	cysteine/xylose[106]
2-Thienol[2,3-b] thiophene	cysteine/xylose,[106] cysteine/glucose,[129] cysteine/cystine/glucose[105]
2-Thiophenoic acid	cysteine/pyruvaldehyde[74]
2,3-Dihydrothiophene	cysteine/xylose[88a]
2,5-Dihydrothiophene	cysteine/xylose[88a]
2-Methyl-4,5-dihydrothiophene	thiamine[28]
Tetrahydrothiophene	cysteine/xylose[88a]
2-Methyltetrahydrophiophene	cysteine/xylose[106]
Dihydro-3(2H)thiophenone	cysteine/xylose/(HVP),[106,88a] cysteine/glucose[129]
2-Methyldihydro-3(2H)thiophenone	cysteine/xylose/(HVP),[106] thiamine[28]
2-Acetyltetrahydrothiophene	thiamine[28]
5-Methyldihydro-2(3H)thiophenone	cysteine/xylose[106]
2-Thiophenethiol	cysteine/glucose[129]
2-Methylthiothiophene	cysteine/glucose[129]
2,3-Benzothiophene	cysteine/glucose[129]
Thiazoles	
Thiazole	cysteine/pyruvaldehyde[74] cysteine/xylose[88a]
2-Methylthiazole	cysteine/pyruvaldehyde,[74] cystine/glucose,[74] cysteine/cystine/ribose,[105] cysteine/xylose[88a]
5- or 4-Methylthiazole	cysteine/pyruvaldehyde,[74] cysteine/xylose[88a]
5- or 4-Ethylthiazole	cysteine/pyruvaldehyde,[74] cysteine/cystine/ribose[105]
2-Ethylthiazole	cystine/pyruvaldehyde[74] cysteine/xylose[88a]
2,5-Dimethylthiazole	cysteine/glucose[74] cysteine/xylose[88a]
2-Propylthiazole	cysteine[134] cysteine/xylose[88a]
4,5-Dimethylthiazole	thiamine[28]
2-Methyl-5- or 4-ethylthiazole	cysteine/pyruvaldehyde,[74] cysteine/cystine/ribose,[105] cysteine/xylose[88a]
2-Methyl-4-propylthiazole	cysteine/xylose[88a]
Trimethylthiazole	cystine/glucose,[74] cysteine/cystine/ribose[105] cysteine/xylose[88a]
2,4-Dimethyl-5-ethylthiazole	cysteine/cystine/ribose,[105] cysteine/xylose[88a]
2,5-Dimethyl-4-ethylthiazole	cysteine/xylose[88a]
2-Propyl-4- or 5-methylthiazole	cysteine/xylose[88a]
2-Propyl-4- or 5-ethylthiazole	cysteine/xylose[88a]
2-Acetylthiazole	cysteine/cystine/ribose[105]
2-Acetyl-4-methylthiazole	cystine/pyruvaldehyde[74]
5-Acetyl-2-methylthiazole	cysteine/cystine/ribose[105]
1-(2-Thiazolyl)-1-propanone	cysteine/cystine/ribose[105]
1-(2-Thiazolyl)-1-butanone	cysteine/cystine/ribose[105]
5-Vinyl-4-methylthiazole	thiamine[28]
Vinyl-2-methylthiazole	cysteine xylose[88a]
2-Allythiazole	cysteine/xylose[88a]
2-(2-Furyl)-thiazole	cysteine/cystine/ribose[105]
2-Methylthiazoline	cystine/glucose,[74] cysteine[134] cysteine/xylose[88a]
2-Ethylthiazoline	cystine/pyruvaldehyde[74] cysteine/xylose[88a]
2-Propylthiazoline	cysteine[134] cysteine/xylose[88a]
2-Methylthiazolidine	cysteine,[40] cystine (P)[40] cysteine/xylose[88a]
Miscellaneous	
Methyl thioacetate	cysteine/xylose/HVP[106]
N,N'-Dibutyrylcysteamine	cysteine/tributyrine[134]
1,3-Dithiolane	cysteine/xylose[88a]

TABLE 6 (Continued)

Sulfur-containing Flavor Compounds Isolated from Meat-simulating Model Systems after Heating

Compound	Model system
2-Methyl-1,3-dithiolane	cysteine/xylose[88a]
3-Methyl-1,2,4-trithiolane	cysteine/xylose[88a]
3,5-Dimethyl-1,2,4-trithiolane	cysteine/xylose(HVP),[106] alanine/methionine/ cysteine/diketone[130]
1,2-Dithiane	cysteine/xylose[88a]
3-Methyl-1,2,4-trithiane	cysteine/cystine/ribose[105]
4,6-Dimethyl-5,6-dihydro-1,3,5-dithiazine	cysteine/xylose[88a]
Thialdine	cysteine/xylose[88a]

HVP = Hydrolyzed Vegetable Protein
(P) = Pyrolysis (270 to 300°C)



Obata and Tanaka[108] found that cooked rice flavor was released in the photolysis of cysteine and cystine in the presence of riboflavine. The latter compound acts as a sensitizer. The compounds formed, hydrogen sulfide, acetaldehyde, ammonia, and carbon dioxide, are together responsible for the flavor. In a later study,[109] these authors found that mercaptans were formed in similar photolysis reactions from S-alkylcysteine.

$$R-S-CH_2-\underset{NH}{CH}-COOH \xrightarrow[\text{riboflavine}]{h\nu} R-SH + NH_3 + CO_2 + CH_3-C\overset{H}{\underset{O}{\lessgtr}} \qquad R{=}H,\ \text{alkyl}$$

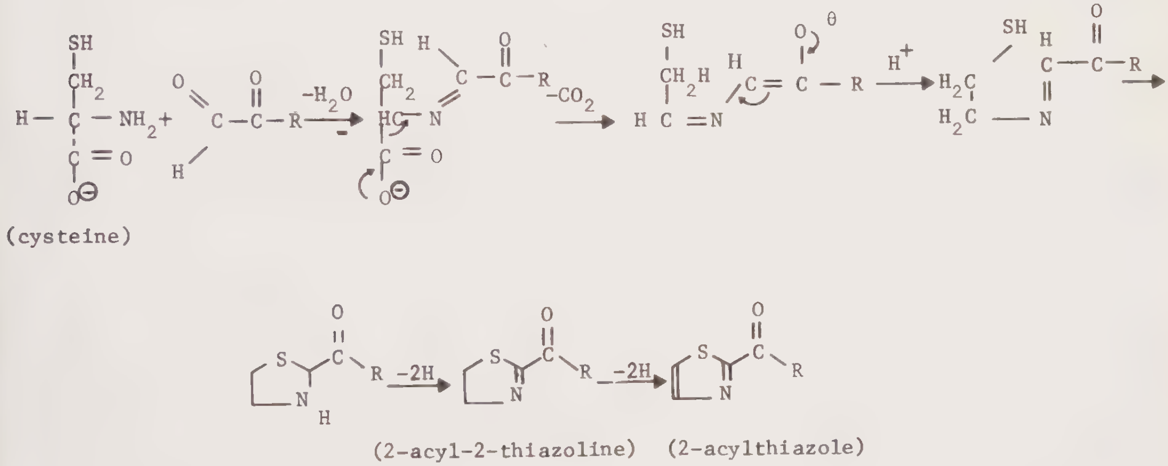
Arroyo and Lillard[3] identified some reaction products of the reaction of the amino acids methionine, cysteine, and cystine with glucose in boiling water. Methionine afforded methane-ethane-, and propanethiol, and dimethyl monosulfide and disulfide. Cysteine and cystine yielded some thiols and hydrogen sulfide. The odor of the methionine-glucose reaction mixture was described as potato-like and that of the cysteine-glucose reaction mixture as egg-like, whereas the odor of the cystine-glucose reaction mixture defied description. No meat-like odors were released.

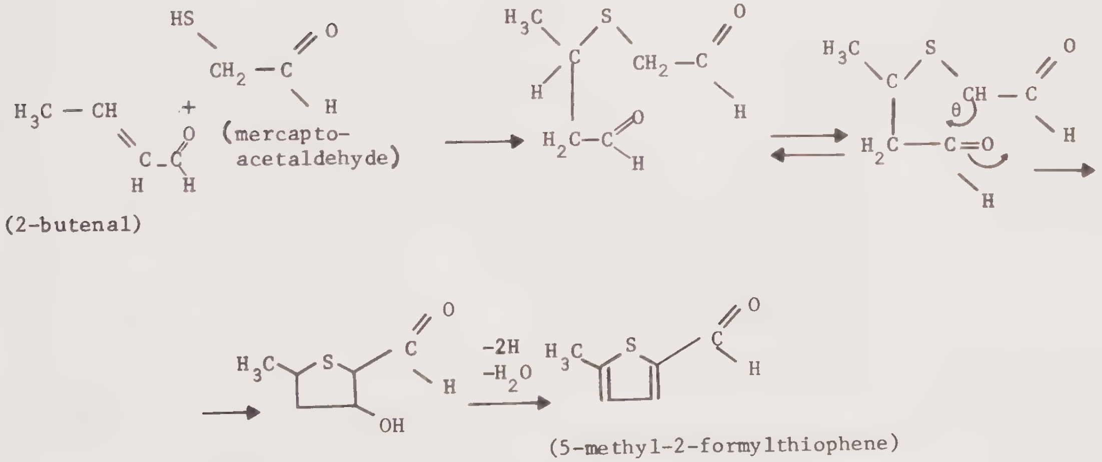
Mussinan and Katz[106] identified 24 sulfur-containing flavor compounds in the reaction products of hydrolyzed vegetable protein (HVP), *L*-cysteine. HCl, *D*-xylose and water, and 15 in a similar system from which the HVP was omitted. Of the latter, 10 compounds were not present in the first reaction product. The most interesting compounds identified in this study were 16 thiophenes, including some thiophenones. Furfurylmercaptan (2-furylmethanethiol), a compound contributing to coffee flavor (see Table 5), was also identified in this investigation. The reaction mixtures had a roasted aroma, reminiscent of meat or coffee.

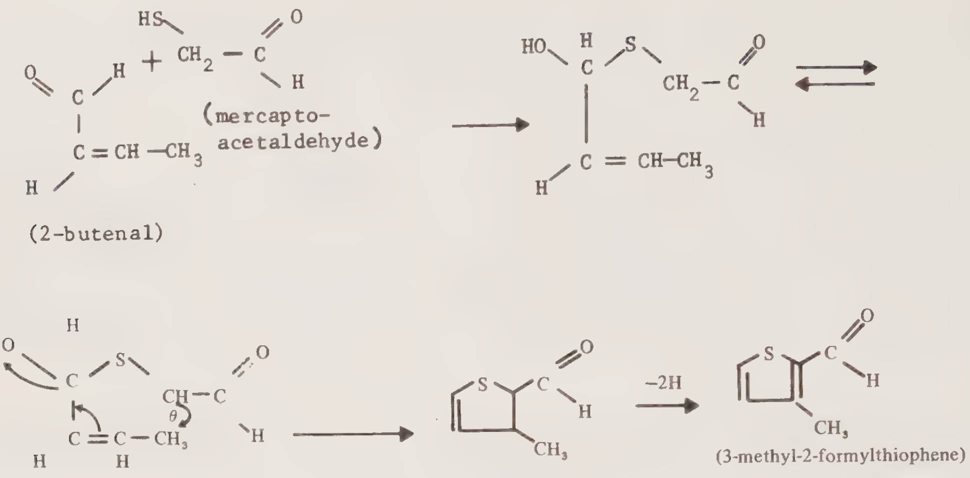
Heating a model system consisting of glutathione, methionine, and diacetyl produced a chicken-like flavor. Taurine gave a serumy character to the mixture and is therefore not regarded as an important chicken flavor precursor.[101]

A large variety of thiazoles and thiophenes were recently identified by Kato et al.[74] in the product of the reaction of cysteine and cystine with glucose or pyruvaldehyde at 160°C. Sesame-like flavors, reminiscent of Japanese rice-crackers, were released. It is somewhat surprising that some 4- or 5-substituted thiazoles were also formed in these reactions. Many thiophenes were isolated from the headspace of the reaction mixture in which D-glucose and L-cysteine HCl were refluxed in distilled water for 15 min.[129] The odor released in this system was reminiscent of stewed chicken at the earlier stages of heating. The pH of the mixture was 1.7 to 1.6. When the same system was buffered at higher pH values, caramel aromas were observed.

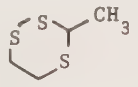
Mulders[105] recently studied the volatile compounds from the nonenzymic browning reaction of a cysteine/cystine/ribose system. These compounds were heated for 24 hr at 125°C in a diethylene glycol/phosphate buffer medium at pH 5.6. Hydrogen sulfide and some volatile thiols were identified and also various thiophenes and thiazoles. The formation of 2-acyl thiazoles and 2-formylthiophene was most notable. The author suggests the following mechanisms for the formation of these compounds from well known intermediates:





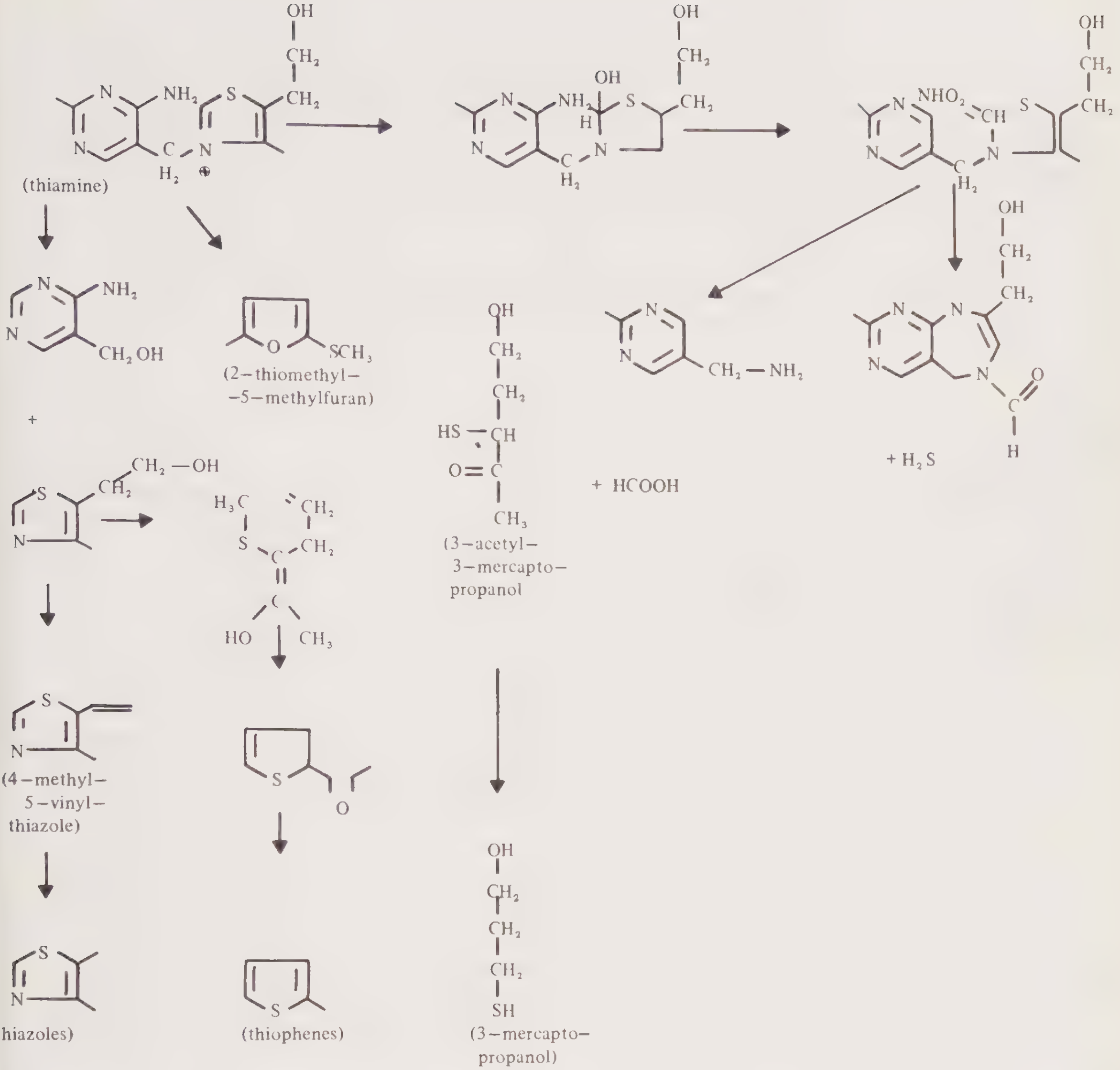


An interesting compound, tentatively identified in this study is 3-methyl-1,2,4-trithiane:

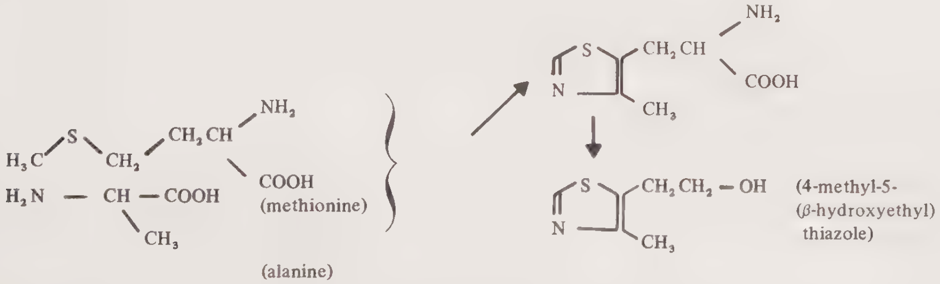


Ledl and Severin[88a] recently identified 76 compounds in the reaction of cysteine and xylose in tributyrine at 200°C, of which 22 thiazoles, 11 thiophenes and 10 other sulfur compounds. Thialdine, dimethyl-dihydro-dithiazine and methyltrithiolane were also formed when methanal and ethanal were treated with ammonia and hydrogen sulfide.[88b]

A compound that almost certainly plays a very important role as a precursor of sulfur-containing flavor compounds is thiamine, also known as vitamin B_1 in its role as a nutrient. Thiamine is reported to have an odor of its own, the threshold value being 39μg/1,[86] though the possibility that this odor is caused by volatile fragmentation products of thiamine should not be excluded. When an aqueous thiamine solution is boiled for several hours, a meat odor with a pungent note is perceived. When glutamic acid is present in this solution, a meaty aroma is released, particularly at pH 6, which is about the pH of cooked meat or meat broth.[86] Some volatile compounds released when a 0.1% solution of thiamine at pH 6 is heated at 121°C for 1 hr, have recently been reported by Dwivedi et al.[28] A major product is 4-methyl-5 (β-hydroxyethyl) thiazole. Two other thiazoles identified, namely 4-methyl-5-vinylthiazole and 4,5-dimethylthiazole, may be derived from this compound. It has been shown that 4-methyl-5 (β-hydroxyethyl) thiazole dehydrates to the 5-vinyl derivative under gas-chromatographic conditions.[140] Hydrogen sulfide, a well-known degradation product of thiamine, is formed after opening of the thiazole moiety. 3-Mercaptopropanol and 3-acetyl-3-mercaptopropanal (4-oxo-3-mercaptopentanal), which were also identified as thiamine degradation products, are formed after cleavage of a sulfur-carbon bond.[29] The mode of formation of 2-thiomethyl-5-methylfuran from thiamine is as yet unclear. Most probably, hydrogen sulfide reacts with other fragments of the molecule to yield a variety of sulfur-containing compounds.[114] Some of the pathways involved in thiamine degradation are shown on the next page:



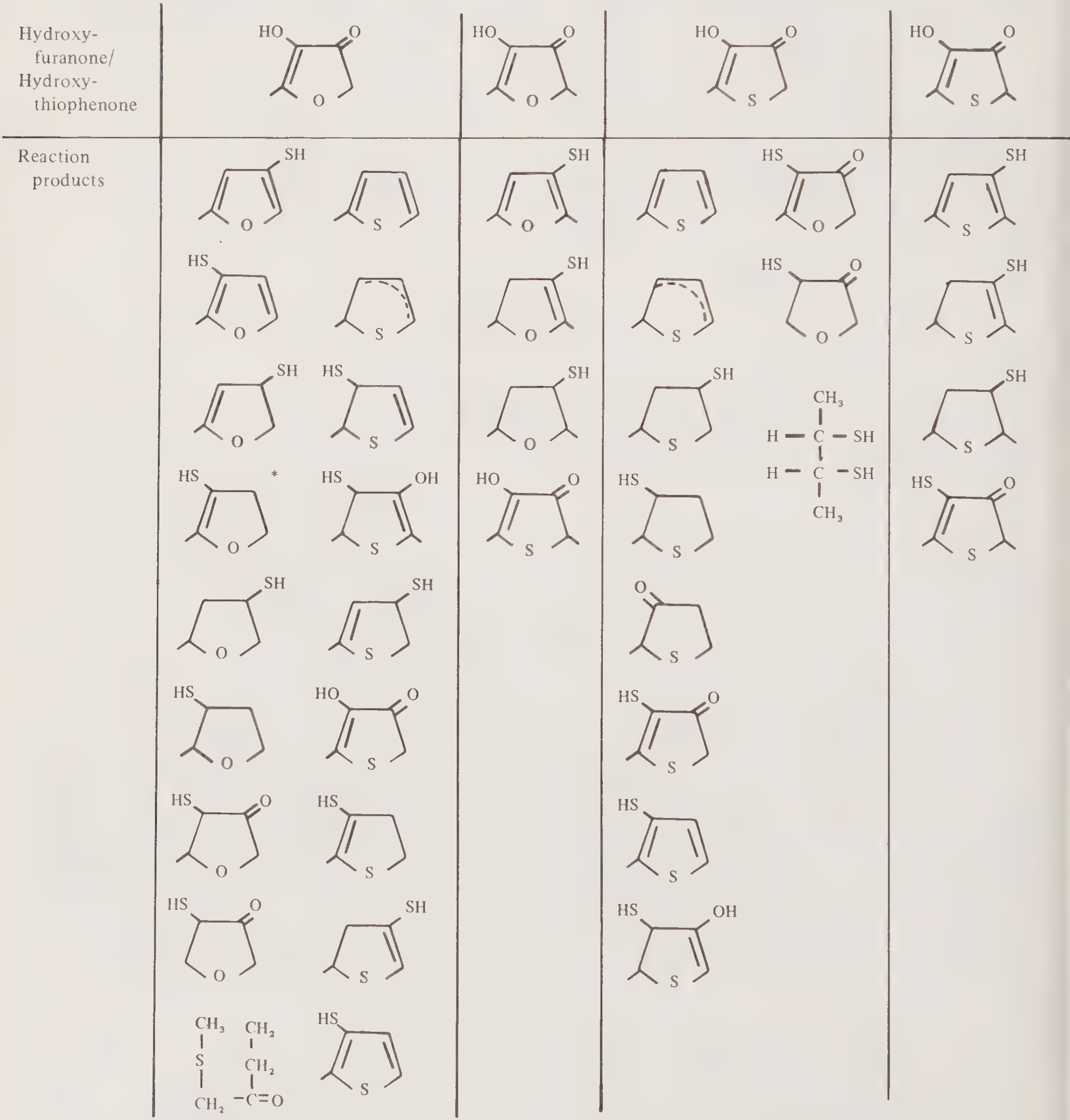
The degradation of thiamine in food products has recently been reviewed by Dwivedi.[29] The processes are not only of importance for flavor formation but also for the understanding of the loss of vitamin B_1 during processing. The degradation of thiamine is just as responsible for the heat-induced flavor of any other food in which it is present, e.g., bread or milk, as it is in meat. Interestingly, studies of Johnson et al.[70] into the biosynthesis of thiamine in yeast showed that the thiazole moiety is derived from alanine and methionine. Thus, the amino acid methionine can equally well be regarded as the precursor of sulfur-containing flavor compounds formed via thiamine.



Reaction products of some model systems of natural precursors have been patented as meat flavors. The compounds isolated by van den Ouweland and Peer[114] are of interest in this respect (see Table 7). The inventors studied extensively the reaction of 5-methyl- and 2,5-dimethyl-4-hydroxy-3-(2H) furanone identified in beef broth by Tonsbeek et al.[145] with hydrogen sulfide. They identified a variety of substituted 3-mercaptofurans and 3-mercaptothiophens in various degrees of saturation. The thiophene analogs of the hydroxyfuranone starting materials were also formed in these reactions. These analogs in

TABLE 7

Sulfur-containing Flavor Compounds Formed by Heating Hydroxyfuranones or Hydroxythiophenones with Hydrogen Sulfide.[114,115]



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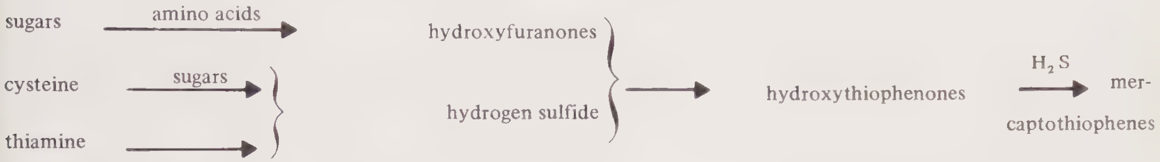
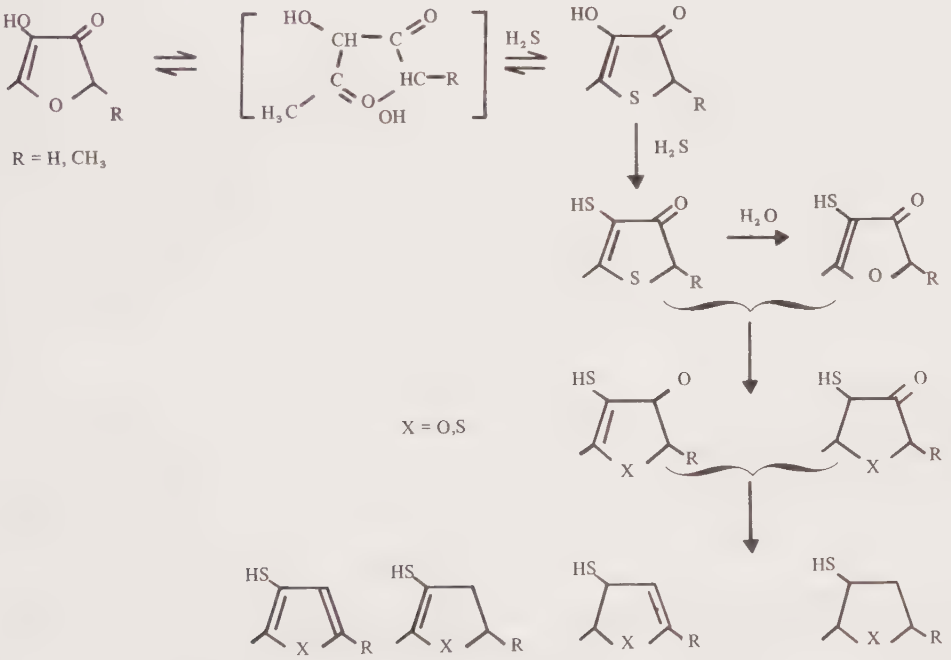
*Also formed from thiamine + cysteine + hydrolyzed vegetable protein.[31]

turn afforded still more mercaptothiophenes and mercaptothiophenones. The reaction systems and even many of the isolated compounds in pure form had meat-like odors.

As the hydroxyfuranones and hydrogen sulfide have been found in boiled beef, it can be expected that the reaction products are also present in natural products, though in such low concentrations that even the most sophisticated analytic tools fail to isolate and identify them. The nose, however, which is the most sensitive detector of flavor compounds, would predict that such compounds contribute to the meat flavor complex. The hydroxyfuranones are derived from sugars or sugar derivatives like ribose-5-phosphate and rhamnose.[62] In Maillard-type reactions, the sugars, undergo the well-known Amadori rearrangement, which is catalyzed by amino acids. As was the case for 1-methylthioethanethiol,[130] a sequence of reactions can be held responsible for the formation of these sulfur containing heterocycles:



The formation of the heterocycles probably follows the reaction sequence as represented below.[115] The dihydrofuran and dihydrothiophene rings split open and in the resulting diketones exchange of sulfur and oxygen can occur readily:



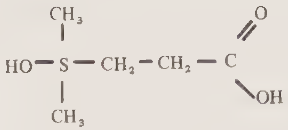
One of these compounds, 2-methylthiophene-3-thiol, was also identified by Evers[31] in a reaction mixture of thiamine, cysteine, and hydrolyzed vegetable protein in water. The corresponding disulfide, an oxidation product of the thiol, was found in relatively large amounts.

Other Foods

Seafood

Relatively little has been published to date on fish and seafood flavor: consequently, little can be said about the flavor volatiles of these foods.

Dimethyl sulfide has been identified in fresh oysters[128] and clams;[100] its odor is reminiscent of oysters and clams, and, therefore, it may make an important contribution to the overall flavor. It has been suggested that dimethyl sulfide stems from the precursor dimethyl-dipropiothetin that occurs in certain plankton species.[100]



$$\mathrm{HO{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{S}}{-}CH_2{-}CH_2{-}C{\overset{\displaystyle O}{\diagup\!\!\diagup}}\!\!{\searrow}OH}$$

(dimethyl-β-propiothetin)

During storage of seafoods, particularly in air, hydrogen sulfide, thiols (e.g., methane- 1 -propane- and 1-butanethiol), and sulfides (e.g., diethyl sulfide, ethyl butyl sulfide, and dimethyl disulfide) are formed,[71] giving rise to an aged or spoiled flavor. They are generated by bacteria.

Some volatile sulfur compounds are released during the cooking of fish.[65] Hydrogen sulfide and methanethiol are reported to be found in herring during the first 30 min of cooking at 100°C. In the period between 30 and 45 min, dimethyl sulfide is released. It is suggested that these compounds are formed in Strecker degradation reactions from cysteine, methionine, and glucose or dicarbonyl compounds, which are all known to be present in fish.

Bread, Chocolate, Coffee, and Roasted Nuts

Bread, chocolate, coffee, and roasted nuts are all foods that have undergone a severe heat treatment before reaching the consumer. The flavor compounds present in these products are for the most part formed from sugars and amino acids during the baking or roasting process in nonenzymic browning reactions. As there are only a limited number of free amino acids and sugars present in food, it is not suprising that in many cases, the same flavor compounds are encountered. The characteristic odor of the particular food depends on the ratio in which the various flavor compounds are present. This in turn is dependent on the level of the amino acids and sugars in the food, on the medium, and on the temperature and duration of the heating process.

As summarized in Table 1, the flavor compounds formed in Maillard reactions may be aldehydes, ketones, phenols, heterocycles such as pyrazines, furans, pyrans, pyrroles, and pyridines, and, of course, sulfur compounds. The sulfur compounds isolated from the foods discussed in this section have been listed in Table 5. Of course, Maillard reactions may also occur during heating of foodstuffs not included in this table; they are responsible, for instance, for the cooked or fried flavors of potatoes and butter and for the "processed" flavors in tomato puree and fruit preserves.

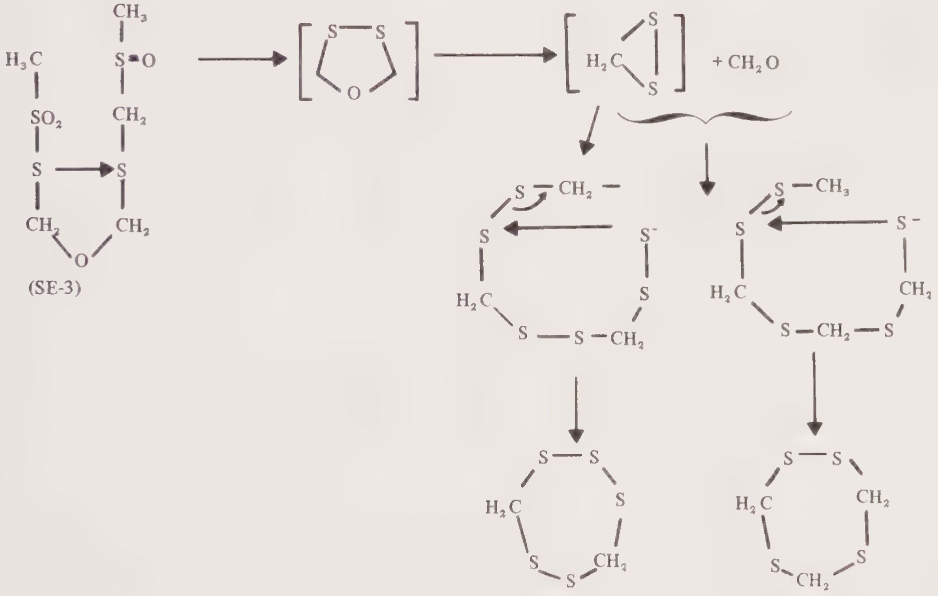
In bread, the characteristic flavor is mainly due to pyrrole derivatives, but pyrazines, lactones, and phenols also play an import role.[143] Sulfur compounds are less important in bread; as yet only some thiophenes and dimethyl mono-, di- and trisulfides have been found.[104] In this context, it is remarkable that compounds like 2-acetylthiazole and 2-acetyl-2-thiazoline, which have a bread-like odor,[146] have so far not been isolated from bread.[105] Sulfur compounds are also of minor importance in chocolate flavor.[127,153] The precursors contributing to the typical chocolate flavor are not sulfur-containing amino acids but mainly valine and leucine.

In coffee, the situation is somewhat different. Walter and Weidemann[157] catalogued all volatile flavor compounds isolated from coffee up to 1968. Only 43 out of the 363 compounds contained a sulfur atom,[164] and only few new sulfur-containing volatiles have been identified in coffee since that time.[139] Nevertheless, one sulfur compound, namely furfuryl mercaptan, makes a large contribution to the flavor of coffee. The precise mechanism of formation of this compound is unknown, but it seems reasonable to assume that the furan moiety is formed in Maillard reactions from sugars, and that the sulfur atom stems from cysteine, which is present in coffee beans. As shown in Table 6, furfuryl mercaptan is also formed in a xylose-cysteine model system.[106]

Pyrazines and pyridines are regarded as the most important flavor compounds in roasted nuts and popcorn.[155] It is, however, very likely that the odoriferous sulfur compounds identified in peanuts[156] and filberts[83] contribute to the overall flavor of these products. The tetrahydrothiophenones in particular can be expected to give a roasted note to the nuts. These compounds are probably formed in a similar way to the meaty flavor compounds listed in Table 7.

Mushrooms

A very interesting flavor compound, 1,2,3,5,6-pentathiacycloheptane, also called lenthionine, has been reported to be the flavor principle of a Japanese edible mushroom, Shiitake.[151] Morita and Kobayashi[102] isolated a sulfur-containing precursor of lenthionine, which they called SE-3 from wet mushrooms. They derived the structure of this precursor from the spectroscopic data and also made a hypothesis for the mechanism of formation of lenthionine and some other thiepanes found in the mushroom from SE-3.



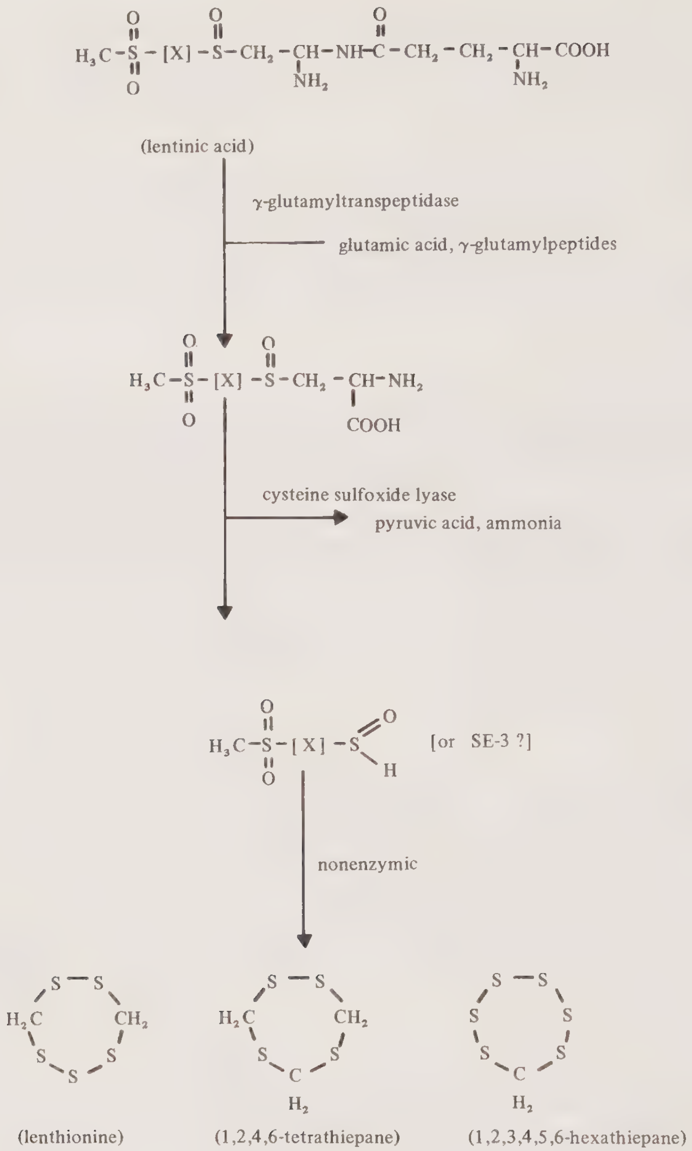
(SE-3)

(lenthionine)

(1,2,4,6-tetrathiepane)

Some support for this mechanism is provided by the synthesis of these compounds from dichloromethane and sodium polysulfide. A methylene disulfide intermediate may also be involved here.

SE-3 could not be isolated from dry mushrooms. This indicates that SE-3 or its direct precursor is formed enzymically during the crushing of the wet mushrooms. Yasumoto et al.[171] isolated a peptide which they showed to release lenthionine as well as the other seven-membered sulfur compounds found by Morita and Kobayashi.[102] This peptide, called lentinic acid, was shown to be an *S*-substituted γ-*L*-glutamyl-*L*-cysteine sulfoxide. Of the remainder of the molecule, only the methyl sulfonate moiety could be indicated. The nmr spectra gave no information about the part of the molecule from which the flavor compounds are formed. Two enzymes cause the subsequent removal of the amino acids, after which a reactive intermediate is formed which is spontaneously converted into the polythiepanes. Yasumoto et al. found no indication that the intermediate involved is SE-3.



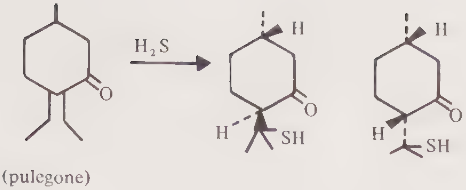
[X] = unidentified part of the molecule

Miscellaneous

Table 1 shows that sulfur compounds are not generally encountered in fruits, dairy products, and alcoholic beverages. There are, however, some exceptions which will be briefly discussed here.

Methyl and ethyl esters of 2-methylthiopropionic acid have been isolated in pineapple flavor concentrates.[32] The methyl ester is even one of the three major components. This compound has a rather unattractive odor.[26] It is, however, unavoidable that it contributes to the flavor of fresh pineapple. It has been suggested that this compound originates from the amino acid methionine.[53]

Two diastereoisomeric thiols have been isolated from buchu oil, the essential oil associated with blackcurrants. The compounds have been identified as (+)-*p*-menth-3-one-8-thiol and (−)-isomenth-3-one-8-thiol.[141] The flavor of the former is particularly characteristic of blackcurrant. The compounds are probably formed by the addition of hydrogen sulfide to pulegone or isopulegone, both present in large amounts in buchu oil.



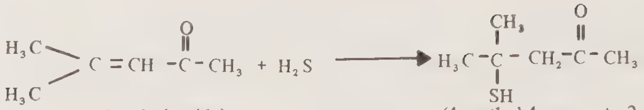
Dimethyl sulfide and dimethyl disulfide are present at or just below their threshold values in fresh milk.[80] In this case, dimethyl sulfide gives the milk a "cowy" fresh flavor;[119] further quantities are formed during processing of the milk, giving rise to off-flavor. It has been detected in concentrated milk and in sour cream; S̃-methyl methionine is identified as its precursor.[27,78] 2-Methylthiophene, dimethyldihydrothiophene, benzothiazole, and hydrogen sulfide have been reported in heated milk, thiamine being held responsible for their formation.[33] The "sunlight" off-flavor in milk is thought to be due to methional; it is noticed at levels of 0.05 to 0.1 μg/kg of methional. Methionine, present in casein, is regarded as the precursor; the methional is formed in a photochemical reaction catalyzed by riboflavin.[118] Benzyl methyl sulfide and benzyl mercaptan, which originate from a weed (land cress), sometimes present in grassland, can also cause off-flavors in milk.[154] The precursors of these compounds, benzyl glucosinolates, have been discussed under the cruciferous vegetables.

During the ripening of cheese, volatile sulfur compounds may be formed from sulfur-containing amino acids. Dimethyl disulfide is even regarded as essential in the flavor of Swiss cheese.[88] On the whole, though, it can be said that sulfur compounds play a very minor role in the characteristic flavor of dairy products. As is the case with milk, they can constitute an off-flavor threat.

Some sulfur-containing flavor compounds have been isolated from Japanese soy sauce.[172] Soy sauce is formed by fermentation of soy protein with yeast. Methionol (3-methylthio-1-propanol), 3-(methylthio)propyl pyruvate, and several half mercaptals and mercaptals have been found. These compounds have been shown to be derived from methionine. Some of these sulfur-containing volatiles have an aroma like that of soy sauce.

Volatile sulfur compounds have not been identified in large numbers in alcoholic drinks. Hydrogen sulfide and traces of ethanethiol have been identified in wine.[1,125] These compounds do not originate from sulfur-containing amino acids but rather from elemental sulfur present in vineyard dust. The hydrogen sulfide is formed during fermentation by yeast. Hydrogen sulfide and acetaldehyde are assumed to yield ethanethiol via the cyclic trimer 2,4,6-trimethyl-1,3,5-trithiane. Schreier and Drawert[129a] recently identified 3-methylthio-1-propanol in German white wine. This compound is formed from methionine, which is present in relatively high levels in grapes used for Riesling wine. The acetate of this alcohol and the related methyl and ethyl esters of 3-methylthiopropionic acid were also reported by these authors as volatile wine constituents.[129b,129c] As mentioned before these esters are known to occur in pineapple flavor.[32] Some low-molecular thiols and sulfides have been found in beer and whiskey.[72] Hydrogen sulfide, thioformaldehyde, thioacetaldehyde, thioacetone[116] and methylthiolesters of butyric, hexanoic, and heptanoic acid are present in beer.[19] The esters originate from the hops. Methanethiol and methional are formed in brewery yeasts. It has been shown that methionine decomposes to these compounds at room temperature, when traces of sulfite and iron or manganous ions are present.[152] 3-Methyl-2-butene-1-thiol, a compound held responsible for the "sun-struck" off-flavor in beer, stems from the action of hydrogen sulfide on isohumulenes, sesquiterpene beer ingredients.[125] Here again, the detection of the sulfur compounds is indicative for the occurrence of off flavors.

While on the subject of off-flavors, a most repellent off-flavor should be mentioned that can occur quite unexpectedly in almost all types of food. This off-flavor is called the "catty taint," being reminiscent of the odor of the urine of tom cats. It is formed when hydrogen sulfide reacts with mesityl oxide to give 4-methyl-4-mercapto-2-pentan-2-one. Catty odors have been detected when the level of mesityl oxide was as low as 20 μ/kg.



$$(H_3C)_2C{=}CH{-}\overset{O}{\overset{\|}{C}}{-}CH_3 + H_2S \longrightarrow H_3C{-}\underset{SH}{\overset{CH_3}{C}}{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}CH_3$$

(mesityl oxide) (4-methyl-4-mercapto-2-pentanone)

Mesityl oxide is a condensation product of acetone that may occur in thinners, in greases, and in can lacquer. Traces of hydrogen sulfide are present in almost all types of food. It is not unexpected, therefore, that catty taints have been reported in food products as varied as canned and frozen meat, soups, peas, carrots, even raspberries, and lemon juice.[2]

III. APPLICATION OF PRECURSORS IN THE FLAVORING OF FOOD

Loss of Flavor During Processing

In the previous chapter, the precursor systems responsible for the formation of volatile flavor substances have been dealt with. It will now be described how knowledge of the mechanisms of formation of flavor compounds can be applied in the flavoring of foodstuffs.

In most processed foods, the characteristic fresh flavor has often been lost or at least diminished or modified as a result of the processing procedures that are necessary to preserve the food during storage. The main methods of preservation are deep freezing, dehydration, and sterilization. In all these processes, microorganisms that are responsible for deterioration of the food are inactivated. Deep freezing retards the action of microorganisms, but even at temperatures as low as -35°C, some slow enzymic reactions may take place. To prevent premature spoilage, therefore, vegetables to be deep frozen are first blanched, i.e., treated with hot water or steam to inactivate the most reactive enzymes. Dehydration of a food lowers its "water activity" to a value at which microorganisms are inactive. In the sterilization of foods, the microorganisms are destroyed by heat or irradiation. Each method of food preservation has its own particular influence on the flavor compounds and their precursors.

The blanching step treatment given to foods to be deep frozen destroys not only enzymes responsible for spoilage but also flavor enzymes. In addition, volatile flavor compounds are gradually lost during deep frozen storage. The amount of flavor precursors present may even be lowered by leaching-out processes during the washing and blanching steps.

In the dehydration of foods, many volatiles are lost in spite of the measures that can be taken to enhance retention in some cases. Moreover, enzymes are inactivated by the heat applied in most drying processes, e.g., hot air drying. Freeze drying, which would diminish this loss, is uneconomical for most foods. As for heat sterilization, or sterilization by irradiation, the flavor enzymes are inactivated, while reactive flavor volatiles and flavor precursors may be lost as a result of undesired chemical reactions.

Precautions can be taken during food processing to reduce loss of flavors and flavor precursors. Thus, food may be washed and blanched with less water, or the washing water may be recycled. Food can be dried at lower temperatures, or preferably freeze-dried. Heat preservation can be carried out in closed containers to preclude the escape of volatiles; the application of high-temperature, short-time sterilization can ensure the destruction of microorganisms before chemical reactions have the chance to go to completion. In-line sterilization and aseptic filling offers the possibility of keeping the heat treatment to a minimum. A discussion of these techniques, however, is beyond the scope of this survey.*

Even if the necessary precautions are taken during the processing, flavor loss and modification cannot be prevented altogether and further steps will have to be taken if the processed foods are to be imparted with a fresh or "home-made" flavor. This is where the flavor chemist can make a most useful contribution.

Natural Precursors

Boosting Precursor Levels by Mineral Nutrition

In the first place, the flavor chemist can team up with the agronomist in an attempt to grow raw materials that possess an optimum amount of flavor precursors. In a series of studies Freeman and

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*An interesting study on the influence of processing and formulation on the aroma of canned beef has recently been published by Persson and von Sydow.[121a]

Mossadeghi[34-37] investigated the influence of sulfate nutrition on the flavor components of vegetables in which sulfur-containing volatiles make a large contribution to the flavor. They found that addition of sulfate to the growing medium of *Allium* plants like onion and garlic resulted in an increase of the amount of volatiles in the prepared vegetables; the increase was particularly high (5- to 16-fold) for sulfur compounds and pyruvic-acid. Sensory appreciation improved considerably. The level of lachrymatory factor in onions was also dependent on sulfate nutrition. Interestingly, growth was retarded in the sulfate-treated plants.

With cruciferous plants like radish, cabbage, and mustard, the amounts of isothiocyanates, i.e., β-phenylallyl isothiocyanate, allyl isothiocyanate, and 4-hydroxybenzyl isothiocyanate, increased with increasing sulfate nutrition. This gave a more pungent taste in these vegetables. No correlation was found between sulfur nutrition and the amounts of other volatile flavors. Evidently, the latter are formed from different precursors. It was found that sulfur dioxide was taken up from the atmosphere by the sulfate-treated plants, and that this contributed to a better taste. In this respect it may be advantageous to grow these vegetables in regions where the air is polluted!

Addition of Flavor Enzymes

The flavor of many processed foods may be enhanced by addition of enzymes just before the final preparation and consumption of the food. This method is particularly effective in vegetables in which enzymic flavor development predominates. The procedure is based on the assumption that the flavor enzymes are destroyed during processing, but that appreciable amounts of flavor precursors are still present. Appropriate enzymes added after processing combine with these remaining precursors to generate flavor volatiles. Hewitt et al.[58] described this principle in a patent specification in which no less than 69 examples are given for various types of foods. The examples for vegetables, however, are the most convincing. Blanched or dehydrated vegetables like onions, leek, cabbage, tomatoes, watercress, and mustard are combined with flavorless enzyme preparations obtained by cold extraction of vegetables and subsequent precipitation with acetone. Addition of the enzymes released fresh and characteristic vegetable flavors that were not present before. The specific flavor enzymes may also be gained from nonedible parts of the vegetables, e.g., pea pods or from microbial sources by fermentation, in which case extensive screening is required to find the suitable culture. It is also claimed that the presence of an antibiotic, e.g., chlortetracycline hydrochloride, may lead to improved flavors, particularly when the rate of formation of the desired flavor is slow compared to the rate of microbial spoilage reactions.

The enzymes originating from different vegetables afford different flavors even if they act on the same precursors.[59] It was thus found that enzymes extracted from cabbage gave a less pungent flavor to dehydrated cabbage than enzymes extracted from mustard. In both cases, isothiocyanates were released, though in different ratios. The mustard enzyme yielded more of the pungent allyl isothiocyanate than the cabbage enzyme, whereas the amounts of *n*-butyl isothiocyanate liberated were similar for both enzymes. Some examples are summarized in Table 8.

Although the principle of imparting a processed food product with a fresh flavor by the addition of enzymes is very sound, it does not seem to have found practical application. The preparation of an economical enzyme concentrate of satisfactory stability presents a major limitation.[126] It can be seen in Table 8 that appreciable quantities of an enzyme source are needed. Another difficulty may be the requirement to sell the processed food and the enzyme preparation in two separate containers.

Nonenzymic Precursor Systems

Compounds responsible for *Allium* flavors may also be liberated chemically from added precursors. Addition of cysteine or other sulfur compounds like homocysteine, homocysteine thiolactone, glutathione, sodium thioglycolate, mercaptosuccinic acid, and particularly 1,4-dithiothreitol (2,3-dihydroxybutane-1,4-dithiol) enhances the intensity of the flavor of dehydrated onions, garlic, leek, chives, etc.[133] This effect is attributed to nonenzymic reactions of these sulfur compounds with other compounds, e.g., thiosulfinates and thiosulfonates, that have been formed previously in enzymic processes. It is suggested that exchange of the sulfur moieties takes place with the consequent production of stable disulfides.

Propanethial S-oxide, the compound identified as the lachrymatory factor in onions,[16] is known to be

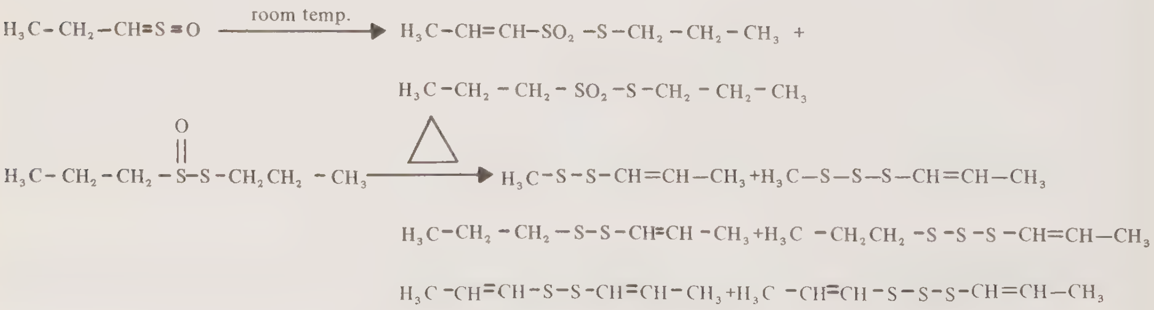
TABLE 8

Enzymic Enhancement of Flavors of Processed Foods[126,132]

Food substrate	Manner in which substrate was processed	Source of enzyme preparation	Parts of substrate per part of enzyme source
Dehydrated onion	Extracted*	Onion	0.25
Tomato	Extracted*	Tomato	2.3
Parsley	Extracted*	Parsley	1.3
Leek	Extracted*	Leek	3.2
Spinach	Extracted*	Spinach	3.3
Celery	Extracted*	Celery	2.3
Peas	Extracted*	Peas	1.0
Watercress	Extracted*	Watercress	0.8
Dehydrated cabbage	Extracted*	Mustard	1.5
Cabbage	Extracted*	Cabbage	0.5
Cabbage	Blanched, dehydrated	Mustard	90
Cabbage	Blanched, dehydrated	Cabbage	3
Horseradish	Blanched, dehydrated	Mustard	30–120
Horseradish	Dehydrated, sulfited	Mustard	5–120
Broccoli	Blanched, frozen	Broccoli	60–120
Beans	Sterilized, cut	Beans	90
Peas	Sterilized, puréed	Peas	110
Carrot	Blanched, dehydrated	Carrots	70
Tomato	Sterilized	Tomato	60–120
Onion	Cooked	Onion	30–60

*Extraction of the substrate with water in order to obtain a flavorless precursor solution.

unstable, thiosulfonates being among the degradation products. These compounds are responsible for a fresh onion flavor. Addition of propanethial S-oxide to foods imparts them with an onion flavor which is mainly caused by propyl, propenyl, and dipropyl thiosulfinate.[17] Dipropyl thiosulfinate may itself be used as a precursor. When it is added to a food product various disulfides and trisulfides are formed during subsequent heating, and a characteristic onion flavor is developed. It has been found that methyl propenyl di- and trisulfide, propyl propenyl di- and trisulfide, and allyl propenyl di- and trisulfide are among the reaction products.[15]



$$H_3C-CH_2-CH{=}S{=}O \xrightarrow{\text{room temp.}} H_3C-CH{=}CH-SO_2-S-CH_2-CH_2-CH_3 +$$

$$H_3C-CH_2-CH_2-SO_2-S-CH_2-CH_2-CH_3$$

$$H_3C-CH_2-CH_2-\overset{\overset{O}{\|}}{S}-S-CH_2CH_2-CH_3 \xrightarrow{\Delta} H_3C-S-S-CH{=}CH-CH_3+H_3C-S-S-S-CH{=}CH-CH_3$$

$$H_3C-CH_2-CH_2-S-S-CH{=}CH-CH_3+H_3C-CH_2CH_2-S-S-S-CH{=}CH-CH_3$$

$$H_3C-CH{=}CH-S-S-CH{=}CH-CH_3+H_3C-CH{=}CH-S-S-S-CH{=}CH-CH_3$$

The product obtained when methionine, with or without a reducing sugar, is heated in oil or fat at 180°C in the presence of a little water is claimed as a potato or potato chip flavor.[25] In all these cases, the knowledge of the flavor precursors in these vegetables has certainly been a great help in the development of these flavor mixtures.

As meat is an important ingredient of many processed foods, it is hardly surprising that numerous patents are devoted to applications of meat flavors.* In many cases, the flavors are based on precursors from which the release of odor compounds takes place via thermally induced reactions. In an early patent, Kipnis and Ornfelt[81] claimed the formation of compounds with a meaty flavor by the reaction of substituted glyoxals with mercaptans. The compounds formed, 2-oxoethanols or monothiohemiacetals, have the general formula R^1-CO-CHOH-S-R^2. When R^1 and R^2 are phenyl groups or when R^1 is a thiophene group, the compounds are said to have meaty odors. Broderick and Linteris[13] used 2-mercaptoacetaldehyde as the sulfur-containing precursor. Upon reaction with reducing sugars in food, it forms all types of acetal linkages, thus generating compounds such as acetals, hemiacetals, monothiohemiacetals, and dithioacetals. These compounds may also be added as such to the food as stabilized forms of 2-mercaptoacetaldehyde. A product that is considered to contribute particularly to the meat flavor is 2-(*D*-xylosylthio)-ethanal. 2,2-Ethoxyethanethiol, or the dimer of 2-mercaptoacetaldehyde, *viz*., 2,5-dihydroxy-1,4-dithiane, may also be used as precursors.

Reaction mixtures with a meat flavor yielded by reaction of hydrogen sulfide with carbonyl compounds are claimed in a number of patents. The hydrogen sulfide may be led through an aqueous solution of carbonyl compounds[5,52] or the hydrogen sulfide may be generated *in situ* from inorganic sulfides, thioamides, thioacids, and 2-mercaptoalkanoic acids and amides.[110] The most suitable carbonyl compounds are reducing sugars, particularly pentoses. Barch[5] believes that reaction products with the general formula R-CHOH-S-CHOH-R are responsible for the meat flavor.

Cysteine is recognized by many inventors as a very effective precursor of hydrogen sulfide. Many reaction mixtures are claimed in which cysteine is made to react in an aqueous system with various other compounds to give meat-like flavors. The other compounds include monosaccharides like ribose, xylose, arabinose, or glucose,[79,82,103,144] aldehydes capable of undergoing aldol condensation reactions;[96] furans with at least one free 2-position in the presence of hydrolyzed vegetable proteins[120] or single amino acids like glutamic acid, arginine, proline or glycine;[95] liquid smoke;[97] ascorbic or isoascorbic acid;[64] or ribonucleotides.[14] The reaction conditions may vary, and other ingredients may be added after the reaction to obtain a better flavor.

Generally, the character of the flavor is that of cooked meat, sometimes chicken, more often beef. In most cases, the flavor is developed by heating the precursors in an isolated system after which the reaction mixture is added to the food. In some cases, however, it is stated that the precursors may also be added as such to food, the flavor being released during the thermal processing steps like heat sterilization or cooking.[95,103]

When amino acids, including cysteine, or amino acid mixtures in the form of hydrolyzed vegetable proteins react with pentoses or hexoses in an oil or in fat at temperatures up to 140°C, a roasted meat flavor or a gravy substitute is obtained.[66,98,136] In these reaction mixtures, a small amount of water is present in the form of crystalline water, while water is formed during the nonenzymic browning reactions. In this sense, the systems are not completely waterfree. On the contrary, the presence of the small amounts of water leads to attractive flavors and prevents the occurrence of burnt off-notes. The reaction conditions in such systems closely simulate the situation during the roasting of meat. In systems in which relatively large amounts of water are present, the conditions are more similar to those prevalent during the boiling of meat. It is hardly surprising, therefore, that roasted meat flavors are formed in the former systems, while boiled meat flavors are formed in the latter. The presence of the fat may also lead to more specific aromas like pork or chicken aroma. This is in agreement with the proposed role of fat in the formation of specific meat flavors.

The role of thiamine as a precursor of meat flavors is stressed in a series of patents.[8,43–45] When thiamine is heated in aqueous systems with proteinaceous substances such as hydrolyzed vegetable proteins and sulfur-containing compounds, such as cysteine, glutathione, hydrogen sulfide, thiols or organic sulfides, meat-like flavors are obtained. Sugars are not necessarily included in these reaction mixtures. The presence of fat is preferable. Addition of pyruvic acid or dihydroxyacetone gives roasted flavors and the presence of methionine leads to pork-like flavors.[43] It is claimed that thiamine may be replaced by 1-hydroxy-3-

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*Application of synthetic meat flavors, particularly in textured vegetable protein products, has recently been published by Wilson and Katz.[166b]

mercapto-4-pentanone,[8] a well-known degradation product of thiamine or by 4,5-substituted thiazoles.[75] The reaction in fat of 4-methyl-5(2-hydroxyethyl) thiazole or homologs or derivatives thereof with amino acid mixtures comprising cysteine affords a chicken-like flavor. Similar reaction mixtures of amino acids, sugars, fats, phosphorus compounds and thiamine are claimed as meat flavors by Yamamoto et al.[168]

Compounds derived from sugars may be used instead of the sugars themselves as reaction partners of sulfur-containing amino acids or other hydrogen sulfide releasing agents. In the development of meat flavor, cyclic carbonyl compounds are known to be formed from monosaccharides in caramelization and nonenzymic browning reactions. Examples are 5-methyl-4-hydroxy-3(2H)furanone, 2,5-dimethyl-4-hydroxy-3(2H)furanone, maltol (2-methyl-3-hydroxy-4-pyrone), and cyclotene (1-methyl-2-hydroxy-1-cyclopenten-3-one).[62] Van den Ouweland and Peer[113] prepared meat flavor mixtures by allowing hydroxyfuranones and pyrones to react with hydrogen sulfide or with hydrogen sulfide releasing agents, such as cysteine, glutathione, thioacetamide, or inorganic sulfides. For instance, a beef flavor was produced by the reaction of 5-methyl-4-hydroxy-3(2H)furanone with cysteine, xylose, and casein hydrolysate. Similar meat flavors were obtained by Katz et al.[76] by the reaction of cyclic carbonyl compounds with hydrogen sulfide or with hydrogen sulfide releasing agents under pressure. Hydroxyfuranones, maltol, ethylmaltol, cyclotene, and 2-hydroxy-3-methyl-2-hexen-4-olide (also known as 3-methyl-4-ethyl-3-hydroxy-2(5H)furanone) are cited as starting materials in the examples. Hydrogen sulfide releasing agents mentioned include furfurylmercaptan, 2-mercaptoethanal, methyl thioglycolate, 3-mercapto-1,2-propanediol, 3-amino-2-dihydro(5H)thiophenone, 4-methyl-5(2-hydroxyethyl)thiazole, glutathione, 1,3-propanedithiol, acetyl methyl disulfide, and thiolacetic acid. Practically all these compounds are powerful flavor compounds themselves.

Recently, the formation of a shellfish-like flavor has been described.[56] A mixture of riboflavine and methionine is heated in water. This example indicates that flavor formation by heat treatment of precursor mixtures may be extended to other types of food.

The patents claiming meat flavors formed by reactions of precursors are summarized briefly in Table 9. Almost all these reactions take place in isolation from the food. A certain parallel can be drawn between these precursor systems and what actually happens during food preparation, particularly with regard to the nature of the precursors and of the flavor compounds formed. The conditions, however, are often exaggerated. This, of course, increases the efficacy of these reactions. In some cases, it has been stated that addition of the precursors to the food product may lead to flavor formation during heat processing steps, e.g., heat sterilization. The addition of such unreacted precursor mixtures to foods is seldom described, as effective patent protection is not feasible. In "reacted" precursor mixtures, on the other hand, the precursor that may still be present in the mixture if the reaction has not been carried out to completion may continue to release flavor compounds in the food.

Synthetic Precursors

In the previous sections, precursors have been dealt with that are based on the natural precursors in unprocessed food. For such systems, those compounds in the raw or fresh food which play an essential role in the release of desirable flavors during food preparation are selected. Since such precursor systems approximate this situation in a natural product, they may be regarded as natual precursor systems, though often the conditions under which the reactions take place are extreme.

Sometimes, however, it may be deemed necessary to accomplish a slow release of a specific flavor substance. Addition of this flavor as such may be impractical, for instance, if the compound is highly volatile or if it is unstable during storage or processing. Gradual release may be achieved by encapsulating the compound, the capsules being ruptured during subsequent treatments of the product. This method is often satisfactory for dry products, as suitable encapsulation techniques have been developed in which the encapsulated material is liberated by addition of (hot) water. For wet products, e.g., canned foodstuffs, encapsulation is not adequate. In these cases, the drawback can be overcome by addition of a nonvolatile derivative of the flavor substance that slowly decomposes during heating, thus releasing the flavoring substance itself.

It has been reported in the previous section that the gradual formation of hydrogen sulfide is sometimes pursued by the use of releasing agents. When releasing agents which are not present in natural materials are designed to perform as such, they must be regarded as synthetic or artificial precursors. Synthetic

TABLE 9

Rough Outline of Some Patents Describing the Formation of Meat Flavors in Nonenzymic Browning Reactions

	Precursors		Reaction conditions		
Inventor(s)	Sulfur source	Other reactants	Medium	Temp (°C)	Time
Kipnis, Ornfelt[81]	mercaptan	2-oxoaldehydes		–	–
I. Flament[32a]	H_2S, $(NH_4)_2S$	carbohydrates	(pyrolysis)	100–500	10 min–2 hr
Broderick, Linteris[13]	2-mercaptoethanal (derivatives)	–	food	pressure processing	–
Barch[5]	H_2S	triethyl citrate	water	room	2–8 hr
Wiener[165]	H_2S, NaHS	pentose, hexose	water, glycerol	100	10 min
Gunther[52]	H_2S, $(NH_4)_2S$	pentose	water	120 pressure	10 min–3 hr
Osborne, Godman[110]	H_2S releasers	pentose	water (fat)	100	15 min–6 hr
Morton et al.[103]	Cysteine, cystine, GSH	pentose, hexose	water, food	100 70	15 min–4 hr 24–30 hr
May[95]	cysteine, cystine, GSH	e.g., furan, MSG	water, food	100 90	15 min–20 hr 18 hr
May, Morton[96]	cysteine, cystine	aldehyde (glyceraldehyde)	water	100 90	15 min–20 hr 18 hr
May, Akroyd[97]	cysteine, cystine	amino acids + liquid smoke	water	100 70	15 min–20 hr 30 hr
Huber et al.[64]	cysteine	(iso)ascorbic acid	water	100 75	1–4 hr 10–25 hr
Kieffer[79]	cysteine, GSH	pentose, hexose	water	90	10 min–6 hr
Perret[120]	cysteine	pentose, hexose + HVP + 5′-ribonucleotides	water	70–100	10 min–4 hr
Thomas[144]	cysteine, cystine	hexose + pentose + glycine	water	70–100	10 min–4 hr
Broderick, Markus[14]	cysteine, cystine	5′-ribonucleotides	water	60–200	evaporation
Kitada et al.[82]	cysteine, cystine	reducing sugar	water pH 8–10	50–120	3–5 hr
Lee[88c]	cysteine, cystine, GSH	deoxyhexose	water	100	1 1.5 hr
May, Soeters[98]	cysteine, cystine	pentose, hexose, HVP	fat (water)	100–140	1 min–4 hr
Shimazaki et al.[136]	cysteine, cystine	reducing sugar	fat	140 160	5 min–2 hr
Jaeggi[66]	cysteine	proline, methionine, ribose	glycerol	110–130	1 hr
Giacino[43]	thiamine + H_2S releasers	HVP	water	100	3–5 hr
Giacino[44]	cysteine, GHS + thiamine	HVP	fat	93 216	15 s–3 hr

TABLE 9 (Continued)

Rough Outline of Some Patents Describing the Formation of Meat Flavor in Nonenzymic Browning Reactions

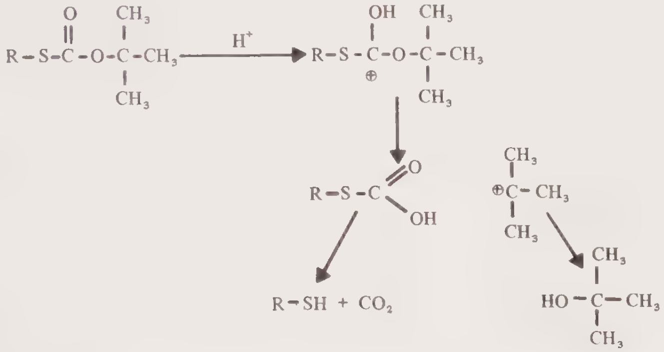
	Precursors		Reaction conditions		
Inventor(s)	Sulfur source	Other reactants	Medium	Temp (°C)	Time
Bidmead et al.[8]	thiamine (derivatives) + cysteine, cystine, GSH, H_2S releasers	carboxylic acid	water pH 4.5–5.5	93–104	15 min–6 hr
Giacino[45]	thiamine + taurine	HVP	water, oil	120–205	15 s–6 hr
Katz et al.[75]	cysteine + thiazole	amino acids	water	103	4 min
			fat	149	30 s
Yamamoto et al.[168]	thiamine	pentose, hexose, P compound	water	100	2 hr
v.d. Ouweland, Peer[113]	H_2S, cysteine, cystine, GSH	cyclic ketone (+ xylose)	water pH 4–7 (food)	100	2–4 hr
Katz et al.[76]	H_2S releasers	cyclic ketone	water	120–190 pressure	30 min–8 hr
Bentz. Scarpellina[7a]	H_2S	aldehyde, ketone	water	room	18–24 hr

, = or
+ = and
() = optionally
GSH = glutathione
MSG = monosodium glutamate
HVP = hydrolyzed vegetable protein
P compound = phosphorus compound

precursors of hydrogen sulfide mentioned in the discussion of patents were thiolcarboxylic acids, thioamides, and 2-mercaptoalkanoic acids, and amides.[110]

Thiols added to foodstuffs as flavoring substances usually disappear readily because of their volatility and reactivity. Moreover, the level at which these compounds impart an attractive flavor is very critical. The use of a thiol-protecting group which decreases the volatility or increases the threshold value and which is sufficiently heat labile to cause a gradual release of the thiol therefore may be attractive.

Schutte and van der Heyden[131] investigated the effect of several thiol-protecting groups in various volatile flavor compounds. They found that thioacetates were generally too stable, and that dithiocarbonates were either too stable or too unstable under the conditions of subsequent heat processing. The O-*t*-alkyl thiocarbonates, however, appeared to have just the right degree of instability. This was substantiated for a variety of thiols listed in Table 10. The O-*t*-hexyl thiocarbonates had the best flavoring characteristics; they are less volatile and therefore have high threshold values and stay longer in the heated food medium. They are thus capable of generating the thiol over longer periods. The O-*t*-butyl esters, however, are easier to prepare and are preferred in most cases. It is interesting that the monothiocarbonates are relatively stable in pure form; they may be purified by distillation. They decompose in aqueous media, though, probably via an acid catalyzed process. It is assumed that the *t*-alkyl group is split off in the first reaction step, and that the carbonic acid then decomposes to the thiol and carbon dioxide.



The advantage of monothiocarbonates as thiol precursors is shown in some patent examples.[60] In one example, it is shown that 1-methylthioethanethiol, when added as such to a dry soup, is lost during boiling. When the precursor O-*t*-butyl-S (1-methylthioethyl) thiocarbonate is added before boiling, the flavor effect in the prepared soup is the same as that when an equivalent quantity of the thiol is added after boiling. In other examples, the precursor was shown to survive the heat sterilization process in the production of canned food and the extrusion process in the preparation of textured vegetable protein from soya fluff. The O-*t*-butyl monothioester of furfuryl mercaptan was shown to have a favorable effect on the flavor of instant coffee.

Toxicological Aspects

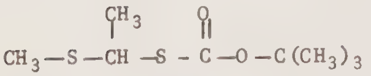
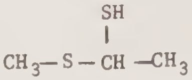
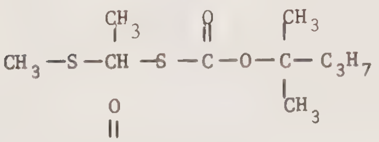
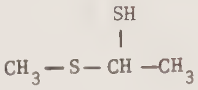
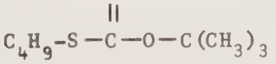
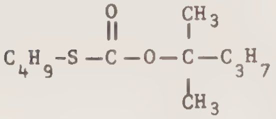
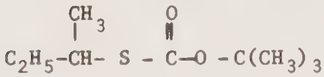
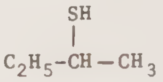
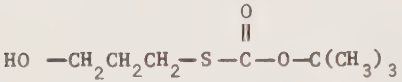
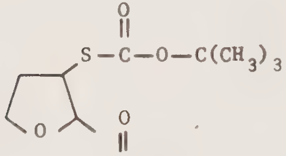
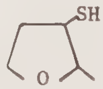
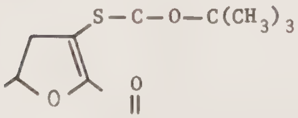
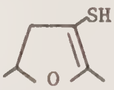
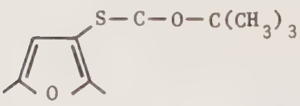
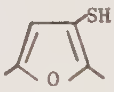
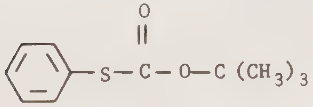
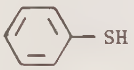
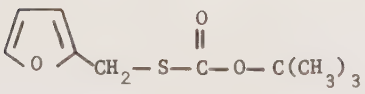
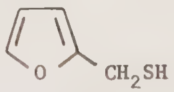
When flavoring substances are to be added to food, their safety must be well-established. In most countries, this responsibility is placed on the manufacturer of the food; in other countries the addition of flavors is restricted by law. For instance, in Germany and Italy, only natural or nature-identical flavors, i.e., synthetics with the same formula as the natural compound, may be used without restriction. A very small number of artificial flavors that are allowed in these countries are listed on a "positive" list.

In the U.S., flavoring substances are "GRAS," (generally recognized as safe) provided they are prepared and used according to good manufacturing practice. An expert panel of the FEMA (Flavor Extract Manufacturers Association) regularly evaluates the data presented for specific compounds before deciding whether to include them in so-called GRAS lists.[41] The Code of Federal Regulations of the FDA title 21, section 121.1163 and 1164 (1971) also gives an advisory list of safe flavorings.

There are, however, indications that the use of flavors in the U.S. will in the future be regulated by a positive list.[87] Similarly in Europe, the Council of Europe is in the course of preparing such a positive list.

TABLE 10

Monothiocarbonates as Synthetic Precursors of Thiol Flavor Compounds.[131]

Precursor	Flavor compound	Release of Thiol*
 $CH_3-S-CH(CH_3)-S-C(=O)-O-C(CH_3)_3$	 $CH_3-S-CH(SH)-CH_3$	++
 $CH_3-S-CH(CH_3)-S-C(=O)-O-C(CH_3)_2-C_3H_7$	 $CH_3-S-CH(SH)-CH_3$	+++
 $C_4H_9-S-C(=O)-O-C(CH_3)_3$	C_4H_9SH	+
 $C_4H_9-S-C(=O)-O-C(CH_3)_2-C_3H_7$	C_4H_9SH	++
 $C_2H_5-CH(CH_3)-S-C(=O)-O-C(CH_3)_3$	 $C_2H_5-CH(SH)-CH_3$	+
 $HO-CH_2CH_2CH_2-S-C(=O)-O-C(CH_3)_3$	$HO-CH_2CH_2CH_2-SH$	+
		++
		+
		+
		++
		+++

*In boiling water at pH 5.5, +++, high; ++, moderate; +, low.

In the preparation of these positive lists, specific flavor compounds are taken into account, irrespective of whether they are nature-identical or artificial.

Urged either by a sense of responsibility or by legal regulations that will be imposed on him, the food manufacturer has to ascertain that the flavors he uses are safe. It is not sufficient to prove that the substances in question occur in nature or in natural foods, since many natural components of food are themselves toxic. It can only be assumed that the addition of a flavor component to a foodstuff in which it occurs naturally is safe if its ultimate level does not exceed the level of the natural flavor. Only then is the daily intake the same. In other cases, the safety of the flavor must be evaluated in animal experiments involving acute toxicity studies, short-term feeding trials, and also limited tests for carcinogenic potential. Feeding studies should be designed to provide a margin of safety (no-effect level) which is at least one hundred times the maximum human daily intake.[150]

A large number of the sulfur-containing flavor compounds mentioned in this study are GRAS; the 88 sulfur compounds listed in Table 11 are on the FEMA GRAS list.[54,55,111,112] This can be mainly attributed to the extremely low levels at which they are used, often far below 1μg/kg food. For the single flavor compounds, therfore, no great problems exist.

TABLE 11

Sulfur-containing Compounds Listed on the FEMA-GRAS List[54,55,111,112,112a,112b]

nr	Compound
Thiols	
2715	methyl mercaptan
2035	allyl mercaptan
3289	3-mercapto-2-butanone
3300	3-mercapto-2-pentanone
3303	2-methyl-1-butanethiol
3304	3-methyl-2-butanethiol
3357	2-keto-4-butanethiol
3180	2-mercaptopropionic acid
3279	ethyl 2-mercaptopropionate
3263	*L*-cysteine
3262	cyclopentanethiol
2439	furfuryl mercaptan
3232	2-pyridinemethanethiol
3299	2-mercaptomethylpyrazine
3230	pyrazineethanethiol
3177	*p*-mentha-8-thiol-3-1-one
3188	2-methyl-3-furanthiol
3062	2-thienylmercaptan
3240	*o*-toluenethiol
3345	2-ethylthiophenol
3314	2-naphthalenethiol
Monosulfides	
3246	methyl sulfide
2042	allyl sulfide
2215	butyl sulfide
3207	1-methylthio-2-butanone
3375	4-methylthio-2-butanone
3376	4-methylthio-4-methyl-2-pentanone
3355	di(butan-3-one-1-yl) sulfide
3206	2-methylthioacetaldehyde
2747	methional
2720	methyl 3-methylthiopropionate
3343	ethyl 3-methylthiopropionate
3374	3-methylthiobutanal
3301	*DL*-methionine
3160	furfuryl methyl sulfide
3161	furfuryl isopropyl sulfide
3238*	2,2′(thiodimethylene)-difuran
3258*	bis(2-furfuryl) sulfide
3259	bis(2-methyl-3-furyl) sulfide
3366	2-methyl-4(methylthio) furan
3189	2-methyl-3,5 or 6-furfurylthiopyrazine

nr	Compound
Trisulfides	
3275	dimethyl trisulfide
3276	dipropyl trisulfide
3308	methyl propyl trisulfide
3253	allyl methyl trisulfide
3265	diallyl trisulfide
Tetrasulfide	
3260	bis(2-methyl-3-furyl) tetrasulfide
Thiolesters	
3282	ethyl thioacetate
3310	methyl thiobutyrate
3385	propyl thioacetate
3329	allyl thiopropionate
3311	methyl thiofuroate
3162	furfuryl thioacetate
3347	furfuryl thiopropionate
3158	2-furanmethanethiol formate
Isothiocyanates	
2034	allyl isothiocyanate
3312	2-methylthiopropyl isothiocyanate
Thiazoles	
3274	4,5-dimethylthiazole
3324	2,4,5-trimethylthiazole
3372	2-(1-methylpropyl) thiazole
3134	2-isobutylthiazole
3313	4-methyl-5-vinylthiazole
3145	2,4-dimethyl-5-vinylthiazole
3204	4-methyl-5-thiazole-ethanol
3205	4-methyl-5-thiazole-ethanol acetate
3192	2-methyl-5-methoxythiazole
3340	2-ethoxythiazole
3328	2-acetylthiazole
3262	2,4-dimethyl-5-acetylthiazole
3256	benzothiazole
3322	thiamine hydrochloride
Thiophenes	
3209	5-methyl-2-thiophenecarboxaldehyde
3266	4,5-dihydro-3(2H) thiophenone
3338	5,7-dihydro-2-methylthieno(3,4-D) pyrimidine

TABLE 11 (Continued)

Sulfur-containing Compounds Listed on the FEMA-GRAS List[54,55,111,112,112a,112b]

nr	Compound	nr	Compound
3231	pyrazinyl methyl sulfide		
3208	(methylthio)methyl pyrazine (mixt)	Miscellaneous	
3210	*o*-methylthiophenol	3039	sulfur dioxide
3412	methyl 4-methylthiobutyrate	3270	*spiro*[2,4-dithia-1-methyl-8-oxabicyclo [3.3.0] octane-3,3′(1′-oxa-2′-methyl)-cyclopentane]
3414	4-methylthiobutanal		
3415	3-methylthiopropanol		*spiro*[2,4-dithia-6-methyl-7-oxabicyclo [3.3.0] octane-3,3′(1′-oxa-2′-methyl)-cyclopentane]
3438	3-methylthio-1-hexanol		
Disulfides			
3201	methyl propyl disulfide		
3228	propyl disulfide		
3227	propenyl propyl disulfide		
3127	allyl methyl disulfide		
3362	methyl furfuryl disulfide		
3168**	2,2′(dithiodimethylene)-difuran		
3257**	bis(2-furfuryl) disulfide		
3323	thienyl disulfide		
3325	phenyl disulfide		

*,**These entries are the same.

The situation is somewhat different for reaction mixtures based on precursors. The addition of precursors, like amino acids and sugars, is formally justified as these compounds are GRAS and the levels used for flavoring are low compared with those for nutrient fortification and sweetening, albeit the latter applications are under discussion. An exception to this is the case of thiamine; the amounts required for flavoring are in the same range as (or higher than) the recommended daily intake of vitamin B_1 (1 to 1.5 mg). Excessive use of this compound for flavoring purposes may easily result in an overdose of vitamin B_1. Although the effects of such an overdose are not clear, excessive use of vitamins may under some legislations (e.g., that in the U.S.) lead to the food being classified as a drug. Although in most other cases addition of precursors is formally justified, they are not added to a foodstuff with the intention of being kept unchanged. On the contrary, the clear purpose is to let them react with each other or with other food ingredients to afford volatile flavor compounds. The exact compositions and amounts of all compounds thus formed are unknown, and, consequently, the toxicological status of the "reaction product" is uncertain. Therefore, it may be questioned whether addition of the precursors is justified merely by their GRAS status.

On the other hand, the same applies for all other ingredients in the food that undergo a change during processing, and it must be emphasized that the reaction of added flavor precursors in the food medium are not principally different from the reactions that normally take place during food preparation. And, when it comes to establishing the safety of a food product with a hundred-fold safety margin, the toxicologist has to admit defeat, because it is impossible to administer the large amounts of food required for such a test to a laboratory animal. In some cases, fractionation or extraction of the food may overcome this problem. For small amounts of reaction products of unknown composition, however, one cannot depend on this technique.

The situation is somewhat different for flavor mixtures that are obtained by reactions of precursors in isolated systems. Although the precursors themselves occur naturally, the reaction conditions can hardly be considered as "natural" since the concentrations of the reactants and often the temperature of reaction are extreme. Hydrolyzed vegetable proteins also belong to this category. Toxicological testing of such mixtures, however, is feasible and perhaps even to be recommended as the findings also give an indication of the safety of precusor systems when they are added as such to foodstuffs. There are of course some difficulties involved. For instance, the necessity of submitting data on the reaction conditions of such mixtures will meet with reluctance on the part of the flavor industry, as this is confidential information. This may help to explain why governmental authorities have as yet made no propositions on how to cope with such reaction mixtures.

IV. CONCLUSIONS

The precursors of sulfur-containing flavor compounds may be subdivided into three categories according to precursor mechanism involved. First, there is the enzymic formation of flavors which is dominant in vegetables. Second, sulfur-containing flavor compounds can be released from natural precursors in nonenzymic browning reactions during the heat treatment of foods; this mechanism prevails in meat and roasted or baked foods. The third mechanism involves the thermal decomposition of artificial precursors. Few volatile sulfur compounds are formed biochemically in the living organism. Examples are the one or two compounds isolated in fruits (blackcurrants, pineapple), 2-isobutylthiazole in tomatoes, and asparagusic acid in asparagus.

Enzymic flavor formation after rupture of the cell tissue is far more important for the production of sulfur-containing volatiles, particularly in vegetables. In this process, flavor precursor and flavor enzymes are brought together, thus enabling the flavor releasing reactions to take place. In cruciferous plants such as mustard, radish, and cabbage, the precursors are glucosinolates and the enzyme myrosinase. The compounds formed, isothiocyanates, have a pungent odor and taste. In allinaceous vegetables such as onion, leek, and garlic, the precursors are S-alkyl cysteine sulfoxides and the enzyme alliinase. Initially, thiosulfinates are formed which readily disproportionate to disulfides and thiosulfonates or monosulfides and sulfur dioxide. These compounds are responsible for the fresh vegetable flavor. As the propenyl moiety is specific for onions, the compound responsible for the lachrymatory effect, propanethial S-oxide, is specific to this vegetable. In subsequent heat treatments, these enzymically formed compounds can rearrange or dissociate and recombine. In boiled *Allium* vegetables, such reactions yield disulfides and trisulfides, whereas in fried onions, dimethylthiophenes contribute to the characteristic flavor. Substantial amounts of the precursors usually survive the processing (i.e., canning, drying, or deep freezing) of cruciferous and allinaceous vegetables. It has been shown that a fresh flavor can be regenerated by addition of suitable enzymes. Specific enzymes are required to generate the flavor characteristic for a particular vegetable. These enzymes can best be extracted from the plant itself, preferably from inedible parts. Nevertheless, this principle is not applied commercially mainly because of the costs of making the specific enzyme preparations. It seems improbable that this state of affairs will change in the near future.

The application of the initial products of the enzymic reaction as precursors for boiled or fried vegetable flavors appears to be more promising. Thus, thiosulfinates can be profitably added to processed *Allium* vegetables as precursors of disulfides and thiosulfonates, while propanethial S-oxide may be used as a precursor of thiosulfinates which impart to foodstuffs a fresh onion flavor. Addition of cysteine to processed vegetables increases the level of disulfides and methionine yields a potato-like flavor.

A very practical approach to improve the flavor of vegetable products is to increase levels of precursors by specific sulfate nutrition of the plants. Furthermore, precautions can be taken during processing to minimize the loss of flavor volatiles, precursors, and if feasible, enzymes.

In meat, the characteristic flavor compounds are formed in thermal reactions from sugars and amino acids. For sulfur-containing volatiles, the paramount source of sulfur is cysteine, either in the free form or as a part of the meat proteins, while thiamine (vitamin B_1) and methionine may also play a role. Hydrogen sulfide, which itself may contribute to the final flavor, is an important intermediate in many of these reactions. Suitable mixtures containing sugars and hydrogen sulfide, cysteine, or thiamine may be heated in water or fat to yield meat-like flavors. The reaction products, which may be regarded as more sophisticated forms of the well-known protein hydrolysates, may be added to foodstuffs to boost the meaty character. Very attractive meat flavors are formed by the reaction of hydroxyfuranones and similar compounds with hydrogen sulfide. Alternatively, the unreacted precursor mixture may be added to the food before

TABLE 12

Survey of Formation of Sulfur-containing Flavor Compounds from Natural Precursors

Class of sulfur compound	Precursor	Formation	Food
Hydrogen sulfide	cysteine	enzymes	seafood, yeast
	cysteine/cystine	heat	meat, eggs
	thiamine	heat	meat
Thiols	methionine	enzymes	yeast
	methionine	heat	meat, fish
	thiamine	heat	meat
Monosulfides	methionine	enzymes	yeast, milk
	methionine	heat	vegetables, meat, seafood
	S-methylmethionine	heat	vegetables
	dimethyl-β-propiothetin	bioformation	seafood
	disulfide	heat	vegetables
Disulfides	sulfide	heat, oxidation	meat, vegetables
	thiosulfinates	heat	*Allium* vegetables
Trisulfides	disulfide	heat, oxidation	*Allium* vegetables
Thiosulfinates	S-alkylcysteine sulfoxide	enzymes	*Allium* vegetables
Thiosulfonates	thiosulfinate	heat	*Allium* vegetables
Isothiocyanates	glucosinolate	enzymes	*Cruciferae* vegetables
Thiocyanates	isothiocyanate	enzymes, heat	vegetables
Methional (derivatives)	methionine	enzymes	yeast, soy sauce
	methionine	heat	vegetables, meat, milk
Thiazoles	cysteine (?)	bioformation	tomato
	cysteine/cystine	heat	meat, coffee, cocoa
	thiamine	heat	meat
Thiophenes	disulfide	heat	onion
	cysteine/cystine	heat	meat, coffee, nuts, bread
	thiamine	heat	meat, milk
	furanones + H_2S	heat	meat
Thiolanes, thianes, thiepanes	peptides(?)	bioformation	asparagus
	peptides	enzymes, heat	mushroom
	hydrogen sulfide	heat, oxidation	potato, meat

processing; the reactions that afford the meat flavor then take place in the food medium during subsequent heating (e.g., sterilization or cooking). These procedures may well find wider application as the replacement of meat by vegetable proteins becomes commercially attractive. Safety clearance of precursor mixtures presents special problems, as very little can be said about the exact identity of the reaction product.

Relatively few precursor mixtures have as yet been reported for other foods in which the flavor is formed in similar nonenzymic browning processes. Exceptions are the formation of a shellfish-like flavor by the reaction of riboflavine with methionine and of a potato flavor by the reaction of methionine in oil. A chocolate flavor is formed in the reaction of valine, glucose, and epicatechin at 180°C, and a bread flavor on heating proline with sugars, but the sulfur compounds are less important here. Precursor mixtures for coffee and roasted nuts may well be developed in the near future.

Undesired or excessive reactions of sulfur-containing precursors can result in off-flavors. Sulfur volatiles, particularly hydrogen sulfide, are released during microbial spoilage. Off-flavors in milk can be caused by glucosinolates originating from weed eaten by the cow. Other off-flavors are induced during the cooking, pasteurizing, or exposure to sunlight of milk. In beer and wine, the occurrence of volatile sulfur compounds is usually indicative for off-flavor.

One more sulfur-containing precursor ought to be mentioned, namely S-methylmethionine. This amino acid, which is present in many vegetables, degrades to dimethyl sulfide. Dimethyl sulfide contributes to the flavor of fresh milk, clams, asparagus, cooked cabbage, and other cooked vegetables. As dimethyl sulfide is released upon heating, it may be one of the compounds that is characteristic for "processed" flavors. These processed flavors are not always regarded as off-flavors; in tomato puree, canned fruits, and jams, for instance, they are generally accepted and appreciated. As processed flavors are usually formed in nonenzymic browning reactions, they may also be induced by precursor systems. The most prominent ways in which the various classes of sulfur-containing flavor compounds are formed from their natural precursors are summarized in Table 12.

The third type of flavor precursors is artificial precursors. These compounds may be prepared by coupling a labile protecting group to a reactive site of the flavor molecule. Such precursors can be created for hydrogen sulfide and for thiols. The main feature of this method is that it enables the specific release upon heating of only one flavor compound. This principle holds promise for the flavor chemist, particularly if specific reactive and highly volatile top-notes are desired for flavor accentuation. It may be extended to flavor compounds without a sulfur moiety, e.g., aldehydes, lactones, amines, and alcohols.

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VOLATILE SULFUR COMPOUNDS IN FOOD FLAVORS

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INTRODUCTION

Flavor is an important quality attribute of foods. It is now recognized as an auxiliary diet factor.[162] The perception of flavor is a complex phenomenon involving olfactory, gustatory, and tactual sensations, mouth feel, pain, temperature, and even sound. The gustatory and the tactual components are concerned with the taste and the texture of the food, respectively. The olfactory component deals with the smell of the food and consists of two distinct factors, viz., the odor and the aroma. Odor is an important factor which has the greatest influence on flavor. It is perceived when the food is smelled, while aroma is sensed by the olfactory receptors during eating and/or drinking the food.

It is well known that very small amounts of some substances can have profound effects on taste and odor sensations. The volatile flavor compounds in foods frequently occur in trace concentrations (ppm or ppb) surrounded by other organic materials and water. The low concentrations of the flavor substances in foods have made their isolation, separation, concentration, and analysis very difficult. To study these compounds, tons of food materials have to be employed to obtain a few grams of odoriferous oils, which are generally very complex mixtures. For example, the coffee flavor that has been most thoroughly investigated showed the presence of 404 volatile components,[85] of which about 350 have been fairly well identified. It has been found that no single compound is totally responsible for the characteristic flavor of a food in question. However, some organoleptically important constituents have been isolated, e.g., ethyl 2-methyl butyrate from apple,[77] 2-methoxy-3-isobutyl pyrazine from bell pepper,[41] nootkatone from grapefruit,[161] 1-(*p*-hydroxyphenyl)-3-butanone from raspberry,[324] alkylidene phthalides and dihydrophthalides from celery,[89] lenthionine from Shiitake mushroom,[308] etc.

Techniques in Flavor Research

Of the various constituents in the food flavor, the sulfur compounds possess a powerful and characteristic odor which contributes to the agreeable as well as the disagreeable flavors of many foods. During the past 10 years there has been an avalanche of reports on the sulfur-containing flavor volatiles; this is largely due to the recent advances in the separation and identification techniques. There exist two approaches in the food odor research, viz., study of all volatile compounds that can be isolated from the food (total volatiles) and study of gaseous odor compounds over the food (headspace gas). Each of these has its own objective, specific merits, and shortcomings. The steps in the analysis consist of detection and identification of the flavor constituents using chemical and instrumental methods. The various instrumental techniques generally used in the flavor analysis are gas chromatography (GC), mass spectrometry (MS), infrared (IR), ultraviolet (UV), and visible spectrometry, nuclear magnetic resonance (NMR), and Raman spectrometry. The GC-MS combination has provided the major means of identifying flavor components during the current decade. NMR and Raman spectra are obtainable with submilligram quantities of purified material. Furthermore, commercial GC-IR and GC-laser Raman spectrometers and the MVS distribution apparatus are gaining popularity in flavor research. Thus, chemical structure determinations can now be made with good certainty with only submilligram quantities. However, the major challenge in flavor research lies in achieving correlation of sensory quality with chemical identity. This study demands that the fractions must be both spectroscopically and organoleptically pure, which is rather difficult to achieve.

Sulfur Compounds

Since sulfur, oxygen, selenium, and tellurium belong to the same group (VI) in the periodic table, one should expect similarities in the behavior of their organic derivatives. For example, water, hydrogen sulfide, hydrogen selenide, and hydrogen telluride are the structurally related compounds. Water has no odor, whereas hydrogen sulfide possesses an unpleasant odor; the property increases progressively in hydrogen selenide and hydrogen telluride. Another interesting group of compounds is methanol, methanethiol, and methaneselenol. Methanol has practically no odor, while methanethiol possesses a powerful and disagreeable odor. Methaneselenol has the maximum penetrating vile odor. The other examples are ethers, thioethers, and selenoethers; isocyanates, isothiocyanates, and isoselenocyanates; and organic sulfur and selenium derivatives[256,257] of carbonic acid, etc. Thus, the replacement of oxygen with sulfur or selenium essentially changes the odor properties. This behavior supports the view[138] that the odor is located in the heteroatoms themselves. From a theoretical point of view, the most important distinction between oxygen and sulfur (or selenium) is the availability of d-orbitals for hybridization and bond formation in sulfur and selenium. Oxygen cannot readily accept valence electrons by expanding its normal valence shell. It could accept valence electrons beyond 8 only by adding them in the third shell which, due to the smaller nuclear charge, results in low stability. On the other hand, sulfur and selenium possess the ability to accommodate up to 10 electrons in their valence shell. Thus, the differences in the electronic behavior and the participation of d-orbitals in the bonding are believed to be the factors responsible for the odor quality of sulfur and selenium compounds. In a recent review article, Klopping[138] pointed out that the odor quality is dependent on the size and shape of the molecule, orientation with respect to the receptor surface, and inherent functional odor group. In addition, the factors such as polarity, mass, volatility, stability, hydrogen bonding, symmetry of the molecule, etc. also seem to contribute to the characteristic odor. In general, compounds containing higher valency sulfur and selenium appear likely to be less odoriferous compared with those containing divalent sulfur and selenium.

Various volatile sulfur compounds may be occurring either naturally in the food or formed as a result of processing and storage conditions. The naturally occurring flavor compounds may be considered as direct metabolites produced in animal or vegetable organisms by intracellular biogenetic pathways. Therefore, the flavor quality depends on the genetic factors. It has been found that the flavor differences in the intercultivars are generally due to the variations in the quantitative composition of the flavor volatiles. For example, the flavor difference in the two cultivars of tomato (Campbell 146 and 1327) has been found to be due to the variation in the content of 2-isobutyl thiazole.[279] Many organic sulfur volatile compounds are formed during the processing and storage of foods. The processing may involve heating, smoking, cooking, frying, roasting, irradiation, enzymatic, etc., which may cause the formation of flavor. The action of light and ionizing radiation may also cause the flavor formation during processing and storage. During heat processing, the following reactions can occur: oxidation, degradation, hydrolysis, dehydration, condensation, decarboxylation, etc. In this connection, it is worth mentioning the important roles of the Maillard reaction and Strecker degradation in the flavor formation of many processed foodstuffs. In a recent review article, Schwimmer and Friedman[247] discussed the genesis volatile sulfur-containing food flavors.

A survey of the sulfur-containing volatiles in foods shows that these contain one of the functional groups, such as thiols, sulfides, sulfoxides, sulfones, thiocyanates, thiosulfinates, thiazoles, thiolanes, etc. A classification of these along with their formulas and occurrence in foods is given in Table 1. One or more of the sulfur compounds may be present in a food, contributing directly or indirectly to the overall flavor. It is well known that the powerful odor substances will have low threshold concentrations; sulfur compounds behave accordingly. Data on the odor threshold values of some of the compounds are given in Table 2. These values depend on the media and are influenced by the presence of other flavoring compounds.

Flavor investigations are greatly simplified if certain volatiles in the product of interest were to exhibit the characteristic aroma of that product. However, such a situation is met only in a limited number of foodstuffs; examples of some character-impact sulfur-containing compounds are given in Table 3.

Information on the various sulfur-containing flavor volatiles in foods, their formation, and significance to the overall flavor will be presented.

TABLE 1

Sulfur-containing Volatiles and Their Occurrence in Foods

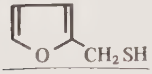
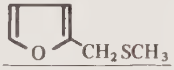
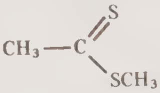
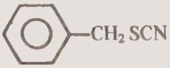
Compound	Formula	Foods
1. **Thiols** (mercaptans)		
Methanethiol	CH_3-S-H	Onion, garlic, leek, coffee, beer, potato
2-Furyl methanethiol		Coffee
1-Methylthioethanethiol	$CH_3SCH(SH)CH_3$	Beef
2. **Sulfides** (thioethers)		
Sym:		
Dimethyl sulfide	CH_3-S-CH_3	Milk, beer, whiskey, onion, garlic, chicken, fish, tea, filbert nut, sweet corn
Diallyl sulfide	$CH_2{=}CHCH_2SCH_2CH{=}CH_2$	Onion, garlic, leek, rakkyo
Asym:		
Methyl ethyl sulfide	$CH_3-S-C_2H_5$	Potato, cocoa, coffee
Methional (3-Methyl mercaptopropanal)	$CH_3-S-CH_2CH_2CHO$	Potato, cheese, milk, bread
Methyl furfuryl sulfide		Coffee
Methyl-(β-methylthio) propionate	$CH_3-S-CH_2CH_2COOCH_3$	Pineapple
3. **Disulfides**		
Sym:		
Dimethyl disulfide	$CH_3-S-S-CH_3$	Potato, rutabaga, cocoa, garlic, onion
Asym:		
Methyl butyl disulfide	$CH_3-S-S-C_4H_9$	Cabbage
Methyl isopropyl disulfide	$CH_3-S-S-CH(CH_3)_2$	Cocoa
Sec. Butyl propenyl disulfide	$CH_3CH_2CH(CH_3)-S-S-CH{=}CHCH_3$	Asafetida
4. **Trisulfides**		
Sym:		
Dimethyl trisulfide	$CH_3-S-S-S-CH_3$	Cabbage, chicken, garlic, onion, caucas
Diallyl trisulfide	$CH_2{=}CHCH_2SSSCH_2CH{=}CH_2$	Garlic, onion, caucas
Asym:		
Methyl allyl trisulfide	$CH_3SSSCH_2CH{=}CH_2$	Garlic, onion, caucas
Methyl-*n*-propyl trisulfide	$CH_3S-S-S-C_3H_7$	Onion, cocoa
5. **Tetrasulfides**		
Diallyl tetrasulfide	$CH_2{=}CHCH_2\text{-S-S-S-S}CH_2CH{=}CH_2$	Onion
Dimethyl tetrasulfide	$CH_3-S-S-S-S-CH_3$	Onion
6. **Thiocarbonyl**		
Methyl dithioacetate		Hops
7. **Thiocyanates**		
Allyl thiocyanate	$CH_2{=}CHCH_2SCN$	Horseradish, onion
Benzyl thiocyanate		Milk
Isobutyl thiocyanate	$(CH_3)_2CHCH_2SCN$	Cocoa

TABLE 1 (continued)

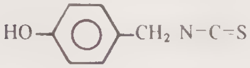
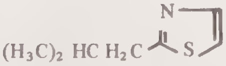
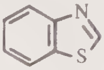
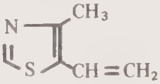
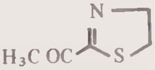
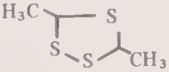
Compound	Formula	Foods
8. **Isothiocyanates**		
Methyl isothiocyanate	$CH_3N{=}C{=}S$	Cabbage, cauliflower, Brussels sprouts
Allyl isothiocyanate	$CH_2{=}CHCH_2N{=}C{=}S$	Black mustard (*Brassica nigra*), cabbage, cauliflower, Brussels sprouts
3-Butenyl isothiocyanate	$CH_2{=}CHCH_2CH_2N{=}C{=}S$	Brown mustard (*B. juncea*)
4-Methylthio-3-butenyl isothiocyanate	$CH_3SCH{=}CHCH_2CH_2N{=}C{=}S$	Radish
p-Hydroxybenzyl isothiocyanate		White mustard (*B. alba*)
9. **Sulfoxides**		
Dimethyl sulfoxide	$(CH_3)_2SO$	Peas
10. **Sulfones**		
Dimethyl sulfone	$(CH_3)_2SO_2$	Milk, butter oil, beef
11. **Sulfenic acid**		
1-Propenyl sulfenic acid	$CH_3CH{=}CH{-}S{-}OH$	Onion
12. **Thiosulfinates**		
Dimethyl thiosulfinate	$CH_3{-}SOSCH_3$	Onion
Allicin (Diallyl thiosulfinate)	$CH_2{=}CHCH_2{-}SOS{-}CH_2CH{=}CH_2$	Garlic
13. **Thiosulfonates**		
Methyl methane thiosulfonate	$CH_3SSO_2CH_3$	Onion
Propyl propane thiosulfonate	$C_3H_7SSO_2C_3H_7$	Onion
14. **Heterocyclics containing sulfur in nuclei**		
a. *Thiophenes:*		
Thiophene		Coffee
2-Formyl thiophene (Thiophene-2-aldehyde)		Coffee, bread
2-Acetyl thiophene		Coffee
Thenyl alcohol		Coffee
b. *Thiazoles*:		
Thiazole		Peanut
2-Isobutyl thiazole		Tomato
Benzothiazole		Potato, cocoa, peanut
4-Methyl-5-vinyl thiazole		Cocoa
2-Acetyl-2-thiazoline		Beef (broth)
c. *Trithiolane*		
3,5-Dimethyl-1,2,4-trithiolane		Potato, beef, filbert nut

TABLE 1 (continued)

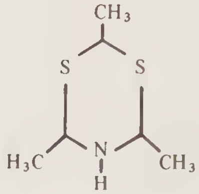
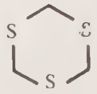
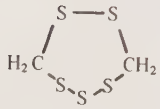
Compound	Formula	Foods
d. *Dithiazine* 2,4,6-Trimethyl-perhydro-1,3,5-dithiazine		Beef
e. *Sym:*Trithiane		Chicken
f. *Pentathiepane* 1,2,3,5,6-Pentathiepane (lenthionine)		*Shiitaké* mushroom *(Lentinus ediodes)*
15. **Miscellaneous**		
Hydrogen sulfide	H_2S	Meat, milk, beer, wine
Thiopropanal-*s*-oxide	$CH_3CH_2CH{=}S{\rightarrow}O$	Onion
Methyl thiohexanoate	$CH_3{-}S{-}CO(CH_2)_4CH_3$	Hops
Carbon disulfide	CS_2	Whiskey, coffee, parsley
Carbonyl sulfide	COS	Cabbage
Sulfur dioxide	SO_2	Onion, garlic, wine

TABLE 2

Odor Threshold of Some Sulfur Compounds

Compound	Threshold concentration (ppm) In water	In air
Hydrogen sulfide[100]	5×10^{-3}	–
Methanethiol[93]	2×10^{-5}	2×10^{-7}
Ethanethiol[5]	–	4.6×10^{-2}
Propanethiol[5]	–	6×10^{-3}
Isobutanethiol[5]	–	8×10^{-3}
Dimethyl sulfide[43,93,100,210,212]	3×10^{-4} to 6×10^{-2}	–
Diethyl sulfide[100]	3×10^{-3}	–
Dipentyl sulfide[5]	–	1×10^{-3}
Methional[43]	2×10^{-4}	–
Dimethyl disulfide[100]	3×10^{-3}	–
Dipropyl disulfide[25]	3.2×10^{-3}	–
Methyl propenyl disulfide[25]	6.3×10^{-3}	–
Propyl propenyl disulfide[25]	2.2×10^{-3}	–
Methyl isothiocyanate[5]	–	1.5×10^{-2}
Allyl isothiocyanate[5]	–	8×10^{-3}
2-Methyl mercapto acetaldehyde[43]	1.6×10^{-2}	–
2-Methyl mercaptoethanol[43]	0.12	–
2-Iso butyl thiazole[43]	3.5×10^{-3}	–
Methyl thiohexanoate[94]	3×10^{-4}	–
Methyl thioheptanoate[94]	2×10^{-3}	–
3,4-Dimethyl thiophene[25]	1.3×10^{-3}	–
Propyl methane thiosulfonate[25]	1.7×10^{-3}	–
Propyl propane thiosulfonate[25]	1.5×10^{-3}	–
Lenthionine[308]	0.27 to 0.53	–

TABLE 3

Character-impact Sulfur Compounds in Foods

Compound(s)	Food
Diallyl disulfide[158,254]	Garlic
Propyl and propenyl disulfides[25]	Boiled onion
Sec. Butyl propenyl disulfide[2]	Asafetida
Allyl isothiocyanate[7,259]	Mustard
4-Methylthio-3-butenyl isothiocyanate[80]	Radish
Propyl thiosulfonate[25]	Fresh onion
2,4- and 3,4-Dimethyl thiophene[25]	Fried onion
Lenthionine[308]	*Shiitaké* mushroom (*Lentinus ediodes*)

MILK AND MILK PRODUCTS

Milk is an important beverage which is consumed as fluid whole milk. Products such as butter, cheese, condensed milk, curd (yoghurt), etc., although derived from the same source – milk, have distinctive flavors much different from milk flavor. The flavors in these are formed during the various stages of processing, including heat treatment.

Milk

It is generally recognized that heat alters the flavor of milk.[240] The chemistry of heated milk flavor may be explained in terms of changes associated with the milk serum proteins[110,116] and changes related to the browning reaction.[208] Pasteurization of milk (143°F, 30 min or 161°F, 15 sec) is considered to have practically no effect on flavor. Dimethyl sulfone, isolated from pasteurized milk,[323] was found to be odorless.[78] However, as the heat treatment becomes severe and exceeds this point, there is a remarkable change in flavor which is evidenced from its intensity. The 'cooked flavor' of milk is evident when the milk is heated to about 74°C.[91,123] This is attributable to the sulfhydryl groups and hydrogen sulfide,[297] which are known to come from the heat denaturation of β-lactoglobulin.[110] Although the origin of these compounds can be traced to the amino acid, cysteine, the mechanism of the reaction leading to their formation has not been established. As the heat treatment of milk intensifies beyond the cooked flavor range, the evolution of volatile sulfides declines and the 'caramelized' flavor becomes evident.

Dimethyl sulfide, which occurs naturally in unheated milk, was first reported by Patton et al.[210] and subsequently by Bassette et al.[15] as possibly contributing to both normal and feed flavor in milk. Apparently this compound, having a low threshold value, also contributes significantly to the heated flavor of sterilized milk.[209] The distinct antioxidant properties of these sulfides are beneficial to the sterilized products which have less oxidized flavor.[73] Reddy et al.[227,228] found the flavor threshold from dimethyl sulfide in milk to be around 9 ppb. They employed a quantitative GC procedure for this compound in milk and found a feed-like flavor defect in some samples attributable to dimethyl sulfide, although this alone was not always the cause. According to Morgan and Pereira,[182] dimethyl sulfide was one of the major compounds detected in the neutral fractions of the volatiles from grass and corn silages which imparted a flavor that resembled some of the characteristics of feed flavor.

Quantitative GC analysis of the volatiles trapped from feed-flavored samples of milk revealed the range of concentration of dimethyl sulfide to be 25 to 45 ppb.[90] It was shown that the dimethyl sulfide content of milk was increased on heating and that this was due to a heat-labile precursor compound present in the skim milk fraction. This precursor was identified as *S*-methyl methionine sulfonium salt.[129]

Patton[207] showed that methional, formed from methionine, is responsible for the "sunlight flavor" of milk. This flavor was found to increase in the presence of riboflavin. According to Walker and Gray,[310] the off-flavor in milk obtained from dairy cows, which are fed with a cruciferous weed called land cress (*Coronopus didymus*), is due to benzyl methyl sulfide and toluenethiol. Benzyl thiocyanate appeared to be a key intermediate in off-flavor formation. Recently, Ferretti and Flanagan[75] found large amounts of dimethyl sulfone and trace quantities of benzothiazole, methylthiobenzoate, and dimethyl sulfoxide in the steam-volatile constituents of stale nonfat dry milk. Dimethyl sulfoxide was considered to be an intermediate compound during the formation of dimethyl sulfide.

Casein

Of the various compounds identified in casein, it appears that methional is the most important flavor compound.[130] Dimethyl disulfide and benzothiazole were isolated from the nonacid steam-volatile flavor fraction of the stored casein[224] and identified by GC and MS. Moreover, benzothiazole was found to constitute 4% of the nonvolatile, nonacid extract of the stored casein, its approximate concentration in casein being 0.1 ppm. It is also possible that the "gluey flavor" of stored casein might be partly due to benzothiazole.

Butter Oil

Butter oil is prepared commercially from butter where the cream is concentrated to 97 to 98% fat. In the manufacture of butter oil, more than in the case of butter, a mild-flavored product free of taints is favored so that some of the more volatile compounds would be lost due to the more severe processing. Forss et al.[78] isolated and identified the presence of dimethyl sulfone and benzothiazole in butter oil, the former in the concentration of 10 ppb and the latter in the range of 0.01 to 10 ppb. However, these were below one tenth of the threshold level. Dimethyl sulfone, an odorless compound found in butter oil, may be the oxidation product of dimethyl sulfide, which has been identified in butter.[69] The threshold of dimethyl sulfide in deodorized butter oil has been found to be 0.009 ppm; this corresponded to 0.02 ppm in fresh butter.[266] According to Forss et al.,[78] the presence of benzothiazole in butter oil might be due to its absorption during milking, the other alternative being that it might be a product of aging.[8]

Cheese

The flavor of cheese is the result of a vast number of chemical and biochemical reactions which take place sequentially or simultaneously in the protein-water-fat-mineral system which constitutes *green* cheese.[74] A great deal of work has been done on the chemical nature of cheese flavor.

Hydrogen sulfide has been identified in the flavor volatiles of cheese. Kristoffersen and Gould[146] reported it has a profound influence on the characteristic Cheddar flavor. Since it is very reactive, it could form a variety of flavorful compounds in the cheese. Keeney and Day[130] studied the role of Strecker degradation of amino acids in the development of cheese flavor. Methional, the degradation product of methionine, was found to be responsible for the cheesy brothy odor.[113,130] The positive presence of this compound has been identified[68,70] as 2,4-dinitrophenylhydrazone in the volatile flavor fraction isolated from the aged Cheddar cheese by distillation of cheese slurries at reduced pressure. This has been further supported by McGugan.[169] Because of its relatively unstable nature, methional has not been isolated. Methional has been found in irradiated sodium caseinate,[67] soft cheeses, and semisoft cheeses,[132] but there is only tentative evidence for its presence in hard cheese such as Cheddar.[151,152] The concentration of methanethiol in Cheddar cheese has been estimated to be between 3 and 30 ppb, nearer the maximum limit (25 ppb) of which it would be detectable organoleptically. The flavor threshold for this compound[66] has been reported to be 2 ppb, although the actual value may be much lower due to the unstable nature of this compound. Dimethyl sulfide has also been isolated[211] and it is probably important in cheese flavor.

MEAT, POULTRY, AND MARINE PRODUCTS

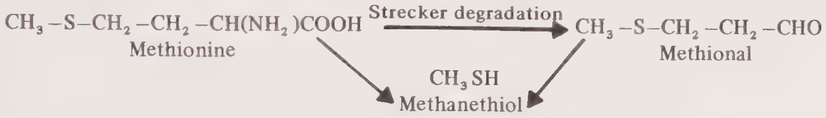
Meat

Meat is seldom consumed in the raw state. Fresh meat is subjected to different processes, such as cooking, smoking, freeze-drying, canning, curing, and irradiation. A characteristic meat flavor is common to all meat and present at varying levels in different meats or different portions of the same meat.[214] Raw meat has little flavor; the potential for the development of flavor resides in the water-soluble extract.[16] Commercial meat extract, which is a concentrate of the hot-water-soluble fraction of meat, is widely used as a source of meat flavor and serves as a useful material for the examination of the substances responsible for the flavor of cooked meat. The extensive heat treatment of meat results in many changes in the organoleptic properties. Very often the product resembles overcooked meat in regard to the texture and flavor. The heat treatment converts the precursors to volatile flavor compounds. It also helps in the release of flavor from the fats and facilitates browning reactions. Recent research has indicated that water-soluble materials in both raw and cooked meat contribute to a basic meaty flavor, whereas fat-soluble compounds are responsible in differentiating the species. Many compounds in meat are capable of entering the flavor formation steps.

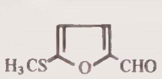
The characteristic "sulfury" meat flavor, which is developed on cooking, is derived from the water-soluble precursors that originate in the fiber. According to Luh et al.,[157] the high-temperature short-time (150°C, 31 sec) product had a "raw" taste and hydrogen sulfide and methanethiol were found among the volatile substances. On the other hand, the retorted product (122°C, 42 min) had a full, good canned-meat flavor with considerably more hydrogen sulfide and no detectable methanethiol. Cysteine, free or combined as its peptide glutathione, seemed to be involved. A possible mechanism of the conversion of cysteine to mercaptoacetaldehyde[184] by Strecker degradation is

$$HS{-}CH_2{-}CH(NH_2)COOH \xrightarrow[\text{decarboxylation}]{\text{Oxidative deamination and}} HS{-}CH_2{-}CHO$$

Mercaptoacetaldehyde is vital for the basic flavor of meat. Similarly, methionine undergoes degradation to form methional (3-methylmercaptopropanal) as well as methanethiol.[12]



It appears that methional is itself capable of further breakdown to odoriferous methanethiol.[212] Methanethiol has been identified as a constituent of meat flavor.[173] Using preparative gas chromatography, Chang and co-workers[60] isolated 18 compounds, of which 2 had a characteristic boiled beef aroma. A small GC peak that had a meaty aroma was identified as 5-thiomethyl furfural[104] (I). Another very small GC peak with a meaty odor is due to the sulfur compound analogous to furfural, viz., thiophene-2-aldehyde (II). The compound could possibly originate solely from amino acids, but may also be formed in

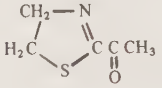


I

II

Maillard-type reactions between amino acids and sugars. The role of elemental sulfur could be played by the sulfur or the thiomethyl group of "active" methionine (adenosylmethionine). Acetone has been shown to be generated from a number of compounds in heated meat. In studies on the flavor of canned meat, Zoltowska[337] showed that methionine had a greater flavor contributing effect in Maillard-type reactions than any other amino acid.

Probably the earliest attempt to study beef flavor was by Crocker,[64] who reported "cooked beef" flavor to be more odoriferous than tasteful and indicated that hydrogen sulfide, amines of several kinds, and (possibly) indole were present. It has been demonstrated[64,144] that cooked and raw beef flavor resided largely in the water-soluble fraction. By means of GC and with the aid of MS, Stahl[275] isolated and identified some sulfur compounds, such as hydrogen sulfide, methane-, and ethanethiols in the meat volatiles obtained from an unirradiated, raw control sample. While suggesting that the characteristic flavor differences in pork and beef reside in their fat, Hornstein and Crowe,[108] demonstrated that the flavor precursors are extractable in cold water. This is in contrast to Wood's[327] opinion. It has, however, been observed that when a lyophilized powder obtained from such an extract was heated, an aroma reminiscent of roast beef developed.[107,108] In contrast, a cold-water solution of the powder developed a boiled beef aroma.[32] Heating the powder under vacuum and trapping the volatiles confirmed the presence of hydrogen sulfide as well as ammonia, ammonium chloride, formaldehyde, acetaldehyde, and acetone. The presence of hydrogen sulfide has been further confirmed by Yueh and Strong.[332] This compound seems to be one of the major components responsible for the characteristic aroma of cooked beef which is liberated during cooking from essentially odorless precursors. It was also noted that the hydrogen sulfide concentration increased when the heating period of beef was increased.[145] These investigators tentatively identified the presence of dimethyl sulfide. An ether extract of beef broth was found to contain 2-acetyl-2-thiazoline[63] (III).



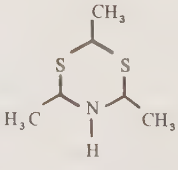
III

Brennan and Bernhard[32] measured the relative retention volumes of some sulfur compounds, such as hydrogen sulfide and methane-, ethane-, propane-, and butanethiols in canned beef.

A problem associated with radiation-sterilization of beef is the production of an unpleasant flavor and odor. Although progress has been made in the isolation and identification of the volatile components of raw and enzyme-inactivated irradiated beef, the relationship of irradiated beef was essentially unknown until Wick et al.[317] observed that volatiles increased with increased radiation. Sulfur- and nitrogen-containing compounds were responsible for much of the irradiation-induced odor and methional was claimed to be a major contributor to the off-odor. Snyder[272] supported the view that the degradation of sulfur-containing amino acids has been responsible for this type of unpleasant odor. Oxidative reactions in solutions of methionine and methionine sulfoxide followed by irradiation led to the formation of malonaldehyde.[4]

Zaika et al.[335] separated the water-soluble and low molecular weight beef aroma precursors by column chromatography. The resultant fractions developed roast beef aroma on pyrolysis (150 to 160°C) but differed in composition. The meaty aroma fraction was found to contain traces of cysteic acid and methionine. A trace constituent, isolated from lean shin of beef and purified by liquid-liquid chromatography, was analyzed by GC and identified as 2-acetyl-2-thiazoline[296] (III) on the basis of its IR and MS. This compound was found to possess an intense aroma of freshly baked bread crusts. The volatile compounds of roast beef, roast beef drippings, and boiled beef that were analyzed by GC and MS revealed the presence of sulfur compounds, such as dimethyl disulfide and dimethyl sulfone.[155] A beef flavor concentrate, which was highly flavorful, represented the original one of shallow-fried beef.[314] Organoleptic tests on the fractions obtained by the silicic acid column chromatography indicated that the various different odors resided in the beef flavor concentrate. The initial fractions of the concentrate had a thiol-like aroma, whereas a later fraction containing methional and benzothiazole had a characteristic rubber odor, which was attributed to benzothiazole. The headspace of a simmering beef broth was analyzed by GC and the components were identified by their mass, IR, and NMR spectra by Brinkman et al.,[36] who have reported the presence of *cis* and *trans* isomers of 3,5-dimethyl-1,2,4-trithiolane (IV) to be a beef flavor component. This compound and 2,4,6-trimethylperhydro-1,3,5-dithiazine (thialdine) (V) were found to form during the isolation procedure. The thialdine that is easily formed from ammonia, hydrogen sulfide, and acetaldehyde has been found to be present in the broth or the headspace of canned meat products. Likewise, 1-methylthioethanethiol, which is present in beef broth, is formed when ethanal, methanethiol, and hydrogen sulfide are heated in aqueous solution at pH 6. These are, in turn, generated under the same conditions from alanine, methionine, and cysteine in the presence of a Strecker degradation agent, such as pyruvaldehyde. These volatile compounds are the immediate precursors of 1-methylthioethanethiol.[242]

IV



V

The same three compounds also give rise to formation of dimethyl disulfide and 3,5-dimethyl-1,2,4-trithiolane in the broth.

Sulfur compounds appear to have both desirable and undesirable effects on the meat aroma. A most undesirable compound, 4-mercapto-4-methylpentane-2-one,[274] has been reported in some samples of canned beef. While it is not a component of meat aroma, it is produced by the reaction of hydrogen sulfide from cooked meat with mesityl oxide. This compound has an unpleasant cat urine odor and is definitely a flavor defect. von Sydow[305] described the importance of some sulfur compounds to canned beef off-flavor by stepwise regression analyses. The compounds, in order of decreasing importance, are 2-methylthiophene, dimethyl sulfide, dimethyl disulfide, thiophene, and methanethiol.

Poultry

Poultry flavor is said to originate in the meaty broth,[214] in the fat,[29,30] and in any tissue in which cooking takes place.[64] Some factors that may be responsible for poultry flavor include sex and age of the bird, stability of lipid components, particularly as related to diet and autoxidation, and the development of labile sulfur and carboxyl compounds.[295] However, the influence of processing steps such as chilling, freezing, packaging, cooking, canning, dehydration, irradiation, and storage cannot be ruled out in this regard. Thus, the importance of gaining insight into the origin of poultry flavor has been increasing for several years.

The characteristic aroma of cooked poultry consists of a blend of compounds. It is hardly possible to define the reactants, products, and reactions that contribute to cooked poultry flavor and aroma. Bouthilet[27-30] demonstrated the presence of hydrogen sulfide in the volatile fraction of cooked chicken and obtained results suggesting the importance of an organic sulfur compound to chicken flavor and Pippen and Eyring[216] reported that other compounds also play an important role in chicken flavor. Minor et al.[178] indicated that the sulfur compounds were responsible for the "meaty" aroma of cooked chicken. Shrimpton and Grey[265] reported the presence of 23 volatile components in chicken muscle. Tentative identification of 15 of these revealed the presence of sulfides and thiols which are given in Table 4A. Nonaka et al.[195] reported more sulfur compounds in boiled chicken meat, which are also included in Table 4A. On cooking, the sulfur compounds were shown to decompose significantly, liberating a variety of flavored by-products.[12,217] In roasted chicken leg meat, Swoboda[292] identified dimethyl trisulfide, at a concentration of 10 ppb, as a very strong aroma component. The volatile components of raw chicken breast muscle as well as the ceca of both living and dead birds have been analyzed;[92] the findings are reported in Table 4B.

Fat of raw poultry, separated from solid tissue and washed with water at temperatures not exceeding 40°C, does not contain cooked poultry aroma and does not develop it when heated, but it acquires more sulfur on cooking. Less than 2% of this sulfur build-up occurs as hydrogen sulfide.[215] In chicken meat heated for 1 hr in the range of 70 to 125°C, about 92% of hydrogen sulfide was produced.[206] This compound is known to evolve continuously from simmering chicken and, hence, contributes to its aroma. The occurrence of hydrogen sulfide in broth of freshly simmered chicken and in the freshly cooked ready-to-eat meat of simmered, roasted, and fried chicken, as well as its contribution directly to the flavor of these products, has been well established.[217] The amount of hydrogen sulfide in fresh cooked chicken is

TABLE 4A

Identification of Sulfur Compounds in Chicken[195,265]

Thiols	Sulfides	Disulfides	Miscellaneous
Methanethiol	Dimethyl sulfide	Dimethyl disulfide	Carbonyl sulfide
Ethanethiol	Diethyl sulfide	Diethyl disulfide	Carbon disulfide
Propanethiol	Dipropyl sulfide		2-Methyl thiophene
1,2-Ethanedithiol	Methyl ethyl sulfide		*Sym.* Trithiane
n-Hexanethiol	Methyl *n*-propyl sulfide		
	Methyl isopropyl sulfide		
	Ethyl *n*-propyl sulfide		

TABLE 4B

Identification of Volatile Components from Breast Muscle[92]

Compound	Source Muscle or cecum
Methanethiol	Cecum
Ethanethiol	Both
Propanethiol	Cecum
Butanethiol	Muscle
Dimethyl sulfide	Both
Dimethyl disulfide	Cecum
Hydrogen sulfide	Both

in the region of 180 to 730 ppb, which is far more than its threshold value. Moreover, freezing, thawing, and reheating can reduce the hydrogen sulfide in the broth to subthreshold levels, thus indicating the transient nature of its direct contribution to aroma. An alternative approach could be that hydrogen sulfide may contribute indirectly to cooked poultry flavor by forming secondary products. The possibility for forming such products by reactions between hydrogen sulfide and carbonyls is particularly interesting because these ingredients occur in poultry and they will react with one another. Symmetric (*sym.*) trithiane (VI) reported in cooked chicken[178] could form from a reaction between hydrogen sulfide and formaldehyde. Thus, hydrogen sulfide is a direct and potentially indirect contributor to cooked chicken aroma.

VI

Potential sulfur precursors in poultry meat are compromised of methionine, cysteine, cystine, taurine, and glutathione. Other sulfur compounds common to natural foods, such as biotin, thiamine, and coenzyme A, are also the possible precursors. However, except for hydrogen sulfide, there is little direct evidence that specifically links the volatile sulfur compounds of cooked chicken to any of these sulfur sources. Koehler and Jacobson[139] identified methionine in fractions from white and dark meat chicken extract. It has been reported that Strecker degradation of methionine gives rise to methional and dimethyl disulfide.[217] Hence, these two sulfur compounds may be formed in cooked chicken by a similar mechanism. Pippen[213] suggested that the presence of thiols and sulfides, linked to alkyl groups (up to hexyl), is an indication that sulfur-containing amino acids break down by a mechanism more complex than the Strecker degradation. Bouthilet[30] was the first to conclude that the true precursor of hydrogen sulfide was glutathione. Later, Mecchi et al.[171] showed that the principal precursor in chicken muscle nonprotein is sulfur, occurring as cysteine and/or cystine in the tripeptide glutathione. This nonprotein isolate from leg muscle began to produce hydrogen sulfide only after 2½ hr boiling. Glutathione, in the amounts found in muscle, caused hydrogen sulfide production of less than 10% of that given by whole muscle. Isolated chicken leg protein was also less efficient (80%) as a hydrogen sulfide producer.[105]

Relatively very little attention has been shown toward the study of the flavor chemistry of eggs. Hydrogen sulfide has been detected and determined in boiled eggs.[291]

Marine Products

It has long been recognized that hydrogen sulfide is an important odoriferous principle in canned salmon.[226,294] The "petroleum odor" of canned chum salmon has been shown to be due to the presence of dimethyl sulfide,[185] which is also reported in frozen haddock.[163,175] This sulfide is formed from dimethyl-β-propiothetin, which is transported from pteropoda (*Limacina helicinia*), a kind of zooplankton, eaten by chum salmon:

$$(CH_3)_2SHCH_2CH_2COOH \longrightarrow (CH_3)_2S + CH_3CH_2COOH$$

TABLE 5

Organo-sulfur Compounds Identified in Oysters[232]

Thiols

Methanethiol
Ethanethiol
1-Propanethiol
2-Propanethiol
1-Butanethiol
2-Butanethiol
2-Methyl-1-propanethiol
2-Methyl-2-propanethiol
3-Methyl-1-butanethiol

Sulfides

Dimethyl sulfide
Diethyl sulfide
Methyl ethyl sulfide
Methyl-*n*-propyl sulfide
Methyl-*n*-butyl sulfide

Disulfide

Dimethyl disulfide

Miscellaneous

Hydrogen sulfide

The formation of the sulfide increases in the presence of volatile phosphoric compounds, as in meat containing bone. On the other hand, the red salmon has no petroleum odor because it seldom eats *Pteropoda*; furthermore, the propiothetin is transformed into methionine during digestion.

Traces of methanethiol have been found in fish.[197,201,204] The unpleasant odor that emanates from codfish[269] has been ascribed to dimethyl sulfide, which may be eliminated considerably by the freeze-drying process. On the other hand, dimethyl sulfide has been reported to be responsible for the characteristic odor of fresh Pacific oysters[232] (*Crassotrea gigas* Thunberg). The volatile organosulfur compounds identified in stored oysters (21°C) are shown in Table 5.

Yueh[331] isolated dimethyl sulfide from fresh raw oysters and hydrogen sulfide, methanethiol, and dimethyl disulfide from boiled oysters. Schiff,[241] Bywood and Challenger,[45] Cantoni and Anderson,[46] Challenger and Simpson,[59] and Challenger et al.[56] observed the evolution of dimethyl sulfide from marine algae and indicated the possible origin from dimethyl-β-propiothetin by enzymic action. Haas,[99] Katayama[127] and Obata et al.[198] also found this sulfide in the volatile compounds of algae.

VEGETABLES

The study of the flavor chemistry of vegetables has received much less attention compared with other foods. A few vegetables such as onion, garlic, cabbage, cauliflower, radish, etc., which possess strong and distinctive flavors, have been studied intensively, whereas beans, peas, carrots, gourds, etc. have been examined superficially. The potato and its products have been studied in detail mainly because of their commercial and economic importance. A few vegetables, such as the tomato, carrot, cucumber, and onion are consumed both in raw and cooked forms, although most of the vegetables are eaten cooked. Many workers have investigated the flavor of raw vegetables as well as cooked vegetables and the changes that occur during storage.

Alliums

Allium is a genus of bulbous herbs, comprising about 500 species. These plants are characterized by their strong odor. Sulfur compounds are responsible, to a large extent, for the characteristic flavor of alliums. The enzymatic development of flavor in allium plants[48,245,249,273] has been known for some time. The general reaction[287] for the flavor genesis in alliums is

$$\underset{S\text{-alk-(en)-yl cysteine sulfoxide}}{R\,S(O)CH_2\,CH(NH_2)\,COOH} \xrightarrow{\text{alliinase}} R\,S(\text{volatile}) + NH_3 + CH_3\,CO\,COOH$$

The kinetics of this reaction has been studied by Schwimmer and Guadagni.[248] The naturally occurring substrates are *S*-substituted derivatives of L-cysteine sulfoxide. The enzyme is called by different names, i.e., alliinase, lyase, etc. The reaction takes place and the flavor compounds are formed only when the cells are ruptured and the enzymes and substrates come into contact. The primary product of the enzyme reaction is believed to be sulfenic acid.[247,273]

$$RSOCH_2CH(NH_2)\,COOH + H_2O \rightarrow \underset{\text{Sulfenic acid}}{RSOH} + NH_3 + CH_3COCOOH$$

The unstable sulfenic acids immediately give rise to thiosulfinates, which in turn decompose into disulfides, thiosulfonates, trisulfides, etc.

$$R_1\,SOH + R_2\,SOH \xrightarrow{-H_2O} \underset{\text{Thiosulfinate}}{R_1\,SSOR_2}$$

$$2RSSOR \longrightarrow RSSR + \underset{\text{Thiosulfonate}}{RSSO_2\,R}$$

$$2RSSOR \longrightarrow RSSR + RSR + SO_2$$

$$2RSSR \longrightarrow RSR + RSSSR$$

Garlic (Allium sativum L.*)*

The earliest work on garlic oil was by Wertheim,[315] who reported that it consists chiefly of diallyl sulfide. In 1892, Semmler[254] reported that there was no diallyl sulfide in garlic oil, but found a disulfide ($C_6H_{10}S_2$) which was considered to be responsible for the garlic odor. Cavallito and Bailey[54] and Cavallito et al.[52,53] extracted ground garlic cloves with alcohol and obtained a colorless liquid, possessing a characteristic odor different from the previously reported odor of sulfides. A compound having an empirical formula of $C_6H_{10}OS_2$ was isolated from the oil and identified as allicin. They also found the evidence for a precursor which, when acted upon by an enzyme present in garlic, gave rise to allicin. Stoll and Seebeck[285] isolated the precursor of allicin, which they designated as alliin. The reaction is

$$\underset{\text{Alliin}}{2CH_2 = CHCH_2\,SOCH_2\,CH(NH_2)COOH} + H_2O \xrightarrow{\text{Alliinase}}$$
$$\underset{\text{Allicin}}{CH_2 = CHCH_2\,SOS\,CH_2\,CH = CH_2} + 2NH_3 + 2CH_3\,COCOOH$$

Fujiwara et al.[81] studied garlic and the related alliums. They reported small amounts of methyl, methyl *n*-propyl, and *n*-propyl allicins, moderate amounts of methyl allyl and *n*-propyl allyl allicins, and large amounts of allyl allicin in garlic. Saghir et al.[234] found methyl allyl disulfide and diallyl disulfide in large amounts, along with small amounts of dimethyl disulfide and diallyl sulfide in garlic. Oaks et al.[196] found the following compounds in the headspace of garlic: dimethyl sulfide, methyl allyl sulfide, dimethyl disulfide, diallyl disulfide, methyl allyl disulfide, dimethyl trisulfide, methyl *n*-propyl trisulfide, and methyl allyl trisulfide. Brodnitz et al.[38] found diallyl thiosulfinate (allicin) as the major component of garlic oil.

Saghir et al.[234] assigned the odor of fresh garlic to allicin and the less pleasant smell of cooked or boiled garlic to di- and trisulfides, which are the breakdown products of allicin. Bernhard and co-workers[21,114]

TABLE 6

Sulfur Volatiles in Garlic*

Thiol

Methanethiol

Sulfides

Dimethyl sulfide
Diallyl sulfide
Methyl allyl sulfide

Disulfides

Dimethyl disulfide
Dipropyl disulfide
Diallyl disulfide
Allyl propyl disulfide
Methyl allyl disulfide

Trisulfides

Dimethyl trisulfide
Diallyl trisulfide
Methyl propyl trisulfide
Methyl allyl trisulfide

Thiosulfinate

Diallyl thiosulfinate

Miscellaneous

Sulfur dioxide

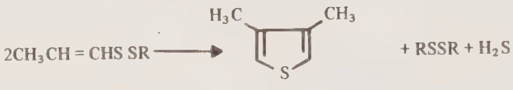
*References 21, 38, 52–54, 81, 114, 196, 234, 254, 285.

reported a number of sulfur compounds in garlic. The various sulfur compounds identified in garlic are listed in Table 6.

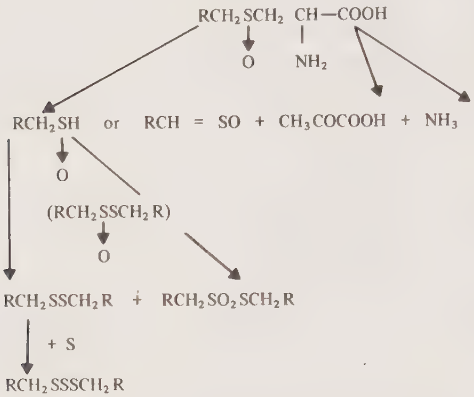
Onion (A. cepa L.*)*

Since Semmler[255] investigated the volatile oil of onion, there have been several thorough studies on the flavor complex of onion. Carson[47] reviewed onion flavor, including the work until 1966. There have been several reviews dealing with the flavor components in alliums[19] and vegetables in general.[118,158,247]

Following the discovery of allyl-*S*-cysteine sulfoxide as the flavor precursor in garlic, methyl, propyl, and propenyl derivatives of L-cysteine sulfoxide were identified in onion.[18,39,50,168, 180,244,245,261] Methyl and propyl-propenyl disulfides have been recognized as important constituents of onion oil.[37] Saghir et al.[234] assigned the common onion odor to dipropyl disulfide. According to Stahl,[275] however, the dipropyl disulfude has a sweet smell but, in combination with propanethiol, gives onion-like odor. Bernhard[18] obtained a correlation between flavor intensity of onion and the disulfide concentration. Recently, Boelens et al.[25] studied the flavor spectrum of fresh, boiled, and fried onion. Their comprehensive studies, using GC, IR, NMR, and MS for identification and sensory studies for correlation, yielded the following results: Propyl thiosulfonate contributes to the fresh onion aroma and boiled onion flavor is due to propyl and propenyl di- and trisulfides. The sweetness of cooked onions is due to *n*-propanethiol (formed during boiling) which is 50 to 70 times sweeter than sucrose. The fried onion aroma is due to dimethyl thiophene. The following mechanisms have been given for the formation of thiophene derivatives and sulfur compounds:[25]



Dimethyl thiophene



R = hydrogen or ethyl

An interesting feature of onion flavor is the lachrymatory factor formed during crushing of onion. The nature of this was studied by various workers. Kohman[140] suggested that it was thiopropanal. Wilkens[320] and Brodnitz and Pascale[39] isolated a compound from onion which they considered to be the lachrymator. This was assigned the structure CH_3CH_2CHSO (thiopropanal- *S*-oxide). In a series of communications, Virtanen and co-workers[180,304] suggested that the lachrymatory factor is derived by enzymatic splitting of the precursor, *S*-propenyl cysteine sulfoxide:

$$CH_3CH=CHSOCH_2CH(NH_2)COOH \longrightarrow CH_3CH{=}CHSOH + NH_3 + CH_3COCOOH$$

Propenyl sulfenic acid

They believed that propenyl sulfenic acid is the lachrymator. Schwimmer and Friedman,[247] after examining the available evidence, suggested that the initial product is the sulfenic acid, with a half-life of 90 sec, which undergoes rearrangement to the more stable isolatable thiopropanal-*S*-oxide.

After examining 25 species of wild alliums of the onion family, Saghir and Mann[235] found that they have no lachrymatory effects. The precursor of the lachrymatory factor was, therefore, presumed to be absent. These authors, however, state that these wild alliums have considerable flavor and aroma. One should, therefore, conclude that the lachrymator is not an important factor in onion flavor.

It should be noted that the flavor compounds of onion originate from the precursors by enzymic action and subsequent rearrangements. Hence, the flavor strength should depend on the flavor precursor available for enzyme action. About 50% of the precursor in onion is present as γ-L-glutamyl peptide and, as such, is insusceptible to the enzyme action. Schwimmer[246] has shown that the peptide bond can be broken down by transpeptidase, enzymes, thereby releasing the flavor precursor to be subsequently acted on by the lyase enzyme. This finding should be of great value in enhancing and supplementing the flavor of dehydrated onion and its products in which the flavor losses are reported to be very high.[18] A number of sulfur compounds have been identified and reported in literature;[49,57,83,193,251,303,307,316,333] these are listed in Table 7.

TABLE 7

Sulfur Volatiles in Onion*

Thiols

Methanethiol
Ethanethiol
Propanethiol
2-Propene-1-thiol
2-Hydroxy propanethiol

Sulfides

Dimethyl sulfide
Diallyl sulfide
Dipropenyl sulfide (three isomers)
Allyl methyl sulfide
Allyl propyl sulfide
Methyl propenyl sulfide (two isomers)
Propenyl propyl sulfide (two isomers)

Disulfides

Dimethyl disulfide
Dipropyl disulfide
Diallyl disulfide
Dipropenyl disulfide
Methyl propyl disulfide
Methyl allyl disulfide
Allyl propyl disulfide
Isopropyl propyl disulfide
Methyl propenyl disulfide (*cis* and *trans*)
Propyl propenyl disulfide (*cis* and *trans*)
Allyl propenyl disulfide (two isomers)

Trisulfides

Dimethyl trisulfide
Dipropyl trisulfide
Diallyl trisulfide
Methyl propyl trisulfide
Methyl allyl trisulfide
Allyl propyl trisulfide
Isopropyl propyl trisulfide
Methyl propenyl trisulfide (*cis* and *trans*)
Propyl propenyl trisulfide (*cis* and *trans*)

Tetrasulfides

Dimethyl tetrasulfide
Diallyl tetrasulfide

Thiophenes

2,5-Dimethyl thiophene
2,4-Dimethyl thiophene
3,4-Dimethyl thiophene
3,4-Dimethyl-2(5H)-thiophene

Thiosulfonates

Methyl methane thiosulfonate
Propyl methane thiosulfonate
Propyl propane thiosulfonate

Thiosulfinates

Dimethyl thiosulfinate
Dipropyl thiosulfinate

Miscellaneous

Hydrogen sulfide
Sulfur dioxide
Allyl thiocyanate
Thiopropanal
2-Thiopropanal
3-Hydroxy thiopropanal
Thiocyanic acid
Thiopropanal-*S*-oxide
Propenyl sulfenic acid

*References 18, 19, 39, 47, 49, 57, 83, 118, 158, 193, 247, 251, 303, 307, 316, 320, 333

Other Alliums

Chive (A. schoenoprasum L.*)*

Saghir et al.[234] studied chives and reported the presence of six sulfur compounds. Wahlroos et al.[309] analyzed the flavor spectrum of chives. They considered the following compounds responsible for its characteristic flavor, viz., 2-methyl but-2-enal, 2-methyl pent-2-enal, dipropyl disulfide, propyl-*cis*-2-propenyl disulfide, and propyl-*trans*-2-propenyl disulfide. The sulfur compounds identified in chives are given in Table 8.

Rakkyo (A. chinense)

Jacobsen et al.[114] and Saghir et al.[234] studied this species of allium. The following sulfur compounds were identified: diallyl sulfide, dimethyl disulfide, methyl propyl disulfide, dipropyl disulfide, allyl propyl disulfide, diallyl disulfide and methyl allyl disulfide.

TABLE 8

Sulfur Volatiles in Chives and Leek[234,251,309,334]

Chives

Sulfide and disulfides

- Diallyl sulfide
- Dimethyl disulfide
- Methyl propyl disulfide
- Methyl allyl disulfide
- Dipropyl disulfide
- Allyl propyl disulfide
- Propyl propenyl disulfide (*cis* and *trans*)
- Diallyl disulfide

Leek

Thiols

- Methanethiol
- Ethanethiol
- Propanethiol

Sulfides

- Dimethyl sulfide
- Diallyl sulfide

Disulfides

- Dipropyl disulfide
- Diallyl disulfide
- Methyl propyl disulfide
- Methyl allyl disulfide
- Allyl propyl disulfide

Thiosulfinates

- Dimethyl thiosulfinate
- Dipropyl thiosulfinate
- Methyl propyl thiosulfinate
- Methyl allyl thiosulfinate
- Allyl propenyl thiosulfinate
- Propyl propenyl thiosulfinate

Miscellaneous

- Hydrogen sulfide

Leek (A. porrum L.*)*

The flavor of leek has been studied by Saghir et al.,[234] Self et al.,[251] and Yoshimura.[334] The compounds identified are included in Table 8.

Caucas (A. victorialis)

Nishimura et al.[194] studied caucas flavor and identified as many as ten sulfur compounds. They are methyl allyl sulfide, dimethyl disulfide, diallyl sulfide, methyl propyl disulfide, methyl propenyl disulfide, methyl allyl disulfide, dimethyl trisulfide, propyl allyl disulfide, diallyl disulfide, and methyl allyl trisulfide.

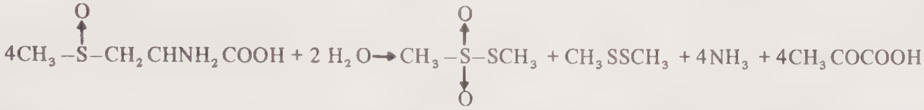
The allicins and sulfides are generally recognized as the principal sources of flavor and aroma in *Allium* species. Bernhard[17,19] correlated the disulfide content with the aroma and flavor of various alliums. The differences in odor among the species are accounted for by the nature and quantity of the sulfur compounds present. For example, allyl disulfide has a distinct garlic-like odor, whereas *propyl disulfide* has the odor of common onion. Other alliums with odors similar to onion are the Japanese bunching onion, chive, and leek. These also contain predominantly propyl disulfide. Rakkyo and Chinese chives (*A. tuberosum*) have high proportions of methyl compounds and their smell resembles that of cabbage. Although the number of sulfur compounds depends on the amino acid precursors, the characteristic odor may be due to only one particular compound. For example, although onion contains methyl, propyl, and propenyl derivatives, the odor is mainly due to propyl sulfides. Saghir and Mann[235] reported that the propyl and allyl content of any species could be roughly estimated by their odor. These two radicals dominate the odor, so that even in species like Chinese chives, where the methyl concentration is very high, the allyl odor is more predominant. Recently, Bernhard[20] studied the distribution of volatile sulfur compounds in a number of "Old World alliums" and used the data for chemotaxonomy. Apart from variations due to species and varietal differences in the flavor, the effect of seasonal and climatic changes on the flavor spectrum of alliums is worth studying.

Cabbage and Related Crops

Cabbage (*Brassica oleracea* L.), Brussels sprouts (*Brassica oleracea* var. *gemmifera*), cauliflower (*Brassica* *oleracea* var. *botrytis* L.), sprouting broccoli (*Brassica oleracea* var. *italica*), and rutabagas (*Brassica napus* or *napobrassica*) are considered in this section.

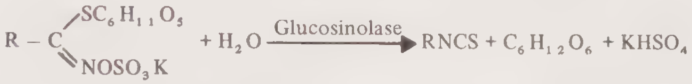
As early as 1929, Konig and Kracht[143] reported the presence of hydrogen sulfide and methanethiol in cabbage. Using paper chromatographic technique, Jensen and Kjaer[117] found the presence of allyl isothiocyanate in white and red cabbage and 3-butenyl isothiocyanate in red cabbage. Clapp et al.[61] converted the isothiocyanates of the cabbage steam distillate into their thioureas and, by employing paper chromatography and infrared spectroscopy, they identified allyl, 3-butenyl, 3-methyl thiopropyl, and 3-methyl sulfinyl propyl isothiocyanates.

Simpson and Halliday[267] were the first to investigate the flavor volatiles of cooked cabbage and found hydrogen sulfide, which was considered to form as a result of the hydrolysis of allyl isothiocyanate. Later, Dateo et al.[65] wrongly concluded the major flavor components to be hydrogen sulfide and dimethyl disulfide. *S*-methyl-*L*-cysteine sulfoxide, isolated by Synge and Wood,[293] accounts for 25% of the free sulfur; it has been shown to be the main precursor of dimethyl disulfide.



$$4CH_3-\overset{\overset{O}{\uparrow}}{S}-CH_2CHNH_2COOH + 2\,H_2O \rightarrow CH_3-\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}-SCH_3 + CH_3SSCH_3 + 4NH_3 + 4CH_3COCOOH$$

MacLeod,[158] however, did not obtain enough dimethyl disulfide to justify its importance and indicated that the precursor might as well produce other volatiles. Challenger[55] reported that the characteristic odor and taste of cabbage are due to complex thioglucosides which, on enzymic hydrolysis, yield glucose, potassium, hydrogen sulfate, and the pungent isothiocyanate, as given below:



$$R-C\begin{matrix}\diagup SC_6H_{11}O_5\\ \diagdown\!\diagdown NOSO_3K\end{matrix} + H_2O \xrightarrow{\text{Glucosinolase}} RNCS + C_6H_{12}O_6 + KHSO_4$$

where R = allyl, 3-butenyl, 3-methyl thiopropyl, or 3-methyl sulfinylpropyl. Bailey et al.[9] used GC-MS in the analysis of cabbage flavor. They examined the volatile fractions obtained by vacuum steam distillation amd fractionation of fresh, dehydrated, and rehydrated cabbage (Table 9).

The identification of five isothiocyanates suggested the presence of the corresponding thioglucosides from which the isothiocyanates are released by enzymatic hydrolysis. In addition, the presence of methyl thiomethyl and methyl thiobutyl isothiocyanates was indicated. The study showed a partial or complete loss of the volatile sulfur compounds in the processed samples compared to the fresh cabbage. The reconstitution of the dehydrated product with water and glucosinolase gave allyl, *n*-butyl, and 3-butenyl isothiocyanates. This suggested the survival of the parent thioglucoside precursors during the dehydration process.

The origin of sulfides was postulated from a number of sulfur compounds such as sulfoxides, thioglucosides, sulfur-containing amino acids, and sulfonium compounds. Carbonyl sulfide, hydrogen sulfide, and carbon disulfide were explained[9] to originate as a result of hydrolysis of isothiocyanates:

$$RNCS + H_2O \rightarrow RNH_2 + COS$$
$$COS + H_2O \rightarrow H_2S + CO_2$$
$$2\,RNCS + 2\,H_2O \rightarrow 2RNH_2 + CO_2 + CS_2$$

Furthermore, the formation of carbon disulfide might also be due to the following reaction:

$$2\,RNCS + H_2S \rightarrow RNHCSSH \rightarrow RNH_2 + CS_2$$

The survival of the nonvolatile, relatively heat-stable precursors is important in the processed foods since, by the addition of proper enzymes, the natural flavor can be restored. For example, Bailey et al.[9] treated dehydrated cabbage with a cabbage glucosinolase during reconstitution and obtained an improved cabbage flavor. Schwimmer[243] used mustard glucosinolase instead and obtained a pungent flavor.

Self et al.[251] studied a large number of cooked foods, including cauliflower and Brussels sprouts, and observed a similar pattern of low boiling volatiles, viz., large amounts of hydrogen sulfide, methanethiol,

TABLE 9

Distribution of Sulfur Compounds in Fresh, Dehydrated, and Rehydrated Cabbage[9]

Compound	Fresh	Dehydrated	Rehydrated
Isothiocyanates			
Methyl isothiocyanate	+	0	0
n-Butyl isothiocyanate	+	0	+
3-Butenyl isothiocyanate	+	0	+
Allyl isothiocyanate	+	0	+
3-Methyl thiopropyl isothiocyanate	+	0	0
Sulfides			
Dimethyl sulfide	+	+	+
Diethyl sulfide	+	0	0
Dibutyl sulfide	+	0	0
Disulfides			
Dimethyl disulfide	+	0	+
Diethyl disulfide	+	0	0
Dipropyl disulfide	+	0	0
Diallyl disulfide	+	0	0
Methyl ethyl disulfide	+	0	0
Ethyl propyl disulfide	+	0	0
Propyl butyl disulfide	+	0	0
Propyl allyl disulfide	+	0	0
Trisulfide			
Dimethyl trisulfide	+	0	0
Miscellaneous			
Hydrogen sulfide	+	0	0
Carbonyl sulfide	+	0	+
Carbon disulfide	+	0	+
Tentative			
Methyl thiomethyl isothiocyanate	+	0	0
Methyl thiobutyl isothiocyanate	+	0	0
Diethyl trisulfide	+	0	0

dimethyl sulfide, and traces of ethanethiol. The higher boiling volatiles were, however, not considered and some of these might be specifically present in one particular vegetable and completely absent in another. The determination of such higher boiling volatiles, as well as the relative proportions of the low boiling components, could be of considerable importance in distinguishing the flavor of cooked vegetables. MacLeod and MacLeod[159] analyzed the volatiles of cooked cabbage, cauliflower, and Brussels sprouts by using gas chromatography and mass spectrometry. They reported the relative abundance of dimethyl sulfide, dimethyl disulfide, methanethiol, methyl propyl disulfide, and the isothiocyanates of methyl, allyl, and *n*-butyl (Table 10). The proportion of these compounds depended very much on the cooking time. The same authors[160] also studied the efects of variation in the period of cooking time (5 to 90 min), the use of microwave radiations on the flavor volatiles of cabbage, and measured the amount of the individual flavor components. In general, sulfur volatiles increased with the time of cooking, and new compounds, such as dipropyl and methyl butyl disulfides, were formed when microwave radiations were employed for cooking. The recent work of Maruyama[166] shows that dimethyl trisulfide is a major aroma component in the cooked brassicaceous vegetables, such as cabbage, cauliflower, broccoli, and Brussels sprouts. The formation of this compound was explained to result from the reaction of unstable sulfenic acid (an intermediate compound formed during dimethyl disulfide formation) with hydrogen sulfide as follows:

$$2CH_3SOH + H_2S \rightarrow CH_3S_3CH_3 + 2H_2O$$

TABLE 10

Relative Amounts of the Sulfur Volatiles in Brassicas[159]

Sulfur compound	Approximate % relative abundance in		
	Cabbage	Brussels sprouts	Cauliflower
Thiol			
Methanethiol	0.5	0.05	0.5
Sulfides			
Dimethyl sulfide	26.5	11.5	26.5
Dipropyl sulfide	–	–	0.05
Disulfides			
Dimethyl disulfide	1.0	1.5	0.5
Methyl propyl disulfide	1.0	1.0	0.5
Butyl methyl disulfide or Propyl isothiocyanate	–	–	0.5
Isothiocyanates			
Methyl isothiocyanate	0.5	0.5	0.5
n-Butyl isothiocyanate	1.0	0.5	0.5
Allyl isothiocyanate	6.5	2.0	4.5

It is generally agreed that the heart of the cabbage has a much stronger flavor than the outer leaves when both are cooked in exactly the same way. The oxidation of the flavor distillates of the inner and outer leaves of cabbage with chloramine-T showed higher content of organic sulfur compounds in the inner leaves,[223] which has been established by MacLeod and MacLeod[160] using gas chromatography. In general, dimethyl sulfide, dimethyl trisulfide, and allyl isothiocyanate seem to contribute to the characteristic cabbage flavor.

Rutabaga

This is a strong-flavored turnip-like vegetable. Hing and Weckel[106] identified hydrogen sulfide, dimethyl sulfide, and dimethyl disulfide and detected the presence of mercaptans and isothiocyanates in the steam distillates of rutabaga. They concluded that these compounds were mainly responsible for the strong pungent odor. 2-Phenyl ethyl isothiocyanate has been reported to occur in turnips.[153,154]

Radish (*Raphanus sativus* L.)

In 1846, Pless[218] reported that steam distillation of radish root gave a sulfur-containing oil, possessing the taste but not the odor of fresh radish. From steam distillates of radish, Bertram and Walbaum[22] obtained an oil which did not react with ammonia. Gadamer[82] ether-extracted the sliced root material and obtained a sulfur-containing oil which possessed the characteristic odor and taste of fresh radish. He believed that the oil was produced by enzymatic decomposition of a glucosidic progenitor. The oil reacted with ammonia to give a product with properties suggestive of a thiourea structure. Many years later, Heiduschka and Zwergal[103] obtained a distilled radish root oil. They isolated a compound which they concluded was either 4-(butyl(thio)-3-butenyl isothiocyanate ($CH_3(CH_2)_3$)-S-CH=CH$(CH_2)_2$NCS) or 4-(butyl(thio) butyl isothiocyanate ($CH_3(CH_2)_3S(CH_2)_4NCS$). Using paper and gas chromatography of methanolic extract of radish, followed by mass and nuclear magnetic resonance spectroscopy, Friis and Kjaer[80] showed that the pungent principle in radishes was 4-methylthio-3-butenyl isothiocyanate ($CH_3SCH{=}CH(CH_2)_4NCS$). This isothiocyanate is probably produced from 4-methylthio-3-butenylglucosinolate by rapid enzymatic hydrolysis. Recently, Brandsma et al.[31] reported the synthesis of this isothiocyanate.

Horseradish (*Armoracia lapathifolia* Gilib)

The principal pungent compounds in the roots of the horseradish have been shown to be allyl and

2-phenyl ethyl isothiocyanates.[112,276,286] Recently, Gilbert and Nursten[87] studied the essences of the volatile components of five samples of horseradish root, viz., English (mineral soil, peaty soil), Hungarian, and dried flakes of Hungarian and Japanese and found the presence of 17 compounds using GC-MS. Five of these have been rigorously identified, viz., allyl thiocyanate, allyl-2-butyl-, 4-pentenyl-, and 2-phenyl ethyl isothiocyanates. Evidence has been shown for the presence of methyl, ethyl, and isopropyl isothiocyanates. Using paper and GC and UV spectroscopy, 2-butyl isothiocyanate was also previously identified in *Wasabi*[187a] and Japanese horseradish.[141,142] The fine odor of Hungarian horseradish (preferred by the manufacturers of processed horseradish products) has been attributed not only to the natural occurrence of 4-pentenyl isothiocyanate but also to its high content of it.

Potato (*Solanum tuberosum* L.)

In a concise review on the varieties of potato, Salaman[237] suggested that the strength of potato flavor was a varietal characteristic. The aroma of boiled potatoes is mainly due to a mixture of low-boiling volatiles; its strength increases when the temperature of the cooking liquor is above 194°F. Kroner and Wegner[147] analyzed the steam volatile constituents of potatoes and detected esters, fatty acids, and a high-boiling sulfur compound. Self et al.,[251,252] Gumbmann and Burr,[97] and, recently, Buttery et al.[42] analyzed the cooked flavor of potato; a list of sulfur-containing volatiles is given in Table 11. Gumbmann and Burr[97] found that dimethyl disulfide and methanethiol constituted 90% of the total sulfide, with dimethyl sulfide and ethanethiol adding a further 7% by weight. Hydrogen sulfide was produced in relatively large amounts (200 to 500 ppb per hr) over extended periods from cooking either fresh or dehydrated potatoes. Potatoes stored for a longer period showed higher concentrations of hydrogen sulfide, methanethiol, and dimethyl sulfide. Self[250] and Neilson and Caul[189] observed that the addition of salt to the cooking potatoes suppressed the amount of dimethyl sulfide, methanethiol, hydrogen sulfide, and other volatile compounds in the headspace. Self et al. and Gumbmann and Burr agreed upon the importance of volatile sulfur-containing compounds in potato flavor.

Raw potatoes do not have any of the characteristic flavors of cooked potatoes. It is, therefore, evident that the odor of cooked potatoes must arise from odorless precursors by enzymic and/or thermal

TABLE 11

Volatile Sulfur Compounds from Cooked Potatoes[42,97,251,252]

Compound	Percent (w/w)
Thiols	
Methanethiol	45.00
Ethanethiol	5.00
n-Propanethiol	0.20
iso-Propanethiol	0.50
tert-Butanethiol	Traces
Sulfides	
Dimethyl sulfide	2.00
Diethyl sulfide	0.05
Methyl ethyl sulfide	0.20
Methyl-*n*-propyl sulfide	Traces
Disulfides	
Dimethyl disulfide	45.00
Methyl ethyl disulfide	0.70
Methyl isopropyldisulfide	1.00
Miscellaneous	
3,5-Dimethyl-1,2,4-trithiolane	Traces
Benzothiazole	Traces

degradation processes. The sulfur volatiles were thought to originate as a result of the thermal degradation of the sulfur-containing amino acids. They may also originate to a lesser extent from the breakdown of the other naturally occurring substances, such as thiamine, biotin, coenzyme A, glutathione, etc. Using model systems containing methionine and ethionine, Casey et al.[51] showed that thiols were produced first and subsequently oxidized to disulfide. The formation of methional is as a result of Strecker degradation of methionine, which on dry heat can produce methanethiol and dimethyl sulfide as well, a reaction of interest in the dried potato products. The formation of hydrogen sulfide and methanethiol has been explained as a reaction of naturally occurring dehydroascorbic acid in potatoes with cystine, cysteine, and methionine.[13] The hydrogen sulfide may also arise from the decomposition of benzothiazole or 3,5-dimethyl-1,2,4-trithiolane. Buttery and Ling[44] studied the nonbasic steam volatile constituents of potato chips and reported the presence of methional and 2-methylmercaptoacetaldehyde. The former was considered an important component in the aroma of potato chips.

Tomato (*Lycopersicum esculentum* Mill.)

In comparison with many vegetables, knowledge of the volatile constituents of tomatoes has, until recently, been limited.[280] Volatiles can exist as such in the whole intact tomatoes or they can develop as artifacts. Many volatile compounds in tomatoes apparently exist in dynamic systems highly dependent on the treatment the tomato receives during its preparation or analysis. It also appears likely that tomato flavor results from a blending of aromas of several compounds, none of which is singly tomato-like.[326] Small amounts of methylsulfide are given off by the raw tomato and appreciable amounts are produced during cooking or prolonged heating. Indeed there is strong evidence that dimethyl sulfide is the principal volatile flavor component of processed tomato products.[177] The GC analysis showed the presence of dimethyl sulfide (3 to 4 ppm) in the tomato juice. This concentration would be 10,000 times its odor threshold in water and, therefore, quite important in the aroma of tomato products.[93] At 100°C and atmospheric pressure, 150 ppb of hydrogen sulfide and 2 to 6 ppm of dimethyl sulfide were formed in an hour from canned tomatoes and juice. Commercially canned tomatoes and juice contained 1.6 to 7.9 ppm dimethyl sulfide. These amounts are far above their odor thresholds in water and probably both compounds modify the overall aroma of processed tomato products. As heating time was increased from 2 to 80 min, both the dimethyl sulfide content and odor intensity of the juices progressively increased and the most desirable aroma quality occurred between 5 and 20 min of heat processing.[95]

There exist qualitative and quantitative differences in the volatile composition of flavor between the raw and heat processed samples.[190] Dimethyl sulfide, which was absent in fresh tomato, was formed during the heating process and its concentration in processed tomato juice was found to decrease on storage. Tomato products contain much more dimethyl sulfide (0.4 to 10.9 ppm) than hydrogen sulfide. These amounts range from 1,200 to 33,000 times the odor threshold of dimethyl sulfide in water. Analysis of the threshold values of pure dimethyl sulfide, the control juice alone, and the dimethyl sulfide control juice mixtures indicated some sort of interaction between juice and dimethyl sulfide, resulting in odor addition or synergism. The interaction appeared to become greater as the dimethyl sulfide concentration was increased.[96] Free amino acid determinations on tomato paste serum indicated the presence of several sulfuramino acids such as cysteine, methionine, and *S*-methyl cysteine sulfoxide or sulfone, methionine sulfone, and lanthionine. Methionine and *S*-methyl cysteine might give rise to dimethyl sulfonium-type salts from which dimethyl sulfide could be produced by heat.

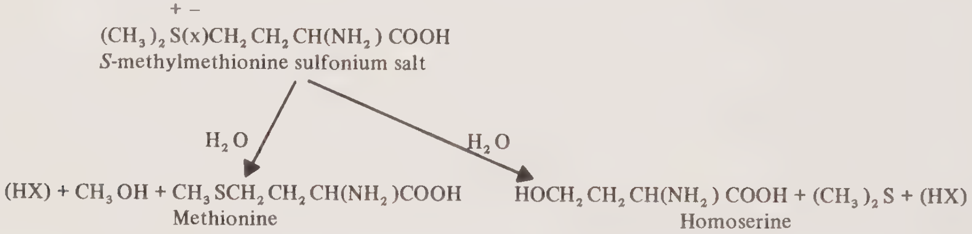
Wong and Carson[326] isolated a sulfonium compound, viz., *S*-methyl methionine sulfonium (3-amino-3-carboxypropyl dimethyl sulfonium) ion (m.p. 139 to 140°C) by a modified procedure of McRorie et al.[170] Calculations based on the amino acid analysis indicated the concentration of the methyl methionine sulfonium salts in the tomato to be on the order of 16 to 35 ppm. Miers[177] found that an exhaustive collection of the volatile materials from tomato preparations contained dimethyl sulfide within this range. These findings show that *S*-methyl methionine sulfonium salt plays an important role in the formation of flavor in heated tomato products.

Notable among the 32 new components isolated by Viani et al.[302] was 2-isobutylthiazole. 2-isobutylthiazole and methional have been identified[128] by GC analysis. Methional, also reported by Ryder,[233] is of particular interest because of its relationship to ethylene production in fruits and vegetables. Its formation could be heat-induced from methionine, as shown by Ballance.[12] This compound was found to be associated with "heated" or "cooked" tomato flavor. Moreover, it showed unusual flavor characteristics. At concentrations of 1 ppm or above, it masked the typical flavor of tomato juice and produced an insipid flavor. Normally, its concentration in volatiles from fresh tomatoes recovered by steam distillation was estimated to be around 0.05 ppm.

A good example of flavor interaction was found with 2-isobutylthiazole. When added to canned tomato juice or tomato paste, it produced a more intense, fresh tomato-like flavor. Also it improved the mouth feel properties of the juice or paste. It was effective in tomato juice at levels from 25 to 50 ppb, depending on the amounts of other volatiles already in the juice. Its threshold value in water was 2 ppb. At higher levels, its flavor became objectionable, being described as "rancid," "medicinal," or "metallic."

Asparagus (*Asparagus officinalis* L.)

Jansen[115] isolated a compound from this and identified it as β,β-dimercapto isobutyric acid ($HS\text{-}CH_2CH(COOH)\ CH_2SH$). This compound undergoes hydrolysis, forming mercaptan, which is subsequently oxidized to disulfide. Johnson[119] developed an ultraviolet spectroscopy method for following the above reaction; this technique helps in establishing the age (freshness) of asparagus. Challenger and Hayward[58] have reported the occurrence of *S*-methyl methionine sulfonium salt (α-amino dimethyl-γ-butyrothetin) in asparagus as possible precursor of dimethyl sulfide, methionine, and homoserine. The formation of these can be explained by the following reactions:



Carrots, Peas, Beans, Parsnip, Parsley, and Celery

The earliest attempt at examining the volatiles of carrot (*Daucus carota* L.) was reported by Konig and Kracht,[143] who found sulfur compounds in cooked carrots. Using gas chromatography, Self et al.[251] studied the low boiling compounds in cooked vegetables, such as carrots, peas (*Pisum sativum* L.), beans (*Phaseolus vulgaris* L.), parsnip (*Pastinaca sativa* L.), and celery (*Apium graveolens* L.). These are listed in Table 12.

Heatherbill et al.[102] identified ethanethiol and dimethyl sulfide in canned carrots using GC-MS. These compounds were not present in the raw carrot but formed during processing. Using GC-MS, Kasting et al.[126] analyzed the headspace vapors of high vacuum distillates of parsley leaves (*Petroselinum sativum*

TABLE 12

Low Boiling Sulfur Volatiles in Cooked Vegetables*[251]

Compound	Carrot	Peas (frozen)	Beans	Parsnip	Celery
Hydrogen sulfide	O	L	S	S	Tr
Methanethiol	S	S	S	S	O
Ethanethiol	Tr	Tr	O	Tr	O
Propanethiol	O	Tr	Tr	O	O
Dimethyl sulfide	L	M	M	VL	VL

*Boiled for 30 min
O = Undetectable, S = Small; M = Medium; L = Large; Tr = Traces; VL = Very large

Hoffm.) and identified dimethylsulfide and carbon disulfide. Using GC-MS, Ralls et al.[222] studied the flavor volatiles of green peas and reported dimethyl sulfide, dimethyl disulfide, dimethyl trisulfide, carbon disulfide, and methanethiol. They showed the formation of dimethyl sulfoxide from dimethyl sulfide in the commercial blanched samples of peas.

FRUITS

Although some fruits are consumed in the fresh state, a major portion of them is processed into a wide range of products, such as slices, juice, juice blends, nectar, squashes, cordials, etc. A considerable amount of the volatile components is lost during processing (canning, bottling, concentration, dehydration, etc.). Although sulfur compounds, particularly thiols, sulfides, disulfides, and isothiocyanates, play an important part in the aroma of vegetables, it is noteworthy that very few volatile sulfur compounds have been isolated from fruits.

Grapes

The extensive use of Concord grape (*Vitis labrusca*) products in the food industry has prompted an investigation of volatiles in the essence. The volatiles of Concord grapes were examined[278] by capillary GC-MS combination. Of the 60 components identified, a possible ethyl alkyl thioester was of particular interest. The structure of this compound is yet to be elucidated.

Grapefruit (*Citrus paradisi* Swingle)

The volatile water-soluble flavor constituents in the canned and stored samples of grapefruit juice have been investigated.[135] Hydrogen sulfide was absent in freshly canned juice and was found in trace quantities in fresh juice and in stored canned juice. The lack of hydrogen sulfide in freshly canned juice is taken to be due to deaeration before canning and its reappearance in the stored juice as evidence of the breakdown of some sulfur compound in the juice.

Orange (*Citrus sinensis* L.)

Hydrogen sulfide has been reported in green oranges and in orange juice.[14,134] Trace quantities of hydrogen sulfide were found[136] during distillation of the fresh and freshly canned juices of the volatile water-soluble constituents of California Valencia orange; none were found in the stored canned juice. Passage of nitrogen through unheated freshly reamed juice showed hydrogen sulfide to be present as such and not as an artifact produced by heating.

Strawberries (*Frageria virginiana* L.)

Dimethyl sulfide has been found in autoclaved strawberry[271] puree, although not detected in raw puree. This compound has not been previously reported as a component of strawberries, although Winter and Willhalm[325] reported other compounds, such as carbonyls, esters, and volatile alcohols. The maximum concentration of dimethyl sulfide was produced after 10 min of heating and was not significantly altered by extending the heat treatment. However, Casey et al.[51] have shown that dimethyl sulfide was formed when methionine was heated in the presence of pectin. Strawberries contain natural pectin which could serve as a methyl donor, although the presence of methionine in strawberries has not been documented as yet. Another possible precursor could be *S*-methyl methionine sulfonium salt.

Pineapple (*Ananas sativus* L.)

Methyl-β-methyl thiopropionate($CH_3SCH_2CH_2COO\,CH_3$), confirmed by synthesis and identified by the synthesis of its sulfone (m.p. 93.6 to 94.0°C), was found in the higher boiling fractions of the volatiles of the cayenne variety of pineapple.[98] The two exceptional major sulfur compounds, viz., methyl-β-methyl thioproionate and ethyl-β-methyl thiopropionate, which do not occur in common fruits, have been identified[62] in the residual oil obtained from the Hawaiian pineapple (approximately 0.2 and 0.1 ppm).

Durian (*Durio zibethinus* Murr.)

Durian is a tree fruit grown and used in Southeast Asia. It has two distinct odors: strong and onion-like and delicate and fruity. Recently, Baldry et al.[11] identified hydrogen sulfide, methanethiol, ethanethiol, propanethiol, dimethyl sulfide, diethyl sulfide, and diethyl disulfide in the flavor volatiles of durian.

Cranberries (*Vaccinium macrocarpon*)

Recently, Anjou and von Sydow[6] analyzed the aroma of American cranberries and identified benzothiazole, 2-hexylthiophene, and 2-heptylthiophene.

BEVERAGES

Beverages are used both for stimulating and refreshing purposes. Beer, wine, etc., are classified as alcoholic beverages, whiskey as distilled liquor, whereas coffee, tea, and cocoa are nonalcoholic.

Beer is a hop-flavored fermented beverage prepared from raw materials, such as malted barley, rice, and corn.

Hops

Hops are plants, the flowers of which contain resin and essential oil (0.2 to 0.4%) which contribute a characteristic bitter taste and a pleasant aroma, respectively, to beer. Using GLC, IR, and mass spectrometry, Buttery et al.[40] identified methyl thiohexanoate and methyl thioheptanoate in the oxygenated fraction of the hop oil. These thioesters occur in small concentrations (0.1%) and contribute very much to the hop aroma. The threshold concentrations[94] (in ppb) of methyl thiohexanoate and methyl thioheptanoate are 0.3 and 2.0, respectively. It is not certain whether these compounds are present in the hops while picking from the vine or formed during sulfuring and drying. Based on mass spectral data, the tentative identification of methyl thioisoheptanoate and methyl thio-2-methyl butyrate has also been indicated.[40] The GLC, MS, and NMR analyses[71] of the aroma concentrate of hops have shown the presence of dimethyl sulfide, dimethyl disulfide, and methyl dithioacetate. Dimethyl sulfide has been considered to contribute much to the hop aroma. The origin of these sulfur compounds is not well understood.

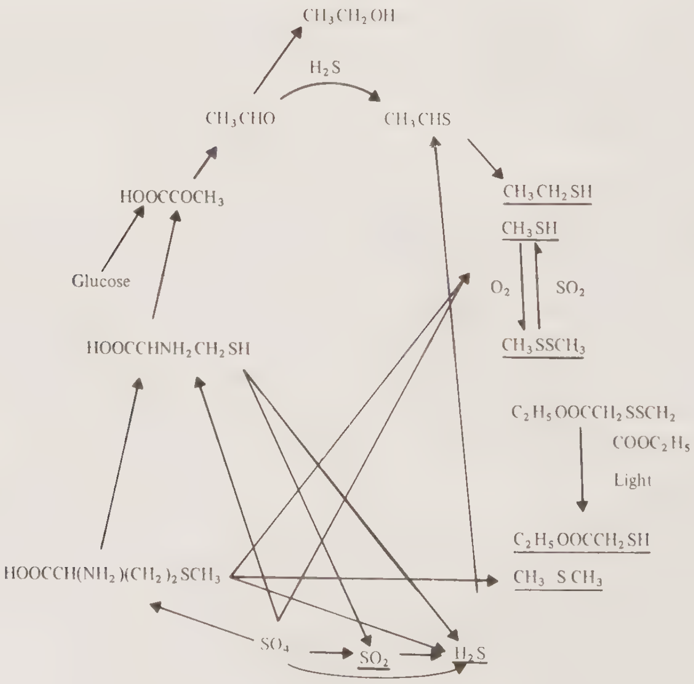


TABLE 13

Hydrogen Sulfide Levels in Beer and its Raw Materials[33]

	Hydrogen sulfide content (ppb)
Raw materials	
Barley	72
Malt	190
Lager yeast (compressed)	1,110
Commercial wort	13–37
Beer	
After main fermentation	11–20
After storage	0–8
Bottled	0–30 (4–6)*

*The value indicates the range in greatest number of samples.

Beer

Brenner et al.[33] examined the hydrogen sulfide levels in brewery raw materials and throughout the brewing process (Table 13). They have also discussed the interrelationships of sulfur compounds produced during the brewing process.

It was pointed out that the transformation indicated above can be brought about by yeasts or other microorganisms or by simple biochemical reactions. Thus, inorganic sulfate ion can be reduced by yeast to H_2S or sulfur dioxide. Cysteine can be dethiolated by yeast under reducing conditions to yield H_2S or to give SO_2 under oxidizing conditions. Methanethiol may arise from SO_4^{--} or from the thiomethyl group split off from methionine.

The scrubbing action of carbon dioxide gas, produced during fermentation, maintains the H_2S at a low level when the fermentation is complete. The organoleptic threshold of H_2S in beer is reported to be 4 to 5 ppb. Ricketts and Coutts[231] concluded that the liberation of H_2S by yeast during fermentation is the result of enzymatic action by a dehydrogenase, probably triose phosphate dehydrogenase, or alcohol dehydrogenase, or both. Stewart et al.[281] showed that a yeast that requires pantothenate (e.g., brewer's yeast) produces copious amounts of H_2S when there is a shortage of this factor in the wort.

Brenner et al.[35] examined a number of malts and found sulfur dioxide in the range of 28 to 47 ppm. During fermentation, SO_2 levels rose from about 1 to 23 ppm in a period of 7 to 8 days. However, the stored beers contained 4 to 13 ppm SO_2, which was attributed to the loss by oxidation and complex formation with aldehydes. The same authors[34] analyzed the thiol content in the brewery raw materials. The range was 30 to 112 ppb in samples of six malts; in samples of nine adjuncts (corn and rice), the level was below 30 ppb. They found that the level of thiols decreased during fermentation and rose again during storage. Kuroiwa and Hashimoto[101,150] did not find any thiols in the unheated beer and suggested that they arise as artifacts due to heating from thioformaldehyde, dithioformaldehyde, and thioacetone, which were identified in fermenting wort and young beer. The presence of thiols in the finished beer is considered deleterious,[167] although Brenner et al.[34] do not agree with this view.

The skunky odor of "sunstruck beer" has been attributed to 3-methyl-2-butene-1-thiol,[149] a product of the degradation of isohumulones in the presence of hydrogen sulfide or a sulfhydryl compound[148] in the nascent state. The thiol is also formed from *S*-prenyl-L-cysteine when exposed to sunlight.[203]

Kepner et al.[131] and Ahrenst-Larsen and Levin-Hansen[3] identified dimethyl sulfide in beer using gas chromatography. Sinclair et al.[268] found the dimethyl sulfide content less than 30 ppb in the British ales and lagers, while the Pilsner-type beers contained about 130 ppb.[72] Harrison[100] pointed out that the dimethyl sulfide has a significant effect on beer flavor and it is probably formed by the action of wort bacteria on wort.[24] A recent study of Niefind[192] showed that diethyl sulfide also occurs in small quantities in beer and contributes to the aroma. Large quantities of dimethyl sulfide and diethyl sulfide are

TABLE 14

Sulfur Volatiles in Alcoholic Beverages*

Beer

Methanethiol
Ethanethiol
3-Methyl-2-butenethiol
Dimethyl sulfide
Diethyl sulfide
Hydrogen sulfide
Sulfur dioxide

Whiskey

Methanethiol
Dimethyl sulfide
Methyl ethyl sulfide
Carbon disulfide

Wine

Ethanethiol
Hydrogen sulfide

*References 3, 33, 35, 101, 124, 131, 149, 150, 192, 225, 231, 236, 319

found, however, only when the wort is infected by fermentation-resistant bacteria. Such infected beers exhibit an astringent, sweet onion aroma, which was synthetically demonstrated by the addition of the two sulfides.

Whiskey

This is a distilled alcoholic beverage made from grains or potatoes. Kahn et al.[124] and Wiley[319] reported carbon disulfide, dimethyl sulfide, ethanethiol, and methyl ethyl sulfide in the flavor volatiles of whiskey.

Wine

This is a fermented alcoholic beverage. The most common raw material is grapes although other fruits are also used. Rankine[225] found traces of hydrogen sulfide and ethanethiol in young wines, while Sainsbury and Maw[236] estimated the volatile thiols in beer. H_2S was shown to form from bisulfite and elemental sulfur (fungicide). The formation of ethanethiol was considered due to the reaction of H_2S with acetaldehyde through a cyclic trithio-acetaldehyde intermediate. The sulfur compounds in the various alcoholic beverages are listed in Table 14. The objectionable odor due to these disappears slowly with time or more rapidly following addition of sulfur dioxide and aeration.

Nonalcoholic Beverages (Coffee, Tea, Cocoa)

The flavor of tea and cocoa is formed both during fermentation and drying, whereas in the case of coffee, it is formed mainly during roasting.

Coffee

The flavor of coffee has been extensively studied in view of its popularity as an instant beverage and its commercial importance. The flavor studies have been carried out on the raw, roasted, and instant coffee. Sulfur volatiles have a profound effect on coffee aroma. As early as 1938, Johnston and Frey[122] obtained a volatile liquid fraction having "a good coffee-like aroma and also a mercaptan-like odor." They detected sulfur, but could not identify the compounds.

Dimethyl sulfide, with its low threshold value, imparts the essential properties of high quality mild coffee when present in parts per billion quantities.[270] Rhoades[230] reported the absence of dimethyl sulfide in instant coffee. However, at less than 10 ppm in the coffee solubles, it is easily noticeable and markedly improves the coffee flavor and aroma. Although possessing unpleasant odor, thiols, thiophenes, and hydrogen sulfide play a significant role in the characteristic aroma of coffee in low concentrations.

According to Staudinger and Reichstein,[277] a natural coffee aroma can be made by mixing fugitive mercaptans and sulfides and reacting them with oxygen- and nitrogen-containing bodies of the type found in natural coffee. It is also claimed[111] that the colorless oil obtained by reacting 2-furylmethanethiol (furfuryl mercaptan) with diacetyl has a "coffee-like" aroma.

Furfuryl mercaptan has been considered to have a great influence on roasted coffee aroma. Reichstein and Staudinger,[229] Giral and Fernandez,[88] and Ongaro[205] found that furfuryl mercaptan, when considerably diluted, has a mild odor resembling that of coffee. On the other hand, according to Hughes and Smith,[109] furfuryl mercaptan, added at ppm levels to coffee, did not result in any improvement to the coffee aroma.

According to the same authors, hydrogen sulfide contributes more of a disagreeable taste sensation. The production of hydrogen sulfide during boiling of coffee may be due to the changes that take place when coffee is overheated or kept for long. This may also partly explain the variations in flavor obtained by different methods of preparation.

According to Gautschi et al.,[84] thiophene compounds are formed from furans, hydrogen sulfide, or some other sulfur being involved in the cyclization step. Cysteine and methionine probably participate in these reactions. Merritt and Robertson[176] found that methyl thiophene is formed from cysteine. Thiazolecarbonyl compounds are believed to originate from a cysteine fragment. Mizutani et al.[179] have shown that cysteine will form thiazolidine compounds very easily by reaction with aldehydes. Subsequent decarboxylation and dehydrogenation can occur under roasting conditions. The same authors have demonstrated that the compounds formed initially will be partly pyrolized to hydrogen sulfide. Several other sulfur compounds have been identified in the coffee aroma.[86,174,181,282,283,290,336] These are listed in Table 15.

Tea

Tea is perhaps the most versatile beverage. It is consumed mainly in three forms: green tea, oolong tea, and black tea. In addition, the instant form of each of the above is becoming popular. In contrast with the voluminous literature available on the chemistry of tea polyphenols and their role in tea flavor, the aromatic constituents have received attention only during recent years. In the tea aroma complex, four sulfur compounds have been reported, viz., hydrogen sulfide, methanethiol, dimethyl sulfide, and methional.[26,188,298]

Dimethyl sulfide is considered to have some influence on the overall aroma of tea. According to Wickremasinghe and Swain,[318] dimethyl sulfide, with its threshold value as low as 3×10^{-4} ppm, should participate in the tea aroma even in ppm quantities. Luc and Dominique[156] have described a computerized method for selecting gas chromatographic peaks corresponding to volatile constituents directly affecting the quality of tea aroma. They have found that the peak in the dimethyl sulfide region is one of the most important with regard to tea quality. Kiribuchi and Yamanishi[137] believe that the "laver-like" odor of green tea is due to dimethyl sulfide. They have suggested *s*-methyl methionine sulfonium salt present in tea extract as the possible precursor to dimethyl sulfide:

$$(CH_3)_2\overset{+}{S}CH_2CH_2CH(NH_2)COOH \xrightarrow{OH^-} (CH_3)_2S + \underset{\text{Homoserine}}{CH_2(OH)CH_2CH(NH_2)COOH}$$

Tsujimura et al.[298] studied the steam distillate of green tea and detected hydrogen sulfide. It was found that the larger the hydrogen sulfide content, the better the quality of the tea. Nakabayashi[188] reported the presence of methional in tea volatiles and suggested methionine as the precursor

TABLE 15

Sulfur Volatiles in Coffee*

Thiols

Methanethiol
Ethanethiol
Propanethiol
2-Furylmethanethiol

Sulfides

Methylene sulfide
Dimethyl sulfide
Methyl ethyl sulfide
Methyl phenyl sulfide
Methyl-(2-hydroxyphenyl) sulfide
Furfuryl methyl sulfide
5-Methyl furfuryl-2-methyl sulfide
Difurfuryl sulfide

Disulfides

Dimethyl disulfide
Methyl ethyl disulfide

Thiophenes

Thiophene
3-Vinyl thiophene
2-Methyl-4-ethyl thiophene
Thiopheno (2,3) thiophene
Benzothiophene
2-Formylthiophene
5-Methyl-2-formyl thiophene
2-Acetyl thiophene
3-Acetyl thiophene
2-Acetyl-4-methyl thiophene
2-Acetyl-3-methyl thiophene
2-Acetyl-5-methyl thiophene
2-Propionyl thiophene
Tetrahydrothiophene-3-one
2-Methyl tetrahydrothiophene-3-one
Thenyl alcohol
Thenyl formate
Thenyl acetate
1-(Thienyl-2)-Propanedione(1,2)
1-(Thienyl-3)-Propane dione(1,2)

Thiazoles

2-Acetyl-4-methyl thiazole
2-Propionyl-4-methyl thiazole

Miscellaneous

Hydrogen sulfide
Carbon disulfide
1-Methyl thiobutan-2-one
Furfuryl-2-thiocarbonic acid methyl ester
Furfuryl thiol acetate
Thienyl-(2)-carbonic acid methyl ester

*References 84, 86, 88, 109, 174, 181, 205, 229, 230, 270, 277, 282, 283, 290, 336

Cocoa

In addition to being used as a beverage, cocoa finds wider use in the manufacture of chocolates and confectionery products. The aroma of cocoa arises from the fermentation and roasting stages. Polyphenols and amino acids have been considered to be the aroma precursors in cocoa. Bailey et al.[10] tried to correlate the cocoa aroma to some specific compounds identified. From quantitative information based on GLC, they concluded that acetaldehyde, isobutyraldehyde, isovaleraldehyde, benzaldehyde, phenyl acetaldehyde, 5-methyl-2-phenyl-2-hexenal, 2-furfuraldehyde, dimethyl sulfide, and isopentyl acetate contribute to cocoa aroma. They also found that a mixture of isovaleraldehyde and dimethyl sulfide in the GLC effluent possessed cocoa-like odor. van der Wal et al.[300] attempted to duplicate the aroma concentrate using the GLC pattern as the guide. Although this synthetic mixture was reminiscent of cocoa, it lacked the pronounced aroma of cocoa extract. Several organic sulfur compounds[76,165,284,288,299,301] have been identified in the flavor volatiles of cocoa, but none of them possessed the typical aroma of cocoa. These are given in Table 16.

TABLE 16

Sulfur Volatiles in Cocoa*

Dimethyl sulfide
Methyl ethyl sulfide
Methyl benzyl sulfide
Methional
Dimethyl disulfide
Methyl isopropyl disulfide
Dimethyl trisulfide
Methyl-*n*-propyl trisulfide
Isobutyl thiocyanate
Benzothiazole
4-Methyl-5-(2-Hydroxymethyl) thiazole
4-Methyl-5-vinyl thiazole
2-Methyl mercapto isobutanal

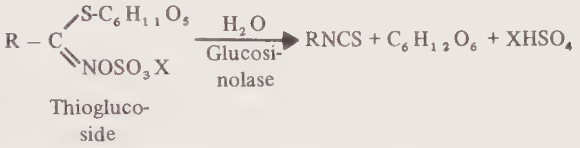
*References 10, 76, 165, 284, 288, 299–301

SPICES

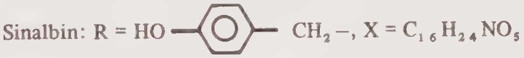
Among the various spices used in foods, the characteristic flavors of mustard and asafetida are due to organic sulfur compounds.

Mustard

Mustard seed provides three kinds of sharp tasting isothiocyanates, viz., allyl, 3-butenyl, and *p*-hydroxybenzyl isothiocyanates.[259] The pungent aroma of black mustard (*Brassica nigra* L.) and brown mustard (*Brassica juncea* Coss.) is due to the volatile allyl isothiocyanate and allyl and 3-butenyl isothiocyanates, respectively. The *p*-hydroxybenzyl isothiocyanate is a nonvolatile compound occurring in white mustard (*Brassica alba* L.), which possesses a sharp taste without pungent aroma. These isothiocyanates are not present as such in the mustard, but are formed from the thioglucoside precursors by the hydrolytic enzyme reaction. Glucosinolase is a naturally occurring enzyme present in black, brown, and white mustard. The flavor of mustard flour, unlike many ground spices, is protected from deterioration and loss by a unique natural phenomenon. Having both a natural protective system and release mechanism, mustard perhaps deserves the distinction of being the earliest entrapped flavor. The formation of the isothiocyanates[7,259] takes place according to the following reaction:



Sinigrin: $R = CH_2 = CH\,CH_2-$, $X = K$



The condimental value of mustard seeds/flour depends on its isothiocyanate content[7] (Table 17). Therefore, the methods of analysis of the isothiocyanates are important in the grading of the quality of the mustard seeds. Recently, a colimetric method[221] for the determination of sinalbin and volumetric methods[219,258,260] for the determination of the pungent constituents in black and white mustard have been developed in this laboratory.

Asafetida (*Ferula alliacea* Boiss)

This is an oleogumresin containing 3 to 20% volatile oil which is responsible for its powerful, pungent, and alliaceous odor. Semmler[253] reported the presence of *sec* butyl propenyl disulfide, to an extent of 45%, in the volatile oil. Later, Mannich and Fresenius[164] analyzed the oil, confirmed the findings of Semmler, and indicated the presence of some more sulfides.

TABLE 17

Isothiocyanate Content in Mustard[7,259]

Mustard variety	Isothiocyanate Allyl %	 *p*-Hydroxybenzyl %
White: *Brassica alba*	–	1.5–3.7
Black: *Brassica juncea*	0.6–0.8*	–
Brassica nigra	0.6–1.5	–

*Includes 3-butenyl isothiocyanate

Some years ago, Sastry and co-workers[238,239,289] and Shivashanker et al.[263,264] studied some analytical aspects of asafetida. Recently, Abraham et al.[1,220] carried out a detailed analysis of the authentic and market samples of asafetida and described a volumetric method for the determination of the volatile oil using chloramine-T reagent. Three sulfur compounds with the formulas $C_7H_{14}S_2$(1), $C_7H_{14}S_3$(2), and $C_8H_{16}S_3$(3), which contributed to the asafetida flavor, were isolated and their spectral data studied.[2] The compound (1) was characterized as *sec* butyl propenyl disulfide. While work was in progress in this laboratory, Naimie et al.[187b] reported the presence of 1-(1-methylthiopropyl-1-propenyl disulfide) ($C_7H_{14}S_3$) and 2-butyl (3-methyl thioallyl) disulfide ($C_8H_{16}S_3$) in the volatile oil of asafetida.

Ginger (*Zingiber officinale* Roscoe)

The headspace analysis[125] of the steam distillate of ginger showed the presence of a substantial amount of methyl allyl sulfide and trace concentrations of diethyl- and ethyl-isopropyl sulfides.

ROASTED FOODS

Peanut

Typical roasted peanut flavor is one of the most desirable flavors and the approach to this problem is to analyze the heated and unheated flavor fractions of raw and roasted peanuts, respectively. It appears that raw peanut is practically devoid of any sulfur compound except the amino acid, methionine, which is reported[191] to be present in raw as well as roasted peanuts of full as well as intermediate maturity. The value ranges from 1 to 1.93 μmol/g of fat-free meal. It has been indicated very strongly that this amino acid could be a precursor of the volatile flavor components in roasted peanuts. Walradt et al.[312] reported 11 sulfur compounds in roasted Spanish peanuts. These are listed in Table 18.

The neutral fraction of roasted peanut volatiles had a very intense roasted peanut aroma but when highly concentrated, the aroma was more "burnt" or coffee-like. This fraction was analyzed by GC-MS and found to consist of sulfur volatiles, such as dimethyl disulfide, 2-acetyl-thiophene, and thiophene-2-aldehyde.[120] Most of the newly identified components can be readily attributed to nonenzymatic browning reactions.

TABLE 18

Compounds Identified from Roasted Peanuts[312]

Sulfide

Methional

Disulfides

Dimethyl disulfide
Dipropyl disulfide
Benzyl methyl disulfide

Thiophenes

2-Acetyl thiophene
Dihydro-2H-thiophen-3-one
2-Methyl dihydro-2H-thiophen-3-one
5-Methyl thiophen-2-carboxaldehyde

Thiazoles

Thiazole
4-Methylthiazole
Benzothiazole

TABLE 19

Sulfur Volatiles in Roasted Filberts[133]

Thiol

Methanethiol

Sulfide

Methional

Disulfides

Dimethyl disulfide
Diethyl disulfide

Trisulfide

Dimethyl trisulfide

Thiophenes

Thiophen-2-carboxaldehyde
Dihydro-1H-thiophen-3-one

Thiazoles

Benzothiazole
4-Methyl-5-vinyl thiazole

Thiolanes

Dimethyl trithiolane
3,5-Dimethyl-1,2,4-trithiolane

Filbert Nut (*Corylus avellana*)

Sheldon et al.[262] carried out the quantitative headspace analysis of filbert oil from nuts dry-roasted in a gas oven at 177°C for different time periods. They reported the appearance of dimethyl sulfide after 10 min roasting which increased to a maximum of 20 min. Also a good roasted flavor was noticed when the concentration of dimethyl sulfide was 0.33 ppm (17.5 min). In a recent study on the roasted filbert volatiles, based on MS data, Kinlin et al.[133] identified 11 sulfur compounds, which are given in Table 19.

Popcorn

Popcorn is another popular food in which the characteristic flavor is produced during heat processing. Since the unique flavor and aroma of popcorn have such wide appeal, knowledge of the important flavor compounds could be used as an aid in developing products with improved flavor. Volatile compounds were isolated from popcorn which was popped conventionally in oil and without oil in a microwave oven. Techniques employing popper headspace gas entrainment and vacuum steam distillation of a slurry of ground popped corn were used. The aqueous condensate and vacuum distillate were extracted with ether, concentrated, and analyzed by GC-MS. Thiazole, 2-pentyl thiophene, 5-methyl-2-thiophenaldehyde, and 2-ethyl-5-butylthiophene were identified.[311]

Barley

The flavor components of roasted barley[313] were found to contain hydrogen sulfide, dimethyl disulfide, and methanethiol, which arise from the breakdown of the sulfur-containing amino acids. Hydrogen sulfide and dimethyl disulfide have been found to contribute significantly toward the roasted barley flavor.

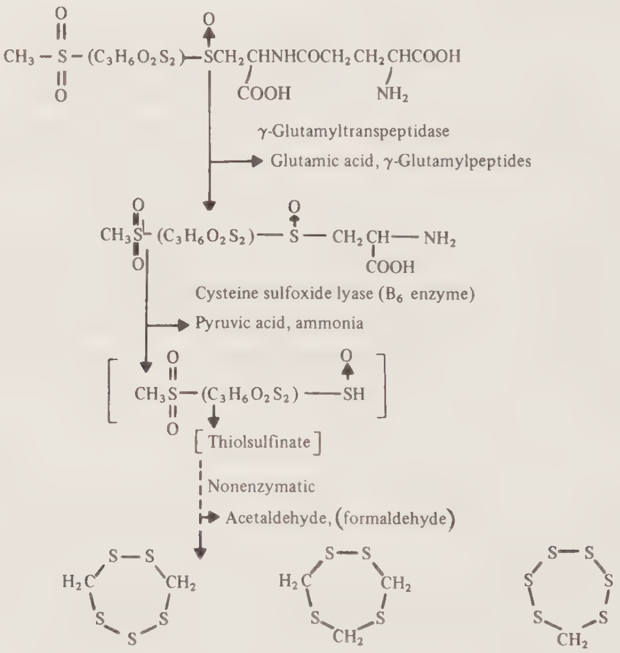
MISCELLANEOUS

Bread

Freshly baked bread has flavor which is subtle, yet very attractive to most individuals. Johnson et al.[121] first reported the presence of methional in bread. This could have been formed from methionine as a result of Strecker degradation. The release of hydrogen sulfide during dough mixing has been reported,[172] the amount varying with temperature. von Sydow and Anjou,[306] analyzed the volatiles of rye crisp bread using GC-MS and identified dimethyl disulfide, 2,3,4-trithiapentane, and 2-formylthiophene in concentration ranges of 0.04, 0.04, and 0.08%, respectively. In a recent investigation employing headspace analysis, Mulders et al.[186] identified at least 93 compounds, including 2-(or 3-)acetylthiophene, dimethyl sulfide, and dimethyl disulfide.

Mushroom

Freise[79] investigated the essential oils of certain mushrooms and found benzyl isothiocyanate ($C_6H_5CH_2NCS$) and phenyl-ethyl thiocyanate ($C_6H_5CH_2CH_2SCN$). *Shiitaké* (*Lentinus ediodes*), a species of mushroom, has long been used as a popular flavorful food in Japan and China. The characteristic odor of this is due to 1,2,3,5,6-pentathiepane (lenthionine),[308] which has threshold values of 0.27 to 0.53 and 12.5 to 25.0 ppm in water and vegetable oil, respectively. A recent analysis[330] of crushed samples of *Shiitaké* mushroom showed the presence of methanethiol, dimethyl sulfide, and dimethyl disulfide, which also appeared to contribute to the mushroom flavor. Morita and Kobayashi[183] reported the synthesis of lenthionine from formaldehyde, methylene chloride, and sodium polysulfide. This compound finds promising use as a flavor additive in egg and beef soups. Recently, Yasumoto et al.[328] isolated the sulfur-containing peptide precursor, lentinic acid, from the fruiting bodies of the mushroom. They showed that the formation of lenthionine was by enzymic reaction as given below:



Soy Products

Obata and co-workers[199,200,202] identified dimethyl sulfide and hydrogen sulfide in soybean meal hydrolysate. The dimethyl sulfide was considered to originate from methionine methylsulfonium compound. Wilkens and Linn[321,322] employed GC-MS in the isolation and identification of the volatile components of whole-fat soybean milk. They have reported the presence of carbonyl compounds, alcohols, hydrocarbons, and benzothiazole and they have also identified dimethyl disulfide in deep fat-fried soybeans. However, the typical green-beany flavor of soy has been ascribed to a mixture of many compounds.

Sweetcorn

Raw corn does not contain dimethyl sulfide; however, the characteristic odor of the corn is often associated with dimethyl sulfide. Self et al.[251] observed that dimethyl sulfide was present in the low-boiling volatiles of several cooked vegetables, including sweetcorn, and suggested the mechanisms[51] through which dimethyl sulfide can arise. In a recent investigation, Bills and Keenan[23] determined the average dimethyl sulfide content in canned or heated sweetcorn to be about 8.7 ppm. Since the flavor threshold of this compound is in the neighborhood of a few ppb, it is undoubtedly one of the more important flavor constituents of heated corn. Heating in excess of the normal canning treatment or in excess of 5 min of autoclaving did not result in further production of appreciable quantities of dimethyl sulfide, thereby indicating that most of it in heated corn probably results from a heat-labile precursor, *S*-methyl methionine sulfonium salt (MMS). According to Keenan and Lindsay,[129] MMS is rapidly degraded to dimethyl sulfide and homoserine at temperatures above 100°C and nearly neutral pH. However, the wide variation in dimethyl sulfide content among commercial samples suggests that further work is necessary to discover the parameters that influence the yield of dimethyl sulfide in canned or cooked corn. The plant geneticist, on the other hand, may be interested in varietal differences in dimethyl sulfide yield and the systematic breeding of corn varieties in which this compound and other flavor compounds are developed at optimum levels.

SUMMARY AND CONCLUSIONS

This survey has shown that the volatile sulfur compounds are generally present in trace amounts in foods. As a rule, these compounds possess a strong and powerful odor and contribute to both agreeable and disagreeable flavor of foods. These compounds may occur either naturally or form due to chemical, enzymic, or microbial reactions.

The major lines of research in flavor chemistry have been isolation and identification of flavor compounds, their mechanism of formation, correlation with sensory qualities, and synthesis. Considerable progress has taken place in recent years with respect to identification because of the availability of sophisticated analytical equipment and techniques. The power of these techniques is being enhanced by fast-scan instruments and by digital computers. However, there is still a need for newer and improved techniques and ultrasensitive instruments for the isolation and identification of the trace volatile components. This may help in understanding the flavor composition in foods.

Despite a few studies made regarding the significance of some sulfur compounds to the overall flavor, much work remains to be done. An insight into the mechanism of flavor formation helps in the development and control of flavors and preventing the incidence of off-flavors. Therefore, this study has attracted the attention of many workers in recent years.

The enzymatic flavor formation in the *Brassicas* and the *Alliums* has been thoroughly investigated and the substrate-enzyme systems characterized. Knowledge of the above study, however, is yet to be utilized in the enhancement of flavor in processed foods. On the contrary, the chemistry of flavor formation due to microorganisms and processing conditions (heat, light, etc.) is not clearly understood.

Most processes employ heat, which helps in the development of characteristic and desirable flavors not present in the raw materials. The heat-induced reactions are very complex in nature, involving Maillard and Strecker degradation. During processing, the volatile flavor constituents are either lost or changed due to evaporation, oxidation, polymerization, etc. The loss by evaporation can be retarded or prevented by suitable fixation of the flavor volatiles.

The study of fixation and stabilization of flavors in natural and processed foods needs great attention both from academic and technological interests. The identification of the naturally occurring key compounds has led to the synthesis of compounds like lenthionine and furfuryl mercaptan, which find application as flavor additives. Attempts are also being made to flavor an artificial foodstuff using nontoxic ingredients so that it smells and tastes like a known food. Of course, this will involve legal and aesthetic problems which will have to be clarified.

The plant geneticists have paid very little attention to the flavor aspect, compared to other factors, such as yield and disease resistance. Flavor genetics is a new area of endeavor and can play an important role in the foreseeable future of plant breeding experiments.

The area of greatest interest in flavor research is understanding the significance of the contribution of the individual components to the overall flavor and correlation of chemical structure with sensory quality. The ultimate aim of flavor research is the creation of synthetic flavors which surpass the natural ones.

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THIAZOLES IN FOODS

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Food flavor is composed of numerous classes of compounds, and traditionally major classes, such as lipids, carbohydrates, alcohols, and carbonyls, have undergone extensive investigation. However, during the past decade more unique classes of compounds, such as pyrazines, amines, and sulfur-containing products, have rejuvenated flavor chemistry studies. The thiazole derivatives are an example of a potent and characteristic class of such flavor compounds that due to improved flavor chemistry isolation and detection techniques have just begun to become appreciated for their organoleptic properties.

During the past several years increasing amounts of food-related thiazole data have appeared, and it is the primary objective of this review to summarize these data in hopes of stimulating new and diversified research in this challenging and rewarding area of flavor chemistry.

Occurrences in Foods

Historically, thiazole and its derivatives have been known by the organic chemist for nearly a century. In the mid 1930's it was reported that vitamin B_1 had a thiazole ring nucleus. However, it was not until 1967 that the natural occurrence of thiazoles in food systems and their potential importance to flavor chemistry was reported. In analyzing an extract from cocoa, Stoll et al.[1] reported that a compound identified as 4-methyl-5-vinylthiazole had a characteristic nutlike odor. This report was closely followed by others identifying thiazole and its derivatives in various food systems. For example Stoll et al.[2] found 2-propionyl-4-methylthiazole and 2-acetyl-4-methylthiazole in coffee; Flament et al.[3] found benzothiazole in cocoa; and Buttery et al.[4] also reported benzothiazole to be present in beer. For the convenience of the reader, food systems from which thiazole derivatives have been isolated are summarized in Table 1.

TABLE 1

Food Systems from Which Thiazole Derivatives Have Been Isolated

Food	Reference(s)
Pressure-cooked beef	31
Beef broth	8
Shallow-fried beef	37
Beer	4
Stored casein	34
Cocoa	1, 3, 36
Coffee	2
Roasted filberts	10, 11
Pressure-cooked pork liver	7
Heated milk	35
Stale non-fat dry milk	33
Sterile concentrated milk	32
Roasted peanuts	39
Popcorn	9
Boiled potato	13
Potato chips	13
Rum	12
Soybean milk	38
Tomato	8, 14, 16, 17
Whisky	12

TABLE 2

Thiazoles Reported in Pressure-cooked Ground Beef[31]

Thiazole
2-Methylthiazole
4-Methylthiazole
2,4-Dimethylthiazole
5-Ethyl-4-methylthiazole
4-Ethyl-2-methylthiazole
2,4,5-Trimethylthiazole
2,4-Dimethyl-5-vinylthiazole
2-Acetylthiazole

TABLE 3

Thiazole Derivatives Reported in Potato Products[13]

Boiled Potato	Potato Chips
2,4,5-Trimethylthiazole	2,4,5-Trimethylthiazole
2-Isopropyl-4,5-dimethylthiazole	2-Isopropyl-4,5-dimethylthiazole
2-Isopropyl-4-methyl-5-ethylthiazole	
2-Isobutyl-4,5-dimethylthiazole	
2-Acetylthiazole	
Dipropylthiazole*	
Ethyldimethylthiazole*	

*Tentative.

However, some caution should be taken in viewing the foods in Table 1, because in some of the products (cocoa, shallow-fried beef, soybean milk, stored casein, heated milk, stale non-fat dry milk, and sterilized concentrated milk) the only thiazole derivative reported was benzothiazole. In light of the observation reported by Ferretti and Flanagan,[5] it would appear that the presence of benzothiazole in flavor concentrates may be an artifact. Ferretti and Flanagan[5] observed the presence of benzothiazole in a model system and could not rationalize its formation. They pointed out that its formation in any food system has not been postulated. They believe that it resulted from rubber tubing used in their isolation process.

Another interesting point concerning the foods listed in Table 1 is that most foods listed have undergone heat treatment or Maillard-type reactions. The only possible exception would be the tomato system reported by Kazeniac and Hall.[6] In this case, biogenetic formation of the thiazole in question, 2-isobutylthiazole, was proposed.

At this point, certain of the foods that are thought to contain non-artifact-induced thiazoles will be discussed in detail. The largest group of naturally occurring thiazoles reported to date from a food was found in pressure-cooked ground meat. These compounds are summarized in Table 2. The authors did concede that rather harsh sample preparation was involved, since the meat was heated to 182°C for 15 min in a pressurized system. No specific pathways for the thiazoles observed were discussed. Similar sample preparation conditions were used by Mussinan and Walradt[7] in identifying 179 compounds from pork liver. However, only thiazole, 4-methylthiazole, and 2-acetylthiazole were found. Interestingly, none of the compounds identified were thought to possess a typical liver character. Earlier, Tonsbeek et al.[8] had reported on the isolation and identification of a thiazole-related compound, 2-acetyl-2-thiazoline, in beef broth. The authors described its aroma as resembling freshly baked bread crust.

As seen in Table 1, several roasted-nut products have been reported as sources of thiazoles. Walradt et al.[39] first reported the occurrence of thiazole and 4-methylthiazole in roasted peanuts. No sensory properties were given, nor were specific formation pathways proposed. Kinlin et al.[10] were the first to report the presence of 4-methyl-5-vinylthiazole in roasted filberts. Sheldon et al.[11] found thiazole to be present in roasted filberts. Thiazole was also identified in popcorn by Walradt et al.[9] Rum and whisky are also examples of products where only thiazole has been reported.[12]

Buttery and Ling[13] have identified various thiazoles from potato products. Their data are summarized in Table 3. Buttery and Ling[13] noted that additional thiazoles may be present in potato chips but were obscured by the presence of other compounds. The concentration of thiazoles in boiled potatoes was calculated to be less than 1 ppm. They also observed that different lots of potatoes varied considerably in thiazole levels.

A unique thiazole, 2-isobutylthiazole, was first reported by Viani et al.[14] to be present in and contributing significantly to the flavor of tomatoes. A patent application was filed in 1969, based on this observation. The patent was granted in 1972 to Kazeniac and Hall,[15] who proposed the addition of 10 to 50 ppb of 2-isobutylthiazole to canned-tomato products as a means of enhancing tomato flavor. Stevens[16] reported on tomato cultivar differences in 2-isobutylthiazole levels. One variety was found to contain 59 ppb, whereas another contained 140 ppb. The sensory threshold of 2-isobutylthiazole was reported to be 1.3 ppb, and thus Stevens also concluded that this compound significantly contributed to tomato flavor. Stevens[16] also reported that 2-isobutylthiazole concentration was genetically determined by a single gene with additive effects. Buttery et al.[17] also found 2-isobutylthiazole in tomatoes and reported its odor threshold to be 3.5 ppb. However, they were not as convinced as earlier investigators that this compound was primarily responsible for tomato flavor.

Structural relationships of thiazole-related compounds reported to be present in foods or investigated for their flavor properties are shown in Figure 1.

Formation Pathways

Thiazoles are unique in that they are heterocyclic rings containing both nitrogen and sulfur. However, few investigators have postulated or reported on possible formation pathways. As mentioned previously, biogenetic pathways, which are not fully understood, constitute one avenue of formation.

One of the most logical explanations for the formation of thiazoles would be the thermal interaction of sulfur-containing amino acids and reactive compounds, such as carbohydrates or carbonyls. For example,

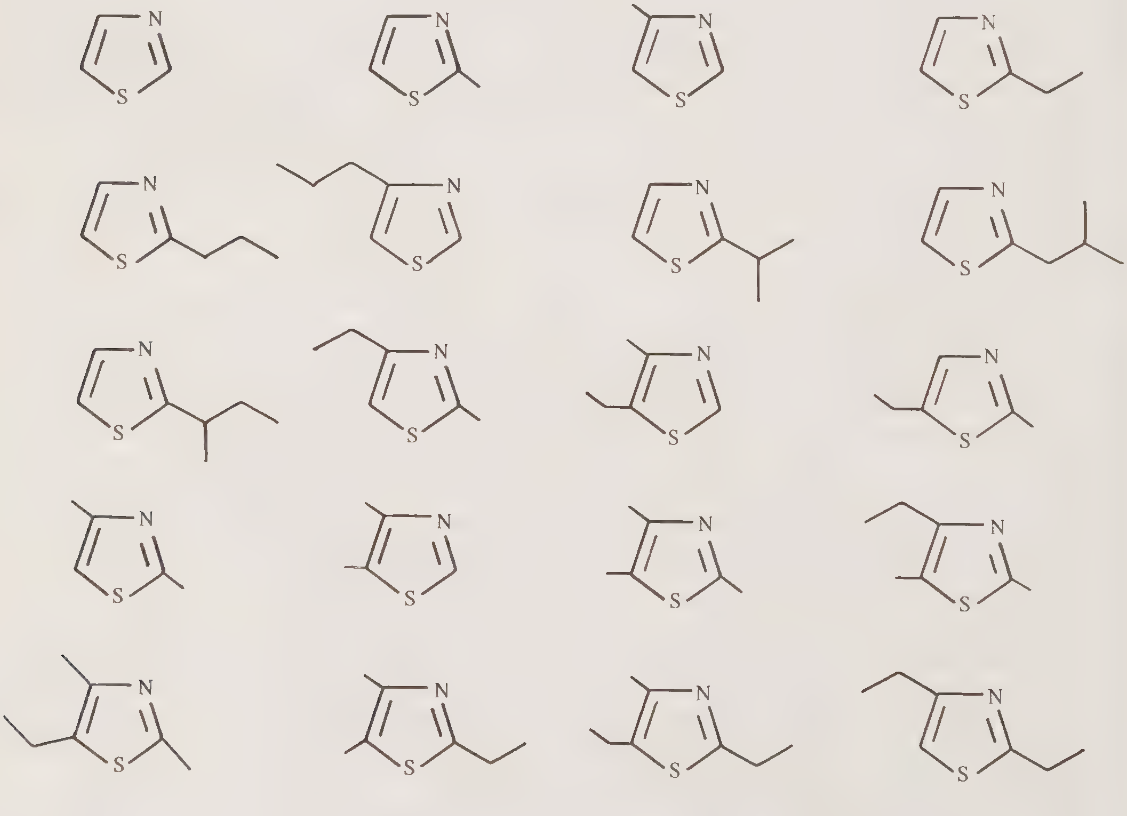

FIGURE 1. Structural relationships of food-related thiazoles.

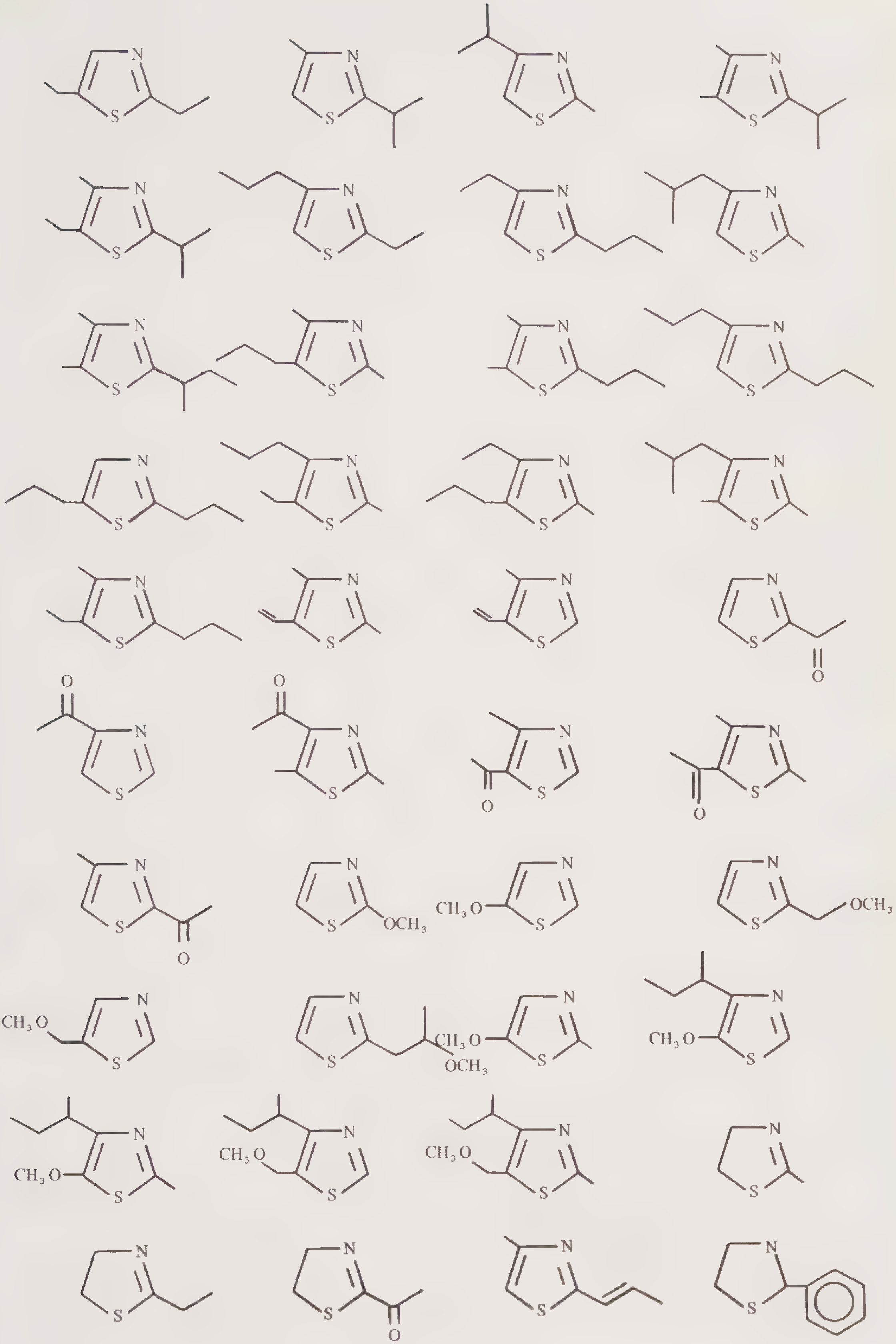

FIGURE 1. (Continued)

TABLE 4

Thiazole Derivative Formation through Amino–Acid Carbohydrate/Carbonyl Thermal Interaction[18]

Thiazole formed	Cysteine + glucose	Cystine + glucose	Cysteine + pyruvaldehyde	Cystine + pyruvaldehyde
Thiazole	–	–	+	–
2-Methylthiazole	–	+	–	+
2-Ethylthiazole	–	–	+	–
2-Methylthiazoline	–	+	–	–
2-Ethylthiazoline	–	–	+	–
2,4(or 5)-Dimethylthiazole	–	+	–	–
5(or 4)-Ethylthiazole	–	–	+	–
2-Methyl-5-ethylthiazole	–	–	–	+
2-Methyl-4(or 5)-ethylthiazole	–	+	–	–
Trimethylthiazole	–	+	–	–
2-Acetyl-4-methylthiazole	–	–	–	+

Kato et al.[18] convincingly demonstrated this possibility (Table 4), using model systems of cysteine, lystine, glucose, and pyruvaldehyde. As seen in Table 4, a wide variety of thiazoles resulted. Also, several thiazolines were identified in the mixture.

Another thiazole formation possibility involves the degradation of vitamin B_1 and/or interactions among its degradation products. This theory deserves further investigation and could easily be performed on a model system basis, similar to the procedures employed by Kato et al.[18]

Synthesis

As suggested by Kurkjy and Brown,[19] numerous alkylthiazoles can be synthesized by reacting appropiate halocarbonyls with thioamides. For example, Kato et al.[18] formed 2-methylthiazole by reacting thioacetamide with chloroacetaldehyde, and Buttery et al.[17] synthesized 2-isobutylthiazole from valeramide and chloroacetaldehyde. Buttery et al.[20] reported on the synthesis of 2-alkylthiazoles, using this technique. They reportedly formed haloketones by direct bromination of the appropriate ketone as described by Catch et al.[21] It should be noted that, when unsymmetrical ketones are used, two bromoketones are formed; however, Buttery et al.[20] reported no difficulty in separating the resulting two thiazoles formed. Buttery et al.[20] suggested the method of Bedoukian[22] for the formation of haloaldehydes. This involves formation of an enol acetate from a saturated aldehyde, followed by addition of bromine and then conversion to the dimethyl acetal; hydrolysis then results in the formation of the appropriate bromoaldehyde. Buttery et al.[20] reported alkylthiazole yields to be approximately 50%.

Recently Pittet and Hruza[23] reported on the synthesis of 11 alkyl-5-acetyl- and 10 alkoxythiazoles. A majority of their alkyl- and acetylthiazoles were also formed by the addition of halocarbonyls to thioamides as outlined by Kurkjy and Brown.[19] Ammonium dithiocarbamate, prepared by the method of Redemann et al.,[24] was reacted with 3-bromo-2-butanone, as outlined by Buchman et al.,[25] to form 4,5-dimethylthiazole. They also prepared 5-alkoxy- and 5-alkoxyalkylthiazoles by the method of Tarbell et al.,[26] which involves the reaction of N-acylamino acid esters with phosphorous pentasulfide. Unsubstituted 5-alkoxythiazoles were also prepared by successive bromination and deamination of 2-aminothiazole, as described by Beyerman et al.,[27] followed by treatment with the appropriate alkoxide. 2-Alkoxythiazole was prepared from 2-bromothiazole, which in turn was synthesized from 2-aminothiazole.[28,29] 2-Acetyl thiazole was prepared from 2-bromothiazole as described by Kurkjy and Brown.[30]

The thiazoline 2-ethylthiazoline has been synthesized by Kato et al.[18] by reacting the thioamide thioacetamide with the haloamine 2-bromomethylamine.

It is apparent that relatively simple methods of synthesis are available, which should encourage synthesis and evaluation of additional thiazole derivatives.

Isolation and Identification Techniques

Isolation techniques that can be used are those typical for the preparation of flavor concentrates. Buttery and Ling[13] have reported that thiazoles were observed in the basic fraction, intermingled with pyrazines, in potato products. Other investigators[7,31] have observed thiazoles in total-flavor concentrates. Thus it would appear that the isolation techniques outlined in a previous review[32a] would be adequate for effective isolation of thiazoles.

As in the case of most trace-level flavor compounds associated with foods, analysis of flavor concentrates obtained from relatively large sample sizes by means of gas chromatography-mass spectrometry combinations has been the primary means of thiazole derivative separation and identification. Several groups have published mass spectral data, and these are summarized in Table 5. In some cases thiazole structure and purity have also been confirmed, using NMR[20,23] or IR.[17] A partial listing of the types of gas-chromatographic columns used in thiazole separations is summarized in Table 6. As can be seen, extensive use has been made of capillary columns, but effective results have also been obtained by using the more traditional packed columns.

At this point perhaps a note should be made concerning a gas-chromatography technique that one investigative group[10] has found to be an aid in the identification of thiazoles. With some modification, a gas chromatograph unit was equipped to simultaneously monitor sulfur, nitrogen, and flame ionization detection signals. Thus, the method provides a means to locate areas in a complex chromatographic scan where sulfur-containing compounds, such as thiazoles, may be present.

Sensory Properties

Although most thiazoles are potent flavor-related compounds, few published data have appeared that discuss their thresholds or characteristic sensory properties. Odor threshold data for several thiazoles have been discussed previously in this review. Hopefully, additional threshold data on this important flavor area will be forthcoming.

To date, one published report has appeared, describing the sensory properties of 26 synthesized thiazoles.[23] These data have been included as a portion of Table 5. The authors reported that the compounds were smelled on blotters and were tasted at appropriate dilutions in water, which were not further specified. As seen in Table 5, a wide variety of characteristic odors were used to describe the various thiazoles.

In this same study efforts were made to compare the sensory properties of certain pyrazine and pyridine derivatives of analogous substitution. Thus, Pittet and Hruza[23] concluded that the lower 2-alkylthiazoles processed green, vegetable-like properties. Pyridines of similar structure were also found to have green odors. However, structurally comparable pyrazines were thought to be more nutty in flavor. Increased substitution (dialkyl- and trialkylthiazoles) added nutty, roasted, and meaty notes, which more closely approximated the di- and trialkylpyrazines.

Insufficient numbers of di- and trialkylpyridines were available to make significant conclusions regarding their flavor properties. The 2-alkoxypyridines were found to have unpleasant phenolic odors, whereas corresponding 2-alkoxypyrazines were sweet and nutty. The sensory properties of the 2-alkoxythiazoles were midway between those of the 2-alkoxypyridines and those of the corresponding pyrazines. Alkoxy substitution in the 5-position resulted in a more sulfury character than the same substitution in the 2-position. When tasted at a high unspecified dilution, the two 5-alkoxy-4-isobutylthiazoles were thought to be equal in strength, but 5 to 10 times stronger than the corresponding 5-alkoxy-4-isobutyl-2-methylthiazole, due to the diluting effect of the added methyl group.

Substituted 2- and 4-acetylthiazoles possessed nutty, cereal, and popcorn odors similar to corresponding pyrazines and pyridines. However, the 5-acetyl alkylthiazoles had more roasted, sulfury, meaty odors.

From the above, Pittet and Hruza[23] concluded that in the case of thiazoles substitution in the 2- or 4-position, adjacent to the ring nitrogen, resulted in more potent and characteristic flavors than substitution in the 5-position. Also, by comparing the three classes of compounds (thiazoles, pyrazines, and pyridines), they concluded that certain functional groups (acetyl, methoxy, and isobutyl), when located adjacent to the ring nitrogen of heterocyclics of similar size, possess similar odor notes. For example, 4-isobutyl-5-methoxythiazole, 2-isobutyl-3-methoxypyrazine, and 2-isobutyl-3-methoxypyridine all had characteristic green-pepper aromas. This would perhaps suggest that pyridines are another potent flavor compound class and deserve increased investigation.

TABLE 5

Chemical and Sensory Properties of Food-related Thiazole Derivatives

Derivative	Reported as naturally occurring	Odor description	Mass spectra	References
Thiazole	Yes	Pyridine-like	85(100), 58(67), 57(15)	18
2-Methylthiazole	Yes	Green vegetable	58(100), 99(57), 45(9), 59(8), 42(6)	23
4-Methylthiazole	Yes	Green, nutty	99, 71, 72, 45, 39, 69	7
2-Ethylthiazole	–	Green, nutty	58(100), 113(81), 112(63), 57(20), 45(20), 98(19)	23
2-Propylthiazole	–	Green, herby, nutty	99(100), 58(55), 112(22), 98(20), 45(14), 59(13), 127(12)	23
4-Propylthiazole	–		99(100), 45(50), 98(48), 71(36), 112(31), 127(25), 39(17), 126(17), 72(14)	20
2-Isopropylthiazole	–	Green vegetable	112(100), 58(53), 127(41), 59(29), 126(23), 27(17)	23
2-Butylthiazole	–	Raw, green, herby	113(100), 112(81), 58(53), 126(43), 59(40), 99(19)	23
2-Isobutylthiazole	Yes	Green-tomato vine	99(100), 58(38), 27(20), 126(17), 41(17), 113(15)	23
4-Ethyl-2-methylthiazole	Yes		127(100), 126(67), 71(68), 45(48), 85(45), 86(29), 112(24), 39(21)	20
5-Ethyl-4-methylthiazole	Yes	Nutty, green, earthy	112(100), 127(70), 45(47), 85(36), 43(26), 39(24)	23
5-Ethyl-2-methylthiazole	–		127(100), 112(67), 71(61)	18
2,4-Dimethylthiazole	Yes			
4,5-Dimethylthiazole	–	Roasted, nutty, green	113(100), 71(73), 45(40), 86(39), 85(30), 27(28)	23
2,4,5-Trimethylthiazole	Yes	Cocoa, nutty	127(100), 86(97), 71(90), 59(42), 85(35), 27(29)	23
4-Ethyl-2,5-dimethylthiazole	–		141(100), 85(86), 126(48), 59(45), 140(39), 100(23)	20
5-Ethyl-2,4-dimethylthiazole	–	Nutty, roasted, meaty	126(100), 141(74), 85(55), 54(31), 113(24), 59(23)	23
2-Ethyl-4,5-dimethylthiazole	–		141(100), 86(69), 71(65), 126(28), 45(24), 59(21), 85(21)	20
2,5-Diethyl-4-methylthiazole	–	Green, nutty	140(100), 155(75), 85(32), 45(30), 154(24), 100(22)	23
2,4-Diethylthiazole	–		141(100), 140(94), 71(58), 45(54), 86(37), 39(20)	20

TABLE 5 (continued)

Derivative	Reported as naturally occurring	Odor description	Mass spectra	References
2,5-Diethylthiazole	–		141(100), 40(67), 126(63), 71(55), 45(45), 140(45), 86(43)	20
2-Isopropyl-4-methylthiazole	–		126(100), 55(60), 141(49), 71(42), 72(38), 45(38), 39(24)	20
4-Isopropyl-2-methylthiazole	–		126(100), 141(51), 45(38), 85(33), 39(17), 140(14), 127(11), 99(10)	20
2-Isopropyl-4,5-dimethylthiazole	Yes		140(100), 155(40), 71(39), 45(30), 86(26), 59(23), 53(21), 39(20)	13
2-Isopropyl-4-methyl-5-ethylthiazole	Yes		154(100), 45(45), 169(42), 41(37), 85(27), 59(26), 155(20)	13
4-Propyl-2-ethylthiazole	–		127(100), 71(44), 45(40), 155(25), 140(21), 126(20), 154(17)	20
2-Propyl-4-ethylthiazole	–		127(100), 45(38), 71(29), 140(23), 85(21), 155(20), 154(17)	20
4-Butyl-2-methylthiazole	–		113(100), 45(35), 71(30), 72(17), 43(13), 155(10)	20
2-Isobutyl-4,5-dimethylthiazole	Yes		127(100), 126(33), 86(22), 71(18), 41(15), 45(14), 59(13)	13
5-Propyl-2,4-dimethylthiazole	–		126(100), 155(30), 85(18), 45(16), 59(11), 41(9), 156(8)	20
2-Propyl-4,5-dimethylthiazole	–		127(100), 126(33), 86(28), 155(21), 45(19), 140(18)	20
2,4-Dipropylthiazole	–		141(100), 71(33), 45(30), 154(22), 169(19), 41(13), 168(11)	20
2,5-Dipropylthiazole	–		141(100), 140(26), 45(23), 154(18), 71(18), 98(16), 169(15)	20
4-Propyl-5-ethyl-2-methylthiazole	–		141(100), 140(66), 169(52), 99(31), 154(27), 59(26), 45(25)	20
5-Propyl-4-ethyl-2-methylthiazole	–		140(100), 169(33), 59(20), 141(18), 45(15), 154(15), 99(15)	20
4-Butyl-2,5-dimethylthiazole	–		127(100), 85(30), 59(28), 140(23), 126(21), 45(16), 41(12)	20
2-Propyl-5-ethyl-4-methylthiazole	–		141(100), 145(31), 45(28), 85(24), 41(22), 169(22), 59(20)	20
5-Vinyl-2,4-dimethylthiazole	Yes			
5-Vinyl-4-methylthiazole	Yes		125, 97, 45, 58, 39, 98	10
2-Acetylthiazole	Yes	Nutty, cereal, popcorn	43(100), 127(41), 99(40), 58(40), 57(32), 112(26)	23

TABLE 5 (continued)

Derivative	Reported as naturally occurring	Odor description	Mass spectra	References
4-Acetylthiazole	–	Nutty, cereal	112(100), 127(60), 43(40), 45(30), 57(29), 84(23)	23
4-Acetyl-2,5-dimethylthiazole	–	Roasted, meaty, sulfury	140(100), 155(97), 43(70), 59(55), 45(43), 99(40)	23
5-Acetyl-4-methylthiazole	–	Roasted, nutty, sulfury	126(100), 43(78), 141(67), 45(48), 71(29), 98(22)	23
5-Acetyl-2,4-dimethylthiazole	–	Roasted, nutty, meaty	43(100), 155(69), 140(61), 45(38), 71(36), 112(29)	23
2-Acetyl-4-methylthiazole	Yes		141(45), 72(31), 113(27)	18
2-Methoxythiazole	–	Sweet, roasted, phenolic	115(100), 56(74), 45(64), 100(54), 58(39), 114(27)	23
5-Methoxythiazole	–	Roasted, meaty, onion	45(100), 115(64), 57(12), 72(10), 73(10), 44(9)	23
2-Ethoxythiazole	–	Phenolic, burnt, nutty	101(100), 73(79), 129(50), 27(49), 29(41), 45(41)	23
5-Ethoxythiazole	–	Cooked onion	45(100), 29(83), 101(75), 27(40), 46(38), 129(34)	23
2-Butoxythiazole	–	Green vegetable	101(100), 25(56), 41(35), 27(30), 57(24), 73(21), 157(19)	23
5-Methoxy-2-methylthiazole	–	Cabbagy, sulfury, vegetable	129(100), 45(81), 59(66), 88(27), 57(26), 73(25)	23
4-Isobutyl-5-methoxythiazole	-	Green pepper	128(100), 129(39), 101(36), 45(31), 171(20), 27(19)	23
4-Isobutyl-5-methoxy-2-methylthiazole	–	Green vegetable	142(100), 101(46), 185(40), 59(28), 143(24), 41(22)	23
4-Isobutyl-5-ethoxythiazole	–	Cucumber, green potato	114(100), 142(44), 27(36), 45(35), 29(32), 185(24)	23
4-Isobutyl-5-ethoxy-2-methoxythiazole	–	Green vegetable, onion	59(100), 128(98), 156(57), 144(37), 27(35), 20(31)	23
2-Methylthiazoline	–		60(100), 101(95), 59(60)	18
2-Ethylthiazoline	–		60(100), 115(53), 45(35)	18
2-Acetyl-2-thiazoline	Yes	Bread crust	42(100), 129(62), 60(58), 59(25)	8
2-Propionyl-4-methylthiazole	Yes			
Benzothiazole	Yes*			

*Possible artifact, as discussed in text.

TABLE 6

Gas-chromatographic Columns Used in the Separation of Thiazoles

Type	Size	Packing (coating)	Reference
Packed	10 m × 8 mm	20% DEGS – 40/60 Chromosorb W	14
Packed	15 m × 8 mm	10% Apiezon L – 40/60 Chromosorb W	14
Packed	16′ × 1/8″	4% OV-1 – 80/100 Chromosorb G	16
Capillary	300′ × 0.01″ i.d.	BDS	9
Capillary	1000′ × 0.03″ i.d.	5% Igepal co-880 – Carbowax 4000	17
Capillary	1000′ × 0.03″ i.d.	5% Igepal co-880 – Carbowax 20M	17
Packed	20′ × 1/4″ o.d.	9% Carbowax 20M – 60/80 Chromosorb P	17
Packed	10′ × 1/4″ o.d.	10% SF-96-350 plus 0.5% Igepal co-880 – 60/80 Chromosorb P	17
Packed	10′ × 1/4″ o.d.	10% DEGS – 60/80 Chromosorb P	17
Capillary	500′ × 0.03″ i.d.	Carbowax 20M	9
Packed	2 m × 1/8″ o.d.	20% Carbowax 20M – 60/80 Embacel	12
Capillary	1000′ × 0.03″ i.d.	Carbowax 20M	10
Packed	10′ × 0.085″ i.d.	15% DEGS – 100/120 Chromosorb G	11
Packed	3 m × 3 mm i.d.	3% SE-30 – 60/80 Chromosorb W	18
Packed	3 m × 3 mm i.d.	10% Carbowax 20M – 60/80 Diasolid L	18
Packed	3 m × 3 mm i.d.	20% Carbowax 20M – 60/80 Diasolid L	18
Capillary	500′ × 0.03″ i.d.	Carbowax 20M	31
Capillary	500′ × 0.03″ i.d.	SF-96	31
Capillary		Carbowax 20M	23
Capillary		SE-30	23
Capillary	300 m × 0.075 cm i.d.	5% Igepal co-880-SF 96(100)	13
Capillary	150 m × 0.075 cm i.d.	5% Igepal co-880-Amine 220	13
Capillary	1000′ × 0.03″ i.d.	Carbowax 20M	7

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FLAVOR POTENTIATION

Flavor potentiators (enhancers) may be defined as compounds exhibiting little or negligible odor and taste *per se*, but they magnify, usually manifold, the characteristic aroma of certain food substrates when used in small or even trace amounts. This behavior may be considered as a particular type of *synergism* (the cooperative action of various factors producing a total effect larger than the sum of the effects contributed by each factor alone). This definition is somewhat generic, however, since it is exclusive of modifying effects by potentiators on certain flavors. According to several investigators, the effect of potentiators consists of rounding-out the flavor, improving the mouthfeel, or, more generally, creating a sense of satisfaction on the sensory organs concentrated on the tongue as well as those placed throughout the oral cavity. It must be noted at this point that although potentiators affect the aroma (*i.e.*, the taste-flavor-odor complex), their effect on flavor has been studied in some depth.

In a broad sense even common salt (sodium chloride) should be classified as a potentiator; the following example may serve to better clarify the definition of potentiator. When adding increasing amounts of salt to a series of identical samples (*e.g.*, unsalted beef bouillon), we note that those containing a very low salt concentration do not exhibit a salty taste. However, for a given salt concentration higher than the threshold value, the characteristic salty flavor becomes perceptible. Those samples that do not have a salty taste nevertheless exhibit a somewhat different flavor as compared to the unsalted bouillon; this flavor depends on the concentration of salt. Therefore, salt, lacking flavor *per se*, still modifies and enhances the flavor of the food substrate to which it is added, in this case the beef bouillon.

The effect of sodium chloride on flavor is modest when compared to monosodium glutamate (MSG), a potentiator widely employed by the food industry. The effects of 5′-nucleotides* (disodium salts of 5′-inosinate and 5′-guanylate) are more impressive. MSG has a salty taste; the flavor becomes perceptible at a concentration of 0.03% in distilled water. In unsalted chicken bouillon the minimum perceptible is lowered to 0.015%, and in carbonated beverages, to only 0.002%. The above limits adequately illustrate the effect of a potentiator. A relevant issue that is better classified as a modification rather than a potentiation of flavor is the effect of MSG on sulfur-containing compounds. The flavor of these compounds (with the exception of thioisocyanates, whose flavor is so much enhanced as to attain intolerable values) is usually depressed by the presence of MSG. In 5′-IMP and 5′-GMP the effects are somewhat more complex. These potentiators exhibit a remarkable synergism in combination with MSG. A solution of 0.01% of disodium 5′-IMP in distilled water has practically no taste, while a solution of equal strength containing in addition 0.1% MSG exhibits a definite taste readily distinguishable from that of a pure MSG solution. In general, small amounts of disodium salts 5′-IMP or 5′-GMP added to a given amount of MSG will yield flavor potentiation equal to that of much larger levels of MSG alone. Essentially this is "potentiating a potentiator." The quantitative values vary widely due to the subjective method of measuring such effects (based chiefly on panel test evaluation).

The end-uses of MSG and the disodium salts of 5′-IMP and 5′-GMP are manifold, ranging from soups, bouillons, condiments, sauces, and protein-rich food products in general. However, products known to be flavor potentiators and used on an industrial scale are very few, even when sodium chloride and maltol are added to the list. The latter acts as a flavor potentiator for fruit juices, fruital aromas, and similar products. The extremely low levels at which flavor potentiators are usually active have rendered their systematic isolation and identification from natural sources extremely difficult. In view of the continuing and expanding research effort on similar compounds, it is conceivable that new ones will continue to become available in the future. Unfortunately, little is known about the mechanism of action of such compounds. Biological action on the sensory organs may be conceivable based on the very low levels at which potentiators are found to be effective. Continuing progress in molecular biology and advanced studies of the mechanism of olfaction and taste are expected to shed more light on these unanswered questions in the future.

* 5′-IMP = 5′-inosinate = 5′-inosinemonophosphate.
5′-GMP = 5′-guanylate = 5′-guanosinemonophosphate.

RELATIONSHIP OF TASTE TO FLAVOR: THE EFFECT OF SWEETENER ON FLAVOR

Flavorists are very well aware of the necessity of maintaining an exact balance between those components responsible for the taste sensation (sweet, sour, etc.) and those responsible for the overall flavor sensation. This statement may give the impression of a play on words. Referring to the universally accepted meaning of taste and flavor, the latter is defined as the resulting effect of two different sensations: taste and olfaction. The fact that any variation in the taste sensation (sweet, bitter, salty, sour) may bring about remarkable changes of flavor quality becomes intuitive. Moreover, if the stimulating sensations are now replaced with the stimulants, *i.e.*, the components of the flavor, it may seem obvious that any slight variation or imperfect dosage (for instance, the sour components in a beverage) may affect the taste as well as the resulting flavor of the beverage.

Although there is extensive literature covering the physiological problems associated with taste, olfaction, and flavor, it is nevertheless important by way of illustration to delve further into an aspect of significant nutritional and economic importance—the effect on the flavor composition of a beverage of synthetic sweeteners (cyclamates, saccharin) as compared to traditional sweeteners such as sucrose. This problem has indeed a great economic importance considering the huge world production of beverages containing both synthetic and natural sweeteners (low-calorie beverages).

What basic guidelines should the flavorist follow in flavoring food substrates (including beverages) sweetened with synthetic sweeteners in place of traditional sucrose? Should the flavorist employ the same flavors used for sucrose-sweetened products, or should he introduce modifications predictable to a certain extent based on experience but requiring experimental control? Will such modifications be capable of duplicating exactly the flavor obtained by formulating with natural sweeteners, or will it be practically impossible to attain the same degree of smoothness and flavor quality?

In order to render a thorough and convincing answer to these questions, a series of panel tests were devised (20 subjects selected on the basis of triangular tests by J. Krum) capable of rating not only the degree of flavor acceptance but also flavor identity and differences. First, two groups of aqueous solutions containing either a synthetic sweetener or sucrose varying in concentration by a dilution factor of 1:5 were panel tested. All subjects in the panel rated the solutions containing sucrose as most acceptable and indicated the bitter-metallic aftertaste of synthetic sweeteners as the chief reason for rejection. The flavor differences between sucrose and synthetic sweeteners became more evident as the concentrations increased from normal palatable levels to over-sweetened doses.

The second experiment consisted of panel testing of two beverages sweetened with either a synthetic sweetener (cyclamate) or with sugar and flavored with identical formulations of the type suitable for flavoring non-alcoholic beverages. Since similarly flavored beverages prepared with sucrose were already a market item, this implicitly vouched for flavor acceptance by the consumer. Test results were conclusive and illuminating; flavors rated to be of good quality and harmonious in sugar-sweetened beverages were found to exhibit disharmony, with consequent mediocre aromatic results, in synthetically sweetened beverages. A peculiarity common to all of the flavors tested was that the top notes and "fragrance" of the beverage were greatly enhanced in the presence of synthetic sweeteners. This behavior can be explained by Henry's law, which states that the vapor pressure of any compound dissolved in a liquid is directly proportional to the solubility in the liquid phase. Obviously sugar, which is an alcohol and in this experiment present in each formulation at 10%, acts by favorably increasing the specific solubility of the flavors. Therefore, a flavor dissolved in an aqueous beverage containing synthetic sweeteners gives the sensation of being more aromatic. The flavor formulations employed in the test were specifically designed for sugar-sweetened beverages and as such were harmoniously balanced. The replacement of sugar with synthetic sweetener decreased the specific solubility of the aromatic components, while it increased the vapor pressure and the relative volatility responsible for the enhanced olfactory sensation by the aroma.

The flavor disharmony resulting from the use of synthetic sweeteners can also be explained by the following concept. A flavor consists of several components having different chemical structures and interacting differently with sugar. When sugar is replaced in the beverage, this affects the vapor pressure of the various components. Since the flavor sensation is partially caused by the olfactory sensation consisting of aromatic molecules migrating from the liquid toward the vapor phase and impinging on the receptors responsible for the olfactory stimuli, the unbalanced volatility of the aroma may account for the unbalanced, uneven, and disharmonious flavor sensation.

Table 1 shows the number of individuals out of 20 who positively identified the four effects indicated in synthetically sweetened beverages formulated with various flavors.

TABLE 1

Flavor	Enhanced olfactory sensation	Flavor "disharmony"	Differential acidity	Identification of synthetic sweetener
Strawberry	20	19	0	20
Raspberry	19	20	0	19
Lemon	15	16	0	19
Lime	16	10	0	20
Orange	18	20	0	20

The results shown in Table 1 clearly indicate the unanimous differentiation between synthetically and sugar-sweetened beverages. Flavor "disharmony" in the presence of synthetic sweeteners was recognized by almost all members of the panel in all cases with the exception of the lime flavor, where the phenomenon was observed by only 10 out of 20 subjects. The enhanced olfactory sensation in the presence of sweeteners was also found by an overwhelming number of the panel members. The acidity of synthetically sweetened as compared to sugar-sweetened beverages could not be differentiated by the panel either qualitatively or quantitatively. All were able to identify the formulations containing synthetic sweeteners.

Once establishing beyond doubt that the flavoring of synthetically sweetened beverages is quite different from beverages containing traditional sucrose, the individual aromatic components or groups of components comprising the flavor formulates were thoroughly scrutinized. Through painstaking efforts flavor formulations suitable for flavoring beverages containing synthetic sweeteners were rebuilt. The flavored beverages were panel tested by the same subjects. Although the panel was always capable of identifying the beverage formulated with synthetic sweetener, few other negative effects were found. In particular flavor disharmony was overcome completely. By introducing suitable modifications in the formulation, *i.e.*, by reformulating the flavor using the same components in slightly different ratios, it has been possible to formulate flavors of a qualitative level identical to aromas compatible with sugar-sweetened beverages. The results of the panel test with reformulated flavors are shown in Table 2.

TABLE 2

Flavor	Enhanced olfactory sensation	Flavor "harmony"	Differential acidity	Identification of synthetic sweetener
Strawberry	15	20	0	17
Raspberry	16	19	0	14
Lemon	15	19	0	15
Orange	17	19	0	15
Lemon-lime	17	20	0	5

Table 2 clearly shows again that the olfactory sensation was greatly enhanced by the presence of synthetic sweeteners. This effect is considered highly desirable when accompanied by a well balanced and harmoniously blended flavor. The results regarding flavor "harmony" support the view that although flavor for beverages containing synthetic sweeteners must be specially formulated, it is perfectly feasible to do so with a high degree of acceptance. As in previous tests, acidity differences associated with the type of sweetener were not distinguishable. It is interesting to note that only 5 out of 20 subjects were able to identify the presence of synthetic sweetener in a lemon-lime flavored beverage. Only 75% of the individuals on the average were able to identify the presence of synthetic sweeteners as compared to the previous test. These results strongly suggest that when properly formulated, flavors may reduce to a large extent negative effects (*e.g.*, metallic-bitter aftertaste) associated with the use of synthetic sweeteners.

A practical example may best recap the above concepts. Let us consider the traditional formulation of a strawberry flavor for use in a beverage sweetened with sucrose:

A

Ethyl caproate
Ethyl butyrate
Amyl acetate
Ethyl acetoacetate
Amyl butyrate
Butyl isovalerate
Ethylfuran carbonate

B

Diethyl acetal
Octanal dimethyl acetal
Aldehyde C_{16}
Geraniol
Phenethyl alcohol
Terpineol
β-Ionone
Neroli essential oil
Vanillin
Maltol

In a formulation developed using the components listed above, it was merely sufficient to vary *the relative ratio* of group A (consisting of esters) to group B (including various functional classes of products) to prepare a strawberry flavor satisfactory for beverages containing synthetic sweeteners.

In conclusion, the experimental evidence indicates that whenever synthetic sweeteners are used (balanced or not by a proper dose of sodium and calcium cyclamates or saccharin and salt mixtures), the flavor formulation created by the flavorist should be quite different from traditional formulations used with sucrose-containing beverages. Remarkable enhancement of the olfactory sensation not disjointed from a satisfactory, well balanced aroma can be attained by lowering the ratio between the highly volatile and the non-volatile components in traditional flavor formulations. This applies especially to compounded and rebuilt fruital flavors. In simple flavors, such as citrus, ambivalence is frequently encountered but becomes more noticeable when the aroma of the terpene fraction overwhelms the flavor of oxygen-containing compounds, as in the lime flavor.

NOMENCLATURE AND CLASSIFICATION OF FLAVOR INGREDIENTS

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Introduction

A few basic concepts regarding the classification of flavor ingredients have already emerged. The classifications that will be discussed below are based on terms that have been widely used, not only in technical literature, but also commercially and by various regulatory agencies.

The regulatory agencies vary in their interpretations. In the United States, a concept widely used in Europe is in disfavor by the Food and Drug Administration, which has repeatedly stated that an ingredient is either "natural" or "synthetic". While they have specifically and categorically stated[1] that criteria of safety are not factors in the difference, the Food, Drug and Cosmetic Act of 1958[2] as amended requires labeling of "artificial ingredients"; therefore it is possible to have both natural (from lemongrass oil) and synthetic citral, for example. Economic adulteration is the bone of contention.

In Europe, however, the concept of "nature-identical" is accepted, whereby a chemical isolated from, or just identified in a natural material, may be used interchangeably with its synthetic counterpart in a "natural" flavor. Not all isolated materials, both in Europe and in the United States, are considered to be safe. Such problems are considered elsewhere in this volume. Readers are cautioned that the regulations regarding the use of any chemical are changing rapidly, and such publications as the U.S. *Federal Register* must be continuously consulted regarding classification of ingredients on the important criterion of "safety" or harmlessness in flavors at the recommended level of use.

The most recent (at this writing, November 1974) proposals of the U.S. Food and Drug Administration set forth three categories of materials that may be used.[3]

1. "Generally recognized as safe" for their intended use. without regard to level.
2. "Generally recognized as safe", but with levels limited to historically used concentrations, since there may be doubt as to safety if use becomes more widespread or concentrations are increased.
3. "Regulated food additives", where the levels are restricted.

All three categories will require adequate testing for toxicological criteria, such as mutagenicity, carcinogenicity, teratogenicity, acute toxicity, and possible allergenicity. Some products will be accepted by virtue of a "grandfather clause" – widespread use (in the United States) prior to January 1, 1958, or "prior sanction". There is a list of banned items, including coumarin and safrole, and some, but not all, of the natural products containing those materials; that is, though they have been identified in other natural ingredients, the level is low and the use restricted. Therefore, while the gradation of safety is a possible means of categorizing flavor ingredients, it is not pragmatic for this discussion.

The physical appearance of a flavor ingredient (solid, liquid, paste, etc.) may be considered as the first criterion of classification; this concept is summarized in Table 3. Also, flavor ingredients are of two general types, either "simple" or "complex". *Simple* ingredients are relatively pure chemical identities *per se*, such as vanillin, citral, *cis*-3-hexenol, or 2-methyl butanol. In many cases a so-called "simple" chemical may be a mixture of isomers when it is an article of commerce; thus, isoamyl alcohol is usually a mixture of 2-methyl butanol and 3-methyl butanol, and perhaps some *n*-pentanol This is frequently ignored in commercial practice, except that a user tries to purchase the same quality with every order, so that he may maintain the flavor characteristics he desires, which may be different from those desired by another user. The nature of

TABLE 3

Physical Classification of Flavor Ingredients

Solids	Liquids	Pastes
Crystals	Essential oils	Soft extracts
Powders	Folded	Resins (natural or prepared)
Freeze-dried	Rectified	Resinoids
Spray-dried	Terpeneless	Concretes
Dried extracts	Sesquiterpeneless	Emulsions (creams)
Plated	Oleoresins	
Encapsulated flavors	Absolutes	
	Fluid extracts	
	Compounded oils	
	Alcoholates	
	Alcolates	
	Tinctures	
	Infusions	
	Distillates	
	Spirits	
	Soluble essences	
	Emulsions	
	Fractions and isolates	
	Concentrated juices	
	Single-strength juices	

the impurity is dependent on the synthetic route and on the type of purification involved. Highly fractionated liquids, relatively free of impurities, will not have the same organoleptic characteristics as a less pure chemical, even when made by the same route.

Simple ingredients may be further classified by their functional groups – aldehydes, ketones, alcohols, mercaptans, etc. There are general relationships among the members of each family, such as the following:

1. Lower members are more volatile, sharper in odor, more water-soluble. Conversely, higher members are "fuller", more oil-soluble, less volatile, and of lower odor strength.
2. Branched chains seem to contribute more flavor and odor character, given the same number of carbon atoms in a molecule.
3. Stereoisomers may have very different odors/flavors and physiological response. Thus, *d*-carvone resembles caraway, and *l*-carvone is spearmint-like (both have been isolated from those natural materials); *l*-menthol has a cooling effect on the skin and in the mouth not shared by *d*- or *dl*-menthol. In other cases the effect is not so pronounced, as with *d*-citronellol and *dl*-citronellol, but *l*-citronellol is more "rosy" in character (it is frequently called "rhodinol").

It must be reemphasized that commercial grades of simple ingredients are not necessarily simple, but are mixtures of simple ingredients. Geraniol isolated from citronella oil (Java or Formosa) is about 60% true geraniol and 40% citronellol, with traces of other chemicals; synthetic geranoil, on the other hand, is quite free of citronellol, but may have 5% or more of its *cis*-isomer, nerol, depending on the route. Certain grades of natural linalool may have linalyl acetate present, as well as linalool oxide. Different suppliers use different methodology, and the product received from one is not always, or even often, interchangeable with the product of another.

The functional-group classification is the one being used by the U.S. Food and Drug Administration for its Scientific Literature Review in its program to affirm the GRAS status of some 1,000 synthetic or isolated flavor ingredients.[4] It is not of great use for purposes of further discussion here.

Of great interest and widespread use are the *complex* ingredients, which will be further discussed below. First it must be stated that both categories are used more often not in their concentrated state, but as dilutions in an appropriate solvent. Most flavors are "compounded", not in the sense of chemical "compounds" (molecular structures of various atoms), but in the sense that they are blends of simple and/or complex ingredients and/or solvents (carriers), which must be selected to give a homogeneous solution, emulsion, or powdered blend compatible with the product in which they are to be used. One or more compounded flavors may then be used in compounding another flavor; this is discussed elsewhere in this volume.

The nature of the solvent or carrier can be of paramount importance for both technical and commercial reasons. Ethyl alcohol (usually called only "alcohol") is the subject of taxation in many countries, and hence contributes cost beyond its cost as a "simple" chemical. In the U.S., 90% of the tax may be recovered as "drawback" when alcohol is used in non-potable (*per se*) beverages,[5] and 100% when exported. The United Kingdom does not distinguish between potable beverages and flavors for tax purposes. Isopropanol is available in a finer grade for solvent use and is widely used in the U.K., but it does impart some flavor. Methanol is prohibited almost universally as being toxic. Propylene glycol (1,2-propanediol), glycerine, 1,3-butanediol, vegetable oils, esters such as triacetin (glyceryl triacetate), dibutyrin (glyceryl dibutyrate), and other functional carriers may be used, but they are not as universally acceptable to regulatory agencies as ethanol, and the permissibility of such use must be checked against current regulations in each country in which the flavor is to be used. Not all of them may be technologically feasible for a given end use.

The balance of our discussion then will center on the *complex* ingredients, subdivided according to their physical characteristics.

Solid Flavor Ingredients

The crystalline aspect of a flavor ingredient suggests a well-defined chemical substance, but there are far fewer crystalline flavor ingredients than there are liquid. Some are powerful, and among them is vanillin, probably the most widely used ingredient (its flavor most popular among consumers), which may be made through several well-known routes. Vanillin was formerly made from eugenol (through isoeugenol), which was considered to give the finest organoleptic quality, but as a result of cost and improved methodology it has been replaced by that derived from lignin (coniferyl alcohol). Before being banned as toxic, coumarin was used in conjunction with vanillin in vanilla flavors. Curiously, the other powders used in large quantities are vanilla-like in character: ethyl vanillin, propenyl guaethol, and heliotropine (piperonal). Maltol and ethyl maltol, sometimes considered flavor enhancers rather than flavorants (yet still "flavor ingredients"), are crystalline solids. The enhancer monosodium glutamate, is a crystalline powder, as are citric acid, tartaric acid, malic acid, and fumaric acid.

Many carriers now being used in compounding flavors are solids: gum arabic, mannitol, lactose, dextrose, sucrose, dextrin (modified starch), etc. These are used in two ways, basically: one is as the substrate on which a flavor (concentrated or as a solution) is "plated", and the other is as an ingredient in spray-drying to get an entrapped or encapsulated flavor compounded, complex, or simple (see discussion later in this section.)

In the plating process, care must be taken to uniformly distribute the flavor (compounded, complex, or even a simple chemical) over the surface, and to allow the solvent to completely evaporate, otherwise the product will lump on standing. This process is not used as much today as it once was, because the extremely large surface area is conducive to oxidative degradation of sensitive materials, such as aldehydes. In certain uses, solid carriers are considered satisfactory. Of significant commercial and technical importance are spice oils and oleoresins plated onto salt; these form a distinct and separate product category. Other carriers are magnesium carbonate, silica gel, etc. The former products are intended for use by the pastry or baking industry and may have suitable dyes added to them; they are not particularly hygroscopic, but they must be stabilized and/or have an anti-caking agent added, because of the previously mentioned tendency to oxidize or to lose the plated material by evaporation. Many of those used are derived from aqueous extracts of herbs or spices (e.g., gentian, quassia, aloe, garlic, onion, etc.)

Spray-dried flavors or flavor ingredients have come into great prominence in recent years. Perhaps more compounded flavors are spray-dried than are simple or complex ingredients. They are relatively non-hygroscopic, free-flowing, stable (vis-à-vis loss by evaporation or degradation by oxidation), and easily soluble when introduced into an aqueous medium, etc. They are used in cake mixes, powdered mixes for beverages, desserts, puddings, pie fillings, etc. The concentration of flavor, however. is limited to about 25%, depending on the nature of the ingredient(s) used for the carrier, since mixtures of solids may be used as carriers. This is discussed more fully later on.[6]

Other flavor ingredients are quite commonly available in powdered form, but they are more or less hygroscopic and should be properly packaged to protect them from moisture until ready for use. Freeze-dried (lyophilized) flavor ingredients are characteristically very hygroscopic, particularly when they contain (naturally or as added ingredients) sugars, which may exist in anhydrous or hydrated forms. Some freeze-dried ingredients are now sold *per se* in the retail market (e.g., coffee and tea); they are obtained from a single source, without the admixture of other ingredients. Sugars, dyes, etc., may be added prior to spray-drying or may be blended into the already dried product.

Microencapsulated flavors or ingredients are the most recent entry into the field. Although they too may contain simple, complex, or compounded ingredients, they are more often used as final products than as ingredients; they exhibit prolonged storage stability, because the encapsulation material tends to surround the active flavor, thereby protecting it from evaporation, moisture, and oxygen, or from other chemical or physical attack. They can be formulated to rupture with pressure; however, cost and patents are factors in their use.[7]

Of lesser importance are the clathrate compounds, wherein a simple ingredient is enmeshed or entrapped within the crystal structure of the host. The clathrate mechanism may be part of the plating process (see above). Also being investigated are flavorants chemically linked to supporting molecular structures or entrapped in matrices from which they may be leached. Techniques similar to those used for time-release medications, seed protection, etc., are being investigated to further coat (and thereby protect) already solid materials, such as the Wurster process and the use of Aeromatic® equipment. These are the subject of patents issued[8] and pending. Some solids are amorphous masses and are considered under the heading Pastes below.

Liquid Flavor Ingredients

Liquid flavors constitute by far the most numerous class of ingredients. Their liquid character is an important asset in the majority of applications, since they diffuse readily into the substrate. They can be oily liquids, such as essential oils and oleoresins, or non-oily when obtained by dissolving in an appropriate solvent. Alcohol in a variety of strengths is the most widely used solvent. Fluid extracts, though they could be solutions of simple ingredients (more generally called just that – a solution), are more generally solutions of complex ingredients. A compounded flavor dissolved in a solvent is usually a flavor – the entire solution being considered the flavor under most conditions. (Note: under present regulations of the FDA in the U.S.A., solvents and carriers are considered "non-flavor ingredients" of the flavor for labeling purposes.)[9]

Compounded oils are properly flavors *per se* rather than ingredients. It is common practice in the industry, however, in order to protect trade secrets or for convenience, to compound certain ingredients into "keys" or "pre-mixes" or "goes-intos", which, when tasted, may have unrecognizable, poor, or even distasteful flavors. Thus, as flavors, they may be alcoholic or non-alcoholic, homogeneous or emulsions, with large, small, or zero proportions of solvent. As such, they are better considered as flavors than as flavor ingredients.

Essential oils are obtained from botanicals by expression or distillation, as will be discussed below. They are distinguished from the "fixed" or non-volatile oils, which have virtually no odor/flavor value. Further treatment of an essential oil results in "folded" oils, rectified, terpeneless, or sesquiterpeneless oils. There are many methods of doing this; most common is vacuum fractional distillation. Others are differential solubility, chromatographic absorption and elution of the oxygenated constituents, counter-current extraction, or combinations of one or more of these methods. These are discussed further on.

There is also a series of products consisting of simple or compounded flavor ingredients that contain alcohol in varying amounts. These flavor ingredients (used mostly in liqueurs and syrups) are derived from essential oils, herbs, or spices, and may also contain isolated products as well as other natural or synthetic flavor ingredients. It must be pointed out that there is no really clear-cut designation into subclasses, for various users have their own names and there is overlapping. In general, the discussion that follows may be applied. Fluid extracts, tinctures, alcolates (or sometimes alcoholates) are closely interrelated. They are generally obtained by maceration or percolation of an herb, spice, oil, etc., or sometimes by re-solution of an oleoresin or solid extract in a solvent, which may be either the one originally used to make the product or a different one; in the latter case there may be some insoluble constituents, which must be separated by filtration or centrifugation. The ratio of extract to substrate may be part of the label information as percent content (or as a ratio), giving the concentration of extracted flavor ingredient. The concentrations for some products may be standardized in official publications, such as the USP, BP, NF, FCC, FDA standard (as for vanilla extract), etc.[10] These products are used in liqueurs, cordials, syrups, vermouth, etc.

There may be specific usage of terms, but care must be taken to assure that the semantics are clear between user and supplier. Some consider that alcoholates are similar to hydrates in that the alcohol becomes molecularly attached to one or more simple ingredients in the complex, or that they are similar to acid salts of amines.

An alcolate is a product obtained by maceration in alcohol of a specific concentration of herbs and spices for a period sufficiently long to effect solution of one or more flavor ingredients. These products are somewhat equivalent to tinctures and are labeled with respect to the percent content of the extracted flavor ingredients.

A tincture is obtained by prolonged maceration or percolation in an alcoholic solution of definite strength. The ratio of flavor ingredient to alcohol is expressed in percent.

An alcoholate is obtained by maceration in maximum-strength alcohol (95–96%). The term implies that the alcohol becomes fixed or part of the flavor ingredient, much as water of hydration or a hydrochlorite.

Distillates are obtained when an alcoholic (usually) extract of a botanical is distilled, carrying with it some of the flavor ingredients by cohobation or coevaporation. This may be done after decantation or filtration of the botanical, expression of the liquid, or in the presence of the plant material (rarely animal material). Water, propylene glycol, or other solvents may be used in the same way as alcohol. If the botanicals are present, mechanical agitation may or may not be used. The distilled material is usually homogeneous, but in some cases an insoluble oil, lighter or heavier than the distillate, must be separated from it. This is particularly true when the solvent itself is a mixture (such as 50% alcohol) of ingredients with different boiling points.

Infusions, sometimes called percolates, are aqueous or alcoholic solutions of flavor ingredients prepared by extraction with a hot solvent.

Spirits are prepared by mixing alcolates, tinctures, and distillates in specific ratios (e.g., sweet spirits of niter).

Soluble essences, which can be alcoholic or non-alcoholic solutions of simple or compounded flavor ingredients, are special products derived from essential oils. The name "soluble essences" derives from their solubility in syrup. They can be considered aqueous solutions of essential oils obtained by removing insoluble terpenes by cold-solvent washing. Soluble essences are used for flavoring syrups employed in the manufacture of carbonated and still beverages.

Emulsions are mixtures of finely divided particles of liquids that are not mutually soluble in each other. The most common emulsion is probably milk. Unheated whole milk, on being allowed to settle, separates into two phases, the lower being primarily an oil (dispersed phase) in water (continuous phase), whereas the cream is some water dispersed in oil. By treatment with a homogenizing agent, the mixture may be made more stable. There are relatively few, if any, flavor *ingredients* that are emulsions, except when one emulsified flavor is used as an ingredient in another; therefore, emulsions are better discussed as being products. They are sometimes encountered as an undesirable stage in the purification or isolation of natural materials.

Juice as pressed from the fruit is called "single-strength"; it contains mostly water and hence occupies much space in storage. Because space is expensive, relatively little juice is kept in this form. The juice may be pasteurized or frozen, either as is or after being depectinized. It is more economical, however, to store the concentrated juice. Before concentrating, however, many juices, particularly berry juices and apple juice, must be treated with enzymes to "depectinize" them. This reaction hydrolyzes polysaccharides to simple sugars (mono- or disaccharides), which do not gel. Otherwise, as water is removed, the juice thickens beyond use, or the polysaccharides precipitate, undesirably, in the flavor later on, or in the product in which the flavor is used. Literature is available from suppliers of enzymes describing their use; they are highly specific, and mixtures must often be used.

Concentrated juices are obtained by evaporating water from single-strength juices. This may be done under vacuum at reduced or elevated temperatures. Valuable ingredients may be lost in the procedure, although processes and equipment are available to condense these materials, often called "essences" and designated by "fold", the reciprocal of the percent removed from the juice; thus, 1 lb of 100-fold essence is obtained from 100 lb of juice; 1 lb of 300-fold essence is obtained from 300 lb of juice. The concentrated juice may be pasteurized or frozen; the essence may be "returned", meaning put back into the concentrated juice, or may be sold with (or separately from) the juice, to be added by the user.

Fractions are obtained by (vacuum) distillation of essential oils and contain different proportions (from 0 to 100% is theoretically possible) of the chemicals present in the whole oil. The degree depends on the conditions selected, the size of the fraction (percent of the distillate), etc.

Isolates may be separated from essential oils, oleoresins, extracts, etc., by extraction, by differential solubility, or by converting to an insoluble adduct, followed by filtration or other physical separation and regeneration of the original material after the undesired constituents are removed.

Oleoresins are viscous materials that fall between liquids and pastes. In the writer's opinion, they are closer to pastes (see below).

Paste Flavor Ingredients

It is difficult to exactly classify flavor ingredients as *liquids* or *pastes.* Some so-called liquids are highly viscous, even semisolid (particularly when cold), or seemingly amorphous solids at room temperature.

"Solid extracts" or soft extracts of herbs, spices, and fruits are obtained by concentrating fluid extracts (or tinctures) to a syrupy constituency. Limited amounts of solvents may be added for convenience in handling, to adjust the product to a uniform flavor strength, or to represent a definite relationship to the botanical extract (e.g., 1:4, meaning 1 lb of extract was obtained from 4 lb of substrate). Typical are S.E. St. John's bread (carob bean), S.E. cover tops, and so forth. Different solvents may be used by the same or by different suppliers to obtain products with altered characteristics from the same botanical, such as S.E. (aqueous) kola nut and S.E. (alcoholic) kola nut.

Resins may be obtained *per se* naturally, or they may be prepared. The natural resins are plant exudates formed by terpene oxidation and are usually, chemically speaking, acids, acid anhydrides, or the esters of polyterpenoids. Sometimes they are the residues obtained after distilling off the monoterpenes and diterpenoids, as rosin is obtained from gum turpentine (from various species of pine trees). Prepared resins are the residues obtained after removal of the aromatic components of oleoresins by extraction. Both types are generally amorphous solids or semisolids, and, if free from water, may form translucent masses. Virtually free of odor, they may be soluble in alkalis (as their alkali salts), but insoluble in water; they are often soluble in undiluted alcohol and hydrocarbons.

Resinoids include balsams, gum resins, oleoresins, natural resins, etc.; they are products of non-cellular plants. Although they vary in texture from solid to tacky, they are homogeneous when freed of the sand, twigs, leaves, stones, ax heads, etc., often found in the crude commercial products gathered by natives of the producing geographical areas. Obviously, they must be treated before being used in food products. Their chemical constituents are resin acids, resin anhydrides, essential oils, sesquiterpenes, waxes, plant pigments, and other hydrocarbon-soluble materials. The crude products are first extracted with petroleum ether (benzin), benzene, hexane, kerosene, acetone, methylene chloride, or other solvents, and then filtered; the solvents are removed by distillation, using particular care to avoid scorching the desired residue. Other solvents, less volatile, may be left in the product when so desired; these include diethyl phthalate, benzyl benzoate, and isopropyl myristate. Care must be taken to use only solvents permitted by regulatory agencies, and/or to leave not more than permitted amounts when the resinoid is concentrated.

Occasionally, some emulsions are heavy enough to be considered creams or pastes. These probably would have the oil as the continuous phase and water as the dispersed phase, but the reverse can be true. There are few such flavor ingredients.

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GENERAL METHODS OF PREPARATION

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Having established that most flavor ingredients can be well characterized, it is important to illustrate general methods of preparation. Each method, although developed along certain generally acceptable manufacturing guidelines, may be modified or combined into rather unique operations. Manufacturers have their individual particular trade secrets regarding, for example, choice of solvent, temperature, construction of equipment, etc., and experience so as to offer a particular quality while achieving superior yields, often resulting in lower costs and greater utilization by the food industry.

As indicated in Figure 1* (see fold-out), flavor-ingredient manufacture can be divided into two major categories: those unit operations utilized for the recovery of ingredients from natural sources, and those prepared by synthetic routes. In the latter case, some of the starting materials can be fractions and isolates derived from natural sources. Products from both lines are then fed into the flavor center for compounding, etc., into finished products.

Although synthetic methods are well known and documented, the criteria for purity used in other industries are not directly applicable to flavor ingredients. Such analytical parameters[7] as heavy-metals determination, pH, and melting point are useful in guaranteeing freedom from toxic substances, intermediates, etc., but the ultimate criterion is organoleptic quality. A simple ingredient, as described earlier, is almost never a 100% pure chemical identity. The trace impurities are often highly desirable to the flavorist or perfumer, and the impurities, or lack of them, in one synthetic route versus another may cause the product of one manufacturer to be much less desirable to the trade. In recent years, new routes to commonly used chemicals were published, but it took many more years before flavorists were able to appreciate the value of the new products. In an established formula, the products are not generally wholly interchangeable, and hence they must be worked into new formulations. In the same way, isolates from natural products may have nuances different from their synthetic "nature-identical" counterparts. With that caution, synthetic materials may be dismissed from further consideration, except to note that many of the general methods below are also used in synthetic processes. Some manufacturers use the same equipment for both natural and synthetic materials, but there is a tendency towards specialization, not only in regard to natural versus synthetic material, but also in the narrowing of synthetic product lines to those in which the manufacturer has superior expertise vis-à-vis his competitors. The general methods described are those used to recover natural flavor ingredients, i.e., products obtained by distillation, extraction, expression, concentration, or isolation.

Distillation

The application of heat to essential oils, as with many organic substances, has a proclivity to cause decomposition. Distillation is a process requiring heat to volatilize the components, and most essential oils boil at elevated temperatures. In addition, each component boils at a different temperature, depending on molecular weight, functional groups present, molecular composition and structure, etc. Many texts are available that discuss the theory of distillation.[8] In general, a mixture is said to boil when the sum of the vapor pressure of each individual component equals the atmospheric pressure (Dalton's Law of the Additivity of Vapor Pressures). If the pressure of the atmosphere is reduced, the temperature required to

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* The editors and CRC Press thank Naarden Inc. for their kind permission to reproduce Figure 1 from their publication *Flavor Thoughts*, No. 4, The Flavor Principle.

cause boiling is lower. It also happens that products immiscible with each other will codistill. Thus, steam blown through an essential oil, or generated by boiling water in the presence of volatile materials, will carry over those materials at a lower temperature than would be necessary for the volatile oil alone to distill. This is a special form of distillation called *steam distillation.*

Most essential oils do not exist as such, but are microdroplets in cells in the plant. The cellulosic materials of the cell walls must first be ruptured to release the oil, which must then come in contact with the water (steam) before it can be carried away from the plant material to a condenser. The separation of oil from the botanical is not, then, an instantaneous process, but is effected only after a more or less prolonged period of contact with water. A number of devices may be employed to hasten the process: grinding, enzyme treatment, use of hypertonic solutions (addition of salt to the batch, to change the osmotic pressure in an endeavor to rupture the cell), or use of non-volatile wetting agents. Different varieties may be treated in different ways, and the optimal methods have been studied by processors.

Aromatic plants are usually distilled when they are fresh (especially herbs, flowers, and leaves). Some, such as roses and orange flowers, must be harvested early in the morning and distilled immediately. If the plants are stacked, even for a few hours, they may ferment; consequently, the delicate perfume of the distillate would be partially destroyed, or at least altered. Plants that can be preserved must be dried in well-ventilated sheds shielded from direct sunlight. The drying process decreases or totally eliminates the water present in the plant. Therefore, dried plants at equal weight yield lower levels of essential oil than fresh plants. With the exception of certain types of roots and seeds, wherever a choice is possible, the distillation of fresh plants is preferred. Although many plants can be dried without alteration, freshly distilled plants generally yield essential oils of superior fragrance and quality to those distilled from dried products. This is probably the result of fermentations not yet well identified that occur during the drying process.

Drying – the volatilization of water – by the same token may also cause codistillation, particularly of lower-boiling, more volatile components. Modern analytical technology (GLC, for example) has enabled the farmer to follow the biogenesis of the desired component and to harvest his crop at the peak concentration for better yield, quality, and composition.

On the other hand, some plants do not develop the desired essential oil until fermentation or enzymolysis has taken place. In mustard and bitter almond, the desired components of the oils exist as glucosides, sinigrin and amygdalin, and cannot be isolated until the linkage is broken by action of the enzymes myrosin and emulsin, which hydrolyze the glucosides, freeing the oil. Therefore it is necessary to grind the plant and keep it wet (macerate) long enough for the reaction to take place before proceeding with isolation.

It is interesting to note at this point that other flavors are developed in plants as a result of fermentation and enzymolysis, such as during the curing of tobacco, tea, coffee, cocoa, and vanilla beans, although these are not usually isolated by distillation at that point.

Distillation may be broken down into six fundamental methods for the isolation of flavor ingredients: (1) direct or dry distillation, (2) wet-steam distillation or cohobation, (3) dry-steam distillation, (4) vacuum distillation, (5) fractionation, and (6) molecular distillation.

Direct-heating Distillation

This method is used for very few products. It is generally destructive when applied to plant materials, and it is best known for the production of tar oil or pyroligneous acid as wood is heated in retorts. Direct heat – the application of flame or hot oil to the still pot - may be used in combination with other methods (see below), but this is not "direct heating" of the plant material.

Wet-steam Distillation

Although sometimes called "direct-heating distillation", referring to the fact that a wood or coal fire, or a gas or oil flame is applied directly to a vessel filled with plant material *and water,* this is really "wet-steam distillation", with the steam being generated *in situ* from the water. Variously shaped stills are used, specifically designed for the distillation of the various types of plants, and even more specifically for the efficient loading and unloading of the plant materials where possible. Where farms or plant-gathering locations are far apart and transportation is poor, the plants must be processed on the spot, and small units, generally quite crude, are all that are available. The "exhausted" plants (after removal of the oil) are often air-dried and used as fuel for subsequent batches. The operation proceeds as follows: the plant is placed in a boiler and covered with water; heat is applied until distillation of water begins; at the beginning of the distillation, only clear water is obtained; when the water turns milky, the essence has started to codistill; by means of Florentine flasks, the water phase is separated and returned to the still; when the condensate runs clear (no second phase present), the batch is considered finished.

This system exhibits several shortcomings: (1) considerable loss of time from the loading and unloading of the material in the still, (2) direct contact of the plant with the metallic container may produce off-flavors because of localized excessive heating, and (3) formation of calcium deposits on the walls of the boiler with loss of heat-transfer efficiency. However, salt may be used to slightly raise the boiling temperature and improve permeability of the cell walls; the recycled water is saturated with the water-soluble ingredients, and they continuously redistill; in methods described below, they may be lost.

Dry-steam Distillation

A more modern method, employed when a central manufacturing plant is located where the harvest from surrounding areas (or, if dried material, from anywhere in the world) may economically be brought to it, is to use "dry" steam. Several versions of equipment are available, all having one feature in common: the plant material is supported away from the boiling water that generates the steam. In turn, the water may be heated directly by a fire or flame, or indirectly by heat exchange from hot oil or from steam generated externally; in other versions, the heat exchanger is a separate vessel. Most frequently, the condensed water is returned to the system; in rare cases, the steam is generated in a separate boiler, passed through the botanical, condensed, decanted, and discarded.

There is a grid located in the (cylindrical) vessel at, say, $\frac{1}{8}$ to $\frac{1}{4}$ the height of the side wall from the bottom of the vessel. If the grid has small openings, the material may be placed directly on it, to be removed when exhausted through a tightly fitted "manhole" in the side. In other construction the grid is coarser, and the plant material is placed in a basket or on a finer plate fitted with lifting chains; the entire top (cover) can be removed, and the charge of exhausted plant may be removed in one fell swoop while still hot; another charge may then be rapidly placed into the still by appropriate mechanical hoists, the cover replaced, the piping reconnected, and another batch processed. This speed is particularly important when fresh plant material is to be processed at the peak of its maturity. In the mint-growing areas of the U.S.A., the carts used to gather the cut mint from the fields are actually the still bodies. They are driven or pulled to the steam-generating area, suitable pipe connections are made, and the spearmint or peppermint oils are distilled from them. Such units are operated by the larger farmers, by cooperatives, or sometimes by brokers dealing in the oils.

The methods noted all have in common the use of saturated ("dry") steam. As the steam is bled through the plant, it strips the volatile principles from the plant, which codistill with the water. The two-phase distillate is condensed, the aqueous phase is separated by decantation in one or more (in series) Florentine decanters, and the water is returned to the system. Decanters may be arranged to separate either oils heavier than water (clove) or oils lighter than water (most others), and may either be continuously discharged or left to the end of the batch. Because some fractionation does occur, the first portions being richer in the more volatile components, the yield from the entire batch must be combined for uniformity of product.

Units in which water is placed below the grid and heated by a direct flame are becoming more rare. Rather, coils are immersed in the water, the vessel is jacketed and insulated, and the heating medium (steam at a higher pressure or other heat-transfer media) is circulated through the coils. The technique where live steam is generated in a separate heat exchanger (reboiler), often of the shell and tube type, is considered to yield the best results; it avoids temperature oscillations and contact of the plant with the metallic still body at elevated temperatures. Material of construction may vary – copper is frequently used, but stainless steel and aluminum are becoming common, particularly for the vapor piping, condenser, and subsequent piping, which comes in contact with the oil. Since this method involves two vessels, it is more costly to build and the operation is somewhat slower; it is less often used than the injection of live steam directly from the primary boiler, where the condensed water may not be recycled and some loss of yield (by solubility in water) may occur.

To avoid losses from solidification of the essence during distillation, apparatus for continuous distillation are employed by large manufacturers. These are equipped with special control devices for the automatic feeding of the water separated by decantation. Although, theoretically, there are no big differences between the various methods of steam distillation, in practice the results may differ remarkably because of side reactions occurring during distillations. Some of these are hydrodiffusion, hydrolysis, and thermal decomposition.

Hydrodiffusion is the phenomenon wherby essential oils and water diffuse through plant membranes. In steam distillation, steam does not effectively penetrate membranes of dry plant cells. The use of superheated steam dries the material completely, whereas the use of saturated steam yields essential oils. Superheated steam can be applied only when the plant cells bearing the essential oil have been set free of the surrounding membranes by means of a preliminary very fine grinding, or by the use of melting agents or enzymes. Diffusion may take place only when the material is thoroughly wetted and the soaked tissue has reached the isotonic point with the circulated steam. It appears that the walls of plant cells are impermeable to essential oils. Unground plants immersed in water for long periods do not yield essential oils; the yields after distillation are also practically nil. If the material is finely ground, thus breaking the wall of the oil-bearing cells, the codistilled water contains considerable amounts of essential oils. Temperature is also an important factor. Where maceration is used and is carried out (sometimes with the addition of salt) in hot rather than in cold water, a larger amount of essential oil is found in the water. When hot water is used, the essential oils dissolve in the water present inside the plant cells, pass through the imbibed cell membrane by osmosis, and reach the external surface, where they are evaporated.

The speed of evaporation depends not only on the volatility of the components, but also on their solubility in water. The lower-boiling, more volatile materials, soluble in water, distill before the water; they remain soluble (do not separate) on condensation, and therefore continue to recirculate with the water, revolatilize with the steam, etc. The higher-boiling, non-soluble materials come over in a ratio depending on their vapor pressure relative to that of the steam. Temperature is dependent on the pressure in the still, which is usually atmospheric pressure, although it is theoretically possible in closed systems to operate either under vacuum or at elevated pressure (and therefore temperature).

Essential oils have components that are somewhat soluble in water, less so at lower temperatures. It is, therefore, important to cool the condensate properly to reduce this solubility. If the steam is "single-pass", the condensate is discarded along with the soluble valuable oxygenated flavor components of the oil, the less valuable terpene hydrocarbon components being less soluble in water. Total yield also is reduced. Recirculation of the condensate into the heat exchanger to generate more live steam minimizes the losses, since the steam already contains the soluble vapors, which are recondensed, etc. Care must also be taken to prevent "channeling" of the steam through the plant charge in order to distribute the steam uniformly through the mass. Condensation that would drain back through the charge and leach soluble materials from the plant is to be avoided. In the best techniques, the stills are insulated, and some coils (or jacket) are placed in the bottom of the still to reevaporate such condensate, although care must be taken that the temperature and physical position is such that the steam is not excessively superheated (dried), if at all.

Hydrolysis, in this case, is the cleavage effected by water on certain constituents of the essential oils. Natural constituents susceptible to hydrolysis include esters, acetals, reaction products of organic acids, and alcohols. In the presence of water, and especially at elevated temperatures, esters tend to decompose, thus forming the corresponding acids and alcohols. Since esterification and hydrolysis reactions are reversible at equilibrium, the system consists of esters, water, alcohols, and acids. If a large amount of water is present, hydrolysis prevails, thus reducing the concentration of the often desired ester components. Hydrolysis thus lessens the quality of the oil and may decrease the yield, since the alcohols are more water-soluble than the esters and tend to remain in the water phase. This is prevalent in distillation with water. In steam distillation hydrolysis is limited and decreases even further if superheated steam is employed. Hydrolysis usually occurs during the contact period between the oil and the water phase. This is particularly disadvantageous, since, under the conditions necessary for this type of distillation, the contact period is rather long.

Decomposition during distillation is usually caused by excessive heat. The temperature of the steam that is bled through the material oscillates during the operation. It may be kept low at the beginning, when low-boiling constituents are vaporized, and increased to evaporate constituents with higher boiling points. Steam finally reaches the temperature of saturated steam at a given pressure. The pressure is controlled by suitable valving in the vapor line from the reboiler to the still body or in the line from the steam generator to the still. If there is no resistance or back-pressure in the still, its vapor line, condenser, etc., the steam will never go above atmospheric pressure.

Although hydrodiffusion, hydrolysis, and decomposition accompanying distillation with water are theoretically distinct, in practice they occur concomitantly. An example of each of the effects would be difficult to give. However, distillation should be carried out at the lowest permissible temperature, since most constituents of essential oils are unstable at elevated temperatures. The temperature of distillation with water or with steam at atmospheric pressure is usually slightly under 100°C. In steam distillation the temperature may be 110°C or more, according to whether the steam is saturated or superheated. It is possible to lower the boiling temperature by using a closed system and reducing the pressure by vacuum pumps, steam jets, etc.

Vacuum Distillation

Steam distillation, among several other methods for extraction of essential oils, is the system generally preferred because of its rapidity. However, this is too violent for products with very delicate and easily alterable constitutions, such as the odorous substance present in the essential oils. This shortcoming is avoided by conducting the distillation at reduced pressure.

Distillation under reduced pressure offers several advantages, as follows:

1. Economy of fuel.
2. Drying and resinification effects are avoided by operating in the absence of air.
3. Ease of separation of the essences from other constituents exhibiting high and very close boiling points under ordinary pressure, thus codistilling with the essence.
4. The chance of reaction between components occurring at more elevated temperatures is lessened.
5. The lowering of boiling points facilitates the distillation of products difficult to distill under ordinary pressure without decomposition or significant losses in yield.

However, how does one heat a plant material at all, to reach whatever boiling point is required at the given vacuum? Special construction is necessary for heat transfer, which is expensive, and therefore vacuum distillation is very rarely used for the *primary* recovery of essential oils from plant material. It is almost always employed in the redistillation and fractionation of essential oils, whatever means were used originally to separate the oils from the plant material.

Fractional Distillation

Fractional distillation solves one of the most important problems in industrial chemistry – the separation in almost pure form of well-defined volatile chemical substances that are found mixed with other volatile substances. Fractionation may take place under increased pressure, as is common practice in the petrochemical industry, but the increased temperatures would be highly detrimental to flavor ingredients. Therefore, the pressure is reduced in a closed vessel to lower the boiling points and sometimes widen the relative difference in boiling points between components, easing their separation. Two major means of creating vacuum are used: (1) mechanical pumps of different styles, and (2) aspiration, based on Bernouli's principle, where a moving stream of water, steam, mercury vapor, etc., at high speed causes a depressed pressure in a suitably constructed device, known as an aspirator, jet evacuator, mercury diffusion pump, and so forth. Both principles are fully exploited in the laboratory and industrially.

It is a general rule to start large-scale fractional distillation only after carefully checking the behavior of the mixture to be fractionated in the laboratory. This is necessary in order to know the exact number and quantity of the fraction to be separated and to establish the proper distillation temperatures. This is then translated to the same operating conditions to be used in the plant. While much has been published on the theory and practice of fractionation of two-component systems, the complications are increased multifold where many components are present, and where the concentration of each component varies from season to season, from field to field, and even from batch to batch. Factors such as the relative volatility of the components and the physical construction of the still must be taken into consideration. In the flavor (and perfume) industry, columns are generally "packed" rather than being of the bubble-cap, tray, sieve-plate, or other similar type, and packings must be selected to give low pressure drop relatively high throughput, relatively uniform efficiency at a range of loadings below the flood point, etc. Many types of packing have been introduced and advertised to the trade, and each has its proponents. Cost is a factor that is not neglected. The HETP (height equivalent to a theoretical plate) under varying conditions of reflux ratio, throughput, etc., affect the degree of fractionation for a given column.

Once the experimental parameters have been established, plant operation must follow the conditions as exactly as possible. Temperature control is important, the degree of heat applied being as little as possible above the boiling point of the most volatile component remaining; the column must be kept as close to equilibrium as possible to effect the best separation of the components; and interruptions must be avoided. Automatic controls are very much indicated, and many have been developed. The practical secret of obtaining good cuts is to maintain conditions as constant as possible, and if upsets do occur, to switch to total reflux for an appropriate time until correct conditions have been reestablished. The boiler must not be filled beyond a certain capacity, and foaming should be avoided. The operation is preceded by degassing and dehydrating, which require particular attention. Once the distillation is started, fractions can be exactly separated by weight, volume, refractive index, GLC, IR, UV, or other analytical parameters.

The most simple vacuum distillations are called *rectification,* with only one or two theoretical plates being employed; hence, little fractionation takes place. Oils may be rectified 2X, 3X, etc., which is effectively the same as a single fractionation using a more efficient column.

Rectification is used primarily to remove residual water and very light fractions from the heads (0.5-0.8%) and heavy, high-boiling components, such as sesquiterpenes and waxes, from the tails (1.0–1.5%) or from resinified components (often colored) that may have formed in old oils. The loss of quality essential oil during rectification should not exceed a maximum ranging between 1.5 and 2.3%, according to the type of essence.

It is sometimes necessary to use chilled water from melting ice, ice/salt, or mechanically refrigerated brine in the condenser in order to assure that no losses occur by failure to condense the low-boiling components, which also act to reduce the efficiency of the pumping system. Suitably chilled traps may be installed in the vacuum line to remove such components, which may seriously impair the ability of the vacuum source to maintain the desired low pressure.

In the deterpenization of essential oils, the product is distilled in a manner to achieve total elimination of the head fractions (terpenes), with subsequent rectification of the main and tail fractions, which are combined after distillation. The exact knowledge of the percentage of terpenes to be removed and of the physical-chemical characteristics of the terpeneless essence obtained in a pilot plant run is indispensable prior to transferring the operation to an industrial scale. The main objective of removing terpenes is to obtain an essence with high solubility and to enhance the top notes of the essence by concentrating the more functional products.

Terpeneless essences exhibit well-defined physical-chemical constants. Special equipment and handling are necessary for different essences, but in general a suitable apparatus for the removal of terpenes can be used for more than one product by varying the conditions employed. That is, where less fractionation is required, a lower reflux ratio may be employed. In rare cases, because of the expense involved, packing may be removed; with suitable valving and piping, it is possible to by-pass part of the column. Although such a mechanical installation is more costly, this cost is compensated later on by the time and labor saved in changeovers and by the gain in operating time. The removal of sesquiterpenes from essential oils is also obtained by rectification. The sesquiterpeneless essence consists of the main fraction of the distillation, with total elimination of the insoluble head and tail fractions, including waxy residues. A sesquiterpeneless essence is even more soluble than one free of terpenes only. The removal of sesquiterpenes is limited to only a few essential oils because of the high cost of the resulting product. The operation may also affect the functionality of the essence.

Commonly employed sesquiterpeneless essential oils include lemon, lime, orange, and sometimes bergamot oils. The equipment used for the distillation is identical to that used for the removal of terpenes. The distillation can be carried out by distilling the main fraction and leaving the tail fraction containing sesquiterpenes and other residues in the boiler; the tail fraction is subsequently discharged.

Continuous distillation is rarely, if ever, employed for essential oils, the quantities involved being too small, but it is being used during production of synthetic simple components manufactured in large quantity, such as citral.

Differential Solubility

Another method of separating the more valuable oxygenated compounds from the terpenes and sesquiterpenes is to take advantage of the varying solubility of the fractions in a particular solvent, such as aqueous alcohol, dimethylsulfoxide, etc. This "cold" method has the disadvantage of being slow and requiring rather more labor. On the other hand, simple equipment and little fuel energy are required for the basic separation. Since solubility is temperature-dependent, for utmost quality uniformity the temperature of the extraction must be controlled. Another advantage is that the oils are not subjected to the high temperatures required by distillation (even under vacuum), which causes flavor degradation in the terpeneless or sesquiterpeneless oils, particularly in citrus oils, and this method, with variations in technology, has been used for many years. Sesquiterpeneless orange, lemon, lime, mandarin, tangerine, and grapefruit oils may be made by this method.

The general procedure described below can be improved by use of modern equipment. For instance, instead of allowing the mixture to settle out and simply separating the phases by gravity, solid-bowl centrifuges (similar to those used for separating cream from milk) may be employed to separate the oily upper layer from the aqueous solvent lower layer when the volume of material to be processed warrants it economically, resulting in much faster as well as more complete separation of the phases, since the force of gravity is multiplied manifold. The temperature of the mixtures, instead of being ambient and therefore varying from winter to summer, may be controlled by circulating water (or other fluid) through the jacket or in coils in the vessel, with the water in turn automatically heated or cooled, as may be required, to maintain constant temperature in the vessel. Such equipment is obviously more expensive than the simple equipment that can be used for small-scale production.

Multistage countercurrent extractors may also be used, wherein the heavier aqueous alcoholic solution containing 50 to 70% alcohol is fed near the top and falls by gravity to the bottom, and the essential oil is fed near the bottom and rises through the solvent as it is displaced by the higher-specific-gravity liquid. Suitable settling areas are provided at top and bottom for separation of the phases, which may be further clarified by centrifugation, filtration, or other methods, as noted below. Solvents other than ethanol likewise may be used.

In order to minimize differences in quality, in large-scale production several lots of essential oils are bulked in large vessels, mixed, and drawn off for use as required or returned to the original drums. Antioxidant may be added, and/or the drums may be flushed with nitrogen, stored in cool areas, or otherwise handled in a manner designed to reduce deterioration prior to use. Stainless-steel, tin-lined, or galvanized drums have been preferred to ordinary iron drums, and several proprietary epoxy-phenolic (and other) linings baked on iron drums have been found to be suitable for prolonged storage. The single-fold oils are generally stored for as long as two years before being processed to the terpeneless, sesquiterpeneless, or "folded" stages. It is sometimes desirable to keep oils derived from specific varieties of fruit, or from "early season," "midseason," and "late season" crops of the same variety, separate because of differing organoleptic values.

Best techniques call for the laboratory evaluation of the exact lot of oil to be processed prior to treating the entire batch, although the "recipe" used by an individual manufacturer may be used without variation for all lots of oil manufactured. The "wobble" so introduced is probably less than the differences inherent in the original fruit due to growing conditions, area, etc. Vacuum fractional distillation is used to remove terpenes and/or sesquiterpenes, and the desired fractions are checked for solubility in aqueous alcohol, frequently in the range of 65 to 70% by volume. If, for example, 1 volume of oil fraction is soluble in 5 volumes or 5.2 volumes of 65% ethanol, then this concentration is used subsequently in the plant; the lowest percentage of alcohol that effects the expected separation is the most desirable. An oil fraction also may be soluble 1:3 in 70% alcohol, but less soluble (cloudy) at 1:10 in the same strength; it may be incompletely soluble at 15°C, but totally miscible at 20°C. Close attention to temperature, therefore, is important; even if simply ambient temperatures are to be used, they are generally well known for the plant in use at a given season.

Having the above information, the following operations are performed:

1. The raw essence (single-fold oil as obtained by expression or distillation) is mixed with the appropriate ratio of solvent as determined above, or from the formula, if a constant ratio is always used. The vessel may be metal, cylindrical with a conical bottom, and equipped with suitable discharge valve(s) and sight glasses, or a large, squat earthenware tank not so equipped. In the latter case, the supernatant layer is skimmed from the surface by hand. After sufficient mixing to allow equilibrium to come about, according to the distribution coefficients of the many chemicals in the complex, at the desired temperature, agitation is stopped. This may be from 3 to 10 hours, depending on the type of agitation used. In some equipment, the agitator must now be physically removed. The vessel is closed to prevent evaporation (and therefore change in concentration), the layers are allowed to separate, and the temperature may be adjusted to a different, cooler value.
2. The insoluble oily upper layer contains very few oxygenated compounds – esters, aldehydes, ketones, alcohols, etc. – and consists almost entirely of terpenes, sesquiterpenes, and waxes. By gravity, the lower layer is removed through the bottom valve; great care must be taken to make a "clean" separation. This must be done slowly, to avoid a vortex that draws down some of the upper layer. Alternately, the upper layer may be siphoned off and/or skimmed from the surface. With the use of a centrifuge, the settling time may be reduced to the point of complete elimination; immediately after agitation is stopped, the mixture is passed through the centrifuge.
3. The lower layer may be treated to assure as complete separation of the oil as may be desired, such as recentrifugation, filtration through paper, etc. If the same vessel is to be used for the next step, it is washed, to be sure that it too is free from oil. In larger production, another vessel, possibly of a different size, is used, and a second batch is started in the first vessel. If a solvent (e.g., alcohol or acetone) is used, the vessel may require drying.
4. The aqueous alcoholic solution is placed in a similar vessel, and the alcohol concentration is reduced to, say, half its original (by adding an equal volume of water), or about 30 to 35%. After good agitation, the batch is allowed to settle as before. In some cases, salt is added to saturation, or to a concentration of about 10% by weight of the entire batch, as may be the experience of the processor; in other cases, this is done to effect a third separation after the diluted batch has been separated. Once again, time of agitation, temperature, and time allowed to settle vary with processor, and the agitator may require physical removal.
5. The top layer is now the one that is wanted; it consists mostly of the alcohols, esters, aldehydes, ketones, etc., which contribute to the odor/flavor value. It is carefully separated as before, dried over sodium sulfate (or other innocuous drying agent), and packaged in airtight containers with or without antioxidant(s), as may be desired and permitted by regulatory agencies.
6. The aqueous layer is saved for recovery of the solvent (alcohol) for economic reasons. It need not be highly fractionated; the distillate must only be made strong enough to be equal to or greater than the concentration originally used. Rough fractions may be taken until the specific gravity or refractive index of the distillate indicates that it is almost free of alcohol, after which the fractions may be combined to give the concentration desired for subsequent batches, with or without enrichment by fresh alcohol or dilution with water. Regulatory problems may be involved due to the tax imposed on alcohol in most countries. The yield of desired oils also may be improved when recycled alcohol is used, because it may be saturated with components from the raw oil even though it has been distilled.

Chromatographic Deterpinization

With the development of analytical techniques for separation of molecular compounds by chromatographic columns, industry followed suit by exploiting the method for commercial separation of ingredients. It is another type of "cold" system for separating hydrocarbons from oxygenated components. The latter have a greater affinity for adsorption on the column packing, very often silica gel, than do the terpenes and sesquiterpenes, and they are preferentially adsorbed when a stream of essential oil is passed through the column. The general method is as follows:

1. A column of chosen diameter and height is carefully filled with clean, dry silica gel. Glass or stainless steel may be used for the column. Voids and channels must be removed; glass permits better control by permitting visual observation. The column is wrapped with heating tape and insulated (see step 6 below).
2. A stream of essential oil is slowly and uniformly fed into the top of the column, using a pump or low nitrogen pressure on a closed vessel.
3. The material passing through the column is depleted of oxygen-bearing components, and the terpenes come out at the bottom and are collected. The stream is fed into the unit until analysis of the effluent indicates that the column has been saturated with oxygenated elements, by virtue of their detection in the stream by any of several means – change in refractive index, ultraviolet or infrared absorption, analysis for aldehyde, etc.
4. Feed is now stopped, and a little nitrogen is allowed to flow through to flush as much free oil as possible from the bed. A non-polar solvent, such as hexane, may also be used to flush out terpenes.
5. An eluting solvent is then fed through the column in the same way. The oxygenated components dissolve in it. Fractions may be taken, the first part being somewhat richer than later fractions, and again the progress of the leaching action may be followed by suitable analytical techniques.
6. The solvent is flushed from the column, using steam, and the silica gel is reactivated by heating under vacuum to at least 150°C for several hours (activation may be required after the initial fill). The process may then be repeated.

For satisfactory results in the plant, it is necessary to conduct preliminary tests in the laboratory to estimate the capacity of the column, the degree of separation expected, and the most desirable eluant for the proposed end use of the terpeneless oil. Suitable eluants include ethyl acetate, ethyl ether, and ethyl alcohol. All traces of moisture must be absent from the column, as moisture inhibits selective adsorption and prevents exact reproducibility of results. Air should be removed by applying vacuum. With proper reactivation, the packing may be reused many times, thereby reducing the cost.

Kirchner and Miller[1] first proposed this method in 1952 and devised a specific technique, later improved by Bravermann and Golomiansky[2] in the case of orange essence. Also, G. and P. Rovesti[3] recently proposed some modification of Bravermann's method for the preparation of terpeneless oils of orange, lemon, and bergamot. Terpeneless peppermint and spearmint oils have also been made by a modified procedure. Many details are proprietary in nature.

For each essential oil chromatographic separation is carried out in the absence of eluant until the percentage of oxygen-containing compounds in the oil reaches approximately 0.2%. Preliminary tests establish the amounts of essential oil that can be treated in a column of given dimensions without exceeding the level of oxygen-containing compounds. After the chromatographic separation of the oil, terpenes are removed from the column, using hexane as the eluant. The oxygen-containing compounds that are still adsorbed on the silica gel are eluted, using ethyl ether. Preference is given to ethyl ether as compared to ethyl acetate used by Kirchner and Miller[1] and by Bravermann and Golomiansky,[2] since the final products prepared by these authors were designed for a specific use. Traces of ethyl acetate may affect the top notes of flavor and perfume compositions. This does not occur when ethyl ether is used as eluant, because its high volatility permits more complete removal from the essence. To obtain the terpeneless essence from the ethereal eluate, it is necessary to distill at ambient temperature under vacuum (ca. 14 mm Hg) and then to remove any traces of eluant at 0.4 mm Hg. Based on the analysis of the prepared products, the chromatographic terpeneless essences are free of the main terpene fraction, but they still contain waxes and natural pigments. Terpeneless essences obtained by this method are orange-colored for orange oil, yellow-green for lemon oil, and olive-green for bergamot oil. If higher solubility is desired, waxes can be removed by cooling to a temperature of –5 to 10°C and then filtering.

Variations may be used. When ethanol (or a water-miscible chemical) is selected as the eluant, it is possible to eliminate the vacuum-heating step above and to wash the excess alcohol from the oil by diluting with water and "salting out" the oil. If the oil is subsequently to be used in a compound containing alcohol, this may be the preferred method.

This method, when transferred to an industrial scale, is straightforward, not too laborious, and can be automated. A great advantage of the method is the almost complete removal of terpenes. The autocatalytic properties of terpenes negatively affect the freshness of the top note of an essence in which terpenes are present in amounts larger than a minimum limit. Currently much investigation is taking place on the "high-pressure liquid chromatography" technique for analysis and identification of components.[9] The detection devices and methodology are very likely to be adapted to production processes as well.

Molecular Distillation

Fractional distillation, consisting of the separation of fractions, their enrichment, and subsequent condensation, has revealed its limitation in proceeding to the further separation of medium- or high-molecular-weight organic compounds. Even when reduced pressure is employed, the high boiling temperatures cause destruction of the molecules. Because of the necessity of distilling and separating high-boiling products, molecular distillation (a technique based on the evaporation of compounds) has been perfected. In normal distillation, the liquid and vapor phase impinge on the cooled surface of the condenser, where they separate. In molecular distillation, some molecules situated on the surface of the hot liquid under reduced pressure pass into the vapor phase and subsequently condense. These molecules obey laws of the kinetic theory of gases. The mean free path, or average distance traveled by any one molecule between two subsequent collisions, is calculated in a way that the mean free path is equal to the distance between the evaporating surface and the condensing surface. In contrast to the idea that molecular distillation may not occur whenever the distance between the evaporating and cooling surface is larger than the mean free path of molecules, Hickmann has demonstrated that this distance can be equal to multiples of the mean free path, up to 20 or 30 times its value.[4] Heating is usually carried out on a descending layer as thin as possible, since, at equal temperature and vacuum, the thickness of the layer is a determining factor for the evaporation speed. Knowing that the temperature is proportional to the mean square of the molecular speeds and that, at a given temperature, the molecular speed of different gases is inversely proportional to the square root of the molecular masses, it is logical to conclude that the thickness of the liquid layer being heated is proportional to the evaporation speed. The speed of evaporation is dependent on the vacuum applied. For example, a decrease from 10^{-3} to 10^{-4} mm Hg implies a decrease in the evaporation speed of about 10%.

Modifications of the equipment have been developed to create the thin film not by a simple descending layer, but by use of centrifuge force to spread the film on a heated rotating dish, for example.

Molecular distillation has made a decisive contribution to the concentration of fruit juices. Special equipment has been built that is suitable for the purpose and that allows the preparation of concentrates while retaining almost intact the original fragrance of the juice by heating for only a very short period of time. The current costs of molecular distillation are almost equal to those of traditional concentrators, but they offer a broader spectrum of use.[4,5]

Azeotropic Distillation

The technique of azeotropic distillation may be best known to chemists as a means of removing water from 95% (BV) ethanol by distilling with benzene, en route to anhydrous ethanol. This methodology can be adapted to the removal of terpenes from oxygenated organic materials at atmospheric or reduced pressures. One drawback is the long (relatively speaking) heating period, even under vacuum, which tends to degrade the quality of the terpeneless oil. As usual in the essential oil, flavor, and fragrance industry, details are proprietory "trade secrets", but the methodology is worth considering in some cases.

Expression

Expression is the operation by which oils and juices are removed from plant sources by applying external pressure. The simple concept of squeezing the fruit pulp has been employed for ages in the preparation of juices. In the preparation of essential oils, however, expression is almost exclusively carried out on citrus fruits (lemon, orange, grapefruit, tangerine, lime, etc.), which exhibit a number of oil-rich cells on the outer portion of the rind. These are sufficiently large in most citrus fruits to render the process economically attractive. In the expression process, citrus fruits are thoroughly washed and then pressed, using either the whole fruit or only the rind. They may be in various stages of ripeness. Cold-expressed essential oils contain impurities, such as mucilage, peel, and juice residues; these are separated from the essence by careful decantation or centrifugation. The quality of the cold-expressed citrus oils is considered superior to oils extracted by other methods. Cold expression does not alter the aromatic constituents of the oil and thereby keeps the flavor and fragrance value intact.

The technology of expressing citrus essential oils is based on one of the following methods:

1. The oil-bearing cells are twisted open, and the essence is collected by gravity.
2. The oil-bearing cells are pierced, using vibrating needle-like prongs, and subsequently the rind is completely shaved; the oil is then obtained by pressing the shavings.
3. The rind is separated from the pulp and expressed directly; the expressed oil is collected by gravity.
4. In the United States, automatic machines express the oils at the same time the juice is collected.[10]

Expressed citrus essential oils can be classified into two broad categories, hand-pressed and machine-pressed oils, which are discussed below.

Hand-pressed Oils

This method of expression is nearly extinct. Using an especially designed knife, the fruit is cut in halves, and the rind is detached from the fruit. Each half is flattened slightly between the fingers, then bent outward with a gentle, quick motion to break the oil-bearing cells. The exuded oil is collected by wiping the rind with a sponge; the oil absorbed on the sponge is drained periodically into a container. The major shortcoming of this method is the very high labor cost.

A second method consists of rubbing the fruits against needle-like prongs protruding from the bottom of a small, hand-held, tin-plated copper container. The oil is collected through a pipe connected to the bottom of the container; the pipe also functions as a handle.

Machine-pressed Oils

The rind alone can be pressed directly, or it is forced to pass through the corrugated surfaces of a machine placed at decreasing distances; the rind undergoes a series of twists and pressures similar to those exerted by hand-pressing. Other machines cut the rind with teeth or needle-like prongs. The exuded essential oil is washed away under a continuous water spray; the oil is separated from the water and from other residual contaminants by centrifugation. In the United States there are also machines capable of separating the juice and the oil in a single operation.[10] The machine consists of a number of opposite pistons, terminated by cups that are equipped with blades. When the upper piston is lowered, the blades cut the rind, breaking the oil-bearing cells. A water spray then washes away the oil. At the same time, a perforated piston located in the center of the lower cup pierces the fruit, and the juice is drained through a channel in the center of the lower cup. Fruit may be used that has been rejected for sale *per se*, because of frost damage, blemishes, etc.

Concentration

Extracted natural flavor ingredients generally consist of rather dilute solutions in which the solvent may or may not contribute to the overall flavor strength. It is, therefore, possible to extend the concept used for the concentration of a solution in general (i.e., an increase in active principles resulting from the partial elimination of the inert solvent) to the concentration of flavor-ingredient solutions as well. For example, a terpeneless lemon oil can be defined as "concentrated", since the resulting increase of active flavor principles (aldehydes and other oxygenated products) is parallel to the decrease in terpene solvent exhibiting only very weak specific flavoring action.

Concentrated Essential Oils

The expanding flavor technology has created a need for essential oils with manifold increases in flavoring strength. These oils, commonly known in the trade as "folded oils", are obtained by removing the inert or unwanted fractions (terpenes, sesquiterpenes, etc.), thus concentrating the original extract. Although an oil can be folded or concentrated to many times its original flavoring strength, the process has limitations; a portion of the flavor ingredient can be lost by concentrating the oil beyond certain limits. In some cases a 2X, 3X, or 5X, folded oil used at $\frac{1}{2}$, $\frac{1}{3}$, or $\frac{1}{5}$ the strength, respectively, may yield almost identical flavoring effects as compared to the unfolded oil; highly concentrated material used at the same strength ratio may yield entirely different results. Folded oils are generally used to create natural flavoring effects. Concentration of essential oils improves the stability of the essence by removing those readily oxidizable constituents that contribute off-flavors. Terpeneless and sesquiterpeneless oils already discussed are, in fact, multifolded oils.

Generally, folded oils are limited to 10-fold and are made by distilling off terpenes under vacuum with some degree of fractionation. This leaves behind the oxygen-bearing ingredients that boil at a higher temperature, the sesquiterpenes, waxes, etc. With proper condensation of the terpenes, the desired proportion of oil may be accurately left behind in the still pot, to be withdrawn after cooling. When low color is wanted, the oil left behind may be "flashed", that is, vacuum-distilled, with little or no fractionation, away from the waxes and color bodies and from the polymers formed during the distillation. Sometimes the last portion of terpenes distilled off is kept separate until the yield of folded oil is known, and the volume of that oil is adjusted to the desired fold by returning an appropriate amount, since the losses that occur most often give a yield of less than the desired proportion (otherwise, more may be distilled off).

Concentrated Fruit Juices

Fruit juices, such as raspberry, strawberry, black and red currant, and blackberry, are of great importance in food technology, since fruit flavors are particularly well accepted by consumers. Great effort has been devoted by the flavor industry to identifying the constituents of the fruital aromas and to duplicating them with synthetic products. A concomitant objective has been the development of suitable methods of concentration to improve storage stability, ease of transportation, and the functional flavoring properties of fruit juices.

A fruit juice can be considered a very dilute solution of water, carbohydrates, acids, mineral substances, and a very small amount of volatile and degradable flavoring constituents. The water content of juices can be reduced by distillation (evaporation); however, undesirable effects may occur during the heating process, such as the following:

1. Destruction of the heat-sensitive vitamins.
2. Loss of codistillable volatile flavor ingredients.
3. Caramelization of sugars, resulting in a thick, dark-brown concentrate.
4. Hydrolytic reactions, causing degradation of the flavor principles.

Industrial methods employed for the concentration of fruit juices include concentration by vacuum distillation, crystallization, lyophilization, spray-drying, and microencapsulation. These various methods are discussed below.

Concentration by Vacuum Distillation

Vacuum distillation lowers the boiling temperature and shortens the heating time, thus reducing caramelization and hydrolysis effects during concentration. It does not prevent the loss of volatile constituents, however; these may be recovered during the concentration process by means of suitable "traps", or they may be completely distilled and condensed prior to concentration. In either case the recovered flavor ingredients are finally added to the concentrated juice. Single- or multiple-effect rising or falling film evaporators are still being used, with and without the recovery of "essence", the low-boiling fractions that require special low-temperature condensing systems to remove them from the vapor stream. The major original breakthrough in this area is the electronic juice evaporator developed by Ralph Sargeant. In this apparatus the energy necessary to effect water evaporation at room temperature is supplied by means of high-frequency radiation, thereby eliminating the heat conduction through the medium undergoing concentration. Electronically concentrated juices exhibit not only unaltered flavor characteristics and vitamin content, but also a reduced viscosity. For instance, the viscosity of an orange juice concentrated by electronic evaporation is approximately 3 times less than that of an orange juice concentrated to the same strength by vacuum distillation. Attempts to concentrate orange juice beyond 50 to 60° Brix by any means produce highly viscous liquids or gels because of an accumulation of pectin. Many juices are treated with pectolytic enzymes prior to concentration, to avoid the problem of gelling during concentration and the formation of gels when the juice is eventually used in a flavor. Five- or six-fold juices of 68° Brix are obtainable.

Crystallization

The technique of concentrating fruit juices by freezing the water and then separating the ice by mechanical means is also employed to circumvent problems encountered with the use of heat. Limitations to this otherwise excellent technique include the following:

1. The mechanical separation of ice results in significant losses of concentrate. Concentration is not carried out beyond $\frac{3}{4}$ the original volume (1:4 concentration), or 4-fold.
2. The costs run somewhat high from the low crystallization temperatures. The optimal temperature required for manufacturing a 1:4 orange juice concentrate (42° Brix) is 17.8°C. However, presently available technology yields concentrates (up to approximately 70° Brix) perfectly acceptable from the standpoint of flavor.

Lyophylization

The total dehydration, and therefore the maximum concentration of the flavor principles in the fruit juice, is obtained by lyophylization or "freeze-drying". Freeze-drying consists of rapidly freezing the solution to a very low temperature (ranging from a minimum of −10°C to a maximum of −70°C) to stop fermentative, enzymatic, and other degradative processes, and then directly subliming the water under high vacuum. Lyophylization differs from regular drying in that the liquid water phase is not in contact with the product undergoing drying. Lyophylized products are characteristically very hygroscopic. Special equipment is employed, and new operating techniques are constantly evolving, following the guidelines of practical experience. Lyophylization has been extensively used for pharmaceutical, biological, and medicinal products. The method is also being employed by the food industry on an industrial scale and finds extremely interesting use in the preparation of flavor-ingredient concentrates.

Spray-Drying

Spray-drying is another method of dehydrating flavor-ingredient solutions.[11] Solutions or suspensions are transformed in a single operation into dried powders. The liquid is "atomized" into minute droplets by centrifugal shear or pressure and then brought into contact with a stream of hot air. The sudden increase in temperature causes instantaneous evaporation of the water; the heat loss caused by evaporation in turn decreases the temperature of the material undergoing spray-drying. These concomitant effects permit the use of elevated air temperatures, thereby reducing to a minimum the spray-drying time and the possible degradation of the spray-dried product.

Spray-drying methods are developed specifically for individual classes of compounds, and sometimes for specific products. The mechanical process or the methods of solution preparation for spray-drying are tailored as much as possible to suit the physical-chemical characteristics of the products undergoing dehydration and those of the final spray-dried product. Equipment design varies widely according to the type of air-heating system employed (direct or indirect), the type of air flow (axial, cocurrent, countercurrent), the type of equipment used for the collection of spray-dried products (cyclones, cloth filters, washers), and the system of spray-drying of the solution (centrifugal or jet). Modifications for special applications can also be included in the design; these include closed-circuit spray-drying, cooling by spray-drying, reaction by spray-drying, crystallization and freezing by spray-drying, and/or the addition of difficult-to-spray-dry products (e.g., sucrose for "instant" products).

While not used so much for ingredients as for flavors themselves, neutral carriers are often incorporated into the process of spray-drying. Based on the serendipitous discovery by Revie and Wilkerson in 1929 that volatile materials are entrapped in the carrier when a solution or suspension is spray-dried, commercial application has been made of the principle. Patents have been issued on the entrapment in various carriers (themselves mixtures of ingredients) of such extremely volatile materials as acetaldehyde and ethanol. Whether these chemicals are occluded in interstices of the carrier or as the center core of a spheroid has not been fully established to the satisfaction of all practitioners. It is, nevertheless, possible to incorporate 15 to 18% oils (by weight) into a carrier system, which may then be spray-dried to give a free-flowing, stable, relatively non-hygroscopic powder useful in cake mixes, dry beverage powders, and dessert mixes such as pie fillings or gelatins, etc. Among the many carriers that may be used *per se* or in admixture with other carriers are gum arabic, dextrin, modified starch (from various sources), lactose, dextrose, hexitols, carboxymethyl cellulose, corn sugar solids, larch gum, etc. The details of technology are often trade secrets, but products of this nature are available from many sources. The oils so entrapped or encapsulated range from single-fold citrus oils through concentrated oils to compounded flavors of all types, from apple to zinger.

Microencapsulation

Microencapsulation of flavor ingredients is a preparatory technique of very recent invention.[12] The main objective is the preparation of flavor ingredients that can be stored for long periods without undergoing degradation from temperature variation. Products can be micro- or macroencapsulated; the dimensions can vary from 0.1 to 4,000 μm. It is possible to encapsulate almost all types of flavor ingredients (e.g., essential oils, oleoresins, extracts, and alcoholic products) by following special procedures. Balassa and Brody[6] present a description of the general principles of microencapsulation and examples of specific applications. The general principles can be summarized as follows:

1. A flavor emulsion is dispersed in a fatty inert substrate.
2. A dehydrating substance is added that absorbs water and in turn keeps the encapsulating gum in solution.
3. The gum solidifies, forming a capsule that envelopes the flavor ingredient.
4. The capsules are separated and cleaned with special handling from the ancillary materials (fat, dehydrant).

The operating technique, specific for each type of production, is very complex. Those industries that have developed microencapsulated flavor ingredients have invested and continue to invest large sums of money for studying and perfecting the preparatory techniques. Potential uses of microencapsulated flavor ingredients are many, and often new applications are discovered during the continuing study of the preparation. A very suggestive use is that of "retarded" or "at will" flavors.

Miscellaneous

It has become evident that further coatings may be added to spray-dried or microencapsulated flavors. The technique is an adaptation of the fluid-bed-drying or reaction scheme.[13] The coating may be additional thickness of the original carrier, thus lowering the speed with which the flavor is released when placed in an aqueous medium. It also further protects the oil from attack by oxygen, which may permeate the surrounding membrane, and from evaporation by osmosis. The added coating may be alcohol- or oil-soluble rather than water-soluble, if desired. Therefore, as noted above, flavor may be released at different times or points in a process.

Very recently it has been shown that a flavor-ingredient molecule may be chemically, but weakly, attached to a supporting "backbone" or comb-like structure, to be released by hydrolysis or enzyme action in a product, or even in the mouth. It could also be more strongly bound and remain attached, exhibiting flavorful properties, but not be absorbed into the body and hence metabolized, passing through the alimentary canal unchanged. To date, fully compounded flavors have not been so treated, and only a few ingredients have been investigated.

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INTRODUCTION AND REFERENCE NOTATIONS FOR PART II

INTRODUCTION AND REFERENCE NOTATIONS FOR PARTS II AND III*

Introduction

The naturally derived and synthetic flavor ingredients listed in Parts II and III represent only those currently employed and approved for use in the United States under provisions of the Federal Food, Drug and Cosmetic Act (November, 1966) as administered by the FDA. While recent developments and changes in the regulations governing the use of flavor ingredients in the United States have been updated and bear the appropriate *date notice*, the reader is cautioned not to use this listing as an "official" statement of current legal status, since it is impossible in a work of this type to post the latest changes. Accordingly, the reader is advised to consult the *Federal Register* for latest official notices applicable under U.S. law.

Regulatory Status Citations

The following general citations are used in Parts II and III with respect to regulatory status:

GRAS Indicates products *generally recognized as safe* when used:

I. in foods as the spice, herb, or botanical and/or

II. in foods when used as the essential oil, oleoresin (solvent-free), and natural extractives, including distillates. All GRAS substances receive this status when prepared and used in accordance with "good manufacturing practice." The reader is advised to consult with FDA for opinions regarding "good manufacturing practices."

§121.1163 Refers to that section of the Federal Food, Drug and Cosmetic Act stating that the indicated natural flavoring substances and natural adjuvants may be used safely in food in accordance with the following conditions:

1. used in minimum quantity required to produce their intended effect and in accordance with all principles of "good manufacturing practice", and
2. they consist of one or more appropriate forms (e.g., plant parts, fluid and solid extracts, concretes, absolute, oils, gums, balsams, resins, oleoresins, waxes, and distillates) used alone or in combination with flavoring substances and adjuvants generally recognized as safe in food, previously sanctioned for use in food, or regulated in any section. The reader is advised to consult the full text of §121.1163 for an official statement of the provision.

§121.1164 Refers to that section of the Federal Food, Drug and Cosmetic Act stating that the indicated synthetic flavoring substances and adjuvants may be safely used in food in accordance with the following conditions:

1. used in minimum quantity required to produce their intended effect and in accordance with all principles of "good manufacturing practice", and
2. they consist of one or more of the appropriate forms used alone or in combination with flavoring substances and adjuvants generally recognized as safe in food, previously sanctioned for use in food or regulated in any section. The reader is advised, as in the case of natural flavoring substances and adjuvants, to consult the full text of §121.1164 for an official statement of the provision.

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*For Part III, see volume 2.

REFERENCES FOR PART II

The following general references have been used in Part II with respect to physical-chemical constants, methods, and use:

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PART II

Natural Flavors

ALMOND, BITTER

Other names

Peach kernel; apricot kernel

Botanical source

Prunus amygdalus Batsch, *P. armeniaca* L., *P. persica* (L.) Batsch

Botanical family

Rosaceae

Foreign names

Amandes amères (Fr.), Bittermandel (Ger.), Almèndra amarga (Sp.), Mandorla amara (It.)

Description

The term *bitter almond* (almond, bitter) refers to the essential oil obtained by steam distillation of the partially de-oleated press-cake of kernels from any of the following: bitter almond (*P. amygdalus*), apricot (*P. armeniaca*), and peach (*P. persica*). The kernels from these and other such fruits contain the glucoside amygdalin, which on enzymatic hydrolysis yields benzaldehyde and HCN. The distilled oil must be rendered free of HCN (prussic acid) prior to its marketing as a flavor ingredient. Very little essential oil is currently made exclusively from bitter almonds or other fruit kernels; specially purified benzaldehyde is often used in its place.

Parts of plant used

Kernels

Physical-chemical characteristics

Essential oil

Bitter-almond oil is obtained by first cold expressing the fixed oils from the comminuted kernels, after which the press-cake is macerated in about 10 parts of water for 12–20 hours to effect the enzymatic hydrolysis of amygdalin. The mixture is then steam distilled to yield about 0.5–0.7 per cent of the essential oil. Oil intended for use as a flavor ingredient then is treated to remove traces of HCN by precipitation as insoluble calcium ferrocyanide. Freshly distilled bitter-almond oil from any of the above sources (kernels) has the following characteristics prior to removing HCN (see reference 2):

Specific gravity at 20°C	1.041–1.066[1]
Refractive index at 20°C	1.5320–1.5440[1]
Optical rotation at 20°C	+0° to +0°10′[1]
Solubility	1:1 to 1:2 in 70% ethanol[1] 1:2 to 1:5 in 60% ethanol
Benzaldehyde content	ca 80%[1]
HCN content	2–4%[1]

Organoleptic characteristics

Intense, almond-like, cherry aroma; a slightly astringent, moldy taste

Uses

Bitter-almond oil (FFPA) has been reported used in the following:[3]

non-alcoholic beverages	80 ppm
alcoholic beverages	130 ppm
ice cream, ices, etc.	66 ppm
candy	97 ppm
baked goods	96 ppm
gelatins and puddings	29 ppm
chewing gum	330 ppm
maraschino cherries	340 ppm

Regulatory status

GRAS (II). Free from prussic acid

ALOE

Botanical source	*Aloe perryi* Baker, *A. barbadensis* Mill., *A. ferox* Mill., and hybrids of this species with *A. africana* Mill. and *A. spicata* Baker
Botanical family	*Liliaceae*
Foreign names	Aloès (Fr.), Aloe (Ger.), Aloe (Sp.), Aloe (It.)
Description	The various species of aloe are plants with stalks about 1 m (39 in.) high, few branches, and succulent basal leaves that are quite elongated and spiny-toothed; the flowers are spicated. The plant is native to southern Africa. The useful product is the juice, extracted by cutting the succulent leaves when turgid; the juice is subsequently concentrated and dried. Technically and commercially dried aloe juices are distinguished by their characteristic cleavage (glassy or waxy).
Parts of plant used	Concentrated juice from leaves
Physical-chemical characteristics	
Essential oil	Aloe juice contains about 2 per cent essential oil. The oil is a mobile, pale-yellow liquid exhibiting a peculiar odor and an extremely bitter flavor. Apparently, the essential oil is of little or no commercial use as a flavor ingredient. Specific gravity 0.863[1] Boiling point 266–271°C[1]
Derivatives	Aloe derivatives include fluid extract, dry and soft extracts, and tincture (10% in 80% ethanol). The main constituent of the juice and its derivatives is aloin, which varies from 5–25 per cent.
Organoleptic characteristics	A very bitter, characteristic flavor
Uses	Extracts and tinctures are sometimes used in liqueur formulations because of the bitter flavor. The bitter principle of aloe must be used judiciously and in appropriate mixture with other aromatic and tonic flavors. Aloe extract has been reported used in the following:[3] non-alcoholic beverages 5–2000 ppm alcoholic beverages 130 ppm
Regulatory status	FDA §121.1163

ALTHEA

Botanical source	*Althaea officinalis* L.
Botanical family	*Malvaceae*
Foreign names	Guimaure officinal (Fr.), Echter Eibisch (Ger.), Altea común (Sp.), Altea officinale (It.)
Description	Althea, or marshmallow, is a perennial herb 50–150 cm (19.5–58.5 in.) high growing preferentially in marshy areas as well as in the lower mountain areas in central

and southern Europe, North Africa, Asia, and North America. The plant (wild or cultivated) has long, spindle-shaped or cylindrical roots (grayish yellow externally, fleshy white internally), erect stems, alternate ovate white leaves, and white or pinkish racemose flowers blossoming from July through September.

Parts of plant used

Roots, flowers, and sometimes leaves

Physical-chemical characteristics

Derivatives

Infusion (3–5%), fluid extract, syrup (for pharmaceutical use), and tincture (20%)

Uses

The derivatives (syrups) are used in pharmacy as a demulcent. The tincture is used for flavoring beverages and in the formulation of aromas for liqueurs. Althea root (FEMA No. 2048) has been reported used in non-alcoholic beverages, 5.7–10 ppm.[3]

Regulatory status

Roots and flowers: FDA §121.1163

AMBERGRIS

Source

Physeter macrocephalus L., *P. catodon*

Foreign names

Ambre gris (Fr.), Grauer Amber (Ger.), Amber gris (Sp.), Ambra grigia (It.)

Description

Ambergris, also called ambra, is the pathological tissue from the intestinal tract of the sperm or cachalot whale. It is occasionally washed ashore (Somaliland, Mozambique, Java, Japan, and Madagascar); more often it is found in whales taken in commercial hunts. Ambergris usually is distinguished commercially in four different qualities, depending on the color and physical appearance:

(1) soft black amber
(2) waxy ash-gray amber
(3) gray amber
(4) white amber.

The latter two qualities are the most valued. Tissues range from 50–150 g in weight, although occasionally much larger pieces are found.

Physical-chemical characteristics

Derivatives

Dried or powdered ambra is never used as such. It usually is used as a tincture (3–5% in 90–95% ethanol), extract, or resinoid (prepared by concentration of the tincture). The alcoholic extract is usually aged in tightly sealed bottles in darkness to allow the full development of odor.

Organoleptic characteristics

Peculiar, sweet, extremely tenacious odor with a seaweed, moss-like undertone

Uses

Ambergris finds application mainly in perfumery. The tincture (traces) may be employed in the formulation of aromas to confer special bouquets to liqueurs, beverages, candy, and ice-cream flavors. All in all, ambra is a rarely used product, although very well popularized via adventure literature.

Ambergris tincture (FEMA No. 2099) has been reported used in the following:[3]

non-alcoholic beverages	2.0 ppm
ice cream, ices, etc.	1.7 ppm
candy	9.7 ppm
baked goods	0.10 ppm

Regulatory status

GRAS

AMBRETTE

Botanical source *Hibiscus abelmoschus* L.

Botanical family *Malvaceae*

Foreign names Ambrette, graines (Fr.), Moschuskörner (Ger.), Abelmosco, semillas (Sp.), Ambretta, semi (It.)

Description The plant, originally from eastern India, is now cultivated in several tropical and equatorial countries. The fruit contains flat, kidney-shaped seeds about 4 mm long and 3 mm thick. The seeds are grayish-red and sometimes greenish. Some of the better-quality seeds come from Martinique.

Parts of plant used Seeds

Physical-chemical characteristics

Essential oil

Raw Essence

The raw essence is obtained by steam distillation of the seeds. It solidifies at 35–39°C, because it contains large amounts of fatty acids (primarily palmitic). The raw essence has the following characteristics:

Specific gravity at 50°C	0.883[1]
Acid value	75–140[1]
Ester value	66–130[1]

Liquid Essential Oil

The liquid essential oil is obtained by removing the fatty acid from the raw essence by solvent extraction (alcohol) or precipitation of the fatty acids as the calcium or magnesium salts. The oil is a clear, yellow to amber-colored liquid with a strong, musky odor of ambrettolide. The main constituents of the oil include farnesol and ambrettolide.

Specific gravity at 25°/25°C	0.898–0.920[2]
Optical rotation	$-2°30'$ to $+3°0'$[2]
Refractive index at 20°C	1.4680–1.4850[2]
Acid value	< 3.0[2]
Saponification value	140–200[2]
Solubility	1:2–1:5 in 80% ethanol[1] 1:0.5 in 90% ethanol[1]

Derivatives Essential oil; a 10% tincture is obtained by maceration of the crushed seeds in 65% ethanol.

Organoleptic characteristics The oil exhibits a characteristic aromatic flavor, but more important it displays a distinctly brandy-like and floral, musky odor with remarkable tenacity.

Uses The dried seeds and tinctures are used primarily in the manufacture of liqueurs, vermouths, and bitters. The essential oil is only of limited use as a flavor ingredient but finds important use in perfumery. The following uses have been reported:[3]

Ambrette Absolute Oil

non-alcoholic beverages	0.14 ppm
ice cream, ices, etc.	0.22 ppm
candy	0.35 ppm
baked goods	0.35 ppm

Ambrette Seed Oil

non-alcoholic beverages	0.30 ppm
ice cream, ices, etc.	0.30–0.50 ppm

candy	0.80 ppm
baked goods	0.80 ppm
Ambrette Tincture	
alcoholic beverages	10 ppm
non-alcoholic beverages	5.0 ppm
ice cream, ices, etc.	1.0–5.0 ppm
candy	0.04–10 ppm

Regulatory status	GRAS (I), (II)

AMYRIS

Other names	West Indian sandalwood
Botanical source	*Amyris balsamifera* L.
Botanical family	*Rutaceae*
Foreign names	Amyris (Fr.), Sandalo delle Indie Occidental (It.)
Description	Small tree (so-called West Indian rosewood) with compound leaves and white flowers; mainly growing in South and Central America and in the West Indies (Haiti and Jamaica). It should not be confused with true sandalwood belonging to the botanical family *Santalaceae*.
Parts of plant used	Wood
Physical-chemical characteristics Essential oil	Amyris oil is obtained by steam distillation of the wood in approximately 2.5–3.0% yields; it is a slightly viscous, clear, pale-yellow liquid. Its main constituents include β-caryophyllene, *d*-cadinene, methanol, and furfural.

Specific gravity at 25°/25°C	0.943–0.976^{2} (0.946–0.978 at 20°/20°C)^{6}
Refractive index at 20°C	1.5035–1.5120^{2} (1.5050–1.5120)^{6}
Optical rotation	+10° to +53°^{2} (+10° to +60°)^{6}
Acid value	3 max^{2} (1.56–3.0)^{6}
Ester value	7.0 max^{2}
Ester value (after acetylation)	115–165^{2}
Solubility	1:3 in 80% ethanol^{2} (1:1 in 90% ethanol)^{6}

Organoleptic characteristics	Wood-like odor reminiscent of sandalwood; burning taste
Uses	Amyris oil is used as a fixative in perfumery, as is the true sandalwood essential oil. The oil also finds limited application in flavors, such as Oriental specialties and liqueurs.
Regulatory status	FDA §121.1163

ANGELICA

Botanical source	*Angelica archangelica* L.
Botanical family	*Umbelliferae*

Foreign names Archangelique (Fr.), Echt Engelwurz (Ger.), Arcangelica (Sp.), Angelica (It.)

Description Herbaceous plant about 1.5 m (59 in.) high, cultivated in Europe, especially France, Belgium, and Germany. The plant is characterized by spindle-shaped, fleshy roots, an erect stalk, alternate leaves, and greenish-yellow flowers with an inferior ovary; the seeds are oblong with an off-white color. The plant blooms from June to August.

Parts of plant used Seeds and roots

Physical-chemical characteristics

Essential seed oil Obtained in 0.6–1.5% yields by steam distillation of seeds harvested in mid-July (Germany). The product is a pale-yellow liquid exhibiting a fresh, peppery odor more delicate than the essential-root oil; it has a bitter, aromatic flavor. One of the main constituents is β-phellandrene.

Specific gravity at 25°/25°C	0.853–0.876[2]
Refractive index at 20°C	1.4800–1.4880[2]
Optical rotation	+4.0° to +16°[2]
Ester value	10–65[2]
Acid value	<7[2]

Essential root oil Obtained by steam distillation of roots. The pale-yellow to deep-amber liquid has a warm, pungent odor with musky or earthy top notes; it has a bittersweet flavor.

Specific gravity at 25°/25°C	0.850–0.880[2]
Refractive index at 25°C	1.4735–1.4870[2]
Optical rotation	0° to +46.0°[2]
Ester value	10–65[2]
Acid value	<7[2]

The main constituents include *d*-α-phellandrene, α-pinene, sesquiterpenes, cyclopentadecanolide, diacetyl, furfurol, methyl and ethyl alcohols, and angelic acid.

Derivatives Fluid extract from roots, tincture (20% root extract and, less often, seed extract in 60% ethanol), essential root oil, and essential seed oil

Organoleptic characteristics The root has a bitter aromatic and tonic flavor; the seeds exhibit a more delicate aromatic flavor.

Uses The dried roots and the corresponding derivatives find extensive use in the formulation of liqueurs. Roots are often employed in the flavoring of vermouths and bitters, while the essential root oil is used for the formulation of compounded oils used in flavoring benedictine and chartreuse-type liqueurs; tinctures and extracts are employed likewise. The dried seeds often are used in combination with roots for distilled liquors; the corresponding essential seed oil is used as a flavor in compounded oils employed in the manufacture of liqueurs.

Angelica seed oil has been reported used in the following:[3]

non-alcoholic beverages	6.3 ppm
alcoholic beverages	32 ppm
ice cream, ices, etc.	1.5 ppm
candy	1.9 ppm
baked goods	2.2 ppm
gelatins and puddings	5.0 ppm

Angelica root oil has been reported used in the following:[3]

non-alcoholic beverages	12 ppm
alcoholic beverages	15 ppm
ice cream, ices, etc.	0.99 ppm
candy	0.86 ppm

baked goods	1.0 ppm
gelatins and puddings	0.03–5.0 ppm
chewing gum	60 ppm

Angelica seed extract has been reported used in the following:[3]

non-alcoholic beverages	1100 ppm
syrups	100 ppm
condiments	10 ppm
candy	10 ppm
baked goods	50 ppm

Angelica root extract has been reported used in the following:[3]

non-alcoholic beverages	49 ppm
ice cream, ices, etc.	46 ppm
candy	44 ppm
baked goods	61 ppm
syrup	1.0–100 ppm

Angelica stem oil has been reported used in the following:[3]

non-alcoholic beverages	0.50–1.5 ppm
ice cream, ices, etc.	0.50–10 ppm
candy	1.0–2.5 ppm
baked goods	1.0–24 ppm
gelatins and puddings	0.50 ppm

Regulatory status	GRAS (I), (II)

ANGOLA WEED

Botanical source	*Roccella fuciformis* Ach.
Description	A lichen, especially *R. tinctoria* and *R. fuciformis*, yielding a blue, red, or violet dyestuff. The liquid extract of the dyestuff made from the lichens is called archil liquor. *R. tinctoria* of Africa and the East Indies is the source of the chemical indicator litmus and of the dye archil, or orseille.
Uses	A bitter principle for alcoholic beverages
Regulatory status	FDA §121.1163. In alcoholic beverages only

ANGOSTURA

Other names	Cusparia
Botanical source	*Galipea officinalis* Hancock (*G. cusparia* DC.)
Botanical family	*Rutaceae*
Foreign names	Angostura (Fr.), Echt Angostura (Ger.), Cuspa (Sp.), Angostura (It.)
Description	Tall tree up to 20 m (66 ft) high with long-stemmed leaves; grows preferentially in South America. It has large, cob-shaped, whitish-red flowers.
Parts of plant used	Bark

Physical-chemical characteristics

Essential oil

Rarely seen as a commercial product. Reportedly obtained in 1–2% yields by steam distillation of the bark. It is a yellowish liquid turning dark with aging. It has an aromatic odor and a burning, bitter flavor.

Specific gravity at 15°C	0.928–0.960[1]
Refractive index at 20 C	1.5074[1]
Acid value	1.8[1]
Ester value	5.5[1]
Ester value after acetylation	35.7[1]
Optical rotation	−7°30′ to −50°[1]
Solubility	1:9 in 90% ethanol[1]

The main constituents include galipoline (a $C_{15}H_{26}O$ sesquiterpene alcohol) at approximately 14%, galipene, and cadinene. The bark also contains alkaloids, such as cusparine, cusparidine, and galipoidine.

Derivatives

Tincture (20% in 60% ethanol), fluid extract, and the essential oil

Organoleptic characteristics

Bitter, slightly aromatic flavor with a pungent aftertaste. The bitter principle is angosturin, $C_9H_{12}O_5$.

Uses

The essential oil is rarely seen and is of no apparent commercial interest. The bark is used for the preparation of aperitifs. The tincture and extract are used for flavoring alcoholic beverages to confer bitter notes. Angostura tinctures and extracts are not to be confused with consumer products having the same name. The extract has been reported used in the following:[3]

non-alcoholic beverages	18 ppm
alcoholic beverages	1700 ppm

Regulatory status

GRAS (I), (II)

ANISE

Botanical source

Pimpinella anisum L.

Botanical family

Umbelliferae

Foreign names

Anis (Fr.), Anis (Ger.), Anis (Sp.), Anice (It.)

Description

Herbaceous annual plant indigenous to Greece and Asia Minor, now extensively cultivated in Europe, Russia, and, to a lesser extent in India. It has a perpendicular root, an erect cylindrical stalk, alternate leaves, yellowish-white flowers, five-edged carpels, and lens-shaped seeds. It flowers in July. The fruits of commerce are grayish-green to dull yellowish-brown in color, 3 to 5 mm long and 1.5 to 2 mm wide, containing about 10% of fixed oil and 1.5% to 4% of essential oil. Currently, the main commercial source of anise oil is Chinese star anise.

Parts of plant used

Fruits, improperly called seeds

Physical-chemical characteristics

Essential oil

Obtained in approximately 3% yields by steam distillation of dried and minutely crushed fruits. The oil is clear to pale yellow with a characteristic sweet odor and flavor reminiscent of anethole; it is liquid but solidifies at low temperature.

Specific gravity at 20°C	0.980–0990[1]
Refractive index at 20°C	1.5520–1.5590[1]
Optical rotation at 20°C	-2° to +1°[1]
Freezing point	14–19°C[1] (15–19°C)[6]
Solubility	1:3 in 90% ethanol[6]

The main constituents include anethol (approximately 90%), methylchavicol, *p*-methoxyphenylacetone, acetic aldehyde, and others.

Derivatives

Fluid extract, tincture (20% in approximately 70% ethanol), infusion (5%), and decoction (4%). Extraction of anise seed yields an oleoresin containing fixed oil and the full anise flavor.

Organoleptic characteristics

Sweet, soft, mild flavor with rich effects

Uses

Dried fruits macerated in alcohol and subsequently distilled with small additions of other aromatic herbs are fundamental for the formulation of traditional liqueurs (Anisette and similar types). The essential oil has limited use, as star anise oil is preferred to anise oil; both have been substituted and replaced by synthetic *trans*-anethol.

Anise has been reported used in the following:[3]

non-alcoholic beverages	2–30 ppm
condiments	96–5000 ppm
meats	1200 ppm
ice cream, ices, etc.	1–4 ppm
candy	3–4 ppm
baked goods	490 ppm

Anise oil has been reported used in the following:[3]

non-alcoholic beverages	7.5 ppm
alcoholic beverages	45 ppm
meats	65 ppm
ice cream, ices, etc.	67 ppm
candy	500 ppm
baked goods	120 ppm
chewing gum	3200 ppm

Regulatory status

GRAS (I), (II)

ARNICA

Botanical source

Arnica montana L., *A. fulgens* Pursh, *A. sororia* Greene, *A. cordifolia* Hooker

Botanical family

Compositae

Foreign names

Arnique montagnard (Fr.), Arnika Wohlverlei (Ger.), Arnica (Sp.), Arnica (It.)

Description

Perennial herbs commonly growing in pastures and mountain areas. *A. montana* grows wild in the U.S.S.R., Scandinavia, northern India, and central and northern Europe. *A. cordifolia* grows wild in the United States, where it is known as mountain tobacco. The plant is 20-60 cm (8-24 in.) tall and has cylindrical rhizomes sprouted with numerous smaller roots; erect stems; basal rosulate leaves; opposite, small, linear, assurgent cauline leaves; terminal solitary buds; and peripheral ligulate yellow flowers (June-July).

Parts of plant used

Flowers (also rhizomes)

Physical-chemical characteristics

Essential oils

Arnica oil is yellow-orange to greenish-blue; it is obtained by steam distillation of flowers. Arnica root oil is obtained from the rhizomes; it is yellow to dark yellow and more viscous than arnica oil. Both oils are quite scarce and expensive.

Presumably some of the aromatic principles of the plant are lost in making the essential oil, and for this reason the absolute, tincture, and resinoid are preferred.

Derivatives
Absolute, infusion (0.5–1.0%), tincture, fluid extract, and resinoid ("resinoine"). An aromatic principle of the absolute is thymohydroquinone dimethylether.

Organoleptic characteristics
Agreeable, herbaceous, sweet odor, somewhat reminiscent of camomile, with a slightly bitter flavor

Uses
Arnica derivatives (and sometimes the oil) find limited use in the formulation of aromas for liqueurs.

Regulatory status
Flowers: FDA §121.1163

ARTEMISIA

Botanical names
Artemisia absinthium L.—wormwood
A. vulgaris L.—common mugwort
A. pontica L.—Roman mugwort; and other species

Botanical family
Compositae

Foreign names
Armoise (Fr.), Vermut (Ger.), Asenzio (Sp.), Assenzio (It.)

Description
A family of bitter aromatic herbs or shrubs that includes several species. The best established and most common variety, *A. absinthium* L., is a perennial herb widespread throughout central Europe and western Asia as well as North America. The plant has stems up to 1 m (39 in.) high, branched rhizomes, alternate and petiolate lower leaves, pubescent radical leaves, and yellowish flowers (July–August).

Parts of plant used
Leaves and flowering tops

Physical-chemical characteristics

Essential oil
Obtained by steam distillation. The oil is a dark-green to yellow-brown (sometimes blue because of the presence of azulenes) liquid exhibiting a characteristic, acrid taste. The physical constants vary widely, depending on the source. An oil of Italian production has the following constants:

Specific gravity at 20°C	0.918–0.943
Ester value	15–37
Ester value (after acetylation)	123
Acid value	<5.6
Solubility	1:0.5–1 in 90% alcohol; 1:1–2 in 80% alcohol

The main constituents include α- and β-thujone, phellandrene, cadinene, pinene, sabinene, myrcene, chamazulene, β-caryophyllene, bisabolene, and terpenes.

Derivatives
Infusion (0.5–1.0%), fluid extract, distillation, water, tincture (20% in 70

Organoleptic characteristics
Bitter tonic, aromatic

Uses
The tincture, fluid extract, and dried product are employed mainly for their bitter tonic flavor in the formulation of vermouths and bitters. The essential oil is normally used in the formulation of compounded oils.

Wormwood, *A. absinthium* L. (FEMA No. 3114), has been reported used in the following:[3]

non-alcoholic beverages	360 ppm
alcoholic beverages	5.0 ppm

Wormwood extract (FEMA No. 3115) has been reported used in the following:[3]

non-alcoholic beverages	15–43 ppm
alcoholic beverages	10–40 ppm
ice cream, ices, etc.	170 ppm
candy	130 ppm

Wormwood oil (FEMA No. 3116) has been reported used in the following:[3]

non-alcoholic beverages	14 ppm
alcoholic beverages	11 ppm
ice cream, ices, etc.	0.50–32 ppm
candy	9.0 ppm
baked goods	2.0 ppm

Regulatory status	FDA §121.1163. Finished food thujone-free

ARTICHOKE LEAVES

Botanical source	*Cynara scolymus* L.
Botanical family	*Compositae*
Foreign names	Artichaut (Fr.), Artischocke (Ger.), Alcachofa (Sp.), Carciofo (It.)
Description	Perennial, herbaceous plant of Mediterranean origin; it can grow taller than 1 m (39 in.). It has rhizomes, an erect stalk, large alternate leaves, blue-violet flowers, and enveloping fleshy bracts.
Part of plant used	Cauline leaves
Derivatives	Decoction (5%), fluid extract (soft and dried), tincture (20% in 60% ethanol). The active principles of derivatives are contained in the fresh leaves from 0.01–0.02%.
Organoleptic characteristics	Bitter-tonic flavor.
Uses	Dried leaves are employed in the preparation of special bitters and liqueurs.
Regulatory status	FDA §121.1163. In alcoholic beverages only

ASAFETIDA

Botanical source	*Ferula assafoetida* L. and related species of *Ferula*
Botanical family	*Umbelliferae*
Foreign names	Asafetide (Fr.), Asant (Ger.), Asafetida (Sp.), Assafetida (It.)
Description	The plant commonly grows in the steppes of Asia (Iran, Afghanistan, Turkestan, Kashmir). The plant is not used as such; only the gum-resin exudate from its roots is used. The resin consists of essential oil (7–12%), gum (25–48%), resin (40–60%), and ashes (1–3% to 10–15%, depending on the plant type).

Parts of plant used Gum resin

Physical-chemical characteristics

Essential oil The oil, obtained by steam distillation of the resin, is a pale-yellow to orange-yellow liquid with a garlic-like odor and slightly bitter, pungent taste. Main constituents include sulfur-containing compounds (methylpropenyl disulfides). Vanillin is also present; it is formed by oxidation of ferulic acid during the aging process of the resin.

Derivatives Fluid extract, tincture (20% in 70% ethanol)

Organoleptic characteristics Strong, garlic-like odor; slightly bitter, pungent taste

Uses The essential oil is used as a fixative in perfumery. The purified resin, the tincture, and the oil are used for flavoring sauces (such as Worcestershire), meats, pickles, condiments, and candies.

Asafetida gum (FEMA No. 2107) has been reported used in the following:[3]

non-alcoholic beverages	5.0 ppm
ice cream, ices, etc.	10 ppm
candy	15–25 ppm
baked goods	15 ppm
condiments	5.0–160 ppm

Asafetida fluid extract (FEMA No. 2106) has been reported used in the following:[3]

non-alcoholic beverages	4.0 ppm
ice cream, ices, etc.	10 ppm
candy	5.0 ppm
baked goods	8.0–10 ppm
condiments	50 ppm
meats	10 ppm
soups	30 ppm

Asafetida oil (FEMA No. 2108) has been reported used in the following:[3]

candy	1.0–15 ppm
baked goods	1.0 ppm
condiments	10 ppm

Regulatory status GRAS (II)

BALM

Botanical source *Melissa officinalis* L.

Botanical family *Labiatae*

Foreign names Mélisse officinale (Fr.), Melissen (Ger.), Melisa (Sp.), Melissa (It.)

Description Wild or cultivated herbaceous plant that grows well in submountainous areas of southern and central Europe and North Africa. The plant is from 20–80 cm (8–32 in.) in height, with a short rhizome, branched stalk, opposite leaves, and white-pinkish or light-blue flowers (June–August).

Parts of plant used Flowering tops and leaves

Physical-chemical characteristics

Essential oil

The 0.1% yield of essential oil obtained by steam distillation depends widely on the origin of the plant and its harvesting time. The physical-chemical constants also vary. An essential oil of Calabrese (Italy) production exhibits the following constants:

Specific gravity at 15°C	0.9026[1]
Optical rotation	−7°48′[1]
Acid value	1.19[1]
Saponification value	44.32[1]
Saponification value (after acetylation)	182.03[1]
Aldehydes (as citral)	31.82%[1]

Derivatives

Infusion (2%), distillation waters, fluid extract, and tincture (20% in 60% ethanol)

Organoleptic characteristics

Citral odor; tonic-like flavor

Uses

The essential oil (very little known and of limited production) can yield good results in the formulation of compounded oils for liqueurs.

Balm oil has been reported used in the following:[3]

non-alcoholic beverages	8.5 ppm
ice cream, ices, etc.	1.7–15 ppm
candy	20 ppm
baked goods	10–60 ppm

Balm leaves extract has been reported used in non-alcoholic beverages, 2,000 ppm.

Regulatory status

GRAS (I), (II)

BASIL, BUSH

Other names

Dwarf basil

Botanical source

Ocimum minimum L.

Botanical family

Labiatae

Description

Fragrant annual herb used in cooking. It is only 6 in. high and a more suitable plant for pot culture than common basil.

Parts of plant used

Leaves and flowering tops

Physical-chemical characteristics

Essential oil

	Ref. 1	**Ref. 2**
Specific gravity at 15°C	0.9102	0.8901
Optical rotation	−11°58′	−13°36′
Acid number	5.3	—
Ester number	12.5	—
Phenol content	14%	—
Solubility	Sol 2 vol 70% alcohol opalescent in 10 vol	Sol 2.5 vol of 70% turbid in 4.5 vol plus more

Organoleptic characteristics	Similar to sweet basil
Uses	Similar to those of sweet basil
Regulatory status	GRAS (I)

BASIL, SWEET

Botanical source	*Ocimum basilicum* L.
Botanical family	*Labiatae*
Foreign names	Basilic (Fr.), Basilikum (Ger.), Albahaca (Sp.), Basilico (It.)
Description	Annual herbaceous plant native to Asia and other tropical regions; it is cultivated as a culinary herb throughout Europe. The plant is 15–45 cm (6–18 in.) high with an erect stem, opposite oblique leaves, and white or purplish flowers arranged in clusters. The plant flowers from May to September and has an intense, pleasant, characteristic odor. Owing to widespread hybridation, several varieties of plants are known as basil, each yielding on distillation essential oils of different aromatic character.
Parts of plant used	Leaves and flowering tops
Physical-chemical characteristics Essential oil	Depending on the growing site and production conditions, the essential oil obtained by steam distillation may exhibit completely different organoleptic and physical-chemical characteristics. Well known types include: (1) the Reunion type produced in the Comoro Islands, (2) the Mediterranean type or true sweet basil, (3) the Bulgarian or methylcinnamate type, and (4) the phenolic type from Java

Mediterranean Type

The Mediteranean type is characterized as a pale-yellow to amber liquid, lacking the harsh camphoraceous note of the Reunion variety. The main constituents of this variety include cineol, *d*-linalool (about 40%), and methylchavicol (about 25%).

Specific gravity at 20°C	0.891–0.924[1]
Refractive index at 20°C	1.4730–1.4900[1]
Optical rotation at 20°C	−7°30′ to −14°50′[1]
Ester value	ca 10[1]
Ester value (after formylation at room temperature)	140–235[1]

Reunion Type

The Reunion variety is a light-yellow oil with a camphoraceous note and somewhat spicy odor similar to estragon.

Specific gravity at 25°/25°C	0.952–0.973[2]
Optical rotation at 25°C	0° to +2°[2]
Refractive index at 20°C	1.5120–1.5190[2]
Acid value	<1.0[2]
Saponification value	4–10[2]
Ester value (after acetylation)	25–45[2]
Solubility	1:4 in 80% ethanol[2]

The main constituents of this variety include *d*-α-pinene, cineol, *d*-camphor, and methylchavicol (about 70%).

The phenolic type of basil *(Ocimum gratissimum)* is readily distinguished from true sweet basil by the presence of approximately 60% eugenol and some thymol in the essential oil.

Derivatives

Infusion (3%), tincture (20% in 60% ethanol), essential oils. A dark-green semisolid oleoresin is obtained by extracting the type with a high methyl chavicol content to yield a product with a delicate characteristic flavor.

Organoleptic characteristics

Warm, intense, spicy aroma with fresh, mint-like flavor; it can have a camphor-like note

Uses

Fresh leaves are used as a seasoning. The tincture finds some use in liqueurs as a flavor modifier. The essential oil is used mostly in perfumery, but it is used also in the formulation of compounded aromas and for flavoring sauces, condiments, vinegars, canned meats, and baked goods.

Basil has been reported used in the following:[3]

non-alcoholic beverages	2.5 ppm
ice cream, ices, etc.	5.0 ppm
candy	5.0 ppm
baked goods	680 ppm
condiments	500 ppm
meats	520 ppm

Basil oil has been reported used in the following:[3]

non-alcoholic beverages	2.0 ppm
ice cream, ices, etc.	2.7 ppm
candy	6.2 ppm
baked goods	4.2 ppm
gelatins and puddings	0.01 ppm
condiments	15.0 ppm
meats	24 ppm

Basil oleoresin has been reported used in the following:[3]

baked goods	16 ppm
condiments	2–5 ppm

Regulatory status

GRAS (I), (II)

BAY OIL

Other names

Myrcia oil, oil of bay

Botanical source

Pimenta racemosa (Miller) J. W. Moore, *P. acris* Kostel.

Botanical family

Myrtaceae

Foreign names

Bay (Fr.), Bay (Ger.), Bay Malagueta (Sp.), Bay (It.)

Description

A small wild tree, native to the West Indies, with large leathery leaves that are harvested in May/June. It is grown in St. Thomas, Puerto Rico, and throughout the Caribbean Islands, where it is cultivated for extractive purposes.

Parts of plant used

Leaves

Physical-chemical characteristics

Essential oil

The essential oil, obtained by steam distillation of leaves in approximately 0.75% to 1.25% yield, is a yellow liquid that tends to darken readily. It has a pleasant odor similar to that of clove buds and a sharp flavor.

Specific gravity at 25°/25°C	0.950–0.990[2]
Specific gravity at 20°C	0.946–0.984[1]
Refractive index at 20°C	1.5070–1.5170[2]
Refractive index at 20°C	1.5060–1.5200[1]
Optical rotation	0° to −3°[2]
Optical rotation at 20°C	−2° to −3°[1]
Phenol content (by volume)	50–60%[2]
Phenol content	57–66%[1]

Its main constituents include eugenol (about 60%), α-pinene, myrcene, α-phellandrene, limonene, dipentene, cineol, citral, and chavicol (about 5%).

Derivatives Essential oil, extract, oleoresin

Organoleptic characteristics Sharp, spicy taste; pungent, clove-like odor

Uses The essential oil is used in combination with other aromatic oils of the same type, such as clove bud oil, for the formulation of compounded aromas for liqueurs and in perfumery. West Indian bay-leaf extract has been reported used in the following:[3]

non-alcoholic beverages	0.67 ppm
ice cream, ices, etc.	2.0 ppm
candy	1.6–2.0 ppm
baked goods	2.0 ppm
meats	54 ppm
soups	0.72 ppm

West Indian bay-leaf oil has been reported used in the following:[3]

non-alcoholic beverages	1.5 ppm
ice cream, ices, etc.	2.3 ppm
candy	4.4 ppm
baked goods	4.6 ppm
condiments	27 ppm
meats	15 ppm

West Indian bay-leaf oleoresin has been reported used in the following:[3]

meats	25 ppm
soups	72 ppm

Regulatory status GRAS (II)

BEESWAX

Other names Cire d'abeille

Source *Apis mellifera* L.

Description Crude yellow beeswax is harvested together with honey and represents a secondary secretion of the bee. Once the honey is recovered from the honeycombs by draining the cells, the waxcombs are washed with water, melted, and poured into molds to harden. Yellow beeswax contains cerolein, a mixture of fatty acids, soluble in cold alcohol; cerotinic acid, saturated aliphatic acid, soluble in hot alcohol and slightly soluble in cold alcohol; myricyl alcohol and myricyl palmitate, insoluble in alcohol. Beeswax is produced worldwide with the same chemical composition. The odor may vary slightly, depending on the source.

Physical-chemical characteristics

Derivatives Beeswax absolute, prepared by alcoholic extraction of the raw wax, is a waxy solid having a light-yellow color and a very mild, sweet odor with a waxy undertone.

Organoleptic characteristics Mild, sweet odor reminiscent of coumarin

Uses

Beeswax absolute is used in perfumery as a modifier (so-called cire d'abeille perfume bases). In flavors beeswax absolute (FEMA No. 2126) has been reported used in the following:[3]

non-alcoholic beverages	0.50 ppm
ice cream, ices, etc.	2.0 ppm
candy	10 ppm
baked goods	10 ppm
honey	5.0 ppm

Regulatory status

FDA §121.1163

BENZOIN

Botanical source

Styrax benzoin Dryand., *S. paralleloneurus* Perkins, *S. tonkinensis* (Pierre) Craib ex Hartwick, or other species of the section *Anthostyrax* of the genus *Styrax*

Botanical family

Styracaceae

Foreign names

Benjoin (Fr.), Benzoë (Ger.), Benjui (Sp.), Benzoino (It.)

Description

Trees of the above species are about 15 m (49 ft) high. Resin flows from incisions made in the bark. *S. tonkinensis* (Siam benzoin) grows extensively in Laos and Tonkin. *S. benzoin* Dryand. (Sumatra benzoin) grows in Sumatra and Malaya. Sumatra benzoin is produced commercially in two basic qualities: "selected tears" and "almonds," or "amygdaloid" forms. The size of the tear-shaped pieces allows a further classification into three or four types. Sumatra benzoin consists of a grayish-red mass intermixed with yellow pieces somewhat resembling almonds. The amount of granules (almonds) as compared to the mass allows a classification into three basic qualities.

Parts of plant used

The above-described resins

Physical-chemical characteristics

Derivatives

Tinctures of various percentages in 95% ethanol, fluid extract, and resinoids.

The chemical differences between Siam and Sumatra varieties derive from the levels of cinnamic and benzoic acids and their corresponding esters; benzoic derivatives prevail in Siam benzoin, while cinnamic derivatives prevail in Sumatra benzoin. Siam benzoin is used in preference to Sumatra benzoin for food flavoring but must be first de-acidified.

Organoleptic characteristics

Sweet, balsamic, pleasant odor; aromatic, acrid, bittersweet taste

Uses

Tinctures can be used to confer a luster to chocolate eggs; in syrups it can be used to produce turbidity. The resin becomes plastic when chewed.

Benzoin resin has been reported used in the following:[3]

non-alcoholic beverages	15 ppm
ice cream, ices, etc.	5.1 ppm
candy	8.7 ppm
baked goods	20 ppm
gelatins and puddings	10 ppm
chewing gum	110 ppm

Regulatory status

FDA §121.1163

BERGAMOT

Other names

Bergamot orange

Botanical source

Citrus bergamia Risso, *C. aurantium* L. subspecies *bergamia* Wright & Arn.

Botanical family — *Rutaceae*

Foreign names — Bergamote (Fr.), Bergamot (Ger.), Bergamota (Sp.), Bergamotto (It.)

Description — A delicate tree similar to other citrus plants, such as orange and lemon. The plant flowers twice a year—in the spring and at the end of the summer—and yields orange-like fruits, only smaller in size. Bergamot grows almost exclusively in Calabria, Italy. A few experimental cultivations started around the Mediterranean basin and on the Atlantic coast of Equatorial Africa have attained only a very limited success.

Parts of plant used — Fruits, leaves, and twigs

Physical-chemical characteristics

Essential oil — Bergamot oil is obtained by cold expression of the pericarp (peels) of unripe fruits. It is a clear, mobile, yellowish-green liquid with a fragrant, sweet, fruity odor. Its physical-chemical constants are as follows (see also reference 2):

Specific gravity at 20°/20°C	0.876–0.884[1] (0.8763–0.8843)[6]
Refractive index at 20°C	1.464–1.468[1] (1.4660–1.4680)[6]
Optical rotation at 20°C	+8° to +30°[1]
Acid value	2 max[6]
Evaporation residue	4.5–6.5%[1]
Solubility	1:1 in 85% alcohol[1] 1:0.4 in 90% alcohol[1]
Saponification value	120–190[6]
Ester content (as linalyl acetate)	30–45%[1]

The main constituents include *d*-limonene, probably dipentene, *l*-linalyl acetate, *l*-linalool, nerol, probably geraniol, aldehydes, terpenes, and sesquiterpenes.

Bergamot essential oil yields a concentrated essential oil by distillation under reduced pressure. Also terpeneless and sesquiterpeneless essential oils can be prepared from bergamot essential oil. A petitgrain bergamot also is manufactured by steam distillation of the leaves and twigs. This oil is only in limited demand and used mainly in perfumery.

Organoleptic characteristics — Fragrant, sweet, fruity odor

Uses — In addition to its extensive use in perfumery, bergamot (cold-expressed) oil is employed in flavor work for the formulation of compounded oils with a citrus note for flavoring pastry and liqueurs. The more soluble terpeneless oil is used for flavoring syrups and carbonated beverages.

Bergamot oil (FEMA No. 2153) has been reported used in the following:[3]

non-alcoholic beverages	8.9 ppm
ice cream, ices, etc.	7.9 ppm
candy	27 ppm
baked goods	29 ppm
gelatins and puddings	5.3–90 ppm
chewing gum	43 ppm
icings	1.0–130 ppm

Regulatory status — GRAS (II)

BIRCH, SWEET

Botanical source — *Betula lenta* L., *B. alba* L.

Botanical family — *Betulaceae*

Foreign names

Bouleau (Fr.), Birke (Ger.), Betula (Sp.), Betulla (It.)

Description

A tree reaching heights of 15–20 m (49–66 ft). *Betula alba* L. grows throughout eastern Europe, Russia, northern China, and Japan. *B. lenta* L. is widespread in North America, from Canada to Ohio.

Parts of plant used

B. alba L: buds, leaves, bark (white)
B. lenta L: bark (reddish-brown)

Physical-chemical characteristics

Essential oil

Betula alba L.

The essential oil of *B. alba* L. is a viscous, yellow-colored liquid with a balsamic odor. It is obtained from buds by steam distillation in 3.5–8% yields. The oil solidifies at low temperature because of its paraffin content.

Specific gravity at 15°C	0.962–0.979[1]
Optical rotation	−2° to −15°[1]
Refractive index at 20°C	1.5015–1.5045[1]
Acid value	1–4[1]
Ester value	35–77[1]
Ester value (after acetylation)	140–183[1]

The essential oil of *B. alba* L. var. *pubescens* Ehrh., obtained from buds in 3.5% yields by steam distillation, has the following constants:

Specific gravity	0.9779[1]
Optical rotation	−2°2′[1]
Refractive index	1.5008[1]

The essential oil of *B. alba* L. obtained from the bark is recovered in 0.4–0.5% yields.

Specific gravity at 15°C	0.895–0.907[1]
Optical rotation	ca −12°[1]

The essential oil of *B. alba* L. obtained from leaves is recovered in 0.4–0.5% yields. Its optical rotation is 0°.[1]

Bud oil contains, among other constituents, betulene, betulenene, *p*-betulenol, naphthalene, and formic acid.

Betula lenta L.

The essential oil of *B. lenta* L. obtained from bark is a pale-yellow liquid with characteristic odor because of its methyl salicylate content.

Specific gravity at 15°C	1.180–1.189[1]
Optical rotation	0°[1]
Refractive index at 20°C	1.5360–1.5376[1]
Ester value	356–365[1]
Ester content (calculated as methyl salicylate)	97–99%[1]

Betula pendula Roth

Finally, an essential oil is obtained by distillation of birch tar, *B. pendula* Roth, which contains phenol, cresol, dimethylphenol, creosote, guaiacol, sesquiterpenes, and other unsaponifiable products. The characteristic leathery and smoky odor is attributed to the latter. Phenolic derivatives can be eliminated by alkaline washing.

Derivatives

Fluid extracts, dried extracts, and essential oils

Organoleptic characteristics

Characteristic wintergreen flavor

Uses

Birch is one of the most popular and typical American flavors for beverages, candy, chewing gum, and other products. Sweet birch oil (*B. lenta* L.) has been reported used in the following:[3]

non-alcoholic beverages	48 ppm
ice cream, ices, etc.	44 ppm
candy	310 ppm
baked goods	110 ppm
gelatins and puddings	0.07 ppm
chewing gum	4,300 ppm
syrups	5.0 ppm

Regulatory status	Not as yet fully defined by FDA

BLACKBERRY

Botanical source	*Rubus fruticosus* L.
Botanical family	*Rosaceae*
Foreign names	Mure (Fr.), Brombeere (Ger.), Zarza (Sp.), Mora di rovo (It.)
Description	Woody shrub, highly branched at the base; grows commonly in woods and hedgerows throughout Europe. Several species are known: *R. tormentosus* Borkh., *R. ulmifolius* Schott., *R. glandulosus* Bell., etc. The plant has prickly-armed branches and berries that are green to red to shiny black when ripe.
Parts of plant used	Berries
Physical-chemical characteristics Derivatives	Fluid extract, tincture (20% in 20% alcohol), and concentrated (4–5 fold) juice. The main constituents include malic, succinic, oxalic, folic, and ascorbic acids, sugar, and volatile substances.
Organoleptic characteristics	Refreshing, sweet flavor
Uses	The berries are consumed as is. The fluid extract and the tincture are used in pharmacy. The concentrated juice is used for flavoring gelatins, chocolate, and candy fillings.

BLACKBERRY, BARK

Botanical source	*Rubus* species of section *Eubatus*
Description	Armed shrubs; stems biennial; leaves mostly 5-foliolate in the first year's growth; fruits not separating from the juicy receptacle, blackish when ripe. More than 30 *Rubus* species are known, the most common being *R. allegheniensis* and *R. sativus.*
Parts of plant used	Bark
Uses	Blackberry bark extract (FEMA No. 2155) has been reported used in the following:[3]

alcoholic beverages	150–10,000 ppm
non-alcoholic beverages	81 ppm
ice cream, ices, etc.	3.0–880 ppm
candy	230 ppm
baked goods	3.0–660 ppm

Regulatory status	FDA §121.1163

BOIS DE ROSE

Botanical source

Aniba rosaeodora Ducke. (*Ocotea caudata* Mer.), *A. rosaeodora* var. *amazonica* Ducke. (*O. parviflora*)

Botanical family

Lauraceae

Foreign names

Bois de rose (Fr.), Rosenholz (Ger.), Bois de rose (Sp.), Legno di rosa (It.)

Description

Evergreen trees growing wild in the forests of the Amazon basin (Brazil, Peru) and in French Guinea. Brazilian and Peruvian bois-de-rose oils are distilled from the same botanical variety (*A. rosaeodora* var. *amazonica* Ducke.). The oils exhibit only slightly different physical characteristics, but they have different odors peculiar to the growing site of the trees. Cayenne bois-de-rose oil, distilled from the variety *A. rosaeodora* Ducke., is considered the best quality of bois-de-rose essential oils. Cayenne bois-de-rose oil is produced in scale as compared to the Brazilian and Peruvian counterparts.

Parts of plant used

The wood

Physical-chemical characteristics

Essential oil

The oil, obtained by steam distillation of the chopped wood, is colorless to pale-yellow. The Brazilian and cayenne oils exhibit a sweet, slightly woody, characteristic odor, whereas the Peruvian quality has a harsher, more camphoraceous top note. Physical-chemical constants for the various quality oils are as follows:

Brazilian[1]

Specific gravity at 20°C	0.871–0.888 (0.873–0.887)[6]
Refractive index at 20°C	1.4620–1.4685 (1.4640–1.4680)[6]
Optical rotation	−2° to +5° (−4° to +5°)[6]
Total alcohols (as linalool)	84–93%
Solubility (in 60% ethanol)	1:3–5
Ester value (after acetylation)	250–270[6]

Cayenne[1]

Specific gravity at 20°C	0.866–0.877
Refractive index at 20°C	1.4610–1.4665
Optical rotation	−10° to −17°
Total alcohols (as linalool)	87% and more
Solubility (in 60% ethanol)	1:4 and more

Peruvian[2]

Specific gravity at 25°C	0.870–0.880
Refractive index at 20°C	1.4620–1.4700
Optical rotation	−2° to +6°
Total alcohols (as linalool)	>82%
Solubility (in 60% ethanol)	1:6

The main constituent of the oil is linalool. The *l*-form is predominant in cayenne oil, whereas the *d*- and *l*-isomers are present in the Brazilian and Peruvian oils. Other constituents of cayenne oil include terpenes, dipentene, methyl heptenol, eugenol, nerol, *d*-α-terpineol, isovaleric aldehyde, furfural, and methyl heptenone. Other constituents of the Brazilian oil include α-terpineol, *p*-methylacetophenone, cineol, and a sesquiterpene fraction.

Organoleptic characteristics

Characteristic, sweet, somewhat woody, floral odor

Uses

The essential oil is used extensively in perfumery. The relative stability of the oil to alkalies makes it useful in soap perfumes. In flavors the oil is used to impart characteristic notes to compounded oil for chewing gum, baked goods, ice cream, candy, and beverages. Bois-de-rose oil is also an excellent starting material for the extraction of linalool. Bois-de-rose oil (FEMA No. 2156) has been reported used in the following:[3]

non-alcoholic beverages	0.65 ppm
ice cream, ices, etc.	2.6 ppm
candy	6.7 ppm
baked goods	9.3 ppm
chewing gum	35 ppm

Regulatory status

GRAS (II)

BOLDO

Other names

Boldus; boldea; boldu

Botanical source

Peumus boldus Mol.

Botanical family

Monimiaceae

Foreign names

Boldo (Fr.), Boldo (Ger.), Boldo (Sp.), Boldo (It.)

Description

Small, wild tree or shrub widespread throughout Chile, Bolivia, and Peru; it is also cultivated in Italy. It has slender branches, opposite, short, petioled, coarse leaves exhibiting a characteristic, pleasant odor reminiscent of melissa and coriander. The plant flowers in winter and spring.

Parts of plant used

Leaves (harvested in autumn)

Physical-chemical characteristics

Essential oil

The oil is obtained by steam distillation of the dried leaves in approximately 1.8–2.6% yields. It is a yellow liquid with a spicy, hydrocarbon-like odor and aromatic, burning taste. The main constituents include *p*-cymene, cineol, ascaridole, eugenol, cinnamic aldehyde, and an ester of acetic acid. An oil of European origin has the following constants:

Specific gravity	0.9150–0.9567[1]
Optical rotation	−1°40′ to +2°[1]
Refractive index at 20°C	1.47916–1.47928[1]
Acid value	1.8–2.4[1]
Ester value	11.2–14.9[1]
Solubility	1:5.5–9 in 70% ethanol[1]

Derivatives

Fluid extract and tincture (20% in 70% ethanol). The fluid extract contains boldine and other alkaloids, including sparteine (0.250–0.535% total), boldoglucin, and flavone derivatives; the last two components are also present in the essential oil.

Organoleptic characteristics

Spicy, hydrocarbon-like odor; aromatic, burning taste

Uses

The flavor industry employs boldo derivatives in several formulations for liqueurs and bitters and in special compounded aromas for flavoring drugs.

Regulatory status

FDA §121.1163. In alcoholic beverages only

BORONIA

Botanical source *Boronia megastigma* Nees.

Botanical family *Rutaceae*

Foreign names Boronia (Fr.), Boronia (Ger.), Boronia (Sp.), Boronia (It.)

Description Shrub up to 2 m (7 ft) high, growing preferentially along the coasts and in marshy areas in western and southwestern Australia. The plant flowers between August and October.

Parts of plant used Flowers

Physical-chemical characteristics

Derivatives

Concrete
The concrete, prepared by extraction of the flowers using petroleum ether, has a butter-like consistency and green color. Main constituents include ethanol ($<59\%$) and ethyl formate, in addition to glycerides, phytosterols, and β-ionone.

Absolute
The absolute, prepared by alcoholic extraction of the concrete, contains the same constituents as the concrete and exhibits a fresh, green, fruital, spicy odor reminiscent of cinnamon and tobacco.

Organoleptic characteristics Rich, fresh, fruital, or slightly spicy odor

Uses Boronia derivatives are used in perfumery and also to impart richness to fruital aromas with an ionone, spicy note for flavoring candy, baked goods, and beverages. Boronia absolute (FEMA No. 2167) has been reported used in the following:[3]

non-alcoholic beverages	4.3 ppm
ice cream, ices, etc.	2.8 ppm
candy	11 ppm
baked goods	10 ppm

Regulatory status Boronia flowers: FDA §121.1163

BRYONIA

Botanical source *Bryonia alba* L. or *B. dioica* Jacq.

Botanical family *Cucurbitaceae*

Foreign names Bryone dioique (Fr.), Rotbeerige Saurübe (Ger.), Brionia (Sp.), Brionia (It.)

Description Perennial herb chiefly growing in woods, thickets, and fields in central and southern Europe, western Asia, the Far East, and North Africa. The plant has glabrous stems; fleshy, long, tuber-like roots (yellowish-white externally, white internally); alternate palmatifid leaves; and dioecious white flowers (May through September).

Parts of plant used Roots

Physical-chemical characteristics

Derivatives Fluid extract, tincture (20% in 60% alcohol), dried water-alcohol extracts, soft

	water-alcohol extract. The fluid extract contains resin, phytosterine, bryonol, enzymes, terpenes, fatty acids, protein substances, and glucosides.
Organoleptic characteristics	Tonic, aromatic
Uses	Bryonia derivatives are seldom employed in flavoring (liqueurs, bitters) but find application in drugs.
Regulatory status	Bryonia root: FDA §121.1163. In alcoholic beverages only

BUCHU

Botanical source	*Barosma betulina* Bartl. & Wendl., *B. crenulata* (L.) Hooker, *B. seratifolia* Willd.
Botanical family	*Rutaceae*
Foreign names	Bucco (Fr.), Bukko (Ger.), Buchú (Sp.), Bucco (It.)
Description	Small shrubs having opposite leaves, white, five-petaled flowers, and penta-follicled fruits. The plant is native to South Africa (Cape of Good Hope).
Parts of plant used	Leaves (harvested in March–April)
Physical-chemical characteristics	
Essential oil	The oil, steam distilled from the dried leaves, is a dark-brown liquid with a sweet odor and fresh, bitter taste. Distillation of the imported buchu leaves is carried out in Europe (mainly Holland) and in the United States (seldom on the growing site). The main constituents include diosphenol (barosma camphor), diosmin (a flavonic glucoside), and hesperidin. Physical-chemical constants are as follows: Specific gravity at 15°C 0.918–0.960[1] Optical rotation −15° to −48°[1]
Derivatives	Fluid extract, tincture (20% in 20% alcohol)
Organoleptic characteristics	Strong, sweet odor; fresh, bitter flavor
Uses	The essential oil is used in perfumery; the fluid extract and tincture, in patent drugs. The oil also is used for flavoring candy, beverages, and condiments. Buchu leaf oil (FEMA No. 2169) has been reported used in the following:[3] non-alcoholic beverages 1.9 ppm alcoholic beverages 0.50 ppm ice cream, ices, etc. 6.8 ppm candy 8.5 ppm baked goods 5.2 ppm condiments 7.0 ppm
Regulatory status	Buchu leaves: FDA §121.1163

BUCK BEAN

Other names	Marsh trefoil; bogbean
Botanical source	*Menyanthes trifoliata* L.
Botanical family	*Gentianaceae*

Foreign names	Menyanthe, Trefle d'eau (Fr.), Fieberklee (Ger.), Trebol fibrino (Sp.), Trifoglio fibrino (It.)
Description	Buck bean is a perennial herb commonly found in bogs or shallow waters in Europe, Asia, and North America. The plant, approximately 50 cm (20 in.) high, has horizontal rhizomes, alternate trifoliolate leaves, erect floral scape, terminated by white-pinkish racemose flowers (May–June).
Parts of plant used	Leaves (harvested during the flowering season)
Physical-chemical characteristics	
Derivatives	Fluid extract, tincture (20% in 20% ethanol); main constituents of the derivatives include rutin, loganin, and gentianin.
Organoleptic characteristics	Bitter tonic, aromatic
Uses	Because of their bitter-tonic flavor, buck bean derivatives find use in the formulation of liqueurs, bitters, and other products.
Regulatory status	Buck bean leaves: FDA §121.1163. In alcoholic beverages only

CACAO (COCOA)

Botanical source	*Theobroma cacao* L.
Botanical family	*Sterculiaceae*
Foreign names	Cacao (Fr.), Kakao (Ger.), Cacao (Sp.), Cacao (It.)
Description	A tree cultivated mainly in Central and South America and Equatorial Africa. It grows naturally to a height of 10–12 m (33–40 ft), bears large, sparse, lanceolated leaves, and produces small blossoms in clusters and fruits (pods) containing many almond-shaped seeds.
Parts of plant used	Seeds (toasted or fermented)
Physical-chemical characteristics	
Essential oil	The essential oil is obtained in 0.001% yields by distillation of seeds. For the most part it consists of linalool (ca 50%), aliphatic acids, and the various corresponding esters. Specific gravity at 15°C 0.9075[1] Refractive index at 20°C 1.4728[1]
Derivatives	Essential oil, tincture, distillate, fluid extract, infusion (typical beverage). Alcoholic extracts are generally obtained by treatment of the partially crushed seeds with 40–70°C alcohol. The distillate has an alcohol concentration of about 65%; it is obtained from the same type of cacao used for the preparation of tinctures as well as from cacao varieties with low-fat content.
Organoleptic characteristics	Cocoa flavor and aroma
Uses	Cacao distillates and tinctures are extremely important raw materials for liqueur formulations, not only when used as is (cacao liqueurs) but also as a base for

	specialties (Marsala types). Of course, the infusions of cocoa are almost universal beverages.
Regulatory status	GRAS (II)

CADE OIL

Botanical source	*Juniperus oxycedrus* L.
Botanical family	*Pinaceae*
Foreign names	Essence de Cadé (Fr.), Kadeoel (Ger.), Cadé (Sp.), Cade (It.)
Description	Branched trees or shrubs, native to southern Europe; linear-subulate, prickly-pointed leaves; flowers in axillary catkins; red, round berries much larger than *J. communis* (common juniper).
Parts of plant used	Woody portion
Physical-chemical characteristics	
Essential oil	A viscous, reddish-brown mass is obtained by destructive distillation of the chopped wood. From the mass a dark, tar-like deposit (juniper tar) separates; this is removed from the transparent oil. The main constituents include *d*-cadinene, a sesquiterpene ($C_{15}H_{24}$), *l*-cadinol, and dimethylnaphthalene. The oil usually is rectified under vacuum to improve color and solubility. A rectified oil has been reported as having the following constants: Specific gravity at 25°C 0.952–0.961[1] Refractive index at 20°C 1.5110–1.5200[1] Optical rotation +4°17′ to +4°40′[1] Solubility 1:5 in 95% alcohol[1]
Organoleptic characteristics	Characteristic smoky, acrid odor; bitter taste
Uses	The oil is used mainly in perfumery. It also is used occasionally to impart a smoky note to canned meats and fish.
Regulatory status	Proposed by Commissioner of FDA for inclusion in §121.1164

CAJEPUT

Botanical source	*Melaleuca leucadendron* L. and other *Melaleuca* species
Botanical family	*Myrtaceae*
Foreign names	Cajeput (Fr.), Cajeput (Ger.), Cajeput (Sp.), Cajeput (It.)
Description	Trees up to 15 m (50 ft) high, commonly growing wild in the Moluccas, Malaya, northern Australia, Queensland, and New South Wales. The lower and younger trees, however, yield the most suitable material for distillation. Cajeput trees also grow in the United States (Florida), but these plants are not used for production of essential oil.
Parts of plant used	Twigs and fresh leaves

Physical-chemical characteristics

Essential oil

The oil, obtained by steam distillation of the leaves and twigs, is an almost colorless, green or yellow liquid with an agreeable, penetrating, camphoraceous odor and aromatic, bitter taste. The main constituents include cineol, valeric and benzoic aldehydes, α-terpineol (free or esterified), *l*-α-pinene, *l*-limonene, dipentene, and sesquiterpenes.

Specific gravity at 25°/25°C	0.908–0.925[2]
Refractive index at 20°C	1.4660–1.4720[2]
Optical rotation at 20°C	±0° to −4°[2]
Cineol content	50–65%[2]
Solubility	1:1 in 80% alcohol[2]

Organoleptic characteristics

Strong, camphoraceous odor; bitter, burning taste

Uses

The oil is used for flavoring candy and beverages; it also is used in perfumery. Cajeput oil (FEMA No. 2225) has been reported used in the following:[3]

non-alcoholic beverages	0.50–2.0 ppm
ice cream, ices, etc.	1.0 ppm
candy	13 ppm
baked goods	11 ppm

Regulatory status

FDA §121.1163

CALAMUS

Other names

Sweet flag; sweet grass

Botanical source

Acorus calamus L.

Botanical family

Araceae

Foreign names

Calamus (Fr.), Kalmus (Ger.), Calamo (Sp.), Calamo (It.)

Description

Various chromosomic species exist (di-, tri-, and tetraploid). It is a perennial water plant, native to India, now widespread. It is about 1 m (39 in.) tall and exhibits a penetrating, pleasant odor. It has cylindrical, nodular, branched rhizomes; long, radical, encased leaves; and erect, spathaceous inflorescence. It flowers from June to August.

Parts of plant used

Rhizomes

Physical-chemical characteristics

Essential oil

The essential oil is obtained by steam distillation of dried rhizomes (average yields, 2–3%). It exhibits varying physical-chemical constants, depending on the origin. The European essential oil is a yellow-brownish liquid with a warm, camphor-like odor and sharp, burning taste. The main constituents include *d*-α-pinene, camphene, cineol, camphor, eugenol, and methyleugenol.

Specific gravity at 15°C	0.960–0.974[1]
Refractive index at 20°C	1.5045–1.5070[1]
Optical rotation	+15°50′ to +18°14′[1]
Solubility	1:0.5 in 90% ethanol[1]

The Indian-type oil is obtained by steam distillation of either the fresh root or unpeeled dried root; it is yellow-brown.

Specific gravity at 25°/25°C	1.060–1.080[2]
Optical rotation	−2° to +6.5°[2]
Refractive index at 20°C	1.550–1.5525[2]
Acid value	<4[2]
Ester value	3–20[2]

Derivatives	Tincture (20% in 65% ethanol), fluid extract, and essential oil
Organoleptic characteristics	Bitter, tonic-like flavor; highly aromatic
Uses	The dried herb as is and its derivatives (extract and tincture) were once useful for the preparation of bitters and in the formulation of vermouths. The essential oil was used for the preparation of compounded oils for liqueurs and sweets.
Regulatory status	*Note:* Calamus and calamus oil are no longer permitted for use in food under U.S. law (*Federal Register*, May 9, 1968).

CALUMBA

Botanical source	*Jatrorrhiza palmata* (*Lam.*) Miers
Botanical family	*Menispermaceae*
Foreign names	Colombo (Fr.), Kolombo (Ger.), Colombo (It.)
Description	Herbaceous shrub a few meters in length with creeping stalks (creeping lianas) originating from the rhizome. Native to the east African coast and cultivated in the East Indies.
Parts of plant used	Roots (commercially offered in sliced discs)
Physical-chemical characteristics	
Derivatives	Tincture (15–20% in 65–70% ethanol) and fluid extract. The dried product and its derivatives contain bitter substances: columbin, palmatine, columbic acid, columbamine, jatrorrhizine, and other alkaloids. An essential oil has been isolated experimentally in minimum yields.
Organoleptic characteristics	Odorless with a bitter-tonic flavor
Uses	The root and its derivatives are used in the formulation of bitters and liqueurs.
Regulatory status	FDA §121.1163. In alcoholic beverages only

CAMOMILE (CHAMOMILE)

Hungarian or German

Botanical source	*Matricaria chamomilla* L.
Botanical family	*Compositae*
Foreign names	Petite camomille (Fr.), Echte Kamille (Ger.), Manzanilla alemana (Sp.), Camomilla volgare (It.)

Description

Annual herbaceous plant, very common in Europe, Asia, the United States, and Australia. It is 20–60 cm (8–24 in.) tall, dark green, with thin roots, erect stalks, alternate leaves, yellowish blossoms, and peripheral white flowers. It has a characteristic odor and bitter-aromatic taste. The plant flowers from May to July.

Parts of plant used

Flowers

Physical-chemical characteristics

Essential oil

Obtained by steam distillation of flowers with variable yields ranging from 0.3% to more than 1%, depending on the area of production. It is a more or less viscous liquid, depending on ambient temperature. It is intensely blue with a characteristic odor and taste. Refractive index and optical rotation are nearly non-measurable because of the intense color. The color changes to green and finally brown on light exposure. The main constituents are chamazulene (approx. 1–15%), sesquiterpene alcohols, and caprinic acid and ester. The flowers also contain, among other ingredients, apigenine, methyl ether of umbelliferone, and fatty acids.

Specific gravity at 20°C	0.913–0.953[1]
Acid value	5–50[1]
Ester value	3–39[1]
Ester value (after acetylation)	66–155[1]

Derivatives

Infusion (2%), tincture (20% in 70% ethanol), soft and dried fluid extract, and the essential oil

Organoleptic characteristics

Bitter-tonic flavor with a characteristic aroma

Uses

The infusion is a common beverage in Europe and is used as a mild sedative and digestive. The spray-dried infusion is used to prepare instants. The bitter-aromatic taste blends very well with sweeteners. The dried herb and the tincture are generally used for the preparation of bitter-tonic beverages and elixirs. The essential oil is useful in the formulation of compounded oils.

Camomile (Hungarian) oil has been reported used in the following:[3]

non-alcoholic beverages	2.6 ppm
alcoholic beverages	1.0 ppm
ice cream, ices, etc.	6.1 ppm
candy	3.8 ppm
baked goods	6.5 ppm
chewing gum	0.80 ppm

Regulatory status

GRAS (I), (II)

CAMOMILE (CHAMOMILE)

Roman or English

Botanical source

Anthemis nobilis L.

Botanical family

Compositae

Foreign names

Camomille Romaine (Fr.), Roemische Kamille (Ger.), Manzanilla Romana (Sp.), Camomilla Romana (It.)

Description

Perennial herb, 15–20 cm (6–8 in.) tall, native to central Europe, now cultivated in various regions. It has a thin creeping rhizome, numerous erect stalks, a strong, pleasant odor, large yellow florets, and white radial flowers. The plant flowers from June to September.

Parts of plant used: Flowers

Physical-chemical characteristics

Essential oil: Obtained by steam distillation of the dried flowers (yields approx. 0.3–1.0%). It is a yellow to greenish-yellow (sometimes blue) liquid with a characteristic odor and bitter-aromatic taste. It contains primarily angelic and metacrylic acid esters, *n*-butyl isobutyrate, and *n*-butyl and isoamyl alcohols.

Specific gravity at 20°C	0.896–0.917[1]
Refractive index at 20°C	1.4380–1.4570[1]
Optical rotation at 20°C	−1° to +4°[1]
Solubility	1:2–1:4 in 80% ethanol[1]
Ester value	205–300[1]
Acid value	approx. 14[1]

Derivatives: Infusion (2%), tincture (20% in 30–50% ethanol), fluid extract, and the essential oil

Organoleptic characteristics: Similar to that of Hungarian or German camomile

Uses: Camomile oil (English) has been reported used in the following:[3]

non-alcoholic beverages	4.1 ppm
ice cream, ices, etc.	0.10–0.50 ppm
candy	1.3–5.0 ppm
baked goods	0.10–5.0 ppm

Camomile oil (Roman) has been reported used in the following:[3]

non-alcoholic beverages	2.3 ppm
alcoholic beverages	20 ppm
ice cream, ices, etc.	3.3 ppm
candy	4.3 ppm
baked goods	4.3 ppm
gelatins and puddings	0.25 ppm

Camomile extract (Roman) has been reported used in the following:[3]

non-alcoholic beverages	13 ppm
ice cream, ices, etc.	9.3 ppm
candy	6.7 ppm
baked goods	10.0 ppm

Regulatory status: GRAS (I), (II)

CAMPHOR, TREE

Botanical source: *Cinnamomum camphora* (L.) Nees & Ebermeier

Botanical family: *Lauraceae*

Foreign names: Camphre (Fr.), Kampfer (Ger.), Alcanfor (Sp.) Canfora (It.)

Description: Tall, majestic trees, native to the Far East (China, Formosa, Japan). The initial or whole camphor oil is obtained by steam distillation of the trees classified as *C. camphora* Sieb. and a number of related varieties: hon-sho, ho-sho, yu-sho, rau-kusu, sho-guy, and ohba-kusu. Hon-sho represents the most important variety, growing mainly in Japan and Formosa. The yu-sho variety grows in China; the sho-guy variety grows in Formosa, but its essential oil does not contain camphor. The ohba-kusu also grows in Formosa; its essential oil contains 95% safrole.

The wild plants yield larger amounts of camphor and essential oil than the cultivated ones. The yield also increases with the age of the plant. Depending on the composition crude camphor oils distilled from the different varieties can be classified as follows:

Camphor Safrole, Hon-sho Variety (Japan)
All parts of the plant contain a camphor-rich oil. The oil from the leaves, wood, and stumpwood contains free crystalline camphor. The oil from the roots is rich in safrole.

Camphor Safrole (Formosa)
The various parts of the plant (hon-sho and yu-sho) yield an essential oil rich in safrole. The oil from leaves has an average safrole content of approximately 80%. Like the Japanese camphor safrole, the hon-sho variety also yields crystalline camphor, whereas the yu-sho variety does not.

Camphor Cineol (Chinese Camphor Oil), Yu-sho Variety
The oil from leaves contains 60% cineol; that from stumpwood, 50% cineol. Neither the root oil nor the oil from wood contains free crystalline camphor. This oil is called apopin oil or eucalyptus oil, Chinese. When purified of terpineol, it is offered as a cheaper substitute for true eucalyptus oil. Chinese camphor oil (apopin oil) does not separate crystalline camphor. The white oil fraction contains from 10–35% cineol.

Camphor Linalool, Ho-sho Variety (Formosa)
The leaf oil (ho leaf oil) contains up to 80% linalool; the oil does not contain free crystalline camphor. Ho leaf oil has replaced to a great extent ho wood oil, or shiu wood oil, distilled from the wood of the same botanical variety. The latter contains linalool (15%) and camphor (42%).

True Camphor Oil
True camphor oil is distilled from the Formosan and Japanese hon-sho varieties. The crude oil that is steam distilled from the wood, stumpwood, and branches contains crude crystalline camphor that is removed by filter-pressing. The filtered oil is subsequently vacuum rectified, yielding additional camphor and three fractions that are sold commercially under the following names:

1. White camphor oil, the light fraction, or camphor oil 860-880.
2. a. Brown camphor oil, the medium-heavy fraction containing a minimum of 80% safrole, or camphor oil 1070.
   b. Yellow camphor oil, the residual oil after removal of safrole from brown camphor oil, or camphor oil 960-980.
3. Blue camphor oil, the heavy fraction containing mainly sesquiterpenes.

Brown camphor oil 1070 is commercially the most important as a source of safrole and in other industrial applications. Blue camphor oil is the least important because of its limited application. Yellow camphor oil is also known as oil camphor sassafrassy because of its striking resemblance to the sassafras odor.

Parts of plant used

Wood, stumpwood, branches, leaves

Physical-chemical characteristics
Essential oil

True Camphor Oil
Steam distilled from the woody portions.

White Camphor Oil 860-880
Colorless liquid with cineol-like odor.
Specific gravity at 25°/25°C 0.855–0.875[2]

Refractive index at 20°C	1.4670–1.4720[2]
Optical rotation	+16° to +28°[2]
Solubility	1:1 in 95% ethanol[2]

Brown Camphor Oil 1070
Pale-yellow to brown liquid with characteristic odor of sassafras.

Specific gravity at 25°/25°C	1.064–1.075[2]
Refractive index at 20°C	1.5100–1.5500[2]
Optical rotation	±0° to +3°[2]
Congealing point	+6°C[2]
Solubility	1:2 in 90% ethanol[2]

Yellow Camphor Oil 960-980
Yellow to brown liquid with a strong, persistent odor suggestive of camphor and sassafras.

Specific gravity at 25°/25°C	0.955–0.980[2]
Refractive index at 20°C	1.4960–1.5010[2]
Optical rotation	+10° to +5°[2]
Solubility	1:0.5 and more in 90% alcohol[2]

Blue Camphor Oil
Viscous, dark-bluish or bluish-brown liquid.

Specific gravity at 15°C	<1.000[1]
Refractive index at 25°C	ca 1.5050[1]
Boiling point	220–300°C[1]
Camphor content	<2.5%[1]

The main constituents of crude camphor oil include acids—acetic, formic, isobutyric, propionic, isovaleric, myristic, lauric, etc.; aldehydes—isovaleric, propionic, acetic, furfural, hexenal, etc.; cineole; safrole; *l*-linalool; geraniol; borneol; citronellol; terpineol; cresol; eugenol; carvacrol; pinene; camphene; camphor; and phellandrene.

Chinese Camphor Oil (Apopin Oil)

Steam distilled from the woody portion. A good first-quality yu-sho white camphor oil has the following constants:

Specific gravity at 15°C	0.972[1]
Refractive index at 20°C	1.4789[1]
Optical rotation	+18°53′ to +29°51′[1]
Cineol content	35% min.[1]

The main constituents include furfural, camphor, cineol, safrole, α-terpineol, α- and β-pinene, camphene, and dipentene.

Ho Wood Oil (Shiu Wood Oil)

Steam distilled from the woody portion in approximately 2% yields. The oil is a colorless to pale-yellow liquid with a sweet, camphoraceous odor. The main constituents include camphor (42%), linalool (15%), cineol (7%), safrole (5%), formaldehyde, eugenol, dipentene, camphene, terpineol (5%), and pinene.

Specific gravity at 15°C	0.870–0.8952[1]
Optical rotation	−0°51′ to −15°30′[1]
Acid value	0.6 max.[1]
Solubility	1:1.8–10 in 70% ethanol[1]

Ho Leaf Oil

Steam distilled from the leaves, ho leaf oil is a colorless liquid with a sweet, floral, delicate odor reminiscent of linalool. The rectified oil is a very good source of linalool and competes very effectively with the linalool isolated from Brazilian bois de rose.

Organoleptic characteristics

See above.

Uses

Camphor oil has a number of applications: as a solvent in paints and varnishes and as a diluent for inks. It is a good antiseptic and disinfectant and a good raw material for the isolation of cineol, safrole, linalool, etc. The oil is used extensively in perfumery (soaps, detergents, deodorants, sprays, etc.). The brown camphor oil is a very useful starting material for the synthesis of isosafrole, heliotropine, and vanillin. In flavors Japanese white camphor oil (FEMA No. 2231) has been reported used in the following:[3]

non-alcoholic beverages	5.4 ppm
baked goods	1.6–48 ppm
condiments	15 ppm

Regulatory status

FDA §121.1163. Safrole free

CANANGA

Botanical source

Cananga odorata Hook & Thoms. (*Canangium odoratum* Baill. f. *macrophylla*)

Botanical family

Anonaceae

Foreign names

Cananga (Fr.), Cananga (Ger.), Cananga (Sp.), Cananga (It.)

Description

For a long time cananga and ylang-ylang trees were considered identical species. A more accurate study classified the true cananga plant as the tree of *Canangium odoratum* Baill. f. *macrophylla*, whereas ylang-ylang was classified as *Canangium odoratum* Baill. f. *genuina*.

Cananga, native to the Moluccas, grows wild or cultivated throughout tropical Asia and the islands of the Indian Ocean. The tree may reach up to 30 m (98 ft) in height. Although it flowers year round, the production peak occurs between October and December.

Parts of plant used

Flowers

Physical-chemical characteristics

Essential oil

The oil, obtained by direct-fire distillation of flowers, is a pale-yellow to deep-yellow liquid. It has a characteristic, slightly woody, floral odor reminiscent of ylang-ylang and a burning taste. Its physical-chemical constants are as follows (see also reference 2):

Specific gravity at 20°/20°C	0.906–0.923[1]
Refractive index at 20°C	1.495–1.503[1]
Optical rotation at 20°C	−30° to −15°[1]
Ester value	13–35[1]
Solubility	1:1 in 95% ethanol with haze[1]

The main constituents include sesquiterpenes, sesquiterpene alcohols, linalool, geraniol, eugenol, isoeugenol, cadinene, benzyl alcohol, methyl salicylate, methyl anthranilate, safrole, nerol, farnesol, and formic, acetic, and benzoic acids. The chemical constitution of cananga oil is identical to that of ylang-ylang oil, except that cananga oil contains more sesquiterpenes and fewer esters than ylang-ylang oil. A rectified oil with inferior fixative properties, but lighter in color and more soluble, is also prepared.

Organoleptic characteristics

Slightly woody, floral odor reminiscent of ylang-ylang; burning taste

Uses

The essential and the rectified oils are used extensively in perfumery. The oils are sometimes used for flavoring beverages and baked goods. Cananga oil (FEMA No. 2232) has been reported used in the following:[3]

non-alcoholic beverages	7.0 ppm
ice cream, ices, etc.	1.0 ppm
candy	2.0 ppm
baked goods	2.0 ppm

Regulatory status

GRAS (II)

CAPERS

Botanical source

Capparis spinosa L.

Botanical family

Capparidaceae

Foreign names

Caprier épineux (Fr.), Kappernstande (Ger.), Taparera (Sp.), Cappero (It.)

Description

Wild or cultivated, prickly, prostrate shrubs, commonly growing in rocky and arid mountain areas in southern Europe, North Africa, and around the Mediterranean basin. The plant has woody, cylindrical, branched, grayish roots, numerous sarmentose stems with alternate leaves, and edible buds.

Parts of plant used

The root bark

Physical-chemical characteristics

Derivatives

Decoction, tincture, and fluid extract. All derivatives contain the glucoside capparirutin.

Organoleptic characteristics

Sour, astringent flavor

Uses

The derivatives were used in pharmacy. The buds are often pickled and used in cooking.

Regulatory status

GRAS (I)

CAPSICUM

Other names

Cayenne pepper; red pepper; paprika

Botanical source

Capsicum minimum Mill., *C. frutescens* L., *C. annuum* L., and similar varieties

Botanical family

Solanaceae

Foreign names

Piment Caraibe or Poivron Rouge (Fr.), Cayenne Pfeffer (Ger.), Pimienta chiles (Sp.), Capsico (It.)

Description

Commercially the fruits of *C. annuum* and its varieties are known under the names of Spanish pepper, poivrons, and paprika. The fruits of *C. frutescens* are known as chiles. The term *chiles* may be used to indicate any variety of capsicum. The orange-red powder of the fruits from which the most pungent parts are removed is known as rosenpaprika; in the United States this is simply paprika.

Capsicum frutescens

C. frutescens is a small shrub similar to other capsicum species native to South America. It has a 2–3 year life span, reaches heights of 1 m (39 in.), has greenish yellow flowers clustered at the base of lanceolate leaves, and small, oblong, intensely red pods 1–3 cm (0.4–1.2 in.) long.

Capsicum annuum

C. annuum is an annual, shrub-like herb smaller than *C. frutescens*, with a woody stem and single, white flowers located at the junction of isolated leaves. The oblong pods (fruits) exhibit varying colors—yellow to red to black. The fruits of *C. annuum* have a taste less pungent than *C. frutescens*.

Parts of plant used

Fruits

Derivatives

Fluid extract, tincture (10% in 90% ethanol, or 20% in 60% ethanol), and oleoresins (also plated onto inert carrier). The best-known constituent accounting for the pungent flavor is decylene vanillylamide (also known as capsaicin).

Capsicum Oleoresin

Capsicum oleoresin (African chillies) is obtained by solvent extraction of the dried ripe fruit of *C. frutescens* L. or *C. annuum* L. var. *conoides* Irish with subsequent removal of the solvent. It is a clear-red, light-amber, or dark-red viscid liquid with a characteristic odor and extremely high bite.

Scoville heat units	480,000 min[2]
Color value	4,000 max[2]
Solubility	Partly soluble in alcohol with separation and/or sediment[2]

Paprika Oleoresin[2]

Paprika oleoresin is obtained by solvent extraction of the pods of *C. annuum* L. with the subsequent removal of the solvent. It is evaluated only on a unit color basis; the bulk of this material has a color value of 40,000–100,000. It is a deep red, somewhat viscid liquid with a characteristic odor; it is partly soluble in water.

Red Pepper Oleoresin

Red pepper oleoresin is obtained by solvent extraction of dried fruits of *C. annuum* L. var. *longum* Sendt. or the hybrid Louisiana Sport Pepper with subsequent removal of the solvent. It is a deep-red liquid with a characteristic odor and high bite.

Scoville heat units	240,000 min[2]
Color value	20,000 max[2]
Solubility	Partially soluble in alcohol[2]

Organoleptic characteristics

Mild to highly pungent

Uses

The dried and finely ground fruits are used as spices; flavorists also prepare compounded aromas for condiments, sauces, and other products using the oleoresins and the finely ground fruits. Capsicum extract has been reported used in the following:[3]

non-alcoholic beverages	120 ppm
ice cream, ices, etc.	15 ppm
candy	12 ppm
baked goods	12–14 ppm
condiments	50–100 ppm
meats	200 ppm

Capsicum oleoresin has been reported used in the following:[3]

non-alcoholic beverages	14 ppm
candy	11 ppm
baked goods	14 ppm

chewing gum	46 ppm
condiments	92 ppm
meats	50–100 ppm

Paprika, *C. annuum* L., has been reported used in the following:[3]

baked goods	1,900 ppm
condiments	970 ppm
meats	7,400 ppm
soups	1,000–7,500 ppm

Paprika oleoresin, *C. annuum* L., has been reported used in the following:[3]

non-alcoholic beverages	1.0–25 ppm
ice cream, ices, etc.	1.0 ppm
candy	0.50 ppm
baked goods	1.2 ppm
condiments	100 ppm
meats	96 ppm

Red pepper, mainly *C. frutescens* but also *C. annuum*, has been reported used in the following:[3]

non-alcoholic beverages	15–240 ppm
baked goods	270 ppm
condiments	630 ppm
meats	310 ppm
pickles	11–59 ppm

Cayenne pepper from *C. annuum* L. var. *longum* Sendt. has been reported used in the following:[3]

non-alcoholic beverages	1.0 ppm
ice cream, ices, etc.	2.0 ppm
candy	2.0 ppm
baked goods	2.0–50 ppm
condiments	610 ppm
meats	910 ppm
soups	100 ppm

Regulatory status GRAS (I), (II)

CARAWAY

Botanical source *Carum carvi* L.

Botanical family *Umbelliferae*

Foreign names Carvi (Fr.), Kümmel (Ger.), Caró (Sp.), Carvi (It.)

Description A biennial herbaceous plant very common in Europe, Asia, Africa, and the U.S.A. It has a tapering, fleshy root, furrowed stem, finely cut primately decompounded leaves, white flowers, and oval fruits. The plant grows to about 2 feet in height and blooms from May to July.

Parts of plant used Fruits, containing approximately 15% of fixed oil and 3 to 7% of essential oil.

Physical-chemical characteristics

Essential oil The essential oil exhibits physical-chemical characteristics specific to the country of origin (Holland, Hungary, Yugoslavia, North America, India). It is obtained by steam distillation with yields varying between 3–6%. The oil is a yellow-amber liquid with a characteristic aromatic odor. Carvone content ranges from 50–76%.

In addition to carvone, the oil contains *d*-limonene, carveol, diacetyl, furfural, methyl alcohol, acetic aldehyde, and others.

Specific gravity at 20°C	0.903–0.931[1]
Optical rotation at 20°C	+66° to +80°[1]
Refractive index at 20°C	1.4840–1.4930[1]

Derivatives

Infusion (3%), decoction (5%), alcoholic distillate in 75% alcohol, and distillation waters. Also, a greenish-yellow liquid oleoresin is extracted from the seed.

Organoleptic characteristics

Warm, biting flavor with a strong, fatty, harsh undertone

Uses

The liquor industry makes large use of the alcoholic distillate and of the essential oil. A specific liqueur is Kümmel. The dried product is used as such to flavor cakes, bread, and various confections. Caraway has been reported used in the following:[3]

non-alcoholic beverages	63 ppm
ice cream, ices, etc.	63 ppm
baked goods	3,000–10,000 ppm
condiments	96 ppm

Regulatory status

GRAS (I), (II)

CARDAMOM

Botanical source

Elettaria cardamomum Maton

Botanical family

Zingiberaceae

Foreign names

Cardamome (Fr.), Kardamom (Ger.), Cardamomo (Sp.), Cardamomo (It.)

Description

The small variety of cardamom (α-minor) cultivated in Malabar is the most valuable variety. This variety has almost entirely replaced in the last fifty years the larger variety, β-major. The plant grows more than 2 m (6.5 ft) tall and exhibits a long rhizome from which the fruit-bearing stalks emerge. The plant has white flowers. The fruits (husks) containing the seeds are harvested prior to ripening, which is completed by exposing them to sunlight. The seeds are subsequently sorted into several commercial qualities based on color, size, and origin (Malabar, Ceylon, Mysore).

Parts of plant used

Seeds

Physical-chemical characteristics

Essential oil

It is obtained by steam distillation of the comminuted seeds with an average yield of 5%. The seeds must be removed from the hulls shortly before distillation, as the essential oil is extremely volatile, which can considerably reduce the yields. The oil is a greenish-yellow liquid with a warm, spicy odor.

Specific gravity at 20°C	0.919–0.936[1]
Optical rotation at 20°C	+22° to +41°[1]
Refractive index at 20°C	1.4620–1.4680[1]
Acid value	up to 3[1]
Ester index	92–150[1]
Solubility	1:2–1:5 in 70% alcohol[1]

Derivatives

Essential oil, tincture (20% in 70% alcohol), fluid extract and oleoresin. The main constituents of the oil are limonene, cineol, *d*-α-terpineol, and terpinyl acetate.

Organoleptic characteristics

Warm, spicy aromatic odor, somewhat pungent and faintly bitter at high concentrations

Uses

Cardamom is commonly used as a flavor ingredient. The dried product and the tincture are used in the formulation of compounded mixtures for liqueurs. The essential oil generally is employed in the manufacture of compounded oils for liqueurs and baked goods. It is also used to flavor canned foods, meats, sauces, and condiments.

Cardamom has been reported used in the following:[3]

non-alcoholic beverages	3.0 ppm
ice cream, ices, etc.	2.0 ppm
candy	2.0 ppm
baked goods	1,700 ppm
condiments	900 ppm
meats	570 ppm

Cardamom seed oil has been reported used in the following:[3]

non-alcoholic beverages	1.9 ppm
alcoholic beverages	10 ppm
ice cream, ices, etc.	1.3 ppm
candy	5.8 ppm
baked goods	57 ppm
chewing gum	2.2 ppm
pickles	10–16 ppm
condiments	8.0 ppm
meats	36 ppm

Regulatory status

GRAS (I), (II)

CAROB BEAN

Other names

St. John's bread

Botanical source

Ceratonia siliqua L.

Botanical family

Leguminosae

Foreign names

Caroube (Fr.), Johannisbrotbaum (Ger.), Algarrobo europeo (Sp.), Carruba (It.)

Description

The plant, originally from the Middle East, is widespread along the southern part of the Mediterranean. The tree, which may reach up to 10 m (33 ft) in height, is cultivated extensively in Spain and Italy. It bears a large number of fruits (pods) rich with seeds. The dried or partially desiccated pulp exhibits a characteristic sweet flavor.

Parts of plant used

Fruits cleaned from the seeds. The seeds are used in some countries for the manufacture of a flour. The extremely hard seeds also provide the highly important industrial gum called carob bean gum or locust bean gum. The gum, classed as a galactomannan, is separated by a special milling process and then powdered. The gum is extensively used in food as a thickener and stabilizer.

Physical-chemical characteristics

Derivatives

Tincture (20–25% in 55–77% alcohol), fluid and soft extracts

Organoleptic characteristics

Sweet

Uses

The tincture and the fluid extract are normally employed in the formulation of liqueurs as a corrective flavor (brandy). In more rare cases these derivatives are used, together with the soft extract, for special beverages and pastry. The dried and powdered endosperm from the seed yields the important locust bean gum, an often superior alternative to gum tragacanth. Carob bean extract has been reported used in the following:[3]

non-alcoholic beverages	66 ppm
ice cream, ices, etc.	93 ppm
candy	180 ppm
baked goods	120 ppm
gelatins and puddings	600 ppm
icings and toppings	500–1,000 ppm

Regulatory status

GRAS (II)

CARROT

Botanical source

Daucus carota L.

Botanical family

Umbelliferae

Foreign names

Carotte commun (Fr.), Moehren (Ger.), Zanahoria (Sp.), Carota (It.)

Description

A biennial, herbaceous plant very common in Europe and many other countries. The plant exhibits a fusiform (spindle-shaped) root of orange-red color, erect stalk, alternate leaves, white and pink flowers, and greenish seeds. It flowers from June to September.

Parts of plant used

Roots and seeds

Physical-chemical characteristics

Essential oil

Prepared from seeds, roots, and the green parts of the plant. It is obtained by steam distillation with variable yields, depending on the parts of the plant used for distillation. The oil is produced in various parts of Europe, Asia, and the United States (for U.S. specifications see reference 2). The most valuable seed oil is that of French production (Graines). It is an amber liquid with a characteristic fatty odor. The main constituents identified in carrot seed oil of French production are carotenol (14–18%) and other constituents normally present in this type of essence —terpenes, terpene alcohols, and sesquiterpenes.

Specific gravity at 20°C	0.866–0.940[1]
Refractive index at 20°C	1.4820–1.4910[1]
Optical rotation	−8°40′ to −37°[1]
Acid number	1–5[1]
Ester index	17–52[1]
Solubility	1:0.5 in 90% alcohol[1]

Derivatives

Decoction (3%), infusion (5% prepared from the roots), and a tincture (20% in 60% alcohol) prepared from the seeds

Organoleptic characteristics

Pleasant, aromatic odor; warm, spicy but sweet, piquant flavor

Uses

The most important use is as a food and a flavor ingredient in cooking (spice blends, seasonings, etc.). The tincture from seeds is employed as a corrective flavor in liqueurs. The essential oil is used in the formulation of compounded oils for sauces, cured meats, and other food applications; it is also used in perfumery.

Carrot oil has been reported used in the following:[3]

non-alcoholic beverages	3.1 ppm
ice cream, ices, etc.	5.5 ppm
candy	5.1 ppm
baked goods	4.4 ppm
gelatins and puddings	0.02 ppm
condiments	15 ppm
soups	1.0 ppm

Regulatory status GRAS (II)

CASCARA SAGRADA

Other names California buckthorn; cascara buckthorn; chittembark

Botanical source *Rhamnus purshiana* DC.

Botanical family *Rhamnaceae*

Foreign names Cascara segrada (Fr.), Amerikanischer Faulbaum (Ger.), Cascara segrade (Sp.), Cascara segrada (It.)

Description Shrub or small tree having loosely pinnate-veined leaves and greenish dioecious flowers in axillary clusters. The plant grows along the Pacific coast of the United States (Washington, California, Oregon) and also in Idaho, Arizona, Colorado, and other states. It is also cultivated in Kenya.

Parts of plant used Bark (from the branches and trunk)

Physical-chemical characteristics

Derivatives Fluid extract; tincture (20% in 70% ethanol), soft aqueous extract, soft hydroalcoholic extract, dried extract. Main constituents include emodin, aloe-emodin, crysophanic acid, barbaloin, anthracene and anthraquinone derivatives, glucosides, and also resin, acids, and enzymes.

Organoleptic characteristics Bitter-tonic flavor

Uses The laxative properties are used in pharmacology. Cascara extracts can be used as a partial substitute for the aloe bitter principle in liqueur formulations and aromas. Cascara bitterless extract (FEMA No. 2253) has been reported used in the following:[3]

non-alcoholic beverages	100 ppm
ice cream, ices, etc.	50 ppm
baked goods	100 ppm

Regulatory status FDA §121.1163

CASCARILLA

Botanical source *Croton eluteria* Benn.

Botanical family *Euphorbiaceae*

Foreign names Cascarille (Fr.), Kaskarillbaum (Ger.), Cascarilla (Sp.), Cascarilla (It.)

Description It is a small tree or shrub that may reach 5 m (16 ft) in height, originally from the Bahamas and West Indies as well as from Peru, Paraguay, and Haiti. It has alternate leaves, monoic flowers, and terminal or axillary clusters.

Part of plant used Bark of thin branches

Physical-chemical characteristics

Essential oil It is obtained by steam distillation of the bark with yields of 2%. It is a yellow-greenish or amber liquid with a warm, spicy taste and odor. The main constituents of the oil are *l*-limonene, *p*-cymene, dipentene, eugenol, and cascarillic acid. The bark contains cascarillin and vanillin. (See reference 2.)

Specific gravity at 15°C	0.898–0.925[1]
Optical rotation	+1° to +13°[1]
Refractive index at 20°C	1.489–1.496[1]
Acid value	2–9
Ester value	5–12[1]
Ester value (after acetylation)	54–72[1]

Derivatives Tincture (20% in 70% alcohol) and fluid extract

Organoleptic characteristics Bitter-tonic flavor with a spicy odor mixture of clove, cardamom, eucalyptus, and nutmeg

Uses The dried product and the derivatives commonly are employed in the manufacture of vermouths and bitters. The essential oil is used in the formulation of compounded oils for liqueurs. Cascarilla bark extract has been reported used in non-alcoholic beverages, 5.0–800 ppm.[3] Cascarilla bark oil has been reported used in the following:[3]

non-alcoholic beverages	2.3 ppm
ice cream, ices, etc.	3.0 ppm
candy	8.7 ppm
baked goods	13 ppm
condiments	50 ppm

Regulatory status GRAS (II)

CASSIE

Botanical source *Acacia farnesiana* (L.) Willd.

Botanical family *Leguminosae*

Foreign names Cassie (Fr.), Cassie (Ger.), Acacia (Sp.), Gaggia (It.)

Description Small tree or shrub native to the West Indies. It grows wild or cultivated in the Mediterranean countries with warm climate (Lebanon, Morocco) and in tropical areas. Cassie was once extensively cultivated on the Côte Azure for extractive purposes. The plant, very delicate and sensitive to cold weather, is commonly grafted onto *A. cavenia* Hook. & Arn., a more resistant variety. The yellow flowers arranged in terminal umbellate clusters are similar to mimosa (*A. dealbata*).

Parts of plant used Flowers

Physical-chemical characteristics

Derivatives Concrete, absolute. The main constituents include aldehydes (benzyl, anisic, decylic, cuminic), benzyl alcohol, and probably geraniol, farnesol, and linalool.

Organoleptic characteristics Warm, floral, intense odor with a balsamic undertone

Uses The absolute is used in high-quality perfumes with a floral note and occasionally in flavors to enhance the bouquet of fruital aromas. Cassie absolute (FEMA No. 2260) has been reported used in the following:[3]

non-alcoholic beverages	0.96 ppm
ice cream, ices, etc.	1.2 ppm
candy	4.1 ppm
baked goods	4.1 ppm
gelatins and puddings	1.0 ppm

Regulatory status Flowers: FDA §121.1163

CASTOR OIL

Botanical source *Ricinus communis* L.

Botanical family *Euphorbiaceae*

Foreign names Olio di ricino (It.)

Description Small trees, up to 5 m (15 ft) high in the tropics. The leaves are large, alternate, peltate, palmately 5–12 lobed; the petioles have conspicuous glands. The seeds are ovoid with a large caruncle; the endosperm is fleshy and oily. The plant thrives in rich, well drained, sandy or clay loam; it is grown in India and the United States. Castor beans have been cultivated from earliest times for the oil of the seeds.

Parts of plant used Oil from seeds

Uses Castor oil (FEMA No. 2263) has been reported used in the following:[3]

non-alcoholic beverages	1.5–140 ppm
ice cream, ices, etc.	3.0–540 ppm
candy	3.0–410 ppm
baked goods	210 ppm

Regulatory status FDA §121.1163

CASTOREUM

Animal source *Castor fiber* L. and *C. canadensis* Kubl.

Animal family *Castoridae*

Foreign names Castoreum (Fr.), Bibergeil (Ger.), Castoreo (Sp.), Castoreo (It.)

Description The name *castoreum* designates the dried preputial follicles and the glandular secretion obtained from mammals of the family *Castoridae*. The animals are widely encountered in Alaska, Canada, and Siberia. Removed from the animal during the skinning operation, castoreum is usually dried in the sun or sometimes dried over burning wood. The fresh pouch contains a yellowish, butter-like mass with a fetid, sharp, aromatic odor. The dried product is dark-brown, hard, and resinous. Canadian pouches are wrinkled, pear-shaped, almost flat, from 6–15 cm (2–6 in.) long and 4–8 cm (2–3 in.) wide. Siberian pouches are ovoid and smooth, slightly larger in size, but less valued commercially.

Parts used Castoreum glands (dried and ground)

Physical-chemical characteristics

Derivatives Tincture, resinoid, absolute. The resinoid is prepared by extraction of the dried, ground pouches using petroleum ether. The absolute is prepared by alcoholic extraction of the resinoid. A resinous and crystalline material (1–2%) has been identified in castoreum, together with a butter-like portion containing albumins, fats, urates, salts, and probably cholesterols.

Organoleptic characteristics Warm, animal, sweet odor, becoming more pleasant on dilution. Sometimes a birch, tar-like, musky odor is also perceptible.

Uses The tincture and the absolute are used in perfumery because of the outstanding fixative properties. Castoreum extracts blend very well with vanilla aromas and are used also for flavoring condiments, toppings, candy, beverages, and other food products. Castoreum extract (FEMA No. 2261) has been reported used in the following:[3]

non-alcoholic beverages	5.0 ppm
ice cream, ices, etc.	5.6 ppm
candy	12 ppm
baked goods	41 ppm
chewing gum	400 ppm
condiments	50 ppm
toppings	2.0 ppm

Castoreum liquid (FEMA No. 2262) has been reported used in the following:[3]

non-alcoholic beverages	3.2 ppm
ice cream, ices, etc.	1.9 ppm
candy	4.9 ppm
baked goods	7.3 ppm
gelatins and puddings	1.2–2.0 ppm
chewing gum	19–60 ppm
toppings	2.0 ppm

Regulatory status GRAS

CATECHU BLACK

Botanical source *Acacia catechu* Willd.

Botanical family *Leguminosae*

Foreign names Acacie au cachou (Fr.), Catechu (Ger.), Catecú (Sp.), Catecu Terracattu (It.)

Description Catechu black must not be confused with either the *Areca catechu* L. (betel) or with the *Uncaria gambir* Roxb. (gambir catechu). It grows as a tree to 20 m (60 ft) tall with a great number of branches. The trunk has a dark bark; the leaves are about 20–50 cm (8–20 in.) long and fall during the dry season. It has very small, cylindrical, spiked flowers.

Parts of plant used Bark

Physical-chemical characteristics
Derivatives

Decoction, obtained by extracting the bark with water. The liquid is then concentrated, poured into molds, and allowed to dry. The resulting product, a dark-brown, porous, fragile mass, yields the flavor ingredient. Tincture, 20% in 80% ethanol (tannin free), is another derivative.

Organoleptic characteristics

Bitter, astringent flavor

Uses

The dried product and the tincture are used in liqueurs as a corrective flavor of specially formulated products. Catechu extract has been reported used in the following:[3]

non-alcoholic beverages	16 ppm
ice cream, ices, etc.	21 ppm
candy	140 ppm
baked goods	140 ppm

Catechu powder has been reported used in the following:[3]

non-alcoholic beverages	45 ppm
ice cream, ices, etc.	27 ppm
candy	43 ppm
baked goods	37 ppm
chewing gum	15 ppm

Regulatory status

FDA §121.1163

CEDAR, WHITE

Other names

Arborvitae; thuja

Botanical source

Thuja occidentalis L.

Botanical family

Pinaceae

Foreign names

Thuja (Fr.), Thuja (Ger.), Thuja (Sp.), Thuja (It.)

Description

A tree (conifer) 10–20 m (33–66 ft) high, widespread in the northeastern United States, eastern Canada, and also Japan, where it is known as Niohihiba. The plant has appressed, imbricate leaves, pointless scales on the cones, and broadly winged seeds.

Parts of plant used

Fresh leaves and twigs

Physical-chemical characteristics
Essential oil

The oil is obtained by steam distillation in approximately 0.6–1.0% yields from at least 15-year-old plants. It is a colorless to yellow-greenish liquid with a strong camphoraceous odor reminiscent of sage and similar taste. In addition to thujone (56.7%), the main constituents include bornyl acetate, camphor, fenchone, terpineol, camphene, limonene, and other terpene hydrocarbons.

Specific gravity	0.910–0.920[2]
Optical rotation	−10° to −14°[2]
Refractive index at 20°C	1.4560–1.4590[2]
Ketone content (as thujone)	Not less than 60%[2]
Solubility	1:3 in 70% alcohol[2]

Organoleptic characteristics

Strong, camphoraceous odor reminiscent of sage

Uses

The oil is used frequently in perfumery (room deodorants and similar commercial products) and sometimes in soaps. The oil employed in flavor work must be thujone-free because of the toxicity of this ketone.

Cedar leaf oil (FEMA No. 2267) has been reported used in the following:[3]

non-alcoholic beverages	0.01–0.50 ppm
alcoholic beverages	16 ppm
ice cream, ices, etc.	0.01–1.0 ppm
candy	12 ppm
baked goods	1.0–20 ppm
meats	15 ppm

Regulatory status

Leaves and twigs: FDA §121.1163. Finished food thujone-free

CELERY

Botanical source

Apium graveolens L.

Botanical family

Umbelliferae

Foreign names

Cèlery (Fr.), Sellerie (Ger.), Apio (Sp.), Sedano (It.)

Description

Annual or biennial herb, approximately 30–60 cm (12–21 in.) high. The plant has a grooved, fleshy, erect stalk, taproot, both radical and stalk leaves, hermaphroditic flowers, and humped seeds. It grows wild or cultivated almost worldwide. It is cultivated for extractive purposes mainly in France, Holland, Hungary, India, and California.

Parts of plant used

Seeds; sometimes roots and leaves

Physical-chemical characteristics

Essential oil

Obtained by steam distillation of the crushed seeds in approximately 1.5–2.5% yields. The oil is a pale-yellow to yellow-brownish liquid, exhibiting a characteristic spicy, aromatic odor and a warm, burning taste. The main constituents include *d*-limonene, sesquiterpene alcohols, palmitic acid, probably guaiacol, and trace phenols. The physical-chemical characteristics of celery seed oil are as follows (also see reference 2):

Specific gravity at 20°C	0.886–0.916 (0.897–0.993)[6]
Refractive index	1.4780–1.4980 (1.4780–1.4900)[6]
Optical rotation at 20°C	+40° to +80° (+48° to +78°)[6]
Acid value	10 max (1.5–4.0)[6]
Ester value	16–86 (30–65)[6]

An essential oil is sometimes steam distilled from leaves and stems. However, this oil is of inferior quality; its addition to celery-seed oil lowers the specific gravity and increases the optical rotation of the latter.

Derivatives

Fluid extract, tincture (from roots mainly for pharmaceutical use), oleoresin (from seeds)

Organoleptic characteristics

Rich, long-lasting, spicy odor with a warm, burning taste

Uses

The plant is used as is in cooking. The essential oil and the oleoresin are used extensively for flavoring sauces, meats, condiments, bouillons, and other food products. Celery seed (FEMA No. 2268) has been reported used in the following:[3]

non-alcoholic beverages	0.37–1,000 ppm
baked goods	1,800 ppm
condiments	2,500 ppm
pickles	13–590 ppm
soups	37–500 ppm
meats	1,400 ppm

Celery seed extract (FEMA No. 2269) has been reported used in the following:[3]

non-alcoholic beverages	240 ppm
ice cream, ices, etc.	5.0 ppm
candy	10 ppm
baked goods	1,900 ppm
condiments	10 ppm
meats	100 ppm
soups	160–500 ppm

Celery seed extract solid (FEMA No. 2270) has been reported used in the following:[3]

non-alcoholic beverages	150 ppm
candy	8.0 ppm
baked goods	12 ppm
condiments	7.0 ppm
syrups	10 ppm

Celery seed oil (FEMA No. 2271) has been reported used in the following:[3]

non-alcoholic beverages	11 ppm
ice cream, ices, etc.	3.0–13 ppm
candy	13 ppm
baked goods	12 ppm
chewing gum	28 ppm
condiments	40 ppm
meats	40 ppm
pickles	10–35 ppm
soups	1.0 ppm

Regulatory status

Celery seeds: GRAS (I), (II)

CENTAURY, MINOR

Botanical source

Centaurium umbellatum Gilib. (*Erythraea centaurium* Pers.)

Botanical family

Gentianaceae

Foreign names

Petite Centaurée (Fr.), Tausendguldenkraut (Ger.), Centaura menor (Sp.), Centaurea minore (It.)

Description

Annual or biennial herb, widespread throughout Europe; grows 10–30 cm (4–12 in.) in height. It exhibits thick, erect, quadrangular, branched stalks with opposite leaves and pink flowers.

Parts of plant used

Flowering tops

Physical-chemical characteristics

Derivatives

Tincture (20% in 20–40% ethanol) and fluid extract. The main constituents include gentiopicrin, oleanolic acid, and erythrocentaurin.

Organoleptic characteristics Bitter tonic

Uses The dried product, the tincture, and the fluid extract blend very well with other bitter flavors, because, while bitter, they contribute little other aromatic flavor. The derivatives therefore are used in special combinations for the formulation of bitters.

Regulatory status FDA §121.1163. In alcoholic beverages only

CHERRY LAUREL

Botanical source *Prunus laurocerasus* L.

Botanical family *Rosaceae*

Foreign names Laurier-cerise (Fr.), Kirschlorbeer (Ger.), Laurel cerezo (Sp.), Lauro ceraso (It.)

Description Evergreen shrub that may reach approximately 10 m (33 ft) in height. It has large, shiny leaves, producing flowers in long clusters (April–May); its berries are black when ripe and contain a round seed. Native to the Middle East, the plant was introduced into Europe around the 16th century. It is also cultivated for ornamental purposes.

Parts of plant used Leaves

Physical-chemical characteristics

Essential oil Obtained by steam distillation with very low yields (0.05%) from comminuted leaves previously treated with water. The water triggers the enzymatic hydrolysis of the glucoside (prulaurasin), yielding hydrogen cyanide and benzaldehyde. The oil used by the food industry must be free of hydrogen cyanide. It is an almost colorless liquid, exhibiting a pronounced odor of benzaldehyde, its main constituent.

Specific gravity at 15°C	1.046–1.067[1]
Refractive index at 15°C	1.539–1.543[1]
Acid value	1.6–10[1]
Solubility	1:1 to 1:2 in 70% ethanol
Prussic acid (HCN) content	0.5–4.1%

Derivatives Distillation waters

Organoleptic characteristics Odor reminiscent of bitter almond

Uses The oil is of very limited use today, as it can be replaced by bitter almond or with synthetic benzaldehyde. Cherry laurel oil (FFPA) has been reported used in the following:[3]

baked goods	75 ppm
maraschino cherries	77 ppm
extracts	50–65 ppm

Regulatory status FDA §121.1163. Not to exceed 25 ppm prussic acid

CHERRY, SWEET AND SOUR

Botanical source *Prunus avium* L., *P. cerasus* L.

Botanical family *Rosaceae*

Foreign names

P. avium: Cerisier (Fr.), Kirsche (Ger.), Cerezo (Sp.), Ciliegio (It.)
P. cerasus: Griotte (Fr.), Sauerkirsche (Ger.), Cerezo acido (Sp.), Amarena (It.)

Description

P. avium (Sweet Cherry)
The tree grows to 12–15 m (39–49 ft) high. Native to western Asia and southern Europe, today the tree is widespread in many countries. It has large white flowers, reddish-brown bark, and edible depressed-globose, red, juicy, sweet fruits (drupes). The most important varieties of *P. avium* are Hearts (firm, light or dark, sweet fruits), Bigarreaux (light or dark, sweet fruits mainly cultivated in California), and Dukes (light, somewhat acid fruits).

P. cerasus (Sour or Morello Cherry)
A tree of lower growth and rounder head than *P. avium*, sour cherry has a gray bark, large flowers, and depressed-globose, red, acid fruits. The most important varieties are Amarella (light-colored) and Morello (dark-colored).

Parts of plant used

The fruits and pits

Physical-chemical characteristics

Derivatives

P. avium: four- to six-fold concentrated (under vacuum or by freezing) juice; two- to four-fold concentrated juice with added alcohol; two- to four-fold concentrated juice stabilized with sugar; distillate (60% alcohol).

P. cerasus: four- to eight-fold concentrated juice; juice partially concentrated with added alcohol; distillates (40%, 50%, and 60% alcohol).

The residue from the expression of the juice together with the crushed pits of sour or sweet cherry is used for the preparation of a distillate (usually containing 60–65% alcohol). This and the fruit distillates are used extensively in liqueurs.

Organoleptic characteristics

P. avium: pleasant, sweet taste

P. cerasus: astringent, sour taste

Uses

P. avium: The juices of varying strength are used to prepare syrups, liqueurs, ice cream, candy filling, and other products. The distillate is used in liquors. The edible fruits are consumed fresh or are preserved in alcohol or syrup, candied, or employed to make marmalades and jellies.

P. cerasus: Juices and preserved fruits are used in a similar fashion to sweet cherry. The distillates are used widely in liqueurs (maraschino type).

Cherry pits extract (FEMA No. 2278) from either cherry variety has been reported used in the following:[3]

non-alcoholic beverages	80–150 ppm
ice cream, ices, etc.	50–60 ppm

Regulatory status

Cherry pits: FDA §121.1163. Not to exceed 25 ppm prussic acid

CHERRY, WILD

Other names

Wild black cherry; rum cherry

Botanical source

Prunus serotina Ehrh., *P. canadensis* Poiret

Botanical family

Rosaceae

Foreign names

Cerisier d'automne (Fr.), Traubenkirsche (Ger.), Cerezo de todos los santos (Sp.), Ciliegio d'autunno (It.)

Description

A large tree having reddish-brown branches, aromatic inner bark, lanceolate leaves, and purplish-black fruits with a slightly bitter, vinous flavor. The plant is native to southern Ontario and widespread also in the United States, Central America, and Europe (England, Germany, Belgium, France). Wild cherry is often confused with *P. virginiana* L. (choke cherry), which has an erect trunk, smoother bark, and more lanceolate and nervate leaves. The late flowering of *P. serotina* (June–July) justifies its botanical name.

Parts of plant used

Bark; also small branches and twigs

Physical-chemical characteristics

Derivatives

Fluid extract, tincture (prepared by diluting the fluid extract with 25% ethanol). The main constituents include a glucoside (prunasin) yielding prussic acid, glucose, and benzaldehyde on enzymatic hydrolysis; a modified coumarin (scopoletin or β-methylesculetin); phytosterols; oil; fatty acids (oleic, linoleic, palmitic); and acids (benzoic and modified homologs). In addition to the above constituents, the leaves contain ursolic acid and the glucoside serotin.

Organoleptic characteristics

Sweet, tart, cherry-like flavor

Uses

The extract and the tincture are used in the formulation of aromas for flavoring beverages, ice cream, and candy and, in rather large doses, in the formulation of cherry fruital aromas. Wild cherry bark extract (FEMA No. 2276) has been reported used in the following:[3]

non-alcoholic beverages	120 ppm
alcoholic beverages	300–800 ppm
ice cream, ices, etc.	140 ppm
candy	200 ppm
baked goods	76 ppm
gelatins and puddings	3.5 ppm
syrups	30 ppm

Regulatory status

Wild cherry bark: GRAS (II)

CHERVIL

Botanical source

Anthriscus cerefolium (L.) Hoffm.

Botanical family

Umbelliferae

Foreign names

Cernefil (Fr.), Gartenkerbel (Ger.), Cerefolio (It.)

Description

Annual herb. It has bright-green leaves that are finely divided, curled, and branched and flowering stems 15–18 in. tall. Chervil has a pungent, aromatic flavor; its sweet-scented leaves are used like parsley for flavoring soups and stews. The plant is grown in the mountain areas of southern Europe and in England; it is also grown commercially in the United States. It contains an essential oil and a fixed oil.

Physical-chemical characteristics

Parsley-like but more aromatic and reminiscent of tarragon (methyl chavicol)

Organoleptic characteristics	Tonic-aromatic, aperitive
Uses	Chervil (FEMA No. 2279) has been reported used in the following:[3] non-alcoholic beverages 100 ppm ice cream, ices, etc. 50 ppm baked goods 150 ppm condiments 60 ppm
Regulatory status	GRAS (I), (II)

CHESTNUT

Botanical source	*Castanea dentata* (Marsh.) Borkh.
Botanical family	*Fagaceae*
Foreign names	Chataignier (Fr.), Edelkastanie (Ger.), Castano (Sp.), Castagno (It.)
Description	*C. dentata* is the U.S. variety of *C. vulgaris* or *sativa* (maroon) and other *Castanea* species. *C. crenata*, the Japanese species, differs in having large fruits. The plant, native to Asia Minor, is widespread in Europe, Asia, and North America. Its large trees have large-toothed, pale-green leaves. The fruits are edible and contain vitamins B and C, starches, proteic substances, sugar, and fats. The bark contains tannin. The leaves contain tannic acid, gallic acid, fats, resin, gum, albumin, and pectin.
Parts of plant used	The nutmeat and leaves
Physical-chemical characteristics	
Essential oil	Reddish-brown, irregularly obovate or obconic nuts, having thin, papery shells and borne in stiff, brown burs. The kernels of small American and Chinese chestnuts are of excellent flavor, while European chestnuts are of mediocre flavor; Japanese chestnuts have poor flavor unless boiled or roasted.
Derivatives	Standardized fluid extract and tincture (20% in 50% alcohol)
Organoleptic characteristics	Astringent, tonic
Regulatory status	FDA §121.1163

CHICORY

Botanical source	*Cichorium intybus* L.
Botanical family	*Compositae*
Foreign names	Chicorée Sauvage (Fr.), Wilde Zichorie (Ger.), Achicoria amarga (Sp.), Cicoria amara (It.)
Description	Annual or perennial herb, growing to 50 cm (20 in.) high; native to Europe and Asia. The plant exhibits leaves stemming directly from the root, similar in shape to those of the related dandelion, but with numerous showy, blue flowers.

Parts of plant used Roots and leaves

Physical-chemical characteristics

Derivatives Tincture (20% in 20–40% ethanol), fluid extract, root tincture (20% in 20% ethanol from roasted roots), and soft and dried extracts from roasted roots. The flowers contain cichoriin (6,7-dihydroxycoumarin-7-glucoside).

Organoleptic characteristics Bitter-tonic flavor

Uses The bitter-tonic flavor of the dried product and its derivatives is employed in the formulation of certain alcoholic and non-alcoholic bitters. The aqueous tincture and the aqueous soft and dried extracts from the roasted roots are used as a coffee substitute. The leaves are used as a vegetable and in preparing broths.

Chicory extract has been reported used in the following:[3]

non-alcoholic beverages	63 ppm
ice cream, ices, etc.	58 ppm
candy	57 ppm
baked goods	100 ppm

Regulatory status GRAS (II)

CHIRATA

Botanical source *Swertia chirata* (Roxb.) Buch.-Ham.

Botanical family *Gentianaceae*

Foreign names Chirette indien (Fr.), Indische Chiretta (Ger.), Chiretta (It.)

Description Annual, herbaceous plant; native to the Himalayas, but also grown in South Africa. It is about 60–70 cm (21–28 in.) high with a thick, branched stalk, small, opposite leaves, and flowering tops.

Parts of plant used The whole plant with small portions of the root

Physical-chemical characteristics

Derivatives Tincture (20% in 20–40% ethanol) and fluid extract. The main constituents include chiratin and ophelic acid.

Organoleptic characteristics Bitter tonic

Uses The dried product and its derivatives are used in the manufacture of liqueurs and in the formulation of vermouths and bitters.

Regulatory status FDA §121.1163. In alcoholic beverages only

CHIVES

Botanical source *Allium schoenoprasum* L.

Botanical family *Liliaceae*

Foreign names Cive (Fr.), Schnittlauch (Ger.), Ceballino ajopardo (Sp.) Cipollina (It.)

Description A perennial plant belonging to the onion family, native to Europe and Asia. The plant grows in compact tufts or clusters formed by the intertangling of the fibrous roots. It has rose-purple flowers. The leaves are numerous, erect, slender, hollow, pointed, and deep green. The tender young leaves are cut and used to season foods.

Regulatory status GRAS (I)

CINCHONA

Red and Yellow

Botanical source *Cinchona succirubra* Pav. or its hybrids (red bark); *C. ledgeriana* Moens or *C. calisaya* Wedd. or hybrids of these with other *Cinchona* species (yellow bark)

Botanical family *Rubiaceae*

Foreign names Quinauina (Fr.), China rinde (Ger.), Quina (Sp.), China (It.)

Description Morphologic characteristics of the different varieties of cinchona differ very little. In general, the trees can reach 25 m (82 ft) in height, with opposite leaves and small flowers clustered as flowery tops. Indigenous to Peru, cinchona is cultivated today in all South and Central American countries, in Madagascar, and in areas of Africa.

Parts of plant used The bark from the branches. Commercially the bark is distinguished as red cinchona (*C. succirubra*) or yellow cinchona (*C. ledgeriana*). The bark is collected from plants more than 15 years old.

Physical-chemical characteristics

Derivatives Tincture, 20% in 70% ethanol (tannin-free or not) or 10% in 60% ethanol (tannin-free or not). Fluid, soft, and dried extracts (the last two can be aqueous or water-alcoholic extracts with or without tannin). The main constituents of the dried product and its derivatives are quinine, quinidine, cinchonidine, cinchonine, and tannin. The total alkaloid content determines the quality of the derivatives. Quinine is about 70% of the alkaloid content.

Organoleptic characteristics Bitter tonic

Uses In addition to its well known pharmaceutical uses, cinchona and its derivatives find widespread use in the manufacture of liqueurs and in a large spectrum of special products because of its characteristic bitter-tonic flavoring action. Quinine salts are largely employed in the formulation of carbonated beverages (tonic water). Red cinchona bark has been reported used in the following:[3]

non-alcoholic beverages	1.5–3.7 ppm
alcoholic beverages	20–300 ppm
ice cream, ices, etc.	3.0 ppm
baked goods	27 ppm
bitters	1,000 ppm

Red cinchona bark extract has been reported used in the following:[3]

non-alcoholic beverages	100 ppm
ice cream, ices, etc.	25 ppm
baked goods	20 ppm
condiments	60 ppm

Yellow cinchona bark has been reported used in the fo'

alcoholic beverages	300 ppm
bitters	100 ppm

Yellow cinchona bark extract has been reported used in alcoholic beverages, 100 ppm.[3] Cinchona extract has been reported used in the following:[3]

non-alcoholic beverages	10 ppm
candy	1.0 ppm

Regulatory status

FDA §121.1163. In beverages only; not more than 83 ppm total cinchona alkaloids in finished beverages (red and yellow cinchona).

CINNAMON

Botanical source

Cinnamomum zeylanicum Nees—Ceylon cinnamon; *C. loureirii* Nees—Saigon cinnamon; *C. cassia* Nees—Chinese cinnamon

Botanical family

Lauraceae

Foreign names

Cannelle (Fr.), Zimt (Ger.), Canéla (Sp.), Cannella (It.)

Description

The Ceylon cinnamon tree can grow to 10 m (33 ft). It has long, lanceolated leaves, small flowers in clusters, and small fruits. It is cultivated by extensive pruning (coppicing). Increasingly significant plantations are available in the Seychilles and in Brazil. The whole outer bark is peeled from the trees every two years; the outer corky layer is removed by careful scraping, and the bark strips are sun-dried. Cinnamon, commercially known as "Saigon cinnamon", has superior odor and flavor and is produced from the bark of trees grown in the Saigon district of Vietnam. Saigon cinnamon is used mainly as a ground spice. Chinese cinnamon or cassia is the dried bark of *Cinnamomum cassia,* a large tree that grows wild in South East Asia.

Parts of plant used

The dried inner bark of the shoots of coppiced trees, and the leaves.

Physical-chemical characteristics

Essential oil

Obtained by steam distillation of the bark. Bark fragments are used, as the better-looking bark is used only as a ground spice. The essential oil is a red-brown liquid with a characteristic spicy odor reminiscent of cinnamaldehyde.

Ceylon Cinnamon Bark

Specific gravity at 25°/25°C	1.010–1.030[2]
Refractive index at 20°C	1.5730–1.5910[2]
Optical rotation at 20°C	0° to −2°[2]
Solubility	1:2–1:3 in 70% ethanol[1]
Aldehyde content (as cinnamic aldehyde)	55–78%[2]
Phenol content (as eugenol)	4–10%[1]

Main components include caryophyllene, β-phellandrene, p-cymene, l-α-pinene, l-linalool, furfural, and various aldehydes.

Ceylon Cinnamon Leaf Oil

Specific gravity at 25°/25°C	1.030–1.050[2] at 20°/20°C)[7]
Refractive index at 20°C	1.5290–1.5370[2]
Optical rotation	+1° to −2°[2]
Phenol content (as eugenol)	80–88%[2]
Aldehyde content (as cinnamic aldehyde)	<7%[1]
Solubility	1:2 in 70% ethanol[1]

Seychelles Cinnamon Leaf Oil

Specific gravity at 25°/25°C	1.040–1.060[2]
Refractive index at 20°C	1.5330–1.5400[2]
Optical rotation	0° to −2°[2]
Phenol content (as eugenol)	87–96%[2]
Solubility	1:1 in 70% alcohol

Cinnamon leaf oil has a quite different aromatic character as compared to the bark essential oil. Main constituents of the leaf oil are eugenol (75–95%), terpenes, β-caryophyllene, cinnamic alcohol, and benzyl benzoate (up to 27%)

Chinese Cinnamon Bark Oil

Specific gravity at 20°C	1.046–1.071[1] (1.052–1.070)[7]
Refractive index at 20°C	1.600–1.610[1] (1.6000–1.6140)[7]
Optical rotation	−1° to +6°[1]
Aldehyde content (as cinnamic aldehyde)	70–90%[1] (80% min)[7]
Acid value	15.0 max[7]

This essential oil has a higher specific gravity than other cinnamon bark oils; it contains a much higher amount of cinnamic aldehyde (about 85% on the average), but no eugenol. The available produce is often contaminated with lead from the lead-soldered tin containers used for storage and transport.

Main constituents include cinnamyl acetate, benzaldehyde, methyl salicylate, salicyaldehyde, and coumarin

Derivatives	Tincture (20% in 60–75% ethanol), fluid extract, essential oil, oleoresin, powdered spice
Organoleptic characteristics	Somewhat bitter flavor, slightly pungent and burning
Uses	The dried product is highly suitable to flavor foods and beverages; industrially both the tincture and the fluid extract are used in place of the dried spice. The essential oil is used particularly in the formulation of compounded oils for liqueurs and confections.

Cinnamon has been reported used in the following:[3]

non-alcoholic beverages	5.6 ppm
ice cream, ices, etc.	53 ppm
candy	10–4,000 ppm
baked goods	1,900 ppm
apple butter	78–450 ppm
condiments	110 ppm
meats	880 ppm

Cinnamon bark extract has been reported used in the following:[3]

non-alcoholic beverages	10–13 ppm
ice cream, ices, etc.	8.5 ppm
baked goods	170 ppm
condiments	40–200 ppm
meats	40 ppm

Cinnamon bark oil has been reported used in the following:[3]

non-alcoholic beverages	5.5 ppm
ice cream, ices, etc.	18 ppm
candy	80 ppm
baked goods	110 ppm
chewing gum	620 ppm
condiments	25 ppm
meats	50 ppm

Cinnamon leaf oil has been used in the following:[3]

non-alcoholic beverages	6.8 ppm
ice cream, ices, etc.	3.4 ppm
candy	32 ppm
baked goods	54 ppm
gelatins and puddings	0.20 ppm
chewing gum	160–520 ppm
condiments	20–78 ppm
pickles	32–48 ppm
spiced fruits	3.0 ppm

Regulatory status	Cinnamon bark—Ceylon, Saigon, and Chinese: GRAS (I), (II) Cinnamon leaf—Ceylon, Saigon, and Chinese: GRAS (II)

CITRONELLA

Botanical source	*Cymbopogon winterianus* (*Andropogon nardus*), *Java de Tong* (Java citronella) *C. nardus* Rendle (*Andropogon nardus*), *Ceylon de Tong* (Ceylon citronella)
Botanical family	*Gramineae*
Foreign names	Citronelle (Fr.), Citronel (Ger.), Citronella (Sp.), Citronella (It.)

Description

Citronella is a perennial herb growing more than 1 m (39 in.) high. The herb is harvested 2–3 times a year in Ceylon; the freshly cut or partially dried herb is steam distilled. The plant yields the largest amount of essential oil around its third year of growth. Citronella is also cultivated and distilled in Java, Guatemala, Formosa, Hainan, Argentina, and New Guinea. The essential oil from Ceylon citronella is considered less valuable than the oil from Java citronella.

Parts of plant used

The fresh or partially dried herb

Physical-chemical characteristics

Essential oil

Ceylon Citronella Oil

It is obtained by steam distillation of the partially dried herb known as the lenabatu variety. The Ceylon oil is a pale-yellow to yellowish-brown liquid with a characteristic citronellal-like odor. The main constituents include geraniol, *d*-citronellal, camphene, limonene, dipentene, methylheptenone, methyleugenol, farnesol, *l*-borneol, nerol, and others. Its physical-chemical constants are as follows (see also reference 2):

Specific gravity at 20°/20°C	0.894–0.906[1] (0.894–0.910)[7]
Refractive index at 20°C	1.479–1.485[1]
Optical rotation at 20°C	–9° to –18°[1]
Solubility	1:2 in 80% ethanol[1]
Total alcohols (as geraniol)	55–65%[1]
Aldehyde content (as citronellal)	7–15%[1]

Java Citronella Oil

Java citronella oil is obtained by steam or water distillation of the freshly cut or partially dried herb known as the maha pengira variety. It differs from the Ceylon citronella oil in both composition and odor. Java citronella oil is a clear, mobile, light-yellow to brownish liquid with a pronounced aldehyde (rose, lemon-like) odor. The main constituents include isobutyl and isoamyl alcohols, *n*-*l*-hexanol, methyl-heptenone, isovaleric aldehyde, furfural, benzaldehyde, *l*-limonene, dipentene, citronellal, *d*-citronellol, geraniol, citral, methyl eugenol, eugenol, geranyl butyrate, and vanillin. Its physical-chemical constants are as follows (see also reference 2):

Specific gravity at 20°/20°C	0.878–0.895[1] (0.880–0.895)[6]
Refractive index at 20°C	1.4660–1.4750[1] (1.4660–1.4730)[6]
Optical rotation at 20°C	–5° to 0°[1]
Total alcohols (as geraniol)	32–35%[6]
Aldehyde content (as citronellal)	30–45%[1]
Solubility	1:2 in 80% ethanol[1]

Organoleptic characteristics

Characteristic citronellal, rose- and lemon-like odor

Uses

Citronella oils (Ceylon and Java) are used for the scenting of soaps, sprays, disinfectants, etc. Java citronella oil is used as a starting raw material for the extraction of geraniol and citronellal. Citronellal is in turn employed to manufacture hydroxycitronellal, *l*-menthol, etc. Citronella oil is used to flavor beverages, candy, and baked goods.

Citronella oil (FEMA No. 2308) has been reported used in the following:[3]

non-alcoholic beverages	17 ppm
ice cream, ices, etc.	26 ppm
candy	25 ppm
baked goods	21 ppm

Regulatory status

GRAS (II)

CIVET

Other names Zibeth; zibet; zibetum

Animal source Civet cats (*Viverra civetta* Schreber and *V. zibetha* Schreber)

Foreign names Civette (Fr.), Zibet (Ger.), Algalia (Sp.), Zibetto (It.)

Description Civet cats are members of the Viverridal family (*V. zibetha* and other *Viverra* species) native to Africa. The animals are also found in India, Malaysia, Indochina, and Indonesia.

The product consists of the odorous glandular secretion of male and female civets. The largest quantities come from Africa, where the animals are kept captive on farms. The animal glands are drained of the secretion approximately once a week. Civet is a yellowish to brownish, honey-like paste with a very strong, putrid odor, becoming sweet on dilution. African civet contains approximately 1.0% skatole. Physical-chemical characteristics of pure civet are as follows:

Acid value (total)*	51[1]
Acid value (volatile soluble acids)	6[1]
Acid value (volatile insoluble acids)	2[1]
Ester value*	26[1]
Iodine value	38[1]
Per cent unsaponifiable matter (after ether extraction)	62[1]

Physical-chemical characteristics

Derivatives Absolute, tincture (10 or 20% after a preliminary maceration in 95% alcohol)

Organoleptic characteristics Sweet, animal-like odor, not very strong but rich and tenacious

Uses The sweet, animal note blends well in perfumes with a honey, floral note. Civet absolute (FEMA No. 2319) has been reported used in the following:[3]

non-alcoholic beverages	1.0 ppm
ice cream, ices, etc.	3.0 ppm
candy	3.7 ppm
baked goods	2.8 ppm
gelatins and puddings	0.10 ppm
chewing gum	2.2 ppm

Regulatory status GRAS

CLARY

Other names Clary sage

Botanical source *Salvia sclarea* L.

Botanical family *Labiatae*

Foreign names Sauge sclarée (Fr.), Muscateller Salbei (Ger.), Salvia muscatel (Sp.), Salvia sclarea (It.)

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*Characteristically, the ester value of civet is approximately one-half the total acid value.

Description

Biennial or perennial plant cultivated for extractive purposes in the Mediterranean basin, central Europe, and Russia. It is about 1.5 m (5 ft) high with a taproot, hairy, erect stalk, wide, wooly, oval leaves, and white or light-violet flowers (July) in terminal clusters.

Parts of plant used

Flowering tops and leaves

Physical-chemical characteristics

Essential oil

The essential oil, sometimes called oil of muscatel, is obtained by steam or water distillation of flowering tops and leaves with yields ranging between 0.7 and 1.5%. It is produced in large quantities in France, Russia, and Morocco. The Italian production is fairly small. The essential oil of French production is a yellow liquid with a characteristic herbaceous odor and wine-like bouquet (also see reference 2). The physical-chemical constants vary, depending on the source; minor components also vary.

Specific gravity at 20°C	0.892–0.909[1]
Refractive index at 20°C	1.4580–1.4710[1]
Optical rotation at 20°C	−6° to −25°[1]
Acid value	2 max
Ester content (as linalyl acetate)	40–70%[1]
Solubility in 80% ethanol	1:3 max[1]

The oil contains C_6, C_7, C_8, and C_9 aldehydes, benzoic aldehyde, linalyl acetate, α- and β-pinene, and camphene.

Derivatives

Tincture (20% in 65% ethanol) and distillate (70–80% ethanol)

Organoleptic characteristics

Herb-like odor and wine-like taste

Uses

The dried flowering tops and their derivatives are used extensively in the flavor industry and also in perfumery. They are used in the formulation of liqueurs and soft beverages. Clary (clary sage) has been reported used in alcoholic beverages, 500 ppm.[3]

Clary (clary sage) oil has been reported used in the following:[3]

non-alcoholic beverages	1.8 ppm
alcoholic beverages	100 ppm
ice cream, ices, etc.	3.9 ppm
candy	5.3 ppm
baked goods	13 ppm
condiments	20 ppm

Regulatory status

GRAS (I), (II)

CLOVE

Botanical source

Eugenia caryophyllata Thunb.

Botanical family

Myrtaceae

Foreign names

Girofle (Fr.), Nelken (Ger.), Jerofle Clavus (Sp.), Garofano (It.)

Description

An evergreen tree that may grow to 20 m (66 ft), with opposite leaves and buds. It is native to tropical Asia—Molucca Islands, Reunion, Penang, Zanzibar, Pemba, and Madagascar.

Parts of plant used

Buds, leaves, stems

Physical-chemical characteristics

Essential bud oil

The oil is obtained by water distillation (also, rarely, by steam distillation) of buds in yields ranging from 15–18%. It is a clear, mobile liquid, nearly colorless to yellow-brown; it tends to darken on aging. It exhibits a strong characteristic clove aroma and a spicy, burning flavor. The bud oil contains primarily eugenol (70–90%), eugenol acetate (the per cent of this constituent decreases during the steam distillation yielding eugenol), caryophyllene and corresponding derivatives, and methyl-*n*-amyl ketone.

Specific gravity at 20°C	1.044–1.057[1]
Refractive index at 20°C	1.528–1.538[1]
Optical rotation at 20°C	0° to –1°5′[1] (–1°30′ to 0°)[7]
Solubility	1:2 in 70% ethanol[1]
Phenol content	85–93%[1]

Essential leaf oil

The oil is obtained by steam distillation of the leaves. It is yellow when freshly distilled but tends to turn dark violet on aging in iron vessels. The oil has a characteristic odor of eugenol.

Specific gravity at 25°/25°C	1.036–1.046[2]
Refractive index at 20°C	1.5310–1.5350[2]
Optical rotation at 20°C	0° to –2°[2]
Solubility	1:2 in 70% alcohol[2]
Phenol content (as eugenol)	84–88%[2]

Essential stem oil

Stem oil is obtained by steam distillation of dried stems after removing buds. It is a yellow to light-brown liquid, turning dark violet on aging in the presence of iron. While stem oil also has a characteristic eugenol odor, it is less pleasant than bud oil and less acceptable for use in flavoring and perfumery.

Specific gravity at 25°/25°C	1.048–1.056[2] (1.041–1.059 at 20°/20°C)[7]
Refractive index at 20°C	1.5340–1.5380[2] (1.5310–1.5360)[7]
Optical rotation	0° to –1°30′[2]
Solubility	1:2 in 70% ethanol[2]
Phenol content (% as eugenol)	89–95%[2] (85–95%)[7]

Derivatives

Tincture (20% in 60–80% ethanol), extract, oleoresins (from buds only), and the various essential oils

Organoleptic characteristics

Spicy, clove-like aroma; warm flavor

Uses

Clove bud oil, in addition to being a source of eugenol and an important starting material in perfumery, is employed in the formulation of a great number of compounded oils in flavoring pastry, special sauces, and condiments. The dried product is used directly in compounded infusions for liqueurs and bitters. The leaf and stem essential oils have only a minor application in the flavor industry.

Cloves have been reported used in the following:[3]

non-alcoholic beverages	20–1,000 ppm
ice cream, ices, etc.	33 ppm
baked goods	1,200 ppm
spiced cherries	500 ppm
meats	810 ppm

Clove bud extract has been reported used in the following:[3]

non-alcoholic beverages	16 ppm
ice cream, ices, etc.	19 ppm
candy	2.0–20 ppm
baked goods	48 ppm
condiments	150 ppm
meats	150–260 ppm

Clove bud oil has been reported used in the following:[3]

non-alcoholic beverages	3.1 ppm
alcoholic beverages	300 ppm
ice cream, ices, etc.	13 ppm
candy	320 ppm
baked goods	37 ppm
gelatins and puddings	0.33–5.0 ppm
chewing gum	1,800 ppm
condiments	55 ppm
meats	75 ppm
spiced fruits	830 ppm
jellies	7.3 ppm

Clove bud oleoresin has been reported used in meats, 100 ppm.[3] Clove leaf oil has been reported used in the following:[3]

non-alcoholic beverages	8.6 ppm
ice cream, ices, etc.	16 ppm
candy	22 ppm
baked goods	30 ppm
gelatins and puddings	510 ppm
condiments	14–40 ppm
meats	670 ppm
apple butter	2.0 ppm
pickles	7.0–16 ppm

Clove stem oil has been reported used in the following:[3]

non-alcoholic beverages	5.9 ppm
ice cream, ices, etc.	4.0–7.0 ppm
candy	91 ppm
baked goods	64 ppm
condiments	30–70 ppm

Regulatory status
Clove bud: GRAS (I), (II)
Clove leaf and stem: GRAS (II)

CLOVER

Botanical source: *Trifolium* species

Botanical family: *Leguminosae*

Foreign names: Trefle (Fr.), Klee (Ger.), Trifoglio (It.)

Description: Tufted or diffuse herbs having trifoliate leaves, usually toothed leaflets, and flowers in dense heads or spikes. More than 80 varieties of this annual or perennial herb are known. *Trifolium pratense* L. grows widely throughout Europe and central and northern Asia. This variety has reddish-pink flowers. *T. repens* L. is very common in Europe, together with *T. incarnatum* L.

Parts of plant used: Flowers

Physical-chemical characteristics

Essential oil: The oil is obtained by steam distillation of the freshly cut or dried flowers (*T. pratense*) in approximately 0.006% and 0.028% yields, respectively. A main constituent is furfural. The oil has very little commercial importance. The oil exhibits a rather intense, unpleasant odor, and has the following constants:

Specific gravity at 20°C	0.9476[1]
Optical rotation	+4°10′[1]

Derivatives Soft dried extract

Organoleptic characteristics Intense, unpleasant odor

Uses Red tops clover, solid extract (*T. pratense*, FEMA No. 2326), has been reported used in the following:[3]

non-alcoholic beverages	2.0 ppm
ice cream, ices, etc.	3.0 ppm
candy	20 ppm
baked goods	9.0 ppm

Regulatory status GRAS (I), (II)

COCA

Botanical source *Erythroxylon coca* Lam. and other species of *Erythroxylon*

Botanical family *Erythroxylaceae*

Foreign names Coca (Fr.), Coca (Ger.), Coca (Sp.), Coca (It.)

Description Tropical shrub 3–4 m (10–13 ft) tall, having slender branches, alternate olive-green leaves, and small, axillary flowers. The leaves have an odor reminiscent of tea and an aromatic, slightly bitter taste. The plant, native to Peru, is cultivated throughout South America and also in Java, India, and Ceylon. From time immemorial Peruvian Indians chewed coca leaves mixed with ashes from other plants to quench hunger and thirst and to relieve body fatigue.

Parts of plant used Leaves

Physical-chemical characteristics

Derivatives Fluid extract, tincture, soft aqueous extract. The average alkaloid content in coca leaves ranges between 0.5–1.5%; Java coca leaves, however, may contain up to 2.5% alkaloids. Cocaine represents approximately 50% of the total alkaloid content. Main constituents include *l*-cocaine, benzoylecgonine, cinnamyl cocaine, α- and β-truxilline, hygrine, cuskhygrine, and an essential oil consisting of methyl salicylate, acetone, and methanol. Derivatives for flavor, therefore, *must be* decocainized. Their pharmacological value derives from their relatively high cocaine content.

Organoleptic characteristics Tonic, slightly bitter, aromatic

Uses The decocainized derivatives are used in flavoring carbonated beverages (cola types) and also in compounded aromas for candy, liqueurs, and bitters. Coca leaf extract, decocainized (FEMA No. 2329), has been reported used in the following:[3]

non-alcoholic beverages	200 ppm
ice cream, ices, etc.	540 ppm
candy	400 ppm

Regulatory status Coca (decocainized): GRAS (II)

COFFEE

Botanical source	*Coffea arabica* L. and other *Coffea* species
Botanical family	*Rubiaceae*
Foreign names	Café (Fr.), Kaffee, (Ger.), Café (Sp.), Caffé (It.)
Description	A shrub originally native to Ethiopia and now cultivated in several tropical and equatorial areas. In the wild it grows to 10 m (33 ft) high; it is pruned to 4–5 m (13–16 ft) when cultivated. It has long branches, persistent leaves, and white flowers. The ovary develops into an ovoidal berry. The berry is red when ripe and contains two seeds (beans) surrounded by pulp. The raw beans are gray or yellowish, depending on their quality; on roasting they darken.
Parts of plant used	Seeds (beans)
Physical-chemical characteristics	
Derivatives	Infusion, soft extract, dried extract, tincture (20% in 40–70% ethanol), distillate (65% proof alcohol). The alkaloids (caffeine, adenine, guanine, xanthine, etc.) are responsible for the stimulant action. The small amount of essential oil in the bean contains furfurol, sulfur derivatives, and volatile acids. The essential oil and the fat, consisting of glycerides and unsaponifiables, are responsible for the flavoring action.
Organoleptic characteristics	Typical aromatic, bitter flavor
Uses	Distillates and tinctures in liqueur formulations; fluid extracts and other extracts in baked confections, syrups, candies, and carbonated beverages. The infusion is an universal beverage.
Regulatory status	GRAS (II)

COGNAC OIL

White and Green

Source	Wine lees and dregs
Foreign names	Lie de vin (Fr.), Cognacoel (Ger.), Vinaccioli (It.)
Description	Cognac oil, also called ethyl oenanthate, is formed during the fermentation of the yeast and other sediments in wine lees. Cognac oil is the constituent responsible for the characteristic cognac aroma in wines.
Physical-chemical characteristics	
Essential oil	Cognac essential oil is obtained by steam distillation of the wine lees or from the residual cakes of wine expression in approximately 0.07–0.12% and 0.036–0.066% yields, respectively. It is a green to bluish-green liquid with the characteristic aroma of cognac. The odor of green cognac oil may be unpleasant at times. Its physical-chemical characteristics are as follows (see also reference 2): Specific gravity at 15°C 0.872–0.883[1] Refractive index at 20°C 1.427–1.436[1]

Optical rotation	−0°3′ to +0°43′[1]
Ester value	25–109[1]
Solubility	1:1.5–5 in 80% ethanol[1]

In order to remove the color, raw cognac oil is rectified, yielding a pale-yellow, oily liquid exhibiting an intense, green, herbaceous odor with a fruital undertone (white cognac oil). Cognac oil is highly aromatic and contains aldehydes (acetaldehyde, cuminaldehyde, formaldehyde), acetone, various esters, acids, and alcohols.

Organoleptic characteristics

Characteristic cognac aroma with a fruital note

Uses

Cognac oil is used extensively in the formulation of fruital aromas and in liqueurs. To a much lesser degree cognac oil is used in perfumery.

Green cognac oil (FEMA No. 2331) has been reported used in the following:[3]

non-alcoholic beverages	5.2 ppm
alcoholic beverages	390 ppm
ice cream, ices, etc.	8.2 ppm
candy	12 ppm
baked goods	14 ppm
chewing gum	56 ppm
condiments	1.0 ppm

White cognac oil (FEMA No. 2332) has been reported used in the following:[3]

non-alcoholic beverages	5.6 ppm
ice cream, ices, etc.	14 ppm
candy	18 ppm
baked goods	24 ppm
gelatins and puddings	0.10 ppm

Regulatory status

GRAS

COPAIBA

Botanical source

South American species of *Copaifera*

Botanical family

Leguminosae

Foreign names

Copahu (Fr.), Copaiva (Ger.), Copaiba (Sp.), Copaive (It.)

Description

The commercially most important species of *Copaifera* are *C. reticulata* Ducke, *C. guayanensis* Benth, *C. multijuga* Hayne, *C. officinalis* L., *C. martii* var. *rigida*, and *C. coriacea*. All species consist of highly branched trees growing in the northern regions of South America (Brazil, Venezuela, and Colombia). The trees yield an oleoresin that gathers in pockets of the tree and is collected by drilling holes in the trunk. This resin, commercially known as copaiba balsam, is a viscous, pale-yellow to yellowish-brown liquid with a characteristic aromatic odor. The physical-chemical characteristics of the resin vary widely between the following limits, depending on the source:

Specific gravity at 15°C	0.888–1.004[1]
Optical rotation	−14°45′ to −37°10′[1]
Acid value	48–86[1]
Essential oil content	26–63%[1]

Parts of plant used

The natural resin

Physical-chemical characteristics

Essential oil

The oil is obtained by steam distillation of the natural resin; the Brazilian quality is preferred because of its higher content of essential oil. It is a colorless to slightly yellow liquid with a characteristic odor and aromatic, slightly bitter, spicy taste. Main constituents include α- and β-caryophyllene, *l*-cadinene, and other sesquiterpenes.

Specific gravity at 25°/25°C	0.880–0.907[2]
Refractive index at 20°C	1.4930–1.5000[2]
Optical rotation	−7° to −33°[2]
Solubility	1:5–10 in 95% alcohol[2]

Organoleptic characteristics

Characteristic aromatic odor; slightly bitter, pungent taste

Uses

The resin and the oil are used as fixatives in perfumery in spicy, woody, and floral notes.

Regulatory status

FDA §121.1163

CORIANDER

Botanical source

Coriandrum sativum L.

Botanical family

Umbelliferae

Foreign names

Coriandre (Fr.), Koriander (Ger.), Gilantro (Sp.), Coriandolo (It.)

Description

Annual, herbaceous plant originally from the Middle East. It grows from 25–60 cm (9–24 in.) in height. It has thin, spindle-shaped roots, erect stalk, alternate leaves, and small, pinkish-white flowers. It flowers from June to July and yields round fruits consisting of two pericarps. When ripe the fruits exhibit a warm, pleasant odor.

Parts of plant used

Ripe fruits (seeds)

Physical-chemical characteristics

Essential oil

The oil is obtained by steam distillation of the fruits (seeds), which are comminuted just before distilling; yields range between 0.3% and 1.1%. It is a clear, mobile, colorless to light-yellow liquid with a characteristic odor of linalool. The main constituents of the oil include *d*- and *dl*-α-pinene, β-pinene, dipentene, *p*-cymene, *d*-linalool, aldehyde C_{10}, geraniol, and acetic acid.

Specific gravity at 20°C	0.862–0.878[1]
Refractive index at 20°C	1.462–1.470[1]
Optical rotation at 20°C	+5° to +13°
Acid value	3–22′ (3.0 max)[7]
Solubility	1:8 in 65% ethanol[1]
Alcohol content (calculated as linalool)	> 65%

Derivatives

Infusion (3%), tincture, and fluid extract. Also, a brownish-yellow liquid oleoresin is produced from selected quality seed.

Organoleptic characteristics

Mild, sweet, warm, aromatic flavor

Uses

The dried product, the tincture, and the fluid extract are used extensively in the liquor industry and in carbonated beverages. The dried product also is used in the formulation of curries and cured meats. The essential oil is used for the formulation of compounded oils for use in liqueurs and in perfumery.

Coriander has been reported used in the following:[3]

non-alcoholic beverages	7.4 ppm
alcoholic beverages	1,000 ppm
ice cream, ices, etc.	1.0 ppm
candy	1.0–20 ppm
baked goods	880 ppm
condiments	54 ppm
meats	1,300 ppm

Coriander oil has been reported used in the following:[3]

non-alcoholic beverages	3.1 ppm
alcoholic beverages	10–30 ppm
ice cream, ices, etc.	4.5 ppm
baked goods	9.3 ppm
chewing gum	7.4 ppm
condiments	12 ppm
meats	47 ppm
candy	8.8 ppm

Regulatory status GRAS (I), (II)

CORK OAK

Botanical source *Quercus suber* L. or *Q. occidentalis* Gray

Botanical family *Fagaceae*

Foreign names Sughero (It.)

Description Evergreen tree that grows to 15 m (50 ft) high. It has a broad, round-topped head and thick, deeply furrowed, spongy, elastic bark; its leaves are ovate to oblong; the fruits are short-stalked; the acorn is ovate with thick scales. It is native to southern Europe, North Africa, East India, and California. *Q. occidentalis* differs chiefly in that its fruits ripen the second year and in its less persistent leaves. Its bark is not distinguished commercially from that of true cork oak.

Parts of plant used Bark

Regulatory status FDA §121.1163. In alcoholic beverages only

CORN SILK

Botanical source *Zea mays* L.

Botanical family *Gramineae*

Uses Corn silk (FEMA No. 2335) has been reported used in the following:[3]

non-alcoholic beverages	16–28 ppm
ice cream, ices, etc.	5.5–10 ppm
candy	12–18 ppm
baked goods	12–21 ppm

Regulatory status GRAS (II)

COSTMARY

Botanical source	*Crysanthemum balsamita* L. (*Tanacetum balsamita* L.)
Botanical family	*Compositae*
Foreign names	Tanaise balsamite (Fr.), Marien balsam (Ger.), Balsamite (Sp.), Balsamite (It.)
Description	Suffrutescent plant similar to tansy; grows to more than 1 m (39 in.) high. The plant is covered by hairs, has a fibrous, spindle-shaped root, alternate green leaves, and small, yellow flowers. The plant grows wild or can be cultivated; it is widespread throughout southern Europe.
Parts of plant used	Leaves and flowers
Physical-chemical characteristics Essential oil	Obtained in approximately 0.6% yields by steam distillation of the whole fresh plant. The light-yellow oil distills between 207–283°C and has an aromatic odor of clary sage. Specific gravity at 15°C: ca 0.943[1] Optical rotation: −43°40′ to −53°48′[1] Solubility: 1:1 in 90% ethanol, hazy upon further addition of alcohol; insoluble in 80% ethanol[1]
Derivatives	Tincture (10% in 65–70% ethanol), essential oil
Organoleptic characteristics	Pleasant clary sage, tansy, or mint-like odor
Uses	It is used as a modifier and blends well with rosemary, clove, bay, cinnamon, sage, and isobornyl acetate. It is also used as a pot herb.
Regulatory status	FDA §121.1163. In alcoholic beverages only

COSTUS

Botanical source	*Saussurea lappa* Clarke (*Aplotaxis lappa* Dec., *A. auriculata* DC.; *Aucklandia costus* Falc.)
Botanical family	*Compositae*
Foreign names	Costus (Fr.), Costus (Ger.), Costus (Sp.), Costus (It.)
Description	Perennial herb, more than 2 m (7 ft) high, with a central stem bearing numerous, almost black flowers. The plant grows wild in the Himalaya highlands (especially in Kashmir) and is cultivated in Nepal and throughout the surrounding areas.
Parts of plant used	Roots (cleaned, sometimes slightly roasted)
Physical-chemical characteristics Essential oil	The oil is obtained in approximately 0.7% yields by steam distillation after maceration in water of the comminuted dried roots. Since the oil contains water-soluble components and has a specific gravity similar to that of water, it is subsequently recovered from the distillation waters by extraction with solvents. The oil is a

viscous, pale-yellow to yellowish-brown liquid with a characteristic persistent odor reminiscent of orris, violet, and vetiver. The main constituents include myrcene, *p*-cymene, *l*-linalool, β-ionone, sesquiterpenes, costolactone, and a small amount of palmitic acid. Physical-chemical characteristics are as follows:

Specific gravity at 25°/25°C	0.995–1.039[2]
Refractive index at 20°C	1.5120–1.5230[2]
Optical rotation	+10° to +36°[2]
Acid value	<42[2]
Ester value	90–150[2]
Solubility	1:0.5 in 90% ethanol[2]

Derivatives

Concrete, commercially known as resinoid (from which an essential oil can be distilled); absolute. The absolute is a semisolid mass with an odor reminiscent of the oil.

Organoleptic characteristics

Peculiar, long-lasting odor reminiscent of orris, violet, and vetiver

Uses

The oil and the absolute are used in perfumery because of their fixative properties. The oil finds limited use in flavors.

Costus root oil (FEMA No. 2336) has been reported used in the following:[3]

non-alcoholic beverages	0.08 ppm
ice cream, ices, etc.	0.90 ppm
candy	1.9 ppm
baked goods	1.2 ppm
gelatins and puddings	0.10 ppm

Regulatory status

Costus root: FDA §121.1163

CUBEB

Botanical source

Piper cubeba L. f.

Botanical family

Piperaceae

Foreign names

Cubébe (Fr.), Kubebe (Ger.), Cubeba (Sp.), Cubebe (It.)

Description

Climbing perennial vine native to Java and Indonesia. It is presently cultivated in Indonesia, tropical Asia, and Africa (Congo). The plant yields small, round berries that are harvested before they are ripe and from which the seeds are extracted.

Parts of plant used

Unripe berries (seeds)

Physical-chemical characteristics

Essential oil

The oil exhibits a characteristic spicy, camphor-like odor; it is obtained by steam distillation of the seeds with yields ranging from 10–18%. It is a pale-yellow to bluish-green, slightly viscous liquid (also see Reference 2). Main constituents of the oil include 1,4-cineol, terpene and sesquiterpene alcohols, and cubebin.

Specific gravity at 15°C	0.915–0.930[1] (0.906–0.924 at 20°/20°C)[6]
Refractive index at 20°C	1.4938–1.4981[1] (1.4920–1.5020)[6]
Optical rotation	-25° to -43°[1] (-12° to -43°)[6]
Ester value	1.9–5.6[1]
Acid value	0.1–1[1] (0.8 min)[6]
Ester index (after acetylation)	25–30[1]
Solubility	<1:10 in 90% ethanol

Derivatives

Fluid extract, oleoresin, tincture (20% in 60% ethanol)

Organoleptic characteristics

Warm, woody, spicy odor reminiscent of guaiac with a bitter-tonic taste. The flavor of the oleoresin obtained by hydrocarbon extraction is bitter, while the alcohol extract is peppery.

Uses

The dried product and its derivatives find use in the formulation of compounded oils and flavors for liqueurs, condiments, and other food applications. Cubeb has been reported used in non-alcoholic beverages, 800 ppm.[3]

Cubeb oil has been reported used in the following:[3]

non-alcoholic beverages	2.4 ppm
ice cream, ices, etc.	0.25 ppm
candy	1.8 ppm
baked goods	4.6 ppm
condiments	33 ppm
meats	25–30 ppm

Regulatory status

FDA §121.1163

CUMIN

Botanical source

Cuminum cyminum L.

Botanical family

Umbelliferae

Foreign names

Cumin officinal (Fr.), Kreuzkümmel (Ger.), Comino comun (Sp.), Comino comune (It.)

Description

Annual herbaceous plant native to Egypt. Grows 20–80 cm (8–32 in.) high, with tapered roots, erect stalk, alternate leaves, white or purple flowers, pubescent fruits, and fusiform seeds. Flowers from June to August. It is commercially cultivated in Morocco, Cyprus, Egypt, India, China, and Iran.

Parts of plant used

Seeds from ripe fruits

Physical-chemical characteristics

Essential oil

The oil is obtained by steam distillation of the finely comminuted seeds in average yields of about 3%. This oil contains cuminaldehyde in high percentage and also α- and β-pinene, *p*-cymene, β-phellandrene, and cuminyl alcohol (see also reference 2). The aldehyde content (calculated as cuminaldehyde) ranges between 35% and 63%. The oil is a yellow-amber liquid that tends to darken on aging.

Specific gravity at 20°C	0.908–0.958[1]
Refractive index at 20°C	1.4940–1.5160[1]
Optical rotation at 20°C	+3° to +6°50′[1]

Derivatives

Infusion (2%), tincture (20% in 60% ethanol), the fluid extract, and an oleoresin.

Organoleptic characteristics

Strong, distinctive aromatic odor of cuminaldehyde; spicy, faintly pungent flavor

Uses

The dried product is used in the manufacture of curries. The oil is used in perfumery and, together with other derivatives, in the formulation of compounded oils for flavoring cured meats, cheese, condiments, and other food products.

Cumin has been reported used in the following:[3]

baked goods	2,500 ppm
condiments	300–3,900 ppm
meats	1,000 ppm

Regulatory status

GRAS (I), (II)

CURRANT, BLACK

Botanical source

Ribes nigrum L.

Botanical family

Saxifragaceae

Foreign names

Groseillier noir (Fr.), Schwarze Johannisbeere (Ger.), Groselheira negra (Sp.), Ribes nero (It.)

Description

Shrubs having woody, erect stems covered by a brown bark; alternate, palmately lobed, toothed leaves covered with tiny yellow glands; flowers arranged in loosely drooping racemes, internally purplish and externally greenish; fruits (June–July) consisting of several clustered, globose, black, fleshy berries, exhibiting a pleasant, slightly acid taste.

The plant, up to 3 m (10 ft) high, grows wild in several European countries and is extensively cultivated in France.

Parts of plant used

Leaves, fruits, flower buds

Physical-chemical characteristics

Essential oil

The oil is obtained by steam distillation of the flower buds in approximately 0.75% yields. It is a mobile, pale-green liquid with a cymene-like odor. Its physical-chemical constants are as follows:

Specific gravity at 15°C	0.8741[1]
Refractive index at 20°C	1.48505[1]
Optical rotation	+2°30′[1]
Ester value	5.6[1]
Solubility	> 1:6.5 in 90% ethanol[1]

Derivatives

Juice (by expression of the fruits), distillation waters (from leaves), infusion (5% from dried leaves), fluid extract (from leaves), concrete, absolute (tincture from flower buds). The main constituents of the leaves include tannin (a resinous material with an aromatic taste, not yet completely identified), an essential oil (yielding cymene and oxidase), several organic acids (chiefly citric and malic), sugars, nitrogen-containing compounds, pectins, and emulsin. Vitamins A and A_1 are found in the fruits.

The tincture is prepared by maceration of flower buds and is not usually available commercially. The extraction of the flower buds, with benzene or petroleum ether, yields a dark-green, strongly scented concrete. The absolute is prepared from the concrete according to traditional methods. The concrete contains approximately 85% terpenes and sesquiterpenes (norpinene, sabinene, caryophyllene, *d*-cadinene), approximately 6% alcohols, phenols, acetyl esters, and a C_{18} hydroxyacid.

Organoleptic characteristics

Strong, aromatic, terpene-like odor. The fruits and the juice exhibit a slightly sour, pleasant flavor.

Uses

The berries, in addition to being used for the fabrication of syrups and juice, are used extensively to prepare marmalades and jellies. The essential oil is rarely, if at all, used in flavors or in perfumes. The tincture, the absolute, and, to a lesser degree, the concrete find application in perfumery and also in the formulation of aromas for liqueurs, beverages, and candy. Black currant bud absolute (FEMA No. 2346) has been reported used in the following:[3]

non-alcoholic beverages	4.7 ppm
ice cream, ices, etc.	8.0 ppm
candy	20 ppm
baked goods	20 ppm
gelatins and puddings	5.0 ppm

Regulatory status	Leaves and buds: FDA §121.1163

DAMIANA

Botanical source	*Turnera diffusa* Willd. var. *aphrodisiaca* (Desvaux) Ward.
Botanical family	*Turneraceae*
Foreign names	Damiana (Fr.), Damiana (Ger.), Damiana (Sp.), Damiana (It.)
Description	Small, branched shrubs having alternate leaves and solitary, axillary, yellow flowers. It is native to dry areas in Mexico, California, Bolivia, Brazil, Antilles, and tropical America in general. The plant is known in Mexico as hierba de la pastora and is believed to exhibit aphrodisiac as well as diuretic and stimulant properties.
Parts of plant used	Leaves
Physical-chemical characteristics	
Derivatives	Fluid extract, dried, aqueous extract, tincture (20% in 25% ethanol). Main constituents of the leaves include 14% resin, 3.5% tannin, and 0.5–1.0% essential oil.
Organoleptic characteristics	Bitter tonic, aromatic
Uses	The derivatives are used mainly in pharmacology and sometimes in liqueurs.
Regulatory status	Damiana leaves: FDA §121.1163

DANDELION

Botanical source	*Taraxacum officinale* Weber and *T. laevigatum* DC.
Botanical family	*Compositae*
Foreign names	Pissenlit (Fr.), Löwenzahn (Ger.), Diente de leon (Sp.), Tarassaco (It.)
Description	Perennial, herbaceous plant, widespread throughout Europe. It grows 15–30 cm (6–12 in.) high, with thick, spindle-shaped roots; long, floral scapes terminated by yellow heads (March–October); and smooth, oblong leaves arranged in a rose-like fashion.
Parts of plant used	Roots

Physical-chemical characteristics

Derivatives

Infusion (5%), fluid extract, dried aqueous extract, tincture (20% in 20% ethanol). Main constituents of the dried product include triterpene alcohols, taraxasterol, vitamins A, B, C, and D, inulin, choline, and levulin.

Organoleptic characteristics

Bitter tonic, aromatic

Uses

The extracts, the tincture, and the infusion are used in pharmacology. The dried product, the extracts, and the tincture find application in the formulation of bitters. Dandelion fluid extract (FEMA No. 2357) has been reported used in the following:[3]

non-alcoholic beverages	35 ppm
ice cream, ices, etc.	6.0 ppm
candy	2.0–8.0 ppm
baked goods	53 ppm

Dandelion root extract solid (FEMA No. 2358) has been reported used in the following:[3]

non-alcoholic beverages	10 ppm
ice cream, ices, etc.	2.5–20 ppm
candy	8.0–40 ppm
baked goods	27 ppm

Regulatory status

Dandelion: GRAS (II)
Dandelion root: GRAS (II)

DAVANA

Botanical source

Artemisia pallens Wall.

Botanical family

Compositae

Foreign names

Davana (Fr.), Davana (Ger.), Davana (Sp.), Davana (It.)

Description

Delicately scented herb, cultivated only on a limited scale in southern India.

Parts of plant used

Flowers

Physical-chemical characteristics

Essential oil

The oil is prepared by steam distillation of newly blossomed flowers harvested at the end of April. It is a brownish-green, viscous liquid with a characteristic, persistent, balsamic aroma.

Specific gravity at 30°C	0.9833[1]
Optical rotation	−25°48′[1]
Refractive index at 30°C	1.4898[1]
Acid value	2.6[1]
Ester value	19.1[1]
Ester value (after acetylation)	78[1]

Organoleptic characteristics

Strong, penetrating, green odor. The chemical composition of the oil is still unknown.

Uses

The oil is used as a modifier in compounded formulations and in perfumery. Its uses are somewhat limited because of the high cost. Davana oil (FEMA No. 2359) has been reported used in the following:[3]

non-alcoholic beverages	3.0 ppm
ice cream, ices, etc.	6.5 ppm
candy	8.0 ppm
baked goods	11 ppm
chewing gum	5.0 ppm

Regulatory status

FDA §121.1163

DILL

Botanical source

Anethum graveolens L.

Botanical family

Umbelliferae

Foreign names

Aneth (Fr.), Gemeiner Dill (Ger.), Aneto (Sp.), Aneto (It.)

Description

Slender, annual herb, approximately 30–120 cm (1–4 ft) high. Native to the Orient, dill grows wild almost everywhere in southern Europe, Asia, and Africa; the plant is cultivated in Europe, Pakistan, the United States, India, and Japan. It has erect, cylindrical stems; alternate, finely dissected leaves; yellow, umbellate flowers; and elliptical fruits (diachenes). It flowers in June–July and yields fruits in September.

Parts of plant used

The herb and fruits (seeds)

Physical-chemical characteristics

Essential oils

Dill Weed Oil

In the United States the essential oil is obtained by steam distillation of the fresh herb (stalks, leaves, and seeds). American dill weed oil is a pale-yellow to yellow liquid with a strong, fresh, somewhat spicy, aromatic odor and a warm, slightly burning taste.

Specific gravity at 25°/25°C	0.884–0.900[2]
Optical rotation	+84° to +95°[2]
Refractive index at 20°C	1.4800–1.4850[2]
Solubility	Soluble in 90% alcohol[2]
Carvone content	25–45%[2]

Dill Seed Oil

Dill seed oil is obtained by steam distillation of the fruits (seeds). The oil is a slightly yellow liquid with a caraway-like odor and flavor because of the higher carvone content as compared to dill weed oil. The physical-chemical constants for an oil of European origin are as follows:

Specific gravity at 25°/25°C	0.890–0.915[2]
Refractive index at 20°C	1.4830–1.4900[2]
Optical rotation	+70° to +82°[2]
Carvone content	42–60%[2]
Solubility	>1:2 in 80% ethanol[2]

The main constituents of dill seed essential oil include carvone, *d*-limonene, phellandrene, paraffins, α-pinene, dipentene, and *d*-hydrocarvone. Dill weed essential oil contains, in addition to the above constituents, myristicin, dillapiole, and unidentified waxes. Indian dill (*A. sowa* DC.) essential oil has a somewhat different chemical composition.

Derivatives

From fruits: infusion, tincture, fluid extract, distillation waters. Also, an oleoresin is extracted from seeds.

Organoleptic characteristics

Strong, fresh, somewhat spicy odor; warm, slightly burning taste

Uses

The dried, comminuted herb harvested prior to the ripening of seeds is used as a household spice in condiments and sauces. In flavors the essential oil is used in the formulation of compounded oils for sauces, condiments, pickles, and baked goods. Dill (FEMA No. 2382) has been reported used in the following:[3]

baked goods	4,800 ppm
condiments	1,400 ppm
meats	1,200 ppm
pickles	8,200 ppm

Dill oil (FEMA No. 2383) has been reported used in the following:[3]

non-alcoholic beverages	1.6 ppm
alcoholic beverages	5.0 ppm
ice cream, ices, etc.	5.8 ppm
candy	9.9 ppm
baked goods	5.0 ppm
gelatins and puddings	20 ppm
chewing gum	3.8–8.0 ppm
condiments	150 ppm
meats	51 ppm
pickles	140 ppm

Regulatory status

GRAS (I), (II)

DILL, INDIAN

Botanical source

Anethum sowa Roxb.; *Peucedanum graveolens* Benth. & Hook.

Botanical family

Umbelliferae

Foreign names

Aneth (Fr.), Dill (Ger.), Eneldo (Sp.), Aneto (It.)

Description

Annual, blue-green, glabrous, aromatic herb having erect, cylindrical stems, branched taproots, alternate petiolate leaves, and yellow flowers in terminal, umbellate clusters. The plant is native to Asia (India, Japan). This variety of *Anethum* should not be confused with *A. graveolens*, or dill weed.

Parts of plant used

Seeds (fruits)

Physical-chemical characteristics

Essential oil

The oil, obtained by steam distillation of the crushed seeds in approximately 1.2–3.5% yields, is a light-yellow to light-brown liquid with a rather harsh caraway-like odor and flavor. This oil differs in its physical properties, odor, and flavor from the European and American dill seed oil. Indian dill seed oil has the following constants:

Specific gravity at 25°/25°C	0.925–0.980[2]
Refractive index at 20°C	1.4869–1.4950[2]
Optical rotation	+40° to +58°[2]
Carvone content	20–30%[2]
Solubility	1:05 in 90% ethanol[2]

The main constituents include carvone (30%), limonene (34.4%), dihydrocarvone (0.1%), dillapiole (18.9%), and traces of eugenol, anisic aldehyde, anethole, and thymol. In an essential oil distilled from the herb, α-phellandrene, eugenol, isoeugenol, and thymol have been identified.

Organoleptic characteristics

Caraway-like odor and flavor

Uses	The essential oil is used to flavor baked goods, meats, and condiments. Commercially it is less important than dill seed oil. Indian dill seed (FEMA No. 2384) has been reported used in the following:[3] baked goods 400 ppm condiments 200 ppm meats 3.3–100 ppm
Regulatory status	FDA §121.1163

DITTANY

Other names	Fraxinella; burning-bush; gas-plant
Botanical source	*Dictamnus albus* L.
Botanical family	*Rutaceae*
Foreign names	Dictame ou Fraxinelle (Fr.), Weisser Diptam, Ascherwurz (Ger.), Dictamo blanco, Fraxinella (Sp.), Dittamo (It.)
Description	Glabrous, perennial herb covered with a tacky gland. The plant is native to the island of Crete and widespread throughout the mountains of southern Europe. It has erect, round, nodulose stems; coriaceous leaves; irregular, white (sometimes red-streaked) flowers arranged in hirsute clusters; and glabose seeds with an outer black, shiny tunic.
Parts of plant used	Roots and bark
Physical-chemical characteristics	Infusion (2%) and tincture (20%). The presence of dictamine (alkaloid) in combination with trigonellin and choline is responsible for the antispasmic properties of dittany derivatives.
Organoleptic characteristics	Tonic, aromatic flavor
Uses	The comminuted roots are used alone or in combination with other comminuted herbs in the formulation of flavors for wine-based aperitifs and, where permitted, non-alcoholic beverages and pastry.
Regulatory status	Dittany roots: FDA §121.1163. In alcoholic beverages only

DITTANY OF CRETE

Other names	Spanish hops
Botanical source	*Origanum dictamnus* L.
Botanical family	*Labiatae*
Foreign names	Origan dictame (Fr.), Dosten Diptam (Ger.), Dictamo (Sp.), Dittamo Cretico (It.)
Description	Wooly shrub native to the eastern Mediterranean coasts (Crete). It grows 25–40 cm (10–16 in.) high, with woody stalks, opposite leaves, purple flowers (and branches); it flowers from June to September.

Parts of plant used Leaves and flowering tops

Physical-chemical characteristics

Derivatives Infusion (3%), tincture (20% in 65% ethanol), and fluid extract. The volatile constituents of the aroma include pulegone and carvacrol.

Organoleptic characteristics The dried product and its derivatives exhibit an intense, pleasant odor and a bitter, aromatic flavor.

Uses The dried product and its derivatives are used mainly for the formulation of vermouths, bitters, and other liqueurs. Dittany of Crete has been reported used in the following:[3]

non-alcoholic beverages	25 ppm
baked goods	8.8 ppm

Regulatory status FDA §121.1163

DOG GRASS

Other names Triticum; quick grass; agropyrum

Botanical source *Agropyron repens* L. Beauv.

Botanical family *Gramineae*

Foreign names Petit chiendent (Fr.), Gemeine Quecke (Ger.), Grama officinal (Sp.), Gramigna (It.)

Description Perennial herb (weed) that has a solitary culm and long, nodulose, creeping rootstocks with several smaller roots. The leaves are flat, linear-lanceolate, forming an enveloping sheath at the base; the greenish flowers are arranged in long, assurgent spikelets. The plant flowers from June to August.

Parts of plant used Rhizomes

Physical-chemical characteristics

Derivatives Fluid extract, soft aqueous extract, dried aqueous extract, tincture, infusion. The main constituents include triticin, malic acid, glucosides, and agropyrene, to which a mild antibiotic action is attributed.

Uses Dog grass extracts, alone or in combination with other flavor ingredients, find use to a limited extent in flavoring baked pastry, ice cream, and non-alcoholic beverages. Dog grass extract (FEMA No. 2403) has been reported used in the following:[3]

non-alcoholic beverages	2.0 ppm
ice cream, ices, etc.	4.0 ppm
candy	6.0 ppm
baked goods	6.0 ppm

Regulatory status GRAS (II)

DRAGON'S BLOOD

Other names Dracorubin

Botanical source *Daemonorops draco* Blume; *D. propinquus* Becc.

Botanical family	*Palmae*
Description	The resin exuding from the fruit of a Malaysian rattan palm (*D. draco*). Most of the Malaysian supply comes from unripe, scaly, cherry-sized fruits of eight species of climbing jungle palms (rattan) belonging to the genus *Daemonorops*. The resin is collected by shaking the dry fruits in baskets filled with cockleshells. The friction detaches the resin, which falls through the bottom of the basket in the form of a gritty powder. The latter is then pounded to dust, softened with hot water, and molded into cakes. The red color of the extracts derives from the presence of dracorubin. The resin also contains benzoic acid and tannin.
Parts of plant used	Resin exudate from fruits
Organoleptic characteristics	Astringent, colorant
Uses	Dragon's blood extract (FEMA No. 2404) has been reported used in non-alcoholic beverages, 300 ppm.[3] It is used in medicine against dysentery and diarrhea and as an astringent in tooth powder.
Regulatory status	FDA §121.1163

DULSE

Botanical source	*Rhodymenia palmata* (L.) Grev.
Description	Any of several coarse, red seaweeds used as a food in Scotland, Ireland, and other northern countries. It is especially abundant along the New England coast, growing on rocks and larger seaweeds. It consists of flat, fan-shaped fronds, solitary or tufted, a good deal divided and sometimes sub-divided. Dulse is eaten raw as a relish, either fresh or dried; plain boiled in water or cooked in butter or milk to be served as a vegetable with fish or meat; and added to stews and similar dishes. It should be washed several times before using. In Scotland it is roasted by twisting it around red-hot tongs. It offers little in the way of nutrition, as its main components are not assimilated; its food merits are confined chiefly to its gelatinous properties, which are useful for thickening soups, beverages, and jams.
Parts of plant used	The entire weed
Uses	As a gelling agent
Regulatory status	GRAS (I), (II)

ELDER

Other names	Sambucus; sweet elder
Botanical source	*Sambucus nigra* L.—for flowers and tree leaves *S. canadensis* L.—for flowers only
Botanical family	*Caprifoliaceae*
Foreign names	Sureau (Fr.), Holunder (Ger.), Sauco (Sp.), Sambuco (It.)

Description	Shrub or small tree that grows wild along rivers and brooks in the mountainous areas of southern Europe and western Asia. It has an erect stalk, opposite leaves, whitish-yellow flowers (June) that are scented and arranged in terminal clusters, and round, black, fleshy berries.
Parts of plant used	Flowers and tree leaves
Physical-chemical characteristics Derivatives	Fluid extract and tincture (20% in 60% ethanol or 15% in 55% ethanol); the essential oil and concrete essence are of experimental production only. The derivatives obtained from leaves contain sambunigrin, a mandelonitrile glucoside; on enzymatic hydrolysis it liberates HCN, which must be removed prior to use.
Organoleptic characteristics	Aromatic, bitter tonic
Uses	The dried product and the tincture are used in liqueur formulations and carbonated beverages. Elder flowers have been reported used in the following:[3] non-alcoholic beverages 340 ppm alcoholic beverages 25 ppm ice cream, ices, etc. 1.0 ppm candy 1.0 ppm baked goods 1.0 ppm
Regulatory status	Flowers: GRAS (I), (II) Tree leaves: FDA §121.1163. In alcoholic beverages only; not to exceed 25 ppm prussic acid in the flavor

ELECAMPANE

Other names	Inula; scabwort
Botanical source	*Inula helenium* L.
Botanical family	*Compositae*
Foreign names	Grande aunée (Fr.), Echter Alant (Ger.), Enula Campana (Sp.), Enula Campana (It.)
Description	Perennial, herbaceous plant, branched and velveted, widespread throughout Europe and western Asia; grows 1–2 m (3–7 ft) high. The plant has cylindrical, erect stalks; nodular, fleshy rhizomes; alternate leaves; and yellow flowers. It blooms from May to August.
Parts of plant used	Rhizomes and roots
Physical-chemical characteristics Derivatives	Decoction (2%), infusion (5%), tincture (20% in 65% ethanol), and fluid and soft extracts. The dried product and its derivatives contain inulin, alantol, helenin, alantic acid, and other substances.
Organoleptic characteristics	Bitter, aromatic flavor

Uses

The dried product and its derivatives are used frequently in liqueurs (vermouths, bitters).

Regulatory status

FDA §121.1163. In alcoholic beverages only

ELEMI

Botanical source

Canarium commune L. or *C. luzonicum* Mig.

Botanical family

Burseraceae

Foreign names

Elémi (Fr.), Elemi (Ger.), Elemi (Sp.), Elemi (It.)

Description

The tree grows wild or cultivated in the Philippines. Elemi, a resin, is the pathological exudate flowing from incisions made on the trunk bark. The largest resin production coincides with the appearance of the leaves at the beginning of the rainy season. The gum-resin outflows as a soft, yellowish-white mass that hardens to a wax-like consistency on exposure to air.

Parts of plant used

Resinous exudate

Physical-chemical characteristics

Essential oil

The oil is steam distilled from the crude resin in 20–30% yields. It is a colorless to pale-yellow liquid with a fresh, pleasant odor reminiscent of phellandrene.

Specific gravity at 15°C	0.880–0.910
Optical rotation	+40°50′ to +64°
Refractive index at 20°C	1.4800–1.4880
Solubility (in 90% ethanol)	1:0.5 to 1:1

The oil is not stable because of the oxidation of terpenes. Freshly distilled oils should be preferred for use in flavor and perfume applications. Main constituents include *α*-*d*-phellandrene, dipentene, elemicin, and sesquiterpene alcohols.

Derivatives

Resinoid (prepared by solvent extraction of the crude exudate)

Organoleptic characteristics

Characteristic green, fresh, lemon-like, agreeable, balsamic odor

Uses

The resinoid and the essential oil are used in perfumery. The purified resin and the essential oil find use in the formulations of flavors for candies, pastry, and baked goods. Elemi gum (FEMA No. 2407) has been reported used in the following:[3]

non-alcoholic beverages	0.13 ppm
ice cream, ices, etc.	0.25 ppm
candy	0.25 ppm
baked goods	0.25 ppm

Elemi oil (FEMA No. 2408) has been reported used in the following:[3]

non-alcoholic beverages	0.71 ppm
ice cream, ices, etc.	0.25–5.0 ppm
candy	0.25–15 ppm
baked goods	7.5 ppm
soups	10 ppm

Regulatory status

FDA §121.1163

ERIGERON

Other names Fleabane

Botanical source *Erigeron canadensis* L.

Botanical family *Compositae*

Foreign names Erigeron (Fr.), Erigeron (Ger.), Erigeron (Sp.), Erigeron (It.)

Description Herbaceous plant widespread throughout Canada, central and northern United States, southern Europe, India, and South Africa. The plant is *not* cultivated but grows as a weed mainly in corn fields. The harvesting for the production of essential oil is done only sporadically; no large-scale production of the oil is known.

Parts of plant used The whole plant (fresh or dried)

Physical-chemical characteristics

Essential oil Fresh plants yield from 0.3–0.6% essential oil, while dried plants seldom yield in excess of 0.2% essential oil on distillation. The oil obtained by steam distillation is a colorless to pale-yellow liquid with a slightly pungent, herbaceous odor. The oil tends to polymerize on exposure to air.

Main constituents include *d*-limonene, *p*-cymene, dipentene, linalool (traces), cuminaldehyde, and ketone. Also methyl octanoate derivatives formed by enzymatic action have been isolated in the oils distilled from other *Erigeron* species.

Derivatives Concrete (seldom prepared)

Organoleptic characteristics Fresh, slightly pungent, herbaceous odor; burning, unpleasant, bitter aftertaste

Uses Erigeron essential oil is used in perfumery almost exclusively to modify the top note of fern and cypress-type perfumes. As a flavor the oil is used in a variety of food substrates, such as condiments, candies, and non-alcoholic beverages. Erigeron oil (FEMA No. 2409) has been reported used in the following:[3]

non-alcoholic beverages	0.13–4.8 ppm
ice cream, ices, etc.	0.25–3.5 ppm
candy	0.25–30 ppm
baked goods	0.25–1.0 ppm
condiments	2.0 ppm

Regulatory status FDA §121.1163

EUCALYPTUS

Other names Globulus

Botanical source *Eucalyptus globulus* Labill.

Botanical family *Myrtaceae*

Foreign names Eucalyptus globuleux (Fr.), Eukalyptusblume (Ger.), Eucalipto (Sp.), Eucalipto (It.)

Description

Tree native to Australia, cultivated in temperate regions. It has opposite, lanceolated leaves and white or pinkish flowers.

Parts of plant used

Leaves of the mature tree

Physical-chemical characteristics

Essential oil

The oil is obtained by steam distillation of the leaves in approximately 1% yields. It is a mobile, pale-yellow to colorless liquid with an odor reminiscent of cineol (also see reference 2).

Specific gravity at 20°C	0.906–0.925[1]
Refractive index at 20°C	1.459–1.461[1] (1.4590–1.4670)[6]
Optical rotation at 20°C	0° to +10°[1]
Solubility	1:5 in 70% ethanol[1]
Per cent cineol	70% min[1]

The oil contains, in addition to cineol (eucalyptol), terpineol, sesquiterpene alcohols, various aliphatic aldehydes, isoamyl alcohol, ethanol, and terpenes.

Derivatives

Infusion (2%), tincture (20% in 80% ethanol), fluid extract, soft water extract, essential oil.

Organoleptic characteristics

Tonic, astringent

Uses

Eucalyptus oil has been reported used in the following:[3]

non-alcoholic beverages	1.7 ppm
alcoholic beverages	1.0 ppm
ice cream, ices, etc.	0.50–50 ppm
candy	130 ppm
baked goods	76 ppm

Regulatory status

FDA §121.1163

FENNEL, COMMON

Botanical source

Foeniculum vulgare Mill. var. *amara*

Botanical family

Umbelliferae

Foreign names

Fenouil amer (Fr.), Bitterer Fenchel (Ger.), Hinojo amargo (Sp.), Finocchio amaro (It.)

Description

Herbaceous, perennial plant, native to the Mediterranean regions; it grows wild or cultivated almost everywhere—central Europe, India, Argentina, United States. Only the cultivated plant is used for extractive purposes. The plant closely resembles sweet fennel, *F. vulgare* Mill. var. *dulce*, with the exception of having somewhat larger seeds. Also sweet fennel does not grow wild; it is cultivated only.

Parts of plant used

Green parts of the plant, dried seeds, roots

Physical-chemical characteristics

Essential oil

The oil is obtained by steam distillation of the dried, comminuted seeds in varying yields, usually from 2.5–6.5%, depending on the plant origin. It is a colorless to pale-yellow liquid with an aromatic, spicy odor and an initially slightly bitter, camphoraceous, then sweet flavor.

Specific gravity at 20°C	0.889–0.921[1]
Refractive index at 20°C	1.4840–1.5680[1]
Optical rotation	+20° to +68°[1]
Congealing point	<−10°C[1]

The main constituents include *d*-pinene, camphene, *d*-α-phellandrene, dipentene, 50–60% anethole, fenchone, methyl chavicol, aldehydes, and anisic acid. Also 2,3- or 1,3-dimethyl butadiene has been identified in a seed oil originally from South Dakota. The essential oil distilled from green parts of the plant (herb oil) contains *d*-α-phellandrene, pinene, a small amount of anethole, methyl chavicol, fenchone, and other substances.

Derivatives

Hydroalcoholic tinctures, fluid extract (from seeds and roots)

Organoleptic characteristics

Warm, camphoraceous odor with bitter, slightly burning flavor

Uses

Dried common fennel seeds have long been used for flavoring liqueurs, pastry, and other food products. The seed essential oil is not used in flavors but only as an extractive source of its main component anethole. Common fennel (FEMA No. 2481) has been reported used in the following:[3]

non-alcoholic beverages	800 ppm
baked goods	300–6,500 ppm
condiments	50 ppm
meats	2,400 ppm

Regulatory status

GRAS (I)

FENNEL, SWEET

Botanical source

Foeniculum vulgare Mill. var. *dulce*

Botanical family

Umbelliferae

Foreign names

Fenouil doux (Fr.), Heller Fenchel (Ger.), Hinojo (Sp.), Finocchio dolce (It.)

Description

Biennial or perennial herb native to and widespread around the Mediterranean. The cultivated variety is annual or biennial, yielding fruits improperly called seeds. The common edible vegetable consists of the fleshy stalk carrying sheath-shaped leaves and a large cylindrical root. Its flowers are yellow umbellae, blooming in the summer.

Parts of plant used

The fleshy stalk (vegetable), seeds, and roots

Physical-chemical characteristics

Essential oil

Obtained by steam distillation of the seeds. It is a yellowish-green liquid with a characteristic anise odor. The main constituents of the oil include anethole (50–60%), *d*-phellandrene, and *d*-limonene.

Specific gravity at 20°C	0.959–0.981[1]
Refractive index at 20°C	1.5330–1.5530[1]
Optical rotation at 20°C	+3° to +16°[1]
Congealing point	+5° to +15°C (depending on anethole content)[1]

Derivatives

From Seeds: tincture (20% in 70% ethanol), fluid extract, and essential oil

From Roots: tincture (20% in 70% ethanol), usually prepared from the fluid extract

Organoleptic characteristics

The oil has a very sweet, slightly earthy or peppery, spicy odor. The flavor is warm, spicy, aromatic, sweet, and slightly burning.

Uses

Anethole can be extracted by freezing from the essential oil from the seeds. The terpenes are employed for the flavoring of cattle feed. The oil is used in the formulation of compounded oils for sweets, pastry, and liqueur applications. Sweet fennel has been reported used in the following:[3]

non-alcoholic beverages	11 ppm
ice cream, ices, etc.	44 ppm
candy	33 ppm
baked goods	33 ppm
meats	40–300 ppm

Sweet fennel oil has been reported used in the following:[3]

non-alcoholic beverages	3.9 ppm
alcoholic beverages	10–20 ppm
ice cream, ices, etc.	0.38 ppm
candy	22 ppm
baked goods	19 ppm
gelatins and puddings	0.10–10 ppm
condiments	2.0 ppm
meats	40–100 ppm

Regulatory status

GRAS (I), (II)

FENUGREEK

Botanical source

Trigonella foenumgraecum L.

Botanical family

Leguminosae

Foreign names

Fénugrec (Fr.), Gelblicher Bockshornklee (Ger.), Fenigreco (Sp.), Fieno greco (It.)

Description

Herbaceous plant indigenous to western Asia, now widespread throughout mountainous and hilly areas of Europe, the Mediterranean, and Asia. The herb is about 0.5 m (20 in.) high, with a velveted, erect stalk, alternate leaves, and whitish-yellow flowers that bloom from June to July. The fruits are linear-compressed with smooth, rounded seeds.

Parts of plant used

Seeds

Physical-chemical characteristics

Essential oil

Very little known; obtained by steam distillation of the seeds with yields varying from 1–3%. Its main constituent is anethole. The dried product and its extracts contain trigonelline (alkaloid).

Derivatives

Infusion (5%), fluid extract, tincture (20% in 30% ethanol), and oleoresin

Organoleptic characteristics

The freshly comminuted seed displays an intensely sweet, spicy, protein-like aroma. The flavor is reminiscent of slightly burnt sugar, with a bitter back note.

Uses

Derivatives are employed as flavorings for imitation maple syrup, vanilla compositions, rum, butterscotch, licorice, pickle, and cheese seasonings. The comminuted seeds are used for curries. Fenugreek has been reported used in the following:[3]

non-alcoholic beverages	470 ppm
ice cream, ices, etc.	15–560 ppm
candy	600 ppm
baked goods	570 ppm
condiments	420–800 ppm
meats	250 ppm
syrups	450 ppm

Fenugreek extract has been reported used in the following:[3]

non-alcoholic beverages	50 ppm
alcoholic beverages	20 ppm
ice cream, ices, etc.	85 ppm
candy	280 ppm
baked goods	99 ppm
gelatins and puddings	30 ppm
chewing gum	7.6 ppm
condiments	150 ppm
icings	37 ppm
pickles	90 ppm
syrups	170 ppm
meats	40–60 ppm

Fenugreek oleoresin has been reported used in the following:[3]

non-alcoholic beverages	290 ppm
ice cream, ices, etc.	72 ppm
candy	90 ppm
baked goods	72 ppm
gelatins and puddings	500 ppm
syrups	300 ppm

Regulatory status	GRAS (I), (II)

FIG

Botanical source	*Ficus carica* L.
Botanical family	*Moraceae*
Foreign names	Figuier (Fr.), Fiege (Ger.), Higuera (Sp.), Fico (It.)
Description	Immense genus of tropical trees and shrubs distinguished by their peculiar fruit (*syconium*) consisting of a pear-shaped or globose receptacle enclosing numerous diclinous flowers. Fairly large trees having numerous branches, large nervate leaves, and edible fruits.
Parts of plant used	The fruits (partially dried in the shade)
Physical-chemical characteristics	
Derivatives	Tincture (20% in 70% alcohol), soft aqueous extract from the partially dried fruits
Organoleptic characteristics	Sweet flavor
Uses	The dried pulp reduced to powder may be used as a carrier for powder flavors. The tincture and the extract may be used for liqueurs, pastes, and sometimes tobacco flavoring.

FIR, BALSAM

Botanical source *Abies balsamea* (L.) Mill.; *A. balsamifera* Mich., *Pinus balsamea* L.

Botanical family *Pinaceae*

Foreign names *Abies balsamea* (L.) Mill. is used worldwide to classify this tree.

Description A tall tree having a characteristic pyramidal shape with numerous branches. The tree is widespread throughout North America, particularly in Canada (Nova Scotia) and the northern United States. A liquid oleoresin is contained in vesicles under the bark of the trunk. This resin, known as Canada balsam, is collected between May and August from incisions made in the bark. The operation is repeated on the same tree every two–three years. Canada balsam is in fact a turpentine consisting mainly of resin and essential oil; the resin does not contain benzoic and cinnamic acids. The balsam is a viscous, pale-yellow to greenish-yellow, translucent mass that slowly dries on exposure to air. It has a characteristic, pleasant turpentine odor.

Parts of plant used Needles, twigs, balsam

Physical-chemical characteristics

Essential oil

Balsam Fir Oil (*Canadian Fir Needle Oil*)

This oil is prepared by steam distillation of the needles and twigs of *A. balsamea*. The oil is a colorless to faintly yellow liquid with a balsamic, pleasant odor reminiscent of spruce or hemlock oil. The oil is produced in limited amounts because of its minor commercial importance. Its physical-chemical constants are as follows:

Specific gravity at 25°/25°C	0.872–0.878[2]
Refractive index at 20°C	1.4730–1.4760[2]
Optical rotation	−19° to −24°[2]
Ester content (as bornyl acetate)	8–16%[2]
Solubility	1:4 in 90% ethanol[2]

Canada Balsam Oil

Canada balsam essential oil is obtained by steam distillation of the balsam (resin) in approximately 15–25% yields. It is an almost colorless liquid with a strong, turpentine-like odor. Its main constituents include *l*-β-phellandrene, α- and β-pinene, esters (bornyl acetate), and alcohols. Its physical-chemical constants are as follows:

Specific gravity at 15°C	0.8614 (0.8605)[1]
Refractive index at 20°C	1.47809 (1.4758)[1]
Optical rotation	−30°36′ (−32°30′)[1]
Ester value	3.7 (2.24)[1]

Derivatives Concrete, absolute. A fir-needle concrete (sometimes called balsam fir needle oleoresin) is prepared by solvent extraction of the needles. Various kinds of fir and spruce needles (*A. alba*, *Tsuga canadensis*) are also employed for extraction, in addition to *A. balsamea* needles. An absolute is prepared from the concrete by alcoholic extraction.

Organoleptic characteristics Balsamic, pleasant, fresh odor reminiscent of spruce or hemlock

Uses Canada balsam is used as an adhesive in microscopy and in medicine. The oil is used mainly for the scenting of soaps and other technical products and in the formulation of aromas for baked goods. The concrete (oleoresin) and the oil are used in flavoring candy and baked goods, as the aroma blends well with citrus oils.

Canada balsam essential oil also may be used in similar applications. Balsam fir oil (FEMA No. 2114) has been reported used in the following:[3]

non-alcoholic beverages	4.5 ppm
ice cream, ices, etc.	0.50–1.5 ppm
candy	5.2 ppm
baked goods	5.2 ppm
gelatins and puddings	0.50–1.0 ppm

Balsam fir oleoresin (FEMA No. 2115) has been reported used in the following:[3]

non-alcoholic beverages	0.20 ppm
ice cream, ices, etc.	1.5 ppm
candy	5.0 ppm
baked goods	5.0 ppm

Regulatory status

FDA §121.1163. Balsam fir, needles, and twigs

FIR, PINE

Botanical source

Abies sibirica Ledeb.—Siberian fir; *A. alba* Mill.—silver or European fir; *A. sachalinensis* Masters or *A. mayriana* Miyabe & Kudo—Japanese fir

Botanical family

Pinaceae

Foreign names

Sapin (Fr.), Fichte (Ger.), Abete (Sp.), Abete (It.). The Latin names are often used to distinguish between the numerous fir varieties.

Description

Pyramidal, tall evergreen trees having horizontal branches, linear perennial leaves, and scaly cones.

A. sibirica, or Siberian fir, grows in the northern part of the U.S.S.R., Finland, and North America.

A. alba, silver fir or European fir, grows extensively in Europe (Germany, Austria, Switzerland, Yugoslavia). The tree has a characteristic whitish bark.

A. mayriana, or Japanese fir, grows specifically in Japan (Hokkaido Island).

Oils distilled from *Picea* and *Pinus* species are often traded under the generic name of fir needles oils.

Parts of plant used

Needles, twigs, cones

Physical-chemical characteristics

Essential oil

A. alba (or *A. excelsa* or *A. picea*) oil is obtained by steam distillation of needles and twigs of European fir in approximately 0.3% yields. The oil is a colorless to pale-yellow liquid with a pleasant, balsamic odor of fir needles and bitter, pungent flavor. Its main constituents include *l*-α-pinene, *l*-limonene, *l*-bornyl acetate, lauric and decylic aldehydes, and probably a sesquiterpene. Its physical-chemical constants follow:

Specific gravity at 25°/25°C	0.867–0.878[2]
Optical rotation	−34° to −67°[2]
Refractive index at 20°C	1.4700–1.4750[2]
Ester content (as bornyl acetate)	4–10%[2]
Solubility	1:7 in 90% ethanol[2]

An essential oil is water or steam distilled also from the crushed cones of *A. alba* (Austria, Yugoslavia, Switzerland, Germany). This so-called templin oil is a colorless to pale-yellow liquid with a fresh, balsamic odor somewhat reminiscent of petitgrain oil. Its physical-chemical constants vary depending on the source. An oil of Austrian origin has the following constants:

Specific gravity at 15°C	0.858[1]
Optical rotation	−77°55′[1]
Refractive index at 20°C	1.4732[1]
Ester content (as bornyl acetate)	2.5%[1]
Total alcohols (as borneol)	6.7%[1]
Solubility	1:8 in 90% ethanol with haze[1]

The composition of fir cones essential oil is very similar to the oil distilled from needles and twigs. It is usually added in small amounts to fir needles essential oil.

A. sibirica oil is obtained by steam distillation of the needles and twigs of Siberian fir. The oil is an almost colorless to very slightly yellow liquid with a fragrant pine-like odor and pungent taste. Its physical-chemical constants follow:

Specific gravity at 25°/25°C	0.898–0.912[2]
Refractive index at 20°C	1.4685–1.4730[2]
Optical rotation	−33° to −45°[2]
Ester content (as bornyl acetate)	32–44%[2]
Solubility	1:1 in 90% ethanol[2]

Organoleptic characteristics

Very pleasant, balsamic, fresh odor; bitter, pungent flavor

Uses

The oil is used extensively to scent soaps, perfumes, disinfectants, room deodorants, and other technical products. It is also used for flavoring candy, baked goods, and beverages because of its pungent taste. Pine (fir) needle oil (FEMA No. 2905) has been reported used in the following:[3]

non-alcoholic beverages	1.5 ppm
ice cream, ices, etc.	0.62 ppm
candy	5.2 ppm
baked goods	2.7 ppm

Regulatory status

Fir, twigs, and needles: FDA §121.1163

GALANGA

Other names

Galangal; Chinese ginger

Botanical source

Alpinia officinarum Hance

Botanical family

Zingiberaceae

Foreign names

Petit Galanga (Fr.), Kleiner Galangant (Ger.), Galangal (Sp.), Galanga (It.)

Description

Perennial herb native to China and cultivated in several Asian countries. The aerial stalk, which originates from a highly branched rhizome and from which additional stalks start, can reach more than 1 m (39 in.) in height. It exhibits distichous leaves and white, red-streaked flowers.

Parts of plant used

Rhizome

Physical-chemical characteristics

Essential oil

Obtained by steam distillation of dried rhizomes with maximum yields of about 1%. The oil is a yellowish liquid exhibiting a fresh, camphor-like odor. Its main constituents include *d*-α-pinene, cineol, linalool (sometimes), and sesquiterpenes.

Specific gravity at 15°C	0.913–0.923[1]
Optical rotation	+3°5′ to 6°50′[1]
Refractive index at 20°C	1.4770–1.4810[1]
Ester value	12–17[1]
Ester value (after acetylation)	40–64[1]

Derivatives Tincture (20% in 60% ethanol) and fluid extract

Organoleptic characteristics The dried product and its derivatives exhibit a bitter-aromatic taste.

Uses The dried product and the tincture frequently are employed in liqueur formulations (vermouths and bitters); the oil is used in the formulation of compounded oils used in pastry, but the product is in short supply.

Galangal root has been reported used in non-alcoholic beverages, 750 ppm.[3]

Galangal root extract has been reported used in the following:[3]

non-alcoholic beverages	0.10–350 ppm
alcoholic beverages	350 ppm
ice cream, ices, etc.	0.30 ppm
candy	0.20 ppm
baked goods	0.10 ppm
bitters	80 ppm

Galangal root oil has been reported used in the following:[3]

non-alcoholic beverages	0.27 ppm
alcoholic beverages	1.0 ppm
ice creams, ices, etc.	0.40 ppm
candy	1.5 ppm
baked goods	2.3 ppm
condiments	2.0 ppm

Regulatory status GRAS (I), (II)

GALANGA, GREATER

Botanical source *Alpinia galanga* Willd.

Botanical family *Zingiberaceae*

Foreign names Galanga (Fr.), Galangant (Ger.), Galangal (Sp.), Galanga (It.)

Description *A. galanga* Willd. is the galanga variety whose rhizomes were originally used for extraction of the essential oil. The plant, native to China, grows wild in Java and Malaysia. Today *A. officinarum* Hance (galanga) is used almost exclusively for extractive purposes.

Parts of plant used Rhizomes

Physical-chemical characteristics

Essential oil The oil, obtained by steam distillation of the comminuted rhizomes, exhibits an odor and flavor quite different from that of *A. officinarum*. Its main constituents include methyl cinnamate (48%), cineol (20–30%), camphor, and probably *d*-pinene. Its physical-chemical constants follow:

Specific gravity at 15°C	0.9847[1]
Optical rotation	+4°20′[1]

Refractive index at 20°C	1.51638[1]
Acid value	1.8[1]
Ester value	145.6[1]
Solubility	1:1 in 80% ethanol[1]

Derivatives Fluid extract, tincture, oleoresin

Organoleptic characteristics Aromatic, pleasant odor; pungent, burning flavor reminiscent of ginger

Uses *See* Galanga

Regulatory status FDA §121.1163. In alcoholic beverages only

GALBANUM

Botanical source *Ferula galbaniflua* Boiss. & Buhse and other *Ferula* species

Botanical family *Umbelliferae*

Foreign names Galbanum (Fr.), Galbanum (Ger.), Galbano (Sp.), Galbano (It.)

Description Herbaceous, tall plant that grows in northern Persia (*F. galbaniflua*) or in southern Persia (*F. rubricaulia* and *F. ceratophylla*). *F. galbaniflua* is widespread also in Turkey and Lebanon. The plant yields a resinous exudate distinguished commercially in two types: Levant galbanum (soft) and Persian galbanum (hard). The resin has a characteristic, aromatic odor and bitter, warm, acrid taste. It contains approximately 15–26% essential oil.

Parts of plant used The dried resinous exudate

Physical-chemical characteristics

Essential oil The essential oil is obtained by steam distillation of the dried resinous gum. It is a pale-yellow to yellow liquid with a balsamic, somewhat spicy, characteristic odor. Its main constituents include myrcene, cadinene, *d*-α-pinene, β-pinene, and sesquiterpene alcohols. Physical-chemical constants of the oil are as follows (see also reference 2):

Specific gravity at 20°C	0.867–0.916[1]
Refractive index at 20°C	1.4780–1.4870[1]
Optical rotation at 20°C	+3° to +20°[1]
Acid value	2 max.[2]
Solubility	>1:6 in 90% ethanol[2]

Derivatives The resinoid once was prepared by hydrocarbon solvent extraction and subsequent evaporation of the solvent; today a high-boiling, odorless solvent is added prior to evaporation; this solvent is left in the finished commercial product. The solvent-free resinoid is a dark-amber, viscous liquid with a characteristic balsamic odor. It yields turbid solutions in alcohol.

Organoleptic characteristics Warm, resinous, somewhat spicy and balsamic odor

Uses The oil and the resinoid are used extensively in perfumery because of their fixative properties. The oil and the resin are used in the formulation of compounded oils for flavoring candy, ice cream, condiments, and baked goods. Galbanum oil (FEMA No. 2501) has been reported used in the following:[3]

non-alcoholic beverages	0.16 ppm
ice cream, ices, etc.	0.84 ppm
candy	1.7 ppm
baked goods	1.8 ppm

Galbanum resin (FEMA No. 2502) has been reported used in the following:[3]

non-alcoholic beverages	0.04–0.25 ppm
ice cream, ices, etc.	0.05–0.50 ppm
candy	1.7 ppm
baked goods	2.4 ppm
condiments	50 ppm

Regulatory status	FDA §121.1163

GAMBIR

Other names	Catechu; gambir catechu; pale catechu
Botanical source	*Uncaria gambir* (Hunter) Roxb.
Botanical family	*Rubiaceae* (*Cinchonaceae*)
Description	Tree native to Malaysia, cultivated in tropical countries. A yellow catechu is derived from the leaves of a Malaysian woody vine (yellow or pale catechu) by boiling or infusing them in water. It is used for chewing with betel nuts and is exported for tanning and dyeing.
Parts of plant used	Leaves and young branches
Physical-chemical characteristics	
Derivatives	Coloring substance. Extracted from leaves and young branches, it consists of small (10–15 g) fragments that are externally reddish-brown and internally yellowish. The main constituents include tannic acid, quercetin, and coloring matter.
Regulatory status	FDA §121.1163

GARLIC

Botanical source	*Allium sativum* L.
Botanical family	*Liliaceae*
Foreign names	Ail (Fr.), Knoblauch (Ger.), Ajo (Sp.), Aglio (It.)
Description	Herbaceous, perennial plant of Mediterranean origin. Its stalk can reach lengths of 1 m (39 in.). The plant exhibits flat, keeled leaves and is terminated by an umbellated flower cluster. The bulb-like root contains several bulbils (cloves) enclosed in a common membrane.
Parts of plant used	Bulbs
Physical-chemical characteristics	
Essential oil	Obtained in 0.1–0.2% yields by steam distillation of the crushed bulbs or cloves; sometimes the whole plant is distilled. The essential oil obtained from bulbs is a

clear, pale-yellow to reddish-orange liquid bearing a very intense mercaptan-like note.

Specific gravity at 25°/25°C	1.040–1.090[2]
Refractive index at 20°C	1.5590–1.5790[2]

The essential oil contains allyl propyl disulfide, allyl di- and trisulfide and probably some allyl tetrasulfide, divinyl sulfide, allyl vinyl sulfoxide, allicin, and other minor components. Allicin is responsible for the characteristic odor of the essential oil and for the odor liberated from the crushed garlic clove. Recent improvements in extraction techniques have permitted the preparation of an oleoresin.

Organoleptic characteristics Pungent, acrid, aromatic, garlic-like

Uses The fresh and dried bulbs (crushed, ground flakes, powders) are used extensively as a condiment. The essential oil finds use in the flavoring of canned foods, meats, bouillons, and sauces. Garlic salts are also widely employed. Garlic oil has been reported used in the following:[3]

beverages	0.01–0.30 ppm
ice cream, ices, etc.	40 ppm
candy	2.9 ppm
baked goods	6.0 ppm
chewing gum	12 ppm
condiments	16 ppm

Regulatory status GRAS (I), (II)

GENET

Botanical source *Spartium junceum* L.

Botanical family *Leguminosae*

Foreign names Genêt (Fr.), Ginster (Ger.), Ginesta (Sp.), Ginestra (It.)

Description Wild or cultivated shrub 2–5 m (7–16 ft) high. It grows on the rocky coasts, in fields, woods, and arid and rocky mountain areas of central and southern Europe and around the Mediterranean basin. The plant has grayish stems with numerous, flexible branches, alternate leaves, and gold-yellow flowers arranged in terminal racemes that blossom in May.

Parts of plant used Flowers

Physical-chemical characteristics

Derivatives Concrete, absolute, tincture, and extract. The concrete is obtained by extracting the dried flowers in approximately 0.1% yields with petroleum ether; the absolute is prepared by alcoholic extraction of the concrete. A tincture also is prepared from the absolute. The concrete is a viscous, brownish mass with a sweet, honey-like, intense odor that characterizes all other derivatives as well.

Organoleptic characteristics Rose and honey-like, persistent odor with a slight, herbaceous note

Uses The derivatives are used in perfumery and, in minute amounts, in the formulation of aromas for flavoring pastry, ice cream, and beverages (honey-like notes). Genet absolute (FEMA No. 2504) has been reported used in the following:[3]

non-alcoholic beverages	0.83 ppm
ice cream, ices, etc.	0.50–1.0 ppm
candy	1.7 ppm
baked goods	1.0–2.0 ppm
chewing gum	12 ppm

Genet extract (FEMA No. 2505) has been reported used in non-alcoholic beverages, 1.4 ppm.[3]

Regulatory status FDA §121.1163

GENTIAN

Botanical source *Gentiana lutea* L.

Botanical family *Gentianaceae*

Foreign names Gentiane jaune (Fr.), Gelber Enzian (Ger.), Genciana (Sp.), Genziana (It.)

Description Perennial, herbaceous plant native to mountainous areas of Europe; it may reach 0.5–1.0 m (2–3 ft) in height. It has large, cylindrical roots (internally yellow); erect chalice; and flowers with a yellow corolla and peduncles. It blooms from July to August.

Parts of plant used Roots (of 2-year-old plants)

Physical-chemical characteristics

Derivatives Infusion (2%), fluid extract, soft and dried aqueous extracts, and tincture (20% in 60% ethanol)

Organoleptic characteristics The dried product and its derivatives exhibit a very bitter flavor.

Uses Extensively used as an aperitive and also in drugs. The dried product and its derivatives, properly selected, enter in the formulation of bitters and in flavors for carbonated beverages with a bitter taste. Gentian root extract has been reported used in the following:[3]

non-alcoholic beverages	26 ppm
alcoholic beverages	13 ppm
ice cream, ices, etc.	47 ppm
candy	120 ppm
baked goods	160 ppm

Regulatory status FDA §121.1163

GENTIAN, STEMLESS

Botanical source *Gentiana acaulis* L.

Botanical family *Gentianaceae*

Foreign name Gentiane acaule (Fr.), Grossblütiger Enzian (Ger.), Génciana acaule (Sp.), Genzianella (It.)

Description Perennial, herbaceous plant native to mountain pastures of central Europe; it grows from 15–40 cm (6–16 in.) high and exhibits a spindle-shaped root, short stem, large lower leaves, stem leaves (almost bracteal), and large, chalice-shaped blue flowers. It flowers from May to July.

Parts of plant used The whole plant

Physical-chemical characteristics

Derivatives Infusion (3–4%), fluid extract, and tincture (20% in 20% ethanol)

Organoleptic characteristics The dried product and its derivatives exhibit a bitter taste.

Uses Similar to those of *Gentiana lutea*

Regulatory status FDA §121.1163. In alcoholic beverages only.

GERANIUM

Botanical source *Pelargonium graveolens* L'Her.—rose geranium; other *Pelargonium* species—*P. roseum*, *P. radula*, *P. capitatum*, *P. fragrans*, *P. odoratissimum* Ait.

Botanical family *Geraniaceae*

Foreign names Geranium (Fr.), Geranie (Ger.), Geranio (Sp.), Geranio (It.)

Description *Geranium macrorrhizum* L. is the only true geranium. A large number of hybrids have been developed from several *Pelargonium* species, from which the essential oil is obtained. *Pelargonium* is a perennial plant when growing in subtropical climates; the plant dies in winter and must be planted annually in temperate climates.

The largest geranium cultivations are on Reunion; more than 50% of the world production of geranium oil comes from this island. The cultivated variety is *P. graveolens*. Other important geranium cultivations occur in Africa (Algeria, Morocco, Congo, Tanzania, Kenya) and in Europe (U.S.S.R., Bulgaria, France, Italy, Spain); South Africa is the only area where geraniums grow wild. The various essential oils are distinguished by the geographical name of the country of origin—Reunion geranium, Moroccan geranium, African geranium, etc.

Parts of plant used Leaves and stems

Physical-chemical characteristics

Essential oil The following essential oils distilled from *Pelargonium* species represent the commercially most important oils; others usually are meant for local consumption.

Reunion Geranium Oil

Also known as Bourbon geranium oil, it is obtained by steam distillation of the fresh plants harvested at the time of initial bloom. The oil is a mobile, clear, yellow-brown to green liquid with a strong, rose-like odor and a characteristic mint-like note. Its physical-chemical constants are as follows (also see reference 2):

Specific gravity at 20°/20°C	0.884–0.893[1]
Refractive index at 20°C	1.461–1.468[1]
Optical rotation	−7° to −14°[1]
Acid value	12 max[1]
Ester content (as geranyl tiglate)	21–32%[1]
Total alcohols (as geraniol)	65–73%[1]
Ketone content (as menthone)	6–13%[1]
Solubility	1:1–3 in 70% ethanol[1]

Algerian Geranium Oil

Algerian geranium oil is obtained by steam distillation of the leaves harvested prior to their turning yellow and shortly before blossoming. It is a light-yellow to deep-yellow liquid with a rose-like odor. The fragrance of Algerian oil is considered superior (less minty) than Reunion (Bourbon) essential oil. Its physical-chemical constants are as follows (see also reference 2):

Specific gravity at 20°/20°C	0.886–0.901[1]
Refractive index at 20°C	1.4635–1.4725[1]
Optical rotation	−6°30′ to −13°[1]
Acid value	9.5 max[1]
Ester content (as geranyl tiglate)	21.1–32%[1]
Total alcohols (as geraniol)	60–75%[1]
Ketone content (as menthone)	8–16%[1]
Solubility	1:4 in 70% ethanol[1]

Moroccan Geranium Oil

Moroccan geranium oil is steam distilled from the freshly cut leaves and stems of *P. roseum*. It is a pale amber-yellow to greenish-yellow liquid with a rose-like, herbaceous odor. Its physical-chemical constants follow:

Specific gravity at 25°/25°C	0.884–0.894[2]
Refractive index at 20°C	1.4640–1.4700[2]
Optical rotation	−8° to −12°[2]
Acid value	1.5–9.0[2]
Ester content (as geranyl tiglate)	14.8–33.8%[2]
Solubility	1:2–4 in 70% ethanol[2]

The main constituents of the various *Pelargonium* oils include geraniol, citronellol, ethanol, dimethyl sulfide, diacetyl, isoamyl alcohol, phellandrene, *l*-α-pinene, methyl hexyl carbinol, *l*-isomenthone, α-terpineol, menthol, linalool, eugenol, and phenethyl alcohol. The oil often is adulterated by the addition of geraniol or citronellol to citronella oil.

Derivatives

Concrete and absolute.

The concrete is prepared by petroleum ether extraction of the leaves and stems as used for the distillation of the essential oil. Morocco is the largest producer of geranium concrete, a dark-green mass with a strong, herbaceous, slightly rosy odor.

The absolute is usually a green or dark-green liquid exhibiting an intense, tenacious odor with a rosy undertone.

Organoleptic characteristics

Strong, rose-like odor with a minty undertone; bitter, rather disagreeable flavor.

Uses

The oil, the concrete, and the absolute find innumerable applications in perfumery. Rhodinol can be isolated by fractional distillation of geranium essential oil. Because of its rose-like aroma, the oil has a limited use for flavoring chewing gum, candy, and baked goods. Rose geranium oil (FEMA No. 2508) has been reported used in the following:[3]

non-alcoholic beverages	1.6 ppm
ice cream, ices, etc.	2.8 ppm
candy	6.9 ppm
baked goods	8.1 ppm
gelatins and puddings	1.1–2.0 ppm
chewing gum	210 ppm
jellies	5.2 ppm

Regulatory status

Rose geranium: GRAS (II)
Geranium species: GRAS (I), (II)

GERMANDER

Other names	Chamaedrys
Botanical source	*Teucrium chamaedrys* L.
Botanical family	*Labiatae*
Foreign names	Germandrée officinale (Fr.), Echter Gamader (Ger.), Xamedrios (Sp.), Camedrio (It.)
Description	Perennial herb widespread from central Europe to Asia and North Africa. It is 10–30 cm (4–12 in.) high with a thin rhizome with stolons, shrubby stalks, and spiked pinkish-red flowers. It blooms from May to September.
Parts of plant used	Flowering tops
Derivatives	Infusion (5%), 10% alcohol extract, and tincture (20% in 60% alcohol)
Organoleptic characteristics	Bitter tonic flavor
Uses	The dried product and its tincture are used in liqueur formulations as well as in vermouths and bitters.
Regulatory status	FDA §121.1163. In alcoholic beverages only

GERMANDER, GOLDEN

Botanical source	*Teucrium polium* L.
Botanical family	*Labiatae*
Description	Low canescent, tomentose, lanate or rarely pilose-hispid shrubs from 2–6 in. high; basal branches procumbent, ascending or rarely suberect; leaves cuneate-oblong or linear, semile, crenate, yellowish hoary, golden or rarely green; white, yellow, or purple flowers. Mediterranean regions and the Orient.
Uses	An extract used in vermouth flavors
Regulatory status	FDA §121.1163. In alcoholic beverages only

GINGER

Botanical source	*Zingiber officinale* Roscoe
Botanical family	*Zingiberaceae*
Foreign names	Gingembre (Fr.), Ingwer (Ger)., Jenijbre (Sp.), Zenzero (It.)
Description	An herbaceous plant native to Asia, it is cultivated in several tropical and subtropical countries—Jamaica, India, Africa, southern China, and more recently in Australia. The plant may reach 60–90 cm (2–3 ft) in height and has tuber-like rhizomes with leaf-bearing and flower-bearing stems. The plant propagates by the splitting of the rhizomes. The African and Cochin qualities are used most frequently for distillation.

Parts of plant used

The dried, unpeeled rhizomes—brown ginger
The dried, skinned rhizomes—white ginger

Physical-chemical characteristics

Essential oil

The oil, obtained by steam distillation of the dried ground rhizomes in approximately 0.25–1.2% yields, is a pale-yellow to yellow liquid with a warm, spicy, aromatic odor; the oil tends to thicken and darken on exposure to air. Its main constituents include sesquiterpenes, farnesene, methyl heptenone, cineol, borneol, geraniol, and linalool. The physical-chemical constants of the essential oil are as follows (see also reference 2):

Specific gravity at 20°C	0.872–0.884[1]
Refractive index at 20°C	1.4870–1.4920[1]
Optical rotation at 20°C	−25° to −52°[1]

Derivatives

Fluid extract, tincture (20% in 60–65% ethanol), oleoresin. The oleoresin is a dark-brown, viscous liquid with the characteristic odor and pungent flavor of ginger. It is prepared by solvent extraction of the dried rhizomes and subsequent removal of the solvent. The main constituents, in addition to those listed for the essential oil, include zingerone (a ketone, probably responsible for the pungent flavor) and gingerol.

Organoleptic characteristics

Warm, sweet, strongly aromatic odor; sharp, pungent flavor. The oil lacks the pungency of the other derivatives.

Uses

The essential oil and the derivatives are used extensively in the formulation of compounded aromas for flavoring candy, baked products, liqueurs, condiments, sauces, and bouillons. The ginger flavor has a well known application in carbonated beverages (ginger ale). The dried, powdered product of African origin is also used as a spice. Ginger (FEMA No. 2520) has been reported used in the following:[3]

non-alcoholic beverages	40 ppm
ice cream, ices, etc.	220 ppm
baked goods	2,500 ppm
meats	1,500 ppm

Ginger extract (FEMA No. 2521) has been reported used in the following:[3]

non-alcoholic beverages	65 ppm
ice cream, ices, etc.	43 ppm
candy	83 ppm
baked goods	100 ppm
condiments	15 ppm
meats	56 ppm

Ginger oil (FEMA No. 2522) has been reported used in the following:[3]

non-alcoholic beverages	17 ppm
ice cream, ices, etc.	20 ppm
candy	14 ppm
baked goods	47 ppm
condiments	13 ppm
meats	12 ppm

Ginger oleoresin (FEMA No. 2523) has been reported used in the following:[3]

non-alcoholic beverages	79 ppm
ice cream, ices, etc.	36–65 ppm
candy	27 ppm
baked goods	52 ppm
condiments	10–1,000 ppm
meats	30–250 ppm

Regulatory status

GRAS (I), (II)

GRAINS OF PARADISE

Other names	Cardamom seed; guinea grains
Botanical source	*Aframomum melegueta* Rosc.
Botanical family	*Zingiberaceae*
Foreign names	Grains de Paradis (Fr.), Paradieskoerner (Ger.), Melegueta (Sp.), Grana Paradisi (It.)
Description	The plant, native to western tropical Africa, yields yellow-orange seeds with a spicy taste. It was once used as a spice under the name of Piper Melegueta.
Parts of plant used	Seeds
Physical-chemical characteristics	
Essential oil	The oil is obtained by steam distillation of the seeds with yields of approximately 0.5%. It is a yellow liquid, scarcely scented, with a taste similar to that of the dried product. The oil is not normally produced; it contains eugenol. Specific gravity at 15 C 0.894[1] Optical rotation ca −3° to −4°[1]
Derivatives	Tincture (20% in 75% ethanol) and the distillate (80% ethanol)
Organoleptic characteristics	Sharp, spicy, pungent taste
Uses	The seeds and their derivatives are used as a spicy flavor in condiments as well as in specific liqueur formulations. Grains of paradise has been reported used in the following:[3] non-alcoholic beverages 43 ppm ice cream, ices, etc. 120 ppm candy 120 ppm
Regulatory status	GRAS (I)

GRAPEFRUIT

Botanical source	*Citrus paradisi* Macfad., *C. decumana* L.
Botanical family	*Rutaceae*
Foreign names	Pamplemousse (Fr.), Pompelmusen (Ger.), Pamplemusa (Sp.), Pompelmo (It.)
Description	A tree, 9–15 m (30–50 ft) high, having a rounded and conical head, ovate glabrous leaves, and smooth, gray-brown bark. The flowers are large, white, and fragrant. The fruits are large, light-lemon or orange with a thin rind and grayish-yellow or flesh pink. Historically and botanically, the origin of the grapefruit is uncertain and appears to have developed from the Shaddok variety native to the West Indies. The plant is cultivated in the United States (Florida, California, Texas), East Asia, West Indies, Brazil, and Nigeria. The *C. decumana* variety yields the largest fruits (up to 10 kg).
Parts of plant used	Fruit and peel

Physical-chemical characteristics

Essential oil

Grapefruit oil is the volatile oil obtained by cold expression of the fresh peels of the fruit. The oil is a yellow, sometimes reddish liquid (often showing a flocculent separation of waxy material) with a pleasant citrus-like odor and flavor. Its physical-chemical constants follow (also see reference 2):

Specific gravity at 20°C	0.8563[1] (0.852–0.860)[7]
Refractive index at 20°C	1.4758[1] (1.4740–1.4790)[7]
Optical rotation at 20°C	+93°28′[1] (+91° to +96°)[7]
Aldehyde content (as C_8 and C_{10})	1.67%[1] (1% min)[7]

Its main constituents include limonene (90%), 2–3% volatile fraction containing oxygen compounds and sesquiterpenes, 7–8% waxy fraction, C_8 and C_{10} aldehydes, geraniol, cadinene, small amounts of citral and dimethyl anthranilate, and acids. A terpeneless oil can be prepared by vacuum distillation, yielding a more soluble and more stable concentrated oil. However, a certain amount of terpenes must be left in the oil to retain the characteristic freshness of citrus flavor.

A lower grade of essential oil that does not have application in flavor work is also obtained by steam distillation of the crushed peels or even from seeds.

Derivatives

Juice and extract. Naringin, a bitter, white, crystalline glucoside, is found in the blossoms and the flavedo of the fruits. Naringin yields rhamnose and naringenin ($C_{15}H_{12}O_5$) on hydrolysis. A naringin extract, prepared from the expressed peels, is used in flavors.

Organoleptic characteristics

Fresh, citrus-like odor; taste reminiscent of sweet and bitter orange to some degree.

Uses

The cold-expressed essential oil and the naringin extract are used in flavors, especially in soft drinks.

Grapefruit oil (FEMA No. 2530) has been reported used in the following:[3]

non-alcoholic beverages	160 ppm
ice cream, ices, etc.	180 ppm
candy	630 ppm
baked goods	370 ppm
gelatins and puddings	250 ppm
chewing gum	1,500 ppm
toppings	400 ppm

Naringin extract (FEMA No. 2769) has been reported used in the following:[3]

non-alcoholic beverages	71 ppm
alcoholic beverages	0.20 ppm
ice cream, ices, etc.	5.7 ppm

GUAIAC

Other names

Guaiacum

Botanical source

Guaiacum officinale L.; *G. sanctum* L.; *Bulnesia sarmienti* Lor.

Botanical family

Zygophyllaceae

Foreign names

Gaiac (Fr.), Guajachol (Ger.), Guajaco (Sp.), Guaico (It.)

Description

Bulnesia sarmienti Lor. is a wild tree 3–4 m (10–13 ft) high, widespread in the woods of Argentina and in the Gran Chaco area of Paraguay. This variety yields the true guaiac. *G. officinale* L., also a tree native to tropical America (Caribbean Islands), grows wild or cultivated in Venezuela, Jamaica, Cuba, and Colombia. This variety yields a resinous substance from which a tincture is prepared.

Parts of plant used

Wood and sawdust from the tree

Physical-chemical characteristics

Essential oil

The oil is obtained by steam distillation of chipped wood of *B. sarmienti* in approximately 3% yields. It is a thick, viscous, orange-brown mass with a woody, rose-like odor reminiscent of tea rose. Sometimes the oil exhibits a smoky note. The main constituent of the oil, also known as champaca wood oil, is guaiol, a sesquiterpene alcohol (85%). Its physical-chemical constants follow:

Specific gravity at 25°/25°C	0.960–0.975[2]
Refractive index at 20°C	1.5020–1.5070[2]
Optical rotation at 20°C	−3° to −12°[2]
Solubility	1:7 in 70% ethanol[2]

Derivatives

Fluid extract, tincture (mainly from *G. officinale* L.). The tincture is generally a 10% solution in 60% ethanol. The fluid extract is a reddish-brown liquid with a pleasant odor and burning, bitter taste.

Organoleptic characteristics

Soft, pleasant, rose-like odor reminiscent of tea roses

Uses

The essential oil is used extensively in perfumery as a fixative. The oil is used also in the formulation of aromas with a woody, rose-like note. The fluid extract and the tincture are used in pharmacology and sometimes in the formulation of aromas for beverages.

Guaiac wood extract (FEMA No. 2533) has been reported used in the following:[3]

non-alcoholic beverages	760 ppm
ice cream, ices, etc.	4.0 ppm
candy	8.0 ppm
baked goods	70 ppm

Guaiac wood oil (FEMA No. 2534) has been reported used in the following:[3]

non-alcoholic beverages	1.1 ppm
ice cream, ices, etc.	4.1 ppm
candy	9.2 ppm
baked goods	8.1 ppm
gelatins and puddings	4.2 ppm
chewing gum	60 ppm

Regulatory status

FDA §121.1163

GUARANA

Botanical source

Paullinia cupana H.B.K. (*P. sorbilis* Mart.)

Botanical family

Sapindaceae

Foreign names

Quarane (Fr.), Guarana (Ger.), Guarana (Sp.), Cupana Guarana (It.)

Description	Climbing shrubs cultivated in Brazil, Uruguay, Venezuela, and other South American countries.
Parts of plant used	Seeds
Physical-chemical characteristics Derivatives	Guarana paste (gum), extracts, and flavor distillates. The comminuted and roasted guarana seeds are mixed with water to form a paste that exhibits a chocolate-like flavor. The main constituents include caffeine (theine), tannic acid, theophylline, theobromine, adenine, guanine, xanthine, hypoxanthine, resins, fixed oil, gums, and saponins. The extract is prepared by alcoholic extraction of the paste.
Organoleptic characteristics	Astringent, tonic, chocolate-like flavor
Uses	In Brazil and other South American countries guarana paste is used as a surrogate for chocolate and coffee and to flavor soft drinks. The Guarany Indians use guarana to cure severe gastric infections. The extracts and the flavor distillates are used for flavoring liqueurs, cordials, and other products. Guarana gum (FEMA No. 2536) is also used in the following:[3] non-alcoholic beverages 12 ppm candy 10 ppm
Regulatory status	FDA §121.1163

GUAVA

Botanical source	*Psidium* species
Botanical family	*Myrtaceae*
Description	The name *guava* includes several tropical plants of the myrtle family that yield delicious fruits. The common guava (*P. guajava*) is a low bush-tree with fragrant, white flowers on solitary axillary stalks. The fruits are larger than a hen's egg, roundish or pear-shaped, smooth, and yellow. The rind is thin and brittle; the pulp is firm, aromatic, sweet, and full of bony seeds. The common guava and the cattley, or strawberry, guava (*P. cattleyanum*) are grown extensively in Florida and southern California. The mara gamba (*P. pygmaeum*) is a dwarf species of Brazil with fruits no larger than gooseberries.
Parts of plant used	Fruits
Uses	The jelly or preserves made from guava fruits are highly esteemed. The juice is used in Hawaiian-type fruit drinks and punches.
Regulatory status	GRAS (II)

HAW, BLACK

Botanical source	*Viburnum prunifolium* L.
Botanical family	*Caprifoliaceae*
Foreign names	Viorne américain (Fr.), Amerikanischer Schneeball (Ger.), Viburno (Sp.), Viburno (It.)

Description

Shrub or small tree, approximately 3 m (10 ft) high, native to the United States (Connecticut, Michigan, Georgia, Arkansas, Mississippi, Florida). The plant has obtuse or slightly pointed leaves similar to the *Prunus* species, ellipsoid or ovoid fruits, and highly flexible branches.

Parts of plant used

The bark (from branches)

Physical-chemical characteristics

Derivatives

Fluid extract, tincture (20% in 60% ethanol), and dried water alcoholic extract. The main constituents include salicin (saligenin glucoside), viburnin, and a trace of essential oil that has never been isolated.

Organoleptic characteristics

Tonic, bitter, aromatic

Uses

The extracts are used in traditional recipes for flavoring pastry and beverages. Black haw bark extract (FEMA No. 2538) has been reported used in the following:[3]

non-alcoholic beverages	5.0–6.0 ppm
ice cream, ices, etc.	2.5 ppm
candy	6.0 ppm
baked goods	6.0 ppm

Regulatory status

FDA §121.1163

HEMLOCK (SPRUCE)

Botanical source

Tsuga canadensis (L.) Carr.—Eastern hemlock
T. heterophylla (Raf.) Sarg.—Western hemlock
Picea glauca (Moench.) Voss.—Canadian, or white, spruce
P. mariana (Mill.) B.S.P.—Canadian black spruce

Botanical family

Pinaceae

Foreign names

Sapin (Fr.), Tanne (Ger.), Puiche (Sp.), Pino (It.)

Description

Hemlock

Nine species of evergreen, mostly hardy, coniferous trees, belong to the genus *Tsuga*. They are medium to large in size and usually pyramid-shaped. Native to North America, Japan, Formosa, China, and the Himalayas, the species has horizontal branches, solitary monoecious flowers, and globose to ovoid or oblong cones with thin, persistent scales. The bark of *T. canadensis* is a valuable source of tannin. *T. heterophylla* is the largest North American species, being 70 m (230 ft) or more in height.

Spruce

P. glauca is a tall tree (15–45 m, or 49–148 ft high) resembling the balsam fir (*Abies balsamea*). White spruce has slender, pale, glaucous leaves and cylindrical cones with thin scales.

P. canadensis is a lower tree of 8–12 m (26–39 ft). It has short, thick, pale bluish-green leaves and short, ovoid or subglobose cones persisting for several years.

Distillation of needles and twigs of the above plants yields hemlock and spruce oils. No attempt is made to keep these species separate for oil production; hence, spruce oil and hemlock oil are used interchangeably in commercial practice.

Parts of plant used

Needles and twigs

Physical-chemical characteristics

Essential oil

The oil is obtained by steam distillation of needles and twigs from the above-mentioned botanical sources. It is a pale-yellow to light-yellow liquid with a pleasant pine-needle odor. Its main constituents include bornyl acetate, borneol, α-pinene, camphene, limonene, β-pinene, and myrcene. Its physical-chemical constants follow:

Specific gravity at 25°/25°C	0.900–0.915[2]
Refractive index at 20°C	1.4670–1.4720[2]
Ester content (as bornyl acetate)	37–45%[2]
Solubility	1:1 or more in 90% ethanol[2]

Organoleptic characteristics

Pleasant, balsamic, fresh, pine-needle odor.

Uses

The oil is used mainly in perfumery—soaps, cosmetics, sprays, deodorants. In flavors hemlock or spruce oils (FEMA No. 3034) have been reported used in the following:[3]

non-alcoholic beverages	6.2 ppm
ice cream, ices, etc.	15 ppm
candy	11 ppm
baked goods	2.0–4.0 ppm
gelatins and puddings	1.0 ppm
chewing gum	44 ppm

HICKORY

Botanical source

Carya species

Botanical family

Juglandaceae

Foreign names

Noyer d'Amérique (Fr.)

Description

It is a gray tree of the walnut family native exclusively to North America. Hickory is a large, strong tree, 18–24 m (60–80 ft) high, with close shaggy bark. It has large pinnately divided leaves, pistillate and staminate flowers, and drooping aments. The fruit is a thick-shelled nut in a tough green husk. Various species are known: *C. ovata*, shagbark hickory, yielding sweeter and better nuts; *C. laciniosa*, kingnut or shellbark; *C. tomentosa*, mockernut, having tough wood; and *C. glabra*, pignut, having bitter, astringent nuts.

Parts of plant used

Bark

Uses

Hickory bark extract (FEMA No. 2577) has been reported used in the following:[3]

non-alcoholic beverages	21–40 ppm
alcoholic beverages	70 ppm
ice cream, ices, etc.	0.01–25 ppm
candy	48 ppm
baked goods	48 ppm
condiments	65 ppm

Regulatory status

GRAS (II)

HOPS

Botanical source *Humulus lupulus* L.

Botanical family *Moraceae*

Foreign names Houblon (Fr.), Hopfen (Ger.), Lupulo (Sp.), Luppolo (It.)

Description Perennial climbing vine that grows wild and also is cultivated extensively in several central European countries, North America, Brazil, and Australia. It has shoots up to 10 m (33 ft) in length, opposite leaves, greenish-yellow flowers (June–September), and ovoidal fruits surrounded by a calix.

Parts of plant used Female flower catkins from the climbing vine and the (lupulin) glandular trichomes dried at 38°C maximum`

Physical-chemical characteristics

Essential oil The oil is present in hops in amounts of approximately 0.5%; yields after distillation range around 0.25%. The oil exhibits different physical-chemical constants depending on the source. The European hop essential oil has the following constants:

Specific gravity	0.825–0.926 at 25°/25°C^{2}	0.855–0.899 at 15°C^{1}
Optical rotation	−2° to +2°5′^{2}	−1° to +2°27′^{1}
Refractive index	1.4700–1.4940 at 20°C^{2}	1.4852–1.4936 at 20°C^{1}
Acid value	$>11^{2}$	0.5–10^{1}
Saponification value	14–69^{2}	
Ester value		13–40^{1}
Solubility		Turbid in 95% alcohol

North American and California varieties exhibit the following characteristics:

	North America	California	
		Lupulin	**Hops**
Specific gravity at 20°C	0.823–0.877^{1}	0.8312^{1}	0.8265^{1}
Optical rotation		−0°73′^{1}	−0°73′^{1}
Refractive index at 20°C	1.4705–1.4856^{1}	1.4735^{1}	1.4720^{1}
Acid value	1–3.6^{1}	0.91^{1}	1.06^{1}
Ester value	44.1–61^{1}	41.3^{1}	41.4^{1}
Solubility	1:3–1:5.4 in 94% ethanol	1:0.95–0.99 in 95% ethanol	

The oil contains β-myrcene, dipentene, α- and β-caryophyllene, humulone, linalool, methyl nonyl ketone, and other substances.

Beer flavor is associated with hops; the bitter flavor is given by the resin, the flavor complex of the essential oil.

Derivatives Infusion (1.5%), fluid extract, tincture (20% in 40% ethanol), concrete, and absolute. The main constituents of lupulin are a bitter resin containing humulone, lupulone, lactaric acid, cerotic acid, and ceryl alcohol.

Organoleptic characteristics Bitter tonic, aromatic flavor.

Uses The large consumption of dried hops is strictly related to the production of beer. To enhance the aromatic value of beer, sometimes the essential oil is added to the finished product. Derivatives may find use in the flavor industry for the formulation of particular bitters, tobacco flavoring, and other products.

Hops oil has been reported used in the following:[3]

non-alcoholic beverages	1.7 ppm
ice cream, ices, etc.	1.7 ppm
candy	2.5 ppm
baked goods	2.9 ppm
chewing gum	2.2 ppm
condiments	20–35 ppm

Hops extract has been reported used in non-alcoholic beverages; 160 ppm.[3]
Hops extract solid has been reported used in the following:[3]

non-alcoholic beverages	8.0 ppm
ice cream, ices, etc.	20–75 ppm
candy	0.70–50 ppm
baked goods	0.80–40 ppm

Regulatory status GRAS (II)

HOREHOUND (HOARHOUND)

Botanical source *Marrubium vulgare* (Tourn.) L.

Botanical family *Labiatae*

Foreign names Marrube blanc (Fr.), Gemeiner Andorn (Ger.), Marrubio blanco, Marroyo (Sp.), Marrubio (It.)

Description Perennial herb indigenous to Britain but commonly growing wild on arid or sandy soils with maritime or mountain climate. The herb is widespread throughout Europe, Asia, and North Africa as well as the United States and Canada.

Parts of the plant used The flowering plant (May–October)

Physical-chemical characteristics

Derivatives Fluid extract and tincture. Marrubiin, a lactone with a diterpene structure, is the characteristic constituent responsible for the pharmacological properties of the extracts.

Organoleptic characteristics Bitter tonic, balsamic

Uses Horehound is used in pharmacology as a replacement for quinine in cases of intolerance for this alkaloid. The extract is used for flavoring beverages and candies. Horehound extract (FEMA No. 2581) has been reported used in the following:[3]

non-alcoholic beverages	8.7 ppm
ice cream, ices, etc.	2.0 ppm
candy	680 ppm
baked goods	2.0 ppm

Regulatory status GRAS (I), (II)

HORSEMINT

Other names Monarda; wild bergamot

Botanical source *Monarda punctata* L.

Botanical family *Labiatae*

Foreign names Monarde ponctueé (Fr.), Monarda (Ger.), Monarda (Sp.), Monarda (It.)

Description Various odorous erect herbs approximately 30–90 cm (12–35 in.) high. *M. punctata* has toothed leaves and large, yellow or white flowers clustered in a few verticles surrounded by bracts. It has petioled, lanceolate leaves narrowing at the base and a nearly smooth corolla, yellowish with the upper lip spotted purple. The plant grows wild in the United States and is used for the extraction of thymol.

Parts of plant used The whole plant

Physical-chemical characteristics

Essential oil The oil is obtained by distillation of the freshly cut or partially dried herb in approximately 1% and 3% yields, respectively. The oil is a yellowish-red to brown liquid with an odor reminiscent of thymol. Its specific gravity at 20°C is 0.930–0.940.[1]

On standing the oil deposits large crystals of thymol (44–61% of the oil). This oil has the following constants:

Specific gravity at 20°C	0.923–0.933[1]
Refractive index at 20°C	1.5020–1.5040[1]
Optical rotation	−2° to +1°[1]

Its main constituents include carvacrol, traces of limonene, and thymol hydroquionone. Other *Monarda* varieties also growing in the United States—*M. fistulosa*, *M. didyma*, and others—contain much less thymol.

Derivatives Fluid extract

Organoleptic characteristics Harsh, burning aromatic flavor; thymol-like odor

Uses Horsemint leaves extract (FEMA No. 2582) has been reported used in nonalcoholic beverages, 600 ppm.[3]

Regulatory status GRAS (II)

HORSERADISH

Botanical source *Armoracia lapathifolia* Gilib. (*Cochlearia armoracia* L. Fries)

Botanical family *Cruciferae*

Foreign names Raifort (Fr.), Petersilienwurzel (Ger.), Rabano picante (Sp.), Rafano rusticano, cren (It.)

Description Perennial, herbaceous plant, native to central-eastern Europe. It has a thick, branched taproot, vertical rhizomes, white flowers, and oval pods.

Parts of plant used Rhizomes and roots

Physical-chemical characteristics

Derivatives Fluid extract, tincture (20% in 25% ethanol), essential oil (experimental production only), and oleoresin. The oil contains sinigrin and sinigrin-derived allyl thioisocyanate, diallyl sulfide, and phenethyl and phenylpropyl thioisocyanate.

Organoleptic characteristics	Sharp, burning, pungent, aromatic flavor; odor similar to mustard seed
Uses	The fresh roots and the various derivatives (although little known) are used in cooking to prepare sharp, piquant sauces.
Regulatory status	GRAS (I)

HYACINTH

Botanical source	*Hyacinthus orientalis* L.
Botanical family	*Liliaceae*
Foreign names	Jacinthe (Fr.), Hyazinthe (Ger.), Jacinto (Sp.), Giacinto (It.)
Description	Bulbous and scapose herbs having a bell-shaped corolla with a prominent tube and short limb. The plant, probably native to Asia Minor or the Balkans, is cultivated extensively for ornamental and extractive purposes, especially in the Netherlands and France.
Parts of plant used	Flowers
Physical-chemical characteristics	
Derivatives	Concrete and absolute. The concrete is extracted from flowers in approximately 0.13–0.22% yields using petroleum ether. It is a greenish-brown, waxy mass. The absolute, prepared by alcoholic extraction of the concrete in approximately 10–14% yields, is a viscous, reddish-brown liquid exhibiting a characteristic, persistent scent of hyacinth flowers.
Organoleptic characteristics	Sweet, floral, slightly green, persistent odor similar to hyacinth flowers
Uses	The concrete and the absolute are used mainly in fine perfumery. Seldom are hyacinth derivatives used in the formulation of aromas for flavoring ice creams and beverages because of their prohibitive cost.
Regulatory status	FDA §121.1163

HYSSOP

Botanical source	*Hyssopus officinalis* L.
Botanical family	*Labiatae*
Foreign names	Hyssope (Fr.), Ysop (Ger.), Hisopo (Sp.), Issopo (It.)
Description	Hyssop is a wild or cultivated shrub native to western Asia; it also grows in the arid and rocky areas of southern Europe. The plant exhibits short, branched rhizomes, opposite leaves, and violet flowers that blossom from July to August. It is 25–70 cm (9–26 in.) high and has a pleasant, aromatic odor.
Parts of plant used	Leaves and flowering tops

Physical-chemical characteristics

Essential oil

It is obtained by steam distillation of the leaves and flowers in low yields (0.15–0.30%). It is a pale-yellow liquid exhibiting an herbaceous, camphor-like odor. The oil contains α- and β-pinene, camphene, hyssopin, and possibly some terpenes, sesquiterpenes, and their alcohols.

Specific gravity at 20°C	0.917–0.965[1]
Refractive index at 20°C	1.4730–1.4860[1]
Optical rotation at 20°C	−6° to −25°[1]
Acid value	<4[1]
Ester value	<36[1]

Organoleptic characteristics

Warm, aromatic, camphor-like odor; warm, sweet, slightly burning flavor

Uses

The dried product and other derivatives are used in the flavor industry for flavoring of sauces, condiments, and canned foods as well as in the formulation of liqueurs. Hyssop has been reported used in bitters, 600 ppm.[3]

Hyssop extract has been reported used in:[3]

non-alcoholic beverages	13 ppm
alcoholic beverages	50 ppm
ice cream, ices, etc.	13 ppm

Hyssop oil has been reported used in:[3]

non-alcoholic beverages	4.7 ppm
alcoholic beverages	5.0–50 ppm
ice cream, ices, etc.	0.25 ppm
candy	14 ppm
baked goods	0.25–33 ppm

Regulatory status

GRAS (I), (II)

ICELAND MOSS

Botanical source

Cetraria islandica (L.) Ach.

Botanical family

Parmeliaceae

Foreign names

Cetrarie d'Islande (Fr.), Islaendisches Moos (Ger.), Liquen de Islandia (Sp.), Lichene islandico (It.)

Description

Perennial plant (lichen) having an erect, branched, gray-greenish thallus. Approximately 12 cm (5 in.) high, the plant grows in rocky areas, woods, and on the bark of conifers in Europe, Iceland, Scandinavia, Greenland, North America, and Asia. It is harvested throughout the year.

Parts of plant used

Thallus

Physical-chemical characteristics

Derivatives

Decoction (3%), fluid extract, tincture (20% in 20% ethanol). The main constituents of the dried product include lichenin, isolichenin, lichenic acids, fatty acid lactones, furan derivatives, and terpene derivatives.

Organoleptic characteristics

Bitter tonic, aromatic

Uses

The bitter-tonic action is exploited in the formulation of specific aromas for liqueurs and bitters.

Regulatory status

FDA §121.1163. In alcoholic beverages only

IMMORTELLE (HELICHRYSUM)

Botanical source

Helichrysum angustifolium DC.

Botanical family

Compositae

Foreign names

Helichrysum Immortelle (Fr.), Helichrysum (Ger.), Perpetua amarilla (Sp.), Elicrisio, Semprevivo (It.)

Description

Small plant growing wild or cultivated in the Mediterranean basin, Africa, and central Asia. Several species of helichrysum are known: *H. italicum* Don., *H. stoechas* DC., *H. kilimandjari*, and *H. arenarium* Mch. *H. italicum*, which could be identified with *H. angustifolium* DC., is a small, densely branched shrub bearing numerous yellow-colored flowers.

Parts of plant used

The flowering tops

Physical-chemical characteristics

Essential oil

The oil, steam distilled from the fresh flowering tops, is a pale-yellow liquid with a strong, pleasant odor. Its main constituents include free and esterified nerol, furfural, eugenol, linalool, valeric aldehyde, and *d*-pinene. The physical-chemical characteristics of the oil vary widely, even between essential oils distilled from the same helichrysum varieties of different origin. An oil of Dalmatian production has the following constants:

Specific gravity at 15°C	0.901–0.911[1]
Optical rotation	−2°20′ to +0°10′[1]
Refractive index at 20°C	1.4735–1.4759[1]
Acid value	0.9–2.8
Ester value	115.7–122.3
Ester value (after acetylation)	141.9–150.3
Solubility	1:0.5 in 90% alcohol

Derivatives

Fluid extract, tincture, concrete, absolute. The concrete and absolute are produced only on a very limited (mostly experimental) scale.

Organoleptic characteristics

Intense, pleasant, sweet odor with a fruity undertone

Uses

The absolute and the essential oil are used in perfumery. The extracts and the essential oil are used as modifiers for certain types of fruit flavors for beverages, pastry, ice cream, and candy. Immortelle extract (FEMA No. 2592) has been reported used in the following:[3]

non-alcoholic beverages	5.2 ppm
ice cream, ices, etc.	16 ppm
candy	11 ppm
baked goods	15 ppm
gelatins and puddings	0.01 ppm
chewing gum	0.50 ppm

Regulatory status

GRAS (II)

IMPERATORIA

Botanical source	*Peucedanum ostruthium* (L.) Koch. (*Imperatoria osthruthium* L.)
Botanical family	*Umbelliferae*
Foreign names	Imperatoire (Fr.), Meisterwurz (Ger.), Imperatoria (Sp.), Imperatoria (It.)
Description	Perennial herbaceous plant, widespread in the mountainous areas of central and southern Europe. Imperatoria may reach 1 m (39 in.) in height. It has woody rhizomes, erect cylindrical stem, alternate leaves, and white and pinkish flowers blossoming from June to July.
Parts of plant used	Rhizomes
Physical-chemical characteristics	
Derivatives	Decoction (5%), infusion (8%), distillate (in 55% ethanol), and tincture (20% in 60% ethanol)
Organoleptic characteristics	Tonic-like
Uses	The dried product and its derivatives are used in the formulation of liqueurs (bitters).
Regulatory status	FDA §121.1163. In alcoholic beverages only

IVA

Other names	Musk yarrow
Botanical source	*Achillea moschata* Jacq.
Botanical family	*Compositae*
Foreign names	Achillea musquee (Fr.), Feldgarbe (Ger.), Achillea musgada (Sp.), Achillea muschiata (It.)
Description	Herbaceous plant growing 15–20 cm (6–8 in.) high, with alternate leaves, white corymb-like flowers, and oblong achenes. The plant blooms between July and August. Iva is often harvested and mistaken for other *Achillea* species, such as *A. herba-rota* All., *A. nana* L., and *A. clavenae* L. These species are similarly aromatic and sometimes offered commercially under the name of Genepi, a term that should be reserved only for *Artemisia glacialis* L.
Parts of plant used	Leaves and flowering tops
Physical-chemical characteristics	
Essential oil	Little known; obtained by steam distillation of the flowers. The oil is blue-green when freshly distilled but fades on aging. The odor is warm and herb-like, resembling hops and tansy oils. Some constituents include borneol, cineol, and ivain.
Derivatives	Infusion (3%), tincture (10% in 60% alcohol), fluid extract, and essential oil

Organoleptic characteristics Bitter tonic, aromatic

Uses Because of its bitter tonic, aromatic flavor, iva once was employed together with other herbs for the manufacture of bitters and liqueurs, such as Benedictine and Chartreuse.

Regulatory status FDA §121.1163. In alcoholic beverages only

JASMINE

Botanical source *Jasminum officinale* L. and other species of *Jasminum*

Botanical family *Oleaceae*

Foreign names Jasmin (Fr.), Jasmin (Ger.), Jazsmin (Sp.), Gelsomino (It.)

Description Jasmine grows extensively around the Mediterranean basin, especially on the Cote Azure and in Sicily. Today the entire Mediterranean area is actively participating in the cultivation of jasmine. The plant normally grows fairly tall; to facilitate the harvesting of the white odoriferous flowers, the plant is pruned so as not to exceed 1–1.5 m (39–59 in.) high. Cultivation is done by transplanting from greenhouses into areas where adequate irrigation is available and where the temperature never drops below 5°C. The species *J. grandiflorum* is sometimes grafted onto *J. officinale* to render the latter more resistant to harsher atmospheric conditions. Jasmine normally blooms from June to September.

Parts of plant used Flowers, which must be harvested before dawn

Physical-chemical characteristics

Derivatives Concrete and absolute essence. The concrete is extracted from flowers using petroleum ether with an average yield of approximately 3%. It is a waxy, brownish-red mass. It smells like jasmine and is partially soluble in 95–96% ethanol.

The absolute essence is obtained by extraction of the concrete with 95–96% ethanol using special techniques. The yields range between 42% and 55%. The physical-chemical constants of the absolute essence vary depending on the origin of the concrete essence. The absolute derived from Italian concrete (yield, approximately 55%) is a yellowish-brown liquid with the following constants:

Specific gravity at 20°C	0.935–0.948[1]
Optical rotation	+3°6′ to +3°54′[1]
Refractive index at 20°C	1.4850–1.4912[1]
Acid value	11–15[1]
Ester value	115–142[1]

It contains alcohols (nerol, nerolidol, terpineol, etc.), benzaldehyde, benzylacetate, linalyl acetate, phenols (*p*-cresol, eugenol), acids, and ketones (jasmone). By distilling the absolute essence with superheated steam at reduced pressure (35–40 mm Hg) and at 88–92°C, an essential oil is obtained in yields up to 23.5%, based on the original concrete.

Organoleptic characteristics Warm, intensely floral aroma

Uses The absolute essence is of great importance in perfumery; it also is used in the formulation of compounded flavors for liqueurs and pastry.

Jasmine absolute has been reported used in the following:[3]

non-alcoholic beverages	0.41 ppm
ice cream, ices, etc.	1.3 ppm
candy	0.80 ppm
baked goods	2.9 ppm
gelatins and puddings	0.10–0.50 ppm
chewing gum	30 ppm

Jasmine concrete has been reported used in the following:[3]

non-alcoholic beverages	0.70 ppm
ice cream, ices, etc.	1.0–1.5 ppm
candy	1.0–3.4 ppm
baked goods	1.0–15 ppm
gelatins and puddings	1.0 ppm

Jasmine oil has been reported used in the following:[3]

non-alcoholic beverages	0.63 ppm
ice cream, ices, etc.	1.6 ppm
candy	3.0 ppm
baked goods	9.3 ppm
gelatins and puddings	0.50–1.0 ppm
chewing gum	1.4 ppm
jellies	0.25 ppm

Jasmine spiritus has been reported used in the following:[3]

non-alcoholic beverages	1.0 ppm
alcoholic beverages	60–2,000 ppm
ice cream, ices, etc.	0.75 ppm
candy	3.0 ppm
baked goods	4.0 ppm
gelatins and puddings	1.0 ppm
condiments	60 ppm
maraschino cherries	10 ppm

Regulatory status GRAS (II)

JUNIPER

Botanical source *Juniperus communis* L.

Botanical family *Pinaceae* (*Cupressaceae*)

Foreign names Genievre commun (Fr.), Heide Wacholder (Ger.), Enebro (Sp.), Ginepro (It.)

Description Thickly branched tree resembling a shrub that may reach several meters in height. Juniper grows in dry areas in Europe, Asia, Africa, and North America. It has an irregular stem, leaves terminated by a sharp thorn, and round blue-violet berries.

Parts of plant used Berries (more or less ripe), wrinkled or dried

Physical-chemical characteristics

Essential oil The oil should be obtained exclusively by steam distillation of the non-fermented berries; because of extensive gin production (obtained from fermented and subsequently distilled berries), the oil results as a by-product of gin distillation. The by-product oil is much less aromatic, lacking the oxygenated fractions. It is almost entirely insoluble in dilute alcohol, even after subsequent rectification, and is not suitable in the formulation of compounded oils.

The essential oil obtained by steam distillation of the dried ripe berries is a colorless to yellow liquid with characteristic odor and an aromatic bitter taste. Its physical-chemical constants follow:

Specific gravity at 25°/25°C	0.854–0.879[2]
Refractive index at 20°C	1.4740–1.4840[2]
Optical rotation	0° to −15°[2]
Solubility	1:4 in 95% ethanol[2]

The oil yield by steam distillation is lower in the case of non-fermented berries (0.5–0.6%) as compared to fermented berries (0.8–1.6%). The dried product of Italian origin may yield up to 2.6% essential oil. The oils in general contain β-pinene, myrcene, *d*-limonene, cymene, camphene, α-terpineol, borneol, and α- and γ-cadinene; the constituents vary, depending on the origin of the plant. The terpeneless or sesquiterpeneless essential oils are destined for specific applications.

Derivatives Infusion (1–3%), distillation waters, distillate (in 60–75% ethanol), and fluid and soft aqueous extracts.

Organoleptic characteristics Aromatic, bitter taste

Uses The distillate is used in the preparation of liquors, as are the terpeneless and sesquiterpeneless essences. The oil is used in the flavoring of special confections and candies.

Juniper berries have been reported used in the following:[3]

alcoholic beverages	60–2,000 ppm
condiments	60 ppm

Juniper extract has been reported used in the following:[3]

non-alcoholic beverages	53 ppm
ice cream, ices, etc.	5.0 ppm
candy	5.0 ppm
baked goods	5.0 ppm

Juniper oil has been reported used in the following:[3]

non-alcoholic beverages	32 ppm
alcoholic beverages	95 ppm
ice cream, ices, etc.	1.9 ppm
candy	4.3 ppm
baked goods	11 ppm
gelatins and puddings	0.01 ppm
chewing gum	0.10 ppm
meats	20 ppm

Regulatory status GRAS (II)

KOLA NUT (COLA NUT)

Botanical source *Cola acuminata* Schott and Endl. and other *Cola* species

Botanical family *Sterculiaceae*

Foreign names Cola (Fr.), Kola (Ger.), Cola (Sp.), Çola (It.)

Description The trees of kola nut are divided into two species. *C. nitida* is the most important and valuable species; its fruits are called large cola nuts. *C. nitida* grows wild in the forests of the Ivory Coast and is cultivated in several areas of tropical Africa and South and Central America.

C. acuminata is the other species; its fruits are called small cola nuts. *C. acuminata* grows wild or is cultivated in Angola, Congo, and other tropical areas in Africa.

Parts of plant used Seeds

Physical-chemical characteristics

Derivatives Tincture (20% in 60% ethanol) and fluid, soft, and dried extracts (also tannin-free). Its main constituents include caffeine, theobromine, theophylline, xanthine, and tannin.

Organoleptic characteristics Bitter flavor

Uses The kola derivatives (usually tannin-free) are employed in the formulation of compounded flavors for bitters, aperitives, and popular carbonated beverages. Kola nut extract has been reported used in the following:[3]

non-alcoholic beverages	120 ppm
ice cream, ices, etc.	220 ppm
candy	160 ppm
baked goods	150 ppm

Regulatory status GRAS (II)

LABDANUM

Botanical source *Cistus* species—*Cistus ladaniferus* L., *C. creticus*

Botanical family *Cistaceae*

Foreign names Ladanum (Fr.), Ladanum (Ger.), Labdano (Sp.), Labdano (It.)

Description Shrubs growing in thickets in several Mediterranean islands (Crete, Cyprus) and countries (Spain particularly). In the Spanish region of Zamora, *C. ladaniferus* L. and its varieties—*C. albiflorus* Dun., *C. stenophyllus* Dun., *C. maculatus* Dun.—are predominant. On the other hand, the extractive use of *C. creticus* growing on the island of Crete is steadily decreasing.

Labdanum resin consists of the secretion of the glandular hairs covering the inferior part of the leaves (spring and summer). The hairy leaves and twigs are treated with boiling water, and the floating resin is skimmed from the surface. Crude labdanum resin is a dark-brown, semi-solid mass with a very pleasant, balsamic odor reminiscent of ambergris and a bitter taste.

In the past the resin was harvested by using a special whip (consisting of several leather strips) to flog the plant. The leather strips would become impregnated with the gum resin, which was subsequently shaved off with special blades. This method is no longer used. To prepare a colorless product, the crude resin can be extracted with filtered ligroin, and finally the solvent is evaporated.

Parts of plant used Leaves and twigs from which the gum resin is removed. The gum resin is used to prepare derivatives.

Physical-chemical characteristics

Essential oil The oil, obtained by steam distillation of the crude gum resin, is a bright-yellow liquid that turns brown with age. It has a strong, balsamic odor reminiscent of ambergris on dilution. Physical-chemical constants of the oil follow:

Specific gravity at 25°/25°C	0.905–0.993[2]
Refractive index at 20°C	1.4920–1.5070[2]
Optical rotation	0°15′ to +7°[2]

Acid value	18–86[2]
Ester value	31–86[2]
Solubility	1:0.5 in 90% ethanol[2]

An essential oil, called cistus oil, is also steam distilled directly from the dried leaves and twigs. This oil is a pale-orange liquid with a characteristic herbaceous odor reminiscent of camomile. It has the following constants:

Specific gravity at 15°C	0.9450 (0.9443)[1]
Refractive index at 20°C	1.4900[1]
Optical rotation	−2°36′ (−3°48′)[1]
Acid value	16.8 (14.56)[1]
Ester value	22.4 (32.9)[1]
Solubility	1:0.5 in 90% ethanol (with haze)[1]

The main constituents that have been identified in labdanum oil are terpenes, benzaldehyde, acetophenone, a ketone with a peppermint odor, acetic acid, and eugenol.

Derivatives

Concrete

The concrete is prepared by hydrocarbon extraction of dried (in the shade) and comminuted leaves and twigs. It is a dark-green mass with a pleasant, balsamic, herbaceous odor. The physical-chemical constants vary widely, depending on the source.

Acid value	71.4–72.8[1]
Ester value	94.3–95.6[1]
Saponification value	167.1[1]
Solubility	85–95% in 95% alcohol[1]

Absolute

The absolute is prepared by alcoholic extraction of the concrete in approximately 55–60% yields. The absolute consists of a semisolid, olive-green mass with a characteristic ambergris odor.

Resinoid and Resin Absolute

The resinoid consists of the hydrocarbon extract of the crude resin. The resin absolute consists of the alcoholic extract of the crude labdanum resin. Since this product is a semi-solid, non-pourable mass, a high-boiling, odorless solvent may be added prior to evaporation of the alcohol to prepare a pourable liquid.

Organoleptic characteristics

Sweet, herbaceous, balsamic odor reminiscent of ambergris with a rich, lasting, animal-like undertone

Uses

The various derivatives (the resinoid and the absolute in particular) and the essential oil are used extensively in perfumery because of their remarkable fixative properties. The oleoresin, the absolute, and the essential oil find application in flavoring candy, beverages, and ice creams. Labdanum absolute (FEMA No. 2608) has been reported used in the following:[3]

non-alcoholic beverages	2.8 ppm
ice cream, ices, etc.	9.8 ppm
candy	5.6 ppm
baked goods	23 ppm
gelatins and puddings	0.06 ppm
chewing gum	1.0–19 ppm

Labdanum oil (FEMA No. 2609) has been reported used in the following:[3]

non-alcoholic beverages	0.41 ppm
ice cream, ices, etc.	0.78 ppm
candy	2.0 ppm
baked goods	0.75 ppm

Labdanum oleoresin (FEMA No. 2610) has been reported used in the following:[3]

non-alcoholic beverages	2.7 ppm
ice cream, ices, etc.	2.0 ppm
candy	5.5 ppm
baked goods	4.0 ppm

Regulatory status — FDA §121.1163

LAUREL

Other names — Bay; sweet bay

Botanical source — *Laurus nobilis* L.

Botanical family — *Lauraceae*

Foreign names — Laurier (Fr.), Lorbeer (Ger.), Laurel (Sp.), Lauro nobile or alloro (It.)

Description — Laurel is an evergreen native to the eastern Mediterranean and cultivated extensively throughout the Mediterranean basin for ornamental purposes. The plant has erect branches; alternate, spear-shaped leaves; yellow or white flowers; and ovoidal fruits (berries) that are black when ripe.

Parts of plant used — Leaves and berries

Physical-chemical characteristics

Essential leaf oil — Obtained by steam distillation with yields between 0.5–1.0%; higher yields are also possible. It is a yellow liquid with a characteristic odor and taste (also see Reference 2). Its main constituents include α-pinene, α-phellandrene, *l*-linalool, cineol (50–70%), geraniol, and eugenol. An oil also is obtained by steam distillation of the berries, but is of little or no use.

Specific gravity at 15°C	0.912 –0.926[1]
Refractive index at 20°C	1.4469–1.4695[1]
Optical rotation	−16°16′ to −18°11′[1]
Saponification value	13–36.6[1]
Solubility	1:1 in 80% ethanol

Bay laurel essential oil should not be confused with the oil of West Indian bay (*Pimenta racemosa*). The latter is quite different in aromatic character.

Derivatives — Infusion (2%), fluid extract, and oleoresin.

Organoleptic characteristics — Aromatic, spicy odor and flavor

Uses — The use of the derivatives in general (and in some cases the oil) is very important for flavoring cured meats, sauces, condiments, preserves, and pastries. The leaves are used in cooking. The oil from berries contains fatty acids used for soap and candle manufacture. Laurel berries have been reported used in non-alcoholic beverages, 450 ppm.[3] Laurel leaf extract has been reported used in spiced vegetables, 5.0 ppm [3]

Regulatory status — Berries: GRAS (II)
Leaves: GRAS (I), (II)

LAVANDIN

Botanical source — *Lavandula hybrida* Rev., hybrid between *L. latifolia* Vill. (spike lavender) and *L. officinalis* Chaix (true lavender)

Botanical family

Labiatae

Foreign names

Lavandin (Fr.), Lavandin (Ger.), Lavandin (Sp.), Lavandino (It.)

Description

Herbaceous hybrid plant that is a cross between lavender and spike lavender. It grows in several varieties, a few of which resemble lavender, while others resemble spike lavender.

Originally the plant grew wild as the result of natural cross-pollination. Today lavandin is cultivated almost exclusively in southern France (Var, Vaucluse, and Drome). Lavandin production from other Mediterranean countries (Italy, Yugoslavia, Spain) is very limited compared to French production.

In the past distillation of lavandin yielded a typical essential oil, the so-called normal type. Through the careful selection of lavandin strains having a high ester content, new varieties of lavandin and, therefore, lavandin essential oils with different characteristics have become available. The variety lavandin abrial has attained great importance in recent years. "Ordinary" or "normal" lavandin oil has an ester content (linalyl acetate) ranging on the average between 20 and 22%; lavandin abrial oil has an average ester content of 30–32%. Lavandin oil exhibits 1:1–1:2 solubility in 65% ethanol. The solubility of essential oils from the same growing site has decreased slightly in the past few years, probably because of a morphological evolution of the plant.

Parts of plant used

The flowering herb

Physical-chemical characteristics

Essential oil

Lavandin Oil

Obtained by steam distillation of the flowering stalks, lavandin oil is a pale-yellow to yellow liquid with a strong, lavender-like, but more pronounced camphoraceous odor. Its physical-chemical constants follow (see also reference 2):

Specific gravity at 20°C	0.885–0.896[1]
Refractive index at 20°C	1.4580–1.4660[1]
Optical rotation	−1° to −7°[1]
Ester content (as linalyl acetate)	22[2]
Solubility	1:3 in 70% ethanol[2]

Lavandin Abrial Oil

Also obtained by steam distillation of the plant material in much higher yields, lavandin abrial oil is a pale-yellow to yellow liquid. The odor of this oil is more earthy and camphoraceous than lavandin oil and also is reminiscent of lavender. Its physical-chemical constants are as follows:

Specific gravity at 25°/25°C	0.885–0.893[2]
Refractive index at 20°C	1.4605–1.4640[2]
Optical rotation	−2° to −5°
Ester content (as linalyl acetate)	28–35%[2]
Solubility	1:2 in 70% alcohol[2]

Terpeneless essential oils with an odor very similar to lavender are also produced by careful vacuum distillation to remove camphor and cineol. The main constituents of lavandin include linalool, linalyl acetate, camphor, cineol, borneol, terpenes, and ethylamyl ketone. The terpene fraction (approximately 7%) contains pinene, camphene, limonene, and dipentene.

Derivatives

Concrete and absolute. The concrete is prepared in approximately 1.5–2.0% yields by solvent extraction (benzene, petroleum ether) of the freshly cut flowering herb. It is a dark-green, viscous mass. An absolute is obtained in approximately 45% yields by distillation of the concrete with diethylene glycol.

Organoleptic characteristics Camphoraceous, fresh, herbaceous odor reminiscent of lavender

Uses The oil is used extensively in perfumery as a less expensive substitute for lavender. The concrete and the absolute are used to a much lesser degree for the same application.

Lavandin oil also is used in flavoring candy, beverages, and baked goods. Lavandin oil (FEMA No. 2618) has been reported used in the following:[3]

non-alcoholic beverages	5.5 ppm
ice cream, ices, etc.	12 ppm
candy	18 ppm
baked goods	18 ppm
chewing gum	0.30 ppm

Regulatory status GRAS (I)

LAVENDER

Botanical source *Lavandula officinalis* Chaix

Botanical family *Labiatae*

Foreign names Lavande (Fr.), Lavendel (Ger.), Lavanda (Sp.), Lavanda (It.)

Description Wild or cultivated shrub having erect, branched stems with a woody lower portion; opposite, whitish-green, narrow leaves; lilac-purple flowers in glomerulate spikes placed at the tip of branches. The plant grows in Mediterranean areas (French-Italian Alps), England, North America, North Africa, and several European countries.

Parts of plant used Flowering tops and stalks

Physical-chemical characteristics

Essential oil The essential oil is obtained by steam distillation of the freshly cut flowering tops and stalks. (A terpeneless oil also is prepared by carefully distilling the essential oil under vacuum.) It is a pale-yellow to yellow-amber, mobile liquid with an ester-like, slightly camphoraceous odor. The yields in essential oil range between 0.6%–1%. The physical-chemical constants vary, depending on the source. A lavender oil of French origin has the following constants:

Specific gravity at 20°/20°C	0.876–0.894[1] (0.876–0.892)[6]
Optical rotation at 20°C	-3° to -11°[1] (-5° to -11°)[6]
Refractive index at 20°C	1.458–1.464[1] (1.4570–1.4640)[6]
Acid value	0.8 max.[1]
Ester content (as linalyl acetate)	30–60% (35–60%)[6]
Solubility	1:2 to 1:3 in 70% ethanol (1:2 in 75% ethanol)[6]

The main constituents of lavender include *l*-linalool, *l*-linalyl acetate, probably furfural, valeric aldehyde, amyl alcohol, α-pinene, cineol, small amounts of *d*-borneol, geraniol, terpenes, and traces of coumarin.

The English lavender oil is distilled from a different lavender variety, *L. intermedia* Loisel. It has a higher linalool, but a lower linalyl ester content that seldom exceeds 10%; French lavender contains from 30% to 60% esters. Lavender essential oil does not withstand prolonged aging. Use of the product within 12–15 months from preparation is advisable. Several hybrid lavender varieties are used today for distillation. These oils are commercially available under different trade names that define somewhat the characteristics of the oil. In France the main types offered commercially are Matheronne and Maillette.

Derivatives

Infusion, tincture, concrete, and absolute. By extraction with benzene or other solvents of the partially dried flowering herb, the concrete is prepared in approximately 1.5–2.0% yields. The absolute is prepared from the concrete in approximately 50–60% yields. The concrete is a more or less liquid, viscous mass with a dark-green color and sweet, herbaceous odor. The absolute is also dark-green and is, sometimes, decolorized using activated charcoal. The main constituents include linalool, linalyl acetate, coumarin, an umbelliferone methyl ether, and coumaric acid.

Organoleptic characteristics

Sweet, herbaceous, slightly floral odor

Uses

Lavender essential oil concrete and absolute are employed in perfumery—colognes, lotions, etc. They also are used in flavoring chewing gum, beverages, and candy. Lavender (FEMA No. 2619) has been reported used in non-alcoholic beverages, 0.08 ppm.[3]

Lavender absolute (FEMA No. 2620) has been reported used in the following:[3]

non-alcoholic beverages	0.20–7.5 ppm
ice cream, ices, etc.	0.40 ppm
candy	2.0–14 ppm
baked goods	2.0–6.3 ppm

Lavender concrete (FEMA No. 2621) has been reported used in the following:[3]

non-alcoholic beverages	0.01–0.20 ppm
ice cream, ices, etc.	0.08 ppm
candy	0.03–0.25 ppm
baked goods	0.25 ppm

Lavender oil (FEMA No. 2622) has been reported used in the following:[3]

non-alcoholic beverages	2.9 ppm
ice cream, ices, etc.	7.8 ppm
candy	5.5 ppm
baked goods	8.3 ppm
chewing gum	220 ppm

Regulatory status

GRAS (I), (II)

LAVENDER, SPIKE

Botanical source

Lavandula latifolia Vill. (*L. spica* DC.)

Botanical family

Labiatae

Foreign names

Aspic (Fr.), Spik (Ger.), Espieglo (Sp.), Spigo (It.)

Description

Herbaceous plant, morphologically very similar to *L. officinalis* (lavender). Spike lavender grows wild in the mountain areas around the Mediterranean basin, especially in Spain and France. It differs from lavender because of its thicker and taller stems and its less blue, more gray flowering tops.

Parts of plant used

Flowering tops

Physical-chemical characteristics

Essential oil

The oil is obtained by steam distillation of the sun-dried flowering tops. It is a pale-yellow to slightly amber liquid with a camphoraceous, herbaceous, earthy odor reminiscent of lavender. The physical-chemical constants vary somewhat, depending on the source. An oil of Spanish origin has the following constants (see also reference 2):

Specific gravity at 20°C	0.894–0.918[1] (0.895–0.907)[6]
Optical rotation at 20°C	-6° to +8°[1] (+1° to +4°)[6]
Refractive index at 20°C	1.4640–1.4680[1] (1.4630–1.4670)[6]
Acid value	<0.8[1] (1.0 max)[6]
Ester content (as linalyl acetate)	1–10.5%[1]
Solubility	1:1.5–2.5 in 70% ethanol[1]

The main constituents include, in order of decreasing importance, linalool, linalyl esters, cineol, pinene, camphor, small amounts of terpene alcohols, geraniol, and sesquiterpenes.

The spike lavender essential oil, also known as aspic oil, has lost most of its commercial value because of the increasing production of the less expensive lavandin essential oil.

Organoleptic characteristics

Characteristic camphoraceous, fresh odor similar to lavender and rosemary.

Uses

Spike lavender oil is used mainly in perfumery (soaps, disinfectants, room deodorants, etc.). The oil blends well with lavender, lavandin, petitgrain, and conifer essential oils. Spike lavender oil is preferred to lavender oil in the formulation of aromas for flavoring candy, beverages, ice cream, and baked goods. Spike lavender oil (FEMA No. 3033) has been reported used in the following:[3]

non-alcoholic beverages	10–11 ppm
ice cream, ices, etc.	10–44 ppm
candy	18 ppm
baked goods	33–50 ppm

Regulatory status

GRAS (II)

LEMON

Lemon Peel and Lemon Petitgrain

Botanical source

Citrus limonum (L). Burm. f.

Botanical family

Rutaceae

Foreign names

Citron (Fr.), Zitrone (Ger.), Limon (Sp.), Limone (It.)

Description

Evergreen tree (shrub) native to the Far East; actual growing site questionable. It was introduced into the Mediterranean region at the time of the Crusades. The plant grows to 6 m (20 ft) high. It has strong, branched roots and an erect trunk with several branches; the lower limbs are sometimes covered with thorns. The tree has alternate oval leaves, white flowers (from February to October), and oval fruits that are yellow when ripe. The rind of the fruits is thin, and the epicarp is rough; the segmented endocarp contains a sour juice and oval seeds.

Parts of plant used

Leaves (and terminal twigs), fruits, and rind

Physical-chemical characteristics

Lemon Petitgrain

Lemon petitgrain is obtained by steam distillation of the leaves. It has small, terminal twigs and small, unripe fruits with yields varying between 0.16–0.23%. It is a clear, mobile, pale-yellow or amber liquid exhibiting the characteristic odor of the leaves.

Specific gravity at 20°C	0.865–0.890[1]
Refractive index at 20°C	1.472–1.475[1]
Optical rotation at 20°C	+15° to +25°[1]
Solubility	1:1 or more in 85% ethanol[1]
Acid value	<1.5[1]
Ester content	14–29%[1]

For flavoring use lemon petitgrain oil must be terpeneless. Its main constituents include *d*-α-pinene, camphene, *d*-limonene, dipentene, *l*-linalool, geraniol, nerol, and the corresponding acetates, esterified cineol, and citral.

Lemon Essential Oil

Lemon essential oil is obtained by cold expression (mechanical or manual) of the peel in yields of approximately 4% based on the weight of the fruit. (A less valuable quality of oil is obtained by steam distillation of the peel.) The expressed oil is a mobile, clear liquid that may become turbid on cooling; it is pale-yellow or greenish-yellow. The physical-chemical constants of lemon essential oil vary, depending on the source of the fruit—Spain, California, Florida, Israel, Italy. The Italian quality exhibits the following constants:

Specific gravity at 20°C	0.852–0.858[1]
Refractive index at 20°C	1.474–1.476[1]
Optical rotation at 20°C	+57° to +65°[1]
Evaporation residue	1.5–3.6%[1]
Acid value	1.4 max[1]
Aldehyde content (as citral)	3–5%[1]

To date more than 40 constituents have been identified in the oil, which contains approximately 90% limonene (by weight). Other important terpenes include α- and β-pinene, myrcene, citral, and γ-terpinene. The non-volatile residue contains citropten (or limettin). From the normal essential oil the terpeneless and sesquiterpeneless oils are obtained by vacuum rectification, washing with dilute alcohol or by column chromatography. Rectification is important to achieve a product with good solubility. Terpeneless oils are also more stable, as they are less sensitive to oxidation.

Soluble essences are prepared by using low-strength ethanol with yields of 1/50, 1/100, 1/200, and 1/400 with reference to formulated syrups.

Derivatives

Using typical extraction techniques, a fluid extract and a tincture (20% in 70% ethanol) are obtained from the dried peel. By properly compounding the essential oil (raw or terpeneless), juice, pectins, and sugars, it is possible to prepare pastes suitable for flavoring carbonated beverages.

The preparation of lemon juice is similar to that of orange.

Evaporation residue	7.5–8.5%[1]
Acid content (as citric acid monohydrate)	4.5–6.5%[1]

It is sold "as is" after stabilization with SO_2 or as concentrates of various strengths.

Organoleptic characteristics

Characteristic lemon-leaf odor; sour, bitter taste

Uses

The fresh fruit is common in cooking, valued for its juice and oil content. The fruit is worked into syrups, and in some instances the peel is candied. The dried peel is used to prepare the tincture and is blended with other flavor ingredients in the formulation of liqueurs. However, the tincture and the fluid extract are used mainly in the formulation of liqueurs. The soluble essences are used to prepare syrups; pastes are used for flavoring carbonated beverages. The oil is used in large quantities in the flavoring of hard candies, pastry, and baked goods.

Lemon extract, *Citrus limonum* (L.) Burm. f., has been reported used in the following:[3]

non-alcoholic beverages	1,000 ppm
ice cream, ices, etc.	540–4,000 ppm
candy	400–12,000 ppm
baked goods	8,900 ppm
icings	10,000 ppm

Lemon oil has been reported used in the following:[3]

non-alcoholic beverages	230 ppm
ice cream, ices, etc.	380 ppm
candy	1,100 ppm
baked goods	580 ppm
gelatins and puddings	340 ppm
chewing gum	1,900 ppm
breakfast cereals	140 ppm
meats	25–40 ppm
condiments	10–80 ppm
syrups	65 ppm
icings	65–600 ppm

Terpeneless lemon oil has been reported used in the following:[3]

non-alcoholic beverages	13 ppm
ice cream, ices, etc.	25 ppm
candy	68 ppm
baked goods	50 ppm
gelatins and puddings	80 ppm
chewing gum	110–670 ppm
toppings	1,000 ppm

Citrus peel extract (*Citrus* species) has been reported used in the following:[3]

non-alcoholic beverages	190 ppm
ice cream, ices, etc.	420 ppm
candy	480 ppm
baked goods	480 ppm

Lemon petitgrain oil has been reported used in the following:[3]

non-alcoholic beverages	8.6 ppm
ice cream, ices, etc.	9.3 ppm
candy	35 ppm
baked goods	35 ppm

Regulatory status

Lemon: GRAS (II)
Lemon peel: GRAS (II)
Petitgrain lemon: GRAS (II)

LEMONGRASS

Botanical source

1. *Cymbopogon citratus* DC or *Andropogon nardus* var. *ceriferus*—West Indian type
2. *C. flexuosus* (Nees.) Stapf. or *Andropogon nardus* var. *flexuosus*—East Indian type

Botanical family

Gramineae

Foreign names

Lemongrass (Fr.), Lemongras (Ger.), Lemongrass (Sp.), Lemongrass (It.)

Description

Herbaceous grasses that grow wild in several tropical and subtropical regions. The East Indian variety is grown in eastern India, Cambodia, Singapore, and Ceylon.

The West Indian type is grown in Madagascar, the Comoro Islands, Guatemala, Honduras, Brazil, Haiti, and Puerto Rico. The East Indian variety yields an alcohol soluble oil (1:2 in 70% alcohol); West Indian lemongrass is soluble 1:10 in 90% alcohol with haze.

Parts of plant used

Herbaceous portion

Physical-chemical characteristics

Essential oil

The oil is obtained by steam distillation of freshly cut (East Indian variety) or partially dried (West Indian variety) grass in approximately 0.2–0.3% and 0.31–0.37% yields, respectively.

East Indian Lemongrass Oil

East Indian lemongrass oil is a pale-yellow to brown-yellowish liquid; it has a characteristic, sharp, pungent, lemon-like odor because of the large amount of citral present (80–85%). Its physical/chemical constants follow (also see Reference 2):

Specific gravity at 15°C	0.899–0.905[1] (0.885–0.901 at 20°/20°C)[6]
Optical rotation	+1°25′ to -5°[1] (+1° to -3°)[6]
Refractive index at 20°C	1.483–1.488[1] (1.4830–1.4890)[6]
Aldehyde content (as citral)	70–85%[1] (73% min)[6]
Solubility	1:1.5–3 in 70% ethanol[1]

In addition to citral, the main constituents of the East Indian oil include citronellal, geraniol, nerol, farnesol, dipentene, methylheptenone, and probably limonene.

West Indian Lemongrass Oil

West Indian lemongrass oil is a pale-yellow to brownish liquid with a pronounced citral odor. Its physical-chemical constants are as follows (see also reference 2):

Specific gravity at 20°/20°C	0.872–0.900[1] (0.872–0.897)[7]
Refractive index at 20°C	1.4830–1.4890[1]
Optical rotation at 20°C	-3° to +1°[1]
Aldehyde content (as citral)	69%[1] (75% min)[7]

Its main constituents include isovaleric aldehyde, furfural, myrcene, dipentene, methylheptenone, aldehyde C_{10}, citronellal, various esters, linalool, geraniol, nerol, and terpenes.

Organoleptic characteristics

Strong, pungent, lemon-like odor

Uses

In spite of the increasing production of synthetic citral, lemongrass essential oil remains the most important natural source for citral extraction. In turn citral is a very important starting material in the manufacture of ionones and ionone substitutes used extensively in perfumes and flavors. Lemongrass oil is used in the preparation of low-cost perfumes for soap and other laundry products.

The oil is also employed in the formulation of aromas for flavor applications. However, the use of the rectified oil or synthetic citral sometimes is preferred.

Lemongrass oil (FEMA No. 2624) has been reported used in the following:[3]

non-alcoholic beverages	4.4 ppm
ice cream, ices, etc.	9.2 ppm
candy	38 ppm
baked goods	38 ppm
gelatins and puddings	290 ppm
chewing gum	220 ppm

Regulatory status

GRAS (II)

LEMON VERBENA

Botanical source *Lippia citriodora* H.B.K.

Botanical family *Verbenaceae*

Foreign names Verbeine odorante (Fr.), Echtes Verbenenkraut (Ger.), Hierba Luisa (Sp.), Verbena (It.)

Description Small shrub that grows to 1.5 m (5 ft) high. Although native to South America, today it is widespread also in Europe. Lemon verbena has woody stems, opposite lanceolate leaves, externally white and internally reddish-blue flowers, and dry drupes.

Parts of plant used Leaves and twigs

Physical-chemical characteristics

Essential oil Lemon verbena oil is obtained by steam distillation of the freshly cut leaves and twigs in approximately 0.1–0.2% yields. It is a yellow-greenish liquid with a characteristic fresh, lemon-like odor. The main constituents, in addition to citral, include cineol, dipentene, limonene, linalool, borneol, nerol, and geraniol. Its physical-chemical constants follow:

Specific gravity at 20°C	0.883–0.900[1]
Refractive index at 20°C	1.4800–1.4900[1]
Optical rotation at 20°C	−9° to −20°[1]
Aldehyde content (as citral)	20–40%[1]

Derivatives Fluid extract, tincture (20% in 50% alcohol), concrete, and absolute

Organoleptic characteristics Intense, fresh, lemon-like odor

Uses Verbena oil and derivatives (concrete, absolute) find extensive use in perfumery, especially in colognes with a strong citral note. The extract and the tincture are used in the formulation of aromas for liqueurs.

Regulatory status FDA §121.1163. In alcoholic beverages only

LICORICE

Other names Glycyrrhiza

Botanical source *Glycyrrhiza glabra* L. and other varieties

Botanical family *Leguminosae*

Foreign names Réglisse (Fr.), Lakritze (Ger.), Orozuz (Sp.), Liquerizia (It.)

Description Herbaceous plant native to southern Europe; it grows wild in eastern Europe. The plant is 1–2 m (3–7 ft) high and has a large creeping root (the secondary roots are branched), erect stalk, alternate leaves, violet flowers (from June to July), and kidney-shaped seeds.

Parts of plant used Stolons and roots (at least 2 years old)

Physical-chemical characteristics

Derivatives

Juice, fluid and soft extract, and tincture (20% in 20% ethanol). The "juice" consists of the dry extract prepared by extraction of stolons and semi-dried roots with hot water. Licorice is sold commerically in large loaves or cylindrical sticks; it exhibits a sweet, rich taste and light, slightly spiced scent. Its main constituent is glycyrrhizin (the potassium-calcium-magnesium salt of glycyrrhizic acid); commercial glycyrrhizin is the ammonium salt of the acid. Glycyrrhizic acid is a glucoside; on hydrolysis it yields glycyrrhetic acid and two moles of glucuronic acid. In addition licorice roots contain triterpene, flavonoids, and B vitamins.

Organoleptic characteristics

Intensely sweet; the sweetening power comes from glycyrrhizin, which is 50 times sweeter than sucrose.

Uses

In the flavor and food industries the sweetening power of licorice is exploited to enhance or subdue the flavor of some bitter formulations. The use is limited only to small dosages, as the characteristic taste of licorice and its derivatives does not permit indiscriminate use.

The liquid juice, or dry extract, is used often in sweets and in pastry recipes, as it blends with anise and menthol flavors. The sweetening power of licorice cannot be employed in acid foods because of its hydrolysis to the non-sweet constituents of the glycoside.

Licorice extract has been reported used in the following:[3]

non-alcoholic beverages	33 ppm
ice cream, ices, etc.	39 ppm
candy	130 ppm
baked goods	84 ppm
gelatins and puddings	4.0 ppm
chewing gum	29,000 ppm
syrups	50 ppm

Licorice extract powder has been reported used in the following:[3]

non-alcoholic beverages	110 ppm
ice cream, ices, etc.	200 ppm
candy	6,500 ppm
baked goods	200 ppm
chewing gum	22,000 ppm

Licorice root has been reported used in the following:[3]

non-alcoholic beverages	130 ppm
candy	460 ppm
baked goods	75 ppm
chewing gum	3,200 ppm

Regulatory status

Glycyrrhiza: GRAS (I), (II)
Glycyrrhiza, ammoniated: GRAS (II)

LIME

Botanical source

Citrus aurantifolia Swingle

Botanical family

Rutaceae

Foreign names

Limette (Fr.), Limett (Ger.), Lima (Sp.), Limetta (It.)

Description

This citrus plant is widespread especially in Central America, Mexico, Florida, Haiti, and Barbados; it also grows well in India. It is cultivated to a limited extent in Calabria (Italy). The varieties from the different countries of origin can be either sweet or sour. The sour varieties are the most important for extractive purposes. This plant (morphologically similar to those of the citrus family) has the peculiarity of yielding flowers and fruits year-round in Central America. The tree is propagated from seeds or by grafting onto bitter orange. The maximum fruit yield occurs after 10 years.

Parts of plant used

Leaves, small unripe fruits, rinds, juice, and twigs

Physical-chemical characteristics

Essential oils

Petitgrain essential oil of lime can be obtained by distillation of leaves, small terminal twigs, or small unripe fruits with yields of about 0.1%. This oil is used in perfumery and has no practical application in the flavor industry. From the rind of not completely ripe fruits, the essential oil is obtained by expression or distillation: the products are called expressed or distilled oils, respectively. The expressed and distilled oils exhibit different physical-chemical and organoleptic characteristics. A distilled oil also is prepared from the sour juice obtained by expression of the whole fruit. The oil in the juice also can be separated from the juice by centrifugation.

Once the lime industry was based on the preparation of the juice, and the essential oil was only a by-product. Today the production of essential oil, especially the distilled oil, represents the most important item. The distilled oil has the following physical-chemical constants (see also reference 2):

Specific gravity at 20°C	0.854–0.864[1]
Optical rotation at 20°C	+34° to +45°[1]
Refractive index at 20°C	1.474–1.478[1]
Evaporation residue	3% max[1]
Aldehyde content (as citral)	0.5–2.6[1]

The expressed essential oil exhibits the following constants (see also reference 2):

Specific gravity at 20°C	0.874–0.882[1]
Optical rotation at 20°C	+35° to 40°[1]
Refractive index at 20°C	1.482–1.486[1]
Evaporation residue	8–13.5%[1]
Aldehyde content (as citral)	4.5–9%[1] (4.5–13.5%)[6]

The main constituents of the oil are *d*-limonene, α- and γ-pinene, dipentene, C_8, C_9, and C_{10} aldehydes, and citral. The essential oils, independently of manufacturing processes, are rectified under vacuum to remove terpenes in order to improve solubility and permit use for flavoring carbonated beverages. The natural lime juice is stabilized (in some countries) by using sulfur dioxide, or it is concentrated by using known techniques.

Organoleptic characteristics

Intensely fresh, citrus aroma; astringent, sweet-sour flavor

Uses

The raw distilled lime oil is used for flavoring soft and hard candies, bitter chocolates, and pastry products. The largest consumption of the soluble (rectified) essential oil is in the preparation of carbonated and cola-type beverages. Expressed essential oil (also centrifuged) is used mainly as a partial substitute for lemon essential oil; the lime oil contained in the rind closely resembles and blends very well with lemon. Consumption of lime oil is considered somewhat limited as compared to the potential number of possible applications.

Lime oil has been reported used in the following:[3]

non-alcoholic beverages	130 ppm
ice cream, ices, etc.	160 ppm
candy	680 ppm

baked goods	370 ppm
gelatins and puddings	200 ppm
chewing gum	3,100 ppm
condiments	20 ppm

Terpeneless lime oil has been reported found in the following:[3]

non-alcoholic beverages	15 ppm
ice cream, ices, etc.	17 ppm
candy	37 ppm
baked goods	22 ppm
gelatins and puddings	26 ppm
chewing gum	0.10 ppm
syrups	8.0 ppm

Regulatory status GRAS (II)

LINALOE

Botanical family *Bursera delpechiana* Poiss. and other *Bursera* species—*B. aloexylon, B. glabrifolia, B. fagaroides*

Botanical family *Burseraceae*

Foreign names Linaloe (Fr.), Linaloe (Ger.), Linaloe (Sp.), Linaloe (It.)

Description The Mexican linaloe (*Burseraceae*) should not be confused with the so-called linaloe cayenne bois de rose from *Aniba rosaeodora, Lauraceae*.

Linaloe is a branched tree or shrub that grows wild, or sometimes is cultivated, in tropical and subtropical areas at approximately 1,000 m (3,280 ft) above sea level. The oil is partially a pathological product of the plant, since the formation is stimulated by repeated incisions made on the trunk at periodic intervals. The plant bears fleshy fruits, ripening between August and September, that also contain an essential oil.

Parts of plant used The wood

Physical-chemical characteristics

Essential oil The oil is obtained by steam distillation of chipped wood using rudimentary stills with a perforated bottom to avoid prolonged contact of the material with the boiling water; this results in extensive hydrolysis of the ester content (linalyl acetate). The essential oil is obtained in high yields (8% or more).

The oil is a colorless to yellow liquid with a pleasant, rose-like, slightly camphoraceous odor; it has the following physical-chemical constants (see also reference 2):

Specific gravity at 15°C	0.883–0.889[1]
Optical rotation	−5°25′ to −13°8′[1]
Refractive index at 20°C	1.4587–1.4612[1]
Acid value	0.8–2.7[1]
Ester content (as linalyl acetate)	14–27%[1]
Total alcohols (as linalool)	>85%[1]
Solubility	1:4 in 60% ethanol[1]

The main constituents include linalool (60–75%), geraniol, nerol, methylheptenol, methylheptenone, myrcene, and various sesquiterpenes.

An essential oil is also steam distilled from the fruits in approximately 3% yields. This oil differs in chemical composition from linaloe wood oil for its content of dextrorotatory linalool. Mexican linaloe wood oil is often adulterated with the oil from fruits, with Japanese shiu oil, or with Brazilian bois de rose oil (steam distilled from *Aniba rosaeodora* var. *amazonica* Ducke).

Organoleptic characteristics Agreeable, flowery, rose-like odor

Uses Linaloe essential oil is used as a raw material for the extraction of linalool. Because of its stability to alkali, the oil sometimes is employed to scent thioglycolates, lotions, cosmetics, and soaps.

The oil is used in the formulation of aromas (in combination with other rose-scented materials or the essential oil of roses) for candy and beverages.

Linaloe wood oil (FEMA No. 2634) has been reported used in the following:[3]

non-alcoholic beverages	4.3 ppm
alcoholic beverages	1.0 ppm
ice cream, ices, etc.	3.8 ppm
candy	16 ppm
baked goods	15 ppm

Regulatory status Linaloe wood: FDA §121.1163

LINDEN

Botanical source *Tilia* species

Botanical family *Tiliaceae*

Foreign names Tilleul (Fr.), Linde (Ger.), Tilo (Sp.), Tiglio (It.)

Description Several linden species are known: *T. parvi*, *T. ulmifolia*, *T. grandifolia*, *T. argentea*, *T. cordata*, *T. platyphyllos*, and others. Linden is a large tree commonly growing in central and southern Europe and Asia Minor. It has thick bark, alternate ovate leaves, white-yellowish flowers (July), and pubescent capsules.

Parts of plant used Flowers (leaves)

Physical-chemical characteristics

Derivatives Infusion (3%), fluid extract, dried aqueous extract, tincture (20% in 40% ethanol). The essential oil and the concrete essence (of experimental production only) have been reported to contain farnesol.

Organoleptic characteristics Soothing, aromatic flavor

Uses The infusion was used in the past as a beverage and a sedative; the extracts were used to flavor galenic products. The tincture may be employed in liqueur formulations for specific flavoring effects.

Regulatory status Linden flowers: GRAS (I), (II)
Linden leaves: FDA §121.1163. In alcoholic beverages only

LOVAGE

Botanical source *Levisticum officinale* Koch.

Botanical family *Umbelliferae*

Foreign names

Livèche (Fr.), Liebstock (Ger.), Levistico (Sp.), Levistico (It.)

Description

Perennial herbaceous plant that grows wild in several areas of Europe; it is cultivated for extractive purposes in France, Germany, Hungary, Czechoslovakia, Belgium, the Netherlands, and Yugoslavia. It has large leaves with a cylindrical stem, branched upper stalks, rhizome-type roots, and yellow-greenish flowers. It grows to 2 m (7 ft) in height.

Parts of plant used

Rhizomes and other parts of the plant

Physical-chemical characteristics

Essential oil

The oil from the green parts normally is not manufactured and exhibits less interesting characteristics than the rhizome oil. Essential oil from rhizomes can be obtained by steam distillation of fresh or dried rhizomes with yields of 0.1–0.2% or 0.6–1.0%, respectively. It is a yellow-amber to greenish liquid exhibiting a strong odor reminiscent of celery and angelica with a sharp, analogous flavor. The main constituents include *d*-α-terpineol, aldehydes, and acids (acetic and isovaleric).

Specific gravity at 25°/25°C	0.960–0.985[2]
Optical rotation	−1° to +5°[2]
Refractive index at 20°C	1.5360–1.5540[2]
Acid value	2–16[2]
Saponification value	238–258[2]
Solubility	1:2 to 1:4 in 80% ethanol[2]

Derivatives

Extract and oleoresin

Organoleptic characteristics

Intensely persistent, warm, celery-like flavor and aroma

Uses

The oil and the oleoresin are used in the formulation of sauces, bouillons, preserves, and condiments. Lovage has been reported used in the following:[3]

non-alcoholic beverages	4.0–30 ppm
ice cream, ices, etc.	18 ppm
candy	28 ppm
baked goods	25 ppm
syrups	0.08 ppm

Lovage extract has been reported used in the following:[3]

non-alcoholic beverages	8.8 ppm
ice creams, ices, etc.	18 ppm
candy	26 ppm
baked goods	24 ppm
condiments	40 ppm
icings	0.07 ppm
syrups	66 ppm

Lovage oil has been reported used in the following:[3]

non-alcoholic beverages	1.3 ppm
ice cream, ices, etc.	0.60 ppm
candy	0.83 ppm
baked goods	2.4 ppm
condiments	3.7 ppm
icings	10 ppm
syrups	6.8 ppm

Regulatory status

FDA §121.1163

LUNGMOSS

Other names	Lungwort
Botanical source	*Sticta pulmonaria* Ach.
Botanical family	*Boraginaceae*
Foreign names	Mousse pulmonarie (Fr.), Lichene polmonario (It.)
Description	A widely distributed lichen (North and South America, Europe) growing on the trunks of trees in moist sub-alpine regions. In Siberia it is used as a substitute for hops. Lungmoss should not be confused with cow's or bullock's lungwort, which is the common mullein (*Verbascum thapsus*). Other plants belong to a genus of European borages (*Pulmonaria*) believed to have medicinal value in lung disease.
Organoleptic characteristics	Astringent, bitter flavor
Uses	In vermouth flavors
Regulatory status	FDA §121.1163

MAIDENHAIR FERN

Botanical source	*Adiantum capillus-veneris* L.
Botanical family	*Polypodiaceae*
Foreign names	Capillaire, Cheveux de Vénus (Fr.), Frauenhaar (Ger.), Capilera (Sp.), Capelvenere (It.)
Description	Cryptogamous perennial fern, commonly grows in shady and damp places; widespread throughout the fields and hillsides of southern and central Europe. The plant owes its botanical name *Adiantum* (Gr., unwetted) to the property of its foliage to repel rain drops. The fronds have black, shiny, hair-thin stipes and bear numerous wedge-ovate or rhomboid pinnules on the terminal portion.
Parts of plant used	Fronds
Physical-chemical characteristics	
Derivatives	Decoctions, infusions, fluid extract, and tincture. The main constituents include tannic acid, gallic acid, and traces of an essential oil.
Organoleptic characteristics	Pleasant, tonic flavor
Uses	The derivatives are used mainly in the formulation of syrups exhibiting a pleasant flavor. The syrups are employed as flavor modifiers in less palatable aromas. The tincture is used in hair lotions.
Regulatory status	FDA §121.1163. In alcoholic beverages only

MALT EXTRACT

Botanical source	*Hordeum vulgare* L. or other grains
Organoleptic characteristics	Tastes like malt candy balls (chocolate-covered)
Uses	Used in flavors (vanilla, chocolate) and in brewing
Regulatory status	GRAS (II)

MANDARIN

Tangerine and Petitgrain Tangerine or Mandarin

Botanical source	*Citrus reticulata* Blanco
Botanical family	*Rutaceae*
Foreign names	Mandarine (Fr.), Mandarine (Ger.), Mandarina (Sp.), Mandarino (It.)
Description	The plant, native to China, was introduced into Europe after the orange. The tree is cultivated throughout the Mediterranean, where the tangerine variety also grows. Tangerine and mandarin are botanically identical, both being *C. reticulata* Blanco. The mandarin fruit is ellipsoidic, while the tangerine fruit common to the United States is more nearly like the original fruit from China; tangerine is more orange in color than mandarin. In Italy mandarin is cultivated together with other citrus fruits in Sicily and Calabria on an industrial scale.
Parts of plant used	Leaves, small twigs, unripe fruits, fruits, and the rind

Physical-chemical characteristics

Petitgrain Mandarin Oil

The petitgrain essential oil of mandarin is obtained by steam distillation of leaves, small twigs, and unripe fruits with yields of about 0.3%. The oil is produced in several mandarin-growing areas (especially Algeria); however, production is somewhat limited. The oil exhibits a fruital odor and a yellow-amber fluorescent color. The oil contains α-pinene, dipentene, limonene, *p*-cymene, methyl anthranilate, geraniol, and methyl methylanthranilate.

Specific gravity at 20°C	0.978–1.044[1]
Refractive index at 20°C	1.5250–1.5470[1]
Optical rotation at 20°C	+2°30′ to +13°15′[1]
Acid value	<1.4[1]
Ester value	170–250[1]
Methyl methylanthranilate content	49–72%[1]
Solubility	1:4–1:20 in 75% ethanol[1] 1:4–1:12 in 80% ethanol[1]

Expressed Mandarin Oil

Cold expression (hand or mechanical) of rind of almost ripe mandarin fruits yields an average of 0.5% mandarin essential oil. The physical-chemical constants of the oil vary, depending on the source (see reference 2). Mandarin oil of Italian production is a clear, mobile liquid, susceptible to turbidity on cooling; the oil ranges from light-orange to reddish-orange in color, and it exhibits a characteristic mandarin odor (also see reference 2). The oil contains decylaldehyde, γ-phellandrene, *p*-cymene, linalool, terpineol, nerol, linalyl and terpenyl acetate, C_8, C_9, C_{10}, and C_{12} aldehydes, citral, citronellal, and *d*-limonene.

Specific gravity at 20°C	0.850–0.885[1]
Refractive index at 20°C	1.474–1.476[1] (1.4730–1.4770)[6]
Optical rotation at 20°C	$+67^\circ$ to $+73^\circ 5'$[1] ($+64^\circ$ to $+75^\circ$)[6]
Carbonyl content	0.5–1.0%[1] (0.4–1.2%)[6]
Solubility	1:0.3 in 96% ethanol[6]

The expressed oil can be vacuum rectified to remove terpenes and sesquiterpenes, thus increasing the solubility, the yield, and the stability of the oil. (For data on expressed tangerine oil, see reference 2.) Mandarin essential oil paste is prepared by procedures similar to those employed for other citrus oils and has a yield in use of 1 to 100.

Derivatives

The fresh rinds are often extracted with 50–60% ethanol to prepare the tincture and the distillate. A 20% tincture and the fluid extract are obtained from the dried rinds by extraction with 60% ethanol. The soluble essence is obtained by treating mandarin essential oil with low-strength alcohol. The soluble essence has a 1–100 or a 1–200 use yield.

Organoleptic characteristics

Pleasant, orange-like odor; sweet-sour taste

Uses

The fruits are consumed extensively as such, preserved in syrup, or candied. In addition to its use in perfumery with petitgrain mandarin essential oil, the expressed essential oil is used in flavoring hard candies, bitter chocolates, and baked products. The terpeneless and sesquiterpeneless oils are used in perfumery and in the formulation of compounded oils for liqueurs. The soluble essence is employed to prepare syrups and in liqueur formulations. In the latter the tincture and the distillate from fresh rinds, as well as the tincture and the fluid extract from dried rinds, are also used. Mandarin paste is employed in flavoring carbonated beverages. Tangerine oil is used mainly in perfumery and cannot be substituted for mandarin in flavoring.

Mandarin oil (FEMA No. 2657) has been reported used in the following:[3]

non-alcoholic beverages	62 ppm
ice cream, ices, etc.	160 ppm
candy	350 ppm
baked goods	190 ppm
gelatins and puddings	30 ppm
chewing gum	83 ppm

Petitgrain mandarin oil (FEMA No. 2854) has been reported used in the following:[3]

non-alcoholic beverages	4.3 ppm
ice cream, ices, etc.	4.1 ppm
candy	4.5 ppm
baked goods	11 ppm
gelatins and puddings	0.43 ppm

Tangerine oil (FEMA No. 3041) has been reported used in the following:[3]

non-alcoholic beverages	90 ppm
ice cream, ices, etc.	160 ppm
candy	160 ppm
baked goods	250 ppm
gelatins and puddings	20 ppm
chewing gum	810 ppm

Regulatory status

Mandarin: GRAS (II)
Tangerine: GRAS (II)
Petitgrain mandarin or tangerine: GRAS (II)

MAPLE, MOUNTAIN

Botanical source	*Acer spicatum* Lam.
Botanical family	*Aceraceae*
Description	Mountain maple is a tall shrub or small tree with diverging limbs. It grows in the temperate regions of the northern United States and Canada. Its leaves turn bright red in summer. *A. spicatum* should *not* be confused with the better known sugar maple varieties (*A. saccharum* and *A. nigrum*), which produce a sap containing up to 6% sugar. Sugar maples can be distinguished also by their height (up to 40 m [131 ft]), their round head, and their gray bark.
Organoleptic characteristics	Deer tongue-like note (coumarin-like)
Uses	Mountain maple is used in tobacco flavoring. Mountain maple, solid extract (FEMA No. 2757), has been reported used in:[3] non-alcoholic beverages 100 ppm ice cream, ices, etc. 8.0 ppm candy 2.0–60 ppm baked goods 44 ppm
Regulatory status	FDA §121.1163

MARIGOLD, POT

Other names	Calendula
Botanical source	*Calendula officinalis* L. (*Caltha officinalis* Moeuch.)
Botanical family	*Compositae*
Foreign names	Souci (Fr.), Gartenringelblume (Ger.), Calendula (Sp.), Calendola, Fiorrancio (It.)
Description	Annual (sometimes biennial) pubescent herb, growing in the Mediterranean region. The plant is covered with glandular hairs and has yellow-orange flowers, alternate greenish-gray leaves (the superior, lanceolate; the radical, oblong), and spindle-shaped roots. Pot marigold should not be confused with tagetes, known also as marigold.
Parts of plant used	Flowers
Physical-chemical characteristics	
Essential oil	An oil of little or no importance is distilled from the dried flowers in approximately 0.02% yields. The main constituents of the oil include a bitter principle (chemically unidentified), saponins, calendulin (a carotenoid), malic and ascorbic acid, and mucilages.
Derivatives	Concrete (extracted with petroleum ether in approximately 0.12% yields), absolute, juice (cold expressed from the leaves), comminuted dried flowers, tincture (10% in 60–65% alcohol) and a fluid extract.
Organoleptic characteristics	Intense herbaceous odor with a slightly bitter, tonic flavor

Uses

The essential oil and the concrete do not have practical applications. The dried product, tincture, and fluid extract are used in the formulation of special aromas. Pot marigold (FEMA No. 2658) has been reported used in the following:[3]

non-alcoholic beverages	11 ppm
ice cream, ices, etc.	44 ppm
candy	33 ppm
baked goods	33 ppm

Regulatory status

GRAS (I)

MARJORAM, POT

Botanical source

Majorana onites (L). Benth. (*Origanum vulgare* L.)

Botanical family

Labiatae

Description

Commonly referred to as *O. vulgare*, pot marjoram appears to be very little known in the United States. *O. vulgare* is a branching, hardy perennial about 2 ft tall, bearing in midsummer pink or purple flowers and small brown oval seeds. It grows wild on the borders of European woods. The plant has a pleasant odor and warm, aromatic, bitter taste.

Parts of plant used

Leaves and shoots

Organoleptic characteristics

It is more sweetly aromatic than *O. majorana*, or *M. hortensis*. The highly aromatic leaves and young shoots are used in the same manner as sweet marjoram (*O. majorana*).

Uses

Pot marjoram, *O. vulgare* L. (FEMA No. 2660), has been reported used in various seasonings.[3] The oil is used in perfuming soaps.

Regulatory status

GRAS (I)

MARJORAM, SWEET

Botanical source

Origanum majorana L. (*Majorana hortensis* Moench.)

Botanical family

Labiatae

Foreign names

Marjolain (Fr.), Marjoran (Ger.), Mejorana (Sp.), Maggiorana (It.)

Description

Herbaceous, perennial plant; annual or biennial in Europe. Native to western Asia and northern Africa, sweet marjoram grows to 0.5 m (20 in.) in height. It has an oblique rhizome, shrub-like stalks, opposite leaves, and white or red flowers (June–September) in clustered bracts.

Parts of plant used

The flowering plant

Physical-chemical characteristics

Essential oil

The oil, obtained by steam distillation with yields of usually less than 0.3%, is a yellow or yellow-greenish liquid. It contains linalool, methyl chavicol, cineol, eugenol, and terpineol. (See also reference 2.)

Specific gravity at 20°C	0.886–0.902[1]
Refractive index at 20°C	1.4700–1.4760[1]

Optical rotation at 20°C	+13° to +24°[1]
Acid value	<1.4[1]
Solubility	1:1–1:2.2 in 80% ethanol[1]

The aromatic character of sweet marjoram oil differs widely from the oils obtained from various species of *Origanum* (wild marjoram). The latter contain a high percentage of carvacrol.

Derivatives Infusion (1.2%), fluid extract, tincture (20% in 60% ethanol) and oleoresin

Organoleptic characteristics Warm, spicy odor; slightly bitter-tonic flavor

Uses The dried product and the tincture are used in the formulation of vermouths and bitters. The oil is employed to formulate compounded oils for flavoring sauces, condiments, canned meats, and other products. Marjoram seed has been reported used in the following:[3]

non-alcoholic beverages	750 ppm
condiments	70–700 ppm
meats	200–3,500 ppm

Sweet marjoram has been reported used in the following:[3]

non-alcoholic beverages	1.9 ppm
baked goods	2,000 ppm
condiments	200 ppm
meats	510 ppm
soups	150 ppm

Sweet marjoram oil has been reported used in the following:[3]

non-alcoholic beverages	4.2 ppm
ice cream, ices, etc.	1.0 ppm
candy	4.0 ppm
baked goods	15 ppm
condiments	8.0 ppm

Marjoram oleoresin has been reported used in the following:[3]

condiments	75 ppm
meats	37 ppm

Regulatory status GRAS (I), (II)

MATÉ

Other names Paraguay tea; St. Bartholomew's tea

Botanical source *Ilex paraguariensis* St. Hil.

Botanical family *Rhamnaceae*

Foreign names Thé du Paraguay (Fr.), Paraguaytee (Ger.), Yerba de Mate (Sp.), Maté (It.)

Description Small trees growing wild in South America (Brazil, Paraguay, and Argentina) or cultivated (Argentina). The trees are usually pruned at intervals for ease of harvesting the leaves. The dried, comminuted maté leaves have been used from time immemorial to prepare an infusion (beverage) largely consumed by South Americans. The resulting beverage, called Paraguay tea, is aromatic, somewhat bitter with refreshing and restorative effects.

Parts of plant used Leaves

Physical-chemical characteristics

Essential oil The oil (not commercially available) was obtained by steam distillation of the fresh leaves in approximately 0.35% yields. The oil exhibited a hay-like, herbaceous odor and refreshing flavor. Its physical-chemical constants follow:

Specific gravity at 20°C	0.885[1]
Refractive index at 20°C	1.447[1]
Optical rotation	Slightly dextrorotatory[1]

Derivatives Concrete, absolute, distilled absolute, infusion. The concrete and absolute, prepared by traditional methods from dried, comminuted leaves, are viscous, semisolid, dark-green masses with a very rich herbaceous, green, leafy odor reminiscent of maté. The distilled absolute yields a pale-colored extract.

Main constituents of the leaves include caffeine, tannic acid, vanillin, and small amounts of essential oil.

Organoleptic characteristics Rich, herbaceous, green odor; somewhat bitter, refreshing taste

Uses The absolute and the tincture find use in perfumery; they blend well with jasmine, oakmoss, lavender, and camomile. The dried, ground leaves are used to prepare the well known infusion. The tincture is used sporadically, if at all, in flavor work.

Regulatory status GRAS (II)

MELILOTUS

Other names Yellow melilot; sweet clover

Botanical source *Melilotus officinalis* (L.) Lam.

Botanical family *Leguminosae*

Foreign names Melilot (Fr.), Meliloten (Ger.), Meliloto (Sp.), Meliloto (It.)

Description Biennial herbaceous plant, sometimes more than 1 m (39 in.) in height; it grows in the highland areas of Europe and Asia. The plant exhibits a long, spindle-shaped root; a smooth, reddish, erect stalk; alternate leaves consisting of three, small, oval leaves; and small, yellow, highly scented flowers (May–September).

Parts of plant used Dried flowering tops

Physical-chemical characteristics

Essential oil The essential oil is little known and only occasionally produced. The scent of melilotus is formed primarily during the drying process, during which coumarin is formed. Free coumarin is the main constituent of melilotus, together with melilotoside and dihydrocoumarin.

Derivatives Infusion (3%), resinoid, and absolute essence

Organoleptic characteristics Sweet, aromatic odor and flavor

Uses The resinoid and the absolute essence are used in perfumery and to introduce a coumarin note for flavoring tobacco or food products (where coumarin is permitted).

Regulatory status Proposed by the Commissioner of FDA for inclusion in Regulation §121.1163 as published in the *Federal Register*, Vol. 31, No. 61, March 30, 1966.

MENTHA ARVENSIS

Other names Corn mint; wild pennyroyal; mint oil

Botanical source *Mentha arvensis* L.

Botanical family *Labiatae*

Foreign names *Mentha arvensis*

Description The name *M. arvensis* is used internationally to indicate both the plant and the essential oil. The most widespread varieties include *M. arvensis* var. *piperascens* Holmes (Brazil, Japan) and *M. arvensis* var. *glabrata* Holmes (China).

M. arvensis is an herbaceous plant from 40–85 cm (16–33 in.) in height; it is cultivated extensively in China, Japan, Brazil, and South Africa. The plant has a long, creeping root with secondary roots, opposite leaves, slender embranched stalk, and flowers growing in round clusters at the joint of the leaves.

Parts of plant used Flowering tops

Physical-chemical characteristics

Essential oil The oil produced in Japan, Brazil, and China is put on the market partially dementholated, as the oil is used to extract menthol. Therefore, the menthol content of the oil is reduced by 40–50%. Yields of distillation vary between 0.5–1.0%, depending on the source of the raw material. The oils are pale-yellow and exhibit a strong, characteristic menthol odor.

Japanese Essential Oil

Specific gravity at 20°C	0.892–0.899
Refractive index at 20°C	1.4590–1.4630
Optical rotation at 20°C	−26° to −30°
Ester content (as methyl acetate)	<12%
Alcohol content (as menthol)	45–56%
Ketone (as menthone)	—
Solubility in 70% alcohol	—

Chinese Essential Oil

Specific gravity at 20°C	0.897–0.905
Refractive index at 20°C	1.4609–1.4628
Optical rotation at 20°C	−26° to −29°
Ester content (as methyl acetate)	7.8–11.1%
Alcohol content (as menthol)	62.5–67.6%
Ketone content (as menthone)	ca 15%
Solubility in 70% alcohol	1:3

Brazilian Essential Oil

Specific gravity at 20°C	0.878–0.898
Refractive index at 20°C	1.4560–1.4610
Optical rotation at 20°C	−22° to −32°
Ester content (as methyl acetate)	—
Alcohol content (as menthol)	46–60%
Ketone content (as menthone)	—
Solubility in 70% alcohol	—

Menthol is separated from the essential oil by crystallization at low temperature and subsequent centrifugation. The main constituents of the oil from the above sources (Japan, China, Brazil) are identical except that their relative ratios vary. The main constituents include α- and β-pinene, limonene, cineol, ethyl amyl carbinol, menthone, isomenthone, menthol, menthyl acetate, piperitone, neomenthol, neoisomenthol, and isomenthol. The dementholated oil subsequently is rectified for flavor use (head and bottom cut losses approximately 14%).

Organoleptic characteristics

Fresh, strong menthol odor and cool mint flavor; less smooth than true peppermint oil

Uses

The essential oil is used for the extraction of menthol. The dementholated, rectified essence is used in flavoring candies, bitter chocolate, toothpaste, and other products in certain countries. *M. arvensis* oil is a common adulterant of true peppermint oil. It is not used as such in the United States.

Regulatory status

Its use in foods is permitted in the United States, but such food products cannot be labeled as peppermint.

MIMOSA

Other names

Black wattle

Botanical source

Acacia decurrens Willd. var. *dealbata*

Botanical family

Leguminosae

Foreign names

Mimosa (Fr.), Mimosa (Sp.), Mimose (Ger.), Mimosa (It.)

Description

Woody plants native to Australia, having pinnate leaves and yellow flower clusters. The plant has become acclimated to the French and Italian Riviera, where it was transplanted in the early 1800's. It is cultivated for ornamental (flowers) and extractive purposes.

Parts of plant used

Flowers

Physical-chemical characteristics

Derivatives

The concrete, which is extracted from flowers in approximately 0.7–1.1% yields using petroleum ether, and the absolute, prepared from the concrete in approximately 20–25% yields. The concrete is a pale-yellow wax with a fatty, floral, slightly sweet odor, reminiscent of beeswax. The absolute is a syrupy, viscous, amber-colored or yellowish liquid with a scent similar to that of flowers. Reported physical-chemical constants for the above derivatives follow:

	Concrete	**Absolute**
Congealing point	48.2°C	—
Acid value	28	28.2
Ester value	44.8	42.3
Specific gravity	—	0.9797
Optical rotation	—	+15°40′
Refractive index at 20°C	—	1.5175

Organoleptic characteristics

Delicate, sweet, floral odor

Uses

The concrete is used in fine soaps because of its outstanding fixative properties and delicate scent. The absolute finds extensive use in perfumery (floral bouquets). The absolute also is employed in the formulation of flavors to modify or enhance specific notes. Mimosa absolute (FEMA No. 2755) has been reported used in the following:[3]

non-alcoholic beverages	0.79 ppm
ice cream, ices, etc.	21 ppm
candy	1.7 ppm
baked goods	17 ppm

Regulatory status	FDA §121.1163

MOLASSES EXTRACT

Botanical source	*Saccharum officinarum* L.
Description	By-product of sugar-refining process: the syrup or the "mother-water" that is separated from the grains of "raw-sugar" in the process of manufacture. Its quality depends on the character and treatment of the cane juices from which it is obtained. Molasses is generally dark brown to bright amber. Black-strap molasses is the final or exhausted molasses of raw-sugar manufacture.
Organoleptic characteristics	Usually sweet; also can taste burnt
Uses	Tobacco flavoring, baking, etc.; its largest use is in animal feed. Black-strap molasses is a rich source of iron.
Regulatory status	GRAS (II)

MULLEIN

Botanical source	**A.** *Verbascum phlomoidea* L., *V. thapsiforme* Schrad. **B.** *V. thapsus* L., *V. latius* Dod.
Botanical family	*Scrophulariaceae*
Foreign names	**A.** Molène médicinale (Fr.), Grossblütige Königskerze (Ger.), Gordolobo (Sp.), Guaragnasco, Tasso Barbasso (It.) **B.** Molène commune (Fr.), Kleinblütige Königskerze (Ger.), Verbasco (Sp.), Verbasco (It.)
Description	Green-yellowish, woolly, biennial herbs existing in two varieties equally widespread in wastelands throughout Europe. *V. phlomoidea* or *V. thapsiforme* are characterized by large leaves; the radical leaves may reach 50 cm (20 in.) in length, whereas the cauline leaves are sessile and only slightly decurrent. *V. thapsum* has smaller, oblong, acute, decurrent, almost petioleless leaves. The plant has taproots, alternate leaves, and yellow flowers clustered in terminal spikes. *V. phlomoidea* is preferred for extractive purposes.
Parts of plant used	Flowers (and sometimes the leaves)
Physical-chemical characteristics	
Derivatives	Infusion and decoction. The main constituents include saponins, sugars, carbohydrates, mucilages, and a trace of essential oil.
Organoleptic characteristics	Bittersweet, tonic flavor

Uses	The derivatives are used in patent drugs and, only to a very limited extent, in flavors.
Regulatory status	Flowers: FDA §121.1163. In alcoholic beverages only

MUSK

Other names	Tonquin musk
Source	*Moschus moschiferus* L. (musk deer)
Family	*Moschidae*
Foreign names	Musc (Fr.), Moschus (Ger.), Almizcle (Sp.), Muschio (It.)
Description	Product of animal origin consisting of a glandular secretion of the male musk deer of Tibet, southern China, northern India, and throughout the Himalayan highlands. The secretion, obtained from adult male musk deer only, is a reddish-brown, paste-like mass with a very strong, penetrating odor. The secretion is found in an internal pouch located under the skin of the abdomen of the animal. The musk pouches are removed from the animal and subsequently dried, thus causing the hardening and darkening of the secretion (so-called musk grains) within the pouch. The dried, unopened pouches of commerce are distinguished by the following names: Tonquin, Blue Skin, Yunnann, Sawko, Cabardin, Nepal, and Assam. Good quality pouches contain approximately 70% musk, while the less valuable ones contain as little as 40% musk. The odorous principle of musk has been chemically identified as a macrocyclic lactone (3-methylcyclopentadecanone-one), also known as muskone.
ysical-chemical aracteristics	
Derivatives	Infusions and tinctures are prepared by alcoholic extraction of musk grains. By concentrating the alcoholic extracts, it is possible to prepare a "musk resinoid." The true resinoid is prepared by petroleum ether extraction of musk grains. A musk absolute is prepared by alcoholic extraction from the resinoid.
Organoleptic characteristics	Potent, penetrating, musk odor with a strong, animal note
Uses	Infusions and the tinctures in high dilutions are used as fixatives in fine perfumes. Musk derivatives are only seldom employed as flavor modifiers to round off tobacco, nut, or candy flavors. Tonquin musk (FEMA No. 2759) has been reported used in the following:[3] non-alcoholic beverages 0.67 ppm ice cream, ices, etc. 0.62 ppm candy 2.0 ppm baked goods 2.7 ppm syrups 3.0 ppm
Regulatory status	GRAS

MUSTARD

Botanical source	*Brassica nigra* (L.) Koch—black or brown mustard *B. juncea* (L.) Cosson—brown mustard *B. hirta* Moench or *B. alba* Boiss—white mustard

Botanical family

Cruciferae

Foreign names

Moutarde (Fr.), Senf (Ger.), Mostaza (Sp.), Mostarda or Senape (It.)

Description

Black or Brown Mustard
Herbaceous, annual plant widespread throughout Europe, North Africa, and northern Asia. It grows more than 1 m (39 in.) high with long primary roots and many secondary ones. It has an erect, branched stalk, alternate leaves, yellow flowers arranged in terminal clusters (June–August), and tiny, reddish-brown seeds.

White or Yellow Mustard
Herbaceous plant widespread in Europe, North and South America, New Zealand, and Japan. The English variety is highly esteemed. The plant is less than 1 m (39 in.) in height; it has a short root, erect branched stalk, alternate leaves, pale-yellow flowers (June to August), and round, reddish-yellow seeds.

Parts of plant used

Seeds

Physical-chemical characteristics

Essential oils

The essential oil of black mustard is produced by steam distillation of the residue (press-cake) obtained after expressing the seeds of the oil. The essential oil of white mustard must be obtained by solvent extraction of the expressed residue (press-cake), because it does not contain a volatile essential oil. Prior to distillation or extraction, it is necessary to hydrolyze the press-cake to release allyl isothiocyanate from the sinigrin glucoside in black mustard or to release sinapine acid sulfate from the sinaldin glucoside in white mustard. The hydrolysis is conducted by maceration of the comminuted seeds in warm water. The aromatic components do not exist in the free state in mustard seeds, but are produced only as a result of the enzymic (myrosin) decomposition of the glycosides when the crushed seeds are mixed with water.

Black Mustard Essential Oil
The essential oil of black mustard is a clear, pale-yellow liquid exhibiting a very intense odor having lachrymatory effects; it has a relatively poor flavor. The essential oil of black mustard is characterized by the following:[3]

Specific gravity at 15°C	1.014–1.022[1]
Refractive index at 20°C	1.5268–1.5290[1]
Optical rotation	±0°[1]
Allyl isothiocyanate content	94%[1]
Solubility in 90% ethanol	1:0.5[1]

White Mustard Essential Oil
The essential oil of white mustard exhibits characteristics quite opposite to those of black mustard, i.e., little odor and a very sharp, pungent taste.

Organoleptic characteristics

Lachrymatory (black mustard only), irritating, sharp odor; pungent, warm taste (white mustard)

Uses

Black mustard essential oil is used extensively to flavor sauces and condiments and to compound mustard sauces. Similar uses are found for black and white mustard flours.

Brown mustard, *B. juncea* (L.) Cosson, *B. nigra* (L.) Koch, has been reported used in the following:[3]

condiments	5,200 ppm
meats	2,300 ppm

Yellow mustard, *B. hirta* Moench, *B. alba* (L.) Boiss, has been reported used in the following:[3]

non-alcoholic beverages	350 ppm
baked goods	20 ppm
condiments	8,200 ppm
meats	1,400 ppm
pickles	2,500–38,000 ppm

Regulatory status

Black or brown mustard: GRAS (I), (II)
Brown mustard: GRAS (I), (II)
White or yellow mustard: GRAS (I), (II)

MYRRH

Botanical source

Commiphora molmol Engl.—Somalian myrrh; *C. abyssinica* (Berg.) Engl.—Arabian myrrh; and other *Commiphora* species

Botanical family

Burseraceae

Foreign names

Myrrhe (Fr.), Myrrhe (Ger.), Mirra (Sp.), Mirra (It.)

Description

Myrrh oleo-gum-resin, also known as heerabol myrrh, consists of the physiological exudate of various *Commiphora* species growing along the coasts of the Red Sea. *Commiphorae* are small trees or shrubs with a grayish bark, dense characteristic foliage, and rather short, thorny branches. The oleo-gum-resin oozing from cracks in the bark, and sometimes from incisions made on the bark, is a yellowish-white milky liquid. On exposure to air, the liquid hardens to irregularly shaped "tears" of reddish-brown color, exhibiting a warm, aromatic, balsamic, slightly pungent odor. The gum resin is commercially available under different names, depending on the botanical source and the manufacturing site. This distinction is often irrelevant, since different lots may be combined together; thus, it becomes difficult to establish the difference in quality. The commercial product usually consists of small fragments ("tears") having an irregular shape and a shiny, granular cleavage. The tears are often hollow and fragile.

Parts of plant used

The oleo-gum-resin exudate

Physical-chemical characteristics

Essential oil

The oil, obtained by steam distillation of the gum in approximately 3–8% yields, is a light-brown to green liquid with a pungent, balsamic, warm odor and corresponding flavor. The oil tends to darken and thicken on exposure to air and light. Physical-chemical constants of the oil follow:

Specific gravity at 25°/25°C	0.985–1.010[2]
Refractive index at 20°C	1.5190–1.5275[2]
Optical rotation	−60° to −83°[2]
Acid value	2–13[2]
Solubility	1:7–10 in 90% alcohol

Main constituents include *d*-pinene, dipentene, limonene, cinnamaldehyde, cuminaldehyde, eugenol, *m*-cresol, sesquiterpenes, and formic and acetic acids.

Derivatives

Tincture (10% in 60–65% ethanol), fluid extract, resinoid. The fluid extract, a dark-green liquid with a pleasant odor and warm flavor, is insoluble in water or sugar syrups; it is readily soluble in 80% ethanol. A resinoid can be prepared by traditional extraction with solvents (benzene, petroleum ether). The product is a viscous, orange-brown paste with a strong, warm, balsamic odor and bitter flavor. The absolute is not prepared from the resinoid but by direct extraction of the gum resin with alcohol. This resin absolute contains 18–20% essential oil and is a very dense. viscous liquid at room temperature. A pourable product is manufactured by adding a high-boiling, odorless solvent prior to evaporation of the alcohol.

Organoleptic characteristics
Warm, balsamic, aromatic odor; bitter, slightly pungent flavor

Uses
The tincture and the fluid extract are used in pharmacology. The essential oil, the resinoid, and the absolute are used in perfumery because of their good fixative properties. The tincture and the essential oil frequently are employed in the formulation of bitters and flavored wines. The purified resin and the essential oil find application in flavoring beverages, candy, and soups.

Myrrh gum (FEMA No. 2765) has been reported used in the following:[3]

non-alcoholic beverages	84 ppm
ice cream, ices, etc.	0.13 ppm
candy	0.13–10 ppm
baked goods	0.15 ppm
chewing gum	1.2 ppm
soups	10 ppm

Myrrh oil (FEMA No. 2766) has been reported used in the following:[3]

non-alcoholic beverages	3.3 ppm
ice cream, ices, etc.	8.3 ppm
candy	13 ppm
baked goods	13 ppm

Regulatory status
FDA §121.1163

MYRTLE

Botanical source
Myrtus communis L.

Botanical family
Myrtaceae

Foreign names
Myrte commun (Fr.), Myrte (Ger.), Mirto (Sp.), Mirto (It.)

Description
Evergreen shrub that grows wild or is cultivated for ornamental purposes throughout the Mediterranean region; it is native to Australia. It grows to 2 m (7 ft) in height, has an erect, highly branched stalk, opposite, oval, or spear-shaped leaves, white, scented flowers (March–June), and round berries with kidney-shaped seeds.

Parts of plant used
Leaves

Physical-chemical characteristics

Essential oil
Myrtle essential oil is obtained by steam distillation with yields of approximately 0.25%. It is a pale-yellow liquid with a characteristic odor. Main constituents of the oil include pinene, camphene, cineol, dipentene, *d*- and *l*-myrthenol, and geraniol.

Specific gravity at 20°C	0.8752–0.8920[1]
Refractive index at 20°C	1.465–1.470[1]
Optical rotation at 20°C	+17° to +30°[1]
Acid value	2.8 max[1]
Ester value	17–35%[1]
Alcohol content	6–20%[1]
Solubility	1:8 in 80% ethanol[1] 1:0.5 in 90% ethanol[1]

Derivatives
Decoction (1%), fluid extract, and tincture (20% in 70% ethanol)

Organoleptic characteristics
Somewhat bitter, astringent, and biting flavor

Uses

The fluid extract generally is employed to modify odor and flavor. The dried leaves and the essential oil find use in liqueurs and, in certain countries, in flavoring sauces and canned meats.

Regulatory status

FDA §121.1163. In alcoholic beverages only

NEROLI BIGARADE

Botanical source

Citrus aurantium L. subspecies *amara* L.

Botanical family

Rutaceae

Foreign names

Neroli (Fr.), Neroli (Ger.), Neroli (Sp.), Neroli (It.)

Description

Neroli bigarade is a product obtained by processing flowers of the bitter orange tree. For additional information see Orange, Bitter.

Parts of plant used

Blossoms of bitter orange tree

Physical-chemical characteristics

Essential oil

The essential oil is obtained in ca 0.1% yields by steam distillation of the flowers. The distillation waters, rich in dissolved essence, are used as is in perfumery, cosmetics, and sweets. Neroli bigarade essential oil, or simply neroli oil, has slightly different physical-chemical properties depending on its origin. Italian neroli oil, qualitatively equal to the French product of much larger production, is a pale-yellow to amber liquid, slightly fluorescent, with an intense, suave, flowery aroma. It has the following constants:

Specific gravity at 20°C	0.866–0.879[1] (0.866–0.881)[7]
Refractive index at 20°C	1.469–1.474[1]
Optical rotation at 20°C	$2^\circ 30'$ to $11^\circ 30'$[1]
Acid value	<2[1]
Ester value	16–44[1] (20–44)[7]
Solubility	1:2–1:5.5 in 75% ethanol[1]
	1:0.5–1:1 in 80% ethanol[1]

The main constituents include pinene, camphene, dipentene, linalool, *l*-linalyl acetate, α-terpineol, geraniol, nerol, nerolidol, methyl anthranilate, indole, farnesol, and phenylacetic acid esters.

Derivatives

Orange flower concrete is obtained in 0.24–0.28% yields by extracting freshly picked flowers with a solvent (usually petroleum ether). Treatment of the concrete with ethanol produces the orange flower absolute in approximately 50% yields. The absolute is a yellow-red liquid with an extremely suave odor typical of the flower.

Organoleptic characteristics

Very powerful floral odor with bitter flavor

Uses

Neroli bigarade is of limited use in flavoring, but, when used in small quantities as a modifier, it can produce elegant effects in candy, liqueurs, and soft drinks.

Neroli bigarade has been reported used in the following:[3]

non-alcoholic beverages	2.0 ppm
ice cream, ices, etc.	3.2 ppm
candy	8.9 ppm
baked goods	16 ppm
chewing gum	14 ppm

Regulatory status

GRAS (II)

NUTMEG

Botanical source

Myristica fragrans Houtt.

Botanical family

Myristicaceae

Foreign names

Muscade (Fr.), Muskatnuss (Ger.), Nuez Moscada (Sp.), Noce Moscata (It.)

Description

Evergreen tree 15–20 m (49–66 ft) in height; grows in Java, Sumatra, Borneo, Penang, Moluccas, and in several other islands of the Indian Ocean. It has alternate leaves and dioecious flowers. Consequently, only female trees bear nuts; male plants are interdispersed in the groves only to insure pollination. The ripe fruits are yellow-red with a fleshy pericarp; the red arillode is tightly wrapped around a woody hull containing the seed.

Note: Mace designates the dried arillodes of nutmeg. The ratio of nutmegs to mace is approximately 10:1. Nutmeg and mace yield different, but sometimes similar, products.

Parts of plant used

Nuts (free of the outer pulp) and arillodes (decolorized with lime). The most commercially important qualities of nutmeg and mace follow:

(1) Banda nutmeg and Banda mace contain 8% and 13% essential oil, respectively;
(2) Jave nutmeg and Java mace contain 6.5% and 11% essential oil, respectively; and
(3) Siauw nutmeg and Siauw mace contain 6.5% and 10–12% essential oil, respectively.

These qualities are further subdivided according to size – large, medium, and small – for extraction and according to appearance – whole, wormeaten, etc.

Physical-chemical characteristics

Nutmeg Essential Oil

The oil is obtained by steam distillation of dried comminuted nutmeg previously treated by hydraulic expression to remove fixed oils; yields are approximately 12%. The hot expression of nutmeg yields a fatty oil with a melting point of about 45°C. Nutmeg essential oil is a colorless to pale-yellow liquid (also see reference 2).

Specific gravity at 20°C	0.866–0.929[1]
Refractive index at 20°C	1.4750–1.4790[1]
Optical rotation at 20°C	+9° to +41°[1]

The oil exhibits a characteristic nutmeg odor and contains α- and β-pinene, camphene, dipentene, *p*-cymene, *d*-linalool, terpineol, geraniol, safrole, eugenol, and isoeugenol.

Mace Essential Oil

Mace oil is obtained by steam distillation of the ground, dried arillodes of the ripe nutmeg seed; yields are approximately 11%. It exhibits a fresher odor than that of nutmeg oil but has a great number of components common to nutmeg. Oil of mace (East and West Indian) is a colorless to pale-yellow liquid with the characteristic odor and flavor of nutmeg.

East Indian Oil of Mace[2]

Specific gravity at 25°/25°C	0.880–0.930 (0.883–0.917 at 20°/20°C)[7]
Optical rotation	+2° to +30° (+8° to +25°)[7]
Refractive index at 20°C	1.4740–1.4880 (1.4750–1.4880)[7]
Solubility	1:3 in 90% ethanol

West Indian Oil of Mace[2]

Specific gravity at 25°/25°C	0.854–0.880 (0.862–0.882 at 20°/20°C)[7]
Optical rotation	+20° to +45° (+20° to +40°)[7]
Refractive index at 20°C	1.4690–1.4800 (1.4720–1.4760)[7]
Solubility	1:4 in 90% ethanol

Derivatives

Nutmeg: tincture (20% in 70% ethanol), fatty oil obtained by expression, and the oleoresin

Mace: tincture, extract, and oleoresin

Uses

Mace and nutmeg essential oils together with their derivatives frequently are employed in the formulation of compounded oils in flavoring liqueurs, condiments, sauces, and other products. Oleoresins preferably are used in the flavoring of sauces, condiments, and cured meats.

Nutmeg has been reported used in the following:[3]

non-alcoholic beverages	700 ppm
ice cream, ices, etc.	550 ppm
baked goods	2,000 ppm
condiments	100 ppm
meats	670 ppm
pickles	100 ppm

Nutmeg oil has been reported used in the following:[3]

non-alcoholic beverages	14 ppm
ice cream, ices, etc.	13 ppm
candy	19 ppm
baked goods	75 ppm
chewing gum	1.2–640 ppm
condiments	21 ppm
meats	150 ppm
icings	2.0–30 ppm
syrups	16 ppm

Mace has been reported used in the following:[3]

non-alcoholic beverages	350 ppm
ice cream, ices, etc.	40 ppm
baked goods	1,300 ppm
condiments	43 ppm
meats	500–2,000 ppm

Mace oil has been reported used in the following:[3]

non-alcoholic beverages	6.0 ppm
ice cream, ices, etc.	4.5 ppm
candy	23 ppm
chewing gum	37 ppm
condiments	12 ppm
meats	33 ppm
baked goods	68 ppm

Mace oleoresin has been reported used in the following:[3]

baked goods	360 ppm
condiments	800 ppm
meats	100–600 ppm
pickles	35 ppm

Regulatory status

Nutmeg: GRAS (I), (II)

Mace: GRAS (I), (II)

OAK, ENGLISH

Botanical source	*Quercus robur* L.
Botanical family	*Fagaceae*
Foreign names	Cheme (Fr.), Eiche (Ger.), Albar (Sp.), Quercia (It.)
Description	Majestic tree up to 35 m (115 ft) high, commonly growing in the mountain woods of central and eastern Europe and the Middle East. The tree has deep roots, crooked branches, alternate leaves, monoic flowers, and pedunculate nuts. The trunk is covered by a corky bark.
Parts of plant used	Wood
Physical-chemical characteristics	
Derivatives	Fluid extract, tincture (10–15% in 85–90% ethanol), distillate (in 85% ethanol)
Organoleptic characteristics	Bitter tonic, astringent
Uses	The aging of wine distillates in oak barrels to enhance the bouquet is a well known practice. Oak derivatives find use in the formulation of compounded oils and alcoholic extracts for liqueurs.
Regulatory status	FDA §121.1163. In alcoholic beverages only

OAK MOSS

Botanical source	*Evernia prunastri* (L.) Ach., *E. furfuracea* (L.) Mann., and other lichens
Botanical family	*Usneaceae*
Foreign names	Mousse de Chêne (Fr.), Eichenmoos (Ger.), Musco de encina (Sp.), Muschio di quercia (It.)
Description	Various lichens belonging to the class *Cryptogamia*; they grow under cool, damp conditions on the trunks and branches of trees such as oak and fir. The lichens are used to prepare resinoids and concrete and absolute essences for a total yearly consumption of approximately 70 tons. *E. prunastri*, the true oak moss, grows on the trunks and branches of oak trees. Like all ascolichens the moss reproduces by fragmentation of soredia and grows by symbiosis yielding an erect, bushy, vegetative form. Other related lichens—*E. furfuracea* and *Usnea barbata*—that grow on spruces and firs are known by the more generic name of tree moss. Oak moss derivatives are light green and exhibit a rich odor, while tree moss derivatives have a grayish-green color and a slight resinous odor. *E. prunastri* yields the most valuable extraction products, while other tree mosses yield products of inferior quality. Oak moss is harvested mainly in France, Yugoslavia, Italy, Morocco, and Hungary. The harvested moss is pressed into bails and shipped to the extractive sites.
Parts of plant used	The lichen
Physical-chemical characteristics	
Essential oil	An essential oil can be obtained by steam distillation of the lichen. However, this product is of little commercial importance because of the very low yields (0.07%). Usually oak moss concrete and oak moss absolute are steam distilled preferably under reduced pressure. Main constituents of the ether-extracted concrete include evernic acid, orcinol, phenols, acids (formic, acetic, stearic, palmitic, and oleic), α- and β-thujone, camphor, borneol, cineol, naphthalene, ketones, terpene alcohols, and traces of vanillin.

Derivatives

Concrete
The concrete is prepared by benzene or petroleum ether extraction in approximately 2–4% and 1.5–3.0% yields, respectively. It is a dark green, waxy mass with a delicate, green, moss-like odor. Usually, the moss is immersed in water for about 6 hours, dried, and finally extracted to improve yields.

Absolute
The absolute is obtained by alcoholic extraction of the concrete. Extraction lasts approximately 5 hours, yielding a dark-green liquid in approximately 60% yields. The alcoholic solution is chilled to 6°C to separate the insoluble waxes. Sometimes the absolutes are decolorized using activated carbon, and the liquid product is vacuum distilled.

Absolute Co-distillates
In order to obtain a good yield of essential oil and to improve the color of the distillate, the absolute is co-distilled under vacuum together with a high-boiling, odorless solvent, thereby yielding the so-called absolute co-distillates. The co-distillates offer a better solubility; they are virtually colorless and retain the characteristic oak moss odor.

Resinoid
The so-called oak moss resinoid is in fact the hot alcohol extract from the lichen. The resinoid is a black-green or brownish-green liquid. This product is not used in flavors, since it contains ethyl everninate formed by esterification of the evernic acid, naturally occurring in oak moss. The ethyl ester is in fact toxic.

Organoleptic characteristics

Delicate, pleasant, green, moss-like odor

Uses

Oak moss derivatives are employed extensively in perfumery whenever refreshing and green notes with long-lasting effects are desirable. The absolute is used in the formulation of aromas, usually at low-use levels and only as a modifier. Oak moss absolute (FEMA No. 2795) has been reported used in the following:[3]

non-alcoholic beverages	1.8 ppm
ice cream, ices, etc.	0.41 ppm
candy	0.81 ppm
baked goods	2.5 ppm
gelatins and puddings	0.15 ppm
condiments	40 ppm
soups	0.50 ppm

Regulatory status

FDA §121.1163. Thujone free

OAK, WHITE

Botanical source

Quercus alba L.

Botanical family

Fagaceae

Foreign names

Quericia (It.)

Description

Oak is a common name used to describe about 400 species of trees and shrubs. They have alternate, simple, deciduous or evergreen leaves and monoecious flowers, the staminate usually in slender pendulous catkins. The pistillate is nearly sessile and solitary or in groups of two or three, developing into acorns that are more or less globular or oblong nuts set in scaly involucres (caps). All species are native to the temperate and colder regions of the northern hemisphere. The bark is used in tanning.

Q. alba is a tree up to 100 ft high with stout, spreading branches forming a broad, open head; bark, light gray; leaves, obovate or oblong-obovate; acorn, oblong-ovate; scales, closely oppressed. The foliage assumes a beautiful deep vibrant red or violet-purple color in fall.

Parts of plant used

Wood chips

Organoleptic characteristics

Astringent

Uses

Oak is used in vermouth flavors and sometimes in medicine. Oak chips extract (FEMA No. 2794) has been reported used in the following:[3]

non-alcoholic beverages	2.5–21 ppm
alcoholic beverages	1,000 ppm
ice cream, ices, etc.	2.5–84 ppm
candy	2.5–63 ppm
baked goods	63 ppm

Regulatory status

FDA §121.1163

OLIBANUM

Other names

Frankincense

Botanical source

Boswellia carterii Birdw. and other *Boswellia* species

Botanical family

Burseraceae

Foreign names

Encens oliban (Fr.), Weihrauch, Olibanum (Ger.), Olibano (Sp.), Olibano (It.)

Description

Olibanum is a gum resin secreted by several *Boswellia* species that grow extensively from South Arabia to Somaliland. The small trees or shrubs yield an exudate after incisions are made on the bark; it consists of a milky liquid that hardens into small, yellowish droplets commercially known as incense tears. The tears are sorted; the most valuable quality (white tears) is sold as burning incense, while the less valuable qualities (powder and fragments) are used in flavors and perfumes because of their more reasonable cost.

Parts of plant used

Gum resin exudate

Physical-chemical characteristics

Essential oil

The oil, obtained by steam distillation of the gum resin, is an almost colorless to pale-yellow liquid with a balsamic, slightly citrine odor. Physical-chemical constants of the oil follow:

Specific gravity at 25°/25°C	0.869–0.889[2]
Refractive index at 20°C	1.4685–1.4820[2]
Optical rotation	15° to +35°[2]
Acid value	<4.0[2]
Ester value	4–30[2]
Solubility	1:6 in 90% alcohol[2]

Derivatives

Resin Absolute, Resinoid, Absolute

Since the gum resin is up to 75% soluble in alcohol, a resin absolute is prepared by filtration and vacuum concentration of the alcoholic solution. The resin absolute is a plastic mass of light-amber color and balsamic odor. The resinoid is obtained by solvent extraction of the resin. Sometimes heat is employed to increase the yields, but this method yields products with a slightly different odor than the cold-extracted resinoid. An absolute also can be prepared by alcoholic extraction of the resinoid.

Uses

The use of resin in the formulation of pomades and ointments is approved by the Swiss Pharmacopoeia. The oil, the resinoid, and the resin absolute find application in perfumery as fixatives in the so-called Oriental notes. Olibanum oil and sometimes its derivatives find a limited use in flavor formulations only to confer a nuance. Olibanum oil (FEMA No. 2816) has been reported used in the following:[3]

non-alcoholic beverages	0.60 ppm
ice cream, ices, etc.	1.2 ppm
candy	3.3 ppm
baked goods	3.7 ppm

Regulatory status

FDA §121.1163

ONION

Botanical source

Allium cepa L.

Botanical family

Liliaceae

Foreign names

Ognon (Fr.), Zwiebel (Ger.), Cebolla (Sp.), Cipolla (It.)

Description

Herbaceous plant originally from the Middle East but today widespread throughout the world because of the large consumption of the edible bulb. The stalk can reach approximately 1 m (39 in.) in height. The bulb consists of several concentric tunics.

Parts of plant used

Bulbs

Physical-chemical characteristics

Essential oil

Obtained by distillation of the bulbs with yields of about 0.02%. The physical-chemical constants vary widely, depending on the origin of the plant. The oil is a yellowish liquid with a characteristic onion odor (also see reference 2). Main constituents of the oil are *d*-*n*-propyl disulfide and methyl-*n*-propyl disulfide.

Specific gravity at 15°C	1.047–1.098[1]
Optical rotation	+1°31′ to +3°53′[1]
Refractive index at 20°C	1.5373–1.5588[1]
Acid value	12–19.8[1]
Solubility	1:10 in 95% ethanol[1]

Derivatives

Oleoresin, fluid concentrated water extract, and the fluid extract. The first two derivatives are obtained by special manufacturing processes from thermally pretreated bulbs in order to enhance some flavor top notes as well as the flavoring strength.

Organoleptic characteristics

Strong, pungent, lasting odor; characteristic onion flavor

Uses

Onion is used as a flavor ingredient in the flavoring of vegetable extracts, canned meats, bouillons, sauces, and prepared condiments.

Onion oil has been reported used in the following:[3]

non-alcoholic beverages	0.50 ppm
ice cream, ices, etc.	0.50 ppm
candy	0.50 ppm
baked goods	1.9 ppm
condiments	2.2 ppm
meats	10 ppm
pickles	16 ppm

Regulatory status

GRAS (II)

OPOPANAX

Other names

Bisabol myrrh; sweet myrrh

Botanical source

Opopanax chironium Koch (true opopanax) or *Commiphora erythraea* Eng. var. *glabrescens*

Botanical family

O. chironium: Umbelliferae
C. erythraea: Burseraceae

Foreign names

Opoponax (Fr.), Opoponax (Ger.), Opoponaco (Sp.), Opopanax (It.)

Description

Opopanax is an oleo-gum-resin that oozes through incisions made on the bark of the tree. The exudate hardens on exposure to air, forming resinous, tear-shaped, more or less regular lumps approximately the size of a nut; these are detached from the bark and used for the manufacture of the essential oil and other derivatives. The trees are native to Somaliland. Once opopanax resin was obtained from *O. chironium* Koch; today the entire production of resin is obtained from *C. erythraea* var. *glabrescens* Eng.

O. chironium crude resin was offered in the form of regular, tear-shaped lumps of a brilliant red color. They were rather soft, shiny, and easily groundable. The strong, aromatic odor was reminiscent of costus and lovage.

The crude oleoresin has a reddish-brown, or sometimes yellowish-brown, color and sweet, balsamic, slightly spicy odor reminiscent of myrrh. The material contains 50–80% of a water-soluble gum, 15–40% alcohol-soluble resin, and 5–9% essential oil. The product is also known as bisabol or sweet myrrh. The adulteration is readily detectable, since opopanax tears in benzene do not react; myrrh tears yield a violet color in the presence of bromine vapors.

Parts of plant used

Oleo-gum-resin exudate

Physical-chemical characteristics

Essential oil

The oil is obtained by steam distillation of the crude resin in approximately 3.5–10% yields. It is a yellow to greenish-yellow liquid with an intense, warm, balsamic odor. The oil tends to resinify on exposure to air. Its main constituents include bisabolene ($C_{15}H_{24}$) and a mixture of alcohols. Its physical-chemical characteristics follow:

Specific gravity at 25°/25°C	0.867–0.932[2]
Refractive index at 20°C	1.4880–1.5050[2]
Optical rotation	−9° to −32°[2]
Acid value	<4.0[2]
Saponification value	4–20[2]
Solubility	1:10 in 90% ethanol[2]

Derivatives
Resinoid and resin absolute. The resinoid, prepared by solvent extraction, is a semisolid mass. To prepare a pourable product, usually a high-boiling, odorless solvent is added prior to evaporation of the extractive solvent. The resin absolute is prepared by direct alcoholic extraction of the crude resin.

Organoleptic characteristics
Fresh, balsamic odor reminiscent of myrrh

Uses
The essential oil and derivatives are used extensively in perfumery because of their good fixative properties. The essential oil is used for flavoring alcoholic beverages (to impart a spicy, warm note) and in some Oriental type specialties.

Regulatory status
FDA §121.1163

ORANGE, BITTER

Botanical source
Citrus aurantium L. subspecies *amara* L.

Botanical family
Rutaceae

Foreign names
Orange bigarade (Fr.), Bittere Pomeranze (Ger.), Naranja amarga (Sp.), Arancio amaro (It.)

Description
Bitter orange is a tall tree, up to 10 m (33 ft) high, with dark-green oval leaves and flowers with five petals. The fruit has a green epicarp that turns yellow-orange on ripening, a spongy mesocarp, and an endocarp consisting of succulent segments. Native to the Far East, bitter orange is cultivated extensively throughout the Mediterranean (especially Sicily), Guinea, West Indies, and Brazil; other nations are minor producers. A commercially important variety grows wild and also is cultivated in Paraguay.

Parts of plant used
Leaves and twigs (petitgrain), flowers (neroli bigarade), and peel

Physical-chemical characteristics

1. *Essential Oil*
From leaves and twiglets. *See* Petitgrain.

2. *Essential Oil*
From flowers. *See* Neroli Bigarade.

3. *Essential Peel Oil*
Bitter orange peel oil can be obtained by the following methods:

   a. Expression of fresh fruit rinds (peel) using suitable machinery that ruptures the oil-bearing cells, followed by separation and purification by centrifugation.
   b. Steam distillation of peels.

The quality of the product obtained by expression is quite different and considered of much higher quality than oil obtained by steam distillation. Oil obtained by expression is deep yellow with a fragrant, bitter flavor; it has the following constants:

Specific gravity at 25°/25°C	0.845–0.851[2]
Optical rotation at 25°C	+88° to +96°[2]
Refractive index at 20°C	1.4725–1.4755[2]
Evaporation residue	2–5%[2]
Aldehyde content (as decylaldehyde)	0.5–1.0%[2]

The main constituents include *d*-limonene, various acids, aldehydes, and diesters.

4. *Derivatives*

Raw bitter orange essence is transformed into bitter orange soluble essence by washing with low-proof alcohol. The soluble essence is used for the manufacture of special syrups and adjusted for strength accordingly (*e.g.*, 1:50, 1:100, 1:200, and 1:400). By removing terpenes and sesquiterprenes by vacuum distillation or cold extraction with low-proof alcohol, the following are obtained:

a. Terpeneless bitter orange essential oil, and
b. Sesquiterpeneless bitter orange essential oil.

The tincture (20% in 65–70% or 90% ethanol) and the fluid extract are obtained from dried peels. *Also see* Neroli Bigarade, Derivatives.

Organoleptic characteristics

All oils and derivatives have a characteristic orange aroma with a bitter flavor.

Uses

Orange blossom absolute has been reported used in the following:[3]

non-alcoholic beverages	1.7 ppm
ice cream, ices, etc.	7.3 ppm
candy	5.7 ppm
baked goods	15 ppm
chewing gum	10 ppm

Orange flowers have been reported used in non-alcoholic beverages, 100–2,000 ppm.[3] Orange leaf absolute has been reported used in the following:[3]

non-alcoholic beverages	0.02 ppm
ice cream, ices, etc.	0.1 ppm
candy	0.25 ppm
baked goods	0.25 ppm

Bitter orange peel essential oil has been reported used in the following:[3]

non-alcoholic beverages	67 ppm
alcoholic beverages	4.0 ppm
ice cream, ices, etc.	71 ppm
candy	150 ppm
baked goods	110 ppm
gelatins and puddings	300 ppm
chewing gum	500 ppm

Regulatory status

Flowers and peel: GRAS (II)

ORANGE, SWEET

Botanical source

Citrus sinensis L. Osbeck; *C. aurantium* var. *dulcis* L.

Botanical family

Rutaceae

Foreign names

Orange Portugal (Fr.), Suesse Pomeranze (Ger.), Naranja dulce (Sp.), Arancio dolce (It.)

Description

Sweet orange is an evergreen tree of Oriental origin, 4–6 m (13–20 ft) high. It has a cylindrical trunk, alternate leaves, and odorous flowers and fruits. The fruit has a green epicarp that turns yellow on ripening; a white, spongy mesocarp; and an endocarp consisting of succulent segments bearing seeds.

The Mediterranean countries in which it is cultivated include Italy (Sicily, Calabria, and Campania), Algeria, Tunisia, Morocco, Spain, and Israel; in addition very important production occurs in California and Florida. It has an enormous worldwide economic importance. In the various countries cultivation is geared toward the production of: (1) fruits for immediate consumption and (2) fruits to be used for the production of juices or essential oils. For this purpose the most suitable varieties have been selected.

Parts of plant used

Leaves (and small twigs), flowers, ripe fruits, small, whole, unripe fruits, peels, and juice

Physical-chemical characteristics

Essential oil

From Leaves; Small, Whole Unripe Fruits; Twigs; and Flowers

Petitgrain oil of sweet orange can be obtained from the above by steam distillation. Its production is low because of its limited application (perfumery).

From Fruits (Peels)

Sweet orange essential oil is extracted from peels of partially ripened fruits in 0.4–0.5% yields using suitable machinery for the rupturing of the oil-bearing cells (expression). A less valuable quality of essential oil is obtained by steam distillation of peels.

Sweet orange essential oil is a clear, mobile liquid, with a yellow to orange color, characteristic odor, and typical aromatic flavor. Physical-chemical characteristics of the oil vary according to origin. Italian qualities have the following constants:

Specific gravity at 20°C	0.844–0.847[1]
Refractive index at 20°C	1.473–1.475[1]
Optical rotation at 20°C	+97° to +99°[1]
Aldehyde content (C_{10})	0.9–2.2%

California Oranges

California produces the Valencia and Washington Navel varieties. Following are characteristics for California cold-expressed oils:

Specific gravity at 25°C	0.842–0.846[1]
Optical rotation at 25°C	+94° to +98°15′[1]
Refractive index at 20°C	1.4723–1.4742[1]
Residue after drying	3.5–5.5%[1]
Aldehyde content (C_{10})	Approx 1%[1]
Solubility	Incomplete in <10 volume of 95% ethanol

Florida Oranges

Florida produces a large variety of oranges, including Parson Brown, Hamlin, Washington Navel, Pineapple, Homosassa, Jaffa, Temple, and Valencia. This production is essentially geared toward the expression of juice, but most converters are equipped to recover the oil. Florida cold-expressed oil exhibits the following characteristics:

Specific gravity at 25°C	0.842–0.846[1]
Optical rotation at 25°C	+96° to +99°[1]
Refractive index at 20°C	1.4723–1.4742[1]
Aldehyde content (C_{10})	0.8–2.1%[1]
Residue after drying	1.6–4.5%[1]
Solubility	Incomplete in <10 volumes of 95% ethanol

Israeli Oranges

Israeli citrus production has reached significant importance in recent times, especially for juice production; types grown include Valencia and Shamuti. Characteristics of Israeli oil include the following:

Specific gravity at 20°C	0.842–0.845[1]
Optical rotation	+95° to +98°[1]
Refractive index at 20°C	1.4745[1]
Acid value	0.2–0.5[1]
Aldehyde content (C_{10})	1.1–1.5%[1]
Residue after drying	2.5–5.0%[1]

The essential oil contains more than 90% limonene and in addition decylic, octylic, nonylic, and dodecylic aldehydes, citral, acids, and esters. From the raw essence of sweet orange, the terpeneless essence can be obtained by vacuum distillation (with heat), by chromatographic separation, or by extraction with low-proof alcohol. By washing the oil with low-proof alcohol, one obtains the soluble essence of sweet orange with yields of 1:50, 1:100, 1:200, 1:400; the essence is used in the flavoring of carbonated beverages, syrups, liqueurs, aperitifs, and other products. Orange pastes for use in carbonated beverages are prepared using terpeneless essential oil, juices, pectins, and sugars.

Derivatives

From Peels
The tincture (20% in 70% ethanol) and the fluid extract are prepared from the dried peel.

From Pulp
Juice is prepared by squeezing the pulp and filtering, using specially designed machinery.

Dry residue	10–12%[1]
Acidity	1–2% (expressed as citric acid)[2]

The juice is subsequently pasteurized and concentrated. Sulfur dioxide and other preservatives may be added. (Check local laws.) It can be distinguished commercially as turbid juice (pasteurized) or clear juice (non-pasteurized). Pasteurization serves to inactivate pectolytic enzymes in the juice that would tend to clarify the product on standing. Both types may contain pulp in varying amounts (large, medium, or fine cells). Concentration is carried out in special equipment (batch, continuous, under vacuum with recovery of "supervolatiles", freezing, etc.) until a volume 5–7 times smaller than original is obtained. A 72° Brix concentrate is usually in large demand.

Organoleptic characteristics

The oils and various derivatives have a mild to highly bitter, astringent flavor and a characteristic aroma. Juices are sweet and acidic or tart.

Uses

Distilled orange oil has been reported used in the following:[3]

non-alcoholic beverages	130 ppm
ice cream, ices, etc.	140 ppm
candy	690 ppm
baked goods	440 ppm
gelatins and puddings	45–500 ppm
chewing gum	930 ppm

Terpeneless orange oil has been reported used in the following:[3]

non-alcoholic beverages	10 ppm
ice cream, ices, etc.	17 ppm
candy	38 ppm
baked goods	25 ppm
gelatins and puddings	230 ppm
chewing gum	13–160 ppm
condiments	25 ppm

The orange peel extract has been reported used in the following:[3]

non-alcoholic beverages	99 ppm
ice cream, ices, etc.	170 ppm
candy	320–330 ppm
baked goods	320–330 ppm

Orange peel oil has been reported used in the following:[3]

non-alcoholic beverages	210 ppm
alcoholic beverages	5 ppm
ice cream, ices, etc.	330 ppm
candy	1,000 ppm

baked goods	430 ppm
gelatins and puddings	1,300 ppm
chewing gum	4,200 ppm
condiments	32 ppm
cereals	49 ppm
icings	190 ppm
meats	10 ppm
syrups	0.34 ppm

Terpeneless orange peel oil has been reported used in the following:[3]

non-alcoholic beverages	43 ppm
ice cream, ices, etc.	83 ppm
candy	190 ppm
baked goods	240 ppm
gelatins and puddings	600 ppm

Regulatory status

Sweet orange: GRAS (II)
Orange leaf: GRAS (II)
Sweet orange flower: GRAS (II)
Sweet orange peel: GRAS (II)

ORIGANUM

Botanical source

Origanum vulgare L. and other *Origanum* species

Botanical family

Labiatae

Foreign names

Origan (Fr.), Dosten (Ger.), Oregano (Sp.), Origano (It.)

Description

Herbaceous plant, widespread throughout all continents; it grows wild in sunny spots or is cultivated. It reaches 30–80 cm (12–32 in.) in height and exhibits an oblique rhizome, erect flower-bearing stalks with lateral sterile stalks, opposite leaves, and purple or white flowers (July to August) that form terminal spikes.

A number of botanical sources are classified under the name "origans". These species differ considerably in both odor and flavor characteristics. The so-called "wild marjoram" is the common herb *Origanum vulgare,* which is cultivated all over the world. The commercially known "oil of wild marjoram" is distilled from the plant *Thymus martichina,* which grows wild in the mountainous areas of central Spain. The latter, in turn, should not be confused with "Spanish origanum" (*Thymus capitatus*), which yields an essential oil with a high (about 50%) carvacrol content.

Parts of plant used

Flowering tops

Physical-chemical characteristics

Essential oil

The oil is obtained by steam distillation of various origanum species with yields of less than 1% In Italy the varieties *O. viride* and *O. virens* are used. Their constants follow:

O. viride

Specific gravity at 15°C	0.918[1]
Optical rotation	$-1°40'$[1]
Refractive index	1.4991[1]
Phenol content	45%[1]
Solubility in 80% ethanol	1:2[1]
Solubility in 75% ethanol	

O. virens

Specific gravity at 15°C	0.9285[1]
Optical rotation	$-1°24'$[1]

Refractive index	1.4967[1]
Phenol content	48.5%[1]
Solubility in 80% ethanol	—
Solubility in 75% ethanol	1:2.4[1]

Thymol comprises the major portion of the phenols in some varieties, while others contain mainly carvacrol. Spanish origanum essential oil belongs to the latter variety (*see Thymus capitatus*).

Derivatives

Infusion (2%) and tincture (10% in 70% ethanol)

Organoleptic characteristics

Fresh, herbaceous odor; warm, burning flavor

Uses

The dried product, the tincture, and the essential oil are used by the flavor industry in certain liqueur formulations. The oil is used in compounded oils for flavoring meat, sauces, and other products. Origanum species have been reported used in the following:[3]

non-alcoholic beverages	320 ppm
baked goods	400 ppm
condiments	2,800 ppm
meats	540 ppm

Regulatory status

GRAS (II)

ORRIS

Botanical source

Iris germanica L. (including its variety *florentina* Dykes) and *I. pallida* Lam.

Botanical family

Iridaceae

Foreign names

Iris (Fr.), Iris (Ger.), Lirio (Sp.), Ireos (It.)

Description

Perennial herbaceous plant that grows wild or can be cultivated. The various species are native to the Far East, but they are well acclimated to the Mediterranean regions as well. Their cultivation in Italy represents a flourishing industry. *I. pallida* Lam. is the best variety for extractive purposes, followed by *I. germanica* and *I. florentina* (which is cultivated mainly for ornamental purposes). Depending on the variety, the plant exhibits blue, deep blue, or whitish-blue veined flowers. It has an erect stem and radical leaves. It has large, horizontal, highly branched and fleshy rhizomes exhibiting a pleasant and persistent odor. The fragrance of *I. pallida* is most persistent.

Parts of plant used

The peeled rhizomes (roots) after two years of aging. Commercial qualities include straight, twisted, and knotty rhizomes

Physical-chemical characteristics

Orris Concrete

Orris butter, or orris concrete, is obtained by steam distillation of dried ground rhizomes with yields ranging between 0.2–0.3%. Special techniques and prolonged distillation are required. It contains 13% to 17% ketones (sometimes more) calculated as irone; 83–86% free or partially esterified fatty acids (*e.g.*, myristic); terpene and sesquiterpene alcohols; aldehydes; and esters. The physical-chemical constants vary, depending on the origin of the rhizomes. At room temperature orris concrete from *I. pallida* Lam. is a light yellow-brown solid mass with a violet-like fragrance; at 40–50 C the product melts to a yellow to yellow-brown liquid.

Melting point	38–50°C[2]
Acid value	175–235[2]
Ester value	4–35[2]
Ketone content (as irone)	9–20%[2]
Solubility	Soluble in ethanol[2]

Orris Absolute
Orris absolute is obtained by alcoholic extraction of the concrete to separate the fatty acids and their esters. It may contain from 55–85% ketones (irone).

Orris Resinoid
The resinoid is prepared by extracting the comminuted rhizomes with yields of 2.4–3.3%, using benzene, or 1–2% using petroleum ether. An absolute can be prepared from the resinoid; this contains 62–78% ketones (irone).

Derivatives
Fluid extract, concrete and absolute essence, resinoid, and the tincture (20% in 50–60% ethanol or 30% in 55% ethanol)

Organoleptic characteristics

Violet-like odor with a fruity undertone

Uses

The dried product and its derivatives are generally employed by the flavor industry in enology, liqueurs, and perfumes. Each derivative has its specific applications. Orris concrete liquid oil (*I. florentina* L.) has been reported used in the following:[3]

non-alcoholic beverages	1.7 ppm
ice cream, ices, etc.	0.52 ppm
candy	1.1 ppm
baked goods	1.3 ppm
gelatins and puddings	1.56 ppm
chewing gum	8.8 ppm
icings	4.0 ppm

Orris root extract (*I. florentina* L.) has been reported used in the following:[3]

non-alcoholic beverages	9.2 ppm
ice creams, ices, etc.	29 ppm
candy	56 ppm
baked goods	31 ppm
gelatins and puddings	2.0 ppm
chewing gum	10–120 ppm

Regulatory status

FDA §121.1163

PALMAROSA

Other names

East Indian geranium

Botanical source

Cymbopogon martini Stapf. var. *motia*

Botanical family

Gramineae

Foreign names

Palmarosa (Fr.), Palmarosa (Ger.), Palmarosa (Sp.), Palmarosa (It.)

Description

Herbaceous plant having long stems and terminal flowering tops. It grows wild or is cultivated on a limited scale in India, Java, Seychelles, and, more recently, on the Comores Islands and in Brazil. The wild grass usually is employed for distillation.

Parts of plant used

The herb (leaves, stems, flowering tops)

Physical-chemical characteristics

Essential oil

The oil is obtained by steam distillation of partially dried plants harvested between September and October. It is a pale-yellow to yellow liquid with a rose-like odor and a characteristic, herbaceous undertone. The physical-chemical constants of the oil follow (see also reference 2):

Specific gravity at 20°C	0.882–0.896[1] (0.882–0.894)[6]
Refractive index at 20°C	1.4715–1.4780[1] (1.4720–1.4780)[6]

Optical rotation at 20°C	−3° to +3°[1]
Ester value	10–70[1] (10–40)[6]
Total alcohol content (as geraniol)	84–94%[1]
Solubility	1:2 in 70% ethanol[1]

Organoleptic characteristics

Sweet, rose-like odor with herbaceous undertone

Uses

The essential oil is used in perfumery as a starting material for the extraction of geraniol. In flavors the oil finds application similar to geranium essential oil in the formulation of aromas for tobaccos, candies, and baked goods. Palmarosa oil (FEMA No. 2831) has been reported used in the following:[3]

non-alcoholic beverages	4.2 ppm
ice cream, ices, etc.	1.7 ppm
candy	12 ppm
baked goods	13 ppm

Regulatory status

GRAS (II)

PANSY

Botanical source

Viola tricolor L.

Botanical family

Violaceae

Foreign names

Violette tricolore (Fr.), Stiefmütterchen (Ger.), Flor de la Trinidad (Sp.), Viola tricolore (It.)

Description

This annual or perennial herb has glabrous, sometimes pubescent stems and spindle-shaped, crooked, nodose roots with several smaller fibrous roots. The lower leaves are roundish or cordate, slightly lanceolate; the upper leaves are oblong and crenate, with a long peduncle that supports the solitary axillary flowers exhibiting a many-colored (yellow, blue, purple) corolla. The fruits consist of dehiscent, loculicidal capsules; the fleshy seeds contain abundant amounts of albumin.

Parts of plant used

Flowers

Physical-chemical characteristics

Derivatives

Decoction and infusion. Main constituents include violanin and violaquercitrin. The latter glucoside yields quercetin, rhammose, and mannose on hydrolysis. A resin, mucilages, and natural gums associated with vegetal albumins and traces of methylsalicylate are also present.

Uses

In alcoholic beverages

Regulatory status

FDA §121.1163. In alcoholic beverages only

PARSLEY

Botanical source

Petroselinum sativum Hoffm. (*Apium petroselinum* L., *Carum petroselinum* Benth. & Hook.)

Botanical family

Umbelliferae

Foreign names

Persil (Fr.), Petersilie (Ger.), Perejil (Sp.), Prezzelmolo (It.)

Description

Parsley is an annual or biennial herb that grows wild or is cultivated throughout the Mediterranean regions, Hungary, Germany, France, Holland, and the United States. The plant has spindle-shaped roots; ternately pinnate, decompound leaves with toothed, ovate leaflets; yellowish-green flowers in umbellate clusters; ovoid fruits; and carpels marked with five prominent ribs.

Parts of plant used

Leaves, flowering tops, ripe seeds, and roots

Physical-chemical characteristics

Essential oils

Parsley Seed Essential Oil

Parsley seed essential oil is obtained by steam distillation of the ripe seeds in approximately 1.5–3.5% yields. It is a more or less viscous, yellowish to yellow-amber liquid that sometimes deposits crystals on being chilled. The oil has a warm, spicy odor with a bitter, warm, aromatic taste. Its physical-chemical constants follow:

Specific gravity at 25°/25°C	1.040–1.080^{2} (1.043–1.083 at 20°/20°C)^{6}
Optical rotation	-4° to -10°^{2} (-4° to -11°)^{6}
Refractive index at 20°C	1.5130–15.220^{2} (1.5100–1.5290)^{6}
Acid value	4 max^{2}
Ester value	2–10^{2}
Solubility	1:4–6 in 80% alcohol^{2} (1:7 in 80% ethanol)^{6}

Main constituents, in addition to apiole, include α-pinene, myristicin, traces of conjugated coumarins, ketones, aldehydes, a solid hydrocarbon (m.p. = 69°C), and traces of phenolic compounds.

Parsley Leaf Oil

Parsley leaf oil is obtained by steam distillation of leaves and flowering tops in very low yields (0.06%). This oil exhibits a much harsher, herbaceous note than the seed oil and has the following physical-chemical constants:

Specific gravity at 15°C	0.948–0.967^{1}
Refractive index at 20°C	1.5087–1.5159^{1}
Optical rotation	−2°55′ to −6°10′^{1}
Saponification number	0.9–7.0^{1}
Solubility	1:10 in 90% ethanol^{1}

Parsley Herb Essential Oil

Parsley herb essential oil is obtained by distilling the whole plant, excluding the root. It is a pale-yellow to greenish-yellow liquid with a pronounced herbaceous odor and a warm, bitter, slightly burning taste. Its physical-chemical constants are as follows:

Specific gravity at 15°C	0.911^{1}
Refractive index	1.5029^{1}
Optical rotation	+6°^{1}
Acid value	1.4
Ester value	8.9
Ester value (after acetylation)	44.8
Solubility	Soluble with opalescence in 95% ethanol; insoluble in 90% ethanol

Derivatives

Infusions and decoctions (from roots; for pharmacological use only), oleoresin (from seeds).

Organoleptic characteristics

Warm, herbaceous, fresh odor; warm, spicy, aromatic, bitter taste

Uses

Parsley essential oils find limited use in perfumery. The herb essential oil distilled from the whole plant is used preferably with the other oils and the oleoresin to flavor cured and canned meats and condiments and in the formulation of compounded aromas for pastry. The fresh herb is widely used in cooking.

Parsley (FEMA No. 2835) has been reported used in the following:[3]

non-alcoholic beverages	3,000 ppm
baked goods	850 ppm
condiments	2,700 ppm
meats	1,000 ppm
soups	200—500 ppm

Parsley oil (FEMA No. 2836) has been reported used in the following:[3]

non-alcoholic beverages	1.4 ppm
ice cream, ices, etc.	0.20—0.25 ppm
candy	4.1 ppm
baked goods	8.5 ppm
condiments	4.9 ppm

Parsley oleoresin (FEMA No. 2837) has been reported used in condiments, 5.0–30 ppm.[3]

Regulatory status

GRAS (I), (II)

PASSION FLOWER

Other names

Passiflora

Botanical source

Passiflora incarnata L.

Botanical family

Passifloraceae

Foreign names

Passiflore purpurine (Fr.), Passionsblume (Ger.), Pasionaria (Sp.), Passiflora (It.)

Description

The passion flower is native to the United States and Brazil; it grows preferably in dry soils. The plant has woody, sarmentose stems covered by a grayish bark; axillary filiform tendrils; alternate, palmate, trilobed, finely dentate leaves terminated by glandular petioles. The solitary, odorous, white flowers are borne by articulate peduncles. The dehiscent berries (fruits) are almost spherical and contain ovate seeds covered by the aril.

Parts of plant used

Leaves and flowers. More frequently the whole branches are used, complete with leaves harvested after the appearance of the first fruits.

Physical-chemical characteristics

Derivatives

Fluid extract, soft aqueous extract, dried extract, alcoholic extract, and infusion (2%). Main constituents include alkaloids (harmine, harmalol, harmane) and a few flavone derivatives.

Uses

Passion flower finds some use in pharmacology as a sedative.

Regulatory status

FDA §121.1163

PATCHOULY

Botanical source

Pogostemon cablin Benth. (*P. patchouly* Pellet. var. *suavis* Hook. f.) and *P. heyneanus* Benth.

Botanical family

Labiatae

Foreign names

Patchouly (Fr.), Patchouli (Ger.), Pachuli (Sp.), Patchouli (It.)

Description

Patchouly is an herbaceous plant having characteristic inferiorly hirsute leaves, slightly lobed and toothed. The true patchouly, known as tilam wangi and dhalum wangi, is cultivated extensively in Indonesia and Malaysia and, to a minor extent, in Madagascar, Seychelles, Brazil, and Paraguay. The largest market centers are, however, Penang and Singapore. In recent years *P. heyneanus* (a flower-bearing wild patchouly variety) has been used for distillation as well.

Parts of plant used

The leaves

Physical-chemical characteristics

Essential oil

The oil is obtained by steam distillation of properly dried leaves in approximately 1.5–3.0% yields. Independent of its origin, the essential oil is a slightly viscous, brown liquid with a typical camphoraceous odor and woody undernote imparted sometimes by adulteration of the oil with gurjum balsam. The classic patchouly odor is recognizable in the high-quality oil manufactured in the Malaysian state of Johore and marketed under the name of Paxamo Special Singapore. The physical-chemical constants vary widely, depending on the source of the oil; the following constants are commonly accepted, however:

Specific gravity at 25°/25°C	0.950–0.975^{2} (0.955–0.990 at 20°/20°C)^{6}
Refractive index at 20°C	1.5070–1.5150^{2} (1.5050–1.5180)^{6}
Optical rotation	−48° to −65°^{2}
Acid value	<5^{2} (4.0 max)^{6}
Solubility	1:10 in 90% alcohol^{2}

Terpeneless and sesquiterpeneless essential oils are also manufactured but have only limited commercial importance.

The main known constituents include benzaldehyde, eugenol, cinnamaldehyde, patchouly alcohol (a tricyclic alcohol, $C_{15}H_{26}O$), two hydrocarbons ($C_{15}H_{24}$), and other minor unidentified components.

Derivatives

Concrete and absolute. Patchouly leaves also can be extracted with solvents (benzene) yielding approximately 5–6% concrete. The absolute is prepared from the concrete in approximately 75–80% yields. The concrete and absolute do not exhibit the slight moldy note of patchouly oil; they have pronounced fixative properties.

Organoleptic characteristics

Characteristic, persistent, slightly camphoraceous odor

Uses

Patchouly essential oil is employed extensively in perfumery and in the making of soap. The patchouly odor blends well with almost any type of perfume composition. The concrete and absolute also are used because of their fixative properties. The use of patchouly oil in flavors is sporadic and highly dependent on the market to which the products are destined. The use of the oil in compounded aromas to flavor chewing gum and baked goods is the most common application.

Patchouly oil (FEMA No. 2838) has been reported used in the following:^{3}

non-alcoholic beverages	0.88 ppm
ice cream, ices, etc.	1.1 ppm
candy	6.3 ppm
baked goods	10 ppm
chewing gum	43–220 ppm

Regulatory status

FDA §121.1163

PEANUT STEARINE

Botanical source	*Arachis hypogaea* L.
Botanical family	*Leguminosae*
Foreign names	Arachide (It.)
Description	The peanut genus has nine species, eight of which are native to Brazil. Its leaves are abruptly pinnate; the flowers are yellow in a dense, axillary, sessile spike. The fruit or nut is really a pod, comparable with a bean pod or pea pod.
Parts of plant used	The nut
Organoleptic characteristics	Fatty odor and taste
Uses	Binding agent for tablets; tablet-releasing agent
Regulatory status	GRAS

PENNYROYAL

Botanical source	*Hedeoma pulegioides* (L.) Pers.—American pennyroyal; *Mentha pulegium* L.—European pennyroyal
Botanical family	*Labiatae*
Foreign names	Menthe pouliot (Fr.), Polei (Ger.), Poleo (Sp.), Menta puleggio (It.)
Description	Herbaceous pubescent plant having characteristic thin, fusiform, fibrillose roots; numerous prostrate stems; opposite, short-petiolate, oblong or ovate, dentate leaves; pinkish flowers arranged in axillary cymose tops; ovoidal, smooth fruits. *M. pulegium* L. grows wild in Spain, Morocco, and other Mediterranean countries. *H. pulegioides* (L.) Pers. belongs to the same botanical family, but grows exclusively in the United States. The U.S. variety yields on distillation an essential oil with a more acrid, distinct mint odor; it is also less rich in pulegone than the European essential oil.
Parts of plant used	The fresh or partially dried flowering plant
Physical-chemical characteristics Essential oil	*M. pulegium* L. European pennyroyal essential oil is obtained by steam distillation of the fresh or partially dried plant. It is a pale-yellow to yellow aromatic oil with a distinct, mint-like, pleasant odor and bitter, somewhat herbaceous flavor. Its physical-chemical constants follow (see also reference 2):

Specific gravity at 15°C	0.936–0.944[1]
Refractive index at 20 C	1.4829–1.4877[1]
Optical rotation	+15°18′ to +23°48′[1]
Pulegone content	85–96%[1]
Solubility	1:45–5.5 in 60% ethanol[1]

Its main constituents include *l*-α-pinene, *l*-limonene, *d*-pulegone, *l*-menthone, *d*-isomenthone, piperitone, menthol, 1-methyl-3-cyclohexanone, *n*-1-octen-3-ol, 1-methyl-3-cyclohexanol, and 1,1,3-trimethyl-4-cyclopentenone.

H. pulegioides (L.) Pers.
American pennyroyal essential oil is obtained by steam distillation in approximately 0.6–1.0% yields. It is a pale-yellow liquid with a much harsher mint-like odor, more bitter and herbaceous than the European oil. The taste is sharp, bitter, slightly burning. Its physical-chemical constants are as follows:

Specific gravity at 15°C	0.925–0.940^1
Optical rotation	+18° to +35°^{1}
Solubility	>1:2 in 70% ethanol^1

The main constituents include *l*-α-pinene, *l*-limonene, dipentene, 1-methyl-3-cyclohexanone, *l*-menthone, *d*-isomenthone, acids (formic, acetic, butyric, salicylic), and a phenol. Pulegone, the main constituent, is present in lower levels than in the European distilled oil.

Derivatives Fluid extract, tincture, infusion (prepared from the dried leaves)

Organoleptic characteristics Aromatic, mint-like odor; bitter taste

Uses The derivatives are sometimes used in medicine. The European essential oil was used for a long time as the starting material for the extraction of menthol (formed by reduction of pulegone). This method can no longer compete with synthetic menthol. Because of the herbaceous, bitter taste, the use of the oil in flavors is very limited. The oil sometimes is employed in the formulation of compounded oils for flavoring candy, beverages and ice cream. The largest use of the oil, however, is in perfumery and other industrial products (soaps, insecticides, etc.).

Pennyroyal oil (FEMA No. 2839) has been reported used in the following:^{3}

non-alcoholic beverages	1.5–5.0 ppm
ice cream, ices, etc.	3.7 ppm
candy	14 ppm
baked goods	20–24 ppm

Regulatory status American and European pennyroyal: FDA §121.1163

PEPPER, BLACK AND WHITE

Botanical source *Piper nigrum* L.

Botanical family *Piperaceae*

Foreign names Poivre (Fr.), Pfeffer (Ger.), Pimienta (Sp.), Pepe (It.)

Description A vine native to southern India; it is cultivated in India, the Sunda Islands, Madagascar, and the Comoro Islands. The plant exhibits a thick, branched stalk; alternate, spear-shaped leaves; sessile flowers arranged in spikes opposite the leaves; and round berries that turn from green to red on ripening. The best known commercial qualities of pepper include Malabar and Lampong.

Whole dried berries, consisting of the epicarp, mesocarp, and endocarp, yield *black pepper*. Berries stripped of the epicarp and the outer portion of the mesocarp (by manual or mechanical maceration) yield *white pepper*. The dried berry contains the aroma distributed as follows:

(1) the epicarp contains the resinous fraction consisting of chavicin, and
(2) the outer portion of the mesocarp contains the essential oil.

Therefore, *black pepper* yields an essential oil and oleoresin, while *white pepper* is used only as a spice. Black pepper retains both the odor and flavor characteristics of pepper, while white pepper retains only the sharp, piquant flavor due to piperine.

Part of plant used

Berries, which are harvested at the onset of ripening

Physical-chemical characteristics

Essential oil

Obtained by steam distillation of berries in yields ranging between 1–2.6%. Pepper essential oil is a pale-yellow liquid with a characteristic odor (also see reference 2). The main constituents of the oil include α- and β-pinene, β-caryophyllene, *l*-limonene, *d*-hydrocarveol, piperidine, and piperine.

Specific gravity at 20°C	0.860 to 0.904[1]
Refractive index at 20°C	1.4800 to 1.5020[1]
Optical rotation at 20°C	−8° to +4°[1]
Ester value	11 max.[1]

Derivatives

The oleoresin is obtained by solvent extraction of dried, unripe berries with subsequent removal of the solvent. It is a dark-green extract usually consisting of an upper oily layer and a lower crystalline portion (see reference 2).

Organoleptic characteristics

Black pepper has a pungent, characteristic odor most apparent when dried whole berries are freshly ground; the flavor is sharp and burning. White pepper has little odor, but the flavor is unusually sharp, biting, and burning.

Uses

The world consumption of black and white pepper as spices is enormous and assessed at several thousands of tons per year. Both the oleoresin and the essential oil retain a large consumer market as well. Aside from a very limited use in perfumery, the products are used "as is" by the flavor industry or blended with other ingredients in flavoring meat, cured meats, condiments, sauces, and other food products. The oleoresin is offered also plated on a salt carrier.

Black pepper has been reported used in the following:[3]

non-alcoholic beverages	30 ppm
baked goods	1,200 ppm
condiments	690 ppm
meats	1,700 ppm
pickles	7.2–230 ppm
soups	27–100 ppm

Black pepper oil has been reported used in the following:[3]

non-alcoholic beverages	2.7 ppm
ice cream, ices, etc.	0.10–20 ppm
candy	5.3 ppm
baked goods	8.5 ppm
condiments	17 ppm
meats	40 ppm

Black pepper oleoresin has been reported used in the following:[3]

non-alcoholic beverages	15 ppm
ice cream, ices, etc.	1.0–20 ppm
candy	1.0–15 ppm
baked goods	1,600 ppm
condiments	370 ppm
meats	230 ppm

White pepper has been reported used in the following:[3]

non-alcoholic beverages	5.9–140 ppm
baked goods	450 ppm
condiments	2,700 ppm
meats	600 ppm
soups	500 ppm

White pepper oil has been reported used in baked goods, 0.60 ppm.[3]
White pepper oleoresin has been reported used in meats, 50 ppm.[3]

Regulatory status

Black pepper: GRAS (I), (II)
White pepper: GRAS (I), (II)

PEPPERMINT

Botanical source

Mentha piperita L.

Botanical family

Labiatae

Foreign names

Menthe poivrée (Fr.), Pfefferminz (Ger.), Mentha pimienta (Sp.), Menta piperita (It.)

Description

Mentha piperita L. Huds. is a hybrid derived from three other species: *M. aquatica* L. and *M. viridis* L.; the latter is in turn a cross between *M. silvestris* L. and *M. rotundifolia* L. *M. piperita* exists in two varieties: *M. piperita officinalis pallens* Camus (white mint) and *M. piperita officinalis rabescens* Camus (black mint). Peppermint is an herbaceous plant cultivated in central and southern Europe, North and South America, and Japan. The plant grows to 80 cm (32 in.) in height; it has an erect green stalk with white flowers (white mint) or a reddish-brown stalk with reddish-brown flowers (black mint). It has opposite leaves, long creeping roots, erect opposite branches, and flowers grouped in clusters and arranged in spikes.

Parts of plant used

Flowering tops

Physical-chemical characteristics

Essential oil

The oil is obtained by steam distillation of the flowering plant with yields ranging from 0.3–0.7%, depending on the origin of the plant. It is a pale-yellow liquid with a characteristic odor. The physical-chemical constants of the oil vary, depending on the source.[1]

	Italian	French	North American
Specific gravity at 20°C	0.900–0.910	0.901–0.916	0.903–0.912
Refractive index at 20°C	1.462–1.464	1.460–1.467	1.460–1.464
Optical rotation at 20°C	−16° to −23°	−10° to −29°	−17° to −28°
Ester value	14–34	14–19	14–19
Ester value (after acetylation)	135–174	135–200	157–193
Ketone content (as menthone)	19–30	15–30	19–32
Solubility in 70% ethanol	1:3.5	1:5	1:5

Raw peppermint essential oil to be used for food flavoring must be rectified. This type of essential oil is commonly known as tri-rectified peppermint essential oil. A good product of Italian origin (Piedmont) exhibits the following constants:

Specific gravity at 15°C	0.907–0.918[1]
Optical rotation	−19° to −27°[1]
Refractive index at 20°C	1.4610–1.4690[1]
Menthol content (total)	50–60%[1]
Menthol content (free)	45–52%[1]
Esterified menthol	4–8%[1]
Solubility in 70% ethanol	1:2 to 1:3[1]

The main constituents are identical in all oil varieties, but the relative ratios vary widely. Constituents include α- and β-pinene, limonene, cineol, ethyl amylcarbinol, menthone, isomenthone menthofuran, menthol, neomenthol, isomenthol menthyl acetate, and piperitone.

The soluble peppermint essence is obtained by solubilization in alcohol of the tri-rectified essential oil. It is used in syrups and liqueurs with yields ranging from 1:100 to 1:400.

Derivatives

Infusion (2%), fluid extract, and tincture (20% in 70% ethanol)

Organoleptic characteristics

Fresh, strong, mint odor; sweet, balsamic taste, often masked by the distinct cooling effect

Uses

The dried flowering tops are used to prepare the beverage peppermint tea and the infusion. They are used also in small quantities in the formulation of liqueurs and special bitters. The fluid extract still retains some pharmaceutical application.

The essential oil (tri-rectified) is extensively used in flavoring candies, bitter chocolates, tobacco, toothpastes, and other products. It is also used in perfumery and cosmetic products; in such applications it is often replaced by menthol. Peppermint oil has been reported used in the following:[3]

non-alcoholic beverages	99 ppm
alcoholic beverages	240 ppm
ice cream, ices, etc.	110 ppm
candy	1,200 ppm
baked goods	300 ppm
gelatins and puddings	75–200 ppm
chewing gum	8,300 ppm
meats	8.0 ppm
icings	5.0–54 ppm
toppings	650 ppm

Regulatory status

GRAS (I), (II)

PERUVIAN BALSAM

Other names

Balsam Peru

Botanical source

Myroxylon pereirae Klotzsch

Botanical family

Leguminosae

Foreign names

Baume du Pérou (Fr.), Perubalsam (Ger.), Balsamo Peru (Sp.), Balsamo del Peru (It.)

Description

The balsam consists of the bark exudate obtained from large trees (up to 15 m [49 ft] high) growing in a rather limited area of Central America (El Salvador). The name Peruvian balsam therefore is a misnomer. The balsam is collected by two methods:

(1) by partially burning the bark, which permits its easy removal after a few days. The bark fragments then are immersed in hot, boiling water, and the oozed balsam is collected at the bottom of the containers;

(2) by wrapping a cloth around incisions made in the bark. The cloth, impregnated with balsam, is then boiled to separate the product. Finally, the residual water is removed from the balsam by direct heating.

The balsam is an oleoresin containing 25–30% resinous material and 60–65% essential oil. Peru balsam is a viscous, transparent, dark-brown mass with a sweet, delicate, lasting odor reminiscent of vanilla. The balsam is readily soluble in 95% alcohol, chloroform, and glacial acetic acid, and only partially soluble in ether and petroleum ether. Its physical-chemical constants follow:

Specific gravity at 26°C	1.152–1.170[1]
Acid value	56.2–83[1]
Cinnamein content	47–59%[1]

Parts of plant used

The balsam (oleoresin)

Physical-chemical characteristics

Essential oil

The oil cannot be steam distilled from the balsam because of its very high boiling point; instead it is co-distilled from the resin in approximately 43–55% yields, using volatile solvents. The oil is a reddish-brown, slightly viscous liquid with a warm, sweet, balsamic, lasting odor and bitter taste. The main constituents include benzyl benzoate, benzyl cinnamate, *n*-nerolidol, farnesol, vanillin, cinnamyl alcohol, cinnamyl cinnamate, and probably stilbene. Its physical-chemical constants are as follows:

Specific gravity at 15°C	1.102–1.122[1]
Optical rotation	+1° to 20°30′[1]
Refractive index at 20°C	1.570–1.580[1]
Acid value	24–52[1]
Ester value	200–250[1]

Derivatives

The resinoid is prepared by extraction of the resin using volatile solvents (benzene, alcohol). The resinoid is a brown, very viscous mass with a pleasant odor. The benzene-extracted resinoid has the following physical-chemical constants:

Specific gravity at 15°C	1.103–1.126[1]
Optical rotation	up to +2°44′[1]
Refractive index at 20°C	1.568–1.582[1]
Acid value	22.4–48.6[1]
Ester value	198–260[1]

Organoleptic characteristics

Warm, sweet, balsamic odor; bitter taste

Uses

The resinoid finds extensive use in perfumery because of its outstanding fixative properties. The oil is used limitedly in flavor work because of the bitter and slightly burning taste.

Peru balsam (FEMA No. 2116) has been reported used in the following:[3]

non-alcoholic beverages	3.0 ppm
ice cream, ices, etc.	5.9 ppm
candy	10 ppm
baked goods	32 ppm
gelatins and puddings	0.05–1.0 ppm
chewing gum	120 ppm
syrups	0.25–7.0 ppm

Peru balsam oil (FEMA No. 2117) has been reported used in the following:[3]

non-alcoholic beverages	3.2 ppm
ice cream, ices, etc.	2.2 ppm
candy	8.4 ppm
baked goods	6.6 ppm

Regulatory status

GRAS (II)

PETITGRAIN

Petitgrain Bigarade and Paraguay Petitgrain

Botanical source *Citrus aurantium* L. subspecies *amara* L.

Botanical family *Rutaceae*

Foreign names Petitgrain, bigarade and Paraguay—Fr., Ger., Sp., It.

Description Petitgrain is a product obtained by processing leaves and twigs of the bitter orange tree. *See* Orange, Bitter, for additional information.

Parts of plant used Leaves and twigs of the bitter orange tree

Physical-chemical characteristics

Essential oil Petitgrain bigarade oil is obtained in approximately 0.2% yields by steam distillation of leaves and twigs of the bitter orange tree; the leaves are the main starting material. Paraguay petitgrain oil (or petitgrain oil, South American) is obtained by steam distillation of the leaves and twigs of a variety of *C. aurantium* L. growing semi-wild or cultivated in Paraguay. Distillation using super-heated steam reduces hydrolysis of esters important for quality aroma. From either petitgrain bigarade or Paraguay petitgrain oil, a terpeneless oil can be prepared by vacuum distillation. Although physical constants vary widely, it is possible to identify the origin by the physical-chemical characteristics.

Petitgrain Bigarade Oil

An Italian product, petitgrain bigarade oil is a pale-yellow to amber liquid with a pleasant, ethereal odor; it is characterized as follows:

Specific gravity at 20°C	0.888–0.898[1]
Refractive index at 20°C	1.4560–1.4620[1]
Optical rotation at 20°C	−6° to +1°[1]
Acid value	<1[1]
Per cent ester (as linalyl acetate)	49–76[1]
Solubility	1:3–1:5 in 70% ethanol[1] 1:1–1:2 in 75% ethanol[1]

Paraguay Petitgrain Oil

A South American product, Paraguay petitgrain oil is a yellow to brownish-yellow liquid with a somewhat harsh, bittersweet odor; it is characterized as follows:

Specific gravity at 25°/25°C	0.878–0.889[2] (0.884–0.892 at 20°/20°C)[7]
Optical rotation	+1° to -4°[2] (0° to -3.5°)[7]
Refractive index at 20°C	1.4580–1.4640[2] (1.457–1.465)[7]
Per cent ester (as linalyl acetate)	45–60%[2] (25–35%)[7]
Acid value	2 max[7]
Solubility	1:2–1:4 in 70% ethanol[2]

The main constituents of the essential oils include *l*-linalyl acetate, linalool, terpineol, and geranyl and nerol esters.

Derivatives Essential oils, terpeneless oils, petitgrain water absolute

Organoleptic characteristics Ethereal to harsh, bittersweet odor; bitter flavor

Uses Petitgrain oil is used extensively in low concentration for fruit and honey flavors; it is used also to round out harsh notes of synthetics. Terpeneless petitgrain finds some use in modifying ginger and honey flavors.

Petitgrain oil has been reported used in the following:[3]

non-alcoholic beverages	1.5 ppm
ice cream, ices, etc.	1.4 ppm
candy	5.3 ppm
baked goods	17 ppm
gelatins and puddings	0.20 ppm
chewing gum	4.1 ppm
condiments	15 ppm

Regulatory status

GRAS (II)

PIMENTA

Other names

Allspice; Jamaica pepper; semen amomi

Botanical source

Pimenta officinalis Lindl.

Botanical family

Myrtaceae

Foreign names

Piment (Fr.), Piment (Ger.), Pimento (Sp.), Pimento (It.)

Description

Pimenta is an evergreen tree growing wild in the East and West Indies and in Central and South America. The tree can reach 9–10 m (29.5–33 ft) in height; its fruits, commonly termed allspice, ripen between September and March. The pimenta tree is commercially exploited only on the island of Jamaica.

Parts of plant used

Leaves and fruits (berry)

Physical-chemical characteristics

Essential Leaf Oil

Obtained by steam distillation of the leaves, the essence is an orange-yellow to reddish-brown liquid with a spicy odor. Two fractions, heavier and lighter than water fractions, are formed during distillation, with a milky emulsion at the interface. The two fractions are combined at the end of the distillation. Main constituents include eugenol (approximately 70%), caryophyllene, acids, and aldehydes.

Specific gravity at 20°C	1.022–1.061[1]
Refractive index at 20°C	1.5300–1.5400[1]
Optical rotation at 20°C	0° to −5°[1]
Phenol content	65–96%[1]

Essential Berry Oil

Obtained by steam distillation of the berry, it is a yellow liquid with a warm, spicy odor and a hot, burning, peppery taste (see reference 2). Main constituents include eugenol, *l*-α-phellandrene, caryophyllene, methyleugenol, and cineol.

Specific gravity at 15°C	1.024–1.055[1] (1.027–1.048 at 20°/20°C)[7]
Refractive index at 20°C	1.525–1.536[1] (1.525–1.540)[7]
Optical rotation	−0° to −5°[1]
Phenol content	65–89%[1] (65% min)[7]
Solubility in 70% ethanol	1:1–1:2[1]

Derivatives

The oleoresin obtained from berries is a viscous, brownish-green to dark-green, non-homogeneous liquid. It exhibits a flavor and an odor more closely related to the dried product. It contains, in addition to the essential oil, resin, tannin, fixed oil, sugar, gum, and alkaloids.

Organoleptic characteristics

Warm, spicy odor and flavor reminiscent of pepper, nutmeg, clove, and cinnamon

Uses

The essential oil and the oleoresin from fruits are used like the dried product in liqueur formulations and in flavoring meat, cured meats, sauces, condiments, and other food products. The essential oil from leaves is used mainly in perfumery and for the extraction of eugenol.

Pimenta leaf oil has been reported used in the following:[3]

non-alcoholic beverages	2.8 ppm
ice cream, ices, etc.	1.3 ppm
candy	34 ppm
baked goods	32 ppm
gelatins and puddings	0.06 ppm
chewing gum	80 ppm
condiments	80 ppm
meats	160 ppm

Allspice has been reported used in the following:[3]

non-alcoholic beverages	120 ppm
ice cream, ices, etc.	1.5–2.0 ppm
candy	2.0 ppm
baked goods	1,400 ppm
chewing gum	40 ppm
condiments	1,000 ppm
meats	670 ppm

Allspice oil has been reported used in the following:[3]

non-alcoholic beverages	18 ppm
alcoholic beverages	5.0 ppm
ice cream, ices, etc.	15 ppm
candy	66 ppm
baked goods	48 ppm
chewing gum	40–1,700 ppm
condiments	70 ppm
meats	110 ppm
pickles	29 ppm
soups	55 ppm

Allspice oleoresin has been reported used in the following:[3]

baked goods	600 ppm
condiments	25–130 ppm
meats	69 ppm

Regulatory status

Pimenta (allspice): GRAS (I), (II)
Pimenta leaf: GRAS (II)

PINE, DWARF

Botanical source

Pinus mugo Turra var. *pumilio* (Haenke) Zenari

Botanical family

Pinaceae

Foreign names

Pin mughus (Fr.), Latschenkiefer (Ger.), Pino mugo (Sp.), Pino mugo (It.)

Description

The dwarf pine is a shrub or small tree that frequently grows bent or close to the ground (horizontal). It is native to the mountainous areas of central and southern Europe, Tyrol, Bavaria, Switzerland, and the Balkans. The trunk is quite twisted and knotty; branches are irregular with linear, twined needles. The flowers are monoic, and the cones have woody scales.

Parts of plant used

Needles and twigs

Physical-chemical characteristics

Essential oil

The essential oil is obtained by steam or steam-water distillation of the comminuted needles and twigs in yields of 0.3–0.4%. The oil is a clear, almost colorless mobile liquid with a characteristic odor. Main constituents include *l*-α-pinene, β-pinene, *l*-limonene, dipentene, *l*-phellandrene, aldehydes, various esters, and alcohols.

Specific gravity at 20°C	0.857–0.873[1]
Refractive index at 20°C	1.4750 to 1.4800[1]
Optical rotation at 20°C	−5° to −12°[1]
Acid value	1.0 max[1]
Ester content (as bornyl acetate)	5–7%[1]
Solubility	1:0.5 in 95% ethanol[1]
	1:8 in 90% ethanol[1]

Derivatives

Fluid extract

Organoleptic characteristics

Pleasant, pine-like odor (sweet, balsamic), somewhat woody. The unique odor apparently comes from traces of lower aliphatic aldehydes.

Uses

Dwarf pine needle oil (FEMA No. 2904) has been reported used in the following:[3]

non-alcoholic beverages	0.39 ppm
ice cream, ices, etc.	0.63 ppm
candy	1.9 ppm
baked goods	1.9 ppm

Regulatory status

FDA §121.1163

PINE, SCOTCH

Other names

Scots pine (United Kingdom); Norway pine (Scandinavia); Baltic redwood (European continent)

Botanical source

Pinus sylvestris L.

Botanical family

Pinaceae

Foreign names

Pin sylvestre (Fr.), Kiefer (Ger.), Pino sylvestris (Sp.), Pino silvestre (It.)

Description

Scotch pine grows to 20–25 m (66-82 ft) in height. It has a reddish-brown bark (rough or cracked) that detaches readily; long blue-green needles (twined) forming a terminal cluster; and flowers from April to May. The staminiferous flowers are clustered at the branch tips, while the pistiliferous flowers are singular, reddish-purple in color, and later yield scaly cones. The tree is widespread throughout Europe, Asia, and North America.

Parts of plant used

Needles and twigs

Physical-chemical characteristics

Essential oil

The oil is obtained by steam distillation of the comminuted leaves (needles). It is a clear, colorless or yellow-green, volatile liquid with a characteristic turpentine odor. It is produced mainly in Tyrol, Russia, and Yugoslavia. The physical-chemical constants vary widely, depending on the plant source.

Specific gravity at 25°/25°C	0.857–0.885[2]
Refractive index at 20°C	1.4730–1.4785[2]

Optical rotation	−4° to +10°[2]
Ester content (as bornyl acetate)	1.5–5%[2]
Solubility	1:6 in 90% alcohol[2]

Main constituents include α- and β-pinene, *d*- and *l*-limonene, aldehydes, *dl*-borneol, alcohols, terpene alcohols, bornyl acetate, phenols, and fatty acids.

Derivatives
An aqueous extract from the needles is available in Germany and Scandinavia; the soft extract is prepared from the distillation waters.

Organoleptic characteristics
Strong pine-turpentine odor

Uses
Scotch pine oil (FEMA No. 2906) has been reported used in the following:[3]

non-alcoholic beverages	6.0 ppm
candy	3.0 ppm
baked goods	2.0 ppm

Regulatory status
FDA §121.1163

PINE, WHITE

Other names
Eastern white pine; Weymouth pine; Canadian white pine

Botanical source
Pinus strobus L.

Botanical family
Pinaceae

Foreign names
The Latin name to distinguish the *Pinus* variety

Description
Tall tree 20–50 m (66–154 ft) high, having slender, glaucous leaves; oval, sterile flowers; fertile, cylindrical, long-stalked catkins; and narrow, thin-scaled cones. The tree grows mainly in the northern United States and Canada but ranges south to Georgia (U.S.).

Parts of plant used
Needles, bark

Physical-chemical characteristics

Essential oil
The production of essential oil from this pine has been abandoned. The needles are probably distilled with those from spruce. A large addition of white pine needles to spruce needles tends to lower considerably the ester content of the distilled spruce oil.

Derivatives
The turpentine content of the oleoresin is 25%. The turpentine consists of 75% *dl*-α-pinene, 15% *l*-β-pinene, and 4% terpene alcohols and ketones.

Regulatory status
FDA §121.1163. In alcoholic beverages only

PINE OIL

Botanical source
Pinus palustris and other *Pinus* species

Botanical family
Pinaceae

Foreign names
Essence de Sapin (Fr.), Fichtenoel (Ger.), Aceite essential de Pino (Sp.), Olio di pino (It.)

Description	True pine oil consists of approximately 2% of the total distillable and extractable material from pine heartwood and stumpwood. The steam-distilled wood yields an oil that is steam distilled or fractionally distilled under vacuum. The lower-boiling fractions yield the so-called wood turpentine. The steam-distilled chips are exhausted by extraction with a hydrocarbon solvent. The solvent is evaporated and the extract subjected to fractional distillation under reduced pressure. Again, the lighter fractions consist of turpentine, while the resinous residue consists of rosin. White or yellow pine oils are obtained after rectification. A pine tar oil can be prepared by destructive distillation of the wood and subsequent rectification.
Parts of plant used	Wood
Physical-chemical characteristics	
Essential oil	Pine oil, prepared by steam distillation and fractional rectification as described above, is a colorless to pale-yellow liquid with a characteristic sweet, balsamic, pine-like odor. Its physical-chemical constants vary depending on the source. Its main constituents include sesquiterpene alcohols, ketones, terpineol, fenchyl alcohol, borneol, fenchone, and estragole.
Organoleptic characteristics	Sweet, balsamic, anisic, pine-like odor
Uses	Pine oil is used mainly for industrial purposes in perfumery, detergents, soaps, and varnishes, as a flotation agent, as a starting material for the extraction of terpineol, for the production of anethole, and in the paper industry. Pine tar oil (FEMA No. 2907) has been reported used in the following:[3] ice cream, ices, etc. 2.0 ppm candy 10 ppm
Regulatory status	FDA §121.1163

PIPSISSEWA

Other names	Chimaphila; bitter wintergreen
Botanical source	*Chimaphila umbellata* (L.) Nutt.
Botanical family	*Ericaceae*
Foreign names	Herbe à pisser (Fr.), Quimafila (Sp.), Chimafila (It.)
Description	Herbaceous plant, 15–30 cm (6–12 in.) tall. It has wedge-lanceolate, sharply serrate, dentate leaves; pale pink to pink flowers in small, terminal, umbellate clusters; loculicidal fruits surrounded by a basal, persistent calyx; and numerous, small seeds. The plant grows in arid or sandy places in the mountains of northern, central, and eastern Europe and in North America.
Parts of plant used	Leaves
Physical-chemical characteristics	
Derivatives	Fluid extract and tincture. Main constituents of the leaves include arbutin, ericolin, chimaphilin, urson, tannin, pectin, sugars, and mucilages.
Organoleptic characteristics	Tonic, aromatic

Uses	The fluid extract is used in the preparation of flavors for beverages and candies. Pipsissewa leaf extract (FEMA No. 2914) has been reported used in the following:[3] non-alcoholic beverages 41 ppm candy 75 ppm
Regulatory status	Pipsissewa leaves: GRAS (II)

POMEGRANATE

Botanical source	*Punica granatum* L.
Botanical family	*Punicaceae*
Foreign names	Grenadier, Pom granate (Fr.), Granatbaum (Ger.), Granado, Mangrano (Sp.), Melograno (It.)
Description	Small tree or thick shrub probably native to Kurdistan; it grows throughout the Mediterranean basin and in other warm regions. Several varieties are known: *P. granatum silvestric* DC (wild), *P. flava* (with yellow flowers), and *P. grandiflora* Hert. *nana* (dwarf variety growing mainly in South America). The plant has an erect trunk with thin, gray bark; subtetragonal branches; and lanceolate, opposite, petiolate leaves without stipules. The flowers are crimson or purple, often growing in trifloral clusters at the tips of branches or in the axilla of the upper leaves. The almost round berries (fruits) are reddish, many seeded, with a crimson pulp.
Parts of plant used	The bark (from branches and roots); the edible fruit pulp
Physical-chemical characteristics	
Derivatives	Decoction (6%), fluid extract, and tincture (prepared from the fluid extract). Main constituents include alkaloids (pelletierine, isopelletierine, methylpelletierine, pseudopelletierine), digallic acid, punicin tannate, calcium oxalate, starches, and mucilages.
Organoleptic characteristics	Characteristic agreeable acid flavor
Uses	The astringent rind has been used in medicine and tanning; the flowers yield a red dye. Pomegranate bark extract (FEMA No. 2918) has been reported used in baked goods, candy, ice cream, and certain condiments.
Regulatory status	GRAS (II)

POPLAR

Other names	Aspen
Botanical source	*Populus balsamifera* L. (*P. tacamahacca* Mill.), *P. candicans* Ait., or *P. nigra* L.
Botanical family	*Salicaceae*
Foreign names	Peuplier (Fr.), Pappel (Ger.), Alamo (Sp.), Pioppo (It.)
Description	Poplar is a slender tree that grows to 25–30 m (82–98 ft) high. It has grayish bark (initially smooth and then cracked); often angular, assurgent branches; green,

	ovate, toothed leaves; scaly buds adherent to the branches, covered with an odorous resinous varnish; ovoid, 4-valved capsules; and dioecious flowers with a tiny perianth. Poplar trees are widespread throughout Europe (especially in Hungary), North Africa, and North America.
Parts of plant used	The buds (sometimes the bark)
Physical-chemical characteristics Essential oil	The oil is obtained by steam distillation from the buds in approximately 0.5% yields. Its main constituent is α-caryophyllene. Its physical-chemical constants vary with its source. An oil of Hungarian production (*P. nigra* L.) has the following constants: Specific gravity at 15°C: 0.890–0.910[1] Optical rotation: +1°54′ to +7°30′[1] Refractive index at 20°C: 1.498–1.500[1] Acid value: 2–11[1] Ester value: 8–9[1]
Derivatives	Tincture, fluid extract, soft extract, and oleoresin (or "concrete"). The oleoresin, obtained by petroleum ether extraction from Canadian poplar buds (*P. balsamifera*), is a yellow-green, viscous liquid with a sweet balsamic odor slightly reminiscent of cinnamon. An essential oil is obtained also by vacuum distillation of the oleoresin in the presence of ethylene glycol. Main constituents include salicin (a glucoside yielding saligenin + glucose on hydrolysis), chrysin (phloroglucin + benzoic acid), tectochrysin, the glucoside populin (yielding salicin + benzoic acid), and small amounts of gallic acid and tannins.
Organoleptic characteristics	Sweet, balsamic odor with a slight cinnamic undertone
Uses	The fluid extracts are used in pharmacology. The essential oil (from buds or from the oleoresin) finds only limited use in perfumery and in liqueurs.
Regulatory status	Poplar buds: FDA §121.1163. In alcoholic beverages only

POPPY

Botanical source	*Papaver somniferum* L. (*P. sativum* Fuchs)
Botanical family	*Papaveraceae*
Foreign names	Pavot somnifère (Fr.), Schlafmohn (Ger.), Amapola (Sp.), Papavero (It.)
Description	Poppy is a bristly, hairy, annual herb native to Asia Minor. It grows wild in the fields and mountain areas of southern Europe (Turkey, Macedonia) and in the Middle East. It is cultivated extensively in Turkey for the extraction of opium for medicinal purposes. The plant has small, slender, spindle-shaped roots; erect, cylindrical, sparsely branched stems; alternate, obovate, irregularly dentate leaves with an ascendent central rib; large, solitary, white or purple flowers; and ovate, globose capsules containing numerous, white, kidney-shaped seeds.
Parts of plant used	Seeds, capsules
Physical-chemical characteristics Essential oil	The fixed drying oil, obtained by cold expression of poppy seeds, is a colorless to

	pale-yellow liquid. The cold-expressed (white) poppy seed oil is used in foods; the red poppy seed oil expressed with the aid of heat is of inferior quality and used mainly in paints and soaps.
Derivatives	Opium is the dried, milky juice obtained by incisions of the unripe capsules. It is a brownish-yellow powder with a faint smell and bitter, acrid taste. Its main constituents include codamine, codeine, cryptopine, gnoscopine, lanthopine, laudanidine, laudamine, laudanosine, meconidine, morphine, narceine, narcotine, neopine, papaveramine, papaverine, protopine, pseudomorphine, rhoeadine, and tebaine. In addition to the above alkaloids, several acids are also present—meconic, lactic, acetic, and phosphoric—together with fats, resin, waxes, and magnesium and calcium salts.
Organoleptic characteristics	Fatty, oily odor and corresponding taste
Uses	Opium is used in pharmacology as an analgesic and sedative. Poppy seed oil (FEMA No. 2919) is used as a salad and cooking oil and also in baked goods (8,600 ppm).[3]
Regulatory status	Poppy seeds: GRAS (I)

PRICKLY ASH

Other names	Xanthoxylum
Botanical source	*Xanthoxylum americanum* Mill.; *X. clava-herculis* L.
Botanical family	*Rutaceae*
Foreign names	Clavalier (Fr.), Zahnwehgelbholz (Ger.), Frassino spinoso (It.)
Description	Shrubs or trees with mostly pinnate leaves; the stems and often the leafstalks are prickly. The plant has small, greenish or whitish flowers and thick, fleshy pods. The aromatic, pungent bark is used in the southern United States as a rustic remedy for toothache.
Parts of plant used	The bark
Organoleptic characteristics	Bitter tonic, aromatic. When taken into the mouth, it actually twinges the tongue.
Uses	Its greatest use is in the flavoring of cordials. Prickly ash bark extract (FEMA No. 2110) has been reported used in the following:[3] non-alcoholic beverages 59 ppm candy 78 ppm baked goods 82 ppm
Regulatory status	GRAS (II)

PRUNE

Botanical source	*Prunus communis* Huds.
Botanical family	*Rosaceae*

Foreign names	Pruneau (Fr.), Pflaume (Ger.), Ciruelo (Sp.), Prugna (It.)
Description	Prune is the dried, edible, fleshy fruit of various species of *Prunus* trees.
Parts of plant used	The dried fruits
Physical-chemical characteristics	
Derivatives	Decoction (3%), fluid extract, tincture (10%, 15%, and 20% in 65% alcohol), a distillate (from dried, fermented plums in the presence of the pits)
Organoleptic characteristics	Sweet, juicy flavor
Uses	The decoction and the fluid extract are used in medicine. The tincture is employed in the formulation of compounded oils and spirits for liqueurs.

QUASSIA

Botanical source	*Quassia amara* L. or *Picrasma excelsa* (Sw.) Planch.
Botanical family	*Simaroubaceae*
Foreign names	Bois amer de Surinam (Fr.), Bitterholz (Ger.), Quassia amarga (Sp.), Quassia (It.)
Description	*Q. amara*, also known as Jamaica quassia, is a tree growing to 5–8 m (16–26 ft) high and native to Brazil. It exhibits a smooth bark, pinnate and lanceolate green leaves with red veins, and flowers in terminal clusters. The tree *P. excelsa*, also known as Surinam quassia, grows to 25 m (82 ft) in height and is native to the Antilles. It has oval, oblong leaves and flowers clustered in spikes.
Parts of plant used	Wood from the branches and trunk
Physical-chemical characteristics	
Derivatives	Fluid extract, soft aqueous extract, and tincture (5%, 10%, and 20% in 70% ethanol). Main constituents of the dried product and its derivatives, which do not contain tannin, include quassin, neoquassin (*Q. amara*), picrasmin, and thiamine (*P. excelsa*).
Organoleptic characteristics	Slight odor with a very bitter taste
Uses	The pure bitter taste is characteristic of the dried product and its derivatives, which find use in the formulation of liqueurs and aperitives. Other uses are of minor importance. Quassia extract has been reported used in the following:[3] non-alcoholic beverages 3.4 ppm alcoholic beverages 3.4 ppm baked goods 50 ppm
Regulatory status	FDA §121.1163

QUEBRACHO

Other names	Aspidosperma
Botanical source	*Aspidosperma quebrachoblanco* Schlecht, or *Schinopsis lorentzii* (Griseb.) Engl. (*Quebrachia lorentzii* Griseb.)
Botanical family	*Apocynaceae*
Foreign names	Quebracho (Fr.), Quebracho (Ger.), Quebracho (Sp.), Quebraco (It.)
Description	Quebracho, an evergreen tree 15–18 m (49–59 ft) high, grows abundantly throughout South America (Argentina in particular). The Argentine variety is characterized by its bright-red bark, rich in tannin, used for dyeing.
Parts of plant used	The bark (from either the trunk or branches)
Physical-chemical characteristics	
Derivatives	Fluid extract, tincture, elixir (alcoholic extract). Main constituents include three crystalline alkaloids—aspidospermine, quebrachine, and quebrachamine (chemically identical to yohimbine)—responsible for the tonic and antispasmodic physiological action.
Organoleptic characteristics	Tonic, aromatic
Uses	In addition to the therapeutic application of quebracho derivatives, the extract is used for flavoring beverages, ice cream, and pastry. Quebracho bark extract (FEMA No. 2972) has been reported used in the following:[3] non-alcoholic beverages 11 ppm ice cream, ices, etc. 23 ppm candy 27 ppm baked goods 28 ppm
Regulatory status	FDA §121.1163; GRAS (II)

QUILLAJA

Other names	Soapbark; quillay bark; Panama bark; quillai
Botanical source	*Quillaja saponaria* Molina
Botanical family	*Rosaceae*
Foreign names	Bois de Panama, Saponarie (Fr.), Seifenholz (Ger.), Quillaja (Sp.), Saponaria (It.)
Description	Perennial tree having thin branches and coriaceous, short-petioled, dentate leaves. It has white flowers clustered in cymose inflorescences and numerous winged seeds.
Parts of plant used	Bark
Physical-chemical characteristics	
Derivatives	Fluid extract and a tincture (20%) prepared from the fluid extract. The active principles contained in the bark are two saponins—quillaja saponin, and quillaic

acid, or quillaja sapogenin. Small amounts of saccharose, starches, calcium oxalate, vitamin C, and a few other unidentified components are also present.

Organoleptic characteristics

Bittersweet, aromatic flavor

Uses

The tincture is sometimes added to hair lotions to combat seborrhea. The use of quillaja or quillaja extracts in food products is essentially limited to beverage flavors. Quillaja (FEMA No. 2973) has been reported used in the following:[3]

non-alcoholic beverages	95 ppm
ice cream, ices, etc.	0.12 ppm
candy	18 ppm
syrups	6.8 ppm

Regulatory status

FDA §121.1163

QUINCE

Botanical source

Cydonia oblonga Miller. (*C. vulgaris* Pers.)

Botanical family

Rosaceae

Foreign names

Coing (Fr.), Quitte (Ger.), Codonyer (Sp.), Cotogno (It.)

Description

The tree, usually from 3–6 m (10–20 ft) high, has an erect trunk with crooked branches. It bears pink or white solitary flowers and has alternate, ovate leaves tapering at one end and fruits resembling a large yellow apple. Each carpel bears many seeds covered by mucilage. The plant is native to central Asia.

Parts of plant used

Fruits and seeds

Physical-chemical characteristics

Derivatives

Decoction (5%), infusion (15% from seeds), fluid extract. The hard, acid flesh of unripe fruits, harvested in October, is used in marmalades, jellies, and preserves. The seeds from the ripe fruits yield quince-seed mucilage, used as a thickening agent in place of tragacanth gum. Amygdalin, which hydrolyzes in the presence of emulsion to yield hydrogen cyanide, benzaldehyde, and glucose, has been reported among various other constituents.

Organoleptic characteristics

Agreeable, slightly acid flavor

Uses

The various extracts are used for flavoring pastry, beverages, and ice creams. Quince seed extract (FEMA No. 2974) has been reported used in the following:[3]

non-alcoholic beverages	0.001–40 ppm
ice cream, ices, etc.	0.06–20 ppm
baked goods	1.0 ppm

Regulatory status

Quince seed: GRAS

RASPBERRY

Botanical source

Rubus idaeus L.

Botanical family

Rosaceae

Foreign names	Framboise (Fr.), Himbeere (Ger.), Frambueso (Sp.), Lampone (It.)
Description	Shrub approximately 1–1.5 m (3–5 ft) high; it grows wild in the underwoods, or is cultivated, in Europe, Asia, and North America. The plant has short, stoloniferous rhizomes, erect stems, alternate branches, alternate leaves, white flowers, and pendulous fruits that are red when ripe (August). The cultivated variety ripens a few months earlier.
Parts of plant used	Berries
Physical-chemical characteristics	
Derivatives	Juice, concentrated (6 to 8 fold) juice, and distillate (50% and 75% alcohol content). Fermentation of the fresh juice yields raspberry wine. Usually synthetic flavors are added to the concentrated juices to improve yields. Main constituents include ketones with a violet-like odor (irones), alcohols, and carbonyl compounds. More than 40 constituents have been identified in raspberry aroma.
Organoleptic characteristics	Sweet-sour flavor
Uses	The expressed juices are consumed as is. The concentrated juices are used in the preparation of syrups, candy, and chocolate fillings. The distillates find application in the formulation of liqueurs or in special compounded oils (cordials).

RHATANY

Other names	Krameria
Botanical source	*Krameria triandra* Ruiz & Pav.—Peruvian rhatany; or *K. argentea* Mart.—Brazilian or Para rhatany
Botanical family	*Leguminosae*
Foreign names	Ratania (Fr.), Ratanhia (Ger.), Raiz para los dientes (Sp.), Ratania (It.)
Description	The shrub has voluminous roots and several erect or prostrate, very thin, 1 m (39 in.) long stems. The stems initially are hirsute, turning glabrous with age. The small, sessile, lanceolate leaves are covered by coarse, silver-white hairs with hairy, externally green, internally red flowers in the axilla of the uppermost leaves. The plant grows in the Andes region of Bolivia, Colombia, Peru, and Brazil.
Parts of plant used	Roots
Physical-chemical characteristics	
Derivatives	Fluid extract, soft water-alcohol extract, dried aqueous extract, and a tincture (20%). Main constituents include tannins and krameriatannic acid.
Organoleptic characteristics	Bitter, astringent
Uses	In addition to pharmacological uses as an astringent, it is employed also for flavoring beverages (alcoholic and non-alcoholic), ice cream, and baked products. Rhatany extract (FEMA No. 2979) has been reported used in the following:[3] non-alcoholic beverages 11 ppm alcoholic beverages 10 ppm ice cream, ices, etc. 31 ppm

candy	40 ppm
baked goods	8.0–63 ppm

Regulatory status	FDA §121.1163

RHUBARB

Botanical source	*Rheum officinale* Baill., *R. palmatum* L., and other species or hybrids of *Rheum* grown in China (rhubarb root); *R. rhaponticum* L. (rhubarb garden root)
Botanical family	*Polygonaceae*
Foreign names	Rabarbaro (It.)
Description	*R. palmatum*, or Chinese rhubarb, is a large, herbaceous, perennial plant with thick rhizomes that branch out after the first 2–3 years of growth. Its radical leaves split when the plant is 2 years old. *R. palmatum* grows in Tibet and western China, especially in high-altitude areas with dry climate. *R. officinale* differs from *R. palmatum* in that the leaves are divided in large, indented lobes; the bark is not red-dotted as that of *R. palmatum*, and the inflorescence is enlarged at the top. The plant flowers after 3 years and forms a flower-bearing stalk up to 2–3 m (7–10 ft) in height, with a long ear consisting of small, white-yellowish flowers (May–June). It grows in the high-altitude areas of Tibet and China. *R. rhaponticum* is a perennial, herbaceous plant growing up to 1–2 m (3–7 ft) in height. It has a thick rhizome, erect stalk, numerous leaves, and white-yellowish flowers in a terminal cluster. It is native to central Asia and extensively cultivated in Europe.
Parts of plant used	The skinned rhizomes and roots of *R. rhaponticum*. The dried product has various appearances, depending on the origin of the plant. Chinese rhubarb is classified by shape—flat, derived from large, cylindrical rhizomes split in the middle, or round. The rhizome is heavy, hard, orange-yellow or reddish-gray, exhibiting irregular, granular fractures. The characteristic star-shaped nodules, not present in the roots, are apparent. The Chinese rhubarb rhizome exhibits a radius larger than that of *R. rhaponticum*. The two varieties may also be differentiated by the harsher odor of *R. rhaponticum* as compared to Chinese rhubarb. Under Wood's fluorescent light the reddish-brown color of Chinese rhubarb remains unaltered, whereas that of *R. rhaponticum* changes from violet to blue on addition of ammonia. Chinese rhubarb contains from 2.5–4.5% anthracene compounds both in the reduced and oxidized state (free or bound as glucosides). It contains chrysophanic acid, rhabarberone, alizarin, cinnamic and gallic acids, and tannins. A main constituent is also calcium oxalate. The content in anthracene compounds of *R. rhaponticum* is 1.9–2.5%. This variety also contains rhaponticin.
Physical-chemical characteristics	
Derivatives	Fluid extract (tannin-free or not), soft aqueous extract, dried aqueous extract, dried alcohol-water extract, and tincture (20% in 65–70% ethanol).
Organoleptic characteristics	Bitter-tonic flavor
Uses	Rhubarb is valued for its characteristic bitter taste. It is used by the flavor industry in formulations for carbonated beverages, syrups, liqueurs, candies, and other food products. By employing the various rhubarb derivatives, the rhubarb note can be the predominant one or can be used to confer a particular bitter-aromatic bouquet to certain formulations. Chinese rhubarb is considered the most valu-

able quality. The use of *R. rhaponticum* is allowed only when the final results in a given formulation do not require high flavor qualities.

Regulatory status

Rhubarb root: FDA §121.1163
Rhubarb garden root: FDA §121.1163. In alcoholic beverages only

ROSE

Botanical source

Rose varieties of interest to the flavor and fragrance industry for the derivatives they yield include *Rosa damascena* Mill., *R. alba* L., *R. centifolia* L., *R. gallica* L., and varieties of these species.

Botanical family

Rosaceae

Foreign names

Rose (Fr.), Rose (Ger.), Rosa (Sp.), Rosa (It.)
The generic name *Rosa* is usually followed by the botanical name and the name of the growing site for exact identification.

Description

Rose grows as a plant, shrub, bush, or thicket. The flowers exhibit a five-petal calyx and a multiple five-petal corolla. Like the corolla, the seeds are inserted in the calyx. The plant is of Asiatic origin. Countries where rose is extensively cultivated for extractive purposes include Bulgaria, Turkey, Morocco, France, and Italy. For an extensive bibliography on the hybridization, cultivation, and extraction of rose, see reference 1.

Parts of plant used

Flowers, buds, leaves, and fruit (hips)

Physical-chemical characteristics

Derivatives

Rose absolute, concrete, leaf absolute, rose oil Moroccan (an essential oil), and rose otto (the Bulgarian essential oil). Also distillation waters, fluid extract, and tincture (20% in 30–40% ethanol and 15% in 60% ethanol). The main constituents of rose derivatives include linalool, β-phenethyl alcohol, *l*-citronellol, nerol, geraniol, eugenol, aldehydes, esters, and stearopten (paraffins).

The choice of rose derivatives for flavor applications often is determined by the feasibility of introducing water-soluble β-phenethyl alcohol into the flavor complex. This component is present in large quantities in the extracts; it is almost absent in distillates and may, therefore, have a significant effect on the resulting aroma.

The physical-chemical constants of extracts and distillates are strongly dependent on the type of material used for extraction. It is not possible to establish a reference standard. We suggest consulting specialized reviews or texts on this subject (see reference 1, pp. 874–875, for bibliography).

Bulgarian rose otto has different physical-chemical constants depending on the growing site. In general this product (from *R. damascena* Mill.) is steam distilled from the flowers, but this requires a high degree of skill. The distillation waters usually are redistilled, and this is combined with the original distillate. Rose otto is a pale-yellow or olive-yellow liquid that precipitates colorless crystals of stearopten at temperatures below 21°C; the liquid supernate is known as the elaeopten.

Specific gravity at 30°C	0.8480–0.8635[1]
Optical rotation	−2°12′ to −4°24′[1]
Refractive index at 25°C	1.4538–1.4646[1]
Congealing point	16–22.5°C[1]
Acid value	0.93–3.8[1]
Ester value	7.4–16.8[1]
Ester value (after acetylation)	194–240[1]
Saponification value	8.4–18.7[1]
Rhodinol content	27.4–56.9%[1]
Stearopten content	16–24%[1]

Organoleptic characteristics

Deep, warm, rich rose odor with a slightly bitter, sharp flavor at high concentrations; pleasant on dilution

Uses

Rose derivatives, including the essential oil, concrete, absolute, and distillation waters, are most important and extensively used by the perfumery and flavor industries. A general review on the potential uses of rose essences and derivatives has been discussed in the paper presented at the Essential Oil Congress in Plovdiv, Bulgaria (May 6–8, 1964) and published in *Rivista Italiana E.P.P.O.S.*, p. 338, 1964, and in *La France et ses Parfums*, p. 285, 1964.

Rose absolute (*R. alba* L., *R. centifolia* L., and varieties of these species) has been reported used in the following:[3]

non-alcoholic beverages	0.63 ppm
ice cream, ices, etc.	1.2 ppm
candy	2.0 ppm
baked goods	1.6 ppm

Bulgarian rose otto oil (*R. damascena* Mill.) has been reported used in the following:[3]

non-alcoholic beverages	0.51 ppm
ice cream, ices, etc.	0.68 ppm
candy	2.6 ppm
baked goods	1.2 ppm
gelatins and puddings	0.01–0.50 ppm
chewing gum	15 ppm
jellies	0.05 ppm

Rose hips extract (*R. canina* L., *R. gallica* L., *R. condita* Scop., *R. rugosa* Thunb., and other rose species) has been reported used.[3] Rose water, stronger (*R. centifolia* L.), has been reported used in non-alcoholic beverages, 100 ppm.[3]

Regulatory status

GRAS (II)

ROSELLE

Botanical source

Hibiscus sabdariffa L.

Botanical family

Malvaceae

Foreign names

Carcadé (Fr.), Carcadé (Ger.), Carcadé (Sp.), Carcadé (It.)

Description

Roselle is an annual herb, native to Africa and cultivated today in various tropical and sub-tropical countries. The plant has wedge-shaped, palmate-nervate leaves (the lower leaves, ovate and cleft; the upper ones, acute and dentate) thickening at the top of the branches and bearing a large, axillary, short-petioled flower. The fruits consist of 5-celled capsules containing glabrous, kidney-shaped seeds.

Parts of plant used

The fleshy calyxes of flowers, commercially available as dried reddish-brown fragments, approximately 3–5 cm (1–2 in.) long

Physical-chemical characteristics

Derivatives

Infusion, concrete, absolute. The infusion is a purple-red liquid with an agreeable, slightly acid taste caused by the presence of tartaric and citric acids. The dark-brown concrete, obtained by petroleum ether extraction, exhibits a faint fruital odor. The absolute is prepared by alcoholic extraction of the concrete.

Organoleptic characteristics

Pleasant, slightly sour flavor with a faint fruital odor

Uses

Wherever permitted, the fleshy calyxes are used to make tarts, jelly, and a sour drink. The derivatives find limited use in liqueur formulations.

Regulatory status

FDA §121.1163. In alcoholic beverages only

ROSEMARY

Botanical source

Rosmarinus officinalis L.

Botanical family

Labiatae

Foreign names

Rosmarin (Fr.), Rosmarin (Ger.), Romero (Sp.), Rosmarino (It.)

Description

Rosemary, a dense, evergreen shrub growing up to 2 m (6.5 ft) high, has highly branched (either erect or prostrate) linear leaves, axillary inflorescences, and light blue flowers. It is native to the Mediterranean regions and is extensively cultivated for extractive use in Spain, France, Tunisia, Morocco, Yugoslavia, and Italy.

Parts of plant used

Entire plant excluding woody parts; also just the leaves

Physical-chemical characteristics

Essential oil

Obtained by steam distillation with yields of approximately 0.5–1.2%. It is a pale-yellow liquid with a characteristic camphoraceous odor and varying physical-chemical constants, depending on the source. Spanish rosemary essential oil has the largest production. Its physical-chemical constants follow:

Specific gravity at 20°C	0.893–0.916[1] (0.895–0.905)[6]
Refractive index at 20°C	1.4670–1.4730[1] (1.4670–1.4740)[6]
Optical rotation at 20°C	−7° to 11°30′[1] (−3° to +10°)[6]
Acid value	1 max[1]
Ester content (as bornyl acetate)	0.6–7.0%[1]
Alcohol content (as bornyl alcohol)	8–18%[1]
Solubility in 80% ethanol	1:4–1:10[1]

Main constituents include α-pinene, camphene, cineol, camphor, and bornyl alcohol (10 to 15%)

Derivatives

Fluid extract, tincture (20% in 70% ethanol) and oleoresin.

Organoleptic characteristics

Strong, fresh, woody, herbaceous odor; warm, spicy flavor

Uses

The essential oil has an important role in perfumery; all other derivatives are used in the formulation of compounded oils for flavoring meat, sauces, bouillons, condiments, and other food products. Rosemary has been reported used in the following:[3]

non-alcoholic beverages	700 ppm
condiments	680 ppm
meats	380 ppm

Rosemary oil has been reported used in the following:[3]

non-alcoholic beverages	3.6 ppm
ice creams, ices, etc.	0.50–40 ppm
candy	7.5 ppm
baked goods	6.3 ppm
condiments	2.9 ppm
meats	40 ppm

Regulatory status

GRAS (I), (II)

RUE

Botanical source *Ruta graveolens* L.

Botanical family *Rutaceae*

Foreign names Rue (Fr.), Raute (Ger.), Ruda (Sp.), Ruta (It.)

Description Biennial or perennial herb widespread in arid areas of southern Europe and North Africa. It has sparse leaves with 2–3 buds and yellow flowers (May–July) with a strong characteristic odor. It grows to 0.5 m (20 in.) in height. Several other varieties of rue are known, including *R. bracteosa*, *R. montana* L., and *R. calepensis*. These display various physical-chemical characteristics.

Parts of plant used Leaves and fresh blooming plants.

Physical-chemical characteristics

Essential oil The oil is obtained by steam distillation of the fresh blossoming plant in 0.5–0.8% yields. The essence exhibits different physical-chemical constants depending on the growing site (see reference 1). The oil is a yellow to yellow-amber liquid with a fatty odor.

Specific gravity at 25°/25°C	0.826–0.838[2]
Refractive index at 20°C	1.4300–1.4400[2]
Optical rotation	−1° to +3°[2]
Ketone content (as methylnonyl ketone)	>90%[2]
Solubility in 70% alcohol	1:2–1:4[2]

Derivatives Infusion (2%), fluid extract, and tincture (20% in 50% ethanol). The main constituents include methylnonyl ketone, methylheptyl ketone (ca 90%), methyl-*n*-octyl ketone, pinene, *l*-limonene, cineol, and acids. The dried product contains rutin, quercetin, furocoumarins, and alkaloids of the quinoline group.

Note: Although rue holds GRAS status in the United States, its sale is controlled in a number of other countries. S. Arctander in *Perfume and Flavor Materials of Natural Origin** states that since the oil produces certain hemorrhage effects when taken internally, it should never be used for perfumery or flavor work.

Organoleptic characteristics Herbaceous odor (fruity, orange note); sharp, burning, acrid taste

Uses The fluid extract and tincture are used by the flavor industry in small dosages to obtain slight bitter notes. Rue oil is an important source of methylnonyl ketone. Rue has been reported used in baked goods, 6.0 ppm.[3] Rue oil has been reported used in the following:[3]

non-alcoholic beverages	1.2 ppm
ice cream, ices, etc.	1.3 ppm
candy	4.1 ppm
baked goods	3.3 ppm
condiments	1.0 ppm

Regulatory status GRAS (I), (II)

SAFFRON

Other names Crocus

Botanical source *Crocus sativus* L.

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*Published by the author, 1960.

Botanical family *Iridaceae*

Foreign names Safran (Fr.), Safran (Ger.), Azafran (Sp.), Zafferano (It.)

Description Several varieties of *C. sativus* L. are known and cultivated in various countries, e.g., France, Spain, Turkey, Greece, and Italy. The varieties *C. sativus thomasii* Ten and *C. orsini* Parl. are commonly cultivated in Italy. This herbaceous plant is approximately 30 cm (12 in.) high, has bulbous roots usually branched by smaller fibrous roots, an erect, white, thin scape terminated by purple inflorescences and 3 red-orange stigmas.

Parts of plant used Dried stigmas

Physical-chemical characteristics

Derivatives Tincture (10% in 80% and also lower-strength ethanol). The dried stigmas contain picrocrocin, crocin, vitamins B_1 and B_2, and a small amount of essential oil (ca 0.30%) that is either solvent-extracted or sometimes steam-distilled for specific uses only. The presence of 2,2,6-trimethyl-4,6-cyclohexadien-al causes the characteristic spicy, warm odor of the dried product and tinctures; crocin yields the characteristic bright orange-yellow color. For coloring purpose, the less expensive dried flowers of the American or Mexican saffron (*Carthamus tinctorius* L.) are used in lieu of saffron. However, these varieties have scarcely perceptible flavor.

Organoleptic characteristics Sweet, spicy, floral odor with a fatty, herbaceous undertone; slightly bitter taste

Uses The tinctures and the dried product are used in the formulation of compounded oils and extracts for flavoring liqueurs and sauces. The dried product is used for seasoning special dishes, such as risotto Milan style and bouillabaise. Saffron (FEMA No. 2998) has been reported used in the following:[3]

non-alcoholic beverages	1.3 ppm
alcoholic beverages	200 ppm
baked goods	10 ppm
meats	260 ppm

Saffron extract (FEMA No. 2999) has been reported used in the following:[3]

non-alcoholic beverages	1.3–7.5 ppm
ice cream, ices, etc.	1.3–9.0 ppm
candy	6.3 ppm
baked goods	1.9–14 ppm
condiments	50 ppm

Regulatory status GRAS (I), (II)

SAGE

Other names Dalmatian sage, English sage

Botanical source *Salvia officinalis* L.

Botanical family *Labiatae*

Foreign names Sauge officinale (Fr.), Salbei (Ger.), Salvia officinale (Sp.), Salvia officinale (It.)

Description Sage is a perennial herb that is cultivated or grows wild throughout southern Europe. It has a long, spindle-shaped root, erect, woody stalk with straight branches, opposite spear-shaped leaves, and large violet flowers (June–July).

Parts of plant used Leaves

Physical-chemical characteristics

Essential oil

Obtained by steam distillation of the partially dried leaves with yields ranging from 0.5–1.0%. Depending on the growing site and even the harvesting time, the oils may exhibit widely different physical-chemical constants. Dalmatian sage oil is considered the best quality (also see Reference 2).

Specific gravity at 20°C	0.914–0.931[1]
Optical rotation at 20°C	−1°6′ to +33°40′[1]
Refractive index at 20°C	1.445–1.470[1]
Acid value	2 (average)[1]
Ester value	6–20[1]
Ester value (after acetylation)	30–60[1]
Ketone content (as thujone)	5%[1]
Solubility	1:1 in 80% ethanol[2]

The oil is a mobile, almost colorless to pale-yellow liquid with a characteristic thujone odor. The oil contains thujone, *d*-α-pinene, cineol, bornyl acetate, camphor, and linalyl acetate. In addition the dried product contains β-sitosterol and triterpenic acids.

Derivatives

Infusion (3%), fluid extract prepared from dried aqueous extract, tincture (20% in 70% ethanol), and oleoresin

Organoleptic characteristics

Warm, spicy odor and flavor

Uses

The essential oil is employed in flavoring condiments, cured meats, liqueurs, and bitters. Fresh sage leaves are used in cooking. Sage also finds application in perfumery.

Sage has been reported used in the following:[3]

non-alcoholic beverages	300 ppm
baked goods	170 ppm
meats	1,500 ppm

Sage oil has been reported used in the following:[3]

non-alcoholic beverages	3.7 ppm
ice cream, ices, etc.	16 ppm
candy	11 ppm
baked goods	14 ppm
chewing gum	30 ppm
condiments	14 ppm
meats	110 ppm
pickles	2.4 ppm

Sage oleoresin has been reported used in the following:[3]

condiments	100 ppm
meats	100 ppm

Regulatory status

GRAS (I), (II)

SAGE, GREEK

Botanical source

Salvia triloba L.

Botanical family

Labiatae

Foreign names

Sauge (Fr.), Salbei (Ger.), Salvia (Sp.), Salvia (It.)

Description

Shrubs mainly growing in Greece and Turkey. The plant has thicker, larger, shorter leaves than *S. officinalis* L.

Parts of plant used

The leaves

Physical-chemical characteristics

Essential oil

The oil, obtained by steam distillation of freshly cut leaves, is a colorless liquid with a harsh, rosemary, spike, camphor-like odor. Its physical-chemical constants follow:

Specific gravity at 20°C	0.9131[1]
Refractive index at 20°C	1.4640[1]
Acid value	2[1]
Ester value	2.4[1]
Ester value (after acetylation)	16.1[1]
Solubility	1:1.4 in 90% ethanol[1]

Organoleptic characteristics

Harsh, rosemary, spike, and camphor-like odor

Uses

The oil is used for medicinal purposes in rural areas of Europe. The dried herb and the oil find applications similar to those of sage in flavor work.

Regulatory status

GRAS (I), (II)

SAGE, SPANISH

Botanical source

Salvia lavendulaefolia Vahl.

Botanical family

Labiatae

Foreign names

Sauge (Fr.), Salbei (Ger.), Salvia (Sp.), Salvia (It.)

Description

Wild herb mainly growing in Spain (Murcia, Almeria, and Granada provinces)

Parts of plant used

The leaves

Physical-chemical characteristics

Essential oil

Spanish sage oil, obtained by steam distillation, is a slightly yellow liquid having a camphoraceous odor with a cineole top note. Main constituents include cineol, linalool, linalyl acetate, linalyl isovalerate, *d*-camphor, probably camphene, pinene, and dipentene. Some oils from the Jaen province have been reported to exhibit a slight laevo optical rotation. Its physical-chemical constants follow:

Specific gravity at 25°/25°C	0.909–0.932[2] (0.913–0.933 at 20°/20°C)[6]
Refractive index at 20°C	1.4680–1.4730[2] (1.4670–1.4730)[6]
Optical rotation	−3° to +24°[2] (−12° to +24°)[6]
Saponification value	14–57[2] (10–57)[6]
Solubility	1:2 in 80% alcohol[2]

Organoleptic characteristics

Camphoraceous, fresh odor with a cineole top note

Uses

This oil is used mainly in perfumery for the scenting of soaps and other technical products. It finds a very limited use in flavor work.

Spanish sage oil (FEMA No. 3003) has been reported used in the following:[3]

non-alcoholic beverages	2.0–11 ppm
ice cream, ices, etc.	2.0–44 ppm
candy	20 ppm
baked goods	20 ppm
condiments	50 ppm
meats	40 ppm

Regulatory status	GRAS (II)

ST. JOHNSWORT

Botanical source	*Hypericum perforatum* L.
Botanical family	*Guttiferae*
Foreign names	Millepertuis officinal (Fr.), Johanniskraut (Ger.), Hipericón (Sp.), Iperico (It.)
Description	Very common and widespread perennial herbaceous plant; grows wild in Italy and in mountainous areas of central Europe, Africa, North America, and northern Asia. The plant is from 20–90 cm (8–35 in.) high, has an erect stem, opposite leaves, and yellow flowers grouped in clusters. It flowers from June to September.
Parts of plant used	Flowering tops, leaves, and caulis
Physical-chemical characteristics	
Essential oil	The essential oil is little known. The oil can be prepared by steam distillation in very low yields. Depending on the origin, the essence can be dextro or laevorotatory and contains α-pinene. The dried product contains hypericin.
Derivatives	Infusion (3%), fluid extract, and tincture (20% in 25% ethanol)
Organoleptic characteristics	Balsamic odor; aromatic taste
Uses	Both the dried product and its derivatives can be employed by the flavor industry in the formulation of liqueurs.
Regulatory status	FDA §121.1163. Hypericin free; alcohol distillate form only; in alcoholic beverages only

SANDALWOOD, WHITE

Other names	Yellow sandalwood; East Indian sandalwood; yellow saunders; white saunders
Botanical source	*Santalum album* L.—East Indian sandalwood; *S. spicatum* (R.Br.) (A.DC); *Eucarya spicata* (R.Br.) Sprag. & Summ.—Australian sandalwood
Botanical family	*Santalaceae*
Foreign names	Bois de santal (Fr.), Sandelholz (Ger.), Sandalo (Sp.), Sandalo (It.)

Description

East Indian sandalwood, also known as sandalwood Mysore, is a tall evergreen tree native to southern India. It grows wild or cultivated in India and throughout Malaysia. East Indian sandalwood should not be confused with *Amyris balsamifera*, or West Indian sandalwood, a small tree growing in the woods and forests of Haiti and Jamaica.

Australian sandalwood is a small shrub native specifically to southern and western Australia.

Only the hard core of the wood and the roots of East Indian sandalwood undergo distillation after removal of the bark and of the soft, external woody layer; whereas the whole trunk, branches, and roots of West Indian sandalwood are used for distillation.

Parts of plant used

Wood from trunk and roots

Physical-chemical characteristics

Essential oil

East Indian sandalwood essential oil is steam distilled from comminuted dried wood chips. It is a pale-yellow to yellow liquid with a strong, warm, woody odor. Its physical-chemical constants follow (see also reference 2):

Specific gravity at 20°C	0.968–0.976[1] (0.968–0.983)°
Refractive index at 20°C	1.5020–1.5090[1] (1.5030–1.5080)[6]
Optical rotation at 20°C	−15° to −22°[1] (−15° to −21°)[6]
Ester value	<10[1]
Total alcohols (as santalol)	<80%[1]
Solubility	1:3–5 in 70% ethanol[1]

Australian sandalwood oil differs from the East Indian oil because of the somewhat harsher, bitter, resinous top note; it exhibits the following physical-chemical constants (see also reference 2):

Specific gravity at 20°C	0.969–0.979[1] (0.968–0.978)[7]
Refractive index at 20°C	1.5040–1.5090[1] (1.5040–1.5100)[7]
Optical rotation	+4°30′ to −9°25′[1] (−3° to −8°)[7]
Acid value	0.8–5[1] (5 max)[7]
Ester value	4.7–18.7[1]
Ester value (after acetylation)	150–207[1]
Total alcohols (as santalol)	66–96%[1]
Solubility	1:3–5 in 70% ethanol[1]

East Indian sandalwood essential oil consists mainly of α-santalol (90%) with traces of phenols, lactones, and terpenes. Australian sandalwood oil contains primarily α-santalol, various sesquiterpene alcohols, and bisabolene (a sesquiterpene believed to be responsible for the characteristic top note of this oil).

Organoleptic characteristics

Strong, persistent, warm, woody odor

Uses

Sandalwood essential oils are used primarily in perfumery because of their outstanding fixative properties. They blend well with ionones and methylionone-based compositions as well as with vetiver and patchouly essential oils. The oils impart a characteristic, woody, Oriental note to perfume compositions. The essential oil is used for flavoring Oriental specialties, and, to a lesser degree, chewing gum, candy, beverages, and ice cream. Yellow sandalwood oil (FEMA No. 3005) has been reported used in the following:[3]

non-alcoholic beverages	2.4 ppm
ice cream, ices, etc.	7.5 ppm
candy	7.7 ppm
baked goods	6.6 ppm
chewing gum	47 ppm

Regulatory status

FDA §121.1163

SANDARAC

Botanical source	*Tetraclinis articulata* (?) (Vahl. Mast)
Botanical family	*Pinaceae*
Foreign names	Sandaraque (Fr.), Sandarakbaum (Ger.), Sandarac (Sp.), Sandarac (It.)
Description	A small conifer growing in the mountains of Morocco and Algeria. The tree has hard, durable, fragrant wood frequently used in building. A natural oleoresin exudes from incisions made on the trunk and branches and solidifies into brittle, faintly aromatic, yellow grains, or tears. The resin finds use primarily in varnishes and as an incense.
Parts of plant used	The oleoresin
Physical-chemical characteristics	
Essential oil	Sandarac oil, prepared by steam distillation of the resin, is a colorless to pale yellow liquid with a fresh, balsamic odor reminiscent of turpentine.
Derivatives	Tincture
Organoleptic characteristics	Turpentine-like, fresh, resinous odor
Uses	The essential oil and the tincture are of very limited importance in both perfume and flavor applications. They find limited use in the formulation of liqueurs.
Regulatory status	FDA §121.1163. In alcoholic beverages only

SARSAPARILLA

Botanical source	*Smilax aristolochiaefolia* Mill.—Mexican sarsaparilla; *S. regelii* Killip & Morton—Honduras sarsaparilla; *S. febrifuga* Kunth—Ecuadorean sarsaparilla; undetermined *Smilax* species—Ecuadorean or Central American sarsaparilla
Botanical family	*Smilacaceae* (*Liliaceae*)
Foreign names	Salsepareille (Fr.), Sarzaparilla (Ger.), Salsaparilla (Sp.), Salsapariglia (It.)
Description	The plant has a very thin stem and large, laminar, petiolate leaves with stipular tendrils that enable it to climb. Several sarsaparilla qualities are commercially available. The roots of Mexican origin (Vera Cruz, Tampico) are usually bigger and exhibit a thicker and more wrinkled skin than other varieties. Honduras sarsaparilla is sold in "cigars" consisting of folded roots externally tied into a small bundle by another root. The so-called Jamaican quality (Brazil, Central America, Colombia) differs from the Honduras product in its redder color.
Parts of plant used	Roots

Physical-chemical characteristics

Derivatives

Fluid extract and dried water-alcohol extract. These derivatives exhibit similar characteristics independently of botanical source. Main constituents include: sarsaponin, parillin, smilagenin, etc.

Organoleptic characteristics

Very little odor; sweet, creamy, licorice, slightly bitter flavor.

Uses

Sarsaparilla and its derivatives are used in flavoring non-alcoholic and carbonated beverages (root beer) and in ice creams.

Sarsaparilla extract (FEMA No. 3009) has been reported used in the following:[3]

non-alcoholic beverages	190 ppm
ice cream, ices, etc.	130 ppm
candy	1,000 ppm
baked goods	2,000 ppm

Regulatory status

FDA §121.1163

SASSAFRAS

Botanical source

Sassafras albidum (Nutt.) Nees

Botanical family

Lauraceae

Foreign names

Sassafras (Fr.), Sassafras (Ger.), Sassafras (Sp.), Sassafrasso (It.)

Description

Tree, common to the United States and Canada, may reach up to 10 m (33 ft) in height. It has trilobed leaves and also oval leaves of various sizes.

Parts of plant used

Root bark and leaves

Physical-chemical characteristics

Essential oils

Root Bark Oil

Sassafras root bark oil is obtained by steam distillation with yields of 6–9% when distilling the bark only, or with yields of 1.8% when distilling the whole root. It is a clear yellow-orange liquid with a characteristic odor and taste. Its main constituents include α-pinene, phellandrene, safrole, eugenol, and *d*-camphor.

Specific gravity at 25°C	1.065–1.076[1]
Optical rotation at 25°C	+2° to +3°38′[1]
Refractive index at 20°C	1.5270–1.5311[1]
Solubility in 90% ethanol	1:1–1:2[1]
Congealing point	4.5–6.9°C[1]

Leaf Oil

The essential oil from leaves has a very pleasant odor reminiscent of lemon and different from root bark oil.

Specific gravity	ca 0.872[1]
Optical rotation	ca +6°[1]

Its main constituents include α-pinene, myrcene, phellandrene, citral, geraniol, and linalool (free or esterified); the commercial product must be free of safrole.

Note: Sassafras oil should not be confused with sassafras oil Brazilian, which is derived from the woody portion of the tree *Ocotea cyrubarum* H.B.K., or with "sassafras artificial", a camphor oil derived by steam distillation of trees classified as *Cinnamonum camphora* Sieb. These oils are not used for food flavoring and represent a source of safrole that is important in perfumery (see reference 2).

Derivatives	Fluid extract and tincture (20% in 60% ethanol)
Organoleptic characteristics	Spicy, aromatic odor and flavor
Uses	Sassafras leaves (safrole-free) have been reported used in soups, 30,000 ppm.[3] Sassafras bark extract has been reported used in the following:[3] non-alcoholic beverages 290 ppm ice cream, ices, etc. 10 ppm candy 100 ppm baked goods 50 ppm
Regulatory status	Sassafras leaves: FDA §121.1163. Safrole-free Sassafras oil: Its use in foods is not permitted in the United States Sassafras root bark: FDA §121.1097. Safrole-free

SAUNDERS, RED

Other names	Red sandalwood
Botanical source	*Pterocarpus santalinus* L.f.
Botanical family	*Santalaceae*
Foreign names	Santal rouge (Fr.), Rotes Sandelholz (Ger.), Santalia (Sp.), Sandalo rosso (It.)
Description	A small tree growing wild mainly in India, Ceylon, and the Philippines; a few *Pterocarpus* varieties also grow in tropical Africa. The wood is not fragrant and does not yield an essential oil on steam distillation. The wood is comminuted into a fine powder that is used as a red dye in a few food products (spice blends and sauces).
Parts of plant used	The wood
Uses	Its primary use is as a dye, although sometimes the powder is used in liqueurs. The wood is not used in perfume or flavor work.
Regulatory status	FDA §121.1163. In alcoholic beverages only

SAVORY, SUMMER

Botanical source	*Satureia hortensis* L.
Botanical family	*Labiatae*
Foreign names	Sarriette des Jardin (Fr.), Bohnenkraut (Ger.), Saborija (Sp.), Santoreggia (It.)
Description	Herbaceous annual plant growing wild or cultivated in the mountain regions of Europe, the Mediterranean basin, and some midwestern areas of the United States. It is an aromatic plant exhibiting a taproot, erect stalk, opposite leaves, and white, red-dotted flowers (June–July) arranged in axillary clusters.
Parts of plant used	Flowering tops

Physical-chemical characteristics

Essential oil

The essential oil is obtained by distillation of the whole dried herb. It is a light-yellow to dark-brown liquid with a spicy, aromatic odor reminiscent of thyme and origanum.

Specific gravity at 25°/25°C	0.875–0.954[2]
Refractive index at 20°C	1.4860–1.5050[2]
Optical rotation	−5° to +4°[2]
Phenol content (as carvacrol)	20–57%[2]
Saponification value	<6.0[2]
Solubility	1:2 in 80% ethanol;[2] 1:10 in 90% ethanol

Derivatives

Infusion (3%), fluid extract, tincture (20% in 60% ethanol), and oleoresin

Organoleptic characteristics

Aromatic, thyme-like odor and flavor

Uses

The tincture and the dried product are used in the formulation of liqueurs (vermouths and bitters). The essential oil is used to flavor sauces, soups, and prepared meats. Summer savory has been reported used in the following:[3]

baked goods	800–850 ppm
condiments	200 ppm
meats	1,100 ppm

Summer savory oil has been reported used in the following:[3]

candy	4.0 ppm
baked goods	4.0 ppm
condiments	10–50 ppm

Summer savory oleoresin has been reported used in the following:[3]

candy	4.0 ppm
baked goods	4.0 ppm
condiments	35–50 ppm

Regulatory status

GRAS (I), (II)

SAVORY, WINTER

Botanical source

Satureia montana L.

Botanical family

Labiatae

Foreign names

Sarriette, Savourée (Fr.), Bohnenkraut (Ger.), Saborija (Sp.), Santoreggia (It.)

Description

Annual herb growing in dense thickets, 10–30 cm (4–12 in.) high, having lanceolate narrow leaves, short whitish bristles, and thick, sunken glands. The plant exhibits a pleasant, aromatic scent and a slightly pungent taste.

Parts of plant used

The whole herb (harvested when flowering and freed from the stems and the larger branches)

Physical-chemical characteristics

Essential oil

Obtained by steam distillation in approximately 0.18% yields. The essential oil is an orange-yellow liquid containing 30–40% carvacrol and small amounts of phenols and cymene-type hydrocarbons. A few varieties of *S. montana* contain, in addition to carvacrol, fairly large amounts of thymol. Until recently, little has been done to standardize and to differentiate the various types of essential oils. The commercial qualities are identified as *S. montana*, or winter savory, oils but a more defined classification would be useful.

Derivatives

Oleoresin

Organoleptic characteristics

Spicy, phenolic odor with a biting, almost bitter flavor similar to summer savory

Uses

The herb, cultivated also for ornamental purposes, is used in cooking and in the manufacture of vermouths (Italy). The essential oil finds some use in perfumery. Winter savory oil (FEMA No. 3016) has been reported used in the following:[3]

candy	4.0 ppm
baked goods	4.0 ppm
condiments	50 ppm

Winter savory oleoresin (FEMA No. 3017) has been reported used in the following:[3]

candy	4.0 ppm
baked goods	4.0 ppm
condiments	50 ppm

Regulatory status

GRAS (I), (II)

SCHINUS MOLLE

Other names

Peruvian pepper tree; Peruvian mastic; California pepper tree

Botanical source

Schinus molle L.

Botanical family

Anacardiaceae

Foreign names

Molée des jardins (Fr.), Weichpfeffer (Ger.), Pimenta falsa, Arvoiera (Sp.), Schino (It.)

Description

Shrubs probably native to the trans-Andean regions in South America and now acclimated and cultivated around the Mediterranean basin. The plant may reach 8 m (26 ft) in height and has characteristic deflexed branches bearing alternate, stipuleless leaves consisting of 15–27 lanceolate, acuminate, dentate leaflets; it has white flowers in axillary terminal clusters, red, globose, fleshy, oil berries, and seeds with a recurved embryo containing very little albumen. The plant blooms between May and June.

Parts of plant used

Fruits (berries)

Physical-chemical characteristics

Essential oil

The oil, obtained by steam distillation of the fruits, is a pale-green to olive-green liquid with a fresh, spicy odor and flavor. Main constituents include carvacrol, phellandrene, thymol, pinene, an unidentified resin, and a few high-molecular-weight ketones. The oil was a popular substitute for black pepper oil during shortages of the latter; today it is used only sporadically in flavor work.

Derivatives

Fluid extract and tincture

Organoleptic characteristics

Warm, spicy odor with biting flavor less pungent than black pepper

Uses	The essential oil is used in the formulation of flavors for condiments and candy. The extract and the tincture find some application in pharmaceuticals. Schinus molle oil (FEMA No. 3018) has been reported used in the following:[3] candy 10 ppm baked goods 10 ppm condiments 3.0 ppm
Regulatory status	GRAS (II)

SENNA

Botanical source	a. **Alexandria senna**—*Senna acutifolia* Nect.; also called *Cassia acutifolia* Delile; incorrectly known as *C. alexandria* Mill. b. **Tinnevelly senna**—*C. medicinalis* Bischoff; also called *C. augustifolia* Vahl. The Tinnevelly variety, also known as *C. lanceolata* Royle, or incorrectly as *C. acutifolia* Delile, belongs to this class. c. *S. italica* Lamk. or *C. senna* Lamk.; also known as *C. obovata* Coll. (Hayne)
Botanical family	*Leguminosae*
Foreign names	Senne (Fr.), Senna (Ger.), Senna (Sp.), Senna (It.)
Description	A shrub up to 2 m (6.5 ft) high; grows in tropical and subtropical countries and is cultivated in India and Pakistan. Some confusion exists in the botanical classification. Some pharmacopeae permit the use of only the Tinnevelly variety, *C. augustifolia* Vahl. This variety is taller and has a thicker foliage and smaller fruits than *C. acutifolia* Delile. Also *C. obovata* is often classified as *C. alexandria*. *C. medicinalis* Bischoff var. Royleana has pinnate leaves consisting of a 7–15 cm long rachis and from 5–9 pairs of short-petioled, lanceolate leaflets with an asymmetric base and acuminate apex. The fruits, commercially known as follicales, are greenish or sometimes brownish.
Parts of plant used	Leaflets
Physical-chemical characteristics	
Derivatives	Tincture, fluid extract, soft aqueous extract, dried aqueous extract, dried purified extract, and a tincture prepared from the fluid extract. The leaves contain sennaemodin, sennanigrin, sennarhamnetin, and anthraquinones.
Regulatory status	*C. acutifolia* Delile: FDA §121.1163

SERPENTARIA

Other names	Virginia snakeroot
Botanical source	*Aristolochia serpentaria* L.
Botanical family	*Aristolochiaceae*
Foreign names	Serpentaire de Virginie (Fr.), Virginische Schlangenwurzel (Ger.), Serpentaria (Sp.), Aristolochia serpentaria (It.)

Description Perennial herb 12–45 cm (5–18 in.) high, having stems branched at the base; ovate or oblong leaves; short-peduncled flowers next to the root; fibrous-aromatic roots. The plant is native to the United States (Virginia, Louisiana, Arkansas).

Parts of plant used The roots

Physical-chemical characteristics

Essential oil The oil, obtained by steam distillation of the dried roots in approximately 1.0–1.2% yields, is a light-brown liquid with an odor reminiscent of valerian and ginger. Its physical-chemical constants are as follows:

Specific gravity at 15°C	0.961–0.990[1]
Refractive index at 20°C	1.4972–1.4980[1]
Optical rotation	+21° to +26°[1]
Acid value	2–3[1]
Ester value	65–80[1]
Solubility	1:15–20 in 80% ethanol[1] 1:0.5 in 90% ethanol[1]

Main constituents include pinene, borneol (esterified), probably tiglic acid, and a terpene.

Organoleptic characteristics Aromatic, spicy odor similar to valerian and ginger

Uses The oil finds limited use in the formulation of aromas for liqueurs.

Regulatory status FDA §121.1163. In alcoholic beverages only

SESAME

Other names Benne

Botanical source *Sesamum indicum* L.

Botanical family *Pedaliaceae*

Foreign names Sesam (Ger.), Sesamo (Sp.), Sesamo (It.)

Description A genus of tropical African and Indian herbs. It is a rough, hairy, gummy, annual plant, about 70–80 cm high, having petiolate, ovate-lanceolate leaves, slightly toothed and mucilaginous. The pale or rose-colored flowers are solitary in the axils. The plant is cultivated for its black or white seeds, which are tiny, but sweet and oleaginous. Sesame oil is second only to coconut oil for culinary purposes, food, and medicine; it is also used as a substitute for olive oil.

Parts of plant used Seed (oil)

Uses In flavoring bread (seeds); oil in baking and flavoring confections

Regulatory status GRAS (I)

SNAKEROOT, CANADIAN

Other names Asarum; wild ginger

Botanical source *Asarum canadense* L.

Botanical family

Aristolochiaceae

Foreign names

Serpentaire du Canada (Fr.), Canadische Schlangenwurzel (Ger.), Asaro (Sp.) Asaro (It.)

Description

The several known *Asarum* species find various applications, depending on the botanical classification. *A. canadense*, not to be confused with *A. europaeum* L., is a perennial herb growing preferably in shady, humid, woody areas in Canada and the northern United States. European asarum differs from the Canadian variety, not only in its main constituents but also in its vegetative form. The essential oil from *A. europaeum* is poisonous and is not prepared for commercial use. Unidentified constituents of the terpene fraction—*not* asarone, as commonly believed—are responsible for the toxicity of the oil.

Parts of plant used

Rhizomes

Physical-chemical characteristics

Essential oil

Canadian snakeroot is first uprooted; the rhizomes are cleaned, dried, and comminuted with water prior to undergoing steam distillation. The steam-distilled essential oil is a yellow to yellow-amber liquid with a spicy odor and flavor reminiscent of ginger oil. Its physical-chemical constants follow (see also reference 2):

Specific gravity at 15°C	0.947–0.998[1]
Optical rotation	0 to −11°20′[1]
Refractive index at 20°C	1.4843–1.5015[1]
Acid value	1.9–7.5[1]
Ester value (after acetylation)	92.4–144.2[1]
Solubility	1:1.5–2.5 and more in 70% ethanol[1]

The distillation waters are often cohobated for the total yield of essential oil of approximately 3.0%. Main constituents include α-pinene, *d*-linalool, *l*-borneol, *l*-α-terpineol, geraniol, eugenol, methyl eugenol, a lactone, an azulene compound, and various fatty acids.

Organoleptic characteristics

Strong, characteristic, spicy odor and flavor reminiscent of ginger

Uses

Snakeroot essential oil is used extensively in flavoring to impart a spicy note to condiments, candy, beverages, and other food products. The oil finds application to a lesser extent in perfumery, in combination with orris derivatives for special effects. Canadian snakeroot oil (FEMA No. 3023) has been reported used in the following:[3]

non-alcoholic beverages	1.9 ppm
ice cream, ices, etc.	1.0–5.0 ppm
candy	8.3 ppm
baked goods	8.3 ppm
condiments	1.4–4.0 ppm

Regulatory status

FDA §121.1163

SIMARUBA

Botanical source

Simaruba amara Aubl. (*Quassia amara*)

Botanical family

Simarubaceae

Foreign names

Simarouba (Fr.), Ruhrrinde (Ger.), Simaruba (Sp.), Simaruba (It.)

Description	Chiefly tropical trees and shrubs having bitter-tonic bark, mainly pinnate leaves, and small 3–5-merous flowers with a prominent disk. The fruit is either a drupe, a samara, or a berry. The bark contains an essential oil and a bitter principle. Most of the *Simarubaceae* contain a bitter principle and sometimes a resinous matter and an oil that is of value as a tonic. Branches of quassia and the pulverized bitter wood of *Simaruba* species are used in tropical America to drive away insects.
Parts of plant used	The bark
Organoleptic characteristics	Tonic, digestive, bitter
Regulatory status	FDA §121.1163. In alcoholic beverages only

SLOE

Other names	Blackthorn
Botanical source	*Prunus spinosa* L.
Botanical family	*Rosaceae*
Foreign names	Prunellier (Fr.), Schwarzdorn (Ger.), Bruniero (Sp.), Prugnolo (It.)
Description	Shrubs with brownish, divaricate, thorny branches; simple, alternate, lanceolate leaves with finely dentate edges; white, solitary or geminate flowers supported by a glabrous peduncle; and globose, blue-violet, sour berries. The plant grows in thickets, along roadsides, and in waste places in areas with mild, temperate Mediterranean climate; it grows also in Iran and southern Siberia.
Parts of plant used	Berries; also the bark and flowers
Physical-chemical characteristics	
Derivatives	Decoctions (from the bark), infusions (from dried flowers), fluid extract (from berries and sometimes the bark). Main constituents of the bark include various tannins and alkaloids. The flowers contain, in addition to amygdalin and traces of an essential oil, gums, resins, and quercetin.
Uses	Sloe bark and sloe flower derivatives are used in patent drugs. Sloe berry extract (FEMA No. 3021) has been reported used in the following:[3]

non-alcoholic beverages	110 ppm
alcoholic beverages	43,000 ppm
ice cream, ices, etc.	50–100 ppm
candy	40 ppm
baked goods	45 ppm

Regulatory status	GRAS (II)

SPEARMINT

Botanical source	*Mentha spicata* Houds or L.
Botanical family	*Labiatae*

Foreign names

Menthe crépue (Fr.), Krauseminz (Ger.), Menta crespa (Sp.), Menta crispa (It.)

Description

Herbaceous plant extensively cultivated in North America, England, Germany, and Holland. The most frequently cultivated varieties are *M. trichoura* Brig., *M. crispata*, and *M. tenuis*. The plant is from 25–75 cm (10–30 in.) high, with an erect, branched stalk exhibiting long, lanceolate leaves, and flowers clustered in the form of spikes.

Parts of plant used

Flowering tops

Physical-chemical characteristics

Essential oil

The oil, obtained by steam distillation, is a pale-yellow to greenish-yellow liquid with an aromatic odor. The oil contains α-pinene, α-phellandrene, *l*-limonene, octyl alcohol, dipentene cineol (in some varieties only), dihydrocarveol, and carvone.

Specific gravity at 20°C	0.915–0.938[1]
Refractive index at 20°C	1.4830–1.4910[1]
Optical rotation	−40° to −60°C[1]
Ketone content (as carvone)	55–71.5%[1]
Solubility	1:1 in 80% ethanol[1]

Organoleptic characteristics

Warm, herbaceous, penetrating odor; sharp, pungent flavor

Uses

The essential oil is used extensively to flavor toothpaste, mouth wash, chewing gum, and candy. Spearmint has been reported used in the following:[3]

non-alcoholic beverages	500 ppm
condiments	1,000 ppm
meats	500 ppm

Spearmint extract has been reported used in the following:[3]

non-alcoholic beverages	2,100 ppm
ice cream, ices, etc.	100 ppm
candy	0.20 ppm

Spearmint oil has been reported used in the following:[3]

non-alcoholic beverages	100 ppm
alcoholic beverages	100 ppm
ice cream, ices, etc.	81 ppm
candy	830 ppm
baked goods	270 ppm
gelatins and puddings	75 ppm
chewing gum	6,200 ppm
jellies	72–1,900 ppm

Regulatory status

GRAS (I), (II)

STAR ANISE

Botanical source

Illicium verum Hook. f.

Botanical family

Magnoliaceae

Foreign names

Anis étoilé (Fr.), Stern Anis (Ger.), Anis estrellado (Sp.), Anice stellato (It.)

Description

Tall evergreen tree up to 10 m (32.5 ft) high, indigenous to southern China and Indochina. The plant has short-stemmed leaves, single axillary flowers from white to red in color, and a whitish bark. Following pollination, the carpels (usually 8 in number and each containing a single tiny seed) swell, assuming the characteristic star shape and a reddish-brown color. The plant flowers all year round.

Parts of plant used Seeds

Physical-chemical characteristics

Essential oil The product obtained by steam distillation of well ripened, brown-colored seeds is known commercially as star anise essential oil. It is a pale-yellow to amber-yellow liquid that tends to solidify at low temperatures. The odor is intensely sweet with a characteristic flavor. The main constituents include anethol (85–90%), *d*-α-pinene, Δ^3-carene, α- and β-phellandrene, *p*-cymene, cineol, *l*-limonene, *d*-terpineol, and others (about 25 total components).

Specific gravity at 20°C	0.979–0.987[1]
Refractive index at 20°C	1.5525–1.5560[1]
Freezing point	ca 15°C[1]

Derivatives Fluid extract, tincture (20% in 60–70% ethanol), and essential oil from which anethol is isolated

Organoleptic characteristics Sweet flavor, apparently not powerful

Uses Star anise is used industrially as the essential oil for the production of anethol and for the formulation of anise-flavored compounded oils used in liqueur formulations (anisette). Because of its limited availability, synthetic *trans*-anethol has been used in its place in flavoring candy, licorice, toothpaste, carbonated drinks, and liqueurs. Star anise has been reported used in the following:[3]

non-alcoholic beverages	13 ppm
alcoholic beverages	40–60 ppm
meats	500–1,000 ppm
ice cream, ices, etc.	18 ppm
candy	83 ppm
baked goods	140 ppm

Star anise oil has been reported used in the following:[3]

non-alcoholic beverages	12 ppm
alcoholic beverages	50 ppm
meats	20–55 ppm
syrups	8.0 ppm
ice cream, ices, etc.	99 ppm
candy	190 ppm
baked goods	230 ppm

Regulatory status GRAS (I)

STORAX

Other names Styrax

Botanical source *Liquidambar orientalis* Mill.—Asian or levant storax; or *L. styraciflua* L.—American storax

Botanical family *Hamamelidaceae*

Foreign names Styrax (Fr.), Storax (Ger.), Esteraque (Sp.), Storace (It.)

Description

Storax is a pathological exudate produced in the sapwood (balsam) and bark tissue of the trees *L. orientalis* and *L. styraciflua*. The pathological condition is caused intentionally in *L. orientalis* by removing sections of the bark and injuring the inner sapwood. The crude storax is collected in cans and occasionally pieces of peeled bark are boiled in water to recover additional material. In *L. styraciflua* (American storax) the exudate accumulates in pockets of older trees; thus it is not necessary to injure the sapwood to stimulate the pathological condition. Both *L. orientalis* and *L. styraciflua* are tall trees (ca 15 m, or 49 ft) growing wild in Asia Minor and in the forests of Central and South America. American storax is further subdivided into two varieties: *mexicana* and *macrophylla*. The trees have leaves similar in shape to maple, with flowers growing in clusters like those of plantain. Another variety known as *Styrax officinalis* is a woody shrub growing in Israel, the Aegean Islands, and Greece; it is used only locally.

Parts of plant used

The pathological exudate (balsam)

Physical-chemical characteristics

Balsams

Asian storax is a semisolid, transparent, sticky brown mass; it is essentially the crude exudate cleaned by boiling in water. American storax (Honduras) is slightly darker but generally of better quality. Main constituents of storax include styracin, cinnamic acid and its esters, vanillin, styrene, and probably styrocamphene.

Essential oil

The crude balsam contains many impurities that are objectionable for use in flavors or in perfumery. An essential oil (storax oil) is obtained by steam distillation of the crude resin in approximately 0.5–1.0% yields. The oil is a colorless to pale-yellow liquid with a balsamic, sweet, slightly spicy odor. Its physical-chemical constants vary with the source.

	Asian (levant) storax	**American storax**
Specific gravity	0.89–1.06	0.975–1.005 at 25°/25°C
Refractive index at 20°C	1.53950–1.56528	1.5300–1.5450
Optical rotation	−38° to +0°30′	0° to +4°
Acid value	0.5–33	30 max
Ester value	0.5–130	5–50
Solubility	1:1 in 70% ethanol	>1:0.5 in 80% alcohol

Derivatives

Storax resinoid is an important derivative because the balsam is so impure that it cannot be used. The true resinoid is prepared by benzene extraction. It is free of water, dirt, sand, etc. It is dark olive-brown in color and very viscous. The true storax absolute is obtained by alcoholic extraction of the resinoid. This is not to be confused with the so-called "resin absolute" prepared from the balsam by direct extraction with ethanol followed by drying over sodium sulfate and mild vacuum stripping of the alcohol.

Organoleptic characteristics

Pleasant, sweet, balsamic, slightly spicy odor

Uses

Storax is used as a fixative in fine soaps. A certain amount of storax is used as the starting material for the production of cinnamyl alcohol. The essential oil exhibits fixative properties and is employed in perfumery to soften or to enhance the bottom notes of floral bouquets. The purified balsam and the extract are used to flavor beverages, candy, and pastry. These are somewhat specific applications of limited use only.

Storax (FEMA No. 3036) has been reported used in the following:[3]

non-alcoholic beverages	2.0 ppm
ice cream, ices, etc.	2.0 ppm
candy	13 ppm

baked goods	23 ppm
chewing gum	300 ppm
toppings	15 ppm

Storax extract (FEMA No. 3037) has been reported used in the following:[3]

non-alcoholic beverages	0.84 ppm
ice cream, ices, etc.	0.25–0.60 ppm
candy	3.5 ppm
baked goods	4.0–6.0 ppm
gelatins and puddings	0.04 ppm

Regulatory status	FDA §121.1163

STRAWBERRY

Botanical source	*Fragaria vesca* L.
Botanical family	*Rosaceae*
Foreign names	Fraise (Fr.), Erdbeere (Ger.), Fraulera (Sp.), Fragola (It.)
Description	Perennial, herbaceous plant; grows wild or cultivated in central-southern Europe, North America, and Asia. The plant has thick rhizomes, radical leaves with long, small, white flowers blossoming from April to July, and fleshy, ovoidal, red berries covered with numerous achenes.
Parts of plant used	Berries
Physical-chemical characteristics	
Derivatives	Concentrated (4–6 fold) juice. Strawberry aroma has been the subject of extensive investigation. Several components have been identified, of which only 7% appear to be responsible for the aroma. Strawberry aroma varies widely with the strawberry variety. The most valuable is the aroma from wild strawberry.
Organoleptic characteristics	Sweer-sour taste; characteristic odor
Uses	The concentrated juice finds extensive application in making syrups, ice cream, candy, and chocolate fillings.

SUGAR BEET EXTRACT FLAVOR BASE

Botanical source	*Beta vulgaris* L.
Botanical family	*Chenopodiaceae*
Uses	Source of sucrose; common in Europe
Regulatory status	FDA §121.1086

TAGETES

Other names	Marigold
Botanical source	*Tagetes patula* L., *T. erecta* L., or *T. minuta* L. (*T. gladulifera* Schrank)

Botanical family *Compositae*

Foreign names Tagetes (Fr.), Tagetes (Ger.), Tagete (It.)

Description Strong-scented herb probably native to Africa or Central America. Among the various *Tagetes* species, *T. gladulifera* and *T. minuta* are the most common varieties. The plant grows wild, its growing sites including Argentina, southern Mexico, South Africa, Australia, Africa, and the Mediterranean. It is frequently encountered in India (*T. patula*). The herb has opposite pinnatifid leaves, showy heads of flowers with yellow or orange rays, and seeds that form after the flowers blossom. Tagetes should not be confused with pot marigold (see p. 161).

Parts of plant used The whole plant

Physical-chemical characteristics

Essential oil The oil, obtained by steam distillation in approximately 0.3–0.4% yields, is a yellow-reddish liquid with an unpleasant, rancid odor and a peppermint-like undertone. Its main constituents are tegetone (an unstable, unsaturated ketone believed to be responsible for the rancid odor), *d*-limonene, and *p*-cymene. The oil tends to solidify to a gelatinous mass on exposure to light and moisture. The Indian variety (*T. patula* L.) yields an oil similar to that of calendula with an herbaceous, faintly lavender-like odor; this essential oil is not commercially available. The flowers of *T. patula* L. codistilled with sandalwood oil yield the so-called attar genda, a product employed in perfumery in India.

Derivatives The absolute, prepared by conventional systems, is a highly viscous, yellowish-green to dark-green liquid with an herbaceous odor and slightly bitter, fruital undertones.

Organoleptic characteristics Characteristic herbaceous, somewhat rancid odor with fruital, bitter undertones

Uses Tagetes essential oil is normally used in perfumery and, to a limited extent, in the formulation of compound aromas for flavoring beverages, candies, and condiments. Tagetes oil (FEMA No. 3040) has been reported used in the following:[3]

non-alcoholic beverages	4.1 ppm
ice cream, ices, etc.	7.4 ppm
candy	9.0 ppm
baked goods	13 ppm
gelatins and puddings	7.0 ppm
condiments	20 ppm

Regulatory status FDA §121.1163. As an oil only

TAMARIND

Botanical source *Tamarindus indica* L.

Botanical family *Leguminosae*

Foreign names Tamarin (Fr.), Tamarinde (Ger.), Tamarindo (Sp.), Tamarindo (It.)

Description Large tree up to 25 m (82 ft) high, native to Africa and tropical Asia. The plant has pinnatifid leaves consisting of several ovoidal leaflets, short white-yellowish, racemose flowers obcompressed about 5–8 cm, and long fruits narrowing between the seeds. The fruits exhibit a woody epicarp, fleshy, black, sweet-sour mesocarp, and a parchment-like, membranous endocarp. Commercial qualities come from Egypt, India, Ceylon, Java, and the Antilles.

Parts of plant used Fruits (skinned of the epicarp)

Physical-chemical characteristics

Derivatives Aqueous concentrated extract (35–40°Be), so-called tamarind concentrated juice or pulp. Main constituents of the extract include organic acids (tartaric, malic, succinic), sugar, and pectins.

Organoleptic characteristics Sweet-sour, agreeable taste

Uses The use of tamarind extract is limited to the preparation of syrups and beverages.

Regulatory status GRAS (II)

TANSY

Botanical source *Tanacetum vulgare* L.

Botanical family *Compositae*

Foreign names Tanaise (Fr.), Rainfarn (Ger.), Tanaceto (Sp.), Tanaceto (It.)

Description Perennial plant about 1 m (39 in.) high that grows wild or cultivated in almost every temperate and cold temperate zone in the world. The plant, native to the Balkans, has oblique, branched rhizomes, erect stalk, alternate leaves resembling fern, and yellow, single-head flowers (June–September).

Parts of plant used Leaves and flowering tops

Physical-chemical characteristics

Essential oil Obtained by steam distillation, the oil distilled from the fresh plant is a green liquid; that from dried leaves and flowering tops is yellow with a warm, sharp, spicy odor. Main constituents include β-thujone, *l*-camphor, borneol, and terpenes.

Specific gravity at 25°C	0.913–0.926[2]
Optical rotation	+28° to +40°[2]
Refractive index at 20°C	1.4570–1.4670[2]
Acid value	2 (max)[2]
Per cent ketones (as thujone)	50–65[2]
Solubility	1:3 in 80% ethanol[2]

Organoleptic characteristics Strong, characteristic, aromatic odor; bitter flavor

Uses Tansy and its derivatives were used in pharmacology as an anthelmintic and only occasionally in flavors. The use in flavors was limited only to minute additions because of its toxicity; 4 cc of essential oil represents a lethal dose. For this reason the use of tansy oil and its derivatives in flavors has been practically discontinued.

Regulatory status FDA §121.1163. In alcoholic beverages only. Finished alcoholic beverage thujone-free

TARRAGON

Other names Estragon; estragole

Botanical source *Artemisia dracunculus* L.

Botanical family *Compositae*

Foreign names Estragon (Fr.), Estragon (Ger.), Estragón (Sp.), Estragone (It.)

Description Herbaceous plant native to eastern and central Europe; it prefers shady growing sites. It grows 30–80 cm (12–31 in.) high, with roots clustered in bundles, a branched stalk, alternate leaves, and yellow flowers. The plant flowers from July to August.

Parts of plant used Flowering tops and leaves

Physical-chemical characteristics

Essential oil The essential oil is obtained by steam distillation in yields varying from 0.3–1.4%. It is a yellow-greenish liquid with an anise odor (also see Reference 2). The physical-chemical constants vary, depending on the plant origin. In general, the oil contains, in addition to a large amount of terpenes, such as pinene and myrcene, anethol (approximately 10%) and up to 60–75% estragole (methyl chavicol).

Specific gravity at 20°C	0.919–0.943[1]
Refractive index at 20°C	1.5100–1.5180[1]
Optical rotation at 20°C	+2° to +6°[1]
Ester value	ca 18[1]

Derivatives Infusion (2%), tincture (20% in 65% ethanol), distillation waters, essential oil, and oleoresin (dark-green, somewhat viscous liquid).

Organoleptic characteristics Sweet, spicy odor; sweet, anisic, fresh, green flavor reminiscent of basil and anise

Uses The tincture is used in enology. Together with the essential oil it finds a variety of applications in liqueurs and canned foods.

Tarragon has been reported used in the following:[3]

baked goods	20 ppm
condiments	23 ppm
meats	260 ppm

Estragon oil (tarragon oil) has been reported used in the following:[3]

non-alcoholic beverages	0.79 ppm
alcoholic beverages	1–3 ppm
ice cream, ices, etc.	0.5–0.7 ppm
candy	0.85 ppm
baked goods	17 ppm
condiments	26 ppm
meats	40 ppm

Regulatory status Natural estragole: GRAS (II)

TEA

Botanical source *Thea sinensis* L.

Botanical family *Theaceae*

Foreign names	Thé (Fr.), Tee (Ger.), Té (Sp.), Thè (It.)
Description	A shrub having lanceolate leaves and rather large, fragrant white flowers. The plant is extensively cultivated in India, Java, Ceylon, China, and Japan for its leaves used in the preparation of the world-known beverage. The seeds of the plant contain a fixed oil that is used for industrial purposes. The green tea leaves contain a very small amount of essential oil (0.014%, spring; 0.007%, summer). The leaves are cured by the following process: the leaves are dried and comminuted, thus liberating the juice containing enzymes necessary to fermentation. Fermentation is carried out for about 4 hours, changing the color of the leaves from green to dark brownish-green. Finally, a stream of hot air is passed over the cured leaves to stop fermentation and to reduce moisture content to approximately 2%.
Parts of plant used	The dried, cured leaves
Physical-chemical characteristics	
Essential oil	This oil is not manufactured on an industrial scale but has been prepared for investigational purposes only. Main constituents of the oil include phenethyl alcohol, *n*-hexyl alcohol, benzyl alcohol, citronellol, geraniol, butyraldehyde, isobutyraldehyde, isovaleraldehyde, acetic acid, capronic acid, traces of methyl salicylate, methylmercaptan, and 2-acetylpyrrole.
Derivatives	Concrete, absolute, and tincture (5–10% in 50% ethanol). The concrete is obtained by solvent extraction of the cured dried leaves. The absolute is prepared by alcoholic extraction of the concrete, or it is sometimes co-distilled or molecularly distilled from the concrete. The distilled products are viscous, amber-colored liquids with a rich, delicate, sweet, woody, herbaceous odor.
Organoleptic characteristics	Sweet, herbaceous, woody, floral odor
Uses	Tea derivatives find application in perfumery. The tincture has a limited use in flavor work and in liquors.
Regulatory status	GRAS (II)

THISTLE, BLESSED

Other names	Do not confuse with *Silybum marianum*, commonly known as holy thistle, lady's thistle, or milk thistle.
Botanical source	*Cnicus benedictus* L.
Botanical family	*Compositae*
Foreign names	Chardon béni (Fr.), Benedicktenkraut (Ger.), Cardo benedito (Sp.), Cardo santo (It.)
Description	Annual Mediterranean herb from 20–50 cm (8-20 in.) tall, having small, spindle-shaped (fusiform) roots. The erect, multiple stalks are covered with light hairs; the alternate, hairy leaves are pale green, and the flowers are yellow. The plant, which flowers from May to August, exhibits a somewhat unpleasant odor and a strong, lasting, bitter taste.
Parts of plant used	Leaves and flowers

Physical-chemical characteristics

Essential oil The oil is obtained by steam distillation of the leaves with a yield of ca 5%; the oil is very little known.

Derivatives Infusion (1.5% in 25% alcohol), tincture (20% in 25% alcohol), fluid extract, and the essential oil

Organoleptic characteristics Bitter

Uses The dried product and the derivatives are primarily used as flavor correctives or modifiers and in the formulation of special bitters and elixirs.

Regulatory status FDA §121.1163

THYME

White, Wild or Creeping, and Spanish "Origanum"

Botanical source *Thymus vulgaris* L.; *T. zygis* L. var. *gracilis* Boiss.—white thyme; *T. serpyllum* L.—wild or creeping thyme; *T. capitatus* Hoff. & Link.—Spanish "origanum"

Botanical family *Labiatae*

Foreign names Thym (Fr.), Thymian (Ger.), Tomillo (Sp.), Timo (It.)

Description Shrubs approximately 50 cm (20 in.) high, commonly growing wild throughout the Mediterranean basin (Spain, France, Italy, Morocco, Turkey, etc.), eastern and central Europe, and North America. The various species exhibit different morphological characteristics. In addition to the thyme species covered by this monograph, known varieties include: *T. mastichina* L. (see also reference 2, Oil of Spanish Marjoram), *T. euserpillum*, and others.

T. vulgaris L. and *T. zygis* L. are commonly used for the distillation of the essential oil. Spain produces the largest amount. *T. serpyllum* L. also is used for distillation (Russia). This oil not only is of limited interest to the flavorist but also commercially rare. *T. serpyllum* extracts have been used to a limited extent in the preparation of galenic products. *T. capitatus* Hoff. & Link. is a variety growing in Sicily, Spain, and North Africa; it also is used for distillation.

Parts of plant used The entire flowering plant, excluding the roots

Physical-chemical characteristics

Essential oil The oil is obtained by water and steam distillation of the partially dried plant of *T. vulgaris* and *T. zygis* in varying yields (0.5–1.2%). It is a brownish-red liquid exhibiting a strong, aromatic odor and a warm, somewhat sharp flavor (red thyme oil). White thyme oil is a pale-yellow liquid obtained by rectification of the distilled red thyme oil, exhibiting similar but milder odor and flavor characteristics. The physical-chemical constants of red thyme oil vary, depending on the source. An oil of Spanish origin has the following constants:

Specific gravity at 20°C	0.911–0.954
Refractive index at 20°C	1.4940–1.5100
Optical rotation at 20°C	−5° to +1°
Phenol content (as thymol)	30–75%
Solubility	2:5 in 70% alcohol; 1:2 in 80% alcohol

Thymol and carvacrol are the two main constituents of the oil. Their relative per cent ratio in the oil varies widely, depending on the botanical source. Other constituents include anisyl alcohol, linalool, borneol, geraniol, camphene, and γ-terpinene.

The essential oil steam distilled from *T. capitatus* is a clear, pinkish to reddish-brown oily liquid with odor reminiscent of origanum (Spanish "origanum"). The oil is somewhat richer in carvacrol than the oil from *T. vulgaris* or *T. zygis*, containing mainly thymol. An oil of Sicilian production exhibits the following physical-chemical constants (see also reference 2, "Oil of Spanish Origanum"):

Specific gravity at 20°/20°C	0.930–0.956
Refractive index at 20°C	1.497–1.511
Optical rotation at 20°C	−2° to +1°
Acid value	3.5 min
Phenol content (as carvacrol)	50–74%
Solubility	>1:1.5 in 80% alcohol

Derivatives

From *T. vulgaris*: Fluid extract, tinctures (20% in 20% and 70% ethanol), absolute

Organoleptic characteristics

Warm, herbaceous odor; spicy, slightly biting taste

Uses

The dried product, tincture (*T. vulgaris* and *T. serpyllum*), and fluid extract are used in the formulation of liqueurs. The essential oils (*T. vulgaris*, *T. capitatus*) find use in flavoring sauces, condiments, meats, etc. and also in perfumery (white thyme oil).

Thyme (*T. vulgaris*—FEMA No. 3063) has been reported used in the following:[3]

non-alcoholic beverages	13 ppm
candy	5.0 ppm
baked goods	550 ppm
meats	360 ppm
soups	500–1,000 ppm

Thyme oil (*T. vulgaris*—FEMA No. 3064) has been reported used in the following:[3]

non-alcoholic beverages	1.0–5.0 ppm
ice cream, ices, etc.	20 ppm
candy	1.0–15 ppm
baked goods	1.5–5.3 ppm
chewing gum	100 ppm
condiments	18 ppm
meats	33 ppm
soups	0.13 ppm

White thyme oil (*T. vulgaris*—FEMA No. 3065) has been reported used in the following:[3]

non-alcoholic beverages	0.01–1.0 ppm
alcoholic beverages	5.0 ppm
ice cream, ices, etc.	0.01 ppm
candy	27 ppm
baked goods	5.4 ppm
condiments	4.0–8.0 ppm
meats	15 ppm

Origanum oil (*T. capitatus*—FEMA No. 2828) has been reported used in the following:[3]

non-alcoholic beverages	0.50 ppm
ice cream, ices, etc.	0.50 ppm
candy	0.50 ppm
baked goods	0.60–33 ppm
condiments	30 ppm
meats	37 ppm

Regulatory status

Thyme: GRAS (I), (II)
Thyme, white: GRAS (I), (II)
Thyme, wild or creeping: GRAS (I), (II)
T. capitatus, Spanish "origanum": FDA §121.1163

TOLU BALSAM

Botanical source

Myroxylon balsamum (L.) Harms.

Botanical family

Leguminosae

Foreign names

Baume du Tolú (Fr.), Tolubalsam (Ger.), Balsamo Tolu (Sp.), Balsamo del Tolú (It.)

Description

Tolu balsam is a luxuriant tree reaching more than 20 m in height; it usually grows in the northern part of South America (Magdalena river valley and Nueva Granada region in Venezuela). The balsam consists of the plant exudate oozing from incisions made on the trunk. The fluid gum that exudes through capillary conduits in the tree is collected in cups placed at different heights along the trunk. The balsam is a semisolid plastic mass, brown or brownish-yellow, with a sweet, aromatic, persistent odor reminiscent of vanilla. Aging and climatic conditions strongly affect the appearance of the balsam. In addition to hardening, the balsam becomes friable with a glassy, clean cleavage on aging. Main constituents of the balsam (in addition to 75–80% resinous substances) include benzyl benzoate, benzyl cinnamate, a small amount of essential oil, and traces of vanillin.

Parts of plant used

The balsam exudate

Physical-chemical characteristics

Essential oil

The balsam can be steam distilled, yielding 2-7%. It is a viscous, pale-yellow to light-orange oil with a pleasant, sweet, resinous odor reminiscent of hyacinth. The physical-chemical constants of the oil are as follows (see also reference 2):

Specific gravity at 15°C	0.907–1.1016[1]
Optical rotation	$+0°5'$ to $-1°20'$[1]
Refractive index at 20°C	1.5075–1.5347[1]
Acid value	24–80[1]
Ester value	153–208[1]
Solubility	1:0.5–1 in 90% ethanol[1]

Derivatives

Resin absolute (resinoid), extract obtained by alcoholic extraction of the balsam in approximately 60–65% yields, is a dark, viscous mass with a pleasant balsamic odor and remarkable fixative properties.

Organoleptic characteristics

Agreeable, sweet, lasting odor similar to hyacinth

Uses

In perfumery the essential oil and the resinoid are used as modifiers in floral notes to impart warmth and to enhance persistency. The gum resin and the extract are used in the formulation of aromas for ice cream and chewing gum.

Tolu balsam extract (FEMA No. 3069) has been reported used in the following:[3]

non-alcoholic beverages	32 ppm
ice cream, ices, etc.	150 ppm
candy	57 ppm
baked goods	71 ppm
chewing gum	2.0–38 ppm

Tolu balsam gum (FEMA No. 3070) has been reported used in the following:[3]

non-alcoholic beverages	2.6 ppm
ice cream, ices, etc.	13 ppm
candy	5.2 ppm
baked goods	8.0 ppm
syrups	3.0 ppm

Regulatory status	FDA §121.1163

TONKA BEANS

Botanical source	*Coumarouna odorata* Aubl. (*Dipteryx odorata* Willd.) and other *Dipteryx* species
Botanical family	*Leguminosae*
Foreign names	Feve de Tonka (Fr.), Tonkabohne (Ger.), Haba Tonca (Sp.), Fava Tonka (It.)
Description	Tree native to Brazil and cultivated in Central and South America. It has large, elliptical leaves, violet flowers, and fruits with only a single seed, as in plums.
Parts of plant used	Seeds (properly dried)
Physical-chemical characteristics	
Derivatives	Tincture (20% in 70% ethanol and 10% in 60% ethanol) and fluid extract. The main constituent of the dried product and its derivatives is coumarin.
Organoleptic characteristics	Rich, sweet, warm, distinctly coumarinic odor and flavor
Uses	Tonka beans or extracts cannot be used wherever coumarin is banned. However, in the past and in those countries where coumarin is permitted, tonka has been used for flavoring tobaccos and baked goods. It has a tremendous masking effect and has been used for flavoring cod liver oil and other poor-tasting pharmaceuticals.
Regulatory status	Its use in foods is not permitted in the United States.

TUBEROSE

Botanical source	*Polyanthes tuberosa* L.
Botanical family	*Amaryllidaceae*
Foreign names	Tubereuse (Fr.), Tuberose (Ger.), Tuberosa (Sp.), Tuberosa (It.)
Description	A plant native to Central America, tuberose is cultivated for ornamental purposes (white, lily-like, paired flowers) and for extractive purposes (solitary flowers), especially in France and Morocco. The flowers, harvested between mid-August and the end of September, are not distilled because of the low yields and the deterioration of the fragrance of the raw material. Extraction of the flowers is carried out exclusively by enfleurage or by the use of volatile solvents. The production of tuberose derivatives is extremely low, less than 5 kg per year!
Parts of plant used	Flowers

Physical-chemical characteristics

Derivatives

Concrete, absolute, and distilled oil. The concrete, obtained in approximately 1.20–1.50% yields, is a soft mass with a yellowish-brown color and sweet, floral, extremely intense odor. The absolute is a viscous, brownish liquid. An oil is obtained in approximately 3–6% yields by distillation of the concrete. Tuberose derivatives contain the following constituents: methyl benzoate, methyl anthranilate, benzyl alcohol, butyric acid, probably phenylacetic acid, methyl salicylate, eugenol, geraniol, nerol, and farnesol. The presence of a ketone ($C_{13}H_{20}O$) is somewhat controversial.

Organoleptic characteristics

Intense, sweet, floral odor particularly agreeable on dilution

Uses

Because of the extremely high price, tuberose concrete and absolute find limited use in the finer perfumes or as modifiers in other absolutes, such as jasmine and rose absolute. To even a lesser degree tuberose is used in flavoring candy, beverages, and baked goods; this type of application should be considered exceptional, however. Tuberose oil (FEMA No. 3084) has been reported used in the following:[3]

non-alcoholic beverages	0.26 ppm
ice cream, ices, etc.	0.45 ppm
candy	1.5 ppm
baked goods	1.7 ppm

Regulatory status

GRAS (II)

TURMERIC

Other names

Tumeric; curcuma

Botanical source

Curcuma longa L.

Botanical family

Zingiberaceae

Foreign names

Curcuma longue (Fr.), Gelbwurzel or Curcuma (Ger.), Curcuma (Sp.), Curcuma (It.)

Description

Several species of *Curcuma* exist: *C. xanthorrhyza*, *C. domestica*, *C. zedoaria*, *C. caesia*, and *C. amada*. Although all these are aromatic plants, *C. longa* is the one used as a flavor ingredient. The plant is originally from South Asia and is widespread throughout India, Malaysia, Ceylon and Japan. It is a perennial herb whose rhizome yields (like that of ginger, which it also resembles) climbing stalks with leaves only or with leaves and flowers. Reproduction occurs through the splitting of the rhizome.

Parts of plant used

Rhizome (dried rhizome as is or after previously boiling in water)

Physical-chemical characteristics

Essential oil

The essential oil of *C. zedoaria* Roscoe is obtained by steam distillation with variable yields (1–15%). It is a greenish liquid exhibiting a spicy odor.

Specific gravity at 15°C	0.982–1.01[1]
Optical rotation	+8° to +17°[1]
Refractive index at 20°C	1.5023–1.5088[1]
Ester value	16–22.4[1]
Ester value (after acetylation)	56–73.4[1]
Solubility	1:1.5–2.0 in 80% ethanol[1]
Acid value	0.3–2.4[1]

The essential oil of *C. longa* also is obtained by steam distillation, with yields ranging between 1.3 and 5.5%. It is a yellow liquid with a spicy odor. The oil contains, in addition to turmerone, free acids, cineol, borneol, zingerone, phellandrene, and 3 to 4% coloring matter (curcumin).

Specific gravity at 15°C	0.9348[1]
Optical rotation	+14°4′[1]
Refractive index at 20°C	1.5118[1]
Ester value	9.8[1]
Ester value (after acetylation)	36.6[1]
Ketones (calculated as turmerone)	53%[1]
Solubility	1:0.6 in 90% ethanol[1]

Derivatives

Tincture (20% in 60% ethanol), fluid extract, and oleoresin

Organoleptic characteristics

Spicy, fresh odor reminiscent of sweet orange and ginger; slightly pungent, bitter flavor

Uses

The dried product is used in the formulation of curries. The derivatives are used largely in the formulation of compounded oils and concentrates to flavor food products, particularly bouillons, soups, precooked beans, and sauces. The finely ground dried product often is used for the same applications. It is used also as the coloring in mustard. The coloring is due to curcumin.

Turmeric has been reported used in the following:[3]

gelatins and puddings	0.05 ppm
condiments	760 ppm
soups	30–50 ppm
meats	200 ppm
pickles	690 ppm

Turmeric extract has been reported used in the following:[3]

non-alcoholic beverages	0.78 ppm
condiments	59 ppm
soups	30–40 ppm
meats	43 ppm
pickles	40 ppm

Turmeric oleoresin has been reported used in the following:[3]

condiments	640 ppm
meats	20–100 ppm
pickles	200 ppm

Regulatory status

GRAS (I), (II)

TURPENTINE

Botanical source

Pinus palustris Mill. and other *Pinus* species that yield terpene oils exclusively

Botanical family

Pinaceae

Foreign names

Essence de Térèbinthine (Fr.), Terpentinoel (Ger.), Trementina (Sp.), Trementina (It.)

Description

Balsam turpentine is the oleo-gum-resin obtained by incisions made on the trunk of several trees belonging to the genus *Pinus*. The common American turpentine comes from *P. palustris*. Crude turpentine contains 75–90% resin and 10–25% oil. It is of paramount importance to use special techniques in making incisions, since the tree otherwise may die in a short time. A gum (gum turpentine) consisting of white incrustations is formed around the incisions in the tree.

Rosin is the resinous residue of the distillation of turpentine. There are several varieties of rosin, varying in color from the palest amber to nearly black and from translucent to opaque, depending on the turpentine source. *Colophony* is the name of the common rosin variety.

Part of plant used

The oleo-gum-resin (turpentine balsam)

Physical-chemical characteristics

Essential oil

Turpentine oil is obtained by steam distillation of the oleo-gum-resin. It is a clear, colorless, mobile liquid with a warm, balsamic, refreshing odor of turpentine. Its physical-chemical constants are as follows:

Specific gravity at 15.5°C	0.860–0.875[1]
Refractive index at 20°C	1.465–1.478[1]
Boiling point	Initially, 150–160°C;[1] >90% distills below 170°C[1]
Optical rotation	+11°19′ (*P. palustris*);[1] −19°19′ (*P. caribaea*)[1]

Note: The oil must be absolutely free of water to avoid oxidation of α- and β-pinene (approximately 80% of the oil).

Organoleptic characteristics

Penetrating and characteristic odor; pungent, bitter taste

Uses

Turpentine oil is the single largest essential oil produced. It finds extensive use in a large number of industrial products (perfumery, sprays, deodorizers, varnishes, and paints). Rosin is used in perfumery as a fixative. Turpentine gum (FEMA No. 3088) has been reported used in baked goods, 15 ppm.

Steam-distilled turpentine (FEMA No. 3089) has been reported used in the following:[3]

candy	11 ppm
baked goods	10–20 ppm
chewing gum	7.1 ppm

Regulatory status

Turpentine: FDA §121.1163
Rosin (colophony): FDA §121.1163. In alcoholic beverages only

VALERIAN

Botanical source

Valeriana officinalis L.

Botanical family

Valerianaceae

Foreign names

Valeriane (Fr.), Baldrian (Ger.), Valeriana (Sp.), Valeriana (It.)

Description

Perennial herb approximately 1.5 m (5 ft) high, native to Europe and Asia. Valerian grows wild on roadsides and in thickets. The plant has short rhizomes, fibrous roots, erect stalk, opposite pinnate leaves, cymose hermaphrodite flowers (March–April) with a pale-pink corolla.

Parts of plant used

Rhizomes and roots (harvested in the spring).

Physical-chemical characteristics

Essential oil

Obtained by steam distillation of the partially dried roots in varying yields (0.4–0.6%). Very old roots should not be used for distillation because of the valeric acid content in the distilled product. The presence of valeric acid strongly affects the odor of the oil. Main constituents include *l*-pinene, valeric acid, terpineol, and α-, β-, γ-, and δ-valene. Reported physical-chemical constants for valerian oil are as follows:

Specific gravity at 15°C	0.953–0.990
Refractive index at 20°C	1.4861–1.5021
Optical rotation	−2°18′ to −28°40′
Acid value	7.0–45.3
Ester value	31.7–106.9

Derivatives

Fluid extract, soft aqueous extract, water-alcohol extract, dried extract, tinctures (20% in 70% ethanol and 20% in ether-ethanol mixture)

Organoleptic characteristics

Warm, balsamic, characteristic odor

Uses

The use of valerian and valerian extracts as sedatives is well known. The essential oil and derivatives find use in flavoring tobaccos, beer, and other products.

Valerian root extract (FEMA No. 3099) has been reported used in the following:[3]

non-alcoholic beverages	25 ppm
ice cream, ices, etc.	35 ppm
candy	65 ppm
baked goods	69 ppm
condiments	24 ppm

Valerian root oil (FEMA No. 3100) has been reported used in the following:[3]

non-alcoholic beverages	0.52 ppm
ice cream, ices, etc.	0.36 ppm
candy	2.6 ppm
baked goods	3.1 ppm
gelatins and puddings	0.02–1.5 ppm

Regulatory status

Valerian rhizomes and roots: FDA §121.1163

VANILLA

Botanical source

Vanilla planifolia Andr.; *V. tahitensis* J. W. Moor (F & B); *V. pompona* Schiede (F.)

Botanical family

Orchidaceae

Foreign names

Vanilla (Fr.), Vanille (Ger.), Vainilla (Sp.), Vaniglia (It.)

Description

A great variety of vanilla plants bearing the vanilla pods, or siliques, exist. Those mentioned above are the most important species. Of special value are those cultivated in Mexico, Madagascar, Java, Tahiti, the Comoro Islands, and Reunion.

The cultivation of vanilla beans is very long and laborious. This creeping plant needs suitable supports in order to grow. Fecundation of flowers is performed (November–December) by perforating the membrane that separates the pollen from the pistil. This is an exacting task requiring skilled hand labor. Natural fecundation occurs when a similar operation is carried out by birds or insects that perforate the membrane in search of food. After a few months clusters of hanging pods (siliques) are formed; these start to yellow at the lower tip in August–September. At this point the siliques are harvested and undergo special treatment that develops the aroma. The siliques are placed in straw baskets and dipped into hot water to rupture the inner cell wall. After a few months the aroma starts developing. Then the siliques are exuded by intermittent exposure to sunlight (by alternately covering and uncovering the siliques with wool blankets).

When exudation is complete, the siliques are oiled with cocoa oil to avoid chapping during drying and finally dried to a suitable residual moisture content. In the final stage of the preparation, the best quality siliques form a vanilla "brine" that crystallizes on the surface of the bean. All in all, the processing of vanilla bean takes more than a year. The most important commercial qualities are brined vanilla, bastard vanilla, and vanilla pompona.

Parts of plant used

Bean

Physical-chemical characteristics

Vanilla tincture: 20–25% in 90–95% ethanol; 10% in low strength ethanol

Absolute: The dried product and also some derivatives contain aromatic principles in addition to vanillin, glucovanillin, vanillic acid, anisic acid, and aldehyde. Vanilla oleoresin as defined by its Standard of Identity; it must be extracted according to standardized techniques, using dilute alcohol.

Organoleptic characteristics

Sweet, ethereal odor and characteristic flavor

Uses

Vanilla bean (silique) and its derivatives are of great importance in food flavoring, especially confections, ice creams, liqueurs, and baked goods. Its use is limited only by price; it is often replaced with synthetic vanillin and ethyl vanillin.

Vanilla (FEMA No. 3104) has been reported used in the following:[3]

non-alcoholic beverages	420 ppm
ice cream, ices, etc.	600 ppm
candy	490 ppm
baked goods	530 ppm
gelatins and puddings	630 ppm
icings	200–630 ppm
syrups	10 ppm
toppings	300 ppm

Vanilla extract (FEMA No. 3105) has been reported used in the following:[3]

non-alcoholic beverages	200 ppm
ice cream, ices, etc.	3,000 ppm
candy	4,000 ppm
baked goods	1,900 ppm
icings	2,000–4,800 ppm
syrups	8.5–54 ppm
toppings	2,700 ppm

Vanilla oleoresin (FEMA No. 3106) has been reported used in the following:[3]

non-alcoholic beverages	190 ppm
ice cream, ices, etc.	290 ppm
candy	210 ppm
baked goods	300 ppm
gelatins and puddings	230 ppm
condiments	200 ppm

Regulatory status

GRAS (I), (II)

VERONICA

Other names

Speedwell

Botanical source

Veronica officinalis L.

Botanical family

Scrophulariaceae

Foreign names

Véronique (Fr.), Echter Ehrenpreis (Ger.), Veronica Macho (Sp.), Veronica (It.)

Description	Perennial herb that commonly grows in the fields, thickets, and roadsides throughout Europe, Caucasus, Azores, and North America. The plant has opposite, obovate-elliptical or wedge-oblong leaves with dentate lip and blue, pinkish, purple-streaked flowers clustered in dense, panicled racemes supported by a rigid peduncle. The fruits consist of obovate-triangular, 2-celled capsules with flat, ovate seeds.
Parts of plant used	Flowering tops
Physical-chemical characteristics	
Derivatives	Infusion (6%), tincture, fluid extract, ground powder, and decoction. The main constituents include glucoside, resins, tannins, mannitol, organic acids, bitter principles, a saponin, and minute amounts of essential oil.
Organoleptic characteristics	Tonic, slightly bitter
Regulatory status	FDA §121.1163. In alcoholic beverages only

VERVAIN, EUROPEAN

Botanical source	*Verbena officinalis* L.
Botanical family	*Verbenaceae*
Foreign names	Verveine officinale (Fr.), Eigenkraut (Ger.), Yerba sacra (Sp.), Verbena (It.)
Description	Herbaceous plant commonly growing in central and southern Europe and also widespread in other continents. The plant should not be confused with *Lippia citriodora* Kunth, native to Chile and now acclimated around the Mediterranean basin, from which verbena oil is prepared. *V. officinalis* grows to 40 cm (16 in.) in height; it has spindle-shaped roots, opposite, coarsely serrate, irregularly crenate leaves, and very small purplish flowers clustering in terminal panicled spikes. *L. citriodora*, on the other hand, is a woody shrub, usually growing more than 1 m (39 in.) high. It has opposite, lanceolate leaves grouped in threes or fours. The leaves exhibit glandulose ciliate edges; the flowers are externally white and internally purplish-blue. While verbena essential oil finds use in perfumery and in flavors, *V. officinalis* L. essential oil is not produced because of the very low oil content in the plant.
Physical-chemical characteristics	
Derivatives	Infusion, fluid extracts, dried comminuted herb
Uses	The whole plant is employed for phytotherapeutic purposes. The infusion or the distillate from *L. citriodora* is generally preferred for the formulation of aromas (liqueurs). Vervain derivatives find some application in pharmacology.
Regulatory status	FDA §121.1163. In alcoholic beverages only

VETIVER

Botanical source	*Vetiveria zizanioides* Stapf.
Botanical family	*Gramineae*

Foreign names

Vetiver (Fr.), Vetiver (Ger.), Vetiver (Sp.), Vetiver (It.)

Description

Herbaceous plant having thin rhizomes and rootlets; it grows wild or cultivated in various tropical countries—southern India, Indonesia, Ceylon, Philippines, East Africa, and Central America. The fibers of the grass are woven into fragrant matting with an aromatic balsamic odor. The largest and industrially most important cultivations of vetiver are found in Reunion Island, Java, Haiti, and southern India.

Parts of plant used

Rhizomes, rootlets

Physical-chemical characteristics

Essential oil

Vetiver oil is obtained by steam distillation of washed and sun-dried rootlets and rhizomes in approximately 1.0–1.5% yields; it is a viscous, light-brown to dark-brown liquid with a characteristic sweet, earthy, woody odor that varies somewhat, depending on the source. The main constituents include vetiverol (a mixture of sesquiterpene alcohols), vetiverone (sesquiterpene ketone mixture), vetiveryl esters, and palmitic and benzoic acids. Its physical-chemical characteristics are as follows (also see reference 2):

Specific gravity at 20°/20°C	0.983–1.022[1]
Refractive index at 20°C	1.515–1.530[1]
Optical rotation at 20°C	
Haiti vetiver	+20° to +40°[1]
Bourbon vetiver	+14° to +30°[1]
Java vetiver	+17° to +46°[1]
Indian vetiver	+10° to +25°[1]
Acid value	38 min[1]
Ester value	2–35[1]
Solubility	1:3 in 80% ethanol[1]

Derivatives

Vetiver acetate, vetiver alcohol aroma. Vetiver acetate is prepared by acetylation of the isolated vetiverol or by direct acetylation of vetiver oil. The low-boiling fraction of the distilled vetiver oil can be extracted separately with low-proof alcohol to yield an alcohol aroma exhibiting a characteristic asparagus, green pea flavor.

Organoleptic characteristics

Sweet, heavy, rich, woody, earthy odor; asparagus, green pea flavor

Uses

Vetiver oil is used extensively in perfumery for its characteristic note and fixative properties. Vetiver alcohol aroma finds limited use in flavoring food substrates, mainly to reinforce the flavor of asparagus.

Regulatory status

FDA §121.1163

VIOLET

Botanical source

Viola odorata L.—sweet violet; *V. calcarata* L.—Swiss violet

Botanical family

Violaceae

Foreign names

Violette (Fr.), Veilchen (Ger.), Violeta odorosa (Sp.), Violetta, Viola Mammola (It.)

Description

Perennial herbaceous plant native to Europe; it grows wild or cultivated in Asia and North America. The plant has short oblique roots, procumbent stoloniferous stalks, ovate leaves, highly scented violet flowers (March–April), and round capsules.

Parts of plant used

Flowers and leaves; the roots are used only for the preparation of galenic products.

Physical-chemical characteristics

Derivatives

Infusion (5%), fluid extract, tincture (20% in 60% ethanol), concrete, and absolute. The concrete is prepared by petroleum ether extraction of flowers or leaves. The absolute essences are obtained by alcohol washing of the concrete. The concrete and absolute from flowers have almost disappeared from the market, because they are uneconomical. The essence from leaves finds use mainly in perfumery. An oil of experimental production only has been distilled from the concrete.

Organoleptic characteristics

Pleasant, delicate floral odor (reminiscent of violet on dilution), and slightly bitter taste

Uses

The dried product, tincture, and fluid extract are used to a limited extent in the formulation of compounded oils for liqueurs. Violet leaves absolute (FEMA No. 3110) has been reported used in the following:[3]

non-alcoholic beverages	2.3 ppm
ice cream, ices, etc.	8.4 ppm
candy	7.6 ppm
baked goods	2.0–24 ppm

Regulatory status

Sweet violet flowers: GRAS (II)
Sweet violet leaves: GRAS (II)
Swiss violet: FDA §121.1163. In alcoholic beverages only

WALNUT

Botanical source

Juglans regia L. and other *Juglans* species

Botanical family

Juglandaceae

Foreign names

Noyer commun (Fr.), Walnuss (Ger.), Nogal (Sp.), Noce (It.)

Description

Majestic tree up to 30 m (98 ft) in height, branched, with large, alternate pinnatifid leaves and staminiferous and pistilliferous flowers (April–June). The fruits have a fibrous mesocarp, woody endocarp, and fleshy, oily seeds edible when ripe (September).

Parts of plant used

Leaves, husks, and edible seeds

Physical-chemical characteristics

Essential leaf oil

The essential oil is obtained by steam distillation of leaves with yields ranging between 0.012–0.029%; it is little known and seldom used. The oil is a yellow to greenish-brown liquid exhibiting a powerful, warm, sweet odor reminiscent of tea and labdanum.[1] Main constituents include juglone, α- and β-hydrojuglone, tannin, geraniol, cineol, and methyl eugenol.

Derivatives

From leaves: decoction (5%), fluid extract, tincture (20% in 20% ethanol), and soft aqueous extract

From husks: fluid extract and petroleum ether fluid extract

Organoleptic characteristics

Bitter-tonic flavor; warm, sweet odor

Uses

The dried leaves and their derivatives, husk derivatives, together with fresh and dried nut derivatives, are employed in the formulation of liquors and special bitters. Walnut hull extract has been reported used in the following:[3]

non-alcoholic beverages	43–90 ppm
ice cream, ices, etc.	100–170 ppm
candy	130 ppm
baked goods	100–130 ppm

Regulatory status

Husks, leaves, and green nuts: FDA §121.1163

WHORTLEBERRY

Botanical source

Vaccinium myrtillus L.

Botanical family

Ericaceae

Foreign names

Myrtille (Fr.), Heidelbeere (Ger.), Gogorza (Sp.), Mirtillo nero (It.)

Description

An European species of blueberry. The shrub is approximately 40–60 cm (16–24 in.) high and grows wild in the mountain areas of Europe and Asia. The plant has erect, branched stems, long creeping rhizomes, alternate oval leaves, white-pinkish flowers, and bluish globose berries. This variety should not be confused with *V. vitio idaea*, whose leaves are used for pharmaceutical purposes (contain arbutin).

Parts of plant used

Berries and leaves

Physical-chemical characteristics

Derivatives

From berries: Fluid extract, tincture (20% in 20% alcohol), concentrated (6–8 fold) juice

From leaves: Infusion (3%), dried aqueous extract

Organoleptic characteristics

Sweet, aromatic, sour, astringent flavor

Uses

The derivatives are used for medicinal purposes. The berries are used in the preparation of marmalades and jellies or consumed as is.

WINTERGREEN

Botanical source

Gaultheria procumbens L.

Botanical family

Ericaceae

Foreign names

Gaultherie (Fr.), Wintergrün (Ger.), Gaulteria (Sp.), Gaulteria (It.)

Description

Evergreen shrub with slender, creeping stems, assurgent, flowering branches with leaves clustered at the top, white, bell-shaped flowers blossoming in July–August, followed by red berries (checkerberries). The plant grows extensively in the woods of Canada and the United States (Pennsylvania).

Parts of plant used

The leaves harvested between June and September

Physical-chemical characteristics

Essential oil

Wintergreen essential oil is water-steam distilled from leaves charged into the still and allowed to macerate for several hours to hydrolyze the gaultherin glucoside (methyl salicylate + glucose). Distillation lasts from 5–6 hours and yields approximately 0.7% essential oil. The oil is often adulterated by intentionally co-distilling sweet birch (*Betula lenta*) bark. The oil is a pale-yellow to pinkish liquid with a strong, sweet, aromatic odor reminiscent of methyl salicylate, its main constituent. The physical-chemical characteristics follow:

Specific gravity at 15°C	1.180–1.193
Optical rotation	−0°25′ to −1°30′
Refractive index at 20°C	1.535–1.536
Ester value	354–356

In the last few years wintergreen essential oil has been replaced in most applications by methyl salicylate.

Organoleptic characteristics

Strong, aromatic odor and flavor similar to methyl salicylate

Uses

The oil, sometimes used in small amounts in fern and cypress type perfumes and in toothpaste, is used mainly to flavor pastry and candies. Wintergreen extract (FEMA No. 3112) has been reported used in the following:[3]

non-alcoholic beverages	10 ppm
candy	900–5,000 ppm

Wintergreen oil (FEMA No. 3113) has been reported used in the following:[3]

non-alcoholic beverages	56 ppm
ice cream, ices, etc.	44 ppm
candy	260 ppm
baked goods	1,500 ppm
chewing gum	3,900 ppm

Regulatory status

Status not fully defined by FDA

WOODRUFF, SWEET

Botanical name

Asperula odorata L.

Botanical family

Rubiaceae

Foreign names

Asperule odorante (Fr.), Waldmeister (Ger.), Asperula (Sp.), Asperula (It.)

Description

A small, slightly sweet-scented perennial herb widespread throughout Europe and the Near East. It has very thin rhizomes, both fertile and sterile stalks, and spear-like oblong leaves arranged about the central axis of the stalk (verticil) as spokes in a wheel. The verticils are spaced along the length of the stalk. The plant has terminal flowers (usually 3) with white petals and blooms from June to July. The dried herb is commercially available throughout Europe.

Parts of plant used

The whole plant

Physical-chemical characteristics

The plant does not yield an essential oil upon steam distillation. While the fresh plant is nearly odorless, it exhibits a coumarin-like fragrance when dried.

Derivatives

Tincture (10% in 65% ethanol), infusion (5%); absolutes and concretes are rarely seen as articles of commerce.

Organoleptic characteristics	Heavy, sweet, tobacco-like flavor and odor
Uses	The tincture is used in the formulation of special bitters as a flavor modifier. It is also used to add flavor to special sweet wines and in a cordial with gastric action manufactured in Germany.
Regulatory status	FDA §121.1163. In alcoholic beverages only

YARROW

Other names	Milfoil; achillea
Botanical source	*Achillea millefolium* L.
Botanical family	*Compositae*
Foreign names	Millefeuilles (Fr.), Gemeine Schafgarbe (Ger.), Abrofia (Sp.), Achillea millefoglie (It.)
Description	Perennial herb having stalks 20–80 cm (8–31 in.) high with branched rhizomes and soft alternate leaves. The leaves are deep green, while the flowers vary from white to pink in terminal corymbs about 3–6 mm long and 1.5–3 mm wide. The plant blooms from June to September.
Parts of plant used	Leaves and flowering tops
Physical-chemical characteristics	
Essential oil	Obtained in approximately 0.2% yields by steam distillation of the fresh plant (preferably the flowers). It exhibits an intense blue color together with an aromatic camphor-like odor. Main constituents include *l*-α-pinene, *d*-α-pinene, *l*-limonene, *l*-borneol, camphor, bornyl acetate, cineol, caryophyllene, azulene, and various acids (formic, acetic, valeric, salicylic). Specific gravity at 15°C 0.900–0.927[1] Optical rotation −1° to −3°[1]
Derivatives	Essential oil, fluid extract, soft extract, tincture (10% in 65–70% alcohol), infusion (5%), and decoction (8%).
Organoleptic characteristics	Leaves, flowers, and their derivatives have an astringent, bitter tonic flavor
Uses	Yarrow, especially as the dried herb, is employed by the wine and liqueur industries in the formulation of bitters and vermouths to impart bitter-aromatic notes. Yarrow herb has been reported used in the following:[3] non-alcoholic beverages 29 ppm alcoholic beverages 5–40 ppm
Regulatory status	FDA §121.1163. In beverages only; finished beverage must be thujone-free[4]

YERBA SANTA

Other names	Bear's weed; mountain balm; eriodictyon
Botanical source	*Eriodictyon californicum* (Hook. & Arn.) Torr.

Botanical family	*Hydrophyllaceae*
Foreign names	Herbe sainte (Fr.), Eriodicton (Ger.), Eriodicto (Sp.), Erba santa (It.)
Description	Herbaceous plants growing mainly in California, Mexico, and Brazil.
Parts of plant used	Leaves
Physical-chemical characteristics Derivatives	Fluid extract, tincture (20%) prepared from the fluid extract, and syrup. Main constituents include flavone derivatives, eriodictyol, eriodictyonone, tannins, resin, and a small amount of volatile oil.
Organoleptic characteristics	Tonic, aromatic
Uses	Yerba santa finds an important use in reducing the very bitter flavor of alkaloid bases present in drugs. The derivatives are used mainly as flavor modifiers in liqueurs and for flavoring pastry, baked goods, and candies. Yerba santa fluid extract (FEMA No. 3118) has been reported used in the following:[3] non-alcoholic beverages 25 ppm ice cream, ices, etc. 200 ppm candy 400 ppm baked goods 400 ppm
Regulatory status	FDA §121.1163

YLANG-YLANG

Botanical source	*Cananga odorata* Hook f. & Thoms. *forma genuina*
Botanical family	*Anonaceae*
Foreign names	Ylang-ylang (Fr.), Ylang-ylang (Ger.), Ylang-ylang (Sp.), Ylang-ylang (It.)
Description	Large tree native to the Philippines, also widespread throughout the Pacific Islands, Madagascar, Reunion, and Nossi-Be Islands; it grows wild or is extensively cultivated in the above-mentioned areas. The botanical distinction between cananga and ylang-ylang is discussed in the cananga monograph. The wild tree may reach up to 20 m (66 ft) in height. For ease of harvesting the flowers, the cultivated plant is pruned at intervals to prevent growth above 4 m (7 ft). The plant has large, hairy, green fruits changing to yellow when ripe.
Parts of plant used	Flowers
Physical-chemical characteristics Essential oil	The flowers are steam distilled a few hours after an early morning harvesting. Distillation may last up to 24 hours, yielding approximately 1% essential oil. The various fractions withdrawn have different commercial values and physical-chemical characteristics. Ylang-ylang essential oil extra consists of the volatile oil steam distilled in the first few hours. The oil represents approximately 35–40% of the total distillation

yield and is considered the most valuable product. This oil is a yellow liquid with a suave, floral odor. Its physical-chemical constants are as follows (see also reference 2):

Specific gravity at 20°C	0.946–0.982[1]
Refractive index at 20°C	1.4980–1.5090[1]
Optical rotation at 20°C	−25° to −40°[1]
Acid value	2.8 max[1]
Ester value	130–182[1]
Solubility	1:0.5 in 90% ethanol[2]

Other grades of oil—first, second, and third quality—are produced by continuing the steam distillation and withdrawing the various fractions by specific gravity. These oils are pale-yellow liquids with a floral odor. Their physical-chemical constants follow (see also reference 2):

	I Quality[1]	II Quality[1]	III Quality
Specific gravity at 20°C	0.928–0.949	0.918–0.933	0.906–0.923[1]
Refractive index at 20°C	1.5000–1.5090	1.5057–1.5117	1.5070–1.5150[1]
Optical rotation at 20°C	−33° to −60°	−40° to −68°	−35° to −67°[1]
Acid value	2.8 max	2.8 max	2.8 max[1]
Ester value	89–130	56–89	34–56[1]
Solubility (in 90% ethanol)	1:0.5	1:0.5 (occasionally)	1:0.5 (sometimes)[2]

A complete ylang-ylang oil consists of the total volatile fractions obtained by steam distillation of the flowers. This oil is a yellow to brownish liquid with a floral odor. Its physical-chemical constants follow:

Specific gravity at 25°/25°C	0.924–0.935[2]
Refractive index at 20°C	1.5050–1.5100[2]
Optical rotation	−45° to −60°[2]
Saponification value	80–100[2]
Solubility	1:0.5 in 90% ethanol[2]

All qualities contain the following components in varying ratios: *d*-α-pinene, *l*-linalool, geraniol, benzyl alcohol and esters, *p*-cresol, *p*-cresyl acetate, eugenol, methyl benzoate, methyl salicilate, and several acids (formic, valeric, acetic, benzoic, salicyclic).

Derivatives

Concrete and absolute. The concrete is obtained by extraction of flowers with petroleum ether or benzene in approximately 1% and 2.5–3.6% yields, respectively. It is usually a liquid with an intense floral, sweet odor. The absolute is obtained by alcoholic extraction of the concrete in approximately 80% yields.

Organoleptic characteristics

Intense, floral, sweet odor; bitter aromatic taste

Uses

The essential oils, the concrete, and the absolute find extensive use in perfumery as modifiers and also as fixatives to impart floral notes. On some occasions the essential oil is used in flavors (candy, chewing gum, baked goods) but only as a modifier to impart floral notes. Ylang-ylang oil (FEMA No. 3119) has been reported used in the following:[3]

non-alcoholic beverages	0.95 ppm
ice cream, ices, etc.	1.4 ppm
candy	2.9 ppm
baked goods	2.9 ppm
chewing gum	18–25 ppm
icing	0.75 ppm

Regulatory status

GRAS (II)

YUCCA

Other names	Joshua tree
Botanical source	*Yucca brevifolia* Engelm
Botanical family	*Liliaceae*
Description	A genus of American plants, sometimes arborescent, having long, pointed, often rigid, fibrous-margined leaves on a woody caudex, and bearing a large panicle of white blossoms (yucca cactus).
Uses	It is used to flavor root beer. *Y. brevifolia* (FEMA No. 3120) has been reported used in the following:[3] non-alcoholic beverages 120 ppm ice cream, ices, etc. 20 ppm
Regulatory status	FDA §121.1163

YUCCA, MOHAVE

Botanical source	*Yucca schidigera* Roezl ex Ortigies (*Y. mohakensis* Sarg.)
Uses	A foaming agent is made from the plant; it is also used to flavor root beer. Mohave yucca extract (FEMA No. 3121) has been reported used in non-alcoholic beverages, 150 ppm.[3]
Regulatory status	FDA §121.1163

ZEDOARY

Botanical source	*Curcuma zedoaria* Rosc.
Botanical family	*Zingiberaceae*
Foreign names	Zedoarie (Fr.), Zitwer (Ger.), Zedoario (Sp.), Zedoaria (It.)
Description	Perennial herb native to India; it is cultivated for edible purposes (rhizomes, leaves). The plant has thick, tuber-like rhizomes, sterile and flower-bearing branches, very large (edible) leaves, flowers with a white calyx, and trigonous capsules containing arillate seeds.
Parts of plant used	Rhizomes (commercially available in disks or long slices)
Physical-chemical characteristics	
Essential oil	Obtained by steam distillation of the rhizomes in approximately 1% yields. The oil is a viscous, dark-green to greenish-amber liquid with a camphoraceous odor reminiscent of ginger. Main constituents include cineol, sesquiterpenes (ca 78%), *d*-α-pinene, and camphor.

Specific gravity at 20°C	0.982–1.012
Optical rotation	+8° to +17°
Refractive index at 20°C	1.5023–1.5088
Acid value	0.3–2.4
Ester value	16–22.4
Ester value (after acetylation)	56–73.4
Solubility	1:0.5–2 in 80% ethanol

Organoleptic characteristics	Characteristic warm, camphoraceous odor; warm, spicy, slightly bitter taste
Uses	The dried product is used as a spice and in the formulation of liqueurs. The tincture and the fluid extract are used in the formulation of compounded oils for liqueurs and bitters. The essential oil is produced only in limited amounts and has few practical applications. Zedoary (FEMA No. 3122) has been reported used in non-alcoholic beverages, 7.5–2,000 ppm.[3] Zedoary bark extract (FEMA No. 3123) has been used in the manufacture of bitters.
Regulatory status	GRAS (I), (II)

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