

# Handbook of natural dyes and pigments

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and  
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Ever since the prehistoric time, mankind took delight in coloring the objects of daily use by employing natural pigments of vegetable, animal, and mineral origin. These coloring substances, known as natural dyes, are the chemical compounds used for coloring fabrics, hair, leather, plastic, paper, food items, cosmetics, and medicines, etc., and to produce artistic colors and inks for paintings and printing.

People always prefer natural dyes and pigments because of their brightness, soothing and non-toxic nature. But after the discovery of synthetic dyes by William Henry Perkin in 1856, the natural dyes gradually lost their utility value in most parts of the world. However, people lately have come to realize the toxic effects of synthetic dyes, especially the azo dyes and benzidine derivatives. Therefore, it has become imperative to revert to the natural dyes as they are user-friendly and eco-friendly, and are harmless to health and environment. Further, natural food colors are more desirable than synthetic dyes from their nutritional point of view as few of the carotenoid pigments are helpful in prevention of few forms of cancers and few are vitamin A precursors, which may be effective antioxidants.

Recently conducted National and International conventions and workshops on natural dyes were of the opinion that there is a great need for the revival of the use of natural dyes in Asia, particularly in India. Therefore, efforts should be made to promote the use of natural dyes, extend the range of their application, and encourage their commercial use rather than restricting them to small scale cottage industries. There is a need to carry out research and development on natural dyes by using modern technology to develop extraction techniques, standardize applications on synthetic as well as natural fibers, leather, and also evaluate their toxicity.

In India, National Handloom Development Corporation (NHDC), Indian Institute of Technology (IIT), New Delhi, Forest Research Institute (FRI), Dehradun, National Botanical Research Institute (NBRI), Lucknow, Alps Industries, Sahibabad, Ghaziabad, U.P., etc., have developed technologies for the extraction of natural dyes from plant materials. These technologies



are being marketed through National Research Development Corporation (NRDC), New Delhi.

Keeping the above in view, this book attempts to revive the glory of natural colors. The book, written in technical style, is profusely illustrated, contains information on 86 natural dyes derived from 350 plant species, 5 animal dyes, and 11 mineral pigments arranged in alphabetical order of their chemical names. The book is mainly focused on sources of natural colors of Indian subcontinent. It will be useful for students, teachers, scientists, researchers, industrialists like textile, food, pharmaceutical, cosmetics, etc.

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**Har Bhajan Singh**  
**Kumar Avinash Bharati**

## Abbreviations

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%	percentage
°C	degree centigrade
°Tw	degree Twaddle
Å	angstrom
c.	circa, about, approximately
ca	centiare (1 m <sup>2</sup> )
cf.	confer, compare
cm	centimetre
e.g.	exempli gratia, for example
et al.	et alii, and others
etc.	etcetera; and so forth, continuing in the same way
ha	hectare
i.e.	id est, that is
lit.	litre
m	metre
mm	millimetre
mp	melting point
ppm	parts per million
psi	pound per square inch
sp.	species; plural spp.
µg	microgram
V/V	volume/volume
viz.	videlicet, namely, that is to say
W/V	weight/volume

Ever since pre-historic time, man has been fascinated to color the objects of daily use employing inorganic salts or natural pigments of vegetable, animal, and mineral origins. These coloring substances, known as dyes, are the chemical compounds used for coloring fabrics, leather, plastic, paper, food items, cosmetics, etc., and to produce inks and artistic colors. Dyes are of two types, i.e. synthetic and natural. Synthetic dyes are based on petroleum compound, whereas natural dyes are obtained from plant, animal, and mineral matters.

Natural dyes are always preferred because of their brightness, soothing and non-toxic nature. But after the advent of synthetic dyes by William Henry Perkin in 1856, the use of natural dyes has gradually gone out of existence from most part of the world. However, natural dyes are traditionally used in certain parts of India despite synthetic dyes insurgency. Lately, people have come to realize the toxic effects of synthetic dyes, especially the azo dyes and Benzedrine derivatives. They release harmful amines, allergens, carcinogens, and other poisonous compounds that caused cancer, allergy and are detrimental to human health and environment. Consequently, many developed countries of the world have imposed a ban on the import, stock, and sale of commodities manufactured from such azo- and Benzedrine-based dyes that came into effect from April, 1996. Therefore, no textile, leather or food products which contain azo or Benzedrine based dyes are to be found in the markets of America, Canada or other Western countries. As a result, the countries' manufacturing and exporting azo based products are losing its sizeable export earnings. Moreover, to preserve public health and to protect the environment, the Union Ministry of Environment and Forests, Government of India, has also imposed a ban through a gazette notification on manufacturing and using of 118 azo- and Benzedrine-based dyes from June 23, 1997. Furthermore, 38 pigments of this category have also followed suits in April 1998. Therefore, it has become imperative to revert to the natural dyes as these dyes are said to be user-friendly and eco-friendly and are harmless to health and environment.

India is harboring enough potential raw materials for manufacturing natural dyes. It is believed that out of 47,000 plant species occurring in India,

over 500 plant species can be used as raw materials for production of natural coloring matters. Besides animal and mineral, raw materials are also available in abundance in India for obtaining natural dyes. Thus there are enough natural resources in India for manufacturing natural dyes, provided that they are judiciously and efficiently exploited.

There is a belief that natural dyes are fugitive and do not produce brilliant and deep shades as synthetic ones. It may be because the natural dyes have been used in the crude form. The crude extract may be a mixture of several coloring matters. So that each coloring matter gives its own hue. Therefore, the color of the natural dyes may not be as brilliant and deep as synthetic one, which is based on a single chemical compound. For example, the natural indigo contains indigotin, indirubin, indigobrown, an amorphous substance of under mined constitution, gluten, the flavonol kaempferol (indigo yellow), and mineral matters. Because of this composition, the natural indigo does not produce as brilliant and deep color as that of synthetic indigo, which in contrast is a hundred percent pure indigotin. Similarly, the crude extracts of the roots of the madder (*Rubia cordifolia* L.) contains about 19 anthraquinone pigments in which alizarin, purpurin, and pseudopurpurin are the major coloring matters. If these coloring matters are not separated, each and every coloring matter produces its own hue. Therefore, the crude extracts of the plant should be subjected to isolation of principal coloring matter in pure form using modern methods of analytical chemistry such as spectroscopy, and chromatography. The coloring matter, thus obtained, would be in no way inferior in shade, depth, tone, etc., to the synthetic one.

Considering the similar approach in mind, the Indian Institute of Technology, Delhi, and Forest Research Institute, Dehradun, have developed a technology for manufacturing natural dyes from vegetable raw materials. By using the same technology, Alps industries of India has set up the world's first vegetable dyes manufacturing unit at Sahibabad, Uttar Pradesh, India, with collaboration of Park. B. Smith Inc., USA.

Keeping the above view in mind, the present book has been written. Hope this would fulfill the aspirations and needs of the industrialists, entrepreneurs, traders, researchers, students, and those who are interested to acquire knowledge in natural dyes.

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## 2.1 Introduction

The concept of natural dyes is by no means a new. The primitive people had revealed the tinctorial properties of the juices of leaves, fruits, crushed flowers, roots, bark, etc., from the stains left on their hands while collecting food. Natural dyes have been used in most of the ancient civilizations of the world, like India, China, Mesopotamia, Egypt, Greece, Aztec, and others. The discovery of red ochre in very ancient burial sites indicates that the use of natural dyes for aesthetic and other purposes is at least 15,000-year old. The art of dyeing cloth is believed to have been known since 3000 BC in China and 2500 BC in India. At relatively the same period (2000 BC), dyeing of cloth in yellow, red, blue, and green was also practiced in Egypt.

Indigo is perhaps the oldest natural dye used by man. It has been known in India for about 4000 years. In northern Europe, another blue dye known as the woad (*Isatis tinctoria*) has been in use since the Bronze Age (2500–800 BC). Another ancient dye, the Tyrian purple derived from the Mediterranean shell fish of the genera *Purpura*, and *Murex* was probably the most expensive dye stuff in history. The Phoenician towns of Tyre and Sidon were the centers of this dye industry in about 800 BC, and the Greek dye factories that produced purple existed all along the Mediterranean coasts. The Tyrian purple was so precious that an extract of it was often dyed over the purple made from a Lichen genus *Rocella*. Gradually, the use of *Murex* died out, until the Lichen (*Rocella*) alone provided the purple dye.

## 2.2 Pre-Vedic period

The history of Indian natural dyes appears to have been started from the Vedic period. From the pre-Vedic period, however, a piece of purple-colored cotton was found from the antiquities of Mohenjodaro (c 3000 BC), which from recent chemical examinations suggests its colouration with madder (*Rubia cordifolia*). It is also believed that the art of dyeing and calico printing had its origin in India. There are numerous references such as *Bhṛighu Samhita*, paintings of *Ajanta* and *Bagh*, relics of Mohenjodaro, Fiazi's illustrated

Ramayana, and Firdausi's Shehnama where the uses of natural dyes have been given. The relics from the excavation of Harrapan culture have yielded evidence of ropes and fabrics dyed with natural colors. The cave paintings of the Ajanta and Bagh still preserve the beauty of natural colors in their fullest splendor.

### 2.3 Vedic period

The tinctorial properties of natural dye substances recognized in the Vedic period, particularly in the Atharvavedic and the succeeding period (c 1000 BC–500 BC) were indigo (*Indigofera tinctoria*), safflower (*Carthamus tinctorius*), madder (*Rubia cordifolia*), lodhra (*Symplocos racemosus*), haridra (*Curcuma longa*), and lac (*Laccifer lacca*).

### 2.4 Post-Vedic period

In the post-Vedic period (c 500 BC–c 3rd century AD), saffron (*Crocus sativus*), indigo (*Indigofera tinctoria*), kermes (*Kermes ilicis*), rocand (a bright yellow substance prepared from cow's urine), and red ochre were the most prevalent natural dyes.

### 2.5 Epic period

In the epic period, there are frequent references to "Pitambar" a yellow garment used by the Gods. Fresco revealed that during this period, men and women used very colorful garments.

### 2.6 The Classical period

The classical age to the medieval period acknowledges the tinting capacity of the number of vegetable, mineral, and animal substances.

The evidence of the use of natural dyes during pre-Muslim and Muslim period in Indian history is much better preserved in the form of dresses, manuscripts, and printings. Some of the records of the court historians (and biographers like Firdausi) are written and illustrated with natural dyes. The palace decorations and the ceilings of the temples of Hallebid and Bellur (in Karnataka) loudly testify to the mastery of the Indian craftsmen in the use of natural dyes. The colored exquisite silk and muslin fabrics of India acquired fame throughout the world during the 16th and 17th centuries. The most prized red dye-stuffs of this period were, *kampillaka* (*Mallotus philippensis*), *pattanga* (*Caesalpinia sappan*), *jatuka* (*Oldenlandia spp.*), and *cochineal*



(*Dactilopius spp.*). In addition to these, some black dyes derived from *Terminalia chebula*, *Embilica officinalis*, *Eclipta alba*, *Indigofera tinctoria*, *Piper longum*, and sakala, a black dye prepared from cow-dung, were in use.

## 2.7 The Medieval period

The Medieval period was marked by the discovery of a mordant; the color fixation property of tuvari, the alum and processes employed for the extraction of the coloring principles from the dye stuff. The late Medieval period (18th century AD) introduced the applications of iron mordant for the fixation of colors like blue, green, and violet, and of aluminum mordant for the fixation of red dye stuff. Just how important were the natural dyes in the economic life of India in the 18th and 19th century is illustrated by the rising of Indigo planters of Champaran in Bihar. Up to the end of the last century, India was the largest exporter of natural dyes such as indigo, lac, safflower, cutch, madder, etc. Although the ancient dyers and printers were not conversant with modern terminology as science and technology of dyeing and printing, yet one cannot but admire the high proficiency achieved by them in application of natural coloring matters. Thus from the remote antiquity to the end of the last century, India's superiority in color, design, and fastness of shades remained undisputed. This was the state of affairs till the discovery of first synthetic dye by William Henry Perkin in 1856 from coal-tar chemicals.

Sir Thomas Wardle (1831–1909), a British textile entrepreneur, had compiled "Specimens of Fabric Dyed with Indian Dyes" in 15 volumes. He had documented about 3,000 dyes extracted from 64 plants. It may be replicated in 30,000 color combinations by using right proportion of dyes and mordants. Further, Wardle had pasted samples of fabrics dyed with different combinations of natural dyes and assigned a number for each color. The detailed description of coloring agents, source, extraction and application methods are provided. The original volumes are still preserved in Botanical Gallery of Indian Museum, Kolkata.

## 2.8 Down fall of the natural dyes

After the discovery of the synthetic dyes, there was a gradual decrease in the use of natural dyes. It was because of the synthetic dyes were cheaper, brilliant, deep in shades, and easy in processing color fastness in comparison to their counterparts. Thus, the importance and reputation of natural dyes was destroyed.

## 2.9 Revival of natural dyes

During the period of World War I (1914–1918), various textile industries of the world were paralyzed on account of the complete stoppage of the export of synthetic dyes from Germany, who held the monopoly till then. Investigations were again carried out in several institutions and organizations in India to revive the ancient, and indigenous natural dye stuff industry. However, these attempts came to a standstill at the end of the World War I. During the span of 21 years, since the termination of World War I and the beginning of World War II (1918–1939), the textile industry along with the dyes tuff industry forged ahead by leaps and bounds. The ultimate result was that the indigenous natural dyes, which were being used by the artisans, practically disappeared from the market, except for few centers in Rajasthan, Andhra Pradesh, Gujarat and a few remote rural areas where the craft is still practiced by the few devoted families.

After independence, one of the policies of the Govt. of India was to revive and preserved the heritage and culture of India. Revival and development of dyeing and printing with natural dyes was also covered under priorities.

Various Government institutions, such as the office of the National Handloom Development Corporation, Weavers Service Centers, Voluntary Organizations and individuals are making efforts to revive the ancient industry that is leading towards extinction. Moreover, environmental awareness throughout the world now seems to rescue the “total fall” of natural dyes. Hazards of chemical industry in general and dyes in particular have forced environmentalists and toxicologists to think in terms of natural products. Trends of greater use of synthetic substitute of natural substances have been reversed. This actually started when people throughout the world in general and West in particular preferred natural dyes. The production of synthetic dyes involves many violent reactions, which are conducted at high temperature and pressure using primary chemicals isolated from petroleum. During the manufacturing process, many carcinogenic chemicals are required. The by-products formed have to be discharged in the rivers, ponds or in the atmosphere. Thus, the effluents from the industries are one of the major causes of environmental pollution. These drawbacks of synthetic dyes have prompted environmentalists to look for eco-friendly products and technologies. With the result, natural products in general and natural dyes in particular are heading towards a period of renaissance. Natural dyes are not only free from this drawback but could also assist the regeneration of environment if the dye yielding plants are to be cultivated on the commercial scale. Looking from the point of the national health, toxicologists are of the opinion that many of these chemicals are hazardous to health and environment. Therefore, it is imperative to use the natural dyes as these are eco-friendly and user-friendly.

## 2.10 Present status

Recently, an international workshop on “quality standards and certification of natural dye” was organized at Hyderabad. Visva Bharati University conducted a seminar and workshop on the application of vegetable dyes on textiles. Several national and international workshops were held on natural dyes as a part of UNDP programme of technical co-operation among developing countries. During these workshops, it was concluded that there is a great potential for the revival of the use of natural dyes in Asia, particularly in India. Therefore, efforts should be made to promote the use of natural dyes, extend the range of their application, and encourage their commercial use rather than restricting it to cottage scale, and a need to carry out R&D on natural dyes, develop extraction technique, standardize applications on synthetic as well as natural fibers, leather, and also to evaluate them for their toxicity.

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### 3.1 Introduction

Traditionally, both dye plant and the material to be dyed were simultaneously boiled together. Such primitive method was used by the craft persons. Though, it is still in use among some native people, but it is non reproducible and suitable for small-scale operations. The vegetable dyes extraction is broadly divided into extraction method and extraction technology.

#### 3.1.1 Extraction methods

The extraction method of vegetable dyes basically depends on the method in which the dye is extracted. There are mainly four methods used in extraction of natural dyes.

- (a) *Aqueous method*: Boil the dyestuff in soft water at 100°C. Filter the dye solution and record the optical density.
- (b) *Alkaline method*: Prepare 1% alkaline solution with addition of sodium carbonate or sodium hydroxide in water. Enter the dye material in it and boil the same at 100°C. Filter the dye solution and record the optical density.
- (c) *Acidic method*: Prepare 1% of acidic solution by adding HCl in soft water. Enter the dye material and boil it at 100°C. Filter the dye solution and record the optical density.
- (d) *Alcoholic method*: Alcoholic solution is made by adding equal amount of alcohol and water. Enter the dye material and boil it at 100°C. Filter the dye solution.

#### 3.1.2 Extraction technology

The extraction can be carried out in aqueous, acid or alkaline medium. At present in India, mostly small scale producers and manufacturers are using these methods. Even the local dyers are using more crude methods for extraction using metallic flax and crude process in refined way using blender condenser, distillation plant and drier, and crystallization unit with the capacity of 300

tons per year. The modern techniques of extraction are carried out with the use of extraction plant, reverse osmosis process, and the latest is supercritical fluid extraction method. This method is very common in developed countries.

#### A. Solvent extraction

Solvent extraction or Soxhlet extraction technique was developed just before the dawn of twentieth century. This is one of the most common extraction techniques used today for solid matrices and now it has been commercialized in recent years. This technology has been improved to reduce waste generation and eco-effectiveness of extraction methodology.

#### B. Microwave-assisted extraction technology

The microwave-assisted extraction technology is a high-speed method used for selectively targeted compounds from various raw materials. The technology uses a microwave applicator as the energy source during solvent extraction, leading to the following advantages:

- Faster processing
- Better yield
- Improved quality
- Lower energy consumption
- Reduced solvent level
- Low capital investments

#### C. Continuous steam distillation process

The continuous steam distillation process, as the name suggests, is a separation process using steam as a media; but instead of batch type, this process is continuous. The process consists of a totally insulated pneumatic conveying system using super heated steam as a carrier gas.

#### D. Enzymatic fermentation extraction

Recently, a novel method of extracting pigments from pigmented plant products has been developed. This method results in extraction with stability far superior to present methods of carotenoid extraction. Because most carotenoids exhibit bright colors, these pigments have much potential use as a coloring agent. Carotenoid pigments have been found to be particularly useful as food colorants or food dyes. A US Patent No. 5,830,738 has been granted for this technology. The process includes the steps of combining shredded plant material with an enzyme. The enzyme breaks down the plant cellular walls releasing the carotenoids contained within the plant cells. The enzymes added to the plant material can be pectinase, cellulase, hemicellulase, or mixture thereof.

In the extraction of natural Indigo, the process involves over-night fermentation of harvested indigo plant using bacteria in specially designed

cement-molded ring tank. After fermentation, the plant debris is removed, and the fermented liquid is oxidized using specially designed mechanical agitator. The precipitated indigo settles down at the bottom of the tank as the slurry is collected, boiled, and sun dried as indigo cakes.

#### E. Supper critical fluid extraction (SFE)

Super critical fluid extraction is a further advancement, making significant steps over the use of conventional solvent extraction technology. It uses  $\text{CO}_2$  as extraction media. It is non-hazardous and subject to minimum waste generation. This technique is used for the extraction of natural products in food, pharmaceuticals, and chemical industries too.

Advantages of supercritical  $\text{CO}_2$  extraction technique: This technique makes it possible to work at moderate temperature without affecting the organoleptic qualities and the active ingredients of the extracts obtained. It is possible to obtain 100% natural extracts, completely free from extraction solvent residues. At the end of extraction, an expansion phase (achieved by reducing pressure) causes the carbon dioxide to change from the supercritical state to the gaseous state, which enables it to be removed completely from the  $\text{CO}_2$  extract obtained. SFE is a two-step process, which uses a dense gas as solvent usually carbon dioxide above its critical temperature ( $31^\circ\text{C}$ ), and critical pressure (74 bar) for extraction. The natural product is powdered and charged into the extractor. Carbon dioxide is fed to the extractor through a high-pressure pump (100–350 bar). The extract charged carbon dioxide is sent to a separator (60–120) via a pressure reduction valve.

At reduced temperature and pressure conditions, the extract precipitates out in the separator. The extract-free carbon-dioxide stream is introduced several times for effective extraction of the entire coloring component from the natural products. The separation of colorants, however, is the only part of the separation task. The solvent is to be separated from the dissolved material. Thus, the extraction unit will consist of two main steps:

- (1) Extraction step
- (2) Separation step

During the extraction step, the soluble material is extracted with high pressure from the solid plant material by solvent from the solid plant–material matrix and transported away by the solvent during the separation step; the dissolved material is removed from the solvent by decreasing the solubilising power of the solvent. Many of the same qualities which makes  $\text{CO}_2$  as SCF ideal for extraction, also makes it suitable for dyeing offering enhanced dyeing rates with preferred fastness properties.  $\text{CO}_2$  as SCF is considered GRAS (generally regarded as safe) solvent. The extract ability depends on the occurrence of functional grouping in the colorant, their molecular weight, and

polarity. Solubility of the natural colorant can be increased by using co-solvent or modifier to increase its polarity and hence its power increases where the natural colorant is sparingly soluble. Ethyl alcohol, ethyl acetate, and water are the best co-solvents for natural colorant extraction. By adding modifiers (1–10%) to the supercritical fluid, it increases the polarity of supercritical  $\text{CO}_2$ .

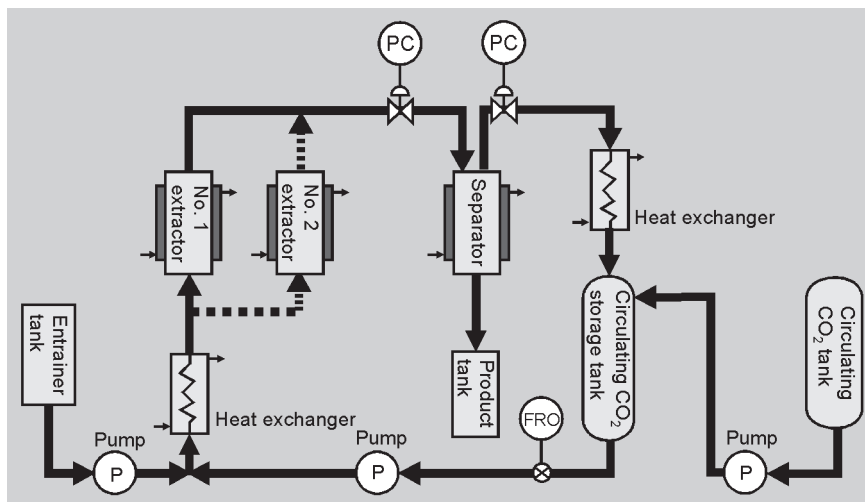


Fig. 3.1 Flow chart for the production of natural dyes

Few colorants are soluble in solvents, and some colorants are soluble in water. For large scale commercial production of natural dyes or colorants, using conventional solvent extraction processes pose regulatory constraints. The serious investigation into the newer process for improvement of recovery and stability of colorants using supercritical  $\text{CO}_2$  is being seriously explored all over the world. For complete extraction and separation of colorant from the matrix, the process needs to be repeated several times.

Therefore, a separation of the extractable proportion according to their solubility can be achieved by a repeated extraction of the raw material with rising dissolving power due to increasing density. Thus certain functional groups like free carboxylic acids, carboxylic acid ester, amides, etc., determine together with the molecular size the interaction and thus the solubility.

Worldwide, SFE is gaining popularity and importance over the conventional techniques for extraction of natural products in food, pharmaceutical, and chemical industries because supercritical carbon dioxide at high densities can extract minute quantities of colorants.

**Table 3.1** Flow chart for the production of natural dyes.

Scheme I	Scheme II
Raw Material	Raw Material
↓	
Size Reduction	Size Reduction
↓	↓
Batch Extraction	Batch Extraction
↓	↓
Phase Separation	Phase Separation
↓	↓
Fine Filtration	Fine Filtration
↓	↓
Evaporation	Precipitation
↓	↓
Spray Drying	Drying Under Vacuum
↓	↓
Finishing	Finishing
↓	↓
Packing	Packing

### 3.2 Raw materials

The raw material for the production of natural dyes is mostly vegetable matter such as seeds, leaves, roots, bark, heart wood, etc., of the plants. The most important part of the production of natural dyes is the sourcing of the raw material. The raw material selected for the extraction of the coloring matter should be easily available at reasonable price and in large quantity throughout the year.

For the procurement of the raw materials, proper specifications in terms of moisture content, ash content, water or alkali, extractable matter, and the absorption spectra must be specified so as to ensure reproducible results.



### **3.3 Size reduction**

The raw materials are required to be ground to powder form so as to facilitate the extraction. The powder should have a fine and uniform particle size distribution. If the particle size becomes very fine then there are chances of swelling and lump formation. Hence for the proper extraction, optimum size between 50 and 100 mesh is required to be adjusted for each raw material depending on its swelling characteristics. Excess heating of the raw material during grinding should be avoided since these raw materials are sensitive to heat.

### **3.4 Batch extraction**

The batch extraction of the coloring component must be carried out in non-corrosive stainless steel (SS) vessel. The coloring component can form metal complexes with the material of construction of the extractor.

Depending on the batch size and the material to liquor ratio, suitable steam jacketed vessel with low speed stirrer is recommended to be used for extraction of the coloring matter. It is important that the water used for extraction should be free from metallic impurities. Hence, soft water with less than 50 ppm hardness is recommended for the extraction of the coloring matter. Other important factors for the proper and reproducible results are the time, temperature, and pH of the water used for extraction. This varies from color to color.

### **3.5 Phase separation**

After extraction, the solids and the liquor are required to be separated. This can be done in various ways such as, by continuous decanting, continuous centrifugation, etc. During this process, the solid waste generated after extraction is separated and disposed off.

### **3.6 Fine filtration**

For removing the fine particle, >5 microns, a sparkler filter with a non-woven filter cloth is recommended. One also uses the reverse osmosis system for eliminating the fine suspended particles.

### **3.7 Precipitation/concentration/drying**

The precipitation of the dye from the extract is brought about with change in pH from alkaline to acidic pH. The precipitated dye is filtered through the

filter press or separated from the liquor by centrifugation. The precipitated dye is dried under vacuum at the low temperature. In some cases, the dye liquor is concentrated under vacuum to a solid content of approximately 30%, and spray dried. The dye powder thus obtained is ground to 200 mesh particle size and formulated to get the standardized natural dyes.

### 3.8 Characterization

Every lot of the dye must be characterized in terms of water soluble matter, ash content, moisture, pH and spectra intensity as well as the strength of the dye (by the dyeing trial).

**Table 3.2** Specification of few natural dyes produced by Alps Industries, using the above-mentioned technology.

S. no	Botanical name	Common name	Moisture (%)	Water soluble matter (%)	PH of 1% solution	Ash (%)	Trade name*
1.	<i>Acacia catechu</i>	Cuth	6.0 + 0.2	95.0 + 2.0	6.0 + 0.4	7.0 + 1.0	Thar
2.	<i>Acacia nilotica</i>	Acasia	3.0 + 1.0	95.0 + 2.0	7.5 + 1.0	27 + 2.0	Capsian
3.	<i>Mallotus philippensis</i>	Kamala	4.0 + 1.0	10.4 + 4.0	6.3 + 0.3	5.0 + 3.0	Basant
4.	<i>Pterocarpus santanilas</i>	Red sandal wood	5.0 + 2.0	29.0 + 2.0	6.0 + 1.0	11.0 + 2.0	Garden
5.	<i>Punica granatum</i>	Pomegranate fruit rind	6.0 + 2.0	95.0+3.0	4.3+0.2	11.0+2.0	Pacific
6.	<i>Quercus infectoria</i>	Gall nuts	5.0 + 1.0	96.0 + 2.0	4.0 + 0.2	6.0 + 1.0	Amber M
7.	<i>Rheum emodi</i>	Himalayan rhubarb	5.0 + 1.5	30.0 + 5.0	3.0 + 1.0	5.0 + 3.0	Desert
8.	<i>Rubia cordifolia</i>	Indian madder	5.0 + 2.0	95.0 + 2.0	8.0 + 2.0	35.0 + 5.0	Indus
9.	<i>Rumex maritimus</i>	Golden dock	12.0 + 1.5	14.0 + 3.0	3.0 + 1.0	3.0 + 1.0	Sahara
10.	<i>Terminalia chebula</i>	Myrobalan	5.0 + 1.0	97.0 + 2.0	3.5 + 0.5	7.0 + 2.0	Kango
11.	<i>Indigofera tinctoria</i>	Indigo	5.0 + 1.0	4.0 + 2.0	5.0 + 1.0	63.0 + 7.0	Nile

\*Trade names of Alps Industries Limited

**Table 3.3** Comparison with other extraction techniques.

S. no	Solvent extraction	SF extraction
1.	Solvent presence is unavoidable. The residue ppm level of the solvent depends on the type of solvent used	Totally free of solvents and hence very pure
2.	Heavy metal content is also unavoidable and depends on the solvent, the recycle method for the solvent, the source of the raw material, and the material of construction of the contact parts of the machinery	Totally free of heavy metals since they are not extractable even if they are present in the raw material. No heavy metals are present in CO <sub>2</sub> and the equipment
3.	Inorganic salt content cannot be avoided, using the same concept as above	Totally free of inorganic salts using the same explanation as above
4.	Polar substances get dissolved along with the lipophilic substances from the raw material due to poor selectivity of the solvent. During solvent removal operation, these polar substances form polymers, which lead to dark color of extract and poor flow characteristic. All this renders the extract to look different from the basic components in the raw material and hence it is more of a pseudo natural extract.	No such possibility since there is very high selectivity of CO <sub>2</sub> and no chance of polar substances forming polymers. In addition, the operating temperature is only 40–50°C
5.	Both polar as well as non-polar colors are extracted	Only non-polar color get extracted
6.	Solvent removal requires extra unit operation, and hence recovery of useful material is lower	No extra unit operations needed and yield of useful material is very high capital cost

## Further reading

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## Mordants and their applications

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### 4.1 Introduction

Natural dyes are either substantive, which need no mordant, or adjective which require one mordant. The majority of natural dyes need a chemical in the form of a metal salt to create an affinity between the fiber and the pigment. These chemicals are known as “mordants,” the name being derived from Latin *mordere*, meaning “to bite”. It was thought at one time that the mordants are away from the surface of the fiber so that the dye could sink in. It was the general opinion that the metallic salt, because of their corrosive nature, made the textiles rough, opened their pores, and made them more receptive to the coloring matters. But it is now regarded as a chemical which can itself be fixed on the fiber and also combines with the dyestuff. A link is, therefore, formed between dyestuff and fiber, which allows certain dyes with no affinity for the fiber, to be fixed. Where the dyes are capable of being dyed directly, the mordant helps to produce faster shades by forming an insoluble compound of mordant and dyestuff within the fiber itself.

Besides metallic salt, tannins and oils are also used as mordants. Generally, cotton is mordanted with these mordants. These mordants impart affinity for basic dyes. They also act as primary mordants for metallic salts. For instance, a cotton cloth on treatment with tannic acid can absorb all types of metallic mordants. The metallic mordants form complex with the carboxylic groups of tannic acid. The cloth thus treated can be dyed with the mordant dyes.

There are three types of mordants namely,

- Metal salt or metallic mordants
- Tannins and tannic acid
- Oils or oil-mordants

#### 4.1.1 Metallic mordants

Originally, only naturally occurring metal salts were used as mordants. But nowadays, metal salts of aluminium, chromium, iron, copper, and tin are used as mordants. Few of the common mordants are alum, potassium dichromate, ferrous sulphate, copper sulphate, stannous chloride, and stannic chloride.

*Alum*

The name alum was originally coined to denote the double sulphate of aluminium and potassium, which crystallized in the shape of octahedra with 24 molecules of water of crystallization. This salt is also called potash alum,  $\text{Al}_2\text{K}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$ . It contains about 36% aluminium sulphate.

The name alum was later extended to a whole class of double sulphates of analogous constitution and in amorphous form. Thus, a great number of alums are known, such as

Ammonium alum	$\text{Al}_2(\text{NH}_4)_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$
Soda alum	$\text{Al}_2\text{Na}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$
Chrome alum	$\text{Cr}_2\text{K}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$
Ferric alum	$\text{Fe}_2(\text{NH}_4)_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$

All these alums crystallize in octahedral and cannot be separated by crystallization when present in solution together.

About 22 g of alum can be dissolved in 100 ml of water at 30°C, and in boiling water up to 357 g alum may be dissolved in same volume. Alum is not dissociated by boiling or by diluting with water. By the addition of sodium hydroxide or carbonate to the solution of alum, so called neutral alum is obtained. By gradually adding the alkali, temporary precipitates are formed, which redissolve on stirring. A solution of alum which has been rendered as basic as possible, without permanent precipitation, is called “neutral alum”. It is however, a basic salt. It can be prepared by boiling a solution of 12 parts of alum with 1 part calcium hydroxide. If the solution is heated above 40°C, precipitate is formed.

*Potassium dichromate*

Potassium dichromate is also referred to as red chromate or dichromate of potash, or chrome. It is manufactured by heating chrome iron ore with lime and potash, when the chromium oxide is oxidized by the atmospheric oxygen, and chromates of calcium and potassium are formed. Potassium dichromate crystallizes in the form of large orange triclinic prisms. It is poisonous, the property common to chromic acid and its salts. Its dust is very harmful to the skin, and cause painful sores. The solutions of dichromate are light-sensitive.

*Ferrous sulphate*

Ferrous sulphate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) is also known as Copperas or Green Vitriol. Ferrous sulphate is prepared on large scale from the iron pyrites. It is also obtained as a by-product in various manufacturing processes. The commercial product forms bluish-green monoclinic crystals, which effloresce in the air and become yellowish by oxidation, though when pure they are perfectly

stable. Ferrous sulphate is readily soluble in water; 100 parts of water dissolve 115 parts of the crystallized salt,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , at  $25^\circ\text{C}$ . Solution of ferrous sulphate does not dissociate either heating or on cooling. It is one of the most important and one of the oldest mordants known, and is still extensively employed.

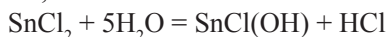
#### *Cupric sulphate*

Cupric sulphate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) is also known as blue vitriol or copper sulphate. Cupric sulphate is manufactured by roasting ores, which contain copper and by dissolving them in sulphuric acid. From this solution, crystals having a different degree of purity are obtained. Cupric sulphate crystallizes in transparent blue triclinic crystals, which contain 5 molecules of water. It is readily soluble in water and 100 parts of water dissolve 49 parts of cupric sulphate at  $30^\circ\text{C}$ .

#### *Stannous chloride*

Stannous chloride ( $\text{SnCl}_2$ ) is prepared by dissolving tin in hot hydrochloric acid. From the aqueous solution, monoclinic crystals are obtained, which contain two molecules of water of crystallization and which are known commercially as tin crystals.

Stannous chloride has a fairly high solubility in water. The clear solution becomes turbid on dilution with water insoluble basic stannous chloride is formed,



Tin crystals are oxidized in the same way on exposure to the air.

#### *Stannic chloride*

Stannic chloride is prepared by the oxidation of stannous chloride with chlorine or potassium chlorate. It is generally sold in the form of monoclinic crystals,  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ . Stannic chloride is highly soluble in water. It is an important mordant for cotton and silk.

### 4.1.2 Tannins and tannic acid

Tannins are primarily used in the preservation of leather. They are also used in glues, stains, and mordants. Vegetable tannins are bitter and astringent substances in plants, often occurring as excretions in the bark and other parts (especially leaves, fruits, and galls). For tanning purposes, the extractions are either employed directly or used in a concentrated form by extraction of the tanning substances.

A number of tannin containing substances are employed as mordants in the dyeing of textile fibers. Few of these are used on account of their lower price

as a substitute for tannic acid in mordanting. Among the tannins, myrabolans and sumach are most important.

#### *Myrabolan*

Myrabolan is the fruit of the tree *Terminalia chebula*. The dried fruits resembling a slightly shriveled plum are about an inch long, very hard, and possess a bitter astringent taste. The bulk of the tannin is in the peel of the fruit. The tannin of the myrabolan is ellagitannic acid. Myrabolan contains a yellowish-brown coloring matter which when removed makes the material a good substitute for tannic acid. It is used in tanning, cotton dyeing and black dyeing of silk. It is locally known as Harda.

#### *Sumach*

Sumach consists of the leaves and twigs of several species of *Rhus*. The sumach from *Rhus coriaria* is the best. It is sold in the form of the whole or crushed leaves, or as a powder. Best sumach contains 15–20% tannin, and has olive-green color. Sumach contains reddish coloring matter that prohibits it from being employed for the dyeing of light and brilliant shades. Sumach contains gallotannic acid.

#### *Tannic acid*

Tannic acid occurs in many tannin containing substances, especially in nut galls, and in sumach. Nut galls contain about 60–77% tannic acid. Tannic acid is light-yellowish colored amorphous powder having a strong astringent taste. It becomes yellowish when exposed to light. It is soluble in six parts of cold water and more freely in hot water. The aqueous solution of tannic acid gradually decomposes on standing by fermentation. Addition of boric acid inhibits the decomposition by fermentation. The alkaline solution of tannic acid rapidly absorbs oxygen from the air and acquires a brown color on decomposition.

### 4.1.3 Oil mordants

Oil mordants are used mainly in the dyeing of turkey-red color from madder. The main function of the oil-mordant is to form a complex with alum used as the main mordant. Since alum is soluble in water and does not have an affinity for cotton, it is easily washed out from the treated fabric. The naturally occurring oil contains fatty acids such as palmitic, stearic, oleic, ricinolic, etc., and their glycerides. The COOH group of fatty acids reacts with metal, salt and gets converted into  $-COOM$  where M denotes the metal, for instance, in the case of alum it would be Al. Subsequently, it was found that the treatment of oils with concentrated sulphuric acid produces sulphonated oils that possess



the better metal binding capacity than the natural oils due to the introduction of sulphonic acid group,  $-\text{SO}_3\text{H}$ . The sulphonic acid can react with metal salts to produce  $-\text{SO}_3\text{H}$ . The bound metal can then form a complex with the mordant dye such as madder to give turkey-red color of superior fastness and hue. Thereafter, the sulphonated oils were called Turkey-Red Oils (TRO).

The term TRO is now used only for the sulphonated castor oil, which was introduced in the market in 1876, almost simultaneously by an English and a French firm. TRO is also the forerunner of the modern synthetic surfactants.

## 4.2 Application of moderants

Mordants not only give the dye an affinity, but in many cases, they produce different colors and improve the fastness of a dye. There are many plants which may yield a color that is brilliant and pleasing but fades easily, unless fixed by using a mordant. There are different agencies of fading such as, light, washing, and perspiration. Few mordants are better preventives of one type of fading than they are of others. Several different methods of applying a mordant are in use, and each has its proper place. The principal methods are as follows:

- Applying the mordant before the dye
- Applying the mordant after the dye
- Applying both together
- Applying both before and after

## 4.3 Mordanting of cotton

Since the metallic mordants are soluble in water and are loosely held by the cotton fibers, these mordants have to be precipitated on the fabric by converting them into insoluble form, or by first treating the fibers with oil or tannic acid and then impregnating the treated fabric with the solution of a mordant, whereby the metallic mordants are held on to cotton via oil or tannic acid.

### 4.3.1 Application of alum mordants

Alum yields about 13% alumina ( $\text{Al}_2\text{O}_3$ ) on cotton. Addition of alkali to alum solution produces basic aluminium sulphate, which is used as a mordant. For mordanting 10 kg of cotton, 1 kg of alum and 0.5 kg of sodium hydroxide are dissolved in 200 l of water to give basic aluminium sulphate of required strength. As stated above, two different methods are employed for mordanting cotton with basic aluminium sulphate.

- The material is impregnated directly with the mordant, and the latter fixed by other chemicals or by ageing.
- The material is first impregnated with a sulphate which attracts the basic sulphate and forms an insoluble compound with alumina (oil mordants, tannic acid).

Direct mordanting with basic aluminium sulphate: The cotton is turned for some time in the described solution of the basic sulphate and left in the bath for three to five hours, warmed and dried. Uneven drying produces unequal decomposition of the basic salt, resulting in nonuniform dyeing. It is therefore, advised to fix the alumina on the fiber by precipitating it in the free-state. The fixation of alumina is carried out by working the material in the luke-warm fixing bath for half an hour. The fixing liquor is prepared so that each litre contains 5–10 g of either of the following salts: sodium carbonate, sodium phosphate, sodium silicate (100°C), ammonium carbonate or ammonia liquor (50 g). A solution containing 1% neutral soap is also sometimes employed.

Fixation of mordants can also be carried out by treatment with cow dung. Dung contains a mixture of phosphates, carbonates, silicates, and chlorides of calcium, potassium, and sodium. The action of cow dung has not been completely explained; the phosphates, silicates, and carbonates doubtless exert a fixing action, but the organic sulphates are not altogether inert. It is asserted that cow dung gives better results than any other substitute, since it acts more slowly and evenly. The dunging bath is principally made up with cow or sheep dung and should not contain too much straw or iron; before being used, it is often allowed to stand for few days with addition of some caustic soda, and subsequently diluted with 50–60 times its volume of water.

*Mordanting with basic aluminium sulphate after previous impregnation of the cotton with other substances.*

The process of mordanting cotton with olive oil or sulphated oil, also with tannic acid, and subsequently with basic sulphate or aluminium is employed extensively for the dyeing of turkey-red color.

For other colors, the cotton is impregnated with a solution of about 100 g neutralized TRO per liter, squeezed, dried at low temperature, and worked for half an hour in the previously described solution of basic aluminium sulphate. Subsequently, the material is washed with water and passed through 1 g/l soap solution to fix alumina thoroughly and to remove superficially held mordant. A final thorough rising in water makes the material ready for drying. In place of TRO, an equal amount of soap may be used. Tannic acid is used in a similar way.

4.3.2      Application of chromium mordants

For the successful application of chrome mordant, it is essential that dichromate is reduced to chromic-oxide before the mordanted material is dyed. In case the goods are treated with dichromate after dyeing, the chromic acid produced acts as the oxidizing agent and chromic oxide, which are thus generated, act as the mordants.

One of the methods of applying chrome mordant on cotton is by chroming bath as described:

800 g	Potassium dichromate and
600 ml	ammonia are dissolved in
200 ml	water along with
800 g	sodium thiosulphate
500 ml	magnesium acetate (52° Tw), and
4000 ml	gum thickening (6%)

Pad the fabric with resulting mixture, dry, and steam for 90–120 min. Chromium oxide and magnesium oxide fixed on the fabric act as mordants. This is long tedious process, and one may get tendered material due to long steaming of the impregnated material.

It is, therefore, suggested that the vegetable fibers, like cotton, should be first mordanted with tannin and subsequently treated with a boiling solution of dichromate. It has been observed that 20% tannic acid is required for full shades. The chroming bath is prepared by dissolving three parts of dichromate along with one part of sulphuric acid (in 100 ml).

4.3.3      Application of iron mordant

Iron salts are very extensively applied in dyeing and printing. The application of iron salts in dyeing for mordanting purposes and for weighting silk, which is to be dyed black are of great importance. These mordants are applied on tannin-treated cotton fabric. The commonest way of applying copper as (ferrous sulphate) in cotton dyeing (especially for blacks) is to first treat the fabric with tannin, pass through clear lime water, and then through copperas solution. By the double decomposition of the calcium tanate and copperas, ferrous tannate is fixed on the fiber and calcium sulphate is formed, which is subsequently removed by washing. The ferrous tannate is rapidly oxidized in the air to ferric tannate, which acts as a mordant.

Ferrous sulphate, if applied alone, leaves very small quantity of iron on the fabric. However in many cases, the material is first impregnated with

a boiling decoction of the natural dyestuff or mixture of dyestuff, such as logwood, fustic, cutch, etc., and subsequently passed through a cold solution of ferrous sulphate.

#### 4.3.4 Application of copper mordants

The light fastness of many colors is vastly improved by an after treatment with copper sulphate, e.g., logwood. Copper salts are employed in cotton dyeing as oxidizing agents for the production of cutch brown and logwood blacks. Copper sulphate is frequently employed in the dyeing of black shade on cotton and for this purpose it is fixed by means of tannin.

#### 4.3.5 Application of tin mordants

The tin mordants produce exceptionally brilliant colors. Stannous salts are very powerful reducing agents and are used in discharge printing. Due to their being very powerful reducing agents, they cannot be used along with oxidizing mordants, such as copper sulphate. The natural dyes which are susceptible to reduction should not be dyed on the tin mordants, lest they may get decolorized.

Stannous salts are not frequently employed as mordants on cotton. Persian berries yield a good yellow to orange shade on the materials previously mordanted with tannin and stannous chloride.

Stannic salts are extensively used as mordants for cotton. Many natural dyes, e.g., logwood, fustic, quercitron, and weld are fixed on cotton with stannic oxide, produced on mordanting. Generally, the material is first mordanted with tannin and then worked in a dilute solution of stannic chloride, and finally washed before dyeing. In these cases, tannic acid present in the tannin acts as a fixing agent for the stannic hydroxide, which is the actual mordant.

#### 4.3.6 Application of tannins

Cotton has a very low affinity for most of the natural dyes. The tannins play an important role in cotton dyeing, and are largely used for preparing cotton, so as to enable it to retain coloring matter permanently. Frequently, the purpose of preparing the vegetable fiber with tannin is not so much to fix the coloring matter, although that is the ultimate aim, as to fix certain metallic salts (notably those of aluminium, copper, tin, and iron) in the form of insoluble tannates. The metal tannates present on the material form insoluble lakes with the natural dyes during dyeing.

Tannic acid is the best tannin for the mordanting of cotton since it is the purest of all, and does not contain the natural impurities, which are partly ineffective, partly injurious in mordanting and dyeing. Tannic acid is

extensively used in the dyeing of light and brilliant shades. For dark shades, extracts of gall nuts, sumach, and myrabolan are largely employed. For light shades, 2–5% (o.w.f.) tannic acid is used; while for dark shades, 5–10% tannin is required. The material is worked in the bath for some time and is allowed to soak overnight.

#### 4.4 Mordanting of wool

Unlike cotton, wool is highly receptive towards mordants. Due to amphoteric nature, wool can absorb acids and bases equally and effectively. When wool is treated with a metallic salt it hydrolyses the salt into an acidic and a basic component. The basic component is absorbed at the  $\text{-COOH}$  groups, and the acidic component is removed during washing.

Wool also has a tendency to absorb the fine precipitates from solutions. These precipitates are superficially absorbed onto the surface of the fibers and the dye attached to these gives poor rubbing fastness.

Alum is less efficient a mordant for wool than aluminium sulphate. In few cases, the sulphate is used without any additions. However, a mixture of the sulphate with tartar (tartaric acid) is required to obtain full and brilliant colors, which do not rub off. For a full shade, about 6–8% aluminium sulphate and 5–7% tartar are required. The material is entered in the cold bath and heated to boil. After about 90 min, the material is taken out and given a thorough wash to remove loosely adhering mordant. The washed wool is ready for dyeing, and it should not be allowed to dry, as it is very difficult to wet out again.

Mordanting of wool with sodium or potassium dichromate is one of the most widely used methods of mordanting wool. It is comparatively cheap, easy to apply, and given full bright shades having fairly good fastness. For mordanting, wool is boiled for 60–90 min in a bath prepared with 2–4% dichromate (o.w.f.). Addition of organic acids such as formic, oxalic or tartaric improves the brightness of the resultant dyeings.

Ferrous sulphate does not give an advantage over dichromate as a mordant for producing black color on wool. Logwood black is better fixed by dichromate than ferrous sulphate. However, it is used as an after treatment in case of the brown colors produced from wood extracts.

Copper sulphate is used in conjunction with aluminium sulphate and ferrous sulphate in the dyeing of logwood blue and logwood black. It has been found to be very useful as an after treatment to the dyed material for improving the light fastness.

Among the tin salts, stannous chloride is used as a mordant for wool. The best method is to mordant with 4% stannous chloride and 2% oxalic acid at the boil. Oxalic acid first precipitates stannous oxalate which is slowly taken

up by the fiber during mordanting. An excess of tin mordant makes the wool harsh and rough.

## 4.5 Mordanting of silk

Like wool, silk is also amphoteric and can absorb both acids as well as bases. However, wool has thiol groups (-SH) from the cystine amino acid which act as reducing agent and can reduce hexavalent chromium of potassium dichromate to trivalent form.

The trivalent chromium forms the complex with the fiber and the dye. Therefore, potassium dichromate cannot be effectively used as a mordant for silk.

Alum is not a preferred mordant for silk. Deposition of alumina results in the lowering of the luster and pliability of silk. In one of the methods of application, 10 parts of alum and 4 parts of sodium thiosulphate are dissolved in 100 parts of water, and the silk is treated in this solution for three hours at 60–80°C. It is then rinsed and dyed.

Iron salts are very important, both for mordanting and weighting of silk. Excellent black colors are produced on iron mordanted silk. For production of black color, silk is first treated with tannin. After it has been saturated with tannic acid, it is worked for a short time in ferrous sulphate solution, wrung, and exposed to air for half an hour, again passed through iron liquor and hung once more, and finally rinsed well in running water and dried. The silk which has lost its luster by these operations is soaped and treated with acidified olive oil. By this treatment, it does not only gain luster but also has scroop.

Stannic chloride is the most important mordant for the mordanting of silk. It is also used as a weighting agent. Weighting of silk results in the lowering of the strength of the material. For mordanting and weighting, the material is steeped in 10–15% solution of stannic chloride until it is thoroughly impregnated with the solution. The material is then rinsed with water and treated with sodium phosphate at boil for 30 min. This treatment with stannic chloride and phosphate is repeated until sufficient quantity of the salt is deposited on the fabric. The fabric not only gains weight but also becomes receptive towards mordant dyes.

In order to preserve the original luster and feel, silk is preferably dyed with substantive dyes, which do not require a mordant for their fixation.

## Further reading

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## Preparation of fiber for dyeing

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### 5.1 Cotton

#### 5.1.1 Scouring and bleaching

Grey yarn or cloth as such is not suitable for dyeing or wet processing as it contains natural impurities such as fats, waxes, coloring matter, broken seeds, etc. In order to make the yarn absorbent and to obtain level dyeing, good penetration of the dye stuff and fast shades the impurities have to be removed. This is done by boiling out the yarn with hot alkaline solution.

When the white yarn is required or when light or pasted shades are to be produced, it is necessary to bleach the yarn. The natural color of the yarn is destroyed by bleaching. Cotton yarn is normally bleached in a solution of bleaching powder. Half bleach is usually sufficient for the yarn intended for dyeing. However, the natural color of the yarn is destroyed by full bleaching to get white color.

#### 5.1.2 Process of boiling and bleaching

Raw cotton contains dirt and dust. It is boiled with soda ash and caustic soda (2% soda ash, and 1% caustic soda) and 0.5% soap for one hour and then thoroughly washed. Cotton has thus become physically clean. It is then bleached with bleaching powder. Half per cent (0.5%) bleaching powder is dissolved in water in wooden or stone or stainless steel tanks and the supernatant water is taken out and poured in another wooden tub. In this way, as much chlorine water as possible is taken out thrice. The residue is then thrown away. In this chlorine water, the loose cotton is kept for one hour under water. If more whiteness is required, the bleaching powder may be increased to 1%. The loose cotton is then squeezed and put under another tap, washed thrice and then squeezed. In another wooden vessel, sufficient water is taken in which sulphuric acid or hydrochloric acid is poured just sufficient to make the water slightly acidic. The loose cotton is then treated in this freely. It is taken out, thoroughly washed, and treated in another bath containing 0.5% of thiosulphate of soda for 15 min and then washed freely, squeezed, and dried in



sun. This last treatment with thiosulphate of soda or hypo removes all traces of chlorine, and that is why it is called “anti chlor”.

For cotton yarn and cloth, there are additional impurities other than natural. They are oily matter (oil used during spinning of cotton yarn) and the material used during sizing and weaving, which contains oil, tallow, starches, etc. They are required to be removed before the yarn and the cloth are bleached or dyed. The process of boiling and scouring of yarn/cloth are the same. The cotton material is vigorously boiled in iron or copper tanks for four hours. It is then thoroughly washed and if bleaching is required, it is treated in the same manner as detailed for raw loose cotton. Unless this process of scouring is done, dyeing pale or deep shades will present numerous difficulties.

## **5.2 Silk**

### **5.2.1 Pure or mulberry silk yarn/cloth in raw state**

Raw silk contains natural grace, and resin called “Ceresone”. This is required to be removed. This process is called “Degumming”. For 1000 g of raw silk in hank form, 10 mg of soda ash and 5 mg of soap are required. Sufficient water is poured in a copper/brass vessel, to which the soda ash is added, and the water is heated to boil. The soap is cut into chips and boiled in a small copper vessel. When completely dissolved, it is added to the boil vessel. The silk hanks are put on brass or wooden rods and entered in the boiling bath, turned freely and boiled for 30 min. During boiling, the silk should be freely moved up and down by inserting a wooden rod tapering at one end. The bottom portion of the boiling silk is brought up and the upper portion of silk down. In this way, the boiling is continued for half an hour. The silk is required to be whiter therefore, sufficient cold water is poured in another copper or brass or wooden tank, to which 0.5% hydrosulphate of soda is added. The wet silk is turned in this way up and down for 40 min, taken out, thoroughly washed, and then treated in cold water (to which a little quantity of sulphuric acid has been added). The silk treated in this acid bath for 15 min is then thoroughly washed and dried in the sun.

## **5.3 Wool**

The color of wool varies from white to very dark brown and black, with all shades of fawn, grey, and brown. The natural colors of wool are not absolutely fast to light but tend to bleach slightly with the sunlight. Wool comes into the market in the following forms:

1. In grease, not having been washed, containing all impurities
2. Washed with some of the grease removed, fairly cleaned
3. Scoured, thoroughly cleaned and all grease removed

Wool can be dyed either as fleece, yarn or as woven cloth. Raw wool always contains a certain amount of natural grease. This should no longer be washed out until it is ready for dyeing; the grease keeps the moth out to a considerable extent. Hand-spun wool is generally spun with the help of the oil to facilitate spinning.

### 5.3.1 Scouring

All the grease and oil must be scoured out before dyeing is begun, and this must be done very thoroughly otherwise the wool will not take the color. Wool which is also a silicate fiber has to be handled very carefully. In the same manner as for silk, sufficient water for wool is poured in a copper or brass pot, and the water is heated to 60°C. The woolen yarn in the hank form is put on brass or wooden rods. Then the woolen yarn is put into hot water containing 2% soda and 1% soap, and treated for 2 h. Care should be taken that temperature of this mixture should not get beyond 60°C. The woolen yarn so treated is thoroughly washed and dried.

### 5.3.2 Bleaching

The scoured wool will be of light color. When pure white wool is required, or when pale shades are to be dyed, the wool may be bleached with hydrogen peroxide.

### 5.3.3 Dyeing

There are five principal methods of dyeing with natural dyes. They are as follows:

1. The material is boiled first with the mordant and then in the fresh bath dye.
2. The material is first dyed in the dye bath and treated in a separate bath containing mordants.
3. The material is dyed in the same bath with dye and mordant together.
4. The material is mordanted and then dyed in a separate bath and again treated in a third bath.
5. Some dyes do not require any mordant and the material can be dyed directly.

The mordanted or non mordanted material according to the color is dyed in the concerned dye to extract for 45 to 60 min. Strict watch should be kept during the process to obtain uniform and even dyeing by keeping the constant strength, temperature, and time. The material to be dyed should constantly be moved up and down in the dye bath.

The capacity of the vessel should be such that the entire cloth or yarn may not only be accommodated in it after thorough soaking, but a sufficient margin is left for working the material in the dye bath by constantly stinging and moving in the dye bath with the help of strong wooden rods.

### 5.3.4 After treatment

Colors thus stand washing with boiling soap and also do not fade in sunlight, and can be regarded as fast colors. All fast colors are not so equal in this respect. Few fast colors are unaffected by the bright sunlight of the tropics. To improve this effect, dyed materials may be given some chemical treatment after dyeing with copper sulphate solution.

### 5.3.5 Soaping

This is a very important treatment. On soaping, the colored material loses the superficial colors and gets the proper development of its true shade. In some cases, this process improves the brightening effect of the color.

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## 6.1 Adinin

Adinin ( $C_{16}H_{14}O_7$ ; mp  $235^{\circ}C$ ), the yellow coloring matter, occurs in the heartwood of Haldu [*Haldina cordifolia* Ridsd. syn. *Adina cordifolia* (Roxb.) Hook. F. ex Brandis]. Adinin is insoluble in cold water but slightly soluble in boiling water and undergoes decomposition on protracted boiling. It is also insoluble in chloroform, carbon tetrachloride, benzene, ether, petroleum ether, and carbon disulphide but slightly and moderately soluble in cold and hot alcohol, acetone, and glacial acetic acid, respectively. It readily dissolves in solutions of alkali hydroxides and less readily dissolves in alkali carbonates and bicarbonates, forming light yellow solutions, from which the coloring matter is reprecipitated unchanged on acidification.

### 6.1.1 Extraction

The wood is powdered and extracted either with alcohol (95%) at room temperature or with boiling water, and then allowed to stand for a week; at the end of which, a crystalline matter is separated in the form of yellow nodules. It is filtered off, washed with alcohol, and dried under reduced pressure. The substance is then freed from waxy impurities by extraction with hot benzene and thus, a purified material is obtained. It is recrystallised several times from hot alcohol. The pure substance crystallizes from alcohol in long, fine, glistening needles with a golden-yellow color, and from glacial acetic acid in small bright yellow prisms. The yield of the dye is about 0.09%.

An alcoholic solution of adinin (1%) on spectrographic examination was found to have a well-defined absorption band between wave length 4250 and 4650 Å with the head of the band or absorption maxima at 4590 Å.

### 6.1.2 Uses

Adinin is used to dye cotton, wool, and silk in yellow. On various mordants, it produces different shades.

### 6.1.3 Sources

Adinin is made from the heartwood of Haldu tree, which is known in different languages of India with different names.

Bengali – Dakom, Keli-kadam, Petpuria; Gujarati – Haldarvo; Hindi – Haldu; Kannada – Arsintega, Yettega; Malayalam and Tamil – Manja-kadambu; Marathi – Heddlī; Oriya-Holondo; Sanskrit – Bahuphala; Telugu – Pasupu-Kadamba; Trade – Haldu; English – Yellow Teak.

It is a large deciduous tree with globose yellow flowers, found scattered in deciduous forest throughout the greater part of India, ascending to an altitude of 900 m in the sub-Himalayan tract. It is also common in the forest of South India, especially in the Eastern Ghats and Karnataka.

This plant is raised by seeds. Seeds are sown in nursery beds containing fine sifted soil with a considerable proportion of sand or powdered charcoal. In about two or three months, seedlings are transplanted.

The wood is even grained, moderately hard, and lemon-yellow in color when freshly cut but turns yellowish-grey on exposure to air. The wood weights 45 pounds per cubic foot. It is suitable for making furniture, combs, and toys. The coloring matter, adinin, is easily removed from the wood by extraction with boiling water or alcohol (95%). The raw material for extraction of dye can be obtained, in form of saw dust, from saw mills.

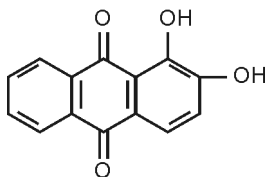
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## 6.2 Alizarin

Alizarin (1,2-dihydroxy anthraquinone; 1,2-dihydroxy-9,10-anthracenedione;  $C_{14}H_8O_4$ , mp 288–289°C), the principal coloring matter, occurs in roots of European Madder, *Rubia tinctorum* L.; Indian Madder, *Rubia cordifolia* L.; Wild madder, *R. peregrine* L.; and in root bark of Chay-root, *Oldenlandia umbellata* L., in the form of a glycoside, ruberythric acid (Alizarin-2-β-primveroside;  $C_{25}H_{26}O_{13}$ , mp 257°C). The glycoside ruberythric acid

readily breaks down to give alizarin and purpurin. The orange or red colored needles or prisms of alizarin are soluble in aromatic solvents, hot methanol and ether, moderately soluble in ethanol and sparingly soluble in water.



Alizarin

Although dye is known for more than 6000 years, the actual coloring matter, alizarin, was isolated from the roots in 1826. Alizarin was the first natural dyestuff to be produced synthetically in 1869 in Von Baeyer's Laboratory. The material is collected in October–November from 2–7 year old plants. Nature of soil and climatic conditions influences the quality and quantity of coloring constituents.

### 6.2.1 Extraction

The dye is extracted from the dried roots of the European and Indian madder, and root bark of the chay-root. The raw material is ground to powder and stored up to four years to increase its tinctorial power, as old plant material is fast in color than fresh one. The yellow powdered root yields maximum coloring matter if it is fermented. Therefore, the powdered root is kept in sealed vessels or in open pits for fermentation. The fermented powder is then boiled either in water, hot methanol or ether for 2–4 h, cooled, and filtered. The filtrate is evaporated or dried up under reduced pressure to get dry powder of the dye. Madder roots contain a mixture of about nineteen anthraquinone pigments, in free-state or as glucosides. Maximum concentration (4%) of these anthraquinones is found in the roots of adult plants. These are separated with the help of chromatographic methods.

### 6.2.2 Uses

The dye is used for dyeing and printing. It is, perhaps, the oldest dye used by men for coloring cotton cloths as it has been identified in the objects excavated from the *Mohenjo-Daro* (c 3000 BC). It was once considered the most important of all dyestuffs used by Calico printers. It yields a famous turkey-red color on aluminium mordanted cotton. It is preferred to use synthetic alizarin for coating the printing foil and dyeing rugs. It is also used in food products, cosmetics, and toothpastes and also used by painters as an artists' color.

Alizarin has been reported to be mutagenic and caused DNA damage in bacterial tests. However in general, it was found inactive in a range of genotoxicity assays in mammalian cells in culture and did not bind to DNA when administered orally to mice. It was of moderate to low acute oral toxicity in mice and may have suppressed the immune system, when administered to mice by repeated intraperitoneal injection. Mild eye irritation had occurred in rabbits.

### 6.2.3 Madder lakes

From the madder dye, madder lakes are also produced. They vary in hue from bluish to yellowish reds and are largely used in oil paints and printing inks. They are unaffected by 5% HCl or 5%  $\text{Na}_2\text{CO}_3$  but turn to violet by strong alkali and are insoluble in water, commonly soluble in oils and waxes, and non bleaching towards soap gel. Madder lakes lack hiding power and paints containing them should always be used with an undercoat. All the madder lakes have very good fastness to light but because they contain purpurincarboxylic acid have a slightly lower fastness than the lakes made from synthetic alizarin. Darken on heating in lithographic varnish at  $148.8^\circ\text{C}$  for 30 min.

Madder lake is produced by boiling garancine (carbon sulphurique; which is made by heating madder with sulphuric acid and then with concentrated sulphuric acid), with dilute alum, filtered hot, cooled the filtrate, separated the precipitate which settled down, and redissolved the precipitate in ammonia, and finally precipitated with alum and/or stannous chloride. Pink madder is the alum lake of Kopp's Purpurin, the precipitate obtained when madder is extracted with cold dil. nitric acid and the extract is heated to  $60^\circ\text{C}$ . It is used to a limited extent as an artists' pigment.

### 6.2.4 Green alizarin

Ground madder is extracted with cold aqueous sulphurous acid (2–3%) to which hydrochloric acid (33%) is added and which is then boiled for two hours. The commercial purpurin which settles down is removed and the extract is boiled for another two hours when a deep precipitate form is obtained which is commercially used under the name of Green Alizarin.

### 6.2.5 Source

Alizarin is made from the roots of the three different madders which are as follows:

*Oldenlandia umbellata* L. (Rubiaceae)

English – Chay-root, Indian Madder; Bengali and Oriya – Surbuli; Hindi – Chirval; Malayalam – Chayaver; Tamil – Chiruver, Imburaver, Saya-wer; Telugu – Cheriveru

It is a diffuse and somewhat woody annual or biennial herb occurring in Bihar, Orissa, and Kerala in India. The root bark, preferably of a two year old plant, is the source of chay-root dye, once employed with mordants for imparting red color to calico, wool, and silk fabrics. Previously, the plant was extensively cultivated in coastal areas of Kerala. The colors obtained by chay-root are similar to those given by madder (*Rubia tinctorum* L.), but the former possesses only about half the dyeing power of madder.

The coloring matter is located mostly in bark. Chay-root resembles madder as it contains alizarin, rubichloric acid, and ruberythric acid. There is mark difference in other constituents like purpurin and purpuroxanthin carboxylic acid that are present in madder. Considerable quantity (1.0%) of yellow crystalline substance is present in chay-root. They contain alizarin ( $\alpha$ -methylether, acetylalizarin,  $\alpha$ -methylether, anthragallol dimethyl ethers, hystazarin monomethyl ether, and  $\alpha$ -hydroxyanthraquinone).

*Rubia cordifolia* L. (Rubiaceae)

English – Indian Madder; Assam – Manjathi; Bhutani – Soth; Hindi – Manjit, Manjith; Kannada – Siomalate, Siragatti, Manjustha; Kashmiri – Dandu; Khasi – Ryhoi, Soh-misem; Lepcha – Vhyem; Malayalam – Poont, Manjetti; Marathi – Manjeshta; Manipuri – Moyum; Naga – Enhu, Chenhu; Nepali – Manjito; Oriya – Barheipani, Manjistha; Punjabi – Kukarphali, Tiuru, Kala-Meshika; Tamil – Shevelli, Manjitti; Telugu – Taamarvalli, Chiranji, Manjistateega

It is a variable prickly creeper or climber, commonly found throughout India, ascending to an altitude of 3,750 m. Root stocks perennial, stem 4–angled, leaves cordate, arranged in whorl. It is a complex group, exhibiting a wide range of morphological characters and is distributed in Africa, Asia, and extending into Australia.

Indian madder of commerce consists of short rootstocks with numerous cylindrical, smooth, and straight roots, covered with a thin, brownish cork, which peels off in flakes, exposing a red brown bark marked by longitudinal furrows. The root is sweetish, followed by acrid and bitter taste. The dye is extracted from the root as well as stem in India; however in Tanzania, the root and fruits are used.

The Indian madder has long been employed in the country for dyeing coarse cotton fabrics, blankets, and carpet. The method of dyeing is much the same all over India, the cloth is steeped in an infusion of the stem or root, and mordanted with alum.



The coloring matter is present in the roots of *R. cordifolia*. Besides Alizarin, the roots contain purpurin and munjistin. In very small quantity xanthopurpurin or purpuroxanthin and psendopurpurin are also found in the root.

*R. tinctorum* L. (Rubiaceae)

English – European Madder, Alizari; Punjabi – Bacho

It is a prickly or scabrid, climbing herb with quadrangular stems, distributed from Kashmir westwards to Spain. Rootstocks perennial with fleshy roots, leaves 4–6 in whorls, usually elliptic, sometimes elliptic-lanceolate. Flowers are greenish yellow in terminal and auxiliary panicles of cymes. Fruit is globose, red to black.

It is an important dye yielding plant that gives brilliant shades of red, known for their beauty and fastness even after light and water. It had been cultivated from antiquity by the Egyptians, Iranians, Indians, and later by Europeans. In India, the cultivation of European madder plant is carried on chiefly in Kashmir. The plant is propagated by buds or sets from the root stocks, and the roots are dug up after two year for use. As the older roots are richer in coloring matter, in few countries the roots are dug up even after three years. The dye is found principally in cortex of the roots. Maximum concentration of the coloring substance is found before and after the flowering period. It is found in the form of glycoside, (2.0–3.5%). Besides ruberythric acid [alizarin-2-(-primveroside)], the other glycosides like galiosin (pseudopurpurin primveroside; present only in fresh roots), rubiadin glucoside (2-methyl purpuroxanthin-3-glucoside), asperuloside, pseudopurpurin, purpuroxanthin, and munjistin have also been isolated from madder roots. Besides roots, the other parts of plant also contain dyestuffs. Stems are easy to harvest, and the total yield (madder-glycosidic content, 2.4–4.2%, dry weight basis of the dye) from stem is reported to be almost twice that of roots. Stem contains more pseudopurpurin than roots and can be used for dyeing wool. Madder yields the famous turkey-red color, on aluminium-mardanted cotton, but now it has almost entirely been replaced by synthetic alizarin which is more effective and cheaper than the natural dyestuff. Nevertheless, synthetic alizarin is reported to lack the luster of natural alizarin, probably due to the presence of pseudopurpurin in the natural dyestuff, which forms lakes of brilliant and light-stable red with aluminum.

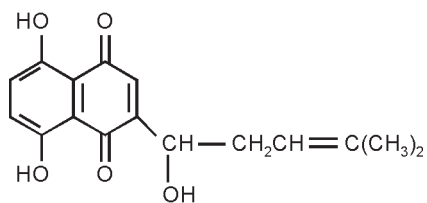
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### 6.3 Alkannin

Alkannin, (S)-5, 8-Dihydroxy-2-(1-hydroxy-4-methyl-3-pentenyl)-1, 4-naphthalenedione; (-)-5, 8-dihydroxy-2-(1-hydroxy-4-methyl-3-pentenyl)-1, 4-naphthoquinone; (1-hydroxy-3-isohexenyl)naphthazarine; 2-(1-hydroxy-4-methyl-3-pentenyl)-5, 8-dihydroxy-1, 4-naphthoquinone; anchusic acid; anchusin; alkanna red natural red 20; alkanet extract; Shikonin; arnebiv IV ( $C_{16}H_{16}O_5$ ; mp 148–149°C), the principal coloring matter, occurs in the roots of Dyer's Bugloss, *Alkanna tinctoria* (L.) Tausch, Ratanjot, *Arnebia nobilis* Reichb., *Onosma hispidum* Wall. ex D. Don, *Arnebia euchroma* (Royle) Johnston, Kashmiri gaozaban, *Arnebia benthamii* (Wall. ex G. Don) Johnston, *A. hispidissima* DC., *A. guttata* Bunge, *Onosma caucasica* Levin, *O. hookeri* C.B. Clarke; *Plagiobothrys arizonicus* (A. Gray) Greene ex A. Gray; *Maharanga emodi* (Wall.) A. DC, Shikon, *Lithospermum erythrorhizon* Siebold & Zucc., Non-Shikon, *L. enchromum* Royle, Gromwell, *L. officinale* L., Corn-Gromwell, *L. arvensis* L., *Arnebia ugamensis* H. Riedl syn. *Macrotomia ugamensis* Popor., *Echium rubrum* Forsk, and *Jatropha glandulifera* Roxb.



Alkannin

The coloring matter alkannin was first isolated under the name of Anchusic acid by Belictier (1818). It is also known under the names pseudo or false alcanna, ox-tongue root, stone-weed, and orcanella. Alkannin forms red-brown needles with a coppery luster. The constitution was elucidated by Brockmann who was able to show that alkannin and shikonin (q.v.) are optical enantiomorphs and possess the same structural formula. Of the two antipodes, alkannin has the (S) and shikonin the (R) configuration. A racemate of alkannin and shikonin also occurs in nature and is known as shikalkin.

Alkannin is slightly soluble in water; very soluble in organic solvents, hydrocarbons, etc., to a red solution. With sodium hydroxide (10%) solution it gives deep blue color. Alkannin forms red-brown needles with a coppery luster. It contains three active hydrogen atoms and thus yields a triacetyl derivative (yellow needles mp 132°C).

### 6.3.1 Extraction

The roots harvested in spring and autumn are dried in shade and ground into a fine powder. It is then extracted with hexane at room temperature for 24 h under continuous stirring. The hexane extract is extracted with methyl alcohol. The methanol extract is evaporated to dryness and the remaining solid mass is further extracted with hexane, which is evaporated and redissolved in hexane and then extracted with aqueous solution of 2% NaOH. The alkaline extract is acidified with dilute  $\text{H}_2\text{SO}_4$  and extracted with hexane, and then evaporated under reduced pressure and gets a solid residue, which is a mixture of naphthaquinone pigments.

With the help of chromatographic methods like TLC and column chromatography, pure alkannin is separated from the other pigments with dichloromethane.

### 6.3.2 Uses

Alkannin has been used since antiquity as a dye. The dye is used for dyeing wool, silk, and cotton. With aluminium, it gives violet shade on cotton and silk. The alcoholic solution of alkannin at 40°C for about 2 h with alum produces from lilac to red shades, but with iron, it produces a tone of grey to violet grey. The colors are very beautiful but not quite fast to light and very sensitive to alkalis and acids. To preserve the blue color, the material is entered in an alkaline solution after bath of ammonia for about a minute. To bring out the purple to red shades, material is dipped briefly in acid bath.

Alkannin is also used as food colorant for coloring oils, butters, wines, confectionery, and sweets. It is also used for coloring pharmaceutical preparations, cosmetics, and as biological stain. Formerly, it was used as a mordant dye for calico-printing. It is also recommended as an indicator and as a reagent for magnesium. It is stabilized for use in cosmetics by impregnating into minute particles of polyethylene, polyvinyl chloride or silicone. A stabilized cosmetic pigment is also prepared by extracting the pigment from root absorbed by powder of aluminium chloride treated mica. A black colorant is prepared by treating alkannin with D-glucosamine and is used in mascara soap, polyamide fibers, and for dyeing wool.

Alkannin paper, anchusin paper, Boettger's paper are also made by impregnated white papers with a 1% alcoholic tincture of alkanet root and then dried. A blue paper can be made from the red paper by treating the latter with a 1%  $\text{Na}_2\text{CO}_3$  solution. This paper acts nearly like litmus paper. With alkalies it changes to green or blue, and with acids it changes to red.

Alkannin is an antioxidant and has an antimicrobial effect against *Straphylococcus aureus* and *S. epidermis*. It is also known to have wound healing, antitumor, and antithrombotic properties.

### 6.3.3 Sources

Alkanin is made from the roots of the following plants:

*Alkanna tinctoria* (L.) Tausch (Boraginaceae)

syn. *Anchusa tinctoria* L.

English – Dyer's Bugloss, Alkanet, Alcanea

It is a velvety, evergreen, 10–60 cm tall plant with hairy leaves and large blue flowers, found all over the sunny and sandy places of Mediterranean and central Europe in wild state. It was cultivated as a dye plant in Europe, and early settlers in North America, probably brought it over for medicinal use but may be as dye plant too. In early days, the gentlewomen of France used to paint their faces with the roots of this plant.

In conventional method, the powdered roots of the plant are extracted in boiling water or alcohol for 2 h and then strained. The liquor is cooled and then cleaned and wetted wool is dipped into it and simmer the bath for 20–40 min. Then wool is dried without rinsing. With alum it yields tan-red to purple-red and gray shades. To preserve the blue color, put the wool in an alkaline after bath of ammonia for about a minute. To bring out the purple to red shades, wool is dipped in an acid bath.

*Arnebia benthamii* (Wall. ex G. Don) I. M. Johnst. (Boraginaceae)

syn. *Macrotomia benthamii* (Wall. ex G. Don) A. DC

Kashmiri – Kashmiri Gaozaban

It is an erect, perennial herb, about 30–90 cm tall with pink to purple flowers, found in the alpine Himalayas from Kashmir to Kumaun, and in Nepal. Its root contains the dye, alkannin.

*A. euchroma* (Royle) I. M. Johnston.

syn. *Macrotomia perennis* Boiss.

It is a perennial herb of about 20–50 cm height with purplish-white to purple or brownish flowers, found in Western Himalayas from Kashmir to Kumaun at altitudes of 3000–4200 m. Its roots contain alkannin which is used as purple or red dye.

*A. hispidissima* (Lehm.) A.DC.

It is a diffuse, hispid herb found in the plains of North-West India. Its roots contain red dye known as alkannin and shikonin.

*Arnebia nobilis* Rech.f. (Boraginaceae)

Ratanjot (trade name) neither occurs in India nor is there any record of its introduction. However, the roots of this plant are imported into India from Afghanistan and sold under the trade name Ratanjot. It is available in the Indian *bazars* as purple-brown pieces of root and rootstocks that are 5–10 cm long and 3–6 cm in diameter, and covered with several layers of thin scaly bark of the same color. An air-dried market sample yielded 2.5% of a very crude viscous red dye which on chromatographic analysis gave seven naphthaquinones designated as arnebins and identified as: arnebin-1 (alkannin), (-dimethylacrylate; yield, 0.375%), arnebin-2 (-dimethylacrylic eater of hydroxyalkannin; yield, 0.047%), arnebin-3 (Alkannin acetate; yield, 0.075%), arnebin-4 (alkannin), arnebin-5 ( $C_{16}H_{18}O_5$ ; mp 111–112°C), arnebin-6 ( $C_{18}H_{20}O$ ; mp 88–90°C) and arnebin-7 [5,8-dinydroxy-2(4'-methylpent-3'-enyl)-1,4-naphthaquinone].

*A. guttata* Bunge

syn. *A. tibetana* Kurz

It is a herb found in the northern part of Kashmir. The roots of the plant are used in Ladakh as cough medicine, they and also yield a red dye. They contain d-alkanin which is called shikonin; a Russian sample yields as high as 4.16% shikonin.

*Jatropha glandulifera* Roxb. (Euphorbiaceae)

Hindi – Jangli Erandi, Undarbibi; Kannada – Totlagida; Malayalam – Atala, Nakadanti; Marathi – Janglerandi; Tamil – Adalai, Eliyamanakku, Puliyanakku; Telugu – Dundigapu; Pakistani – Ratanjot (wood)

It is an evergreen shrub with stout branches and a smooth papery bark which is commonly found in the black cotton soils from Krishna River southwards, particularly near the sea coast. Leaves are simple, and palmately lobed below the middle. Its flowers are greenish-yellow.

The derivative compounds of shikonin responsible for the dark-red color of the wood are 3, 3-dimethylacrylyl shikonin (yield 0.68% of dry weight) and acetyl shikonin (yield 0.66%) obtained from the dried wood of the plant. These compounds on hydrolysis with 2% NaOH solution yield shikonin, the coloring matter.

*Lithospermum erythrorhizon* Sieb. and Zucc. (Boraginaceae)

Japanese – Murasaki, Shikon

It is an erect perennial, 40–70 cm tall herb with course hirsute stem, thick, purple stained root, and white flowers, commonly found in grassy slopes of the mountains and hills in Japan, Korea, and China.

The roots of the plant have been widely used as a dye or a drug in Japan. The root yields shikonin, and other derivatives of shikonin like: isobutyl shikonin ( $C_{20}H_{22}O_6$ ; mp 89%) and  $\beta$ ,  $\beta$ -dimethylacryl-shikonin ( $C_{21}H_{22}O_6$ ; mp 113–114°C) as the coloring principles.

Recently, shikonin has been derived successfully from the callus cell cultures on skoog medium supplemented with IAA and Kinetin.

*L. arvense* L.

English – Corn Gromwell

It is an erect, annual herb of about 30–60 cm height that is found from Kashmir to West ward. Leaves are cauline, lanceolate, strigose, lower leaves petioled, obovate-oblong. Flowers are white, rarely bluish, arranged in racemes.

A red dye, shikonin is extracted from the roots and bark of the plant, which is used for coloring ointments, etc.

*L. officinale* L.

English – Gromwell

It is an erect, hispid hairy, perennial herb of 0.6–1.2 m height, found in Kashmir and Kumaun at an altitude of 1,500–2,700 m. Leaves are oblong-lanceolate rough, strigose. Flowers are white, fading yellowish, small in size, and arranged in racemes.

*Maharanga emodi* (Wall.) A. DC. (Boraginaceae)

syn. *Onosma emodi* Wall.

It is a herb that is frequently found in the Himalayas from Garhwal to Bhutan at altitudes of 3,500–4,000 m and in Napa hills of Assam. It is also reported to be found in Bhutan, Nepal, and China. Its root yields alkannin, a red dye, used for coloring wood and silk.

*Onosma hispida* Wall. ex D. Don (Boraginaceae)

Bengali and Hindi – Ratanjot

It is a perennial herb, occurring in western Himalayas from Kashmir to Kumaun at an altitude of 2,000–4,500 m. Its roots are tapering and purple in color, and flowers are whitish or pale yellow. It has been reported to be a source of Ratanjot, a red dye, used for coloring foodstuffs, oils, cotton, woolen and silk textiles, and medicinal preparations.

The roots of *Onosma hookeri* C.B. Clarke, a herb found in Sikkim and Bhutan also yields the dye which is used locally by lephas.

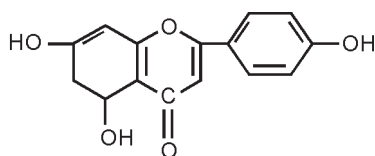
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## 6.4 Apigenin

Apigenin, (4',5,7-Trihydroxyflavone; 5,7-dihydroxy-2-(4-hydroxyphenyl)-4H-1-benzopyran-4-one;  $C_{15}H_{10}O_5$ ; mp 347–348°C), the yellow coloring matter present in free state or in the form of the glycoside apiin, ( $C_{26}H_{28}O_{14}$ ; mp 228°C) in the dried flower heads of the Roman chamomile, *Chamaemelum nobile* (L.) All. syn. *Anthemis nobilis* L., German chamomile, *Matricaria chamomilla* L., Yellow dahlia, *Dahlia pinnata* Cav. syn. *Dahlia variabilis* L., Field daisy, *Leucanthemum vulgare* (Vaill.) Lam. syn. *Chrysanthemum leucanthemum* L., and in leaves, stem, and seeds of Parsley, *Petroselinum crispum* (Mill.) Airy-shaw, and Manchurian Kaoliong, *Sorghum nervosum* Bess. ex Schult. The other glycosides of apigenin like cosmosiin or cosmetin,

( $C_{21}H_{20}O_{10}$ ; mp 1780,2030, 227–2300), occurs in flowers of *Cosmos bipinnatus* and *Zinnia elegans*; 7-(-D-Glucouronide ( $C_{21}H_{18}O_{11}$ ) occurs in Snap dragon, *Antirrhinum majus*, vertiaflavone or thevetiaflavone, ( $C_{16}H_{12}O_5$ ; mp 263°C) occurs in the seeds of yellow oleander, *Cascabela thevetia*; 4',5,7-Trimethoxyflavone ( $C_{18}H_{16}O_5$ ; mp 156–157°C) occurs in the leaves of *Senna siamea*. These glycosides on hydrobysis yield the coloring matter apigenin. It is soluble in alcohol and insoluble in water.



Apigenin

#### 6.4.1 Extraction

For the extraction of the dye, the dried flower heads are put in alcohol for 2–4 h at 60°C and then filtered. The extract is dried under reduced pressure to get yellow crystals of the dye. The dye is purified further with the help of chromatographic methods.

#### 6.4.2 Uses

Apigenin is used as a pale yellow dye in hair washes, especially in combination with henna for blonde hair. It is also used in dry shampoos and for dyeing liquors. Apigenin is also reported to be very potent anti-cancer. Besides, it is also reported anti-inflammatory, anti-spasmodic, and acts as an antioxidant.

#### 6.4.3 Sources

*Chamaemelum nobile* (L.) All. (Asteraceae)

syn. *Anthemis nobilis* L.

English – Roman Chamomile; Hindi – Babuna-Ke-phul; Kannada – Sime Shyamantige; Malayalam – Shimajavanti; Tamil – Shimaichamanti; Telugu – Shima-chaamanti

It is a perennial and pleasantly scented herb, cultivated in the temperate regions of the Himalayas for medicinal purposes. It has run wild at several places. Its flower heads are yellow-centered, white, and solitary. It is cultivated in France, England, Belgium, Italy, Czechoslovakia, Egypt, and other countries for the production of an essential oil. The cultivation of Roman chamomile for the production of an essential oil has recently attracted the attention of Indian



scientists and technologists. The plants are regenerated through seeds. The plant starts growing and flowering in the end of December and January. The flowers have been used as a dye to lighten hair. This plant is considered to be antiseptic, antimicrobial, disinfectant, and vermifuge.

The flower heads make a good yellow dye consisting of flavonoids like apigenin and luteolin and its 7-glucosides. The stems and leaves, like flowers, also make good yellow dye.

*Antirrhinum majus* L. (Scrophulariaceae)

English – Snap dragon

It is an erect, simple or branched annual–perennial herb of 1.8 m height, usually grown as an annual ornamental in gardens, both in the plains and in the hills. Leaves are ovate-elliptic to oblong; flowers are white, red or variegated, in many flowered, terminal racemes. Snap dragons are propagated from seeds which are sown mixed with sand to ensure uniform distribution of the seeds. They thrive best on light soils rich in lime and require plenty of sunlight. About 7–8 cm height seedlings are planted into beds. About four months old plants produce flowers. Flowers of different colors yield different type of flavonoid pigments but apigenin-7-glucuronide glycoside is found in all types, except in albino types.

*Senna siamea* (Lam.) H. S. Irwin and Barneby (Fabaceae)

syn. *Cassia siamea* Lam.

English – The Iron Wood Tree, The Siamese Senna; Bengali – Minjri; Gujarati – Kasid; Kannada – Hiretangadi, Sema-Tangedu; Marathi – Kassod; Tamil – Manja-Konnai; Telugu – Sima-Tengeedu

It is a small or medium sized evergreen tree of 6–18 m height, commonly found from Punjab to Arunachal Pradesh and Tripura, extending into Peninsular India, up to an altitude of 1,220 m, and in the Andaman Islands. Its leaves are 12–30 cm long with 6–14 pairs of leaflets. Flowers are bright yellow, in up to 60 cm long auxiliary and terminal panicles. Pods are slightly curved at posterior end flattened.

The tree grows well on both flat terrain and hill slopes. It thrives under a variety of climatic conditions within the tropics, but cannot withstand frost, though it is fairly resistant to drought. The leaves contain apigenin, and its glycoside which on hydrolysis yields the coloring matter apigenin.

*Leucanthemum vulgare* (Vaill.) Lam. (Asteraceae)

syn. *Chrysanthemum leucanthemum* L.

English – Field-Daisy, Marguerite, Moon-Daisy herb, Ox-Eye-Daisy

It is a perennial herb, cultivated in gardens but also found as an escape. Root stock is rhizomatous; stem is erect, simple or branched; leaves are ovate-

oblanceolate or lanceolate-oblong, toothed to pinnatifid; flower heads are solitary, long-stalked, and white in color. Ray florets contain glycoside apigenin which yields the coloring matter apigenin.

The other varieties of the garden chrysanthemum yield 7-o-glucoside of apigenin which also gives a coloring matter apigenin.

Numerous cultivars, highly variable in growth, size, shape, and color of flowers, respond to environment and cultural practices. The plant is cultivated on commercial scale in peninsular India, particularly around Coimbatore, Dharmapuri, Madurai, Bangalore, and Ahmad Nagar.

For its cultivation, the field is ploughed 3–4 times during June–July and brought to a fine tilt. About 50 tonnes of farm yard manure is incorporated per hectare. Beds of 4 × 3 m are formed, and about 2.5 lakh suckers or rooted cuttings are planted per hectare in April and August. The crop is irrigated once in 8–10 days but does not tolerate water loggings. The flowers come after 3–4 months of its plantation.

*Cosmos bipinnatus* Cav. (Asteraceae)

It is a glabrous or somewhat pubescent annual herb of 2–3 m height. Leaves are bipinnately cut into remote linear, entire lobes; flower heads are of white, pink, and crimson in color with yellow colored disk. It is a native to Mexico, introduced to Indian gardens.

The flower contains a glycoside cosmetin or cosmosiin which yields a coloring matter apigenin.

*Dahlia pinnata* Cav. (Asteraceae)

syn. *Dahlia variabilis* (Wild.) Desf.

It is a genus of tuberous rooted perennial herbs with showy flowers, cultivated in gardens for its beautiful flowers of various colors.

The flowers have an extraordinary strong dye in their petals. The color varies with the color of the petals, from yellow to orange-red. One can get a dye from the flowers which are ready to be thrown out after a week in a flower vase. Thus, the flowers of Dahlia serve a double purpose as for beauty and as dye.

Besides coreopsin, flower head of Dahlia also contains other coloring principles like apigenin, luteolin, diosmetin, and butein. Besides above mentioned anthoxanthins, some anthocyanins (3.1–4.2%) like pelargonidin, delphinidin-3, 5-diglucoside, malridin, and cyanidin-3-glucoside have also been isolated from the Dahlia flowers. Thus, the color extracted from Dahlia flowers is highly soluble in water and alcohol, and contains 36–38% dry matter and 55–60 mg/kg of coloring substances. Since the preparation was not found toxic at 10 g/kg, and did not contain heavy metals, it has been recommended for use as a substitute

for amaranth for coloring pharmaceutical preparations. It is efficient for coloring confectionery, bakery products, syrups, beverage, and other food products, and pharmaceutical preparations.

*Matricaria chamomilla* L. (Asteraceae)

English – German Chamomile; Punjabi – Babuna, Suteigul

It is a much branched, aromatic, annual herb cultivated in gardens and also found as an escape in Punjab, Himachal Pradesh, and Upper Gangetic plains.

Its plants are raised by seeds. The seeds are sown in nursery in September and the seedlings are transplanted in fields in November; flower heads are produced in March – April. Two crops of this can be obtained in a year. The flower heads contain apigenin and its glycoside contains apiin.

*Petroselinum crispum* (Mill.) Nyman ex A.W. Hill (Apiaceae)

syn. *P. sativum* Hoffm.; *P. hortense* Hoffm.; *Apium crispum* Mill.

English – Parsley; Kannada – Achu Mooda

It is a hardy, aromatic, and biennial herb that produces a rosette of finely divided radical leaves in the first year and a flowering stalk in the second year on which yellow or yellowish-green flowers in compound umbels are produced. There are two main types of horticultural parsley; those cultivated for the leaves (*crispum*), and those grown for their turnip like root (*radicosum*); only former type is cultivated in India.

Parsley is a cool weather crop that grows best in a rich and moist soil, amenable to deep cultivation. Seeds are sown in March–May on the hills and August–November in the plains. Seeds are germinated after 15 days of sowing, but they can be germinated before if they are soaked in water for few hrs before sowing. Because of the slow rate of germination and tenderness of newly sprouted seedlings, it is preferable to sow the seeds in nursery beds and later transfer the seedlings (5–8 cm) to the site. Leaves are ready for harvesting in about three months. A hectare of land yields c 2,500 dozen bunches at each cutting, and 2–5 cuttings are possible for each plant.

The leaves, stems, and fruits contain a glucoside apiin which on hydrolysis yields the coloring matter apigenin. The fruits of the plants from Delhi are reported to yield 2.2% apiin. The coloring matter can be obtained from the waste material remained after isolating essential parsley oil.

*Sorghum bicolor* (L.) Moench (Poaceae)

syn. *Sorghum nervosum* Bess. ex Schult.; syn. *Andropogon sorghum* Brot.

English – Manchurian Kaoliangs

It is a stout grass, up to 5 m tall and 3 cm in diameter, and it is one of the most important grain crops of Manchuria. It is commonly cultivated in eastern Asia, particularly in China from where it has been introduced into Japan and India. In India, a few forms of the typical variety *nervosum* have been introduced into Bihar, Orissa, and Maharashtra. The dye apigenin is isolated from the plant.

A red dye suitable for food, medicine, and cosmetics is also manufactured from the husk of the sorghum by immersing the sorghum husk in 60–70°C water to remove tannin and then immersing in 0.05–0.2% hydrochloric acid to remove impurities, and then followed to be immersed in 55–70% ethanol at 35–45°C for 40 h. It is then filtered, concentrated, separated, and dried under reduced pressure to get a dry powder which is then grinded. The dye is soluble in alcohols and water, and imparts bright red color.

*Zinnia elegans* Jacq. (Asteraceae)

English – Youth- and Old-Age

It is a beautifully erect, annual, and up to 1 m tall plant that is native to Mexico and later introduced into the Indian gardens; also met with as an escape. Stems are pilose strigose; leaves are clasping, cordate-ovate or elliptic; flower heads vary from white, yellow, orange, pink, red, scarlet or lilac-purple, but usually red in wild plants.

Zinnias are warm season plants which remain stunted in cold places. The plants thrive in the plains and grow best after rains. They are, therefore, planted soon after the monsoon showers; in the hills they can be grown from March onwards. They prefer deep and loamy soils, rich in organic material. The floral pigments include glucosides of razilin, pelargonidin, and flavonoids. The yellowish-white and double flowered type has been found to contain an apigenin-7-glucoside called cosmetin ( $C_{21}H_{20}O_{10}$ ; mp 218–220°C; decomposes), which yield a coloring matter apigenin, yields at the rate of 1% glucoside.

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## 6.5 Azure blue

Azure blue, a blue coloring dye, principally derived from the mineral azurite,  $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$  copper ore, commonly found in Maharashtra, Madhya Pradesh, Rajasthan, Andhra Pradesh, Tamil Nadu, Himachal Pradesh, Bihar, and Uttar Pradesh in India. Azurite occurs both as an earth and in a crystalline form. The crystals are deep blue and the earth is a lighter blue in color.

### 6.5.1 Extraction

For the extraction of azure blue, azurite is ground to a fine powder and then boiled in aqua regia or in a hot concentrated solution of sodium hydroxide (NaOH); thus a precipitate is obtained, which is filtered and discarded. The filtrate solution is azure blue liquor, which is dried up under reduced pressure to get a powder of azure blue. An artificial azure blue or blue verditer, basically copper carbonate,  $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$  is produced by the action of lime on a solution of copper sulphate. Such pigments are not well acceptable because they have a strong tendency to thicken with the linseed oil when used as a tube color. It is not permanent to light and air contact as a natural azure, and is useless for permanent paintings.

### 6.5.2 Uses

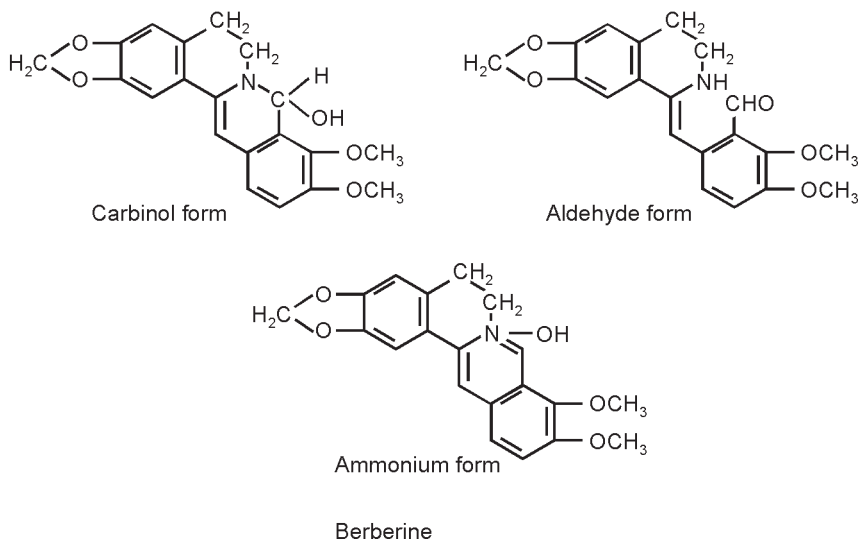
The azure blue was extensively used in paintings in China, but rarely in Indian paintings. It is used as an artists' color.

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## 6.6 Berberine

Berberine, 5,6-Dihydro-9, 10-dimethoxybenzo[g]-1, 3-benzodioxolo[5,6-a]quinolizinium; 7,8,13,13a-tetrahydro-9,10-dimethoxy-2,3-(methylenedioxy)berbinium; umbellatine ( $\text{C}_{20}\text{H}_{18}\text{NO}_4$ ; mp  $145^\circ\text{C}$ ) an alkaloid, is the only known natural basic dye, found in the stem and root bark of several species of the genera, *Berberis* L. and *Mahonia* Nutt.; stem wood of false calumba or tree turmeric, *Coscinium fenestratum* Colebr., roots or rhizomes of Colombo, *Jateorhiza palmate* (L.) Miers, golden seal, *Hydrastis canadensis* L., and in some species of the genus, *Thalictrum* L.



Berberine forms yellow needles that are freely soluble in hot water and less soluble in alcohol. It exists in three forms i.e., carbinol form, aldehyde form, and ammonium form. Its base is unstable and assumes the aldehyde form berberinal, whereas its salts are derived from ammonium form. It behaves as a quaternary base, forming salts by replacement of OH groups.

### 6.6.1 Extraction

Stem, root bark, roots, and stems are cut into small pieces, steeped in water and boiled for 2–4 h and then strained. The strained extract again is boiled and evaporated till a dark brown sticky mass is obtained. It can also be extracted through steam-jacket extractor. In this method, the small pieces of the raw material are put in steam-jacket extractor, and boiled for 4–5 h. The extract is removed and the material is again boiled repeatedly for 3–4 times till the pieces of wood are completely exhausted. The extract is then filtered and evaporated in a steam pan to a thick-semisolid mass. In crude preparation, much of berberine is decomposed due to overheating.

Berberine is also extracted as its hydrochloride by cold percolation method. Raw material is powdered and percolated successively with 2.5% acetic acid for 12 h. It is then filtered; hydrochloric acid is added and kept at 20–50°C. The golden-yellow precipitate of berberine chloride is separated and dried in vacuum. Similarly, berberine sulphate is extracted by using 20% sulphuric acid. The chromatographic methods are employed for getting pure dye from the aqueous extract.

### 6.6.2 Uses

Berberine is used for dyeing wool, silk and leather from a fainty acid bath at 500–600°C or cotton mordanted with tannin and tarter emetic. With alum it gives bright yellow to the wool, but with tin imparts stronger yellow color. Formerly, it was used as a food dye but later banned because of its toxic nature. It has also been used as a flouochrome in microscopy. It has long been used as a yellow dye among European peasants. Berberin is considered as antibiotic. It has been used in the treatment of trachoma and leishmaniasis.

### 6.6.3 Sources

Berberine is found in the stem and root bark of several species of the genera which are stated as follows:

*Berberis aristata* DC. (Berberidaceae)

English – The Indian Barberry; Bengali – Darhaldi; Hindi – Chitra, Darhald, Kashmal, Rasaut; Malayalam – Maradarisina; Marathi – Daruhald; Sanskrit – Daruharidra; Tamil – Maramanjai

It is an erect thorny bush of about 3–6 m height with yellow flowers and bright red fruits, found in Himalayas from 2,000–3,500 m altitude, and also in Nilgiri hills of South India. Root bark yields about 4% berberine.

*B. asiatica* Roxb. ex DC.

Kumaun – Kilmora; Garhwal – Kingora

It is an evergreen, pretty, thorny bush of about 1.8–2.4 m height with yellow flowers, commonly occurring in Himalayas from Himachal Pradesh to Bhutan and Assam at 1,500–1,800 m altitude, and on Parasnath hills in Bihar, Pachmarhi hills in Madhya Pradesh, and Mount Abu in Rajasthan. The plant contains 2.09–1.29% berberine in its root and stem, respectively.

*B. chitria* Buch.-Ham. ex Lindl.

Kumaun – Chitar, totar

It is an erect, thorny bush that is up to 3.6 m tall with deep yellow flowers and dark brown fruits found in the Himalayas from Kashmir to Nepal at an altitude of 1,500–2,400 m. The root and stem yield 5.0–4.2% berberine, respectively.

*B. lycium* Royle

It is a sub-erect, rigid, and thorny bush of 2.7–3.6 m height with entire leaf margins, pale yellow flowers, and black fruits, commonly found in the Himalayas from Kashmir to Kumaun at 900–2,700 m altitude. It is also commonly met with moist temperate forests of Chamba in Himachal Pradesh. It yields about 2% berberine from its roots.

*B. tinctoria* Lesch.

English – Common Nilgiri Barberry; Kannada – Baagisutra; Malayalam – Maramanjali; Tamil – Mullukala, Oosipila

It is a thorny bush of 1.8–2.4 m height, found in Nilgiri and Palni hills at 1800 m of altitude and also on Shevaroy hills of South India. It yields 2.3% berberine.

*B. vulgaris* L.

English – Common barberry

It is a thorny bush, commonly found in Europe, Eastern Asia, South and North America. Formerly it was found to grow as wild bush in England, but the belief that it affects the growth of corn caused it to be banished from the hedge-rows. It has long been used as a yellow dye among European peasants.

*Coscinium fenestratum* Colebr. (Menispermaceae)

English – False Columba, Tree Turmeric; Hindi – Jhar-I-Huldi; Kannada – Maradaarashina; Malayalam and Tamil – Moramajal; Marathi – Jhade-Halade; Telugu – Manu, Pasupu; Sanskrit – Daru Haridra

It is a woody climber with a cylindrical and internally yellowish color stem, occurring wild in Western Ghats, Nilgiri, and Thiruvananthapuram in Southern India. The stem has long been used in South India and Sri-lanka as a yellow dye and bitter tonic. It is also used as a substitute for razili [*Jateorhiza razili* (Lam.) Miers]. The dye is used either alone or in combination with turmeric and other coloring materials. The stem yields 3.5% berberine.

*Hydrastis canadensis* L. (Hydrastidaceae)

English – Goldenseal, Orangeroot

It is a herb of about 30 cm height with thick and yellow rhizome and greenish white flowers. It's a native of Japan, commonly found in Vietnam, and North-East America. It was used both as a tonic and as a dye. Due to the ruthless collection of the rhizome, the plant is almost exterminated. Hydrastis does best in rich moist soil with plenty of leaf mold. It can be propagated by seeds or by division of the rhizome.

*Jateorhiza palmata* (Lam.) Miers. (Menispermaceae)

syn. *J. calumba* Miers.; *Cocculus palmatus* DC.

English – Columba

It is a woody climber with densely pubescent shrub, commonly found in East Africa, South Africa and Mauritius in low-land rainforest and reverines forest from sea level up to 1,500 m. It is cultivated in Kolkata garden. Its root yields berberine and is used for dyeing clothes and also as a tonic.

*Mahonia napaulensis* DC. (Berberidaceae)

syn. *M. acanthifolia* G. Don; *Berberis nepalensis* Spreng in part.



Nepali – Chattri, Kesari, Chutro

It is a tall and evergreen bush with yellow flowers and blue-black fruits, found in Sikkim, North Bengal, Darjeeling, and Nepal at an altitude of 1,200–2,400 m. The root yields about 0.5% berberine. The other species like *M. borealis* Takeda, *M. griffithi* Takeda, *M. leschenaylti* Takeda, *M. manipurensis* Takeda, *M. sikkimensis* Takeda, and *M. simonssii* Takeda, found in North-West India and Lushai hills, Bhutan, hills of South India, Manipur, Sikkim, and Khasi hills, respectively also contain berberine in their roots. They can also be used as a source of yellow dye.

*Thalictrum foliolosum* DC. (Ranunculaceae)

Bengali – Gurbiani; Hindi – Pilazari, Mamiri; Kashmiri – Chaitra; Kumauni – Barmat, Penglazari; Marathi – Mamiran; Punjabi – Chireta

It is an erect perennial bush of about 2.5 m height, found in the temperate Himalayas from 1,500–2,400 m; in Khasi hills from 1,200 to 1,800 m, and in Kashmir, Punjab, Uttar Pradesh, Bihar, Orissa, and Andhra Pradesh. The rhizome contains about 0.35% berberine. It is used locally as a yellow dye.

*T. minus* L.

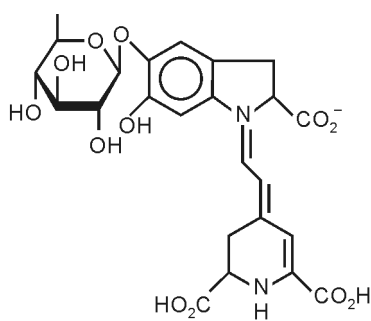
It is an erect herb of about 30–60 cm height, found in valleys of the temperate Himalayas and in the Western Tibet between 2,700 and 3,600 m and also found in Kashmir and Simla, in Himachal Pradesh. The rhizome of the plant is used as a source of yellow dye and as a bitter addition to beer. Rhizome yields berberine along with magnoflorine and thalictrimine alkaloids.

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## 6.7 Betanin

Betanin or phytolaccamin ( $C_{24}H_{27}N_2O_{13}$ ), the water soluble red pigment occurs in the roots of beet root, *Beta vulgaris* L. As a food additive, its E number is E162. Betanin degrades when subjected to light, heat, and oxygen; therefore, it is used in frozen products, products with short shelf life and products sold in dry state. The color of betanin depends on pH between 4 and 5. It is bright-bluish red, and becomes blue-violet as the pH increases. Once the pH reaches alkaline levels, betanin degrades by hydrolysis.



Betanin

Beet root is a rich source of a group of red and yellow pigments known as betalains, comprising red-violet betacyanins and yellow betaxanthins. Betanin (75–95%) is the major constituent of red pigment and vulgaxanthin I, the principal pigment of yellow betaxanthin group. Another yellow pigment, betalamic acid, derived directly from cleavage of betanin is probably the key intermediate in all betalaines.

### 6.7.1 Extraction

Betanin is obtained from red beet extract, which is available as beet juice concentrate, dehydrated beet root, and spray-dried extract. The red color bodies of betanin can be isolated from the concentrate of beet root with the help of chromatographic methods.

The contents of betacyanins can be increased 5–7 times by fermentation of the extracted juice with *Torulopsis utilis*. Fresh red-beet juice is purified by a strain of *Aspergillus major* Van Tiegh. by removing sugar. The fermentation reduces total solids without significant alteration of pigment.

### 6.7.2 Uses

Betanin is used to color food and pharmaceutical products. It is successfully used to color meat substitutes, summer sausage, gelatin, desserts, and dairy products. The root juice is employed to intensify the color of tomato products like tomato sauce, puree, and catch-up. The 10% concentrate of the juice at pH 6.3–6.6 gives most stable natural meat color. This is available as beet-root concentrate, dehydrated beet, and spray dried extract.

### 6.7.3 Sources

*Beta vulgaris* L. (Chenopodiaceae)

English – Beet Root, Garden Beet or Table Beet; Bengali – Bitpalang; Hindi – Chukander; Sanskrit – Palanki; Tamil – Beet Kilangu

Beet root plant is a succulent, tuberous herb, cultivated throughout India as a vegetable. The plant produces a large, swollen, fleshy root, and a rosette of leaves. Beet root is known to have originated in the Mediterranean region and the adjacent regions of Central and West Asia. Beet root is a cold season crop. The plant requires sunshine weather and optimum temperature of 16°C for its growth. The crop is sown from mid-August to December in the plains and during March to July in the hills. However, in some parts of South India, the crop is sown throughout the year. The beet root crop is ready for harvesting within 2–3 months from sowing. The yield of beet roots varies between 20–25 tonnes per acre.

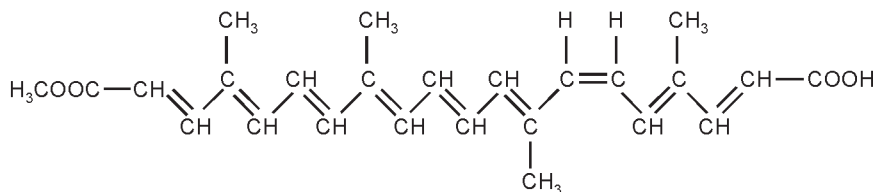
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## 6.8 Bixin

Bixin (6,6'-diapo-carotenedioic acid monomethyl ester;  $C_{25}H_{30}O_4$ ; mp 198°C), a red coloring matter, occurs in the outer covering of the seeds of Annatto, *Bixa*

*orellana* L. Bixin which is an oil soluble, and highly stable coloring ingredient. The saponification of methyl ester group to form dicarboxylic acid yields water soluble form of bixin called norbixin ( $C_{24}H_{28}O_4$ ; mp  $250^\circ\text{C}$ ). Bixin, the chief coloring constituent, varies from 10 to 12% in crude annatto dye.



Bixin

The pulp of seed cover contains 70–80% of total pigment in seed and is rich in tannin but contains a mixture of eight colorants of carotenoid group of which the main two are orellin or norbixin, water soluble yellow pigments, and bixin. Bixin forms red-brown rhombic crystals. In addition to bixin and orellin, methylbixin,  $\beta$ -carotene, cryptoxanthin, lutein, and zeaxanthin have also been reported. Bixin is the main pigment of oil-soluble annatto preparations, and norbixin (Orellin) is the principal coloring matter of water soluble products. Annatto preparations are pH-sensitive and at low pH of food products, color turns pink.

### 6.8.1 Extraction

Various methods have been used for extracting crude color and bixin. Butter color is obtained by treating seeds with a vegetable oil like castor oil, preferably at  $1200^\circ\text{C}$ . The extract is then diluted to specifications. A concentrate containing 20% bixin is obtained by mechanical agitation of the seeds. According to a report, chloroform ethanol (25:75 V/V) solvent gives highest yield of bixin dye. At 1:4 seed: solvent ratio (W/V), the extraction yield is 76.48%. Supercritical carbon-dioxide has also been used for extraction of the pigment at a pressure of 3000–7000 psi and at a temperature range of  $400$ – $550^\circ\text{C}$ . Maximum solubility of pure bixin is 0.003. Efficiency of annatto pigment extraction increases in the presence of oil.

According to one Japanese patent, stabilized bixin preparation is obtained by holding bixin in alcoholic solution at pH 4.5 for one hour before spray-drying. In another process, the seeds or crude annatto color is stirred with aqueous alkali or aqueous alcohol, filtered, and pH of the filtrate is adjusted to 5–6 to give bixin.

Yet in another process, the colorant is extracted by counter-current method using water during simultaneous mechanical friction on the surface of seeds. The suspension thus obtained is evaporated in vacuum, which on subsequent drying and powdering can be used for coloring various food products like candies.

Commercial cheese color is an alkaline solution which contains norbixin and is obtained by using sodium or potassium hydroxide. Powdered norbixin has been prepared by spray drying of 1–2% of aqueous solution, using a seed solution ratio of 1:1.3 for 10–20 min at ambient temperature (dissolved solid content 10–200 Brix). The spray dryer is operated at an entrance temperature of 150–200°C and an exit temperature of 80–100°C.

For extraction of dye, seeds are bruised, and pulp is macerated with hot water and soaked for several days. The coloring matter forms a fine suspension. Thereafter, seeds are removed and allowed brie containing dye to ferment for about a week. The dye which settled down at the bottom is separated and dried into cakes. The yield of the dye is about 5–6% by weight of seeds.

In this method, the seeds are boiled with sodium carbonate solution and filtered. The filtrate is then acidified. The dye is sometimes coagulated by boiling it with common salt, filtered, washed, and dried. The dye can also be extracted by boiling seeds with ethyl acetate and then purified with the help of chromatographic methods.

In the crude domestic method, the seeds are soaked in water for about a week and then the whole mass is boiled after addition of few drops of edible oil. The colored water is then filtered out and white clothes are soaked in it, which imparts a deep orange color to silk and cotton.

### 6.8.2 Uses

Annatto is one of the oldest food colorant and is used for coloring foodstuff such as butter, ghee, margarine, cheese, chocolate, etc. Mixture with paprika deoresin yield red color and may be used in processed cheese. Water soluble preparations, consisting mainly of norbixin (about 0.1–3.0%), in aqueous potassium hydroxide or tablets of potassium carbonate are applied in coloring cheese, cereals, and ice cream. An insoluble powder is available for coloring spices and meat. Mixture with curcumin is yellow in color and is claimed to be more stable. Annatto is also used in textile, medicine, and cosmetic industries. It has been used to dye silk and cotton, but it is not a fast dye. It is also used for floor polishes, shoe polishes, hair oils, etc. The bixin toxicity has been studied on rats, but it showed no toxic effects.

### 6.8.3 Sources

*Bixa orellana* L. (Bixaceae)

English – Annatto Tree; Bengali and Hindi – Latkan; Kannada – Rangmale; Marathi – Sendri; Tamil and Telugu – Japhara

It is a shrub or a small tree that is up to 2.5 m tall, found throughout tropical part of India. The plant is cultivated in Brazil, Guiana, Mexico, and in Antilles. In India and to some extent in Orissa, Andhra Pradesh and Maharashtra it is reported to be cultivated for its seeds. It is also found in Karnataka, Tamil Nadu, Kerala, West Bengal, and Assam. It occurs in two forms, one with white flowers and green capsules and the second with pink flowers and red capsules. The latter variety is preferred for its seeds.

The tree is found to thrive at elevation of 600–900 m where the annual rainfall ranges from 125 to 175 cm. The mean temperature of 15.5–26.5°C during October–December seems to be congenial for its growth, flowering, and fruiting. In general, it prefers cool places and well-drained and rich loamy soil. Natural regeneration is through seeds which get germinated by falling on the ground. The tree can also be propagated by stem cutting. Generally, seeds from freshly gathered capsules are used because older seeds lose viability. Seeds, preferably red ones, are sown in shaded nursery. They germinate in 8–10 days and when the seedlings are 15–25 cm tall, they are transplanted in the fields. However, sometimes, the seeds may be sown directly in the fields. Planting is seldom done in an organized way with regular spacing between the plants; though the spacing 4.5–6.0 m between every two plants is recommended. The seedlings should be planted in 60 cm pits filled with sufficient farmyard manure and should be watered immediately after planting.

Annatto starts bearing flowers in its second year of planting, but full bearing starts after the third year. Flowering begins in the last week of August and continues up to mid October. After about 30 days of flowering, capsules begin to appear on the tree, which are ready for harvest by January. At full maturity, the color of the capsules turns bright red or bronze. In the case of pink flowered variety, the seeds at this stage appear to be thinly coated with deep vermilion paint; whereas in the case of white variety, the seeds turn yellow or pale red. As soon as the capsules attain the characteristic color, they are harvested as they burst open later. Good quality seeds are generally obtained from the fully mature and dried fruits. Seeds which are dry, hard, bright red, and have a characteristic smell are considered good for dyeing. Annatto has long been used by American Indians to make body paint, especially for the lips.

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## 6.9 Blanc-fixe

Blanc-fixe, a white coloring principle, obtained as a precipitate of barium sulphate ( $\text{BaSO}_4$ ) from the Barite, is the natural ore of barium. It is also popularly known as heavy spar. Barytes or barite is a colorless or white mineral; often tinged with yellow, red, brown, and sometimes blue. The crystalline system is rhombic. Barytes is found sometimes as transparent crystals, but generally it is opaque. Barytes is widely distributed throughout the world. In India, it is commonly found in Andhra Pradesh, Bihar, Himachal Pradesh, Madhya Pradesh, Maharashtra, Rajasthan and Tamil Nadu.

Barium sulphate is insoluble in water and aqueous alkaline and slightly soluble in strong acids. It shows considerable opacity in water, but settles quickly, and is more or less transparent in oil.

### 6.9.1 Extractions

Blanc-fixe is extracted from Barite. Barite is ground into a fine powder and dissolved in sulphuric acid containing free sulphur trioxide. The solution is then poured into water and then it gets a precipitate of barium sulphate. The precipitate is filtered and evaporated to get a crystalline substance, the barium sulphate or

Blanc-fixe. A good cream-floated razili is about 99%. Barium sulphate with small amount of silica, iron oxide, and alumina is of white lower grades.

### 6.9.2 Uses

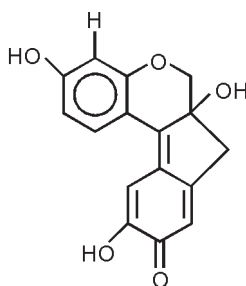
Blanc-fixe is used as a water color by artists. It is extensively used as base for lake colors, for para red, and for paper coating. In fact, natural ground Barite and blanc-fixe are widely used in paint and pigment industry. It has main application as filler in paints, coatings, pigments and plastics, and as functional additive in batteries.

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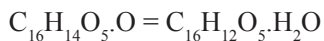
### 6.10 Brazilein

Brazilein ( $C_{16}H_{12}O_5$ ), a red coloring matter is obtained by oxidation of brazilin ( $C_{16}H_{14}O_5$ ; mp  $250^\circ C$ ). Brazilin was first isolated from the Brazil wood, *Caesalpinia violacea* (Mill.) Standl. syn. *C. braziliensis* L. by Chevreul as colorless silky needles. The term brazil-wood is derived from the Portuguese word Braza, meaning glowing like fire. When Portuguese explorers discovered the area of South America that had abundance of trees which produce brilliant red colors, they named the area Brazil. Among the other woods which also contain brazilin are: Fever nut or Penambuco wood, *Caesalpinia bonduc* (L.) Roxb. syn. *C. cristata* L., Sappan or Lima wood, *C. sappan* L., and, Peach wood, *C. echinata* Lam. Brazilein is slightly soluble in water. It yields a deep red solution with NaOH (10%), which turns brown. Brazilein is obtained by the oxidation of the brazilin as follows:



Brazilin





Brazilin, the amber-yellow crystals are soluble in water, ether, alcohol, and in alkali hydroxides and make colorless solution in NaOH (10%), which change to deep red solution as it brazilin to brazilein by atmospheric oxygen. The specific color produced by the pigment depends on manner of preparation, in an acidic solution it gives yellow color but in an alkaline preparation it gives red.

### 6.10.1 Extraction

For extraction of the dye, the wood is cut into small pieces or pounded into a powder and then boiled in water for 6 hours. It is filtered and concentrated under vacuum. The pure dye is isolated with the help of chromatographic methods. The wood can be extracted with sodium hydroxide solution (10%) and filtered. Thus, obtained liquor is changed to a deep red solution, which is dried up under reduced pressure. It can be crystallized with alcohol. For further purification, chromatographic methods could be adopted.

### 6.10.2 Uses

Brazilin has been used since the middle ages to dye fabric, and has been used to make paints and inks as well. Brazilin is used in calico printing for producing steam-red and pinks. Aluminium acetate or stannic oxalate is used as mordant in combination with an oxidizing agent (potassium chlorate or copper sulphate). With cotton fabrics, mordanted by tannin and alum, it produces a bright reddish-orange shade. In combination with indigo, purple shades are obtained. Wool and silk can be dyed using alum, potassium dichromate or iron salts as mordants, but the shades produced are not fast. It is also used for chrome and vegetable tanned leather, mainly as a ground for topping with synthetic dyes. In conjunction with carmine it produces Florentine lake, a valuable pigment for face creams and lipsticks. *Gulal*, a red starch much used in India during *Holi* festival, is colored with brazilin. It is also used as a food coloring agent and biological stain. Brazilin dye is reported to have anti-inflammatory activity. It is also used in manufacturing of facials which are resistant to light, heat, and water and are non irritant to skin.

### 6.10.3 Sources

*Caesalpinia bonduc* (L.) Roxb. (Fabaceae)

syn. *C. cristata* L.; *C. nuga* Sit.

English – Fever Nut, Penambuco wood; Bengali – Netu, Shingrilota; Gujarati – Kachka; Malayalam – Kakamullu, Kazanji; Telugu – Mullutiga

It is a large woody climber, found on the banks of rivers in tidal forests near the eastern sea-coast of Orissa, and Western sea-coast from Konkan Southwards and in Sundarbans in West Bengal and also in Madhya Pradesh and Himachal Pradesh. The plant is readily propagated from seeds. The wood contains brazilin, which is used as natural food color.

*C. echinata* Lam.

English – Brazilwood

It is a tree with spiny stem, yellow flowers, and is about 7–8 cm long with oblong fruit, found in Tropical America. Its wood contains the coloring matter brozilin.

*C. sappan* L.

English – Brazil Wood, Sappan Wood; Bengali and Hindi – Bakam, Patang; Gujarati – Bakam; Kannada – Pattanga; Malayalam – Chappa, Sappannam; Marathi – Patang; Oriya – Bacom; Sanskrit – Bharyavriksha, Surangada; Santal – Teri; Tamil – Parthangi, Patungam; Telugu – Bakamm

It is a small, thorny tree of 3–10 m height, found wild and as an escape in South India, West Bengal, Orissa, and Madhya Pradesh and also cultivated in Malaysia and Philippines for obtaining natural dye.

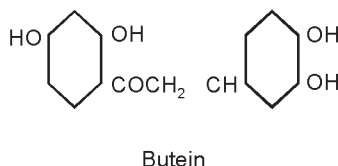
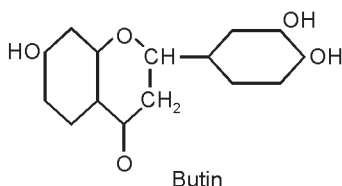
The tree is cultivated in gardens for its yellow flowers. It is propagated from seeds. It is a very fast growing tree. The wood is orange-red, hard, very heavy, and straight-grained with a fine and even texture. The wood was formerly used in calico printing of cotton, wool, and silk. It is now, however, replaced by synthetic dyes. Heart wood contains brazilin the coloring matter.

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## 6.11 Butein and butin

Butein, [1-(2,4-dihydroxyphenyl)]-3-(3,4-dihydroxyphenyl)-2-propen-1-one;  $C_{15}H_{12}O_5$ ; mp 213–215°C), the principal coloring matter, occurs as butyrin ( $C_{27}H_{32}O_{15}$ ), and isobutyryn, the mono and diglycosides along with butin (7,3',4'-trihydroxyflavanone;  $C_{15}H_{12}O_5$ ; mp 224–226°C) in the flowers of Palas, *Butea monosperma* (Lam.) Taub. Butein and butin are slightly soluble in hot water but freely soluble in alcohol. Butin is also converted by ring-fission on boiling with potassium hydroxide into butein. Butein with sodium hydroxide (10% solution) gives a deep orange-red color, whereas butin gives pale orange-red color.



### 6.11.1 Extraction

The dried flowers are ground into powder and extracted with petroleum ether or carbon tetra chloride after soaking for 30–40 h to remove waxy material. The powder is then extracted with alcohol (95%) for 30 h. The alcoholic extract is distilled under reduced pressure to remove the solvent and the residue is treated with boiling water and then allowed to cool. The solution is then extracted with ether. The ether extract is shaken in the cold with aqueous sodium bicarbonate (1%). The alkaline aqueous layer turns red and is separated from the ether layer. The ether layer is distilled and dissolved in alcohol (95%). The alcoholic solution is kept for a week. Later, an orange-yellow crystalline solid settles down that is separated out later. This is recrystallised from dilute alcohol in the form of golden-yellow stout needles or rods of butein.

The alcoholic mother liquor from which butein is separated is allowed to concentrate by evaporation for one week. It is then boiled with water and filtered. The aqueous filtrate slowly deposits a pure yellow crystalline solid in the form of broad rectangular plates of butein.

Under conventional method, the flowers yield a brilliant but very fugitive yellow dye. It is obtained in the form of a decoction or an infusion in water from dried flowers. Addition of alum, lime or an alkali deepens the color to orange and also makes it less fugitive. The decoction is used to dye cotton fabrics, sola articles, and woolen carpets.

### 6.11.2 Uses

It has long been used as food additive and as an herbal medicine throughout Asia. Butein is known to exhibit anti-inflammatory, anticancer, and anti-fibrogenic activities. The dye is used to color cotton, silk, and wool from yellow to brownish-black depending on the mordants used. The dye with alum, lime or an alkaline deepens the colors to orange and also makes it less fugitive. It can also be used for coloring foodstuffs. The decoction of the flowers is used during Holi, the festival of colors in India.

### 6.11.3 Sources

*Butea monosperma* (Lam.) Taub. (Fabaceae)

syn. *B. frondosa* Koenig ex Roxb.

English – Bestard Teak, Bengal Kino Tree, Flame of the Forest; Bengali, Malayalam and Marathi – Plas; Hindi – Dhak, Palas; Kannada – Muttuga; Oriya – Porasu; Sanskrit – Palasa; Tamil – Parsa, Pilasu; Telugu – Mooduga, Palasamu; Punjabi – Dhak

It is a deciduous, small tree of about 15 m height, commonly found throughout India, except in the arid regions. It contains bright orange-red and sometimes yellow colored flowers and one-seeded pods.

The tree is culturally important as it is commonly found in the plains of India and is capable of thriving where most species cannot grow. Leaves of the tree begin to fall during November–December, and by the end of January, the tree is leafless or nearly so. It flowers from January to April.

The seeds lose their viability within a year. In nature, seeds are germinated in rainy season. In artificial regeneration, the pods are sown while maintaining a distance of 25–30 cm, lightly covering with soil and watering afterwards. This tree can be raised by transplantation also. Seeds are sown in nursery beds long before the rainy season. Seedlings appear in 7–15 days and are transplanted during the first rainy season after the stem is pruned to 5 cm and the taproot is of 23 cm. The plant is also cultivated for rearing the lac insects.

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## 6.12 Calendulin

Calendulin, a carotenoid is the principal yellow coloring substance found (0.8–1.0%) in dried petals of Marigold, *Calendula officinalis* L., along with other coloring compounds like lycopene, rubixanthin, and violaxanthin. Calendulin is soluble in hydrocarbons and hot water.

### 6.12.1 Extraction

The dry petals, pre-treated with alcohol, are extracted with petrol for 24 h and then filtered. The filtrate is solidified under reduced pressure. Thus obtained product is a mixture of carotenoids like calendulin, lycopene, rubixanthin, and violaxanthin. With the help of chromatographic methods, these coloring compounds are separated in pure form.

### 6.12.2 Uses

Calendulin is used for coloring soups, stews, salads, rice, milk, butter, cheese, omelettes, buns, bread, and puddings.

### 6.12.3 Sources

*Calandula officinalis* L. (Asteraceae)

English – Calendula, English Garden Marigold, Post Marigold, Mary-Bud, Gold-Bloom, Holligold; Hindi – Zergul; Punjab – Akbelulmulk, Saladbargh; Tamil – Thulukka Saamanthi

It is an aromatic, erect, annual herb, up to 60 cm tall, native to Southern Europe, commonly cultivated in India as an ornamental plant and often met with as an escape. It contains light yellow to deep-orange flowers.

It is easy to cultivate on any soil, except clay soil. It is cultivated during June–July and October–November in the plains and during February–March

and September in hills. The seeds are treated with IBA at 10 or 20 ppm before sowing that give maximum (80%) germination. Early sowing i.e., in June–July is reported to favor quick and better germination, vigorous vegetative growth and better quality flowers. Regular watering over a week and application of liquid manure at the time of flowering is beneficial. The period of blooming can be prolonged by removing old blooms regularly.

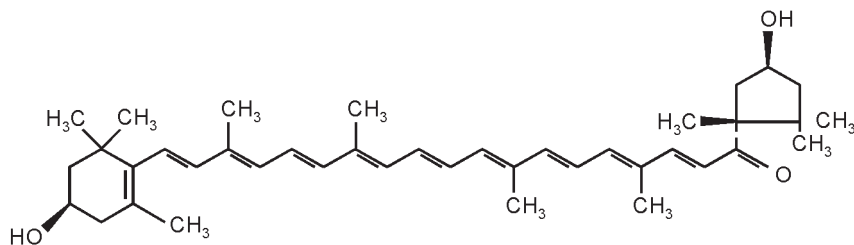
Besides coloring and flavoring properties, calendula flowers also provide the drug calendula which has stimulant, bitter, tonic, sudorific, febrifuge, carminative anti-emetic, and anthelmintic properties. They are used in ointments for treating wounds, malignant ulcers, frost-bite, skin-damage, and scars.

### For further reading

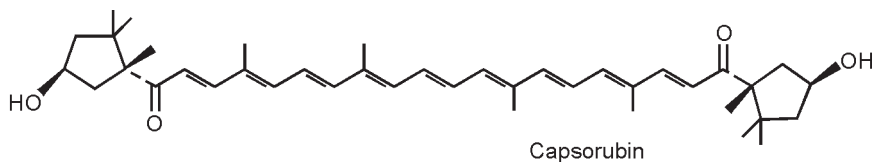
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## 6.13 Capsanthin

Capsanthin, (all-E, #R,3'S,5'R)-3, 3-dihydroxy- $\beta$ , k-carotene-6'-one;  $C_{40}H_{56}O_3$ ; mp 175–176°C) the principal red coloring substance is present with capsorubin ( $C_{40}H_{56}O_4$ ; mp 201°C) in paprika, the oleoresin obtained from ripe fruits of Red chillis or Paprika, (*Capsicum annuum* L.) and in the anthers of Tiger Lily, *Lilium lancifolium* Thunb. Capsanthin is readily soluble in acetone, chloroform and also soluble in oil, less soluble in methanol, ethanol, ether and benzene, and sparingly soluble in carbon disulphide. It crystallizes from carbon disulphide in deep carmine-red round grains. From petrol, the pigment is obtained in needles and from methanol in prism. Capsanthin in ethanol gives deep-red solution, and in petroleum it gives lemon to orange-yellow solution.



Capsanthin



### 6.13.1 Extraction

*Capsanthin:* Paprika pods without shells and seeds are dried at 35–40°C. The finely ground material is then extracted at room temperature. The solution is diluted with a threefold volume of ether, and 30% methanol potassium hydroxide is added, and then the mixture is allowed to settle for 1–2 days at room temperature. After that, the free phytoxanthins are dissolved in ether. The solution is washed, until it shows a neutral reaction, dried over sodium sulphate and most of the solvent is evaporated under reduced pressure. The ethereal residue is diluted with much petroleum ether and allowed to settle in cold for 24 h. In this way, about 1.2–2 g of crude capsanthin is obtained from 1 kg of high quality paprika. The crude capsanthin is the mixture of esters of capsanthin, capsorubin, zeaxanthin, cryptoxanthin, carotenoids, violaxanthin, and cryptocapsin. Capsanthin is separated out from other carotenoids by chromatography on calcium carbonate or zinc carbonate. Carbon disulphide is employed as solvent for developing the chromatograph. A mixture of benzene and ether (1:1) is also suitable for this purpose.

*Capsorubin:* From paprika extract, another red coloring substance capsorubin ( $C_{40}H_{60}O_4$ ; mp 201°C) can also be isolated. Capsorubin crystallizes from a mixture of benzene and petrol in violet-red needles. From carbon disulphide, the dye is obtained in rhombic plates. It is readily soluble in alcohol and acetone, sparingly soluble in ether, benzene, and carbon disulphide, and almost insoluble in petroleum ether. The chromatographic behavior of capsorubin is similar to that of capsanthin.

For extraction of capsorubin, paprika pods are pre-treated with ethanol, and then extracted with petroleum ether. The combined extracts are concentrated in vacuum and the dye is chromatographed on calcium carbonate. After repeated chromatographic absorption, the capsorubin ester is saponified with methanol potassium hydroxide, and the dye is finally chromatographed repeatedly on calcium carbonate from carbon disulphide solution. For further purification, the dye is crystallized from the mixture of benzene and petrol. The yield of pure dye is about 260 mg from 1 kg of pods. Recently, paprika oleoresin has been extracted by supercritical carbon dioxide method.

### 6.13.2 Uses

Capsanthin and capsorubin are used for coloring food stuffs and pharmaceutical preparations.

### 6.13.3 Sources

*Capsicum annuum* L. (Solanaceae)

syn. *C. frutescens* C.B. Clarke

English – Chili, Purple, Red or yellow chili, Sweet pepper, Paprika; Bengali – Dhanilanka, Lalmorich, Lanka, Morich; Gujarati – Lalmarchan, marchan; Hindi – Gachmarich, Lalmirich; Kannada – Menasinakkayi; Malayalam – Chalie, Chuvanna-mulaku, Kappalmulaku, Milagu; Marathi – Mirchi; Oriya – Lalmoricho, Lankamoricho, Moricho; Tamil – Mulagay, Usimulagay; Telugu – Soodimura-pakaaya; Kashmiri – Marchawangun

Chili is essentially a crop of tropics and grows better in hotter regions. It is cultivated over large areas of the countries of Asia, Africa, South and Central America, part of USA and Southern Europe, both under tropical and sub-tropical conditions. The major chili growing countries are India, Nigeria, Mexico, China, Indonesia, Japan, and South Korea.

In India, chili is grown all over the country. But Andhra Pradesh, Karnataka, and Maharashtra account for 75% of the country's net area under crop.

Chili is a rich source of red color. The total quantity of color is higher in the fruits of the first harvest than that of second. Depending upon the solvent used, the total yield of the coloring matter varies from 19.7% with alcohol to 67.7% with acetone. The pigment in chili ranges from 0.1 to 0.5%, whereas in paprika, the oleoresin, from 0.1 to 0.8%. The major red coloring matters present in it are capsanthin and capsorubin. Apart from these, capsanthin-5, 6-epoxide, capsochrome, and capsanthin 3, 6-epoxide are the major carotenoids present in paprika.

*Lilium lancifolium* Thunb. (Liliaceae)

syn. *L. tigrinum* Ker-Gawl.

It is a stout herb of about 0.6–1.2 m height, native to China and Japan and cultivated in Indian gardens. Bulbs are spherical, white or pale yellow; flowers are bright salmon-red spotted purplish black. Bulbs are eaten and are used for ovarian neuralgia. Stamens of the plant yield capsanthin, a red coloring matter which is used as to dye foodstuff and pharmaceutical preparations.

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## 6.14 Caramel

Caramel, a dark-brown, thick liquid or solid material, is made by heating sugar or glucose above its melting point (above 186°C) by adding small quantities of alkalies, alkaline carbonate or a trace of mineral acid. It is soluble in water and dilute alcohol but insoluble in benzene, chloroform, ether, acetone, petroleum ether, and turpentine oil.

### 6.14.1 Uses

Caramel is used in confectionaries and in coloring beverages and foods. Good tinctorial effects of caramel are observed in the range of 1000 ppm. Various shades from yellowish-tan to red-brown can be obtained. A foaming caramel is frequently used in root bear, and a non-foaming caramel in cola drinks.

Caramel color used in carbonated beverages must be acid proof and be free from undesirable taste and odor. Caramel color reacts with ingredients in the carbonated beverage formula to cause an off flavor. Therefore, it is necessary to test the caramel color for its being acid free and reaction free with the formulation in which it is used in order to determine its acceptability. An acid proof quality test can be undertaken by taking 5% solution of caramel color with 2.5% phosphoric acid or 1% hydrochloric acid and observe clarity after 24 hours. If no sediment appears, the caramel is acid proof.

### 6.14.2 Toxicity

The toxicity studies as evaluated by Joint FAO/WHO Expert Committee on Food Additive (JECFA) in 1987, showed pigmentation of mesenteric lymph nodules and caecal enlargement but were considered to be non-specific effects. The evaluated ADZ value is 0–200 mg/kg body weight.

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## 6.15 Carbon

Carbon, a black coloring matter is obtained from wood, charcoal, lampblack, bone black, coke, asphalts, and graphite.

### 6.15.1 Uses

Carbon has been used since ancient times for various purposes. It is used as a black dye for calico printing, artist's colors, and printing ink, and to color rubber, plastic, paper, cement, and flooring tiles as a pigment in paint industry.

### 6.15.2 Sources

Carbon is obtained from the following sources:

#### *Charcoal black*

This is one of the oldest black pigments known to mankind. In ancient times, it was made by carbonizing wood and wood waste in specially constructed heaps or piles. But nowadays it is prepared in closed carbonization kiln or retorts. Thus obtained charcoal is boiled with nitric acid for 5–6 h and washed thoroughly with water till completely free from acid. It is then dried in the air, crushed, and sieved.

In United States, resinous woods are used after extraction of resin and turpentine oil by solvents. In France, it is produced from the dry grape husk. In India, charcoal is prepared from the twigs and wood of tamarind (*Tamarindus indica* L.), and shells of almonds (*Prunus amygdalus* Stokes), and coconut (*Cocos nucifera* L.).

#### *Lamp black*

Lamp black, known as *kajal* in India is prepared by burning oil in a lamp and depositing the soot on an earthen bowl. It can be prepared by burning wax, fat, coal gas, turpentine, tar, petroleum, acetylene, etc., in the presence of air. Thus obtained black powder is further purified by successive washing with

benzene, alcohol, and ether so as to remove hydrocarbons. The powder is then dried in air and in the oven at 150°C. It contains about 93% carbon.

### *Bone black*

Bone black is made by heating bones or bone cuttings in closed retorts. Before heating, bones are degreased by steam or benzene. The extracted bones are then reduced to small pieces and burnt for about 6 hours in retorts. Thus obtained char is removed from the retorts, cooled down, and finally crushed. In this form, it is used in the sugar industry for refining the sugar. The waste bone black remained after being used in sugar industry is washed and reground. It is used in paint and color trades under the name of drop black.

### *Coke*

Coke is obtained as a residue in dry distillation of coal, i.e. by heating coal in a closed vessel out of contact with air in which gas, tar, and ammonia are obtained as byproducts. Coke generally contains 85–90% of carbon. Properties of coke depend upon the nature of coal from which it is obtained and the way the coal is cooked. The main varieties of the coke are (a) soft coke – the porous, black and brittle and (b) hard coke – dark grey in color with bright luster.

### *Asphalts*

Asphalts are the varieties of naturally-occurring bitumen. Asphalts are also produced as a petroleum byproduct. Both substances are black and largely soluble in carbon disulphide. They are of variable consistency, ranging from highly viscous fluid to a solid. Asphalts occur with or without mineral matter.

Many types of asphalts occur as viscous impregnations in sand stones, silt-stones, and lime-stones. After treatment to remove water and volatile constituents, the asphalts are fused at 54–60°C and contain about 83% carbon. Most of the asphalts are of marine origin and consist of the high-molecular weight compounds normally present in petroleum residue.

### *Graphite*

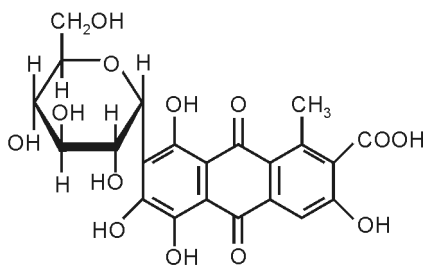
Graphite, the black coloring material, also known as plumbago or black lead, usually occurs in foliated or granular masses. Its color is iron-black or dark steel-grey, with a metallic luster. It gives a cold touch owing to its high thermal conductivity. The organic part is nearly pure carbon, and this is associated with varying proportions of impurities such as silica, alumina, iron, and oxoxide. Graphite occurs in irregular masses in formations of limestone, mica schists, granite, and gneiss. It is widely distributed throughout the world, and in India it occurs in Kerala, Orissa, Bihar, Rajasthan, and Sikkim.

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### 6.16 Carminic acid

Carminic acid (7-(-D-Glucopyranosyl-9,10-dihydro-3,5,6,8-tetrahydroxy-1-methyl-9,10-dioxo-2-anthracene-carboxylic acid;  $C_{22}H_{20}O_{13}$ ; mp 189–190°C), the principal red coloring matter, occurs in the female cochineal insects, *Dactylopius coccus* Costa, *D. confusus* Cookerell, *D. indicus* Green, *D. tomentosus* Lam., *Anthracoccus uvaursi* L., *Porphyrophora polanica* L. and *P. hameli* Brandt., which flourishes on cactus species *Nopalea cochenillifera* (L.) Salm-Dyck syn. *Opuntia cochenillifera* (L.) Mill., commonly found in Mexico, Central America, Russia and Middle East.



Carminic Acid

Carminic acid is soluble in water, alcohol, ether, acid and alkaline solutions and insoluble in benzene, chloroform and petroleum. Addition of alkalis or neutral lead acetate, carminic acid changes from scarlet red shade to bluish red. Addition of saturated solution of uranium acetate, which is a characteristic test for carminic acid, gives a pea-green color. Its red color changes according to pH (being yellowish at pH 8 and bluish-red above pH 6.2).

After the discovery of Mexico and exploitive tactics of Cortez and Spanish King, Charles V, cochineal replaced kermes as the major reddish-orange on the continent, a monopoly that continued for over 300 years. In 1858, the introduction of aniline red finally broke the market of Mexican-Spanish corner. Such a state of secret was the source of this new world of dye. Even as late as 1725, it was commonly believed that cochineal was the seed of an American tropical plant. In fact, cochineal is obtained from an insect

which feeds on the cactus *Nopalea cochinellifera*. Even before the conquest of Spaniards, the value of the dye was legend. It is reported that Aztecs used it as a tribute. In 1480, Montezuma extracted modern Oaxaca, a yearly tribute of twenty sacks of cochineal from the state of Huaxyacas. Considering that ca 155,000 dried insects are required to produce one kilogram of cochineal dye, the value of such a tribute is enormous.

### 6.16.1 Extraction

The mature female insects that are 90–110 days old, and contain the highest percentage of carminic acid are collected just before they begin to lay their eggs. They are killed either by immersing in hot water followed by drying or dried directly by exposure to the sun, steam or hot air. The immersion technique produces a black grain that later turns to silver grain and is then contaminated with white waxy powder. The grains are completely dried. These grains are defatted with acetone and extracted with 70% aqueous ethanol (one part in five parts) at 80°C. On evaporation, it gives carminic acid.

In earlier method, ground insect mass is cooked with water and purified by acetic acid and filtered. The sulphuric acid is added to the filtrate and left overnight. Gradually, carminic acid crystals get deposited in the bottom that are drained out and dried.

### 6.16.2 Uses

Though the traditional dyes of biological origin have been replaced by synthetic ones, cochineals have managed to survive, till date. Its brilliant, permanent nature, fastness and high saturation are its major characteristics. Cochineal dye is applied in food, drinks, cosmetics, and in pharmaceutical products. It is used to dye sugar coated pills, sauce, and meat substitutes. Bulk amount of dye goes into the pork sausage and pie industry; dried fish, shrimps, ice cream, jams, jellies, yoghurt, fruit in syrup, aperitif alcoholic and soft drinks, chocolate, fillings, sweets cider, vinegar, etc.

It is also used in dyeing and printing, especially leather and wool. Two shades of red color are obtained upon wool. Crimson is produced by using aluminium sulphate as mordant and scarlet using stannous and stannic chlorides. Wool mordanted with potassium dichromate gives a purple color which with ferrous sulphate and tartar produces a purplish, slate or lilac. Cochineal dye is employed in dyeing shawls in Ludhiana and Kashmir; silk fabrics to obtain permanent shades of deep, crimson and red in Mysore, India. Carminic acid is also used as biological stain for nucleic acids as well as protein.

### 6.16.3 Insects

Cochineal insects are indigenous to the new world, Central and South America. Later, they have been transported and naturalized in the old world countries like South Africa, India, Sri Lanka, and Australia. Out of total nine species of the genus *Dactylopius*, reported in the world, five species viz. *D. ceylonicus* Green, *D. coccus* Costa, *D. costa* Costa, *D. Confusus* Cockerell and *D. tomentorus* Lamark are found in India.

Cochineal insects are of two types, the cultivated superior ones and the wild ones. The cultivated one, *D. coccus* gives the true cochineal or Grana fina, which is a genuine dyestuff and the wild cochineals or Grana Silvestre, an inferior quality of dye.

*Cultivation of the insects:* Cochineal insects need care for cultivation. Dry summer season is suitable, while wind and rain are destructive to them. In spring, the females are brought out and put in little straw nests fastened to the cactus, 8–10 females are swept into a small bag made of cotton gauze or tissue paper pierced with small holes and tied at the bottom of cactus stem. The nymphs escape and spread themselves over the surface of the stem. Bright sunny days are selected for such operations. Nymphs may be transferred to fresh cactus plants to facilitate propagation. For winter crop, cactus is infested in October–November, and the cochineal is ready for harvest in February–March. When infected in March, they are collected in the next October–November. The female insects are believed to contain large amount of dye, maybe half of its body weight while the male accounts negligible. Carminic acid is present about 10% in the insect of dry commercial quality. The life cycle of an average insect lasts for a period of 60–130 days. Under suitable conditions, 3–5 generations can be raised in a year.

### 6.16.4 Lakes

Carmine is the aluminium-calcium lake of carminic acid. Aluminium and aluminium-tin lakes are made and find their use as pigments.

Lakes of cochineal are formed on starch, alumina or blanc fixe. They have poor fastness to light and weather, but they are transparent and are used as artists' water colors for coloring confectionery, cosmetics and occasionally in printing ink.

Cochineal digested with ammonia to which gelatinous alumina was added, formed a blue dye which was used to bleach cotton blue.

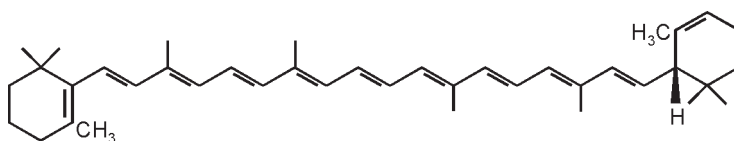
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## 6.17 Carotene

Carotene ( $C_{40}H_{56}$ ; mp  $181^{\circ}\text{C}$ ), a yellow coloring principle is widely distributed in plants and animal kingdom. Carotene has been first isolated by Wackenroder in 1831 as ruby-red crystals from the common carrot, *Daucus carota* L. var. *sativa* having mp  $184^{\circ}\text{C}$ . But Kuhn (1930) has shown that the natural product contained three isomers:  $\alpha$  (mp  $188^{\circ}\text{C}$ ),  $\beta$  (mp  $184^{\circ}\text{C}$ ) and  $\gamma$  or lutein (mp  $178^{\circ}\text{C}$ ). The  $\beta$ -isomeric form is most common and an average composition of  $\alpha$ ,  $\beta$  and  $\gamma$  is 15, 85, and 0.1% respectively is generally found in carotinoids of red varieties of *Daucus* spp. One kg of carrots and palm oil yield 1 g and 1.2–2.0 g carotene, respectively. The  $\beta$ -form is similar to lycopene, the red coloring matter found in tomatoes and other fruits. Carotene is soluble in water.



$\alpha$ -Carotene

### 6.17.1 Extraction

Carotinoids have been extracted by two extraction methods namely, traditional solvent extraction and supercritical fluid extraction. Under the traditional methods, carrots are finely cut, dried, ground and extracted with petroleum ether at room temperature. The extract is then concentrated at  $30\text{--}40^{\circ}\text{C}$  under reduced pressure and diluted with an equal volume of carbon disulphide. From this mixture, the crude carotene is precipitated with ethanol and filtered. Spirit of wine is added to the precipitate in small quantities at 2–5 min intervals. As soon as the carotene crystals are formed, the colorless material is separated by rapid filtration. The mother liquor is then diluted with alcohol and is allowed to stand for 20 h at  $10^{\circ}\text{C}$ . After that the crude carotene is filtered

off, dissolved in carbon disulphide, precipitated with ethanol, extracted with little warm petroleum ether to remove remaining impurities, and finally recrystallised from a large volume of petroleum ether. Then with the help of chromatographic methods, the fractions of  $\alpha$ ,  $\beta$ , and  $\gamma$  or lutein carotenes are separated. Enzymatic method can be used for extraction of the carotene. However, carotenoids extracted by using supercritical  $\text{CO}_2$  recovered  $\alpha$ ,  $\beta$  and  $\gamma$  or lutein carotenes and also showed high anti-oxidant activity. Recently, a new method, pressurized fluid extraction (PFE) has been developed under which conventional solvent is utilized at controlled temperature and pressure, requires less solvent and shorter extraction time.

### 6.17.2 Uses

Carotene is used as colorant in foods and ingested drugs. It is also used for coloring margarine, fats, oil, etc.

### 6.17.3 Sources

*Daucus carota* var. *sativa* Hoffm. (Apiaceae)

English – Cultivated Carrot; Bengali, Hindi, Gujarati and Punjabi – Gajar; Kannada – Gajjari; Marathi – Gazara; Sanskrit – Shikha-Mula; Tamil – Gajarakkilangu, Karettukizhagu

It is an annual or biannual herb cultivated throughout India, as a winter crop in North Indian plains and throughout the year in hills. The crop is raised by seeds. Seeds are sown either by broadcast or by drill in lines, from August to November in the plains and from March to September in hills. The fields are irrigated soon after sowing the seeds. Seedlings appear in 10–12 days. Crop needs watering once a week during dry months and once a fortnight during winter. Carrots are harvested after 2–4 months when the roots are of sufficient size for use. Carrots can be stored for 5–6 months without loss in quality of food value.

The carotene contents of the roots of most varieties increase till maturity. It does not accumulate in the roots of the white varieties. Carotene content is about 60–120 mg/100 g roots but some varieties can contain up to 300 mg/100 g. Larger size roots are usually richer in carotene than smaller ones. The  $\beta$ -carotene formed 60–80% of the total carotenoids in red varieties. The principal pigment of orange color varieties is  $\beta$ -carotene while light yellow, yellow, pink and violet-color varieties contain xanthophyll.

### For further reading

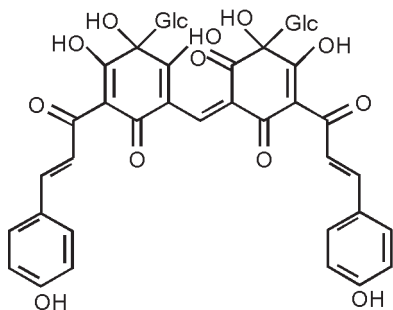
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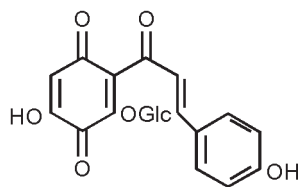
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## 6.18 Carthamin

Carthamin (6-(-D-glucopyranosyl-2-[(3-(-D- glucopyranosyl-2,3,4-trihydroxy-5-(3-(4-hydroxyphenyl)-1-oxo-2-propenyl]-6-oxo-1,4-cyclohexadien-1-yl]methylene]-5-6-dihydroxy-4-[3-(4--hydroxyphenyl)-1-oxo-2-propenyl]-4-cyclohexene-1,3-dione; carthemic acid; safflor carmine; safflor red;  $C_{43}H_{42}O_{22}$ ), the principal red coloring matter, occurs in the petals of Safflower, *Carthamus tinctorius* L. and *C. oxyacanthus* M. Bieb. along with a yellow coloring matter, Safflower yellow A ( $C_{27}H_{30}O_{15}$ ).



Carthamin



Carthamone

Carthamin is a dark red, granular powder with green luster. It is slightly soluble in water and readily soluble in dilute alkali carbonates and alcohols, but insoluble in ether. On oxidation carthamin yields a stable red coloring matter, carthamone ( $C_{21}H_{20}O_{11}$ ).

Safflower originated in Turkey and in north of India, and is cultivated in the east of the Mediterranean basin, especially in Egypt. It is recorded that the grave clothes of the ancient Egyptian mummies were dyed with the safflower dye. Though, due to impermanent nature of the dye, plant was abandoned as a source of dye stuff even before the advent of synthetic dye, but is still used in India for dyeing cloth for ceremonial occasions.

### 6.18.1 Extraction

The flowers of safflower contain principally two coloring matters, the carthamin, insoluble in water, and safflower yellow a, that is soluble in water. The water soluble yellow coloring matter, which was discarded previously, is now used as dye because soluble matter gets converted to carthamone on standing for some time. For the extraction of the dye, the florets are collected and dried in shade. The dried material is repeatedly washed with acidulated water till all the water-soluble yellow coloring matter is oxidized by pro-oxidize enzyme into carthamone. The left over residual mass is treated with sodium carbonate, and then carthamin is precipitated out with the help of dilute acid. Pure carthamin has also been extracted using organic solvents and enzymes to give improved yield and quality of dye.

### 6.18.2 Uses

Carthamin is used to give cherry-red color for dyeing silk and cotton. The red carthamin present in abundance (26–36%) is oxidized to carthamone. Carthamone imparts different shades of colors (cherry-red, rose-pink, crimson or scarlet) to cotton and silk. It is also employed for coloring cakes and biscuits. It is the first important substitute for saffron. It is a fugitive dye to light and air and sensitive towards alkali, chlorine, and sulphuric acid. Citric acid (70%) is found to have a color fixing effect. It is also used for coloring toys.

### 6.18.3 Toxicity

When the dye is used in large quantities for making eatables, it acts as a cathartic.

### 6.18.4 Sources

*Carthamus tinctorius* L. (Asteraceae)

English – Bastard Saffron, False Saffron, Safflower; Bengali – Kusukphal, Kusum; Gujarati – Kasumbo; Hindi – Karrah, Kusum; Kannada – Kusumba, Kusume; Marathi – Kardai, Kurdi; Sanskrit – Kusumbha; Tamil – Kusumba, Sethurangam, Telugu – Kusembalu

It is a much branched annual herb of 45–60 cm height with orange-red or yellow flower heads, native to Europe and Asia and cultivated throughout India. Safflowers have been cultivated for centuries as a source of dye but recently it is also used as edible oil and is popular in many countries especially India, China, Egypt, Italy, Spain, USA, Mexico, Australia, and Russia. In India, it is cultivated in the states of Maharashtra, Karnataka, and Andhra Pradesh.

For production of dye, the crop is cultivated as a pure crop. The crop is raised through seeds. Seeds are treated with agrosan GN or ceresan fungicides before sowing and also pre-soaked in water for 24 h. Seeds are sown by the end of September or middle of October at the rate of 17–20 kg seeds per hectare. For dye, the fully grown flower heads are collected at second or third day of flowering. Delay in collection causes loss in dye. Cloudy weather or rain during flowering also reduces the yield of dye. The flower heads are dried and petals are separated for extraction.

The crop can be grown for dual purpose of dye and oil production. The petals are collected after fertilization and the seeds are allowed to ripe so that both dye and seeds are obtained from the same crop.

*Carthamus oxyacanthus* M.Bieb.

syn. *Carthamus polyacantha* M. Bieb.

English – Wild safflower

It is a stout, strongly armed, generally much branched, 1.0–1.5 feet tall plant, found in dry open places of Afghanistan, Azerbaijan, India, Iran, Iraq, Kyrgyzstan, Pakistan, Tajikistan and Turkmenistan. It is a common weed of wheat field. The flower contains two major pigments, the water soluble yellow carthamidin and the orange-red coloring matter carthamin. *Carthamus oxyacanthus* had long been grown for the dye extracted from flowers. Depending on the dyeing procedure and addition of mordants, it imports a yellow, red, brown or purple color to cloth. Flowers are generally mixed with rice, bread, pickles, and other food materials to give them an attractive orange color.

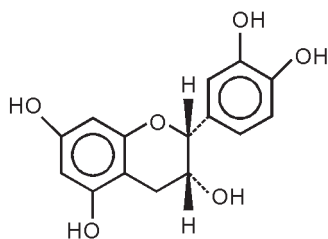
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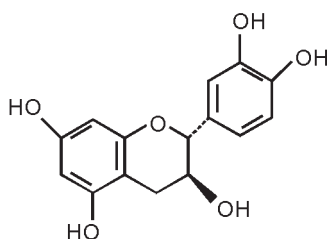
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## 6.19 Catechin

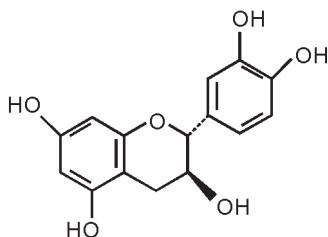
Catechin (2-(3,4-Dihydroxyphenyl)-3,4-dihydro-2H-1-benzopyran-3,5,7-triol; catechol; 3,3',4',5,7-flavonpentol; catechinic acid; catechuic acid; cyanidol;  $C_{15}H_{14}O_6$ ; m p 93-96°C, 175-177°C when anhydrous; the principal coloring matter, is extracted from the heart wood of Bengal cutch, *Acacia catechu* (L. f.) Willd.; fruits of betel nut, *Areca catechu* L.; leaves and twigs of Gambier, *Uncaria elliptica* R. Br. ex G. Don. syn. *Uncaria gambier* Roxb.; leaves and bark of Black babool, *Acacia nitotica* (L.) Delile subsp. *indica* (Benth.) Brenan, leaves of tea, *Camellia sinensis* (L.) Kuntze, and rhizomes of Pashaanbhedha, *Bergenia ciliata* (Haw) Sterub., and *B. stracheyi* (Hook. f. and Thomson) Engl.



(-)-Epicatechin



Catechin



Catechin

Catechin has two racemic and four optical forms-d-, l- and r- Catechin and d-, l- and r-epicatechin. In catechin and epicatechin, the H and OH in 2, 3-positions have trans and cis configurations, respectively.

During dyeing, catechin is converted into catechu tannic acid that is oxidized to a brown product of unknown constitution is fixed on the fiber and yields pale yellow on the alum and brown on the iron mordant.

The dl-form is slightly soluble in cold water, ether; readily soluble in hot water, alcohol, glacial acetic acid, and acetone but insoluble in benzene, chloroform, and petroleum ether.

### 6.19.1 Extraction

The raw material is turned into small pieces or in dust form and boiled in water and then filtered. The filtered extract is further concentrated till it attains the consistency of syrup. Unnecessary heating should be avoided to prevent the conversion of catechin into catechu tannic acid which retards the crystallization of catechin in thick solution. The concentrated extract is cooled and set aside for few days. The crystals of the catechin settled down are filtered through fine muslin cloth. Thus collected catechin is then washed with pure cold water to remove all traces of catechu tannic acid.

### 6.19.2 Uses

Catechin has been used for centuries for dyeing cotton, silk, and wool, and also as a food and hair dye. It has been used for tanning and dyeing leather and for rot proofing fishing cloths, paper maker felts, etc.

In India, two types of catechu are marketed; *katha* (the pale catechu), and *cutch* (the dark catechu). *Katha* is used in pan preparations and in medicine, and the *cutch* is used for printing and dyeing purposes. The *cutch* contains tannins (56–62.5%), catechin (13.5–17.8%), extractives (20–32%), insoluble (2.9–5.6%), and ash (1.2–1.5%). The catechu is mainly used for dyeing cotton and silk, and in calico printing. The well known catechu-brown or cutch-

brown on cotton is obtained by steeping the material in a boiling solution of cutch to which copper sulphate has been added. Catechu-brown dyed by this method is reported to be very fast to light and to acid and alkali solutions, and also to bleaching powder.

Cutch may be used in admixture with direct dyes, chosen with regard to their ability to withstand the action, the process being cheaper than topping with basic dyes. Cutch is also used in the dyeing of ship sails and mail bags. Materials dyed with cutch exhibit greater fastness to weather and sea-water conditions than those dyed with coal-tar dyes. Cutch is also used in printing brown and drabs, and brown in combinations with red, chocolate, and purple.

### 6.19.3 Sources

*Acacia catechu* (L.f.) Willd. (Fabaceae)

English – Bengal Catechu, Cutch Tree; Assami – Khorja; Bengali – Khayar; Gujarati – Kherio-Baval; Hindi – Khair; Kannada – Kachu, Kaggali, Kanti; Malayalam – Khadiram; Marathi – Kaderi, Khair; Oriya – Khairu; Punjabi – Khair; Sanskrit – Khadira; Tamil – Kadiram, Karnagalli; Telugu – Kachu, Kadiramu, Sandra

It is a moderate sized deciduous tree with a light feathery crow, occurring throughout India in dry type of mixed forests on a variety of geological formations and soils. Khair is common throughout the sub-Himalayan tract from Punjab to Assam.

Khair grows best on porous alluvium and on loam or gravel with varying proportions of sand and clay; it also grows on black cotton soil. The plant is grown by seeds that are sown in lines. They germinate readily with moderate rain or watering. The seedlings grow very fast. The heartwood of 20–30-years-old tree yields the best catechu.

*Acacia nitotica* (L.) Delile subsp. *indica* (Benth.) Brenan

syn. *Acacia arabica* (Lam.) Willd., *Mimosa nilotica* L.

English – Black Babool, Indian Gum Arabic Tree; Bengali – Babla, Babul; Bihari – Babulo; Gujarati – Babaria, Baval; Hindi and Punjabi – Babul, kikar; Kannada – Gobbli, Jaali, Kari Jaali; Malayalam – Karive lam; Marathi – Babul, Vedibabul; Oriya – Bambuda, Bambra; Tamil – Karu Ve Lamaram, Karuvelei; Telugu – Nallatamma, Tumma

It is a moderate sized, ever green tree, found throughout the drier parts of India. It thrives best on riverain alluvium subject to inundation; and also grows well on black cotton soil, and alluvial loan in the plains of northern India; on loamy soil in the peninsula, and in tank beds in Tamil Nadu. It also survives well in saline soil.

This plant is propagated through seeds that are sown either in nursery beds or polythene bags filled with good soil. Within a year or two, new plants attain a height of 1.5–2 m and are ready for plantation. New plants are planted in rainy season. About 620 plants are planted in a hectare.

The leaves, bark, and fruits are the source of tannin (12.20%) which contains catechin, epicatechin, dicatechin, quercetin, gallic acid, and lencocyanidin. Catechin, the principal coloring matter is extracted from the aqueous extract of leaves, bark, and fruit.

*Areca catechu* L. (Arecaceae)

English – Areca Nut, Betelnut Palm, Areca Palm; Areca Palm; Pinang Palm; Andaman – Ah-Bud-Dah, Ah-Purvud Dah, Tambul; Bengali – Gua, Supari; Gujarati – Sopari; Hindi and Marathi – Supari; Kannada – Adika, Betta, Chikaniyadika, Puga; Malayalam – Adakkamarom, Kavungu, Kazhangu; Sanskrit – Gubak, Poojiphalam, Tantusara; Tamil – Kamugu, Paakkumaram, Pugam; Telugu – Gautupoka Kolapoka, Oppuvakkulu, Vakka

It is a tree with annulated stem, 12–18 m in height, and widely distributed in the coastal regions from Maharashtra to Kerala and Tamil Nadu and in Deccan Plateau in Assam, Meghalaya, West Bengal, and Andaman and Nicobar Islands.

Areca nut is mostly propagated by seeds, though few branched types are propagated by air layering. The fully ripe seeds collected from 25–30 year old plants are sown in the primary nursery seed beds. Whole nuts with husk are arranged vertically with calyx end-upwards, covered with a thin layer of sand and mulched with grass or straw. Watering is done daily till the seeds are sprouted. Germination starts about 40 days after sowing and may extend up to 94 days. Three months old seedlings bearing 2–3 leaves are transplanted into secondary nursery during monsoon season. Then after 12–18 months, seedlings are planted in well ploughed fields at  $1.8 \times 3$  m distance and about 90 cm depth. For good crop, about 100 g of Nitrogen, 40 g of Potash, and 140 g of potassium, 12 kg each of green manure and compost or cattle manure, and 450 g lime is recommended for per plant per year.

The palm comes into bearing in about 10–12 years after its plantation. Fruits are harvested when they are ripe. Each tree on an average yields two to three bunches of 150–250 fruits per year. Nuts contain tannin (18%); non-tannin (7–15%), and insoluble (42–43%). The tannins, commonly known as chogaru, are predominantly catechol or catechin type, which is used for tanning and coloring leather and for treating fishing nets and for making inks. It is also used as a substitute of synthetic food colors.

*Bergenia ciliata* (Haw) Sterub. (Saxifragaceae)

Sanskrit – Paashanabheda, Shailagarbhaja

It is a perennial herb with stout rootstock, found in the temperate Himalayas between 900 and 3000 m of altitude.

The rhizome is the source of tannin (14.2–16.3%) that is used for tanning and coloring leather. The tannin contains catechin, the principal coloring matter.

*B. stracheyi* (Hook.f. and Thomson) Engl.

It is a perennial herb, commonly found from Kashmir to Uttar Pradesh at an altitude of 2,400–4,800 m. The rhizome is the source of tannin (25%) and it imparts heavy, pale chocolate color to leather. It contains catechin, the principal brown coloring matter.

*Camellia sinensis* (L.) Kuntze. (Rubiceae)

English – Tea Plant; Bengali and Hindi – Chai, Chha; Gujarati – Cha; Kannada – Cha, Chaha, Theyale; Malayalam – Chaya, Theyila; Marathi – Chaha; Oriya – Cha; Sanskrit – Chaha, Chavika; Tamil – Karupputteyilai, Pachocitteyilai, Teyilai; Telugu – Nellateyakua, Teyaku; Urdu – Chai

It is a variable evergreen shrub or a small tree, found from Assam and hilly regions to the east and south of it. It is also cultivated in the hilly districts of North and South India, and elsewhere for its leaves which furnish the tea of commerce.

Tea is a sub-tropical species and is grown on a plantation scale in many parts of the world where the climate is moist and warm and the winter is not too cold. It flourishes where the optimum range of temperature is between a mean maximum of 29.5°C. Tea can be grown on a well-drained and friable loam or in soil rich in organic matter.

Tea is generally propagated from seeds, but in recent years the use of high yielding clonal material has become popular. Tea can be vegetatively propagated by budding, grafting on root stocks or by layering or cuttings. Propagation by cuttings has now been widely adopted as the most successful and practical means of vegetative multiplication. Cuttings from primary shoots, when the terminal and auxiliary buds are active or nearly active, are used for propagation. Single-node cuttings from green and semi-hard wood are preferred. Cuttings are kept in water to preserve their normal turgidity. The cuttings are planted in shaded propagating beds or in polythene.

Clonal plants from rare individuals can be obtained through tissue culture technique in a short period of time.

Leaves are rich in catechins (17.0–26.5%), the principal coloring matter. Besides catechins, theaflavins, and thearubigins, yellow and red or brown coloring matters are also present in the leaves. The thearubigins constitute



about 10–20% by weight of tea. In tea waste also, the theaflavins, thearubigins, and catechins are present from 10 to 15%.

The yellow-brown and green colors derived from tea have been used for coloring confectionery products such as sugar lozenges, fruit paste, ice-cream, and soft drinks. Tea extracts are also used as dyeing material for silk.

*Uncaria elliptica* R.Br. ex G.Don. (Rubiaceae)

syn. *Nauclea dasyoneura* (Korth.) Walp.; *Uncaria dasyoneura* Korth.

English – Gambier, Pale catechu; Bengali – Khayer; Bombay – Chinai-katha; Hindi – Kath-Kutha; Kannada – Sanakachu; Telugu – Ankudukurra

It is a small woody climber, found in tropical South-East Asia and cultivated in Indonesia, Malaysia, and Singapore for the production of gambier that is used for tanning and coloring leather.

Gambier or pale catechu, extracted from the heartwood of the plant is very much similar to cutch or dark catechu, obtained from *Acacia catechu*. Gambier contains catechin (7.33%), catechutannic acid (22–50%), mineral matters (3–5%), and in small quantity of (+)-epicatechin, catechu red, quercetin, wax, sugars, starch, cellulose, and weak acids.

Gambier is being imported into India from Indonesia, Malaysia, and Singapore. It has been used for dyeing and tanning leather. The brown coloring matter, catechin, is also isolated from the gambier. If the gambier is melted with 1% potassium chromate, preferably in presence of copper sulphate, it gives much redder dye than gambier itself.

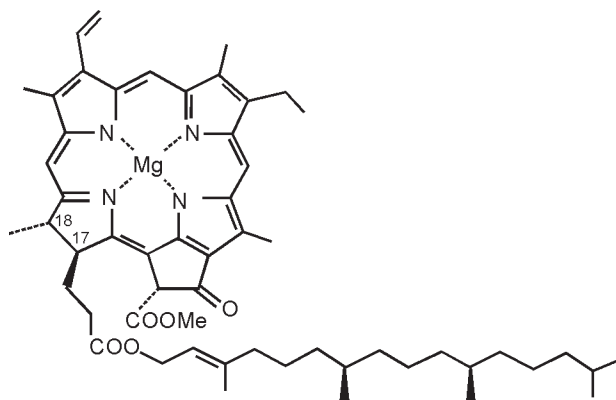
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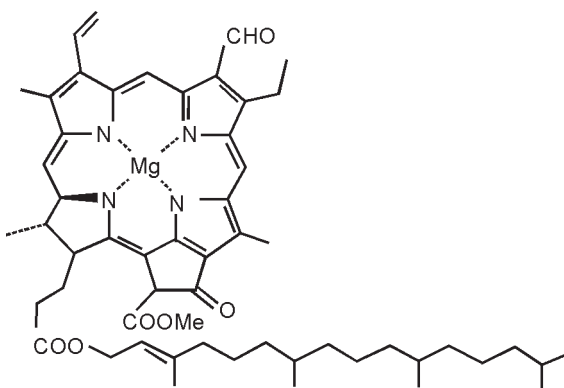
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## 6.20 Chlorophyll

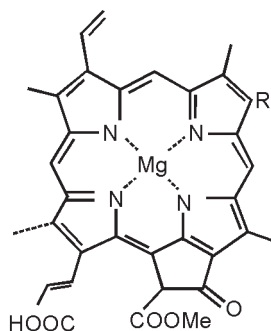
Chlorophyll, the photosynthetic green pigments of the leaves, occurring as a mixture of chlorophyll a ( $C_{55}H_{72}MgN_4O_6$ ) and chlorophyll b ( $C_{55}H_{70}MgN_4O_6$ ), is a dark green powder in the ratio of approximately 3:1 along with yellow, orange, and red colored bodies. Though chlorophyll is found in all the green plants, but commercially it is derived from the leaves of stinging nettle, *Urtica dioica* L., spinach, *Spinacia oleracea* L., Alfalfa, *Medicago sativa* L., and Corn, *Zea mays* L.



Chlorophyll a



Chlorophyll b



Chlorophyll c

### 6.20.1 Extraction

The leaves and tops of the plants are first extracted with petroleum ether to remove a majority of the carotenoids, fats, and waxes and then followed by another extraction with 80% acetone and then filtered. Low boiling petroleum ether is added to this extract and then acetone is removed by washing with distilled water. It is again extracted with 85% methanol to remove most of the yellow pigments. The methanol is removed from the petroleum ether by washing with water; the chlorophyll is precipitated, which is isolated from the petroleum ether by centrifuging. The complete process must be done in subdued light to prevent photodecomposition of the dissolved chlorophyll. The chlorophyll a and b are separated through chromatographic methods using a dried solution of the product in one part benzene and 10 parts petroleum ether with fine sugar as the absorbing medium. The separation is accomplished with Girard Reagent T (Trimethylamino-acetylhydrazide chloride) which reacts with the formyl group of chlorophyll b, giving a water soluble product, whereas chlorophyll a remains unreacted and insoluble.

In few commercial products, the Mg is replaced by copper or iron. For this purpose, the raw material is extracted with ethyl alcohol in copper vessels, usually in the presence of concentrated aqueous copper sulphate. The alcohol is distilled off and the residue is extracted with benzol. The residue after distillation forms the basis of the various commercial preparations. Blue shaded products are prepared with copper complex, while yellow shaded products without copper. In some cases, iron replaces the magnesium or copper. Oil-soluble products are formed by mixing with natural or mineral oils. Water-soluble products are obtained by saponifying with aqueous caustic soda.

### 6.20.2 Uses

Chlorophyll is used extensively for coloring soaps, resins, inks, waxes, and candles. Because it is physiologically harmless, it is used for the coloring of edible fats and oils, chewing gums, confectionery, gelatin, cosmetics, liniments, lotions, mouthwashes, perfumes, and also for coloring leather.

### 6.20.3 Sources

*Medicago sativa* L. (Fabaceae)

English – Alfalfa, Lucerne; Gujarati – Vilayti-Hullu; Hindi – Rigka; Punjabi – Lusan; Marathi – Ati-Gavat

It is an erect herb with purple or violet flowers in dense auxiliary racemes and 2–3 spiraled pods, native of south-west Asia, cultivated as a legume fodder in warm temperate or cool-sub-tropical regions. In India, it is cultivated in Punjab, Uttar Pradesh, Maharashtra, Gujarat, Tamil Nadu, and West Bengal. Lucerne is hardy and draught resistant. It grows well in plains as well as in hills up to 2,400 m altitude. Lucerne is propagated by seeds which are soaked in water before sowing and then sown during the cold weather from mid October to mid November. Seeds are sown broadcast or drilled in lines or on ridges. The crop is ready for cutting just before or immediately after flowering; subsequent cuttings are made at intervals of 1.0–1.5 months. Under favorable conditions, 8–12 quintal/acre are obtained in a year and the yield is sustained for 6–7 years.

Chlorophyll is extracted from ground lucerne meal on a commercial scale.

*Spinacia oleracea* L. (Chinopodiaceae)

English – Garden Spinach; Bengali – Palang, Pinnis; Hindi, Marathi, and Gujarati – Palak; Kannada – Spinachsoppu; Oriya – Pataksag; Punjabi – Palak; Tamil – Vasayleykiray; Telugu – Dumpabachhali, Matturbac hhali

It is an erect annual herb which is cultivated throughout India up to an altitude of 2100 m. Spinach is a cold season crop. It is sown during September–November in the plains and during February–April in the hills. The seeds are sown broadcast or drilled in, 30 cm apart. The seed rate varies from 30 to 40 kg/ha. It is short season crop and is ready for harvest in 6–8 weeks after sowing. The leaves are reported to be a raw material for the manufacturing of chlorophyll.

*Urtica dioica* L. (Urticaceae)

English – Stinging-Nettle; Hindi – Bichhu Booti

It is a robust herb, up to 2 m tall, with grooved stems abundantly armed with stinging hairs, found in the Himalayas from Kashmir to Kumaun at the altitudes of 2100–3200 m.

Nettle contains chlorophyll (15.7 mg/100 g fresh wt.). In Russia, the plant has been used as a source of green pigment for confectionery. Extraction of plant with alcohol (95%), after boiling with water, followed by draining and drying, gives a yield of 17.4% of green pigments on dry weight basis.

*Zea mays* L. (Poaceae)

English – Corn, Maize; Bengali – Janar, Bhutta; Gujarati – Makkari, Makkai; Hindi – Makai, Makka, Bhutta, Kukri; Kannada – Mekkejota; Malayalam – Cholam; Marathi – Maka, Makai, Buta; Oriya – Maka Buta; Tamil – Makka-Cholam; Telugu – Mokka-janna

It is a robust, annual grass, cultivated in the plains and hills. It is essentially a warm weather crop. The crop is raised by seeds which are sown in June–July in the northern plains, April–May in the hills and May–June in South India. The seeds are generally sown in rows, either with the help of drill or by dropping seeds in furrows behind the plough. Maize crop is generally ready for harvest in 80–100 days from sowing.

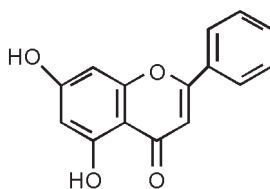
Besides chlorophyll, maize contains carotene and lutein. Chlorophyll is extracted from the leaves on commercial scale.

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## 6.21 Chrysin

Chrysin (5,7-Dihydroxyflavone;  $C_{15}H_{10}O_4$ ; mp 275–290°C), a yellow coloring matter, occurs in the leaf buds of Lombardy popular, *Populus nigra* L. var. *italica* Koehne, stem and root barks of Ullu, *Oroxylum indicum* vent, stem bark, and leaves of Pine, *Pinus roxburghii* Sarg., and *P. wallichiana* A. B. Jackson, and in whole plant of Sculicap, *Scutellaria galericulata* L. It is insoluble in water; soluble in alkali hydroxide solutions but slightly soluble in alcohol, chloroform and ether. A small amount of a second coloring matter, tectochrysin ( $C_{16}H_{12}O_4$ ; mp 163–165°C) is also found along with chrysin.



Chrysin

### 6.21.1 Extraction

The raw material is powdered and extracted with alcohol, and then the alcohol is removed from the extract under demised pressure. The residue is heated with water that is about eight times its weight, and then it is cooled and filtered. The residue is dried and then thoroughly extracted with hot benzene for 72 h. The benzene extract is concentrated, cooled, and filtered. The greenish-yellow crystals obtained are washed with petroleum ether to remove adhering oil. Thus obtained crude contains a number of other pigments. The pure chrysin is obtained from this crude product with the help of chromatographic methods.

### 6.21.2 Use

Chrysin is a feeble dye. It yields bright yellow, pale yellow-orange, and chocolate brown shades on wool with aluminium, chromium, and iron mordants, respectively. It is also used to dye silk.

### 6.21.3 Sources

*Oroxylum indicum* Vent (Bignoniaceae)

Assam – Tognna, Bhatghila, Dirgari; Bengali – Sona, Nasona, Sonpatti; Gujarati – Aralu, Tentu; Hindi – Ullu, Arlu, Saona; Kannada – Tigdu,

Bunepale, Sonepatta; Marathi – Tetu; Malayalam – Palagapaiyani; Oriya – Phapni, Phonphonia; Punjabi – Mulin, Tatmorong; Tamil – Achi, Peiarlanthei; Telugu – Dundilum, Pampini; Sanskrit – Shyonaka

It is a small to medium sized tree, up to 12 m in height, found throughout the greater part of India up to an altitude of 1200 m.

The tree reproduces naturally by seeds which germinate in the beginning of the rainy season. Artificial reproduction may be done by sowing the seeds in nursery during March–April and planting the seedlings in the first or second rainy season.

The root bark, yellow to grey in color, is a well known drug in Ayurvedic system. The stem and root bark contain three coloring matters viz. Chrysin (0.35%); Oroxylin A (5:7-dihydroxy 6-methoxyflavone,  $C_{16}H_{12}O_5$ ; mp 219–220°C); and Baicalein, (5:6:7-trihydroxyflavone,  $C_{15}H_{10}O_5$ ; mp 265–266°C).

*Pinus roxburghii* Sarg. (Pinaceae)

syn. *P. longifolia* Roxb.

English – Chir Pine, Himalayan Long-Leaved Pine; Hindi – Chir, Chil, Sarala

It is a tall tree, found in the Himalayas from Kashmir to Bhutan and in the Siwalik hills at altitudes of 450–2,400 m.

Natural regeneration of the chir takes place through seeds which germinate as soon as sufficient moisture is available.

Artificial regeneration of chir is done through the transplantation of nursery-raised seedlings or by direct sowing. Seeds are sown in nursery during March–April. The seedlings are picked out in July. One or two year old seedlings are transplanted at the beginning of rains. The pine needles and the bark yield a yellow coloring matter chrysin.

*P. wallichiana* A.B. Jackson

syn. *P. excelsa* Wall. ex D. Don.

English – Blue pine, Bhutan Pine; Hindi – Kail

It is a tall, evergreen tree with spreading or drooping branches, found in the Himalayas from Kashmir to Bhutan at altitude of 1800–3,700 m. Blue pine also regenerates as *P. roxburghii* Sarg.

The bark and the needles yield a fair amount of coloring matter and are sometimes used for dyeing silk and wool. It gives a fine yellow color on corah silk, and deep orange color on wool.

*Populus nigra* L. var. *italica* Koehne (Salicaceae)

English – Lombardy Poplar; North West Himalayas – Frast, Farsh, and Sufeda

It is a large tree, up to 30 m tall and 3 m in girth, with a narrow pyramidal crown and viscid buds, cultivated in the north-west Himalayas at altitude of 900–3,700 m; also planted in avenues, especially in Kashmir.

The plant rarely flowers in India and is raised from stem or root cuttings, and also from root suckers, which are produced after the tree is cut down.

The leaf buds yield a yellow coloring matter, chrysin (0.25%). It also contains a small amount of second coloring matter tectochrysin (chrysin monoethyl ether) along with chrysin.

*Scutellaria galericulata* L. (Lamiaceae)

English – Scullcap

It is an erect, perennial marsh plant, 70–100 cm tall, growing in small clusters in Kashmir at elevations of 1,500–2,400 m. Its leaves contain coloring matter chrysin along with other flavonoid glycoside, scutellarin and pyrocatechol tannin (2.9–3.5%).

## For further reading

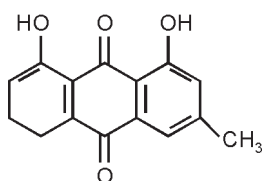
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## 6.22 Chrysophanic acid

Chrysophanic acid also known as Chrysophanol (1,8-Dihydroxy-3-methyl-9, 10-anthracenedione;  $C_{15}H_{10}O_4$ , mp 196°C), the principal yellow coloring matter, occurs in the free state as well as in the form of chrysophanol (1,8-Dihydroxy-3-methylanthraquinone) in several species of the genera *Chamaecrista* (L.) Moench, *Cassia* L., *Senna* Mill., *Rumex* L.,



*Rheum* L., *Asphodelus* L., *Frangula* Mill., and in the lichen *Parmelia parietina*. Chrysophanol, on oxidation, yields chrysophanic acid, the coloring principle. It is slightly soluble in water and petroleum ether but fairly soluble in organic solvents like alcohol, benzene, chloroform, ether, glacial acetic acid, acetone, and in solutions of alkali hydrides, and in hot solutions of alkali carbonates. It gives a pale yellow solution which turns red on adding alkali and sulphuric acid.



Chrysophanic Acid

### 6.22.1 Extraction

For the extraction of the dye, the plant material is ground into powder and extracted with ethyl alcohol (95%) or benzene. The alcoholic extract is treated with alcoholic KOH, followed by extraction from the acidic medium with ether. In addition, the alcoholic extract is treated with dil. HCl gives brown powder which affords, after purification – a mixture of pure free anthraquinones. With the help of the chromatography, the chrysophanol is separated along with other anthraquinones like bichrysophanol, aloë-emodin, emodin, and a chrysophanol glycoside.

### 6.22.2 Uses

Chrysophanic acid dyes the wool yellow directly, but red on the chrome mordant. It is also used in conjunction with lawson, derived from henna (*Lawsonia innermis* L.) for blonde hair dyes. Chrysophanic acid has anticancer activity. It is also reported to be used as skin diseases.

### 6.22.3 Sources

*Asphodelus tenuifolius* Cav. (Liliaceae)

English – Asphodel; Gujarati – Dungrun; Hindi – Bokar, Pyajhi; Punjabi – Binghar-bij, Bokar, Piazi

It is erect, glabrous, and annual with short rhizomes, found abundantly as a field weed and often as a troublesome weed of cultivation in most parts of the plains from West Bengal westwards to Gujarat and Punjab.

It grows extensively in wheat fields and fallow lands in the winter season. It contains chrysophanol which on oxidation yields chrysophanic acid, the principal coloring matter.

*Chamaecrista absus* (L.) H. S. Irwin and Barneby (Fabaceae)

syn. *Cassia absus* L.

Gujarati – Chimar, Chimed, Chinol; Hindi – Banar, Chaksu; Malayalam – Karinkolla; Marathi – Kankuti; Sanskrit – Arangakulitthika, Drikaprasada, Kulanasha; Tamil – Edikkol, Karunkanam; Telugu – Channupaalavittulu

It is an erect, annual herb, covered with grey, bristly, viscous hairs, distributed almost throughout India, and ascending up to 1,500 m in the Himalayas.

The root yields the chrysophanol which on oxidation gives chrysophanic acid, the principal coloring matter.

*Cassia fistula* L.

English – Golden-shower, Indian Laburnum; Bengali – Amultas, Banderlati Sundali; Gujarati – Garmalo; Hindi – Amaltas, Bandarlauri; Kannada – Kakkemara, Rajataru; Malayalam – Kanikonna, Karitmalam, Svarnaviram; Marathi – Bahava, Boya, Chimkani; Oriya – Soturongulo, Sunari; Sanskrit – Aragwadha, Kritmala, Svannavriksha; Tamil – Arakkuvadham, Konnei; Sarak-kondai; Telugu – Aragvadamu, Kolaponna, Rellachettu; Urdu – Amaltas

It is a medium-sized tree, up to 24 m in height, found both in wild and cultivated areas almost throughout India. It contains bright yellow, pendulous flowers; cylindrical, pendulous smooth, hard, dark brown or black pods.

The plant grows under a wide range of climatic and edaphic variations. It is found in a variety of geographical formations, and can grow on poor, shallow soil.

The plant can be regenerated either through direct sowing or transplanting the nursery raised seedlings or stump-planting. The seeds are sown in seedbeds in March or April, and regularly watered. The seeds take 6–52 days to germinate. Transplantation of 15–30 cm tall seedlings is done during the rainy season.

The leaves and wood contain chrysophanol which on oxidation yields chrysophanic acid, the principal coloring matter.

*Cassia grandis* L.f.

English – Brazilian-Cassia, Coral-or Pink-Shower, Horse-Cassia; Kannada – Dodda-dogare

It is a small-or medium-sized tree, up to 15 m tall, native to tropical and Central America, and the West Indies, later introduced into India and grown for ornamental purpose in gardens and avenues, and also for shade.

Seeds contain chrysophanol which on oxidation yields chrysophanic acid, the principal coloring matter.

*C. italica* (Mill.) Lam. ex F.W. Andr.

syn. *C. obovata* Collad.

English – Country Dog, Italian, Jamaican, Senegal, Spanish or Sudan Senna; Gujarati – Bhony-Awal, Mindiawel, Surati-sonamukhi; Hindi – Chhota-taroda; Kannada – Kadusoonamukhi, Nelavareke; Malayalam – Seruvanni, Sunnamaki, Vattantakara; Marathi – Bhonya taravad, Mendial; Sanskrit – Bhuniyathuli, Bhutalapota; Tamil – Kuttunilavarai, Nilavearai, Vellaipponnavarai, Telugu – Neelaponna, Sunamukhi; Rajasthani – Bhinda-anwal, Goral, Sonamukhi

It is a perennial, 30–120 cm tall herb, found in Punjab, Delhi, Rajasthan, Madhya Pradesh, Gujarat, Maharashtra, Karnataka, Kerala, and Tamil Nadu, up to an altitude of 300 m.

The leaves and pods yield chrysophanol which on oxidation gives chrysophanic acid, the principal coloring matter.

*C. javanica* L.

English – Apple-Blossom Senna, Javanese Cassia; Hindi – Java-Kirani; Marathi – Mazeli; Tamil – Konne, Vakai

It is a beautiful, small or medium sized tree with widely spreading and almost horizontal branches, showy blossoms and is native to Java, introduced into Indian gardens, found mainly in and around Central India.

The leaves and seeds contain chrysophanol which on oxidation gives chrysophanic acid, the principal coloring matter.

*C. occidentalis* L.

English – Coffee-Senna, Foetid Cassia, Negro-coffee, Rubbish Cassia, Stinking-week; Bengali – Kalkashunda; Gujarati – Kasodari, Kasundari; Hindi – Badikasondi, Chakunda, Kasonda; Kannada – Anecogate, Doddtagase; Malayalam – Natramtakara, Ponnnaviram; Marathi – Kasonda, Rankasvinda; Oriya – Kasundri; Sanskrit – Kasmarda; Tamil – Ponnnavarai, Ponthagarai; Telugu – Kasinda, Pedda-Kasinda; Urdu – Kasonji

It is an erect, fetid, annual herb or under shrub, 60–150 cm in height, found throughout India, up to an altitude of 1,500 m.

The leaves, seeds, and roots contain chrysophanol which on oxidation yield chrysophanic acid, the coloring matter.

*C. roxburghii* DC.

syn. *C. marginata* Roxb.

English – Ceylon Senna, Red Indian Laburnum; Malayalam – Katakkon; Tamil – Karungondrai, Kondaru, Vagai; Telugu – Erramunga, Simareelachettu, Urimidi

It is a small or medium sized tree, found in most parts of Central and Southern India; often planted for ornament and along the roads for shade.

The leaves, wood, and seeds contain chrysophanol the precursor of chrysophanic acid, the principal coloring matter.

*Rheum australe* D. Don. (Polygonaceae)

syn. *Rheum emodi* Wall. ex Meissn.

English – Himalaya Rhubarb, Indian Rhubarb; Bengali – Bangalarevanchini; Gujarati – Gamni-revanchini; Hindi – Hindirevanchini, Dolu; Kannada – Nat-reva-chinni, Revalchini; Ladakh – Lachu; Marathi – Mulka-charevalchini; Punjabi – Chutail, Chuki, Lachu, Rewand-chini; Telugu – Nattupasupu-chinuigadda, Nattu-revalchini; Tamil – Nattu-ireval-chinni, Nattu-manjal-china-kizhangu

It is a stout herb, 1.5–3.0 m in height, distributed in the Himalayas from Kashmir to Sikkim at an altitude of 3,300–5,200 m. It is also cultivated in Assam for its leaves as a vegetable.

This plant is the main source of the Himalayan rhubarb drug. Annually roots are dug out in huge quantity from Himachal Pradesh, Kumaun, Sikkim, and Nepal. It has been suggested to cultivate it in its natural geographical regions to meet its essential requirements.

The herb is drought-resistant and can be propagated either through rhizome cuttings or seeds, the former method is preferred. The cuttings are planted in early spring at a spacing of 1.2–1.5 m. The rhizomes and roots are dug up in September from 3 to 10 years old plants.

Indian rhubarb is used as a purgative and astringent tonic. The root is used along with madder (*Rubia tinctorium* and *R. cordifolia*) and potash for dyeing fabrics in red color.

The rhizome contains chrysophanol, which on oxidation yields chrysophanic acid, the coloring principle. Besides chrysophanol, it also contains emodin, aloe-emodin, rhein, and gallic acid.

*R. rhaponticum* L.

English – Rhapontic Rhubarb, Pie-Plant, Garden-Rhubarb

It is a perennial herb, probably indigenous to Southern Siberia and China, extensively cultivated for its edible roots all over Europe and America. In India, it is cultivated to a small extent in the Khasi hills in West Bengal and Nilgiri hills.

The root-stocks contain chrysophanic acid, the principal coloring matter.

*Rumex acetosa* L. (Polygonaceae)

English – Garden Sorrel; Bengali – Chukapalam; Hindi – Khatta Palak

It is an erect, perennial herb, found in Western Himalayas from Kumaun to Kashmir at 2,400–3,600 m elevation.

The root contains chrysophanic acid (3.3% on dry basis), which is used to dye wool red when mordanted with chromium.

*R. crispus* L.

English – Yellow Dock, Curled Dock

It is a perennial, erect, and glabrous herb, 50–100 cm tall, native of Europe and reported from Mt-Abu in India.

The root contains chrysophanic acid and emodin. It also contains rumicin, an isomeric of chrysophanic acid.

*R. dentatus* L.

Hindi – Ambavah, Amrule, Lal bibi, Jangli Palak

It is an erect, deep rooted, annual herb, 30–100 cm in height, found in the Himalayas up to an altitude of 300 m, and in the plains from Assam to Western and Southern India. It contains *red-colored* root and grooved stem.

Roots contain chrysophanic acid and emodin. They yield a dye and are also used as astringent applications in coetaneous disorders.

*R. maritimus* L.

English – Golden Dock; Bengali – Bun-Palung; Hindi – Jub-Palum, Jangli-Palak; Punjabi – Khattikan, Bijband

It is a stout, erect, annual plant, 30–120 cm high, occurring in the temperate Himalayas and on wet grounds along the river banks in the plains of North India and in marshes in Assam and Bengal, Western Ghats, Nilgiri, and Palni hills at 1200–1300 m elevation.

Its roots contain chrysophanic acid, the principal coloring matter.

*R. nepalensis* Spreng.

Bengali – Pahari Palang; Kashmiri – Palak; Kumauni – Kulii

It is a tall, robust, annual or perennial plant, 60–120 m tall, found in temperate Himalayas from Kashmir to Bhutan and in the Western Ghats, Nilgiri, and Palni hills at altitudes between 1,200 and 2,700 m.

The root contains chrysophanic acid, the yellow coloring matter. Besides chrysophanic acid, the root also contains nepodin ( $C_{18}H_{16}O_4$ ; mp 158°C) a derivative of protocatgechuic acid. It is also contains tannin (12%) which can be used for tanning purposes.

*Senna alata* (L.) Roxb. (Fabaceae)

syn. *Cassia alata* L.

English – Candlebush, Candlestick senna, Ringworm Senna; Bengali – Dadmardan, Dadmari; Hindi – Dadmurdan, Datkapat, Senamakhi, Vilaytie aghatea; Kannada – Dood-dastangade, Seemal-agasae; Malayalam – Puzhukadi-konna, Seemagati; Marathi – Dadmardana; Oriya – Dadumorddona,

Jadumari; Sanskrit – Dadhrugna, Dvipagsti; Tamil – Malanthakerai, Seemai-agathi; Telugu – Seematangeedu, Simaavisa

It is a large, handsome shrub or a small tree, introduced into India from West Indies and cultivated in the gardens, and also found wild almost throughout India and in Andaman Islands. It contains bright yellow flowers in dense panicle racemes, and 10–20 cm long winged pods.

The leaves and the seeds contain chrysophanol which on oxidation yields chrysophanic acid, the principal coloring matter.

*Senna auriculata* (L.) Roxb.

syn. *Cassia auriculata* L.

English – Tanner's Cassia, Tanners Senna; Gujarati – Aval; Hindi – Awal, Tarval; Kannada – Ararike, Ollehangadi; Malayalam – Avara, Aviram, Ponnnaviram; Marathi – Assual, Taravada; Sanskrit – Avartaki, Hemapushpam, Mayahari; Tamil – Avaram, Semmalai; Telugu – Merakatangeedu, Tangeedu; Rajasthani – Anwala

It is a much branched shrub, with auricled or rotunda-semi form leaves and yellow flowers, found in the dry zones of Southern, Western, and Central India extending up to Rajasthan in the north. It is also cultivated in some parts of Punjab, Haryana, Uttar Pradesh and West Bengal, and often planted in gardens for ornamental purpose and as hedges.

It is a fast growing plant. Its rate of growth is 45–53 cm in a month and 1.4–2 m in a full season. The flowers appear from October to May and fruits are available from January to June. Seeds are viable for about 10 months and they take about 15 days to germinate.

The pod yields chrysophanol, which on oxidation gives chrysophanic acid, the principal coloring matter.

*Senna didymobotrya* (Fresen.) H.S.Irwin and Barneby

syn. *Cassia didymobotrya* Fresen.

It is a shrub or a small tree of 2.5–3.0 m height, occasionally reaching 6 m, native of East Africa, introduced into India for ornament, found both as cultivated and wild in Tamil Nadu and also found in Dehradun and Delhi. It contains orange-yellow flowers and flat hairy pods.

The leaves contain chrysophanol which is converted into chrysophanic acid, the principal coloring matter. Besides chrysophanic acid, the principal coloring matter and chrysophanol, leaves also contain aloe-emodin and rhein, other coloring matters.

*Senna floribunda* (Cav.) H.S.Irwin and Barneby

syn. *C. floribunda* Cav.; *C. laevigata* Willd.

English – Hill-Cassia, Smooth-Senna, Wild-Senna

It is a shrubby herb, 1.0–1.3 m in height, introduced into India from Tropical America, now naturalized and found wild in the hills of Uttar Pradesh, Punjab, West Bengal, Sikkim, Meghalaya, Manipur, Karnataka, and Tamil Nadu, up to an altitude of 1,650 m.

The pods and seeds yield chrysophanol which on oxidation yields chrysophanic acid, the principal coloring matter.

*Senna obtusifolia* (L.) H. S. Irwin and Barneby

syn. *Cassia obtusifolia* L.; *C. tora* Baker.

Mundari – Cakonda, Huring; Konkani – Daba; Rajasthani – Pandia, Pumarai; Santal – Chakaodaorak; Uttar Pradesh – Banarh, Chakwar, Rosangi

It is an annual herb or under shrub, distributed from Jammu and Himachal Pradesh to West Bengal and in Orissa, Madhya Pradesh, Rajasthan, Gujarat, and Maharashtra, up to an altitude of 1200 m.

Seeds and roots contain chrysophanol which oxidize into chrysophanic acid, the principal coloring matter.

*Senna alexandrina* Mill.

syn. *Cassia senna* L. var. *senna*; *C. acutifolia* Delile; *C. angustifolia* Vahl; *C. obovata* Baker.

English – Alexandrian, Bombay or Tinnevely Senna; Bengali – Sannamakki, Sonpat; Gujarati – Middiawal, Sennamakki; Hindi – Bhuikhakhasa, Hindsona; Kannada – Nelavarike, Soonamukhi; Malayalam – Nilavaka, Sunamukhi; Marathi – Bhuitarvada, Shonamukhi; Oriya – Shonamukhi; Sanskrit – Bhunuari, Pitapushpi, Swarnamukhu, Swarn-patrika; Tamil – Nattunelavarai, Nelavagai, Sooratrnila avarai; Telugu – Neelaponna; Rajasthani – Senna

It is a variable, branching, erect shrub, up to 1.8 m in height, introduced into India, naturalized in some parts and also cultivated.

The plant is cultivated for its glycoside, sennosides which is a well known medicinal glycoside. It is highly drought resistant and may be suitable for deserts. It is largely cultivated on marginal lands in about 10,000 ha in Tamil Nadu where it is grown as a cash crop in Tirunelveli, Ramanathapuram, Tiruchchirappalli and Madurai districts and also cultivated in Andhra Pradesh, Karnataka and Maharashtra.

The leaves, pods, seedlings, and roots contain chrysophanol (2.8%) which on oxidation yields chrysophanic acid, a principal coloring matter.

*Senna siamea* (Lam.) H.S.Irwin and Barneby

syn. *Cassia siamea* Lam.

English – Tron wood Tree, Siamese Senna; Bengali – Minjri; Gujarati – Kasid; Kannada – Hiretangadi, Sima-tangedu; Marathi – Kassod; Tamil – Manja-konnai; Telugu – Sima-Tangeudu; Tripura – Minjori, Mirjiri

It is a small or medium sized evergreen tree, 6–18 m in height, commonly found from Punjab to Arunachal Pradesh and Tripura, extending into Peninsular India, up to an altitude of 1,220 m and also in Andaman Islands.

The tree is propagated either through direct sowing or transplanting. The former is the best method for raising plantations. The seeds germinate in about 10 days. They are sown in beds and transplanted when they are 15–30 cm high.

The leaves, stem-bark, root-bark, and heartwood yields chrysophanol, which on oxidation gives chrysophanic acid, a principal coloring matter.

*Senna sophera* (L.) Roxb.

syn. *Cassia sophera* L.

English – Pepper leaved Senna, Senna Sophera; Bengali – Kalkashunda; Gujarati – Kasundari, Kuwadice; Hindi – Banar, Kasondi, Kasunda; Kannada – Kasamarda; Malayalam – Ponnantagara-ela; Marathi – Kasondi, Ratankala; Oriya – Kasundri, Kolakasunda; Sanskrit – Kasamanda, Suvarnamayaheri; Tamil – Nalal, Peravirai, Ponnavairei, Sularai; Telugu – Konda Kasinda, Nooti-kasinda, Paiditangeedu; Urdu – Kalkasonji

It is a diffuse, sub-glabrous shrubby herb or under shrub, found throughout India, ascending to the Himalayas, up to an altitude of 750 m.

The flowers, heartwood, and root-bark contain chrysophanol, which on oxidation yields chrysophanic acid, the principal coloring matter.

*Senna tora* (L.) Roxb.

syn. *Cassia tora* L.

English – Foetid Cassia, Sicklesenna, Wild Senna; Bengali – Chakunda, Panevar; Gujarati – Kawario, Konaria; Hindi – Chakavat, Chakunda, Panevar; Kannada – Gandutogache, Taragasi; Malayalam – Chakramandarakam, Takara; Marathi – Takala, Tankli, Tarota; Oriya – Chakunda; Sanskrit – Chakramarda, Dadamari, Prisnaparni; Tamil – Senavu Tagarai, Vindu; Telugu – Chinnakashinda, Tellakasinda

It is a fetid, annual herb or under shrub, found as weed throughout India, ascending up to an altitude of 1,550 m in the Himalayas.

Seeds contain chrysophanol which is then oxidized into chrysophanic acid, a coloring matter. Seeds have also been used to dye clothes yellow, blue, and red.

## For further reading

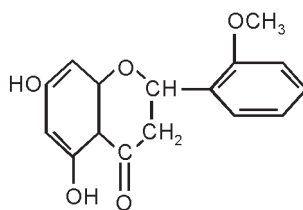
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## 6.23 Citronetin

Citronetin (5,7-Dihydroxy-2-methoxy-flavone;  $C_{16}H_{14}O_5$ ; mp 224–225°C), the yellow coloring matter occurs in the peels (rind) of the fruit of Bergamot Orange, *Citrus medica* L. and Lemon, *Citrus lemon* (L.) Burm. f. in the form of a glycoside, citronin (5-hydroxy-2-methoxyflavone 7-rhamnoglucoside;  $C_{28}H_{34}O_{14}$ ; mp 235°C). Citronin on heating with alcohol (50%), containing phosphoric acid  $H_3PO_4$  (5%) and water, at 110°C for three hours yields the coloring matter citronetin. It is soluble in alcohol but insoluble in water.



Citronetin

## 6.23. Extraction

Air dried peel is extracted with alcohol (80%) at 60°C and the alcohol is distilled off. Thus a powder of the glucoside citronin is obtained. It is then boiled with alcohol (50%) which contains phosphoric acid ( $H_3PO_4$ ; 5%) at 110°C for three hours and then poured into water. Then it yields citronetin. It is further crystallized with alcohol.

### 6.23.2 Uses

Citronetin has been used to dye silk in India.

### 6.23.3 Sources

*Citrus medica* L. (Rutaceae)

syn. *Citrus aurantium* L. var. *bergamia* (Risso) Brandis; *C. bergamia* Risso and Poit.

English – Bergamot Orange

It is a small to medium sized thorny tree of irregular growth habit with pale green leaves, white, fragrant flowers, yellow, round or slightly necked fruits, thin rind. It is of Mediterranean origin, rarely met within India. It is a source of Bergamot oil, a base for toilet waters and perfumes.

The rind of the fruit is reported to contain citronin, a glucoside of citronetin which is a yellow coloring matter.

*Citrus limon* (L.) Burm.f.

English – Lemon; Bengali – Baranebu, Goranebu; Gujarati – Motu Limbu; Hindi – Baranibu, Jambira; Kannada – Bijapura, Bijuri; Marathi – Idalimbu, thoralimbu; Tamil – Malai Elumichai; Telugu – Bijapuram

It is a medium sized, thorny tree with purple flowers in the bud, native to India, commonly cultivated throughout the country.

The rind of the fruit is reported to contain the glycoside citronin which on hydrolysis yields a yellow coloring matter citronetin.

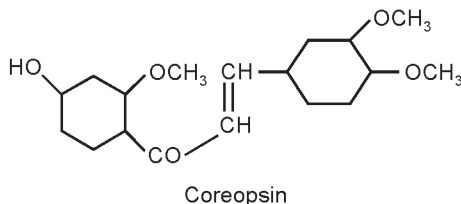
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### 6.24 Coreopsisin

Coreopsisin (4'-glucoside;  $C_{21}H_{22}O_{10}$ ; mp 190–95°C), a glucoside of butein, is the principal yellow coloring matter that occurs in the flower heads of *Cosmos sulphureus* Cav., *Coreopsis basalis* (A. Dietr.) S. F. Blake and yellow dahlia, *Dahlia pinnata* Cav. It also occurs as a glucoside of butein, the coloring principle present in the flowers of palas, *Butea monosperma* (Lam.) Kuntze.

Coreopsin gives an olive-brown color with ferric chloride and deep-red color with alkalis.



### 6.24.1 Extraction

The flower heads are boiled in water for 10–15 min and filtered. The aqueous solution is treated with neutral or basic lead acetate solution by which a precipitate is obtained. The precipitate is suspended with rectified spirit and then decomposed with hydrogen sulphide. Thus a clean glucoside solution is obtained. This solution is concentrated and repeatedly recrystallized from aqueous methanol. Thus, an amorphous yellow coreopsin is obtained.

### 6.24.2 Uses

Coreopsin is used to dye wool and cotton yellow without any mordant but on alum and chrome mordanted wool it gives yellow to bronze-gold and orange color respectively. It is also used to dye food stuffs and pharmaceutical preparations.

### 6.24.3 Sources

*Coreopsis basalis* (A. Dietr.) S. F. Blake (Asteraceae)

syn. *Coreopsis drumondii* Torr. and Gray; *C. picta* Hort; *C. tinctoria* Nutt

English – Golden Wave

It is a 40 cm tall, glabrous to hispid annual herb with 1–3 pinnate leaves, yellow flowers, native to Texas, grown in gardens in India as an ornamental plant in winter season.

*Cosmos sulphurius* Cav. (Asteraceae)

It is a pubescent, annual plant of about one meter height, with orange-yellow flowers, native of Mexico, and is commonly grown in Indian gardens during the summer season. Besides coreopsin, flower heads contain luteolin, quercetin glucoside (iso-quercitrin), and sulphuretin, the other coloring matters.

*Dahlia pinnata* Cav. (Asteraceae)

It is a genus of tuberous rooted perennial herbs with showy flowers, cultivated in gardens for its beautiful flowers of various colors.

The flowers have an extraordinarily strong dye in their petals. The color varies with the color of the petals, from yellow to orange-red. One can get a dye from the flowers which are ready to be thrown out after a week in a flower vase. Thus, the flowers of Dahlia serve a double purpose as for beauty as well as dye.

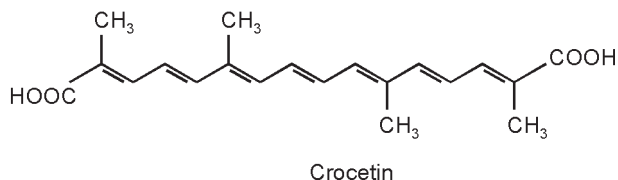
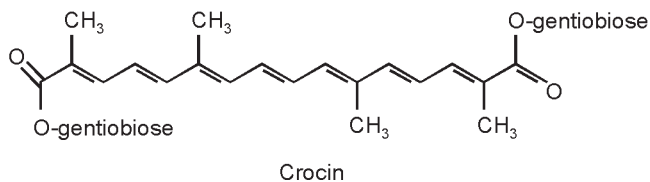
Besides coreopsin, flower head of Dahlia also contains other coloring principles like apigenin, luteolin, diosmetin and butein. Besides above mentioned anthoxanthins, some anthocyanins (3.1–4.2%) like pelargonidin, delphinidin-3, 5-diglucoside, malvidin and cyanidin-3-glucoside have also been isolated from the Dahlia flowers. Thus, the color extracted from Dahlia flowers is highly soluble in water and alcohol, and contains 36–38% dry matter and 55–60 mg/kg of coloring substances. Since the preparation was not found toxic at 10 g/kg; and did not contain heavy metals, it has been recommended for the use as a substitute for amaranth for coloring pharmaceutical preparations. It is efficient for coloring confectionery, bakery products, syrups, beverage and other food products and pharmaceutical preparations.

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### 6.25 Crocin and crocetin

Crocin, (8,8'-Diapo- $\gamma$ ,  $\gamma$ -carotenedioic acid bis(6-O-b-D-glucopyranosyl-b-D-glucopyranosyl) ester; a-crocin; di-gentiobiose ester of crocetin ( $C_{44}H_{64}O_{24}$ ; mol wt 977.00). Crocin ( $C_{44}H_{64}O_{26}$ ; mp 186°C) the principal coloring matter found as a glycoside in the stigmas of Saffron, *Crocus sativus* L., fruits of Unki, *Gardenia jasminoides* J. Ellis and the flowers of Night Jasmine, *Nyctanthes arbor-tristis* L., and Indian Mahogany tree or Toon, *Toona ciliata* M. Roem. Crocin, a water soluble pigment is a digentiobioside ester of crocetin. On hydrolyses, crocin yields digentiobiose and the carotenoid pigment crocetin ( $C_{20}H_{24}O_4$ ; mp 285–287°C), a dicarboxylic acid. Crocin is freely soluble in hot water giving an orange-colored solution. It is sparingly soluble in absolute alcohol, ether, and other organic solvents.



### 6.25.1 Extraction

Crocin is extracted when dried stigmas of saffron or fruits of unki or wongsky or flowers of night jasmine or toon are pulverized in water and heated at 50°C for two or more hours and filtered. The filtrate is used either as such, or it can be solidified under reduced pressure and redissolved in methyl alcohol and then isolated through chromatographic methods.

### 6.25.2 Uses

Crocin finds its applications in coloring food stuffs. It is capable of dyeing wool, silk, and cotton directly with optional mordanting by alum or tin. Colors obtained are sulphure-yellow and a magnificent orange-yellow. In England, saffron was formerly used for dyeing silk and glove leather. Unki is used to dye silk and wool directly golden-yellow and orange; tin mordanted cotton is dyed orange. It is also used as a constituent of scarlet.

Wongsky is used in China for yellow, as a component of greens and in conjunction with safflower for dyeing textiles; combined with turmeric used to produce the sulphur yellow or *basanti*. The flowers of night jasmine boiled with aqueous potash and lemon juice yield a bright golden-yellow, a direct cotton dye used in India. However, toon flowers are used as yellow, red, and brown dye in India.

### 6.25.3 Sources

*Crocus sativus* L. (Iridaceae)

English – Saffron, Meadow-crocus; Bengali – Jafran, Kesur; Gujarati and Marathi – Kesar; Hindi – Kesar, Kumkum; Kannada – Kasari, Kum kuma,

Kash.-Kong.; Malayalam – Kum kumapurva; Sanskrit – Agnishikha, Kesara, Kumkuma; Tamil – Kum kum, Kungumapu; Telugu – Kum kumapuru; Urdu – Zaafran, Zaafranekar

It is a perennial herb of 28–45 cm height, native to Southern Europe and Asia Minor; cultivated in Jammu and Kashmir at 1700–1900 m height. It is also introduced and successfully cultivated on the hills of Himachal Pradesh and Uttar Pradesh.

The name of the plant comes from the Arabic word *Zafaran*, meaning yellow. It is believed to have originated in Greece, Asia Minor, and Iran, wherefrom it spread east wards to North India and China. Saffron is cultivated in Spain, France, Italy, Greece, Turkey, India, Japan, China, Australia, Germany, and Switzerland. Spain is the largest producer and accounts for 90% of the world production.

During the Greek and Roman times, saffron enjoyed a variety of uses. Not only was it their principal dye of the ancient times, it was also extensively used as a spice, as an ingredient of medicinal formulations, and as a perfume in public baths. Latter in the Middle Ages, it was found that when used as a mordant on paper with iron, realistic emulation gold could be obtained. This made possible the beautiful illuminated manuscripts which were produced by monasteries, and which are still treasured as valuable art works.

#### 6.25.4 Cultivation

The crop thrives well in cold regions with a warm or subtropical climate, at altitudes of 1,500–2,400 m, but it flourishes and blooms best up to 2,100 m. The best saffron is produced when the weather is dry and not very humid at the time of flowering. It needs moisture during the spring, moderate showers during the summer and bright, cool, and dry autumn for flowering.

Saffron requires a rich, well drained, sandy or loamy, and alkaline soil. Once the crop is established, no manure or fertilizer is required. However, timely application of farmyard manure, ammonium sulphate, superphosphate, and potassium nitrate or potassium sulphate improve the yield.

The crop is propagated through corms or bulbs. They remain dormant during May–August. Before planting, corms are peeled and exposed to the sun and dipped in copper sulphate solution (95%) to protect them from soil born diseases. Pre-treatment of corms with gibberellic acid (100 mg/l) or a single application of the apical notch (100 or 500 g/corm) for 4 h at the time of transplanting increases the yield of saffron. The corms are planted in rows in the months of July–August. About 5 tonnes of corms are needed for a hectare. After a month, the corms start sprouting and about two months later, the plant comes in bloom. Each plant produces three flowers in succession.

Saffron remains in bloom only for 15 days. The flowers are harvested in the morning before the sun becomes too hot, as this stage yields maximum saffron. The flowers are collected on alternate days and are cut close to the ground. The flowers are cleaned and the stigmas are separated from the perianth on the same day. They are then dried in thin layers in air under shade or in warm furnace. Approximately 100,000 flowers give nearly 5 kg of fresh stigmas, reduced to 1 kg on drying, containing about 10 g crocin and 60 g crocetin as actual dye components.

The stigma contains a water soluble yellow dye with a very high tinctorial power. The principal pigment is crocin, the digentiobiose ester of crocetin. It is accompanied by small amount of lycopene, carotene, carotene, and zeaxanthin.

### 6.25.5 Sources

*Gardenia jasmanoides* J. Ellis  
syn. *G. florida* L.

English – Cape jasmine; Bengali, Hind, Oriya, and Sanskrit – Gandhraj, Unki; Marathi – Karinga

It is a variable evergreen shrub or a small tree, native to China and Japan, commonly cultivated in Indian gardens. It has large, double, creamy white and highly fragrant flowers, and an ovoid about 5 cm long, fleshy, ribbed, orange-colored fruits. The plant is propagated easily by cuttings and layering during rainy season.

The fruit contains water soluble and a red amorphous coloring matter, crocin. The water extract of the fruits is reported to be used in China for dyeing fabrics yellow or scarlet.

It is a green dye that can also be obtained from the extract of the fruits. The dried fruits are pulverized in water and heated at 50°C for about 8 h. It is then filtered and concentrated under reduced pressure. The same extract is redissolved in water in the ratio of 10 g of extract and 500 ml of water and adjusted to pH 5 and treated with the enzyme acylase for 45 h followed by heating at 90°C for 15 min to inactivate the enzyme. It is again concentrated under reduced pressure and stirred with 92% Ethyl alcohol and water (75:25) and allowed to stand for separation. The bottom layer (solid phase) is recovered for use as a blue color, which has been recommended as a colorant for foods, pharmaceuticals, and cosmetics (chemical abstract, 1987, 106, 195058).

*Nyctanthus arbor-tristis* L.

English – Night Jasmine, Coral Jasmine; Bengali – Sephalica, Seoli; Gujarati – Jayaparavati; Hindi – Harsingar, Seoli; Kannada – Harsing, Parijata;

Malayalam – Pavizhamalli, Parijat – Akom; Marathi – Khurasi, Parijatak; Oriya – Godokodiko, Gunjo, Seyoli, Singarohari; Sanskrit – Parijata, Sephalika

It is a shrub or small tree, up to 10 m in height, native of India, occurring wild in the sub-Himalayan region from Chenab to Nepal up to 1500 m of altitude, and in Chhota Nagpur, Rajasthan, Madhya Pradesh, and South wards of Godavari. It is cultivated in gardens almost throughout India for its fragrant flowers. The plant is easily propagated by seeds or cuttings. The plant blooms from August to December and remains leafless from April to May. It contains white colored flowers of which corolla tube is bright orange in color.

A bright golden-yellow color, fast to light and washing is obtained from the corolla tube of its flowers. The corolla tube contains a pigment, first named nictanthin, which was subsequently found to be the same as crocin, the pigment found in saffron. It occurs in the material in a concentration of 0.1%, probably as a glucoside.

Cotton, silk, and tussar are dipped in the hot or cold decoction of the flowers, followed by mordanting with alum and lemon juice to dye in a yellow buff color. The dye is often dyed in combination with turmeric and indigo.

*Toona ciliata* M. Roem. (Meliaceae)

syn. *Cedrela tonna* Roxb.

English – Toon, Red Cedar, Moulmein Cedar, Indian Mahagony Tree; Assamiz – Pama; Bengali and Hindi – Gunari, Tun, Mahanim; Kannada – Mandurike; Malayalam – Malaveppu; Marathi – Kuruk; Tamil – Santhanavembu, Tunumarum; Telugu – Nandichettu; Sanskrit – Nandivriksha, Tunna

It is a large tree, attaining a height up to 35 m and a girth of trunk up to 3 m, found in the sub-Himalayan tracts and outer Himalayas up to an altitude of 1500 m and in Assam, Bengal, Chhota Nagpur, in Western Ghats and other hills of Deccan peninsula.

The plant flourishes best in deep, rich, moist, and loamy soil. It is a moderate light demander. Young plants need protection from sun. The plants are raised by the seeds that are collected in May from the tree and sown in raised nursery beds during rainy season.

Flowers contain a flavonic-yellow pigment quercetol, some phlobaphenes or tannic acid originating from the condensed tannins and particularly an orange-red dye, identical to crocin or crocetin.

Colors obtained are yellow, red, and brown that are fast to light. In India, the decoction of the flowers served to dye silk and cotton directly in yellow and red colors. This dye is known as gunari or gulfari in Bengal.

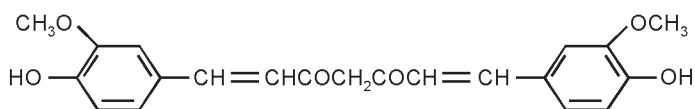


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## 6.26 Curcumin

Curcumin ( $C_{21}H_{20}O_6$ ; mp  $183^{\circ}\text{C}$ ), the principal yellow coloring matter, occurs in the rhizomes of Turmeric, *Curcuma longa* L., *C. amada* Roxb., *C. aromatica* Salisb., *C. viridiflora* Roxb., and *Boesenbergia rotunda* (L.) Mansf. Curcumin is an orange-yellow compound soluble in water, ethanol, ether, acetone, glacial acetic acid, and petroleum ether. It gives brownish red color with alkalis, and yellow color with acids (pH range 7.4–8.6).



Curcumin

### 6.26.1 Extraction

The powdered rhizomes are refluxed with ethanol for about 8 h and then centrifuged to remove the insoluble fraction. The supernatant is then concentrated in a flash evaporator. The dried material is washed with petroleum ether and recrystallized in hot ethanol. The end product obtained with orange needles is a curcumin.

### 6.26.2 Uses

Curcumin is used for dyeing wool, silk, and unmordanted cotton to which it imparts yellow shade in an acid bath. It is used as a coloring matter in pharmacy, confectionery, and food industry. It is also used to dye paper, which is an official reagent, in the British Pharmacopoeia for testing alkalinity. It also contains antioxidant properties. Curcumin is also used as biological stain. It showed anticancer activity in mice. It is also reported to act as a cholagogue causing the contraction of the gall bladder.

### 6.26.3 Sources

*Curcuma amada* Roxb. (Zingiberaceae)

English – Amada, Mango Ginger; Bengali – Amada; Hindi – Am Haldi; Marathi – Amla-Haldi; Sanskrit – Amargandhi, Karpura, Haridra; Tamil – Mangai cujil; Telugu – Mannidiallam

It is a rhizomatous annual herb that is found in West Bengal, Maharashtra, Karnataka, Tamil Nadu and in the hills of Western Coast.

Mango ginger with the aroma of raw mangoes is grown in kitchen gardens. In the fields it is planted along with turmeric as their cultural requirements are similar. Amada is planted any time from February to June. The seed rate of 1.0–1.5 kg per plot of 3 m × 3 m is required and planted on ridges or flat beds at a depth of 5–15 cm.

Germination begins in two weeks and may continue for a month. The rhizomes are fully formed by the eighth to tenth month. The crop needs copious watering but without the fields getting undated. By the tenth month the leaves start withering, which indicates the maturity of the rhizomes.

Harvesting commences in October and continues till January. The rhizomes are collected, cleaned, and dried in shade. On an average, 10–12 kg per plot of 3 m × 3 m may be obtained or a yield of nearly 10,000 kg/ha at field level is expected with proper cultivation. Rhizome yields curcumin, the coloring matter.

*C. aromatica* Salisb.

English – Wild Turmeric, Yellow Zedoary; Bengali – Ban-Halud; Hindi – Jangli Haldi; Kannada – Kasturi-Arishina; Marathi – Ban-Halada; Tamil – Kasturi-Manjal; Telugu – Kasturi-Pasupu

It is an erect, perennial herb, found throughout India, and also cultivated in some parts of West Bengal and Kerala. It contains yellow, orange, red, and aromatic tubers.

The plant occurs as a weed near tea estates. The tubers are orange-red in color and possess a camphoraceous odor, sometimes used as a substitute for turmeric. Tubers contain the yellow-orange coloring matter curcumin,

demethoxy curcumin, and bis-demethoxycurcumin, which showed anticancer activity against Sarcoma-180 in mice.

*C. longa* L.

syn. *C. domestica* Val.

English – Turmeric; Bengali – Halod; Gujarati – Huldhar, Haldi; Hindi – Haldi; Kannada – Arishina; Malayalam – Manjal; Marathi – Haldi, Halkund; Sanskrit – Haridra; Tamil – Manjal; Telugu – Pasupu

It is an erect, perennial, annual herb, grown in India, China, South-East Asia, Indonesia, and East Indies. In India, it is cultivated in Andhra Pradesh, Tamil Nadu, Kerala, Orissa, Karnataka, West Bengal, Maharashtra, Bihar, and Assam. It is also grown to a small extent in the lower hills of Meghalaya and Himachal Pradesh.

Turmeric was known in India since ancient times. The origin of the turmeric is believed to have been in South-East Asia. The cultivated species are naturalized in some areas of north-eastern parts of India and the island of Java. Turmeric is thought to have reached East-Africa in the 8th century and West Africa in the 13th century. Hence, the crop is distributed throughout the tropical belt.

Turmeric is grown generally as an annual crop. It requires a warm and humid climate. Turmeric thrives in well-drained, fertile, sandy and clayey, black-red or alluvial loams, rich in humus, uniform in texture, and easily workable soil.

The land is deeply dug or ploughed 4–6 times to bring the soil to a fine tilt. Turmeric can be propagated through seeds and rhizomes, but rhizomes are always preferred. The mother rhizomes are cut into two; each having at least one sound bud which is sown in the months of mid April and August. But the short duration varieties are planted in the second fortnight of May; the medium duration ones are planted in the first fortnight of June, and the long duration varieties between 15th June and 15th July. The rhizomes or fingers are planted at 30–35 cm × 20 cm space for beds and 45–60 × 25–30 cm for ridges and furrows. About 2000–2500 kg rhizomes are required for planting a hectare. The crop is ready for harvesting in about 9–10 months when the lower leaves turn yellow. The yield is variable, ranging from 13440 to 24640 kg/ha and sometimes it reaches 28000 kg/ha.

The rhizomes of turmeric contain 1.5–2.0% crystalline coloring matter, the curcumin, diferuloyl methane. It dissolves in concentrated sulphuric acid, giving a yellow-red coloration.

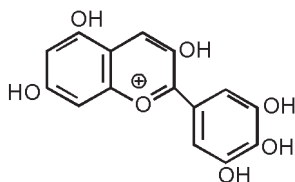
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## 6.27 Delphinidin

Delphinidin, Delphinidole or Awobanin, (3,3',4,5,5',7-Haxahydroxyflavylium;  $C_{15}H_{11}O_7$ ; mp 202–203°C), the principal coloring matter occurs either in free state or in the form of the glycoside, Delphinidine-3, 5-Diglucoside, in the flowers of Azure, *Commelina communis* var. *hortensis* Makino, and *Anemone coronaria* L., fruits and flowers of Black current, *Ribes nigrum* L., leaves of *Cinchona calisaya* Wedd., *Eucalyptus obliqua* L'Hér., and *Eucalyptus regnans* F. Muell., and in seed coat of Pomegranate, *Punica granatum* L. The glycoside 3,5-diglucoside on acid hydrolysis followed by hydrogen peroxide hydrolysis yields delphinidin.



Delphinidin, Delphinidol

### 6.27.1 Extraction

Air dried raw material (leaves, flowers or seed coat) is extracted with methanol and then filtered. The alcoholic extract on hydrolysis with hydrochloric acid furnishes a dark-red color solution. It is concentrated in vacuum, washed with hexane and ethyl acetate and further concentrated and purified through chromatographic methods to get a pure powder of the dye.

### 6.27.2 Uses

Awobanin or delphinidin is used in Japan to make awobana paper. It is also used to dye silk; as colorants for food stuffs, pharmaceutical preparations, and cosmetics.

### 6.27.3 Sources

*Anemone coronaria* L. (Ranunculaceae)

It is a 30–45 cm tall herb, with brownish root stock, lobed leaves, cup shaped and multicolored flowers, native to Europe and Central Asia, grown in Indian gardens. Petals of flowers contain delphinidin, pelargonidin, and cyanidin anthocyanins.

*Cinchona calisaya* Wedd. (Rubiaceae)

syn. *Cinchona ledgeriana* Moens ex Trimen.

English – Ledger or Yellow bark

It is a weak, straggling, but fast growing tree that is native to Peru and Bolivia, grown in West Bengal, Tamil Nadu, Meghalaya, Assam, and Tripura. It forms nearly 75% of the *Cinchona* plantations and it is the richest source of quinine. The leaves contain quercetin, kaempferol, reynoutrin, and delphinidin.

*Commelina communis* L. var. *hortensis* Makino. (Commelinaceae)

English – Azure-blue flower

It is a herb that has blue flowers, also known as azure, found in Japan. It is used in the preparation of awobana paper. The flower pigment contains delphinidin diglucoside as the main constituent and p-cumaric acid and awobanol.

*Eucalyptus obliqua* L'Hér. (Myrtaceae)

It is a tall tree with persistent fibrous bark and thick leaves, commonly found in Nilgiris. Besides 17.2% tannin, the leaves also contain delphinidin-3, 5-diglucoside which on acid hydrolysis yields the coloring matter delphinidin.

*E. regnans* F. Muell.

It is a very tall tree, cultivated on Simla hills in Himachal Pradesh. It is sensitive to draught, but is capable of withstanding snow. The leaves yield delphinidin-3, 5-diglucoside, which on acid hydrolysis yields the coloring matter delphinidin.

*Punica granatum* L. (Punicaceae)

English – Pomegranata; Bengali – Dalim; Gujarati – Dadam; Hindi – Anar; Kannada – Dalimba; Malayalam – Matalam; Marathi – Dalimba; Tamil – Madulai

It is a shrub or small tree, native to Iran, Afghanistan, and Baluchistan, found growing wild in the warm valleys and outer hills of the Himalayas and cultivated throughout India.

The pomegranate is a subtropical fruit tree that grows best in semi-arid climate where cool winters and hot summers prevail. It grows well in a deep loamy soil, although it thrives well on comparatively poor soil where other fruits fail to flourish. The pomegranate is propagated by seeds as well as by hard wood cuttings. The hard wood cuttings, 25–25 cm long, from the previously seasons growth are taken. These are planted in beds, leaving only one or two buds exposed. After one year, the rooted cuttings are lifted out with a ball of earth and transplanted to the orchard. It starts fruiting in about four years after transplanting.

The flower contains a glycoside, pelargonidin-3, 5-diglucoside, which on acid hydrolysis yields pelargonidin, a red dye. The seed coat yields a red dye delphinidin-3, 5-diglucoside and malvidin pentose glycoside in the juice and a mixture of pentose glycoside (malvidin derivative along with some petunidin derivative) in the rind. The rind also contains isoquercetin.

*Ribes nigrum* L. (Grossulariaceae)

English – Black Currant; Kumauni – Papear; Punjabi – Muradh, Nabar-Beli, Shaktekas

It is an erect shrub with greenish purple pendulous flowers, globose, black, strong aromatic berries, found wild from Kumaun to Kashmir at an altitude of 2100–3600 m.

Fruits and flowers are reported to contain delphinidin 3,5-diglucoside along with other coloring matters like kaempferol, quercetin, myricetin and cyanidin. The juice of the fruits with alum mordant wool gives a deep pink, and with tin mordant wool gives deep-purple colors.

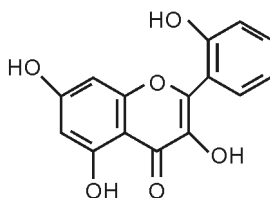
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## 6.28 Datiscetin

Datiscetin (3,5,7-Trihydroxy-2-(2-hydroxyphenyl)-4H-1-benzopyran-4-one; 2',3,5,7-tetrahydroxyflavone; 2'-hydroxycrystidenolon 1493.  $C_{15}H_{10}O_6$ ; mol wt 286.23; mp 271°C), the principal yellow coloring matter, present in the roots and leaves of the Bastard Hemp, *Datisca cannabina* L. A glycoside, datiscin ( $C_{27}H_{30}O_{15}$ ,  $4H_2O$ ; mp 192–193°C) is also found in the roots and leaves of the plant in 6–10%, which on hydrolysis yields datiscetin, the coloring principle and rutinose, a disaccharide containing rhamnose and glucose. With concentrated sulphuric acid and sodium hydroxide solution it gives yellow color. It is soluble in alcohol ether and other organic solvents and sparingly soluble in hot water. Datiscetin can be obtained directly ( $\approx 4\%$  yield) from the alcoholic extract of the root.



Datiscetin

### 6.28.1 Extraction

The roots and leaves are ground into a fine powder and then extracted with alcohol for 2–4 h and then filtered. The liquor is dried under reduced pressure to get a dried powder of the dye. It is further purified with the help of chromatographic methods.

### 6.28.2 Uses

The dye has been extensively used in Kashmir and throughout the Himalayas as yellow dye stuff, chiefly on alum mordanted silk. It is also used for dyeing

wool and cotton. It dyes wool olive yellow with chromium and bright yellow with tin mordants. Cotton with aluminium mordant is dyed bright yellow.

### 6.28.3 Source

*Datisca cannabina* L. (Datisceae)

English – Bartard Hemp; Hindi – Akalbir; Kashmir – Woftangal; Punjabi – Bhagjata, Bujrabanga

It is a bush of about 1–2 m height, found in India from Kashmir to Nepal at elevations of 300–2000 m. The plant looks like a true hemp, *Cannabis sativa* L. The plant is propagated by seeds or cuttings.

The roots of the plant, known as *Akalbir*, have been used in Kashmir and throughout Himalayas as yellow dye stuff. Roots and leaves of the plant contain a glycoside datiscin and a tetrahydroxy flavone detiscetin. Besides, another yellow coloring matter, corresponding to the formula  $C_{15}H_{12}O_6$ ; mp  $237^{\circ}C$ , a resin, tannin, and an essential oil, are also reported to be present in the plant.

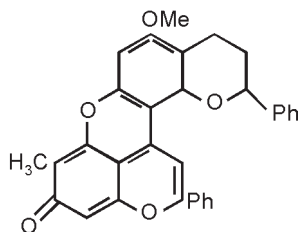
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## 6.29 Dracocarmin

The dracocarmin or dracorubin ( $C_{32}H_{24}O_5$ ; mp  $320^{\circ}C$ ), and drachorhordin ( $C_{17}H_{14}O_3$ ; mp  $168^{\circ}C$ ) are the principal coloring matters found in the resinous secretion of the fruits of Dragon's blood, *Daemonorops draco* (Willd.) Blume, *D. kurziana* Hook.f. ex Becc., and from the resinous secretion of the stem of sokotra Dragon's blood, *Dracaena cinnabari* Balf.f., and Arabian Dragon's blood, *Dracaena schizantha* Baker.





Dracorubin

### 6.29.1 Collection of resin

The resinous matter is collected by rubbing or shaking the fruits in bags, or collected directly from the stems of the *Dracaena* spp. A product of inferior quality is obtained by heating the crushed fruits with water or by tapping the stems. It is odorless, and almost tasteless and gritty when chewed. The pure resin is almost entirely soluble in alcohol. The alcohol soluble resin contains 50–60% of dracoresinotanol, mostly in the form of benzoic acid and benzoyl acetic ester, 13% of yellow resin, and 2.5% of dracoalban and also abietic acid.

### 6.29.2 Extraction

The powdered resin is extracted with boiling benzene for four hours and then filtered. The filtered extract is mixed with a solution of picric acid in benzene and heated under reflux for six hours, until gelatinous brown precipitate, which has separated initially, becomes granular. Next day the solid is collected, washed with benzene, air-dried, and triturated with a little methanol or alcohol to remove resinous material, leaving the impure picrate as a bright orange powder which does not darken on exposure to air. On decomposition of this product in 95% alcohol with 25% aqueous sodium hydroxide at room temperature and then 40°C for one hour gives crude dracorubin which is collected, washed with boiling water, and dried. It is further extracted with chloroform, leaving a small amount of a brown residue. The chloroform extract is poured on a column of aluminium oxide, and after the lower bluish-purple zone is washed through the column with much chloroform, the main red zone containing dracorubin is eluted with methanol-chloroform (1:9). Thus, obtained red solution is concentrated in a vacuum gives crystalline dracorubin which is further purified by repeated chromatography on aluminum oxide to remove traces of other accompanying pigments.

### 6.29.3 Uses

Dragon's blood is used for coloring lacquers varnishes and plasters and also in zinc live engraving for protecting those portions of the metal not to be etched from the action of the acids. It is also used in printing trade for preparing half tone plates for multicolor printing.

### 6.29.4 Sources

*Daemonorops draco* (Willd.) Blume syn. *D. propinquus* Becc., commonly known as Dragon's Blood, found in Sumatra and Borneo, are the main sources of the resin from which the dye is extracted.

*D. kurziana* Hook.f. ex Becc. (Arecaceae; Palmae)  
syn. *D. grandis* Kurz.; *Calamus grandis* Griff.

English – East Indian Dragon's Blood; Hindi – Aprang, Hiradukhi; Marathi and Gujarati – Hiradakhani; Tamil – Kondamural rattam

It is a lofty, climbing, thorny plant that is found in South Andaman Islands. It is the only Indian species which yields a red resin, known as East-Indian Dragon's Blood. The plant yields canes of about 2.5 cm in diameter that are also used for basketry.

The stems of Zanzibar Drops or Socotra Dragon's Blood, *Dracaena cinnabari* Balf.f., and Arabian Dragon's Blood, *D. schizantha* Baker, occurring in East Africa and Southern Arabia respectively, exude a red resin which resembles true dragon's blood obtained from *Daemonorops* spp. It occurs in tears with a glassy feature and differs from true dragon's blood in containing no fruit scales and is not emitting, the odor of benzoic acid when heated. The resin is imported in India from their respective countries.

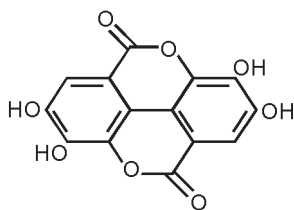
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### 6.30 Ellagic acid

Ellagic acid (2,3,7,8-Tetrahydroxy [I] chromeno [5,4,3-cde] chromene-5,10-dione; (C<sub>14</sub>H<sub>6</sub>O<sub>8</sub>; mp above 360°C), the principal coloring matter, found in fruits of Divi-Divi, *Caesalpinia coriaria* (Jacq.) Wild, leaves of Chestnut spp., *Castanea sativa* Mill, *Castanopsis concinna* (Champ. ex Benth.) A. DC., *Castanopsis eyrei* (Champ. ex Benth.) Hutch., and *Castanopsis faberi* Hence, fruits, wood and bark of several species of myrobalan, *Terminalia alata* Heyne ex Roth., *T. arjuna* (Roxb. ex DC.) Wight and Arn., *T. bellirica* (Gaertn.) Roxb., *T. catappa* L., *T. chebula* Retz., and *T. paniculata* Roth, and in Kinos of several species of *Eucalyptus* sp. and in tannins which contain ellagitannin. It is slightly soluble in water or alcohol; soluble in alkalis and pyridine but insoluble in ether.



Ellagic Acid

#### 6.30.1 Extraction

The raw material is chopped and turned into small pieces and then milled to make fine powder of dust. The powdered material is put into warm water or methanol for 3–4 h and then filtered. The filtered solution is concentrated to less than half of its bulk. The dark viscous residue is diluted with ether. The mixture is shaken thoroughly and kept overnight. The lower layer is separated from the ether layer which is washed several times with water and then extracted successively with saturated sodium bicarbonate, 1 N sodium bicarbonate, and 3 N sodium hydroxide. The extract is acidified with dilute sulphuric acid, and shaken with ether. The ethereal solution is further shaken with water and the aqueous sodium bicarbonate to get a brown amorphous

solid crude ellagic acid. This crude is dissolved in acetone and passed through a column of alumina, which is prepared in acetone containing 5% glacial acetic acid. The eluate is evaporated. The remaining dark viscous residue stirred with ethyl acetate yields a brown amorphous solid of ellagic acid that is separated. It is collected and washed with ethyl acetate and methanol. The crude material may also be crystallized from pyridine and separated as brownish-yellow needles of ellagic acid.

### 6.30.2 Uses

Ellagic acid is soluble in hot water. It is used for dyeing fast yellows on chromed wool. The yellow alkaline solution turns green on addition of  $\text{FeCl}_2$ . Ellagic acid shows antioxidant properties. It is also been used as a dietary supplement as it exhibits benefits against cancer and heart disease.

### 6.30.3 Sources

*Caesalpinia coriaria* (Jacq.) Willd. (Fabaceae)

English – American Sumac; *Divi-Divi*; Bombay – Libidiki; Kannada – Vilayati aldekayi; Tamil – Hodivaelam, Inkimaran, Tivi-Divi; Tel – Divi-Divi

It is a medium sized, unarmed tree, native to Central America and West Indies, introduced into India and cultivated in the gardens of the different parts of India, particularly in Andhra Pradesh and Tamil Nadu. It is also found as an escape in Uttar Pradesh, West Bengal, Gujarat, and Karnataka.

The tree is propagated by seeds that are sown in shaded nursery beds or in bamboo baskets, and are kept moist. They germinate in about a week. The seedlings are planted when they are of about 30 cm height. Watering is done till the seedlings are a metre tall. About 250 plants per hectare are planted. The tree generally begins to bear fruits after 3–4 years of planting. Flowering and fruiting occur twice a year. The pods are harvested as soon as they are ripe. They are collected daily as they drop down from the tree. The tree usually begins to yield 2 kg of pods per tree when it is 3–4 years old, but yields 45 kg after 20 years.

All the parts of the tree are rich sources of tannins. Tannin is present in leaves (44.3%), pods (69.4%), stem bark (51.1%), and root bark (70%). The tannins are of pyrogallol type and consist of gallotannin and ellagitannin, from which ellagic acid is derived.

The infusion of divi-divi produces, on standing, a bloom on account of deposition of ellagic acid. This is caused by the activity of an enzyme present in the pods. Pods have been used for tanning and coloring leather. It gives leather with a light-yellow tint. Sometimes it is used mainly as a dye.

*Castanea sativa* Mill. (Fagaceae)

syn. *C. vulgaris* L.

English – Spanish or Sweet Chestnut; Kashmir – Panjaeb Gour, Singhara  
It is a tree of up to 15 m height, native to South Europe and North Africa, cultivated in Orc throughout the Himalayas up to Assam and Meghalaya between 2000 and 3000 m altitudes.

Chestnut requires a cool climate with a moderate rainfall. It is a moderate light demander. It grows well on deep fertile loams. The tree is propagated from seeds. Ripe nuts are selected and stored in moss or in deep trenches for at least two months before sowing to ensure better germination. During the storage period, the nuts develop sprouts and are ready to be sown immediately in autumn, in nursery beds at a depth of 7–10 cm. Seedlings are planted in orchards in autumn. Tree can be regenerated vegetatively by means of grafting and budding. The leaves and heartwood contain ellagic acid. Heartwood also contains hydrolysable tannin (61.4%) that is used for coloring and tanning leather.

*Castanopsis* spp. (Fagaceae)

The leaves of the *Castanopsis conccina*, *C. eyrei* and *C. fabri*, found in Hong Kong, yield ellagic acid (3–5%).

*Eucalyptus calophylla* R.Br. (Myrtaceae)

It is a medium to large sized tree, bearing dense foliage of ovate-lanceolate leaves, large clusters of white, cream-colored, rarely pink flowers and urn-shaped fruits. It is cultivated in the Nilgiri hills of Tamil Nadu.

The kino is collected from the plant which is known as Botany Bay Kino, contains ellagic acid.

The other species of Eucalyptus like *E. corymbosa* Sm., *E. maculata* Hook, and *E. hemiphloia* Benth. A have also been reported to contain ellagic acid.

*Terminalia alata* Heyne ex Roth. (Combretaceae)

syn. *T. tomentosa* Wight.

Bengali – Asan; Hindi – Asan, Sain, Saj.; Gujarati – Sadar; Kannada – Sadala; Marathi – Ain; Oriya – Sahaju; Tamil – Karramarda; Telugu – Tam; Trade – Laurel

It is a large and deciduous tree, found in the Himalayas from Kangra eastwards of Himachal Pradesh to Goalpara Division of Assam and Southwards throughout the peninsula and grown almost all over India.

The plant is propagated by seeds and also vegetatively by means of root and shoots cuttings. The seeds are sown in shade nurseries, soon after collection during March–April. Germination takes place in 2–5 weeks. The

seedlings are ready for transplantation early in the rainy season. Ellagic acid is isolated from leaves and fruits.

*T. arjuna* (Roxb. ex DC.) Wight & Arn.

Assam – Orjun; Bengali – Arjhan; Hindi – Arjuna; Gujarati – Sadado; Kannada – Maddi; Marathi – Sanmadat; Sadaru, Vellamarda; Oriya – Arjuno, Sahajo; Punjabi – Arjan; Tamil – Vellamatta; Telugu – Yerramaddi; Trade – Arjun

It is a large, evergreen tree with a spreading crown and drooping branches, found commonly in most parts of India.

The tree is a moderate shade-bearer. It prefers loose, moist, fertile, and alluvial soil. The tree is propagated by seeds and also by layers. The seeds are sown in the end of July. They germinate in about 21 days. The early growth of the plant in nursery is rapid. The 75 days old seedlings are planted after removing all the leaves except of the top pair.

The bark contains tannin (20–24%). The tannin is of a mixed type. It contains both pyrogallol and catechol tannins. The tannin yields ellagic acid and b-sitosterols.

*T. bellirica* (Gaertn.) Roxb.

Bengali – Belliric Myrobalan, Bhairah; Hindi – Bahera; Malayalam – Thani; Marathi – Baheda; Oriya – Bhara; Tamil – Tani; Telugu – Tani; Trade – Bahera  
It is a handsome tree that is up to 40 m tall, found in deciduous forests throughout the greater part of India but not in arid regions.

The plant is a light demander, but can withstand slight shade in its young stage. The ripen fruits are collected young and cleaned. The pulp is removed and the seeds are dried in the sun. Seed retains viability for about a year. Seeds are soaked in water for 24 h before sowing and then sown either direct in the field or by transplanting the nursery raised seedlings that are one year old. Seeds are sown in nursery in the months from March to May and watered. Germination commences in about 15 days and is completed in 30 days. Seedlings are transplanted in fields in July when they are two or four months old.

The ellagic acid is found in fruits, heartwood, and bark. The fruits contain tannin (21.4%). Tannin is a condensed and hydrolysable type. It has been used for coloring and tanning leather. The fruits are also used to make ink.

*T. catappa* L.

English – Indian Almond Tree; Andaman – White Bombway; Bengali – Bangla Badam; Hindi – Deshi Badam; Malayalam – Adamarram; Tamil – Natvadam; Telugu – Badamuchettu, Vedam

It is a large, handsome, and deciduous tree, 18–24 m tall, found in the Andaman and is also cultivated in gardens for edible fruits. The tree is confined to the sandy or slightly shingly soil. It prefers moist tropical climate.

The plant is raised by seeds either by direct sowing or by entire planting. The freshly collected fruits are sown in the nursery in the month of July, and the seedlings are transplanted in the south west monsoonal rains of the following year.

The wood, bark, leaves, and fruits contain ellagic acid, the coloring matter that is soluble in water and produces light brownish yellow, light drab, golden fawn, and slate colors in silk; light drab, olive, and grey in cotton; pale brown in wool by various processes.

*T. chebula* Retz.

English – Chebulic Myrobalan; Assam – Silikha; Bengali – Haritaki; Hindi – Harra; Gujarati – Hardo; Marathi – Hirda; Oriya – Harida; Punjabi – Har, Harar; Tamil – Kadukkai; Telugu – Karakkai; Trade – Myrobalan

It is a tree of 15–24 cm height, found throughout the greater parts of India, particularly in the sub-Himalayan tracks from the Ravi, east wards to West Bengal and Assam.

The plant is a demander of strong light. It requires direct overhead light and cannot tolerate shade or a cramped situation. It is frost hardy and drought resistant to a considerable extent.

The fruits are collected in first-half of January from the ground soon after they are fallen. They are soaked in water for 36 h before sowing. Seeds are sown in nursery under shade. They germinate in 15 days. One year old seedlings are transplanted in fields during rainy season. The tree can also be raised vegetatively by root and shoot cuttings.

The dried fruits constitute one of the most important vegetable tanning material and have been used in India from a long time. The dried flesh of the fruit yields tannin (30–32%). The tannin belongs to the pyrogallol type. The hydrolysable tannins, chebulagic acid ( $C_{41}H_{30}O_{27} \cdot 10H_{20}$ ; mp 240°C), chebulinic acid ( $C_{41}H_{32}O_{27}$ ) and carilagin, are the major tannin constituents present that belong to ellagitannin class. They are accompanied by varying proportions of the following products of their complete and incomplete hydrolysis: chebulic acid, ellagic acid, gallic acid, and b-D-glucogallin.

The tannin has been used for coloring and tanning leather for a long period of time. The tannic acid, extracted from the myrobalan tannin, is used to make ink. The ellagic acid, a coloring matter, extracted from the tannin, is used for coloring cotton, wool, and silk in various shades.

Besides fruits, tannin is also present in the roots, bark, wood, and leaves.

*T. paniculata* Roth.

English – Flowering Murdah; Malayalam – Pilamuruthu, Pillamurda; Marathi – Kinjal; Tamil – Pekadukkai; Telugu – Neemeeri; Trade – Kindal

It is a large deciduous tree, found in the tropical semi-evergreen and

tropical moist deciduous forests of the western and Eastern Ghats up to 1200 m altitude.

The tree prefers fairly moist situations. It requires a well drained soil, and is not found on water logged grounds.

The tree is regenerated by seeds that are sown in nurseries under shade. One year old seedlings are transplanted in fields. The growth of the tree is slow. It attains a diameter of 45–52 cm in 100 years and 61–69 cm in 150 years.

The heartwood is a rich source of ellagic acid. Besides ellagic acid, it also contains 3,3'-O-di-methyl ellagic acid-4-glucoside, O-pentamethyl flavellagic and b-sitosterol. Bark contains tannin (14%) which is used for dyeing and tanning leather.

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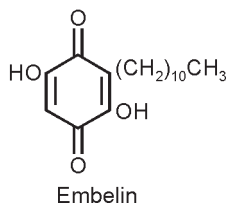
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## 6.31 Embelin

Embelin (2,5-Dihydroxy-3-undecyl-2,5-cyclo-hexadiene-1,4-dione; 2,5-dihydroxy-3-undecyl-p-benzoquinone; “Embelic acid”.  $C_{17}H_{26}O_4$ ; mol wt 294.39; mp 142–143°C), the principal yellow coloring matter, formerly termed embelic acid, occurs in the berries of the Baberang, *Embelia ribes* Burm. f., and *E. tsjeriam-cottam* (Roem and Schult) A. DC., and in fruits and seeds of *Myrsine Africana* L., *M. semis errata* Wall., and *Rapanea capitellata* (Wall.)



Mez. It is insoluble in water but soluble in the usual or hot organic solvents or in alkali hydroxide solutions, and very slightly soluble in petroleum ether.



### 6.31.1 Extraction

The dried and powdered berries are extracted with any one of the organic solvents like ether, benzene, ligroin, ethyl acetate, hexane, ethyl alcohol, and methyl alcohol, and then the residue is evaporated and crystallized with methanol and recrystallized with chloroform, yields embelin as orange-red plates. It is further purified by dissolving it in hot alcohol and allowing it to crystallize slowly. At first, deep-red colored crystals are deposited which on several repetitions of this process, give a pure, orange color plates of embelin.

### 6.31.2 Uses

Embelin is used to dye silk and wool yellow. It produces beautiful shades on wool and silk from alcoholic solution, and to give various deeply colored lakes with different metallic salts and hydroxides. In the latter respect, embelin behaves as a polygenetic dyestuff like alizarin or purpurin.

### 6.31.3 Sources

*Embelia ribes* Burm.f. (Myrsinaceae)

Bengali – Biranga, Baibirang; Gujarati – Vyvirang, Vavading; Hindi – Baberang, Wawrung; Kannada, Tamil, and Telugu – Vyuvilanga; Malayalam – Vizhal; Marathi – Kakannie, Uavdinga; Sanskrit – Vidanga, Vrishanasana

It is a large scandent shrub with gland-dotted leaves that are dull-red to nearly black-colored, found throughout India, up to an altitude of 200 m.

Fruit contains embelin (2.5–3.1%) which is used to dye silk and wool.

*E. tsjeriam-cottam* (Roem. and Schult.) A. DC.

syn. *E. robusta* Roxb.

It is a shrub or small tree, with gland dotted leaves, longitudinally striated fruits, found throughout greater part of India up to an altitude of 200 m.

Fruit contains embelin (1.6%) which is the yellow coloring matter.

*Myrsine Africana* L. (Myrsinaceae)

Garhwali – Rikhdalmi; Kashmiri – Gugil; Kumauni – Ghani; Punjabi – Bebrang, Kakhum, Shamshad

It is an erect shrub or small tree, with sharp toothed leaves, white minute flowers, dark purple, small globose fruits, and found in outer Himalayas from Kashmir to Nepal and Khasi hills between 300 and 2700 m altitude.

Fruits and seeds contain embelin (3%). Fruits also contain quercitol (1%).

*M. semiserrata* Wall.

Garhwali – Bains, Gaunta; Kumauni – Chupra; Lepcha – Singgun; Nepali – Shalame

It is a shrub or small tree that is up to 1.8 m tall, occasionally up to 4.5 m with sharply toothed leaves towards the tip; pinkish flowers; bluish or pinkish-purple fruits when ripe, found in the outer Himalayas between Beas and Bhutan, in North Bengal and in Khasi, Jaintia, Aka, and Lushai hills at an altitude between 900 and 2700 m. Seeds contain embelin (0.4%) and quercitol.

*Rapanea capitellata* (Wall.) Mez. (Primulaceae)

syn. *M. capitellata* Wall.

Assami – Kachidria; Khasi – Dieng-ching; Nepali – Phalamkath

It is a very variable shrub or small tree that is found in Nepal, Bhutan, North Bengal, Assam, Khasi, Jaintia, and Aka hills. Seeds contain embelin (1.6%).

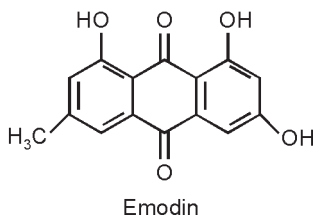
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## 6.32 Emodin

Emodin or frangula emodin, rheum emodin, archin, frangulic acid (1,3,8-Trihydroxy-6-methyl-9,10-anthracenedione; 1,3,8-trihydroxy-6-

methylantraquinone; 4,5,7-trihydroxy-2-methylantraquinone); ( $C_{15}H_{10}O_5$ ; mol wt 270.23; mp 259–260°C), a yellow coloring matter occurs in certain species of *Rhamnus* L.; *Aloe* L.; *Rheum* L.; *Cassia* L., and in wood of *Sonneratia caseolaris* Engl. Emodin is present as a glucoside frangulin ( $C_{27}H_{30}O_{14}$ ; mp 215°C) in the bark of *Frangula dodonei* Ard. syn. *Rhamnus frangula* L. and as rhamnocathartin, which contains emodin, rhamnose and a hexose as structural unit in the Purging Buckthorn *Rhamnus cathartica* L. It is readily soluble in organic solvent and less soluble in water.



### 6.32.1 Extraction

For the extraction of the dye, the material is defatted and extracted with organic solvents. It is extracted with ethyl alcohol (95%), concentrated and treated with either hydrochloric acid (10%) or potassium hydroxide (KOH, 10%), followed by the extraction from the acidic medium with ether. It gives a brown colored precipitate, a mixture of pure and free anthraquinones. With the help of chromatographic methods, the emodin and other anthraquinones present in the extract are separated.

### 6.32.2 Lakes

The berries are extracted with boiling water and the extract is evaporated under reduced pressure; the greener and rougher the berries, the better the extract.

It is used in calico printing with tin, alum, and chrome mordants for steam yellows, oranges, browns, and olive, and for shading logwood printing blocks. It is suitable for dyed styles on printed or discharged mordants and in combination with basic dyes for which Persian Berries act as a mordant, for bright yellows and greens.

Alum is added to fresh aqueous extract of Persian Berries and precipitated with soda to obtain yellow to orange lakes. It is unstable to heat but moderately fast to light and unaffected by sulphur dioxide or hydrogen sulphide. It was formerly used in calico printing, coloring foods, and as a lime-color in distempers, wall paper printing, etc.

Yellow to dark-orange lakes are obtained by adding stannous chloride to a fresh aqueous extract of Persian Berries and precipitated with soda. It is formerly used for coloring paper, leather, soaps, oils, waxes, etc., in distempers and in calico and wall paper printing.

The natural-green colored lake is prepared by crushing the almost ripe berries of *Rhamnus cathartica* L. or similar species of Buckthorn, fermenting it for 10 days, pressing them and treating the extracted juice with alum and potash, evaporating the mixture to thick syrup, and then packing it in bladders. A similar product is obtained by mixing the juice of the ripe berries with lime and evaporating it to dryness.

It was formerly used for coloring paper and leather, and to some extent in artist's water colors.

### 6.32.3 Uses

Emodin is used for coloring paper, leather, wool, and to some extent in artist's water colors. It is also used for calico printing, coloring food, and is used to dye silk and wool in a range of colors using various mordants. Colors obtained are yellow without any mordant, brown with copper, olive-green with iron, red-violet with chromium and bright yellow with tin mordants. The dye is fast to light and washing. Emodin showed anticancer effect on several human cancers.

### 6.32.4 Sources

*Aloe vera* (L.) Burm.f. (Asparagaceae)  
syn. *A. barbadensis* Mill.

English – Barbados Aloe, Curacao Aloe, Indian Aloe, Jafrabad Aloe; Bengali and Sanskrit – Ghrita-kumari, Kanya; Gujarati – Kumarpathu, Kunawar; Hindi – Ghee-Kanwar, Ghi-Kuvar; Kannada – Kolasoare, Komarika, Maulisara; Malayalam – Katta-vazha; Marathi – Korphad; Oriya – Kumari, Mushaboro; Tamil – Bhottu-Katrashae, Chirukattalai, Kottaalai; Telugu – Kalabanda

It is a perennial plant with a short stem with leaves that are 30–60 cm long, full of juice, leathery and spiny teeth on both sides. It is found in semi-wild state in many parts of India.

It is a well known medicinal plant that possesses cathartic properties due to the glycosides alone. Aloe can be easily cultivated in almost all parts of India, even under constant drought conditions. Aloe also contains free anthraquinones, such as aloe-emodin, isoemodin, and resins. The isoemodin is used to prepare a dye which gives purple color to silk, black to wool, and pink to linen.

*Cassia* spp., *Chamaecrista* spp., *Senna* spp. (Fabaceae)

Several species of *Cassia*, *Chamaecrista*, *Senna*, like *Cassia javanica* L. (leaves), *Chamaecrista mimosoides* (L.) Greene (leaves and seeds), *Chamaecrista nigricans* (Vahl) Greene (leaves and pods), *Chamaecrista pumila* (Lam.) K. Larsen (plant), *Senna alata* (L.) Roxb. (pods), *Senna auriculata* (L.) Roxb. (leaves and pods), *Senna floribunda* (Cav.) H. S. Irwin and Barneby (roots), *Senna italica* Mill. (herb), *Senna obtusifolia* (L.) H. S. Irwin and Barneby (roots), *Senna occidentalis* L. (seeds, roots, and flowers), *Senna podocarpa* (Guill. and Perr.) Lock (leaves), *Senna alexandrina* Mill. (leaves and pods), *Senna sophera* (L.) Roxb. (heart wood) and *Senna tora* (L.) Roxb. (leaves and stem bark) contain emodin in the parts mentioned under parenthesis in respective species. All the species have been dealt in detail under the dye chrysophanic acid.

*Frangula purshiana* Cooper (Rhamnaceae)

syn. *Rhamnus purshiana* DC.

English – Cascara or Cascara Sagrada, Bearberry

It is a deciduous shrub of about 6 m height, occurring in the North-West USA and Canada. It constitutes the drug cascara or cascara sargada which is used as a laxative and tonic, and contains emodin (1.4–4.0%). Besides, it also contains aloe-emodin ( $C_{15}H_{10}O_5$ ; mp 323°C), Chrysophanol ( $C_{15}H_{10}O_4$ ; mp 196°C) and barbaloin (aloin,  $C_{21}H_{22}O_9$ ; mp 146–148°C).

Cascara is imported into India from its native countries. Attempts have been made to cultivate the plant at Dehradun, Kashmir, Himachal Pradesh, and Nilgiris in India and Bhutan.

*Rhamnus infectoria* L.

syn. *R. lycioides*

English – Avignon Berry; Persian – Berries (unripe fruits)

It is a small plant, about a meter high, growing in Mediterranean region of Portugal, Greece, and the nearby islands. The dye is extracted from the unripe fruits that are used fresh or preferably dried. They are plucked from mid July to mid August. The coloring matter comprises mainly of flavonols. Those existing free are quercetrol, kaempferol, rhamnetol, rhamnazol, and rhamnocitol, but they are mainly found in the form of rhamnosides (heterosides specific to the plant) of which the oldest known is the xanthorhamnoside. The berries also contain small amount of anthraquinoid pigments, especially emodin that gives the shades an orangish tint.

In the beginning of 20th Century, silk and wool were dyed in yellow and orange-yellow color with this dye. The yellows thus obtained tend to turn red or brownish with time, which could be due to the presence of anthraquinones in the dye, which do not fade as quickly as the less fast flavonol pigments.

Dye yields a pure yellow to lively-orange color having good fastness to washing and light, while tin and chrome of tartar are used as mordants. When copper sulphate is used, a very fast olive-green is obtained.

*Rheum* spp. (Polygonaceae)

The Rhubarb, a well known drug, consists of the dried rhizomes and roots of some *Rheum* species. It is a mild anthraquinone purgative. There are three main types of rhubarb, viz. the Chinese rhubarb, the Indian Rhubarb of the Himalayas, and Rhapontic Rhubarb. It contains about 25–30% of extractive soluble anthraquinone derivatives like emodin, physcione (emodin-3-monomethyl ether), chrysophanol, aloë-emodin (9,10-dihydro-1,8-dihydroxy-3-dihydroxymethyl-9,10-dioxoanthracene) and rhein.

The Indian rhubarb consists of the rhizomes of *Rheum australe* D. Don. syn. *R. emodi* Wall. ex Meisn., and *R. webbianum* Royle. The rhizomes and roots of *Rheum spiciforme* Royle syn. *R. moorcroftianum* Royle are also reported to be mixed with the drug. The details of the above mentioned species have already been made under the dye, chrysophanolic acid.

*Sonneratia caseolaris* (L.) Engl. (Sonneratiaceae)

syn. *S. acida* L. f.

Bengali – Orcha, Archā, Archaka, Ora; Kannada – Kandale; Malayalam – Thirala, Blatti; Marathi – Tiwar, chipi; Oriya – Sundarignua; Tamil – Kinnari. It is a small to moderate sized tree, found along almost the entire coast of India and in the Andaman Islands. It bears solitary, large, dark rose colored flower, cushion shaped berries of 50 cm in diameter.

The wood contains two coloring matters, archin (2%) and archinin, ( $C_{15}H_{10}O_4$ ; mp 197°C; 1.5%). Archin and archinin have been shown to be identical with 1,3,8-trihydroxy-3-methyl anthraquinone and 1,8-dihydroxy-3-methyl anthraquinone, respectively.

The two coloring matters are extracted and separated. Powdered wood is extracted and concentrated and then put in the refrigerator for a few days. Then the crude coloring matter that is crystallized is filtered and washed with small quantities of ether. It is then purified by precipitating extraneous impurities with petroleum ether. The yellowish-red clear filtrate on concentration and cooling yields crystals of both the coloring matters, from which both archin and archinin are separated through extraction with hot benzene. The benzene-insoluble residue mainly consists of crude archin, while the benzene solution on concentration and cooling yields crude archinin. The pure archin is obtained after repeated crystallization from ethyl acetate that finally gives pure archin in the form of orange-red needles.

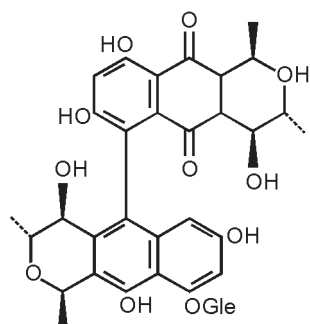
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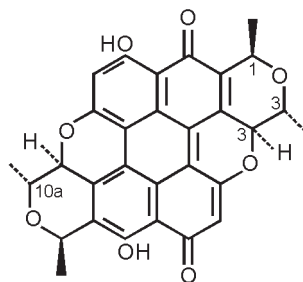
## 6.33 Erythroaphins

Erythroaphins (1, 3, 3a, 8, 10, 10a-Hexahydro-7-13, dihydroxy-1, 3, 8) o-tetramethyl-6H,14H-2, 4, 8, 11-tetraoxadibenzo (bc, kl) coronene-6,14-dione, the red coloring matters found in two forms, i.e. fb. (IR, 3R, 3aR, 8R, 10R, 10aR)-form and erythroaphin sl. (IR, 3R, 3aS, 8R, 10R, 10aR)-form ( $C_{30}H_{22}O_8$ ; mp 250°C) in the common bean aphid or black aphid, *Aphis fabae*, and willow tree aphid (*Tuberolachnus salignus*), respectively. The common bean aphids or black aphids are feed upon the broad bean, *Vicia faba* L. and willow tree aphids on *Salix Alba* L. The coloring matter is not actually present in the living insects but arises from yellow precursor after their death. The haemolymph of the living insects contains a yellow coloring matter protoaphin fb and sl, respectively ( $C_{36}H_{38}O_{16}$ ; mp 210°C) which converts rapidly enzymically after the death of the insect into yellow fat soluble fluorescent xanthoaphins fb and sl ( $C_{30}H_{26}O_{10}$ ; mp 210°C). Xanthoaphin are unstable and undergoes into conversion, particularly in presence of acids, first into the fluorescent orange chrysoaphin fb and sl ( $C_{30}H_{24}O_9$ ; mp 250°C) and then fluorescent carmine red colored erythroaphin, fb and sl, the stable products

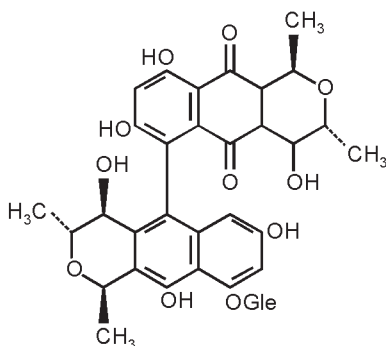
of the series. The erythroaphins fb and sl are isomeric compounds having identical ultraviolet and visible absorption spectra but differs in infrared absorption, solubility, crystalline habit, and optical rotation.



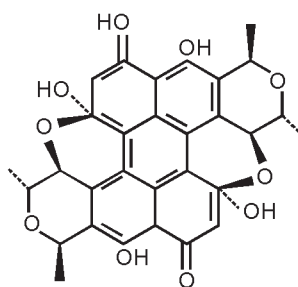
Protoaphin FB



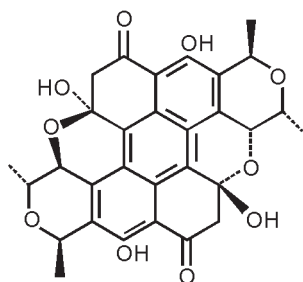
Erythroaphin FB



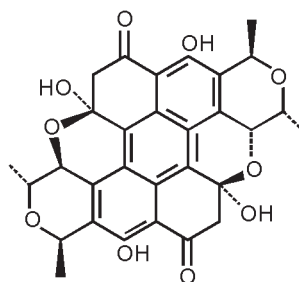
Protoaphin SL



Xanthoaphin FB



Xanthoaphin SL-1



Xanthoaphin SL-2

Protoaphins can be isolated only from the freshly collected insects that are killed by quick heating method at 70°C, which simultaneously inactivate



the enzymes responsible for the conversion of protoaphin to xanthoaphin, then to chrysoaphin, and then to erythroaphin. The conversion of erythroaphin from protoaphin occurs spontaneously in crude extracts of the insects and appears to be independent of the presence of air, though they are enormously accelerated by heat or by acids or alkalies.

Erythroaphin is moderately soluble in chloroform or carbon tetrachloride, somewhat less so in pyridine, acetone, benzene, dioxin, ether, acetic acid or acetic anhydride; sparingly soluble in ethanol or ethyl acetate and quite insoluble in water. Neutral or acid solutions in organic solvents are red with an orange-red fluorescence.

### 6.33.1 Extraction

Live insects are washed off with cold water from the plants and crushed with Sorensen buffer and then left at room temperature for one hour. Then the insects are extracted with a mixture of ether and carbon tetrachloride solution and filtered liquor is evaporated under reduced pressure. The residue is taken up in chloroform and then formic acid is added. The mixture is then heated for 20 min. Most of the solvent is removed by distillation and then warm alcohol is added. The solution is then concentrated until crystallization. It is then set aside overnight by which the small deep-carmine red colored needles of erythroaphin settle down which are then filtered and separated.

The crude erythroaphin is further purified by dissolving in alcohol-free chloroform and shaken with sulphuric acid, whereupon the pigment passes into the acid layer. The acid solution is washed with chloroform and then diluted with sulphuric acid and extracted with chloroform; the red pigment is passed into the chloroform, leaving a brownish aqueous layer. The chloroform extract is separately washed with water, dried, and concentrated under reduced pressure. Then ethanol is added until turbidity appears, and then the mixture is warmed to bring into solution and set aside over night whereupon pure erythroaphin is separated.

Erythroaphin can also be obtained from the insects preserved in cold storage. They are thoroughly extracted with acetone and light petroleum, and then evaporated. Viscous red oil is received after evaporation of the mixture. The viscous red oil is freed from residual acetone under reduced pressure at room temperature. It is then boiled with small amount of light petroleum for 10 min by which most of the fat is removed with little loss of coloring matter. The residue, now a granular red powder, is washed with light petroleum and dissolved in chloroform and then carbon tetrachloride and formic acid are added. The solution is then concentrated until crystallization. On cooling, erythroaphin is separated.

### 6.33.2 Uses

Erythroaphin is used to dye cotton, silk, and wool in red color.

### 6.33.3 Aphids

The bean aphids (*Aphis fabae*) are commonly known as black aphids which attack cultivated broad beans, *Vicia faba* L. during early summer; it also occurs on a variety of other hosts that are members of the brassicaceae family. These aphids are industriously milked by ants, which increases the rate of production of honeydew and thus of juice intake. Consequently, there is more rapid growth rate and hence, a greater multiplication of the aphids. This aphid is very much prevalent in Britain. The aphid contains pigment at the rate of 0.8% of the weight of live insects.

The willow tree aphids (*Tuberolachnus salignus*) parasitizes especially on white willow tree (*Salix alba*). These aphids form large colonies of brown color on the underside of the branches from late summer until the first severe frost. The coloring matter content is at the rate of 2% of the weight of live insect.

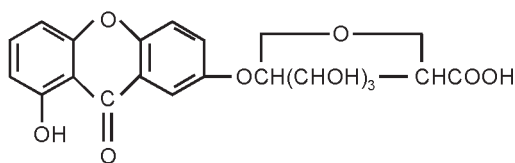
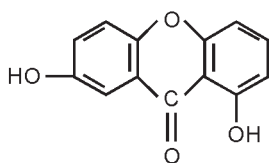
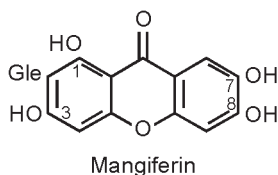
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## 6.34 Euxanthic acid

Euxanthic acid ( $C_{19}H_{16}O_{10}$ , mp 162°C), the coloring principle, is derived from the glucoside mangiferine ( $C_{19}H_{18}O_{11}$ ; mp 280–281°C), which occurs in the

leaves, heartwood, and bark of the mango, *Mangifera indica* L. Euxanthic acid readily breaks down into euxanthone ( $C_{13}H_8O_4$ ) and glycuronic acid, ( $C_6H_{10}O_7$ ). Euxanthic acid was formerly used in India in paints and also for the manufacturing of oil and water colors for artists. It was obtained by feeding the leaves of mango to cows. The coloring matter was excreted in the urine to the extent of 56 g per day per cow.



### 6.34.1 Extraction

Fresh air-dried bark, leaves or heartwood is turned into powder form and extracted with boiling light petroleum for about six hours to remove fatty matter, and then with cold acetone for 24 h to remove tannins, and finally with 70% ethyl alcohol for six hours. The alcoholic extract is concentrated under reduced pressure and a yellow amorphous powder is obtained. It is recrystallized from 70% ethyl alcohol that gives pale yellow needles. With aqueous solutions of  $Na_2CO_3$  and NaOH, it gives deep yellow color. In alcoholic solution with  $FeCl_3$  it gives deep-green color; with Mg and HCl it gives an orange-red color; with Zn and HCl (boiling) it gives red color. With HCl and alcoholic  $FeCl_3$  it produces a greenish-yellow precipitate.

### 6.34.2 Uses

Euxanthic acid produces beautiful, though light, yellow shades on cotton, silk, and wool. In conjunction with turmeric and lime it gives cotton a bright rose-pink color. It is used for painting wood work in yellow color. It is also used to develop green color on indigo dyed material and for topping turmeric dyed materials to improve fastness, and with a little alum to get greenish-yellow. It

is an ancient dye. In older days, it was obtained from cow's urine by feeding cows on the leaves of mango tree. The urine was heated and thus, a precipitate was obtained that was separated out and used as a yellow dye. This dye is commonly known as Indian yellow, rocana, pioury, pinari, purrea, arabicu, purree or pevirang. Prolong feeding of leaves may result in the death of the animals.

### 6.34.3 Sources

*Mangifera indica* L. (Anacardiaceae)

English – Mango; Bengali – Aam; Gujarati – Aamri; Hindi – Aam, Amb; Kannada – Mavu; Malayalam – Amram, Cutam, Mavu; Marathi – Amba; Tamil – Manga, Mau; Telugu – Mamidi, Mavi

It is a large, evergreen tree of about 10–45 m height, cultivated throughout India on a large scale. It has been cultivated in India for at least 4000 years and was originated in the Assam, Myanmar, and Thailand regions where truly wild mango trees have been recorded. A large number of mango types, estimated at over 1,000 are grown in various parts of India.

Mango flourishes in tropical or nearly tropical climate. It grows well in humid as well as dry climate, but yields better production in the regions with a rainfall of 75–250 cm from June to September, followed by a rainless period of months. Mango thrives in a wide variety of soils. It grows in rich clayey loams as well as on poor, sandy, and gravelly soil. Mango is easily propagated from seeds and vegetatively by grafting. The latter is always preferred. The root-stock is raised from seeds and when it is about a year old, it is grafted with a branch of the scion tree. Since mango seeds lose their germinating power within 20–30 days, they are sown as soon as they are extracted from ripe fruits.

The grafted plants are planted in pits of 60 cm in diameter and 60 cm deep in the months of July–August, and watered regularly.

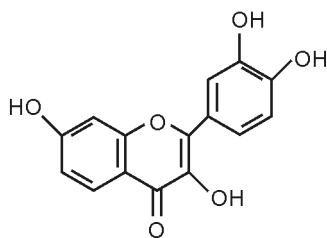
The most serious diseases of mango are powdery mildew, anthracnose, and bunchy top caused by *Oidium marginiferae* Berthet., *Colletotrichum gloeosporioides* Penz., and due to various species of mites, respectively. The powdery mildew is controlled by dusting with sulphur thrice at intervals of 15 days. While spraying Guesarol 405–450 containing 5% DDT and 50% sulphur, it gives good results in controlling both mildew and jassid hoppers. Thracnose can be controlled effectively by spraying Bordeaux mixture 2–3 times at intervals of 3–4 months during dry period; the only preventive measure of bunchy top is to remove and burn affected inflorescence as soon as they appear.

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### 6.35 Fisetin

Fisetin (3,3',4',7-Tetrahydroxyflavone;  $C_{15}H_{10}O_6$ ; mp  $330^{\circ}\text{C}$ ), the principal yellow coloring matter, is obtained from the wood of Smoke Tree, *Cotinus coggygia* Scop., East African Copal or Zanzibar, *Hymenaea verrucosa* Gaertn, and Kidney Vetch, *Anthyllis vulneraria* L. It is readily soluble in hot water, alcohol, acetone, and acetic acid. With sodium hydroxide it gives yellow color, which becomes brown on exposure to air. It occurs as the glycoside of tannic acid, fustin tannide, which readily hydrolyses to brown-olive on iron and bright reddish-orange on tin.



Fisetin

#### 6.35.1 Extraction

The wood is ground into fine powder and extracted either with hot water mixed with NaOH (10%) solution or ethanol. The extract is dried under reduced pressure. The dried extract is known as cotinin. It is a mixture of several other compounds. These compounds can be separated with the help of chromatographic methods, and thus a pure fisetin is obtained.

### 6.35.2 Uses

It is used in the textile and leather industries. It dyes mordanted wool orange with alum, reddish brown with chrome, brownish olive with iron, and reddish yellow with tin mordants. It has poor fastness to light and wet treatment. Formerly, it was used in UK for red-brown on chrome and oranges in tin mordants and for scarlet with cochineal. It was also used in the combination of peach wood, *Caesalpinia echinata* Lam., and logwood to dye alum mordanted silk brown. It is also used to dye feathers and light leather.

### 6.35.3 Sources

*Cotinus coggygia* Scop (Anacardiaceae)  
syn. *Rhus cotinus* L.

English – Smoke-Tree, Wig-Tree, Venetian Sumach, Indian Sumach; Kashmiri – Darengri; Kumauni – Gadtung; Punjabi – Tunga, Manu, and Paan

It is a small tree or bush found throughout the western Himalayas up to an altitude of about 2000 m, chiefly as undergrowth in pine forests. It commonly occurs in Jaunsar, Tehri-Garhwal, and Kumaun. It is also grown in gardens for the filmy effect of its large plumose fruiting panicles, and the yellow and purple autumn tints of the leaves.

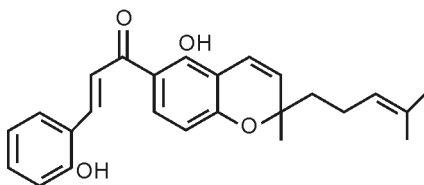
The yellow wood from the stem and larger branches are the young fustic of commerce and the source of the fisetin. Its leaves and bark yield tannin (18–22%), used in the tanning industry.

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### 6.36 Flemingín

Flemingín ( $C_{25}H_{26}O_5$ ; mp 148–150°C), the principal coloring matter occurs in the resinous powder, obtained from the pods of *Flemingia grahamiana* Wight and Arn syn. *Flemingia rhodocarpa* Baker and *F. macrophylla* (Willd.) Merr. Flemingín forms orange-red needles which readily dissolve in cold alkali to give deep orange-red solution. On fusion with alkali, flemingín yields salicylic acid and O-hydroxycinnamic acid.



Flemingín A

This powder is variously known as Warrus, Wurrus, Wars, and Varas. It is similar to Kamala powder obtained from the dried pods of *Mallotus philippensis* (Lam.) Müll. Arg.

#### 6.36.1 Extraction

Warrus is a dull purplish powder which under microscope is seen to consist of non-glandular and glandular hairs. It is obtained from the dried pods of the plants by gentle shaking and rubbing to denude them of their outer hairy covering. The warrus is extracted with hexane for four days to remove wax. The residue is then extracted with dichloroethylene for five days and then filtered. The filtered extract is concentrated, and it yields a red resin which is treated with cold chloroform or dichloroethylene and then solidified. This crude extract contains flamingín A, ( $C_{25}H_{26}O_5$ ; mp 148–150°C) B, and C (both  $C_{25}H_{26}O_6$ ; mp 176–178°C and 180–182°C, respectively) and homoflemingín ( $C_{26}H_{30}O_6$ ; mp 160–162°C) that are separated with the help of chromatographic methods.

#### 6.36.2 Uses

Flemingín is used to dye silk and to a lesser extent wool, but not cotton. In Arabia, it is employed as a cosmetic.

#### 6.36.3 Sources

*Flemingia grahamiana* Wight and Arn. (Papilionaceae; Fabaceae)  
syn. *Moghania grahamiana* Kuntze

It is a low, erect shrub with tomentose young shoots found in Nilgiri, Anamalai, and Pulney hills, and in the hills of Thiruvananthapuram. Pods are covered with viscous-red glandular and non-glandular hairs.

The fruits ripen in November towards the close of the north-east monsoon, when they are covered with garnet colored glandular hair. For collecting warrus, the fruits are gathered, spread on boards or paper, and dried by exposure to the over sieves. The powder collected is again sieved through fine muslin or lawn. Warrus so prepared is a purplish-red granular powder without any marked odor or taste that contains about 72.83% resinous coloring matter.

*F. macrophylla* (Willd.) Kuntze ex Prain

syn. *Moghania macrophylla* Kuntze; *Flemingia congesta* Roxb.

Assami – Samnaskhat; English – Wars, Wurrus, Black Kamala; Bengali and Hindi – Bara-salpan, Bhalia; Malayalam – Kamatter, Korkattachedi; Marathi – Dowdowla; Oriya – Bonokandulo

It is an erect, 1–2 m tall shrub with sulcate and silky young branches, occurring at lower elevations throughout India and in Andaman Islands. The plant is also grown in gardens. Pods yield warrus, the major source of the dye.

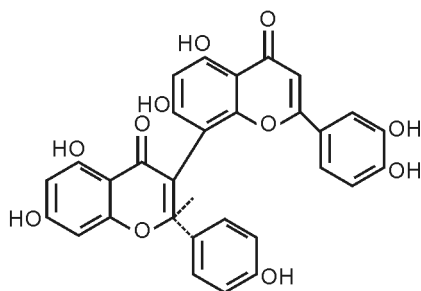
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## 6.37 Fukugetin

Fukugetin or Morelloflavone ( $C_{30}H_{20}O_{11}$ ; mp 244–245°C), the principal yellow coloring matter is found in the bark of Fukugi, *Garcinia spicata* Hook.f. It is soluble in alkalis and concentrated sulphuric acid. It gives a yellow solution on treatment with 50% caustic potash solution.





Fukugetin

### 6.37.1 Extraction

Air-dried bark is ground into a fine powder and extracted with petroleum ether. The extract is then dissolved in Acetone, and then the acetone solution is extracted with 5% aqueous sodium carbonate solution to remove acidic compounds. The acetone layer is then washed with water, dried, and chromatographed. The fractions containing yellow pigments are purified with aqueous methanol to get yellow needles of fukugetin.

### 6.37.2 Uses

The dyeing properties of the fukugetin are similar to those of luteolin, obtained from *Reseda luteola* L. It is used in Japan under the name *fukugi* to produce yellow dyes.

### 6.37.3 Sources

*Garcinia spicata* Hook.f. (Guttiferae; Clusiaceae)

syn. *G. ovalifolia* Hook.f.

Malayalam – Manja Nangu; Marathi – Haldi; Tamil – Kokattai; Telugu – Pidatha; Japanese – Fukugi

It is a medium sized or tall tree, found in the evergreen forests of Western Ghats from Konkan South-wards to Trivandrum at low elevations and on the Eastern Coast from Ganjam to Pudukottah. It is also found in Ceylon and Japan, especially in Ryukyu Islands where its bark is used as a raw material of yellow dye. Its bark is scaly and grey in color.

The Japanese dyestuff Fukuji, available in the form of brittle rectangular cakes of yellowish-brown color and used as a mordant dyestuff in Japan, is obtained from the bark of this tree. The Garcinin, a second coloring matter

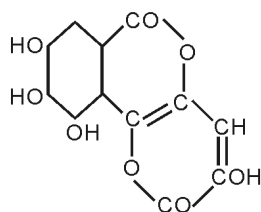
reported to be present in the bark, is probably impure fukugetin. In Japan, the coloring matter is extracted from the bark by water, the solution boiled with hydrochloric acid to bring about hydrolysis of the glucoside, and free pigment is taken up in alcohol and further purified.

### For further reading

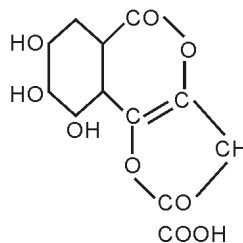
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## 6.38 Galloflavin and isogalloflavin

Galloflavin ( $C_{12}H_6O_8$ ; decomposing at  $290^\circ\text{C}$ ), together with isogalloflavin is a yellow mordant dye obtained by aerating aqueous sodium or potassium gallates ( $\text{NaGa}_2\text{O}_3$ ;  $\text{KGa}_2\text{O}_3$ ). It is readily soluble in acetic acid and aniline; slightly soluble in water, alcohol, and ether. It is fast to light, milling, washing, acids, and alkalis. With concentrated sulphuric acid, it gives a reddish-yellow solution which on dilution yields a white precipitate.



Galloflavin



Isogalloflavin

### 6.38.1 Extraction

The dye is obtained by aerating sodium gallate ( $\text{NaGa}_2\text{O}_3$ ) or potassium gallate ( $\text{KGa}_2\text{O}_3$ ). The sodium gallate is obtained from the tailing of aluminium and

zinc ores. The tailings of aluminium and zinc ores, left after the extraction of aluminium and zinc, mixed with the solution of caustic soda gives a solution of sodium gallate. The sodium gallate solution is then accreted at 0°C for about 5 h yields a yellow precipitate of galloflavin. The precipitate of galloflavin is then filtered and redissolved in water, and then dried under reduced pressure. Thus, pale yellow prisms of galloflavin are obtained.

### 6.38.2 Isogalloflavin

(C<sub>12</sub>H<sub>6</sub>O<sub>8</sub>; decomposition at 275–280°C)

A solution of galloflavin in 10% potassium hydroxide rapidly becomes dark and after 45 min at room temperature, concentrated hydrochloric acid is added carefully until the precipitate first formed just redissolves. Warming on the water bath precipitates crude isogalloflavin as a dark solid which is collected and repeatedly extracted with hot methyl alcohol. The pale residue is insoluble in the usual organic solvents but after treatment with boiling water, a monohydrate is obtained which crystallizes from hot methyl alcohol in colorless needles, decomposing at 275–280°C.

### 6.38.3 Uses

It is used to dye chrome mordanted wool in olive-yellow color. It is also used to dye chrome mordanted cotton in greenish-yellow color which is sensitive to chlorine.

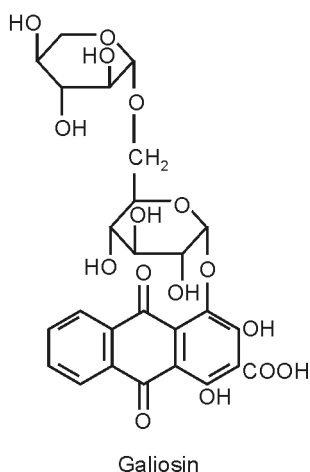
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## 6.39 Galiosin

Galiosin {9,10-dihydro-1,3-dihydroxy-9,10-dioxo-4-[(6-O-b-D-xylopyranosyl)-b-D-gglucopyranosyl) oxy]-2-anthracenecarboxylic acid; C<sub>26</sub>H<sub>26</sub>O<sub>16</sub>; mp >100°C}, is the principal red coloring matter occurs as glycoside of purpurincarboxylic acid in the fresh stem and roots of cheese Rennet, *Galium verum* L., and Madder, *Rubia tinctorum* L., respectively. Galiosin forms yellow needles which decompose above 100°C and dissolve in dilute alkalis

with a deep-orange coloration. On hydrolysis under mild conditions, it yields purpurin-3-carboxylic acid and rubiadin primeveroside (6-b-d-xylopyranoside-d-glucose). Galiosin differs from the other known hydroxyanthraquinone glycosides in being extremely unstable. Galiosin behaves as an acid in that it decomposes sodium bicarbonate and lithium carbonate. On drying in vacuum or at 50° in the air, crystalline galiosin forms an amorphous red product which gives crystalline galiosin again on addition of water.



### 6.39.1 Extraction

For extraction of the dye, the fresh roots or stem, or both are ground into powder and extracted with hot water or butyl alcohol or ether for 2–4 h and then filtered. The filtered liquor is a mixture of several other anthraquinone compounds. For the separation of the galiosin, the extract is either cooled in the ice-chest so that yellow needles of the dye are crystallized, or it could be crystallized from water in vacuum or at 50°C in air by which an amorphous red product is formed which on dissolving again in water crystallizes into galiosin. It is further purified with the help of chromatographic methods.

### 6.39.2 Uses

The galiosin, a red dye, is employed for dyeing woolens. In its color reactions with alkalis and on mordanted silk galiosin, it differs markedly from alizarin, purpurin and quinizarin, but closely resemble xanthopurpurin and munjistin. Galiosin also resembles munjistin in the strong yellow color of the free substance and in that its solutions in alkalis showed general absorption without giving sharp absorption bands.

### 6.39.3 Sources

*Galium verum* L. (Rubiaceae)

English – Cheese Rennet

It is a slender, perennial herb of 30–90 cm height with erect angular stem. It is commonly found wild in Kashmir, Lahul in Himachal Pradesh, and other West Himalayan regions at an altitude between 1500 and 3500 m.

The plant is easily propagated in gardens and is particularly well adapted for rockeries in temperate regions.

*Rubia tinctorum* L.

See under the dye Alizarin.

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## 6.40 Gamboge

Gamboge, also known as Camboge, is a hard, brittle gum resin that is obtained from the latex of *Garcinia morella* (Gaertn.) Desr. and *G. hanburyi* Hook.f. Gamboge is reddish-yellow or brownish-orange in color with a smooth, uniform, conchoidal fracture. It is odorless and tasteless or slightly acidic. It forms a yellow emulsion with water and a clear, deep-orange solution in dilute ammonia. It is almost completely dissolved by successive additions of alcohol and water. The resin is precipitated from alkaline solutions by acids. Three acids  $\alpha$ ,  $\beta$ , and  $\gamma$ -garcinolic acids ( $C_{23}H_{28}O_6$ ;  $C_{25}H_{32}O_6$  and  $C_{23}H_{28}O_5$ ) have been separated from it.  $\gamma$  Garcinolic acid is colored red by alkali.

### 6.40.1 Extraction

Gamboge is gathered by making spiral incision in the lower part of the stems and collecting the effluent sap in bamboo. These are allowed to dry for a month and heated over fire until the contents have hardened.

### 6.40.2 Uses

Gamboge is esteemed as a pigment on account of the brilliancy of its color. It is used in the preparation of water colors and gold colored spirit varnishes

for metals. In Burma, it is used for dyeing silk robes of Buddhist priests. In Thailand, a golden-yellow ink is prepared from it for writing on black paper.

### 6.40.3 Sources

*Garcinia hanburyi* Hook. f. (Guttiferae; Clusiaceae)

It is a dioecious tree with leathery, leural like leaves, small yellow flowers and usually square-shaped, four-seeded fruits. It is indigenous to Cambodia, parts of Thailand, and South Vietnam.

Gamboge is obtained principally from these species. Its juice, when hardened constitute gamboge, is contained in ducts in the middle layer of the bark. When it is procured by making incisions, bamboo joints are being placed to receive it as it exudes.

*Garcinia morella* (Gaertn.) Desr.

English – Indian Gamboge tree; Assami – Kuje-thekera; Bengali, Hindi, and Marathi – Tamal; Kannada – Hardala, Deranabuli, Jarize; Malyalam – Chigri, Daramba, Karukkampuli, Pinnarpuli; Tamil – Makki, Soliappuli; Telugu – Pasupurvarne, Revalchinni.

It is a small or medium sized evergreen tree, found in evergreen forests of Assam, Khasi, and Jaintia Hills, Bengal and in Western Ghats from N. Kanara southwards to Thiruvananthapuram.

It is the indigenous source of gamboge, but no effort appears to have been made to collect it on the commercial scale and it is mostly imported from Thailand (Siam). Gamboge contains 70–80% resin and 15–25% gum and gambogic acid.

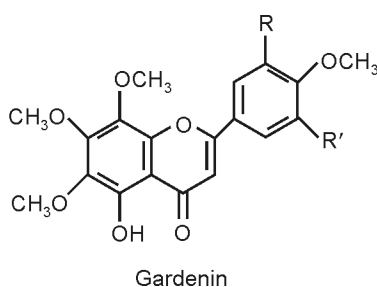
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### 6.41 Gardenin

Gardenin (5-hydroxy 6,7,8,3',4'5'-hexamethoxyflavone;  $C_{21}H_{22}O_9$ ; mp 161–162°C) is a yellow colouring matter which is present in Dikamali or

Cumbi gum, the resinous exudation of the leaf-bud of *Gardenia gummifera* L.f. and *G. resinifera* Roth syn. *G. lucida* Roxb. Gardenin is insoluble in cold 5% alkali, but dissolves to a yellow solution on heating. The alcoholic solution of gardenin produces red color with magnesium and hydrochloric acid. Recent studies showed that gardenin is a group of flavones like gardenin A, referred to in early literature as gardenin; gardenin B ( $C_{19}H_{18}O_7$ ;  $R=R'=R''=H$ , mp 176–177°C; gardenin C ( $C_{20}H_{20}O_9$ ,  $R=OH$ ,  $R'=OCH_3$ ; mp 179–180°C); gardenin D ( $C_{19}H_{18}O_8$ ;  $R=OH$ ,  $R''=H$ ; mp 190–192°C); gardenin E ( $C_{19}H_{18}O_9$ ,  $R=R'=OH$ ; mp 234–235°C).



### 6.41.1 Extraction

The dikamali or cumbi gum is digested with hot alcohol and then cooled, filtered, and dried under reduced pressure. It is then dissolved in chloroform and diluted with diluted rectified spirit, therefore yellow needles are formed. When they settle down, they are separated out. This process is repeated three or four times till melting point become constant. Finally, it is crystallized from absolute alcohol.

### 6.41.2 Uses

Gardenin is used to dye textile fibers of wool, cotton, and silk. It is also used to dye food stuffs and pharmaceutical preparations.

### 6.41.3 Sources

*Gardenia gummifera* L.f. (Rubiaceae)

Bengali, Hindi, and Marathi – Dikamali; Gujarati – Kamarri, Dikamali; Malayalam – Cittubikke, Kambimena, Dikkemalli; Oriya – Gurudu, Bryddikoli; Tamil – Kambilippicin, Dika-malli; Telugu – Manchi, Bikki, Cittamata; Sanskrit – Pindava, Nadi-hingu

It is a large shrub or a small tree, often with a crooked stem and rough twisted branches, found throughout the Deccan Peninsula, extending northwards to Bundelkhand and parts of Bihar.

The resin or dikamali or cumbi gum is secreted freely in the form of tears. The shoot and buds are broken off with the tears of resin attached and marketed either in this form or after agglutination into cakes or irregular masses. The resin is transparent, greenish yellow, with a sharp pungent taste and a peculiar offensive odor.

*G. resinifera* Roth

syn. *G. lucida* Roxb.

Gujarati, Hindi, and Marathi – Dikamali

It is a shrub or small tree, resembling *G. gummifera*, but has a darker bark and longer, distinctly stalked leaves, found in Central India and Deccan Peninsula and also commonly cultivated in gardens.

Dikamali or cumbi gum collected from this species is identical with that of *G. gummifera* and also yields gardenin, the coloring matter.

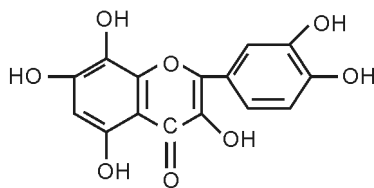
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## 6.42 Gossypetin

Gossypetin (3,5,7,8,3',4'-hexahydroxy flavone;  $C_{15}H_{10}O_8$ ; mp 310–314°C), the principal coloring matter present in the form of its 7-glucoside, gossypitrin (gossypetin-7-glucoside;  $C_{21}H_{20}O_{13}$ ; mp 250–252°C); together with quercetin (3,5,7,3',4'-pentahydroxy flavone;  $C_{15}H_{10}O_7$ ; mp 314°C); herbacitrin (7-glucoside of herbacetin;  $C_{21}H_{20}O_{12}$ ; mp 247–249°C); and herbacetin (3,5,7,8,4'-pentahydroxy flavone;  $C_{15}H_{10}O_7$ ; mp 280–283°C), in the petals of the Indian cotton, Uppam, *Gossypium herbaceum* L. Gossypin ( $C_{28}H_{24}O_{18}$ ; mp 230–231°C) another glycoside of gossypetin is also found in *Gossypium arboreum* L. syn. *G. indicum* Lamk. It is slightly soluble in water and freely soluble in rectified spirit. During dyeing, it readily oxidises to gossypetone ( $C_{15}H_8O_8$ ) that has strong affinity for mordanted wool. The coloring matter is also isolated from calyces of *Hibiscus sabdariffa* L.





Gossypetin

### 6.42.1 Extraction

Dry petals are powdered and extracted with boiling rectified spirit till the pigments are completely removed. On allowing it to stand for some days, a deep-yellow crystalline solid is deposited. It is filtered, washed with alcohol and boiled with water, decanted, and filtered. It gives gossypitrin on dissolving in dilute acetic acid.

The filtrate remained after removing yellow crystalline solid is boiled with 7% sulphuric acid for two hours, yields crystals of aglucone which is recrystallised from rectified spirit and come out as yellow flat needles of gossypetin.

### 6.42.2 Uses

Gossypetin dyes wool in bright orange-yellow without a mordant but with alum it dyes orange-brown; with chrome dull-brown, with iron dull-olive and with tin orange-red. It is also used together with turmeric and pomegranate rind dyes to dye iron mordanted cloth orange-brown to deep-olive.

### 6.42.3 Sources

*Gossypium herbaceum* L. (Malvaceae)

English – Uppam, Levant

It is important dry-land cotton, grown widely in South India since it is well adapted to withstand drought. The flower petal is yellow with deep crimson spot near the base. About five cultivated races of this species are recognized. These are race persicum found in South-Central Asia, race kuljianum in Chinese Central Asia, race acerifolium in North Africa and Arabia, race wightianum in Western and South India and race africanum in South Africa. The race wightianum is a large annual shrub, distributed throughout the cotton growing India from Cutch to Tamil Nadu. The centre of its variability in India

is Gujarat where almost the whole range of different forms is found. Cotton is propagated mostly by seeds. It can also be propagated vegetatively by cuttings. Seeds are soaked in water over night before sowing and are usually sown broadcast or in lines by drill. Plants start blossoming in 7–10 weeks after planting. The flowers remain open only for a day and pollinate shortly after opening. After pollination, flowers are collected for extraction of the dye.

In orthodox method, the cotton flowers are steeped in water for about 15–20 min. Then they are strained off and cleaned, and after that wetted cotton clothes are entered into it. Then the bath is brought just under the boiling point and kept at this temperature for about half an hour. For a tan color, cotton clothes are entered in a hot after-bath of vinegar and chrome and simmered for 10–15 min. After-bath is kept covered; the cotton clothes are rinsed and dried.

### *Hibiscus sabdariffa* L.

English – Roselle, Jamaica Sorrel, Red Sorrel; Hindi – Lal-Ambari, Patwa; Lal-Mistra, Patwa, Chukar; Marathi – Lal-Ambadi, Patwa; Telugu – Yerra Gogu; Tamil – Pulichchai Kerai, Gogu; Kannada – Pulachakiri, Pundibija; Malayalam – Polechi, Pulichchai; Assami – Chukiar

It is annual, erect, and bushy, up to 2.5 m in height, trailing with many branches, prickly; stem is red, and leaves are alternate 7.5–12.5 cm long, green in color with reddish veins. There are single flowers in leaf axils; calyx red, five sepals, epicalyx. This species is native of Indian subcontinent. It is under cultivated in tropics and subtropics of the globe, mainly in West Indies and Central America. Roselle is cultivated in India mainly for food and fiber. The calyces are rich in calcium, niacin, riboflavin and iron, and used in salads. The red color dye is isolated from calyces and it is used as coloring agent for food products.

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### 6.43 Green Earth

Green earth or terre verte,  $(K,Na)(Fe_3,Al,Mg)_2(Si,Al)_4O_{10}(OH)_2$ , is a natural earth, consisting chiefly of the minerals glauconite and celadonite, which are hydrous iron, magnesium, and aluminum potassium silicate. Green earth is found all over India, but only certain varieties are suitable to be used as a dye. The color of the green earth depending on its source varies from place to place. The shades are from olive-green, yellow-green to greenish-grey or blackish-green. The color is durable but often deficient in opacity and full in color intensity.

#### 6.43.1 Extraction

The green earth is ground to a fine powder and mixed with *till* oil to make colors for painting.

#### 6.43.2 Uses

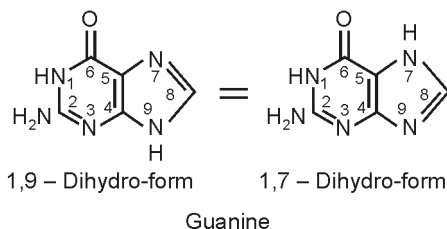
Green earth or terre verte has been used as a pigment for paintings since mediaeval times under the name “Terra di Verona”. Its chief use is as an absorbent and as a base in lake making. Having a strong affinity for basic dye stuffs, it is used for organic dye products such as auromine and malachite green. Earth with pale-green shade and fairly high ferrous silicate content is best for this purpose.

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## 6.44 Guanine

Guanine ( $C_5H_5N_5O$ ; mp  $300^\circ\text{C}$ ), the natural white dye, occurs widely in animal and plant tissues but commercially extracted from fish scales, swimming bladders, and from guano..



### 6.44.1 Extraction

Fish scales or guano is heated for a little while at  $65\text{--}100^\circ\text{C}$  and then suspended in rectified spirit. The guanine crystals settle down at the bottom and a mucous material comes out on the upper surface. It is then filtered and separated. The pearl essence, a silvery bright preparation made from fish scales such as of herring and tarpon contains guanine crystals. It is usually a suspension of 11% of guanine crystals in a cellulose nitrate lacquer except when the lacquer is to be used in a plastic when the cellulose nitrate should be substituted by the particular plastic. The guano is the droppings of various fish eating sea birds such as pelicans, gannets, gulls, petrels, penguins, and cormorants. Guano is also a valuable fertilizer, rich in nitrogen and phosphorus.

Guano accumulates in rainless coastal regions or on islands where birds gather, such as the Chincha Islands off the coast of Peru, Galapagos Islands of Ecuador and also on other Islands of Latin America, Pacific Islands, and Grand Canyon Bat cave in Arizona.

### 6.44.2 Uses

Guanine is used for pearly or lustrous effect and for coloring artificial pearls and other artificial jewellery and fancy goods. It is also used in nail polishes and wherever a pearl or mother of pearl effect is required. The lacquers and plastic containing pearl essence is used to decorate many articles such as mirror backs, minicure, toilet sets, jewellery boxes, handles, etc.

### For further reading

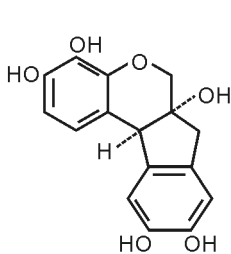
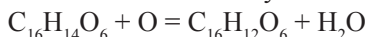
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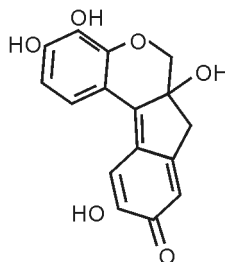
## 6.45 Haematoxylin

Haematoxylin {7,11b-Dihydrobenz [b]indro[1,2-d] pyran-3,4,6a, 9,10 (6H)-petol;  $C_{16}H_{14}O_6$ ; mp 100–120°C}, the coloring matter, occurs in the heartwood of logwood, *Haematoxylum campechianum* L., a tree that grows in Central and North-South America. Haematoxylin, on oxidation, yields haematein ( $C_{16}H_{12}O_6$ ; mp 250°C), a dark violet crystalline body with a green metallic luster, is the real coloring matter. Haematoxylin is the result of the decomposition of a glucoside in the fresh wood. It, when perfectly pure, forms white prismatic crystals which quickly become colored on exposure to air, with the formation of haematein. Haematoxylin is slightly soluble in cold water and fairly soluble in hot water, whereas haematein is slightly soluble in hot water. With sulphuric acid and sodium hydroxide, haematein gives deep-red and deep-violet colors, respectively.

Haematein is formed by oxidation of haematoxylin as follows:



Haematoxylin



Haematein

### 6.45.1 Extraction

For the extraction of the dye, small pieces or chips are made from the heartwood. These chips are either put into water and boiled and then extracted (French method), or treated with 15–30 Lb steam (American method) and then concentrated under vacuum or evaporated and the solid is extracted. From

this haematein is obtained by passing air through an ammoniacal solution of haematoxylin and forms red scintillating crystals of haematein.

### 6.45.2 Uses

Logwood dye is a mordant dye. Colors obtained with different mordants are: blue to black with chromium, grayish violet with alum, grey to black with iron, greenish blue with copper and red violet with tin. The extracts of logwood find their chief application in cotton dyeing and calico printing, but are also used to dye silk, wool, nylon, viscose rayon, coir, jute, furs, and skins. In some countries, haematein is a permitted dye for food and tobacco. The dye is also used as a biological stain for coloring plant tissues.

Logwood extract is used in both the oxidized and unoxidised forms. The unoxidised haematein is used for weighting and dyeing of silk, nylon, furs, skins, wood, and straws in black shades. The oxidized haematein is used to dye leather and viscose rayon. The hair is dyed black with chrome mordanted haematin followed by fixing hair with iron salt. Hematoxylin has been reported hazardous in case of eye contact (irritant), of ingestion and inhalation.

### 6.45.3 Logwood lakes

The various kinds of lakes such as bronze lake, logwood black, noir reduit, and steam black, etc., have been made from the logwood extract. Purple to black lakes are made by boiling logwood extract with iron or chromium in presence of an oxidizing agent usually potassium dichromate, on a base of aluminium hydroxide. Bronze lake is prepared (a) by the precipitation of logwood extract with  $\text{Al}_2(\text{SO}_4)_3$  and then  $\text{K}_2\text{Cr}_2\text{O}_7$  and neutralizing it with chalk or soda after 12–15 h, (b) by treating cold logwood extract with concentrated sulphuric acid and  $\text{SnCl}_4$  and then hot  $\text{K}_2\text{Cr}_2\text{O}_7$  and stirring for one hour, and (c) with the addition of  $\text{SnCl}_4$  and  $\text{KClO}_3$  to the extract and brought to  $75^\circ\text{C}$  and stand for one week with occasional stirring. The logwood black is obtained by stirring the extract with sulphuric acid and  $\text{K}_2\text{Cr}_2\text{O}_7$ . A brownish lake is obtained, if hydrochloric acid is used instead of sulphuric acid. The black lake can also be obtained by heating logwood extract with potassium dichromate and copper sulphate. It is dense black but has a poor fastness to light.

Noir Reduit Lake is obtained with the addition of acetic acid to the logwood extract which is then dissolved in  $\text{NaHSO}_3$ . It produces various hues by the addition of quercitron bark extract (*Quercus velutina* Lam. syn. *Quercus tinctoria* Bartram) or iron acetate. The steam black lake is obtained on the addition of iron nitrate or ferrous sulphate and ammonia to the cold extract. The lake thus obtained needs short steaming for fixation on cotton.

*Uses of lakes:* The bluish-black to black lakes are used with size to color paper and with varnish bleachable printing inks and artists colors. Solutions of lakes in oxalic acid are used as inks. Mixed with oil or spirit lacquers they are used for fancy goods, leather, celluloid, etc. Noir reduit and steam black are used for printing cotton. Steam black printed on cellulose, silk or wool with chromium acetate or chrome and iron give blacks of excellent fastness to light and washing; good fastness to chlorine and fair fastness to rubbing.

#### 6.45.4 Sources

*Haematoxylon campechianum* L. (Mimosaceae)

English – Logwood, Champechy Wood Tree, Black wood; Bengali – Bokkan; Hindi – Patang; Kannada – Partanga; Telugu – Gabbi

It is a small, rarely medium sized thorny tree, native to Central and North-South America, also grows in Mexico, Haiti, San Domingo, Cuba, Honduras, and Mauritius. In India, it is often cultivated in Indian gardens for its delicate leaves and fragrant flowers; sometimes grown as a hedge plant. The tree is propagated by seeds and by cuttings.

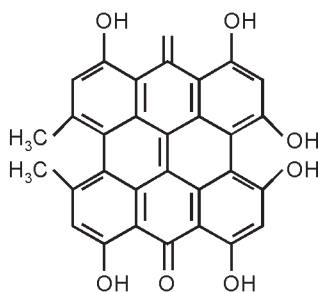
The heartwood constitutes the logwood of commerce which yields a well known dye of darker tints of grey, violet, blue, and black. The wood is very hard and heavy and of a deep orange-red color. It yields its color both to aqueous and spirituous menstruate. A decoction of this wood is of deep-violet or purple color, which after a while changes to a yellowish tint, and finally becomes black.

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## 6.46 Hypericin

Hypericin, also known as hypericum red [1,3,4,6,8,13-Hexahydroxy-10,11-dimethyl-phenanthro (1,10,9,8-opqra) perylene-7,14-dione; 4,5,7,4',5',7'-hexahydroxy-2,2'-dimethyl naphtho dianthrone;  $C_{30}H_{16}O_8$ ; mol wt. 504.43; Decompose at  $320^{\circ}\text{C}$ ] is a red coloring matter that occurs in several species of St John's wort, *Hypericum* spp. and the mealy bugs, *Nipaeococcus aurilanus* Maskell. However, commercially it is extracted from common St John's wort, *H. perforatum* L.



Hypericin

Hypericin is freely soluble in pyridine and methanol, and yields cherry-red solutions with red fluorescence. Though it is insoluble in most other organic solvents, it is soluble in aqueous solutions of alkaline; below pH 11.5, solutions are red and above pH 11.5, solutions are green with red fluorescence.

### 6.46.1 Extraction

An air dried plant material is ground to fine powder and extracted with pyridine or methanol for four hours and then filtered. The filtered liquor is reduced to dryness by flash evaporation at  $40^{\circ}\text{C}$ . The residue is redissolved in ethyl ether and then column chromatographed on silica gel to remove the chlorophyll. The reddish hypericin is then eluted with methanol. This eluate is further evaporated and the residue is redissolved in methanol. For further purification it is chromatographed by high performance liquid chromatography (HPLC).

### 6.46.2 Uses

Hypericin, which is also known as hypericin red, dyes wool and silk deep violet-red. When boiled with alum, however, it is said to produce a yellow dye. Hypericin is believed to act as antibiotic and non-specific kinase inhibitor.



### 6.46.3 Sources

*Hypericum perforatum* L. (Hypericaceae)

English – Common St. John's wort; Hindi, Punjabi, and Kashmiri – Bassant, Balsana, Dendhu

It is a rhizomatous perennial herb up to one meter high, native to Mediterranean region, now widely distributed as a weed in Europe, Asia, North Africa, North and South America, Canada, Australia, and New Zealand. In India, it is distributed in western Himalayas from Jammu & Kashmir to Kumaun at altitude of 1000–3500 m. The plant has two ribbed stem; sessile, opposite, oblong, ovate or linear, black dotted leaves; yellow flowers with numerous stamens in three bundles and three styled ovary.

The herb has a characteristic balsamic odor and a bitter, resinous and somewhat astringent taste. Besides hypericin, it also contains pseudohypericin, rutin, quercitrin, isoquercitrin, quercetin, and hyperoside flavonoidic compounds. They can be separated and may be used as dyes. Recent studies demonstrated that the level of hypericin is lowest in May and highest in Midsummer. Hypericin levels range from 121 to 804  $\mu\text{g g}^{-1}$  dry weight was found in Canadian and Australian plant material, respectively. Hypericin content in shoot of field collected *H. perforatum* was 370–1460 ppm for Australian material and about 980 ppm for French material. It was reported that foliar levels of hypericin are three to four times higher in the narrow level (in var. *angustifolium*) than in the round leaved (in var. *perforatum*). Hypericin levels also varied widely within plants and were found higher in the flowers, seed capsules, and upper leaves than in the stems or basal foliage.

*Nipaecoccus aurilanus* Maskell

English – Mealy bugs

Black colored mealy bugs found on *Araucaria* spp. in Australia contain hypericin (0.03%). Besides hypericin, the bugs also contain emodin.

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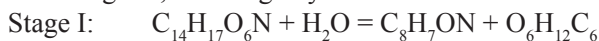
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## 6.47 Indigo or indigotin

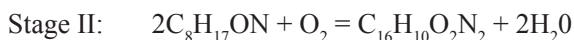
Indigo or indigotin is one of the oldest natural dyes used by man. It was known to the people of Asia for over 4000 years as its method of preparation is described in ancient Vedic literature (The Atharvaveda), and Egyptian tombs have mummies wrapped in clothes dyed with indigo.

Indigotin ( $C_{16}H_{10}O_2N_2$ ; mp 390–392°C), the principal blue coloring matter, also known as indigo, is extracted from the leaves of Bengal or Java Indigo, *Indigofera arrecta* A. Rich., West Indian or Anil Indigo, *I. suffruticosa* Mill., common or Indian Indigo, *I. tinctoria* L., Pala Indigo or Kul Kudai, *Wrightia tinctoria* R. Br., Osak or Assam Indigo, *Strobilanthes cusia* (Nees) Imlay, Riyong, *Marsdenia tinctoria* R. Br., Woad, *Isatis tinctoria* L., Dyers Knot-grass, *Persicaria tinctoria* (Aiton) H. Gross syn. *Polygonum tinctorium* Aiton, and Gara, *Philenoptera cyanescens* (Schum. and Thonn.) Roberty syn. *Lonchocarpus cyanescens* (Schum. and Thonn.) Benth., and from the roots of the wild Indigo, *Baptisia tinctoria* (L.) Vent.

Indigotin is found in the form of a soluble colorless glucoside, Indican ( $C_{14}H_{17}O_6N$ ; mp 180°C) which hydrolyses into glucose and indoxyl ( $C_8H_7ON$ ; mp 85°C). Indoxyl readily reacts with atmospheric oxygen to form insoluble pigment indigotin, the indigo dye. The chemical reactions are as follows:

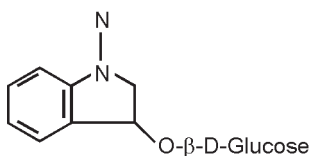


INDICAN → INDOXYL

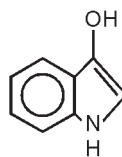


INDOXYL → INDIGOTIN

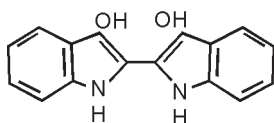
The average yield of indigo is 25% of the total extractable material. Besides indigotin, natural indigo contains indirubin (indirubin or indigo red;  $C_{16}H_{10}N_2O_2$ ; 2–4%), indigo brown, an amorphous substance of undermined constitution (probably derived from indoxyl), gluten, the flavonol kaempferol (Indigo-yellow), and mineral matter. It is because of this composition that the natural indigo dye is not as deep or as reproducible as that of synthetic indigo, which is 100% indigotin.



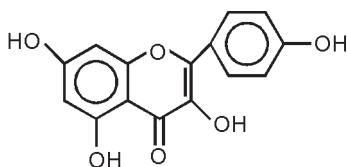
Indican



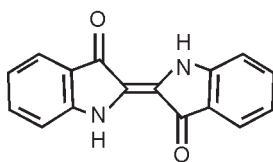
Indoxyl



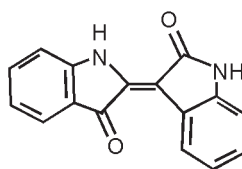
Indigo White



Indigo-Yellow



Indigotin



Indirubin

### 6.47.1 Extraction

The indigo dye is extracted by two methods: (1) the wet method and (2) the dry method. In wet method, freshly harvested plants are steeped in water in especially constructed vats; the water is warmed if necessary to 32°C and left overnight. Fermentation sets in and the glucoside indican breaks down by the action of an enzyme indimuslin, naturally present in the plant, to glucose and indoxyl. Fermentation is completed in 10–15 h. The yellow liquor is run into beating (oxidising) vats equipped with paddle wheels. When the wheels are rotated, the liquor is thrown up into the air as a fine spray and the indoxyl gets oxidized to indigotin or indigo, which settles down as a fine blue mud at the bottom of the vat. The supernatant water is then drawn off. Better yields are obtained by fermenting the leaves under acid conditions and affecting oxidation by blowing ammonia, steam, and air simultaneously into the fermented liquor by means of an injector. Addition of sodium nitrate or Dhak gum, *Butea monosperma* (Lam.) kuntze facilitates the setting of indigo mud. The oxidized product is stirred with boiling water containing a little dilute sulphuric acid, which is then allowed to settle and the clear liquor decanted.

It is then washed with boiling water, filtered through cloth, and pressed. The product is cut into about 7.5 cm cubes and air dried to about 6% moisture. The cubes are brushed to remove surface mould growth (if any), polished and packed in wooden chests.

In dry method, the leaves are air dried prior to steeping in water. They are then macerated with water in a vat and fermented for about two hours. The fermented liquor is treated in the same manner as described under wet process. The advantage of the dry process lies in the short duration of fermentation and the indigo thus obtained is reported to be more uniform. However, some loss of indigo may occur during the air drying of leaves, thereby resulting in lower yield.

High grade indigo has a deep violet-blue shade and shows a coppery luster when scratched with finger nail; it is also light and porous. On the other hand, inferior quality of indigo is heavy, hard, and dull grey in color and does not show a coppery luster when scratched.

### 6.47.2 Uses

Indigo finds use in dyeing and printing cotton and rayon, and for dyeing wool. It has been employed in the preparation of pigments for paints, lacquers, rubber, plastic, and printing inks. It is also used to a small extent by artists and in wall paper.

### 6.47.3 Sources

*Baptisia tinctoria* (L.) Vent. (Fabaceae)

English – Horsefly, Horsefly Weed, Rattle Weed, Wild Indigo

It is a North American herb of about one meter height, having bright yellow flowers, cultivated in America during summer as a fodder crop. Its root contains indigotin which was formerly used as an inferior substitute for indigo.

*Indigofera arrecta* A. Rich. (Fabaceae)

English – Natal Indigo, Java Indigo, Bengal Indigo

It is native of Ethiopia and was introduced into India through Java. It is an erect, deep green, leafy plant of about one to two meter height with compound leaves of 7–8 pairs of leaflets, small pinkish-red colored flowers that are arranged in auxiliary racemes.

It is most important because of its higher dye content (0.8–1.0%) compared to the other two species. At present, it is grown in Andhra Pradesh and Tamil Nadu for green manuring purposes.

The seeds of *I. arrecta* possess hard coat and unless specially treated before sowing, show poor germination. Therefore, seeds are usually scarified in a machine or treated with concentrated sulphuric acid and sown in lines on well ploughed, manured and levelled soil in the middle of October at the rate of 5–7 kg of seeds per hectare. The crop is ready for the first cut by the end of May or the beginning of June. The plants are cut about three cm above the ground and a second crop is taken after an interval of six weeks or more. It yields heavily with the application of the super phosphate.

The crop is affected by wilt which causes serious damage. Wilting can be checked by pruning, soil aeration, and application of organic manure and soluble phosphate.

*I. suffruticosa* Mill.

syn. *I. anil* L. var. *polyphylla* DC.

English – West Indian Indigo, Anil Indigo

It is a shrub, 1–2 m tall, native to tropical America and West Indies. It was introduced into India, Myanmar, China, Philippines, Java, and other South-East Asian countries. It has very small flowers of pale-orange color and two to four seeded curved pods.

It is a hardy plant and can be grown on well drained soil. It is propagated by seeds. The seeds are sown at the rate of about 9–10 kg per hectare. At present, it is grown as a cover crop in coffee and tea plantations and as a green manure crop in Indonesia, Malaysia, Sri Lanka, and Africa. In India it has been replaced by *I. arrecta* as the latter yields higher quantity of vegetative matter as well as the coloring matter.

*Isatis tinctoria* L.

syn. *I. sumatrana* Gaertn.

English – Common Indigo, Indian Indigo; Hindi and Bengali – Nil; Gujarati – Gali, Gari, Nil; Malayalam – Nilam; Marathi, Tamil and Kannada – Nili; Telugu – Aviri, Nili

It was once grown extensively for extraction of the indigo dye. The plant is about 1–2 m tall, found nearly throughout India, mainly as an escape from cultivation. It contains compound leaves with 9–13 leaflets, red flowers and slightly curved or straight fruits. It is considered to be Asian in origin, though it has been occurring wild in Africa. It was cultivated in India, China, and other countries of the East as the source of the indigo dye, but was replaced first by *I. suffruticosa* and latter by *I. arrecta* in India.

*Marsdenia tinctoria* R. Br. (Apocynaceae)

North Bengali – Riyong; Lepcha – Ryom; Assami – Mei-ni-buli-likur, Mani; Nepali – Kali Lara

It is a tall and stout climber, found in eastern Himalayas and Assam. The plant is occasionally cultivated. It is propagated from layers, slips, and cuttings.

The leaves yield a dye indigotin or indigo similar to as obtained from the *Indigofera* spp. The cultivation of the plant for dual purpose of dye and fiber, obtained from bark, has been suggested.

*Persicaria tinctoria* (Aiton) H. Gross (Polygonaceae)

syn. *Polygonum tinctorium* Aiton

English – Dyers Knot Grass

It was at one time grown in China and the Caucasus. It also contains indican.

*Strobilanthes cusia* (Nees) Imlay (Acanthaceae)

syn. *S. flaccidifolius* Nees

English – Osak Rum, Assam Indigo; Assam – Rum, Rampat; Sibsapar – Raspat; Lushai – Tiny; Manipur – Khuma, Khum

It is a perennial glabrous shrub found in Assam, Meghalaya, North Bengal, and Manipur. Leaves elliptic-ovate, acute; flowers purple, in dense panicles; pods 1.8 cm long.

The plant yields a blue dye and is cultivated by the hill tribes throughout the regions of its distribution. It is propagated by root cuttings made in May or June or earlier if rains set in. It flourishes on higher dry lands and is pruned twice or thrice a year, in April–May and again during September–October. The indican contents of the leaves have been reported to be 0.4–1.3%.

The twigs are cut and steeped in water to which lime is added. When fermentation sets in, the water is stirred well and the precipitated blue dye is collected. The dye in combination with turmeric, lime, and safflower produces shades of green, deep blue, and purple, respectively.

*Wrightia tinctoria* R. Br. (Apocynaceae)

English – Pala Indigo-plant, Ivory Woad Tree; Bengali – Inderjau; Hindi – Indrajau, Mitha-idrajau; Gujarati – Indrajau, Runchallodudhlo, Dudhlo; Kannada – Kodamurki, Bepalle, Kodesige; Malayalam – Kotakappala, Aiyapala; Marathi – Kala-kuda, Indrajau; Oriya – Pita Karuan, Dudhokriya, Krya; Tamil – Yeypale, Irumpalai, Thonthapalai; Telugu – Tedlapaala, Amkuda, Jeddapaala; Sanskrit – Hyamaraka

It is a small tree, up to 1.8 m tall, native to India, occurs in Rajasthan, Madhya Pradesh, and the Peninsular India, ascending to an altitude of about 1,200 m in the hills.

The leaves are a source of blue dye, indigo, called Mysore Pala Indigo (yield, 0.33–0.5%). Besides leaves, seeds and roots also have been reported to

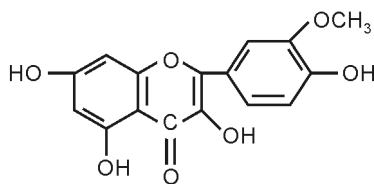
have indigo yielding glucoside, the indigotin. The dye is extracted in the same way as extracted from *Indigofera* spp. The tree is a moderate light demander, and is often found as an undergrowth species in deciduous forests. It requires a mixture of peat, loam, and sand. It can be propagated by seeds or cuttings which readily root in sand under the sun in rainy season. It produces root suckers. The growth is slow to moderate, the annual increase in girth being 1.16–2.3 cm.

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### 6.48 Isorhamnetin

Isorhamnetin (3,4',5,7-tetrahydroxy-3'-methoxyflavone;  $C_{16}H_{12}O_7$ ; mp 305°C), the principal yellow coloring matter is present in the dried fruits and flowering stem of Asbarg, *Delphinium zalil* Aitch. and Hemsl., and in red clover, *Trifolium pratense* L., in the leaves of Senna, *Senna alexandrina* Mill. syn. *Cassia senna* L. and in lesser Indian Reed-Mace, *Typha australis* Schum and Thonn. It is soluble in hot water. Isorhamnetin is less reddish-yellow than quercitrin.



Isorhamnetin

### 6.48.1 Extraction

The plant material is ground into powder and put into hot water for 2–4 h and then filtered. The filtrate is treated with sulphuric acid and again boiled for 15 min. It is then cooled and dried. After drying, a brownish-yellow powder is obtained. The powder is digested with boiling alcohol, which dissolves the coloring matter. Then a dark colored solution is obtained. It is evaporated to a small bulk and poured into a large volume of ether, and washed with water until the washings are colorless. It is then agitated with alkali to free the substance from impurity of wax. The alkaline liquid is acidity to get yellow flocks of the coloring matter, which is still contaminated with some impurity of acidic nature. To remove this, excess of sodium hydrogen carbonate is added to the mixture and the product is extracted with ether and then evaporated to get a yellow colored powder of isorhamnetin.

### 6.48.2 Uses

This is used to dye cotton and silk and also in calico printing. It produces gand-kaki, a sulphur yellow on silk with akalbir, *Datisca cannabinn* L. dye. With different mordants it yields various shades. With aluminium, chromium, iron, and tin it gives golden-yellow, brownish-orange, brown-olive and a bright-orange color, respectively.

### 6.48.3 Sources

*Senna alexandrina* Mill. (Fabaceae)

syn. *Cassia senna* L.

See under the dye chrysophanic acid or chrysophanol.

*Delphinium zalil* Aitch. and Hemsl. (Ranunculaceae)

English – Zalil Larkspur; Hindi and Punjabi – Asbarg; Marathi – Trayaman, Gul-zalil

It is a large and evergreen herbal plant, distinguished by its bright yellow flowers, commonly available in Iran, Afghanistan, and Baluchistan, and also



cultivated in Europe. The dye is obtained from the flowers and their stalks. Once dried and packed in boxes, they are exported as the dye for silk.

The entire plant is rich in flavonols-quercetol and isorhamnetol. Silk is dyed in a sulphur-yellow color called ghandhaki in the presence of alum, and green called *abi sangar*, with copper sulphate.

*Trifolium pretense* L.

For the details of the plant, see the dye-pratol.

*Typha australis* Schum. and Thonn. (Typhaceae)

syn. *T. angustata* Bory and Chanb.; *T. elephantiana* Grah

English – Lesser Indian Reed-Mace; Bengali – Kaw, Hogla; Gujarati – Ghabajario, Punjabris, Pario; Hindi – Patera; Kannada – Aanechondu, Aapu, Maribala; Marathi – Pankauis, Pun, Jangli-bajri; Tamil – Sambu; Telugu – Jammugaddi, Dabbujammu, Jammu

It is a perennial, robust, up to four meter tall plant, commonly found in marshy places throughout India. It has a creeping rhizome and semi cylindrical,  $3 \times 2.5$  cm leaves, cylindrical spikes bearing male and female flowers, sometimes on different plants. Male spikes are 25–50 cm long, consisting of deep-yellow anthers; female spikes are 22–38 cm long, pale brown, flowers mixed with clavate pistillodes.

The plant contains isorhamnetin, the coloring matter.

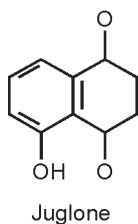
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## 6.49 Juglone

The isomeric compound of lawsone, commonly called Juglone, Nucin, or Regianin, found in the leaves and shells of unripe walnut, *Juglans regia* L., and Pecan, *Carya illinoensis* (Wangenh.) K. Koch has been identified as

a-hydrojuglone glucoside ( $C_{16}H_{18}O_8$ ) which on hydrolysis yield glucose and a-hydrojuglone (1,4,5-trihydroxynaphthalene); the latter on oxidation yield juglone (5-hydroxy, 1,4-naphthoquinone,  $C_{10}H_6O_3$ ; mp 153–155°C). Juglone is slightly soluble in hot water; freely soluble in chloroform, benzene, alcohol, and ether.



### 6.49.1 Extraction

The glucoside forms up to 15% of the total indophenol dye by reducing material in immature wall nut shells or mature hulls. Its concentration is particularly high in very young fruits and in resting buds and catkins. The shells are ground, fermented for two days, and extracted with hot water. In this process, the colorless hydroform undergoes air oxidation to yield the quinone structure that dyes natural fibers in yellow-brown hue. For isolation, pure juglone, i.e. the unripe walnut hulls are crushed and macerated in ether. The solvent is then allowed to evaporate at room temperature. On evaporation it leaves a dark scaly residue, which on sublimation yields crude juglone. This is then chromatographed and gets pure juglone. Besides the unripe walnut hulls, the leaves of walnut tree and pecan also contain juglone. For the extraction of juglone from the leaves, the leaves are immersed, immediately after harvesting, in a solid  $CO_2$  ( $-78^\circ C$ ), and ground in the mixture of chilled chloroform and methanol (2:1) and filtered. The filtrate is concentrated by vacuum distillation and chromatographed. The fraction is collected by elution with methanol. The methanol eluate on further concentration yields an orange pigment which on hydrolysis at reflux with 1:3 N HCl for one hour in 50% aqueous methanol yields juglone. It is then separated by thin layer chromatography by spraying dichloromethane and pentane (1:3).

### 6.49.2 Uses

Juglone is an ancient dye which has been used in tapestries since 17th century. It imparts a brownish-yellow color on mordanted wool and rose tint on mordanted cotton. The colors are inferior to synthetic dyes in fastness, particularly against light; mordants do not improve the color fastness.

### 6.49.3 Sources

*Carya illinoensis* (Wangenh.) K.Koch (Juglandaceae)

syn. *C. pecan* Engl. and Graebn

English – Pecan nut tree and Hickory nut tree

It is handsome, deciduous, and up to 60 m tall tree. It has been successfully introduced in Kangra valley of Himachal Pradesh and in the Kumaun and Garhwal hills of Uttar Pradesh.

The trees thrive well in sub-temperate climate. Under normal conditions seedlings can be raised from seeds, but such trees bear nuts after 20 years; hence propagation by various budding and grafting methods is recommended.

The leaves contain juglone, the coloring matter. The content of juglone in leaves and nuts is low in early season and increases through July. The level of coloring matter in nuts continues to increase to a high level in the late season while that in leaves decreases to near zero.

*Juglans regia* L. (Juglandaceae)

English – Common Walnut, Persian Walnut, and European Walnut; Hindi – Akhrot; Trade – Akhrot, Arkut, Akhor, Krot

It is a large deciduous tree with tomentose shoot, found throughout the Himalayas and hills of Assam at altitudes between 1000 and 3500 m. It is also cultivated in Kashmir, Punjab, Himachal Pradesh, and Uttar Pradesh.

Walnut requires a frost free climate in spring and extreme heat in summer. It thrives well in areas with an annual rainfall of 75 cm or more. The deep and well drained silt loam soil containing abundant organic matter gives the best result. The hard pan, subsoil or alkali soil does not give good results.

The plants are generally raised from seedlings. Nuts are sown in rows, about five cm deep in soil immediately after harvesting in December. The distance between plant to plant and row to row should be 30 cm. Germination starts in the beginning of March and seedlings are ready for transplantation in the second year.

Walnut is also propagated by vegetative methods like whip grafting, cleft grafting, inlay bark grafting, and patch budding in early spring. Irrigation helps growth and trees come into bearing early. Irrigation should be continued till the maturity of fruits as it reduces nut falls.

The tree starts to bear crop at the age of 8–10 years. The yield of nuts varies according to the age, size, and variety of tree. A grown up big tree may yield 150–200 kg of nuts.

Green walnut hulls, shells, bark, and leaves yield juglone and tannin which after isolation and purification are used for dyeing and tanning. The alcoholic extract of the green walnut shells is used as hair dye, after mordanted with alum.

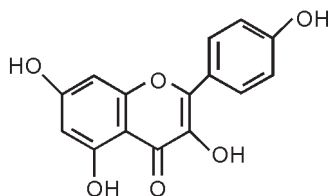
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## 6.50 Kaempferol

Kaempferol (3,4,5,7-tetrahydroxy flavone;  $C_{15}H_{10}O_6$ ; mp 276–278°C), the principal yellow coloring matter occurs in the bulbs of Kulanjan, *Alpinia officinarum* Hance, rhizome of bracken fern, *Pteridium aquilinum* (L.) Kuhn, bark of Utis, *Alnus nitida* (Spach) Endl. flowers and leaves of Chinese primrose, *Primula sinensis* Sabine ex Lindl., leaves of tea, *Camellia sinensis* (L.) Kuntze, in whole plant of field horstail, *Equisetum arvense* L., seeds of Akashbel, *Cuscuta reflexa* Roxb. flowers of *Consolida regalis* Gray syn. *Delphinium consolida* L., *Prunus spinosa* L., *Crocus asturicus* Herb., *C. speciosus* M.Bieb., and in berries of *Rhamnus cathartica* L.

Kaempferol also occurs as glycosides, robinin ( $C_{33}H_{40}O_{15}$ ; yellow needles, mp 196–197°C), from *Robinia pseudacacia*, multiflorin ( $C_{27}H_{30}O_{15}$ ; yellow needles, mp 147–170°C) from *Rosa multiflora*, kaempferin ( $C_{27}H_{30}O_{16}$ ; yellow needles, mp 185–186°C) from *Cassia angustifolia*., kaempferitrin (indigo yellow), a 3-rhamnoside, ( $C_{27}H_{30}O_{14}$ ; colorless needles, mp 201–203°C), from *Indigofera arrecta* and dyers' knot grass (*Polygonum tinctorium*), from which kaempferol can be obtained after hydrolyzing the glycosides with acid.



Kaempferol

Kaempferol is slightly soluble in water but readily soluble in boiling alcohol and dissolves in alkaline solution with pale yellow colors.

### 6.50.1 Extraction

The raw material ground into fine powder and extracted with hot methyl alcohol. The alcoholic extract is then boiled in water and filtered. Then ether is mixed with the aqueous alcoholic extract to get kaempferol. It is recrystallized from methyl alcohol yields yellow needles of kaempferol.

### 6.50.2 Uses

Kaempferol is used in calico printing and dyeing. It is used to dye cotton, wool, and silk and imparts various colors with different mordants. It gives brownish-yellow, yellow, lemon yellow and deep olive brown with chromium, aluminium, tin and iron respectively.

### 6.50.3 Sources

*Alnus nitida* (Spach) Endl. (Betulaceae)

English – West Himalayan Alder; Kashmiri – Selong, Seril; Punjabi – Sharol; Uttar Pradesh – Kunis utis

It is a large deciduous tree, up to 30 m tall and 4 m in girth, distributed in Western Himalayas from the Yamuna westwards to Kashmir at altitudes between 900 and 2,700 m.

Bark yields kaempferol, the coloring matter.

*Alpinia officinarum* Hance (Zingiberaceae)

English – Lesser Galangal

It is a perennial herb with thick, creeping, reddish-brown rhizome, and white flowers, native of China. It can be cultivated in the plains of West Bengal and Assam and in the Eastern Himalayas.

Like ginger, it can be propagated from the rhizomes. As it is imported from China, it is not available in genuine form and in the market it is found to be adulterated with the rhizomes of *Acorus calamus*.

The alcoholic extract of the rhizome contains the coloring material kaempferol and quercetin.

*Camellia sinensis* (L.) Kuntze. (Theaceae)

English – Tea plant; Bengali and Hindi – Chai; Gujarati – Cha; Kannada – Cha, Chaha, Theyale; Malayalam – Chaya, Theyila; Marathi – Chaha; Oriya – Cha; Sanskrit – Chaha, Chevika; Tamil – Karupputteyilai, Pachaitteyilai, Teyilai; Telugu – Nellatcyakua, Teyaku; Urdu – Chai

It is an evergreen shrub or small tree that is found from Assam and hilly regions to the east and south of it. It is cultivated in the hilly districts of North and South for its leaves which furnish the tea of commerce.

Tea is a subtropical species and is grown on a plantation scale in many parts of the world where the climate is moist and warm and the winter is not too cold. A well distributed rainfall varying from about 125 to 750 cm is needed for tea cultivation. Tea can be grown on a well drained and friable loam or in soil rich in organic matters.

Tea is generally propagated from seeds; but in recent years, the use of high yielding clonal material has become popular. It can also be vegetatively propagated by budding, grafting or root stocks or by layering.

The fresh leaves as well as green tea contain kaempferol and quercetin which are responsible for the yellow color. The waste also contains pigments like theaflavins, thearubigins, and catechins, which have been used for coloring confectionery products such as sugar lozenges, fruit paste, ice cream, and soft drinks and form good substitutes for coal-tar based food colors which are being discontinued because of their carcinogenic properties and other harmful side effects. Fukuda, Monnosuke of Japan developed a method for dyeing silk by using a mordant. For example, 1.5 kg green tea in a cloth bag is immersed in 40 l water which is then boiled at 80°C, treated with burnt deep-green soul. Silk (500 gm) with light brown bottom is dipped in a solution for 24 h to give a fast dye, retaining the brown color. A patent developed by Bokuchava and Pruidze (1967) described the preparation of green and yellow colors directly from extracts of green and black tea. A red dye is obtained by coupling with beetroot pigments and mixing these with the ethyl-acetate-soluble portion produces an orange dye. A black color is produced by treating the tea extracts with iron lactate solution.

*Equisetum arvense* L. (Equisetaceae)

English – Field Horsetail

It is a rush like perennial plant with deep creeping rhizomes from which arise erect or scrambling, hollow, and jointed aerial branches. Leaves are reduced to scales which sheathe the joints. The plants inhabit swampy ground and sandy banks of streams and rivers at high altitudes in the Himalayas.

The plant yields a red dye which is used for polishing wooden articles. It yields a number of coloring principles like kaempferol, equisetin, and apigenin.

*Onychium japonicum* (Thumb.) Kuntze (Polypodiaceae)

It is a small and handsome fern with creeping rhizome and pinnatifid fronds found in Kumaun, Missouri, Garhwal, Khasi, Aka, and Lushai hills at altitudes of 900–2,400 m. The fern is well suited for indoor decoration.

Plant yields a glycoside ( $C_{27}H_{30}O_{14}$ ) which on hydrolysis gives kaempferol and rhamnose.

*Primula sinensis* Sabine ex Lindl. (Primulaceae)

English – Chinese Primrose

It is a woody herb, native to China, and reported to be cultivated in gardens in Uttar Pradesh, Nilgires, and Bangalore.

This species has a large number of cultivated type plants with large fringed flowers of blue, white, red, rose, orange-red, scarlet or carmine-purple color.

The flowers and leaves contain three major coloring principles: lole lae, ferp, Qiercetom and myricetin.

*Pteridium aquilinum* (L.) Kuhn (Polypodiaceae)

syn. *Pteris aquiliva* L.

English – Bracken, Brake; Lushai – Katchat; Malayalam – Tavi; Punjabi – Deo, Kakei, Kakhash, Lungar; Tamil – Parnai

It is a tufted, fast growing fern with a stout, creeping rhizome, producing numerous fronds that grows on exposed grassy lands in the hills throughout India, at altitude of 600–3,600 m.

Bracken is an ornamental fern, grown for borders and rockeries and also planted in pots for indoor decoration. It can be propagated through division of rhizomes, or from spores.

Rhizome yields a dark-yellow dye which contains yellow coloring matter kaempferol. It also contains other flavonoids like astragalin, isoquercetin, and rutin. It also contains catechol tannin (66%), which is used for tanning and dyeing leather.

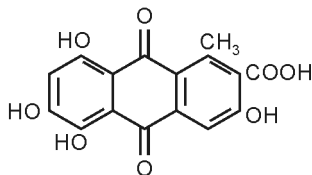
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## 6.51 Kermesic acid

Kermesic acid (9,10-Dihydro-3,5,6,8-tetrahydroxy-1-methyl-9,10-dioxo-2-anthracenecarboxylic acid;  $C_{16}H_{10}O_8$ ; mp>320°C) is the principal red coloring matter, similar to that of carminic acid, that occurs in the galls of dried females of a coccid kermes, *Kermes ilicis* (= *Kermococcus ilices*; *Coccus ilices* and *Kermes vermilio* Planchon), the kidney or heart shaped, reddish-brown with black strip insects which thrive on the leaves and stems of alder oak trees, *Quercus coccifera* L., and holm-oak Ilex, *Q. ilex* L., and are commonly found in North America, Middle East, and Europe.



Kermesic Acid

The name kermes is derived from an American word which means “little worm” for which the later Latin equivalent was *Vermi-culus*. The basis of the English word vermilion is the color this insect dyes natural fibers in. It was particularly important during the Golden Age of Venice, when its dyeing rivaled the fabled tyrian royal purple, and the search for additional sources



stimulated world exploration. These insects have been collected historically by women; it being noted that they allowed their finger nails to reach a more than normal length in order to assist them in their work. One woman could pick about a kilogram of insects per day in candlelight before day break, when the dew had not yet evaporated and the thorny holly or oak leaves were still soft.

### 6.51.1 Extraction

For the extraction of the dye, the insects are collected in the month of June and killed by exposure to the vapors of acetic acid and then dried. The dried insects are boiled in water and filtered. The filtered liquor, the crude kermes dye contains two dyes namely, kermesic acid and flavokermesic acid ( $C_{13}H_8O_6$ ). The two dyes are separated as both the dyes have different solubilities in sodium acetate solution. Five kilograms of crude dried insects yield approximately 50–55 g of kermesic acid and 3 g of flavokermesic acid. The flavokermesic acid gives golden-yellow color from acid bath and a dull orange shade on tin mordant.

The kermesic acid or kermesic dye, popularly known as Ajred dye in ancient Greece and Rome, is the oldest of all the insect dyes except lac dye.

### 6.51.2 Uses

Kermesic acid is slightly soluble in cold water but commonly soluble in hot water and gives a yellowish-red solution. On dissolving in concentrated sulphuric acid, it produces a violet-red which turns blue on the addition of boric acid. It gives brilliant scarlet when mordanted with alum. It dyes wool orange-red from an acid bath and gives scarlet-red, the less blue than those of carminic acid, on a tin mordant. It has been widely used in south France, Spain, Morocco, and Turkey for dyeing leather and woolens.

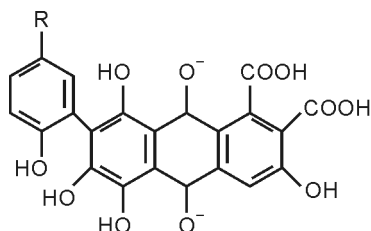
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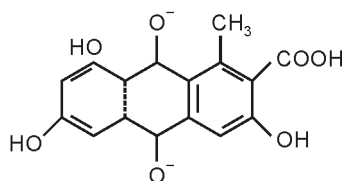
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## 6.52 Laccaic acid and erythrolaccin

The stick lac, resinous protective secretion of the tiny lac insects, *Kerria lacca* Kerremans (formerly *Laccifer lacca* Kerr) contains two pigments, the water soluble red dye, the laccaic acid (Hydroxy anthraquinone carboxylic acid;  $C_{20}H_{14}O_{10}$ , mp  $180^{\circ}C$  decomposed) and an alkali and spirit soluble yellow dye, the erythrolaccin (1,2,5,7-tetrahydroxy-4-methyl anthraquinone,  $C_{15}H_{10}O_6$ ; mp  $314^{\circ}C$ ). Laccaic acid is slightly soluble in cold water but readily soluble in hot water and alcohol. It is crystallized from water or methanol in bright red needles. It forms purple solution in aqueous sodium bicarbonate, sodium carbonate, and sodium hydroxide. It gives a bluish-grey coloration with ethanolic ferric chloride and a purple with methanolic magnesium acetate. Its purple solution in aqueous sodium hydroxide turns red on treatment with sodium hydrosulphite and remains red after air oxidation. It is similar to alizarin and is a mixture of at least five closely related compounds such as laccaic acid A ( $C_{26}H_{19}NO_{12}$ ), B ( $C_{24}H_{16}O_{12}$ ), C ( $C_{25}H_{17}NO_{13}$ ), D, and E. It is acidic in nature and is generally present as its sodium or potassium salts are completely soluble in cold water, whereas the pure dye is sparingly soluble in cold water but soluble in boiling water. The dye is also soluble in methyl alcohol, amyl alcohol, acetone, acetic acid, and formic acid but insoluble in ether, chloroform, ligrorin, and benzene.



Laccaic A.B.C



Laccaic Acid D

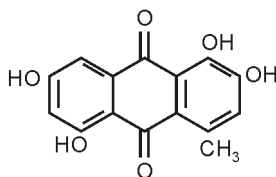
### 6.52.1 Extraction

Different methods of extraction of the lac dye have been developed by the scientists at Lac Research Institute, Ranchi. Few of them, which are simple and economical, are as follows:

- (A) The crushed stick-lac is washed thoroughly with water (slightly alkalined), and the washings are allowed to settle and then supernatant liquid is decanted off. The residual stick-lac is again washed in the same manner. The combined extracts are then filtered and brought to pH 8 by the addition of caustic soda solution and treated with the calcium chloride. The calcium salt of the dye is precipitated. It is filtered and washed to remove soluble matters. This calcium salt of the dye is treated with hydrochloric acid; steam is passed for half an hour and then allowed to stand for a week. The needles of red dye are crystallized, filtered, and dried at 50°C.
- (B) The waste effluents of lac processing units are treated with sulphuric acid (0.1%), precipitate out the solid which is either decanted or filtered. The filtered liquor is treated with lime which yields insoluble calcium salt. Now this calcium salt is converted into soluble sodium salt which is then passed through cation exchange resin column and then the eluate is concentrated to give pure red dye crystals.
- (C) The dye can be obtained through a direct method in which the stick-lac is washed in water and filtered. The filtered water is passed through cation exchange resin column and the resulting solution is concentrated to yield red lac dye.

### 6.52.2 Erythrolaccin

The erythrolaccin is soluble in alkali and spirit but insoluble in water. It has been employed for dyeing silk, wool, and leather. It is also used for decorative painting of hands and feet by ladies.



Erythrolaccin

The erythrolaccin, a yellow dye, is extracted from the seed lac or button-lac from which the water soluble red dye is removed. The seed lac is soaked either in industrial alcohol (spirit) or alkali solution for over 2–4 h and then filtered. The yellow dye is soluble in spirit, and alkali is then crystallized under reduced pressure.

### 6.52.3 Uses

The lac dye has been used in India from ancient times for dyeing wool and silk as mentioned in *Atharvaveda* (1500 BC). It is fast on animal fibers like wool and silk but not on vegetable fibers like cotton. It has been found non-toxic, therefore, it is used for coloring food materials and products and cosmetics. It is used for coloring juice, soft drinks, and products like ham-sausage, bean-jam, etc. It has also been used to dye leather and leather products.

### 6.52.4 Lac and lac insects

Lac is the resinous protective secretion of the tiny lac insect, *Kerria lacca* Kerr syn. *Laccifer lacca* Kerr, a pest on several plants. There are over a hundred species of plants on which lac insects have been found but from the point of view of large scale production, Palas, *Butea monosperma* (Lam.) Kuntze, Ber, *Ziziphus abyssinica* Hochst. ex A.Rich. syn. *Ziziphus mauritiana* Lam., Arhar, *Cajanus cajan* (L.) Mills), and Khair, *Acacia catechu* Willd. are the most important. The insects secrete a thick resinous fluid which envelops their bodies. The secretions from individual insects coalesce and form a hard continuous encrustation over the twigs. The twigs are broken off just before the time of hatching and exposed to the sun to kill the insects; the obtained product is stick-lac.

Presently only two nations in the world, India and Thailand, are the main producers of lac. India produces approximately 20,000 tonnes per year, involving about 3 million tribal people of Bihar, Madhya Pradesh, Maharashtra, Orissa, West Bengal, and Uttar Pradesh. About 15–20% of the total production is consumed locally and the rest is exported to various countries.

The commonest and the most widely occurring species of lac insect in India is *Kerria lacca* syn. *Laccifer lacca* which produces the bulk of commercial lac. Besides this, the species like *K. mysorensis* and *K. communis*, found in Central India; *K. fici* Wild. found in Bihar, Delhi, Jammu and Kashmir; and *K. sindica* found in Sind in Pakistan are also reported to produce commercial lac.

### 6.52.5 Lac cultivation

*Introduction:* Lac cultivation has been carried on by peasants in forests, sub-forests, and hinterland areas where suitable host plants exist, as a subsidiary occupation. The lac cultivation is initiated from brood lac, which is the twig of host tree carrying lac encrustation, with larvae about to emerge from mother cell. The twigs are cut, bundled, and tied at convenient places on a fresh host plant, so that the emerging larvae can swarm and settle on nearby succulent

shoots.

*Pruning:* The twigs on which lac encrustations have been deposited are pruned after 3–4 months of inoculation for *katki* crop and 8–9 months for *baisakhi* crop.

*Harvesting:* Encrustations of lac are separated from the twigs by scraping. The scraped material, green lac or stick-lac, as it is called, is spread thinly (10–15 cm deep) in a covered and well-ventilated place and periodically raked until dry. The stick-lac thus obtained is then bagged for storage or for the market.

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## 6.53 Lapachol

Lapachol, (2-Hydroxy-3-(3-methyl-2-butenyl)-1,4-naphthoquinone;  $C_{15}H_{14}O_3$ ; mp 139–140°C), a reduced product of desoxylapachol, is a principal yellow coloring matter that occurs in the heartwood of teak, *Tectona grandis* L.f., Taigu or lapachol wood, *Catalpa ovata* G.Don., and Rodhia tree, *Tecomella undulata* (Sm.) Seem., and *Zeyhe digitalis* (Vell.) Hoehne, and also in bark and roots of few species of the Bignoniaceae family.

Lapachol, also known as lapachic acid, taiguic acid, teconin or

greenheartin soluble in alcohol, chloroform, benzene, acetic acid, and alkali is slightly soluble in ether and hot water. In aqueous sodium hydroxide solutions it forms a bright red sodium salt solution.

### 6.53.1 Extraction

The wood is powdered and extracted successively with benzene. It is recrystallized with ethyl alcohol to give lapachol, which can further be purified with chromatographic methods.

The crude aqueous extract, which contains a number of other pigments, is extracted by heating chopped wood with water or preferably with sodium carbonate solution (1%). Then the dye is precipitated from the extract and extracted with ether.

### 6.53.2 Uses

Until recently, it was mostly used for the manufacture of high quality bows and fishing rods. It is also used to dye textile fibers.

### 6.53.3 Toxicity

Lapachol is reported to cause allergic eczema or severe itching to few people. However, it has exhibited an antitumor activity against walker 256 carcinoma.

### 6.53.4 Sources

*Tecomella undulata* (Sm.) Seem (Bignoniaceae)  
syn. *Tacoma undulata* G.Don; *Begonia undulata* Sm.

English – Rohida Tree; Marathi – Roira, Lahuri, Lohero, Rakhtreora; Hindi – Rugtrora; Marathi – Rakhtreora, Rakhtrohi, Rakhtroda; Marwari – Roira, Rohera; Punjabi – Rohira, Roira, Lahura, Luar; Rajasthani – Roira, Rohera; Sanskrit – Rohi

It is a deciduous ornamental shrub or a small tree, found in the drier parts of the North-West and Western India, extending eastwards to the river Yamuna and ascending to an altitude of 1200 m in the outer Himalayas.

The tree is grown in gardens for its handsome yellow or deep orange colored flowers. The plant is very hardy and resistant to drought and is used for afforestation and landscaping of dry tracts.

The tree is propagated by seeds, and vegetatively by cuttings and succeeds well in well-drained fibrous loam soil. It requires plenty of water in summer. The heartwood contains a good amount of lapachol, which is toxic and responsible for the fungus and termite resisting properties of the wood.

*Tectona grandis* L. (Bignoniaceae)

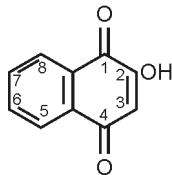
See under tectoleaf-quinone.

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## 6.54 Lawsone

Lawsone (2-hydroxy, 1,4-naphthoquinone;  $C_{10}H_6O_3$ ; mp 195–196°C), the principal coloring matter found in the leaves of Henna, *Lawsonia inermis* L., and Balsam, *Impatiens balsamina* L. to the extent of about 1.0–1.4% of the weight of dried leaf. It is very sparingly soluble in cold water; slightly soluble in chloroform, bromoform, acetic acid, and petroleum ether; moderately soluble in alcohol, benzene, and ether; and easily soluble in solutions of alkalis, carbonates, bicarbonates, and hydroxides, and forms orange-red solutions which quickly undergo decomposition when boiled. The substance is fairly acidic in reaction and produces a brisk evolution of carbon dioxide from sodium bicarbonate, although not from sodium carbonate.



Lawsone

Henna is a rare example of a dye plant which is very ancient in origin and

is still used today. Egyptian mummies found in tombs had their nails dyed with henna, exactly like their descendants in the present times. Henna is a very fast dye. It is harmless and causes no irritation to the skin.

### 6.54.1 Extraction

Leaves are dried and ground in a fine powder and then extracted with sodium bicarbonate solution (5%) for a period of 24 hours. It is then acidified with strong sulphuric acid diluted with an equal volume of water. The resultant precipitate, which contains crude coloring matter, is filtered and dried off. The crude substance is then extracted with dilute ammonium hydroxide, filtered, and the filtrate is precipitated with concentrated hydrochloric acid and again filtered. The obtained precipitate is dried and then extracted with benzene. The benzene is distilled off and the coloring matter is obtained in the form of orange-yellow crusts. It is then dissolved in sodium carbonate solution, filtered, and the orange-yellow filtrate is precipitated with concentrated hydrochloric acid. The precipitate is filtered, washed with distilled water until free from chloride, dried, and repeatedly crystallized from benzene color in the crystalline and a lemon-yellow color in the powdered state known as Lawsone.

### 6.54.2 Uses

Lawsone is used to dye wool and silk in orange shade. The dye has also long been used by the people, especially the ladies of India and the middle Eastern countries for tinting finger nails and the palms of their hands a reddish-brown, dyeing the hair and eyebrows and for other forms of personal adornment. This is also used for coloring leather and for the tails and manes of horses.

A wide range of colors from orangish to brownish-red may be obtained by treating henna-dyed fabrics in acid baths containing various metal salts. Cotton previously treated with acidified ferrous sulphate solution is colored cement-grey when dyed with henna extract. The use of henna as a textile dye has declined since the advent of synthetic dye stuffs. It can also dye leather, skin, and hair in a brownish-red color, and is still used for this purpose in Muslim countries and also in India.

### 6.54.3 Sources

*Impatiens balsamina* L. (Balsaminaceae)

English – Garden Balsam; Bengali – Dupati; Gujarati – Gulmendi, Pantambol; Hindi – Gulmendi; Malayalam – Mecchingom; Marathi – Terada; Oriya – Haragaura; Punjabi – Bantil, Trual, Halu, Tatura, Tilphar, Juk; Sanskrit – Dushpatrijati

It is an erect, branched, succulent annual of 20–75 cm height, with



shortly stalked or stalk less, serrate leaves; solitary or fascicled, purple, pink or nearly white flowers; capsular, hairy fruits; found throughout the tropical and subtropical parts of India, and is found growing gregariously as forest undergrowth. It is variable and is found in many forms, often separated as varieties that are cultivated in gardens. The flowers and leaves yield the dye lawsone.

Balsams are very easy to cultivate throughout the year. It needs a very rich variable, open, well-drained soil, and open, sunny situation and a very liberal supply of water during growth. Seeds are sown thinly in well-drained seed beds and shaded till germination begins. When the plants have grown about six leaves, they are transplanted into beds or field by setting those 25 cm apart in regular rows. If very large blooms are required, all the side shoots are pinched off. Plants are kept in a moist atmosphere and sprayed in dry weather. Liquid manure may be given once a week for better growth. The plants are attacked by mildew all year long. Bordeaux mixture or copper oxy-chloride should be sprayed for checking the disease. Blooms appear in 60–65 days after sowing; blooming period lasts for about 15 days.

#### 6.54.4 Sources

*Lawsonia inermis* L. (Lythraceae)

syn. *L. alba* Lam.

English – Henna, Egyptian Privet; Bengali – Mehendi, Mendi; Gujarati – Medi, Mendi; Hindi – Mehndi; Kannada – Mayilanchi, Gorante; Malayalam – Mailanchi, Pontlasi; Marathi – Mendhi; Oriya; Benjati; Punjabi – Mehandi

It is a much branched shrub or small tree, cultivated as a hedge plant throughout India and as a commercial dye crop in Punjab, Haryana, Gujarat, Madhya Pradesh, and Rajasthan. The more important centres of production of *mehandi* are: Faridabad in Gurgaon district (Haryana) and Bordoli and Madhi in Surat district (Gujarat) which together account for 87% of the total production of henna leaves.

#### 6.54.5 Cultivation

Henna plant can grow on any type of soil from light loam to clay loam, but does best on heavy soils which are retentive of moisture. It can tolerate a little alkalinity in the soil. Propagation is done by seeds and cuttings. Seeds are sown in nursery beds and kept flooded with water for few days before sowing. Seeds are first soaked in water for 20–25 days with frequent change of water for sprouting and then sown in March–April. About 3.0–4.5 kg of seeds is required to raise enough seedlings and when they are 40–60 cm tall, they

are transplanted in the field (in July–August) after cutting out the roots and shoots. Once established, the plants continue to flourish and yield successive crops of leaves for about 100 years. For hedging, propagation by cuttings is convenient. The crop is harvested twice a year (April–May and October–November) from the second year onwards. Plants are cut close to the ground, dried in shade, and leaves are separated by beating.

The yield of dry leaves is low during the first 2–3 years and varies from 80–400 kg per acre; it increases later to 450–800 kg. The yield from irrigated fields is reported to be 1000 kg per acre per annum. The harvest during October–November (summer crop) accounts for 75–85% of the total yield. About 15% of the total production is consumed within the country in the form of powder; the rest is exported in the form of dried leaves for making powder. The principal importing countries are France, the United Kingdom, South Africa, Syria, Algeria, Tunis, Bahrein, Jordan, and the United States.

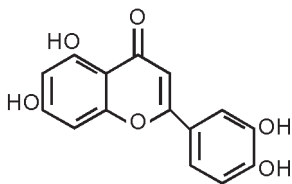
The quality of henna powder is determined by its color, purity, and fineness. Henna powder is adulterated with sand, stems and fruits of henna plant, and husk of paddy, arhar, moong, etc. Leaves are sometimes adulterated with the leaves and twigs of other shrubs. Leaves also contain flavonic pigments such as luteolin and tannins (6% gallic acid) which act as organic mordants helping to make the color dark and fast.

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## 6.55 Luteolin

Luteolin 2-(3,4,5,7-Tetrahydroxy-flavone;  $C_{15}H_{10}O_6$ ; mp 328–330°C), a yellow principal coloring matter, occurs together with apigenin, the other coloring matter, in all parts of Dyer's Rocket or Weld, *Reseda luteola* L., and in flowers of Dyer's Broom or Greenwood, *Genista tinctoria* L. It is slightly soluble in hot water but readily soluble in alcohol.



Luteolin

### 6.55.1 Extraction

The plant material is put in water and heated slowly for 2–4 h. Plant material is strained off and the liquor is cooled. In another method, the plant material is ground into powder and extracted in alcohol. The alcoholic or aqueous extract is dried under reduced pressure and yellow-colored needles are obtained from the dye. The needles are redissolved in alcohol and pure luteolin is isolated with the help of chromatographic methods.

### 6.55.2 Uses

Luteolin is perhaps the oldest European dye. At one time, it was considered as an important yellow dye for alum-mordanted silk and wool. It also dyes wool in yellowish-olive on chrome, olive on iron, and greenish-yellow on tin mordants. It is reputed to be the best dye to light fastness other than any other natural yellow dye. In Europe, it is still used for dyeing leather.

### 6.55.3 Lakes

A lake is also obtained from the aqueous extract of the dye. The alum is added to the extract and then followed by soda to get a precipitate of the lake dye. It is then separated and dried. It is used for coloring oils and for making water colors.

### 6.55.4 Sources

*Reseda luteola* L. (Resedaceae)

English – Dyer's Rocket, Weld, Dyer's weed, Wild mignonette

It is a small, glabrous herb of 50–150 cm height, indigenous to Western Europe, and grown in gardens in India, but also found as an escape from cultivation. For many centuries it was used as a dye plant in Britain. It is still found wild on the chalk downs in England. All parts of the plant contain the coloring matter. It must be gathered before it seeds; otherwise it loses its coloring properties. It also contains apigenin, another yellow coloring principle. It is good for dyeing silk, wool, and cotton.

In conventional methods, the weld is put in cold water and heated slowly for 2–3 h. Then the plant is strained off and the liquor is cooled. Then the clean and wetted wool is entered into it and the bath is simmered for about an hour. For olive, iron is added for last 15 min. Then wool is rinsed two times and dried. With alum and cream of tartar it gives lemon-yellow; with chrome it gives golden-yellow; with tin it gives bright orange-yellow, and iron gives olive with alum-mordanted wool.

For cotton fabrics, the pieces of the plant are put into cold water and then simmered for 3 h. Then plant material is strained off and stirred in chalk and copper sulphate. The clean and wet cotton or cotton fabric is entered into it and heat under boiling point for 1.5–3.5 h, then rinse and dried. With alum-tannin, alum mordant gives yellow color.

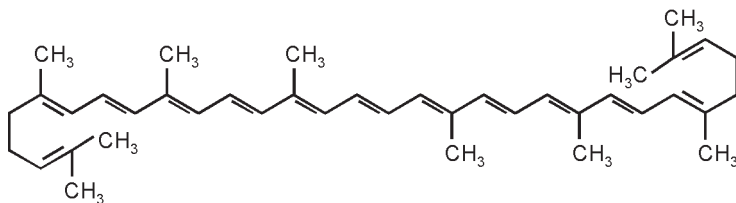
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## 6.56 Lycopene

Lycopene ( $\psi$ ,  $\psi$ -carotene;  $C_{40}H_{56}$ ; mp 175°C), the isomer of carotene, a dark-red crystalline pigment, present in the ripe fruits of tomato, *Lycopersicon*

*esculentum* Mill., and in palm oil, *Elaeis guineensis* Jacq. It is also found in a number of other plants and in animals, though often only in small quantities.



Lycopene

### 6.56.1 Extraction

The well-ripen fruits are ground in 95% ethanol. The mixture is then passed through a fine cloth under slight pressure. The red-colored residue is dried at 40–50°C, finely ground and extracted with carbon disulphide. The solvent is removed by distillation under reduced pressure at 40°C in the presence of dry carbon dioxide. The dark reddish-brown paste, which remains, is diluted with ethanol. After some time a crystalline mass is settled down, which is filtered and the residue is washed with cold petroleum ether. Thus the crude lycopene is obtained, which can be further purified either by dissolving in carbon disulphide and precipitated with ethanol or by recrystallisation by petroleum ether.

### 6.56.2 Uses

Lycopene is used to color food stuffs, medicines, oils, etc.

### 6.56.3 Sources

*Lycopersicon esculentum* Mill. (Solanaceae)

English – Tomato; Bengali and Hindi – Tamatar, Vilayithi baingan; Gujarati – Vilayithi vangan; Marathi – Vel vangi; Tamil – Takkali

It is an unarmed, spreading, hairy herb, cultivated throughout the world for vegetable. For the proper development of color in the fruit, warm and sunny days, and moderately cool nights are necessary.

A well-drained, light, fertile loamy soil with a fair capacity to hold moisture is best suited for tomato.

The plant is propagated mostly by seeds that are sown in nursery beds, and later the seedlings are transplanted in the field. In India, tomatoes are grown nearly throughout the year. In the hills, seeds are sown from middle

of March to middle of May or June. In the plains, three crops are raised; two early crops and one main crop; seeds are sown in June–August for the first crop; August–October for the second crop; and October–November for the third crop. Seeds take 7–10 days to germinate, and the seedlings are ready for transplantation in 4–6 weeks.

Seedlings are transplanted on flat beds or on the sides of raised beds. Soon after transplantation, fields are irrigated. Fruits are set during cool and wet weather, particularly in low temperature. For better crop, few plant growth regulators like *b*-naphthoxy acetic acid, *a*-chlorophenoxy acetic acid, and *p*-chlorophenoxyacetic acid are used. Tomatoes are harvested when the plants are about 3-month old.

The carotenoids ( $\beta$ -carotene and lycopene) constitute the chief coloring matter of tomato. Lycopene is absent in green tomato and appears when the fruit just begins to turn red; as the fruit ripens further, the lycopene content increases rapidly. Ripening of fruit by the use of ethylene has ten lycopene formation but fruits contain less  $\beta$ -carotene. Both lycopene and carotene increase in the tomatoes which ripen at 50–86°F; at higher temperature, lycopene formation is inhibited and only carotene is formed.

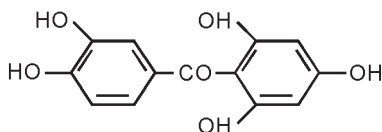
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## 6.57 Maclurin

Maclurin (2,3',4,4'-Pentahydroxybenzophenone;  $C_{13}H_{10}O_6$ ; mp 222–222.5°C), the yellow coloring principle occurs along with morin in the heartwood of Dyer's Mulberry, *Maclura tinctoria* (L.) D. Don ex Steud. syn.

*Chlorophora tinctoria* (L.) Gaudich, Osage Orange, *Maclura pomifera* (Raf.) C. K. Schneid., white Mulberry, *Morus alba* L., and *Mangosteen*, *Garcinia × mangostana* L. It is soluble in 190 parts of water; freely soluble in alcohol or ether. Maclurin is degraded by alkali to phloroglucinol and protocatechuic acid.



Maclurin

### 6.57.1 Extraction

The dye is extracted from the heartwood. The wood is ground into fine powder and extracted with either hot benzene or hot chloroform. The powder is extracted with hot benzene for 60 h and then solvent is removed, and thus a dark brown extract is obtained. The benzene extracted wood powder is further extracted with hot acetone for 60 h and then the solvent is evaporated; thus a pale brown solid is obtained. From this solid, the maclurin is crystallized, collected, and recrystallized from benzene and ethyl acetate (5:1). Maclurin can also be extracted from the heartwood with hot chloroform. Thus a dark brown filtrate is obtained, which is further concentrated into a powder. Maclurin is isolated as the pentamethyl ether after methylation of the powder.

### 6.57.2 Uses

Maclurin has been used for centuries as one of the best yellow dyes for wool. With chrome and copper, maclurin gives tones of aged-gold, olive, and bronze colors which are very fast to washing and light. Maclurin imparts pale yellow, yellowish-green or pale grey on alum, chrome, and iron mordanted wool, respectively. Formerly it was used as an intermediate in the manufacture of fustine. Maclurin is also used as a base for dyeing wool black with logwood after pretreatment of wool with chrome; silk mordanted with iron; with indigo to make saxon-green and mordanted with chrome to make drab. It is also used as a background for dyeing of cotton brown. It is used with chrome as a dye or as a base for dyeing nylon. It is also used for tanning and coloring leather.

### 6.57.3 Sources

*Garcinia × mangostana* L. (Clusiaceae)

English – Mangosteen; Bengali, Hindi, Malayalam, and Tamil – Mangustan, Mangustana

It is a small- or medium-sized tree with deep-green leathery leaves, found in Myanmar, Siam, Indo China, Sri Lanka, and Philippines. In India it is cultivated in Nilgiri and Tirunelveli districts of Tamil Nadu. Mangosteen is a tropical tree and adapted to the regions of heavy and well-distributed rainfall. It requires a wet but well-drained soil and a humid atmosphere. It does not withstand frost and drought. It is propagated by seeds, which are sown within 5 days of their collection. They are sown in well-drained soil that is rich in organic matter. About 2-year-old seedlings are transplanted under semi-shade in July–August with about  $10 \times 10$  m or  $12 \times 12$  m space. In the first two years, light shade is necessary at least during summer months.

The growth rate is slow and even in the most favorable conditions it does not bear fruits till 7–10 years old. The wood is dark brown and heavy, rather hard and fairly durable. It yields the flavone, maclurine, the principal yellow coloring matter.

*Maclura pomifera* (Raf.) C.K.Schneid. (Moraceae)

syn. *M. aurantiaca* Nutt.

English – Osage Orange

It is a spiny tree with spreading branches, indigenous to United States, especially in Texas, Oklahoma, Louisiana, Mississippi, and Pennsylvania. It has been introduced into India and is grown in gardens.

The plant is propagated by seeds, root cuttings, and layers. It is hardy against frost and drought, and thrives well in deep soil. The leaves of the plant may be used for rearing mulberry silk worm.

The wood is very hard, tough, heavy, strong, and bright orange in color, which becomes brown on exposure. The aqueous extract contains tannin (9–10%), maclurin, and morin. Its dyeing properties are similar to those of old fustic, but it yields clearer, less reddish dyeings of better fastness to light. It is widely used on chrome-mordanted wool and nylon, tin weighted silk, and chromed leather. The fastness on chrome-mordanted nylon (AATCC tests) light, 8; washing, 5; and perspiration, 5. Nylon dyed with osage orange shows less loss in tensile strength than any other dyewood. It is also used in conjunction with logwood. Its high tannin content has led to its being used as a replacement of Gambier on silk and leather. The aqueous extract of the wood has also been used for tanning and dyeing leather.

*Morus alba* L. (Moraceae)

English – White Mulberry, Mulberry; Bengali – Tut; Gujarati – Shetur; Hindi – Tut, Sahtut, Tutri, Chinni, Jaleba; Kannada – Hipperle; Kashmiri – Tut; Kumauni – Siah tut; Marathi – Tut, Ambat; Oriya – Tuto, Tuticoli; Punjabi – Tut, Tutri; Tamil – Musukette, Kamblichedi; Telugu – Reshme chattu



It is a moderate size tree, indigenous to China, cultivated throughout the plains of India and in the hilly areas of the Himalayas, up to an elevation of 3,300 m.

White mulberry regenerates itself naturally from seeds which are dispersed by birds and human beings. It is propagated artificially by seeds, cuttings, grafting, and budding. It grows well under varying conditions of soil and climate. Seeds are collected from the tree and sown within a month of their collection in shaded nursery beds. Before sowing, seeds are treated with camphor water to ward off the diseases. Seeds sprout in 9–14 days according to the season. Seedlings are transplanted in the field when they are about 1 m of height.

The sapwood is white or yellowish-white; heartwood is bright yellowish-brown or golden-brown which darkens after exposure. The heartwood contains tannin (32%) and the flavons maclurin and morin, the coloring matters. Wood has been used for a long time to color clothes yellow and also for coloring and tanning leather.

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## 6.58 Malachite

Malachite [ $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$ ], the copper ore is commonly found in Bihar, Andhra Pradesh, Rajasthan, Sikkim, and Uttar Pradesh in India. It usually occurs in nature as earthy or compact modular mass, sometimes with a fibrous structure. It is distinguished by its green color. The term malachite is derived from a Greek word meaning “marshmallow”, as it resembles the color of the leaves of this plant. Malachite has been used in jewelry, larger decorator works, and as a source of green color for paintings for many centuries.

Malachite yields a green coloring principle, the basic copper carbonate,  $\text{Cu(OH)}_2 \cdot \text{CuCO}_3 \cdot \text{H}_2\text{O}$ . It is soluble in dilute acids or ammonia and insoluble in water and alcohol.

### 6.58.1 Extraction

For the extraction of the color, the malachite ore or stones are ground into fine powder, sieved, and then boiled in aqueous solution of ammonia. A green precipitate of basic copper carbonate is obtained. It is filtered, dried, ground, and then mixed with linseed oil.

### 6.58.2 Uses

The green precipitate of basic copper carbonate produces bright green shade and is used in paintings as an artist's color.

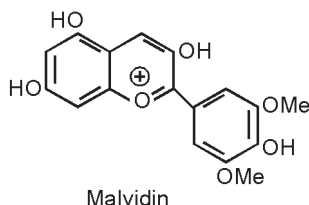
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## 6.59 Malvidin

Malvidin, 3,4',5,7-Tetrahydroxy-3',5'-dimethoxyflavylium 3,5,7-Trihydroxy-2-(4-hydroxy-3,5-dimethylphenyl)-1-benzopyrylium, 9Cl. Malvidin 3',5'-Dimethyldelphinidin Denidin. Syringidin. Malvidol. Enidin ( $\text{C}_{17}\text{H}_{15}\text{O}_7$ ; mp  $300^\circ\text{C}$ ), an anthocyanin, the principal red coloring matter, occurs in the form of malvidin-3-glycoside in the skins of black or blue grapes or concord grapes, *Vitis vinifera* L. subsp. *sylvestris*, together with the other coloring matters like

delphinidin ( $C_{15}H_{11}O_7$ ), petunidin ( $C_{16}H_{13}O_7$ ), poenidin ( $C_{16}H_{13}O_6$ ), cyanidin ( $C_{15}H_{11}O_6$ ), quercitin, and quercitrin. It is soluble in absolute alcohol, giving a violet-red solution, and sparingly soluble in water.



### 6.59.1 Extraction

Grape waste from industrial processing units such as wine or juice is an excellent source of anthocyanin pigments. The grapes filter-trim (tartrate sludge), the industrial waste, is extracted at room temperature by absolute ethanol containing 0.01% citric acid. It is then concentrated under vacuum and dried into fine powder, which can be used, as such, for coloring a wide variety of food products. The obtained powder contains a number of anthocyanin pigments like, malvidin (41.2%); delphinidin (3.4%); petunidin (5.0%); peonidin (10.1%); caffeoyl bearing pigments (13.6%); and p-coumaroyl-bearing pigments (26.5%). On chromatography of the crude extract, each and every coloring matter is separated. And then each band of each pigment is rechromatographed in 15% acetic acid which yields a complete purified compound.

### 6.59.2 Uses

The crude dry powder of the grape is used in dry mix beverages and gelatin desserts. The isolated malvidin is used to color food stuffs and pharmaceutical preparations.

### 6.59.3 Sources

*Vitis vinifera* L. subsp. *sylvestris* (C.C. Gmel) Hegi (Vitaceae)

English – Common Grape Vine, Wine Grape, European Grape; Bengali – Angurphal, Drakhyaluta; Hindi – Angur, Dakh; Gujarati – Darakh, Draksha; Kannada – Angura, Draksha; Malayalam – Mundiri, Gostani; Marathi – Draksha; Oriya – Drakya, Anguro, Gostani; Tamil – Kodimundiri, Gostanidraksha; Telugu – Draksha, Gostanidraksha

It is a large and deciduous climber with ovoid to globose purplish or bluish-black fruits, cultivated in South-West Asia, South and Central Europe,

extending up to West Germany. In India, grapes are cultivated in Andhra Pradesh, Maharashtra, Karnataka, Punjab, Tamil Nadu, and Haryana.

Grape vines are propagated by stem-cuttings; though reproduction by seeds, layers or grafts may be done for specific purposes. Cuttings are taken from the pruning during August–November in South India, in October in Western India, and in February in North India.

Cuttings may be taken from any part of the vine and should be 30–40 cm long and over 8 mm in diameter. The cuttings are planted in well-drained soil. It takes about 90 days for rooting and to give out 4–5 leaves. The rooted cuttings are planted in previously prepared pits or trenches during October–November or January–February in Peninsular India and in February in North India. The vine may commence to yield some fruits in the second or third year of its planting, but good-sized crop is expected after the 3rd year.

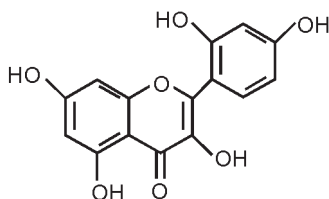
Generally, the coloring matter of grapes is found only in the cells of the skin. The green color of immature grapes is due to chlorophyll; this color fades during ripening. The true color of the grape, previously masked-manifest, red color in red, blue, purple and black grapes is due to anthocyanins; and this red pigment has been identified as Oenin (malvidin 3-glucoside). Anthocyanins from the skin of grapes is extracted and used as a colorant of carbonated and other beverages, under the trade name “Enocyanin”. Enocyanin is used in cosmetics, dentifrices, and carbonated soft drinks.

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## 6.60 Morin

Morin (2',3',4',5,7-Pentahydroxyflavone;  $C_{15}H_{10}O_7$ ; mp 303–304°C), the principal yellow coloring matter is found in the heartwood of Jack wood, *Artocarpus heterophyllus* Lam., and Kala Lakuch Tree, *A. gomezianus* Wall. ex Trécul, and also found together with maclurin in the heartwood of Dyer's Mulberry, *Maclura tinctoria* (L.) D. Don ex Steud. syn. *Chlorophora tinctoria* (L.) Gaudich, Osage Orange, *Maclura pomifera* Schneid, and white Mulberry, *Morus alba* L. Morin is freely soluble in alcohol; slightly soluble in ether and acetic acid. It is soluble in aqueous alkali solutions with intense yellow color which turns brown on exposure to air.



Morin

### 6.60.1 Extraction

The heartwood is ground to a fine powder and then extracted with boiling water, filtered, and cooled. On cooling, the crystals of impure morin get deposited at the bottom. It is separated and purified by several crystallizations from alcohol and dilute acetic acid.

### 6.60.2 Uses

Morin has been used for centuries as one of the best yellow dye for wool, cotton, and silk. It imparts various shades with different mordants. With chrome and copper, it yields gold, olive, and bronze colors which are very fast to washing and light. It also imparts pale yellow, yellowish-green or pale grey on alum, chrome or iron mordants.

Calico yellow is obtained by the action of bisulfate on fustic extract which consists mainly of the bisulfate compound of morin ( $C_{15}H_{10}O_7 + NaHSO_3$ ) and is used in calico printing. The calico yellow of commerce is a good source of morin for the laboratory. The bisulfate is removed by HCl.

### 6.60.3 Sources

*Artocarpus gomezianus* Wall. ex Trécul  
Hindi – Kala Lakuch

It is a tall tree that is up to 40 m in height, found in Andaman Islands. The wood is hard and durable. The heartwood contains a flavone, morin, the yellow coloring matter along with few other flavones which are found in *A. heterophyllus*.

The details of *chlorophora tinctoria*, *maclura pomifera*, and *Morus alba* have been given under the dye maclurin.

*A. heterophyllus* Lam. (Moraceae)

syn. *A. integrifolia* Hook.f.

English – Jack Fruit; Jack Wood; Bengali – Kanthal; Gujarati and Marathi – Phanas; Hindi – Kanthal, Kathal, Ponas; Kannada – Halasu, Hebhalasu; Khasi – Dieng-Soh-phan; Malayalam – Chakka, Pilavu; Oriya – Ichodopholo, Kantokalo, Ponoso; Sanskrit – Ashaya, Atibrihatphal, Panas, Phanasa; Tamil – Murasabalam, Pala, Pila, Pila-palani; Telugu – Panasa, Verupanas; Urdu – Kathal

It is a large tree, 10–15 m tall, and commonly found in evergreen forests of the Western Ghats and cultivated throughout the warmer parts of India.

Jack tree requires a moist tropical climate and deep, rich, well-drained alluvial or open textured loamy or literate soil. It is commonly grown from seeds, cuttings, grafting, and budding. Seeds are soaked in water for 24 h before sowing. Large holes are dug and then filled with rich soil; two or three seeds are sown together in each hole. A space of  $9 \times 12$  m is recommended between two holes.

The wood is moderately hard; sapwood is pale; heartwood is bright yellow which darkens on exposure. The heartwood contains a flavone, morin, a yellow coloring matter. Besides morin, the other flavons like dihydromorin, cyanomaclurin, artocarpin, isoartocarpin, artocarpin, artocarpesin, and artocarpnone have also been isolated from the heartwood.

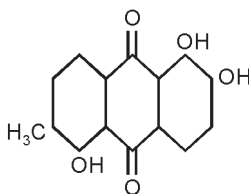
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## 6.61 Morindone

Morindone (1,2,5-Trihydroxy-6-methylantraquinone;  $C_{15}H_{10}O_5$ , mp  $284^{\circ}\text{C}$ ), the principal coloring matter, occurs in the form of the glycoside morindin ( $C_{27}H_{30}O_{14}$ , mp  $264.5^{\circ}\text{C}$ ), in the root bark of Al or Ach, *Morinda citrifolia* L., *M. angustifolia* Roxb., *M. coreia* Buch.-Ham., *M. umbellata* L., Kuthan, *Hymenodictyon orixense* (Roxb.) Mabb. syn. *Hymenodictyon excelsum* Wall., and an Australian plant, *Coprosma lucida* var. *lucida* syn. *Coprosma australis* (A. Rich.) B. L. Robinson. The morindin on hydrolysis with dilute acid yields glucose, rhamnose, and morindone. Morindone is soluble in hot water and alcohol.



Morindon

### 6.61.1 Extraction

Air dried and finely ground root bark is exhaustively extracted with ethanol for 2–4 h. On cooling it gives brown liquor which yields fine yellow needles. On crystallization from acetone, it yields morindin as orange needles; which are separated. On heating under reflux with 2% aqueous sulphuric acid for 10 h, it yields a brown precipitate which is separated from the cooled solution. The precipitate is further dissolved in boiling acetone and filtered. After cooling of the filtered liquor, the morindone is crystallized as orange needles which are separated and dried up under reduced pressure.

### 6.61.2 Uses

Morindone is used for dyeing cotton, wool, and silk. With mordants it produces red, purple, and chocolate shades which are fast to soap. It dyes wool and silk in orange shade, although the tint becomes more violet in the presence of soap.

### 6.61.3 Sources

*Coprosma lucida* var. *lucida* (Rubiaceae)

syn. *Coprosma australis* (A. Rich.) B. L. Robinson.

syn. *C. grandifolia* Hook.f.

It is a shrub or a small tree with thin trunk, 4–7 m in height, occurs in Australia and New Zealand. It contains up to 17% of its dry weight in anthraquinone dyes morindon, soranjidiol rubiadin, and dimethyl ether of the coparrolatin.

The extract of bark, in combination with conventional mordants, offers a range of colors from dull pink to brown-red, which are fast to light and washing.

*Hymenodictyon orixense* (Roxb.) Mabb. (Rubiaceae)

syn. *Hymenodictyon excelsum* Wall.

Assami – Kodom, Ding-Dolong-Sir, Phurkundi; Bengali – Lati Karum; Gujarati – Amarchala, Dondro; Hindi – Bhaulan, Kukurkat, Bhurkur; Kannada – Bandarayanni, Vilari; Marathi – Bhoursal, Dancelo; Malayalam – Itthilei, Nichan, Vella-Katampu; Nepali – Latikaram; Oriya – Bodoka, Konoo; Punjabi – Kukarhat, Barthoa; Sanskrit – Bhramarchhallika, Uragandha; Tamil – Vellei-kadambu, Sagapu, Peranjoli; Telugu – Dudippa, Dadiyetta, Burja

It is a medium to large-sized deciduous tree, found scattered in the dry mixed deciduous forests throughout the greater part of India.

The plant is a strong light demander. It is propagated by seeds which are sown in nurseries, and about 1-year-old seedlings are transplanted in fields. It grows fairly fast.

The leaves and root bark contain coloring matter morindone.

*Morinda angustifolia* Roxb. (Rubiaceae)

Assami – Asugoch; Bengali – Acho, Darhharidra; Nepali – Barrhardi; Lepcha – Huldi-Kung; Khasi – Dieng-Nong, Dieng-Seroi; Garo – Chhennong; Lushai – Kawnpel

It is a shrub or a small tree that is found in eastern Himalayas, Assam, Bihar, Orissa, and Andhra Pradesh, up to an altitude of 1800 m.

Root yields morindone which is used as a yellow dye for dyeing cotton yarn and cloth; red shades are obtained on mordanted yarn by using cold water extracts of the root.

*M. bracteata* Roxb.

syn. *M. citrifolia* var. *bracteata* Hook.f.

It is a shrub or a small tree, found in the coastal forests of Bengal and Deccan Peninsula and Southern India.



*M. citrifolia* L.

syn. *M. tomentosa* Heyne ex Roth.

Bengali, Hindi, Gujarati and Marathi – Al, Ach, Surangi, Bartundi; Kannada – Ainshi, Tagase, Maddi; Malayalam – Kattapitalavam, Mannanatti; Oriya – Achu, Pindra; Tamil – Nuna, Togaru; Telugu – Maddi, Togaru

It is a small tree with a straight trunk, formerly cultivated throughout the greater part of India and now found only in wild state or as an escape in parts of Bengal, Bihar, Orissa, and Western Coast of Andaman Islands. It is also found in Sri Lanka, Malaysia, and Indonesia.

It was formerly cultivated as a field crop on an extensive scale and its roots exploited as a source of Al dye. Under the conditions of cultivation, the plant begins to bear flowers and fruits within 2–3 years of plantation. The roots are dug out when the plants are 3–4 years old, dried, and sorted out for use as the dyeing trade. The coloring matter resides in the root bark and is present to the maximum extent when the plants are 3–4-years-old. The use of Al dye has been virtually abandoned since the advent to synthetic dye.

In addition to the glycoside morindin, it contains rubichloric acid, alizarin x-methyl ether, rubiadin-1-methyl ether, two isomeric dihydroxy methylantraqui none (morindadiol,  $C_{15}H_{10}O_4$ ; mp 244°C and soranjidiol,  $C_{15}H_{10}O_4$ ; mp 276°C), and two trihydroxy methylantraquinone monomethyl ethers, (mp 216 and 172°C).

The plant is grown as a shade tree and as a support for pepper vines.

*M. coreia* Buch.-Ham.

syn. *M. tinctoria* Roxb.

It is a small- to medium-sized tree, found in dry forests throughout the greater part of India. It is also cultivated in few other places.

The root bark contains morindone and its glucoside morindin. The heartwood contains three anthraquinone pigments namely, morindone, damnacanthal ( $C_{16}H_{10}O_5$ ; mp 212°C), and nor-damnacanthal ( $C_{15}H_8O_5$ ; mp 218–220°C).

*M. umbellata* L.

It is a diffuse or climbing shrub that is found in Khasi hills, Bihar, and Deccan Peninsula at an altitude of 1500 m.

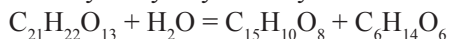
The root bark in addition to morindone and morindin contains rubichloric acid and trihydroxymethyl anthraquinone methyl ether, mp 216°C; morindanigrin, ( $C_{16}H_{10}O_5$ ; mp 210°C); 1,3-dihydroxy-6-methyl anthraquinone, mp 269°C, a derivative of dimethyl anthraquinone, ( $C_{16}H_{12}O_6$ ; mp 258°C); and a hydroxy-methyl anthraquinone carboxylic acid, ( $C_{16}H_{10}O_5$ ; mp 198–199°C).

## For further reading

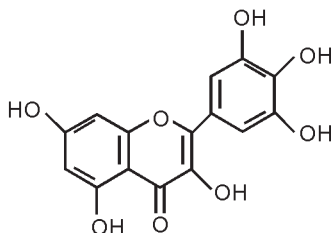
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## 5.62 Myricetin

Myricetin (3,3',4,5,5',7-Hexahydroxyflavone;  $C_{15}H_{10}O_8$ ; mp 357–360°C), the principal yellow coloring matter, occurs in the bark of Kaiphal, *Myrica esculenta* Buch.-Ham. ex D. Don and *Myrica rubra* (Lour.) Siebold and Zucc., Sicilian Sumac, *Rhus coriaria* L., Smoke Tree, or Indian Sumac, *Cotinus coggygria* Scop., and from the leaves of Star-Apple, *Chrysophyllum cainito* L., Mastic tree, *Pistacia lentiscus* L., Bullet wood, *Mimusops elengi* L., South Indian Mahua, *Madhuca longifolia* (Koenig) Macb., in the form of the glycoside, myricitrin (myricetin 3-rhamnoside,  $C_{21}H_{22}O_{13}$ ; mp 199–200°C) which on hydrolysis yields myricetin as follows:



Myricetin is soluble in alcohol, sparingly soluble in boiling water but insoluble in chloroform and acetic acid.



Myricetin

### 6.62.1 Extraction

The air-dried raw material is ground to a fine powder and digested for 6 h with ten times its weight of boiling water and then filtered. Then a solution of lead acetate is added to the filtrate when a bulky yellowish precipitate is obtained, which on prolong boiling becomes dirty white; this consists almost entirely of the lead compound of tannin matter. This is removed by filtration, washed with water, and the filtrate is further treated with more lead acetate solution until a precipitate is no longer formed. The lemon-yellow lead compound is then collected, washed, and decomposed, while still moist, by means of boiling dilute sulphuric acid. The brown liquid, which now contains the coloring matter, is removed from the lead sulphate by decantation and then extracted twice with ether. The yellow crystalline residue left after evaporating the ethereal extract is dissolved in a little alcohol; the solution is diluted with boiling water and then cooled. On cooling, crystals are formed. These crystals are separated, collected, and then extracted two or three times with small quantities of boiling acetic acid in order to remove a colorless wax like substance which is present in some quantity. It is then washed with water and recrystallised from dilute alcohol, by which the coloring matter myracetin is obtained in pure form.

### 6.62.2 Uses

The dye is used to dye *piazi* color on wool. Depending on the mordants used, the colors obtained vary from ochre to grey and exhibit good fastness to light and fair to washing. It gives red-brown, brown-orange, and bright red shades with chromium, aluminium, and tin mordants, respectively.

### 6.62.3 Sources

*Chrysophyllum cainito* L. (Sapotaceae)

English – West Indian Star Apple, Cainito

It is a much branched, laticiferous tree, 9–18 m and sometimes 30 m tall, native to Central America and the West Indies, occasionally grown in warmer parts of India for its edible fruits and as avenue tree.

The tree thrives well on well-drained sandy soil, but it is sensitive to frost. It is propagated through seeds and cuttings.

The leaves contain myricetin and myricitrin, the coloring matters.

*Madhuca longifolia* (Koenig) Macb. (Sapotaceae)

syn. *Bassia longifolia* Koenig.

English – South Indian Mahua, Mowra Butter Tree; Bengali – Mahwa, Maul, Mahula; Gujarati – Mahuda; Hindi – Maluca, Mohwa, Manwa;

Kannada – Hippe; Malayalam – Poonam, Ilupa; Marathi – Mahwa, Mohwra; Oriya – Mahula, Moha, Madgi; Tamil – Illupe, Elupa; Telugu – Ippa

It is a large and evergreen tree, found in South India and cultivated as an avenue tree. It is common in the monsoon forests of Western Ghats from Konkan southward, usually along the banks of rivers and streams. Plants are propagated by seeds that are sown in nurseries in July–August. Seedlings are transplanted into fields from the nursery during the first rainy season, a few weeks after germination.

The leaves contain myricetin, quercetin, myrcitrin, and quercitrin, the principle coloring matters.

*Mimusops elengi* L. (Sapotaceae)

Assami – Gokul; Bengali – Bakul; Gujarati – Barsoli, Balsari; Hindi – Maulsari; Kannada – Bakula, Pagade; Malayalam – Elengi, Ilanni; Marathi – Owalli; Tamil – Vagulam, Magadam, Ilanji; Telugu – Pogada; Trade – Bullet wood

It is a small to large sized evergreen tree, found in the Deccan Peninsula and Andaman Islands, and frequently cultivated in gardens for ornament and also grown as an avenue or shade tree throughout the greater part of India.

The plant is propagated by seeds that are sown in baskets; planting out seedlings in the field takes place usually after 2 years in the rainy season.

The leaves contain myricetin, the coloring principle.

*Myrica esculanta* Buch.-Ham (Myricaceae)

syn. *M. nagi* Hook.f.

English – Box-Myrtle; Bengali – Kaiphal, Satsarila; Gujarati – Kariphal; Hindi – Kaiphal; Kannada – Kirishivani; Malayalam – Kaya-phala; Tamil – Marudam; Telugu – Kaidaryamu

It is a small or moderate sized tree, found in subtropical Himalayas from Ravi eastwards to Assam and in Khasi Jaintia, Naga, and Lushai hills at an altitude of 900–2,100 m. It contains grey or brownish-grey, rough, with deep vertical, wrinkled bark.

The bark contains a yellow coloring matter, myrcetin and is rich in tannin. It has been used occasionally as a tanning and dyeing material. It produces on mordanted wool shades similar to those obtained with quercitrin bark (from *Quercus* sp.); on mordanted cotton, it produces shades similar to those obtained with old fustic, *Maclura tinctoria* (L.) D. Don ex Steud. syn. *Chlorophora tinctoria*. The tannins of the bark belong to the pyragallol group and c 73% of the total tannin can be extracted with water. Hides tanned with the bark are somewhat darker in color than those tanned with wattle bark. The bark is also used as an astringent carminative and antiseptic.

*M. rubra* Siebold and Zucc.

It is a small to moderate sized tree, having deep red-purple edible fruits. The plant is commonly found in Japan, South China, Korea, and Philippine Islands. In India, it is cultivated in gardens.

Bark yields the coloring matter myrcetin. Fruits are edible and also used for making a drink.

*Pistacia lentiscus* L. (Anacardiaceae)

English – Mastic Tree

It is a variable, evergreen shrub or a small tree, up to 4 m in height, with pinnate leaves and small globose black fruits, found chiefly in the Mediterranean region, especially in the south-east corner of the island up to an altitude of 500 m. Propagation is done by cuttings.

The leaves contain myricetin, the coloring matter.

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## 6.63 Ochres

Ochres are the mixtures of clayey or siliceous material with 15–80% iron oxide (limonite, goethite, or hematite). They are characterized by their performance in color, opacity to ultra-violet light, and excellent covering power. They are non-bleeding, produce hard and impervious paint films which resist weathering, give good protection to wooden or metal structures and can be used in either oil or water media. They are fast to light in self colors and tint to lime. They are generally inert and may decompose under some conditions by certain acids. Three types of ochres like red, yellow, and green are found in India. Red and yellow ochres are commonly available in Andhra Pradesh, Bihar, Gujarat, Himachal Pradesh, Jammu and Kashmir, Madhya Pradesh,

Tamil Nadu, Maharashtra, Karnataka, Orissa, Rajasthan, Uttar Pradesh, and West Bengal, whereas green ochre is found in Golhalli in Tumkur district of Karnataka.

### 6.63.1 Red ochre (geru, gairika or hirmaji)

They contain about 15–65% hematite (anhydrous iron oxide) as the red coloring principle, disseminated in a siliceous or clayey base. Though the ochres have been used since 15,000 years for aesthetic and other purposes, red ochre became popular in India from the post-Vedic period in connection with textile dyeing. It was also used as an ingredient in the recipes for yellow dyeing. There are both anhydrous ( $\text{Fe}_2\text{O}_3$ ) and hydrous ( $\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$ ) forms of red ochre. The anhydrous oxide is red, while the hydrated varieties range from red to dull yellow. This is a very stable compound and is not affected by light and alkalis. Red oxide is also produced artificially, and there are hardly any differences, chemical or physical, between the two varieties, except that the artificial variety is very finely divided and mono generous. Fine red ochre is obtained by washing and lavigation of the crude variety.

### 6.63.2 Yellow ochre (ramraj or haldimati)

They contain about 15–30% limonite (hydrous iron oxide) as the coloring principle, mixed with varying quantities of clayey or fine sand. They vary in color from lemon-yellow to golden-yellow with low specific gravity but of medium or high  $\text{Fe}_2\text{O}_3$  contents and staining power.

Like red ochre, yellow ochre is the most important yellow pigment used from earliest times. In yellow ochre, the colors are on account of the presence of various hydrated forms of iron oxide, particularly the mineral goethite ( $\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$ ). The pigment is prepared from the natural earth by selection, grinding, washing, lavigation, and drying. Because it is a natural product, it is found in a number of shades.

Artificial ochre is prepared by precipitating a mixture of soluble iron salt (ferrous sulphate) and alum with an alkali like lime or potash. The depth of the yellow color can be controlled by the proportion of alum used. The final product is a mixture of ferric and aluminium hydroxides and gypsum. On heating this yellow pigment, various shades of orange, red, brown, and violet are obtained.

### 6.63.3 Uses

Ochres are principally used as a pigment or stain in paint manufacturing and also in color washes, distempers, and paper and linoleum making. They are

also employed for coloring textile, paper, and certain roofing and lime bricks. Yellow ochre is calcined to burnt ochre, whereby it is converted to a hydrous red ferric oxide. Burnt ochre, used as artistic color, is quite permanent.

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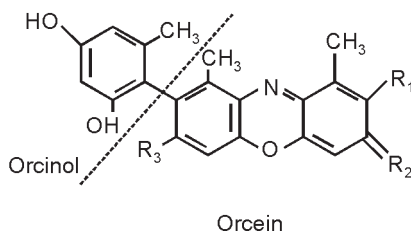
## 6.64      Orchil or archil

Orchil or archil, a purple or red-violet dye contains lecanoric acid ( $C_{16}H_{14}O_7$ ; mp  $175^\circ\text{C}$ ) and erythrin ( $C_{20}H_{22}O_{10}$ ,  $H_{20}$ ; mp  $156\text{--}157^\circ\text{C}$ ) found in some species of lichen.

The tinctorial property of the orchil is due to the presence of orcein. Under the combined influence of ammonia and atmospheric oxygen, lecanoric acid and erythrin give first orcin or orcinol ( $C_7H_8O_2$ ; mp  $58^\circ\text{C}$ ) and subsequently orcein, the coloring matter of the orchil. Orcein is a mixture of three compounds, 7-oxyphenoxazon, 7-aminophenoxazon, and 7-aminophenoxazin. If sodium or potassium carbonate is present at the same time, the reaction proceeds further and azolitmin along with erythrolitmin, the coloring matter of litmus, are produced.

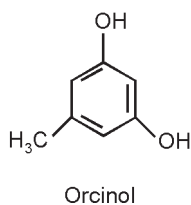
Lecanoric acid (ammonia + oxygen)	Orcin	Orcein
Erythrin (ammonia + oxygen)	Orcin	Orcein

The lecanoric acid gives a blood-red color with bleaching powder and a stable violet color with ferric chloride. The erythrin gives an orange-red color with bleaching powder and an alcoholic solution of it turns violet on the addition of a drop of ferric chloride solution, while with an excess of the reagent it turns reddish-brown.



Lecanoric acid (2,4-Dihydroxy-6-methylbenzoic acid 4-carboxy-3-hydroxy-5-methylphenyl ester),  $9C_1$ , 4-Carboxy-3-hydroxy-5-methylphenyl 2,4-dihydroxy-5-methylbenzoate. P-Diorsellinic acid. Glabratric acid,  $C_{16}H_{14}O_7$ , occurs in numerous lichens.

Orcinol (5-Methyl-1, 3-benzenediol; 5-methylresorcinol; orcin; 3,5-dihydroxytoluene.  $C_7H_8O_2$ ; mol wt 124.13°C), occurs in many species of lichens. Monohydrate crystals are sweet but unpleasant taste and redden on exposure to air due to oxidation; mp about 58°C; 107°C when anhydrous, freely soluble in water, alcohol, ether; less soluble in benzene, slightly soluble in chloroform or carbon disulfide.



### 6.64.1 Extraction

The sun-dried lichen is pulverized and boiled in soft water; treated with few drops of ammonia and then allowed to cool over night. The extract is evaporated and then gets a solid mass, which on further drying under reduced pressure yields a dried powder of Orchil.

### 6.64.2 Uses

Before the discovery of synthetic dyes, the archil had considerable economic importance as a dyestuff. It was mentioned by the ancient "Greeks" and apparently used widely in the "Mediterranean region", especially as the source of a valuable purple dye. Once it was used for dyeing wool and silk. It is still used in the production of high quality Harris Tweed cloth and also for calico printing.



### 6.64.3 Sources

*Parmelia abessinica* Kremp.

It is crustaceous lichen found in rocky areas of Bellary, Anantpur, and Cuddapah districts of Andhra Pradesh. It is also available in large quantities in market.

It contains 3.3% lecanoric acid. Owing to its high content of lecanoric acid, it is a source for the production of orcinol and litmus.

*P. tinctorum* Despr.

It is foliage lichen, common in the plains of India and in the Himalayas on tree barks and rocks. A sample of coorg, from Karnataka, yields 5% lecanoric acid while from Kumaun region it contains 20–25% lecanoric acid.

*Rocella montagnei* Bel.

It is fruticose lichen that occurs in abundance in waltair and the neighborhood, and is chiefly found on the cashew nut, mango, pongamia, tamarind and banyan trees. It contains lecanoric acid, erythrin, and orcinol coloring matters.

*R. tinctoria* Lam. and DC.

It is fruticose lichen, commonly found in Sri Lanka and Tamil Nadu in India. In olden days, India used to supply this lichen to Britain and then the dye was imported into America, ready for use. The thallus contains lecanoric acid and erythrin.

*R. fuciformis* is an allied species of *R. tinctoria*, commonly found on mango trees in Pondichery which also yields the dye.

Besides these, a number of lichen species like *Parmelia arnoldii*, *P. conspurcata*, *P. corniculata*, *P. furfuracea*, *P. himalayensis*, *P. hyporyslea*, *P. manshurica*, *P. meizospora*, *P. nimandairana*, *P. perforata*, *P. perlata*, *P. quercina*, *P. soledica*, *P. sulcata*; *Lecanora tartarea*, *L. calcarea*; *Dendographa leucophaea*, and *Aspicilia calcarea*, yield orchil dye.

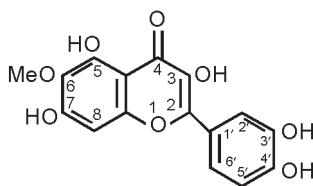
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## 6.65 Patuletin

Patuletin (3,3',4',5,7-Pentahydroxy-6-methoxyflavone;  $C_{16}H_{12}O_8$ ; mp 262–264°C), the principal yellow coloring matter, present in the flowers of French Marigold, *Tagetes patula* L. Patuletin is soluble in alkalis and produces orange-yellow solutions. It produces brownish-green color with ferric chloride.



Patuletin

### 6.65.1 Extraction

The dried petals of the flowers are extracted with boiling alcohol for 12 h, and the extract is further concentrated on boiling the extract and then filtered. The filtrate is diluted with large amount of water; a yellow crystalline solid is precipitated which is filtered and washed with water. As it is still impure and sticky, it is dissolved in a little pyridin and then water is added to the solution till the impurities are separated out as a suspension. They are coagulated by the addition of calcium chloride and filtered off. The clear filtrate is concentrated till the dye gets separated out as yellow needles. For further purification of the substance, it is crystallized twice from alcohol.

### 6.65.2 Uses

The dye is used to dye wool, cotton, and silk fabrics. It gives yellow color on alum, golden-yellow on chrome mordanted wool, and also gives yellow on alum-tannin-alum mordanted cotton and silk. It is also used in chicken feed to enhance the yellow color for chicken skin and eggs.

### 6.65.3 Sources

*Tagetes patula* L. (Asteraceae; Compositae)

English – French Marigold; Bengali and Hindi – Genda; Marathi – Machamul, Guljaphini; Oriya – Gendu; Punjabi – Gonda; Sanskrit – Tangla; Telugu – Seemabanthi

It is an annual bushy plant, native to Mexico, cultivated in gardens all over India, up to an altitude of 1,350 m. It is very popular as a garden plant owing to its bright colored flowers i.e., lemon-yellow to orange in color which yields a shining orange dye. The flowers bloom abundantly from the beginning of summer up to autumn. Even faded flowers are quite rich in dyeing matter; hence several plucking can be done in a season, which stimulates the blossoming of more buds.

Besides patuletin, flower contains patulitrin and cyanidin diglycoside coloring matter.

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## 6.66 Phycocyanin

Phycocyanin, the blue coloring matter occurs as phycocyanobilin ( $C_{33}H_{38}O_6$ ) in some species of the blue-green algae, like *Nostoc muscorum*, *Anabena cylindrica*, *Synechococcus lividus*, *Phormidium luridum*, and *Plectonema boryanum*. Phycocyanin is not localized in a definite pigment-bearing body or plastid but is frequently diffused in the outer zone of protoplasm.

### 6.66.1 Extraction

Blue-green algae is extracted with methanol at room temperature to remove water and the bulk of carotenoids, chlorophyll, etc. It is then boiled with methanol, 1% ascorbic acid, and incubated at 60°C for 8 h and then filtered. The filtered extract is evaporated and dried under reduced pressure. It is again stirred in water for 10 min and centrifuged to give a blue solution containing phycocyanin which is free from chlorophyll and carotene.

Blue-green algae are the unicellular plant bodies containing, in addition to chlorophyll, a bluish pigment, the phycocyanin. They are commonly grown in regions having a warm climate; develop elsewhere in great abundance during the summer and warmer seasons of the year. Blue-green algae can be cultured in a medium containing sodium nitrate ( $\text{NaNO}_3$ ), potassium hypo phosphate ( $\text{K}_4\text{P}_2\text{O}_6$ ), magnesium sulphate ( $\text{MgSO}_4$ ), metal salts in trace, and distilled water at  $50^\circ\text{C}$  under 2000–5000 by illumination for 10 days. After centrifugation, the cells are collected, suspended in phosphate buffer at pH 6.0, and extracted. The extract is ultra filtered on a dialysis membrane to get phycocyanin.

### 6.66.2 Uses

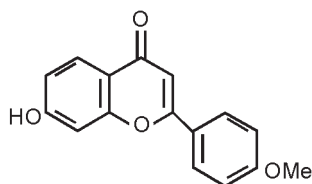
Phycocyanin is useful as a coloring material for pharmaceuticals, cosmetics, and food stuffs. It is also used as one of the ingredient of eye shadow which contains linolin, zinc stearate, kaolin, magnesium carbonate, and talc.

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### 6.67 Pratol

Pratol (7-hydroxy-4'-methoxyflavone,  $\text{C}_{16}\text{H}_{12}\text{O}_4$ , mp  $263\text{--}264^\circ\text{C}$ ), the yellow coloring principle, occurs in the flowers of the red clover, *Trifolium pratense* L., and crimson clover, *T. incarnatum* L. It is soluble in water and alcohol.



Pratol

### 6.67.1 Extraction

The dye is extracted from the flowers. The fresh or dry flowers are put into water or ethyl alcohol and boiled for 2–4 h. The extract is filtered and dried under reduced pressure to get the yellow crystals of the dye.

### 6.67.2 Uses

Pratol was formerly used for dyeing wool, silk, and cotton fabrics yellow.

### 6.67.3 Sources

*Trifolium incarnatum* L.

English – Crimson Clover

It is an upright annual with bright red, large, comical flower heads. It is grown in the Mediterranean region, Central Europe, and USA for hay and pasture and as a cover crop. It can grow on both clayey and sandy soil, but on poor soil the growth is stunted. It has been introduced into India and successfully grown at Kodai Kanal in Tamil Nadu. The flowers yield yellow coloring matter pratol.

*T. pretense* L. (Papilionaceae; Fabaceae)

English – Red Clover, Purple Clover, Broad Leaved Clover; Punjabi – Trepatra, Chit-batto

It is a small and hairy plant, found from Kashmir to Garhwal at altitudes of 1,200–2,400 m. It contains small purple flowers in ovoid or rounded heads. The plant is also introduced into Nilgiris and has run wild.

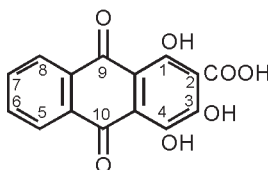
The flowers contain a yellow coloring matter pratol. Besides pratol, it also contains a number of phenolic compounds such as daidzein, genistein, isotriflorin, isorhamnetin, prantensol, triflorin, and an antifungal compound triflorhizin.

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## 6.68 Pseudopurpurin

Pseudopurpurin or purpurin-3-carboxylic acid (1,3,4-Trihydroxyanthraquinone;  $C_{15}H_8O_7$ ; mp  $222.4^\circ\text{C}$ ), the major red coloring matter found in the fresh root of madder, *Rubia tinctorum* L., wild madder, *Rubia peregrina* L., cleavers or goose grass, *Galium aparine* L., and lady's bed straw or rennet, *Galium verum* L. in the form of a glycoside galiosin ( $C_{26}H_{26}O_{16}$ ; mp  $<100^\circ$ ). The glycoside galiosin is extremely unstable. It decomposes on standing with cold dilute hydrochloric acid, with  $\text{Na}_2\text{CO}_3$  solution or by boiling for a few hours with either alcohol or distilled water. Galiosin on hydrolyzing with N/10 hydrochloric acid at  $40^\circ\text{C}$  yields pseudopurpurin, the main coloring principle. It produces orange-red solution in hot water. Its alum lake is unusually brilliant. The superiority of natural madder lakes over the synthetic products is probably due to the presence of pseudopurpurin.



Pseudopurpurin

### 6.68.1 Extraction

Pseudopurpurin can be extracted by two methods as follows:

- (i) The clean and fresh roots are extracted with boiling water until all the yellow color is extracted and filtered. To the clear filtered solution, 0.5–1.0% hydrochloric acid and about 30 cc of toluene are added. Then it is warmed for about half an hour at  $50^\circ\text{C}$ . Resulting of this, the glycoside galiosin, present in the mixture, is converted into pseudopurpurin. It is further extracted with toluene and crystallized with ethyl alcohol, yields red leaflets of pure pseudopurpurin.
- (ii) The cleared fresh roots are cut into small pieces and put into a mixture of toluene and hydrochloric acid (5:1 of 10% HCl) and then left for 2 days. It is then heated to about  $100^\circ\text{C}$  in water bath for about half an hour. Then the glycoside, galiosin, present in the extract is decomposed and the coloring matter pseudopurpurin is passed into the toluene. It is then crystallized with ethyl alcohol to get pure crystals of pseudopurpurin.

### 6.68.2 Uses

Pseudopurpurin is used in the manufacture of acid and chrome dyes. Once it was the most important dye in calico printing for reds, pinks, and chocolates. It had extensive use in lake making and was a permitted dye for food stuffs in few countries. It is used to dye cotton, silk, and wool and produces various shades on different mordants. The aqueous solution of the roots of madder and bedstraws have been used at times for dyeing reds on alum mordants, turkey-reds on cotton mordanted with alum in presence of lime; pink on silk mordanted with basic aluminium sulphate.

### 6.68.3 Sources

*Galium aparine* L. (Rubiaceae)

English – Cleavers Goose Grass

It is a trailing or climbing shrub, commonly found in temperate Himalayas up to an altitude of 4000 m. Its leaves are arranged in whorls of 6–8; flowers are white tinged with green, on auxiliary stalks; and fruits are small with hooked hair.

The root of the plant contains glycosides, galiosin and asperuloside ( $C_{17}H_{24}O_{11}$ ; mp 125–127°C).

*G. verum* L.

English – Cheese Rennet, Lady's Bedstraw

It is a slender, perennial herb of up to 1 m height with linear leaves, 6–8 in a whorl, and yellow flowers, angular stem, found in Kashmir, Lahul in Himachal Pradesh, and other parts of the Western Himalayas at altitudes of 1500–3500 m. Plant can easily be cultivated in gardens and is well-adapted for rockeries in temperate regions.

The stem and tops of the plant yield a yellow dye. It was used formerly for coloring cheese and butter. It is used to dye alum mordanted wool yellow. Root of the plant yields a red dye which is employed in few places for dyeing woollens. The coloring matters in the root occur as glycosides galiosin and rubiadin primeroside. They on hydrolyzing with dilute alkalis and acids yield pseudopurpurin and rubiadin, respectively. A third coloring matter, the ruberythric acid, a glycoside of alizarin is also present in the roots in traces.

Aqueous extract of the root gives different shades on wool with various mordants. It gives red with chrome, light orange with alum and chrome, and purplish-red with chrome and iron mordants.

*Rubia tinctorum* L.

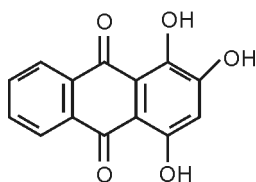
Please see under the dye alizarin.

## For further reading

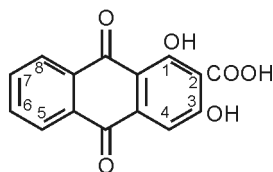
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## 6.69 Purpurin and munjistin

Purpurin (1,2,4-trihydroxyanthraquinone;  $C_{14}H_8O_5$ ; mp  $259^\circ\text{C}$ ) and munjistin (1,3-dihydroxyanthraquinone-2-carboxylic acid;  $C_{15}H_8O_6$ ; mp  $229\text{--}230^\circ\text{C}$ ), the principal coloring matters occur together in root and stem of madder (*Rubia cordifolia* L., *R. tinctorum* L. and *R. sikkimensis* Kurz.), in the form of the glycoside. An appreciable amount of purpurin is not found in fresh roots of madder but it is formed during the storage of the roots. Although it is a dye itself, it is usually considered as an undesirable contaminant of the dye alizarin. Purpurin is slightly soluble in hot water but readily soluble in alcohol and ether. The munjistin, an orange dye, is sparingly soluble in hot water but readily soluble in acetic acid. The aqueous alkaline solution of the munjistin gives red color and with concentrated sulphuric acid it gives intense yellow colors. It is moderately fast to light, washing, and soda boiling on cotton, silk, and wool.



Purpurin



Munjistin

### 6.69.1 Extraction

The raw material (root and stem) is ground into a fine powder and then extracted either with boiling water or alcohol or ether for 2–4 h and then filtered. The



filtered extract is dried under reduced pressure to form a powder. That extract is crude purpurin. It consists of purpurin, munjistin, purpuroxanthin, and pseudopurpurin. In preparing pure purpurin and munjistin, the crude extract is treated with boiling alum liquor and filtered. Doing this, the traces of alizarin are removed. The filtered liquor is again treated with boiling alum liquor and filtered. The hydrochloric acid is added to the filtered solution and then a precipitate is obtained. It is collected, washed, and then treated with boiling alcohol. Some part of the precipitate is dissolved in boiling alcohol and filtered. This can be recrystallized with alcohol to get pure purpurin.

The undissolved portion of the precipitate is collected, washed, and dried to make a powder. This powder is further treated with boiling alcohol to which a little hydrochloric acid is added. It dissolves and yields a small quantity of a crystallized substance of purpuroxanthic acid or munjistin. It is crystallized with alcohol to get pure munjistin.

### 6.69.2 Uses

Purpurin, in the form of a crude madder extract, has long been employed in India for dyeing human hair, coarse cotton fabrics, woolen clothes, blankets, carpets, cane and bamboo articles, decorations for spears and ornaments. When alum is used as mordant; the crude extract of the plant dyes cotton fabrics into a bright scarlet-red. It is also used for coloring medicinal oils.

The freshly prepared purpuroxanthic acid or munjistin dyes alumina mordants an orange and iron mordants a brown color. These colors are however, very fugitive and disappear entirely on treatment with boiling soap-liquor.

### 6.69.3 Sources

*Rubia cordifolia* L. (Rubiaceae)

English – Indian Madder; Assami – Manjathi; Bhutani – Soth; Hindi – Manjit, Manjith; Kannada – Siomalate, Siragatti, Manjustha; Kashmiri – Dandu; Khasi – Ryhoi, Soh-misem; Lepcha – Vhyem; Malayalam – Poont, Manjetti; Marathi – Manjeshta; Manipur – Moyum; Naga – Enhu, Chenhu; Nepali – Manjito; Oriya – Barheipani, Manjistha; Punjabi – Kukarphali, Tiuru, Kala-Meshika; Tamil – Shevelli, Manjitti; Telugu – Taamarvalli, Chiranji, Manjistateega

It is a variable prickly creeper or climber, commonly found throughout India, ascending to an altitude of 3,750 m. Root stocks are perennial, stems are 4-angled, leaves are cordate and arranged in whorls. It is a complex group, exhibiting a wide range of morphological characters and is distributed in Africa, Asia, and extending to Australia.

Indian madder of commerce consists of short root stocks with numerous cylindrical, smooth, and straight roots, covered with a thin, brownish cork, which peels off in flakes, exposing a red-brown bark that is marked by longitudinal furrows. The root is sweetish, followed by acrid and bitter taste. The dye is extracted from root as well as stem in India, however in Tanzania, roots and fruits are used.

The Indian madder has long been employed in the country for dyeing coarse cotton fabrics, blankets, and carpet. The method of dyeing is much the same all over India, the cloth is steeped in an infusion of the stem or root and mordanted with alum.

The coloring matter present in the roots of *R. cordifolia* is a mixture of purpurin and munjistin. Purpurin is the main coloring principle in the roots, while munjistin, an orange dye, occurs in the form of a glycoside and is accompanied by isomarine (C<sub>15</sub>H<sub>8</sub>O<sub>6</sub>; mp 202°C). Besides purpurin and munjistin, the roots contain small amount of xanthopurpurin or purpuroxanthin and pseudopurpurin.

A variety of *R. cordifolia* var.  *khasiana* Watt., commonly found throughout Assam and Manipur and extending westward to Nepal is reported to be richer in dye content than either *R. cordifolia* or *R. sikkimensis*.

*R. sikkimensis* Kurz.

English – Naga Madder; Manipuri – Moyum

It is a stout, scabrid, much branched climber, commonly found in Nepal eastwards to Assam, Nagaland, and Manipur, ascending to an altitude of 1,500 m.

This is the main dye yielding species in Eastern India. Dried roots have rough and fluted appearance; it differs from the round, smooth roots of *R. cordifolia*. Roots as well as stems yield a brilliant red dye which is used by hill tribes for dyeing woolen clothes, human hair, decorations for spears and ornaments, and cane and bamboo articles.

Roots contain purpurin (0.37–0.5%), as the principal coloring matter. Besides purpurin, munjistin and purpuroxanthin are also present.

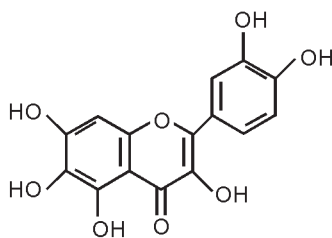
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## 6.70 Quercetagetin

Quercetagetin, 2-(3,4-Dihydroxyphenol)-3,5,6,7-tetrahydroxy-4H-1-benzopyran-4-one; 3,3',5,6,7-hexahydroxyflavone; 6-hydroxycyanidenolon;  $C_{15}H_{10}O_8$ ; mp 318–320°C), the yellow coloring matter, occurs in flowers of French marigold, *Tagetes patula* L., and also in the form of 7-glucoside, quercetagitritin ( $C_{21}H_{20}O_{13}$ ) in the flowers of the African marigold, *Tagetes erecta* L., and in Garland chrysanthemum, *Chrysanthemum coronarium* L. It is readily soluble in boiling alcohol and sparingly soluble in boiling water in which the impure pigment is fairly soluble.



Quercetagetin

### 6.70.1 Extraction

Air-dried petals are first extracted with chloroform for an hour and then with alcohol. The alcoholic solution is then concentrated under reduced pressure and filtered while it is hot to remove the dark brown resinous matter. After cooling, ether and water are mixed to the filtrate and then the ether layer is removed. Thus a bright yellow residue is obtained, which on acetylation by means of acetic anhydride and pyridine yields a colorless crystalline powder.

It is crystallized with alcohol-acetic acid, and recrystallised from methanol, gives colorless silky needles which are then hydrolysed in boiling glacial acetic acid (50 cc) and concentrated hydro chloric acid (50 cc). Boiling water is then added, and on cooling, quercetagenin is separated in the form of long, silky, pale brownish needles. It is further crystallized from alcohol to get a pure substance.

### 6.70.2 Uses

Quercetagenin is used to dye cotton, silk, and wool fabrics. It imparts yellow color with alum and golden color with chrome mordants.

### 6.70.3 Sources

*Chrysanthemum coronarium* L.

English – Garland chrysanthemum; Bengali – Babir; Gujarati and Hindi – Guldauri; Kannada – Hale; Malayalam – Jevanthi; Marathi – Gule sevati; Sanskrit – Shevantika; Tamil – Sevanthipoo; Telugu – Chamanti; Urdu – Gulechini

It is an erect, leafy, annual herb, grown in Indian gardens. It has yellow to yellowish-white colored flowers. The plant is also cultivated as a leafy vegetable in West Bengal. The petal of the flower contains coloring matter quercetagenin in the form of 7-glucoside, quercetagenin.

*Tagetes erecta* L. (Asteraceae)

English – Aztec, African Marigold; Bengali and Hindi – Genda; Gujarati – Guljharo, Makhana; Kannada – Seemeshamantige, Chandumallige; Malayalam – Chendumalli; Marathi – Rajia-cha-phul, Zundu; Oriya – Gendu; Punjabi – Tangla, Mentok, Genda; Tamil – Tulukka-samandi; Telugu – Bentichettu; Sanskrit – Sthulapushpa, Sandu, Gendnga

It is a stout, branching herb of about 60 m tall, native to Mexico, commonly cultivated as an annual in gardens all over India; also met with as an escape. It is a very popular garden plant for cut flowers, owing to its bright yellow flowers.

The flowers contain several pigments from which quercetagenin and quercetagenin, present only in early season flowers, have been isolated from Indian types whereas kaempferitin and helenien are found in Rumanian varieties and xanthophyll from United States varieties, which are used in chicken feeds to enhance the yellow color of chicken skin and eggs.

*Tagetes patula* L.

For details see under the dye patuletin

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## 6.71 Quercetin

Quercetin (3,3',4,5,7-Pentahydroxy flavone,  $C_{15}H_{10}O_7$ , mp 313–314°C), the yellow coloring matter, occurs in bark of dyers oak, *Quercus velutina* Lam., which is commonly known as quercitron and also commercially available in the market as flavine; and also occurs in the outer skin of red onion, *Allium cepa* L.; and in the hulls of ground nut, *Arachis hypogaea* L. Quercetin also occurs in many plants as glycosides of quercetin, which on hydrolyzing with sulphuric acid yields quercetin. The glycosides like quercitrin ( $C_{21}H_{20}O_{11}$ ; mp 182–185°C) found in horse chest nut, *Aesculus hippocastanum* L., in the flowers of Damask rose, *Rosa damascena* Mill., and in French rose, *R. gallica* L.; isoquercitrin ( $C_{21}H_{20}O_{12}$ ; mp 217–219°C) in *Vaccinium* spp.; quercimetrin ( $C_{21}H_{20}O_{12}$ ) in cotton flowers (*Gossypium arboreum* L. syn. *Gossypium indicum* L. and *G. hirsutum* L.); incarnatrin ( $C_{21}H_{20}O_{12}$ ; decomposing at 242–245°C) in *Trifolium incarnatum*; rutin ( $C_{27}H_{30}O_{16}$ ; mp 180–190°C), a 3-rutinoside occurring in flower buds of Japanese Pagoda tree, *Styphnolobium japonicum* (L.) Schott syn. *Sophora japonica* L., and in common Rue, *Ruta graveolens* L. The glycosides of quercetin, together with those of isoquercetin, luteolin, and other flavones have also been found in Field Horsetail, *Equisetum arvense* L. Quercetin is soluble in glacial acetic acid, boiling alcohol, and in aqueous alkaline solution with yellow color; slightly soluble in hot water, but insoluble in cold water.

### 6.71.1 Extraction

Air-dried raw material is ground to a powder and washed with salt solution to remove impurities. It is then extracted with cold dilute ammonia. The extract

when neutralized with dilute sulphuric acid deposits a brown amorphous precipitate, containing little or no coloring matter, is filtered off, and the remaining clear yellow solution is acidified with sulphuric acid and boiled. It yields crystals of quercetin which are separated on cooling. Then these crystals are collected with the mixture (still warm) in order to prevent their contamination with a brown flocculent matter which is usually separated out on further cooling. The product consists of almost chemically pure quercetin, and this can further be purified by recrystallisation from dilute alcohol, or more rapidly by extracting with a mixture of ether and chloroform. On evaporating the extract, the crystals of pure quercetin get separated as they are practically insoluble in chloroform.

### 6.71.2 Uses

The quercetin is used to dye fabrics. It yields brownish-orange on alum, reddish-brown on chrome, olive-black on iron, and bright orange-brown on tin mordants. On chrome mordanted wool or nylon it yields brownish-olives, on alum mordant it yields dull yellow, on iron greenish-olive, and on tin dull reddish-yellow. It is used chiefly for steam olives and browns on chrome in calico printing and for shading logwood printing blocks; also used for dyed styles on printed or discharged mordants.

### 6.71.3 Sources

*Aesculus hippocastanum* L. (Sapindaceae)

English – Horse Chestnut Tree; Punjabi – Pu

It is a large tree of 18–25 m height. It contains panicles of showy flowers and prickly capsules. It is endemic to the mountains of the Balkan Peninsula. It has been introduced into India and is occasionally grown as an ornamental tree. Horhammer *et al.* (1959), isolated quercitrin, from the tree. The extract of the wood is also used as a black dye for silk.

*Allium cepa* L. (Liliaceae)

English – Onion; Bengali – Palandu, Piyaj; Gujarati – Dungali; Hindi – Piyaz; Kannada – Irulli; Malayalam – Ulli; Marathi – Kanda; Sanskrit – Nripakana, Palandu, Rakta-kanda; Tamil – Ira-Vengayam, Irulli, Vela-Vengayam; Telugu – Nirulli, Vulli-Gaddalu

It is a bulbous biennial that is cultivated throughout India. Onion comprises of the edible swollen bases of green foliage leaves and fleshy scales. The outermost dry papery skins are the best source of the flavonoid quercetol. Besides quercetin, kaemferol, quercetin-3-glucoside and some tannin are also present in them.

The traditional dyeing method comprises of boiling the mordanted material with onion skins. Alum and crome of tartar together give brilliant orange color, while copper and iron gives brown and tins an orangish color. Because of its high substantivity and good fastness properties, several studies have been carried out on this dye. Recently, a French patent for the hair dye was made from onion skins, and it has been combined with indigo to dye a green color on cotton.

*Arachis hypogaea* L. (Fabaceae)

English – Groundnut, Peanut, Monkeynu; Bengali – Chini-Badam; Gujarati – Mughphali; Hindi – Mungphali, Vilayati-Mung; Kannada – Nela-Gadale; Malayalam – Kappalandi, Nela-Kadala; Marathi – Bhuni-Mung; Sanskrit – Buchanaka; Tamil – Nela-Kadalai, Verkadalai; Telugu – Nelasenagalu, Verusenagalu

It is a small, prostrate, diffuse or erect, branched, annual herb of 30–60 cm height. Groundnut is believed to be native of Brazil and it was cultivated as early as 950 BC by the Indians in Brazil and Peru.

The occurrence of quercitrin (0.1%), the glycoside of quercetin, in groundnut hulls has been reported. A process for the preparation of quercitrin from groundnut hulls has been patented in USA (Wender, US Pat, no.2557164, 1951).

*Equisetum arvense* L. (Equisetaceae)

English – Field Horsetail

It is a bush like perennial plant with deep creeping rhizome from which arises erect or scrambling, hollow, jointed aerial branches. The leaves are reduced to scales which sheathe the joints. It is found in swampy grounds and sandy banks of streams and rivers at high altitudes in the Himalayas.

The plant is reported to contain quercetin, apigenin, and kaempferol as the coloring matters. The saprophyte is also reported to contain rhodoxanthin, a red coloring matter. In Norway, *E. sylvaticum* stems are used dry or fresh to produce a grayish-yellow dye.

*Quercus velutina* Lam. (Fagaceae)

syn. *Q. tinctoria* Willd.

English – Black Oak

It is a tree that is indigenous to Pennsylvania, Georgia, and Carolina of United States. It is distinguished by its downy twigs and hairy buds from the other oak trees. The leaves are green and glossy above, pale brown below. The dye is obtained from the inner bark which is called quercitron bark. Quercitron extract finds its application under the name flavin in dyeing and more especially in printing. The patent bark or quercetin is industrially

obtained by boiling the bark with dilute sulphuric acid, thrice as strong as the bark.

Flavine-yellow shade is prepared by extracting the bark with high pressure steam and consists mainly of quercitrin. It can be separated out as yellow crystals with the extraction of aqueous extract from dilute methanol or ethanol (mp 176–179°C); from water (mp 167°C). It is practically insoluble in cold water and ether but soluble in alcohol and moderately soluble in hot water. It has been used as a textile dye. It yields golden-yellow on alum, brownish-yellow on chrome, lemon-yellow on tin and deep olive on iron mordants. Formerly it was used on wool mordanted with tin and alum in a single bath to produce brilliant yellows which could not be matched with yellow synthetic acid dyes because of the physical difference between the two.

Flavine-red shade is prepared by rapidly extracting the bark with dilute ammonia and boiling the extract with sulphuric acid which mainly consists of quercetin. It yields brownish-orange on alum, reddish-brown on chrome, olive-black on iron, and bright orange-brown on tin mordants. The flavines have approximately 16 times the color value of the bark.

*Rosa damascena* Mill. (Rosaceae)

English – Damask Rose, Summer Damask Rose; Hindi – Bussorah, Fasli Gulab

It is an erect shrub of about 2 m height, widely grown in gardens throughout India. It contains sweet scented red, pink or white colored flowers.

The damask rose is believed to have been introduced from the Middle Eastern regions into European countries by the returning crusaders. It is most important of all perfumery roses, and is planted extensively in Bulgaria. In India, it is under cultivation on a large scale in a few areas of Uttar Pradesh for preparation of rose-water and attar, the volatile oil (yield, 0.025–0.050%).

Besides rose-water and essential oil, the flowers contain the red coloring matter cyanin (9–10% on dry weight basis) and a yellow coloring glycoside of quercetin, quercitrin.

The other coloring matters like lycopene,  $\beta$  and  $\gamma$ -carotenes, rubixanthin, zeaxanthin, xanthophyll, and taraxanthin can also be extracted from the plant.

*R. gallica* L.

English – French rose

It is an erect plant of about 1.0–1.2 m height with slender pickles and solitary pink or crimson flowers. It is considered to be one of the foundation species from which most of the garden roses have been bred, and is sometimes grown in Indian gardens.

Besides essential oil (0.027–0.036%) and rose-water, petals yield the coloring matters like cyanin (up to 10%), cyamidin, and quercitrin.



*Ruta graveolens* L. (Rutaceae)

English – Garden Rue

It is a strong-scented, erect, glabrous herb of 30–90 cm height, native of the Mediterranean region and sometimes cultivated in Indian gardens.

The plant contains about 2% rutin, the glycoside of quercetin, which on hydrolyses yields the coloring matter quercetin.

*Styphnolobium japonicum* (L.) Schott (Fabaceae)

syn. *Sophora japonica* L.

English – Japanese Pagoda Tree, Chinese Scholar Tree, Umbrella Tree

It is a medium sized deciduous tree of up to 25 m height. It is grown in Kashmir for ornamental purpose.

The flower buds are very rich source of rutin (16.0–23.0% dry wt basis), the 3-rutinoside, the glucoside of quercetin; rutin from the buds can be extracted with hot water which gives 80% yield. Pods and flower buds are reported to yield a yellow dye which is used in batik work.

*Trifolium incarnatum* L. (Fabaceae)

English – Crimson Clover

It is an upright annual, with bright red, large, conical flower heads. It is grown in Mediterranean region, Central Europe, and United States for hay and pasture, and as a cover crop. It has been successfully introduced at Kodai Kanal in Tamil Nadu.

Flower heads are reported to have a glucoside incarnatrin which on hydrolyzing yields the coloring matter quercetin.

*T. repens* L.

English – White Clover, Dutch Clover, and Shamrock

It is a perennial, creeping herb, considered to be a native of the northern parts of USA and Canada, commonly found in the temperate and alpine Himalayas, up to an altitude of 4,800 m. It has been introduced into the Nilgiris in Tamil Nadu. Its stem is solid, rooting at the nodes; flowers are white or pinkish with globose heads.

The flowers owe their tinctorial property to quercetin which is present as the glucoside incarnatrin.

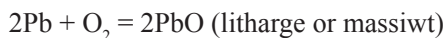
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## 6.72 Red lead or minium

Red lead or minium ( $\text{Pb}_3\text{O}_4$ ), also known as *sindur* in Hindi, is not found in the mineral form but is made by heating litharge, which is the yellow mono-oxide of lead or white lead, a lead carbonate. It can be obtained directly by oxidation of lead.



### 6.72.1 Extraction

For using it as a coloring matter, *sindur* is treated with manasila (realgar). In this preparation, *sindur* is rubbed up for one and a half day in water. Realgar is then ground without being combined with water. Both the substances are mixed together with the aid of water and kept preserved for five days. The entire mass is then ground again and preserved in a vessel. As a dye matter, *sindur* is combined with some oleaginous substances for durability of the color.

### 6.72.2 Uses

The pigment is bright orange-red and has been used in Indian paintings in abundance. It has, however, a defect that on prolonged exposure to light and

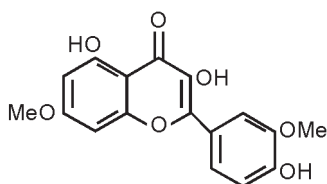
air it turns brown or black. Red lead or *sindur* is also found to be used as a red dyeing material in the medieval period.

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## 6.73 Rhamnazin

Rhamnazin (3,4',5-Trihydroxy-3',7-di-methoxyflavone;  $C_{17}H_{14}O_7$ ; mp 216–218° a yellow coloring matter, occurs in Persian berries, *Rhamnus infectoria* L., Water pepper or pepper wort, *Persicaria hydropiper* (L.) Delarbre, and as 4'-glycoside hibiscatin ( $C_{23}H_{24}O_{12}$ ; mp 160°C) in *Hibiscus surattensis* L. and 3-glucoside alboside ( $C_{23}H_{24}O_{12}$ ; mp 178–180°C) in *Salix alba* L. The glycosides absoside and hibiscatin on hydrolysis with 1N HCl for 1 h yield aglycone rhamnazin, the principal coloring matter. Rhamnazin is moderately soluble in boiling toluene, less moderately in boiling acetic acid, and very sparingly soluble in alcohol. It dissolves in alkalies forming orange-red solutions which on treatment with lime water yield orange-red insoluble precipitate.



Rhamnazin

### 6.73.1 Extraction

The dry, powdered material is extracted with ethanol (95%) for 10 hours. The ethanol is recovered, and the residue is extracted with water. The aqueous solution is extracted with ethyl acetate for 6 hours. The ethyl acetate is recovered under reduced pressure and the residue is re-dissolved in water. The aqueous solution is treated with lead substance solution and the resultant precipitate is filtered and removed. The filtrate is treated with  $H_2S$  and the precipitate formed is filtered off. The filtrate is concentrated and then extracted with ethyl acetate. The ethyl acetate solution is concentrated to dryness and the residue redissolved in water and then separated out through chromatographic methods.

### 6.73.2 Uses

Rhamnazin dyes orange-yellow shades on aluminum mordants. With iron mordants it gives a pale brown color; with alum mordanted it gives a faint yellow tinge.

### 6.73.3 Sources

*Hibiscus surattensis* L. (Malvaceae)

syn. *Hibiscus furcatus* Roxb.

Assami – Kiasi; Kannada – Huligowri, Gumchi; Malayalam – Naranampupuli, Paccapuli; Oriya – Piri-Pirika; Telugu – Adavi Gogu, Konda gogu, Dana-soni Gogu

It is an erect or trailing prickly herb with large yellow flowers and 3–7 lobed leaves, found as an undergrowth in the forests of Assam, Chota Nagpur, Orissa, Andhra, and Karnataka; it occurs in the Ghats and forests from Konkan southwards to Kerala, up to an elevation of 1000 m.

The flowers contain flavonol glucoside, hibiscatin, along with gossypin and gossypitrin. The glucoside bibiscatin on hydrolysis with hydrochloric acid yields a coloring matter rhamnazin.

*Persicaria hydropiper* (L.) Delarbre (Polygonaceae)

syn. *Polygonum hydropiper* L.; *P. flaccidum* Meissn.

English – Water Pepper; Pepper-Wort; Bengali – Packur Mul, Pani-Maricha

It is a glabrous, often glandular reddish, annual or perennial herb, found throughout India in wet places.

The herb dyes wool in yellow, as it contains several flavone compounds (2.0–2.5%) viz. quercetin, quercitrin, kaempferol, rutin, hyperoside, persicarin, and rhamnazin.

*Salix alba* L. (Salicaceae)

English – European Willow, White Willow; Kashmiri – Vivir; Punjabi – Bis, Malchang, Bhushan, and Madnu

It is a large tree with olive-green, yellow or purple branches, frequently cultivated in the Western Himalayas up to an altitude of 2,400 m.

The tree is frost-hardy and grows best on moist and fertile soil that is free from water logging. It is propagated by cuttings during February–March, mainly along the watercourses or on swampy grounds. The cuttings are washed and then kept in water till the roots appear; it is necessary to change the water every day. The transplanting is done from November to March. The transplanted sets grow into trees in about 4–6 years.

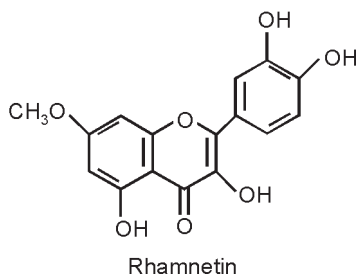
The leaves contain phenolic glucoside alboside, which on hydrolysis yields a coloring matter rhamnazin. The bark is also used for dyeing and tanning purposes as it contains tannin catechin (5–7%).

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### 6.74 Rhamnetin

Rhamnetin (3,3',4',5-Tetrahydroxy-7-methoxyflavone;  $C_{16}H_{12}O_7$ ; mp 294–296°C) occurs as glucoside xanthorhamnin ( $C_{34}H_{42}O_{20}$ ) in dried unripe berries of various species of buck-thorn and Persian berries like *Rhamnus alaternus* L., *R. amygdalinus* L., *R. catharticus* L., *R. infectorius* L. *R. lycioides* subsp. *oleoides* (L.) Jahand. and Maire and *R. saxatilis* Jacq. as a glucoside 7-O-methylrutin (rhamnotin 3-rutinoside;  $C_{24}H_{20}O_{11}$ ) in *Suriana maritima* L. The glucosides xanthorhamnin and 7-O-methylrutin when boiled with dilute acids yield the coloring matter rhamnetin. Rhamnetin when hydrolyzed with hydrochloric acid yields quercetin, the coloring matter of quercitron bark.



Rhamnetin is soluble in boiling phenol, slightly soluble in hot water, alcohol, glacial acetic acid, and acetone, freely soluble in dilute alkalis with intense yellow color. Rhamnetin, 2-(3,4-Dihydroxyphenyl)-3,5-dihydroxy-7-methoxy-4H-1-benzopyran-4-one; 3,3',4',5'-tetrahydroxy-7-methoxyflavone; 7-methylquercetin; b-rhamnocitrin; cyanidenolon-7-methyl ether ( $C_{16}H_{12}O_7$ ; mol wt. 1537).

### 6.74.1 Extraction

The unripe and dried berries are extracted with boiling water for about 6 h and the extract is then evaporated under reduced pressure. Thus the dry powder obtained is a crude commercial xanthorhamnin. This crude xanthorhamnin is a mixture of three coloring matters namely, rhamnazin, rhamnetin, and quercetin. These coloring matters can be separated with the help of chromatographic methods from the crude commercial xanthorhamnin.

For the separation of these coloring matters, the crude xanthorhamnin is extracted with methyl alcohol. The alcoholic solution is chromatographed in the prewash with 2% hydrochloric acid, then with distilled water, and Whatman chromatographic paper by a solvent mixture of n-butyl alcohol-chloroform-acetic acid-water (4:4:1:1 by volume). Each of the three fractions, developed on the chromatographic paper, is eluted with methyl alcohol and hydrolyzed with 2% sulphuric acid. The first fraction yields aglycone rhamnazin, second fraction rhamnetin, and the third fraction quercetin. Thus pure coloring matters can be obtained. The coloring matter from the *Suriana maritima* can be obtained from the methanol in the following way:

The dried powdered material is extracted with methanol and concentrated, and then diluted with water which results in the deposition of a generous quantity (0.55% of the dry weight of plant) of a yellow crystalline crude material which contains rutin and 7-O-methylrutin (Rhamnetin 3-rutinoside). This crude material is crystallized from methanol and yellow needles of 7-O-methylrutin are obtained. It is hydrolyzed by refluxing for 2 h in methanol containing 10% aqueous sulphuric acid. On cooling and filtration it affords a yellow crystalline solid of rhamnetin.

Rutin, the other coloring matter can also be obtained from the mother liquor remained after the initial recrystallization of the crude yellow solid. Several successive concentrations of, and recrystallization from, this mother liquor, yields rutin, which on hydrolyses yields quercetin.

### 6.74.2 Uses

Rhamnetin has been used for dyeing wool and cotton.

### 6.74.3 Sources

*Rhamnus* spp. (Rhamnaceae)

Buckthorn or Persian berries belong to Rhamnaceae. About 150 species are found all over the world. They are mostly deciduous shrubs and small trees, chiefly found in temperate regions of Northern Hemisphere, a few in Brazil and South Africa. Few are grown as ornamentals for their foliage and fruits. A few species yield dyes of economic value and few have medicinal uses because of the purgative properties of drugs in the bark. The species of *rhamnus* are propagated by seeds sown in autumn or stratified, by cuttings and grafting. The following species yield dye:

*R. alaternus* L.

English – Italian Buckthorn

It is about 6 m high, ever green or partly so shrub or a small tree, found in Southern Europe and also cultivated in United States. The unripe berries of the plant yield a number of coloring matters like kaempferol, quercetin, rhamnetin, xanthorhamnin, emodin, frangulin, and rhamnazin. They have been isolated, separated, and purified with the help of chromatographic methods.

*R. caroliniana* Walt.

English – Indian Cherry, Carolina buckthorn

It is a small, about 9 m tall, deciduous, shrub or a small tree, found in USA. It is a source of traditional commercial dye, and has a vast amount of dye in its various parts. The twigs, the smooth grayish bark, and the berries that are red and later turn black all are the source of the dye. The berries are gathered when not quite ripe for drying, but they can also be used fresh.

Aqueous extract of the berries gives lemon-yellow color to mordanted wool with alum and cream of tartar; alum alone gives bright yellow, chrome gives warm brown, chrome and cream of tartar gives golden color, tin gives orange, iron and cream of tartar added to the dye bath gives greenish-yellow.

*R. cathartica* L.

English – Common Buckthorn

It is a deciduous shrub of about 4 m height with spines at ends of branches and black fruits, found in Europe, West and North Asia, cultivated in USA for hedges.

Unripe berries yield rhamnetin, a yellow coloring matter. Green coloring matter can also be obtained by crushing the almost ripe berries of the species, fermenting for 10 days, pressing them and treating the extracted juice with alum and potash, evaporating the mixture to a thick syrup and then packing in

bladders. A similar product is obtained by mixing the juice of the ripe berries with lime and evaporating to dryness.

*R. infectoria* L.

English –Avignon Berry or Persian Berries

It is a deciduous, spiny shrub of about 2 m height with black fruits found in Southern Europe to Iran. The unripe fruit called “Persian berries” are the source of the dye.

*R. saxatilis* Jacq.

English – Rock Buckthorn

It is a low spreading, spiny, deciduous shrub of below 1 m height, found in Central and Southern Europe. The other coloring matter like rhamnazin, quercetin, kaempferol, and emodin are also present in the berries.

*Suriana maritima* L. (Simaroubaceae)

It is a pantropical shrub or small tree, common to coral coasts of Pacific Indian Ocean islands and the coast of Florida.

The plant yields two coloring matters, 7-O-methylrutin (rhamnetin 3-rutinoside) and rutin. On acid hydrolysis both yield rhamnetin and quercetin, respectively.

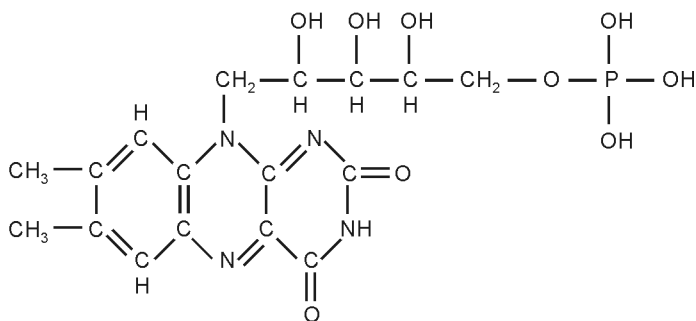
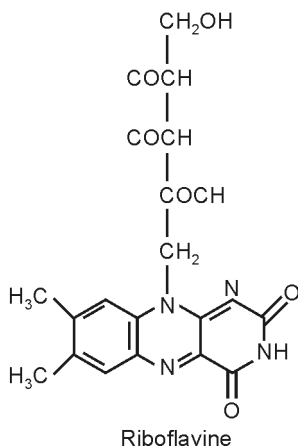
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## 6.75 Riboflavin

Riboflavin [7,8-dimethyl-10-(D-ribo-2,3,4,5-tetrahydroxypenty Disoalloxazine; 7,8-dimethyl-10-ribitylisoalloxazine; Beflavine; Flavaxin; Ribipca ( $C_{17}H_{20}O_6$ ; mol wt 367.36), also known as vitamin G, lactoflavin, hepatoflavin, ovaloflavin, uroflavin and verdoflavin], is the principal yellow coloring matter, found in milk, eggs, malted barley, liver, kidney, heart, some bacteria, some fungi and algae, and in higher plants. The richest natural sources of the riboflavin are yeast and whey. Minute amount is present in all plant and animal cells. It occurs in free form only in the retina of the eye, whey, and urine. The principal forms occurring in tissues and cells are flavine mononucleotide (FMN, riboflavine-5-phosphate) and flavine-amine dinucleotide (FAD).



Riboflavin crystallizes from 2N acetic acid, alcohol, water or pyridine in fine orange-yellow needles. It decomposes at 278–282°C. When dry, it is not

appreciably accepted by diffused light, but in alkaline solution it deteriorates quite rapidly. Riboflavin is odorless and has a bitter taste. It is easily soluble in water and ethanol and soluble in dilute alkalis, slightly soluble in amyl alcohol, cyclohexanol, benzyl alcohol, and phenol or amyl acetate but insoluble in ether, acetone, chloroform or benzene. Natural solutions of riboflavin have a greenish-yellow color. It gives a red-violet color with concentrated sulphuric acid, which changes to yellow on dilution. When heated with 50% NaOH solution, riboflavin produces a green color that changes to red on dilution.

### 6.75.1 Extraction

In order to liberate riboflavin from its natural protein-bound form, it is necessary to treat the mashed tissues with suitable solvents at room temperature or at the boiling point of the solvent. Methanol, ethanol, acetone, undiluted or diluted with water, and aqueous acid solutions have been used for extraction of the vitamin. For instance, riboflavin from fresh or dried plants has been extracted in good yields by boiling the material with 70% methanol for 45 minutes.

For the isolation of riboflavin from the extracts, it sometimes is useful first to remove lipids by extraction with ether, in which the vitamin is insoluble. Salts and glycogen in few cases can be eliminated from riboflavin concentrates by fractionate precipitation with alcohol or acetone. Impurities from fermentation liquors may be precipitated by means of acetone, and crude riboflavin can be recovered from the concentrated filtrate by the addition of more acetone. The vitamin can be extracted with butanol and then precipitated from the extract by addition of petroleum ether. In the isolation of riboflavin from whey, the accompanying creatinine is removed by picric acid precipitation.

Precipitation of riboflavin occurs with lead acetate and with silver nitrate in neutral solution, or with phosphotungstic acid in  $\text{N H}_2\text{SO}_4$ ; from the latter precipitate, the phosphotungstic acid can be extracted with amyl alcohol. Silver nitrate or mercuric sulfate in acid solution leaves the vitamin in solution but precipitates few accompanying substances.

Good adsorbents for riboflavin are fuller's earth in acid solution, florisil, flordin XXF, and frankonit in neutral solution. One of the best eluents is pyridine, diluted with aqueous methanol or ethanol, ammonia, triethanolamine, 0.1 N  $\text{NaO}_2$  in 60% ethanol, boiling 60% ethanol, 80% acetone, and polyhydric alcohols have been used for elution. Vitamin  $\text{B}_2$  is adsorbed by charcoal very strongly; however, elution is difficult from this adsorbate. Adsorption occurs furthermore with lead sulfide, when this is precipitated in a riboflavin solution; the vitamin can be extracted with hot water from the precipitate. Riboflavin is not adsorbed by kieselguhr, kaolin, tale, aluminum oxide, or calcium carbonate.

A combination of precipitation and adsorption methods mostly will be necessary to isolate pure riboflavin. As an example, the isolation of riboflavin from egg white, egg yolk, and whey might be mentioned. A general method for the preparation of pure D-riboflavin from natural sources has been described, which is based on adsorption on fuller's earth, fractionation with immiscible solvents and acetone, and crystallization from an aqueous acetone-petroleum ether mixture; aqueous alcohol solutions have been used for elution of the adsorbates.

### 6.75.2 Uses

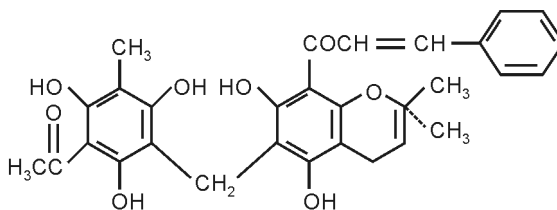
Besides its therapeutic applications, riboflavin is used to color few food products including cheese, as it has been permitted as a food coloring matter under the PFA Act of India. Riboflavin is an essential nutrient for all animals and many micro-organisms. No toxicological effects were reported in humans whom high levels of riboflavin were fed in the toxicological monograph prepared by JECFA in 1980 for riboflavin and riboflavin-5'-Phosphate (FNM).

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### 6.76 Rottlerin

Rottlerin or mallotoxin, ( $C_{30}H_{28}O_8$ ; mp 206–207°C), the principal coloring matter, occurs in the orange-red powder which is found as a glandular pubescence on the fruits of Kamala, *Mallotus philippinensis* Muell. syn. *Rottlera tinctoria* Roxb. Rottlerin is insoluble in cold water, slightly soluble in boiling water, and freely soluble in alkalis, alcohols benzene and ether, and forms a deep red solution. The coloring matter comprises of several chalcones, the rottlerin and isorottlerin (mp 180–182°C). Together they constitute about 11% of the weight of the Kamala powder. In addition to these, Kamala powder also contains a small amount of homorottlerin (mp 192–193°C), a dark resin (60% mp 60°C) and a yellow resin (5%, mp 121–122°C), and a wax (2%, mp 82°C), in traces a volatile oil, tannins, gum, and citric and oxalic acids.



Rotterin

### 6.76.1 Extraction

The red pubescence is separated from the ripe fruits by beating and shaking them in canvas bags. It may also be obtained by stirring the fruits vigorously in water. The pubescence settles down as sediments, which is later collected and dried. The yield of powder is 1.4–3.7% of the weight of fruits. It is granular reddish-brown resinous powder, almost without odor and taste. From the Kamala powder, rottlerin is obtained by boiling it in any one of the solvents like carbon bisulphide, ethyl alcohol or benzene. The extraction of rottlerin can be done by the following ways:

*By carbon bisulphide:* Rottlerin can be isolated by using both cold and hot carbon bisulphide. Well-dried kamala powder is extracted in six times its bulk of cold carbon bisulphide for about 24 h while occasionally shaking. The dark red extract thus obtained is filtered and the bulk of the carbon bisulphide is distilled off. Thus, obtained product is a crude rottlerin and contains a small quantity of a yellow compound. It is removed easily by recrystallisation of the crude rottlerin from toluene.

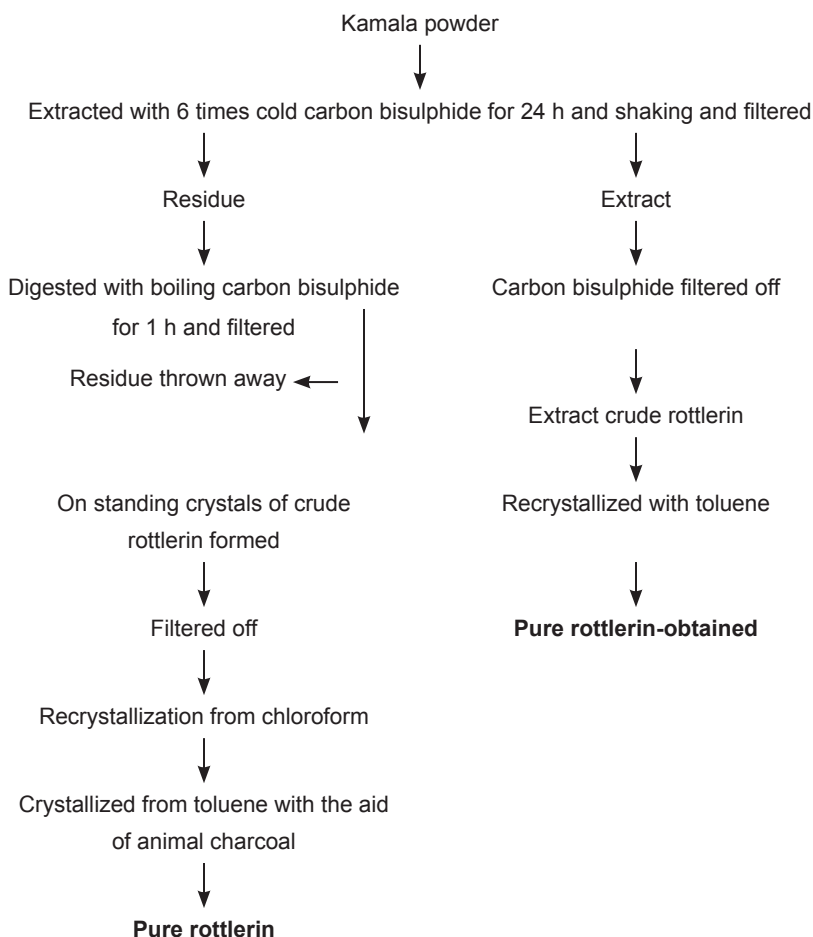
The residue left after extraction with cold carbon bisulphide is digested with a large quantity of boiling carbon bisulphide for an hour and the dark red liquid is filtered off. This on standing becomes thick, owing to the separation of a large quantity of gelatinous matter, which on subsequent concentration gradually becomes crystalline and is separated by filtration. Then the residue is extracted several times with boiling carbon bisulphide until the extract becomes nearly colorless. Thus, rottlerin is obtained which is a pure compound. It is further purified by two or three crystallizations from chloroform, which remove a small quantity of a sparingly soluble substance and lastly crystallize from toluene with the aid of little animal charcoal.

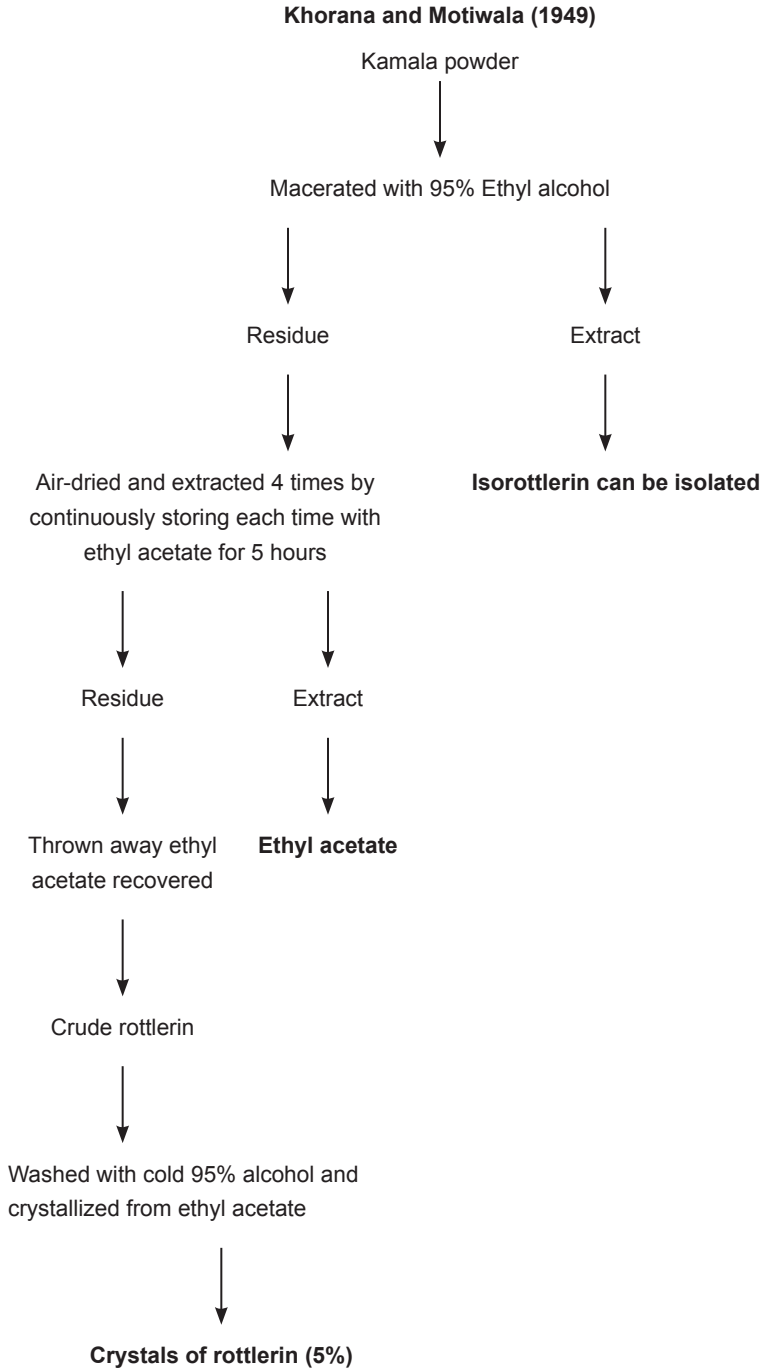
*By benzene:* Rottlerin can also be isolated from hot benzene. Finely powdered kamala is refluxed for 6 h with hot benzene and then filtered while it is hot. This is repeated four times. The combined filtrates are then concentrated to one fourth of their volume under reduced pressure, and allowed to stand overnight and filtered. Thus, obtained residue is washed with

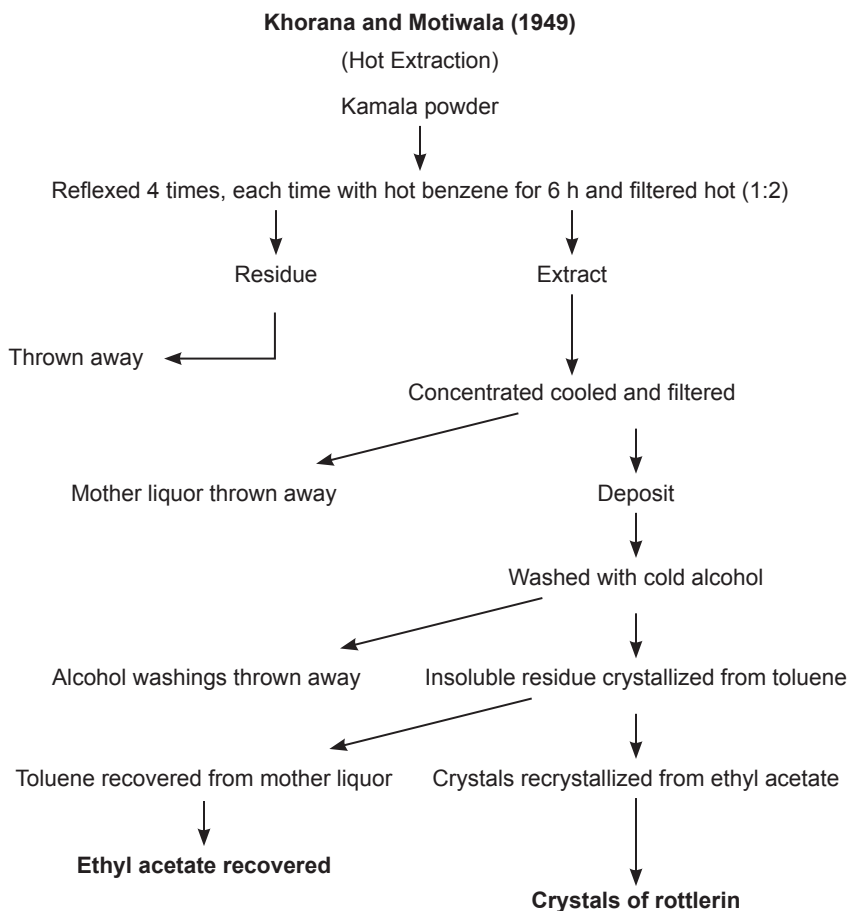
cold 95% alcohol and then crystallized from toluene and further recrystallized from ethyl acetate. Thus pure glistening reddish-yellow plates of rottlerin are obtained.

*By alcohol:* Rottlerin can also be isolated from alcohol. Kamala powder is macerated with 95% ethyl alcohol and then filtered. Thus, obtained residue is air-dried and then extracted four times by continuously stirring each time with ethyl acetate for 5 h and then extracted. From the extract, ethyl acetate is recovered and thus crude rottlerin is obtained. It is washed with cold 95% alcohol and then crystallized from ethyl acetate. Thus, pure crystals of rottlerin are obtained.

**Rottlerin extracted from cold and hot carbon bisulphide (Perkin 1893)**







### 6.76.2 Uses

Rottlerin is used for dyeing silk and wool. It produces a bright orange or flame color which is fairly fast to soap, alkalis, and acids but fades somewhat in sunlight. It is used for coloring food stuffs and beverages. It is used as an antioxidant for ghee, vegetable oil, and shortening. It is stable and harmless, without taste and odor, and imparts a light yellow color. It shows anthelmintic activity. Kamala dye powder is also used as a sindur or kumkum by women in India.

### 6.76.3 Sources

*Mallotus philippensis* Muell. Arg. (Euphorbiaceae)  
syn. *Rottlera tinctoria* Roxb.

Assami – Jarat losan; Bengali – Kamala; Hindi – Kamala, Sindur, Rohini; Marathi – Shendri; Gujarati – Kapilo; Tamil – Kapli, Kungumam, Kurangumanjanatti; Telugu – Kunkuna, Sinduri, Chendiramamu; Kannada – Kunkumadamara; Malayalam – Manjana, Kuramadakku; Oriya – Sinduri, Kumkumom Kapilogundi; Nepali – Sindure; Lepcha – Puroakung

It is a shrub or a small and evergreen tree, found throughout India, occasionally ascending to 1,500 m in the outer Himalayas. It contains globose, 3-lobed, 3-valved, densely covered with reddish-brown glandular pubescence fruits.

Kamala tree is widely distributed in northern-central, western and southern India. It is commonly found in sal and certain scrub and mixed forests. Natural reproduction takes place by seeds which fall to the ground in the beginning of the hot season and germinate in the ensuing rainy season. Artificial propagation is done by sowing fresh seeds by April. The 1-year-old seedlings are planted in the fields. The tree also reproduces from root suckers. About 100–120 g of rottlerin are obtained from 1 kg of Kamala fruits.

## For reading reading

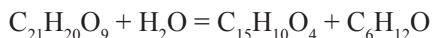
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## 6.77 Rubiadin

Rubiadin (1,3-dihydroxy-2-methyl-anthraquinone; 1,3-dihydroxy-2-methyl-9,10-anthracenedione;  $C_{15}H_{10}O_4$ ; mp 290°C), a yellow coloring matter, occurs



in the form of a glucoside ( $C_{21}H_{20}O_9$ ) in the roots of Madder, *Rubia tinctorum* L., Karamu, *Coprosma lucida* Forster, *C. acerosa* Conuingham and *C. australis*, *Morinda citrifolia* and *M. jasmanoides* and also as a primoveroside ( $C_{26}H_{28}O_{13}$ ; mp 248–250°C) in *Galium verum* L. The glucoside undergoes hydrolysis to form glucose and rubiadin on heating with dilute mineral acids as follows:



Rubiadin is insoluble in cold water and nearly soluble in boiling water but easily soluble in ether, alcohol, benzene, and glacial acetic acid. Its alkaline and acidic solutions are red and yellow, respectively.

### 6.77.1 Extraction

In order to extract the dye, fresh roots or root bark is ground into powder and extracted with boiling water or 50% aqueous alcohol. Thus a dark brown extract is obtained, which is mixed with an excess solution of lead acetate, which gives an abundant reddish-purple precipitate. The precipitate is filtered off and an excess of ammonia is added to the dark yellow filtrate, which gives a voluminous red precipitate and then the liquid becomes colorless. This precipitate is collected, washed with water, and treated with an excess of dilute sulphuric or hydrochloric acid. The excess acid is removed with lead carbonate and then the lead is removed by hydrogen sulphide.

Thus, a yellow filtrate from the lead sulphide is evaporated to about one half and then acidified with sulphuric acid or hydrochloric acid, and boiled for some time. During the boiling, a dark green precipitate is gradually formed, and the liquid becoming much paler in color. The green precipitate is collected, washed, and then treated with boiling alcohol, and filtered. To the liquid, filtered boiling hot alcoholic solution of lead is added; this gives a dark purple precipitate which is filtered off. Thus, a yellow filtrate is got which is evaporated to dryness and then the residue is treated with water in order to remove the excess of lead acetate and the residue is collected, washed, and treated with boiling baryta water. The latter dissolves rubiadin, and gives a red solution from which barium rubiadin is crystallized out on cooling. The red substance is left undissolved by the baryta water, which is the barium compound of the glucoside; this is decomposed with dilute hydrochloric acid, and the glucoside, after collection and washing, is dissolved in boiling alcohol, from which rubiadin is crystallized on cooling. Rubiadin is then collected, washed, dried, and purified by crystallization, first from alcohol and then from benzene. As the aqueous or alcoholic liquor is a mixture of several anthraquinone compounds, these compounds can be separated by chromatography, usually over columns of magnesium carbonate-supercel (1:1) and then pure rubiadin may be isolated.

### 6.77.2 Uses

Rubiadin, a pale yellow dye, is used for coloring cheese and butter. It is also used to dye woolens.

### 6.77.3 Sources

*Galium verum* L.

See under the dye galiosin.

*Morinda citrifolia* L.

See under the dye morindone.

*Rubia tinctorum* L.

See under the dye alizarin.

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## 6.78 Rubrobrassicin

Rubrobrassicin (Cyanidin 3-Sophoroside-5-glucoside;  $C_{28}H_{33}O_{16}$ ), the principal coloring matter occurs in the leaves of red cabbage, *Brassica oleracea* var. *capitata* L.f. *rubra*, and in the roots of red globe radish, *Raphanus sativus*, in the form of rubrobrassicin chloride ( $C_{28}H_{33}O_{16}Cl$ ).

### 6.78.1 Extraction

The cabbage leaves and radish root skins are macerated and extracted with boiling water or aqueous  $\text{SO}_2$  solution at room temperature for 16 h. It is then concentrated under reduced pressure and dried up into fine powder, which can be used as such for coloring a wide variety of food products. A pure rubrobrassicin is obtained through chromatographic methods. The crude extract contains cyanidin 3,5-diglucoside, cyanidin 3-sophoroside-5-glucoside, and cyanidin 3-sophoroside-5 glucoside acylated with one and two equivalents of sinapic acid. For the purification of the pure pigment, the powder is washed with dilute aqueous hydrochloric acid and then the anthocyanins are eluted with the mixture of methyl alcohol and hydrochloric acid solution. The fractions thus obtained are chromatographed on Whatman no. 3 paper in solvent BAW (butan-1-ol-acetic acid-water, 4:1:5, v/v) to get pure pigment rubrobrassicin.

### 6.78.2 Uses

The dye is used to color food stuffs, soft drinks, and pharmaceutical preparations.

### 6.78.3 Sources

*Brassica oleracea* var. *capitata* L.f. *rubra*. (Brassicaceae)

English – Red cabbage; Bengali – Bandhakapi, Kopi; Gujarati – Kobij; Hindi – Bandgobi, Patagobhi; Kannada – Yeleksu; Malayalam – Muttakose; Marathi – Kobi; Mundari – Arakubi, Kubiafa; Tamil – Muttai; Telugu – Aalugobi

It is a small biennial herb, native to the Mediterranean region and introduced into India where it is cultivated on a large scale as an annual both in hills and in the plains. It has a red head and that is why it is known as red cabbage.

The culture of cabbage dates back to some 4,000–8,000 years. The seedlings are raised in nursery beds and later transplanted in the fields when they are 30–45 days old. A number of varieties of the red cabbage have been developed but major are large blood red, red rock mammoth, and red cabbage.

Red cabbage is considered as a source of the anthocyanin pigments. It contains cyanidin 3,5-diglucoside, cyanidin 3-sophoroside-5 glucoside, cyanidin 3-diferuloylsophoride-5-glucoside; cyanidin 3-P-coumaroylsophoroside-5-glucoside, and two unidentified pigments. The anthocyanin powder is used as a dry soft drink mix colorant.

*Raphanus sativus* L. (Brassicaceae)

English – Red Globe, Radish; Bengali, Gujarati, Hindi, and Marathi – Muli, Mula, Mura, Muri; Kannada, Malayalam, Tamil, and Telugu – Mullangi

It is an annual or biennial bristly herb with a white or brightly colored tuberous tap root, which is cultivated throughout India.

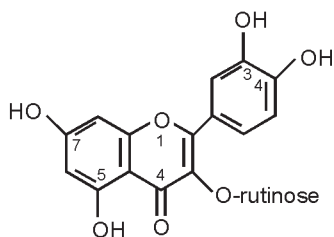
The colored radishes contain anthocyanin pigments which occur naturally acylated either with ferulic or with p-coumaric acid. Red skinned radish yields cyanidin-5-glucoside-3-phosphoride, whereas scarlet skinned radish yields the corresponding pelargonidin diglycoside. Cyanidin diglycoside and catechol are also reported in the red types.

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### 6.79 Rutin

Rutin (3,5,7,3',4'-Pentahydroxy flavone-3-rhamnoglucoside; quercetin 3-β-D-rutinoside ( $C_{27}H_{30}O_{16}$ ; mp 214–215°C), the principal coloring matter, present in the leaves and blossoms of Buck wheat, *Fagopyrum esculentum* Moench.; Duckwheat, *F. tataricum* (L.) Gaertn., Garden Rue, *Ruta graveolens* L.; in the buds of the Japanese Pagoda Tree, *Styphnolobium japonicum* (L.) Schott syn. *Sophora japonica* L., and in the leaves of tobacco, *Nicotiana tabacum* L. in Forsythia, *Forsythia suspensa* (Thunb.) Vahl. var. *fortunci* (Lindl.) Rehd in hydrangea, *Hydrangea paniculata* Sieb., and also in number of other plants. Rutin is a yellow crystalline powder, slightly soluble in water, more soluble in alcohol, acetone, and alkaline solutions and insoluble in chloroform, ether, and hydrocarbons. On acid hydrolysis it yields quercetin, rhamnose, and glucose.



Rutin

### 6.79.1 Extraction

The solvents employed for the extraction of rutin are hot water, dilute isopropyl alcohol or ethanol; but the isopropyl alcohol was found more efficient solvent in case of buckwheat, whereas hot water was preferred in case of *Eucalyptus macrohyncha*. The plant raw-material is ground into powder and extracted with isopropyl alcohol. From the extract the alcohol is distilled off and the fat, which settles, is strained off. The crude rutin is crystallized from the remaining extract on standing and cooling. It is then redissolved in hot water and treated with silica gel to remove the red pigments and thus pure rutin is crystallized from the filtrate.

### 6.79.2 Uses

Rutin does not hydrolyze on dyeing. It yields brownish yellow-orange on alum-mordanted wool. It has the same dyeing properties as quercetron bark dye has. It yields several shades with different mordanted wool, silk, and cotton. Rutin dyes brown direct but green on iron mordant.

Besides a dye, rutin is also an important pharmaceutical product. It is known as “P” factor or a substance possessing vitamin “P” like activity. Besides its medicinal properties it has also been shown to provide protection against harmful effects of X-rays, indicating that it may be used to cure the people exposed to dangerous atomic radiations.

### 6.79.3 Sources

*Eucalyptus macroorhyncha* F. Muell. (Myrtaceae)

English – Red Stringybark, Mountain Stingybark

It is a medium sized tree with reddish to brown, persistent, and stingy bark. It is indigenous to the solerophyll forest of the Central and Southwestern slopes of New South Wales and Victoria and in South Australia near Clare. In India it is grown in Nilgiris, in Tamil Nadu. It would probably do well in the Himalayas at an elevation of 2000 m. It is xeromorphic in nature and can be cultivated in the areas of moderate rainfall. It can stand in drought and hot spells. Being xeromorphic plant adated to long period with sparse water, its leaves have a very thick cuticle and the laminae ore borne vertically downwards.

Leaves are very rich source of rutin (10–24%). Quercetin can be prepared from rutin in a high state of purity by simple acid hydrobysis.

*Eucalyptus youmanii* Blakely and McKie

It is a moderate sized tree of about 12–20 m height and 0.45–0.90 m diameter. It is usually heavily branched and moderately large to dense crown and grown

on the low hills of northern tablelands of NSW in Australia in sclerophyllous eucalyptus forests. Seeds of this species are obtained from Australia. They have successfully been grown in Nilgiris and Palani hills of South India and at Palampur in Himachal Pradesh. Seeds are sown in nurseries. It takes about six months for the plants to gain a height of 15–25 cm when they are transplanted in the field. The best time of sowing the seeds is January–February. Seeds treated with 50 ppm concentration of gibberellic acid and kept soaked overnight were found to take less time, whereas germination percentage increases three times. The maximum rutin content is obtained in the month of July and rutin percentage is found more in young leaves near the tip of the twig than in mature leaves.

*Fagopyrum esculentum* Moench. (Polygonaceae)

English – Common Buckwheat, Brank; Assami – Doron; Hindi – Kotu, Phaphra; Punjabi – Daran, Okul, Phaphar

It is an annual herb of 1–1.75 m height with alternate hastate leaves, pinkish-white flowers, native of Central Asia, and cultivated in various countries as a food or fodder crop. In India it is grown as a minor grain crop from Kashmir to Sikkim, Khasi hills, and Manipur, and in Nilgiri in Tamil Nadu.

Buckwheat plant is a promising commercial source of rutin (3–5%). The leaves and blossoms of the plant contain most of the rutin (80–90%); only a small percentage is present in the stems and none in fruits. The rutin content varies with the age of the plant, reaching a maximum in the early blossoming stage. However, because of the extra growth of the plant, the maximum yield of rutin per acre is obtained when Buckwheat is harvested at full bloom just before the fruits have set. With further growth, the rutin content decreases due to the faster growth of the stem tissue, atrophy of the leaf tissue, and replacement of flowers by fruits.

Rutin is obtained from fresh or dried leaves and flowers. Green plants should be processed as quickly as possible after harvesting, as there is a rapid loss of rutin in slow field drying. A process for rapid dehydration of leaves, using alfalfa dryers, has been developed for retaining rutin contents under ordinary storage conditions for at least a year.

Buckwheat is a quick growing crop and prefers a moist and cool climate, and a well-drained sandy soil. It is considered an excellent crop for soil improvement, particularly for lands newly opened or poor soils which do not support any other cereal crop. It acts as a soil binder, preventing erosion during heavy rainfall.

In North India, buckwheat is usually grown as a rainy season crop that is sown in July and harvested in October. In Nilgiris, it is generally sown in April and harvested in August.

*F. tataricum* Gaertn

English – Duckwheat, Tartary or Indian Buckwheat; Hindi – Kaspat; Punjabi – Brapu, Chin, Ugal

It is an annual plant with small, greenish or yellowish flowers, cultivated in the higher Himalayas especially in the colder parts of Ladakh, Zaskar, and Western Tibet. It stands both heat and cold better than common buckwheat.

Duckwheat is a better source of rutin than common buckwheat, as it contains 45–80% more rutin than the latter. Due to its continuous growth habit, it produces a higher proportion of leaves. Further, it maintains its high rutin content for a longer period as it is slower to mature and the harvest period is not limited as in the case of buck wheat.

*Ruta graveolens* L. (Rutaceae)

English – Garden Rue

It is a strong-scented herb of 30–90 cm height, native to Mediterranean region and sometimes cultivated in Indian gardens.

The plant contains rutin (2%). The plant is often cultivated for its aromatic leaves used as an ingredient in salad, stews, and ragouts. It grows well at high altitudes but can also be cultivated at medium elevations. It prefers a well-drained, calcareous, clayey soil. The plant is propagated by seeds, cuttings, layerings or divisions. Seeds may be sown in pots during October and the seedlings can be later transplanted in fields. Subsequent plantings may be done by cuttings from well-established plants.

*Nicotiana tabacum* L. (Solanaceae)

English – Tobacco; Bengali, Gujarati, Hindi, and Marathi – Tamaku, Tambaku; Kannada – Hogesoppu; Malayalam – Pokala; Tamil – Pugaiyilai; Telugu – Pogaku

It is a 1–3 m tall annual plant, native to north-western Argentina and adjacent to Bolivia, cultivated in most of the countries of the world.

Tobacco contains several substances of phenol, polyphenol, and tannin classes, mostly in the form of glycosides. The principal polyphenols is rutin, which occurs about 1% in green leaves, but its concentration decreases during curing.

Tobacco is reported to have been introduced into India by the Portuguese sometimes in the beginning of the 17th Century, and its cultivation seems to have been soon taken up in earnest. The important tobacco cultivating areas in India lie in Andhra Pradesh, Gujarat, Maharashtra, Karnataka, Tamil Nadu, Uttar Pradesh, Bihar, and West Bengal.

Tobacco thrives well under tropical, subtropical, and temperate climates. It grows well in drained and aerated soil. The desirable soil pH is 5.0–6.0. It is propagated by seeds. Seeds are sown in nursery beds from first week of

July to the third week of September. Seedlings are ready for transplantation in 5–9 weeks after sowing. Transplanting is done by hand. Planting is generally done on a rainy day or irrigating the field or also in dry soil and the field is immediately irrigated. The plants are topped when they are 90–100 cm high or 5–6 weeks old. Rutin occurs to the extent of c 1% in green leaves, but its concentration decreases during curing.

*Styphnolobium japonicum* (L.) Schott (Fabaceae)

syn. *Sophora japonica* L.

English – Japanese Pagoda Tree, Chinese Scholar Tree, Umbrella Tree

It is a medium sized, deciduous tree of about 25 m height, grown in Kashmir as ornamental.

Flower buds are a very rich source of rutin (16–23%; dry weight basis). The aqueous extract of the flower buds and pods yield a yellow dye which contains rutin that is used in butik work.

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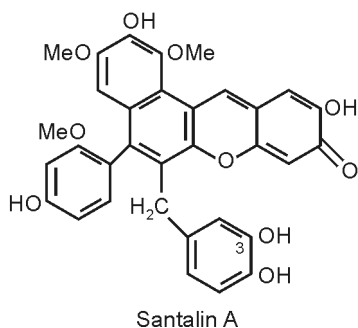
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## 6.80 Santalin

Santalin ( $C_{33}H_{26}O_{10}$ ; mp 302–303°C) the principal red colouring matter, occurs in the wood of Sanders or red sandal wood, *Pterocarpus santalinus*



L.f., Andaman padank or Andaman redwood, *P. dalbergioides* DC., and Malay Padauk, Narra, *P. indicus* Willd. It is soluble in organic solvents but insoluble in water. Santalin yields a blood-red solution with alcohol, yellow with ether, and violet with ammonia and caustic alkaline. Santalin appears to be present also in the wood of *Baphia nitida* Afzol.



### 6.80.1 Extraction

The wood is ground into powder and extracted either with alcohol, ether or alkali and then filtered. The filtered liquor is a mixture of the santalin, desoxysantalin, santal, and two unidentified pigments A and B. These compounds are separated through chromatographic methods to get pure santalin.

### 6.80.2 Uses

Santalin is used for dyeing wool, cotton, and leather. It is also used for coloring pharmaceutical preparations and food stuffs and is suitable for coloring paper pulp. Santalin dyes brick-red directly, orange-red and red with alum, brownish-red on chrome, brown on copper, maroon on iron, and red on tin mordants. It has also been used as a histological stain in biological studies.

### 6.80.3 Sources

*Pterocarpus dalbergioides* Roxb. (Fabaceae)  
syn. *P. indicus* Baker non Willd.

English – Andaman Padauk, Andaman Redwood; Andaman – Chalangada, Da; Tamil – Vengai; Telugu – Yerravegisa

It is a very large, buttressed tree, up to 45 m in height and 5.5 m in girth, found in Andaman Islands and also cultivated in West Bengal and Southern India.

The whole pods are sown for regeneration of the tree. Nursery raised 1-year-old seedlings are transplanted into fields. The rate of growth of the tree is moderate, with the mean annual girth increment being about 2.8 cm.

The sapwood is grey, heartwood very much variable in color, though shades of light yellowish-pink to usually gorgeous reddish with dark lines. The wood contains a red pigment santalin and a yellow flavonoid santal.

*P. indicus* Willd.

English – Malay Padauk, Narra; Tamil – Vengal; Telugu – Yerravegisra

It is a large, buttressed tree, up to 36 m in height and 3.6 m in girth, native to Malaysia, planted in Andaman Islands, West Bengal, Tamil Nadu, and Maharashtra as garden and avenue tree.

The tree requires a deep and well-drained soil and tropical climate. It grows readily from seeds or cuttings, and the rate of growth is extremely rapid.

The wood is yellow to red in color. It contains red coloring matters namely, santalin, narin, and angolensih. Narrin is a dark red amorphous powder which yields phloroglucinol and resorcinol on fusion with alkali. The wood is said to be used in Philippine for preparation of a red dye often used for staining light colored wood.

*P. santalinus* L.f. (Fabaceae)

English – Red Sander, Red Sandal Wood; Bengali and Hindi – Raktachandan, Lalchandan; Gujarati – Ratanjali; Kannada – Agar, Honne, Kempugandha Chekke; Malayalam – Patrangam, Tilaparnni; Marathi – Tambada chandana; Tamil – Atti, Sivappu Chandanam; Telugu – Agarugandhamu, Rakta Gandhamu, Yerra chandamu

It is a small to medium sized tree, founds on dry, hilly, often rocky grounds in Andhra Pradesh, Tamil Nadu, and Karnataka states at altitudes of 150–900 m.

The plant is raised through seeds in nursery. One-year-old seedlings are transplanted from the nursery into bamboo baskets and then planted in prepared pits during rains at a spacing of 3.5–4.5 m. The rate of growth is slow with mean annual girth increments of 1.3–2.0 cm. The tree can be raised to some extent from cuttings, provided these are irrigated regularly.

The wood is heavily impregnated with reddish-brown gum and contains a red dye, santalin, for which it has been valued in the past. It yields 16% santalin. A histological stain has been prepared from the alcohol soluble fraction of the heartwood.

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## 6.81 Sepiomelanin

Sepiomelanin or sepia is a brown dyestuff with a trace of violet, derived from the raw ink which comes out from the ink sac of the common cuttlefish (*Sepia officinalis* L.). A black coloring principle, sepiomelanin, is present in the raw ink as a suspension of small, dark granules in colorless plasma. Sepiomelanin in the dry form is an amorphous, hygroscopic, black powder, insoluble in all solvents.

### 6.81.1 Uses

Ink made from sepia was widely used in ancient times. Sepiomelanin, refined from the raw ink is used as painter's black color.

### 6.81.2 Sources

*Sepia officinalis* L.

English – Cuttlefish or Common Sepia

Cuttlefish, a soft, boneless mollusk related to the squid and octopus family is found in the Mediterranean sea, pacific, and Atlantic oceans. It is characterized by a body shape that is dorsoventrally compressed and oval. It has the conspicuous zebra like, brown to violet cross patterning on the upper surface and a spotted bluish-green belly. Inside the body there is a porous, oval piece of shell known as cuttlebone, the source of minerals for cage birds and as a tooth powder.

The ink of cephalopods is used as both defense and escape mechanism. When alarmed, the cuttlefish ejects an inky fluid to cloud the water and confuse its enemies.

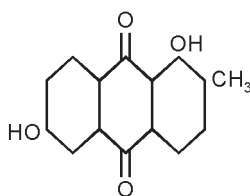
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## 6.82 Soranjidiol

Soranjidiol (1,6-dihydroxy-2-methyl anthraquinone;  $C_{15}H_{10}O_4$ ; mp  $295^{\circ}C$ ), a dark reddish-brown coloring matter, occurs as free anthraquinone and their glycosides in the stem and root bark of suranji, *Mammea longifolia* Planch. and Triana, Al, *Morinda citrifolia* L., and *M. umbellata* L., *Coprosma acerosa* A.Cunn., and *C. lucida* J. R. Forst. and G. Forst. Soranjidiol is soluble in cold water and ethyl alcohol.



Soranjidiol

### 6.82.1 Extraction

For the extraction of the dye, the material does not require boiling as the dye is soluble in cold water and alcohol. The root bark is ground into powder and extracted with methanol and filtered. The filtered liquor is dried up under reduced pressure to get a dark viscous residue which is dissolved in water and hydrolyzed by boiling with hydrochloric acid. The dark precipitate of anthraquinones is obtained which is extracted with acetone and the dissolved products separated by chromatography to give soranjidiol.

Another method for the extraction of soranjidiol is as follows:

Air dried, finely ground bark is extracted with light petroleum for 70 h and then the solvent is evaporated. A yellow solid, obtained after evaporation of the light petroleum, is dissolved in acetone and subjected to column chromatography on freshly calcined magnesias.

The bark is then extracted with benzene for 70 hours. On cooling it yields a yellow insoluble substance, lucidin. It is filtered off from the extract. The residue from the benzene extract is dissolved in acetone and subjected to column chromatography on freshly calcined magnesias.

The residual bark is then extracted with alcohol for 70 h to remove the glycosides. The residue from the alcoholic extract is dissolved in cold water and filtered off. The aqueous solution of the glycosides is hydrolyzed by boiling it with 10% sulphuric acid for 36 h and then extracting with boiling acetone. Thus obtained precipitate is filtered off. The acetone solution is then chromatographed on freshly calcined magnesia. As a result of this, the bands developed from the light petroleum, benzene, and alcoholic extracts are same in number and color, the material from all three chromatograms are combined and the material is absorbed on a series of developed columns. The material from each column is liberated by dissolving magnesia with hydrochloric acid. Then a column of sorangidol is purified after sublimation at 150°C 0.1 mm and then crystallized from alcohol to obtain yellow needles of pure soranjidiol.

### 6.82.2 Uses

Soranjidiol dyes clothes brighter than madder dye, *Rubia tinctorum* L. It is moderately fast to light, washing, and soda boiling on cotton, silk, and wool.

### 6.82.3 Sources

*Mammea longifolia* Planch. and Triana (Clusiaceae)

syn. *Ochnocarpus longifolius* Benth. and Hook.f; *Calysaccion longifolium* Wight.

Bengali – Nagesar; Gujarati – Ratinagkesar; Hindi – Nagkesar; Kannada – Wundi, Suragi, Gargundi; Malayalam – Seraya; Marathi – Punzag, Suringi; Oriya – Churiana; Sanskrit – Nagakesara; Tamil – Nagappu, Nagesarpu; Telugu – Suraponna

It is a large tree, found in the evergreen forests of Western India from Khandala Southwards to Malabar and Coimbatore, ascending to an altitude of 600 m.

The root bark and flower buds contain soranjidiol, the coloring principle which is used to dye cotton, silk, and wool red.

*Morinda citrifolia* L. and *M. umbellata* L.

Please see under the dye morindone.

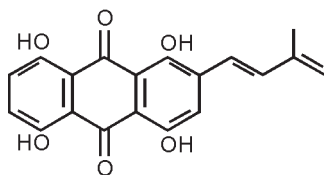
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## 6.83 Tectoleafquinone

Tectoleafquinone (1,4,5,8-Tetrahydroxy anthraquinone;  $C_{19}H_{14}O_6$ ), yellow or red coloring principle, occurs in the leaf of teak, *Tectona grandis* L.



Tectoleafquinone

### 6.83.1 Extraction

The dry leaves are extracted with cold acetone and the wax and chlorophyll removed from the extractives through digestion with petroleum ether. The dark red solid thus obtained is a complex mixture of a number of quinonoid pigments.

The crude dye is fractionated by extraction with benzene and further fractionated by column chromatography on silica gel, which affords a dark red crystalline compound, tectoleaf-quinone.

The crude dye which is a complex mixture of several pigments can be commercially extracted by heating chopped leaves with water or preferably with 0.25% sodium carbonate solution. The best yield of the dye is obtained from the leaves collected during May–August.

### 6.83.2 Uses

Tectoleafquinone is used to dye silk, cotton, and wool. It can be used as a substantive dye for wool and silk, but for cotton a mordant is required. Wool and silk obtain better and stable shades with mordants. Silk and wool when dyed with aqueous leaf extract without any mordant, develop caledonian-

brown color; with  $\text{FeSO}_4$  or  $\text{CuSO}_4$  (5%) they get grey or slaty colors, whereas with  $\text{K}_2\text{Cr}_2\text{O}_7$  or stannous chloride (5%) solution they get flesh color, and with dye extracted with 0.25% sodium carbonate get a lilac color without any mordant. Cotton gets olive-brown and medium gray shades with tannic acid or tanninol or thiotan MS mordants, respectively.

Crushed leaves of teak are known in India since early times to produce a red color when rubbed with saliva; this test had been used to recognize genuine teak. It has been a common practice among women in Kerala state to crush the tender leaves into paste and rub it in their palms to get them dyed in a light reddish shade.

### 6.83.3 Sources

*Tectona grandis* L.f. (Verbenaceae)

English – Teak; Bengali – Segun; Gujarati – Saga, Sagach; Hindi – Sagun, Sagwan; Kannada – Jodi, Sagwani, Tega, Tyagadamara; Malayalam – Thekku, Tekka; Marathi – Sag, Saga, Sagwan; Oriya – Singuru; Tamil – Tekkumaram, Tekku; Telugu – Adaviteeku, Peddateeku; Teeku; Sanskrit – Saka

It is a tree with rounded crown, variable in size, found in India, Myanmar, Thailand, Java, and Indonesia. In India, teak occurs in Peninsular India, Madhya Pradesh, parts of Rajasthan, Southern Uttar Pradesh, and Orissa. Outside of its natural habitat, teak has been cultivated in the forests, parks, and gardens in West Bengal, Assam, Bihar, and Andaman.

The tree contains very large size leaves of about  $30\text{--}60 \times 20\text{--}30$  cm. The tree is generally found leafless throughout the greater part of the hot season. The new leaves appear from April–June but in the wet season they sprout early. The tree comes in bloom from June to August or September.

Teak thrives best and reaches its largest dimension in a fairly moist, warm, tropical climate, although it occurs even in dry localities, subjected to great heat and drought during the hot season. It requires normal rainfall varying from 125–250 cm, with a marked dry season of 3–5 months, but it is known to grow, though not adequately well, in places with a rainfall as low as 75 cm or even less.

Teak shows very good development on the fertile lower slopes of the hills where the soil is deep, but in shallow soil and along dry ridges it becomes stunted. It comes up on soils produced by a variety of geological formations like traps, basalt, granitic gneisses, calcareous crystalline rocks, phyllites, and schists. It also grows well on easily disintegrable sandstones. The soils having a lower silica sesquioxide ratio, lower dispersion coefficient, and a very low or very high water level are unfavorable for good growth of teak. Teak prefers rich soil. Deficiency of nitrogen causes stunted growth, strong chlorosis,

premature defoliation, and absence of branching in seedlings. If phosphorus is deficient, the seedlings exhibit scorched leaf margins and chlorosis followed by necrosis. Potassium deficiency causes intervenal chlorosis and scorching of margins in younger leaves. The surface wrinkles and margins curl inwards.

Teak can be raised directly or by transplanting nursery-raised seedlings. Direct sowing can be done by broadcasting or dibbling seeds, but transplantation of seedlings is preferred and is most prevalent. Before sowing, seeds are soaked in water and then dried in sun till the seed coat becomes soft. It may take a few days or more than a month, depending upon the toughness of the seed coat for germination.

The seeds are sown in nursery beds, generally during April–May, depending upon the local conditions, but it may also be sown as early as March, as in North Bengal, or as late as June, as in parts of Karnataka. The quantity of seeds required for sowing in standard sized bed of 12 m × 1.2 m is from 6 to 12 kg. After sowing, seeds are covered with fine soil, 1.0–2.5 cm thick. Mulching with straw or brushwood is done, but mulch is removed as soon as the germination starts. Whereas no watering is done in moist areas, in drier regions the beds are watered during dry period to hasten germination and growth.

Seedlings having a thickness of 1–2 cm are fit for making stump: while preparing the stump, 1.5–5.0 cm of shoot and 15–25 cm of tap root are retained. Lateral roots are trimmed. Stumps are made in April and are planted during the rainy season. It has been found better to raise the stumps in the polythene tubes in nursery and plant them in the field when the weather is favorable. The stumps are planted in crowbar-holes as early as possible after first good shower. The seedlings do not withstand competition with weeds, hence regular weeding is necessary. The rate of growth varies considerably, depending upon the suitability of site. Under favorable conditions, the growth of teak in its earlier years is very fast; a mean girth of 5 cm per annum and a mean height of 1.8 m per annum for the first few years is not unusual on a good site, when the crop is properly tended.

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## 6.84 Titanium dioxide

Titanium dioxide ( $\text{TiO}_2$ ) is extracted from a large number of naturally occurring titanium minerals, but most important are ilmenite a titaniferous iron ore ( $\text{FeO} \cdot \text{TiO}_3$ ) and rutile ( $\text{TiO}_2$ ). Ilmenite and rutile are widely distributed in India, mainly at coastal areas of Andhra Pradesh, Kerala, Maharashtra, Orissa, and Tamil Nadu. The principal use of ilmenite and rutile are as a source of titanium dioxide which is a valuable white pigment. Titanium dioxide is the whitest of all white pigments known today. It has an excellent hiding power or opacity and is chemically inert and non-toxic.

### 6.84.1 Extraction

Titanium dioxide is produced by dissolving the ore in sulphuric acid solution and precipitating the iron compound solution, and finally hydrolyzing it. The precipitate is then calcined to convert it into  $\text{TiO}_2$ , resulting in a micro-crystalline product. This is subject to careful grinding in water, drying, and air floating before coming on to the market.

### 6.84.2 Uses

Titanium dioxide finds universal application as a whitening and brightening agent, and is extensively used in the paint, textile, rubber, plastic, paper, cosmetic, leather, ceramic, and food industry. In less purified grades, it is the basic natural pigment used in white house paint. There are two crystalline modifications of titanium dioxide: rutile and anatase. Only the anatase variety finds its use as a color additive for foodstuffs. The principal uses of this natural white pigment are in sub-coating of confectionery panned goods and in drinks. As with the other food grade pigments it must be dispersed to give full coloring power. It disperses quite easily in liquids. It remains suspended only in viscous liquids and semi-solid materials. Titanium dioxide is also used along with sugar syrup for usage in the sub-coating of tabletted products. This color additive has a permanent place in the list of food additives.

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## 6.85 Ultramarine blue

Ultramarine blue is the oldest and most brilliant of the blue pigments. It first appeared as a pigment in the region around Afghanistan where it has been found in 6th and 7th century wall paintings in the cave temples of Bamiyan. Its most interesting property is its permanence. A few 15th century paintings and illuminated manuscripts containing the color (as found in nature) still retain their brilliance.

In 1437, natural ultramarine was used by Jan Van Eyck in his painting St. Barbara. It continued to be used in paintings and illuminated manuscripts until synthetic ultramarine was developed. The synthetic product was identical in composition and structure to the natural one.

Ultramarine blue (lajward in Hindi), is a blue coloring principle, obtained from the mineral lapis lazuli, or lazurite,  $3(\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2) \cdot \text{Na}_2\text{S}_4$ , which is a semiprecious stone, commonly found in Afghanistan, Tibet, China, Siberia, Iran, and Chile and also reported from Colorado and Baffin Islands.

It is said that lapis lazuli was imported to India from Afghanistan. It reached Europe from Afghanistan through the port of Venice, a great center of orient trade in medieval days. The name ultramarine is derived from “Azurro ultramarino”, the blue beyond the sea.

### 6.85.1 Extraction

For the extraction of the blue dye from lapis lazuli, the stones are finely ground, dried, and then reduced to fine, smooth paste in water and again dried. It is finally kneaded into dough with a little linseed oil or wax in a weak solution of potash or soda lime. By this means the finest particles settle out, the dough retains the foreign matter or gänge. The extraction of it gives the finest blue.

A process for refining the blue was developed by Cennino Cennini in Italy in the 12th and 13th centuries. Cennini kneaded a paste of ground lapis lazuli, beeswax, resin, gum mastic, and linseed oil in dilute alkaline solution. In this process, the foreign matter, calcite, and pyrite, is retained by the oil phase while the fine particles of ultramarine disperse in the alkaline solution and are decanted several times. The particles of blue are recovered by settling. This process increases the brilliance of the blue to a great extent.

Ultramarine blue can also be manufactured by mixing, grinding, and heating of calcined China clay, sulphur, soda ash, sodium sulphate, carbon (charcoal, pitch, and/or rosin), and silica, at 780–800°C for 50–150 h. Thus formed raw blue is crushed and separated from its soluble salts (principally sodium sulphate) by several hot water washes. The color is then ground and separated into a number of fractions, based on particle size and reground. This is identical in composition and structure to the natural one.

### 6.85.2 Uses

Ultramarine blue has been used in miniature paintings in India. As an artist's color, it is an absolutely permanent, fast to light, and can be mixed with other durable colors. It is also used in textile printing, cosmetics, rubber, laundry blue soaps, floor covering granules, food packaging applications, and in plastic, oil and water paints, and as a color in printing inks.

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## 6.86 Ventilagin

Ventilagin ( $C_{15}H_{14}O_6$ ; mp  $110^{\circ}C$ ), the derivative of methylanthraquinone, occurs in the root bark of Pitti or Raktavalli, Ventilago, *Ventilago maderaspatana* Gaertn. The root bark yields about 8–10% dye. Ventilagin is a red-brown brittle resinous product. It dissolves in alkalis to purple-red solutions, and on distillation with zinc dust yields a-methyl-anthracene.

### 6.86.1 Extraction

The dye is extracted from the root bark and also from the wood of stem. In addition to physion, the naphthoquinone, ventilagin, which is close in structure to alkannin, is also present in the plant. The air dried, powdered root bark extracted with acetone yields a dark brown residue. The residue is dried and chromatographed with benzene and ethyl acetate (9:1). It is further rechromatographed, which on crystallization with acetone yields ventilagin. It can also be obtained by extracting the powdered root bark with carbon disulphide in the cold, and then separating the accompanied impurities by precipitation with alcohol.

### 6.86.2 Uses

The dye is used for coloring mordanted cotton, wool, and tasar silk. The colors obtained on cotton are bordeaux red, on alum; lilac, on iron; and violet-brown on alum and iron mordants. It is an excellent dye for silk and tassar,

even when undergummed. Colors obtained are chocolate brown on alum, and violet on iron mordanted silk. In dyeing of wool, calcium acetate is added to the bath to adjust the acidity of the mordanted fiber. Colors obtained are bordeaux red on alum, red on tin, violet-brown on chromium, and violet on iron mordanted wool.

### 6.86.3 Sources

*Ventilago maderaspatana* Gaertn. (Rhamnaceae)

Assami – Bor-kalia; Gujarati – Ragatarohado; Bengali – Raktapita, Ruktupita; Khasi – Sher-kharuong; Hindi – Pitti; Kannada – Pupli, Papudi; Marathi – Kanvel, Lokhandi; Oriya – Roktopitta, Sajumalo, Toridi; Tamil – Papilli, Surali, Surulbattaikhodi, Vembadam; Telugu – Ettasurugudu, Ettashirattalativva, Suralatige, Surgugudu, Suratichekka (wood)

It is a large, woody, creeping bush, commonly available in Sri Lanka, Burma, Java, Bhutan, and India. In India, it is found in the Western Ghats from Konkan southwards and also reported from Orissa, Central India, Bihar, West Bengal, and Assam.

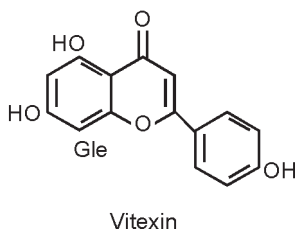
The root bark is the source of the dye. The dye was extracted from the bark of the root, and also the wood of stems in Karnataka up till the end of 19th century for local use as well as for being sold to other regions in combination with the root of chay root, *Hedyotis umbellata* (L.) Lam. The bark is marketed in the form of dark red or brown chips or savings, sold under the names raktapita, pappilichakka, suralpattai, lokhandi, and konwail. Besides ventilagin, the root bark contains emodin monomethyl ether and trihydroxymeth-ylanthranol monomethyl.

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### 6.87 Vitexin

Vitexin ( $C_{21}H_{20}O_{11}$ ; mp 269–270°C), a yellow coloring principle, occurs along with homovitexin ( $C_{18}H_{18}O_8$  or  $C_{16}H_{16}O_7$ ), as glycosides, in the wood and bark



The wood or bark is boiled for 8 h with 10 volumes of water, and the extract is evaporated. The residue is then warmed with alcohol, filtered, and the filtrate once more evaporated. The orange resin so obtained contains the pigment still in the form of glycoside, which is hydrolyzed by dilute hydrochloric acid at room temperature. The semi-solid mass which is thus precipitated is treated with boiling alcohol; a yellow crystalline powder remains and is washed with alcohol until the filtrate becomes colorless. This product, after further purification with alcohol affords pure vitexin.

Vitexin dyes mordanted wool and cotton a pure but weak yellow, somewhat similar to that obtained with apigenin. With aluminum, chromium, tin, and iron mordants it gives bright yellow, pale greenish-yellow, pale brown, somewhat dull and very pale yellow shades, respectively.

### 6.87.3 Sources

*Cyathea spinulosa* Wall. ex Hook. (Cyatheaceae)

Leaves of the tree fern, found in Andhra Pradesh, yield vitexin. The other species of *Cyathea* like *C. faurieri* Copel., *C. tueckheimii* Maxon, and *C. onusta* Christ., found in Costa Rica, have also been reported to contain vitexin.

*Sphenomeris chinensis* (L.) Maxon (Polypodiaceae)

syn. *S. chusana* (L.) Copel.

It is a graceful fern with tufted fronds arising from a short, creeping rhizome, covered with shining brown scales, found in the Himalayas from Kumaun to Bhutan and Meghalaya, and in Bihar and the Western Ghats at elevations of 300–2100 m. Its leaves contain vitexin.

*Vitex altissima* L.f. (Verbinaceae)

Assami – Ahoi, Ashoi, Jharua; Kannada – Myrole, Bulgi, Balgay; Malayalam – Mayila; Marathi – Balage, Banalgay; Tamil – Maila, Mailai; Telugu – Nemiliadogu; Trade – Milla

It is a moderate to large sized tree, with grey, scaly bark, 3–5 foliolate leaves, blue flowers found in Assam, Meghalaya, and the Deccan Peninsula, up to an altitude of 1200 m in the hills. The heartwood, leaves, and bark contain a flavonoid, vitexin, the coloring matter.

*V. lucens* T. Kirk

syn. *V. litoralis* A. Cunn.

It is an ornamental tree with pink flowers, attractive hanging bunches of marble-sized, rose-red, rounded drupes, native to New Zealand, introduced in the Government Botanical Garden, Ootacamund. It can be propagated from seeds, suckers, layers or cuttings. Wood and bark contain vitexin (2%).

*V. peduncularis* Wall. ex Schauer

Assami – Ashoi, Silaosai; Bengali – Boruna, Goda, Ashot; Hindi – Minjurgorwa, Nagpheni; Kannada – Navaladi; Oriya – Mado, Chulia, Eratatka; Santal – Marakata, Bhadu

It is a small to moderate sized tree with a grey, thick, exfoliating in irregular flakes bark, 3-foliolate leaves, and white flowers, found in Assam, West Bengal, parts of Bihar, Orissa, and Andhra Pradesh. Leaves and bark contain vitexin, 0.05 and 0.07%, respectively.

*V. pinnata* L.

syn. *V. pubescens* Vahl

Assami – Ahoi, Bhodia, Dieng-lakhiet-dkhar; Malayalam – Atta Mayila; Oriya – Dhalasingha; Tamil – Myladi; Telugu – Nowlieragu, Nevaladugu; Tripura – Arekodol

It is a moderate to large sized ornamental tree that contains pale yellowish-grey or ash colored bark, 3–5 foliolate leaves, violet-blue flowers, and black, when ripe, fruits, surrounded by the enlarged cup shaped calyx; found in South India, Orissa, Assam, and Tripura. Its bark contains vitexin that yields a yellow dye which is used by locals.

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## Appendices

### Appendix 1: List of coloring matter, color, sources, and uses

S. No.	Coloring matter	Color (color and shade varies depending on the mordant, pH, base, etc.)	Source	Uses
1.	Adinin	Yellow	<i>Haldina cordifolia</i> (Roxb.) Ridsdale	Cotton, wool, silk
2.	Alizarin	Turkey-red color; bluish to yellowish-reds (madder lakes), green (green alizarin)	<i>Oldenlandia umbellata</i> L.; <i>Rubia tinctorum</i> L.; <i>Rubia cordifolia</i> L.; <i>Rubia peregrine</i> L.	Textile, printing
3.	Alkannin	Lilac to red shades, purple to red shades, tone of grey to violet-grey, deep blue	<i>Alkanna tinctoria</i> (L.) Tausch; <i>Arnebia benthamii</i> (Wall. ex G. Don) Johnston; <i>Arnebia euchroma</i> (Royle) Johnston; <i>Arnebia guttata</i> Bunge; <i>Arnebia hispidissima</i> DC.; <i>Arnebia nobilis</i> Reichb.; <i>Arnebia ugamensis</i> H. Riedl; <i>Echium rubrum</i> Forsk; <i>Jatropha glandulifera</i> Roxb.; <i>Lithospermum arvensis</i> L.; <i>Lithospermum erythrorhizon</i> Siebold and Zucc.; <i>Lithospermum officinale</i> L.; <i>Maharanga emodi</i> (Wall.) A. DC; <i>Onosma hispida</i> Wall. ex D. Don; <i>Onosma hookeri</i> C.B. Clarke; <i>Plagiobothrys arizonicus</i> (A. Gray) Greene ex A. Gray	Wool, silk, cotton, pharmaceutical preparations, cosmetics, biological stain
4.	Apigenin	Pale yellow	<i>Antirrhinum majus</i> L.; <i>Chamaemelum nobile</i> (L.) All; <i>Cosmos bipinnatus</i> Cav.; <i>Dahlia pinnata</i> Cav.; <i>Leucanthemum vulgare</i> (Vaill.) Lam.; <i>Matricaria chamomilla</i> L.; <i>Petroselinum crispum</i> (Mill.) Nyman ex A.W. Hill; <i>Senna siamea</i> (Lam.) H.S.Irwin and Barneby; <i>Sorghum bicolor</i> (L.) Moench; <i>Sorghum nervosum</i> Bess. ex Schult; <i>Zinnia elegans</i> Jacq.	Hair, dry shampoos, liquors
5.	Azure blue	Blue	Azurite (mineral)	Paintings (extensively in China)



6.	Berberine	Yellow	<i>Berberis aristata</i> DC.; <i>Berberis asiatica</i> Roxb. ex DC.; <i>Berberis chitria</i> Buch.-Ham. ex Lindl.; <i>Berberis lycium</i> Royle; <i>Berberis tinctoria</i> Lesch.; <i>Berberis vulgaris</i> L.; <i>Coscinium fenestratum</i> Colebr.; <i>Hydrastis canadensis</i> L.; <i>Jateorhiza palmate</i> (Lam.) Miers.; <i>Mahonia napaulensis</i> DC.; <i>Thalictrum foliolosum</i> DC.; <i>Thalictrum minus</i> L.	Wool, silk, leather, cotton, flouochrome in microscopy
7.	Betanin	Red (pH between 4 and 5); bright bluish-red, blue-violet as the pH increases	<i>Beta vulgaris</i> L.	Food, medicines
8.	Bixin	Red, pink (at low pH)	<i>Bixa orellana</i> L.	Food products, textile, medicine, cosmetic, floor polishes, shoe polishes, hair oils
9.	Blanc fixe	White	Barite (ore)	Water color by the artists' (used as base), paints, coatings, plastics, additive in batteries
10.	Brazilein	Red, pink, bright reddish-orange shade, purple (with indigo)	<i>Caesalpinia violacea</i> (Mill.) Standl; <i>Caesalpinia echinata</i> Lam.; <i>Caesalpinia bonduc</i> (L.) Roxb.; <i>Caesalpinia sappan</i> L.	Food, paints, inks, leather, creams, lipsticks, gulal (used in India during Holi festival), fabric
11.	Butein and Butin	Deep orange-red (Butein); orange-red (butin); yellow to brownish-black	<i>Butea monosperma</i> (Lam.) Taub.	Foodstuffs, colors for Holi
12.	Calendulin	Yellow	<i>Calendula officinalis</i> L.	Food products
13.	Capsanthin	Red	<i>Capsicum annum</i> L.; <i>Lilium lancifolium</i> Thunb.	Food stuffs, medicine
14.	Caramel	Dark brown	Sugar/glucose	Food, beverages
15.	Carbon	Black	Wood; Charcoal; Lampblack; Bone black; Coke; Asphalts; Graphite	Printing, artist's colors, rubber, plastic, paper, flooring tiles, paint industry
16.	Carminic acid	Red, yellowish (pH 8), bluish-red (above pH 6.2)	<i>Dactylopius coccus</i> Costa; <i>Dactylopius confusus</i> Cookerell; <i>Dactylopius indicus</i> Green; <i>Dactylopius tomentosus</i> Lam.; <i>Anthraccoccus uvaeursi</i> L.; <i>Porphyrophora polanica</i> L.	Food, drinks, cosmetics, medicine, printing, leather, wool
17.	Carotene	Yellow	<i>Daucus carota</i> var. <i>sativa</i> Hoffm.	Foods, ingested drugs
18.	Carthamin	Cherry-red, rose-pink, crimson or scarlet	<i>Carthamus tinctorius</i> L.; <i>Carthamus oxyacanthus</i> M.Bieb.	Silk, cotton

19.	Catechin	Brown, catechu-brown or cutch-brown, pale yellow (alum mordant), brown (iron mordant)	<i>Acacia catechu</i> (L.f.) Willd.; <i>Areca catechu</i> L.; <i>Uncaria elliptica</i> R.Br. ex G.Don; <i>Acacia nitotica</i> (L.) Delile subsp. <i>indica</i> (Benth.) Brenan; <i>Camellia sinensis</i> (L.) Kuntze; <i>Bergenia ciliata</i> (Haw) Sterub.; <i>Bergenia stracheyi</i> (Hook.f. and Thomson) Engl.	Cotton, silk, wool, food, hair dye, leather, fishing cloths, printing
20.	Chlorophyll	Green	<i>Urtica dioica</i> L.; <i>Spinacia oleracea</i> L.; <i>Medicago sativa</i> L.; <i>Zea mays</i> L.	Edible fats and oils, chewing gums, confectionery, gelatin, cosmetics, liniments, lotions, mouthwashes, perfumes, leather soaps, resins, inks, waxes, candles
21.	Chrysin	Yellow, pale yellow, orange and chocolate-brown shades with aluminium, chromium and iron mordants, respectively	<i>Populus nigra</i> L. var. <i>italica</i> Koehne; <i>Oroxylum indicum</i> Vent; <i>Pinus roxburghii</i> Sarg.; <i>Pinus wallichiana</i> A.B.Jackson; <i>Scutellaria galericulata</i> L.; <i>Asphodelus tenuifolius</i> Cav	Cotton, wool, silk
22.	Chrysophanic acid	Yellow; red (chrome mordant)	<i>Chamaecrista absus</i> (L.) H.S.Irwin and Barneby; <i>Cassia fistula</i> L.; <i>Cassia grandis</i> L.f.; <i>Cassia italica</i> (Mill.) Lam. ex F.W. Andr.; <i>Rheum australe</i> D. Don.; <i>Rheum rhaponticum</i> L.; <i>Cassia roxburghii</i> DC.; <i>Cassia occidentalis</i> L.; <i>Cassia javanica</i> L.; <i>Rumex acetosa</i> L.; <i>Rumex crispus</i> L.; <i>Rumex dentatus</i> L.; <i>Rumex maritimus</i> L.; <i>Rumex nepalensis</i> Spreng.; <i>Senna alata</i> (L.) Roxb.; <i>Senna auriculata</i> (L.) Roxb.; <i>Senna didymobotrya</i> (Fresen.) H.S.Irwin and Barneby; <i>Senna floribunda</i> (Cav.) H.S.Irwin and Barneby; <i>Senna obtusifolia</i> (L.) H.S.Irwin and Barneby; <i>Senna alexandrina</i> Mill.; <i>Senna siamea</i> (Lam.) H.S.Irwin and Barneby; <i>Senna sophora</i> (L.) Roxb.; <i>Senna tora</i> (L.) Roxb.	Wool
23.	Citronetin	Yellow	<i>Citrus medica</i> L.; <i>Citrus limon</i> (L.) Burm. f.	Dye silk
24.	Coreopsin	Yellow; olive-brown (ferric chloride), deep red color (alkalis alum); yellow to bronze-gold, orange	<i>Coreopsis basalis</i> (A.Dietr.) S. F. Blake; <i>Cosmos sulphureus</i> Cav.; <i>Dahlia pinnata</i> Cav.	Food stuffs, pharmaceutical, wool, cotton
25.	Crocin and Crocetin	Sulphure-yellow, orange-yellow, golden-yellow, orange, yellow, scarlet, red, green, blue, browns fast	<i>Crocus sativus</i> L.; <i>Gardenia jasminoides</i> J. Ellis; <i>Nyctanthes arbor-tristis</i> L.; <i>Toona ciliata</i> M. Roem.	Food stuffs, silk, wool, cotton

26.	Curcumin	Orange-yellow ; brownish-red color (with alkalis), yellow (with acids)	<i>Curcuma longa</i> L.; <i>Curcuma amada</i> Roxb.; <i>Curcuma aromatica</i> Salisb.; <i>Curcuma viridiflora</i> Roxb.	Wool, silk, cotton, pharmacy, Confectionery, food, paper
27.	Datisctetin	Yellow	<i>Datisca cannabina</i> L.	Silk, wool, cotton
28.	Delphinidin	Red, deep pink, deep purple	<i>Commelina communis</i> var. <i>hortensis</i> Makino; <i>Eucalyptus obliqua</i> L'Hér.; <i>Anemone coronaria</i> L.; <i>Ribes nigrum</i> L.; <i>Punica granatum</i> L.; <i>Cinchona calisaya</i> Wedd.; <i>Eucalyptus regnans</i> F. Muell.	Silk, food stuffs, medicine, cosmetics
29.	Dracocarmine	Red	<i>Daemonorops draco</i> (Willd.) Blume; <i>Daemonorops kurziana</i> Hook. f. ex Becc; <i>Dracaena cinnabari</i> Balf. f.; <i>Dracaena schizantha</i> Baker.	Lacquers, varnishes, plasters, printing
30.	Ellagic acid	Fast yellows, green (with FeCl <sub>2</sub> )	<i>Caesalpinia coriaria</i> (Jacq.) Willd.; <i>Castanea sativa</i> Mill.; <i>Castanopsis concinna</i> (Champ. ex Benth.) A.DC.; <i>Castanopsis eyrei</i> (Champ. ex Benth.) Hutch; <i>Castanopsis faberi</i> Hance; <i>Terminalia alata</i> Heyne ex Roth.; <i>Terminalia arjuna</i> (Roxb. ex DC.) Wight and Arn.; <i>Terminalia chebula</i> Retz.; <i>Terminalia bellirica</i> (Gaertn.) Roxb.; <i>Terminalia paniculata</i> Roth.; <i>Terminalia catappa</i> L.; <i>Castanopsis eyrei</i> (Champ. ex Benth.) Hutch.; <i>Castanopsis faberi</i> Hance; <i>Eucalyptus calophylla</i> R.Br.	Wool, leather, silk
31.	Embelin	Yellow	<i>Embelia ribes</i> Burm.f.; <i>Embelia tsjeriam-cottam</i> (Roem. and Schult.) A.DC.; <i>Myrsine africana</i> L.; <i>Myrsine semiserrata</i> Wall.; <i>Rapanea capitellata</i> (Wall.) Mez.	Silk, wool
32.	Emodin	Yellow, brown with copper, olive-green with iron, red-violet with chromium, bright yellow with tin mordants	<i>Frangula dodonei</i> Ard.; <i>Aloe vera</i> (L.) Burm.f.; <i>Chamaecrista mimosoides</i> (L.) Green; <i>Cassia javanica</i> L.; <i>Chamaecrista pumila</i> (Lam.) K.Larse; <i>Senna alata</i> (L.) Roxb.; <i>Senna italica</i> Mill.; <i>Senna obtusifolia</i> (L.) H. S. Irwin and Barneby; <i>Chamaecrista nigricans</i> (Vahl) Greene; <i>Senna floribunda</i> (Cav.) H. S. Irwin and Barneby; <i>Senna occidentalis</i> L.; <i>Senna alexandrina</i> Mill.; <i>Senna podocarpa</i> (Guill. & Perr.) Lock; <i>Senna tora</i> (L.) Roxb.; <i>Chamaecrista mimosoides</i> (L.) Green; <i>Senna sophora</i> (L.) Roxb.; <i>Rhamnus infectoria</i> L.; <i>Rheum australe</i> D. Don.; <i>Rheum webbianum</i> Royle.; <i>Rheum emodi</i> Wall. ex Meisn.; <i>Rheum spiciforme</i> Royle; <i>Sonneratia caseolaris</i> (L.) Engl.	Paper, leather, wool, artist's water colors

33.	Erythroaphins	Red	<i>Aphis fabae</i> (black aphids); <i>Tuberolachnus salignus</i> (willow tree aphids)	Cotton, silk, wool
34.	Euxanthic acid	Light yellow, bright rose-pink, green	<i>Mangifera indica</i> L.	Cotton, silk, wool, paints, oil, and water colors for artists
35.	Fisetin	Yellow, orange with alum, reddish-brown with chrome, brownish-olive with iron, and reddish-yellow with tin mordants	<i>Cotinus coggygria</i> Scop.; <i>Hymenaea verrucosa</i> Gaertn.; <i>Anthyllis vulneraria</i> L.	Textile, leather, wool
36.	Flemingin	Orange-red	<i>Flemingia grahamiana</i> Wight and Arn; <i>Flemingia macrophylla</i> (Willd.) Merr.	Silk, wool, cosmetics
37.	Fukugetin	Yellow	<i>Garcinia spicata</i> Hook.f.	Silk, wool, cotton
38.	Galiosin	Red	<i>Galium verum</i> L.; <i>Rubia tinctorum</i> L.	Wool
39.	Galloflavin and isogalloflavin	Yellow	Potassium gallates	Wool, cotton
40.	Gamboge	Reddish-yellow or brownish- orange	<i>Garcinia morella</i> (Gaertn.) Desr; <i>Garcinia hanburyi</i> Hook.f.	Silk, ink, water colors, gold colored spirit, varnishes for metals
41.	Gardenin	Yellow	<i>Gardenia gummifera</i> L.f.; <i>Gardenia resinifera</i> Roth	Wool, cotton, silk, food stuffs, medicines
42.	Gossypetin	Bright orange-yellow, orange-brown, dull brown, olive	<i>Hibiscus sabdariffa</i> L.; <i>Gossypium herbaceum</i> L.; <i>Gossypium arboreum</i> L.	Cotton
43.	Green earth (terre verte)	Olive -green, yellow-green to greenish-grey or blackish-green	Glauconite and celadonite (minerals)	Paintings
44.	Guanine	White	Guano and fish scales	Coloring artificial pearls, artificial jewellery, nail polishes
45.	Haematoxylin	Deep red (Sulphuric acid) and deep violet (sodium hydroxide); blue to black with chromium, grayish-violet with alum, grey to black with iron, greenish-blue with copper and red-violet with tin mordant	<i>Haematoxylum campechianum</i> L.	Biological stain, cotton dyeing, calico printing
46.	Hypericin	Deep violet-red (hypericin red), yellow (with alum)	<i>Hypericum perforatum</i> L.; <i>Nipaecoccus aurilanus</i> Maskell.	Wool and silk

47.	Indigo or Indigotin	Blue	<i>Baptisia tinctoria</i> (L.) Vent.; <i>Indigofera arrecta</i> A.Rich.; <i>Indigofera suffruticosa</i> Mill.; <i>Isatis tinctoria</i> L.; <i>Marsdenia tinctoria</i> R. Br.; <i>Persicaria tinctoria</i> (Aiton) H.Gross; <i>Strobilanthes cusia</i> (Nees) Imlay; <i>Wrightia tinctoria</i> R. Br.	Cotton, rayon, wool, paints, lacquers, rubber, plastic, printing inks
48.	Isorhamnetin	Yellow; with aluminium, chromium, iron and tin it gives golden-yellow, brownish-orange, brown-olive, and bright orange colors, respectively	<i>Trifolium pratense</i> L.; <i>Delphinium zaili</i> Aitch. and Hemsl.; <i>Senna alexandrina</i> Mill.; <i>Typha australis</i> Schum. and Thonn.	Cotton, silk, calico printing
49.	Juglone	Brownish-yellow, rose-tint	<i>Juglans regia</i> L.; <i>Carya illinoensis</i> (Wangenh.) K. Koch	Wool, cotton
50.	Kaempferol	Yellow; brownish-yellow, yellow, lemon-yellow and deep olive-brown with chromium, aluminium, tin and iron, respectively	<i>Alpinia officinarum</i> Hance; <i>Pteridium aquilinum</i> (L.) Kuhn; <i>Alnus nitida</i> (Spach) Endl.; <i>Primula sinensis</i> Sabine ex Lindl.; <i>Alnus nitida</i> (Spach) Endl.; <i>Primula sinensis</i> Sabine ex Lindl.; <i>Camellia sinensis</i> (L.) Kuntze; <i>Equisetum arvense</i> L.; <i>Cuscuta reflexa</i> Roxb.; <i>Consolida regalis</i> Gray; <i>Prunus spinosa</i> L.; <i>Crocus asturicus</i> Herb.; <i>Crocus speciosus</i> M.Bieb.; <i>Rhamnus cathartica</i> L.; <i>Onychium japonicum</i> (Thumb.) Kuntze; <i>Pteridium aquilinum</i> (L.) Kuhn	Calico printing, cotton, wool, silk
51.	Kermesic acid	Red, orange-red; brilliant scarlet (with alum mordant)	<i>Kermes ilicis</i> (coccid kermes)	Leather, wool
52.	Laccaic acid and Erythrolaccin	Red	<i>Kerria lacca</i> Kerremans	Food materials, cosmetics, cotton, wool, silk, leather
53.	Lapachol	Yellow	<i>Tectona grandis</i> L.f.; <i>Catalpa ovata</i> G.Don.; <i>Zeyheria digitalis</i> (Vell.) Hoehne; <i>Tecomella undulata</i> (Sm.) Seem.	Bows, fishing rods, textile fibers
54.	Lawson	Reddish-brown, orange	<i>Lawsonia inermis</i> L.; <i>Impatiens balsamina</i> L.	Skin and hair, cosmetics, wool, silk, leather
55.	Luteolin	Yellow	<i>Reseda luteola</i> L.; <i>Genista tinctoria</i> L.	Coloring oils, water colors
56.	Lycopene	Dark red	<i>Lycopersicon esculentum</i> Mill.; <i>Elaeis guineensis</i> Jacq.	Food stuffs, medicine, oils
57.	Maclurin	Yellow; tones of aged-gold, olive and bronze colors (with chrome and copper); pale yellow, yellowish-green or pale-grey on alum, chrome and iron mordanted wool, respectively	<i>Maclura tinctoria</i> (L.) D.Don ex Steud.; <i>Maclura pomifera</i> (Raf.) C.K.Schneid.; <i>Morus alba</i> L.; <i>Garcinia x mangostana</i> L.	Wool

58.	Malachite	Green	Copper ore	Paintings
59.	Malvidin	Red	<i>Vitis vinifera</i> L. subsp. <i>sylvestris</i> (C. C. Gmel) Hegi	Food stuffs, pharmaceutical preparations
60.	Morin	Yellow; gold, olive and bronze, pale yellow, yellowish-green or pale grey on alum, chrome or iron mordants, respectively	<i>Artocarpus heterophyllus</i> Lam.; <i>Artocarpus gomezianus</i> Wall. ex Trécul; <i>Maclura tinctoria</i> (L.) D. Don ex Steud.; <i>Maclura pomifera</i> Schneid; <i>Morus alba</i> L.	Wool, cotton, silk
61	Morindone	Orange , red, purple, chocolate	<i>Morinda citrifolia</i> L.; <i>Morinda coreia</i> Buch.-Ham.; <i>Morinda umbellata</i> L.; <i>Hymenodictyon orixense</i> (Roxb.) Mabb.; <i>Coprosma lucida</i> var. <i>lucida</i>	Cotton, wool, silk
62.	Myricetin	Yellow, ochre to grey, red-brown, brown-orange and bright red shades with chromium, aluminium and tin mordants, respectively	<i>Myrica esculenta</i> Buch.-Ham. ex D. Don; <i>Myrica rubra</i> (Lour.) Siebold and Zucc.; <i>Chrysophyllum cainito</i> L.; <i>Madhuca longifolia</i> (Koenig) Macb.; <i>Mimusops elengi</i> L.; <i>Myrica esculenta</i> Buch.-Ham; <i>Pistacia lentiscus</i> L.	Wool
63.	Ochres	Red, yellow, green	Natural earth pigment containing hydrated iron oxide	Paint, color washes, distempers, paper, linoleum makings, artistic colors
64.	Orchil or Archil	Purple or red-violet	<i>Parmelia abessinica</i> Kremp.; <i>Parmelia tinctorum</i> Despr.; <i>Rocella montagnei</i> Bel.; <i>Rocella tinctoria</i> Lam. and DC.	Wool, silk, calico printing
65.	Patuletin	Yellow	<i>Tagetes patula</i> L.	Wool, cotton, silk
66.	Phycocyanin	Blue	<i>Nostoc muscorum</i> C. Agardh; <i>Anabaena cylindrica</i> Lemmermann; <i>Synechococcus lividus</i> Copeland; <i>Phormidium luridum</i> (Kützing) Gomont; <i>Plectonema</i> and <i>Boryanum</i> Gomont	Pharmaceuticals, cosmetics, food stuffs
67.	Pratol	Yellow	<i>Trifolium pratense</i> L.; <i>Trifolium incarnatum</i> L.	Wool, silk , cotton
68.	Pseudopurpurin	Red, pinks, chocolates	<i>Rubia tinctorum</i> L.; <i>Rubia peregrina</i> L.; <i>Galium aparine</i> L.; <i>Galium verum</i> L.	Cotton, silk, wool
69.	Purpurin and Munjistin	Red (Purpurin), orange dye (Munjistin), red, yellow	<i>Rubia cordifolia</i> L.; <i>Rubia sikkimensis</i> Kurz.	Human hair, course cotton, wool, ornaments, medicinal oils
70.	Quercetagetin	Yellow, golden color with chrome mordants	<i>Tagetes erecta</i> L.; <i>Chrysanthemum coronarium</i> L.; <i>Tagetes patula</i> L.	Cotton, silk, wool fabrics

71.	Quercetin	Yellow, brownish-orange on alum, reddish-brown on chrome, olive-black on iron and bright orange-brown on tin mordants, respectively	<i>Quercus velutina</i> Lam.; <i>Allium cepa</i> L.; <i>Aesculus hippocastanum</i> L.; <i>Arachis hypogaea</i> L.; <i>Equisetum arvense</i> L.; <i>Rosa damascena</i> Mill.; <i>Rosa gallica</i> L.; <i>Ruta graveolens</i> L.; <i>Styphnolobium japonicum</i> (L.) Schott; <i>Trifolium incarnatum</i> L.; <i>Trifolium repens</i> L.	Fabrics
72.	Red lead or minimum	Bright orange-red	Litharge	Paintings, sindur
73.	Rhamnazin	Yellow, orange-yellow (aluminum), pale brown (iron), ; faint yellow (alum mordants)	<i>Hibiscus surattensis</i> L.; <i>Persicaria hydropiper</i> (L.) Delarbre; <i>Salix alba</i> L.	Textile
74.	Rhamnetin	Yellow	<i>Rhamnus alaternus</i> L.; <i>Rhamnus amygdalinus</i> L.; <i>Rhamnus catharticus</i> L.; <i>Rhamnus infectorius</i> L.; <i>Rhamnus lycioides</i> subsp. <i>oleoides</i> (L.) Jahand. and Maire; <i>Rhamnus saxatilis</i> Jacq.; <i>Rhamnus caroliniana</i> Walt.; <i>Suriana maritima</i> L.	Wool, cotton
75.	Riboflavin	Yellow	Yeast; whey	Food products
76.	Rottlerin	Orange -red	<i>Mallotus philippinensis</i> Muell.	Silk, wool
77.	Rubiadin	Pale yellow	<i>Galium verum</i> L.; <i>Morinda citrifolia</i> L.; <i>Rubia tinctorum</i> L.	Cheese, butter, wool
78.	Rubrobrassicin	Red	<i>Brassica oleracea</i> var. <i>capitata</i> L.f. rubra.; <i>Raphanus sativus</i> L.	Food stuffs, soft drinks, pharmaceutical preparations
79.	Rutin	Yellow	<i>Eucalyptus macroorhyncha</i> F. Muell.; <i>Eucalyptus youmanii</i> Blakely and McKie; <i>Fagopyrum esculentum</i> Moench.; <i>Fagopyrum tataricum</i> Gaertn; <i>Ruta graveolens</i> L.; <i>Nicotiana tabacum</i> L.; <i>Styphnolobium japonicum</i> (L.) Schott	Wool, silk, cotton
80.	Santalin	Brick red; orange-red and red with alum, brownish-red on chrome, brown on copper, maroon on iron and red on tin mordants	<i>Pterocarpus santalinus</i> L.f.; <i>Pterocarpus dalbergioides</i> DC.; <i>Pterocarpus indicus</i> Willd.	Wool, cotton, leather, histological stain in biological studies
81.	Sepiomelanin	Black	<i>Sepia officinalis</i> L.	Ink, painter's black color
82.	Soranjidiol	Dark reddish-brown	<i>Mammea longifolia</i> Planch. and Triana; <i>Morinda citrifolia</i> L.; <i>Morinda umbellata</i> L.	Cotton, silk, wool

83.	Tectoleafquinone	Yellow or red; caledonian-brown color; grey or slaty colors (with $\text{FeSO}_4$ or $\text{CuSO}_4$ ), flesh color (with $\text{K}_2\text{Cr}_2\text{O}_7$ or stannous chloride), lilac color (extracted with 0.25% sodium carbonate without any mordant), olive-brown and medium gray shades (with tannic acid or Tannin or Thiotan MS)	<i>Tectona grandis</i> L.	Silk, cotton, wool
84.	Titanium dioxide	White	Ilmenite (ore); Rutile (ore)	Paint, textile, rubber, plastic, paper, cosmetic, leather, ceramic, food industry
85.	Ultramarine blue	Brilliant blue	Lazurite	Paintings, textile printing, cosmetics, rubber, laundry blue soaps, floor covering granules, ink, oil, and water colors
86.	Ventilagin	Purple-red	<i>Ventilago maderaspatana</i> Gaertn.	Cotton, wool, tsar silk
87.	Vitexin	Yellow; bright yellow (with aluminum mordant)	<i>Cyathea spinulosa</i> Wall. ex Hook.; <i>Sphenomeris chinensis</i> (L.) Maxon; <i>Vitex altissima</i> L.f.; <i>Vitex lucens</i> T. Kirk; <i>Vitex peduncularis</i> Wall. ex Schauer; <i>Vitex pinnata</i> L.	Wool, cotton



**Appendix 2: Application of coloring matter**

Material	Coloring matter [principal color(s)]
Food and beverages	Apigenin (pale yellow); Betanin (red); Bixin (red, pink); Brazilein (red); Butein (deep orange-red); orange-red (butin); Calendulin (yellow); Capsanthin (red); Caramel (dark-brown); Carminic acid (red); Carotene (yellow); Catechin (brown); Chlorophyll (green); Coreopsin (yellow); Crocin and Crocetin (yellow); Curcumin (orange-yellow); Delphinidin (red, deep pink); Gardenin (yellow); Laccaic acid and Erythrolaccin (red); Lycopene (dark red); Malvidin (red); Phycocyanin (blue); Riboflavin (yellow); Rubiadin (pale yellow); Rubrobrassicin (red); Titanium dioxide (white)
Cosmetics and medicines	Alkannin (red); Apigenin (pale yellow); Betanin (red); Bixin (red); Brazilein (red); Butein (deep orange-red); Butin (orange-red); Capsanthin (red); Carminic acid (red); Catechin (brown); Chlorophyll (green); Coreopsin (yellow); Curcumin (orange-yellow); Delphinidin (red); Flemingin (orange-red); Gardenin (yellow); Laccaic acid and Erythrolaccin (red); Lawsone (reddish-brown); Lycopene (dark red); Malvidin (red); Phycocyanin (blue); Purpurin (red); Munjistin (orange); Riboflavin (yellow); Rubiadin (pale yellow); Rubrobrassicin (red); Titanium dioxide (white); Ultramarine blue (brilliant blue)
Leather	Berberine (yellow); Brazilein (red); Carminic acid (red); Catechin (brown); Ellagic acid (yellows); Emodin (yellow); Fisetin (yellow); Kermesic acid (red); Laccaic acid and Erythrolaccin (red); Lawsone (reddish-brown); Santalin (brick red); Titanium dioxide (white)
Painting (artists' color)	Azure blue (blue); Blanc fixe (white); Brazilein (red); Butein (deep orange-red) and Butin (orange-red); Carbon (black); Catechin (cutch brown); Chlorophyll (green); Emodin (Yellow); Euxanthic acid (yellow); Gamboge (reddish-yellow or brownish- orange); Green earth (olive green); Haematoxylin (deep red); Indigo or Indigotin (Blue); Luteolin (yellow); Malachite (green); Ochres (red, yellow, green); Red lead or minium (orange-red); Santalin (brick red); Sepi melanin (black); Titanium dioxide (white); Ultramarine blue (brilliant blue)
Textile	Adinin (yellow); Alizarin (turkey-red color); Alkannin (red); Berberine (yellow); Bixin (red); Brazilein (red); Carminic acid (red); Carthamin (red); Catechin (brown); Chrysin (yellow); Chrysophanic acid (yellow); Citronetin (yellow); Coreopsin (yellow); Crocin and Crocetin (yellow); Curcumin (orange-yellow); Datisctetin (yellow); Delphinidin (red); Ellagic acid (yellow); Embelin (yellow); Emodin (yellow); Erythroaphins (red); Euxanthic acid (yellow); Fisetin (yellow); Flemingin (orange-red); Galiosin (red); Galloflavin and Isogalloflavin (yellow); Gamboge (reddish-yellow or brownish- orange); Gardenin (yellow); Haematoxylin (red); Hypericin (deep violet-red); Indigo or Indigotin (blue); Isorhamnetin (yellow); Juglone (brownish-yellow); Kaempferol (yellow); Kermesic acid (red); Laccaic acid and Erythrolaccin (red); Lapachol (yellow); Lawsone (reddish-brown); Maclurin (yellow); Morin (yellow); Morindone (red); Myricetin (yellow); Orchil or Archil (purple or red-violet); Patuletin (yellow); Pratol (yellow); Pseudopurpurin (red); Purpurin (red); Munjistin (orange dye); Quercetagetin (yellow); Quercetin (yellow); Rhamnazin (yellow); Rhamnetin (yellow); Rottlerin (orange red); Rubiadin (pale yellow); Rutin (yellow); Santalin (brick red); Soranjidiol (dark reddish-brown); Tectoleaquinone (yellow or red); Titanium dioxide (white); Ultramarine blue (brilliant blue); Ventilagin (purple-red); Vitexin (yellow)

\* Different colors and shades are produced from principal color(s), and it depends on the pH, use of bases, mordant, and mixing of other colors



*Acacia catechu* (L.f.) Willd.\_0101



*Aloe vera* L



*Anacardium occidentale* L.



*Antirrhinum majus* L.



*Areca catechu*



*Artocarpus heterophyllus*



*Bergenia ciliata* (Haw.) Sternb.



*Bixa orellana* L.



*Bombax ceiba* L.





*Butea monosperma*



*Caesalpinia coriaria* (Jacq.) Willd.



*Cajanus cajan* (L.) Millsp.



*Calendula officinalis* L.



*Camellia sinensis* (L.) Kuntze



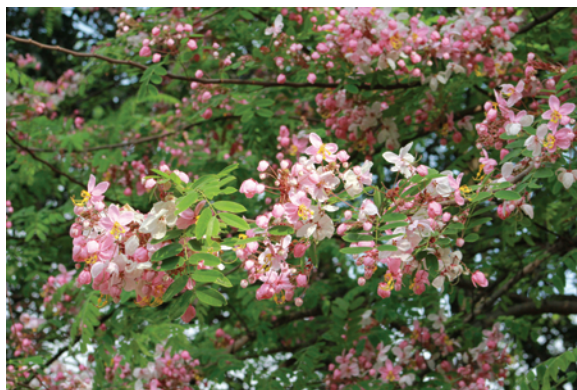
*Canna indica* L.



*Capsicum annuum* L.



*Carthamus tinctorius* L.



*Cassia javanica* subsp. *nodosa* (Roxb.) K.Larsen & S.S.Larsen



*Cassia roxburghii* DC.



*Celosia argentea* var *cristata* (2)



*Citrus aurantiifolia* (Christm.) Swingle





*Cocos nucifera* L.



*Cosmos bipinnatus* Cav.



*Curcuma amada* Roxb.



*Curcuma longa*



*Dahlia variabilis* (Willd.) Desf.



*Equisetum arvense* L.



*Erythrina variegata* L.



*Gossypium herbaceum* L.



*Haldina cordifolia* (Roxb.) Ridsdale



*Hibiscus rosa-sinensis* L.



*Lawsonia inermis* L.



*Lycopersicon esculentum* Mill.





*Madhuca longifolia* (J.Koenig ex L.) J.F.Macbr.



*Mallotus philippensis* (Lam.) Müll.Arg.



*Mangifera indica* L.



*Mimusops elengi* L.



*Morinda citrifolia* L.



*Morus alba* L.



*Nyctanthes arbor-tristis* L.



Ochre red



Ochre yellow





*Persicaria hydropiper* (L.) Delarbre



*Phyllanthus emblica* L.



*Pinus roxburghii* Sarg.





*Piper longum* L.



*Plumbago zeylanica* L.



*Psidium guajava* L.



*Pterocarpus santalinus* L.f.



*Punica granatum* L.



*Rosa x damascena* Mill.



*Rumex dentatus* L.



*Rumex nepalensis* Spreng.



*Schleicheria oleosa* (Lour.) Merr.



*Senna alata* (L.) Roxb.



*Senna insularis* (Britton & Rose) H.S. Irwin & Ba



*Senna siamea* (Lam.) H.S. Irwin & Barneby





*Senna sophora* (L.) Roxb.



*Sepia officinalis* L



*Sorghum bicolor* (L.) Moench



*Tagetes erecta* L.



*Tagetes patula* L.



*Tamarindus indica* L.



*Tectona grandis* L.f.



*Terminalia arjuna* (Roxb. ex DC.) Wight & Arn.



*Terminalia bellirica* (Gaertn.) Roxb.



*Terminalia catappa* L.



*Terminalia chebula*



*Toona ciliata* M.Roem. (2)





*Typha australis* K. Schum. & Thonner



*Zea mays* L.



*Ziziphus mauritiana* (3)

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