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Plant-Derived Pigments and Dyes Used By Artists

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PLANT-DERIVED PIGMENTS AND DYES USED BY ARTISTS

by

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HISTORY

Uses of Biologically-derived Products in Painting

Throughout history man has relied heavily on plant-derived materials in the production of paintings. Plant products have been used to fulfill each of the material requirements of painting. The ground or surface upon which an artist applies paint is usually of plant origin, such as woven fabrics and paper. The ancient Egyptians painted on canvas (from *Linum usitatissimum* L.), papyrus, (from *Cyperus papyrus* L.), and wood (Lucas, 1934:149-150, 201-203; Laurie, 1910:17, 31-32).

At the time of Theophilus leather parchment, preferably of horsehide, was popular for painting (Bazzi, 1960:13). After parchment, walls and wooden panels were most important for medieval painting. Usually solid panels of native woods were employed. In northern Europe the old masters favored oak (*Quercus*), linden (*Tilia*), pine (*Pinus*), fir (*Abies*), larch (*Larix*), birch (*Betula*), beech (*Fagus*), walnut (*Juglans*), and ash (*Fraxinus*). In Italy and the south of Europe chestnut (*Castanea sativa* L.), poplar (*Populus*), and cypress (*Cupressus*, probably Italian

cypress, _Cupressus sempervirens_ L.) were most used. Panels of cedar (various members of the Pinaceae), olive (_Olea europaea_ L.), and pear (_Pyrus communis_ L.) wood were also popular (Bazzi, 1960:13; Taubes, 1964:18; Doerner, 1962:33). Panels were selected for density and firmness and required lengthy processing. The old masters placed panels under running water for long periods of time to remove resins, gums, and tannins. Today this is accomplished by steam treatment (Bazzi, 1960:13). Also, panels must be exposed to air and dried for a year or more to prevent shrinkage and warping. Paintings on wood panels have been better preserved than canvas paintings and can be repaired more easily (Taubes, 1964:16).

Today the most popular panels are made of mahogany (usually _Swietenia mahogoni_ Jacq.) and cottonwoods (_Populus_), as well as birch (_Betula_) plywood and composition board. Solid panels are less desirable today because they are heavy and the wood must be well-seasoned and prepared, making them quite expensive.

Perhaps the earliest instances of painting on cloth were the decoration of procession banners when embroidery was too costly and time consuming. During the Renaissance canvas of hemp and linen was popular. Botticelli's "Birth of Venus," dating probably from

around 1480, is believed to be the earliest example of a large scale painting on canvas for indoor decoration (Thompson, 1956:37-38). After this time canvas became more important. It had the advantages of being cheaper, lighter, and more portable than wood.

Artists' canvas has been made chiefly of flax (*Linum usitatissimum* L.), hemp (*Cannabis sativa* L.), jute (*Corchorus capsularis* L.), and cotton (*Gossypium*). The best canvas is woven from pure flax fiber and is very durable (Laurie, 1930:65). Hemp was used for the large easel paintings of the Venetian School, for instance those by Tintoretto and Veronese. Cotton has been used generally for smaller canvases (Doerner, 1962: 4). Paper has occasionally been used for oil painting; for instance, such notable artists as Rembrandt and Delacroix used oils on it. Paper has also long been favored for watercolor painting. Pasteboards made partially of wood fibers and linoleum panels have also been employed as oil painting surfaces.

The barks of certain trees have been used as grounds by primitive cultures. In recent years a good deal of interest has centered on the paintings of the Australian aborigines. The aboriginal artists use eucalyptus bark panels as grounds for symbolic paintings (Scougall, 1965:47). They make a paint by mixing

"the sap from an orchid bulb or swamp-root oil" and water (Kalamazoo Art Center, 1965:2). It has also been observed that on some Pacific islands natives make paintings on bark-cloth. Natural plant colors are used (Herberts, 1958:25).

Most painting today is accomplished with animal hair brushes, but the ancient Egyptians made paint brushes solely from plant fibers (Lucas, 1934:204-207), with *Ceruana pratensis* Forsk. (Compositae) and halfa grass, *Stipa tanacissum* L. (Graminae), yielding suitable fibers for their artisans. Segments of the midrib of the leaves of the date palm, *Phoenix dactylifera* L., were also used for brush fibers. Often a reed or twig was cut to length and the fibers at one end separated and softened to produce a simple, functional paint brush.

Perhaps the greatest material determinant of the nature of paintings is the paint[1] itself, that which is applied and arranged to produce a visual stimulus pattern. The range and limitations of the paint

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[1]An artists' paint may be said to consist of two main components, a pigment or pigments and a vehicle or medium. In painting, pigments are substances which impart their colors to a surface when applied in a layer over the surface. A pigment is usually employed in the form of an insoluble powder which is suspended in a liquid medium by grinding and mixing to produce a paint.

employed is of primary importance to the artist's end product. It is in the manufacture of paints that plants have been of greatest use to the artist.

Plant-derived Paint Constituents

Organic pigments were employed in some of the earliest known art works. The pigments used in the paleolithic European cave paintings include charcoal and other carbon blacks, as well as animal blood. Some authorities believe that vegetable sugars may have been employed as one of the media for cave painting (Myron, 1964:10; Herberts, 1958:25). Primitive man used only vegetable dyestuffs (Leggett, 1943:86), and some of these may have been incorporated into art works.

The ancient Egyptians used many organic coloring agents. Their blacks were almost always carbon blacks such as charcoal or soot from the burning of vegetable oils (Laurie, 1910:26; Lucas, 1934:204-207; Mekhitarian, 1954:34). Greys were mixtures of such black pigments with gypsum.

Egyptians are believed to have employed yellow vegetable dyes, one from safflower[1] (Laurie, 1910:24, 32; Lucas, 1934:199-200). A yellow obtained from the peel of the fruit of the pomegranite tree, Punica granatum L., was used for dyeing leather. The peel, which contains 26% tannin (Uphof, 1959:301), is also the

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[1]The specific source is discussed later.

source of a tanning material used by the Egyptians. The yellow dye from henna, Lawsonia alba Lam., was used by the Egyptians to paint their bodies. It has been found on the nails of mummies (Heath and Milligan Mfg. Co., 1897:12).

Madder lake, a red obtained from the roots of the madder plant (Rubia tinctorum L.), was used in Egyptian painting. Madder on a base of gypsum yielded a pink pigment used on Egyptian coffins and tomb paintings. The pigment was identified by Russell on Egyptian paintings of the Graeco-Roman Period (Lucas, 1934:137-138; Laurie, 1914:10, 95).

The Egyptians had other vegetable dyes which later found use as artists' pigments. Among these are Indian indigo[1] and woad[1]. Woad was cultivated in Egypt at the time of Christ and may have been used much earlier.

It is very likely that gum arabic obtained from the acacia (Acacia senegal (L.) Willd. and other species) was a popular medium for Early Egyptian painting. The gum was readily available and conveniently soluble in water. Even today nearly all artists' watercolors are made with gum arabic. Some natural resins were used by Egyptian artisans as varnishes, although there

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[1]The specific sources are discussed later.

is no evidence that pigments were mixed with these (Heath and Milligan Mfg. Co., 1897:11; Mekhitarian, 1954:34; Lucas, 1934:150-155).

The Greeks and Romans used many plant-derived pigments and dyes in their painting. A partial list (Laurie, 1914:8-11, 16-17; Laurie, 1910:44-47) of such colors known by the time of Pliny includes:

Reds -- madder, dragon's blood

Yellows -- weld, Persian berries, quercitron

Greens -- sap green

Blues -- Indian indigo, woad

Blacks -- lampblack, charcoal black

Madder may have been known to the early Greeks, and the Romans found that the dregs of wine, carbonized, yielded a good black (Heath and Milligan Mfg. Co., 1897:31).

Though drying oils were known, there is no conclusive evidence that they were used at this time as painting media (Laurie, 1910:64-65).

Other early cultures made use of plant colors. Dragon's blood red[1] and yellows from gamboge[1], saffron[1], and aloes[1] have long been used in the Orient as coloring matters (Heath and Milligan Mfg. Co., 1897:44). Also,

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[1]The specific sources are discussed later.

the American Indians had many organic dyes and may have used them in ornamental painting.

Throughout the medieval period to the 20th century the greatest advances in painting occurred in Europe. More vegetable pigments were added to the artist's palette and innovations of paramount importance were made in the use of media. Drying oil vehicles such as linseed[1], poppyseed[1], and walnut oils[1] became popular. These slow drying vehicles allowed the artist to work longer at details and permitted thin, transparent glazes of color. Moreover, oil paintings were usually more durable and have been retained in better states of preservation. Drying oils were mixed with different resins and oleoresins to form media of proper drying time, consistency, and durability to suit the individual artist. Venice turpentine from the common larch, *Larix decidua* Mill., and Strasbourg turpentine from the silver fir, *Abies pectinata* DC., were two of the most used oleoresin ingredients in the media of many old masters.

Many other organic materials were used both as media and to coat and prepare surfaces for painting. Gums, honey, and glycerine were used in formulas for priming canvas, as were some drying oils. Venetian

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[1]The specific sources are listed on page 11.

masters made a rye paste for use in oil painting grounds. Many animal substances have been used in grounds, including milk, eggs, gelatine, and glues. The Chinese were known to use pig's blood in preparations for painting on cardboard (Bazzi, 1960:21-26).

During medieval times the materials used by the artist were often strictly regulated by the guilds. The preparation of pigments, oils, and other materials was largely undertaken in the artist's atlier; thus, the studio really became a laboratory. Apprentices obtained or extracted the pigments and mixed and ground them with vehicles. Panels, canvas, oils, and brushes were prepared on the spot and considerable apparatus for these operations was a necessary part of the studio (Constable, 1954:21-22).

Pigments were prepared as needed and immediately used in painting. Later, paints were kept in bags of skin, in which they could be retained in usable form for short periods. It was not until the 19th century that metal tubes came into use (Constable, 1954:23), freeing the artist from the need to be part botanist and chemist as well as painter. Pigments and media could be stored and marketed, thus, commercial suppliers supplanted the "studio-laboratory" situation.

Plant-derived paint constituents can be grouped

into two major divisions: media and pigments. Media serve several functions, but chief among them is to bind the pigmented substances together and to a surface. Plant-derived media include:

a. Drying oils, such as:

Linseed oil -- from _Linum usitatissimum_ L.

Poppyseed oil -- from _Papaver somniferum_ L.

Walnut oil -- from _Juglans regia_ L.

b. Essential oils, such as:

Oil of turpentine -- from species of _Pinus_

Oil of spike lavender -- from _Lavandula latifolia Chaix._

c. Oleoresins, such as:

Venice turpentine -- from _Larix decidua_ Mill.

Canada balsam -- from _Abies balsamea_ (L.) Mill.

Strasbourg turpentine -- from _Abies pectinata_ DC.

d. Resins, such as:

Copals -- from species of _Copaifera_

Damars -- from several species of the Dipterocarpaceae

Mastic -- from _Pistacia lentiscus_ L.

e. Gums, such as:

Gum arabic -- from _Acacia senegal_ Willd.

Gum tragacanth -- from _Astragalus gummifer_ Lab.

Pigments constitute that portion of a paint which supplies the desired color. The coloring substance used

as an insoluble powder suspended in a medium is known as a pigment. If the coloring substance is dissolved it is technically called a stain or dye. In this study I propose to consider the sources, preparation, and uses of the plant-derived pigments and dyes used historically, as well as those employed by painters today.

ORGANIC PIGMENTS

In 1856 an organic dye was synthesized for the first time, initiating the possibility of an even greater range of organic tools for the artist. Today there are over 2000 organic color compounds in constant industrial use, while not many more than 100 inorganic colors are employed (Research Laboratories of the International Printing Ink Corp., 1935:8). Most organic colors are now synthesized, as it is usually less expensive to do so.

Nearly all organic colors are composed of ring rather than chain structure; a high ratio of carbon to hydrogen is apparently required for color production in organic substances. Small structural differences can cause differences in color. Many pigments are isomers of other pigments, yet they do not produce the same hue.

Most of the red, blue, and purple pigments of flowers, stems, fruits, and leaves belong to a group of glycosides called anthocyanins. These are normally water-soluble, dissolved in the cell sap, although they sometimes occur in an amorphous or crystalline state in the plant (Mallette, Althouse, and Clagett, 1960: 197; Bentley, 1960:24). Most of the yellow pigments

are glycosides known as anthoxanthins. These include the flavones (such as hematoxylin from logwood), xanthones (such as gentisin from gentian root), flavonols (such as quercetrin in the bark of oaks), flavanones (such as hesperidin in oranges), and flavins (an example of which is riboflavin, vitamin B) (Miller, 1957:59-62).

Organic pigments exhibit certain distinct advantages over inorganic colors. Brighter and more varied hues are normally obtained from organic pigments, and they usually have higher tinctorial strengths (Chatfield, 1962:174). Their intensity and opacity is less diminished by mixing with other colors. Most of the natural plant dyes and pigments have the regretable tendency to fade rather quickly, though a few are reasonably stable. But they do have an advantage over synthetic colors in that as they fade they remain a shade of their original color (Kierstead, 1950:77). Many synthetic colors fade to a very different color, and this, of course, is especially undesirable in works of art. There are many considerations to make in choosing durable organic pigments.

In industry attention is given to the resistance of a color to the action of light, heat, solvents and chemicals. The artist is concerned primarily with the

effects of light and the effects of exposure to the chemical action of the atmosphere.

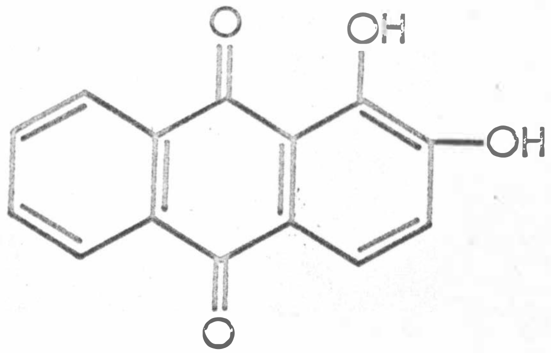
Historically, the natural organic plant colors are without doubt among the most important artists' colors. Some are still widely used and preferred to synthetic pigments, although most are unstable. The more important plant-derived coloring substances employed by artists will be discussed according to their hues.

REDS

Madder

Perhaps the most important natural organic pigment used in painting is madder red, which is also known as laque de garance or Turkey red. The main coloring principle is found in the form of a glycoside, rubierythric or ruberythric acid, which is common principally in the cortex of the long slender roots of the madder plant, Rubia tinctorum L. (Mayer, 1947:119; Schery, 1954:242). The coloring substance alizarin is obtained from this glycoside. Chemically alizarin is 1,2-dihydroxy-anthraquinone ($C_{14}H_8O_4$) (Mayer, 1947:119; Gettens and Stout, 1934:91).

The roots of Rubia tinctorum L. (Rubiaceae) are the primary source of madder red, although other members of the genus yield similar dyestuffs. The plant is an herbaceous perennial native to Greece and the Mediterranean region. The best coloring matter is extracted from the roots of plants which are from 18 to 28 months old and have been grown in calcareous soil (Gettens and Stout, 1934:126). The roots are washed and then ground. They are next fermented and finally hydrolized with dilute sulphuric acid to produce the



Alizarin

(from Mayer, 1947:118-119)

madder extract which has long been favored as a dye.

The madder plant grows wild in much of the eastern Mediterranean. It has been cultivated in Holland, France, Turkey, Belgium, Italy, Germany, India, and in North and South America. Madder has been an important source of red dye since antiquity. Red was important as a symbol of courage, and the red of madder was more brilliant and lightfast than other dyes, regardless of color. Madder was probably first used in India, and it seems to have been well-known to ancient Persians and Egyptians. It has been identified on Egyptian tomb paintings. Madder was mentioned by Herodotus around 450 B.C. (Kierstead, 1950:40).

Rubia tinctorum L. was grown in medieval Europe in fields left fallow. Later, in France, such crop rotation was strictly enforced for a long time. Madder was introduced into Holland during the 16th century. Colbert introduced it into Avignon in 1666, and Frantzen brought it to Alsace in 1729; however, madder did not become very important here until the period between 1760 and 1790 (Perkin and Everest, 1918:23). During the French wars of the Republic the madder industry was for the most part abandoned. Madder was cultivated again on a large scale after 1815.

Holland had controlled the madder market for about 300 years. Through the 16th and 17th centuries Holland was the greatest producer of madder, and it was not until the onset of the 1700's that France began to seriously challenge this domination. The madder industry was seriously affected by the economic unrest which accompanied and followed the French Revolution, and many efforts were made to bolster the industry. In 1840, King Louis Philippe ordered that the trousers and caps of the French army uniforms be dyed red with madder (Leggett, 1943:111). Earlier, the "redcoat" uniforms of England had been colored with madder dye.

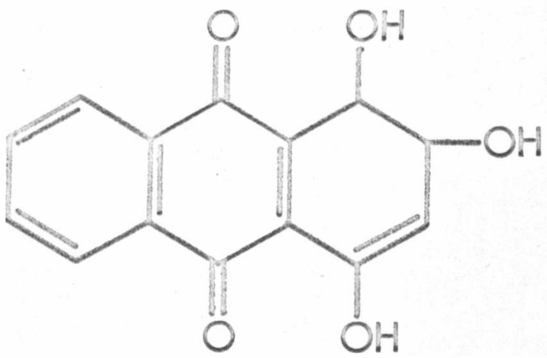
Madder had also been popular elsewhere in Europe. It was introduced as a cultivated plant into Italy at the time of the Crusades and was grown in Spain by the Moors during the 16th century. Its cultivation subsided greatly after alizarin was synthesized by chemists in 1868 (Gettens and Stout, 1934:91). Today madder is still cultivated in a few countries, chiefly to supply the artists' pigment, which is still used (Winsor and Newton Ltd., 1892:6, 9) and often preferred to the synthetic product.

The natural extract does have slightly different qualities. It contains several additional coloring substances besides alizarin and can be identified because it flouresces in ultraviolet light.

The roots of Rubia tinctorum contain a mixture of glucosides, the most important of which is ruberythric acid ($C_{26}H_{28}O_{14}$) (Remington and Francis, 1954:172). On hydrolysis this yields two molecules of glucose and one molecule of alizarin. Alizarin is considered an "adjective" dyestuff. These are compounds which are not normally colored in themselves, but exhibit a marked affinity for metallic mordants, with which they form colored substances (Martin and Morgans, 1954:8).

Other pigments present in Rubia tinctorum are xanthin, chlorogenin, and purpurin. Of these, purpurin, 1,2,4-trihydroxyanthraquinone ($C_{14}H_8O_5$), is most important (Mayer, 1947:119; Gettens and Stout, 1934:126). It probably occurs in the plant as a glycoside. Purpurin is not as lightfast as alizarin and is slightly more orange in color. It gives the natural madder red a more delicate hue but tends to fade or lose brilliance upon exposure to strong sunlight. Purpurin has been prepared synthetically by oxidizing alizarin (Yakobi and Plakidin, 1964:27).

Madder red and similar dyestuffs can be obtained from several species of the Rubiaceae. Rubia tinctorum L. has already been discussed as the most common source of madder. R. peregrina L., called wild madder or Levant madder, was formerly of great importance in



Purpurin

(from Wakeman, 1919:882; Mayer, 1947:140)

England as the source of madder dye (Mairet, 1917:29). This plant grows in the Near East, the Caucasus, and in Europe (Leggett, 1943:87). R. cordifolia L., which can be found growing in northeast Africa, Java, India, Asia Minor, China, and parts of Europe, is the source of a less important red dye. The plant contains purpurin but no alizarin (Perkin and Everest, 1918:41). Other plants which are used as purpurin dye sources are R. munjista Roxb., R. khasiana Kurz. (Khasia madder), and R. sikkimensis Kurz. (Sikkim madder), all of India.

In India there is another member of the Rubiaceae which is an important source of a madder-like dye. This is the chay root, Oldenlandia umbellata L., which is also known as chay-aver, turbuli, cheri-vello, ché or chay, sayawer, and imburel. It is a small bush or herb which is found on sandy soils near seacoasts. The chief constituent of the dye extract is alizarin, however, unlike the extract of R. tinctorum no purpurin is present (Perkin and Everest, 1918:36-37).

For painting, madder lake is prepared from the madder extract. A lake is an insoluble coloring compound formed by precipitating an organic dye upon an inorganic or inert base or extender (Laurie, 1930:96; Research Laboratories of the International Printing Ink Corp., 1935:17; Chatfield, 1962:177; Fischer, 1930:17, 125; Parker, 1905:4; Martin and Morgans, 1954:33).

The madder extract is a water-soluble dye and may be used directly for fabric coloring, but this is usually unsuitable as an artists' paint, chiefly because of the insufficient opacity of dyes. The extract is precipitated on a base such as alumina. It will then leave a relatively opaque layer on a painted surface. Opacity may be controlled by the artist through the amount and nature of the vehicles employed in applying the pigment. Almost any water-soluble vegetable dye can be prepared to yield an insoluble lake pigment (Chatfield, 1962:177), and most plant-derived artists' pigments are of this form.

Madder lakes are very versatile and may be mixed with gums for watercolors or with drying oils and resins to form oil paints. Madder is among the most stable of the natural organic colors, which explains in part its persistent popularity. It is perhaps the most highly recommended natural organic pigment and has been taken as the standard of lightfastness for organic pigments, having been assigned an arbitrary value of 10 on a scale of resistance to light (Martin and Morgans, 1954:35).

Depending on the mordant with which it is used, madder can give shades of red, pink, orange, lilac, brown, or black. It is best known for the bright reds

which can be obtained. Madder extract is regarded as one of the best natural dyes for wool, linen, and cotton.

Madder does not seem to be extremely important in painting prior to the 14th century. It has been cultivated in parts of France at least since late in the 13th century and perhaps long before. The principal use of madder in medieval painting was in making a compound red called "sinopis," which sometimes included brazilwood lake (Thompson, 1956:121-124). The madder lakes manufactured in 17th and 18th century Italy became the most highly regarded red lake pigments and have retained this position up to recent times (Thompson, 1956:122).

The permanency of madder lake is regarded as excellent when used full strength and very good when used in tints (Gardner and Sward, 1946:46-47). Also, it has very good resistance to alkalis and is reasonably resistant to heat. Most organic colors tend to be broken down by high temperatures. Madder is regarded as a transparent pigment, even in large amounts, and is excellent for making transparent washes and glazes.

Of the various hues of madder available to artists the darker shades of red and violet are regarded as more permanent (Doerner, 1962:76). Madder dries slowly

in drying oil paints and is usually mixed with linseed oil and varnish for oil painting. Madder cannot be used in fresco painting because the lime of the plaster will destroy the pigment.

Though madder lakes are usually durable, mixing with certain other pigments can be detrimental. Durability of madder is sometines reduced when mixed with the natural earth colors, raw sienna, raw umber, or raw ochres, due to the presence of iron hydroxide in these pigments (Weber, 1923:17). Also, such pigments as white leads, chrome yellows, Naples yellows, and chrome greens tend to bleach madder lakes.

Brazilwood

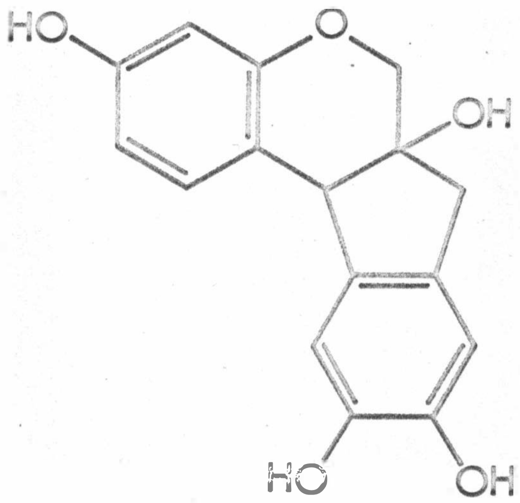
Another natural red dye is obtained from the wood of Caesalpinia echinata Lam. of the legume family. During the middle ages the dye was obtained from sappanwood, C. sappan L., native to India and Malaya. It was known as "brazilwood." Early Portuguese explorers found a very similar tree, C. echinata Lam., growing in South America, and they named the new land for the resemblance to the wood of the old world tree (Foster and Foster, 1945:168-169; Hill, 1952:128; Thompson, 1956: 116-117). The red dye is also obtained from Pernambuco wood, C. crista L., of Jamaica and Brazil. Other trees of the Leguminosae yield similar dyestuffs.

The word "brazil" is believed to be derived from the Spanish "brasas" or the Italian "brage," meaning "glowing coals" (Eastlake, 1960:115). The wood of C. sappan may have been supplied to medieval Europe by Venetians and Moors who brought it from India. Huge quantities of brazilwood were used both for dyeing and painting during the Middle Ages. It was easier and less expensive to make than were the insect dyes such as kermes. Enormous amounts were used especially by painters, and brazilwood lakes were highly esteemed for panel painting and for manuscript painting. Brazilwood was used all over Europe from the 12th century on

and probably earlier (Thompson, 1956:120-123). Today brazilwood lakes are seldom if ever used in painting as the color is fugitive in sunlight.

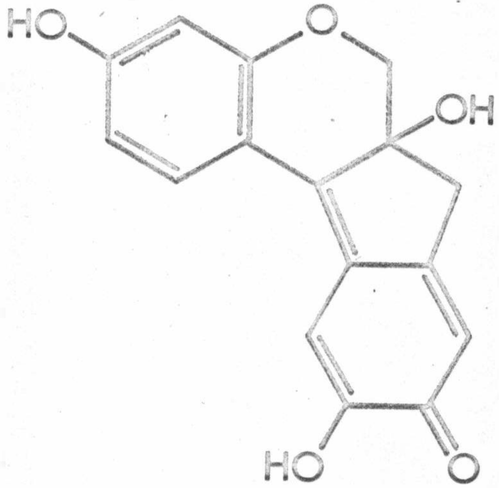
The heartwood of the brazilwood tree is a light color which turns deep red on exposure to the atmosphere. The dye is extracted by cutting heartwood into fine chips and boiling them in water. This yields the coloring material brazilin ($C_{16}H_{14}O_5$) (Bentley, 1960:74). When exposed to the air brazilin is oxidized to brazilein ($C_{16}H_{12}O_5$) which is deep red to brown in color and is more brilliant than brazilin (Gettens and Stout, 1934:99; Bentley, 1960:86-87). This is chemically very similar to hematoxylon from logwood. These two pigments have a type of structure not found in any other naturally occurring substance.

Brazilwood lakes may be prepared in different mordants and produce bright cherry to deep red pigments.



Brazilin

(from Bentley, 1960:86-87;
Gore et al., 1962:235)



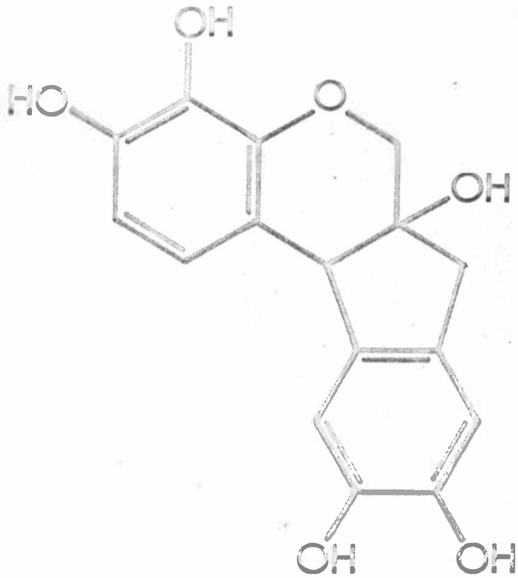
Brazilein

(from Bentley, 1960:86-87)

Logwood

From the wood of Haematoxylon campechianum L. of the Leguminosae comes one of the oldest and most important dyestuffs, logwood. This small tree is native to Mexico, Central America, and the West Indies and has been introduced widely in the tropics. The dye contained in the heartwood is haematoxylin ($C_{16}H_{14}O_6$), a hydroxybrazilin (Gettens and Stout, 1934:125; Bentley, 1960:78-79). This is changed to red-brown haematin ($C_{16}H_{12}O_6$) when exposed to air (Gettens and Stout, 1934: 125). Logwood not only yields an important fabric dye, but is the source of a red stain useful in histology and microscopy.

Haematin is the coloring matter which has been used in artists' paints. It is obtained by boiling heartwood chips in water over steam under pressure. Brown, red-brown, black, and blue-black lakes can be made from logwood extracts by the use of different precipitation agents. Logwood lakes have been used by artists primarily in watercolor paints. These pigments have a tendency to be fugitive in light and are currently avoided when more stable pigments are available.



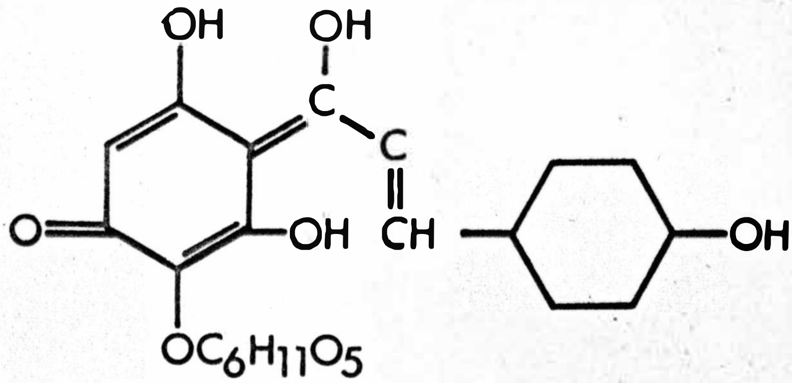
Haematoxylin

(from Bentley, 1960:78-79; Gore et al., 1962:235)

Safflower

Safflower or carthame is a natural red extracted from the dried petals of <u>Carthamus tinctoria</u> L. This member of the Compositae has been called safflower, dyer's thistle, bastard saffron, carthame and safflor. It is a native of India and has been cultivated in China, India, Persia, Egypt, Central and Southern Europe and South America (Rowe, 1924:297). It is now widely distributed in the tropics. The seeds are a source of a valuable drying oil which is also an important edible oil in some areas. The oil cake after decortication is one of the most valuable cattle foods in Europe (Remington, 1950:63).

The plant grows best in dry sandy soils. The red color found in the flowers is due to the presence of carthamin ($C_{21}H_{22}O_{11}$) (Mayer, 1947:208). Remington (1954:173) gives the formula as $C_{14}H_{10}O_7$. Carthamin is present in the flower petals to the extent of about 0.5% to 5% (Perkin and Everest, 1918:594; Remington and Francis, 1954:173; Remington, 1950:63). A soluble yellow substance is found in amounts of about 30%, but this is useless as a paint pigment or effective dye and is therefore removed and discarded. Carthamin mixed with French chalk has been often used as a cosmetic. This is known as "vegetable rouge."



Carthamin

(from Mayer, 1947:208)

To prepare the dye the petals are picked, dried, and then steeped in a cold dilute sodium carbonate solution (Gettens and Stout, 1934:154). The dye was once extremely popular in Europe and was also used as a wood stain. That it was used by artists is certain, but to what extent and in what manner is not clear. It was most probably used with watercolor media.

Safflower was used for many centuries by the Chinese to dye silk shades of rose, scarlet, purple, and violet. The Egyptians used it to dye linen scarlet. Kierstead (1950:48) said that textiles found in the tomb of King Tutankhamen may have been dyed with safflower. The coloring substance is edible and was once used to color liquors and confectionery.

Poppy Red

Poppy red is expressed from the petals of certain members of the genus Papaver, in the Papaveraceae. Different coloring principles are present in different species. The red color is generally due to the presence of cyanidin and pelargonidin derivatives. The distribution of these and other pigments has been useful in the taxonomy of the genus. Generally the pelargonidins are concentrated in the petals, while the cyanidins are found in the stamens and petal bases (Acheson et al., 1962:256, 260).

One of the best sources of poppy red is Papaver rhoeas L., the common red poppy or corn poppy. Among the floral pigments of this poppy are cyanin chloride ($C_{27}H_{31}O_{16}Cl$), the 3,5-diglucoside of cyanidin chloride, which is also present in the red rose, Rosa gallica L. The dark red mekocyanin chloride ($C_{21}H_{31}O_{16}Cl$) is also found in the flower (Mayer, 1947:225; Perkin and Everest, 1918:293). Another red pigment sometimes found in P. rhoeas L. is mekopelargonin (Mayer, 1947:224), the aglucon of which ($C_{15}H_{12}O_6Cl$) appears to be a pelargonidin with a firmly bound water of crystallization.

Acheson, Jenkins, Harper, and McNaughton (1962:257-258) in their study of poppy floral anthocyanins

list several species which contain cyanidin and pelargonidin derivatives. Those containing both types of pigments are:

Papaver rhoeas L.

P. dubium L.

P. lecoquii Lamotte

P. argemone L.

P. hybridum L.

P. apulum Ten.

P. pavonimum Fisch. and Mey.

P. polonicum Mey.

P. glaucum Boiss. and Hausskn.

P. somniferum L.

P. bracteatum Lindl.

P. oriental L.

Papaver species containing only pelargonidins include:

P. pilosum Sibth. and Smith

P. rupifragum Boiss. and Reut.

P. heldreichii Boiss.

P. mudicale L. (red varieties)

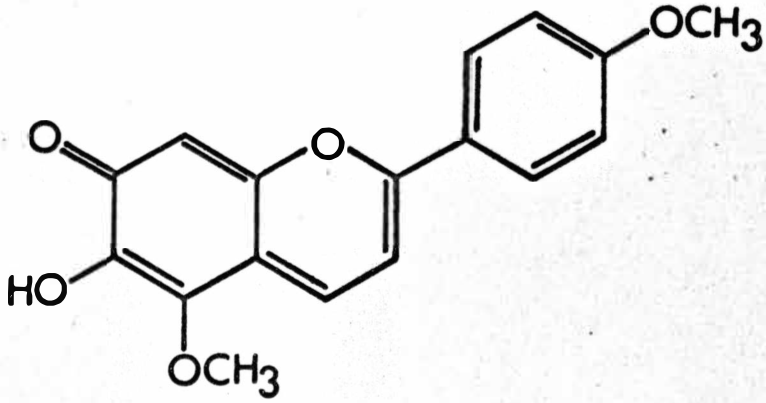
Red pigments are present in greater or lesser quantities and which of these species has or has not been used as a source of poppy red is open to question.

There is little information available on dyeing with poppies, though an oriental poppy has been used for this purpose (Kierstead, 1950:89). A dye may be extracted by drying the petals and placing them in alcohol. The pigment obtained from the extract is unstable, but Bazzi (1960:50) has recorded it as a pigment useful to artists.

Chica Red

Chica red, also called crajura or carajura, is a somewhat rare dye extracted from the flowers and leaves of the American chica plant, Bignonia chica Humb. and Bonpl., a South American tree of the Bignoniaceae (Bazzi, 1960:50; Mayer, 1947:202; Uphof, 1959:52). Two substances are responsible for the color, red carajurin ($C_{17}H_{14}O_5$) and scarlet red carajurone ($C_{15}H_9O_5 \cdot OCH_3$). The leaves are treated with water and the extract treated with a powder from the bark of "aryane." Precipitation of the coloring matter is accelerated by the powder, probably due to the enzymatic fission of the glycoside. A red cake containing 4% pigment is formed and sent to market. The coloring matter is then commercially purified for use (Mayer, 1947:202).

The Indians of the Rio Meta and Orinoco use chica red to paint their bodies (Bentley, 1960:44), as do other Indians of Brazil, Bolivia, Guiana, and Central America (Perkin and Everest, 1918:341-342). When Darwin landed in South America he reported that certain of the naked tribes higly prized a bright red pigment with which they painted their entire bodies (Heath and Milligan Mfg. Co., 1897:60). This may have been chica red.



Carajurin

(from Mayer, 1947:202; Bentley, 1960:44)

It is not certain that the red pigment is obtained from the same species in all cases. Some South American Indians use "ula" leaves from an unknown species of Bignonia. It is reported that a brighter lake pigment is obtained from the leaves of a "brushrope" of British Guiana (Perkin and Everest, 1918:342). It gives a dye with alizarin-like shades and may be chica red, although it seems different in some ways. This difference could merely be due to the relative concentrations of carajurin and carajurone, the latter being a much brighter red.

Chica red lakes are not very stable and are expensive. They have been used by artists probably more because of their color and exotic appeal rather than durability.

Archil

Archil, also called orchil, orseille, and litmus red, has long been used in artists' paints, as a dye for silks and wool, as a pH indicator, and as a coloring additive to wines and liqueurs. It apparently was used by the Romans before the time of Pliny. After the fall of the Roman Empire it was not used again until about 1300 A.D. (Uphof, 1959:314). The name archil was once orchil, which, in turn, was derived from "oricella," from the Florentine family of dye makers (Oricellari) that popularized it in the 14th century.

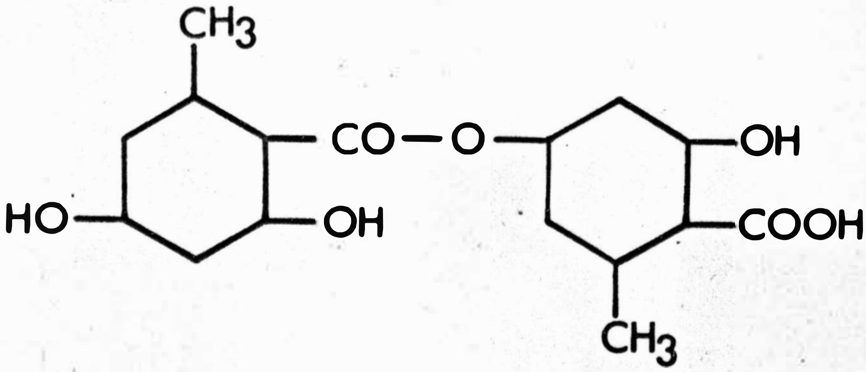
The coloring matter was known in commerce in three forms, as a paste (archil), as a drier mass (persis), and as a red powder (cudbear). The dye is obtained from lichens, chiefly from species of *Roccella* (Roccellaceae) and *Lecanora* (Lecanoraceae).

Roccella tinctoria DC. and other *Roccella* species which are sources of the dye grow on rocky coasts of the Azores, Canaries, Cape Verde Islands, Cape of Good Hope, Madiera, Corsica, Sardinia, Chile, and other tropical and subtropical countries (Perkin and Everest, 1918:540, 556; Mairet, 1917:39). The dye is also obtained from *Ochrolechia tartarea* (L.) Mass. (Lecanoraceae), called crotal, crottle, or cockur,

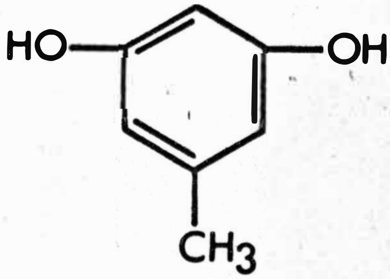
which grows in Sweden and Norway. Lecanora tartarea Mass., of Sweden and the British Isles, is another source of archil. Similar dyes are derived from many other lichens.

All of these lichens have lecanoric acid or other similar colorless acids which are dervatives of orcin. These acids can be converted to colored substances. Lecanoric acid ($C_{16}H_{14}O_7$) (Asahina and Shibata, 1954:59) can be split to orsellinic acid and to orcin ($C_6H_3(OH)_2CH_3$) (Remington and Francis, 1954:173). Orcin, when exposed to atmospheric oxygen and ammonia, will yield a purple substance called orcein. This is a mixture of substances including red orcein ($C_{28}H_{24}N_2O_7$) and a yellow compound ($C_{21}H_{19}NO_5$) (Remington and Francis, 1954:173; Rowe, 1924: 297; Perkin and Everest, 1918:556). Orcein and other related dyes are blue in the presence of bases and red in acids. Azolitmin, the main coloring substance of litmus, is prepared from orcein (Perkin and Everest, 1918:559).

There are many ways of preparing archil. An early method used in Scotland was to treat the lichens in slaked lime and stale urine, the urine providing the ammonia source necessary to convert orcin to orcein (Mairet, 1917:37-40). In Shetland the lichens were collected in May and June, steeped in stale urine for



Lecanoric acid



Orcin

(from Perkin and Everest, 1918:557; Asahina and Shibata, 1954:59, 144)

several weeks, and maintained in a warm condition. When the mixture became thick in texture it was made into small cakes, wrapped in dock leaves, and hung to dry in peat smoke. Thus prepared, it would keep for several years, requiring only the addition of water to form a dye.

Mairet (1917:41) gives a general outline for preparing archil from lichens. First, the lichens are washed, dried, and impurities are removed. They are next pulverized into a pulp with water, and ammonia of a specified concentration is added in regulated amounts. The fermenting mass must be stirred frequently to insure exposure to oxygen. In some cases alkalis such as potash or soda are added to heighten color. Reds, purples, and blues may be obtained depending on preparation.

Litmus is obtained in a manner similar to archil. The reaction is more prolonged, requiring 40 days instead of the usual six or seven, and is carried out in the presence of potassium carbonate. This process results in the formation of the litmus pigments azolitmin and erythrolitmin (Rowe, 1924:297).

Archil is a substantive or nonmordant dye. It has been used at least since about 1300 A.D. (Perkin and Everest, 1918:529), chiefly as a fabric dye. It

was made into a pigment which did have some importance in medieval painting (Thompson, 1956:158), but has been largely abandoned as a paint constituent.

Dragon's Blood

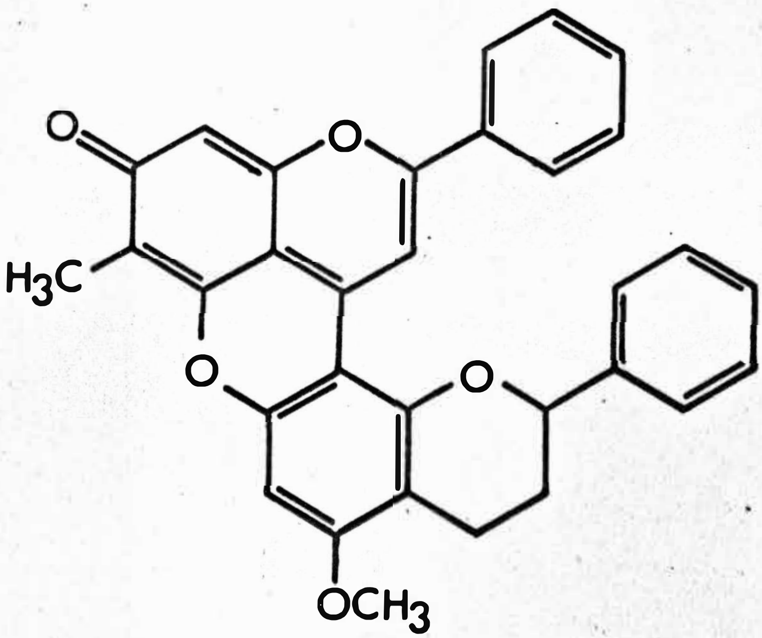
A dark red resinous exudation from the fruit of the rattan palm, _Daemonorops draco_ Blume (Palmaceae), is the source of Sumatra dragon's blood (Gettens and Stout, 1934:111; Uphof, 1959:121; Hill, 1952:161). This palm is indigenous to eastern Asia. Several other Asiatic and South American plants yield similar resins (Dieterich, 1920:201-202; Robertson and Whalley, 1950: 1882). Socotra dragon's blood is obtained from _Dracaena cinnabari_ Balf. (Liliaceae) of southeast Asia, Socotra, and the East Indies. Other "dragon's bloods" are obtained from _Dracaena ombet_ Kotschy (Socotra "vera" dragon's blood), from _D. schizantha_ Baker ("sicut dicta," Arabian dragon's blood), and from _D. draco_ L. (the Indian dragon blood tree). An American dragon's blood is obtained from _Pterocarpus draco_ L. (dragonblood padauk) of Mexico and the West Indies and an African dragon's blood can be obtained from _P. erinaceus_ Lam. (African kino, African rosewood) which grows in northern Nigeria. These resins differ widely in composition. Sumatra dragon's blood is regarded as the best and has been the only one on the market commercially in recent years.

Dragon's blood is a brittle resinous product with

a melting point of about 120° C. (Chatfield, 1953:249). The dragon's blood recieved on the market contains the optically active pigment dracorubin ($C_{32}H_{24}O_5$) (Bentley, 1960:46-50). This compound is an anhydro-2,4-diphenylbenzpyranol which may be derived from the 7-hydroxy-2,4-diphenylbenzpyranol, dracorubanol (Collins *et al.*, 1950; Robertson and Whalley, 1950:1882). A minor pigment also present is dracorhodin.

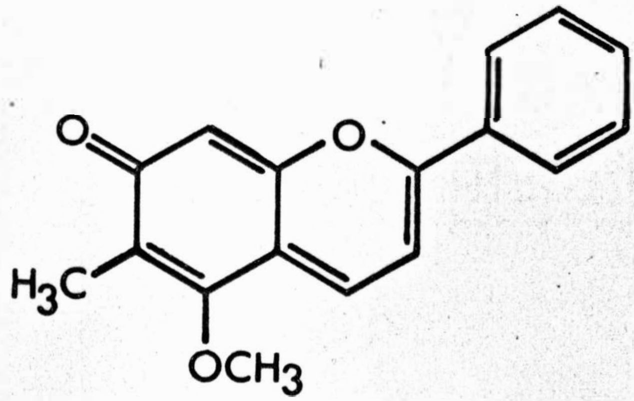
The odorless resin is collected from wounds in the bark and fruit. This is heated, molded into sticks, wrapped in palm leaves, and sent to market. The resin is soluble in alcohol and other organic solvents, yielding a red solution. The resin is most often used in varnishes for metals and for making zinc line engravings. It has also been used for centuries in the manufacture of fine violins.

Considerable myth and legend surrounded the color in the past. It was believed to be derived from the blood of dragons or from the mingling of dragon blood with the blood of a traditional enemy, the elephant (Gettens and Stout, 1934:111; Laurie, 1910:46-47). The pigment and resin has been known for a very long time. Classical Greek writers called it "Indian cinnabar" (Thompson, 1956:124), and Pliny mentioned it in his *Naturalis Historia*, ca. 77 A.D. (Weber, 1923:52).



Dracorubin

(from Bentley, 1960:46-50)



Dracorhodin

(from Bentley, 1960:46-50)

Dragon's blood was used as a pigment in medieval times chiefly by book and manuscript painters. For this purpose it was often mixed with yellow gamboge resin. It was used most in painting during the early Middle Ages and passed somewhat out of favor during the 14th and 15th centuries (Thompson, 1956:124). Since then artists have used it occasionally.

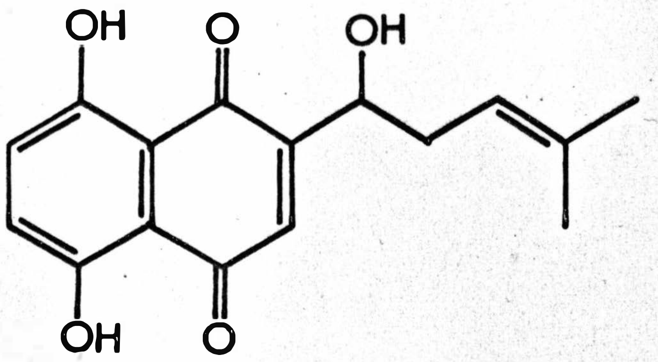
Dragon's blood dries poorly in drying oil media. The color may be destroyed by mixing with certain metallic pigments such as white lead. It is useful in painting for making transparent red glazes, and the color is reasonably durable if locked in a resin film by varnishing.

Alkannin

Alkannin, anchusin, and alkanet are names applied to the coloring substance obtained from the roots of Alkanna tinctoria (L.) Tauch. of the Boraginaceae. The plant is also called false alkanet, orcanette, ox-tongue root, stone-weed, orcanella, or dyer's bugloss. Originally the name alkanet was applied to henna, Lawsonia alba Lam. (Perkin and Everest, 1918:72).

Alkanet is an ancient dyestuff which was well-known to the Romans. The chemical formula of the coloring compound, called alkannin, has long been disputed. Bentley (1960:204) gives the formula as $C_{16}H_{16}O_5$ and describes it as a quinoid pigment. Perkin and Everest (1918:72) report that the roots of alkanet contain 5 to 6% alkannin.

Alkannin forms a red powder which is blue in alkaline solutions. It is still used to color wines, pomades, hair oils, and sweets since it is harmless to ingest. It can also be used to indicate pH. Alkannin has been used to form a violet-carmine lake used in painting. The lake is semi-transparent and the color is not permanent (Weber, 1923:120).



Alkannin

(from Bentley, 1960:204)

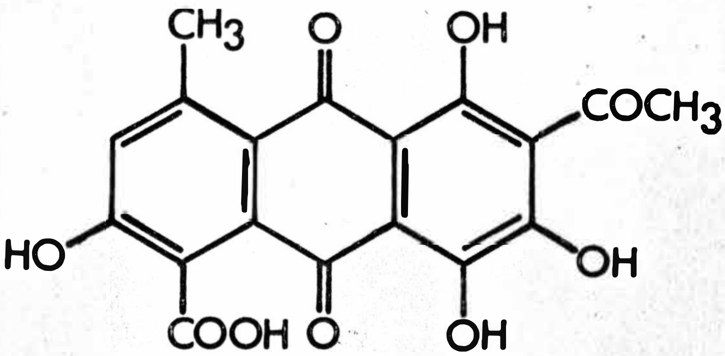
Animal Reds

Kermes

There are several organic animal colors worthy of mention in that they are formed by insects which are associated with certain plants and were originally thought to be plant products.

Kermes may be the most ancient dyestuff on record. It was known to Moses and was used in the East in very early times (Perkins and Everest, 1918:95; Heath and Milligan Mfg. Co., 1897:26). Kermes was once called vermiculus (a little worm) or vermiculara, from which was derived the name of a similar hued inorganic pigment, vermilion. Kermes was very important in medieval dyeing and painting, and it is more permanent than cochineal and brighter than madder (Mairet, 1917:67).

The dye is derived from the dried body of the female *Kermoccus ilicis* L., an insect found on a Mediterranean oak, *Quercus coccinea* Wangenh. The coloring compound is kermesic acid ($C_{18}H_{12}O_9$) (Gettens and Stout, 1934:123; Bentley, 1960:208-209). Flavokermesic acid ($C_{13}H_8O_6$), a yellow or orange substance, is also present in small quantities (Mayer, 1947:144). For a long period the dried red clusters were thought to be berries and the dye was considered a plant product.



Kermesic acid

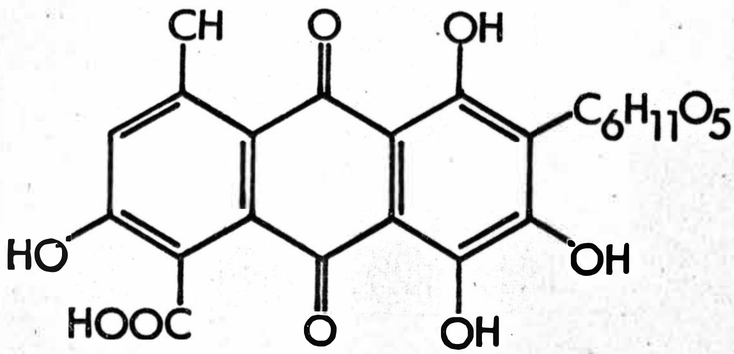
(from Bentley, 1960:208-209)

Cochineal

Cochineal is very closely related to kermes and is obtained from the female of a scale insect, *Dactylopius coccus* Costa, which is found on *Nopalea coccinellifera* (L.) Salm.-Dyck., an opuntia cactus of Central America. The coloring substance of cochineal is carminic acid (Mayer, 1947:137), and the pigment as used by artists is called carmine lake. The discovery of the more brilliant cochineal by Spanish explorers in Mexico in 1518 (Heath and Milligan Mfg. Co., 1897:60) led to the demise of the kermes industry. In turn, cochineal has been largely replaced by the synthetic azo dyestuffs.

Indian lake

The lac insect, *Laccifera lacca* Kerr, from which we obtain shellac, is also the source of a pigment called Indian lake. The insect is found mainly on trees of the genera *Butea, Ficus,* and *Croton,* but especially on the species *Ficus religiosa* L. (peepul tree, bot tree) of the Moraceae, *Zizyphus jujuba* Mill. (common jujub, Chinese jujub) of the Rhamnaceae, and *Butea superba* Roxb. (bastard teak, Bengal kino) of the Leguminosae (Perkin and Everest, 1918:90; Gore *et al.*, 1962:134). These are all Asiatic species. Most of the



Carminic acid

(from Mayer, 1947:137)

commercially marketed lac dye is obtained from trees on the hilly banks of the Ganges River in India, although it is collected and used elsewhere in the Far East.

According to Weber (1923:64) the gravid female insect punctures the bark of the tree and becomes enclosed in the exuding juice or resin. The resin hardens and the young develop in the body of the dead female. When the young insects emerge they leave a red substance in the resinous deposit. This resin is collected by breaking the deposits off of the twigs of the tree. The red color is due to the presence of laccaic acid.

Indian lake is an old pigment and was used in manuscript painting at least as early as the 13th century (Weber, 1923:63). It was used in painting until the synthetic organic pigments became widely available. It produces a less brilliant red than the other insect pigments and is not permanent.

YELLOWS

Gamboge

Gamboge, called also gambogium, gummigutt, gomaguta, gommegutte, and gomma gutta, is a rich yellow-orange gum resin and was used for painting from early times in the Far East. It is obtained from species of *Garcinia* (Guttiferae) found usually in the East Indies, China, India, Ceylon, and Thailand. The major commercial sources are *Garcinia hanbryi* Hook., the Siam gamboge tree, and *G. morella* Desv. Other important gamboge sources are *G. cochinchinensis* Chois., *G. cambogia* Desv., *G. pictoria* Roxb., and *G. travancorica* Hook. (Uphof, 1959:166).

The gum resin was once important in European commerce and was treasured by early Flemish painters for use with drying oil media (Gettens and Stout, 1934: 115; Remington and Francis, 1954:202). Today it is used in watercolors and in alcohol varnishes and gold lacquers. Gamboge is mixed in varying proportions with Prussian blue to form Hooker's green.

The gum resin is obtained by making spiral incisions in the lower bark and collecting the effluent milky liquor in hollow bamboo canes. It is dried for about a month, heated until hard, and then transported.

It consists of about 18 to 25% gum, 64 to 80% resin, and various impurities such as wax, ash and vegetable detritus (Dieterich, 1920:389-391; Remington and Francis, 1954:202; Chatfield, 1953:248).

Gamboge is poisonous and has strong purgative properties; it has been used medicinally. The coloring constituents are present in the resin portion. These are α-, β-, and γ-garcinolic acids ($C_{23}H_{28}O_6$, $C_{25}H_{32}O_6$, and $C_{23}H_{28}O_5$) (Mayer, 1947:258-259). The resin itself is chiefly gambogic acid ($C_{30}H_{35}O_6$) (Dieterich, 1920:389; Chatfield, 1953:248).

Gamboge is normally fugitive in light and shows a gloss when used in thick layers because of its resin content (Doerner, 1962:67). Eastlake (1960: 441-444) considers gamboge superior to other vegetable yellows for oil painting. There are several processes whereby the gum portion of gamboge may be removed, thereby improving its properties in oil paints. In one process gamboge is dissolved in ether; the gum and impurities settle out, being insoluble. When mixed with oleoresins and varnishes the color is regarded as permanent. Mixed only with drying oil, gamboge has faded badly, but it has lasted very well with Venice turpentine, varnish, and even oil of turpentine. The Dutch mixed it with amber resin varnish, and it has also been used quite successfully with copal resin

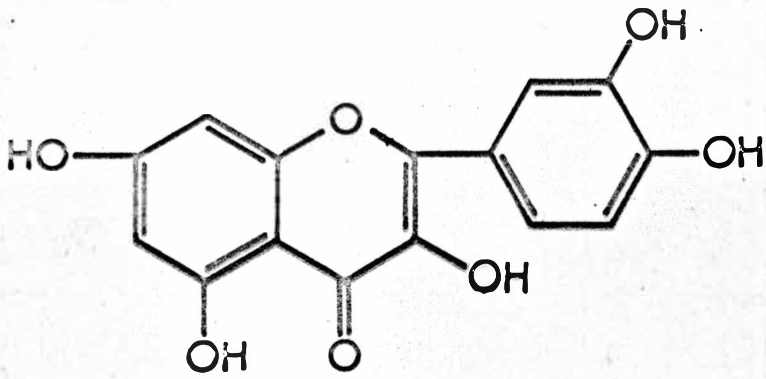
varnishes and wax. It is difficult to explain why it is used almost exclusively as a watercolor today when it is so well suited to oil painting techniques.

Quercitron

Quercitron lake, also called yellow lake or flavine lake, is a yellow pigment derived from the inner bark of the black oak, *Quercus velutina* Lam. (Fagaceae), an oak of eastern North America used in the tanning industry (Hill, 1952:131; Uphof, 1959: 305; Gettens and Stout, 1934:151). Other oaks can also supply lesser amounts of quercitron (Kierstead, 1950: 62; Remington and Francis, 1954:173). The dye substance is quercitin, a tetrahydroxyflavonol ($C_{15}H_{11}O_7$), which is a flavonol also present in corn (*Zea*), ragweed (*Ambrosia*), and certain varieties of apple (*Malus*) (Bentley, 1960:10; Mallette *et al.*, 1960:199). Quercitin-like substances occur also in cauliflower, lettuce, grapefruit peel, spinach, orange peel, lemon peel, and the petals of white, yellow, and red roses. Quercitin is believed to exist in the bark of the oak in the form of the glycoside quercitrin ($C_{21}H_{20}O_{11}$) (Mayer, 1947:188). The dye is extracted from the bark with hot water.

Quercitron was discovered and introduced in 1775 by Bancroft (Perkin and Everest, 1918:186). The tree is found mainly in the middle and southeastern United States and grows to a height of 60 to 80 feet.

Quercitron has been used as a lake for printing



Quercitin

(from Mallette *et al.*, 1960:197)

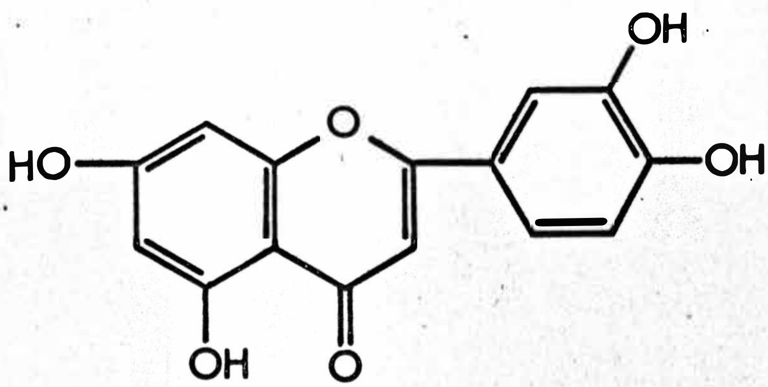
and painting. It is rapidly faded by sunlight but may retain its color well under artificial lighting conditions. In several paintings over 200 years old it has endured rather well.

Weld

Weld is processed from *Reseda luteola* L., called wild woad, weld, or dyer's herb, which was often cultivated in Central Europe in the past and has apparently been used for its dye since neolithic times (Leggett, 1944:47-49; Uphof, 1959:308). It was used by the Gauls and other peoples north of the Alps in the time of Julius Caesar. The coloring compound is luteolin or 5,7,3',4'-tetrahydroxyflavone ($C_{15}H_{10}O_6$) (Mayer, 1947:179; Gettens and Stout, 1934:174). This is the oldest known European dye (Bentley, 1960:1) and also produces the purest, most stable shades of all plant yellows. Made into an artists' pigment it is called gaude yellow and still finds limited use.

Reseda luteola L. of the Resedaceae is an annual found in sandy waste places. It was formerly cultivated to a large extent in France, Germany, and Austria. The plants are gathered in June and July, dried in the shade, and then tied into bundles. The whole plant is used, excepting the roots. The color is extracted by boiling in water or in a weak alum solution. Luteolin is present throughout the plant but occurs in greater amounts in the upper extremities and seeds (Perkin and Everest, 1918:153).

Weld became very important in Europe after the

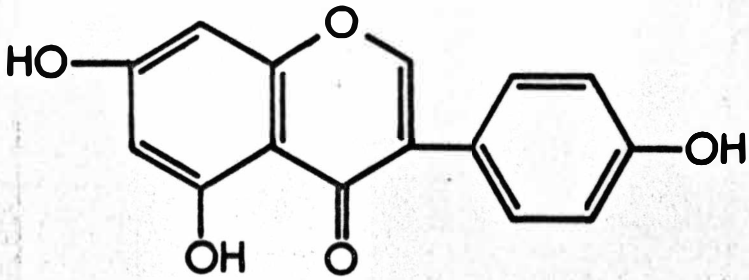


Luteolin

(from Miller, 1957:66)

13th century. It is still grown in Normandy for use in dyeing silk (Thompson, 1956:187-188).

Another yellow used similarly to weld and often called by the same name is obtained from *Genista tinctoria* L., dyer's broom, greening weed, or dyer's greenwood, a small shrub or half shrub of the Leguminosae. It was once much used for making blue wool more green. It grows in Europe, Ural, Caucasia, Asia Minor, and southwest Siberia. The twigs, leaves, and flowers are used as the dye source. *Genista tinctoria* L. contains luteolin as does *Reseda luteola* L. (Miller, 1957:66; Mayer, 1947:179). *G. tinctoria* also yields a similar colored compound, genistein, 5,7,4'-trihydroxyisoflavone ($C_{15}H_{10}O_5$) (Mayer, 1947: 195-196). It exists in the plant as the glucoside genistin ($C_{21}H_{20}O_{10}$). Colored substances of this type are closely related to xanthophyll and are widely distributed in plants, especially in yellow flowers (Kuhn and Winterstein, 1931:754).



Genistein

(from Gore et al., 1962:251)

Saffron

Saffron is a golden yellow from the dried stigmas of the saffron crocus, Crocus sativus L. of the Iridaceae. It contains crocin ($C_{44}H_{64}O_{26}$), a yellow glycoside (Mayer, 1947:71-79). It was known to the ancient Hebrews as "karcom" and is referred to in the Songs of Solomon. The ancient Greeks called it "krokus" and to the Romans it was "karkom." The Arabs introduced its cultivation into Spain, and saffron water was sprinkled on the benches of the theatre in olden days because of its fragrance (Kierstead, 1950:45-46). There are many old recipes which call for saffron as a food flavoring. Kierstead (1950:46) reports that it is said that Henry VIII was so fond of saffron in his food that he forbade the use of it by court ladies for a hair dye. It was often used in the past for decorating book pages, but it is fugitive in light.

Persian Berries

Persian berries lake is a yellow pigment prepared from the dried unripe berries of various Mediterranean and Near Eastern shrubs of the genus Rhamnus (Rhamnaceae). There are several yellow coloring principles in these buckthorns and they may be present in varying quantities in different species. Some have entirely different constituents. Important source species include:

Rhamnus oleoides L. -- from Turkey and Persia

R. saxatilis L. -- from Turkey and Persia, also Spain

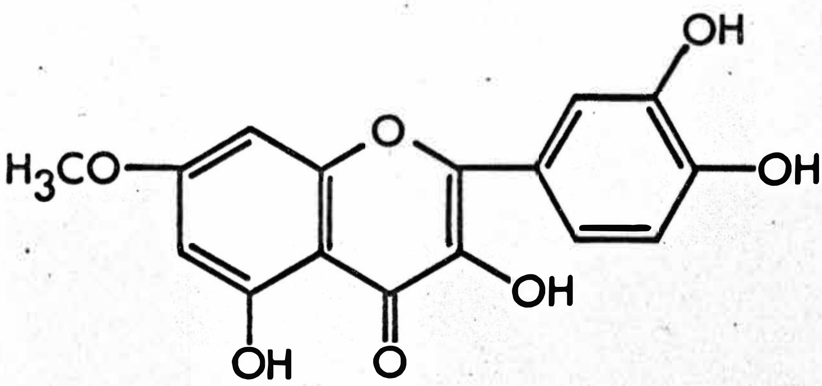
R. infectorius L. -- Avignon or French berries, also from Italy

R. alaternus L. -- Avignon or French berries

R. cathartica L. -- Hungarian berries, also from North Africa and Asia

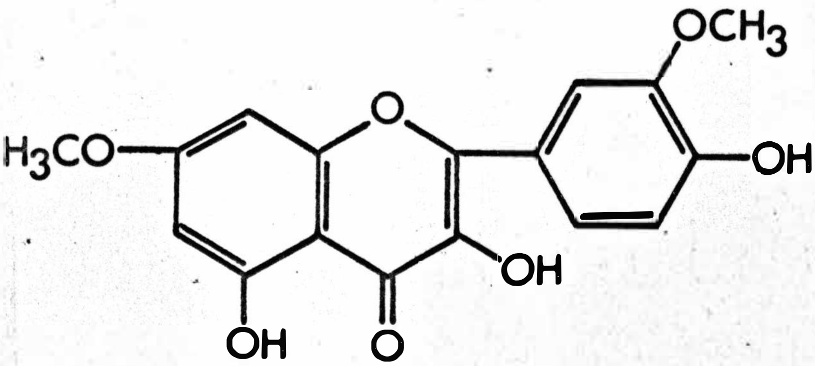
R. graecus Boiss. and Reut. -- from Greece

The characteristic color is usually due to rhamnetin ($C_{16}H_{12}O_7$), which is the 7-methyl ether of quercitin. It usually occurs as a glucoside, the 3-trirhamnoside xanthorhamnetin ($C_{34}H_{42}O_{20}$), and is most abundant in the berries of R. saxatilis L. and R. oleoides L. On hydrolysis with acid this glucoside yields a sugar and rhamnetin (Perkin and Everest, 1918: 206-207; Mayer, 1947:189). Normally accompanying rhamnetin in species of Rhamnus is rhamnazin ($C_{14}H_{14}O_7$),



Rhamnetin

(from Mayer, 1947:189)

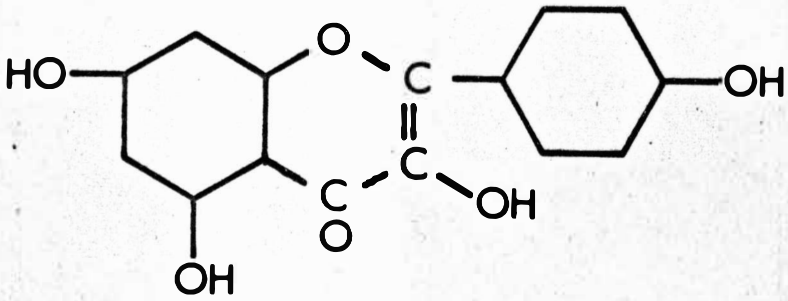


Rhamnazin

(from Mayer, 1947:190)

the 3′-7-dimethyl ether of quercitin. This substance gives orange-yellow shades on aluminum mordants (Mayer, 1947:190) and is present as a glucoside. Glucosides of quercitin are also sometimes found in the berries. Kaempferol ($C_{15}H_{10}O_6$) is a trihydroxy-flavonol present in the berries of R. cathartica L. This is soluble in alkaline solutions with a yellow color. It will dye lemon yellow to olive brown with different mordants (Perkin and Everest, 1918:179-180).

The dyes are usually obtained by boiling the berries in water, and were once very important in dyeing. By precipitating on a base of stannous chloride, rather than the usual alum, a bright orange lake was produced and was popular with calico printers. The lakes are moderately stable in light and were popular with 18th century English and French painters (Gettens and Stout, 1934:136).



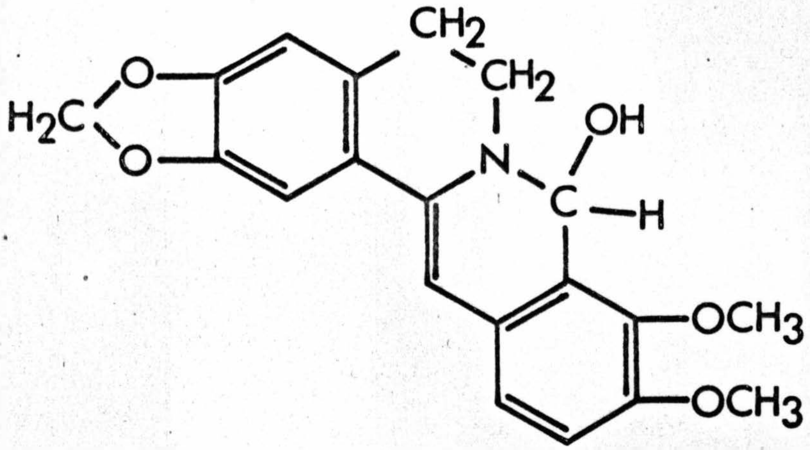
Kaempferol

(from Perkin and Everest, 1918:179)

Brown Stil de Grain

The wood, roots, and bark of the barberry, *Berberis vulgaris* L., are the sources of brown stil de grain. The yellow color is due to berberine ($C_{20}H_{19}O_5$) (Mayer, 1947:317). *B. vulgaris* L. is a compact bush which grows wild in Europe and North America. Berberine occurs in many other plants. Among them are *Jateorhiza miersii* Oliv. of the Menispermaceae (columbo root), *Hydrastis canadensis* L. of the Ranunculaceae (golden seal), from which North American Indians made a dye, and *Mahonia aquifolium* (Lindl.) Don. of the Berberidaceae (Oregon grape) (Rowe, 1924:294).

Berberine is obtained by simmering the cut bark and wood in soft water. It is the only natural basic dyestuff known (Perkin and Everest, 1918:567). The crushed berries of the barberry can also be cooked in water to give a coral colored dye (Kierstead, 1950:65). The lake was once added to oils or varnishes for easel painting.



Berberine

(from Mayer, 1947:318)

Curcuma

Curcumin ($C_{21}H_{20}O_6$) is a yellow substance obtained from the powdered rhizomes and shoots of _Curcuma longa_ L. and other species of _Curcuma_ (Mayer, 1947:93). It is called by various names, including curcuma, turmeric, and terra merita. The plant is indigenous to South Asia and is cultivated in India and China. The best quality is Chinese turmeric and is called "safran d'Inde" (Rowe, 1924:295). In Malaysia it is called the Cha-Kiang root and is used in almost every dish of cookery as well as being the leading yellow dyestuff (Heath and Milligan Mfg. Co., 1897:47).

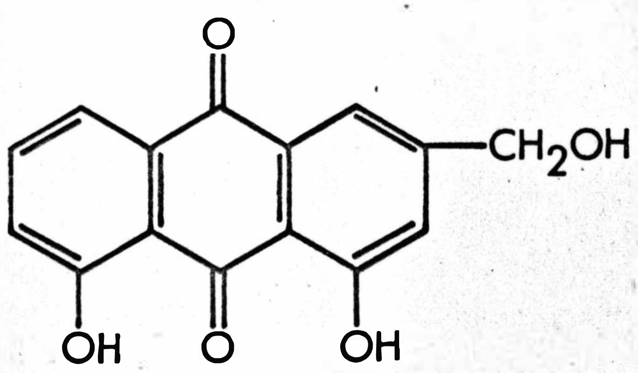
Other good sources of curcumin are _Curcuma viridiflora_ Roxb. and _C. rotunda_ L. Perkin and Everest (1918:388) reported that the rhizomes of a West African plant of the Cannaceae yield a substance which is reputed to be identical with Indian turmeric in taste, smell, and chemical reaction. It is called "African turmeric" and the plant is cultivated in Sierra Leone.

Curcuma has long been used in China for dyeing silk, paper, and wood. It is also used in foods and painting and has been used in Europe. It produces a transparent yellow and was used in miniatures and in the transparent varnish glazes of the Flemish Masters (Bazzi, 1960:50).

Aloin

Many species of *Aloe* of the Liliaceae yield anthraquinones which may be used in dyeing. These were, however, most used medicinally. Aloin is an exudate of the leaves and is a bitter, resinous juice. Leaves are cut transversely and the juice collected and evaporated to dryness.

There are many aloin sources and varying constituents. *Aloe vera* L., one of the sources of Barbadoes aloes and Curacao aloes, is now cultivated in Hawaii. The leaves contain about 45% of a mucilaginous layer. In this a glucomannan is present containing equal quantities of D-glucose and D-mannose (Smith and Montgomery, 1959:349-350). The colored substances aloe-emodin and chrysophanic acid can be prepared from the mucilage. Curacao aloes contain the yellow substances iso-emodin and aloe-emodin (Brody, Voigt, and Maher, 1950). The aloin of some sources has been shown to yield arabinose and aloe-emodin on hydrolysis (Mayer, 1947:135). The chemical formula for aloin and some of its constituents has been long disputed and may still be partially unresolved. It is known that aloe-emodin ($C_{15}H_{10}O_5$) is 4,5-dihydroxy-2-hydroxymethylanthraquinone (Mayer, 1947:135). Its color is orange to yellow.



Aloe-emodin

(from Mayer, 1947:135)

The first attempts to dye fabrics with aloes were made by Boutin in 1840 (Perkin and Everest, 1918:64). He used them to dye wool brown. Aloin will give red colors in acid solutions and orange and yellows with bases. They were used by early Flemish oil painters for making transparent yellow varnish layers (Bazzi, 1960:50).

The chief commmercial sources of aloin (Perkin and Everest, 1918:64; Uphof, 1959:18) include:

Barbadoes aloes from _Aloe vera_ L.

Socratine aloes from _A. africans_ Mill., _A. spicata_ Baker.

Cape aloes from _A. perryi_ Baker., _A. ferox_ Mill.

Curacao aloes from _A. vera_ L.

Jafferabad aloes from _A. abyssinica_ Lam.

Natal aloes from _A. candelabrum_ Tod.

This is merely a sample list as there are many other species in use. Most of the commercially available aloin comes from parts of Africa and the Near East. Yellow emodin pigments are found in many other plants. Wakeman (1919:886) lists some of these species, and included in his list are:

Cassia occidentalis L. -- coffee senna, Leguminosae

C. sophora L. --

C. tora L. -- sickle senna

C. angustifolia Vahl. -- Tennevelley senna

Polygonium cuspidatum Sieb. and Zucc. -- Japanese fleeceflower, Polygonaceae

Rheum officinale Baill. -- medicinal rhubarb, Polygonaceae

R. palmatum L. -- sorrel rhubarb

Rhamnus cathartica L. -- buckthorn, Rhamnaceae

R. japonica Maxim. -- Japanese buckthorn

R. purshiana DC. -- Cascara buckthorn, bearberry, bearwood

R. frangula L. -- alder buckthorn

Sunflower Yellow

The flowers of the sunflower, Helianthus annuus L. (Compositae), have a transparent yellow which was used by Flemish Masters in varnish glazes (Bazzi, 1960:50). A yellow sunflower dye was also used by the American Indians (Uphof, 1959:182). No studies of the floral pigments of H. annuus L. could be located, but Beal (1949) reported the presence of quercitin-like substances from other members of the genus Helianthus. Whether such yellow substances are responsible for sunflower yellow is undetermined.

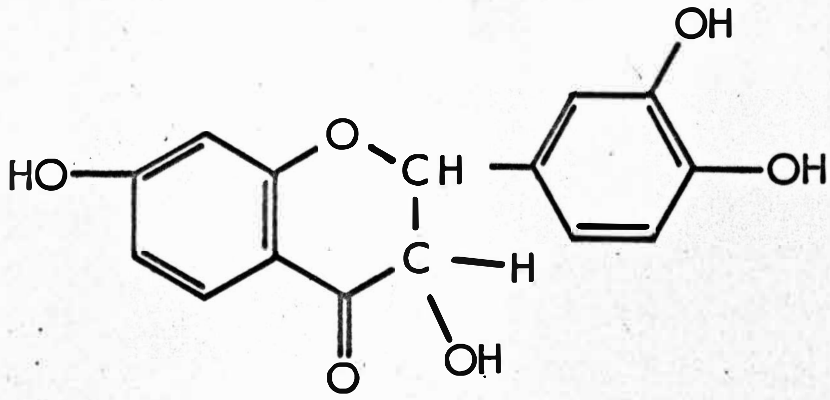
Fustic

Young fustic

Young fustic is obtained from the common smoke tree or Venetian sumac, *Rhus cotinus* L. (syn. *Cotinus coggyria* Scop.), of the Anacardiaceae. In 15th century Italy it had some importance in making lakes for painters, as well as in dyeing (Thompson, 1956:188). The small tree is native to southern Europe and the coloring matter is obtained from the wood of the stem and larger branches.

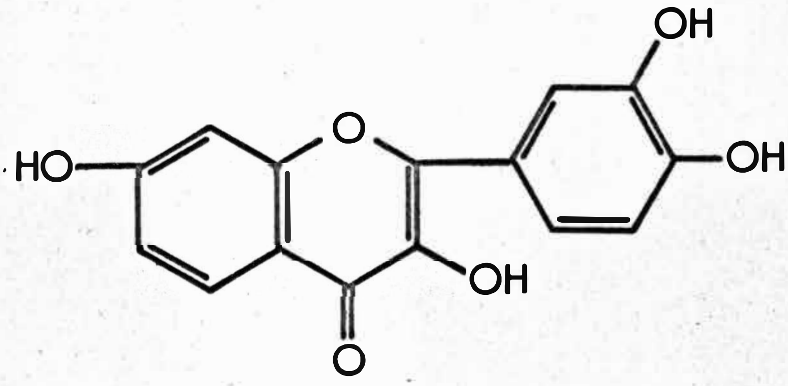
The main yellow coloring substance is fisetin ($C_{15}H_{10}O_6$), 3,7,3',4'-tetrahydroxyflavone (Mayer, 1947:184; Rowe, 1924:292; Remington and Francis, 1954:173; Perkin and Everest, 1918:182). It occurs as a glucoside combined with tannic acid in the heartwood of *Rhus cotinus* L. and in the wood of *Quebrachia lorentzii* Griseb. (Anacardiaceae), quebracho colorado. Another yellow substance, fustin ($C_{15}H_{12}O_6$), may be obtained after removing tannic acid from fisetin (Mayer, 1947:184).

The color is usually extracted by boiling the wood in water. Fisetin is a stong coloring substance and gives hues almost identical to quercitin and rhamnetin (Perkin and Everest, 1918:182-183).



Fustin

(from Mayer, 1947:184)



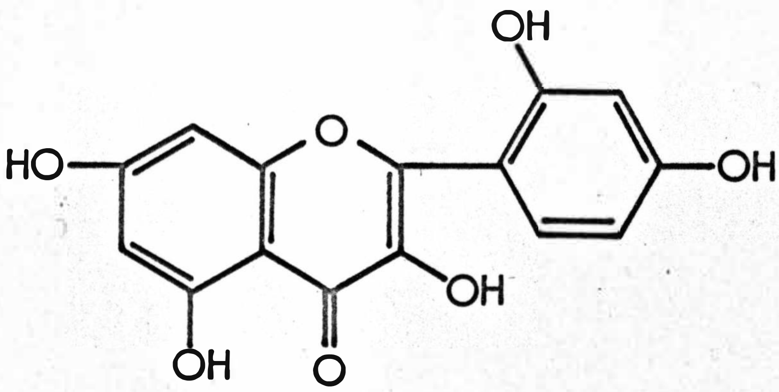
Fisetin

(from Perkin and Everest, 1918:183;
Rowe, 1924:292; Mayer, 1947:184)

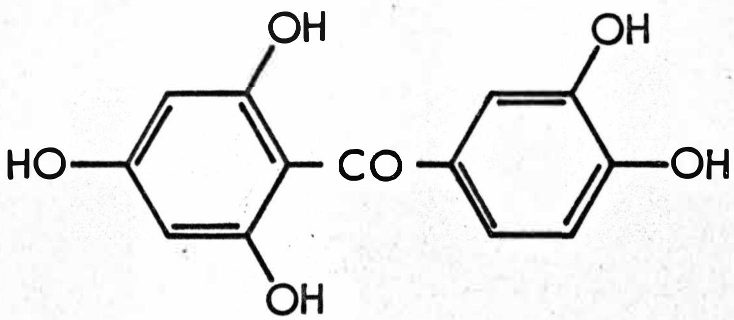
Old fustic

Old fustic is sometimes substituted for young fustic and vice versa. Old fustic is a yellow or olive dye from the heartwood of *Chlorophora tinctoria* (L.) Gaud. (Schery, 1952:245), a shrub or tree of tropical America. The tree grows wild, often to a height in excess of 60 feet. It is transported as debarked logs, the best quality being shipped from Cuba. Brazil, Costa Rica, Nicaragua, Panama, Salvador, Columbia, Venezuela, and Jamaica also supply the wood. Old fustic is sometimes called cubawood, yellow brazilwood, bois jaune, or gelbholz.

In 1864, Hlasiwetz and Pfaundler found two yellow constituents in old fustic (Perkin and Everest, 1918: 115). These are morin ($C_{15}H_{10}O_7$), 3,5,7,2',4'-pentahydroxy-flavone, and maclurin ($C_{13}H_{10}O_6$), 2,4,6,3',4'-pentahydroxy-phenone (Mayer, 1947:187; Remington and Francis, 1954: 173; Rowe, 1924:292). These same substances are found in the bark and roots of the osage orange tree, *Maclura pomifera* (Raf.) Schneid., of the Moraceae. The dye obtained from the osage orange tree gives slightly purer shades of yellow, is more fast to light, and has a high tannin content, making it a good dye for leather (Rowe, 1924:292).



Morin



Maclurin

(from Perkin and Everest, 1918:117;
Rowe, 1924:292; Mayer, 1947:187)

Old fustic has been used primarily as a dye for wool. It is the most important yellow dyestuff for this purpose (Mairet, 1917:87; Perkin and Everest, 1918:218).

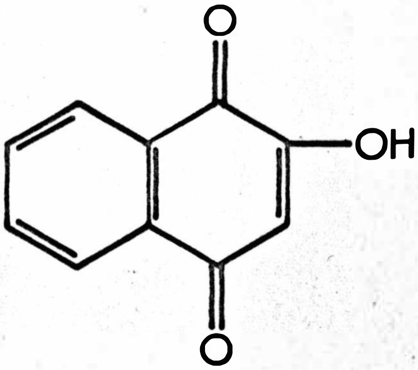
Celandine

The juices of saffron and of the greater celandine, *Chelidonium majus* L., are mentioned in medieval manuscripts in paint recipes for imitating the color of gold (Thompson, 1956:184). Celandine is a member of the Papaveraceae and is a perennial herb of Europe and Asia. It has been introduced into North America.

In Europe, *C. majus* L. grows as a weed along roadsides and waste places, and when bruised exudes a yellow or orange colored latex. The juice is bitter and has a disagreeable odor. It contains several alkaloids, is used in pharmacy as a drug, and was once considered a cure for warts and boils. The juice of the root is more orange than that of the stems and leaves. The color is due, at least in part, to the presence of berberine (Perkin and Everest, 1918:578), already mentioned in connection with *Berberis vulgaris* L.

Henna

Henna is another old dye probably used in early art. There is reference in Isa. 49:16 and in other places in the Bible to the art of tattooing by rubbing powder of henna into punctures in the flesh (Heath and Milligan Mfg., 1897:27). Henna is obtained from <u>Lawsonia alba Lam.</u> of the Lythraceae and is also called camphire. In India it is an ornamental garden or hedge shrub. The yellow color is due to the presence of lawsone ($C_{10}H_6O_3$), 2-hydroxy-1,4-naphthaquinone (Mayer, 1947:105). This occurs in the leaves and is extracted by aqueous sodium carbonate. It is used to dye wool and silk orange.



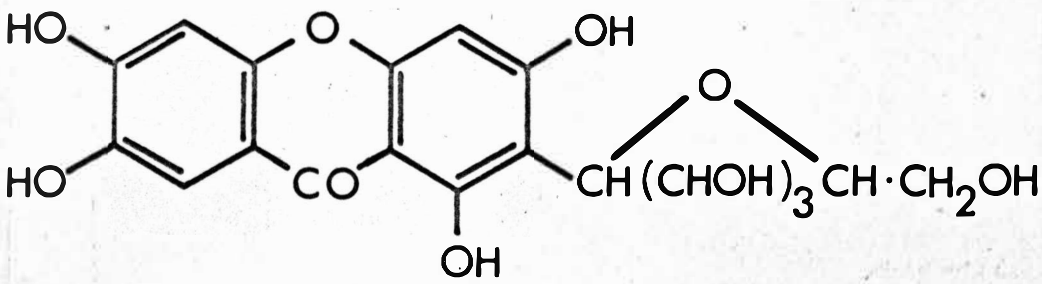
Lawsone

(from Mayer, 1947:105)

Indian Yellow

Indian yellow is especially interesting in that it is produced by interaction between a plant and an animal. It is prepared in India from the urine of cows fed on the leaves of the common mango, *Mangifera indica* L. (Anacardiaceae). Mangiferin ($C_{19}H_{18}O_{11}$) is a constituent of various parts of *M. indica* L. and is a precursor of Indian yellow (Gore *et al.*, 1962:331-333). The coloring substance of Indian yellow is a magnesium or calcium salt of euxanthic acid ($C_{19}H_{16}O_{11}Mg$). The dried extract is sent to market in lumps which are later powdered and purified.

Indian yellow, also called Monghr piuri and other names, is used both in watercolor and oil painting in the form of a lake. In oil it is a poor dryer and requires the addition of a varnish. It is a very expensive pigment and has therefore been frequently adulterated. This has had a detrimental effect on its reputation. Actually, pure Indian yellow lake is very resistant to light and is rated as a permanent pigment (Doerner, 1962:66; Uphof, 1959:238). Direct sunlight will bleach it very slowly (Gettens and Stout, 1934:119). Its color is a rich, warm golden yellow which is transparent and excellent for glazing.



Mangiferin, probable structure
(Gore et al., 1962:332-333)

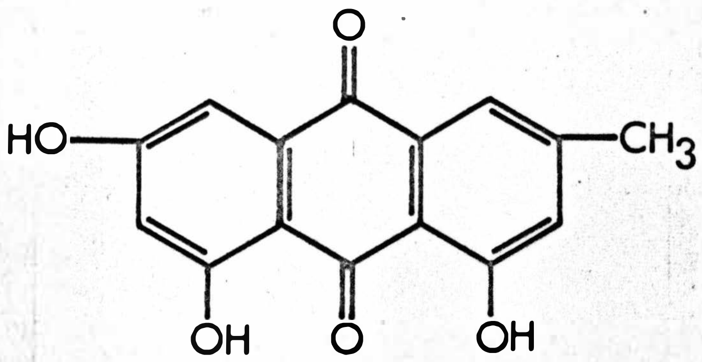
Miscellaneous Trees

It is known that the wood and bark of many trees were sources of yellows for medieval and Renaissance painters in Europe, but all the species which have been used for this purpose are no longer known. Quercitron, berberine, and fustic have already been considered. In all probability yellow plant pigments used by painters were first discovered and employed by dyers. To some extent it is known what dyes were used during these times and which trees and shrubs will yield yellow dyestuffs. From this knowledge we can speculate as to what plants may have been used by painters.

Little known yellows that were definitely used by artists were obtained from the bark of walnut trees (*Juglans*) and from the bark of apple trees (*Malus*) (Thompson, 1956:188). Apple tree yellow was used in 15th century Germany. Kierstead (1950:84) states that crab and other apple barks will make beautiful green-yellow dyes, the color depending on the mordant used and the variety of apple. The husks of the fruit of several species of *Juglans* have been used in dyeing, and these will give orange, yellow, tan, brown, and gray dyes on extraction with

hot water (Kierstead, 1950:90; Uphof, 1959:200; Schery, 1952:244).

The fresh inner bark of the European ash, Fraxinus excelsior L. (Oleaceae), yields a yellow dye. Another yellow is obtained from the bark of Rhamnus frangula L. and R. cathartica L. Mayer (1947:130) states that the yellow coloring compound emodin ($C_{15}H_{10}O_5$) occurs as the glycoside frangulin in the barks of species of Rhamnus. The bark and shoots of the Lombardy or Italian poplar, Populus nigra var. itálica Du Roi (syn. P. pyramidalis Borkh.) of the Salicaceae, give a yellow dye, and a yellow may be obtained from sweet willow, Salix pentandra L. (Salicaceae) (Mairet, 1917:32). Yellows for dyeing may be obtained from the leaves of several European trees, including the pear tree, Pyrus communis L. (Rosaceae), the plum tree, Prunus domestica L. (Rosaceae), and species of poplar and willow. Dyes of a more brown shade are obtained from the bark of the black or European alder, Alnus glutinosa Medic. (Betulaceae), from the bark of a birch, Betula pubescens Ehrh. (Betulaceae), and from the leaves of a larch (Larix) (Mairet, 1917: 30-32).



Emodin

(from Mayer, 1947:130)

Lily Pollen

Thompson (1956:188) states that lily pollen is mentioned in medieval recipes for yellow artists' paints. It has been disclosed that the pollen of *Lilium candidum* L. (Madonna lily, Annunciation lily, or Bourbon lily) of the Liliaceae contains flavone pigments (Cappelletti and Tappi, 1948). These are believed to be of the oxyflavone type and probably account for the useful yellow color. Exactly how the color was used is not clear, but it probably made a convenient water-soluble yellow for use as a transparent watercolor.

GREENS

Bladder Green

Bladder or sap green is a dark, rich, transparent green which is usually rather olive in color. It is obtained from the berries of the common or purging buckthorn, Rhamnus cathartica L. (Rhamnaceae), which grows in Europe. The main constituent of bladder green is kaempferol ($C_{15}H_{10}O_6$), 3,5,7,4'-tetrahydroxyflavone (Mayer, 1947:183). This substance was synthesized by Kostanecki and Tambor in 1904 and is soluble in alkaline solutions, giving a yellow color. Kaempferol will dye lemon yellow to olive brown depending on the mordant used. Also present in the berries are glucosides of rhamnetin, quercitin, and xanthorhamnetin (Perkin and Everest, 1918:211).

Sap green is more yellow or more green depending on the ripeness of the berries. The juice of the berries was added to temper and enrich the green pigment verdigris which was popular in medieval painting. Sap green was used only as a watercolor, and the sticky juice of the berries was sometimes used without any additional binding medium. Usually the juice was allowed to dry and thicken to a dense syrup. Gum could be added to improve its adhesive properties.

The color is very fugitive, though it is less so when added to alum (Thompson, 1956:170-171). It was valued especially as a glazing color because of its transparent nature.

Chinese Green

Chinese green or locao is obtained from *Rhamnus globosa* Bge. and *R. utilis* Decne., two oriental members of the Rhamnaceae. It is used in the form of a powder made from the bark or leaves. It forms a lightfast blue-green dye which is used by the Chinese for coloring cotton and silk (Mayer, 1947:254). It has long been used in oriental painting.

The constitution of Chinese green is still uncertain. Natural green coloring matters are comparatively rare, and it is possible that Chinese green is a mixture of substances. The presence of yellows, such as emodin, in species of *Rhamnus* has already been discussed. If a blue compound were also present they would together give a green color. Blue indigo may have been isolated from at least one species of *Rhamnus* and this species is listed in the section concerned with indigo.

Iris Green

Iris green was the chief rival of bladder green in late medieval manuscript painting. The color was most often prepared as a "clothlet" (Thompson, 1956: 171). Pieces of cloth were first dipped in an alum solution and dried. Then they were dipped in the juice of the flowers, dried, and the whole process repeated several times more. Occasionally the juice was just mixed with alum and thickened.

Iris germanica L. and the Florentine iris, *Iris florentina* L. (Iridaceae) were apparently the species most used. Their flowers give a purple juice which becomes clear, bright green when alum is added. This green was highly favored by artists during the 14th and 15th centuries and even into the 17th century. Kierstead (1950:87) reports that iris blossoms may be used for dyeing, giving yellows, greens, blues, and grays depending on the flower used.

The specific constituents which make up the iris green dye have apparently not been investigated, however, work has been done with iris floral pigments. Guilliermond (1931) states that the formation of anthocyanin pigments in the sepals and petals of *Iris germanica* L. is preceded by the secretion of

oxyflavonols. During the course of development of the flower these become anthocyanin pigments with color changes through browns and reds to violet. The presence of both yellow flavonols and a blue or purple anthocyanin could together result in a green color, or the green could be formed by reaction of one of the pigments with the alum mordant. Eastlake (1960:458) reports that the liliengrün used by painters in the 17th century came from the purple flowers of *Iris germanica* L. The purple anthocyanin may give a green in alum.

Thompson (1956:172) also mentions that a yellow discussed in 14th and 15th century recipes for painting may have been obtained from iris pollen. Blues from iris were also used in painting at this time.

Miscellaneous Greens

There were several other natural greens used in medieval painting. In most cases the specific source is not well recorded or is questionable. Greens known in the 14th century and probably earlier include a green from the flowers of a plant called "aquileia" and a green from the berries of a honeysuckle. Green paints from leaves were used in the early 13th century and possibly in earlier times. The leaves of nightshades (Solanum), elders (Sambucus), and mulberries (Morus) were most used. Thompson (1950:172-173) states that in all these greens chlorophyll was probably the chief pigmentary constituent.

Bazzi (1960:50) mentions the use of violet green, stramonium green, tobacco green, and Spanish ennel green. She states that these were extracted from pressed petals and mixed with water and alum or sometimes lime. They were used for watercolors as a substitute for sap green.

BLUES

Woad

When the Roman army invaded England in 55 B.C. they found descendants of an ancient Celtic race. They were called painted people or "Picts" after their custom of painting their bodies. They punctured their skin with tools of flint and rubbed a dye from the woad plant, Isatis tinctoria L., into the cuts to form blue designs on the body (Kierstead, 1950:15).

Isatis tinctoria L. (Cruciferae) is native to Greece and Italy and has been grown from antiquity in Egypt, England, and Sweden. Woad is considered a "gross feeder," and it will exhaust the land it grows on unless the salts that it uses are continually replaced. Much land was exhausted in medieval Europe because of constant woad cultivation. Woad was a very important source of potash in medieval England. The stems, roots, and waste of woad plants from dye making were burned. Potassium carbonate and other mineral salts were recovered from the ashes in the form of a lye by washing with water (Thompson, 1956: 136-137).

Woad was important in English economy for a long

period, dating at least from the 13th century, and was closely allied to the English wool industry. Kierstead (1950:30) declares that it was the most important dye of the Middle Ages. It was sometimes added to kermes or madder to make a purple dye, or added to a yellow to make a green. Even a black dye was made from it. It was used by medieval artists and manuscript painters who called it "flower of woad." The color is due to the presence of indigo, the same substance derived from the indigo plants, species of *Indigofera*.

There are many ways to prepare woad dye. The following method, given by Kierstead (1950:32), is an old process apparently used in medieval England. The leaves of the woad plant were cut at the base and quickly crushed or ground to a pulp. This was put into small heaps and allowed to drain. When sufficiently dry to knead into lumps they were made into balls three to five inches in diameter. These were placed on wicker trays and allowed to dry in ventilated sheds for about one month. After drying or storage the balls were ground to a fine powder and fermented. Fermenting was done by spreading the powder two or three inches deep in a roofed shed open

to the air and soaking it with water. The resulting paste was kept wet and turned frequently for about nine weeks. The paste was then cooled and packed in cakes for marketing. Woad making in England became an extremely profitable industry. It was estimated that nine pounds of woad leaves would yield one pound of prepared woad. "As the woad plant was abundant and hardy, this was considered fair return, and in average years, profit derived from it was often greater than the value of the land on which it was grown" (Kierstead, 1950:32).

In making "woad vat" for dyeing the prepared woad was heated in water and a mordant, usually alum, was added. This was heated for several hours and during this time a blue scum would rise to the surface. This by-product of woad dyeing was the material employed by artists. It was collected, dried, powdered, and used as a paint pigment.

Indigo

The blue dye substance obtained from indigo plants is indigo ($C_{16}H_{10}O_2N_2$). This is the same substance responsible for the blue of woad. The precursor of indigo is the glucoside indican ($C_{14}H_{17}O_6N$), which is present primarily in the leaves of woad, *Isatis tinctoria* L., and of the true indigo plant, *Indigofera tinctoria* L., and other species of *Indigofera* (Mayer, 1947:316). The yield of woad is much lower.

Since the coloring matters of woad and indigo plants are the same it is impossible to distinguish between them visually or chemically. This has presented some difficulty in attempts to determine which plants were grown and used by different cultures or what the sources were for pigments appearing in certain paintings.

There are ancient records in Sanskrit which describe the method of indigo preparation and indicate that indigo may have been known to the people of Asia as a dye and cosmetic for over 4000 years (Kierstead, 1950:34; Perkin and Everest, 1918:475). The indigo plant is native to India and has been used for dyeing and painting in the Far East from very early times.

The Early Egyptians used indigo, but it is believed that they cultivated woad and obtained indigo from this source. The Romans used the indigo coloring matter in painting and used it to decorate parade shields around 200 A.D. Indigo was supposedly named after India by the Romans because this is where their supply was obtained. In 1295, Marco Polo (Heath and Milligan Mfg. Co., 1897:45) said:

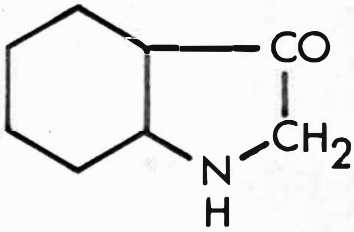
> Indigo, of excellent quality and in large quantities, is made here [Coulan, India]. They procure it from an herbaceous plant, which is taken up by the roots and put into tubs of water, where it is suffered to remain until it rots, when they press out the juice. This, upon being exposed to the sun and evaporated, leaves a kind of paste, which is cut into small pieces of the form in which we see it brought to us.

In the 17th century Indian indigo began to be imported to Europe in large quantities. This destroyed the European woad industry as woad has a lower yield and was consequently a more expensive source of indigo. The indigo plant has been grown throughout much of the world. It was first grown in the New World in 1744 when it was introduced by Eliza Pinckney in South Carolina (Kierstead, 1950:34). In 1880 Baeyer synthesized indigo (Gettens and Stout, 1934:120) and cultivation has declined greatly since 1900 due to the availability of inexpensive synthetic dyes.

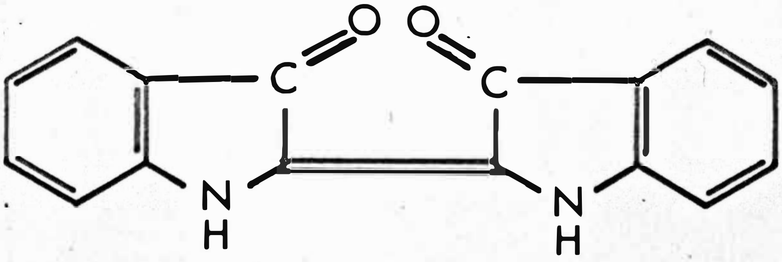
Of prime importance in indigo plant cultivation is the weight of indigo yield per acre, which in turn depends on the percentage of leaf present on the plants and the amount of indican present in the leaves. A good plant will be 40% to 65% leaf. Indigo yield usually increases through the year. The leaves of young plants are relatively low in indican, while the young leaves of an old plant are relatively high in indican (Perkin and Everest, 1918:478-479).

The glucoside indican ($C_{14}H_{17}O_6N$) is believed to be hydrolized by the enzyme indemulsin which exists in the plant, and also by dilute acids (Remington and Francis, 1954:170). The products of this are the colorless indoxyl and a sugar. Upon exposure to atmospheric oxygen two indoxyls join to form one molecule of indigo. Natural indigo, especially the East Indies types, contain the impurity indigo red or indirubin ($C_{16}H_{10}O_2N_2$) (Mayer, 1947:316).

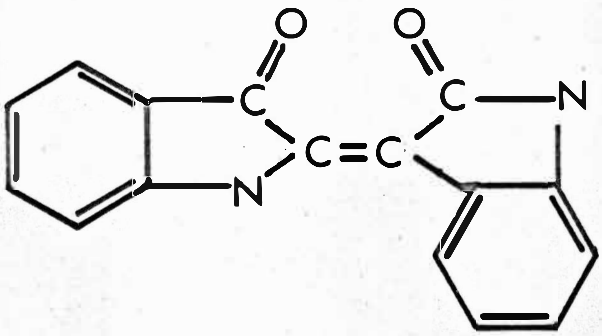
As with woad, there are many methods for the preparation of indigo. The early processes were done by hand. The following early method is given by Kierstead (1950:35). The leaves of the indigo plant were cut early in the morning and steeped in water, one pound of leaves to a gallon of water. After nine



Indoxyl (from Remington and Francis, 1954:171)



Indigo (from Mayer, 1947:316)



Indirubin (from Mayer, 1947:316)

to fourteen hours of soaking, the liquid was run off into a large container. Here it was beaten violently with bamboo sticks to expose as much surface as possible to atmospheric oxygen. The indigo precipitated out and settled to the bottom after which the liquid was drawn off. The indigo was then strained, sterilized by boiling, dried, and cut into blocks. The blocks were powdered by pounding to prepare a pigment for painting.

Indigo is first mentioned in medieval European painting in the 11th century (Eastlake, 1960:120). It is found in Italian painting before the 15th century and was used by the Flemish both in watercolor and drying oil media. Mixed with a resin, the pigment has survived centuries in perfect condition in a few Flemish masterpieces (Bazzi, 1960:50). In other works it has faded. Indigo is slightly similar to Prussian blue in color and is good for covering and glazing when used with drying oil media (Wild, 1929:30).

There are a great many plants which are sources of indigo. These include (Perkin and Everest, 1918: 475-476; Mayer, 1947:316; Remington and Francis, 1954: 170; Rowe, 1924:299; Uphof, 1959:150):

Indigofera tinctoria L. -- true indigo plant, Indian indigo plant; Leguminosae

I. disperma L. --

I. argentea L. --

I. arrecta Hochst. -- Natal indigo plant

I. paucifolia Delile -- Madagascar indigo plant

I. secundiflora Poir. -- Guatemala indigo plant

I. anil L. --

I. pseudotinctoria R. Br. --

I. angustifolia L. --

I. arcuata Willd. --

I. caroliniana Walt. --

I. cinerea Willd. --

I. longeracemosa Boiv. --

I. coerulea Roxb. --

I. endecaphylla Jacq. --

I. glabra L. --

I. hirsuta L. --

I. indica Lam. --

I. mexicana Benth. --

I. leptostachya DC. --

Lonchocarpus cyanescens Benth. -- Yoruba indigo, West Africa; Leguminosae

Tephrosia tinctoria Pers. -- Leguminosae

Strobilanthes flaccidifolius Nees. -- Acanthaceae

Polygonium tinctorium Ait. -- cultivated in Japan, China, and Russia; Polygonaceae

Isatis tinctoria L. -- woad, cultivated in Europe; Cruciferae

Gymnema tingens Spreng. -- Asclepiadaceae

Marsdenia tinctoria R. Br. -- Asclepiadaceae

Eupatorium laeve DC. -- Compositae

E. indigofera Perodi. -- Compositae

Phaius grandiflorus Reich. -- Orchidaceae

Calanthe veratrifolia R. Br. -- Orchidaceae

Other plants which may contain indican are:

Mercurialis perennis L. -- Euphorbiaceae

Fagopyrum esculentum Moench. -- common buckwheat; Polygonaceae

Fraxinus excelsior L. -- European ash; Oleaceae

Baptista tinctoria (L.) R. Br. -- Yellow wild-indigo, rattle weed; Leguminosae

Rhamnus alaternus L. -- Rhamnaceae

Turnsole

Turnsole, also called folium, is obtained from the fruit of *Chrozophora tinctoria* Juss., a member of the Euphorbiaceae which grows in southern Europe. Turnsole has not been used for a long time and it seems that no information is available on its coloring constituents. Turnsole acts as an indicator substance and is red in acid solutions, violet in neutral solutions and blue in bases (Gettens and Stout, 1934:162; Thompson, 1956:126). It was used most as a violet or blue.

Turnsole was not used prior to medieval times and probably had a rather late introduction. It was not prominent until the 14th century but may have been used in the 12th century. Turnsole was not much used as a dye, but was used mostly for painting, writing and flourishing in books and manuscripts. The blues and violets of turnsole were held in high regard in 14th century Italy. Manuscript painters used turnsole in combination with the mineral pigment azurite to form a rich blue. Turnsole gives a transparent blue and shades of violet and red can also be obtained (Thompson, 1956:141-144).

Turnsole was usually prepared in "clothlets" which were a convenient way of preparing vegetable dyes for painting. Many dyes were made this way for medieval painting but turnsole was the most popular. Thompson (1956:143) gives the method of preparing turnsole clothlets. The fruit of *Chrozophora tinctoria* Juss. were collected in the summer and a juice was expressed from them. Linen cloths were soaked in the juice and dried. This process was repeated until the cloth had soaked up a large amount of dye. If a violet dye was desired the cloths were soaked in lime water and dried prior to dipping in the juice. This neutralized the natural acidity of the expressed juice. In order to prepare a more blue color the violet dye soaked cloths were exposed to ammonia vapors. In the presence of a base the dye became more blue but later tended to return to violet.

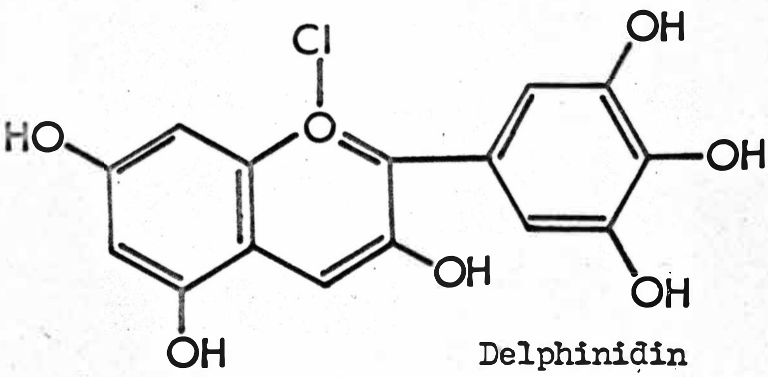
The clothlets were a convenient way of using dyes for painting. The coloring substances were used as water-soluble stains rather than precipitated lake pigments and gave very transparent colors. A clothlet of desired color was wet with water to get a solution of the stain. Glair, a medium prepared from egg white, or gum was added as a binding medium (Thompson, 1956:144).

Indigo and turnsole appear to have been the most important blues of medieval times. Their names were applied to substitute blues obtained from elderberries (*Sambucus*), mulberries (*Morus*), bilberries (*Vaccinium*), and centaureas (*Centaurea*). Perkin and Everest (1918:565) mention a "tournesol en drapeaux" which was long manufactured in France. Judging from the method of preparation and the color reactions this was undoubtedly the turnsole of *Chrozophora tinctoria*. It is supposed to have been used in its red condition by the Dutch to color the outside of cheeses.

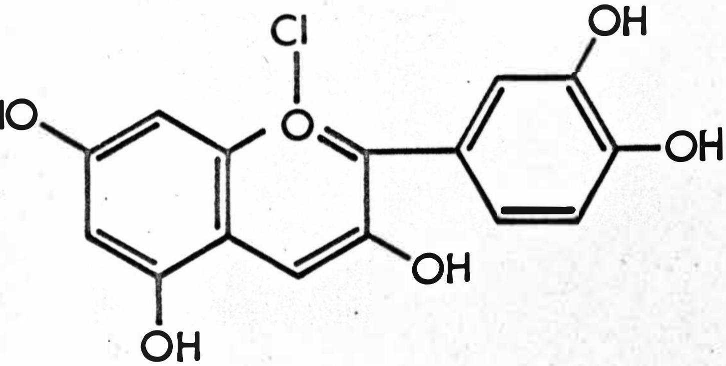
Cornflower Blue

Cornflower blue was prepared from Centaurea cyanus L., a European composite often grown in North America. In medieval times the dried petals were soaked in alcohol to yield a purple-blue dye which was used in watercolor painting (Bazzi, 1960:50). This color is interesting in that the blue anthocyanin, cyanidin, was first isolated from the flowers of C. cyanus L. by Willstatter and Everest and paved the way for anthocyanin studies (Perkin and Everest, 1918: 279; 288-289). Cyanidin belongs to a group of similar substances including pelargonidin, cyanidin, and delphinidin. Blueness increases in these substances, in the order given, with the increase in the number of hydroxyl groups which have been substituted on the lateral benzene ring (Miller, 1957:60).

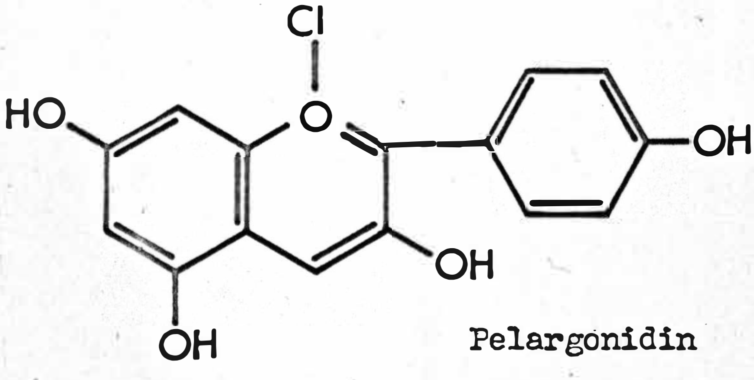
These substances are very common in plants. Cyanidin is present in many flowers and fruits and its derivatives are widespread. It is most easily isolated in its chloride which is red.



Delphinidin



Cyanidin



Pelargonidin

(from Miller, 1957:60-61)

Elderberry

A blue from the berries of the elder was used in medieval painting. A blue dye was obtained from Sambucus nigra L. (Mairet, 1917:29), and this was probably the source of the stain used in painting. The blue or purple-blue juice obtained from the fruit has been used as an ink, as a fabric dye, for homemade wines, and in painting. The juice is believed to contain cyanidin and delphinidin (Harborne, 1963:92; Nolan and Casey, 1928).

BLACKS

Carbon Blacks

The term "carbon black" as used in this paper means black pigments whose principal ingredient, carbon, is left as a residue of combustion. It was previously mentioned that such black pigments, perhaps from plant sources, had been used in early cave paintings. Black inks are mentioned in the Ebers Papyrus dating from the 16th century B.C., and analysis indicates that early Egyptian black inks had a carbon base. These were probably made from animal or vegetable charcoal (Venuto, 1953:1).

Carbon blacks are by far the most important black pigments to the artist, being made by partial burning of natural gases, seed oils, woods, bone, and other organic materials. These are stable, not effected by light, air, or acids, and have excellent covering power (Gettens and Stout, 1934:103). Varieties in shade are due to impurities, particle size, and amount of amorphous carbon.

Lampblacks

Lampblacks are generally considered most durable and are made in several ways. Detailed instructions for preparing a lampblack were given by Vitruvius (30 B.C. - 14 A.D.), but this was not a true impingement black. The ancient Chinese made the first true impingement black pigments. Oils such as tung oil (from species of *Aleurites*) and sesame oil (from *Sesamum indicum* L.) were burned and the flame permitted to impinge on the inner surface of smooth porcelain cones. The carbon deposited by the flame was scraped off for use in inks and paints (Venuto, 1953:1). In medieval times lampblack was made by burning a beeswax candle or a lamp with linseed oil (from *Linum usitatissimum* L.), hempseed oil (from *Cannabis sativa* L.), olive oil (from *Olea europaea* L.), or other vegetable oils and allowing the flame to play on a cold surface. Sometimes incense or pitch was burned for this purpose. The soot was collected and could be mixed with a gum to make an ink or paint (Thompson, 1956:83). The best lampblacks are generally made from fatty oils (Weber, 1923:32, 79), usually seed oils of plants. Fats, grease, tallow, and resins have also been used. Today most lampblack carbon is obtained from controlled

oxidation of waste coal tar products (Martin and Morgans, 1954:14). Lampblacks are generally slow drying in oil media but are adaptable to all techniques. They usually give black-blue tints when mixed with white pigments (Toch, 1925:96-103).

Vegetable blacks

Many carbon black pigments have been made from the residue of burning plant materials. These include (Bazzi, 1960:49; Doerner, 1962:89-90; Gettens and Stout, 1934:103-104):

oak black -- from the wood of species of *Quercus*

vine black -- from grapevine, *Vitis vinifera* L.

cocoanut shell black -- from the fruit of *Cocos nucifera* L.

almond shell black -- from the fruit of *Prunus amygdalus* Stokes.

cork black -- from the outer bark of *Quercus suber* L.

peach stone black -- from the fruit of *Prunus persica* Sieb. and Zucc.

Blacks are also made by the dry distillation of woods heated in kilns. The best are obtained from willow (*Salix*), basswood (*Tilia*), beech (*Fagus*), maple (*Acer*), and other even textured woods (Gettens and Stout, 1934:104; Toch, 1925:102). Pine wood is also sometimes used.

Bistre

Bistre is a brown-black watercolor made from the tarry soot of burned resinous wood, especially beechwood. It is similar to asphaltum in color and composition and can vary from saffron yellow to black depending on source and treatment. The tarry soot is ground and mixed with a gum and glycerine. It is suitable only for painting in thin washes because of its tarry nature and is discolored by sunlight. Such tarry materials of wood have been employed for centuries. Bistre was used in Italian book illustration during the 14th century and by Rembrandt in wash drawings (Gettens and Stout, 1934:97). Bistre is still used as a watercolor (Doerner, 1962:88).

Asphaltum

Asphaltum, also called bitumen, mineral pitch, Antwerp brown, and mummy, is a resinous or pitchy substance soluble in drying oils. There are many types of asphaltum and their occurrence is widespread. They are black-brown substances, primarily hydrocarbons, which are the product of the decompositon of plant and animal matter. Some are formed as the residue of the distillation of asphaltic petroleum oils.

Asphaltum materials were used for waterproofing and as preservatives by the early Egyptians and Babylonians. They appear to have been used in masonry which has been dated at between 5000 and 3000 B.C. (Taylor and Marks, 1961:13-15). These were probably crude, naturally occurring substances. Today asphaltums are refined to give a more uniform product which is useful as a waterproofing and protective agent.

Asphaltum is pulverized and heated in oil until it dissolves. It does not dry well and a drying oil medium such as linseed oil must usually be added (Doerner, 1962:88). It was used in painting at least as early as the 16th century. The Flemish painters used it and the Dutch used common coal as a pigment (Eastlake, 1960:463, 466-467). French painters of the

school of David painted with asphaltum and added wax to it to prevent it from flowing once applied. It enjoyed popularity in the 18th century English School and in the Munich School, and was employed by such great artists as Rembrandt and Albert Ryder. Rembrandt used asphaltum effectively as a thin glaze (Doerner, 1962:89).

Asphaltum is now generally held to be an exceedingly poor artists' material and is seldom used. When applied in layers thick enough to be opaque the asphaltum tends to crack and to migrate on the canvas (Mayer, 1948:54). Also, its color is not permanent. It tends to be brown in color, but organic substances present will oxidize in light to leave a residue of carbon (Weber, 1923:23). This makes the color more black and may severely darken a painting.

Oak Gall Inks

Insect galls which are formed on twigs of the Aleppo oak, Quercus infectoria Oliv., have long been a source of tannin. The Aleppo oak is a small Mediterranean shrub and the galls, formed in response to insect injuries, have a very high tannin content. Tannin combines with iron salts to give a blue-black dye and inks of this sort were described as early as the 11th century (Hill, 1952:125). Inks from oak galls were used by medieval European artists (Thompson, 1956: 81) and are still important today.

SUMMARY

From antiquity painters have depended very heavily on biologically-derived products. Most of the important paint media are from plants. Media constituents derived from plants include drying oils, essential oils, oleoresins, resins, and gums. Pigments and dyes obtained from plant sources represent a wide range of hues and are more than adequate in satisfying the artist's need for a variety of colors. Organic colors are generally more brilliant and more varied than inorganic pigments. The chief drawback to most plant-derived pigments is that they tend to be fugitive. Because of this most of these pigments have been replaced by synthetic organic pigments derived from coal and coal tar distillation. Synthetic organic pigments generally have fewer impurities, are more uniform in composition, and are sometimes more lightfast than natural colors. Madder, gamboge, and Indian yellow are exceptions and are frequently preferred to synthetic substitutes. Also, the best black pigments are carbon blacks obtained from the combustion of woods and seed oils.

As previously mentioned, plant products are used not only in paints, but also in fulfilling other material needs of the painter. Some uses are obscure

but interesting. Carnauba and other waxes have been used to give a protective coat to paintings. Also, coffee was once rubbed over oil paintings by forgers in order to give the patina of age (Hubbard, 1939:43).

The list of plant-derived artists' materials is extensive. Painting as an art form had its inception at a time when natural organic and earth pigments were the only ones available. Many of the plant media were also used from antiquity. The nature of these materials has in great measure shaped and determined the art products man has been able to produce and many of the traditions that surround their creation. Some plant materials have been replaced, but there is still no substitute for many of the artist's favorite tools.

ALPHABETICAL LIST OF SPECIES DISCUSSED IN THIS STUDY WHICH ARE SOURCES OF COLORING SUBSTANCES USED IN PAINTING

Alkanna tinctoria (L.) Tauch. -- Alkanin (Red)

Alnus glutinosa Medic. -- see Miscellaneous Trees (Yellow)

Aloe abyssinica Lam. -- Aloin (Yellow)

A. africana Mill. -- Aloin (Yellow)

A. candelabrum Tod. -- Aloin (Yellow)

A. ferox Mill. -- Aloin (Yellow)

A. perryi Baker. -- Aloin (Yellow)

A. spicata Baker. -- Aloin (Yellow)

A. vera L. -- Aloin (Yellow)

Berberis vulgaris L. -- Brown Stil de Grain (Yellow)

Betula pubescens Ehrh. -- see Miscellaneous Trees (Yellow)

Bignonia chica Humb. and Bonpl. -- Chica Red

Butea superba Roxb. -- host of lac insect, Indian Lake (Red)

Caesalpinia crista L. -- Brazilwood (Red)

C. echinata Lam. -- Brazilwood (Red)

C. sappan L. -- Brazilwood (Red)

Calanthe veratrifolia R. Br. -- Indigo (Blue)

Cannabis sativa L. -- Lampblack

Carthamus tinctoria L. -- Safflower (Red)

Centaurea cyanus L. -- Cornflower Blue

Chelidonium majus L. -- Celandine (Yellow)

Chlorophora tinctoria (L.) Gaud. -- Old Fustic (Yellow)

Chrozophora tinctoria Juss. -- Turnsole (Blue)

Cocos nucifera L. -- Vegetable Black

Crocus sativus L. -- Saffron (Yellow)

Curcuma longa L. -- Curcuma (Yellow)

C. viridiflora Roxb. -- Curcuma (Yellow)

C. rotunda L. -- Curcuma (Yellow)

Daemonorops draco Blume -- Dragon's Blood (Red)

Dracaena cinnabari Balf. -- Dragon's Blood (Red)

D. draco L. -- Dragon's Blood (Red)

D. schizantha Baker. -- Dragon's Blood (Red)

Eupatorium indigofera Perodi -- Indigo (Blue)

E. laeve DC. -- Indigo (Blue)

Ficus religiosa L. -- host of lac insect, Indian Lake (Red)

Fraxinus excelsior L. -- see Miscellaneous Trees (Yellow)

Garcinia cambogia Desv. -- Gamboge (Yellow)

G. cochinchinensis Chois. -- Gamboge (Yellow)

G. hanbryi Gook. -- Gamboge (Yellow)

G. pictoria Roxb. -- Gamboge (Yellow)

G. travancorica Hook. f. -- Gamboge (Yellow)

Genista tinctoria L. -- Weld (Yellow)

Gymnema tingens Spreng. -- Indigo (Blue)

Haematoxylon campechianum L. -- Logwood (Red)

Helianthus annuus L. -- Sunflower Yellow

Hydrastis canadensis L. -- Brown Stil de Grain (Yellow)

Indigofera angustifolia L. -- Indigo (Blue)

I. anil L. -- Indigo (Blue)

I. arcuata Willd. -- Indigo (Blue)

I. argentea L. -- Indigo (Blue)

I. arrecta Hochst. -- Indigo (Blue)

I. caroliniana Walt. -- Indigo (Blue)

I. cinerea Willd. -- Indigo (Blue)

I. coerulea Roxb. -- Indigo (Blue)

I. disperma L. -- Indigo (Blue)

I. endecaphylla Jacq. -- Indigo (Blue)

I. glabra L. -- Indigo (Blue)

I. hirsuta L. -- Indigo (Blue)

I. indica L. -- Indigo (Blue)

I. leptostachya DC. -- Indigo (Blue)

I. longeracemosa Boiv. -- Indigo (Blue)

I. mexicana Benth. -- Indigo (Blue)

I. paucifolia Delile. -- Indigo (BLue)

I. pseudotinctoria R. Br. -- Indigo (Blue)

I. secundiflora Poir. -- Indigo (Blue)

I. tinctoria L. -- Indigo (Blue)

Iris florentina L. -- Iris Green

I. germanica L. -- Iris Green

Isatis tinctoria L. -- Woad (Blue)

Jateorhiza miersii Oliv. -- Brown Stil de Grain (Yellow)

Lawsonia alba Lam. -- Henna (Yellow)

Lecanora tartarea Mass. -- Archil (Red)

Lilium candidum L. -- Lily Pollen (Yellow)

Linum usitatissimum L. -- Lampblack

Lonchocarpus cyanescens Benth. -- Indigo (Blue)

Mahonia aquifolium (Lindl.) Don. -- Brown Stil de Grain (Yellow)

Mangifera indica L. -- Indian Yellow

Marsdenia tinctoria R. Br. -- Indigo (Blue)

Nopalea coccinellifera (L.) Salm.-Dyck. -- host of the cochineal insect, Cochineal (Red)

Ochrolechia tartarea (L.) Mass. -- Archil (Red)

Oldenlandia umbellata L. -- Madder (Red)

Olea europaea L. -- Lampblack

Papaver apulum Ten. -- Poppy Red

P. argemone L. -- Poppy Red

P. bracteatum Lindl. -- Poppy Red

P. dubium L. -- Poppy Red

P. glaucum Boiss. and Hausskn. -- Poppy Red

P. heldreichii Boiss. -- Poppy Red

P. hybridum L. -- Poppy Red

P. lecoqii Lamotte -- Poppy Red

P. mudicale L. -- Poppy Red

P. oriental L. -- Poppy Red

P. pavonimum Fisch. and Mey. -- Poppy Red

P. pilosum Sibth. and Smith -- Poppy Red

P. polonicum Mey. -- Poppy Red

P. rhoeas L. -- Poppy Red

P. rupifragum Boiss. and Reut. -- Poppy Red

P. somniferum L. -- Poppy Red

Phaius grandiflorus Reich. -- Indigo (Blue)

Polygonium tinctorium Ait. -- Indigo (Blue)

Populus nigra L. var. italica Du Roi. -- see Miscellaneous Trees (Yellow)

Prunus amygdalus Stokes. -- Vegetable Black

Prunus domestica L. -- see Miscellaneous Trees (Yellow)

Prunus persica Sieb. and Zucc. -- Vegetable Black

Pterocarpus draco L. -- Dragon's Blood (Red)

P. erinaceous Lam. -- Dragon's Blood (Red)

Pyrus communis L. -- see Miscellaneous Trees (Yellow)

Quebrachia lorentzii Griseb. -- Young Fustic (Yellow)

Quercus coccinea Wangenh. -- host of kermes insect, Kermes (Red)

Q. infectoria Oliv. -- Oak Gall Ink (Black)

Q. suber L. -- Vegetable Black

Q. velutina Lam. -- Quercitron (Yellow)

Reseda luteola L. -- Weld (Yellow)

Rhamnus alaternus L. -- Persian Berries (Yellow)

R. cathartica L. -- Persian Berries; also, see Miscellaneous Trees (Yellow); also, Bladder Green

R. frangula L. -- see Miscellaneous Trees (Yellow)

R. globosa Bge. -- Chinese Green

<u>R. graecus</u> Boiss. and Reut. -- Persian Berries (Yellow)

<u>R. infectorius</u> L. -- Persian Berries (Yellow)

<u>R. oleoides</u> L. -- Persian Berries (Yellow)

<u>R. saxatilis</u> L. -- Persian Berries (Yellow)

<u>R. utilis</u> Decne. -- Chinese Green

<u>Rubia cordifolia</u> L. -- Madder (Red)

<u>R. khasiana</u> Kurz. -- Madder (Red)

<u>R. munjista</u> Roxb. -- Madder (Red)

<u>R. peregrina</u> L. -- Madder (Red)

<u>R. sikkimensis</u> Kurz. -- Madder (Red)

<u>R. tinctoria</u> L. -- Madder (Red)

<u>Sambucus nigra</u> L. -- Elderberry (Blue)

<u>Salix pentandra</u> L. -- Miscellaneous Trees (Yellow)

<u>Sesamum indicum</u> L. -- Lampblack

<u>Tephrosia tinctoria</u> Pers. -- Indigo (Blue)

<u>Vitis vinifera</u> L. -- Vegetable Black

<u>Ziziphus jujuba</u> Mill. -- host of the lac insect, Indian Lake (Red)

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