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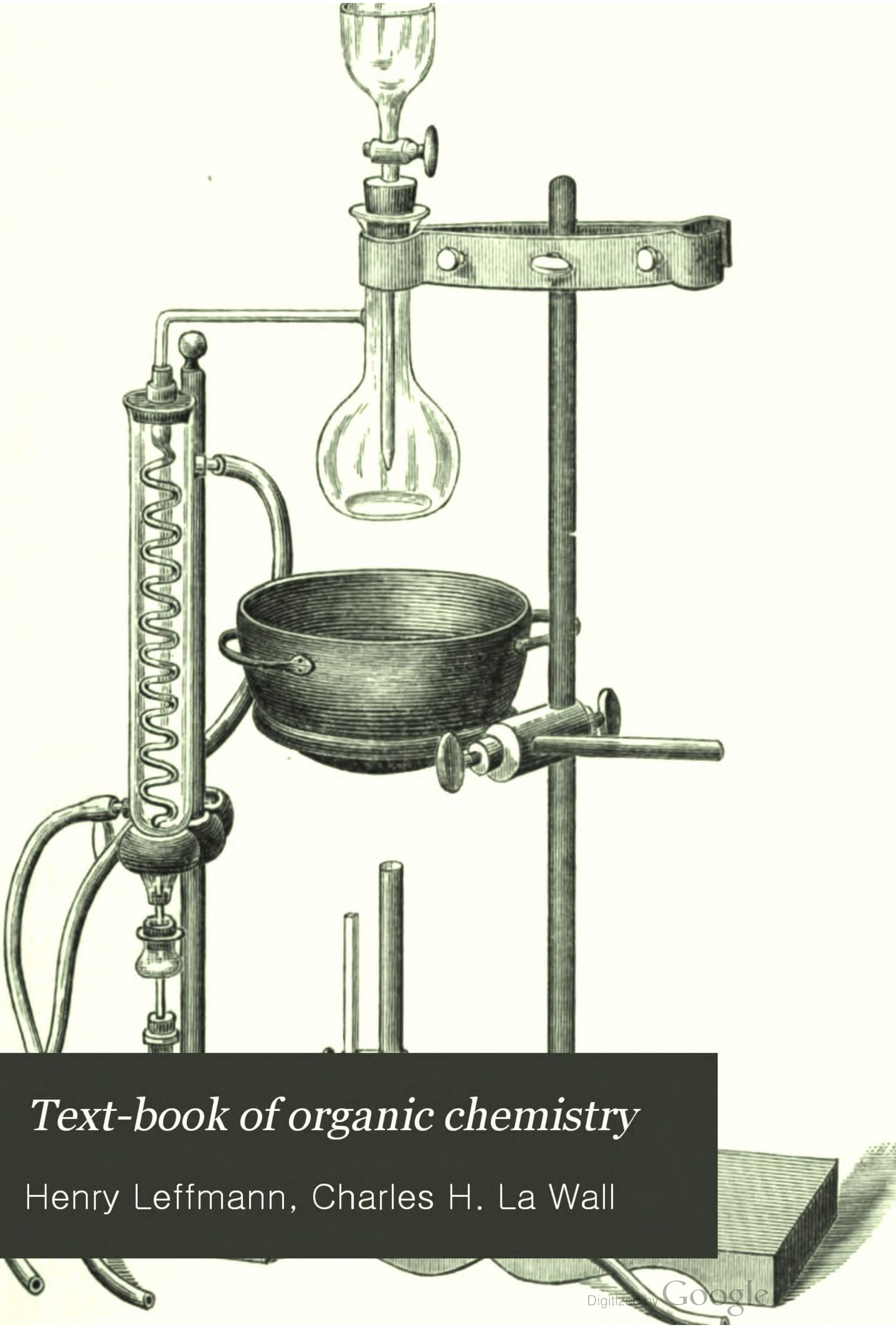
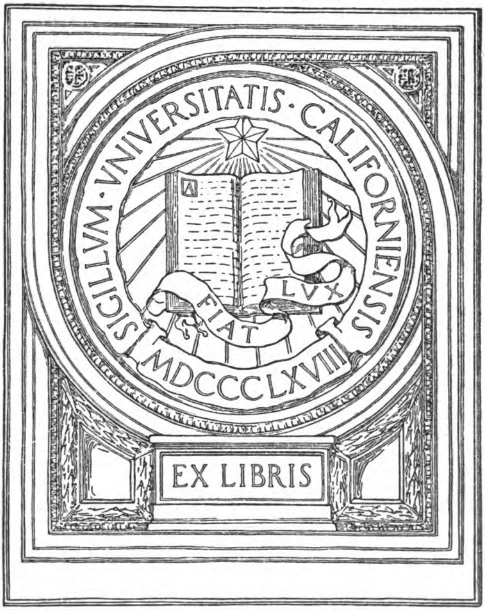


# Text-book of organic chemistry

Henry Leffmann, Charles H. La Wall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# TEXT-BOOK

OF

# ORGANIC CHEMISTRY

BY

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AND

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WITH ILLUSTRATIONS AND EXPERIMENTS

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# PREFACE.

This book is offered as an aid to the study of organic chemistry in connection with general and professional college courses. The difficulty in the preparation of such a work is to determine what to exclude. We have endeavored to give consideration to the more important features of the science, especially in its applications. Polarisation of light has been treated in some detail on account of the importance of it in the study of molecular structure.

Some descriptive topics that are often passed over very briefly have been given considerable space. Among these are to be noted the sections on Enzyms, Purins, Alkaloids and Proteids.

The experiments have been selected with a view of illustrating all the important types of organic compounds and reactions, and at the same time avoiding danger to the student and tediousness and complexity of manipulation.

All temperatures are centigrade.

119 South Fourth St., Philadelphia,
October, 1904.

H. L.
C. H. L.

# CONTENTS.

# ORGANIC CHEMISTRY.

## PRINCIPLES.

ORGANIC CHEMISTRY is primarily the chemistry of substances produced by living tissues. These are very numerous, and other bodies can be obtained from them, which are analogous to the primary organic bodies, and are included in the same groups. Transformations and modifications may be carried so far as to produce substances which are clearly inorganic, consequently it is not possible to establish a distinct boundary between inorganic and organic chemistry. It was formerly supposed that organic bodies are distinct in that the original compounds could only be produced by vital action, but, in 1828, Wöhler succeeded in producing urea by heating ammonium cyanate, and thus set aside the supposed distinction. Since that time many similar results have been obtained, and it is now generally believed that the chemical affinities concerned in the formation of compounds by living tissues are the same as those operating in inorganic bodies. It must, however, not be supposed that the chemistry of vital action has been solved, or even brought into entire analogy with inorganic chemistry. Many points yet remain to be explained.

A characteristic of the products of vital action is that they all contain carbon, hence it has been proposed to substitute for organic chemistry the title "Chemistry of the Carbon Compounds." No special advantage is gained by this. Moreover, several compounds containing silicon in combinations analogous to natural organic bodies have been obtained, so that the later title is equally insufficient.

Carbon, hydrogen, oxygen and nitrogen are most abundant in organic compounds; sulphur and phosphorus are present in the complex forms that are found in tissues of higher function. Iron is found in several, among which are the coloring matters of blood and green vegetable tissue. Copper is also noted in a few cases. By laboratory methods many substances have been obtained into which other elements, *e. g.*, chlorine, bromine, iodine, mercury and arsenic, have been introduced. These are often analogous in many ways to natural organic bodies, but not equivalent to them in biologic function.

The following list of bodies from natural sources will illustrate the degrees of complexity exhibited by organic compounds:

| | |
|---|---|
| $C_{10}H_{16}$ | Terpene. |
| $C_{12}H_{22}O_{11}$ | Cane sugar. |
| $C_{10}H_{14}N_2$ | Nicotine (from tobacco). |
| $C_{17}H_{19}NO_3$ | Morphine (from opium). |
| $C_2H_7NSO_3$ | Taurin (from bile). |
| $C_3H_9PO_6$ | Glycerophosphoric acid (from brain tissue). |
| $C_{32}H_{32}FeN_4O_6$ | Hematin (from blood corpuscles). |

**Proximate and Ultimate Composition.**—The tissues of plants and animals, or the immediate products of their transformations, are generally mixtures of several independent substances. Butter is a mixture of four or five fats common rosin contains two or sometimes three distinct bodies; opium and Peruvian bark are still more complicated, and brain and muscle structures are so complex that as yet complete analyses have not been made of them. The substances which thus exist naturally in a state of mixture are called *proximate principles;* the separation and identification of them is called *proximate analysis*, and such of them as give characteristic qualities to the articles in which they occur are often called *active* or *essential principles;* atropine, for instance, is the active principle of belladonna, for although many different bodies are contained in belladonna, atropine is the one upon which its physiological activity mainly depends. The *ultimate constituents* of any substance are the elements, *e. g.*, carbon and hydrogen, that it contains; the detection of these elements and determination of their amount is *ultimate analysis*. This is simple in principle but in practical operation involves much care and skill. The following is an outline of the more important procedures:

Carbon and hydrogen are determined by burning a weighed portion of the substance in a current of oxygen or in contact with some oxidising agent. The carbon is converted into carbon dioxide, the hydrogen into water. These are absorbed by suitable materials in separate vessels and the increase in weight of these will permit of calculation of the carbon and hydrogen in the substance. If oxygen is the only other element present it is determined by difference. Nitrogen is determined either by measuring it free, or by conversion into amine (ammonia), $NH_3$. A method now much used is to heat the substance with strong sulphuric acid with or without special oxidising agents, by which the nitrogen is converted into ammonium sulphate. This is termed the Kjeldahl method. Chlorine, iodine, and other unusual elements require special methods that need not be described here. Sulphur is usually converted into sulphate by oxidation.

Nitrogen may be detected in many substances by conversion into cyanide. For experimental illustration of this, see under "Cyanogen."

**Physico-chemical data (constants)** are of value in identifying organic bodies, ascertaining purity and elucidating formulas. The following are the more widely applicable methods:

*Specific Gravity.*—Specific gravities of liquids and solids are generally expressed by comparison with water. Confusion and inconvenience have arisen from the fact that results have been referred to water at different temperatures as unity. The temperatures of observation and comparison should always be expressed. $\frac{100^\circ}{15.5^\circ}$ indicates a determination at 100° and comparison with water at 15.5° as unity. It is best to compare the substance and the standard at the same temperature.

*Pyknometer or Specific-gravity Bottle.*—This is a generally applicable means of determining specific gravity, and is capable of furnishing good results. It is a bottle—with a perforated stopper—adjusted to hold a certain weight of water at a standard temperature, usually 15.5°. Bottles as sold are often inaccurate. The weight of water that a bottle holds should be carefully determined.

*Sprengel Tube.*—This is a form of pyknometer with which a high degree of accuracy is attainable; it is especially suitable for determinations at the boiling-point of water. It consists essentially of a thin glass U-tube terminating in two capillary ends bent at right angles and each provided with a ground cap. One of these capillary tubes must have a smaller caliber than the other—not larger than 0.25 mm. The larger tube should bear a mark at *m*. The tube is filled by immersing *b* in the liquid under examination, connecting the smaller end with a large glass bulb, and applying suction to the latter by means of a rubber tube. If now the rubber tube be closed, the glass tube will fill automatically. It is placed in water, the ends being allowed to project, and the water is brought to the proper temperature. A conical flask may be used to contain the water, the ends of the Sprengel tube being supported by the neck. The mouth of the flask should be loosely covered. As the liquid expands it will drop from the larger orifice. When this ceases, the liquid is adjusted to the mark at *m*. If beyond the point, a little may be extracted by means of a roll of paper. The tube is then taken out of the bath, the caps adjusted, the whole thoroughly dried, allowed to cool, and weighed. The same operation having been performed with dis-

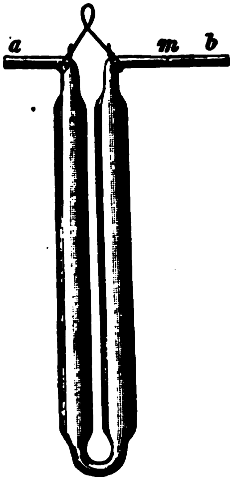


FIG. 1.

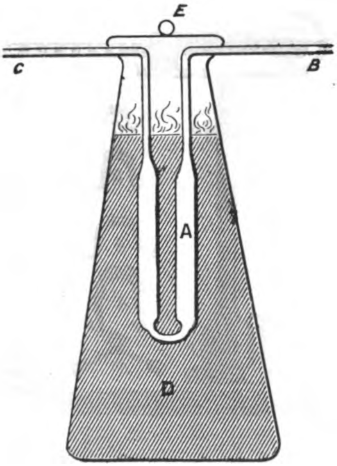


FIG. 2.

tilled water, the calculation of the specific gravity is made as usual.

*Westphal Balance.*—This affords a convenient means of determining specific gravity. It consists of a delicate steelyard provided with a counterpoised plummet. The latter, being immersed in the liquid, the equilibrium is restored by means of weights or riders, the value of which is directly expressed in figures for the specific gravity without calculation.

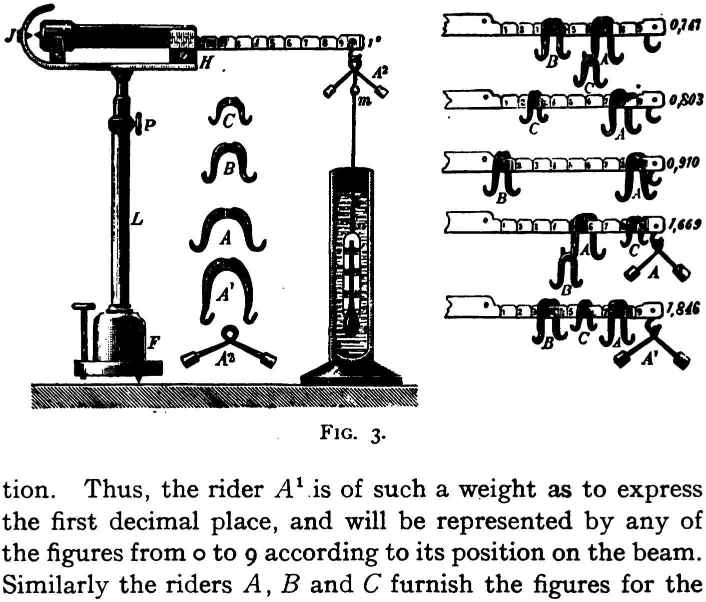


FIG. 3.

Thus, the rider $A^1$ is of such a weight as to express the first decimal place, and will be represented by any of the figures from 0 to 9 according to its position on the beam. Similarly the riders $A$, $B$ and $C$ furnish the figures for the second, third and fourth decimal places respectively. The weight $A^2$ is used in the case of liquids heavier than water.

The ordinary form of Westphal balance is untrustworthy, but good instruments are made by some European manufacturers.

The principle of the hydrostatic balance may be applied by using a plummet (that sold with the Westphal balance will serve) with the ordinary analytic balance. Testtubes weighted with mercury and sealed in the flame may also be used. The plummet is suspended to the hook of the balance by means of a fine platinum wire. The specific gravity of any liquid may be determined by noting the loss of weight of the plummet when immersed in the liquid and dividing this by the loss in pure water.

*Hydrometers* are much used for the determination of the specific gravity of liquids, but the indications are less reliable than by the foregoing methods. Sensitive hydrometers with slender stems, and accurately graduated, are now obtainable. These are capable of furnishing good results. Care should be taken to make the reading at the top, center or bottom of the meniscus according to the method used in the graduation of the instrument. Instruments intended for use with opaque liquids should be graduated to be read at the top of the meniscus.

The actual specific gravity of any substance is the ratio of its density at a given temperature to that of water *at the same temperature*. Statements made upon any other basis than this may be converted into actual specific gravity by calculation from the table of density of water. Thus, a determination of specific gravity of 0.8000 at $\frac{100^\circ}{15^\circ}$ may be converted into actual specific gravity ($\frac{100^\circ}{100^\circ}$) as follows:

Density of water at 15° = 0.99916
" " 100° = 0.95866

$$\frac{100^\circ}{15^\circ} \qquad \frac{100^\circ}{100^\circ}$$

Therefore, 95866 : 0.99916 : : 0.8000 : 0.8337 (actual specific gravity at 100°).

*Melting and Solidifying Points.*—The determination of these is often difficult. Many substances, especially fats, assume conditions exhibiting abnormal melting-points, and also frequently solidify at a temperature very different from that at which they melt. If, in the preparation of any substance for determining its melting-point, it is necessary to make a previous fusion, the mass should be allowed to rest not less than twenty-four hours after solidification before making the experiment. Chemists disagree as to whether the melting-point should be considered to be that at which the substance begins to be liquid or that at which the liquid is perfectly clear. Ordinary thermometers are frequently inaccurate, the error amounting to a degree or more. No observations in which precision is required should be made with unverified instruments.

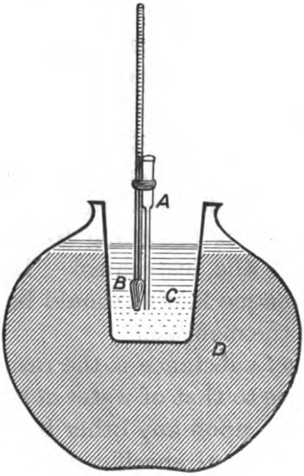


FIG. 4.

The following method for determining melting-points is suitable for many technical purposes. By substituting strong brine or glycerol for the water in the bath observations may be made at temperatures beyond the limits of 0° and 100°.

The substance is heated to a temperature slightly above its fusing-point, drawn into a very narrow glass tube, and allowed to solidify for not less than twenty-four hours. The tube, open at both ends, is attached by a wire or rubber ring to a thermometer so that the part containing the substance is close to the bulb. The apparatus, immersed in water, is heated at a rate not exceeding 0.5° per minute until fusion takes place, when the temperature is noted. The temperature is allowed to fall and the point at which the substance becomes solid is also observed. To insure uniform and gradual heating, it is necessary to immerse the vessel containing the thermometer and tube in another vessel filled with water (Fig. 4).

*Boiling-point.*—For the determination of boiling-point the apparatus shown in Fig. 5 is convenient. The thermometer is inclosed in an outer tube, so that the portion of the scale to which the mercury rises is immersed in the vapor. If this is not done, a correction must be applied for the error produced by the cooling of the thermometer tube. The bulb of the thermometer does not reach into the liquid. A few fragments of pumice-stone or broken clay pipestems will prevent bumping. The exit-tube at the lower end of the wide tube connects with a condenser. The barometric pressure must always be noted and allowance made for the variation from the standard pressure, 760 mm.

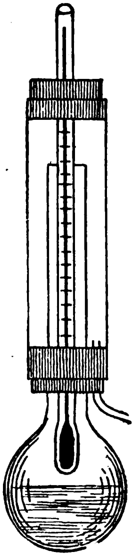


FIG. 5.

*Vapor Density.*—This is the density of the substance in a state of gas as compared with some standard (generally hydrogen) at the same temperature and pressure. The determination is largely used in organic chemistry, and several methods of procedure have been devised. The following, due to Victor Meyer, is the simplest:

Fig. 6 shows the apparatus. A narrow glass tube *BA* is expanded at the closed end and arranged at the open end to receive a caoutchouc stopper. *C* is a short delivery tube which passes under the collecting tube in the pneumatic trough. The outer cylinder *F*, containing the tube *BA*, is filled with some liquid of known boiling point higher than that of the substance to be tested. A portion of the substance to be tested is weighed into a small tube and dropped into the inner tube. It vaporises and drives out an equal volume of air which is collected in the tube *E*. By this means the volume of vapor produced by a given weight of the body is determined, and by calculation with necessary corrections the vapor density is obtained.

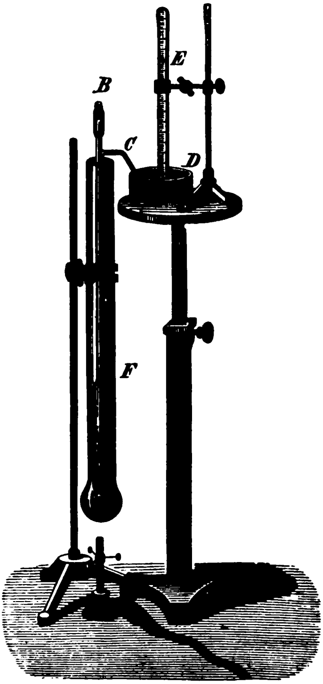


FIG. 6.

*Freezing Point of Solution, Cryoscopy.*—This method, originally applied for determination of molecular weights, is also used as a clinical test, observations being made especially with urine and blood. The depression of the freezing point of these is regarded as of considerable value in diagnosis. In this clinical application calculations of molecular weight are not made, the data being interpreted by comparison with the average of normal fluids.

An apparatus shown in Fig. 7 is used. The inner tube *A*, provided with a thermometer, stirrer and a side tube, contains the solution to be tested. It is fastened by a cork in the wider tube *B* and the whole is supported in the vessel *C* (about 2500 c.c. capacity) by means of a metallic cover. In *C* is the freezing mixture which can be stirred by means of the rod shown. By this arrangement the solution is separated from the cooling mixture by air and the cooling is uniform and gradual. For accurate determination the thermometer should read at least to 0.02°. It is not necessary to observe actual temperatures, but merely the degree of depression as compared with the freezing point of the pure solvent.

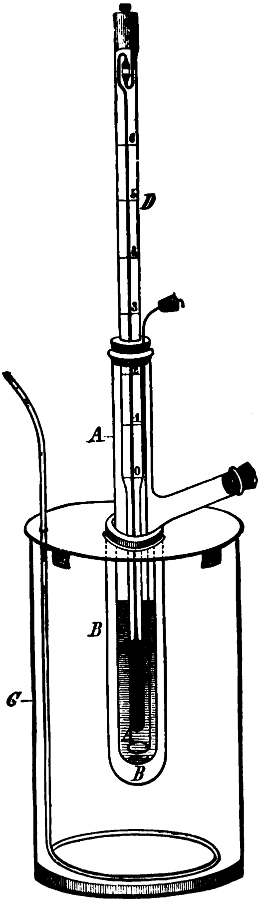


FIG. 7.

*Polarimetry.*—Polarimeters are instruments used to measure the extent and direction of the rotation of the plane of polarised light. They consist essentially of a Nicol's prism as polariser, a tube carrying the substance to be tested, and a second Nicol's prism or analyser, by which the extent of rotation is measured. In all forms some condition of the field of vision is fixed upon as the zero point, and the rotation of the analyser or other manipulation necessary to restore this standard field affords the measurement of the rotation caused by the interposed substance. Several types of instrument have been devised, of which two are most important. In one form, devised by Soleil, white light is used and a colored field, known as the transition tint, is taken as the zero point. In the other type white light or monochromatic (yellow) light is used and the zero point determined by equalising the brightness of the field. Instruments of the first form are unsatisfactory by reason of the difference in susceptibility in the eyes of different persons to color-contrasts. The instruments of the second type, commonly designated shadow instruments (more correctly "penumbral") are now more generally employed; they have been brought of late years to a high degree of accuracy and convenience.

In the Laurent apparatus, shown in Fig. 8, the monochromatic light passes through the collimating lens A and is polarised by the Nicol's prism B, which is so placed that it may be moved, on its axis, over a small arc by means of the lever C and clamped at any point; by this the brightness of the field may be varied and the sensitiveness of the instrument increased or diminished as may be needed. The polarised beam then passes through a quartz plate of even thickness, cut exactly parallel to the optic axis, and placed so that it covers a semicircle of the field. At the other end of the apparatus is the analysing prism E and the eyepiece F fixed to a graduated disk. This combination can be rotated upon its axis in a complete circle. Attached arms carry view-lenses for reading the angle of rotation, and the instrument is set at zero by an independent adjustment by which the analysing prism is rotated without disturbing the position of the graduated disk. Verniers are provided for close measurement. The monochromatic light must be obtained from a sodium flame, since the thickness of the quartz plate is adjusted to these rays.

In use, the tube is filled with water, the instrument directed to the source of light, and the adjusting milled head turned until the disk is set at zero. The two portions of the field should now appear equally illuminated. If this is not the case, the position of the analyser must be altered by means of the independent adjustment, the index remaining undisturbed at the zero point.

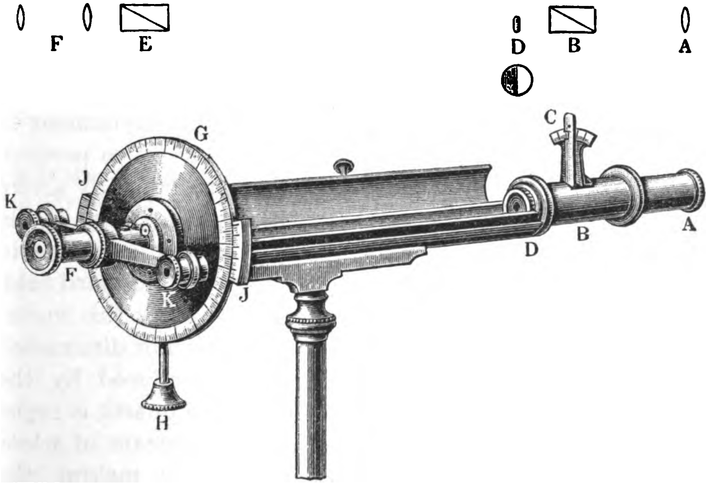


FIG. 8.

The tube is filled with the liquid to be tested and again placed in the instrument. If optically active, the plane of the polarised light will be rotated and one-half of the field of observation will appear darker. The extent of rotation, which will depend upon the nature of the substance and its amount, is measured by rotating the analyser to the right or left, as the case may be, until the halves of the field become equally illuminated.

This form of instrument can be employed to measure the rotatory power of all classes of substances, but other forms give accurate indications only with substances which have the same dispersive power as quartz, unless monochromatic light be used. In the Schmidt and Hänsch penumbral instrument the division of the field is obtained by a special construction of the polarising prism and the restoration is accomplished by the adjustment of compensating quartz-wedges constructed so as to produce in the zero position no rotation. When an optically active substance is interposed in the path of the ray, one of the quartz-wedges must be moved to an extent sufficient to overcome this rotation in order to restore the standard field. The effect is dependent upon the fact that by this movement the thickness of the quartz is increased or diminished until it compensates for the rotation produced by the solution. The extent of movement of the quartz is registered upon a linear scale, which is read by means of a lens and vernier. White light is employed in making the observations. A form of the Laurent instrument, with quartz-wedge compensation, and employing white light, is made. An instrument has been devised in which the field is divided vertically into three zones, the central one being a broad band. Duplicate Nicol prisms are so arranged that the lateral zones agree in tint, thus making stronger contrast with the central zone.

*Specific Rotatory Power.*—The specific rotatory power of a substance is the amount of rotation, in angular degrees, produced by a solution containing 1 gram of the substance in 1 c.c. examined in a column one decimeter long. It is usually represented by the symbol $[\alpha]$. To indicate the light employed in the observation, $[\alpha]_D$ or $[\alpha]_j$ is used. D stands for light of wave length corresponding to the D line of the solar spectrum (sodium flame) and j (*jaune*) for the transition tint, which in the case of sugar solutions furnishes results corresponding to the "mean yellow ray." It is usual also to indicate in the same symbol the temperature of observation; thus, $[\alpha]^{20}_D$.

Under ordinary methods of observation the specific rotatory power is represented by the following formula:

$$[\alpha]_D = \frac{100\,a}{cl}\text{; in which}$$

$[\alpha]_D$ is the specific rotatory power for the light of the sodium flame,
$a$ is the angular rotation observed,
$c$ is the concentration expressed in grams per 100 c.c. of liquid,
$l$ is the length of the tube in decimeters.

## DERIVATIVES AND SYNTHETIC COMPOUNDS.

The list of substances designated organic is increased by transformation of natural compounds and by formation of compounds from simpler bodies or elements. The latter method is called "synthesis."

**Transformations.**—Many methods are known. The following are of frequent use:

HEAT.—Many organic bodies melt at a moderate heat and at a higher point volatilise unchanged. The effect is usually termed distillation if the substance is a liquid, and sublimation if a solid. Some substances can be melted but not volatilised except by decomposition; a few pass apparently directly from the solid to the gaseous condition. When a high heat is applied many organic bodies undergo irregular decomposition by which a mixture of new compounds is obtained, none of the original body distilling. This is termed "*destructive distillation.*" It is applied largely to wood and natural bituminous substances (coal and shale), and is the source of many valuable compounds.

Destructive distillation may be illustrated by heating a few pieces of wood or a fragment of soft coal in a small testtube. Combustible vapors are given off and tar is deposited on the cooler part of the tube. If a few fragments of bone or glue be heated, offensive vapors will be emitted, due principally to the nitrogen compounds present.

The extent of decomposition and the substances formed in destructive distillation being dependent on several conditions, no general reaction can be given. In a few instances the action is definite. When pyrotartaric acid is heated for some time above 200°, it decomposes as follows:

$$\overset{\text{Pyrotartaric acid}}{C_5H_8O_4} = \overset{\text{Butyric acid}}{C_4H_8O_2} + \overset{\text{Carbon dioxide.}}{CO_2}$$

Oxygen.—Most organic bodies when exposed to the action of oxygen at high temperature burn, the carbon forming carbon dioxide and the hydrogen forming water. Nitrogen may be liberated in the free state or in the form of hydrogen compounds. Sulphur and phosphorus are oxidised. At low temperatures, free oxygen acts on but few substances, but by the use of oxidising agents different effects may be obtained according to the conditions of the action. Oxygen may be added to the molecule, hydrogen may be removed without addition of oxygen, or oxygen may be substituted for hydrogen in the proportion of O for $H_2$. The following reactions illustrate these actions:

$$\overset{\text{Alcohol}}{C_2H_6O + O} = \overset{\text{Aldehyde.}}{C_2H_4O + H_2O}$$

$$\overset{\text{Aldehyde}}{C_2H_4O + O} = \overset{\text{Acetic acid.}}{C_2H_4O_2}$$

$$\overset{\text{Alcohol}}{C_2H_6O + O_2} = \overset{\text{Acetic Acid.}}{C_2H_4O_2 + H_2O}$$

Whether aldehyde or acetic acid is formed in one reaction from alcohol, depends on the energy of the oxidising agent.

So-called Natural Changes.—The principal of these are *Fermentation*, *Putrefaction* and *Decay*.

Fermentation and Putrefaction, are processes by which organic bodies are converted into new substances simpler in composition. They are dependent on the action of minute organisms and enzyms. Substances that prevent these actions are called *antizymotics*.

Some important forms of fermentation are:

1. The Vinous, producing alcohol, $C_2H_6O$, and carbon dioxide, $CO_2$.
2. The Acetous, producing chiefly acetic acid, $C_2H_4O_2$.
3. The Lactic, producing chiefly lactic acid, $C_3H_6O_3$.
4. The Butyric, producing chiefly butyric acid, $C_4H_8O_2$.

Each fermentation is dependent upon and produced by special enzyms, which are often the products of particular forms of microörganisms.

PUTREFACTION is usually limited to changes in nitrogenous bodies. The more complex forms of these contain sulphur and phosphorus, which are converted into gaseous compounds of offensive odors.

These transformations are largely by hydrolysis, but other actions, especially oxidation, occur. The products will differ according as the action occurs in the presence of air (aërobic) or out of contact of air (anaërobic). Substances that prevent the growth of microörganisms or the action of their enzyms will prevent putrefaction and are termed *antiseptics*.

DECAY.—This is the decomposition of organic bodies by the slow action of oxygen. It takes place too slowly for any increase of temperature to be noticed, and it is rarely complete, that is, some portions of the elements escape action. When wood burns with a flame it leaves nothing but the incombustible mineral matter or ash, but when it decays a brown powder is left, which contains some of the original carbon and hydrogen. Decay requires the access of air, the presence of moisture and a temperature above the freezing point.

HYDROLYSIS.—This term is applied to transformations accompanied by the taking up of water with production of one or more substances, in which neither water nor the original body remains. It is brought about by action of enzyms, dilute acids or acid salts. The manner in which the hydrolysing body acts is not understood; it is usually not permanently affected by the reaction that it produces. These reactions take place only in the presence of excess of water, but usually the equation is written without the hydrolysing agent or the excess of water, since these are unchanged. Thus, the hydrolysis of cane sugar is written

$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6$$

although the hydrolysing agent and much additional water are present.

Dehydrolysing Agents.—These are commonly called dehydrating agents, but the latter term should be applied only to substances that remove water existing as such from other bodies. Anhydrous copper sulphate and calcium chloride, for example, are used in the preparation of absolute alcohol to remove the small amount of admixed water that cannot be removed by distillation. The true dehydrolysing agents (many of which are also dehydrating agents) remove hydrogen and oxygen in the proportion of $H_2$ to O, and form water, although the water-molecule does not exist in the original substance. In many cases an intermediate combination is produced that breaks up yielding water. For an illustration of this, see the process for making ether.

When cane sugar is mixed with strong sulphuric acid, water is formed, which unites with the acid, and carbon is set free. Among the most used dehydrolysing agents are sulphuric acid, phosphoric anhydride and zinc chloride. Heat often acts as a dehydrolysing as well as a dehydrating agent.

Nitric Acid.—The action of this differs with the temperature and degree of concentration. When strong cold acid is used, a substitution of $NO_2$ for H usually occurs, producing "nitro-compounds." When the acid is weak or hot a direct addition of oxygen may take place, according to methods noted in a preceding paragraph. An illustrative reaction of the formation of nitro-compounds is:

$$C_6H_6 + HNO_3 = C_6H_5NO_2 + H_2O$$

CHLORINE, BROMINE AND IODINE.—These sometimes form compounds by addition, but more frequently substitute hydrogen or other monads. In structural formulas, they are generally in direct association with carbon. The following are illustrative reactions for additive and substitutive actions:

**Additive** **Benzene dichloride.**

$$C_6H_6 + Cl_2 = C_6H_6Cl_2$$

**Substitutive** **Dichlorbenzene.**

$$C_6H_6 + Cl_4 = C_6H_4Cl_2 + 2HCl$$

SODIUM AND POTASSIUM.—These expel hydrogen, atom for atom, when it is in the hydroxyl position. An illustrative reaction is:

**Alcohol** **Sodium ethylate.**

$$C_2H_5HO + Na = C_2H_5NaO + H$$

SULPHURIC ACID.—The action of this as a dehydrolysing agent, in which respect it is very powerful, has already been noted. Acting on bodies that contain no oxygen or closed-chain compounds, with or without oxygen, sulphuric acid displaces an atom of hydrogen by substituting the molecular residue, $HSO_3$ forming a molecule of water at the same time. The substitutions thus obtained are termed "sulphonic acids." The following reaction illustrates their formation:

$$\underset{\text{Benzene}}{C_6H_6} + H_2SO_4 = \underset{\text{Benzene sulphonic acid.}}{C_6H_5HSO_3} + H_2O$$

By duplication of the reaction, polysulphonic acids (di, tri, etc.) may be obtained. In many cases sulphuric acid exchanges one or both of its hydrogen atoms for hydrocarbon radicles, producing esters.

Dilute sulphuric acid often produces hydrolysis, being itself unaffected by the reaction.

FRACTIONAL DISTILLATION.—When a liquid contains two or more substances of different boiling points, a partial separation of these may be made by distillation, changing the receiver from time to time. Each liquid distils over at about its boiling point. The most volatile constituent distils first and as each constituent passes off, a thermometer immersed in the vapor shows steadily rising temperature. The separate portions are termed *fractions*. It is usually not possible to separate compounds completely by this method. The adhesion between liquids and vapors causes some of the material of higher boiling point to be carried over at a lower temperature. Thus, a mixture of common alcohol and water can be distilled so as to reduce the amount of water to about 5 per cent. of the distillate, but absolute alcohol cannot be so obtained.

Fractional distillation is largely used in the separation of the hydrocarbons of petroleum and coal-tar.

LIGHT AND ELECTRICITY.—Many organic bodies are affected by light, but the action is usually superficial unless fresh portions are constantly exposed. A mixture of gelatin and potassium dichromate is rendered insoluble, and commercial betanaphthol is slowly darkened by light. The other forms of radioactivity probably also cause changes.

Electricity produces combination and decomposition of organic bodies. Electrolysis can be obtained with many compounds. By passing continuous or interrupted discharges from carbon poles in contact with some gases synthetic actions may be obtained.

## STRUCTURE OF ORGANIC MOLECULES.

**Percentage Composition and Formula.**—The composition of any substance may be expressed without use of symbols, or indication of the number of atoms of the elements present. The *parts by weight* of each element contained in *one hundred parts* of the substance may be given. The composition of ordinary sugar may be stated as:

| | |
|---|---|
| Carbon | 42.1 |
| Hydrogen | 6.4 |
| Oxygen | 51.5 |
| | 100.0 |

These figures represent *percentage composition.*

Such methods of expression, though simple and representing facts alone, are not convenient. No satisfactory comparison as to the composition of different compounds can be reached except by the construction of formulas in which the elements are represented by the relative numbers of atoms probably present.

By dividing each figure by the atomic weight of the element, and clearing of fractions, as nearly as can be done conveniently, the number of atoms of each element will be obtained. For example:

$$\begin{array}{rcrcrcrcl} 42.11 & \div & 12 & = & 3.51 & \times & 3.4 & = & 11.93 \\ 6.43 & \div & 1 & = & 6.43 & \times & 3.4 & = & 21.8 \\ 51.56 & \div & 16 & = & 3.24 & \times & 3.4 & = & 11.01 \end{array}$$

The last column indicates the formula, $C_{12}H_{22}O_{11}$; that is, this formula, when calculated to percentage composition, will give figures practically identical with those actually obtained by analysis of a sample of cane sugar.

It is evident that any multiple of this formula would also correspond to the percentage composition, hence it is necessary to fix the numbers more rigidly. The lowest term is by no means always the proper formula. The following list exemplifies this. Each formula is correct only for the body indicated; a multiplication or division of it is inaccurate.

| | | Molecular weight. |
|---|---|---|
| Formaldehyde | $CH_2O$ | 30 |
| Acetic acid | $C_2H_4O_2$ | 60 |
| Lactic acid | $C_3H_6O_3$ | 90 |
| Tetrose | $C_4H_8O_4$ | 120 |
| Arabinose | $C_5H_{10}O_5$ | 150 |
| Dextrose | $C_6H_{12}O_6$ | 180 |
| Mannoheptose | $C_7H_{14}O_7$ | 210 |

The formula is fixed in each case by the molecular weight. The determination of this becomes, therefore, an important matter. Several methods are in use: among the most frequently employed are determinations of *vapor density*, *freezing point of solution* and *combining weight.* The procedures for the first two are described in connection with determination of physico-chemical data.

*Vapor Density.*—This method of ascertaining molecular weight is of wide application and great value. Its use depends upon the fact that when a substance is capable of volatilising without decomposition, the density of its vapor compared to hydrogen as unity will be half the molecular weight.

For example: One liter of vapor of common ether is 37 times as heavy at 1 liter of hydrogen gas, the conditions of temperature and pressure being the same. The molecular weight of ether will be, therefore, 74. This corresponds to the formula $C_4H_{10}O$. ($C_4=48$; $H_{10}=10$; $O=16$ $=74$). No multiple of this formula will correspond to the observed vapor-density. The further elucidation of this formula, expressing its rational form $(C_2H_5)_2O$, is attained by other methods.

All the members of the homologous series of hydrocarbons, beginning with $CH_2$, have the same percentage composition, their formulas being multiples of the lowest formula, but the vapor densities steadily increase as shown in the annexed table ($CH_2$ has not been obtained).

| Formula. | Density. | Molecular weight. |
|---|---|---|
| $C_2H_4$ | 14 | 28 |
| $C_3H_6$ | 21 | 42 |
| $C_4H_8$ | 28 | 56 |
| $C_5H_{10}$ | 35 | 70 |

The exact formula of each member of the series can be fixed by a determination of the molecular weight.

Many organic bodies are decomposed by heat and their vapor density cannot be obtained.

*Freezing Point of Solution.*—The general rule is that when different substances are dissolved in amount proportional to their molecular weights in separate portions of the same solvent, the depression of the freezing point is the same. Experiment has shown that if the dissolved substance and the solvent are in the ratio of 1 molecule of the former to 100 molecules of the latter the depression of the freezing point of the solvent will be 0.62°. The method is not widely applicable, being satisfactory only with substances of low chemical activity. Active bodies, such as acids, bases or salts, give abnormal results.

*Combining Weight.*—If an organic body forms a definite compound with any element or with any compound, the molecular weight of which is known, such combination can be utilized in determining the molecular weight. For example, silver oxide reacts with acetic acid to form silver acetate and water. Silver acetate has the percentage composition:

| | |
|---|---|
| Silver | 64.6 |
| Carbon | 14.4 |
| Hydrogen | 1.8 |
| Oxygen | 19.2 |
| | 100.0 |

Proceeding as indicated on page 31, that is, dividing each percentage by the corresponding atomic weight and multiplying these quotients by a number which will practically eliminate fractions (in this case 1.66), the following figures are obtained:

$$64.6 \div 108 = 0.6 \times 1.66 = 0.99$$
$$14.4 \div 12 = 1.2 \times 1.66 = 1.99$$
$$1.8 \div 1 = 1.8 \times 1.66 = 2.98$$
$$19.2 \div 16 = 1.2 \times 1.66 = 1.99$$

The ratio of the numbers in the last column is substantially 1 : 2 : 3 : 2, hence the formula of silver acetate is $AgC_2H_3O_2$. Here, as in the instance explained on page 31, any multiple of the formula, for example, $Ag_2C_4H_6O_4$, would satisfy the percentage composition. This uncertainty is eliminated by determining the degree of basic power of acetic acid. If it is a monobasic acid silver acetate will have but one atom of silver; if a dibasic acid then the salt will have two atoms of silver. Experiment shows that acetic acid forms but one series of salts, hence silver acetate must be $AgC_2H_3O_2$, and acetic acid $C_2H_4O_2$. The latter formula can be confirmed by a determination of the vapor density.

Several other methods for determining molecular weight are known, but do not need description here. Many organic bodies exist to which no known method is applicable; hence the formula is not definitely assigned. Starch, for example, has a percentage composition corresponding to the ratio $C_6H_{10}O_5$, but the molecular weight cannot be ascertained by any of the methods available. The origin and transformations of starch suggest complex structure; it is probable that $C_{60}H_{100}O_{50}$ is an approximation to its formula. In such cases the formula is often expressed in the lowest terms with a provisional indefinite coefficient, thus $nC_6H_{10}O_5$.

**Empirical, Rational and Structural Formulas.**—The formulation of organic molecules is based upon the assumption that the valencies of the principal elements are not subject to irregularity. Carbon is always taken as a tetrad, hydrogen as a monad, oxygen as a dyad and nitrogen as either triad or pentad. Phosphorus is usually considered as a pentad; sulphur as either a dyad or hexad. It is, however, freely assumed that polyvalent elements may combine by more than one bond to another atom, even another of the same nature. Thus carbon is assumed to be capable of forming the groups:

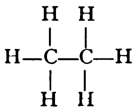
$$\equiv C-C\equiv \qquad =C=C= \qquad -C\equiv C-$$

Oxygen is frequently represented as combining by both its bonds, as in the group: $H-O-C=O$. The double and triple linkings are often termed "unsaturated."

It must not be supposed that a linking by two bonds is a stronger union than by one bond. Valency is a standard of capacity of affinity, not of intensity; in fact, acetylene which is supposed to contain the triple linking is more easily decomposed than ethane in which the single linking is assumed.

$H—C \equiv C—H$

**Acetylene**

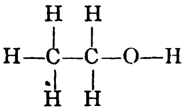


$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & — & C & — & C & — & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

**Ethane**

Some recent researches have shown the existence of compounds in which carbon is apparently a triad, and others in which oxygen is apparently a tetrad, but the theories in regard to valency are provisional only. For the great majority of organic compounds, the valencies noted above are satisfactory.

A formula that shows only the number of atoms of each element in the compound is an *empirical* formula; if any supposed arrangement is exhibited the formula is termed *rational.* When the symbols are displayed so as to indicate probable relations of the atoms to each other the formula is termed *structural* (sometimes *graphic*). The following formulas exemplify these terms:

| Empirical. | Rational. | Structural. |
|---|---|---|
| $C_2H_6O$ | $C_2H_5HO$ |  $\begin{array}{ccccccccc} & & H & & H & & & & \\ & & \vert & & \vert & & & & \\ H & — & C & — & C & — & O & — & H \\ & & \vert & & \vert & & & & \\ & & H & & H & & & & \end{array}$ |

Some authorities distinguish between *empirical* and *molecular* formulas, applying the former term to the simplest formula that corresponds to the *percentage composition*, and the latter term to formulas that correspond to the *molecular weight*. Under this distinction, $CH_2O$ would be the *empirical* formula of all the bodies in the list on page 31 and would be the *molecular* formula of *formaldehyde* only. In this work, the terms will be used synonymously.

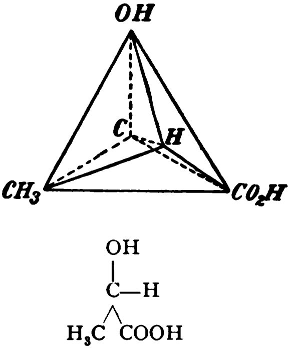
In some substances the atoms are subject to changes of position without altering the identity of the substance. Thus phloroglucol, $C_6H_6O_3$, can be represented by either of the following formulas:

| Symmetric trihydroxybenzene. | Triketohexamethene. |
|---|---|
| $C_6H_3(HO)_3$ | $(CH_2)_3(CO)_3$ |

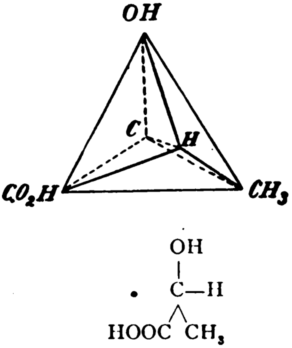
Molecules that exhibit this variability are termed *tautomeric* or, rarely, *desmotropic*.

A *general formula* is an algebraic expression for representing the formulas of a group of bodies, for illustration of which see "Homologous Series."

Ordinary structural formulas represent the atoms arranged upon the same plane, but as molecules occupy space it is desirable to formulate them on a three-dimensional system. As a basis for this, the carbon atom is represented as a tetrahedron. It is not assumed that this is the shape of the atom, but the four apexes of this solid correspond to the four valencies usually manifested by carbon. Such formulas are termed "*stereochemic*." They are most satisfactorily shown by models, but the annexed figures show the usual methods of exhibiting them.



Dextrolactic acid



Levolactic acid

Union of carbon atoms by two bonds is shown by joining the tetrahedrons by edges (see page 40); union by three bonds, by joining them by faces.

**Optical Activity. Asymmetric Atoms.**—*Optical activity* is the power to rotate polarised light. It is possessed by many bodies, but in organic chemistry is of importance only when exhibited by substances in liquid form, by fusion or solution. The rotation may be either to the right or left. Substances exhibiting the former action are termed dextrorotatory, indicated by + or d; substances showing left-handed rotation are termed levo- (laevo) rotatory, indicated by — or l.

*Asymmetric Atoms.*—Any atom that has each of its bonds united to an atom or molecule of different nature is asymmetric. Asymmetric carbon is the most important example. In structural formulas, it will be indicated by an italic symbol. (See, for example, the formula of tartaric acid, page 88.)

A general relation exists between this position of the carbon atom and the optical activity, expressed by the rule that "every carbon compound that, in the liquid condition, rotates polarised light, will have in its molecule at least one atom of asymmetric carbon." The reverse of the proposition is not true. Asymmetric carbon may be present in substances that do not rotate polarised light. In fact, in most cases, molecules containing asymmetric carbon exist in three conditions, dextro- and levorotatory, and inactive. The inactive condition may depend upon either the antagonistic influence of the asymmetric carbon atoms within the molecule (neutralisation by internal compensation) or by the presence of equivalent quantities of the opposing active substances (neutralisation by external compensation).

The dibasic acid represented by the empirical formula $C_4H_6O_6$ exists in four forms, each of which has the rational formula $H_2C_2H_4O_6$.

| | | | |
|---|---|---|---|
| Ordinary tartaric | acid.... | Dextrorotatory. | |
| Levotartaric | " .... | Levorotatory. | |
| Racemic | " .... | Inactive. | (Mixture of + and —.) |
| Mesotartaric | " .... | Inactive. | (Not a mixture.) |

In racemic acid the neutralisation is due to presence of equivalent amounts of the + and — forms, in mesotartaric acid to the existence of antagonistic asymmetric carbon atoms. The latter condition cannot exist in bodies having but one asymmetric carbon atom in the molecule. The association of molecules of opposing optical conditions is termed "racemism."

**Isomerism, Metamerism and Polymerism.**—The properties of bodies depend on the elements present in them and the arrangements of these elements with respect to each other. Different arrangements may be made with the same constituent atoms, and thus will arise bodies having the same constitution but not identical. To all such instances the term *isomeric* is often applied, but it is more satisfactory to limit it to the instances in which the bodies are analogous in structural formula. When the identity is in percentage composition and in molecular weight, the structures being of different types, the term *metameric* is applicable. When the identity is in percentage composition, the molecular weights being multiples, but the structure analogous, the relation is termed *polymeric*. True isomerism is often indicated by the addition of the prefix "iso" to the name of one of the substances. Polymerism is sometimes indicated by the similar addition of "para" to one of the names. The following illustrations will show the application of these principles:

**True isomerism.**

$H—C\equiv N$ cyanogen. $C\equiv N—H$ isocyanogen.

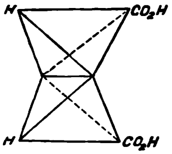
**Metamerism.**

$(CH_3)_2O$ methyl oxide. $C_2H_5HO$ alcohol.

**Polymerism.**

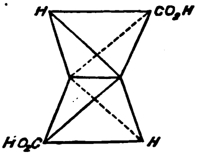
$C_2H_4O$ aldehyde. $C_6H_{12}O_3$ paraldehyde.

Instances of isomerism dependent on slight differences in the spatial relation of the constituent atoms are frequently observed in complex molecules. These can only be shown by stereochemic formulas. The term "*allo-isomerism*" proposed for this phase, has not been generally adopted, the usual designation is "stereochemic isomerism." The distinctive nomenclature of these isomers is incomplete. One of the methods is shown in the annexed formulas, in each of which a pair of double-linked carbon atoms are shown by tetrahedrons joined by edges.



Maleic acid

Plane symmetric
(or cis-) form



Fumaric acid

Axial symmetric
(or trans-) form

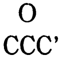
The syllables "cis" and "trans" are used because, in one case, the similar radicles are on the same side of the carbon chain, in the other case on opposite sides.

**Organic Radicles.**—Any unsaturated molecule may be considered a radicle, and hence the number of radicles in the formula of any body will be limited only by the number of divisions that may be assumed. Many of the groupings thus obtained, having no coherence or independent function, are not regarded. Any grouping that confers characteristic properties or reactions upon the molecule or that remains unchanged through a series of reactions, is a true radicle. Some of these are of frequent occurrence, are always distinguished in rational formulas and often indicated in the name of the compound. The following are instances:

HO, *Hydroxyl.*—The hydrogen of this is easily replaceable by positive elements such as potassium and sodium. When subjected to the action of certain chlorine compounds the entire group is replaced, not the hydrogen alone, as occurs when hydrogen is united to carbon. The presence of one or more hydroxyl groups in a compound is often indicated by the termination "ol," *e. g.*, phenol, $C_6H_5HO$.

HOCO, *Carboxyl.*—This confers acid properties upon the molecule containing it. The basic capacity is proportional to the number of such groups present. Thus acetic acid has but one carboxyl group and is monobasic; tartaric acid has two and is dibasic; citric acid has three and is tribasic.

HCO, *Aldehyde Group.*—The hydrogen is joined to the carbon atom and is not replaceable by positives. Compounds containing this group generally show reducing power.



$C\overset{O}{C}C$, *Ketonic Group.*—Carbon united to oxygen by two bonds and by its remaining bonds to carbon atoms that are *not* united to a negative body. This group generally confers reducing power on the molecule containing it.

The foregoing groups, it will be noted, do not contain asymmetric carbon and, therefore, do not produce optical activity.

$NH_2$, *Amidogen.*—This generally confers capacity for combining with acids which is often proportional to the number of groups present. It is indicated by the syllables "amin" or "amid."

NH, *Imidogen.*—This resembles in function amidogen. It is indicated by the syllables "imin" or "imid."

**Homologous Series.**—Any series of compounds in which the formulas differ by $CH_2$ or some multiple of this difference by a whole number, is termed a *homologous series*, and the members thereof are *homologues.* These terms are not limited to hydrocarbons. The following are examples of homologous series:

| Paraffins. | Alcohols. | Esters. |
|---|---|---|
| $CH_4$ | $CH_3HO$ | $(CH_3)_2SO_4$ |
| $C_2H_6$ | $C_2H_5HO$ | $(C_2H_5)_2SO_4$ |
| $C_3H_8$ | $C_3H_7HO$ | $(C_3H_7)_2SO_4$ |
| $C_4H_{10}$ | $C_4H_9HO$ | $(C_4H_9)_2SO_4$ |

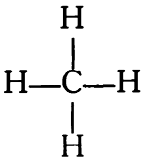
In the third column the constant difference is $(CH_2)_2$, but the series is still homologous. A series intermediate between each member is known, but even if these latter were non-existent, the homology would not be lost.

**General Formulas.**—The existence of homologous series, renders it possible to express by one formula the molecule of any member of the group. Thus, in the first series, the atoms of hydrogen are always two more than twice the carbon atoms. The general formula, $C_nH_{2n+2}$, in which *n* represents any number of atoms, will stand for any member of this series. If it be required, for instance, to write the formula of the sixth member the rule is simple. As the carbon increases regularly one atom at a time, the sixth member will have $C_6$. Twice six plus two is fourteen; the formula is, therefore, $C_6H_{14}$. The general formula of the second series above given is $C_nH_{2n+1}HO$; of the third series $(C_nH_{2n+1})_2SO_4$.

These formulas are sometimes used instead of the series-names. Thus the series beginning with $CH_4$ is often designated as the series $C_nH_{2n+2}$.

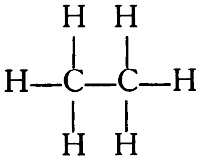
**Carbon Chains.**—The valency of each member of a homologous series is the same. The explanation of this is the supposition that, in forming the molecules, the carbon has in part satisfied itself, so that each atom of carbon added carries into the molecule only two degrees of valency, which $H_2$ satisfies. Structural formulas will exemplify this supposition.

**Methane, $CH_4$.**



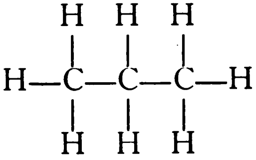
$$\begin{array}{ccc} & H & \\ & | & \\ H- & C & -H \\ & | & \\ & H & \end{array}$$

**Ethane, $C_2H_6$.**



$$\begin{array}{cccc} & H & H & \\ & | & | & \\ H- & C- & C & -H \\ & | & | & \\ & H & H & \end{array}$$

**Propane, $C_3H_8$ (tritane).**

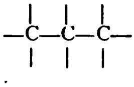


$$\begin{array}{ccccc} & H & H & H & \\ & | & | & | & \\ H- & C- & C- & C & -H \\ & | & | & | & \\ & H & H & H & \end{array}$$

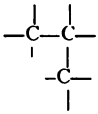
These linked carbon atoms have been called, somewhat fancifully, perhaps, "carbon skeletons." The forms shown above are termed "*open chains.*" In other cases the carbon is arranged in a ring of three or more atoms forming "*closed chains.*"

**Properties of Bodies in the Homologous Series.**—The relation of homologous bodies is not a mere accidental relation in formulas. By comparing different members of the same series analogies either in origin, general properties, or chemical relations appear. The series beginning with $CH_4$ is characterised by general indifference to chemical action. The hydroxides of the series beginning with $CH_3HO$ constitute a series of alcohols which possesses specific physiologic action. In each series fusing and boiling points, specific gravity and other constants vary with considerable regularity. The molecular weight, of course, increases regularly.

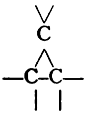
**Isomeric Modification in Homologous Series.**—Many organic bodies occur in two or more forms not sufficiently distinct to consider them as essentially different, and yet not identical. In such cases, the diagrammatic method of showing the linking of the carbon atoms may be utilised to show that the difference may be due to different positions of the carbon atoms, with respect to each other and to the other elements present. When the number of carbon atoms is less than four, fundamental variation of the structure is not possible, except by closing the chain, as shown below:



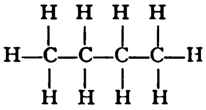
is identical with



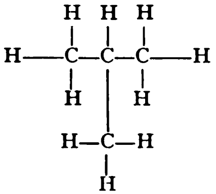
but not with



With four carbon atoms two forms may be obtained, as exemplified in the hydrocarbon, $C_4H_{10}$:



Normal butane



Isobutane (methyl propane)

The number of possible variations increases rapidly with the number of carbon atoms, so that the higher members of the series show numerous instances. The structural formulas given above may be condensed as follows:

| Normal butane. | Isobutane. |
|---|---|
| $CH_3CH_2CH_2CH_3$ | $CH_3CH(CH_3)CH_3$ |

## CLASSIFICATION AND NOMENCLATURE OF ORGANIC COMPOUNDS.

Many organic bodies are, in formulas, structurally analogous to inorganic bodies, and may be classified and named on the same systems as used in inorganic chemistry. The groups termed acids, alkalies and salts, are well represented in organic chemistry. Oxides, sulphides and halogen compounds are also abundant. The phenomena of isomerism, polymerism, tautomerism and homology are practically peculiar to organic chemistry, and hence the methods of classification and nomenclature must be much more elaborate. Unfortunately the systems of naming and arranging organic compounds are still incomplete and unsatisfactory.

In classifying organic bodies it is most convenient to begin with the binary forms—the hydrocarbons. These are very numerous and cannot be named according to their formulas, as is so easily done with binary inorganic compounds. Each hydrocarbon has a name referring to some property, source, use or other incidental, often fanciful, relation.

Thus methane, $CH_4$, the fundamental hydrocarbon of organic chemistry, because the simplest of all known ones in structure, was called *marsh gas*, because it was detected in the emanation from the mud of marshes. The name, methane, is due to the relation of the hydrocarbon to methyl alcohol and that name, in turn, is really a misnomer, for it refers to a Greek word meaning "wine," to which methyl alcohol has no direct relationship. Similarly the hydrocarbon, butane, is so named owing to its structural relations to butyric acid, which is obtained from butter. "Butyric" is derived from the Greek word for butter.

Suggestions have been made to name compounds by syllable systems, according to which the elements should be indicated by their symbols and the number of atoms in each by the vowels in the usual alphabetic order, *i. e.*, a = 1; e = 2, etc. By this system $CH_4$ would be "Caho." These methods have not received serious attention, as they produce jargon.

Nomenclature in organic chemistry is in the main based on the principle that the name shall show the molecular structure or immediate relationships of the body. It is not usual to base it on properties, but two well-marked instances of this are to be noted. Nitrogenous organic bodies termed "enzyms" or "non-organised ferments" are generally distinguished by the termination "ase." Nitrogenous bases are distinguished by the termination "ine." Many substances are as yet not definitely classifiable. For these the termination "in" is provisionally used.

The following is a summary of the principal groups of organic bodies:

Hydrocarbons.
Ethers, Alcohols, Aldehydes, Ketones, Esters.
Oils and Fats.
Acids and Salts.
Carbohydrates.
Cyanogen and derivatives.
Amine and derivatives.
Alkaloids, Ptomaines and Leucomaines.
Azo-, Diazo- and Hydrazo-compounds.
Proteids.
Enzyms.

The distinction between the groups is not well defined; many bodies may be included in more than one group, their molecules exhibiting mixed structure. Thus lactic acid has alcoholic as well as acidic structure. Dextrose which is classed among the carbohydrates has alcoholic and aldehydic structure.

Organic compounds are sometimes divided into two groups, termed respectively:

(1) Open-chain or aliphatic compounds, and (2) closed-

chain or cyclic compounds. This division is also imperfect, in that many bodies cannot be assigned positively to either group.

Organic compounds that show analogy to inorganic compounds may be designated by analogous terms. Thus, the formula of common alcohol may be written $C_2H_5HO$, showing a structural analogy to KHO. $C_2H_5$ is called ethyl, hence alcohol is termed ethyl hydroxide.

To assist in distinguishing organic bodies, many syllables have been applied as prefixes or suffixes. A few examples of the more important will be here given. Other less important ones will be mentioned in connection with the compounds that exemplify the use.

"Ane," "ene," "ine," "one," etc., are used for different series of hydrocarbons. The system may be extended by using other vowels and diphthongs. In these syllables the first vowel is long. Care must be taken not to confuse these terminations with others apparently similar, namely "one" used to indicate a special form of oxygen compound, called a ketone, and the use of "ine" (in which "i" is short) as a termination for basic substances.

"ase" indicates an enzym;

"ose" indicates a carbohydrate, but is also applied to some intermediate products of proteid hydrolysis;

"ol" indicates hydroxyl;

"yl" indicates a radicle, generally one of uneven valency;

"in" has no exact significance; it is employed largely for bodies not definitely classifiable. It is used for some common enzym, but it would be best to use the proper termination for these;

"al" indicates an aldehyde;

"mono," "di," "tri," etc., are used with analogous significance to that in inorganic chemistry;

"nitro," "chloro," "bromo," "iodo," refer respectively to the presence of $NO_2$, Cl, Br, I;

"nitroso" indicates the group NO;

"azo" and "diazo" indicate the group $—N=N—$;

"hydrazo" indicates the group $=N—N=$;

"amin" or "amid" indicates the group $NH_2$;

"imin" or "imid" indicates the group NH;

"thio" indicates sulphur;

"sulpho" is often used instead of "thio";

"pyro" is used to indicate a body that has been obtained by heat;

"sulphonic" indicates the group $HSO_3$; a salt of this, by replacement of H, is a "sulphonate."

# DESCRIPTIVE CHEMISTRY.

## Aliphatic or Open-chain Hydrocarbons.

Compounds of carbon and hydrogen are very numerous. Carbon being a tetrad, the greatest number of atoms of hydrogen that can combine with one of carbon is four. This compound $CH_4$, commonly known as methane, is the type of the aliphatic or open-chain hydrocarbons; all other compounds of this class are capable of being regarded as derived therefrom by subtraction or substitution, or both.

Substituting all or part of the hydrogen in $CH_4$ by any other element or group of elements, does not disturb the saturation; the molecule remains a saturated hydrocarbon. Hence the compounds $CCl_4$, $CHCl_3$, $CH_2Cl_2$, $CH_3Cl$ will all be referable to the same group as $CH_4$.

By successive subtractions of H from $CH_4$, are obtained a series of unsaturated molecules, known as radicles, the valency of which will be, in each case, equal to the number of hydrogen atoms removed. $CH_3$ is a monad radicle because it lacks one atom of hydrogen; $CH_2$ is a dyad, CH a triad, while C, of course, is a tetrad. From each of these molecules—termed hydrocarbon radicles—derivatives may be obtained, comparable in the main to similar derivatives from the elements themselves. Thus $CH_3$ forms a chloride, bromide, hydroxide, sulphate, each analogous in formula to the similar compound formed by the elements of the potassium group. $CH_2$ yields compounds analogous in formulas to those from dyad metals, and so on. In addition these radicles have substitution power, that is, they may replace the hydrogen of other organic compounds. Each of them and each of their derivatives is the first member of a homologous series. A system of nomenclature by terminations has been adopted to distinguish the different series; the vowels are used in regular order, and the syllable *yl* indicates uneven valency. The number of carbon atoms is indicated, except in the first two members of each series, by syllables formed from Greek numerals.

The following table will be sufficient to show the principle of the above classification:

| Series 1 | Series 2 | Series 3 | Series 4 | Series 5 |
|---|---|---|---|---|
| Gen. Formula | Gen. Formula | Gen. Formula | Gen. Formula | Gen. Formula |
| $C_nH_{2n+2}$ | $C_nH_{2n+1}$ | $C_nH_{2n}$ | $C_nH_{2n-1}$ | $C_nH_{2n-2}$ |
| Paraffins | Alkyls Monatomic Alcohol Radicles | Olefins | Methylenes | Acetylenes |
| Methane<br>$CH_4$ | Methyl<br>$CH_3$ | Methene<br>$CH_2$ | Methenyl<br>CH | Methine<br>C |
| Ethane<br>$C_2H_6$ | Ethyl<br>$C_2H_5$ | Ethene<br>$C_2H_4$ | Ethenyl<br>$C_2H_3$ | Acetylene<br>(Ethine)<br>$C_2H_2$ |
| Propane<br>(Tritane)<br>$C_3H_8$ | Propyl<br>(Trityl)<br>$C_3H_7$ | Propene<br>(Tritene)<br>$C_3H_6$ | Propenyl<br>(Tritenyl)<br>$C_3H_5$ | Allylene<br>(Propine)<br>$C_3H_4$ |
| Butane<br>(Tetrane)<br>$C_4H_{10}$ | Butyl<br>(Tetryl)<br>$C_4H_9$ | Butene<br>(Tetrene)<br>$C_4H_8$ | Tetrenyl<br>$C_4H_7$ | (Crotonylene)<br>Butine<br>$C_4H_6$ |
| Pentane<br>$C_5H_{12}$ | Amyl<br>(Pentyl)<br>$C_5H_{11}$ | Pentene<br>$C_5H_{10}$ | Pentenyl<br>$C_5H_9$ | (Valerylene)<br>Pentine<br>$C_5H_8$ |
| Hexane<br>$C_6H_{14}$ | Hexyl<br>$C_6H_{13}$ | Hexene<br>$C_6H_{12}$ | Hexenyl<br>$C_6H_{11}$ | Hexine<br>$C_6H_{10}$ |

It does not necessarily follow that all of these bodies have been obtained, but most of them are known and the others could doubtless be prepared. The members of each vertical column are homologous with each other.

The members of the first series being saturated hydrocarbons, are practically indifferent to chemical reagents. Common paraffin consists of several of them, and the series has therefore been called the "*paraffin series*"; those of the second series; because their compounds are on the type of the alkali-metals, are termed "alkyls"; the members of the third series have been called *olefins*, from the older name of one of the members of it.

## PARAFFIN OR METHANE SERIES.

The members of this series are saturated molecules not easily affected by chemical agents. Many of them are found in petroleum.

*Methane*, *Marsh Gas*, $CH_4$.—This is a colorless and odorless gas which is formed at the bottom of marshes and stagnant pools (whence the name *marsh gas*) as the result of the slow hydrolysis of cellulose.

$$C_6H_{10}O_5 + H_2O = 3CH_4 + 3CO_2$$

This decomposition is probably due to the presence of microörganisms. The gas may be collected by filling a bottle completely with water, inserting a funnel, and stirring the decaying vegetable matter in the bottom of the pool while holding the bottle and funnel in an inverted position under the surface of the water. The bubbles which arise may be guided through the funnel into the bottle in order to displace the water.

*Methane* is a product of ordinary putrefaction and also results from the slow decomposition of certain varieties of coal. When mixed with air it constitutes *firedamp* that causes explosions in coal mines. Coal-gas manufactured for illuminating purposes consists of nearly 50 per cent. of methane; the natural gas, largely used for fuel and illuminating purposes in some parts of the United States, is almost pure *methane* (about 90 per cent.). Methane may be produced artificially in several ways: the most convenient method for experimental purposes is to strongly heat a mixture of anhydrous sodium acetate, sodium hydroxide and calcium oxide.

*Experiment* 1.—Mix intimately, by rubbing in a mortar, equal parts of dried sodium acetate and quicklime. Introduce the mixture into an ignition tube and apply strong heat. Methane will be evolved and may be ignited at the mouth of the tube. A portion of the gas may be collected over water and its explosive qualities tested after mixing it with air.

*Ethane*, $C_2H_6$, is a colorless and odorless gas, found in natural gas in small amounts and also existing in crude petroleum.

*Propane*, $C_3H_8$; *Butane*, $C_4H_{10}$; *Pentane*, $C_5H_{12}$; *Hexane*, $C_6H_{14}$ and *Heptane*, $C_7H_{16}$, are all found in crude petroleum.

*Butane* is more commonly known as "Cymogene" and is used as an anesthetic in surgery.

*Pentane*, commonly called "Rhigolene" is used as an anesthetic and solvent. The vapor of *pentane* is used as a standard in determining the illuminating power of gas and electric lamps.

*Hexane*, commonly known as "Gasolene," is used as a solvent and for illuminating and heating purposes.

The hydrocarbons or petroleum products boiling between 70° and 120° and having a specific gravity between 0.685 and 0.690 are known under the name of "Ligroin."

The use of the terms benzine, benzin and benzolene has led to great confusion between the petroleum products and benzene, $C_6H_6$, (benzol), the principal constituent of coal-tar naphtha.

*Heptane* exists in petroleum spirit and also constitutes the greater portion of the oil from *Pinus Sabiniana*. It is used as a solvent under the trade designation of "Abietene."

*Kerosene*, or *Coal Oil*, is that mixture of the hydrocarbons which is most suitable for burning in lamps. The name kerosene is a contraction of keroselain or "wax oil" and was originally a trade-mark for a certain fraction of petroleum oil.

The hydrocarbons from $C_{16}H_{34}$ to $C_{20}H_{42}$ constitute the various grades of *petrolatum*. Some members of the olefin series are also associated with the paraffins in these compounds. The different consistencies, colors and melting-points of petrolatum preparations are obtained by different methods and represent varying degrees of purification. Commercial products not differing materially from petrolatum are sold under various trade names, as cosmoline, vaseline.

A mixture of hydrocarbons having a higher melting point than the petrolatums constitutes the product known as *paraffin*. The name paraffin, from *parum*, without, *affinis*, affinity, has also been applied to the entire group of saturated hydrocarbons, indicating the difficulty of inducing chemical change. Common paraffin is a white, waxy solid, having a melting point of from 45° to 65° and a metallic sound when struck. It has an extensive use as a substitute and adulterant for beeswax and spermaceti.

A small amount of these hydrocarbons is sufficient to form explosive mixtures with a large volume of air. This may be illustrated by pouring a few drops of one of the volatile products into a 100 c.c. beaker, covering it with a glass plate, and, after a few minutes, removing the plate and applying a light.

*Synopsis of the Paraffin Series.*—The lowest members of the series at ordinary temperatures are gaseous, the intermediate members liquid and the higher members solid. The boiling points rise with the molecular weights and in the higher members of the series the specific gravities and melting points show a regular increase. The following tables illustrate these facts:

| | | Structural Formula. | Boiling point below 760 mm. |
|---|---|---|---|
| $C_3H_8$ | **Propane** | $CH_3.CH_2.CH_3$ | —45° (B. 27, 3306) |
| $C_4H_{10}$ | **Normal Butane** | $CH_3.CH_2.CH_2.CH_3$ | + 1° (B. 27, 2768) |
| | **Trimethyl Methane** | $CH_3.CH(CH_3)_2$ | —17° |
| $C_5H_{12}$ | **Normal Pentane** | $CH_3.(CH_2)_3.CH_3$ | +38° |
| | **Dimethylethyl Methane** | $CH_3.CH_2.CH(CH_3)_2$ | +30° |
| | **Tetramethyl Methane** | $C(CH_3)_4$ | +10° |
| $C_6H_{14}$ | **Normal Hexane** | $CH_3(CH_2)_4CH_3$ | +71° |
| | **Methyldiethyl Methane** | $CH_3(C_2H_5)_2CH$ | +64° |
| | **Dimethylpropyl Methane** | $CH_3.CH_2.CH_2.CH(CH_3)_2$ | +62° |
| | **Di-isopropyl** | $(CH_3)_2.CH.CH.(CH_3)_2$ | +58° |
| | **Trimethylethyl Methane** | $CH_3.CH_2.C(CH_3)_3$ | +43°—48° |

| | | Melting Point. | | B. P. | Sp. Gr. | |
|---|---|---|---|---|---|---|
| Heptane | $C_7H_{16}$ | ... | | 98.4° | 0.7006(0°) | |
| Octane | $C_8H_{18}$ | ... | | 125.5° | 0.7188(0°) | |
| Nonane | $C_9H_{20}$ | — 51° | | 149.5° | 0.7330(0°) | |
| Decane | $C_{10}H_{22}$ | — 32° | Under 760 mm. pressure. | 173° | 0.7456(0°) | |
| Undecane | $C_{11}H_{24}$ | — 26.5° | | 194.5° | 0.7745 | At their M. P. |
| Dodecane | $C_{12}H_{26}$ | — 12° | | 214° | 0.773 | |
| Tridecane | $C_{13}H_{28}$ | — 6.2° | | 234° | 0.775 | |
| Tetradecane | $C_{14}H_{30}$ | + 5.5° | | 252.5° | 0.775 | |
| Pentadecane | $C_{15}H_{32}$ | + 10° | | 270.5° | 0.775 | |
| Hexadecane | $C_{16}H_{34}$ | + 18° | | 287.5° | 0.775 | |
| Heptadecane | $C_{17}H_{36}$ | + 22.5° | | 303° | 0.776 | |
| Octadecane | $C_{18}H_{38}$ | + 28° | | 317° | 0.776 | |
| Nonadecane | $C_{19}H_{40}$ | + 32° | | 330° | 0.777 | |
| Eicosane | $C_{20}H_{42}$ | + 36.7° | Under 15 mm. pressure. | 205° | 0.777 | |
| Heneicosane | $C_{21}H_{44}$ | + 40.4° | | 215° | 0.778 | |
| Docosane | $C_{22}H_{46}$ | + 44.4° | | 224.5° | 0.778 | |
| Tricosane | $C_{23}H_{48}$ | + 47.7° | | 234° | 0.778 | |
| Tetracosane | $C_{24}H_{50}$ | + 51.1° | | 243° | 0.778 | |
| Heptacosane | $C_{27}H_{56}$ | + 59.5° | | 270° | 0.779 | |
| Hentriacontane | $C_{31}H_{64}$ | + 68.1° | | 302° | 0.780 | |
| Dotriacontane | $C_{32}H_{66}$ | + 70.0° | | 310° | 0.781 | |
| Pentatriacontane | $C_{35}H_{72}$ | + 74.7° | | 331° | 0.781 | |
| Dimyricyl | $C_{60}H_{122}$ | + 102° | | ... | ... | |

Derivatives of the Paraffins.—Paraffins are not easily acted upon by chemical agents. Substitution compounds may be obtained by direct action of chlorine and bromine upon all of them, and nitro-compounds may also be produced directly from some of the higher members.

By successive substitution of the hydrogen in $CH_4$ four derivatives are obtained which will serve as an illustration of the nomenclature of this class of compounds.

| | |
|---|---|
| Methane | $CH_4$ |
| Monochlormethane (methyl chloride) | $CH_3Cl$ |
| Dichlormethane (methene chloride) | $CH_2Cl_2$ |
| Trichlormethane (methenyl chloride) | $CHCl_3$ |
| Tetrachlormethane (carbon tetrachloride) | $CCl_4$ |

The first substitution product, *monochlormethane* or *methyl chloride*, $CH_3Cl$, may be made by the direct action of chlorine on methane or by the action of hydrochloric acid gas on methyl hydroxide. It is gaseous at ordinary temperatures but is liquefied under a pressure of several atmospheres. This liquid is sometimes used to produce local anesthesia.

The second product, *dichlormethane* or *methylene chloride*, $CH_2Cl_2$, may be prepared by the action of chlorine upon methane or upon methyl chloride. It is a colorless liquid boiling at 41° and has been used as an anesthetic.

The third substitution, *trichlormethane*, is the important body, *chloroform*, $CHCl_3$. It may be made by the direct action of chlorine upon methane but it is usually made by the action of chlorinated lime upon alcohol or acetone.

When pure it is a colorless, fragrant, mobile, volatile liquid, sp. gr. 1.49, boiling point 60°, sparingly soluble in water, soluble in all proportions in alcohol, ether, petroleum spirit and fixed and volatile oils. It is not readily inflammable, but vapor from boiling chloroform burns with a greenish flame. It is used in analytical chemistry as a solvent. It has marked antiseptic powers. When inhaled it produces deep anesthesia; when swallowed it acts as an irritant. Pure chloroform is unstable; the commercial article contains about 1 per cent. of alcohol which acts as a preservative.

*Experiment* 2.—Mix 100 grams of chlorinated lime with about 500 c.c. of water in a large flask provided with a thistle tube and a distillation tube which is connected with a well-cooled condenser. Add gradually, through the thistle tube, about 30 c.c. of acetone and apply a gentle heat until the chloroform begins to distil over, when the heat may be regulated according to the rapidity of the distillation. Purify the chloroform by first washing it with water, then with a small quantity of sulphuric acid, and finally with a solution of sodium carbonate, after which it may be distilled on the water bath.

Instead of the thistle tube and delivery tube, the arrangement shown in Fig. 57 may be used. The acetone is placed in the stoppered funnel tube and the addition of it is easily controlled. The hemispherical dish (the bowl of an ordinary water-bath) contains water heated gently by the burner. The bowl is moved up so as to include the lower half of the flask. Cold water passes through the condenser. This arrangement of apparatus is suitable for many distillations.

*Carbon tetrachloride*, $CCl_4$, is the final result of the successive substitution of the hydrogen of methane by chlorine. It is a colorless liquid having an odor resembling chloroform; sp. gr. 1.56. It boils at 68°. It is a powerful anesthetic but is most largely used at the present time as a non-inflammable solvent in manufacturing and technical operations.

*Bromoform*, $CHBr_3$, is analogous in composition to chloroform and is used mainly as an anesthetic.

*Iodoform*, $CHI_3$, is also analogous to chloroform, and is largely used as an antiseptic in surgery. It cannot be obtained by direct substitution of iodine in the methane group, but it is made by the action of iodine on alcohol or acetone in the presence of an alkali. It has a penetrating, disagreeable odor. It crystallises in bright yel-

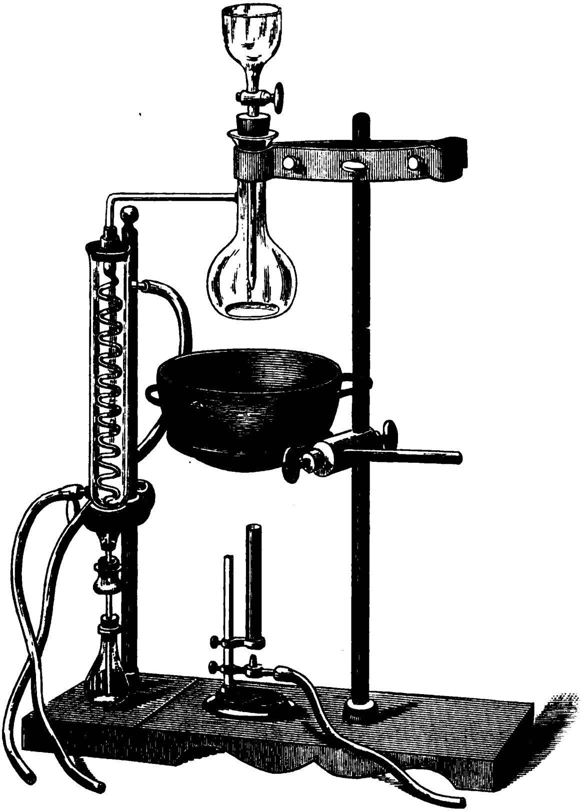


FIG. 9.

low hexagons which are soluble in chloroform, ether and petroleum spirit.

*Experiment* 3.—Dilute 2 c.c. of acetone to make about 10 c.c., and add a solution of 1 gram of potassium iodide and 1 gram of sodium hydroxide dissolved in about 5 c.c. of water; then add solution of sodium hypochlorite drop by drop, observing the separation of yellow crystals of iodoform, which may be collected on a filter paper, dried and tested for solubility in water, alcohol and ether.

ALKYLS, MONATOMIC ALCOHOL RADICLE SERIES.—This is a series of monad radicles sometimes called the *methyl* series, often the alcohol radicles, because their hydroxides are the common alcohols. The term alkyls is most convenient. The following derivatives are obtained from this series:

Normal oxides called ETHERS:

$(CH_3)_2O$, methyl ether, analogous to $Na_2O$, sodium oxide.
$(C_2H_5)_2O$, ethyl ether, analogous to $Na_2O$, sodium oxide.

Compounds with halogens, also sometimes called ETHERS:

$CH_3Cl$, methyl chloride, analogous to NaCl, sodium chloride.
$C_5H_{11}Cl$, amyl chloride, analogous to NaCl, sodium chloride.

Compounds derived from acids called ESTERS or COMPOUND ETHERS:

$C_2H_5NO_2$, ethyl nitrite, analogous to $NaNO_2$, sodium nitrite.
$C_5H_{11}C_2H_3O_2$, amyl acetate, analogous to $NaC_2H_3O_2$, sodium acetate.

The compounds analogous to the acid salts are sometimes called VINIC ACIDS:

$C_2H_5HSO_4$, sulphethylic or sulphovinic or ethylsulphuric acid, analogous to $KHSO_4$.

Hydroxides called Alcohols:

$CH_3OH$, methyl alcohol, analogous to $KOH$, potassium hydroxide
$C_2H_5OH$, ethyl alcohol.
$C_5H_{11}OH$, amyl alcohol.

Compounds containing two different radicles are called Mixed Ethers:

$(CH_3)(C_2H_5)O$, methylethyl ether.

Each compound here mentioned is a member of a homologous series.

In general, when alcohols are oxidised by a limited amount of oxygen, two atoms of hydrogen are removed and no oxygen is added. When oxidised in a free supply of oxygen, an atom of oxygen takes the place of the removed hydrogen. In this way is obtained:

$$\overset{\text{Ethyl alcohol}}{C_2H_5OH} + O = \overset{\text{Ethyl aldehyde.}}{C_2H_4O} + H_2O$$

$$C_2H_5OH + O_2 = \overset{\text{Acetic acid.}}{C_2H_4O_2} + H_2O$$

Thus each alcohol or hydroxide may be made to yield an *aldehyde* (from *al*cohol *dehyd*rogenatum) and an acid, each of these being one of a homologous series.

The series of acids is very important; many of them are obtained from fats and oils, hence have been called fatty-acids. The following table gives an outline of some of the important derivatives of this series. One atom of the hydrogen in the acid is replaceable by any positive element or radicle, so that it is generally written apart from the other atoms as in $HC_2H_3O_2$, *acetic acid.* In this table only a few of the esters are given.

Isomeric modifications are possible in these bodies, except with methyl, ethyl and some of their derivatives.

| Radicles. | Oxides, Ethers. | Hydroxides, Alcohols. | Aldehydes. | Acids. | Esters. |
|---|---|---|---|---|---|
| $CH_3$<br>Methyl. | $(CH_3)_2O$<br>Methyl ether. | $CH_3HO$<br>Methyl alcohol. | $CH_2O$<br>Methyl aldehyde.<br>Formaldehyde. | $HCOOH$<br>Formic acid. | $CH_3COOCH_3$<br>Methyl acetate. |
| $C_2H_5$<br>Ethyl. | $(C_2H_5)_2O$<br>Ethyl ether. | $C_2H_5HO$<br>Ethyl alcohol. | $C_2H_4O$<br>Ethyl aldehyde.<br>Acetaldehyde. | $CH_3COOH$<br>Acetic acid. | $C_2H_5NO_2$<br>Ethyl nitrite. |
| $C_3H_7$<br>Propyl. | $(C_3H_7)_2O$<br>Propyl ether. | $C_3H_7HO$<br>Propyl alcohol. | $C_3H_6O$<br>Propyl aldehyde. | $C_2H_5COOH$<br>Propionic acid. | $(C_3H_7)_2SO_4$<br>Propyl sulphate. |
| $C_4H_9$<br>Butyl. | $(C_4H_9)_2O$<br>Butyl ether. | $C_4H_9HO$<br>Butyl alcohol. | $C_4H_8O$<br>Butyl aldehyde. | $C_3H_7COOH$<br>Butyric acid. | $C_4H_9NO_3$<br>Butyl nitrate |
| $C_5H_{11}$<br>Amyl. | $(C_5H_{11})_2O$<br>Amyl ether. | $C_5H_{11}HO$<br>Amyl alcohol. | $C_5H_{10}O$<br>Amyl aldehyde. | $C_4H_9COOH$<br>Valeric acid. | $C_5H_{11}NO_2$<br>Amyl Nitrite. |

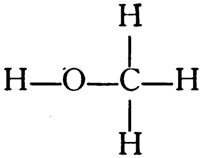
**Methods of Forming the Compounds of the Methyl Series.**—The starting point is generally the alcohols. The ethers, simple and compound, are produced by the action of acids on the alcohols. The aldehydes are produced by partial oxidation, the acids by complete oxidation; many of the acids exist ready formed in nature.

The alcohols will be described first. They are often called the monatomic alcohols, because they contain a monatomic (*i. e.*, monad) radicle.

CONSPECTUS OF MONATOMIC ALCOHOLS.

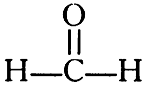
| FORMULA. | SYSTEMATIC NAME. | COMMON NAME. | SOURCE. |
|---|---|---|---|
| $CH_3OH$ | Methyl | Wood spirit | Distillation of wood. |
| $C_2H_5OH$ | Ethyl | Alcohol | Fermentation. |
| $C_3H_7OH$ | Propyl | Propyl alcohol | " |
| $C_4H_9OH$ | Butyl | Butyl " | " |
| $C_5H_{11}OH$ | Pentyl | Amyl "<br>Fusel oil | " |
| $C_6H_{13}OH$ | Hexyl | Caproic alcohol | |
| $C_7H_{15}OH$ | Heptyl | Ænanthic " | Action of KHO on castor oil. |
| $C_8H_{17}OH$ | Octyl | | From parsnip oil. |
| $C_9H_{19}OH$ | Nonyl | | |
| $C_{10}H_{21}OH$ | | | |
| $C_{12}H_{25}OH$ | | | |
| $C_{14}H_{29}OH$ | | | |
| $C_{16}H_{33}OH$ | Hexadecyl | Cetyl " | Spermaceti. |
| $C_{18}H_{37}OH$ | | | |
| $C_{30}H_{61}OH$ | | Triakontyl (myricyl alcohol) | Beeswax. |

*Methyl alcohol*, $(CH_3)HO$, *wood spirit*, is usually made by distilling wood. The crude material is purified to such an extent that it has very little odor and closely resembles ethyl alcohol in its physical properties. Pure methyl alcohol is a colorless, inflammable liquid of pleasant odor and soluble in water, ethyl alcohol, ether and glycerol. It boils at 66.5°. The effects on the animal system are so dangerous as to even prohibit its use in small proportions in making preparations intended for internal administration; the most prominent effect following its use is blindness, due to atrophy of the optic nerve. *Methylated spirit*, a mixture of 90 parts common alcohol with 10 parts of crude methyl alcohol, was formerly largely used in Great Britain as a tax-free substitute for ordinary alcohol, the presence of the methyl alcohol rendering it unfit for use in any preparations to be given internally.



$$H-O-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-H$$

Hydroxymethane
(Methyl alcohol, carbinol)



$$H-\overset{\overset{O}{\|}}{C}-H$$

Methyl aldehyde
(Formaldehyde)

The presence of methyl alcohol in ethyl alcohol may be determined as follows: The suspected sample (which may be first fractionally distilled) is diluted with water to reduce the strength to about 10 per cent. A copper spiral, made by winding copper wire closely around a lead pencil or similar cylindrical body, for a distance of about 5 c.c., is heated to redness and plunged into the diluted alcohol; this operation is repeated five or six times, after which the liquid is gently boiled for a few minutes and filtered if necessary. The effect of the heated copper spiral is to reduce both the ethyl and methyl alcohols to the corresponding aldehydes. The ethyl aldehyde being more volatile is removed by boiling after which the remaining liquid may be tested for the presence of formaldehyde by any of the standard methods. This process will detect as small a quantity as 2 per cent. of methyl alcohol in ethyl alcohol.

*Ethyl alcohol*, $(C_2H_5)HO$, *common alcohol, grain alcohol, spirit of wine*, is produced in the vinous fermentation of sugar, carbon dioxide being the only other product formed in large amount; it can also be prepared synthetically. The fermented spirit is concentrated by distillation in a rectifying still and column, but the strongest thus prepared contains about 5 per cent. of water and constitutes the ordinary alcohol of commerce. To withdraw all water it is necessary to distil with quicklime, anhydrous copper sulphate or calcium chloride, by which *absolute alcohol* is formed.

*Alcohol* is a colorless, transparent, inflammable liquid, of a faint but characteristic odor and a sharp burning taste, sp. gr. about 0.825, boiling point 78°. It is soluble in all proportions in water, ether and glycerol and is largely used as a solvent. *Absolute alcohol* is a slightly better solvent than ordinary alcohol for some volatile oils and resins. It attracts moisture so readily from the air that it is difficult to preserve it in the absolute condition.

Proof-spirit contains, by weight, 50.8 parts of absolute alcohol to 49.2 of water and has a sp. gr. of 0.920. *Alcohol* is contained in wine, beer and spirits. Whisky, brandy and other spirits contain from 40 to 50 per cent. of alcohol; wines, from 17 (port and madeira) to 7 or 8 (hock and light clarets) per cent.; porter and strong ale contain from 6 to 8 per cent., lager beer about 3.5 per cent.; the mild fermented liquors known as mead, root-beer, spruce-beer, contain from ½ to 1 per cent. The effervescence of fermented liquids is due to the carbon dioxide which is produced with alcohol:

$$C_6H_{12}O_6 \text{ breaks up into } \overset{\text{Alcohol.}}{2C_2H_6O} + 2CO_2$$

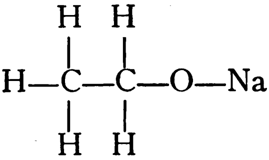
The carbon dioxide in sparkling alcoholic beverages, is retained by bottling the liquid before the fermentation is over.

In the production of alcohol by fermentation other substances are formed, some of which contaminate the product even after repeated distillation. One of these, known as *fusel oil*, consists of a mixture of several of the higher members of the same homologous series. The presence of this impurity is usually determined by the characteristic odor which is left on filter paper after a small quantity of the alcohol has been allowed to evaporate from it. Aldehyde, which is an oxidation product of alcohol; is sometimes present and may be detected by the brown color which it produces with a solution of potassium hydroxide.

*Experiment* 4.—Place about 5 c.c. of absolute alcohol in one testtube and about 5 c.c. of ordinary alcohol in another testtube. Add about 0.5 gram of anhydrous copper sulphate to each and note the difference in the effect.

*Experiment* 5.—Dissolve about 100 grams of cane sugar in 1000 c.c. of water and place the solution in a large bottle or wide-mouthed jar. Add to this solution about one-fourth of a cake of compressed yeast and stand the mixture aside for fermentation to take place. When the fermentation is complete, which may be known by no more bubbles of carbon dioxide being given off, transfer the solution to a large distilling flask and collect about 100 c.c. of the first distillate which comes over. Test this distillate for alcohol by means of the iodoform reaction.

*Sodium ethylate* is obtained by the action of sodium upon alcohol. The substitution takes place rapidly, hydrogen being evolved, but only the hydroxyl group is attacked. The resulting compound is a solid, very soluble in water and alcohol, and corrosive. It saponifies fats more rapidly than an aqueous solution of sodium hydroxide.



$$\begin{array}{ccccccccc} & & H & & H & & & & \\ & & | & & | & & & & \\ H & — & C & — & C & — & O & — & Na \\ & & | & & | & & & & \\ & & H & & H & & & & \end{array}$$

Sodium ethylate
(Sodium ethoxide)

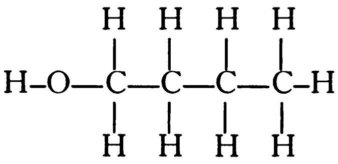
*Amyl alcohol*, *Pentyl alcohol*, $C_5H_{11}HO$.—Eight isomers, four primary, three secondary and one tertiary (see below) are possible; all have been obtained. Several have asymmetric carbon. Some of the amyl alcohols are by-products in vinous fermentations and hence are found in alcoholic beverages. They are especially noticeable in the fermented liquor from potato starch (hence the name "amyl" alcohol, from a Greek word for starch). These alcohols may be separated in part by distillation. The mixture of them thus obtained is known commercially as "fusel oil." It is supposed to be very poisonous and to give very injurious properties to liquors containing even small amounts, but these points are not established. The pure amyl alcohols are colorless liquids, nearly insoluble in water and of a hot, acrid taste.

The higher alcohols are mostly oily liquids or wax-like solids.

*Isomeric Forms of Alcohols.*—Methyl and ethyl alcohols present only one form, but a number of isomers of the higher alcohols have been obtained. Comparison of these isomers has led to their division, according to an assumed arrangement of the carbon atoms, into three groups, primary, secondary and tertiary alcohols.

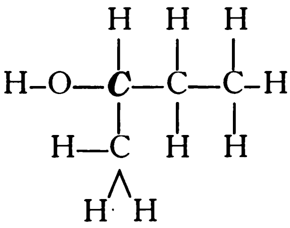
Primary alcohols contain the group $CH_2OH$ joined to *one* alcohol radicle; secondary alcohols contain the group CHOH joined to *two* radicles; and tertiary alcohol contains the group COH, joined to *three* radicles.

Illustrations of these principles are found in the structural formulas of the three butyl (tetryl) alcohols. The secondary form contains asymmetric carbon indicated by italic symbol:

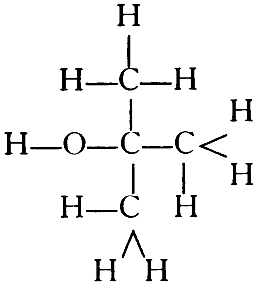


$$\begin{array}{ccccccccccc} & & & & H & & H & & H & & H & \\ & & & & | & & | & & | & & | & \\ H & - & O & — & C & — & C & — & C & — & C & - & H \\ & & & & | & & | & & | & & | & \\ & & & & H & & H & & H & & H & \end{array}$$

Primary butyl alcohol



Secondary butyl alcohol



Tertiary butyl alcohol

## ETHERS.

The primary alcohols, by the action of bodies which have an affinity for water (sulphuric and phosphoric acids), are converted into oxides, called ethers. A *compound* *ether* or *ester* is the replacement of the hydrogen of an acid by one or more molecules of a hydrocarbon. The only simple ether of any importance is:

*Ethyl oxide*, $(C_2H_5)_2O$, ether, often wrongly called sulphuric ether, made by the action of sulphuric acid upon alcohol. Acid ethylsulphate is first formed and then decomposed:

$$\underset{\text{Alcohol.}}{(C_2H_5)HO} + H_2SO_4 = \underset{\text{Acid ethylsulphate.}}{(C_2H_5)HSO_4} + H_2O$$

Another molecule of alcohol is then acted upon, thus:

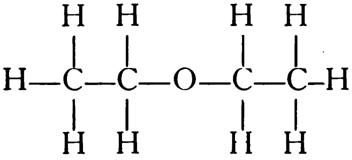
$$(C_2H_5)HO + (C_2H_5)HSO_4 = H_2SO_4 + \underset{\text{Ether.}}{(C_2H_5)_2O}$$

It will be seen from these reactions that in theory the sulphuric acid is continuously re-generated. This is not true in practice on account of reactions between the sulphuric acid and the impurities in the alcohol.

Ether is a colorless mobile, very volatile liquid, of a characteristic odor, boiling at 37°. Sp. gr. 0.723. Its vapor is inflammable and very heavy. It is insoluble in water, soluble in alcohol and is a solvent for fats, fixed and volatile oils, resins and many other proximate principles. Its vapor is anesthetic.

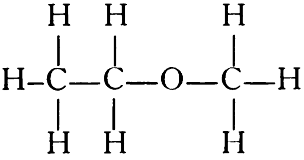
*Experiment* 6.—Warm a beaker of about 250 c.c. capacity slightly in the flame of a bunsen burner; pour into it a few c.c. of ether and cover the beaker with a watch glass for a few moments. Take another beaker of the same size and, having removed the watch glass, invert the beaker containing the ether vapor over the empty beaker, with a motion similar to that used in pouring liquids from one vessel to another. Test the vapor in the second beaker for inflammability, using a lighted taper. This shows that the vapor of ether is considerably heavier than atmospheric air.

The molecular structure of simple and mixed ethers is illustrated by the annexed formulas:



$$\begin{array}{ccccccccccccc} & & H & & H & & & & H & & H & & \\ & & | & & | & & & & | & & | & & \\ H & — & C & — & C & — & O & — & C & — & C & - & H \\ & & | & & | & & & & | & & | & & \\ & & H & & H & & & & H & & H & & \end{array}$$

Ethyl ether.



$$\begin{array}{ccccccccccc} & & H & & H & & & & H & & \\ & & | & & | & & & & | & & \\ H & - & C & — & C & — & O & — & C & — & H \\ & & | & & | & & & & | & & \\ & & H & & H & & & & H & & \end{array}$$

Methylethyl ether.

*Heavy oil of wine* is a by-product in the manufacture of ether and consists of a mixture of sulphuric esters of the hydrocarbons. When mixed with an equal volume of ether it constitutes *ethereal oil* which is one of the constituents of the official *compound spirit of ether* (*Spiritus ætheris compositus*), commonly known as *Hoffman's anodyne.*

**Esters, Compound Ethers.**—Many of these have characteristic odors and are the flavoring materials of flowers and fruits. They can be made synthetically.

The usual method of preparation is to heat a mixture of the sodium salt of the proper acid, the alcohol containing the proper radicle and sulphuric acid. Thus to produce ethyl acetate, sodium acetate, ethyl alcohol and sulphuric acid are used:

$$C_2H_5HO + NaC_2H_3O_2 + H_2SO_4 = C_2H_5C_2H_3O_2 + NaHSO_4 + H_2O$$

Mixtures of esters are used as imitation flavors. The following are the more important:

*Methyl acetate*, $CH_3C_2H_3O_2$, is a colorless liquid used as a solvent. In association with acetone, it dissolves pyroxylin.

*Methyl salicylate* $C_6H_4OHCOOCH_3$ constitutes the greater portion of oil of wintergreen and oil of birch.

*Ethyl acetate*, $C_2H_5C_2H_3O_2$, is a colorless liquid of a characteristic agreeable fruity odor. It is largely used in compounding fruit essences.

*Ethyl butyrate*, $C_2H_5C_4H_7O_2$, is also largely used in artificial flavoring extracts.

*Ethyl bromide*, $C_2H_5Br$, is an anesthetic.

*Ethyl nitrite*, $C_2H_5NO_2$, is the active ingredient of the official spirit of nitrous ether, commonly known as sweet spirit of nitre. (*Spiritus ætheris nitrosi.*)

*Amyl nitrite*, $C_5H_{11}NO_2$, is made by the action of nitric acid upon amyl alcohol. It is a yellowish liquid, of well-marked odor, boiling at 96°. It is used in medicine by inhalation, for the relief of angina pectoris.

*Amyl acetate*, $C_5H_{11}C_2H_3O_2$, is another of the esters largely used in compounding artificial fruit flavors. It is also used as a solvent, especially in preparing the lacquering solutions and the so-called pyroxylin varnishes.

*Experiment* 7.—In a tubulated retort place 5 grams of red phosphorus and 25 c.c. of absolute alcohol. Connect the retort with a well-cooled condenser. and insert a separatory funnel provided with a glass stop-cock through the tubulure of the retort, making a tight joint by means of a rubber stopper. Place 25 grams of bromine in the separatory funnel, and, having ascertained that all the connections are perfect, allow the bromine to flow into the mixture of red phosphorus and alcohol drop by drop. After allowing the flask to stand for several hours, apply a gentle heat to the flask and collect the *ethyl bromide* (bromethane) which distils over. Wash the distillate with water in a separatory funnel; dry it by adding calcium chloride and allowing it to stand; then redistil and make notes of the boiling point, odor and specific gravity.

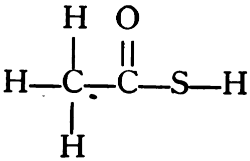
*Experiment* 8.—Mix equal quantities of alcohol and acetic acid in a testtube, cautiously add a little concentrated sulphuric acid and warm the mixture gently. The fragrant odor of *ethyl acetate* will be observed. This reaction may be used as a test for the presence of either acetic acid or alcohol.

*Experiment* 9.—Dissolve about one gram of sodium nitrite in 2 c.c. of water in a testtube. Add about 1 c.c. of alcohol and then cautiously pour in a mixture, previously made, of 1 c.c. of sulphuric acid and 2 c.c. of water. The vapor of ethyl nitrite ($C_2H_5NO_2$) is evolved, which may be recognised by the fragrant ethereal odor resembling apples.

*Experiment* 10.—Cautiously mix equal volumes, 5 c.c., of concentrated sulphuric acid and alcohol and dilute the mixture with about ten times its bulk of water. Add barium carbonate in small portions until effervescence ceases and the liquid is neutral. Filter and examine the clear filtrate for barium. This is a soluble compound of barium with sulphuric acid, called barium ethylsulphate, $Ba(C_2H_5SO_4)_2$.

**Sulphur Alcohols, Mercaptans.**—The oxygen of organic bodies, as of inorganic bodies, may be replaced by any other element of the oxygen group. Ethyl alcohol, for instance, has a corresponding sulphur compound, $C_2H_5HS$, called *mercaptan*. This is a condensation of a Latin phrase meaning "to take mercury" on account of its action on that element. The proper name is ethyl hydrosulphide. The mercaptans when oxidised form sulphonic acids which will be taken up later. Corresponding ethers also are known; thus $(C_2H_5)_2S$, ethyl sulphide. These derivatives are mostly strong-smelling and irritating compounds. A few of them exist ready-formed in the secretions of animals and plants. The essential oils of mustard, garlic and horseradish are examples, and are noticed elsewhere.

When the oxygen of carboxyl is replaced by sulphur the prefix "thio" is generally employed. The following structural formula shows one of the positions of the sulphur atom. These bodies are, as exemplified by those just mentioned, mostly of strong, disagreeable odor.



$$\begin{array}{ccccccccc} & & H & & O & & & & \\ & & | & & \| & & & & \\ H & - & C & - & C & - & S & - & H \\ & & | & & & & & & \\ & & H & & & & & & \end{array}$$

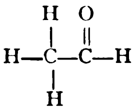
Thiacetic acid

When both atoms of oxygen are replaced the prefix "dithio" is used.

**Aldehydes.**—These compounds are formed by the removal of two atoms of hydrogen from the corresponding alcohols, and stand intermediate between the alcohols and the acids.

*Ethyl aldehyde*, *ethanal*, usually called *acctic aldehyde*, or simply *aldehyde*, $C_2H_4O$, is often present in liquors, especially in raw forms of commercial spirits, and probably gives to such articles some injurious qualities. It is a colorless, volatile liquid, lighter than water, and boiling at 21°, having a powerful affinity for oxygen, and therefore a reducing action. It presents several isomeric modifications, one of which, *paraldehyde*, a polymeric form, to which the formula $C_6H_{12}O_3$ has been assigned, has hypnotic properties. All the aldehydes of the series form complicated compounds, as yet of little practical value.

The structural formula of common aldehyde is:



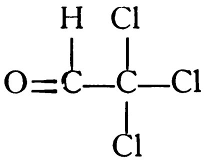
$$\begin{array}{ccccccc} & & H & & O & & \\ & & | & & \| & & \\ H & - & C & - & C & - & H \\ & & | & & & & \\ & & H & & & & \end{array}$$

It will be noted that no hydroxyl is present, and hence aldehyde has neither acid nor basic properties.

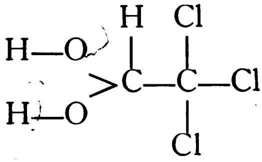
*Chloral.*—The substitution of three atoms of hydrogen in aldehyde, by chlorine, produces a colorless liquid heavier than water (sp. gr. 1.18), and boiling at 94°. This is trichloraldehyde, $C_2HCl_3O$, chloral. It combines with one molecule of water to form a crystalline, pungently-smelling solid, soluble in water, which is now used under the name of chloral hydrate. In alkaline solution chloral is decomposed as shown in the following equation:

$$\overset{\textbf{Chloral.}}{C_2HCl_3O} + \overset{\textbf{Sodium Hydroxide.}}{NaHO} = \overset{\textbf{Sodium Formate.}}{NaCHO_2} + \overset{\textbf{Chloroform.}}{CHCl_3}$$

The so-called chloral hydrate (*chloral*) is trichlorethene glycol, $C_2HCl_3(HO)_2$. It is a hypnotic and sedative. It is often used for drugging liquor to assist in the commission of robbery or rape. It is decomposed by alkalies in the same manner as chloral.



Trichloraldehyde (chloral)



(So-called) Chloral hydrate

If a few grams of chloral hydrate in a narrow testtube be covered by strong sulphuric acid, the mixture will soon form in two layers; the upper one is *chloral*, formed by dehydrolysis.

*Experiment* 11.—Dissolve about 1 gram of potassium dichromate in about 10 c.c. of water and add an equal volume of alcohol. Cautiously add about 3 c.c. of concentrated sulphuric acid, note the change in the appearance of the liquid and observe the odor given off. The odor is that of aldehyde and the green color of the liquid indicates that the potassium dichromate has been reduced to chromic sulphate.

*Experiment* 12.—Prepare formaldehyde from methyl alcohol, by the process given on page 62, under the test for methyl alcohol in ethyl alcohol.

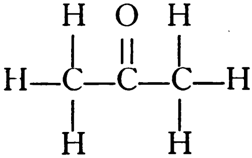
*Experiment* 13.—Dissolve 0.1 gram of silver nitrate in distilled water; add solution of sodium hydroxide, drop by drop, until no more precipitate forms, and then add ammonium hydroxide until the solution becomes clear. Clean a testtube thoroughly by washing it with soap, by the aid of the testtube brush or swab, and rinsing well with water. Pour in the prepared silver solution, add a few drops of aldehyde (or paraldehyde) and immerse the tube in boiling water. Silver will be set free by the reducing action of the aldehyde. If the tube is clean, a mirror will be formed on the glass, but otherwise the precipitate will be loose and black.

*Formaldehyde*, $CH_2O$, has much practical as well as theoretic interest. It is produced by the action of heated copper oxide upon the vapor of methyl alcohol. It is a powerful antiseptic, preserving thoroughly many perishable articles. The use of formaldehyde in preserving articles of food and drink is forbidden by law, as it forms insoluble compounds with many proteid substances, and therefore affects the digestibility of the substances thus preserved. It is also a powerful reducing agent. Formaldehyde is considered by plant physiologists as the starting-point in the formation of the so-called "carbohydrates" of the vegetable kingdom. Its formula multiplied by five gives $C_5H_{10}O_5$, pentose, forms of which are common in plants, and by easy changes may produce the sugars and starches. The commercial formaldehyde (formalin) consists of a 40 per cent. solution of the gas in water. This solution readily polymerises with the formation of paraformaldehyde, $C_3H_6O_3$, which upon strongly heating again decomposes into formaldehyde, $CH_2O$.

**Ketones.**—By the destructive distillation of calcium acetate, a body called *acetone*, $C_3H_6O$, is formed, differing from aldehyde, $C_2H_4O$, by $CH_2$.

$$(CH_3COO)_2Ca = CH_3COCH_3 + CaCO$$

*Acetone* is the type of a group termed *ketones*. They contain carbonyl, CO, united to two monad radicles. They are reducing agents, form "osazones" (see page 100) and form compounds with sulphites.



$$\begin{array}{ccccccc} & H & & O & & H & \\ & | & & \| & & | & \\ H- & C & - & C & - & C & -H \\ & | & & & & | & \\ & H & & & & H & \end{array}$$

Acetone
(Dimethyl ketone)

Acetone is produced in the destructive distillation of wood and is used as a solvent in many technical processes. It is a colorless, transparent liquid, of a characteristic, ethereal odor, soluble in all proportions in water, alcohol and ether and resembling the latter liquid in its solvent effect on fats, oils and waxes. It is also used as a solvent for pyroxylin.

*Experiment* 14.—Prepare a saturated solution of sodium acid sulphite in water, and shake this with an equal volume of acetone. A sulphite compound will be formed and precipitate in the strong solution, but will be dissolved on addition of water.

## FATTY-ACIDS.

This term, applicable strictly to only a few of the series, is applied to the homologous bodies derived from the alcohols by substitution of two atoms of hydrogen by one atom of oxygen. It is an extensive and important class; nearly all are natural products. The fixed oils and fats yield some of the higher members of the series. Some have been produced synthetically by a reaction, of which the following is a type:

$$\underset{\text{Ethyl alcohol.}}{C_2H_6O} + O_2 = \underset{\text{Acetic acid.}}{C_2H_4O_2} + H_2O$$

Each of the acids so produced contains one carboxyl group, COOH, the hydrogen of which can be replaced by a positive element or radicle, and this fact may be shown by writing each formula with the carboxyl distinguished. The lower members of the series are freely soluble in, and miscible with water, strongly acid and irritating, but as the quantity of carbon and hydrogen increases, the compounds become more and more oily, and the higher members are fatty, feebly acid, insoluble in water, but soluble in alcohol and ether.

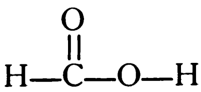
**Formic Acid,** HCOOH, was originally obtained by distilling the liquid in which the bodies of a species of ant (Lat., *formica*) had been macerated. It can be prepared in quantity by heating oxalic acid with glycerol. Glycerol-formic ester is produced and then decomposed. The equation shows that hydrolysis and dehydrolysis occur.

$$C_3H_5(HO)_3 + (COOH)_2 = C_3H_5(HO)_2CHO_2 + CO_2 + H_2O$$
$$C_3H_5(HO)_2CHO_2 + H_2O = HCOOH + C_3H_5(HO)_3$$

The glycerol being reproduced, a small amount will suffice for the conversion of much oxalic acid. Formic acid is supposed to exist in the secretions of some stinging animals and plants.

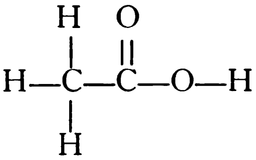
*Experiment* 15.—Place about 10 c.c. of glycerol in a testtube with about 3 grams of oxalic acid and apply heat gradually, by means of a bunsen burner, taking care not to raise the temperature much above the boiling point of water. Test the vapors occasionally with moistened blue litmus paper and when acid vapors are evolved, cautiously note the pungent, irritating odor which is due to formic acid.

Although formic acid has a higher percentage of oxygen than any other member of its series, it has the greatest reducing power. This is mainly because it contains an aldehydic structure, the group HCO, which is not the case with the other normal fatty-acids. The structural formula in comparison with that of acetic acid shows this point:



$$H-\overset{\overset{\displaystyle O}{\|}}{C}-O-H$$

Formic acid



$$H-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle O}{\|}}{C}-O-H$$

Acetic acid

Formic acid is a colorless, highly irritating liquid.

**Acetic Acid,** $CH_3COOH$.—This occurs in small quantities in animal and plant juices. In the dilute form it constitutes vinegar, which contains from 3 to 6 per cent. of the acid, and is usually made by oxidising very weak alcohol in the presence of a ferment. Acetic acid is also produced in the distillation of wood. The first distillate is, in this case, generally contaminated with tar and phenol-compounds and is called pyroligneous acid. It is used commercially in preserving meats, and is often sold under the name "Liquid Smoke." Pure acetic acid is a colorless, corrosive liquid, solidifying at 17° (hence often called "*glacial acetic acid*"), and boiling at 119°. The dilute forms are less active, and in vinegar its effects are quite mild.

ACETATES.—The most important of these are:

*Potassium acetate*, $KC_2H_3O_2$, a deliquescent salt, much used in medicine as a diuretic.

*Sodium acetate*, $NaC_2H_3O_2$, which forms efflorescent crystals, containing $3H_2O$.

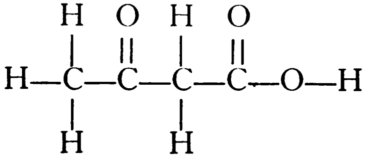
*Ammonium acetate*, $(NH_4)C_2H_3O_2$, is used in medicine in the form of a freshly prepared solution in water, called spirit of Mindererus. (*Liquor ammonii acetatis.*)

*Lead acetate*, $Pb(C_2H_3O_2)_2$, *sugar of lead*, made by dissolving lead monoxide in acetic acid, forms white crystals, soluble in water. By boiling this solution with lead monoxide, a considerable amount of the latter is dissolved, and the *subacetate*, more correctly oxyacetate, is formed, called *Goulard's extract*, in concentrated solution (*Liquor plumbi subacetatis*), and when much diluted, *Lead water* (*Liquor plumbi subacetatis dilutus*).

*Copper acetate*, $Cu(C_2H_3O_2)_2$, is not important; but an irregular and variable compound of it with copper hydroxide, known as *verdigris*, is made by exposing alternate layers of sheet copper and refuse grape skins to the air; ethyl alcohol is formed and then converted into acetic acid which acts on the copper.

*Zinc acetate*, $Zn(C_2H_3O_2)_2+2H_2O$, is a white efflorescent salt which is used as an astringent.

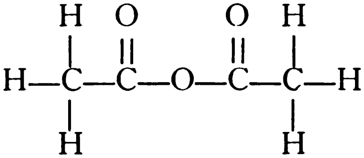
A derivative of acetic acid, *acetoacetic acid*, the structural formula of which is given, is of some theoretic interest. Its ethyl ester, obtained by the action of sodium upon ethyl acetate, the hydrogen of the carboxyl being replaced by ethyl has, contrary to what theory indicates, acid qualities and takes up sodium in exchange for a hydrogen atom that is in union with carbon. The reason for this unusual action has not been ascertained, but there is probably tautomerism in the formula.



$$\begin{array}{ccccccccccccc}
 & & H & & O & & H & & O & & & & \\
 & & | & & \| & & | & & \| & & & & \\
H & - & C & - & C & - & C & - & C & - & O & - & H \\
 & & | & & & & | & & & & & & \\
 & & H & & & & H & & & & & &
\end{array}$$

Acetoacetic acid

*Acetic anhydride*, $(C_2H_3O)_2O$, used in some analytic and research operations, is obtained by distilling anhydrous sodium acetate with phosphoric oxychloride. Structurally, it resembles the ethers, but acid radicles, not hydrocarbons, are united by oxygen.



Acetic anhydride

HOMOLOGOUS SERIES OF FATTY-ACIDS.

| Common Name. | Empirical Formula. | Properties. | Natural Source. |
|---|---|---|---|
| Formic..... | $CH_2O_2$ | Colorless volatile liquid. | In red ants and some other insects and in some stinging plants. |
| Acetic...... | $C_2H_4O_2$ | Colorless pungent liquid. | Oxidation of alcohol and sugar. |
| Propionic... | $C_3H_6O_2$ | Crystalline solid. | |
| Butyric..... | $C_4H_8O_2$ | Colorless liquid of disagreeable odor. | Butter and other animal secretions. |
| Valeric..... | $C_5H_{10}O_2$ | Colorless liquid of disagreeable odor. | Valerian root. |
| Caproic .... | $C_6H_{12}O_2$ | Colorless oily body. | Butter and coconut oil. |
| Enanthylic.. | $C_7H_{14}O_2$ | Slightly soluble in water; has an agreeable odor. | Oxidation of castor oil. |
| Caprylic.... | $C_8H_{16}O_2$ | | Butter, coconut and castor oils. |
| Pelargonic.. | $C_9H_{18}O_2$ | Crystalline solid. | Geranium leaves. |
| Capric ..... | $C_{10}H_{20}O_2$ | Crystalline mass having the odor of sweat. | Butter and coconut oil. |
| Lauric ..... | $C_{11}H_{22}O_2$ | Silky crystals. | In coconut oil. |
| Myristic.... | $C_{14}H_{28}O_2$ | Crystalline scales. | In nutmeg and coconut oil. |
| Palmitic.... | $C_{16}H_{32}O_2$ | Fat-like solid. | Most natural fats. |
| Margaric... | $C_{17}H_{34}O_2$ | " " | |
| Stearic..... | $C_{18}H_{36}O_2$ | " " | " " " |
| Arachidic... | $C_{20}H_{40}O_2$ | White crystalline fatty solid. | Peanut oil. |
| Behenic .... | $C_{22}H_{44}O_2$ | " " " " | Oil of ben. |
| Hyenic..... | $C_{25}H_{50}O_2$ | 'Resembles cerotic. | |
| Cerotic..... | $C_{27}H_{54}O_2$ | Crystallises in small grains. | Free in beeswax. |
| Mellissic.... | $C_{30}H_{60}O_2$ | | Derived from beeswax. |

**Butyric (Tetrylic) Acid,** $C_3H_7COOH$.—This may be obtained from butter-fat, from some fruit flavors, and by fermentation of sugar with cheese and chalk. It is a colorless liquid having the disagreeable odor of rancid butter. Ethyl butyrate is produced by heating butter-fat with alcoholic solution of sodium hydroxide. The reaction is not known.

**Valeric (Pentylic) Acid,** $C_4H_9COOH$, is found in valerian root and in other plants. Four isomeric modifications are possible. The ordinary form is a colorless liquid of a disagreeable odor. Several valerates, often called valerianates, are used in medicine; among these are those of zinc and ammonium.

**Stearic Acid,** $HC_{18}H_{35}O_2$, can be obtained from most of the solid animal fats, and from some vegetable fats. It is a white, crystalline body which can be distilled. It is insoluble in water, slightly soluble in alcohol. The white candles called stearin are generally made of stearic acid. Its only use in medicine is with sodium carbonate, with which it forms a soap, a vehicle for the administration of glycerol in suppositories.

**Salts of Fatty-Acids Soaps.**—By substituting the single atom of replaceable hydrogen of the fatty-acids a series of bodies is obtained all of which might be called "soaps," but it is only with the higher members of the series that the peculiar physical and chemical characters of the soaps are noticeable. The derivatives of the lower members are generally soluble in water, but in the higher members most of the compounds are insoluble, except those formed by potassium, sodium and ammonium. Lead, calcium and zinc, for instance, form insoluble soaps.

The soluble soaps are those which are valuable for their detergent properties. When sodium hydroxide is used in combination with olive oil, a "castile" soap is produced which is a hard soap. Potassium hydroxide produces the so-called soft-soaps; the official soft or green soap (*Sapo mollis*), being made from potassium hydroxide and linseed oil. Among the insoluble soaps which are of common occurrence may be mentioned: Lead plaster which is lead oleo-stearate, made by saponifying olive oil with lead oxide, glycerol being obtained as a by-product. The so-called Carron oil, made by adding lime water (solution of calcium hydroxide) to linseed oil is an insoluble calcium soap formed with the fatty-acids of linseed oil.

## SUBSTITUTION DERIVATIVES OF THE FATTY-ACIDS.

The hydrogen that is part of the radicle of these acids may be substituted by members of the chlorine group, particularly by chlorine itself. From acetic acid we get three compounds, which resemble the original acid:

| | |
|---|---|
| $HC_2H_3O_2$ | Acetic acid. |
| $HC_2H_2ClO_2$ | Monochloracetic acid. |
| $HC_2HCl_2O_2$ | Dichloracetic acid. |
| $HC_2Cl_3O_2$ | Trichloracetic acid. |

These compounds are usually obtained by the direct action of chlorine. By indirect means, the use of phosphoric chloride, $PCl_5$, for instance, the chlorine may be made to replace the hydroxyl of the acid; in this manner the acid properties are removed, and chlorides formed with the acid radicles. Acetic acid gives the following:

$$\overset{\text{Acetic acid.}}{CH_3COOH} + PCl_5 = \overset{\text{Acetyl chloride.}}{CH_3COCl} + POCl_3 + HCl$$

Similar compounds may be obtained with bromine.

## Olefins or Methene Series.

*Methene*, the first member of the series, has not yet been obtained. *Ethene*, $C_2H_4$, *ethylene*, the second member of this series, was called, when first discovered, olefiant (oil-making) gas, because it combines with chlorine to form an oily liquid; for this reason the series has been called the *olefins*. They are dyad radicles, which form alcohols, ethers and other derivatives; but these derivatives are greater in number than from monad radicles, on account of the higher valency. Two series of acids are yielded by the action of oxygen on the alcohol, instead of one, as in the case of the monad radicles.

The ratio between the weights of the hydrogen and carbon is the same in all members of the series, hence the percentage composition is the same, but the molecular weight increases. The members of the series are polymeric isomers.

Derivatives of Olefins.—The olefins combine directly with the halogens. Ethene dichloride $C_2H_4Cl_2$, was originally called *Dutch liquid*, because discovered by an association of Dutch chemists.

By indirect means, oxides esters and hydroxides may be formed. The hydroxides contain two molecules of HO and are known as Diatomic Alcohols or Glycols. Each of these alcohols yields by oxidation *two* acids, one derived by the replacement of two atoms of hydrogen by one atom of oxygen, and the other by the replacement of four atoms of hydrogen by two atoms of oxygen. The first is the *lactic acid* series; the second, the *oxalic acid* series. For instance, ethene glycol gives the following:

$$C_2H_4(HO)_2 + O_2 = H_2O + \overset{\text{Glycolic acid.}}{HOCH_2COOH}$$

$$C_2H_4(HO)_2 + O_4 = H_2O + \overset{\text{Oxalic acid.}}{COOHCOOH}$$

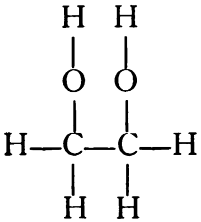
Oxalic acid is, therefore, dicarboxyl. Methene glycol, $CH_2(HO)_2$, has not been obtained. By oxidation it could form but one acid, carbonic, $(HO)_2CO$, which may be regarded as the first member of the first series.

| Radicle. | Oxides, Ethers. | Hydroxides, Alcohols. | Acids by first oxidation. | Acids by second oxidation. |
|---|---|---|---|---|
| $C_2H_4$ | $C_2H_4O$ | $C_2H_4(HO)_2$ | Glycolic acid.<br>$C_2H_4O_3$ | Oxalic acid.<br>$C_2H_2O_4$ |
| $C_3H_6$ | $C_3H_6O$ | $C_3H_6(HO)_2$ | Lactic acid.<br>$C_3H_6O_3$ | Malonic acid.<br>$C_3H_4O_4$ |
| $C_4H_8$ | $C_4H_8O$ | $C_4H_8(HO)_2$ | Oxybutyric acid.<br>$C_4H_8O_3$ | Succinic acid.<br>$C_4H_6O_4$ |

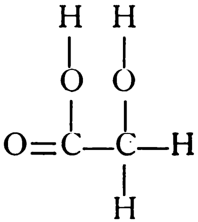
The acids of the first series, containing one molecule of alcoholic hydroxyl and one molecule of carboxyl, are called hydroxy-acids.

*Ethene oxide*, $C_2H_4O$, is isomeric (more accurately, metameric), with common aldehyde. It is a three-membered closed chain, the oxygen atom being one member of the chain (see under "Heterocyclic" compounds).

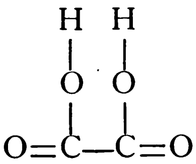
The structural relations of ethene (ethylene) glycol and its two acid derivatives, together with two important salts of oxalic acid are shown in the annexed formulas:



Ethene glycol
(Dihydroxyethane)

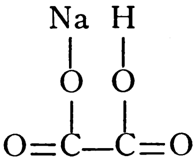


Glycolic acid.



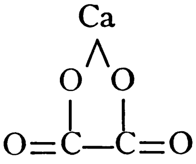
$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ & & O & & O & & \\ & & | & & | & & \\ O & = & C & — & C & = & O \end{array}$$

Oxalic acid
(Dicarboxyl)



$$\begin{array}{ccccccc} & & Na & & H & & \\ & & | & & | & & \\ & & O & & O & & \\ & & | & & | & & \\ O & = & C & — & C & = & O \end{array}$$

Acid sodium oxalate



$$\begin{array}{ccccccc} & & & Ca & & & \\ & & / & & \backslash & & \\ & & O & & O & & \\ & & | & & | & & \\ O & = & C & — & C & = & O \end{array}$$

Calcium oxalate

**Acid Derivatives of the Glycols.**—These are the most important. The first (lactic) series is monobasic, that is, has a single atom of replaceable hydrogen; the second (oxalic series) is dibasic, that is, has two atoms of replaceable hydrogen.

LACTIC SERIES.

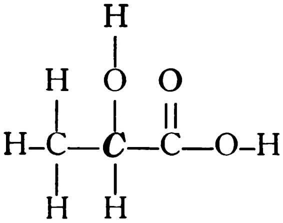
| Name. | Formula. | Source. |
|---|---|---|
| Glycolic.......... | $C_2H_4O_3$ | By oxidation of ethene glycol. |
| Lactic ........... | $C_3H_6O_3$ | By fermentation of milk sugar. |
| Oxybutyric...... | $C_4H_8O_3$ | By oxidation of butyric acid. |
| Oxyvaleric ...... | $C_5H_{10}O_3$ | By oxidation of valeric acid. |
| Leucic ........... | $C_6H_{12}O_3$ | Occurs in animal products; also formed by decomposition of horn and glue. |

Glycolic acid is found in unripe grapes. It is of no commercial importance.

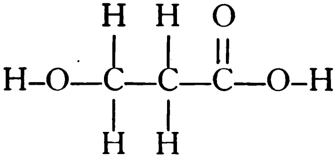
**Lactic Acid,** $(HO)C_2H_4(COOH)$.—This important acid exists in four modifications.

*Ordinary lactic acid* is a product of fermentation of milk sugar and is therefore found in sour milk and koumyss. It is a colorless, syrupy, very sour liquid, which has not yet been obtained in the solid state. It can be obtained in quantity by allowing a mixture of cane sugar, cheese, sour milk and chalk, or zinc oxide to ferment for several days. The resulting calcium or zinc lactate can be purified and lactic acid obtained from it. It is optically inactive, but consists of equal parts of dextro- and levorotatory forms, which can be separated by several methods. Such separation of isomers is termed "mesotomy" (*Gr.* cutting midway). Dextrolactic acid occurs in the juice of flesh and is sometimes called sarkolactic acid.

*Ethene-lactic* acid is obtained synthetically by several methods. It is optically inactive. The following formulas show the stereochemistry of these compounds. Asymmetric carbon is present only in one arrangement.



Active lactic acid
Paralactic and ordinary lactic acid
(Ethylidene lactic acid)



$\mathrm{H{-}O{-}CH_2{-}CH_2{-}C({=}O){-}O{-}H}$

Ethene-lactic acid
(Ethylene lactic acid)

d + 1 = lactic acid of fermentation

Several lactates are used in medicine particularly ferrous lactate and strontium lactate. Lactic acid is one of the products of the growth of fungi around the teeth, and is an important factor in dental caries. When lactic acid is heated in dry air, several anhydrides are formed as follows:

$$2C_3H_6O_3 - H_2O = C_6H_{10}O_5, \text{ lactic anhydride}$$
$$C_6H_{10}O_5 - H_2O = C_6H_8O_4, \text{ lactide}$$

Lactide is a stable compound.

*Experiment* 16.—To 5 c.c. of a dilute aqueous solution of phenol add ferric chloride to obtain the characteristic violet reaction. Add to this solution a single drop of *lactic acid* and observe that the color of the solution changes from violet to a bright canary-yellow. This is *Uffelmann's reaction* for detecting lactic acid in gastric juice.

## OXALIC SERIES.

| Name. | Formula. | Source. |
|---|---|---|
| Oxalic ......... | $H_2C_2O_4$ | Oxidation of sugar, starch, and cellulose. |
| Malonic ........ | $C_3H_4O_4$ | Oxidation of malic acid. |
| Succinic ........ | $C_4H_6O_4$ | Distillation of amber; oxidation of fatty-acids. |
| Pyrotartaric .... | $C_5H_8O_4$ | Action of heat on tartaric acid. |
| Adipic ......... | $C_6H_{10}O_4$ | " " nitric on sebacic acid. |
| Pimelic ......... | $C_7H_{12}O_4$ | " " potassium hydroxide on camphoric acid. |
| Suberic ......... | $C_8H_{14}O_4$ | Action of nitric acid on cork or castor oil. |
| Anchoic......... | $C_9H_{16}O_4$ | Action of nitric acid on coconut oil. |
| Sebacic ......... | $C_{10}H_{18}O_4$ | Distillation of oleic acid. |
| Rocellic ........ | $C_{17}H_{32}O_4$ | Exists in some lichens. |

**Oxalic Acid,** $(COOH)_2$.—The free acid and its salts, especially acid potassium oxalate and calcium oxalate occur in many plants, generally in the form of crystals—called raphides—deposited in special cells. It is now made by fusing cellulose, in the form of sawdust, with potassium hydroxide. It is decomposed by strong heat or the action of dehydrating agents with the production of $CO_2$, CO and $H_2O$. When it is heated with glycerol, formic acid is produced.

Oxalic acid forms colorless crystals, having the composition $H_2C_2O_4,2H_2O$. It is freely soluble in water, and is one of the most rapidly fatal poisons known. Death has occurred in ten minutes after administration. Soluble oxalates are also poisonous, hence the antidote must be some material that will produce an insoluble compound. Lime is the only available substance. Preparations of the acid are sold under the misleading names of salt of sorrel, and salt of lemon, and used for removing ink stains.

*Cerium oxalate*, $Ce(C_2O_4)_3 + 9H_2O$, is the only salt of oxalic acid that is used in medicine. It is a permanent white powder; odorless and tasteless.

*Ammonium oxalate*, $(NH_4)_2C_2O_4$, forms white crystals, soluble in water, and much used as a test for calcium compounds.

*Calcium oxalate*, $CaC_2O_4$, is colorless and insoluble in water. It is usually found in the urine in microscopic octohedral or dumbbell crystals. In larger masses it constitutes mulberry calculus.

*Experiment* 17.—Heat cautiously together in a flask 5 grams of sugar and 40 c.c. of nitric acid. After the reaction has ceased and red fumes cease to be evolved, concentrate the liquid, neutralise with soda and test for *oxalic acid*, as in the following experiment:

*Experiment* 18.—Add a solution of oxalic acid to a dilute solution of calcium chloride or to lime water and observe the white precipitate of *calcium oxalate*, $CaC_2O_4$. Collect the precipitate, dry and ignite it. The residue is calcium carbonate, $CaC_2O_4 = CaCO_3 + CO$. Treat the residue with acetic acid and note the effervescence.

*Experiment* 19.—Prepare a dilute solution of potassium permanganate, add an equal volume of solution of oxalic acid, acidulated strongly with sulphuric acid, and observe the discharge of color of the permanganate solution according to the following reaction:

$$5H_2C_2O_4 + K_2Mn_2O_8 + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 8H_2O + 10CO_2$$

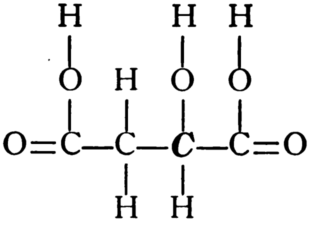
**Succinic Acid,** $C_2H_4(COOH)_2$.—This occurs in amber and other resins; also in small quantities in some animal secretions. It forms colorless crystals, soluble in water.

## ACIDS DERIVED FROM TRIATOMIC ALCOHOLS.

Somewhat related to the series just described, although not necessarily referable to the same radicles, are two important vegetable acids, malic and tartaric. The relation is especially with succinic acid, from which they differ only in amount of oxygen:

| | Empirical formulas. |
|---|---|
| Succinic | $C_4H_6O_4$ |
| Malic | $C_4H_6O_5$ |
| Tartaric | $C_4H_6O_6$ |

**Malic Acid,** $H_2C_4H_4O_5$, occurs in many sour fruits, as apples, pears, mountain ash berries and the fruit of *Rhus glabra*. It may be made artificially from succinic acid by replacing an atom of H with OH, or from tartaric acid by reduction and removal of O. It is crystalline, sour, soluble in water and alcohol. The malates are mostly soluble in water. Sweet cherries contain potassium malate. The annexed formula will show the presence of asymmetric carbon in malic acid:

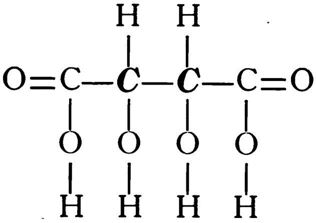


$$\begin{array}{ccccccccccc} & & H & & & & H & & H & & \\ & & | & & & & | & & | & & \\ & & O & & H & & O & & O & & \\ & & | & & | & & | & & | & & \\ O & = & C & — & C & — & C & — & C & = & O \\ & & & & | & & | & & & & \\ & & & & H & & H & & & & \end{array}$$

Malic acid

**Tartaric Acid,** $(HO)_2C_2H_2(COOH)_2$, is found in many plants, but especially in grapes, in which it exists as acid potassium tartrate, $KHC_4H_4O_6$. This is somewhat soluble in water, but insoluble in dilute alcohol; and hence, in the manufacture of wine, as the fermentation advances, the quantity of alcohol increases, and the tartrate deposits as a red mass called *argol* or *tartar*. When this is dissolved in water and purified by crystallisation it constitutes *cream of tartar*. Tartaric acid is obtained from argol by decomposition with sulphuric acid. It is the dextrorotatory form of four stereochemic isomers, two of which are, respectively, dextro- and levorotatory, and two optically inactive. One of these owes its inactivity to internal antagonism of the asymmetric carbon atoms, the other is a mixture of equivalent quantities of the two active forms. By inoculating a solution of this form with a common mold (*Penicillium glaucum*) the dextrorotatory form is gradually broken up by the organism, leaving the other form unchanged. This method was discovered by Pasteur to whom the initial investigation in this line is due. There are other methods of mesotomy for these optical isomers.

*Racemic acid.*—This is the naturally occurring mixture of the two optically active forms. It is found associated with tartaric acid and can be prepared synthetically.



Tartaric acid

*Acid potassium tartrate*, cream of tartar, is a white crystalline body, very sour, and not very soluble in cold water. It is used in baking powders because it liberates $CO_2$ from alkaline carbonates and acid carbonates.

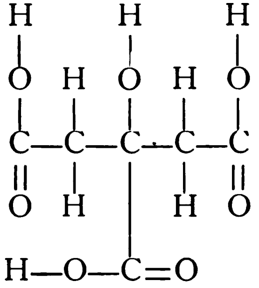
*Potassium tartrate*, $K_2C_4H_4O_6$, is called soluble tartar.

*Sodio-potassium tartrate*, $NaKC_4H_4O_6 + 4H_2O$ is known as *Rochelle salt.*

*Tartar emetic* is made by boiling acid potassium tartrate with antimonous oxide, by which an atom of hydrogen is replaced by the molecule SbO. The formula for tartar emetic is $K(SbO)C_4H_4O_6$, potassium antimoxyl tartrate. It crystallises with one molecule of water of crystallisation to two molecules of the salt, the formula being $2K(SbO)C_4H_4O_6 + H_2O$.

**Citric Acid,** $(HO)C_3H_4(COOH)_3$, is the acid present in lemons, limes and oranges, and is also found in some other fruits. It is usually prepared from lemons and limes, which contain from 7 to 10 per cent., but it has also been produced from solutions of cane sugar by the action of certain microscopic fungi. It is normally present in milk. It contains no asymmetric carbon.

It is a crystalline body, very sour and easily soluble in water. It is used in the preparation of effervescing mixtures, but some of the so-called effervescing citrates contain tartaric instead of citric acid. At a high temperature citric acid is decomposed into aconitic acid, $C_3H_3(COOH)_3$ and $H_2O$.



Citric acid

## Methylene (Methenyl) Series.

These are triad radicles. The first member, CH, methenyl, may be regarded as existing in chloroform. The most important member of the group is *tritenyl*, $C_3H_5$, also called *propenyl*, *propylene* and *glyceryl*. Its hydroxide, $C_3H_5(HO)_3$, is glycerol. Many of the common oils and fats are propenyl esters, and when treated with alkalies, such as sodium hydroxide, are broken up; a new salt and propenyl hydroxide are formed. On propenyl stearate (one of the ingredients of common animal fat) sodium hydroxide—common lye—would act thus:

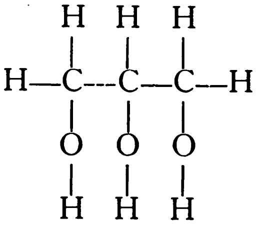
$$\overset{\text{Propenyl stearate.}}{(C_3H_5)(C_{18}H_{35}O_2)_3} + 3NaHO = \overset{\text{Sodium stearate.}}{3NaC_{18}H_{35}O_2} + \overset{\text{Glycerol.}}{C_3H_5(HO)_3}$$

Sodium stearate is a *soap*, and the process is saponification. The formation of glycerol can also be brought about by the use of superheated steam. This method is now generally used, since it gives the fatty-acids in the free condition, thus:

$$C_3H_5(C_{18}H_{35}O_2)_3 + 3H_2O = C_3H_5(HO)_3 + 3HC_{18}H_{35}O_2$$

**Glycerol (glycerin),** $C_3H_5(HO)_3$.—Pure glycerol is a colorless, viscid liquid, miscible in all proportions with water. Sp. gr. 1.2659. It has a sweet taste, absorbs water from the air, but does not otherwise change. Under certain conditions of pressure it can be distilled without decomposition, but under ordinary conditions it decomposes at the boiling point. It solidifies at about —40°. It dissolves a great many substances, standing next to water in its range of solvent powers. It is produced in small quantity during the fermentation of sugar, hence is often found in ordinary liquors. It is sometimes called the "sweet principle of fats," but it does not exist in fats, and possesses no chemical analogy to them. It is an alcohol, and is probably somewhat analogous to the sugars. Its use, therefore, as an application to the skin as a substitute for the emollient oils has no chemical justification, and owing to its strong affinity for water, which it abstracts from the tissues, it often produces irritation when applied in the undiluted state.

When treated with strong nitric acid, it forms propenyl nitrate, $C_3H_5(NO_3)_3$, known as *nitroglycerin.* This is a high explosive. It is now extensively used as a blasting agent, being generally mixed with some inert power such as paper pulp or diatomaceous earth, in which form it constitutes *dynamite.*



Glycerol

## FATS AND FIXED OILS.

The fats and fixed oils are almost all esters of propenyl (glyceryl). Most of the natural forms are mixtures of two or more distinct esters. Names are applied to them according to the acid from which the ester is derived. (See below.) The fixed oils are fats with a low melting point, and may be divided into two classes; drying oils, which absorb oxygen from the air, and become hard and resinous, such as linseed and poppy oil; non-drying oils, which remain fluid, as castor and sperm oils. Many fats and oils undergo partial decomposition in the air, producing acids, the condition being known as rancidity. When an alkali is added to a fat, decomposition takes place, a salt is formed, constituting a soap, and glycerol is produced. Soaps produced by potassium hydroxide are usually soft; those from sodium hydroxide hard; those made from other oxides are mostly insoluble in water. This latter fact explains the curdling action of limestone waters. The calcium and magnesium compounds in these waters produce insoluble soaps. When soluble soaps are treated with cold water they decompose into acid salt, which precipitates and makes the soapsuds, and a basic salt, which dissolves and gives the cleansing action.

The fatty-acids may be obtained by adding a strong acid to ordinary soaps.

The fats are all insoluble in water, but are soluble in ether, chloroform, benzene, petroleum spirit and carbon disulphide. They are decomposed by heat, and consequently cannot, under ordinary circumstances, be distilled.

The proximate constituents of the common fats are given under condensed names, the significance of which is as follows:

Stearin is propenyl stearate.
Palmitin is propenyl palmitate.
Margarin is propenyl margarate.
Butyrin is propenyl butyrate.
Olein is propenyl oleate.

Oleic acid is not a member of the same series with the other acids. It belongs to a series beginning with acrylic acid, $C_3H_4O_2$, and is elsewhere described.

*Glycerophosphoric Acids.*—Several of these are possible, but the only one of importance is that having the formula $C_3H_5(HO)_2H_2PO_4$. The structural formula of this is shown in connection with that for lecithin in the section on Proteids. Some of the complex esters that are found in higher tissues, *e. g.*, brain, nerve-tissue and egg-yolk, are derivatives of this acid. Calcium, sodium and strychnine glycerophosphates are used in medicine. The acid can be prepared by the action of glycerol on orthophosphoric acid.

*Experiment* 20.—Heat together in an evaporating dish, 40 grams of linseed oil, 9 grams of potassium hydroxide, 5 c.c. of alcohol and 50 c.c. of water. Continue the heat, with constant stirring, until a small portion of the mixture is found to be completely soluble in hot water. This process is called saponification and is analogous to the method used in making *Sapo mollis* of the Pharmacopœia. The potassium hydroxide reacts with the linseed oil, forming soap and glycerol. By using olive oil and sodium hydroxide a hard or *soda-soap* is obtained which may be precipitated from its aqueous solution by the addition of sodium chloride which causes it to separate in the form of curdy masses.

*Experiment* 21.—Dissolve a small quantity of the soap made in the previous experiment in water, and add it gradually to a solution of copper sulphate (1 to 20). The separation of an insoluble *copper-soap* will take place. The addition of the soap solution to a solution of calcium chloride will cause the precipitation of an insoluble *calcium-soap*.

*Experiment* 22.—Dissolve about 5 grams of soap in 100 c.c. of water by the aid of heat and add to the solution 5 c.c. of diluted sulphuric acid. The *fatty-acids* of the soap will separate in the form of an oily layer upon the surface of the liquid.

*Experiment* 23.—Heat about 5 c.c. of ethyl acetate in a flask, connected with a reflex condenser, with an excess of sodium hydroxide (about 4 grams), dissolved in a little water. The odor of ethyl acetate disappears owing to saponification with the formation of sodium acetate and alcohol, according to the following reaction:

$$C_2H_5(C_2H_3O_2) + NaOH = Na(C_2H_3O_2) + C_2H_5OH$$

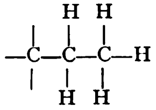
*Experiment* 24.—Melt about 10 grams of butter in a testtube by immersing it in boiling water; pour off about 2 c.c. of the melted butter into another testtube and saponify by boiling for a few moments with an alcoholic solution of sodium hydroxide. After the saponification is complete, evaporate the solution to dryness on the water bath and redissolve it in a small quantity of water. Add an excess of dilute sulphuric acid and heat. Observe the odor which is evolved. This is due to the volatile acids of the butter, such as butyric, caproic and their homologues; the greater portion of the fatty-acids of the butter, being non-volatile, remains floating on the surface of the liquid as an oily layer.

*Experiment* 25.—Boil together, in an evaporating dish, 6.4 grams of lead monoxide, 12 grams of olive oil and 5 c.c. of water, replacing the water from time to time as it is lost by evaporation. A thick tenacious compound is formed which solidifies upon cooling. This is the official *lead plaster, lead oleopalmitate.* Observe the sweetish taste of the water with which the compound has been boiled, due to *glycerol* formed in the reaction, as follows:

$$2(C_3H_5C_{18}H_{33}O_2)_3 + 3PbO + 3H_2O = 3Pb(C_{18}H_{33}O_2)_2 + 2C_3H_5(HO)_3$$

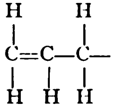
**Allyl and Derivatives.**—Allyl, $C_3H_5$, is isomeric with propenyl, but is a monad, the carbon atoms neutralising the valency of each other more completely than in the case of propenyl. By structural formulas the difference may be thus represented:

Propenyl, *triad.*



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ -C & - & C & - & C & - & H \\ | & & | & & | & & \\ & & H & & H & & \end{array}$$

Allyl, *monad.*



$$\begin{array}{ccccc} H & & & & H \\ | & & & & | \\ C & = & C & - & C - \\ | & & | & & | \\ H & & H & & H \end{array}$$

Allyl alcohol is $C_3H_5HO$. It is obtained by the distillation of glycerol in the presence of oxalic acid which acts as a dehydrolysing and reducing agent. Allyl is interesting on account of the occurrence in nature of two of its compounds, allyl sulphide, $(C_3H_5)_2S$, which is the essential *oil of garlic*, and allyl thiocyanate, $C_3H_5CNS$, *volatile oil of mustard*. Allyl aldehyde, $C_3H_4O$, *acrolein*, is one of the products of the decomposition of fats by heat, and is the main cause of the irritating vapors which are caused by such decomposition. It is formed by the dry distillation of glycerol according to the following reaction:

$$C_3H_5(OH)_3 = C_3H_4O + 2H_2O$$

*Experiment* 26.—Heat about 5 c.c. of glycerol in a dry testtube and observe the irritating vapors of *acrolein*, $C_3H_4O$, that are evolved.

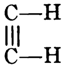
The oxidation of allyl aldehyde gives acrylic acid, which is the first member of a series of acids derived from some of the fats. The most important of this list is oleic acid.

*Oleic acid*, $C_{17}H_{33}(COOH)$, exists in most natural fats and non-drying oils as olein, propenyl oleate. Above 15° it is a clear liquid, lighter than water, and insoluble in it, but soluble in alcohol and ether. Crude oleic acid, is used in soap making, under the name of *red oil*. Various oleates, *e. g.*, copper, bismuth, zinc and mercury oleates, are now used in medicine to produce the physiological effect of the medicament by local application. They are usually prepared by the reaction of sodium oleate with some suitable compound. Thus, copper oleate is formed by precipitating solution of copper sulphate with solution of sodium oleate.

The derivatives of this series are often termed unsaturated compounds because they are capable of taking up negatives without substitution of hydrogen. The latent valency of the group $=C=C=$, which is in all of them, is developed. Iodine is especially adapted to this action and the proportion of it taken up under specified conditions is known as the "iodine number." It is an important datum in the analytic examination of fatty substances, tar and petroleum products. Some of the fatty bodies containing these unsaturated groups absorb oxygen rather rapidly from the air, becoming viscous. This is commonly termed "drying" and is a property of the oils used in the preparation of paints.

## Acetylene Series.

This is a series of unsaturated radicles of which the first member, Methine, is C. The second member, Ethine, more commonly known as *acetylene*, has the formula $C_2H_2$. The structural formula may be expressed thus:



$$\begin{array}{l} C-H \\ ||| \\ C-H \end{array}$$

The production of acetylene by the direct combination of carbon and hydrogen is an example of absolute synthesis, since both materials are obtainable from inorganic sources. The apparatus is shown in Fig. 10. Hydrogen is allowed to flow through the flask while a succession of electric

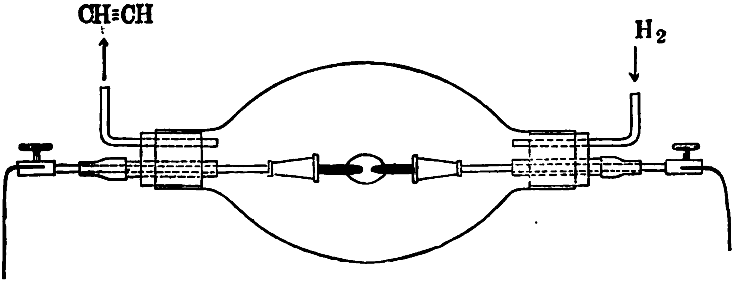


Fig. 10.

sparks is passed through the carbon poles. Acetylene flows out at the other opening. From acetylene many other organic bodies can be made by synthesis.

Other members of the series, of less importance, are: Allylene $C_3H_4$, Butine $C_4H_6$, Pentine $C_5H_8$ and Hexine $C_6H_{10}$. The members of this series are produced in the destructive distillation of many organic compounds. Acetylene is produced by a number of other methods, involving the reduction of methane, ethane, ethylene, etc. The incomplete combustion of illuminating gas, as when the flame in a bunsen burner or gas stove strikes back and burns at the base, yields some acetylene. Acetylene is produced commercially for illuminating purposes by the decomposition of metallic carbides (usually calcium carbide, $CaC_2$) with water. Acetylene is a colorless gas

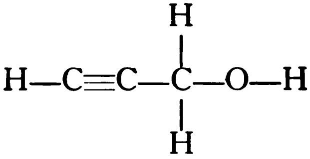
$$CaC_2 + 2H_2O = Ca(HO)_2 + C_2H_2$$

with a peculiar penetrating odor. It burns with a sooty flame from an ordinary burner, but with specially constructed burners a flame is produced which is brighter and more intense than the ordinary illuminating-gas flame. Acetylene can be liquefied by cold and pressure. The liquid is liable to explode. Acetylene dissolves freely in acetone; the solution is stated to be not explosive.

The hydrogen of acetylene can be replaced by strong positives producing carbides. The compounds formed by members of the potassium and calcium groups are stable, except in presence of water and alcohol, but those of silver and copper are explosive. Although these compounds are simply carbides, yet as they are obtained by reactions with acetylene, an organic body, they are classed as organic compounds. This is, therefore, an instance of the indefiniteness of the term organic.

The alcohols of this series are but little known. The only one of interest is:

*Propargyl alcohol, Propine hydroxide.*—The structural formula of this is annexed. It is a mobile liquid with an agreeable odor. It forms silver and copper compounds by exchanging hydrogen for these elements, but not the hydroxyl-hydrogen. As with the acetylene derivatives, it is the hydrogen that is attached to the triple-linked carbon that is replaced.



$$\mathrm{H{-}C{\equiv}C{-}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}{-}O{-}H}$$

Propargyl alcohol

*Experiment* 27.—Add a small fragment of calcium carbide, about 1 gram, to about 500 c.c. of water contained in a large evaporating dish. Apply a lighted taper to the gas which is evolved and observe its ready inflammability. This gas is *acetylene*. By generating the gas in a flask and allowing it to pass into an ammoniacal solution of cuprous chloride, a reddish-brown precipitate of copper carbide is formed, which is explosive when dry.

*Experiment* 28.—Add a small fragment of calcium carbide to about 5 c.c. of a saturated solution of zinc chloride contained in a testtube. *Acetylene* is not evolved as is the case when pure water is used.

## CARBOHYDRATES.

This term was originally applied to sugars, starch and allied bodies, because they contain carbon, hydrogen and oxygen, the latter two being in the proportion in which they exist in water, namely, $H_2$ to O. Two formulas will illustrate this:

| | |
|---|---|
| Cane sugar | $C_{12}H_{22}O_{11}$ |
| Dextrose | $C_6H_{12}O_8$ |

This limitation is now known to be inapplicable. Substances strictly analogous to the true carbohydrates, and exhibiting other ratios of hydrogen to oxygen have been discovered. Some compounds that exhibit this ratio, acetic acid, $C_2H_4O_2$, for instance, are not included in the group. The term is, however, too well fixed in the nomenclature of chemistry to be displaced at present.

The number of substances included within this group is large. They are mostly of vegetable origin, soluble in water, optically active and readily susceptible to the action of enzyms and microörganisms, by which they are at first usually hydrolysed and then split into simpler forms, changes that are exemplified in the common forms of fermentation.

The group of carbohydrates is subdivided as follows:

| | **Examples.** |
|---|---|
| MONOSACCHARIDS | Dextrose, arabinose. |
| DISACCHARIDS | Sucrose, lactose. |
| TRISACCHARIDS | Raffinose. |
| POLYSACCHARIDS | Starch, cellulose. |

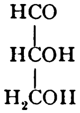
The carbohydrates have moderate reducing powers, especially in alkaline solution. Many of them form with phenylhydrazin characteristic crystalline precipitates called "osazones."

Hydroxyl is a predominating group in the carbohydrates; several molecules are present in even comparatively simple forms. They are, therefore, as a class, alcoholic. They break down through the action of certain fungi, especially yeasts, into simpler bodies which are distinctly alcoholic, such as ethyl alcohol, some forms of butyl and amyl alcohol, and glycerol. Methyl alcohol does not appear to be a result of these actions. Many carbohydrates show feebly the properties of acids, but they are not true acids. Several of the sugars, for instance, will form compounds with calcium oxide. A solution of cane sugar will dissolve a notable amount of lime; the compound formed has been termed calcium saccharate or saccharate of lime.

Aldehyde and ketone groups are frequently present in the carbohydrates. The structural formulas of several hexoses are accurately known and some of them have been obtained synthetically. One of the synthetic methods is by reactions between glycerose and formaldehyde. A carbohydrate that contains an aldehydic group is called an *aldose;* a carbohydrate that contains a ketone group is called a *ketose*. A carbohydrate may contain all three of these groupings, and be, therefore, aldehydic, alcoholic and ketonic, a condition that might be condensed into "aldalcoketose" to show the three types and the carbohydrate structure.

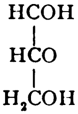
MONOSACCHARIDS.—Under the group monosaccharids are included substances containing different numbers of carbon atoms, indicated by the terms monose, diose, triose, etc. Of these the pentoses and hexoses are the most important. Formaldehyde may be considered a monose.

*Glycerose*, $C_3H_6O_3$, is apparently a triose, but is a mixture of two carbohydrates obtained by the oxidation of glycerol. One of these is an aldose, the first glycerol aldehyde, that is, the product obtained by removing $H_2$ from glycerol without introducing oxygen; the other, a ketose, is the ketone derivative of glycerol. The formulas of these derivatives are, respectively:



$$\begin{array}{c} HCO \\ | \\ HCOH \\ | \\ H_2COH \end{array}$$

Aldehyde



$$\begin{array}{c} HCOH \\ | \\ HCO \\ | \\ H_2COH \end{array}$$

Ketone

Glycerose is of no practical interest, but its application in the synthesis of carbohydrates has given it theoretic importance.

*Pentoses* exist in many plant tissues and have an important bearing on the nutritive value of vegetable materials, but the details belong to physiology rather than chemistry.

HEXOSES.—Two important hexoses require detailed consideration:

*Dextrose*, *Glucose*, *Grape sugar*, $C_6H_{12}O_6$.—This exists in many fruit juices and in honey. It is present in small amount in many animal fluids and excretions; in some diseases the amount is greatly increased. In fruit juices and honey it is associated with levulose. Dextrose can be obtained by the hydrolysis of many carbohydrates by dilute acids or enzyms. Starch, dextrin, cellulose and cane sugar are easily hydrolysed in this manner.

The principal commercial source of dextrose is by the hydrolysis of starch, usually corn starch, by dilute sulphuric acid. If the resulting solution is not concentrated beyond the syrupy condition, it will contain, in addition to dextrose, maltose, dextrin and several unfermentable carbohydrates not yet clearly isolated. If the material be evaporated to solid form, it will consist almost entirely of dextrose. The syrupy liquid is commercially always called "glucose" and the solid form "grape sugar."

Pure dextrose is a white, crystalline substance, freely soluble in water, to which it imparts moderate sweetness. The solution has strong dextrorotatory power and is easily fermentable by yeast into carbon dioxide and alcohol. In alkaline solution, dextrose has marked reducing power, liberating copper, lead, silver, gold and platinum from their compounds. It forms with phenylhydrazin an osazone that crystallises in yellow stellate tufts.

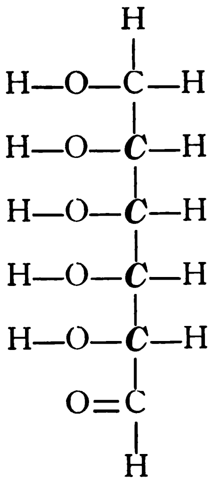
Commercial glucose is largely used as a substitute for other carbohydrates in the fermentation industries, and also as a substitute and adulterant for honey, molasses and maple syrup.

*Levulose*, $C_6H_{12}O_6$, *d-Fructose*, *Fruit sugar.*—This is associated with dextrose in fruit juices and in honey, and is produced in equal amount with dextrose in the hydrolysis of sucrose. It can be obtained pure by heating inulin with water at the boiling point for twenty-four hours.

Levulose is soluble in water, forming a sweet liquid that is strongly levorotatory at ordinary temperatures; less so when hot. It ferments with yeast to carbon dioxide and alcohol, but not so readily as dextrose, hence many fruit-juices, become levorotatory when fermented, the dextrose being removed much faster than the levulose.

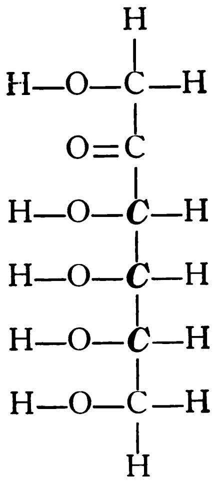
Notwithstanding the strong levorotatory power of ordinary levulose, it is, on account of certain structural relations, usually termed d-fructose.

Ordinary dextrose and levulose are alcohols, but are not stereo-isomers. The former is an aldehyde, the latter is a ketone. There is, therefore, a form of dextrose having left-handed rotation and one of levulose having right-handed rotation; in fact, theory indicates, and research has confirmed, the existence of numerous isomeric hexoses and derivatives. The annexed formulas show the structure of some of these bodies. Asymmetric carbon is present in all. In forming osazones, dextrose and levulose lose the characteristic groupings, that is, dextrose loses the aldehyde group and levulose loses the ketone group. Hence these hexoses, though not stereo-isomers, yield the same osazone.



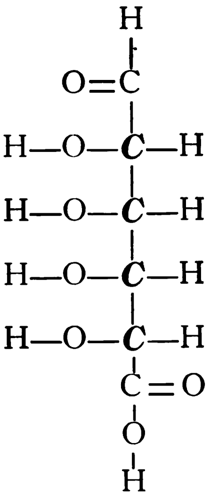
$$\begin{array}{rcl} & \mathrm{H} & \\ & | & \\ \mathrm{H{-}O{-}} & \mathrm{C} & \mathrm{{-}H} \\ & | & \\ \mathrm{H{-}O{-}} & \boldsymbol{C} & \mathrm{{-}H} \\ & | & \\ \mathrm{H{-}O{-}} & \boldsymbol{C} & \mathrm{{-}H} \\ & | & \\ \mathrm{H{-}O{-}} & \boldsymbol{C} & \mathrm{{-}H} \\ & | & \\ \mathrm{H{-}O{-}} & \boldsymbol{C} & \mathrm{{-}H} \\ & | & \\ \mathrm{O{=}} & \mathrm{C} & \\ & | & \\ & \mathrm{H} & \end{array}$$

**Dextrose**

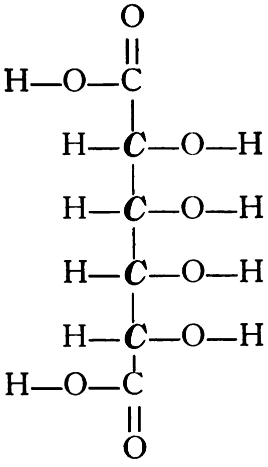


$$\begin{array}{rcl} & \mathrm{H} & \\ & | & \\ \mathrm{H{-}O{-}} & \mathrm{C} & \mathrm{{-}H} \\ & | & \\ \mathrm{O{=}} & \mathrm{C} & \\ & | & \\ \mathrm{H{-}O{-}} & \boldsymbol{C} & \mathrm{{-}H} \\ & | & \\ \mathrm{H{-}O{-}} & \boldsymbol{C} & \mathrm{{-}H} \\ & | & \\ \mathrm{H{-}O{-}} & \boldsymbol{C} & \mathrm{{-}H} \\ & | & \\ \mathrm{H{-}O{-}} & \mathrm{C} & \mathrm{{-}H} \\ & | & \\ & \mathrm{H} & \end{array}$$

**Levulose**



Glycuronic acid



Saccharic and Mucic acids

It will be noted that glycuronic acid is an alcohol, aldehyde and acid. Saccharic and mucic acids which are products of oxidation of several carbohydrates and stereo-isomers, are alcoholic and acid only.

Hexose Alcohols.—These contain hydroxyl groups but no aldehydic nor ketonic groups. They resemble the ordinary hexoses in many ways but do not reduce Fehling's solution and are not fermented by yeast. The most important is:

*Mannite, Mannitol*, $C_6H_{14}O_6$, which is seen not to correspond in its empirical formula to the ordinary definition of a carbohydrate. Mannite exists in three isomeric forms, dextro- and levorotatory and inactive. The dextrorotatory form is a natural product, occurring in several plants, especially in the manna, an exudation from *Fraxi-*

*nus ornus.* It may be prepared synthetically by the action of sodium amalgam upon levulose.

*Sorbite*, from mountain ash berries, and *dulcite*, from a manna from Madagascar, are similar in composition to mannite. Care must be taken not to mistake the termination in these names for the syllable used in the names of some salts. The terms sorbitol and dulcitol would be preferable for these bodies.

DISACCHARIDS.—*Sucrose*, *Cane sugar*, $C_{12}H_{22}O_{11}$.—This exists in the juices of many plants, but is commercially obtained from few sources: sugar-cane, beet-root, maple and sorghum. It is a colorless solid, easily crystallised and very soluble in water. The solution is very sweet and has high dextrorotatory power. It does not reduce Fehling's solution, nor form a precipitate with phenylhydrazin. It ferments readily with yeast, but this effect is preceded by a hydrolysis under the influence of an enzym present in the yeast-cell. By this hydrolysis, one molecule of sucrose takes up one molecule of water, and divides into one molecule of dextrose and one of levulose. The equation of the reaction is:

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6$$

The proportions by weight are 95 parts of sucrose to 5 parts of water, yielding 50 parts of dextrose and 50 parts of levulose. As the specific rotatory power of levulose is, at ordinary temperatures, higher than that of dextrose, the resulting mixture is slightly levorotatory, and is termed "*invert sugar.*" The same transformation can be brought about by the action of dilute acids and many mineral salts. It is technically known as an "*inversion.*" The yeast-enzym that inverts sucrose is called "*invertase.*" The fermentation that ensues is produced by other enzyms not yet definitely isolated, and affects the dextrose more actively than the levulose.

*Maltose*, $C_{12}H_{22}O_{11}$, is produced together with dextrins by the action of common enzyms on starch. It is abundantly present in malt. It is sweet, soluble in water, readily fermentable with yeast, reduces Fehling's solution and forms a characteristic osazone.

*Lactose*, $C_{12}H_{22}O_{11}$, is the characteristic carbohydrate of cow's milk. It probably exists in the milk of many other animals. Richmond obtained from the milk of a species of buffalo, domesticated in Egypt, a similar body to which he gave the name "tewfikose."

Ordinary lactose, obtained from the whey of cow's milk, crystallises in colorless, gritty masses moderately soluble in cold water and with slight sweetness. The solution ferments readily to lactic acid, but yields alcohol only under the influence of special ferments. In alkaline solution, lactose reduces compounds of silver and copper promptly. It yields a characteristic osazone and differs from sucrose in not being carbonised by strong sulphuric acid, and in reducing Fehling's solution.

The principal medicinal use of lactose is in the preparation of tablets and triturates of powerful drugs. In its ordinary form it is associated with one molecule of water of crystallisation, which may be driven out by gentle heating. A freshly made solution in water shows exceptionally high optical activity (termed "birotation") but on standing for some hours, or promptly on boiling, the normal rotating power is developed. Boiling with sulphuric acid slowly hydrolyses lactose into a mixture of equal parts of two hexoses, ordinary dextrose and galactose.

The TRISACCHARID, *Raffinose*, is found in association with beet sugar.

POLYSACCHARIDS.—*Cellulose*, $nC_6H_{10}O_5$ is the colorless material of woody fibre. It is seen in cotton or linen in a nearly pure form. It dissolves in an ammoniacal solution of cupric hydroxide but is insoluble in water, ether or alcohol. Strong sulphuric acid converts it either into a soluble substance, like dextrin, or into a substance, giving a blue color with iodine. By long-continued action of dilute sulphuric acid, cellulose is converted into dextrose.

*Paper* is nearly pure cellulose obtained by boiling vegetable structures with solutions that dissolve the cementing materials. For the best grades of paper, made from linen and cotton, weak solutions of sodium hydroxide in open vessels are used, but much paper is made from wood, by boiling with strong solutions of sodium hydroxide or magnesium sulphite under pressure. The inferior grades of commercial paper contain much ground wood not chemically treated.

When paper is treated for a short time with a cold mixture of two volumes of sulphuric acid and one of water, it becomes tough and waterproof, and is termed *parchment paper*.

Cellulose may be dissolved and reprecipitated. By mechanical methods the precipitate may be obtained in threads or thin sheets, thus producing artificial textile materials.

*Pyroxylin*, *Gun-cotton*.—Cellulose yields with nitric acid a series of nitric esters, having explosive properties. The composition differs with the strength of the acid, temperature and time of immersion. All the products retain the general physical appearance of the original material, but become rapidly combustible, burn with a bright smokeless flame disengage much gas, and leave no appreciable residue. They dissolve, or gelatinise, in liquids which do not affect cellulose. When the degree of nitration is low, *e. g.*, the composition, $nC_6H_8(NO_2)_2O_5$, the product is soluble in a mixture of alcohol and ether and is called *soluble* or *negative cotton*. The latter term refers to its use in preparing photographic negatives. When the formula contains larger proportions of the nitric acid radicle, the material is highly explosive, less soluble and is known as *gun-cotton*. It is used alone as an explosive and also in the preparation of smokeless powders.

*Collodion* is formed by dissolving pyroxylin in a mixture of ether and alcohol. This is called *plain collodion.*

*Celluloid* is a mixture of pyroxylin and camphor.

*Glycogen*.—This is an animal product and is a white, amorphous powder, which gives a brown color with iodine and by the action of ferments or dilute acids is converted into dextrose. It therefore resembles starch, but is soluble in cold water.

*Starch*.—This term is applied to a carbohydrate found widely distributed in the vegetable kingdom, in different tissues, but especially seeds, rhizomes and tubers. It is intimately connected with the formation of the cellular structure of vegetables. The conditions of its development have been carefully studied owing to its importance in vegetable physiology. It is not unlikely that the first step in its formation is the synthesis of formaldehyde under the influence of sunlight in accordance with the following equation:

$$CO_2 + H_2O = CH_2O + O$$

From the formaldehyde, by polymerisation, complex carbohydrates and finally starch is produced.

The percentage composition of starch corresponds to the empirical formula $C_6H_{10}O_5$; the molecular weight is unknown but is certainly high. The rational formula is also unknown.

Starch is deposited in the cells of plants in minute granules which are sufficiently characteristic in form to permit the source of the starch to be recognised by microscopic examination. In most cases, the granules are spherical or spheroidal. They are often marked by concentric rings and by a spot, termed the hilum.

Starch is not appreciably soluble in cold water; hot water breaks up the granules, dissolves some of the material and forms with the remainder a jelly of very low diffusive power. The solution has high dextrorotatory power. With free iodine, starch produces a deep blue compound, sometimes called starch iodide, but the exact nature of it is not known. It is dissociated by heating the liquid, the mixture becoming colorless, but the color returns on cooling. The solid starch also gives the blue with iodine.

Many enzyms, especially those of malt, saliva and pancreatic secretion, quickly convert starch-jelly by hydrolysis into a mixture of maltose and dextrin. Dilute acids also hydrolyse starch, producing much dextrose with some dextrin.

*Inulin* is a carbohydrate that exists in the roots of many Compositæ, such as dahlia and chicory. By boiling with water for some time it is completely converted into levulose.

*Dextrin.*—This term includes several substances that have not been clearly distinguished. Their composition corresponds to the formula $nC_6H_{10}O_5$. They are produced from starch by direct heating with water and by hydrolysis with dilute acids and many enzyms. They are amorphous, light yellow powders, insoluble in alcohol, soluble in water, forming an adhesive mucilage. The solution is strongly dextrorotatory and does not reduce Fehling's solution. By boiling with dilute acids, the dextrin may be converted into dextrose.

The dextrin obtained by heating starch with water under pressure is sometimes called *British gum*. It is used as an adhesive.

*Gum Arabic*, an exudation from species of *Acacia*, consists chiefly of the calcium and magnesium arabates. It is used in the preparation of mucilage.

*Gum Tragacanth*.—This is composed of several carbohydrates, some of which are soluble in water and others that do not dissolve, but absorb water in large amount and swell, making an adhesive paste.

Several vegetable gelatinising materials, such as agar-agar, are probably carbohydrates or closely related to them.

*Experiment* 29.—Prepare starch solution as follows: (Arrow-root starch is best but corn starch will serve.) Fifty c.c. of water are brought to the boiling point; a few grams of starch are stirred well with 10 c.c. of *cold* water and this mixture poured into the boiling water with constant stirring. The liquid is allowed to become quite cold. Portions of about 10 c.c. are used for the experiments.

*Experiment* 30.—Test a portion of the starch solution with solution of potassium iodide; no color will appear. Add a few drops of solution of iodine; a blue color at once appears. Heat the mixture just to boiling; it will become paler or colorless, and on cooling the color will return. The compound formed by the starch and iodine is apparently dissociated by heat.

*Experiment* 31.—Add to a portion of the starch solution a small amount of either diastase, takadiastase, pancreatic extract or saliva, and allow the mixture to stand for a few moments. Test portions of about 1 c.c. every few minutes with iodine solution. The starch reaction will soon be replaced by a dark, brownish color, which will soon be followed by a reddish brown, indicating the completion of the hydrolysis. (See under "Enzyms.")

*Experiment* 32.—Add 10 c.c. of the starch solution to 10 c.c.

of water and a few drops of sulphuric acid. Boil the mixture for five or ten minutes, cool, add slaked lime in small portions until litmus paper is not reddened by the liquid, filter and test for reducing sugar as noted below.

*Experiment* 33.—Treat starch solution with any one of the enzyms noted in Experiment 31 and test the resulting mixture for reducing sugar.

*Experiment* 34.—Make separate solutions of sucrose, dextrose and lactose by dissolving about 5 grams of each in 50 c.c. of water. The water may be heated if necessary to hasten the solution, but should be allowed to cool. For the dextrose solution, the common glucose or grape-sugar will answer. Portions of 10 c.c. of each of these should be taken for the experiment. Each experiment given below should be repeated with each sugar.

*Experiment* 35.—Test the reducing action by boiling with copper sulphate rendered alkaline with sodium hydroxide solution.

*Experiment* 36.—Test the action by boiling with a pinch of bismuth subnitrate and sodium hydroxide solution.

*Experiment* 37.—Test the reducing action with solution of silver nitrate rendered alkaline with ammonium hydroxide.

*Experiment* 38.—Make a solution of 10 grams of sucrose in 100 c.c. of water, and divide it into two approximately equal portions. Grind a cake of fresh, compressed yeast with 20 c.c. of water, filter the liquid and add one-half the filtrate to each of the sucrose solutions. To one of the solutions also add a few drops of a strong alcoholic solution of thymol, and a drop of acetic acid. Place both solutions in flasks and keep them for twenty-four hours at a temperature between 35° to 40°. The flasks may be loosely stopped with a little cotton wool or by covering with watch-glasses. They should not be tightly stopped. The solution containing the thymol will be converted into invert-sugar without fermentation; the other solution will soon begin to ferment, give off carbon dioxide and form alcohol. Both solutions will acquire levorotatory power.

*Experiment* 39.—Make a solution of sucrose containing about 5 grams in 100 c.c.; add 1 gram of citric acid and boil the liquid for ten minutes, replacing the water as it is lost. Allow the solution to cool and examine it for invert-sugar by any of the standard tests, such as reduction of Fehling's solution, reduction of bismuth subnitrate, formation of osazone by phenylhydrazin or rotatory power.

## GLUCOSIDES.

This term includes a large number of substances, mostly of vegetable origin, that are easily decomposed into several simpler bodies, one of which is dextrose or an analogous carbohydrate. Dilute acids and some enzyms are the usual means of producing these changes, the action is, in most cases, by hydrolysis. A glucoside may, therefore, be regarded as an ester of the carbohydrate yielded by it.

Most glucosides are non-nitrogenous. Many are the active principles of the plants in which they occur, but in some cases this activity is due to the products of decomposition and not to the glucoside itself. This is the case with mustard, bitter almonds and wild cherry bark. As a rule, the glucosides are associated with the enzym necessary for their decomposition. Starch and some of the other carbohydrates may be regarded as glucosides as they yield dextrose by hydrolysis.

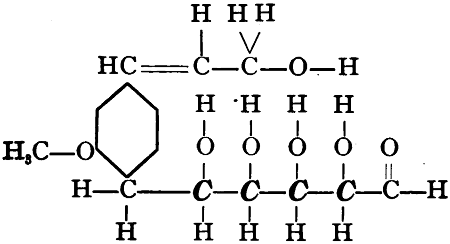
*Amygdalin*, $C_{20}H_{27}NO_{11}$, exists in tissues, especially seeds, of many plants of the order Rosaceæ, in association with an enzym called *synaptase*. This acts on the amygdalin, when the seeds are crushed in cold water; but boiling alcohol coagulates the synaptase and dissolves the undecomposed amygdalin. The latter is a white, crystalline body, soluble in alcohol and water, but not in ether. The decomposition to which it is susceptible is explained in connection with the description of hydrogen cyanide.

*Salicin*, $C_{13}H_{18}O_7$, is found principally in the bark and leaves of the poplar and willow. It crystallises in white needles; insoluble in ether, but soluble in water and alcohol. Salicin decomposes as follows:

$$C_{13}H_{18}O_7 + H_2O = C_7H_8O_2 + C_6H_{12}O_6$$

$C_7H_8O_2$ is called *saligenin*.

The structural formula of salicin shows open and closed chains. The significance of the hexagon is explained under Benzene. The structure of dextrose is also evident, and a methyl ether group ($H_3C—O$) is present.



*Tannins.*—These are astringent principles, widely diffused in the vegetable kingdom. They dissolve in water and have an acid reaction; hence are often called tannic acids. Many forms are known; they possess the common property of precipitating gelatin and giving dark-colored precipitates with ferric salts. Their action on gelatin is utilised in the preparation of leather, and their action with ferric salts in making ink.

*Ordinary tannin*, *gallo-tannic acid*, occurs in nutgalls—excrescences formed on a species of oak by puncture by an insect—and sumach. It is usually seen as a loose, brittle, light-yellow, non-crystalline mass, very soluble in water and highly astringent. It gives a bluish-black precipitate with ferric salts. The common form is not entirely a glucoside but contains a large amount of digallic acid, $C_{14}H_{10}O_9$.

When tannin is boiled with dilute acids, or mixed with water and exposed to moist air, it forms gallic acid by hydrolysis of the glucoside or digallic acid.

Thus:—

$$\overset{\text{Tannin (glucoside).}}{C_{27}H_{22}O_{17}} + 4H_2O = \overset{\text{Dextrose.}}{C_6H_{12}O_6} + \overset{\text{Gallic acid.}}{3C_7H_6O_5}.$$

$$\overset{\text{Digallic acid.}}{C_{14}H_{10}O_9} + H_2O = \overset{\text{Gallic acid.}}{2C_7H_6O_5}.$$

The formation of gallic acid is a loss in the manufacture of leather, since it has no tanning qualities. The change can be prevented by antiseptic substances, such as sulphurous and boric acids, and solutions of these are sold under the name of *antigalline*. The process of tanning consists essentially in the tannin rendering the gelatinous matter of the hide insoluble, and therefore not liable to decomposition.

*Sinigrin, Potassium Myronate,* $KC_{18}H_{10}NS_2O_{10}$.—The seed of the black mustard contains this body and also an enzym, *myrosin*, which decomposes the sinigrin according to the following equation:

$$KC_{10}H_{18}NS_2O_{10} = C_3H_5CNS + C_6H_{12}O_6 + KHSO_4.$$

$C_3H_5CNS$ is allyl thiocyanate, to which the irritating action of mustard is due. Preparations of it should not be made with hot water as this will injure the enzym and prevent the decomposition. It will be noted that this is not hydrolysis. By direct action of amine, allyl thiocyanate is converted into thiosinamin (allyl thiocarbamide).

White mustard seed contains a glucoside, *sinalbin*, and an enzym, *myrosin*.

*Indican*, $C_{52}H_{62}O_{34}$, occurs in several plants, especially those of the genus Indigofera. By boiling with acids it yields the color known as *indigo blue* (indigotin). Indigo blue is obtained from the plants containing indican, by macerating them with water, and exposing to the air until fermentation occurs and blue is deposited.

## Cyclic Hydrocarbons.

In these compounds, carbon atoms are connected into one or more closed series or chains. Three is the smallest number of atoms that can form such a chain. When the chain is composed of one kind of atoms, the molecule is *homocyclic* or *isocyclic*. This term is generally applied to carbon chains, although obviously not necessarily so limited. The nucleus of three nitrogen atoms in azoimide is homocyclic. As with the open-chain compounds, some of the valencies may be latent, that is, two atoms may be connected by more than one bond. These latent valencies are developed only under special conditions, giving origin to *additive* compounds.

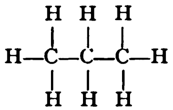
When the chain includes atoms of different elements, it is termed *heterocyclic*. The more important instances of this arrangement are rings containing two or more carbon atoms linked with an atom of oxygen, sulphur or nitrogen.

These closed-chain compounds may have the same empirical formula as open-chain compounds. The former are, therefore, not infrequently named by attaching the prefix "cyclo" to the name of the open-chain compounds. Thus, trimethene $(CH_2)_3$, isomeric with $C_3H_6$, propane, is called "cyclopropane."

### HOMOCYCLIC COMPOUNDS.

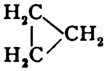
Of all these series, the most important and interesting, both from practical and theoretic points of view, is the six-carbon homocyclic series, commonly termed the Benzenes, from the name of the fundamental hydrocarbon. It will be sufficient to note a few points in regard to other groups.

*Three-membered Rings.*—An instance of this is found in *cyclopropane*, *trimethylene* or *trimethene*, isomeric with propane, the difference in structure being shown in the annexed formulas:



$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

Propane



Cyclopropane

*Four-membered Rings.*—The compounds of this type have as yet but little practical interest. Methyl tetramethene, $(CH_2)_3CH(CH_3)$, is an instance.

*Five-membered Rings.*—A considerable number of derivatives of this type are known. Common camphor yields methene derivatives of this type, but the reactions by which these are produced are not yet known.

Seven-membered rings are also known but they tend to reduce to six-carbon rings.

## SIX-CARBON HOMOCYCLIC COMPOUNDS.

Three subgroups of these are distinguished:

**Benzenes (aromatic hydrocarbons).**
**Terpenes (essential oils).**
**Polynucleated compounds.**

## BENZENES.

*Historical Note.*—In the manufacture of illuminating-gas by the destructive distillation of bituminous coal and shale and in the manufacture of coke, many products are obtained, some gaseous at ordinary temperatures, others liquid and solid. The liquid and solid bodies are collected in mixture as a dark, thick liquid, with an odor recalling that of the gas. This is known as *coal-tar*. For a long while it was a useless by-product and its disposal a serious problem. In 1825 Faraday obtained, by compressing coal gas, a hydrocarbon, which is now known to be identical with that obtained by Mitscherlich in 1834, by distilling calcium benzoate, which, on account of this source, was called "*benzene*." In 1845 Hofmann discovered the same body in coal-tar, and not long afterwards, Mansfield, a pupil of Hofmann, prepared it in practicable quantity from the tar. Mansfield lost his life while preparing a sample for public exhibition.

Experiments with benzene soon showed that it is capable of yielding many derivatives, and while showing no isomeric modifications itself, its derivatives show many instances thereof. The chemical nature of benzene was imperfectly understood up to 1865, when Kekulé suggested that its molecule consists of six carbon atoms in a closed chain with six latent valencies and six other valencies satisfied by hydrogen. By this theory, so far, all the numerous derivatives can be formulated consistent with their isomerisms and relations. Moreover, the properties of benzene itself are explained by the theory. Benzene ordinarily exhibits the functions of a saturated hydrocarbon, but, under special conditions, it is capable of forming additive compounds, this addition taking place by the simultaneous action of two valencies.

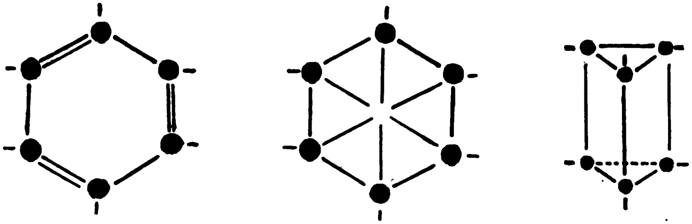
Kekulé's view has been generally accepted, and extended to many other classes of compounds. Some difference of opinion exists as to the manner in which the latent valencies are disposed, but it is not necessary to discuss this point.

Coal-tar contains many substances that are structurally related to benzene; these may be separated, but usually somewhat imperfectly by fractional distillation. It is known that benzene obtained from tar, unless especially purified, contains a compound in which sulphur takes the place of two carbon atoms. This will be noted under the heterocyclic compounds. Among the important bodies associated with benzene in coal-tar, are toluene, phenol, anthracene, naphthalene and pyridin. The benzene occurs in the most volatile portion of the tar, termed light oils. Crude benzene is known in commerce as "benzol," a name which has, unfortunately, been much used for benzene itself.

*Benzene*, *phene*, $C_6H_6$, is a colorless mobile, volatile liquid with an odor that suggests coal-tar. It melts at 5.4° and boils at 80.4°. The solid benzene resembles common paraffin. The sp. gr. of the liquid is 0.899. It has high solvent powers for many substances, notably fats, waxes and resins. It is readily inflammable, burning with a smoky flame, but does not undergo direct oxidation by ordinary oxidising agents. Benzene, as already noted, forms two classes of derivatives, *additive* and *substitutive*. The former are of little practical interest, but the latter are very numerous and important. Additive compounds of monad elements are formed with even numbers of atoms, *e. g.*, benzene chlorides are $C_6H_6Cl_2$; $C_6H_6Cl_4$; $C_6H_6Cl_6$. The substitution of monad elements or radicles may take place singly, chlorbenzenes, $C_6H_5Cl$; $C_6H_4Cl_2$; $C_6H_3Cl_3$; $C_6H_2Cl_4$; $C_6HCl_5$; $C_6Cl_6$, being known.

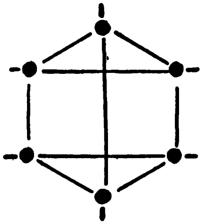
It is necessary to distinguish clearly between these two classes of derivatives. The nomenclature used is exemplified above. Additive compounds are named in the same manner as the binary compounds of inorganic chemistry (compare benzene dichloride, $C_6H_6Cl_2$, with zinc dichloride, $ZnCl_2$). Substitution compounds are named by attaching to the fundamental name syllables indicating the nature of the substituting bodies and also numerical syllables; thus, $C_6H_4Cl_2$ is *dichlorbenzene.*

The assumed structure of the molecule of benzene is shown in the following diagrams of the carbon nucleus—the carbon atoms represented by dots—and arrangement of valencies. Several diagrams are given, showing suggestions as to manner and disposition of the latent valencies.



Kekulé Armstrong Ladenburg's prism

Carbon atoms in benzene (various suggestions)



Ladenburg's prism modified

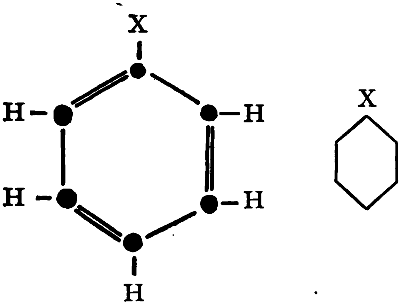
Benzene derivatives obtained by substituting the hydrogen by equivalent atoms or groups are numerous and show many instances of isomerism. These are best explained by tridimensional (stereo-chemic) formulas but such a method is not here available and the ordinary structural formulas must suffice.

The following compounds illustrate these substitutions and the nomenclature of them:

| | |
|---|---|
| $C_6H_5Cl$ | chlorbenzene. |
| $C_6H_4Cl_2$ | dichlorbenzene. |
| $C_6H_3(HO)_3$ | trihydroxybenzene. |
| $C_6H_4(COOH)(HO)$ | carboxyhydroxybenzene. |

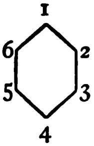
For convenience in naming compounds, $C_6H_5$, is frequently called phenyl, and $C_6H_4$, phenylene.

The term "hydroxy" in these names is often abbreviated to "oxy." Thus, $C_6H_5HO$ is called oxybenzene. The conditions of symmetry in benzene are such that no isomerism is to be expected (and none has been observed) in the compounds formed by a single substitution of the hydrogen. Hence, phenol, hydroxybenzene, is identical in nature no matter how prepared. When two or more hydrogen atoms are replaced, isomerism at once becomes possible, and instances become very numerous when several different substituting molecules are introduced. To aid in expressing the formulas of these isomeric bodies, and also in distinguishing them by name, the normal benzene-molecule is represented by a hexagon which, when unmodified, stands for $C_6H_6$; it is termed a "ring-symbol." A symbol or formula at any angle of this hexagon indicates that an atom of hydrogen is replaced by the body represented by that symbol or formula. The annexed diagrams will show the detailed structural formula and ring-symbol. The carbon atoms are here again represented by dots. X represents any monad elements or radicle.

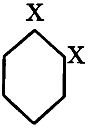


Substitution compound and ring symbol
$=C_6H_5X$

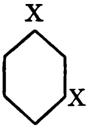
The position of the substituting body is immaterial in this case, but it is usually placed at the upper angle. When two hydrogen atoms are replaced three isomeric bodies will be formed, whether the replacement is by the same or different bodies. To assist in indicating, the angles are distinguished by numbers in the order of those on a clock, thus:



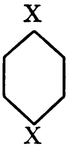
Substitution of two hydrogen-atoms are shown in the annexed ring-symbols.



1–2
ortho



1–3
meta

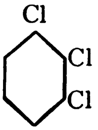


1–4
para

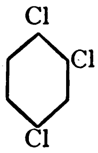
X, as before, represents any monad element or radicle. It will be seen that 1–5 and 1–6 are identical, respectively, with 1–3 and 1–2, so that three and only three isomeric forms are to be expected. This accords with all known facts. Moreover, the rule applies to cases in which two different substituting molecules appear. The numerical nomenclature is not generally used in these instances, the compounds being designated by prefixing the following syllables:

ortho for 1–2
meta for 1–3
para for 1–4

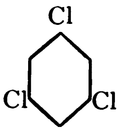
Substitutions of three hydrogen atoms by three atoms or molecules of the same kind give rise to three isomeric forms which are exemplified in the annexed formulas of the three trichlorbenzenes together with distinctions by the two systems of nomenclature in vogue.



1–2–3
Consecutive
or adjacent

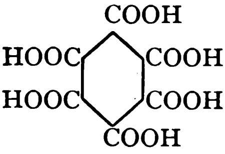


1–2–4
Unsymmetric



1–3–5
Symmetric

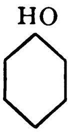
If the three substituting bodies are not identical, the isomerism becomes complex, and substitutions of four or five hydrogens still more so, but substitution of six hydrogens by identical bodies gives only one form. The latter point is exemplified in the annexed formula:



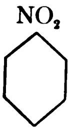
Mellitic acid, hexacarboxybenzene.

No uniform system is available for representing additive compounds by ring-symbols. A provisional method is adopted in this book for the few instances in which such representation is required. Additive elements or groups are indicated by placing the proper sign at a short distance from the angle and connected by a bond. There is also no uniform method of indicating cyclic combinations containing less than six carbon atoms nor those containing atoms of different elements (heterocyclic). Some chemists use a truncated hexagon for five-membered rings. For indicating the heterocyclic (pyridin) ring, $C_5H_5N$, the benzene hexagon with a small N close to an angle will be used in this book. Both these methods are exemplified in the formula for pyridin hydride.

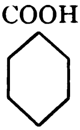
For illustration and comparison, the ring-symbols of a few compounds are given here. The substances are described in the following pages.



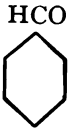
Hydroxybenzene
(Phenol)



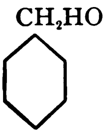
Nitrobenzene



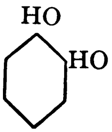
Carboxybenzene
(Benzoic acid)



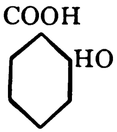
Benzaldehyde
(Bitter-almond oil)



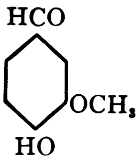
Benzyl alcohol



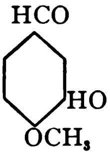
Resorcinol



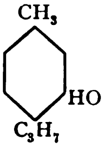
Salicylic acid



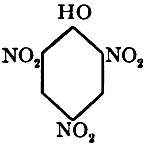
Vanillin



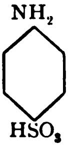
Isovanillin



Thymol



Picric acid

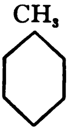


Sulphanilic acid
1–4 Amidobenzene-sulphonic acid

HOMOLOGUES AND DERIVATIVES OF BENZENE.—Benzene is the first member of a series of the general formula $C_nH_{2n-6}$ of which the following compounds are examples:

| | | | |
|---|---|---|---|
| Benzene, | $C_6H_6$ | | |
| Toluene, | $C_7H_8$ | $C_6H_5(CH_3)$, | methylbenzene |
| Xylene, | $C_8H_{10}$ | $C_6H_4(CH_3)_2$, | dimethylbenzene |
| Cumene, | $C_9H_{12}$ | $C_6H_3(CH_3)_3$, | trimethylbenzene |
| Cymene, | $C_{10}H_{14}$ | $C_6H_2(CH_3)_4$, | tetramethylbenzene |

*Toluene* is a colorless liquid, of sp. gr. 0.870. It boils at 110°. A substitution of one atom of the benzene-hydrogen of toluene must produce three isomeric forms, since the substituting group must take a position either 1–2 (ortho), 1–3 (meta), or 1–4 (para), with reference to the methyl group, for, as the structural formula and systematic name of toluene indicates, it is not a seven-carbon chain but a substitution of methyl for one of the hydrogen atoms of benzene. It is obvious, however, that the substitution may take place in the methyl group. This, which is termed "*side-chain*" substitution, gives rise to bodies which show, in empirical formulas, isomerisms with the ordinary benzene substitutions. This phenomenon of side-chain substitution is now receiving special attention in pathological chemistry, and in connection with theories of immunity, but the subject is still imperfectly developed and is too complex for more than mention here.



Methyl-benzene
(Toluene)

*Hydroxytoluene*, $C_6H_4(HO)(CH_3)$, of which there are three forms is isomeric but not identical with $C_6H_5CH_2HO$. The latter might be called hydroxymethylbenzene for distinction. It is, however, known as *benzyl alcohol* and is considered to be the true alcohol of this formula.

*Nitrobenzene*, $C_6H_5NO_2$.—This is easily prepared by the action of strong nitric acid on benzene. It is a colorless liquid, with an odor somewhat like that of essential oil of bitter almonds, for which it has been used as a substitute in flavoring soaps and cosmetics. It is known commercially as *oil of myrbane*. The reaction for its production is:

$$C_6H_6 + HNO_3 = C_6H_5NO_2 + H_2O$$

*Aniline, Phenylamine, Amidobenzene*, $C_6H_5NH_2$.—This is made by the action of nascent hydrogen on nitrobenzene, *e. g.*, by mixing nitrobenzene with tin and hydrochloric acid or with iron filings and acetic acid. The reaction is:

$$C_6H_5NO_2 + H_6 = C_6H_5NH_2 + 2H_2O$$

Aniline is a liquid, boiling at 182°. It is an active poison. By the action of oxidising agents it becomes converted into bodies of complicated composition, some of them having coloring powers of great beauty and variety, so-called "aniline or coal-tar colors." Crude aniline, commonly known as "aniline oil," contains homologous substances, such as toluidines (methyl anilines) and xylidines (dimethyl anilines).

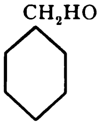
*Phenol, Hydroxybenzene*, $C_6H_5HO$, *Carbolic acid, Phenic acid, Phenylic acid.*—This exists in coal-tar, and can be made artificially by several processes. It forms colorless crystals, deliquescent, and soluble in water, melting at 34° and boiling at 187°. It has an odor like that of kreasote. It is sometimes called "coal-tar kreasote." The commercial article usually has a pink tinge. Applied to mucous membranes, phenol promptly produces blanching and then an eschar. Strong alcohol is antidotal in action. The hydrogen in the hydroxyl of phenol can easily be replaced by positives yielding a series of compounds termed "phenates" or "phenylates." The sodium compound being readily soluble in water and less corrosive than phenol, is used as an antiseptic and as a wash for removing skin-parasites from domestic animals.

*Benzaldehyde*, $C_6H_5HCO$, is oil of bitter almonds. Its formation from amygdalin by a species of fermentation is pointed out elsewhere. It is a colorless liquid, heavier than water, and, as usually made, has the smell of hydrogen cyanide, since that body is formed from amygdalin at the same time as the benzaldehyde. Oil of bitter almonds has been used in confectionery as a flavor. It is sometimes substituted by nitrobenzene.

*Benzoic acid*, carboxybenzene, $C_6H_5COOH$, occurs in various resins, especially in *benzoin*, and can be made artificially by several methods. The usual method is by oxidation of toluene; another is from hippuric acid. Benzoic acid is a white crystalline solid, with faint odor and disagreeable taste. It dissolves but slightly in cold water, but more so in hot water and alcohol. It sublimes at a temperature below its boiling point. It is an antiseptic.

*Sodium benzoate* is a white crystalline solid with faint odor. It is soluble in water; the solution has a somewhat nauseous taste. It has marked antizymotic properties and is now used as a preservative in foods liable to ferment.

*Benzyl alcohol, Phenyl carbinol*, $C_6H_5(CH_2HO)$, is of little practical importance, but is interesting because it is the true alcohol of this series. It is isomeric with the hydroxytoluenes (cresols) but entirely of a different nature and quite different in properties.

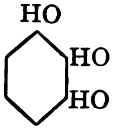


Benzyl alcohol

*Resorcinol, Resorcin, Metadihydroxybenzene*, $C_6H_4(HO)_2$

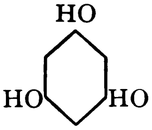
(for structural formula see p. 124). This can be obtained from the resins of galbanum and asafetida and also synthetically from several benzene derivatives. It is a colorless, crystalline body soluble in water, alcohol and ether. It is antiseptic.

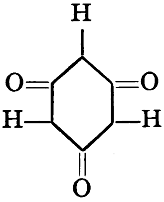
*Pyrogallol, Pyrogallic acid,* $C_6H_3(HO)_3$, 1–2–3 trihydroxybenzene, was originally obtained, as its name indicates, by heating gallic acid. It is a colorless, crystalline body, soluble in water. It absorbs oxygen from the air and decomposes. The action is especially rapid in alkaline solution and is utilised in developing photographic negatives and in the analysis of gaseous mixtures containing free oxygen.



Pyrogallol

*Phloroglucol, Phloroglucin,* $C_6H_3(HO)_3$.—The molecule of this body is supposed to be tautomeric. The annexed formulas show two possible forms. One form is 1–3–5 trihydroxybenzene, the other form is triketohexamethene.



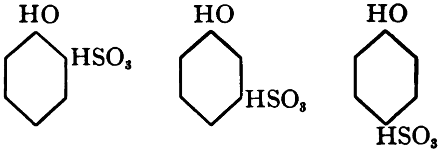


Originally obtained from a glucoside, *phloridzin*, of certain root-barks, it is now made from resorcinol. It is a colorless, crystalline body, soluble in water and alcohol. The alcoholic solution is used in mixture with a solution of vanillin for detection of hydrochloric acid in gastric juice. A solution of phloroglucol and dilute hydrochloric acid is used for detecting some forms of woody tissue. When the solution is added to materials containing these tissues, a bright red stain is produced. This reaction depends upon the existence of substances somewhat similar to vanillin. A solution of phloroglucol in dilute sodium hydroxide is used as a test for formaldehyde.

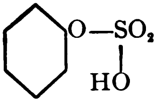
*Phenolsulphonic acids*, $C_6H_4(HO)(HSO_3)$.—Three of these are possible; all are known, but only 1–2 and 1–4 can be obtained by the direct action of phenol upon sulphuric acid. The first form tends to pass into the 1–4 form, slowly when cold, rapidly when hot. These acids are capable of forming salts which are strongly antiseptic and have been used as disinfectants.

*Phenylsulphuric acid*, *Phenyl acid sulphate*, $C_6H_5HSO_4$, is empirically isomeric with the phenolsulphonic acids but quite different in structure. Its potassium salt occurs in urine, and is one of the so-called ethereal sulphates the formation of which is supposed to be dependent on the putrefactive processes taking place in the intestinal canal.

The structural formulas will show the relations of the four bodies.



**Phenolsulphonic acids**



**Phenylsulphuric acid**

*Thymol* (see structural formula p. 124), isopropylmetahydroxytoluene, is one of the ingredients of oil of thyme, and can be prepared synthetically. It forms colorless crystals that melt at 50°. It has an odor recalling that of the oil of thyme. An isomeric form is known called *carvacrol.* Thymol has marked antiseptic powers. Its odor prevents its use as a food-preservative. Its principal medical use is as a vermifuge in the treatment of *uncinariasis*, a disease due to the presence of minute worms in the intestinal canal.

*Guaiacol*, 1–2 hydroxymethoxybenzene, $C_6H_4(HO)(CH_3O)$; is a mixed ether of phenyl and methyl with alcoholic hydroxyl also present. It is the important constituent of kreasote from beechwood tar. When pure it is a white solid with but slight irritating qualities. Commercial guaiacol is a liquid, often very impure, and decidedly irritating to mucous membranes. By treatment with carbonyl chloride, $COCl_2$, a derivative having the formula $(C_6H_4OCH_3)_2CO_3$ is obtained. It has been used as a therapeutic agent under the name *guaiacol carbonate.*

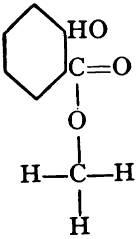
*Vanillin* methylprotocatechuic aldehyde see p. 124) is the principal flavoring constituent of vanilla, which contains from 1 to 2 per cent. It is now made artificially from eugenol. It forms colorless, needle-like crystals, with the well-known agreeable odor. It is freely soluble in alcohol, but not very soluble in water.

*Picric acid*, $C_6H_2(NO_2)_3HO$, is the *trinitrophenol* in which the nitro-groups are arranged symmetrically with regard to each other and to the hydroxyl. The other forms are but little known. Picric acid is obtained by the oxidation of indigo, silk, wool and leather, and synthetically by the oxidation of phenol. Phenolsulphonic acids mixed with nitrates produce some picric acid, but several lower nitrophenols are also formed. Picric acid may be produced by the direct oxidation of phenol with nitric acid, but the action is apt to be violent. Picric acid is a deep yellow solid, soluble in water. It dyes silk and wool without a mordant. It coagulates albumin. It is very bitter, a property to which the name refers. With care it can be sublimed without decomposition, but under some conditions explodes with great violence. The high explosive called "lyddite" is picric acid. As the formula shows, it is not a carboxyl acid, but the nitro-groups give the hydrogen of the hydroxyl acid function. This hydrogen may be replaced by positives, forming salts, most of which are explosive.

*Salicylic acid*, orthohydroxycarboxybenzene, oxybenzoic acid, $C_6H_4(COOH)(HO)$ (see p. 124), differs in formula from benzoic acid by an additional atom of oxygen, hence the name oxybenzoic acid. It is usually made from sodium salicylate obtained by the action of carbon dioxide on sodium phenate.

$$\underset{\text{Sodium phenate.}}{NaC_6H_5O} + CO_2 = \underset{\text{Sodium salicylate.}}{NaC_7H_5O_3}$$

Salicylic acid forms colorless prismatic crystals, sparingly soluble in water. The solution gives a deep violet color with ferric salts. It has high antiseptic qualities and is much used as a preservative in foods and beverages. Its methyl ester exists in the volatile oils of wintergreen, (*Gaultheria procumbens*) and birch (*Betula lenta*). By saponifying these, the natural acid can be obtained; this is preferable for therapeutic use on account of its freedom from the dangerous by-products occasionally present in the acid made from phenol. Salicylic acid has a marked restraining action on several starch-converting enzyms.



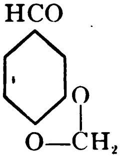
Methyl salicylate

*Cresols*, $C_6H_4(CH_3)HO$, methyl phenols, cresylic acids. These have the same relation to toluene, $C_7H_8$, that phenol has to benzene. Phenol is hydroxybenzene; cresol is hydroxytoluene. They exist in coal-tar. Three isomeric forms are known. They are often present in commercial phenol.

*Lysol*, now much used as a surgical antiseptic, is a mixture of the cresols saponifed by caustic soda and thus rendered soluble in water.

*Eugenol, allyl guaiacol*, $C_6H_3(C_3H_5)(OCH_3)(OH)$. This forms the greater portion of oil of cloves, and occurs in other essential oils. It differs from vanillin in containing the monad allyl radicle, $C_3H_5$, in place of the aldehyde group HCO. By oxidation allyl may be converted into HCO, and vanillin obtained. This is now the commercial source of synthetic vanillin.

*Piperonal.* The structural formula shows this to be an aldehyde-ether. It bears some relation to vanillin and benzaldehyde. It is a liquid of pleasant odor. .



Piperonal

QUINONES.—The substitution of oxygen for hydrogen in the proportion of $O_2$ for $H_2$ in closed-chain compounds, gives rise to a series of bodies termed *quinones*. Some of them are analogous in structure to hydrogen dioxide, and like it are active oxidising agents. Two series have been obtained, representative of 1–2 and 1–4 substitutions. The latter series *true*, or *paraquinones*, are of the greater importance. Some of them are probably tautomeric, oscillating between a peroxide and a ketonic structure. In the latter condition they have reducing power.

The structural formulas of these forms is illustrated by benzoquinone :

**Benzoquinone**

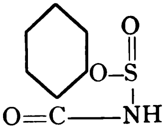
**Peroxide form** $C_6H_4O_2$ **Ketonic form** $C_4H_4(CO)_2$

*Quinone*, *benzoquinone*, the type substance, may be prepared in many ways. The usual method is by oxidising aniline with chromic acid. It forms yellow crystals which have a penetrating disagreeable odor and irritate the skin.

*Phthalic acids*, dicarboxybenzenes, $C_6H_4(COOH)_2$.—These are the final products of the oxidation of side-chains of benzene derivatives and their preparation is, therefore, valuable as a means of ascertaining the position of these chains, since the forms of acid yielded will be dependent on the position of molecules oxidised. There are, of course, three forms of these acids: 1–2, 1–3, 1–4. The methods used depend upon the form of the acid desired. The most important is:

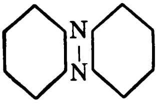
*Phthalic acid*, $C_6H_4(COOH)^1(COOH)^2$, 1–2 dicarboxybenzene.—This is obtained by the oxidation of naphthalene, by which the extra ring is broken and its carbon converted in carboxyl. It is a colorless, crystalline body soluble in water. It is prepared in large quantity for the manufacture of commercial synthetic products. Its preparation from naphthalene is the first step in the manufacture of artificial indigo-blue.

*Saccharin*, *Benzosulphinide*, $C_7H_5NSO_3$.—The structural formula shows the nature of this body. It is an imido-derivative of benzosulphonic acid. It is a white crystalline solid soluble in water; the solution is very sweet. Saccharin has been estimated as several hundred times as sweet as cane sugar. It has marked antiseptic powers, and is much used as a substitute for sugar and sometimes as a preservative.

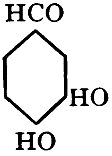


Saccharin

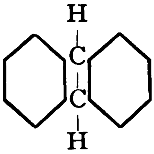
The following formulas show several benzene derivatives, some of which do not need special description:



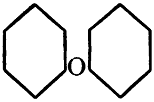
Phenazine



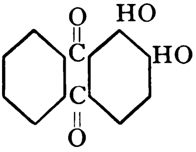
Protocatechuic aldehyde



Anthracene
$=C_{14}H_{10}$



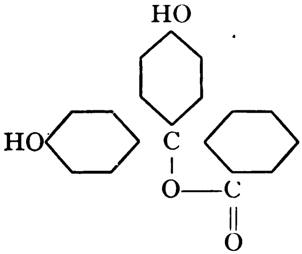
Phenylether



Alizarin

PHTHALEINS.—These are complex derivatives of phthalic acid. Some of them have acquired much importance on account of their value as dyes and indicators, and one of them, fluorescein, on account of its optical properties. The general nature of the structural formula is shown by that for *phenolphthalein* given below. The phthaleins must not be confounded with the "*phthalins*," a less important group, not requiring special consideration here.

*Phenolphthalein* is a light yellow powder almost insoluble in water but freely soluble in alcohol. The solution is nearly colorless when neutral or acid, but becomes bright red when alkaline. It is much used as an indicator.



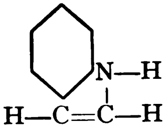
Phenolphthalein

*Resorcinolphthalein, fluorescein,* is a reddish powder which dissolves in strong alkaline solutions to produce a dark-red solution, but when highly diluted the liquid shows a vivid green fluorescence. The coloring power of fluorescein is so great that large bodies of water may be made distinctly fluorescent by moderate quantities of the material, and it has been used for tracing underground connections between streams and springs.

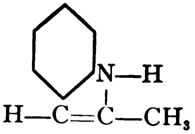
EOSINS, RHODAMINS.—These classes of colors, now well-known on account of their use in coloring foods, beverages and confections, are derivatives of the phthaleins. The *eosins* are bright red dyes; most of them are fluorescent. Eosin proper is tetrabromofluorescein, and erythrosin, tetraiodofluorescein. The *rhodamins* are the phthalein derivatives of 1-3 amidophenol; they are also brilliant dyes of different shades of red and fluorescent.

*Indol*, $C_8H_7N$. According to the system of nomenclature now generally used, this body should be termed "indin." The structural formula shows it to be a union of a pyrrol ring with a benzene ring. It is of considerable importance because of its occurrence among the products of putrefaction, and pancreatic digestion of proteids, and also its relation to the principal coloring matter of indigo.

*Skatol* is a methyl substitution of indol. It occurs with indol and is a characteristic ingredient of the contents of the intestinal canal.



Indol (Indin)



Skatol (Skatin)
(Methyl indin)

*Indigotin*, $C_{16}H_{10}N_2O_2$, the principal coloring matter of indigo, is a duplicated indol with substitution of two oxygen atoms for four hydrogen atoms. It exists in the indigo plant in the form of a glucoside, "indican," which is hydrolysed by dilute acids or by enzyms. The change can be brought about by exposing the macerated plant-tissues to air. Indigotin is insoluble in water. It is of a bright blue color, and in masses has a copper lustre. Natural indigotin is contaminated with other coloring matters. To render indigo available for dyeing it is made soluble, either by converting it into a sulphonic acid or into indigo-white, a compound containing two additional hydrogen atoms obtained by fermentation methods, The sulphonic acid dyes directly; the indigo-white is soluble and impregnates the fibre and when exposed to the air reverts. to indigotin and becomes blue and insoluble.

The synthesis of indigotin has been accomplished in several ways: The following method, now employed on a practical scale, illustrates the general methods of organic synthesis.

Naphthalene from coal-tar is converted into phthalic acid, $C_6H_4(COOH)_2$ this phthalimide, $C_6H_4(CO)_2NH$, this into anthranilic acid, $C_6H_4(COOH)(NH_2)$, this into a body of the formula $C_6H_4(COOH)(NH)(CH)(COOH)$, which is then converted into indoxylcarboxylic acid, $C_6H_4(CO)(NH)(CHCOOH)$, from which indigotin is obtained.

*Experiment* 40.—Make an intimate mixture of benzoic acid with twice its weight of quicklime, and heat the mixture strongly in an apparatus provided with a condenser. If it be desired to obtain considerable benzene a hard glass flask and condensing apparatus must be used, and the distillate must be purified by shaking with sodium hydroxide and then with calcium chloride and redistilling. For the purpose of illustrating this method of obtaining pure benzene, a distillation of 10 grams of benzoic acid with 20 grams of quicklime will be sufficient. A testtube with bent delivery tube will serve. The residue in the retort is principally calcium carbonate. After cooling, it may be treated with boiling water, filtered, and the material collected on the filter and tested with hydrochloric acid. The presence of a carbonate will be shown by effervescence.

*Experiment* 41.—Add 4 c.c. of sulphuric acid slowly to 5 c.c. of nitric acid, stirring during the addition. Allow the mixture to cool, place the vessel containing it in cold water and add, with stirring, 1 c.c. of benzene in small portions, stirring between each addition. Allow the mixture to stand until the action is complete; add considerable water, stir and allow to stand for a time. Nitrobenzene settles as in an emulsion with water. It should be washed several times by shaking it with water and allowing the mixture to settle. The characteristic odor will be noticed. Note also that the product floats in the mixture of acids but sinks in water. The experiment may be conveniently performed in a testtube with foot, as heat is not required.

*Experiment* 42.—Mix about equal volumes (1 c.c. of each) of nitrobenzene, water and hydrochloric acid, and a little granulated tin, or fine tinfoil, cut into very small pieces. Care should be taken not to use common foil as this is largely lead. It may be necessary to warm the mixture slightly to maintain the evolution of hydrogen. The nitrobenzene will be converted into aniline. To detect the latter, slightly dilute the mixture and add a fresh solution of bleaching powder or solution of chlorinated soda. A transient bluish-violet tint will appear.

*Experiment* 43.—Add a few drops of a dilute solution of ferric chloride to a small amount of salicylic acid in a watch glass or porcelain basin. A violet solution is produced.

*Experiment* 44.—Mix about 0.1 gram of salicylic acid with 20 c.c. of water, to which a few drops of sodium hydroxide have been added, and shake the liquid until the acid has been dissolved. If the solution does not occur in a few minutes add more sodium hydroxide. The solution will contain sodium salicylate. Add enough sulphuric acid to render the liquid slightly acid, then add 10 c.c. of ether and shake well. Allow the mixture to stand until some ether separates, pour this off, evaporate it and test the residue for salicylic acid as noted above. This is an extraction with an "immiscible solvent."

*Experiment* 45.—Test a small amount of benzoic acid by the method given in Experiment 43. A brown precipitate will be formed.

*Experiment* 46.—Prepare sodium benzoate and extract benzoic acid from it by the method of Experiment 44, substituting benzoic acid for salicylic. Test the benzoic acid by odor and reaction with iron.

*Experiment* 47.—Mix a very little aniline with a drop of chloroform, add a few drops of a strong solution of sodium hydroxide in alcohol, and heat the mass gently by immersing it in warm water. A peculiar and very disagreeable odor will be developed, due to a body called phenylcarbamine or isonitrile, $C_6H_5NC$.

*Experiment* 48.—Mix 1 gram of phenol with 6 c.c. of strong sulphuric acid and 1 c.c. of water; stir and heat for a short time by immersing the testtube in boiling water; 1–2 and 1–4 phenolsulphonic acids are formed. The 1–3 form cannot be obtained by this method.

*Experiment* 49.—Liquefy phenol by adding a few drops of water to a gram of the crystals; add some of this liquid to some white of egg. The albumin is coagulated. This is a distinction between phenol and true kreasote, as the latter does not coagulate albumin.

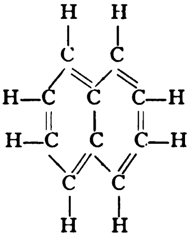
*Experiment* 50.—Place about 20 c.c. of bromine water in a beaker and stir it with a glass rod carrying a small drop of liquid phenol. A yellowish-white precipitate of tribromphenol is produced.

*Experiment* 51.—Dissolve about 0.1 gram of potassium nitrate in a few drops of water; evaporate the solution to dryness in a watch glass over the steam bath and add to the residue a few drops of the phenolsulphonic acids obtained in Experiment 48 and smear the liquid over the glass with a glass rod. It will assume a yellow tint owing to the formation of nitrophenols, including picric acid. Add more water and pour the liquid into a small beaker, dilute further with water and then neutralise with ammonium hydroxide or sodium hydroxide. A deep yellow color is developed owing to the formation of a picrate.

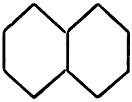
If the mixture of phenol and sulphuric acid be heated for several hours in boiling water, it is mostly changed into a phenoldisulphonic acid, and the yield of picric acid from this is much greater than that obtained in the above experiment.

*Experiment* 52.—Dissolve a little saccharin in water, acidulate slightly with sulphuric acid and proceed as in Experiment 44. The saccharin will be left as a crystalline residue, the nature of which is easily recognised by its taste.

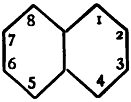
*Naphthalene*, $C_{10}H_8$, often called coal-tar camphor, is obtained from coal-tar, in the form of white, somewhat fragrant, crystalline scales. It melts at 80°. It is slightly soluble in boiling water. It is used extensively to protect goods against moths. Naphthalene consists of a double ring of carbon atoms saturated with hydrogen; thus:



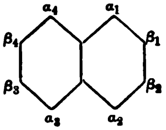
This formula is usually expressed by



The naphthalene-ring may be oriented in the same manner as the benzene-ring, beginning at the upper right hand angle and numbering in the direction of the numbers on a clock.



or



A substitution of one atom of hydrogen in naphthalene may produce two isomeric derivatives, depending on the position of the substituting body. Substitution at points

1, 4, 5 or 8 are termed "alpha" derivatives; substitutions at 2, 3, 6 or 7 are termed "beta" derivatives. Each may be more definitely indicated as shown in one of the ring-symbols.

*Naphthols, hydroxynaphthalenes*, $C_{10}H_7HO$.—When naphthalene is dissolved, in strong sulphuric acid, a mixture of alpha- and betanaphthalenesulphonic acids is obtained. If these be separated and saponified with sodium hydroxide, each will yield the corresponding hydroxide (naphthol). The two naphthols are much alike, being white, crystalline bodies, freely soluble in alcohol, sparingly in water and possessing marked antiseptic and germicide powers. Betanaphthol is almost exclusively used.

*Betanaphthol*, (*naphthol*), is a colorless crystalline powder, soluble in about 1000 parts of cold water, 75 parts of boiling water, very soluble in alcohol, ether, chloroform and alkaline solutions. It becomes slightly yellow on exposure to light. It is used as an antiseptic and preservative.

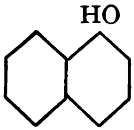
The naphthols yield sulphonic acids and nitro-derivatives exhibiting numerous instances of isomerism. A few of these are of considerable practical importance.

*Dinitro-alphanaphthols*.—One form is known as *Martius' yellow* and *naphthol yellow*. It is a bright yellow powder of high coloring power and has been used as a color for food and confections, but the fact that in large doses it produces functional disturbances, has led to the prohibition of this use.

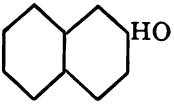
*Naphthol yellow S*, a sulphonated derivative of naphthol yellow, is a yellow powder of high coloring power, and being apparently much less active than the latter has displaced it as a food color.

*Abrastol*, *Asaprol*.—These are trade names of a calcium betanaphtholsulphonate, used as a food preservative.

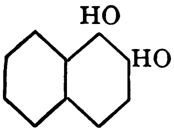
The following structural formulas show several naphthalene derivatives.



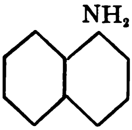
α-naphthol
α-hydroxynaphthalene



β-naphthol
β-hydroxynaphthalene



α-β-naphthol



α-amido-naphthalene

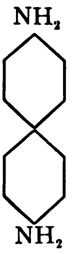
*Anthracene*, $C_{14}H_{10}$ (for structural formula see p. 135).—This is present in in the higher-boiling portions of coal-tar. It crystallises in colorless scales that show violet fluorescence. It melts at 213° and distils at about 360°. It is insoluble in water and only slightly in cold alcohol, benzene and carbon disulphide. An important use of anthracene is for the synthetic production of alizarin, the coloring matter of madder-root. The first step in this synthesis is the treatment of anthracene with chromic acid, by which anthroquinone, $C_{14}H_8O_2$, is formed. Anthroquinone is converted by means of strong sulphuric acid into a monosulphonate, and this, treated with sodium hydroxide and potassium chlorate, yields alizarin. This method of production has proved so satisfactory that the cultivation of madder (*Rubia tinctoria*) has been discontinued.

*Anthraquinone*, $C_{14}H_8O_2$, is a diphenyldiketone (see under Quinones, p. 133), obtained by the oxidation of anthracene with chromic acid. It forms yellow crystals. It is not an oxidising agent, and, unlike some other quinones, is not reduced by sulphurous acid. Its production from anthracene is a standard method of assaying the crude forms of the latter substance.

*Experiment* 53.—Dissolve 1 gram of commercial anthracene in 45 c.c. of glacial acetic acid; filter if necessary, bring to boiling and add a solution of chromic acid in acetic acid by small portions. The chromic acid solution is made by dissolving 10 grams of chromic anhydride in 10 c.c. of 50 per cent. acetic acid. This solution should be added until the boiling mixture produces a red stain on a piece of silver which shows that the chromic acid is no longer reduced. Allow the mass to cool, dilute with 150 c.c. of water, allow to stand a few hours, collect the precipitate on a filter, wash with water, then with solution of sodium hydroxide and again with water.

*Benzidin*, *diamidodiphenyl*, $(C_6H_4)_2(NH_2)_2$, belongs to the class of polynucleated cyclic compounds that is constituted of independent rings joined directly at one point, as contrasted with duplicated rings, such as naphthalene and phenanthrene, or conjugated rings such as phenyl ether, phenazin, anthracene and alizarin.

Benzidin has lately been brought into notice as applicable to the volumetric determination of sulphuric acid and sulphates on account of the insolubility of benzidin sulphate. A solution of benzidin hydrochloride is used in this process. Many of its derivatives are valuable dyes.



Benzidin

*Diphenyl*, $C_6H_5C_6H_5$, is another compound of the same class as benzidin.

*Carbazol* 1–2 *imido-diphenyl*, $(C_6H_4)_2NH$.—This exists in crude anthracene as a potassium derivative. It is employed in the preparation of synthetic colors and as a test for nitrates.

## COAL-TAR COLORS.

The coal-tar colors are a very numerous group of compounds obtainable from the hydrocarbons present in the tar. They are all closed-chain derivatives, but not all from benzene. The first color discovered was a violet which Perkin obtained, in 1856, while experimenting with aniline. Hofmann (1859) produced a brilliant red color magenta, from aniline, and the following year the manufacture of it was begun. From that date the number rapidly increased and they began to displace the natural colors. In 1868 alizarin, the coloring matter of madder, was obtained by synthesis from anthracene and recently indigo has been made from naphthalene.

On account of the almost exclusive use of crude aniline in the manufacture of these colors in the early period, they were termed "aniline colors" a name which is still largely used, although some of the most used are not made from aniline or its immediate derivatives.

As a class these bodies are brilliant in tint, of high coloring power and soluble in water and alcohol. They include every known shade and have to a great extent replaced the natural dyes. They are much used for coloring foods, beverages and household articles, and their sanitary relations have been the subject of much investigation and discussion.

Their composition is, as a rule, very complex, but as nearly all of them are produced from simple substances (*e. g.*, benzene, naphthalene, anthracene) by synthetic methods, the structural formulas are mostly known with certainty. The commercial colors include representatives of all the larger groups of closed-chain derivatives. The important ones are considered in connection with the groups to which they belong. The following list will indicate the variety of types they represent. A few colors not classified elsewhere are here described:

*Nitro- and Nitroso-colors.*—Picric acid, naphthol yellow, naphthol yellow S, naphthol green.

*Azo-colors.*—Methyl orange, Bismarck brown, Congo red.

*Ketonic Colors.*—Alizarin, chrysophanic acid.

*Phenylmethane Derivatives.*—Auramin, magenta (fuchsin), malachite green, phenolphthalein, fluorescein, eosins, rhodamines, methyl violet.

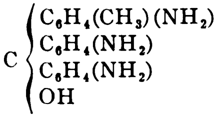
*Sulphur Derivatives.*—Methylene blue.

As the systematic names of these bodies are generally long and awkward, they are almost always known by commercial titles which are arbitrary and often fanciful. Abbreviations are used to indicate shade, special condition or manufacturer. A few of these abbreviations are here noted:

Letters such as J, JJ, B, BB, OOOO, are descriptive of the shades. Eosin J indicates an eosin with a yellow shade (Fr. *jaune*); German chemists often use G for this. JJ means a stronger yellow shade; OOOO a strong orange shade. S generally means sulphonation; naphthol yellow S is the sulphonated derivative of naphthol yellow. BASF (Badische Anilin und Soda Fabrik) is an example of a manufacturer's name.

A few of these colors are insoluble in water. Some azo-colors insoluble in water are soluble in oils, to which they impart an orange or yellow tint. They are now often used in coloring fatty foods, especially butter and cheese. Many colors are affected by acid or alkaline solutions and are used as indicators.

*Rosaniline.*—This is produced whenever crude aniline, which always contains toluidines (methylanilines), is treated with oxidising agents. Arsenic acid, nitrobenzene and mercuric nitrate are the oxidising agents practically used. The arsenic acid method was the first and hence all the rosaniline products were liable to contain arsenic. Rosaniline is generally formulated as a derivative from methane by substitution of all its hydrogen by monad groups.



$$C\begin{cases} C_6H_4(CH_3)(NH_2) \\ C_6H_4(NH_2) \\ C_6H_4(NH_2) \\ OH \end{cases}$$

Rosaniline forms salts with acids some of which are important dyes. One of these is: *magenta*, *fuchsin*, *aniline red*, *rosaniline hydrochloride.* It is soluble in water producing a brilliant red solution of high coloring power. It is used largely for coloring foods and beverages. The name "magenta" is an interesting instance of the fanciful source of these color-names. It refers to the battle at Magenta, Italy, fought in the year in which the color was first prepared.

*Methylene blue*, $C_{16}H_{18}N_3SCl$.—This is a complicated sulphur derivative, which has been used as a therapeutic agent and also for staining pathologic and bacteriologic preparations.

*Methyl violet*, $C_{24}H_{28}N_3Cl$, is a product of oxidation of dimethylaniline. It is of very high coloring power and is also an antiseptic. It is used in treatment of ulcers and wounds under the trade name "pyoktanin blue."

## TERPENES.

The *terpenes* are cyclic hydrocarbons having the general formula $(C_5H_8)_n$. When oxidised they form camphors and resins. The *terpenes* may be considered as cyclic compounds in which one or more latent valencies exist.

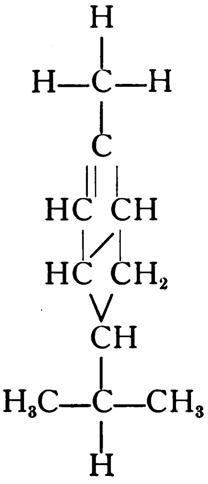
The formulas on page 148 are suppositions, and only suggestive, but indicate the complexity of the structure of these compounds.

Many *essential oils* consist almost entirely of *terpenes*, others of a mixture of *terpenes* with oxygenated bodies. The *terpenes* are capable of polymerisation, and often show optical activity. The natural forms are sometimes composed of equivalent proportions of dextro- and levorotatory modifications.

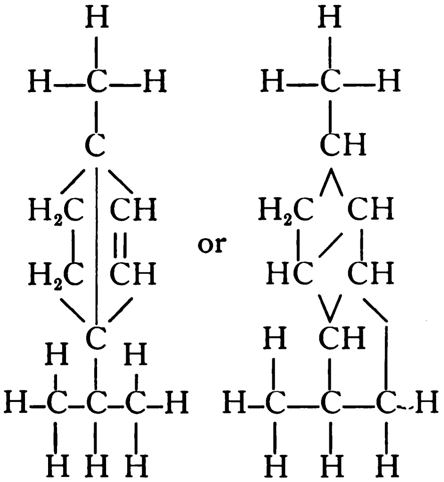
The following classification of the *terpenes* is based upon the differences in their molecular weights:

| | |
|---|---|
| 1. Hemiterpenes, | $C_5H_8$ |
| 2. Terpenes, | $C_{10}H_{16}$ |
| 3. Sesquiterpenes, | $C_{15}H_{24}$ |
| 4. Diterpenes, | $C_{20}H_{32}$ |
| 5. Polyterpenes, | $n(C_{10}H_{16})$ |

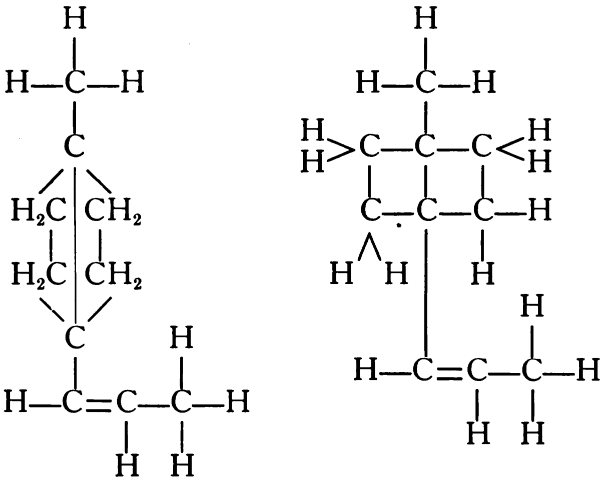
*Pinene*, $C_{10}H_{16}$, constitutes the principal portion of oil of turpentine. It is a colorless liquid possessing an aromatic odor. It unites with hydrochloric acid to form pinene hydrochloride, $C_{10}H_{17}Cl$, which, from its resemblance in physical properties to camphor, has been called "artificial camphor." When oil of turpentine is mixed with alcohol and nitric acid and allowed to stand for several days, a crystalline compound separates which has the composition $C_{10}H_{18}(OH)_2 + H_2O$, and is known as *terpin hydrate*. This compound forms colorless tabular crystals possessing a slightly aromatic odor and a bitter taste, and is used in medicine as an expectorant.



Pinene



Camphene



Terpinene
(Two arrangements of the suggested formula.)

*Camphene*, $C_{10}H_{16}$, is a white crystalline solid, which can be oxidised to form camphor.

*Limonene*, also known as *hesperidene*, *carvene* and *citrene*, constitutes almost the entire portion of several of the volatile oils, notably oil of orange peel. Oil of lemon peel consists of a mixture of pinene and limonene. Many of the volatile oils such as orange and lemon consisting almost entirely of terpenes, lose their characteristic odor upon standing and acquire the odor of oil of turpentine, the change being due to some obscure molecular rearrangement. This change is usually accompanied by a thickening and resinification of the oil, due to partial oxidation of the terpenes.

*Dipentene*, *Sylvestrene*, *Terpinolene*, *Terpinene* and *Phellandrene*, all have the formula $C_{10}H_{16}$ and possess similar properties to the terpenes already described.

*Terebene* is a mixture of several of the terpenes (pinene, terpinene and dipentene) and is produced by the action of sulphuric acid on oil of turpentine.

Members of the classes *sesquiterpenes*, $C_{15}H_{24}$, and *diterpenes*, $C_{20}H_{32}$, are found in some volatile oils.

*Colophene*, $C_{20}H_{32}$, is a diterpene, which is formed as a by-product in the manufacture of terebene.

*Polyterpenes* $(C_{10}H_{16})_x$, exist in caoutchouc and gutta percha and may be formed by the polymerisation of oil of turpentine.

## CAMPHORS.

The *camphors* are oxygenated derivatives of the terpenes. They are sometimes called *stearoptenes* to distinguish them from the *eleoptenes* or liquid portions of the volatile oils in which they usually occur. Some of them are alcohols while others resemble the ketones. They are completely volatile without decomposition and may be purified by sublimation.

Ordinary *camphor*, $C_{10}H_{16}O$, sometimes called *Japan camphor*, is obtained by distilling the wood of a species of cinnamon (*Cinnamomum camphora*) in a current of steam. It has also been obtained synthetically from oil of turpentine by converting the pinene into camphene which readily yields camphor by oxidation.

Camphor is a crystalline solid, possessing a characteristic odor and a pungent, afterward a cooling, taste. It is sparingly soluble in water but readily soluble in alcohol, ether, chloroform, petroleum spirit and fixed and volatile oils, the solution of the natural product being dextrorotatory. It can be ignited readily and burns with a luminous, smoky flame. With bromine, camphor forms a derivative known as monobromated camphor, $C_{10}H_{15}BrO$, which forms colorless, prismatic crystals, melting at 76° with a slight odor and a pungent camphoraceous taste.

*Borneol* or *Borneo camphor*, $C_{10}H_{18}O$, is obtained in a similar manner to ordinary camphor from the wood of *Dryobalanops aromatica*. It may be obtained from ordinary camphor by the action of sodium.

*Linalool*, $C_{10}H_{17}OH$; *Geraniol*, $C_{10}H_{17}OH$; *Citral*, $C_{10}H_{16}O$, and *Citronellal*, $C_{10}H_{20}O$, are odorous bodies belonging to this class, obtained from certain volatile oils, *citral* being present in oil of lemon.

*Menthol*, $C_{10}H_{20}O$, is the stearoptene obtained from volatile oils of several varieties of peppermint. *Menthol* forms colorless, needle-shaped crystals melting at 46° having a warm mint-like taste, followed by a cooling sensation when air is inhaled through the mouth.

## ESSENTIAL OILS.

*Essential oils*, often called *volatile oils*, are the liquid proximate constituents to which the characteristic odors of plants are due. They are obtained from flowers, seeds, leaves, stems, barks and roots, mostly by distillation with water, the volatile oil passing over with the steam and condensing with it. Some of the aromatic waters used in medicine, such as rose water and orange flower water, are obtained as by-products in the distillation of the essential oils. The essential oils are usually mixtures of terpenes and camphors although some consist of esters, aldehydes or ketones.

The ESSENTIAL OILS are distinguished by their complete volatility, comparative insolubility in water and complete solubility in alcohol, ether, chloroform and similar solvents. They are sometimes obtained by expression, as with oils of orange and lemon, and may be extracted from the plant tissues by the use of appropriate solvents. They may be divided into four classes, viz.:

Terpenes: Oils consisting mainly of members of the class of terpenes, as oil of lemon.

Oxygenated: Oils consisting of aldehydes, esters or ketones often associated with small amounts of terpene, as oil of cinnamon.

Sulphurated: Containing sulphur, as oil of mustard.

Nitrogenated: Containing nitrogen, as oil of bitter almond.

It will be impossible to give more than a brief outline of some of the important volatile oils.

Oil of turpentine is obtained by the distillation of the natural oleoresin of *Pinus palustris:* it consists almost entirely of pinene.

Oil of anise is principally composed of anethol, a methoxy-derivative of benzene.

Oil of black mustard is allyl isothiocyanate associated with a small amount of carbon disulphide.

Oil of cinnamon is principally cinnamic aldehyde.

Oil of cloves and oil of pimenta consist mainly of eugenol (allylguaiacol).

Oil of lavender flowers consists almost entirely of linalool and geraniol.

Oil of lemon consists of pinene, limonene (a dextrorotatory terpene), citral and a small amount of citronellal.

Oil of orange peel consists mainly of limonene and geraniol.

Oil of pennyroyal contains several ketones, the principal one being pulegone.

Oil of peppermint is very complex in its constitution. It contains pinene, limonene, aldehydes, alcohols and esters.

Oil of rose contains geraniol associated with a hydrocarbon having the formula $C_{20}H_{42}$.

Oil of sassafras contains safrol, eugenol, pinene and a benzene derivative.

Oil of sweet birch and oil of gaultheria consist of methyl salicylate, associated with a small amount of terpene.

Oil of violets, so called, is a product obtained from essential oil of orris. In concentrated form it bears very little resemblance in odor to violets, but when largely diluted with alcohol the odor is similar.

## RESINS.

The resins are also products resulting from the oxidation of the terpenes and are associated in plant tissues with other proximate principles, such as volatile oils and gums. They usually exhibit the characters of acids or anhydrides and are decomposed by strong heat. They are divided into three groups: 1, true resins; 2, oleoresins; 3, gum-resins.

The hard or true resins, of which ordinary resin or colophony (sometimes called rosin) is a type, are fusible solids capable of crystallisation under favorable conditions, insoluble in water, but soluble in one or more of the following solvents: alcohol, ether, chloroform, carbon disulphide, acetone, petroleum spirit, benzene and fixed or volatile oils. They often combine with alkaline hydroxides to form compounds known as resin soaps. They are contained in various plant tissues and are often obtained as exudations from living plants, in which case they may be pathological products, caused by wounding the tissues in which they exist.

*Colophony* or common resin is obtained as a residue when the oleoresin of the pine tree is distilled for obtaining oil of turpentine. It consists largely of abietic anhydride, $C_{44}H_{62}O_4$, which is converted into abietic acid by the action of alcohol and water.

*Dammar*, *Copal* and *Amber* are fossil resins used in the manufacture of varnishes and lacquers.

*Lac* is a resinous exudation from several species of oriental trees, occasioned by the puncture of an insect.

*Shellac* is the purified product occurring in thin, transparent layers.

*Guaiac resin* exists in the bark and heartwood of a West-Indian tree. It yields protocatechuic acid when fused with potassium hydroxide and is decomposed by destructive distillation into *guaiacol* and allied products.

*Crude turpentine*, *Burgundy pitch* and *Copaiba* are natural oleoresins, the consistency being liquid or semi-solid according to the amount of volatile oil associated with the resin.

*Balsams* are oleoresins which are associated with aromatic products, such as benzoic or cinnamic acid. The principal balsams are *Benzoin*, *Balsam Peru*, *Balsam Tolu* and *Storax*, all of which are used in medicine.

The *gum resins* usually exist in the plants from which they are derived, in the form of a milky juice. Upon fusing the gum resins with potassium hydroxide they yield resorcin and protocatechuic acid. The principal *gum resins* are *Asafetida*, *Ammoniac*, *Myrrh* and *Gamboge*.

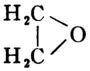
Caoutchouc and gutta percha are polyterpenes which exist in many plants in the form of an emulsion or milky juice.

## HETEROCYCLIC COMPOUNDS.

The closed chains so far described are assumed to contain only carbon atoms. Many compounds are known in which the ring consists of carbon atoms with an atom of oxygen, sulphur or nitrogen. These are termed *heterocyclic compounds*. Nitrogen carries with it one hydrogen atom (see Pyrrol).

The following is a synopsis of the most important groups of this type:

THREE-MEMBERED RINGS.—Among these are found bodies which might be classed as open-chain compounds, such as ethene oxide, $C_2H_4O$, of which the structural formula must be:



FOUR-MEMBERED RINGS.—In these is included betaine, the structural formula of which is given in the section on Ptomaines. The ring is the series NOCC.

FIVE-MEMBERED RINGS.—These include several important types of compounds.

*Furfurane:* four carbon and one oxygen atom.

*Thiophene:* four carbon and one sulphur atom.

*Pyrrol:* four carbon and one nitrogen atom.

Of the very many derivatives that these bodies may yield, only a few of special importance can here be noted.

*Furfurane*, $C_4H_4O$, is present in the materials collected from the distillation of pine wood. It is of less interest than its aldehyde.

*Furfural*, $C_4H_3(HCO)O$, often termed furfurol, is produced in the destructive distillation of, or action of strong acids upon, bodies containing carbohydrates, and in small amount in alcoholic fermentation. Lately, a suggestion has been made that the comparatively higher poisonous action occasioned by newly-prepared alcoholic beverages is due to furfural and not, as formerly supposed, to ordinary aldehyde or amyl alcohols. Furfural is a colorless liquid with an aromatic odor. It has well marked aldehydic properties. It is used for a few special tests in food analysis.

*Experiment* 54.—Ten grams of wheat bran are mixed in a 500 c.c. flask with 70 c.c. of water and 3 c.c. of sulphuric acid. The flask is connected with a condensing arrangement and the mixture cautiously distilled until about 20 c.c. have passed over. The distillate contains furfural. For a test for it, see under Phenylhydrazin.

*Coumarin.*—This is a crystalline principle existing in the tonka bean. Its odor is sufficiently like that of vanillin, to cause the tonka bean to be used very much as a substitute for vanilla. The molecule of coumarin is a combination of an oxidised furfurane ring with a benzene ring.

*Thiophene*, $C_4H_4S$, may be regarded as benzene in which two atoms of carbon are replaced by sulphur. The principal interest attaching to it is that it is a frequent impurity of benzene. It gives color reactions that hydrocarbons do not give, but its presence in benzene was long unrecognised and its reactions were ascribed to benzene itself until the impurity was discovered. Thiophene resembles benzene in many properties.

*Pyrrol*, $C_4H_4NH$, is found in bone oil and coal-tar. It can be prepared synthetically. It is a colorless liquid with an odor recalling that of chloroform.

According to the system of nomenclature now in vogue the termination "ol" is not appropriate to this compound. The name "pyrrin" would be more systematic.

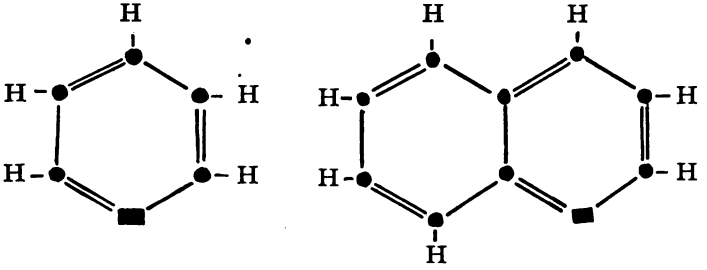
SIX-MEMBERED RINGS, PYRIDINS.—This is a series of bodies that contain nitrogen atoms in a closed chain with carbon atoms. This grouping, known as the "pyridin ring," is a stronger molecular linking than even benzene, and the opportunities for isomerism are also greater than with benzene. The type compound is:

*Pyridin*, $C_5H_5N$.—This was first noted in the offensive liquor obtained by distilling bones, formerly used in medicine under the name "Dippel's animal oil." It is found in coal-tar. Pyridin is a liquid with a disagreeable odor, boiling at a temperature somewhat above that of boiling water. It is a monacid base combining, as is usual with nitrogen bases, with the entire acid molecule. It also unites with alkyl iodides, such as methyl iodides; these compounds decomposed by silver hydroxide, yield hydroxyl bases analogous to the substitution ammoniums.

*Quinolin.*—The pyridin ring associated with a benzene ring, gives rise to quinolin, which bears the same structural relation to pyridin that naphthalene does to benzene.

The structural formations of these two bodies are shown in the annexed drawings in which the atoms are represented by special signs. It is to be noted that while pyridin cannot exist in more than one form, since the nitrogen atom may be placed at any angle of the chain without altering the relations of the other atoms to it, the quinolin group is capable of two modifications as shown. Neither pyridin nor quinolin contains asymmetric carbon and, therefore, has no optical activity.

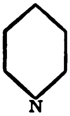
Quinolin is a colorless liquid of high dispersive power. It is produced in the destructive distillation of coal, bones and many alkaloids. It has been obtained synthetically. Pyridin and quinolin are of much interest not only on account of the large number of derivatives they yield, but principally because their molecular structure is present in many alkaloids.



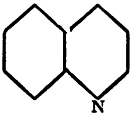
Pyridin Quinolin

The round dots represent carbon atoms; the rectangular represent nitrogen atoms
(Diagrammatic formulas.)

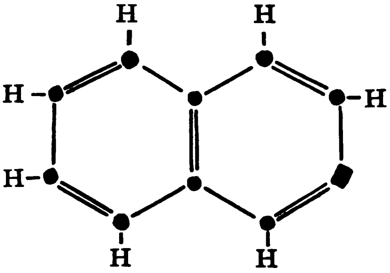
yet no uniform method of representing the
In this book it is represented by benzene
ith a small "N" attached close to one of the
wn in the annexed formula:



Pyridin symbol $=C_5H_5N$



Quinolin symbol $=C_9H_7N$



Iso-quinolin

*Homologous Derivatives.*—The hydrogen of all these molecules may be replaced by the alkyl radicles, thus forming homologous series. A few of these deserve mention.

*Methyl Pyridins.*—These are:

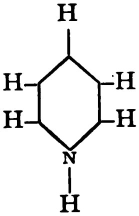
Picoline, $C_5(CH_3)H_4N$
Lutidine, $C_5(CH_3)_2H_3N$
Collidin, $C_5(CH_3)_3H_2N$

The first substitution will exist in three forms, the methyl radicle standing either in the 1–2, 1–3 or 1–4 position to the nitrogen. The further substitutions will show still more numerous instances of isomerism.

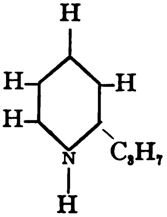
*Additive Compounds.*—As with benzene and naphthalene the latent valencies of these closed chains may be developed, and a series of derivatives obtained in which the original hydrogen is not disturbed.

*Piperidin, Pyridin hydrid,* $C_5H_{11}N$, is closely related to conine, as the annexed formulas show.

*Conine* is a substitution of propyl (trityl), $C_3H_7$, for the additive hydrogen atoms in piperidin nearest to the nitrogen, and is therefore, 1–2 propylpiperidin. The introduction of the alkyl radicle makes the carbon atom to which it is attached asymmetric. Conine is known to exist in several forms, respectively, dextro- and levo-rotatory, and inactive. The natural conine is dextro-rotatory.

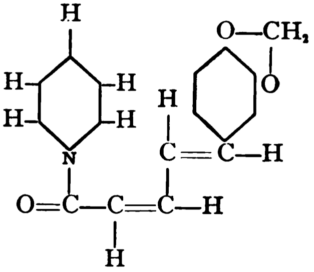


Pyridin hydrid
(Piperidin)



Conine

*Piperin.*—This substance is an abundant ingredient of all forms of pepper. Its empirical formula is identical with that of morphine, but it is not an alkaloid, and is structurally wholly different from morphine as the annexed formula shows. It contains a pyridin and a benzene ring. Piperin must not be confounded with the diamine, *piperazin.*



Piperin

## Cyanogen and Derivatives.

Nitrogen and carbon do not combine by simple contact, but if nitrogen be passed over a mixture of carbon and potassium carbonate, *potassium cyanide*, $KCN$, is formed. From this, other cyanides may be obtained. By heating mercuric cyanide, $Hg(CN)_2$, free cyanogen, $C_2N_2$, is formed. This is a colorless, poisonous gas.

Cyanides may be formed from proteid matters. This may be illustrated by placing a small piece of dried albumin and a little sodium in the closed end of a glass tube, heating to redness for about a minute and dipping the heated portion into a little water. The tube will break and its contents partly dissolve. The solution will react to the tests for cyanides, as given below.

Two forms of cyanogen compounds are known termed, respectively, cyanides and isocyanides, as follows:

| **Potassium cyanide.** | **Potassium isocyanide.** |
|---|---|
| $K—C \equiv N$ | $C \equiv N—K$ |

In the former nitrogen is triad, in the latter, pentad.

*Potassium Cyanide*, $KCN$.—This body, prepared usually by decomposing some more complex cyanides, is a snow-white mass, very soluble in water, and easily decomposed even by the carbonic acid of the air, hydrogen cyanide being formed. Potassium cyanide dissolves many silver compounds that are insoluble in water. It is used in making solutions for silver-plating and in photography, also in very small doses as a medicine. It is an active poison. Oxidising agents convert it into potassium cyanate. Commercial potassium cyanide generally contains cyanate and sodium cyanide.

*Hydrogen Cyanide*, HCN.—This is generally called *hydrocyanic* or *prussic acid.* When pure, it is a colorless liquid, easily decomposed and intensely poisonous, As sold for medical purposes (*Acidum hydrocyanicum dilutum*), it is very dilute, consisting of two parts of acid to ninety-eight of water. It has, even when much diluted, a strong odor suggesting bruised peach kernels; in fact, hydrogen cyanide is formed from these substances by the decomposition of nitrogenous principles when the seeds are crushed with cold water. This occurs under the influence of enzyms, for if these are first coagulated by boiling alcohol, no decomposition occurs. The reaction by which hydrogen cyanide is formed when bitter almonds are macerated with water consists in the hydrolysis of a crystalline principle called *amygdalin*, under the influence of an enzym called *synaptase*:

$$\overset{\text{Amygdalin.}}{C_{20}H_{27}NO_{11}} + 2H_2O = \overset{\text{Benzal-dehyde.}}{C_7H_6O} + \overset{\text{Hydrogen cyanide.}}{HCN} + \overset{\text{Glucose.}}{2C_6H_{12}O_6}$$

Hydrogen cyanide may also be made by decomposing other cyanides by strong acids, thus:

$$2KCN + H_2SO_4 = K_2SO_4 + 2HCN$$
$$AgCN + HCl = AgCl + HCN$$

The latter reaction is utilised in the pharmaceutical preparation of the dilute acid.

*Complex Cyanides.*—The potassium group cyanides show a great tendency to combine with other cyanides, especially those of the iron group, to form complex cyanides, in which some properties of the simpler cyanides, especially the poisonous qualities, are much diminished. The iron series is the most important. Two well-marked compounds are known.

*Potassium ferrocyanide*, $K_4C_6N_6Fe$, often called *yellow prussiate of potash*, is made by heating a mixture of nitrogenous organic matter, iron scraps, and potassium carbonate, treating the mass with water and allowing it to crystallise. Large lemon-yellow crystals are formed, which are not actively poisonous. Oxidising agents convert it into:

*Potassium ferricyanide* $K_3C_6N_6Fe$, commonly called *red prussiate of potash*. It forms large ruby-red crystals, soluble in water. The reactions with some substances are so distinct as to constitute very delicate tests. With ferrous compounds, for instance, the ferricyanides give a dark-blue precipitate; ferric salts give, with ferrocyanides, a similar blue precipitate—Prussian blue. The two precipitates are nearly identical in composition. An intermediate compound is known as *soluble* Prussian blue, being soluble in pure water, but insoluble in water containing ordinary mineral salts.

*Nitroprussic acid.*—By the action of nitric acid upon potassium ferrocyanide, an acid-like body is formed, the structure of which is not understood. It is provisionally termed nitroprussic acid. Its importance lies in the fact that its sodium salt, $Na_2Fe(CN)_5NO$, generally called *sodium nitroprussid*, is a test for sulphur and for formaldehyde.

*Tests for Cyanides.*—The recognition of cyanogen is a matter of importance in toxicology. The tests can be directly applied only to the simple cyanides; the double cyanides usually give the reactions after being decomposed by acids.

Silver nitrate gives a white precipitate of silver cyanide, which is soluble in boiling nitric acid.

A mixture of ferrous sulphate and sodium hydroxide, when agitated with a cyanide and then treated with acid, will produce a blue precipitate.

When hydrogen cyanide is brought into contact with ammonium sulphide, a compound called ammonium thiocyanate is formed, which gives, with ferric chloride a blood-red color.

*Experiment* 55.—Dissolve about 0.5 gram of potassium cyanide in 20 c.c. of water. Put a few drops of this solution in a watch-glass, add a drop of dilute sulphuric acid, and invert over the mixture another watch-glass containing a drop of silver nitrate solution. *Hydrogen cyanide* will be formed and some of it will pass off as vapor and form *silver cyanide* on the upper glass.

*Experiment* 56.—Repeat Experiment 55, substituting a drop of ammonium sulphide for the silver nitrate. The vapor of hydrogen cyanide will form *ammonium thiocyanate.* After about five minutes, touch the spot in the upper glass with a rod dipped in ferric chloride. A bright red stain of *ferric thiocyanate* will appear.

*Experiment* 57.—To 5 c.c. of the potassium cyanide solution, in a testtube, add a few drops of ferrous sulphate solution and then a little sodium hydroxide. A precipitate consisting principally of ferrous hydroxide forms. Pour the mass from one testtube to another for a short time, then add, cautiously, hydrochloric acid in slight excess. A precipitate of *ferric ferrocyanide* (Prussian blue) will be obtained. This is destroyed by excess of alkali but re-formed by acid.

*Experiment* 58.—Heat in a small glass tube, sealed at one end, a small amount of mercuric cyanide. *Cyanogen* is liberated and will burn at the mouth of the tube with a characteristic peach-blossom flame. At the upper part of the tube a brown deposit of a polymeric form, termed *paracyanogen* will collect.

*Cyanogen hydroxides, Cyanic acids.*—Cyanogen unites with hydroxyl to form several compounds that have the same percentage composition, but some are stereo-isomers, others polymers. Both forms of cyanogen form these compounds. Three important forms are:

| | | |
|---|---|---|
| $N\equiv C-O-H$ | $H-N=C=O$ | $C\equiv N-O-H$ |
| **Cyanic acid** | **Isocyanic acid** | **Fulminic acid** |

*Cyanuric acid*, $H_3C_3N_3O_3$, is of more complex structure. Fulminuric acid has the same empirical formula as cyanuric acid, but is a nitro-derivative and, therefore, of entirely different type.

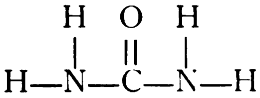
The important derivatives of these acids are the cyanates and fulminates.

*Potassium cyanate.*—The common cyanate is isocyanate, KNCO. It exists in considerable amount in commercial potassium cyanide and can be obtained by heating cyanides with lead oxides.

*Ammonium cyanate*, $NH_4NCO$, is of interest because it may be transformed by heating into urea, $(NH_2)_2CO$. This transformation was the first instance of organic synthesis and its accomplishment broke down the lines between organic and inorganic chemistry. The change is a rearrangement as follows:

$$H_4N{-}N{=}C{=}O$$

Ammonium cyanate



$$H{-}\overset{\displaystyle H}{\overset{|}{N}}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}\overset{\displaystyle H}{\overset{|}{N}}{-}H$$

Urea

*Fulminates.*—As the name indicates, many of these are explosive. *Mercuric fulminate*, $Hg(CNO)_2$, is prepared by heating a mixture of alcohol, nitric acid and mercuric nitrate. It crystallises in needles. It explodes violently on percussion, and is the material used in percussion caps for firearms.

*Silver fulminate*, AgCNO, is more explosive than the mercuric salt.

*Thiocyanates.*—These compounds, often called *sulphocyanates*, are analogous to the cyanates and are obtained in a similar manner, that is, by direct addition of sulphur, but the molecular arrangement is not identical in the two actions.

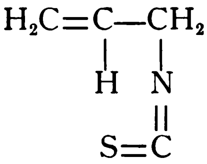
The common cyanate is isocyanate, as already noted (See formula of potassium cyanate.) Oxygen attaches itself in preference to the carbon and nitrogen atoms, but sulphur attaches itself to the other positive element, hydrogen or metal. The contrast is shown in the structural formulas:

$K{-}N{=}C{=}O$
Common potassium cyanate
(Isocyanate)

$N{\equiv}C{-}S{-}K$
Common potassium thiocyanate

The soluble thiocyanates produce with ferric compounds a bright red solution of ferric thiocyanate. This reaction is a delicate test for ferric compounds. No color is produced with ferrous compounds.

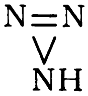
The known esters of thiocyanic acid are of the isothiocyanic type. They are sometimes termed "mustard oils," as the volatile oil of black mustard is allyl isothiocyanate, $(C_3H_5)NCS$. As noted elsewhere, it does not exist in the seed, but is produced by a decomposition under the influence of a special enzym.



$$\begin{array}{ccc} H_2C & = C & — CH_2 \\ & | & | \\ & H & N \\ & & \| \\ & S = & C \end{array}$$

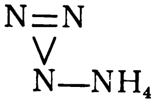
Allyl isothiocyanate
(Mustard oil)

*Azoimide*, *Hydrazoic acid*.—An interesting connecting link between inorganic and organic chemistry is furnished by this substance. It has the empirical formula $N_3H$. The structural formula is considered to be:



$$\begin{array}{c} N{=}N \\ \vee \\ NH \end{array}$$

Azoimide
(Hydrazoic acid)



$$\begin{array}{c} N{=}N \\ \vee \\ N{-}NH_4 \end{array}$$

Ammonium hydrazoate

It was first prepared from an amine derivative of benzene, benzoyl nitride, by treatment with sodium ethylate, the following reaction occurring:

$$\begin{array}{ccccccc} \text{Sodium ethylate.} & & \text{Benzoyl nitride.} & & \text{Sodium hydrazoate} & & \text{Ethyl benzoate.} \\ NaC_2H_5O & + & C_6H_5CON_3 & = & NaN_3 & + & C_6H_5CO_2C_2H_5 \end{array}$$

Hydrazoates may be prepared by several other methods some of which are not strictly organic. From the salt the hydrogen compound may be obtained. It is a colorless mobile liquid of very disagreeable odor, and highly explosive. It resembles the halogen acids in many properties. Its ammonium salt, $NH_4N_3$, has the empirical formula $H_4N_4$.

## AMMONIUM DERIVATIVES.

**Amines and Amides.**—Amine, $NH_3$, ammonia, is always found, either free or combined, among the products of decomposition of nitrogenous matter. One of the most striking properties of free amine is its power to neutralise acids. When certain organic bodies containing nitrogen were found to have a similar property, a similar constitution was assigned to them. Morphine and quinine, which, like amine are decidedly alkaline, and contain considerable nitrogen, have been regarded as ammoniacal in character. Although efforts to produce these bodies synthetically have succeeded only to a limited extent, yet many substances resembling them in composition have been obtained, and no doubt need now exist as to the essential nature of these products, or as to the possibility of ultimately producing them. Many of the synthetic bases now known are produced by the substitution of the hydrogen or nitrogen in amine, $NH_3$, or ammonium, $NH_4$, by different elements or radicles. The number of compounds so produced is greatly increased by the fact that these molecules are capable of polymerism, so that one set of compounds may be formed on the type $NH_3$, and another on that of $N_2H_6$, and so on. A very complete and systematic nomenclature has been adopted for these compounds. In the first place, the character of the replaceable radicles, and, to a certain extent, therefore, the character of the compound itself, is indicated by the termination. When the radicle is positive, and especially when it does not contain oxygen, "*ine*" is used; when negative and containing oxygen, "*ide*" is used. When the nitrogen is replaced by some member of its group (B, P, As, Sb and Bi), some distinct syllables of these names are added. The names of all the radicles entering into the compound are attached. If the molecule is duplicated, the syllables "*di*," "*tri*," etc., are used to indicate the degree of duplication. If the compound is derived from the type $NH_4$ it has the termination "onium." The following list will show all these points:

$NH_3$, amine; $N_2H_6$, diamine; $N_3H_9$, triamine; $N_4H_{12}$, tetramine.
$PH_3$, phosphine; $P_2H_6$, diphosphine.
$AsH_3$, arsine.
$SbH_3$, stibine.
$NH_4$, ammonium; $N_2H_8$, diammonium; $N_3H_{12}$, triammonium.
$PH_4$, phosphonium.
$AsH_4$, arsonium.
$SbH_4$, stibonium.

The polymerisation of the molecules takes place by introduction of radicles of dyad or higher valency. The methods of producing these substitution compounds are various; one of the simplest is by heating solutions of amine with bromides or iodides of the radicles to be substituted. Thus, an alcoholic solution of amine and ethyl iodide heated for some hours in a sealed tube, gives the reaction:

$$NH_3 + (C_2H_5)I = (C_2H_5)H_3NI$$

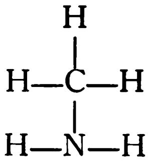
As $NH_4I$ is ammonium iodide so the above compound is called ethylammonium iodide. By further action the whole of the hydrogen may be replaced by ethyl, and we get $(C_2H_5)_4NI$, tetrethylammonium iodide. Each of the hydrogen atoms may be replaced by a different radicle, by which great complexity in structure and nature arises. Thus:

| | |
|---|---|
| $(C_2H_5)_2(C_5H_{11})HNI$ | diethylpentylammonium iodide. |
| $(C_2H_5)_3(C_5H_{11})NI$ | triethylpentylammonium iodide. |
| $(CH_3)(C_2H_5)(C_3H_7)(C_4H_9)NI$ | methylethylpropylbutylammonium iodide. |

From $NH_3$ we may derive:

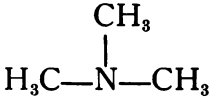
| | |
|---|---|
| $(C_2H_5)H_2N$ | ethylamine. |
| $(C_2H_5)_2HN$ | diethylamine. |
| $(C_2H_5)_3N$ | triethylamine. |

When but one-third of the hydrogen is substituted, the body is said to be *primary;* when two-thirds are substituted, it is *secondary;* when all is substituted, the body is *tertiary.* Ethylamine for instance, is a primary monamine. The following structural formulas show some of these bodies:



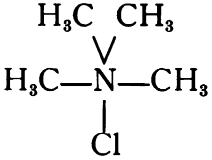
$$\begin{array}{ccc} & H & \\ & | & \\ H- & C & -H \\ & | & \\ H- & N & -H \end{array}$$

**Methylamine**



$$\begin{array}{ccc} & CH_3 & \\ & | & \\ H_3C- & N & -CH_3 \end{array}$$

**Trimethylamine**



$$\begin{array}{ccc} & H_3C\ \ CH_3 & \\ & \vee & \\ H_3C- & N & -CH_3 \\ & | & \\ & Cl & \end{array}$$

**Tetramethylammonium chloride**

*Diamines and diammoniums.* These always contain $N_2$:

$(C_2H_4)H_4N_2$ ............... ethenediamine (ethylenediamine).
$(C_2H_4)H_6N_2(HO)_2$ ........ ethenediammonium hydroxide.

*Triamines, and triammoniums, tetramines and tetrammoniums,* are formed on the same principle.

The following formulas show some of the compounds obtained by these elaborate substitutions and when the nitrogen is replaced by other members of its group:

**Ethyl phosphine.** $(C_2H_5)H_2P$
**Diethyl phosphine.** $(C_2H_5)_2HP$
**Triethyl phosphine.** $(C_2H_5)_3P$
**Trimethyl arsine.** $(CH_3)_3As$
**Tripentyl stibine.** $(C_4H_{11})_3Sb$
**Triethyl bismine.** $(C_2H_5)_3Bi$
**Triethyl borine.** $(C_2H_5)_3B$
**Tetrethylphosphonium hydroxide.** $P(C_2H_5)_4HO$
**Tetrethylstibonium iodide.** $Sb(C_2H_5)_4I$

By a combination of radicles of different valencies we may get such a body as:

$(CH_3)_3(C_2H_5)_3(C_2H_4)H_4P_3I_3$, trimethyltriethylethenetriphosphonium iodide.

Several complex amines are used in medicine. Among these are:

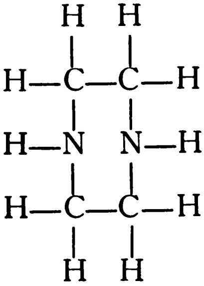
*Hexmethenetetramine*, $(CH_2)_6N_4$, which is made by adding ammonium hydroxide to formaldehyde. The reaction is a dehydrolysis:

$$6CH_2O + 4NH_4HO = (CH_2)_6N_4 + 10H_2O$$

The product is a colorless, almost inodorless, crystalline mass, soluble in water. It is now sold under proprietary names—*e. g.*, formin, cystogen, urotropin—for the treatment of purulent affections of the kidneys and bladder. When taken internally it is decomposed into formaldehyde and ammonium hydroxide. The former is largely excreted by the kidneys and thus exercises its antiseptic action over the mucous membranes of the genito-urinary tract.

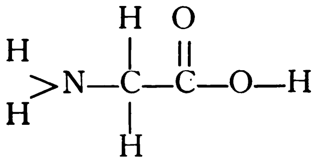
*Experiment* 59.—To 10 c.c. of commercial formaldehyde solution add small amounts of ammonium hydroxide, testing between each addition by a drop of the solution on red litmus paper, until the reaction becomes alkaline. Allow the mixture to stand for some hours and then evaporate it at a low temperature. The tetramine will separate as a white crystalline mass.

*Piperazin* is ethenediamine (ethylenediamine). It forms yellowish crystals, soluble in water. It is strongly basic, and has been used in the treatment of diseases supposed to be associated with excessive excretion of uric acid, as piperazin urate is very soluble in water. Piperazin must not be confounded with piperin.



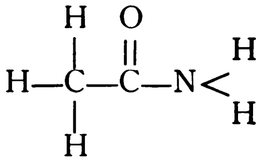
Piperazin

**Amides.**—All primary monamines may be expressed as substitutions of amidogen, $NH_2$, for other monads. When the amidogen is associated with a substantially positive group, the compound is basic and is called an amine, but when associated with negative groups it may form either acid or neutral bodies which are called amides. Thus, amidogen may be substituted for the hydrogen of benzene, giving rise to $C_6H_5NH_2$, amidobenzene, which is basic, and is therefore an amine. Substituted for the hydrogen of acetic acid it gives amidoacetic acid, in which some of the acid properties are retained; but substituted for the hydroxyl of acetic acid it entirely removes the acid function, forming a body called acetamide. These facts are shown by structural formulas:



$$\begin{array}{cccccc} & & \mathrm{H} & & \mathrm{O} & \\ \mathrm{H} & & | & & \| & \\ & >\mathrm{N}- & \mathrm{C} & - & \mathrm{C} & -\mathrm{O}-\mathrm{H} \\ \mathrm{H} & & | & & & \\ & & \mathrm{H} & & & \end{array}$$

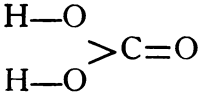
Amidoacetic acid



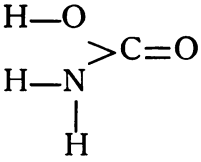
$$\begin{array}{cccccc} & \mathrm{H} & & \mathrm{O} & & \\ & | & & \| & & \mathrm{H} \\ \mathrm{H}- & \mathrm{C} & - & \mathrm{C} & -\mathrm{N}< & \\ & | & & & & \mathrm{H} \\ & \mathrm{H} & & & & \end{array}$$

Acetamide

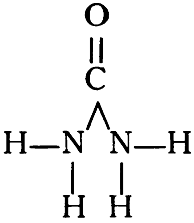
*Urea, carbonyl diamide*, $(NH_2)_2CO$, is the most abundant solid ingredient of normal human urine. It is a colorless solid, crystallising readily and is freely soluble in water and alcohol. Most of its salts are also soluble, but the nitrate and oxalate are but sparingly so, hence the addition of nitric or oxalic acid to urines rich in urea will produce a precipitate. Urea is strictly a diamide, that is, formed by the substitution of an acid radicle—the group CO—but this overcomes only one of the amidogen groups, hence urea forms salts with one equivalent of acid, not as do the diamines with two equivalents. As with all other compounds of these types, the whole molecule of the acid acts; urea hydrochloride is $CH_4N_2O,HCl$. The following structural formulas will show the relation of urea to carbonic acid through the intermediate body, carbamic acid:



Carbonic acid



Carbamic acid



Urea

Urea is not liable to decomposition when in pure solution, but in presence of proteid matters and exposed to the air it soon hydrolyses to ammonium carbonate. This is the ordinary reaction by which urine becomes alkaline on standing:

$$CH_4N_2O + 2H_2O = (NH_4)_2CO_3$$

This change is due to enzyms formed by microbes.

Urea is decomposed by hypochlorites and hypobromites with evolution of carbon dioxide and nitrogen. This reaction is utilised in the quantitative determination of urea in urine. Urea can be prepared synthetically by heating ammonium cyanate. This was the first discovered instance of synthesis. The change is merely a rearrangement. (See under Cyanates.)

*Experiment* 60.—Melt in a sand crucible of about 50 c.c. capacity, 10 grams of commercial potassium cyanide and stir in, gradually and slowly, 40 grams of lead monoxide (litharge). When the entire amount has been added pour the mass out upon an iron plate, and allow to cool. Separate as far as possible the reduced lead from the potassium cyanate that has been formed; powder the latter and dissolve in 50 c.c. of cold water, filtering if necessary. Add a cold saturated solution of 12 grams of ammonium sulphate, heat the mixture slowly on the water-bath to a temperature of 60° and maintain it at that point for an hour. The ammonium cyanate which is the first product of the reaction is changed to *urea*. This may be obtained by evaporating the solution to dryness in shallow basins on the water-bath and extracting the residue with boiling alcohol. The urea crystallises from the cold alcohol. It is not quite pure but will show the characteristic properties.

Many complex bodies of these types are found in the fluids of living tissues and among products of putrefaction. Some of these are described in the section on Purins, others in the section on Ptomaines and Leucomaines. Some others of considerable importance are here described.

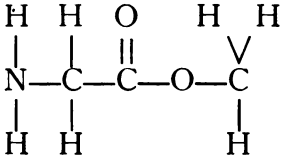
*Taurin, amidothylsulphonic acid*, $C_2H_4(NH_2)HSO_3$, is obtained by hydrolysis of taurocholic acid of bile; especially ox bile, by hydrochloric acid, forming taurin and cholic acid. Taurin forms colorless crystals very soluble in water. As it contains $NH_2$ and $HSO_3$ it has both acid and basic properties.

*Amidoacetic acid, glycocoll, glycin*, $HC_2H_2(NH_2)O_2$.—This may be obtained by several methods, among which are boiling glue with sulphuric acid, warming monochloracetic acid with dry ammonium carbonate, and decomposition of glycocholic acid (of bile) by potassium hydroxide. Amidoacetic acid is a crystalline solid, soluble in water; the solution has a sweetish taste. It is both an acid and a base. It easily forms salts with ordinary positives and also combines with common acids forming, for example, the following compounds: $CuC_2H_4NO_2$ and $C_2H_5NO_2HCl$, both of which are crystalline bodies.

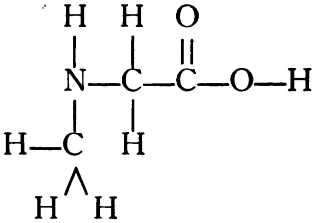
Amidoacetic acid forms esters with the alkyl radicles and also amine derivatives of which the following will serve as examples:

*Ethyl amidoacetate*, $C_2H_5C_2H_4NO_2$.—This is a volatile liquid with an odor resembling that of cacao.

*Methylamidoacetic acid*, $HC_2H_2NH(CH_3)O_2$, *methyl glycocoll*, *sarkosin*, was first obtained as a decomposition product of kreatin.

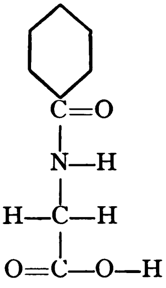


Methyl amidoacetate



Methylamidoacetic acid
(Sarkosin)

*Hippuric acid*, *benzoyl glycocoll*.—The structural formula of this shows that it contains residues of both amidoacetic acid and benzoic acid; in fact, its empirical formula may be obtained by adding the formulas of these acids and deducting $H_2O$. By hydrolysis and also by the action of acids or alkalies, hippuric acid may be decomposed into benzoic acid and amidoacetic acid. As hippuric acid occurs in considerable proportion in the urine of herbivorous animals, it has been a commercial source of benzoic acid.



Hippuric acid.

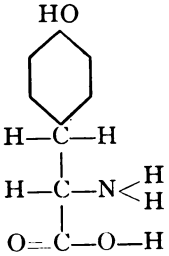
*Trimethyl glycocoll* is *betaine*, a ptomaine described in another section.

Amido-derivatives of the higher acids exhibit numerous instances of isomerism. Among these are:

*Leucins.*—Under the name leucins several analogous substances with the empirical formula, $C_6H_{13}NO_2$, have been included. They are found among the products of digestion of proteids, especially under the influence of trypsin, and are often associated with tyrosin.

One form of leucin, probably an amidocaproic acid, is derived from casein and has also been prepared synthetically; another form is a derivative of butylacetic acid. Some of these forms contain asymmetric carbon and are, therefore, optically active.

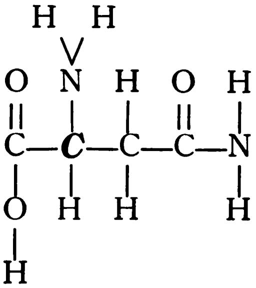
*Tyrosin*, 1-4 phenolamidopropionic acid.—This is produced in many transformations of proteid matters, such as boiling horn, hair or albumin with sulphuric acid, digesting proteids for some time with pancreatic secretion and by putrefactive actions. It has been prepared synthetically.



**Tyrosin**

*Cystin*, $C_6H_{12}N_2O_4S_2$, probably an amidothiolactic acid derivative occurs as a crystalline sediment in human urine and sometimes forms a calculus.

*Asparagin* is an example of the presence of amidogen in two positions in a molecule. It is succinic acid with one hydroxyl group replaced by amidogen, and another amidogen group replacing a hydrogen atom attached to carbon so that both the amine and amide structures are exhibited. *Asparagin* has asymmetric carbon. It is found in the seeds of many plants and in the sprouts of asparagus and vetch. The asparagin in asparagus is levorotatory; that in vetch is mostly the same, but the dextrorotatory form also is found. The natural occurrence of a levorotatory body in predominating quantity is unusual, since most natural bodies that are optically active are dextrorotatory.



Amido-succinamic acid
(Asparagin)

*Purins*, *Alkaloids*, *Ptomaines*, *Leucomaines*.—These are groups of nitrogenous compounds many of which are amines or amides. The important bodies of each type are described in connection with the group named.

## Azo-, Diazo- and Hydrazo-compounds.

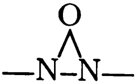
When two atoms of nitrogen are joined by two bonds, and the remaining bonds are joined to similar radicles, a group is formed called an azo-compound. When the radicles are dissimilar, a diazo-compound (diazonium) is formed. When an atom of oxygen is inserted between the nitrogen atoms, an azoxy-compound is formed. When one bond of each nitrogen atom is united to an atom of hydrogen, the body is called a hydrazo-compound. These points are exemplified in the following formula:

$=N-N=$

Hydrazo- group

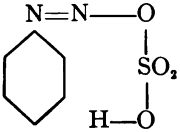
$-N=N-$

Azo- group

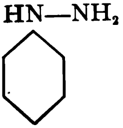


$\overset{O}{-N-N-}$

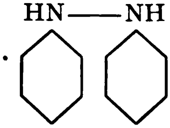
Azoxy- group



Diazobenzene
(diazonium) sulphate



Phenylhydrazin



Hydrazobenzene

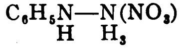
**Hydrazins.**—The hydrazins agree with the diazo-compounds in containing dissimilar radicles, but differ in the fact that the union between the nitrogen is by one bond only.

The difference is shown in the following formulas:

Diazo-benzene nitrate.

$C_6H_5N = N—(NO_3)$

Phenylhydrazin nitrate.



$C_6H_5\underset{H}{N}—\underset{H_3}{N}(NO_3)$

Azo-compounds are now of considerable practical importance. Many of them are brilliant in color and less liable to fade than some of the other forms of synthetic colors. Some of them have the valuable property of dyeing cotton without a mordant. A few are quite insoluble in water but soluble in oil.

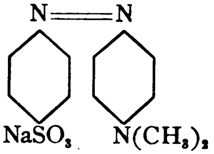
Azo- derivatives are usually produced through the intermediate development of diazo-compounds, by reaction of amine derivatives with nitrous acid. This method called "diazotising," was discovered by Griess. It is regularly used in manufacturing operations, the nitrous acid being obtained by the action of a strong acid, acetic, sulphuric or hydrochloric, on sodium nitrite.

A few of the azo- colors are insoluble in water but soluble in alcohol and in oils. They are used for coloring fatty foods, especially butter and butter-substitutes. Several of them have been designated by the fanciful term Soudan, and distinguished by appended letters, as noted in the general description of synthetic colors.

Soudan I is betanaphtholazobenzene, $C_6H_5N=NC_{10}H_6OH$.

These derivatives are capable of "sulphonation," that is, conversion into sulphonic acids by treatment with sulphuric acid. By this means many of them are rendered more soluble and, apparently, in a few instances, less toxic. From the sulphonic acids salts may be formed with any of the metals, and thus derivatives analogous to the mineral salts are obtained.

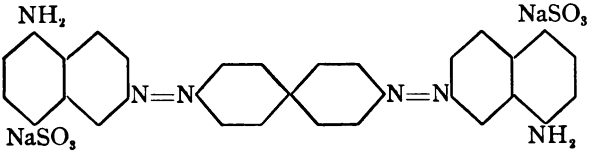
*Methyl orange*, *helianthin*, Porrier's *tropeolin D*, *Orange III*, *gold orange*, *mandarin orange*.—Sodium dimethyl 1–4 amido-azobenzenesulphonate. This series of commercial synonyms is given merely as an instance of the nomenclature of these bodies. Methyl orange is the ordinary name. Its composition is seen from the structural formula, but obviously other positive elements can replace sodium, giving derivatives of the same type but slightly different in properties. Methyl orange dyes bright orange. It is used in coloring textiles and sometimes in foods, and has a special use as an indicator in acidimetry and alkalimetry. It is an orange-yellow powder, freely soluble in water, producing a yellow solution which becomes red-orange by addition of any mineral acid.



**Methyl orange**

*Bismarck brown* is the hydrochloride of a complex azo-derivative. It is used for coloring imitation wines, fruit juices and in confectionery, as well as in dyeing textiles.

*Congo Red.*—This color belongs to a group termed "tetrazo-compounds" because they contain the azo-group twice. The term diazo is appropriated to a special form of azo-compounds. The tetrazo-compounds are chiefly interesting to dyers, but Congo red, the structural formula of which is here shown, is used in the laboratory as an indicator, having the striking property of assuming colors the reverse of litmus and other common vegetable colors. Congo red is blue in acid solution and red in alkaline. It is not a very delicate indicator, but is much used in testing stomach-contents for free hydrochloric acid. It dissolves in water. It is used generally in the form of test-papers.



**Congo red**

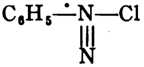
The addition of a strong acid liberates the free sulphonic acid which is blue, but its salts are red.

Diazo-compounds.—As previously noted, this term is applied when the nitrogen atoms are united by more than one bond and the residual bonds are not in union with the same type of radicle. The exact nature of the molecular structure has been disputed among chemists. Present opinion tends to regard them as more closely analogous to ammonium than to amine, and hence they are often termed "diazonium" compounds. The difference between these views is shown in the formulas for diazobenzene chloride:

**Amine type.**

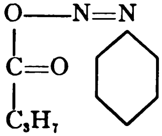
$C_6H_5N=N-Cl$

**Ammonium type.**



$$C_6H_5\overset{\cdot}{-}\underset{\underset{N}{|||}}{N}-Cl$$

These compounds are generally unstable. Many of them are explosive and some highly poisonous. It has been thought that some are formed in the putrefaction of proteids, especially milk-proteids, and that this accounts for the violently poisonous properties of some spoiled foods. They do not appear to be present in advanced states of putrefaction, but when the food is merely stale. As they are mostly easily decomposed by heat, cooking of such food often takes away the poisonous action. In the common cases of cheese and ice-cream poisoning, diazo-benzene (diazonium) salts have been supposed to be present, and one, provisionally termed "tyrotoxicon" (*Gr.* cheese-poison), may be diazobenzene butyrate (diazonium buty-



Diazobenzene butyrate
(Tyrotoxicon)

rate), the structural formula of which is annexed, but the products will differ with different conditions. The small amounts in which the bodies are produced and the ease with which they are decomposed, makes identification of them uncertain.

The hydroxides of the group are unstable but they form derivatives analogous to sodium ethylate which are not so easily decomposed. For example, a potassium compound of the empirical formula, $C_6H_5N_2OK$, is known. Esters have also been prepared. These bodies have as yet little practical importance, but it is not improbable that useful high explosives may be prepared from some members of the group.

*Experiment* 61.—Prepare the following solutions. The proportions given are suggestive only; it is not necessary to adhere strictly to them:

0.05 gram phloroglucol in 5 c.c. alcohol;

0.05 gram vanillin in 5 c.c. alcohol;

0.1 gram sulphanilic acid in 10 c.c. of water and 5 c.c. hydrochloric acid;

0.1 gram alphaamidonaphthalene in 10 c.c. of water and 5 c.c. hydrochloric acid;

0.1 gram sodium nitrite in 10 c.c. of water;

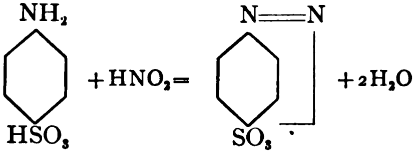
0.1 gram betamidonaphthalene in 10 c.c. of water and 5 c.c. of hydrochloric acid.

The solution of sulphanilic acid and amidonaphthalenes may be slow. It will not be necessary to wait until all the material is dissolved. Care should be taken not to get the alphaamidonaphthalene on the hands, as it has a persistent, disgusting odor. The sodium nitrite solution should be fresh. The others keep well.

*Experiment* 62.—To 10 c.c. of water add 1 drop of the sodium nitrite solution and then about 1 c.c. each of the solutions of sulphanilic acid and alphaamidonaphthalene. A pink tint will soon appear and deepen in about ten minutes.

*Experiment* 63.—Repeat Experiment 62, using no sodium nitrite. No color will appear.

The changes that occur in Experiment 62 are as follows:



1–4 amidobenzenesulphonic acid (Sulphanilic acid)

Diazobenzenesulphonic anhydride

The diazo-compound reacts with the amidonaphthalene to produce the azo-derivative as follows:

$$C_6H_4N=NSO_3 + C_{10}H_7NH_2 = C_{10}H_6(NH_2)N=NC_6H_4HSO_3$$

Alpha-azo-amidonaphthaleneparazobenzenesulphonic acid

The above reactions are analogous to those occurring in a urine test now much used under the name "Ehrlich's diazo-reaction." This depends on the formation of a red azo-derivative by the reaction of the diazo-compound produced in the above manner with bodies not yet isolated, occurring in urine in some diseases. The test is made by adding to the urine solutions of sodium nitrite and sulphanilic acid when, if the pathologic condition exists, a red color is produced.

The reaction is also used for the detection of nitrites in water. In this case the sulphanilic acid and amidonaphthalene are added in acid solution to a sample of the water. If nitrite is present the color is soon produced. No reaction occurs with nitrates. The test is very delicate; 1 part of nitrogen as nitrite in 1,000,000,000 parts of water can be easily detected, using only about 5 c.c. of the sample.

*Experiment* 64.—Repeat Experiment 62, substituting betamidonaphthalene for the alpha-form. A pale yellow color will be developed. By the comparison of these experiments it will be seen that a slight difference in arrangement of atoms may produce great difference in properties. The two amidonaphthalenes are close stereo-isomers, yet they give markedly different azo-derivatives.

*Experiment* 65.—Repeat Experiment 62, substituting for the naphthalene derivative, weak solutions of the following substances: phenol, aniline, vanillin, coumarin, alphanaphthol, betanaphthol, each as a separate test.

*Experiment* 66.—Add a few drops of hydrochloric acid to 1 c.c. of the phloroglucol solution and with this mixture make tests of the following substances, but touching them with rods dipped in the mixture: cotton, linen, fine writing paper, common printing paper (newspaper). If any of these materials contain raw wood fiber, a bright red color will be quickly developed at the point at which the liquid is applied. Common newspaper contains about 80 per cent. ground wood and shows the color strongly. Cotton, linen and high-class writing paper being pure cellulose do not give any color.

If ground olive stones, almond shells or other materials containing the so-called "stone-cells" be tested with this solution the color will also be obtained, and by examining the powder under a power of about 100 the stained cells will show clearly.

HYDRAZINS.—In these the nitrogen atoms are united by a single bond. They are therefore structurally more like the diamines than are the azo-derivatives. The important member is *phenylhydrazin*, $C_6H_5HN—NH_2$ on account of its reactions with ketones and aldehydes.

*Phenylhydrazin hydrochloride.*—This substance is now largely used as a test for sugar. It is a fawn-colored, crystalline powder with an odor recalling that of the geranium. It irritates the skin, producing in some persons an annoying eruption. It is liable to decomposition, becoming dark and pasty and of offensive odor. It should not be used in experiments or tests unless it is in good condition. Phenylhydrazin hydrochloride forms with ketonic and aldehydic bodies characteristic compounds, insoluble in water, termed "*osazones*." The osazones are obtained in several ways. A common method is to heat the carbohydrate, phenylhydrazin compound and sodium acetate for some time in boiling water when the osazone separates.

Dextrose and levulose yield the same osazone, as molecules of the hydrazin group attach themselves to the two terminal carbon atoms breaking up, therefore, the aldehydic and ketonic structures which are, respectively, characteristic of the two bodies.

Lactose and maltose yield osazones; sucrose does not.

*Experiment* 67.—Dissolve 0.5 gram ordinary glucose in 10 c.c. of water in a testtube, add 1 gram of sodium acetate and 0.5 gram of phenylhydrazin hydrochloride. The proportions need not be followed strictly but should be approximately as given. The phenylhydrazin should not be allowed to come in contact with the skin as it may irritate it severely. Immerse the mixture in boiling water for fifteen or twenty minutes. A yellow crystalline deposit of phenylglucosazone will form. This should be examined under a power of about 40 or 50 when the stellate crystals will be seen.

*Experiment* 68.—Repeat the above experiment using the substances *separately* and note the differences: 0.5 gram sucrose; 0.5 gram lactose; 0.5 gram starch. Only lactose forms a precipitate, but commercial sucrose may contain impurities, and yield a slight deposit of the glucosazone.

*Experiment* 69.—Test a portion of the furfural distillate, obtained in Experiment 54, by heating it with a few drops of acetic acid and a small amount of phenylhydrazin hydrochloride. *Furfurosazone* will be formed.

If a small quantity of phenylhydrazin hydrochloride be added to a weak solution of formaldehyde, then a few drops of a fresh solution of sodium nitroprusside, and then a little sodium hydroxide solution, a deep blue liquid is formed. This is a delicate and useful test for formaldehyde. With milk, the color is greenish.

## ALKALOIDS.

The *natural bases* or *alkaloids* are so called because they possess the power of neutralising acids, with which they form distinct and crystallisable compounds. They may be divided into two classes: (1) *Non-volatile alkaloids* consisting of C, H, N and O. These are solids, usually crystallisable, sometimes possessing a definite melting point and often capable of sublimation, though generally with partial decomposition. (2) *Volatile alkaloids*, consisting of C, H and N. These are liquids capable of partial vaporisation at ordinary temperatures, and usually having very high boiling points. The salts of the volatile alkaloids are non-volatile, crystallisable solids.

The *alkaloids* bear a close resemblance to the substitution amines, but they are more complex in constitution, especially as regards the presence of oxygen, which is not contained in the common substitution amines.

As regards the general properties of the non-volatile alkaloids, they are solids, almost insoluble in water to which they impart an alkaline reaction. They are usually soluble in alcohol, from which they may be readily crystallised. They are mostly soluble in one or more of the immiscible solvents, such as chloroform, ether, petroleum spirit, benzene and amyl alcohol, in which solvents, however, their salts are insoluble; the salts are almost invariably soluble in water. This difference in the solubilities of the alkaloids and their salts is utilised for their separation and purification. *Separation by immiscible*

## IMPORTANT ALKALOIDS.

| NAME. | EMPIRICAL FORMULA. | SOURCE. | DESCRIPTION. |
|---|---|---|---|
| Conine . . . | $C_8H_{17}N$ | Water hemlock (*Conium maculatum*). | Liquid; boiling point 167°. |
| Nicotine . . | $C_{10}H_{14}N_2$ | Tobacco (*Nicotiana Tabacum*). | Liquid; boiling point 247°. |
| Sparteine . . | $C_{15}H_{26}N_2$ | Broom (*Spartium scoparium*). | Liquid; boiling point 287°. |
| Morphine . . | $C_{17}H_{19}NO_3$ | Opium (*Papaver somniferum*). | Prismatic crystals soluble in about 5000 parts of water. |
| Codeine . . | $C_{18}H_{21}NO_3$ | | More freely soluble in water than other alkaloids. |
| Narcotine . . | $C_{22}H_{23}NO_7$ | | |
| Apomorphine | $C_{17}H_{17}NO_2$ | By heating morphine with hydrochloric acid to 150°. | Is distinguished by being emetic instead of narcotic. |
| Quinine . . | $C_{20}H_{24}N_2O_2$ | Various species of cinchona bark (*Peruvian bark*). | Quinine and cinchonidine are levorotatory; cinchonine and quinidine are dextrorotatory. Quinine and quinidine give the thalleioquin reaction (see Experiment 70), the others do not. |
| Quinidine . | $C_{20}H_{24}N_2O_2$ | | |
| Cinchonine . | $C_{19}H_{22}N_2O$ | | |
| Cinchonidine | $C_{19}H_{22}N_2O$ | | |
| Atropine . . | $C_{17}H_{23}NO_3$ | Belladonna (*Atropa Belladonna*). | Used as a mydriatic. |
| Homatropine | $C_{16}H_{21}NO_3$ | From atropine. | Preferred to atropine because the effect is not as lasting. |
| Hyoscyamine | $C_{17}H_{23}NO_3$ | Henbane (*Hyoscyamus niger*). | |
| Hyoscine . . | $C_{17}H_{21}NO_4$ | Henbane (*Hyoscyamus niger*). | |

| | | | |
|---|---|---|---|
| Strychnine | $C_{21}H_{22}N_2O_2$ | Nux vonica (*Strychnos Nux Vomica*).<br>St. Ignatia bean (*Strychnos Ignatia*). | Powerfully toxic. |
| Brucine | $C_{23}H_{26}N_2O_4$ | | |
| Hydrastine | $C_{21}H_{21}NO_6$ | Golden Seal (*Hydrastis canadensis*). | Used as an antiseptic. |
| Hydrastinine | $C_{11}H_{11}NO_2$ | Hydrastine. | A powerful oxytoxic. |
| Caffeine (Theine) | $C_8H_{10}N_4O_2$ | Tea, coffee, kola, guarana. | Very feebly basic. |
| Cocaine | $C_{17}H_{21}NO_4$ | Coca (*Erythroxylon Coca*). | A local anesthetic. |
| Theobromine | $C_7H_8N_4O_2$ | Cacao (*Theobroma Cacao*). | Resembles caffeine. |
| Theophylline | $C_7H_8N_4O_2$ | With Theobromine. | Diuretic; now made synthetically. |
| Aconitine | $C_{30}H_{47}NO_{11}$ | Aconite (*Aconitum Napellus*). | A powerful poison. |
| Veratrine | $C_{32}H_{49}NO_9$ | Sabadilla (*Asagræa officinalis*). | Used locally in neuralgia; rarely internally. |
| Colchicine | $C_{22}H_{25}NO_6$ | Colchicum (*Colchicum autumnale*). | |
| Pilocarpine | $C_{11}H_{16}N_2O_2$ | Jaborandi (*Pilocarpus Jaborandi*). | A powerful sialagogue and diaphoretic. |
| Pelletierine | $C_8H_{13}NO$ | Pomegranate (*Punica Granatum*). | A tenicide. |
| Physostigmine (Eserine) | $C_{15}H_{21}N_3O_2$ | Calabar bean (*Physostigma venenosum*). | A powerful myotic. |
| Gelsemine | $C_{24}H_{28}N_2O_4$ | Yellow Jasmine (*Gelsemium sempervirens*). | |
| Emetine | $C_{30}H_{44}N_2O_4$ (?) | Ipecac (*Cephaëlis Ipecacuanha*). | |
| Sanguinarine | $C_{20}H_{15}NO_4$ | Bloodroot (*Sanguinaria canadensis*). | |
| Berberine | $C_{20}H_{17}NO_4$ | *Hydrastis canadensis.* | |

*solvents* is the basis of most of the drug-assay processes of the Pharmacopœia.

Many alkaloids are bitter, acrid or pungent; most of them have decided physiological properties and are the proximate principles upon which the medicinal activities of the plants containing them depend. A synopsis of the formulas, sources and characteristics of the principal alkaloids is given on pages 186, 187.

The alkaloids are distinguished from all other plant principles by the fact that the aqueous solutions of their salts are precipitated by the following reagents: potassium-mercuric iodide, iodine, platinic chloride, auric chloride, picric acid and tannin. They often produce characteristic color-reactions with the inorganic acids and may be identified by the concurrence of several of these tests which, singly, are of little value.

The alkaloids differ from inorganic bases in forming salts by direct union with the acid, not by substituting the hydrogen. Thus, morphine forms with hydrochloric acid the compound $C_{17}H_{19}NO_3HCl$; it is, therefore, called morphine hydrochlorate (sometimes hydrochloride), not morphine chloride. This is due to the fact that the alkaloids are analogous to $NH_3$ rather than to $NH_4$, and the reaction between morphine and hydrochloric acid is similar to the reaction $NH_3 + HCl = NH_4Cl$, in which the hydrogen is not replaced; in fact, the hydrogen of the acid may be regarded as combining with the morphine to form a new molecule, $C_{17}H_{19}NO_3H$, analogous to ammonium and called *morphium*; the compound formed would be *morphium chloride*.

*Heroine*, $C_{17}H_{17}(C_2H_3O_2)NO_3$, is a diacetyl ester of morphine obtained by synthesis. It is used as a substitute for morphine.

*Daturine*, from stramonium (*Datura Stramonium*), is a mixture of atropine and hyoscyamine.

The classification of the alkaloids in a group based on the property of forming definite salts with acids brings together compounds of very different structure. Moreover, the basic power differs considerably in different members of the group. Strychnine, morphine and quinine, for instance, form stable and definite compounds. Caffeine is a weak base, many of its salts being easily decomposed.

Several essentially different types of molecular structure are exemplified in the alkaloids.

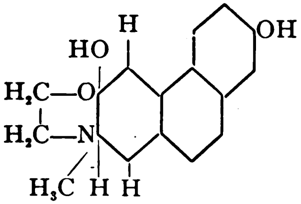
*Amine type.*—Betaine is an example of this structure. Its sources and composition are described under Ptomaines.

*Pyridin type.*—Many alkaloids are of this type, containing either the simple pyridin ring or the duplicated (quinolin) ring. When either of these is present, the molecular structure is stable and the substance resists the action of many reagents.

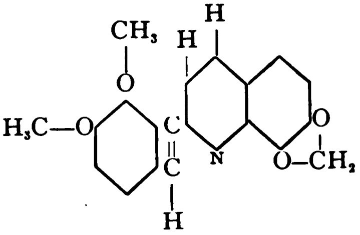
*Purin type.*—This is exemplified in caffeine and theobromine. The former is the characteristic alkaloid of tea, coffee and maté, and is present in small amount in cacao; the latter is the principal alkaloid of cacao. Their structural formulas are given in connection with the descriptions of the Purins.

Hydroxyl and hydrocarbon groups are often present. The latter can often be oxidised by mild oxidising agents to carboxyl groups, thus converting the alkaloids into acids. Several alkaloids, *e. g.*, theophyllin and conine, have been obtained synthetically. Isomers of quinine have also been obtained synthetically, but they have not the medicinal properties of the natural alkaloid.

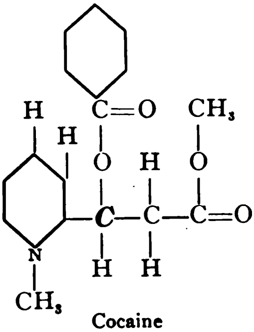
The annexed structural formulas are in some respects provisional but they represent atomic arrangements suggested by the reactions and transformations of the substances. It will be seen that morphine contains the phenanthrene ring and no pyridin. It is more easily decomposed than some other alkaloids. Cocaine and berberine contain the benzene ring; the former contains asymmetric carbon.



Morphine



Berberine



Cocaine

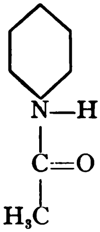
Basic nitrogenous bodies occur in, and are produced by, the decomposition of animal tissues. These are called *ptomaines* and *leucomaines* and are sometimes referred to, respectively, as the *cadaveric* or *animal alkaloids*. They are described below.

Many artificial alkaloids or allied compounds have attained prominence in therapeutics during recent years. Some of these possess the specific power of reducing the animal temperature, and are collectively known as *antipyretics*. They are sometimes called the "coal-tar synthetics" in recognition of their origin. They are generally known by trade-names which may be either abbreviations of their systematic names or purely arbitrary. The following are the more important of these:

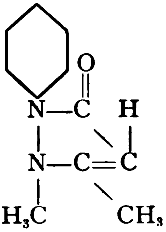
*Acetanilid*, *antifebrin*, $C_6H_5NH(C_2H_3O)$.—This is obtained by the reaction of aniline with acetic anhydride. It forms colorless and odorless crystals, soluble in 200 parts of cold water, much more freely in boiling water, alcohol, ether and chloroform. It is used as an antiseptic dressing and internally as an antipyretic. It is the basis of several proprietary antipyretics and is usually present in so-called "headache powders."

*Antipyrin*, *phenazone*, *phenyldimethylpyrazolon*, $C_{11}H_{12}N_2O$.—This is prepared by the action of phenylhydrazin on ethyl acetoacetate. It forms colorless crystals, freely soluble in water, alcohol and chloroform.

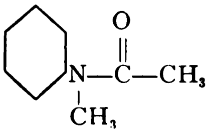
*Phenacetin*, *acetphenetidin*, $C_6H_4(NHCH_3CO)OC_6H_5$.—This is prepared by the action of glacial acetic acid on paraphenetidin. It forms colorless crystals slightly soluble in cold water, alcohol, ether and chloroform.



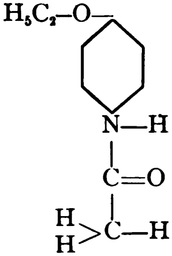
Acetanilid



Antipyrin



**Methyl acetanilid**
**(Exalgin)**



**Phenacetin**

*Experiment* 70.—Dissolve 0.1 gram of quinine sulphate in 10 c.c. of water. Add two drops of bromine water and afterward an excess of ammonium hydroxide. The liquid will assume a bright emerald-green color. This is known as the *thalleioquin reaction* and will also be given by quinidine or its salts.

*Experiment* 71.—Dissolve .02 gram of morphine sulphate in 2 c.c. of water and add several drops of solution of ferric chloride. A blue color will be produced which is destroyed by heating.

*Experiment* 72.—Add a small quantity of morphine or one of its salts to a drop of nitric acid upon a porcelain surface. An orange-red color will be produced which rapidly fades.

*Experiment* 73.—Dissolve .01 gram of strychnine in about 5 c.c. of water and transfer the solution to a small separatory funnel. Add about 2 c.c. of chloroform and then render the aqueous liquid alkaline with sodium carbonate. Upon shaking the separatory funnel the liberated alkaloid enters into solution in the chloroform, which may be drawn off, evaporated, and the residue tested as under Experiment 74.

*Experiment* 74.—Dissolve a minute quantity of strychnine, or one of its salts, in a few drops of concentrated sulphuric acid on a white porcelain or glass surface, and add a small crystal of potassium dichromate. Upon stirring the crystal of dichromate around with a glass rod a blue color will be at first produced, which changes to purplish blue and gradually fades through red to yellow. Ceroso-ceric oxide, manganese dioxide or similar oxidising agents will produce the same effect as potassium dichromate.

*Experiment* 75.—Rub together 4 parts of hydrastine and 1 part of morphine and treat a minute quantity as in Experiment 74. A color similar to the strychnine will be produced, which does not fade out as rapidly but is more permanent. Tests with morphine and hydrastine separately will fail to show any color.

*Experiment* 76.—Heat a small quantity of atropine with several c.c. of sulphuric acid. A peculiar aromatic odor is evolved recalling a mixture of rose and orange flower. Add a small fragment of potassium dichromate and the odor will change to that of bitter almond oil.

*Experiment* 77.—Add a small amount of colchicine to a drop of nitric acid on a white porcelain or glass surface. A blue color will be produced which fades in a short time.

*Experiment* 78.—Rub a small quantity of veratrine with a few drops of sulphuric acid on a white porcelain or glass surface and observe the intense red color which is produced, which does not fade even after several hours.

*Experiment* 79.—Dissolve a small quantity of caffeine in a few drops of hydrochloric acid, add a few small crystals of potassium chlorate and heat over a water bath until a dry residue remains. Expose the residue to the vapor of ammonium hydroxide and observe the characteristic rich purple color which it assumes. This is known as the *murexid test.* Uric acid will give the same reaction, being closely analogous in structure to caffeine.

## PTOMAINES AND LEUCOMAINES.

The chemical changes classed under the terms *fermentation* and *putrefaction* are caused by living organisms, mostly very minute, and included under the general title "microbes." It seems probable that all such transformations are due to enzyms. The principal action is the breaking down of complex nitrogenous ingredients of the living tissues, often by hydrolysis, but also by other types of action, especially oxidation when the action occurs in the presence of air. It follows, therefore, that if air be excluded, the chemical changes will be somewhat different, and hence a distinction is made between the usual (aërobic) decompositions and those that occur out of contact with free oxygen (anaërobic). The latter class has not been as yet extensively studied.

The products of aërobic fermentation and putrefaction have been of late studied with great zeal. Many of them are distinctly basic resembling the alkaloids. Furthermore, the normal pathologic processes of animals give rise to basic bodies. It is hardly necessary to distinguish these different classes, but such distinction has been made. The basic bodies produced by microbes are called "*ptomaines*," those produced in animals, "*leucomaines*." The latter term is not much used. Care must be taken not to confuse the products of animal tissues (leucomaines) with the products of microbes inhabiting the tissues, fluids or cavities of animals. The latter are ptomaines, for they are the result of fermentation or putrefaction apart from the vital action of the animal. As such resulting bodies cause disease by absorption into the fluids of the animal they are sometimes termed "toxins." By special methods, bodies (antitoxins) antagonistic in physiologic effect can be obtained and used in the treatment of diseases caused by toxins.

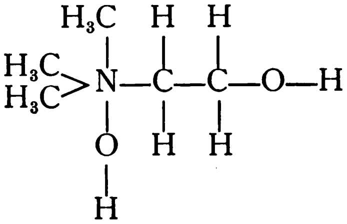
Microörganisms either directly or by intermediate action of enzyms, may produce alcohols, acids, neutral substances, cyclic compounds and nitrogenous derivatives; in fact, representatives of any class of organic compounds. The term ptomaine is derived from a Greek word meaning a dead body, and following out the analogy we might apply the same term to all the products of the decomposition of organic bodies under the influence of microörganisms, distinguishing the different classes by the proper terminations. Thus ptomols would be alcohols, produced by such action. Lactic and butyric acids are ordinarily produced by the action of microbes and are therefore ptomic acids.

It is to be noted, therefore, that the ptomaines are not peculiar as a class among basic organic bodies, nor are they the only products of decompositions.

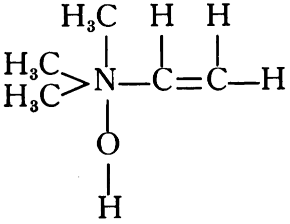
All ptomaines contain nitrogen, but the relation of this to the other atoms is dependent on the nature of the original molecule and the microbes or enzyms which bring about the transformation. Of the different types of combination that nitrogen may exhibit, amido-, azo- and diazo-groups are the most common. Pyridin compounds are not usual among the products of ordinary putrefaction; nitro- and nitroso-groupings are never observed.

The amines observed range in complexity from true basic monamines to tetramides with acid function.

Of the simpler type are some common ptomaines, such as *putrescine*, $N_2H_4(CH_2)_4$, tetramethene diamine, and *cadaverine*, $(NH_2)(CH_2)_5$, pentamethenediamine. A synthetic product used in medicine is also of analogous structure, *piperazin*, diethenediamine, $N_2H_4(C_2H_4)_2$. Similar but more complicated bodies are indicated in the annexed structural formulas. They are of the general type of the true bases and it will be seen that alcoholic and acid groupings are also represented.



**Choline**



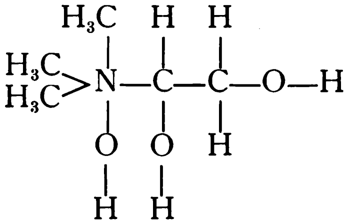
**Neurine**

*Choline.*—Salts of this base occur in many animal and vegetable tissues. It was originally extracted from bile to which the name refers. Its glycerophosphate exists in lecithins. As will be seen from the structural formula it is a complex derivative of ammonium hydroxide. It is strongly alkaline, absorbing water and carbon dioxide from the air. It forms a crystalline chloroplatinate.

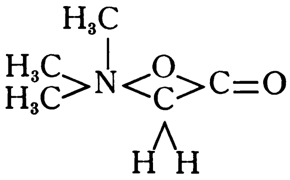
*Neurine.*—This is obtained by boiling choline with barium hydroxide and is produced in some putrefactions.

*Muscarine* occurs associated with choline in poisonous mushrooms.

*Betaine* occurs in the sugar beet and is also produced by the cautious oxidation of choline.

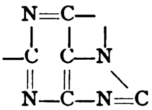


Muscarine

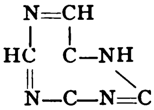


Betaine

Purins.—*Alloxuric bodies, Xanthin bases.*—Under these terms, the first being now much in vogue, is included a number of bodies of complex structure which it has been proposed to regard as derived from a hypothetical radicle termed the "purin nucleus." From this, by association with other radicles, such as amidogen, imidogen, hydroxyl and carbonyl, formulas of the members of the series may be obtained. The following formulas show the relations of some of the members of the series to the purin nucleus and to purin itself:



Purin nucleus

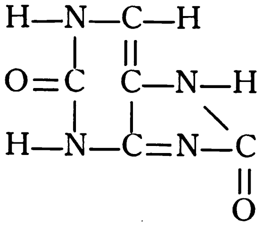


Purin

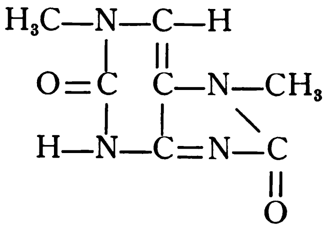
It will be seen that purin is, in a measure, a duplicated urea, the oxygen being absent and part of the hydrogen replaced by carbon. The purin bodies are at present attracting much attention owing to their supposed relation to animal nutrition and metabolism. They exist in many foods and abundantly in tea, coffee, maté and cacao.

The following table gives the empirical formulas of some members of this group, and a few structural formulas are annexed:

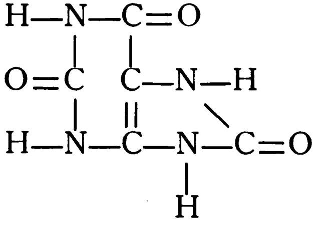
| | |
|---|---|
| Uric acid | $C_5H_4N_4O_3$ |
| Xanthin | $C_5H_4N_4O_2$ |
| Hypoxanthin | $C_5H_4N_4O$ |
| Paraxanthin | $C_7H_8N_4O_2$ |
| Guanine | $C_5H_5N_5O$ |
| Theobromine | $C_7H_8N_4O_2$ |
| Caffeine | $C_8H_{10}N_4O_2$ |
| Adenine | $C_5H_5N_5$ |



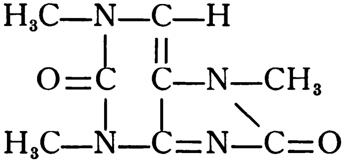
Xanthin



Theobromine



Uric acid



Caffeine

Of these bodies caffeine and theobromine are described in connection with the group of alkaloids in which they are usually classified, but they possess only feebly basic properties, and their formulas are structurally very different from those in the majority of that group.

*Uric acid*, *trioxypurin*, $C_5H_4N_4O_3$.—This occurs in small amount in the urine of mammals and abundantly in that of birds and reptiles. It can be obtained by strongly acidulating urine with hydrochloric acid and allowing the mixture to stand for some hours. Uric acid separates as a crystalline precipitate, usually brownish, from adherent coloring matter. When pure it is in colorless crystals, almost insoluble in cold water and only slightly soluble in boiling water. It forms several derivatives with sodium, potassium and ammonium, usually called "urates," which are more soluble in water than the acid itself. Uric acid does not contain the carboxyl radicle, but the group HNCO, which occurs thrice in the molecule, confers nominal acidity.

*Xanthin*, *dioxypurin*, $C_5H_4N_4O_2$.—This occurs in small amount in urine, but is more abundant in flesh juice, hence is found in commercial meat-extract. It is colorless, crystalline and nearly insoluble in cold water. It is dissolved by alkaline solutions.

*Hypoxanthin*, *oxypurin*, $C_5H_4N_4O_2$.—This is found associated with xanthin. It is crystalline and but slightly soluble in cold water.

*Paraxanthin*, *dimethylxanthin*, $C_7H_8N_4O_2$, is isomeric with theobromine.

*Adenine*, *amidopurin*, $C_5H_5N_5$.—This occurs in several animal fluids, but is most abundant in tea-leaves. It contains no oxygen.

Purin bodies are without nutritive value to the higher animals, hence any that are present in the food are passed off as promptly as possible by the excretions. The ordinary waste of tissue (destructive metabolism) in the animal produces purins, hence the excretions will contain both those in the food and those formed in the body. The former are termed "exogenous purins," the latter "endogenous purins."

Many analyses of food stuffs have been made in order to determine the amount of purins, so that the diet may be regulated to secure the minimum amount of exogenous purins when these are especially objectionable. Meats, some wines and cereals contain considerable amounts of purins; milk, eggs and cheese small amounts. Comparatively few natural purins have been isolated, but over one hundred derivatives have been prepared synthetically.

The endogenous purins are regarded as derived largely from the nucleoproteids by successive dissociation, with probably both hydrolysis and oxidation under the influence of enzyms. If these processes be carried to a considerable extent, as occurs when the functions of nutrition and excretion are well balanced, the purin derivatives are mostly converted into a simple diamido-compound urea, which constitutes the principal result of the waste of nitrogenous tissues in the higher animals and is the most abundant solid ingredient of normal human urine.

Urea and some closely related excretory substances are described elsewhere.

## PROTEIDS OR ALBUMINOIDS.

Proteids or albuminoids are complex bodies that form the essential portions of living tissues. They all contain hydrogen, oxygen and nitrogen; most of them contain also sulphur; a few contain phosphorus, and a few contain iron. Even copper has been found in some, and it is not unlikely that elements, not usually existing in natural organic bodies, are present in proteids having highly specialised function or developed under exceptional conditions.

Little is known as to the structural formulas of proteids, except that they are all very complex, containing open and closed carbon chains. The nitrogen is probably in a pyridin ring and partly in a cyanogen or amine form. Some authorities distinguish between proteids and albuminoids, limiting the latter term to gelatin and closely analogous bodies. Other authorities limit the term proteid to substances that yield monamido-acids on decomposition by certain processes. These distinctions, however, can not be regarded as final, and it is sufficient for present study to classify a considerable number of bodies under the general terms here used, even though appreciable differences in properties are noted. The proper classification will be made when the rational formulas become known.

Proteids are generally colorless or faintly yellow amorphous solids, soluble in water, but some require for this purpose the coincident presence of certain salts. Some proteids dissolve in alcohol. Water solutions putrefy promptly, under ordinary conditions, but this is merely the result of the action of microbes. In the presence of antiseptics or in sterile solution proteids are practically permanent. They are ordinarily eminently colloid, hence have very low diffusive power, but one proteid has been obtained in a distinctly crystalline form, and there is no reason to doubt that all of them are capable of crystallising under certain conditions. Solutions of proteids have marked levorotatory power.

A satisfactory classification of proteids is impossible in the present imperfect state of knowledge. In many cases several bodies are probably included under one name; in other cases a supposed natural proteid is a product of the methods employed in obtaining it. The classifications usually followed take but little account of vegetable proteids, although these are quite numerous. The following classification is that of Hammarsten; it is merely an incomplete index to the animal proteids.

Simple proteids or albumins:

Albumins proper: Ovalbumin, seralbumin, lactalbumin.
Globulins: Fibrinogen, vitellin, myosin, crystallin.
Nucleoalbumin: Casein.
Albuminates: Acid albuminate, alkali albuminate.
Albumoses.
Peptones.
Coagulated proteids: Fibrin, coagulated albumins.

Compound proteids:

Hemoglobins.
Glyco-proteids: Mucins, hyalogens, amyloid.
Nucleoproteids: Nucleohiston, cytoglobin.
Albuminoids: Keratin, elastin, collagen.

Many proteids are precipitated from their solution in water, in forms that are not capable of re-solution without chemical change. This, which is termed "coagulation," is brought about by heat in some cases, by different chemical agents in others; each proteid requiring particular methods. When quite dry, proteids show little tendency to change. By strong heating they are converted in a mixture of substances, among which pyridin and some of its derivatives are especially noticeable.

*Coagulated Proteids.*—Under this term are included proteids rendered insoluble in their normal solvents, pure water or saline solutions, as the case may be. In some cases they may be identical with the original body, but in most cases they are probably modified either by hydrolysis or oxidation with or without division into two or more new substances. Most of them can be converted into proteoses and finally into peptones by the action of some enzyms, and on this fact depends the digestibility of many articles that are prepared by cooking, by which the proteids are coagulated.

ALBUMINS PROPER.—This group includes *ovalbumin* (*egg albumin*), *seralbumin* (*blood albumin*) and *lactalbumin* (*milk albumin*). Care must be taken not to confuse "albumin" with "albumen." The latter term refers to the nutritive material surrounding an embryo. It contains one or more proteids which may or may not be albumins. White of egg is the "albumen" of the egg. It contains ovalbumin, water and other bodies. The seeds of many plants contain a large amount of material around the embryo. This is called the "albumen" of the seed. In the common cereals this albumen contains several proteids, with much starch and some fatty matter and salts.

The albumins are soluble in water and in weak saline solutions. In strong saline solution they are coagulated at a temperature of about 60°. Alkalies and very small amounts of acids do not precipitate them, but larger amounts do, as also many neutral salts, among which are ammonium sulphate and mercuric chloride.

Globulins.—Globulins are insoluble in water, but soluble in dilute solutions of sodium chloride. They are precipitated unchanged from these solutions by dilution with pure water.

*Vitellin* is obtained from egg-yolk; it resembles somewhat the nucleoalbumins. It has not been obtained free from lecithin.

*Crystallin* is obtained from the crystalline lens.

*Fibrinogen.*—This exists in blood plasma. When blood clots, the fibrinogen is converted into fibrin, which forms the clot and encloses the blood corpuscles. This coagulation occurs under the influence of another substance, termed "fibrin-ferment," or "thrombin" which also exists in the blood plasma. The nature of thrombin is not known, but it is probably an enzym.

*Myosin* is obtained from muscles. According to some authorities, the fluids in living muscles contain a proteid termed myosinogen which is converted after the death of the tissue, when the stiffening (*rigor mortis*) sets in, into myosin.

Nucleoalbumins.—These are distinguished from most other proteids by containing notable amounts of phosphorus. The most important is casein, the principal portion of the fresh curd of cow's milk. Some authorities apply the term "*caseinogen*" to the material as it exists in milk, and the term "casein" to the separated proteid. In fresh milk the casein (caseinogen) exists in association with some calcium phosphate and is probably partly in a jelly-like condition, not in true solution. Most acids, many mineral salts, and several enzyms coagulate milk, but much proteid remains in solution, and it is probable that hydrolysis occurs, and the original proteids are split into several substances some of which precipitate and others remain dissolved. A solution of mercuric nitrate in excess of nitric acid precipitates all the proteids of cows' milk.

Cheese is proteid matter obtained from milk either by the action of acids or by rennet, a preparation of enzyms from the stomach of the calf. The acid usually employed is lactic, the result of the natural souring of milk by fermentation of milk sugar. Cheese, even when fresh, does not contain the same proteids as milk, and in ripe cheese further changes have occurred through the action of microbes and enzyms, by which amine bodies have been produced. Ammonium compounds are present in well-ripened cheese. Sometimes ptomaines, either amine derivatives or azo-compounds are present, thus making the cheese poisonous.

ACID-ALBUMINATES AND ALKALI-ALBUMINATES.—Many proteids combine to a limited extent with acids or with alkalies, producing compounds that have characteristic properties. The exact nature of the combination is not known. By the action of somewhat strong solutions of alkali on natural proteids, chemical changes are produced in the latter, among which are the elimination of nitrogen and sulphur. By dissolving proteids in hydrochloric acid, acid-albuminates may be obtained. Both these products have certain properties in common. They are nearly insoluble in water and dilute solution of sodium chloride, but are dissolved by water on the addition of a little acid or alkali. The solution is not coagulated by heat, but can be precipitated without heat by neutralising the solvent substance, that is, adding acid to the alkali-albumin and alkali to the acid-albumin. Strong mineral acids precipitate both classes of albuminates.

*Syntonin* is an acid-albuminate obtained by the action of acids on myosin.

*Albumoses and Peptones.*—The action of hydrolysing enzyms, such as those in the gastric juice and pancreatic secretions on proteids, results finally in the formation of a substance or mixture of substances, similar to the common proteids in many ways but much more diffusible and much less coagulable. This is called *peptone*. In the course of its formation from the original proteid, several intermediate transformations occur, the products of which are, collectively, called *proteoses* or *albumoses*. These products differ with the conditions of action and the proteid and enzym, and much remains to be determined in regard to them. At present it is the custom to consider all the proteid matter that is not precipitated by saturated solution of ammonium sulphate, as peptone; that which is so precipitated as either unaltered proteid or some form of proteose.

HEMOGLOBIN.—This is the coloring matter of blood-corpuscles. It is distinguished from many other proteids by containing iron, which is part of the molecule and not, as with some proteids, merely due to adherent mineral matter. Chlorophyl, the green coloring matter of plants also contains iron, and its functions are analogous to those of hemoglobin. In some animals the iron in hemoglobin is partly or wholly replaced by copper.

Hemoglobin is very soluble in water, producing a red solution that shows characteristic absorption bands. It can be obtained in a crystalline form. Its principal property is the power to take up oxygen and to give this up again under the influence of different substances. The oxygen compound differs slightly in composition according to the pressure of the gas from which the absorption takes place. As a rule, hemoglobin absorbs only free oxygen. It has affinity for other bodies, such as nitrous oxide, nitric oxide, hydrogen sulphide, carbon monoxide, carbon dioxide and acetylene. The affinity for carbon monoxide and nitric oxide is stronger than the affinity for most of the other substances. All these derivatives of hemoglobin give characteristic absorption bands. By exposing oxyhemoglobin for some time to the action of free oxygen or to mild oxidising agents, a substance known as *methemoglobin* is formed. It is believed that in this the oxygen is more strongly combined than is the case with oxyhemoglobin. The associated oxygen of oxyhemoglobin can be driven out by reducing the pressure or by passing through a current of nitrogen or any of the bodies mentioned above as forming compounds with it.

*Hematin* is obtained by the action of alkalies or acids on hemoglobin. Its composition approximates the formula $C_{32}H_{32}N_4FeO_4$. Hematin heated to about 80° with glacial acetic acid and a little sodium chloride, yields a chlorine derivative termed *hemin*. It is regarded as a hydrochloric ester of hematin. It forms characteristic crystals, sometimes termed Teichmann's crystals. The reaction is one of the standard tests for blood.

Oxyhemoglobin gives with a mixture of guaiacum tincture and hydrogen dioxide a blue solution, the production of which is also a test for blood.

MUCIN.—Under this term several proteids are included. They are found in the secretion of mucous membranes, in connective tissue, tendons and the submaxillary gland. Proteid matter that coagulates with nitric acid, frequently appears in urine. It is also termed mucin, but many authorities regard it as essentially different from true mucin, and properly a nucleoalbumin. True mucin may, however, be present in urine containing a large amount of mucus. By the action of acids, mucin can be hydrolysed and a reducing carbohydrate formed.

NUCLEINS.—These are a series of bodies containing notable amounts of phosphorus. They are widely distributed in the vegetable and animal kingdom, and have been classified in two groups: Nucleins proper, which yield proteids, phosphoric acid and xanthin bases; and pseudonucleins that yield no xanthin bases. The true nucleins are obtained as insoluble residues in the digestion of nucleoproteids by gastric juice. By the action of alkalies, nucleates are formed, from which nucleic acids may be obtained. All nucleins, by boiling with dilute acids, yield a series of nitrogenous bodies termed the *xanthin* or *nuclein bases.* They have close structural relations to some alkaloids, leucomaines and uric acid. It has been suggested that they are all derived from a body having the formula $C_5H_4N_4$ to which the name *purin* has been applied. Hence the group is often called the "purin bases." (See Purins.)

KERATIN is the chief proteid constituent of horny structures, hair and nails. Some of its reactions are similar to those of the proteids proper, but it is not digested by gastric or pancreatic secretions.

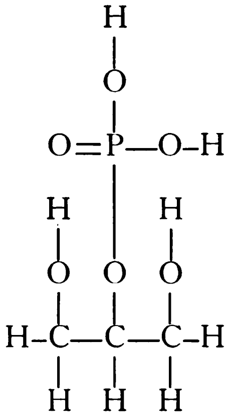
ELASTIN occurs in connective tissue, especially the cervical ligament. It is insoluble in water, and dissolves only slowly in alkalies and acids.

COLLAGEN is the material in connective tissue and bone from which gelatin is obtained. GELATIN is prepared by boiling the tissue with water. The process is very slow at ordinary pressure, but in a closed vessel, the temperature can be raised considerably and the gelatin rapidly produced. The change is doubtless a hydrolysis.

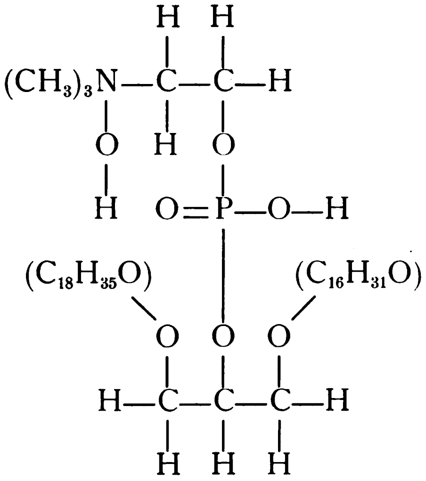
The food material called *isinglass* is probably a collagen that is easily converted into gelatin. Ordinary gelatin dissolves in hot water, and the solution on cooling sets to a jelly if considerable of the gelatin is present. Solutions of gelatin are promptly precipitated by tannins, common tannins. The tanning of skins is dependent on the reaction by which the albuminoids are rendered insoluble and non-putrescent. This was originally carried out by the use of tannins, but several other methods are now in use. Formaldehyde converts gelatin into a mass insoluble in water.

VEGETABLE PROTEIDS.—As a purely vegetable diet will support life satisfactorily for a long period, it is reasonable to suppose that the vegetable proteids are of the same general character as the animal proteids, but the isolation and classification of the former are as yet very incomplete. Recently, careful investigations have been made into the proteids of important cereals. The principal proteids of wheat flour are *gliadin* and *glutenin*. The former, which constitutes nearly half the proteid matter of the grain, is soluble in pure water and in dilute alcohol, but almost insoluble in water containing the mineral matters of the wheat-grain. Glutenin is insoluble in water, dilute saline solutions and dilute alcohol. The glutinous property of wheat flour is due to both the proteids, the gliadin giving the adhesiveness and glutenin the solidity.

LECITHINS.—These are complex bodies that occur in the protoplasm of many forms of cells, either alone or in combination, or close association, with proteids. A lecithin is an ester derived from glycerophosphoric acid by substitution of two of the hydrogen atoms of the latter by two molecules of radicles of the fatty-acids and the other hydrogen atom by a base "*choline*." Since the substituting radicles may differ, a considerable number of bodies of the same type may be produced. The annexed structural formulas show glycerophosphoric acid and one of the common lecithins.



Glycerophosphoric acid



Lecithin

*Experiment* 80.—Beat a raw egg to a foam, allow the mass to stand until most of the insoluble matter has subsided, dilute with about five times the bulk of water and filter through a plaited filter. This solution does not keep, and hence must be made fresh as needed. Portions of about 10 c.c., unless otherwise directed, should be used for the following experiments.

*Experiment* 81.—Heat a portion of the solution to boiling. It will not coagulate, add a few drops of acetic acid and boil again, if coagulation does not occur, add more acetic acid and boil, and proceed in this way, adding small quantities of the acid and boiling for a few seconds, until coagulation is obtained.

*Experiment* 82.—Test separate portions of about 5 c.c. of the liquid with a few drops each of sulphuric acid, hydrochloric acid and nitric acid.

*Experiment* 83.—Add 5 c.c. of the albumin solution to 20 c.c. of water; divide the solution into two equal portions and test one with a few drops of syrupy phosphoric acid (orthophosphoric acid) and the other with metaphosphoric acid. The former will not coagulate, the latter will produce immediate coagulation. If 0.1 gram metaphosphoric acid be dissolved in water and the solution kept boiling for half an hour the coagulating property will be lost, as the acid hydrolyses to orthophosphoric.

*Experiment* 84.—Place about 1 c.c. of strong nitric acid in a narrow testtube and overlay it with a few c.c. of solution of albumin. It is best to use a somewhat diluted solution for this. The overlaying can be done by inclining the tube very much and pouring the albumin solution down the side. The coagulated albumin forms a ring at the point of contact between the two liquids. This is known as Heller's test.

*Experiment* 85.—Portion of the albumin solution may also be tested by the following: saturated solution of picric acid; solution of copper sulphate; solution of mercuric chloride.

*Experiment* 86.—Prepare Millon's reagent by adding 0.5 c.c. of mercury to 5 c.c. of strong nitric acid. It may be necessary to complete the action by gentle warming, but the liquid should not be boiled. When the mercury is dissolved, the liquid is diluted with twice its volume of water, allowed to stand for some hours and decanted from any deposit that may have formed. It does not keep long.

*Experiment* 87.—Treat a solution of albumin with some of this reagent. A white precipitate is formed which turns brick-red on boiling. Other proteids give similar effects

*Experiment* 88.—Treat a solid proteid, such as a little dried white of egg or a piece of wool or silk with strong nitric acid. A yellow color will appear. If ammonium hydroxide be added to the mass, the color will change to orange. This is termed the *xanthoproteic* reaction.

*Experiment* 89.—Prepare a stiff jelly from gelatin and water, observing that it can be liquefied by the application of heat. Add a few drops of formaldehyde solution to a small portion of the jelly and allow it to cool. The formaldehyde combines with the gelatin to form an insoluble compound which will char without melting.

## ENZYMS.

Enzyms are nitrogenous bodies analogous in composition and general properties to ordinary proteids, but are distinguished by power to bring about transformations without being themselves permanently affected. Nothing is known as to their empirical formulas; in fact, they have not been prepared in a perfectly pure condition. They are usually amorphous, colorless or slightly yellow, soluble in water, but not appreciably in other solvents. The solution in water soon putrefies. Some enzyms are affected injuriously by light, and all of them lose their characteristic functions when heated, resisting, however, this treatment better when dry than in solution. Many substances restrain the action of enzyms; some of these, such as salicylic acid, boric acid and benzoic acid are largely used for controlling or preventing their action. Enzyms are often termed "*non-organised ferments*," ordinary microbes being designated "*organised ferments*."

Each enzym has its peculiar "optimum" condition, that is, that under which it is most active. Conditions that favor one enzym often restrain or interrupt the action of others. Thus, pepsin (pepsase), the principal enzym of gastric juice, is favored by the presence of a small amount of hydrochloric acid, but restrained by a larger amount. Trypsin (trypsase), the corresponding enzym of the pancreatic secretion is favored by the presence of a feebly alkaline body.

The manner of action of enzyms is not known. It has been suggested that they combine temporarily with the substances involved in the reaction and are set free unchanged when new molecules are formed. Thus, the hydrolysis of sucrose by invertase would consist in, first, a combination of sucrose molecules and water, one to one, with a molecule of the enzym; then, an intermingling of the water molecule and sucrose molecule to the exclusion of the enzym, which is thus liberated. The molecule formed by the intermingling of the water and carbohydrate is immediately broken into dextrose and levulose. The enzym is free to repeat its action. In theory, therefore, it is inexhaustible; in practice, the accumulation of products and the constantly increasing dilution interfere with and ultimately suspend the action. It has been found experimentally that invertase can hydrolyse 100,000 times its weight of sucrose and still be active.

Enzyms may be regarded as the connecting link between living and non-living matter. They have some of the characteristics of each class, but they have, as far as known, no power of reproduction.

The following are some important enzyms, with their source and characteristic actions:

*Diastase.*—From malt. Converts starch into maltose and dextrin by hydrolysis. Favored by mild alkalinity of solution and restrained by acidity and by salicylic acid.

*Takadiastase* (Japanese, *taka*, strong).—From a fungus that grows on bran. Similar to diastase in its action.

*Amylopsin* (*amylopsase*).—From pancreatic secretion, similar to diastase.

*Invertase.*—From yeast, hydrolyses sucrose to a mixture of equal parts of dextrose and levulose (invert-sugar). Favored by very slight acidity.

*Synaptase.*—From tissues, especially seeds, of plants of the order Rosaceæ. It converts amygdalin by hydrolysis into benzaldehyde, dextrose and hydrogen cyanide.

*Myrosin* (*myrosase*).—Exists in white and black mustard. It hydrolyses sinalbin in the former and sinigrin in the latter, producing the irritating materials upon which the local action of mustard depends.

*Pepsin* (*pepsase*).—The principal enzym of gastric juice. It hydrolyses proteids to proteoses and finally to peptones, but the peptonising action is slow and often incomplete. Pepsin is most active in the presence of a small amount of hydrochloric acid.

*Trypsin* (*trypsase*).—One of the enzyms of the pancreatic secretion. It hydrolyses proteids to proteoses and then to peptones, being more rapid than pepsin. It acts best in feebly alkaline solution. By prolonged action peptones are hydrolysed to leucin and tyrosin.

*Ptyalin* (*ptyalase*).—This is the characteristic enzym of saliva. It hydrolyses starch to maltose and dextrin, and sucrose to dextrose and levulose.

*Steapsin* (*steapsase*).—An enzym of the pancreatic secretion. It hydrolyses fats to glycerol and free acids.

A similar enzym exists in the castor bean.

The juice of the papaw (*Carica papaya*) contains enzyms capable of digesting proteids and starch. The juice of the pineapple contains an enzym that digests proteids.

*Catalase.*—An oxidising enzym obtained from fresh leaf-tobacco, but probably widely distributed. It decomposes hydrogen dioxide.

*Rennin* (*rennase*) is found in gastric juice, especially in that of the fourth stomach of the calf. It is sometimes called chymogen. Its characteristic action is the coagulation of milk which is due to a hydrolytic change in the caseinogen, by which this is split into several proteids some of which precipitate and others remain in solution. The precipitate and liquid are termed, respectively, "curds" and "whey." Rennase in solution is rendered inactive by exposure to a temperature of 60° to 70° which is somewhat lower than that required for most enzyms.

Milk contains several enzyms that have digestive and limited oxidising powers, but they have not been satisfactorily isolated.

The terms proteolytic (proteid-hydrolysing) and amylolytic (starch-hydrolysing) are used in connection with enzyms.

*Experiment* 90.—Make a fresh solution of a small amount of 1–2 diamidobenzene (paraphenylene diamine, $C_6H_4(NH_2)_2$) in water, and add portions of it to boiled and unboiled milk in separate testtubes. Add a few drops of hydrogen dioxide to each tube. A deep blue color is produced with the unboiled milk at once, but no appreciable color with the boiled milk until a considerable time has elapsed. The color is due probably to the action of enzyms in the milk which are injured by the heating.

If two samples of milk be heated, respectively, to 75° and 82°, it will be found that the portion heated to the lower temperature will, when cold, give the above reaction, while that heated to the higher temperature will not give it. At some point between these temperatures is the "death point" of the enzym. The so-called "pasteurising" temperature lies below this death point. It is possible, therefore, to distinguish between pasteurised and boiled (sterilised) milk by this test.

*Experiment* 91.—Repeat the procedures indicated in Experiment 31 with the variation that, before adding the enzyms, about 0.1 gram of salicylic acid is added to each starch solution. It will be found that the action of the enzym will be suspended, very little if any transformation of the starch taking place. It is possible that this is an *inhibitory* rather than an *enzymocide* action.

*Experiment* 92.—Add 1 c.c. of strong, pure hydrochloric acid to 150 c.c. of distilled water, and dissolve, without heat, in this solution 0.009 gram of good pepsin. Mix well and divide the liquid into three equal parts. It contains about 0.2 per cent. absolute hydrochloric acid and 0.003 per cent. pepsin, being approximately equivalent to normal gastric juice.

To one of the portions of solution add 0.1 gram of boric acid; to another portion add about 0.3 gram of sodium sulphite. To all three solutions add 1 gram each of finely-chopped raw meat, and keep them at a temperature of from 38° to 40° for six hours. It will be found that the sulphite solution has a marked restraining action on the pepsin and the boric acid very little, if any. The actions are probably inhibitory rather than enzymocidal.

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