

# **DYES , COLORS & PIGMENTS**

**Writing By**

**TAREK ISMAIL KAKHIA**

# Natural dye



*Skins of wool colored with natural plant dyes.*

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## - Introduction :

**Natural dyes** are dyes or colorants derived from plants, invertebrates, or minerals. The majority of natural dyes are **vegetable dyes** from plant sources – roots, berries, bark, leaves, and wood — and other organic sources such as fungi and lichens.

Archaeologists have found evidence of textile dyeing dating back to the Neolithic period. In China, dyeing with plants, barks and insects has been traced back more than 5,000 years. The essential process of dyeing changed little over time. Typically, the dye material is put in a pot of water and then the textiles to be dyed are added to the pot, which is heated and stirred until the color is transferred. Textile fiber may be dyed before spinning (*dyed in the wool*), but most textiles are *yarn-dyed* or *piece-dyed* after weaving. Many natural dyes require the use of chemicals called mordants to bind the dye to the textile fibers; tannin from oak galls, salt, natural alum, vinegar, and ammonia from stale urine were used by early dyers. Many mordants, and some dyes themselves, produce strong odors, and large-scale dyeworks were often isolated in their own districts.

Throughout history, people have dyed their textiles using common, locally available materials, but scarce dyestuffs that produced brilliant and permanent colors such as the natural invertebrate dyes Tyrian purple and crimson kermes became highly prized luxury items in the ancient and medieval world. Plant-based dyes such as woad, indigo, saffron, and madder were raised commercially and were important trade goods in the economies of Asia and Europe. Across Asia and Africa, patterned fabrics were produced using resist dyeing techniques to control the absorption of color in piece-dyed cloth. Dyes from the New World such as cochineal and logwood were brought to Europe by the Spanish treasure fleets, and the dyestuffs of Europe were carried by colonists to America.

The discovery of man-made synthetic dyes in the mid-19th century triggered the end of the large-scale market for natural dyes. Synthetic dyes, which could be produced in large quantities, quickly superseded natural dyes for the commercial textile production enabled by the industrial revolution, and unlike natural dyes, were suitable for the synthetic fibers that followed. Artists of the *Arts and Crafts Movement* preferred the pure shades and subtle variability of natural dyes, which mellow with age but preserve their true colors, unlike early synthetic dyes, and helped ensure that the old European techniques for dyeing and printing with natural dyestuffs were preserved for use by home and craft dyers. Natural dyeing techniques are also preserved by artisans in traditional cultures around the world.

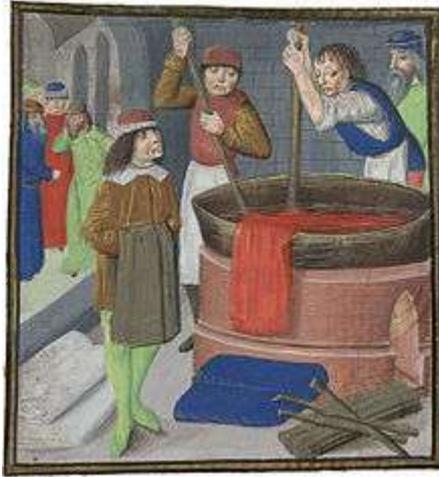
### **1 - Origins :**

Colors in the "ruddy" range of reds, browns, and oranges are the first attested colors in a number of ancient textile sites ranging from the Neolithic to the Bronze Age across the Levant, Egypt, Mesopotamia and Europe, followed by evidence of blues and then yellows, with green appearing somewhat later. The earliest surviving evidence of textile dyeing was found at the large Neolithic settlement at Çatalhöyük in southern Anatolia, where traces of red dyes, possible from ochre (iron oxide pigments from clay), were found. Polychrome or multicolored fabrics seem to have been developed in the 3rd or 2nd millennium BCE. Textiles with a "red-brown warp and an ochre-yellow weft" were discovered in Egyptian pyramids of the Sixth Dynasty (2345-2180 BCE).

The chemical analysis that would definitively identify the dyes used in ancient textiles has rarely been conducted, and even when a dye such as indigo blue is detected it is impossible to determine which of several indigo-bearing plants was used. Nevertheless, based on the colors of surviving textile fragments and the evidence of actual dyestuffs found in archaeological sites, reds, blues, and yellows from plant sources were in common use by the late Bronze Age and Iron Age.

## 2 - Processes :

For more details on this topic, see Glossary of dyeing terms.



*Dyeing wool cloth , 1482*

The essential process of dyeing requires soaking the material containing the dye (the *dyestuff*) in water, adding the textile to be dyed to the resulting solution (the *dyebath*), and bringing the solution to a simmer for an extended period, often measured in days or even weeks, stirring occasionally until the color has evenly transferred to the textiles.

Some dyestuffs, such as indigo and lichens, will give good color when used alone; these dyes are called *direct dyes* or *substantive dyes*. The majority of plant dyes, however, also require the use of a mordant, a chemical used to "fix" the color in the textile fibers. These dyes are called *adjective dyes*. By using different mordants, dyers can often obtain a variety of colors and shades from the same dye. Fibers or cloth may be pretreated with mordants, or the mordant may be incorporated in the dyebath. In traditional dyeing, the common mordants are vinegar, tannin from oak bark, sumac, or oak galls, ammonia from stale urine, and wood-ash liquor or potash (potassium carbonate) made by leaching wood ashes and evaporating the solution.

We shall never know by what chances primitive man discovered that salt, vinegar from fermenting fruit, natural alum,

and stale urine helped to fix and enhance the colours of his yarns, but for many centuries these four substances were used as mordants.

Salt helps to "fix" or increase "fastness" of colors, vinegar improves reds and purples, and the ammonia in stale urine assists in the fermentation of indigo dyes. Natural alum (aluminum sulfate) is the most common metallic salt mordant, but tin (stannous chloride), copper (cupric sulfate), iron (ferrous sulfate, called *copperas*) and chrome (potassium dichromate) are also used. Iron mordants "sadden" colors, while tin and chrome mordants brighten colors. Additional chemicals or *alterants* may be applied after dyeing to further alter or reinforce the colors.



*A dye-works with baskets of dyestuffs  
skeins of dyed yarn, and heated vats for dyeing.*

Textiles may be dyed as raw fiber (*dyed in the fleece* or *dyed in the wool*), as spun yarn (*dyed in the hank* or *yarn-dyed*), or after weaving (*piece-dyed*). Mordants often leave residue in wool fiber that makes it difficult to spin, so wool was generally dyed after spinning, as yarn or woven cloth. Indigo, however, requires no mordant, and cloth manufacturers in medieval England often dyed wool in the fleece with the indigo-bearing plant woad and then dyed the cloth again after weaving to produce deep blues, browns, reds, purples, blacks, and tawnies.

In China, Japan, India, Pakistan, Nigeria, Gambia, and other parts of West Africa and southeast Asia, patterned silk and cotton fabrics were produced using resist dyeing techniques in which the cloth is printed or stenciled with starch or wax, or tied in various ways to prevent even penetration of the dye when the

cloth is piece-dyed. Chinese *ladao* is dated to the 10th century; other traditional techniques include tie-dye, batik, Rōketsuzome, katazome, bandhani and leheria.

The mordants used in dyeing and many dyestuffs themselves give off strong and unpleasant odors, and the actual process of dyeing requires a good supply of fresh water, storage areas for bulky plant materials, vats which can be kept heated ( often for days or weeks ), and airy spaces to dry the dyed textiles. Ancient large-scale dye-works tend to be located on the outskirts of populated areas, on windy promontories.

### 3 - Common dyestuffs :



*The Hunt of the Unicorn Tapestry, dyed with weld (yellow), madder (red), and woad (blue).*

#### 3 – 1 - Reds and pinks :

A variety of plants produce red dyes, including a number of lichens, henna, alkanet or dyer's bugloss (*Alkanna tinctoria*), asafoetida and madder. Madder (*rubia tinctoria*) and related plants of the *Rubia* family are native to many temperate zones around the world, and have been used as a source of good red dye (rose madder) since prehistory. Madder has been identified on linen in the tomb of Tutankhamun, and Pliny the Elder records madder growing near Rome.<sup>[18]</sup> Madder was a dye of commercial importance in Europe, being cultivated in Holland and France to dye the red coats of military uniforms until the market collapsed following the development of synthetic

alizarin dye in 1869. Madder was also used to dye the "hunting pinks" of Great Britain.

Turkey red was a strong, very fast red dye for cotton obtained from madder root via a complicated multistep process involving "sumac and oak galls, calf's blood, sheep's dung, oil, soda, alum, and a solution of tin ." Turkey red was developed in India and spread to Turkey. Greek workers familiar with the methods of its production were brought to France in 1747, and Dutch and English spies soon discovered the secret. A sanitized version of Turkey red was being produced in Manchester by 1784, and roller-printed dress cottons with a Turkey red ground were fashionable in England by the 1820s.

Munjeet or Indian madder (*Rubia cordifolia*) is native to the Himalayas and other mountains of Asia and Japan. Munjeet was an important dye for the Asian cotton industry and is still used by craft dyers in Nepal.

Puccoon or bloodroot ( *Sanguinaria canadensis* ) is a popular red dye among Southeastern Native American basketweavers. Choctaw basketweavers additionally use sumac for red dye. Coshattas artists from Texas and Louisiana used the water oak (*Quercus nigra* L.) to produce red.

A delicate rose color in Navajo rugs comes from fermented prickly pear cactus fruit, *Opuntia polycantha*.<sup>[26]</sup> Navajo weavers also use rainwater and red dirt to create salmon-pink dyes.

### **3 – 2 – Oranges :**

Dyes that create reds and yellows can also yield oranges. Navajo dyers create orange dyes from one-seeded juniper, *Juniperus monosperma*, Navajo tea, *Thelesperma gracile*, or alder bark.

### 3 – 3 – Yellows :

Yellow dyes are "about as numerous as red ones", and can be extracted from saffron, pomegranate rind, turmeric, safflower, onion skins, and a number of weedy flowering plants . There is limited evidence of the use of weld (*Reseda luteola*), also called mignonette or dyer's rocket before the Iron Age, but it was an important dye of the ancient Mediterranean and Europe, and is indigenous to England. Two brilliant yellow dyes of commercial importance in Europe from the 18th century are derived from trees of the Americas: quercitron from the inner bark of oaks native to North America and fustic from the dyer's mulberry tree (*Maclura tinctoria*) of the West Indies and Mexico.

In rivercane basketweaving among Southeastern tribes, butternut (*Juglans cinerea*) and yellow root (*Xanthorrhiza simplicissima*) provide a rich yellow color. Chitimacha basket weavers have a complex formula for yellow that employs a dock plant (most likely *Rumex crispus*) for yellow. Navajo artists create yellow dyes from small snake-weed and brown onion skins, and rubber plant (*Parthenium incanum*). Rabbitbush (*Chrysothamnus*) and rose hips produce pale, yellow-cream colored dyes.

### 3 – 4 - Greens

If plants that yield yellow dyes are common, plants that yield green dyes are rare. Both woad and indigo have been used since ancient times in combination with yellow dyes to produce shades of green. Medieval and Early Modern England was especially known for its green dyes. The dyers of Lincoln, a great cloth town in the high Middle Ages, produced the Lincoln green cloth associated with Robin Hood by dyeing wool with woad and then overdyeing it yellow with weld or dyer's greenweed (*Genista tinctoria*), also known as dyer's broom. Woolen cloth mordanted with alum and dyed yellow with dyer's greenweed was overdied with woad and, later, indigo, to

produce the once-famous Kendal green. This in turn fell out of fashion in the 18th century in favor of the brighter Saxon green, dyed with indigo and fustic.

Soft olive greens are also achieved when textiles dyed yellow are treated with an iron mordant. The dull green cloth common to the Iron Age Halstatt culture shows traces of iron, and was possibly colored by boiling yellow-dyed cloth in an iron pot. Indigenous peoples of the Northwest Plateau in North America used lichen to dye corn husk bags a beautiful sea green.

Navajo textile artist Nonabah Gorman Bryan developed a two-step process for creating green dye. First the Churro wool yarn is dyed yellow with sagebrush, *Artemisia tridentata*, and then it is soaked in black dye afterbath. Red onion skins are also used by Navajo dyers to produce green.

### **3 – 5 – Blues :**

Blue colorants around the world were derived from indigo dye-bearing plants, primarily those in the genus *Indigofera*, which are native to the tropics. The primary commercial indigo species in Asia was true indigo (*Indigofera tinctoria*). India is believed to be the oldest center of indigo dyeing in the Old World. It was a primary supplier of indigo dye to Europe as early as the Greco-Roman era. The association of India with indigo is reflected in the Greek word for the dye, which was *indikón* (ινδικόν). The Romans used the term *indicum*, which passed into Italian dialect and eventually into English as the word *indigo*.

In Central and South America, the important blue dyes were Añil (*Indigofera suffruticosa*) and Natal indigo (*Indigofera arrecta*).

In temperate climates including Europe, indigo was obtained primarily from woad (*Isatis tinctoria*), an indigenous

plan of Assyria and the Levant which has been grown in Northern Europe over 2,000 years, although from the 18th century it was mostly replaced by superior Indian indigo imported by the British East India Company. Woad was carried to New England in the 17th century and used extensively in America until native stands of indigo were discovered in Florida and the Carolinas. In Sumatra, indigo dye is extracted from some species of *Marsdenia*. Other indigo-bearing dye plants include dyer's knotweed (*Polygonum tinctorum*) from Japan and the coasts of China, and the West African shrub *Lonchocarpus cyanescens*.

### **3 – 6 – Purples :**

In medieval Europe, purple, violet, murrey and similar colors were produced by dyeing wool with woad or indigo in the fleece and then piece-dyeing the woven cloth with red dyes, either the common madder or the luxury dyes kermes and cochineal. Madder could also produce purples when used with alum. Brazilwood also gave purple shades with vitriol (sulfuric acid) or potash.

Choctaw artists traditionally used maple (*Acer* sp.) to create lavender and purple dyes . Purples can also be derived from lichens, and from the berries of White Bryony from the northern Rocky Mountain states and mulberry (*morus nigra*) (with an acid mordant).

### **3 – 7 – Browns :**

Cutch is an ancient brown dye from the wood of acacia trees, particularly *Acacia catechu*, used in India for dyeing cotton. Cutch gives gray-browns with an iron mordant and olive-browns with copper.

Black walnut (*Juglans nigra*) is used by Cherokee artists to produce a deep brown approaching black . Today black walnut is primarily used to dye baskets but has been used in the past for fabrics and deerhide. Juniper, *Juniperus monosperma*, ashes

provide brown and yellow dyes for Navajo people, as do the hulls of wild walnuts (*Juglans major*).

### **3 – 8 - Greys and blacks :**

Choctaw dyers use maple (*Acer* sp.) for a grey dye. Navajo weavers create black from mineral yellow ochre mixed with pitch from the piñon tree (*Pinus edulis*) and the three-leaved sumac (*Rhus trilobata*). They also produce a cool grey dye with blue flower lupine and a warm grey from Juniper mistletoe (*Phoradendron juniperinum*).

### **3 – 9 – Lichen :**

Dye-bearing lichen produce a wide range of greens,<sup>[37]</sup> oranges, yellows, reds, browns, and bright pinks and purples. The lichen *Rocella tinctoria* was found along the Mediterranean Sea and was used by the ancient Phoenicians. In recent times, lichen dyes have been an important part of the dye traditions of Wales, Ireland, Scotland, and among native peoples of the southwest and Intermontane Plateaus of the United States.<sup>[37]</sup> Scottish lichen dyes include cudbear (also called archil in England and litmus in Holland), and crottle.

### **3 – 10 – Fungi :**

Miriam C. Rice, (1918—2010) of Mendocino, California, pioneered research into using various mushrooms for natural dyes. She discovered mushroom dyes for a complete rainbow palette. Swedish and American mycologists, building upon Rice's research, have discovered sources for true blues (*Sarcodon squamosus*) and mossy greens (*Hydnellum geogenium*).<sup>[46]</sup> *Hypholoma fasciculare* provides a yellow dye, and fungi such as *Phaeolus schweinitzii* and *Pisolithus tinctorius* are used in dyeing textiles and paper.

## 4 - Luxury dyestuffs

From the second millennium BCE to the 19th century, a succession of rare and expensive natural dyestuffs came in and out of fashion in the ancient world and then in Europe. In many cases the cost of these dyes far exceeded the cost of the wools and silks they colored, and often only the finest grades of fabrics were considered worthy of the best dyes.

### 4 – 1 - Royal purple :

The premier luxury dye of the ancient world was Tyrian purple or royal purple, a purple-red dye which is extracted from several genera of sea snails, primarily the spiny dye-murex *Murex brandaris* (currently known as *Bolinus brandaris*). Murex dye was greatly prized in antiquity because it did not fade, but instead became brighter and more intense with weathering and sunlight. Murex dyeing may have been developed first by the Minoans of East Crete or the West Semites along the Levantine coast, and heaps of crushed murex shells have been discovered at a number of locations along the eastern Mediterranean dated to the mid-2nd millennium BCE. The classical dye known as Phoenician Red was also derived from murex snails.

Murex dyes were fabulously expensive - one snail yields but a single drop of dye - and the Roman Empire imposed a strict monopoly on their use from the reign of Alexander Severus (225–235 CE) that was maintained by the succeeding Byzantine Empire until the Early Middle Ages. The dye was used for imperial manuscripts on purple parchment, often with text in silver or gold, and *porphyrogenitos* or "born in the purple" was a term for Byzantine offspring of a reigning Emperor. The color matched the increasing rare purple rock porphyry, also associated with the imperial family.

## 4 – 2 - Crimson and scarlet :

Tyrian purple retained its place as the premium dye of Europe until it was replaced "in status and desirability" by the rich crimson reds and scarlets of the new silk-weaving centers of Italy, colored with kermes. Kermes is extracted from the dried unlayered eggs of the insect *Kermes vermilio* or *Kermococcus vermilio* found on species of oak (especially the Kermes oak of the Mediterranean region). The dye is of ancient origin; jars of kermes have been found in a Neolithic cave-burial at Adaoutse, Bouches-du-Rhône. Similar dyes are extracted from the related insects *Porphyrophora hamili* of the Caucasus region, *Coccus polonicus* (Polish cochineal or Saint John's blood) of Eastern Europe, and the lac-producing insects of India, Southeast Asia, China, and Tibet.

When kermes-dyed textiles achieved prominence around the mid-11th century, the dyestuff was called "grain" in all Western European languages because the desiccated eggs resemble fine grains of wheat or sand. Textiles dyed with kermes were described as *dyed in the grain*. Woollens were frequently dyed in the fleece with woad and then piece-dyed in kermes, producing a wide range of colors from blacks and grays through browns, murreys, purples, and sanguines. By the 14th and early 15th century, brilliant *full grain* kermes scarlet was "by far the most esteemed, most regal" color for luxury woollen textiles in the Low Countries, England, France, Spain and Italy.

Cochineal (*Dactylopius coccus*) is a scale insect of Central and North America from which the crimson-coloured dye carmine is derived. It was used by the Aztec and Maya peoples. Moctezuma in the 15th century collected tribute in the form of bags of cochineal dye.<sup>[55]</sup> Soon after the Spanish conquest of the Aztec Empire cochineal began to be exported to Spain, and by the seventeenth century it was a commodity traded as far away as India. During the colonial period the production of cochineal (in Spanish, *grana fina*) grew rapidly. Produced almost

exclusively in Oaxaca by indigenous producers, cochineal became Mexico's second most valued export after silver.<sup>[56]</sup> Cochineal produces purplish colors alone and brilliant scarlets when mordanted with tin, and cochineal, which produced a stronger dye and could thus be used in smaller quantities, replaced kermes dyes in general use in Europe from the 17th century.

#### **4 – 3 - The rise of formal black :**

During the course of the 15th century, the civic records show brilliant reds falling out of fashion for civic and high-status garments in the Duchy of Burgundy in favor of dark blues, greens, and most importantly of all, black. The origins of the trend for somber colors are elusive, but are generally attributed to the growing influence of Spain and possibly the importation of Spanish merino wools. The trend spread in the next century: the Low Countries, German states, Scandinavia, England, France, and Italy all absorbed the sobering and formal influence of Spanish dress after the mid-1520s.

Producing fast black in the Middle Ages was a complicated process involving multiple dyeings with woad or indigo followed by mordanting, but at the dawn of Early Modern period, a new and superior method of dyeing black dye reached Europe via Spanish conquests in the New World. The new method used logwood (*Haematoxylum campechianum*), a dyewood native to Mexico and Central America. Although logwood was poorly received at first, producing a blue inferior to that of woad and indigo, it was discovered to produce a fast black in combination with a ferrous sulfate (copperas) mordant. Despite changing fashions in color, logwood was the most widely used dye by the 19th century, providing the sober blacks of formal and mourning clothes.

#### **5 - Decline and rediscovery :**

The first synthetic dyes were discovered in the mid-19th century, starting with William Henry Perkin's mauveine in 1856,

an aniline dye derived from coal tar. Alizarin, the red dye present in madder, was the first natural pigment to be duplicated synthetically, in 1869, leading to the collapse of the market for naturally grown madder. The development of new, strongly colored aniline dyes followed quickly: a range of reddish-purples, blues, violets, greens and reds became available by 1880. These dyes had great affinity for animal fibers such as wool and silk. The new colors tended to fade and wash out, but they were inexpensive and could be produced in the vast quantities required by textile production in the industrial revolution. By the 1870s commercial dyeing with natural dyestuffs was fast disappearing.



*Indigo-dyed and discharge-printed textile, William Morris, 1873*

At the same time the Pre-Raphaelite artist and founding figure of the Arts and Crafts movement William Morris took up the art of dyeing as an adjunct to his manufacturing business, the design firm of Morris & Co. Always a medievalist at heart, Morris loathed the colors produced by the fashionable aniline dyes. He spent much of his time at his Staffordshire dye works mastering the processes of dyeing with plant materials and making experiments in the revival of old or discovery of new methods. One result of these experiments was to reinstate indigo dyeing as a practical industry and generally to renew the use of natural dyes like madder which had been driven almost out of use by the commercial success of the anilines. Morris saw dyeing of wools, silks, and cottons as the necessary preliminary to the production of woven and printed fabrics of the highest excellence; and his period of incessant work at the dye-vat

(1875–76) was followed by a period during which he was absorbed in the production of textiles (1877–78), and more especially in the revival of carpet- and tapestry-weaving as fine arts. Morris & Co. also provided naturally dyed silks for the embroidery style called art needlework.

Scientists continued to search for new synthetic dyes that would be effective on cellulose fibers like cotton and linen, and that would be more colorfast on wool and silk than the early anilines. Chrome or mordant dyes produced a muted but very fast color range for woollens. These were followed by acid dyes for animal fibers (from 1875) and the synthesis of indigo in Germany in 1880. The work on indigo led to the development of a new class of dyes called vat dyes in 1901 that produced a wide range of fast colors for vegetable fibers. Disperse dyes were introduced in 1923 to color the new textiles of cellulose acetate, which could not be colored with any existing dyes. Today disperse dyes are the only effective means of coloring many synthetics. Reactive dyes for both wool and cotton were introduced in the mid-1950s, and are used both in commercial textile production and in craft dyeing.

In America, synthetic dyes became popular among a wide range of Native American textile artists; however, natural dyes remained in use, as many textile collectors prefer natural dyes over synthetics. Today, dyeing with natural materials is often practiced as an adjunct to hand spinning, knitting and weaving. It remains a living craft in many traditional cultures of North America, Africa, Asia, and the Scottish Highlands.

## **6 – Notes :**

- International Mushroom Dye Institute
- Cochineal Master's Thesis-History and Uses

## **Dyes :**

### **Techniques :**

Batik • Dyeing • Kalamkari • Katazome • Leheria • Mordant • Reactive dye printing • Resist • Ring dyeing • Rōketsuzome • Shibori • Tie-dye • Tsutsugaki

### **Types of dyes**

Dyes • **Natural** • Acid • Reactive • Solvent • Substantive • Sulfur • Vat • Disperse

### **Traditional textile dyes**

Black walnut • Bloodroot • Brazilin • Cochineal (Polish cochineal) • Cudbear • Cutch • Dyewoods • Fustic • Henna • Indigo • Kermes • Logwood • Madder • Saffron • Turmeric • Tyrian purple • Weld • Woad

### **History**

Trade and use of saffron • Traditional dyes of the Scottish Highlands

### **Craft dyes**

Dylon • Procion

### **Reference**

Glossary of dyeing terms • List of dyes

# Dye



*Yarn drying after being dyed in the early American tradition, at Conner Prairie living history museum.*

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### **1 – Introduction :**

A **dye** is a colored substance that has an affinity to the substrate to which it is being applied. The dye is generally applied in an aqueous solution, and may require a mordant to improve the fastness of the dye on the fiber.

Both dyes and pigments appear to be colored because they absorb some wave lengths of light more than others. In contrast with a dye, a pigment generally is insoluble, and has no affinity for the substrate. Some dyes can be precipitated with an inert salt to produce a lake pigment, and based on the salt used they could be aluminum lake, calcium lake or barium lake pigments.

Dyed flax fibers have been found in the Republic of Georgia dated back in a prehistoric cave to 36,000 BP. Archaeological evidence shows that, particularly in India and Phoenicia, dyeing has been widely carried out for over 5000 years. The dyes were obtained from animal, vegetable or mineral origin, with no or very little processing. By far the greatest source of dyes has been from the plant kingdom, notably roots, berries, bark, leaves and wood, but only a few have ever been used on a commercial scale.

## **2 - Natural dye :**

The majority of natural dyes are from plant sources – roots, berries , bark , leaves , and wood , fungi , and lichens . Textile dyeing date back to the Neolithic period. Throughout history, people have dyed their textiles using common, locally available materials. Scarce dyestuffs that produced brilliant and permanent colors such as the natural invertebrate dyes Tyrian purple and crimson kermes were highly prized luxury items in the ancient and medieval world. Plant-based dyes such as woad , indigo , saffron , and madder were raised commercially and were important trade goods in the economies of Asia and Europe. Across Asia and Africa, patterned fabrics were produced using resist dyeing techniques to control the absorption of color in piece - dyed cloth. Dyes from the New World such as cochineal and logwood were brought to Europe by the Spanish treasure fleets , and the dyestuffs of Europe were carried by colonists to America .The discovery of man - made synthetic dyes late in the 19th century ended the large - scale market for natural dyes.

## **3 - Synthetic dye :**

The first human - made ( synthetic ) organic dye , mauveine , was discovered serendipitously by William Henry Perkin in 1856. Many thousands of synthetic dyes have since been prepared .

Synthetic dyes quickly replaced the traditional natural dyes. They cost less, they offered a vast range of new colors, and they imparted better properties to the dyed materials.<sup>[5]</sup> Dyes are now classified according to how they are used in the dyeing process.

#### 4 - Dye types :

**I - Acid dyes** are water-soluble anionic dyes that are applied to fibers such as silk, wool, nylon and modified acrylic fibers using neutral to acid dye baths. Attachment to the fiber is attributed, at least partly, to salt formation between anionic groups in the dyes and cationic groups in the fiber. Acid dyes are not substantive to cellulosic fibers. Most synthetic food colors fall in this category.

**II - Basic dyes** are water - soluble cationic dyes that are mainly applied to acrylic fibers, but find some use for wool and silk. Usually acetic acid is added to the dye bath to help the uptake of the dye onto the fiber. Basic dyes are also used in the coloration of paper.

**III - Direct or substantive dyeing** is normally carried out in a neutral or slightly alkaline dye bath, at or near boiling point, with the addition of either sodium chloride ( Na Cl ) or sodium sulfate ( Na<sub>2</sub> SO<sub>4</sub> ) . Direct dyes are used on cotton, paper, leather, wool, silk and nylon. They are also used as pH indicators and as biological stains.

**IV - Mordant dyes** require a mordant, which improves the fastness of the dye against water, light and perspiration. The choice of mordant is very important as different mordants can change the final color significantly. Most natural dyes are mordant dyes and there is therefore a large literature base describing dyeing techniques. The most important mordant dyes are the synthetic mordant dyes, or chrome dyes, used for wool ; these comprise some 30% of dyes used for wool, and are especially useful for black and navy shades. The mordant, potassium dichromate, is applied as an after-treatment. It is

important to note that many mordants, particularly those in the heavy metal category, can be hazardous to health and extreme care must be taken in using them.

**V - Vat dyes** are essentially insoluble in water and incapable of dyeing fibres directly. However, reduction in alkaline liquor produces the water soluble alkali metal salt of the dye, which, in this leuco form, has an affinity for the textile fibre. Subsequent oxidation reforms the original insoluble dye. The color of denim is due to indigo, the original vat dye.

**VI - Reactive dyes** utilize a chromophore attached to a substituent that is capable of directly reacting with the fibre substrate. The covalent bonds that attach reactive dye to natural fibers make them among the most permanent of dyes. "Cold" reactive dyes, such as Procion MX, Cibacron F, and Drimarene K, are very easy to use because the dye can be applied at room temperature. Reactive dyes are by far the best choice for dyeing cotton and other cellulose fibers at home or in the art studio.

**VII - Disperse dyes** were originally developed for the dyeing of cellulose acetate, and are water insoluble. The dyes are finely ground in the presence of a dispersing agent and sold as a paste, or spray-dried and sold as a powder. Their main use is to dye polyester but they can also be used to dye nylon, cellulose triacetate, and acrylic fibres. In some cases, a dyeing temperature of 130 °C is required, and a pressurised dyebath is used. The very fine particle size gives a large surface area that aids dissolution to allow uptake by the fibre. The dyeing rate can be significantly influenced by the choice of dispersing agent used during the grinding.

**VIII - Azoic dyeing** is a technique in which an insoluble azo dye is produced directly onto or within the fibre. This is achieved by treating a fibre with both diazoic and coupling components. With suitable adjustment of dyebath conditions the two components react to produce the required insoluble azo dye. This technique of dyeing is unique, in that the final color is

controlled by the choice of the diazoic and coupling components. This method of dyeing cotton is declining in importance due to the toxic nature of the chemicals used.

**IX - Sulfur dyes** are two part "developed" dyes used to dye cotton with dark colors. The initial bath imparts a yellow or pale chartreuse color, This is aftertreated with a sulfur compound in place to produce the dark black we are familiar with in socks for instance. Sulfur Black 1 is the largest selling dye by volume.

### **5 - Food dyes :**

One other class that describes the role of dyes, rather than their mode of use, is the food dye . Because food dyes are classed as food additives , they are manufactured to a higher standard than some industrial dyes . Food dyes can be direct , mordant and vat dyes , and their use is strictly controlled by legislation . Many are azo dyes, although anthraquinone and triphenylmethane compounds are used for colors such as green and blue . Some naturally - occurring dyes are also used .

### **6 - Other important dyes :**

A number of other classes have also been established, including:

- Oxidation bases, for mainly hair and fur
- Laser dyes : see, for example, rhodamine 6G and coumarin dyes.
- Leather dyes, for leather
- Fluorescent brighteners, for textile fibres and paper
- Solvent dyes , for wood staining and producing colored lacquers , solvent inks , coloring oils , waxes .
- Carbene dyes , a recently developed method for coloring multiple substrates
- Contrast dyes, injected for magnetic resonance imaging, are essentially the same as clothing dye except

they are coupled to an agent that has strong paramagnetic properties .

## 7 - Chemical classification :

By the nature of their chromophore, dyes are divided into :

- Category : Acridine dyes, derivatives of acridine
- Category : Anthraquinone dyes, derivatives of anthraquinone
- Arylmethane dyes
  - Category : Diarylmethane dyes, based on diphenyl methane
  - Category:Triarylmethane dyes, derivatives of triphenyl methane
- Category:Azo dyes, based on  $-N = N-$  azo structure
- Diazonium dyes, based on diazonium salts
- Nitro dyes, based on a  $-NO_2$  nitro functional group
- Nitroso dyes, based on a  $-N = O$  nitroso functional group
- Phthalocyanine dyes, derivatives of phthalocyanine
- Quinone-imine dyes, derivatives of quinone
  - Category : Azin dyes
    - Category : Erythrosin dyes
    - Category : Safranin dyes , derivatives of safranin
  - Indamins
  - Category : Indophenol dyes, derivatives of indophenol
  - Category : Oxazin dyes , derivatives of oxazin
  - Oxazone dyes , derivatives of oxazone
  - Category : Thiazin dyes, derivatives of thiazin
- Category:Thiazole dyes, derivatives of thiazole
- Xanthene dyes, derived from xanthene
  - Fluorene dyes, derivatives of fluorene
    - Pyronin dyes
  - Category : Fluorone dyes, based on fluorone

- Category : Rhodamine dyes , derivatives of rhodamine

## **8 - See also**

- Biological pigment , any colored substance in organisms
  - Hair coloring
  - Blue Wool Scale
  - Paper dyeing
  - Phototendering
  - Stain
  - Category:Natural dyes
  - Category:Pigments
    - Category:Inorganic pigments
  - List of dyes
  - Laser dyes

## Category : Animal dyes

### C

- Carmine
- Cochineal

### H

Hexaplex trunculus

### K

- Kermes (dye)

### L

- Lac

### P

Polish cochineal

### T

- Tekhelet
- Tyrian purple

## Category : Food colorings

### A

- Alkanna tinctoria
- Alkannin
- Allura Red AC
- Amaranth (dye)
- Annatto
- Apocarotenal
- Astaxanthin
- Azorubine

### B

- Betanin
- Black 7984
- Brilliant Black BN
- Brilliant Blue FCF
- Brown FK
- Brown HT

### C

- Canthaxanthin
- Caramel
- Caramel color
- Carmine
- Carotene
- Carthamin
- Chrysoine resorcinol
- Citranaxanthin
- Citrus Red 2
  
- Cochineal
- Crocin
- Curcumin

## **D**

- Ditaxis heterantha

## **E**

- Erythrosine

## **F**

- Fast Green FCF
- Fast Yellow AB
- FD&C Orange Number 1
- Flavin mononucleotide
- Flavoxanthin
- Food orange 7

## **G**

- Green S

## **I**

- Indanthrene blue RS
- Indigo carmine

## **J**

- Juglone

## **K**

- Kitchen Bouquet

## **L**

- Linner hue index
- Lithol Rubine BK
- Lutein
- Lycopene

## O

- Orange B
- Orange GGN
- Orcein

## P

- Patent Blue V
- Ponceau 4R
- Ponceau 6R

## Q

- Quinoline Yellow WS

## R

- Red 2G
- Red no. 40
- Red yeast rice
- Rhodoxanthin
- Riboflavin
- Rubixanthin

## S

- Safflower
- Saffron
- Scarlet GN
- Sudan I
- Sudan Red G
- Sunset Yellow FCF

## T

- Tartrazine
- Titanium dioxide
- Turmeric
- Turnsole

## **V**

- Violaxanthin

## **Y**

- Yellow 2G

## **Z**

Zeaxanthin

## Category : Natural dyes

\* **Animal dyes**

\* **Plant dyes**

### Pages in category "Natural dyes"

Natural dye

A

Aurantininidin

B

Betalain

C

Chica ( dye )

Crimson

Curcumin

F

Filipendula ulmaria

H

Haematoxylin

J

Juglone

L

Lawsone

M

Morindone

Mushroom dye

O

Orcein

P

Phaeolus schweinitzii

S

Stil de grain yellow

T

Traditional dyes of the Scottish Highlands

## Category : Plant dyes

A

*Alkanna tinctoria*

*Cota tinctoria*

B

*Bixa orellana*

Bloodroot

C

*Caesalpinia echinata*

Catechu

Common Tormentil

*Cordeauxia edulis*

*Cryptocarya alba*

D

Dyewoods

E

*Eucalyptus fibrosa*

Eurasian smoketree

G

*Gardenia jasminoides*

*Genista tinctoria*

H

*Haematoxylum campechianum*

*Haemodorum coccineum*

Henna

I

Indigo dye

*Indigofera*

*Indigofera suffruticosa*

*Indigofera tinctoria*

*Isatis tinctoria*

J

*Juglans nigra*

*Juglans regia*

L

Lincoln green

Lithospermum caroliniense

M

Maclura tinctoria

Mallotus discolor

Mallotus philippensis

Malva sylvestris

Morinda citrifolia

Morinda tinctoria

O

Oldenlandia umbellata

P

Pentaglottis sempervirens

Pogonolobus

Pokeweed

Pomegranate

Psorothamnus emoryi

Q

Quercitron

Quercus lusitanica

Quercus velutina

R

Reseda ( plant )

Reseda luteola

Rubia

Rubia cordifolia

S

Safflower

Saw - wort

T

Tansy

Taraxacum officinale

1,2,4-Trihydroxyanthraquinone

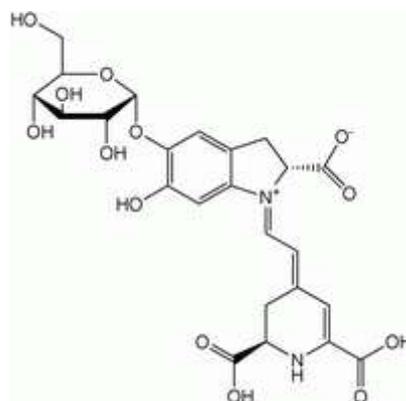
Turmeric

W

Wild Angelica

Wrightia tinctoria

## Betanin



### IUPAC name :

4-(2-(2-carboxy-5-(beta-D-glucopyranosyloxy)- 2,3-dihydro-6-hydroxy-1H-indol-1-yl)ethenyl)-2,3-dihydro-(S-(R\*,R\*)))-2,6-pyridinedicarboxylic acid

### Properties

Molecular formula	$C_{24}H_{27}N_2O_{13}$
Molar mass	551.5 g / mol

**Betanin**, or **Beet root Red**, is a red glycosidic food dye obtained from beets; its aglycone, obtained by hydrolyzing away the glucose molecule, is betanidin. As a food additive, its E number is E162. Betanin degrades when subjected to light, heat, and oxygen; therefore, it is used in frozen products, products with short shelf life, or products sold in dry state.<sup>[1]</sup> Betanin can survive pasteurization when in products with high sugar content. Its sensitivity to oxygen is highest in products with high content of water and/or containing metal cations (e.g. iron and copper); antioxidants like ascorbic acid and sequestrants can slow this process down, together with suitable packaging. In dry form betanin is stable in presence of oxygen.

Betanin is usually obtained from the extract of beet juice; the concentration of betanin in red beet can reach 300-600 mg/kg. Other dietary sources of betanin and other betalains

include the opuntia cactus, Swiss chard, and the leaves of some strains of amaranth.

The color of betanin depends on pH ; between four and five it is bright bluish-red, becoming blue - violet as the pH increases. Once the pH reaches alkaline levels betanin degrades by hydrolysis, resulting in a yellow-brown color.

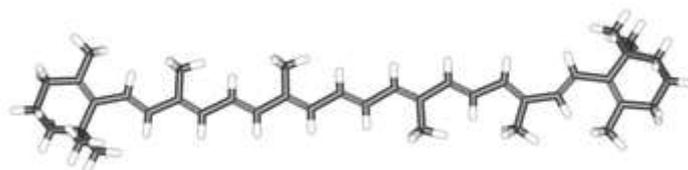
Betanin can be also used for coloring meat and sausages.

The most common uses of betanin are in coloring ice cream and powdered soft drink beverages; other uses are in some sugar confectionery, e.g. fondants, sugar strands , sugar coatings, and fruit or cream fillings. In hot processed candies, it can be used if added at the final part of the processing. Betanin is also used in soups as well as tomato and bacon products.

Betanin absorbs well from the gut and acts as an antioxidant.

Betanin is a betalain pigment, together with isobetanin, probetanin, and neobetanin. Other pigments contained in beet are indicaxanthin and vulgaxanthins.

# Carotene



*β-Carotene represented by a 3-dimensional stick diagram*



*Carotene is responsible for the orange colour of the carrots and many other fruits and vegetables.*

## Contents :

- 1 Molecular structure
- 2 Dietary sources
- 3 The multiple forms
- 4 β - Carotene and cancer
- 5 β - Carotene and cognition
- 6 β - Carotene and photosensitivity
- 7 β - Carotene and nanotechnology
- 8 α - carotene and risk of death
- 9 Carotenemia
- 10 Production
  - 10.1 Total synthesis
- 11 Nomenclature

## Introduction :

The term **carotene** ( also **carotin**, from the Latin *carota*, or carrot ) is used for several related hydrocarbon substances having the formula  $C_{40}H_x$ , which are synthesized by plants but

cannot be made by animals. Carotene is an orange photosynthetic pigment important for photosynthesis. Carotenes are all coloured to the human eye. They are responsible for the orange colour of the carrot, for which this class of chemicals is named, and for the colours of many other fruits and vegetables (for example, sweet potatoes and orange cantaloupe melon). Carotenes are also responsible for the orange (but not all of the yellow) colours in dry foliage. They also (in lower concentrations) impart the yellow colouration to milk-fat and butter. Omnivorous animal species which are relatively poor converters of coloured dietary carotenoids to colourless retinoids have yellowed-coloured body fat, as a result of the carotenoid retention from the vegetable portion of their diet. The typical yellow-coloured fat of humans and chickens is a result of fat storage of carotenes from their diets.

Carotenes contribute to photosynthesis by transmitting the light energy they absorb from chlorophyll. They also protect plant tissues by helping to absorb the energy from singlet oxygen, an excited form of the oxygen molecule  $O_2$  which is formed during photosynthesis.

$\beta$ -Carotene is composed of two retinyl groups, and is broken down in the mucosa of the human small intestine by  $\beta$ -carotene 15,15'-mono oxygenase to retinal, a form of vitamin A.  $\beta$ -Carotene can be stored in the liver and body fat and converted to retinal as needed, thus making it a form of vitamin A for humans and some other mammals. The carotenes  $\alpha$ -carotene and  $\gamma$ -carotene, due to their single retinyl group (beta-ionone ring), also have some vitamin A activity (though less than  $\beta$ -carotene), as does the xanthophyll carotenoid  $\beta$ -cryptoxanthin. All other carotenoids, including lycopene, have no beta-ring and thus **no** vitamin A activity (although they may have antioxidant activity and thus biological activity in other ways).

Animal species differ greatly in their ability to convert retinyl (beta-ionone) containing carotenoids to retinals. Carnivores in general are poor converters of dietary ionine-

containing carotenoids, and pure carnivores such as cats and ferrets lack  $\beta$ -carotene 15,15'-mono oxygenase and cannot convert any carotenoids to retinals at all (resulting in carotenes **not** being a form of vitamin A for these species).

## **1 - Molecular structure :**

Chemically, carotenes are polyunsaturated hydrocarbons containing 40 carbon atoms per molecule, variable numbers of hydrogen atoms, and no other elements. Some carotenes are terminated by hydrocarbon rings, on one or both ends of the molecule. All are coloured to the human eye, due to extensive systems of conjugated double bonds. Structurally carotenes are tetraterpenes, synthesized biochemically from eight isoprene units.

Carotenes are found in plants in two primary forms designated by characters from the Greek alphabet: alpha-carotene ( $\alpha$ -carotene) and beta-carotene ( $\beta$ -carotene). Gamma, delta, epsilon, and zeta ( $\gamma$ ,  $\delta$ ,  $\epsilon$ , and  $\zeta$ -carotene) also exist. Since they are hydrocarbons, and therefore contain no oxygen, carotenes are fat-soluble and insoluble in water (in contrast with other carotenoids, the xanthophylls, which contain oxygen and thus are less chemically hydrophobic).

## **2 - Dietary sources :**

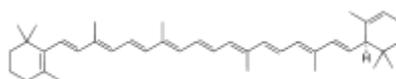
The following foods are particularly rich in carotenes ( also see Vitamin A article for amounts ) :

- sweet potatoes
- carrots
- wolf berries (goji)
- cantaloupe melon
- mangoes
- apricots
- Persimmon
- spinach
- kale

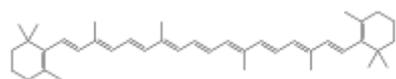
- chard
- turnip greens
- dandelion greens
- beet greens
- mustard greens
- collard greens
- water cress
- cilantro
- fresh thyme
- broccoli
- parsley
- romaine lettuce
- ivy gourd
- rose hips
- winter squash
- pumpkin
- cassava

Absorption from these foods is enhanced if eaten with fats, as carotenes are fat soluble, and if the food is cooked for a few minutes until the plant cell wall splits and the colour is released into any liquid. 6  $\mu\text{g}$  of dietary  $\beta$ -carotene supplies the equivalent of 1  $\mu\text{g}$  of retinol, or 1 RE (Retinol Equivalent). This is equivalent to  $3\frac{1}{3}$  IU of vitamin A.

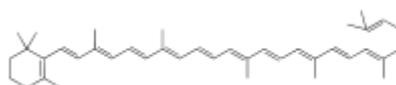
### 3 - The multiple forms :



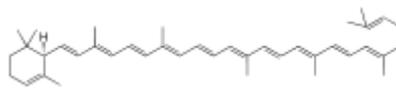
*$\alpha$ -carotene*



*$\beta$ -carotene*



*$\gamma$ -carotene*



*δ-carotene*

The two primary isomers of carotene,  $\alpha$ -carotene and  $\beta$ -carotene, differ in the position of a double bond (and thus a hydrogen) in the cyclic group at one end (left in the diagram here).

$\beta$ -Carotene is the more common form and can be found in yellow, orange, and green leafy fruits and vegetables. As a rule of thumb, the greater the intensity of the orange colour of the fruit or vegetable, the more  $\beta$ -carotene it contains.

Carotene protects plant cells against the destructive effects of ultraviolet light.  $\beta$ -Carotene is an anti-oxidant.

#### **4 - $\beta$ -Carotene and cancer**

It has been shown in trials that the ingestion of  $\beta$ -carotene at about 30 mg / day (10 times the Reference Daily Intake) increases the rate of lung cancer and prostate cancer in smokers and people with a history of asbestos exposure.

An article on the American Cancer Society says that The Cancer Research Campaign has called for warning labels on  $\beta$ -carotene supplements to caution smokers that such supplements may increase the risk of lung cancer.

The New England Journal of Medicine published an article<sup>[13]</sup> in 1994 about a trial which examined the relationship between daily supplementation of  $\beta$ -carotene and vitamin E (alpha-tocopherol) and the incidence of lung cancer. The study was done using supplements and researchers were aware of the epidemiological correlation between carotenoid-rich fruits and vegetables and lower lung cancer rates. The research concluded that no reduction in lung cancer was found in the participants using these supplements, and furthermore, these supplements may, in fact, have harmful effects.

The Journal of the National Cancer Institute and The New England Journal of Medicine published articles in 1996<sup>[14][15]</sup> about a trial that was conducted to determine if vitamin A (in the form of retinyl palmitate) and  $\beta$ -carotene had any beneficial effects to prevent cancer. The results indicated an increased risk of lung cancer for the participants who consumed the  $\beta$ -carotene supplement and who had lung irritation from smoking or asbestos exposure, causing the trial to be stopped early.

A review of all randomized controlled trials in the scientific literature by the Cochrane Collaboration published in JAMA in 2007 found that  $\beta$ -carotene *increased* mortality by something between 1 and 8 % ( Relative Risk 1.05, 95 % confidence interval 1.01-1.08). However, this meta-analysis included two large studies of smokers, so it is not clear that the results apply to the general population.

### **5 - $\beta$ -Carotene and cognition :**

A recent report demonstrated that 50 mg of  $\beta$ -carotene every other day prevented cognitive decline in a study of over 4000 physicians at a mean treatment duration of 18 years.

### **6 - $\beta$ -Carotene and photo sensitivity :**

Oral  $\beta$ -carotene is prescribed to people suffering from erythropoietic protoporphyria. It provides them some relief from photosensitivity .

### **7 - $\beta$ -Carotene and nano technology :**

$\beta$ -Carotene and lycopene molecules can be encapsulated into carbon nanotubes enhancing the optical properties of carbon nanotubes. Efficient energy transfer occurs between the encapsulated dye and nanotube — light is absorbed by the dye and without significant loss is transferred to the SWCNT. Encapsulation increases chemical and thermal stability of carotene molecules; it also allows their isolation and individual characterization.

## 8 - $\alpha$ -carotene and risk of death :

Higher dietary intake and blood serum levels of alpha-carotene are associated with significantly lower risk of death. ( See alpha-carotene for details and refs ) .

## 9 - Carotenemia :

Carotenemia or hypercarotenemia is excess carotene, but unlike excess vitamin A, carotene is non-toxic. Although hypercarotenemia is not particularly dangerous, it can lead to an orangening of the skin (carotenodermia), but not the conjunctiva of eyes (thus easily distinguishing it visually from jaundice). It is most commonly associated with consumption of an abundance of carrots, but it also can be a medical sign of more dangerous conditions.

## 10 - Production:

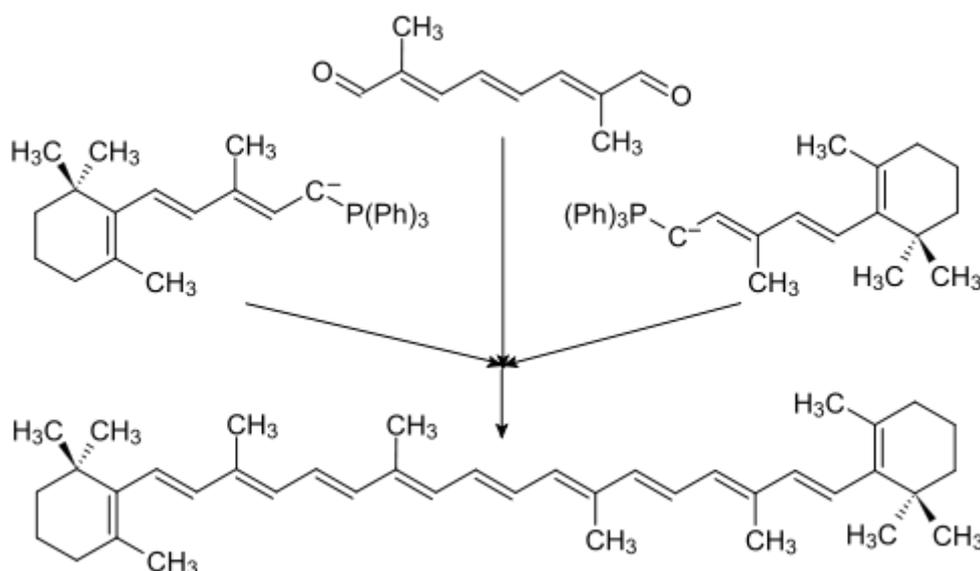
Most of the world's synthetic supply of carotene comes from a manufacturing complex located in Freeport, Texas and owned by DSM . The other major supplier BASF also uses a chemical process to produce  $\beta$ -carotene. Together these suppliers account for about 85 % of the  $\beta$ -carotene on the market. In Spain Vitatene produces natural  $\beta$ -carotene from fungus *Blakeslea trispora*, as does DSM but at much lower amount when compared to its synthetic  $\beta$ -carotene operation. In Australia, organic  $\beta$ -carotene is produced by Aquacarotene Limited from dried marine algae *Dunaliella salina* grown in harvesting ponds situated in Karratha, Western Australia. Cognis Australia Pty. Ltd., a subsidiary of the Germany-based company Cognis, is also producing  $\beta$ -carotene from microalgae grown in two sites in Australia that are the world's largest algae farms. In Portugal, the industrial biotechnology company Biotrend is producing natural all-*trans*- $\beta$ -carotene from a non genetically modified bacteria of the *Sphingomonas* genus isolated from soil.

Carotenes are also found in palm oil, corn, and in the milk of dairy cows, causing cow's milk to be light yellow, depending on the feed of the cattle, and the amount of fat in the milk (high-fat milks, such as those produced by Guernsey cows, tend to be more yellow because their fat content causes them to contain more carotene).

Carotenes are also found in some species of termites, where they apparently have been picked up from the diet of the insects.

### 10 – 1 - Total synthesis :

There are currently two commonly used methods of total synthesis of  $\beta$ -carotene. The first was developed by the Badische Anilin- & Soda-Fabrik (BASF) and is based on the Wittig reaction with Wittig himself as patent holder :



The second is a Grignard reaction, elaborated by Hoffman-La Roche from the original synthesis of Inhoffen et al. They are both symmetrical; the BASF synthesis is  $C_{20} + C_{20}$ , and the Hoffman-La Roche synthesis is  $C_{19} + C_2 + C_{19}$ .

## 11 - Nomenclature

Carotenes are carotenoids containing no oxygen. Carotenoids containing some oxygen are known as xanthophylls.

The two ends of the  $\beta$ -carotene molecule are structurally identical, and are called  **$\beta$ -rings**. Specifically, the group of nine carbon atoms at each end form a  $\beta$ -ring.

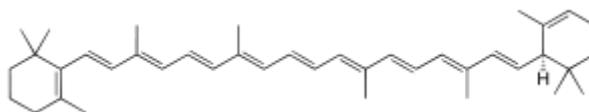
The  $\alpha$ -carotene molecule has a  $\beta$ -ring at one end; the other end is called an  **$\epsilon$ -ring**. There is no such thing as an " $\alpha$ -ring".

These and similar names for the ends of the carotenoid molecules form the basis of a systematic naming scheme, according to which:

- $\alpha$ -carotene is  **$\beta,\epsilon$ -carotene**;
- $\beta$ -carotene is  **$\beta,\beta$ -carotene**;
- $\gamma$ -carotene (with one  $\beta$  ring and one uncyclized end that is labelled *psi*) is  **$\beta,\psi$ -carotene**;
- $\delta$ -carotene (with one  $\epsilon$  ring and one uncyclized end) is  **$\epsilon,\psi$ -carotene**;
- $\epsilon$ -carotene is  **$\epsilon,\epsilon$ -carotene**
- lycopene is  **$\psi,\psi$ -carotene**

$\zeta$ -carotene is the biosynthetic precursor of neurosporene, which is the precursor of lycopene, which, in turn, is the precursor of the carotenes  $\alpha$  through  $\epsilon$ .

## *alpha* – Carotene



### 1 - Introduction :

**$\alpha$ -Carotene** is a form of carotene with a  $\beta$ -ring at one end and an  $\epsilon$ -ring at the other. It is the second most common form of carotene.

#### Properties

Molecular formula	$C_{40}H_{56}$
Molar mass	538 g / mol

### 2 - Human physiology

In US adults the mean concentration of serum  $\alpha$ -carotene was 4.79  $\mu\text{g} / \text{dL}$ , including 4.22  $\mu\text{g} / \text{dL}$  among men and 5.31  $\mu\text{g} / \text{dL}$  among women ( to convert to micromoles per liter, multiply by 0.01863 ).

### 3 - Health effects :

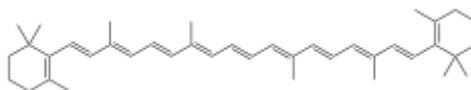
Dietary intake affects blood levels of  $\alpha$ -carotene which was associated with significantly lower risk of death, in one study.

### 4 - Dietary sources :

The following vegetables are rich in alpha-carotene :

- Yellow- orange vegetables : Carrots (the main source for US adults ) , Sweet potatoes, Pumpkin, Winter squash
- Dark-green vegetables : Broccoli, Green beans, Green peas, Spinach, Turnips greens, Collards, Leaf lettuce

## *beta* – Carotene



### Contents :

- 1 Pro-vitamin A activity
  - 1.1 Symmetric and asymmetric cleavage
  - 1.2 Conversion factors
    - 1.2.1 International Units
    - 1.2.2 Retinol Equivalents (REs)
    - 1.2.3 Retinol Activity Equivalents (RAEs)
- 2 Sources in the diet
- 3 Side effects
  - 3.1  $\beta$ -Carotene and lung cancer in smokers
- 4 Compendial status

### Introduction :

**$\beta$ -Carotene** is a strongly-coloured red-orange pigment abundant in plants and fruits. It is an organic compound and chemically is classified as a hydrocarbon and specifically as a terpenoid (isoprenoid), reflecting its derivation from isoprene units.  $\beta$ -Carotene is biosynthesized from geranylgeranyl pyrophosphate. It is a member of the carotenes, which are tetraterpenes, synthesized biochemically from eight isoprene units and thus having 40 carbons. Among this general class of carotenes,  $\beta$ -Carotene is distinguished by having beta-rings at both ends of the molecule.

Carotene is the substance in carrots that colours them orange and is the most common form of carotene in plants. When used as a food colouring, it has the E number E160a.

The structure was deduced by Karrer et al. in 1930. In nature,  $\beta$ -carotene is a precursor (inactive form) to vitamin A via the action of beta-carotene 15,15'- mono oxygenase.

Isolation of  $\beta$ -carotene from fruits abundant in carotenoids is commonly done using column chromatography. The separation of  $\beta$ -carotene from the mixture of other carotenoids is based on the polarity of a compound.  $\beta$ -Carotene is a non-polar compound, so it is separated with a non-polar solvent such as hexane. Being highly conjugated, it is deeply colored, and as a hydrocarbon lacking functional groups, it is very lipophilic.

**IUPAC name** : *beta,beta*-Carotene

**Other names**

Betacarotene

$\beta$ -Carotene

Food Orange 5

1,1'- ( 3,7,12,16 -Tetramethyl -1,3,5,7,9,11,13,15,17- octa deca nonaene-1,18-diyl ) bis [ 2,6,6 - rimethyl cyclo hexene]

**Properties**

Molecular formula	$C_{40} H_{56}$
Molar mass	$537 \text{ g mol}^{-1}$
Appearance	Dark orange crystals
Density	$0.94 \text{ g cm}^{-3}$
Melting point	$180 - 182 \text{ }^\circ\text{C}$
Boiling point	$633 - 677 \text{ }^\circ\text{C}$
log P	14.764
Flash point	$103 \text{ }^\circ\text{C}$

**1 – Pro -vitamin A activity :**

Plant carotenoids are the primary dietary source of pro-vitamin A worldwide, with  $\beta$ -carotene as the most well-known pro-vitamin A carotenoid. Others include  $\alpha$ -carotene and  $\beta$ -cryptoxanthin. Carotenoid absorption is restricted to the duodenum of the small intestine and dependent on Class B scavenger receptor (SR-B1) membrane protein, which are also responsible for the absorption of vitamin E (  $\alpha$ -Tocopherol ) . One molecule of  $\beta$ -carotene can be cleaved by a specific intestinal enzyme into two molecules of vitamin A.

Absorption efficiency is estimated to be between 9-22%. The absorption and conversion of carotenoids may depend on the form that the  $\beta$ -carotene is in (cooked vs. raw vegetables, in a supplement), intake of fats and oils at the same time, and the current levels of vitamin A and  $\beta$ -carotene.

Researchers list the following factors that determine the pro-vitamin A activity of carotenoids :

- Species of carotenoid
- Molecular linkage
- Amount in the meal
- Matrix properties
- Effectors
- Nutrient status
- Genetics
- Host specificity
- Interactions between factors

### **1 – 1 - Symmetric and asymmetric cleavage "**

In the molecule chain between the two cyclohexyl rings  $\beta$ -carotene cleaves either symmetrically or asymmetrically. Symmetric cleavage is done by an enzyme called  $\beta$ -carotene-15,15'-dioxygenase in the human body, requiring the antioxidant alpha-tocopherol . This symmetric cleavage gives two equivalent retinal molecules and each retinal molecule further reacts to give retinol ( vitamin A ) and retinoic acid.  $\beta$ -Carotene is also asymmetrically cleaved into two asymmetric products. The product of asymmetric cleavage is  $\beta$  - apocarotenal ( 8' ,10' , 12' ) . Asymmetric cleavage reduces the level of retinoic acid significantly.

### **1 – 2 - Conversion factors :**

Until recently, vitamin A activity in foods was expressed as international units ( IU ) . This is still the measurement generally used on food and supplement labels. How ever, it is difficult to calculate the total vitamin A activity in the diet in

terms of IU, because both the absorption and conversion of carotenoids, as compared with retinol, are variable. The unit retinol equivalent (RE) was developed by the Food and Agriculture Organization of the United Nations / World Health Organization ( FAO / WHO ) in 1967. More recently in 2001, the US Institute of Medicine proposed retinol activity equivalents (RAE) for their Dietary Reference Intakes.

### **1 – 2 – 1 - International Units :**

1 RE = 3.33 IU vitamin A activity from retinol

1 RE = 10 IU vitamin A activity from  $\beta$ -carotene

( In Canada, Health Canada sets 1 RE = 6.667 IU from  $\beta$ -carotene ) .

### **1 – 2 – 2 - Retinol Equivalents ( REs ):**

1 RE = 1  $\mu$ g retinol

1 RE = 6  $\mu$ g  $\beta$ -carotene ( In Canada, Health Canada sets 1 RE = 2  $\mu$ g  $\beta$ -carotene ) .

1 RE = 12  $\mu$ g other provitamin A carotenoids

### **1 – 2 – 3 - Retinol Activity Equivalents ( RAEs ) :**

1 RAE = 1  $\mu$ g retinol

1 RAE = 2  $\mu$ g all-*trans*- $\beta$ -carotene as a supplement

1 RAE = 12  $\mu$ g of all-*trans*- $\beta$ -carotene in a food matrix

1 RAE = 24  $\mu$ g other provitamin A carotenoids in a food matrix

## **2 - Sources in the diet :**

$\beta$ -Carotene contributes to the orange color of many different fruits and vegetables. Vietnamese gac (*Momordica*

*Cochinchinensis* Spreng.) and crude palm oil are particularly rich sources, as are yellow and orange fruits, such as mangoes and papayas, orange root vegetables such as carrots and yams and in green leafy vegetables such as spinach, kale, sweet potato leaves, and sweet gourd leaves. Vietnam gac and crude palm oil have by far the highest content of  $\beta$ -carotene of any known fruit or vegetable, 10 times higher than carrots for example. However, Gac is quite rare and unknown outside its native region of SE Asia, and crude palm oil is typically processed to remove the carotenoids before sale to improve the color and clarity.

The average daily intake of  $\beta$ -carotene is in the range 2–7 mg, as estimated from a pooled analysis of 500,000 women living in the USA, Canada and some European countries.

The U.S. Department of Agriculture lists the following 10 foods to have the highest  $\beta$ -carotene content per serving.

<b>Item</b>	<b>Grams per serving</b>	<b>Serving size</b>	<b>Milligrams <math>\beta</math>-carotene per serving</b>	<b>Milligrams <math>\beta</math>-carotene per 100 g</b>
Carrot juice, canned	236	1 cup	22.0	9.3
Pumpkin, canned, without salt	245	1 cup	17.0	6.9
Sweet potato , cooked , baked in skin , without salt	146	1 potato	16.8	11.5
Sweet potato , cooked , boiled , without skin	156	1 potato	14.7	9.4
Spinach , frozen , chopped or leaf , cooked , boiled , drained , with out salt	190	1 cup	13.8	7.2

Carrots , cooked , boiled , drained , without salt	156	1 cup	13.0	8.3
Spinach , canned , drained solids	214	1 cup	12.6	5.9
Sweet potato, canned , vacuum pack	255	1 cup	12.2	4.8
Carrots, frozen, cooked, boiled, drained, without salt	146	1 cup	12.0	8.2
Collards , frozen , chopped , cooked , boiled , drained , without salt	170	1 cup	11.6	6.8

### 3 - Side effects :

The most common side effect of excessive  $\beta$ -carotene consumption is carotenoderma, a physically harmless condition that presents as a conspicuous orange skin tint arising from deposition of the carotenoid in the outermost layer of the epidermis.<sup>[16]</sup> Chronic, high doses of  $\beta$ -carotene supplements have been associated with increased rate of lung cancer among those who smoke.<sup>1</sup> Additionally, supplemental beta-carotene may increase the risk of prostate cancer, intracerebral hemorrhage, and cardiovascular and total mortality in people who smoke cigarettes or have a history of high-level exposure to asbestos.

$\beta$ -Carotene is stored in the liver and many other organs ("golden ovaries"). Rat studies show that the body cannot convert such stored  $\beta$ -carotene into vitamin A, even if a deficit develops. A result of heavy consumption of synthetic  $\beta$ -carotene from a great variety of foods to which it is added, plus from natural sources, may result in saturating the liver's storage

capacity for fat soluble vitamins, so that reserves of other fat soluble vitamins, e.g. vitamin D and vitamin A, are not created - in countries far from the Equator, the summer storage of vitamin D, to be drawn upon during the darker winter, may be particularly important, not least in preventing osteoporosis and other vitamin D-deficiency related problems. In many cases the food color annatto can be used instead of  $\beta$ -carotene, and is not deposited in the body.

$\beta$ -Carotene has a high tendency to oxidize, more so than most food fats, and may thus to some extent hasten oxidation more than other food colours such as annatto.

### **3 – 1 - $\beta$ -Carotene and lung cancer in smokers :**

High dose  $\beta$ -Carotene supplementation increases the probability of lung cancer in cigarette smokers(15). The effect is specific to supplementation dose as no lung damage has been detected in those who are exposed to cigarette smoke and who ingest a physiologic dose of  $\beta$ -carotene (6 mg), in contrast to high pharmacologic dose (30 mg). Therefore, the oncology from  $\beta$ -carotene is based on both cigarette smoke and high daily doses of  $\beta$ -carotene.

There have been at least two suggestions for the mechanism for the observed harmful effect of high-dose  $\beta$ -carotene supplementation in this group. None has so-far gained wide acceptance.

A common explanation of the high dose effect is that when retinoic acid is liganded to RAR-beta (Retinoic Acid Receptor beta), the complex binds AP1 (Activator Protein 1). AP1 is a transcription factor that binds to DNA and in downstream events promote cell proliferation. Therefore, in the presence of retinoic acid, the retinoic acid:RAR-beta complex binds to AP1 and inhibit AP-1 from binding to DNA. In that case, AP1 is no longer expressed, and cell proliferation does not occur. Cigarette smoke increases the asymmetric cleavage of  $\beta$ -carotene, decreasing the level of retinoic acid significantly. This can lead

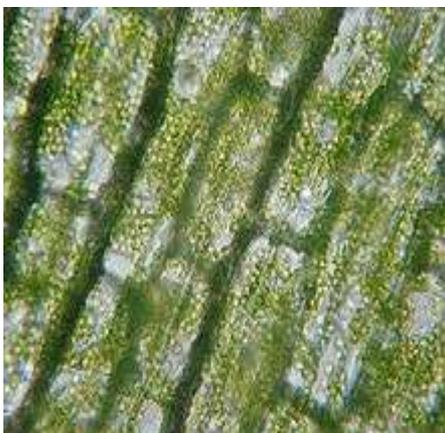
to a higher level of cell proliferation in smokers, and consequently, a higher probability of lung cancer.

Another  $\beta$ -carotene breakdown product suspected of causing cancer at high dose is *trans*- $\beta$ -apo-8'-carotenal (common apocarotenal), which has been found in one study to be mutagenic and genotoxic in cell cultures which do not respond to  $\beta$ -carotene itself.<sup>[20]</sup>

#### **4 - Compendial status :**

- British Pharmacopoeia

# Chlorophyll



*Chlorophyll is found in high concentrations in chloroplasts of plant cells.*



*Chlorophyll gives leaves their green color and absorbs light that is used in photosynthesis.*

## Contents

### 1 Chlorophyll and photosynthesis

#### 1.1 Why green and not black

### 2 Chemical structure

### 3 Spectrophotometry

### 4 Biosynthesis

### 5 Measuring chlorophyll

### 6 Culinary use

### 7 See also

## **Introduction :**

Chlorophyll (also chlorophyl) is a green pigment found in almost all plants, algae, and cyanobacteria. Its name is derived from the Greek words chloros ("green") and, phyllon ("leaf"). Chlorophyll is an extremely important biomolecule, critical in photosynthesis, which allows plants to obtain energy from light. Chlorophyll absorbs light most strongly in the blue portion of the electromagnetic spectrum, followed by the red portion. However, it is a poor absorber of green and near-green portions of the spectrum; hence the green color of chlorophyll-containing tissues. Chlorophyll was first isolated by Joseph Bienaimé Caventou and Pierre Joseph Pelletier in 1817.

### **1 - Chlorophyll and photosynthesis :**

Chlorophyll is vital for photosynthesis, which allows plants to obtain energy from light.

Chlorophyll molecules are specifically arranged in and around photosystems that are embedded in the thylakoid membranes of chloroplasts. In these complexes, chlorophyll serves two primary functions. The function of the vast majority of chlorophyll (up to several hundred molecules per photosystem) is to absorb light and transfer that light energy by resonance energy transfer to a specific chlorophyll pair in the reaction center of the photosystems.

The two currently accepted photosystem units are Photosystem II and Photosystem I, which have their own distinct reaction center chlorophylls, named P680 and P700, respectively. These pigments are named after the wavelength (in nanometers) of their red-peak absorption maximum. The identity, function and spectral properties of the types of chlorophyll in each photosystem are distinct and determined by

each other and the protein structure surrounding them. Once extracted from the protein into a solvent (such as acetone or methanol), these chlorophyll pigments can be separated in a simple paper chromatography experiment and, based on the number of polar groups between chlorophyll a and chlorophyll b, will chemically separate out on the paper.

The function of the reaction center chlorophyll is to use the energy absorbed by and transferred to it from the other chlorophyll pigments in the photosystems to undergo a charge separation, a specific redox reaction in which the chlorophyll donates an electron into a series of molecular intermediates called an electron transport chain. The charged reaction center chlorophyll (P680<sup>+</sup>) is then reduced back to its ground state by accepting an electron. In Photosystem II, the electron that reduces P680<sup>+</sup> ultimately comes from the oxidation of water into O<sub>2</sub> and H<sup>+</sup> through several intermediates. This reaction is how photosynthetic organisms such as plants produce O<sub>2</sub> gas, and is the source for practically all the O<sub>2</sub> in Earth's atmosphere. Photosystem I typically works in series with Photosystem II; thus the P700<sup>+</sup> of Photosystem I is usually reduced, via many intermediates in the thylakoid membrane, by electrons ultimately from Photosystem II. Electron transfer reactions in the thylakoid membranes are complex, however, and the source of electrons used to reduce P700<sup>+</sup> can vary.

The electron flow produced by the reaction center chlorophyll pigments is used to shuttle H<sup>+</sup> ions across the thylakoid membrane, setting up a chemiosmotic potential used mainly to produce ATP chemical energy; and those electrons ultimately reduce NADP<sup>+</sup> to NADPH, a universal reductant used to reduce CO<sub>2</sub> into sugars as well as for other biosynthetic reductions.

Reaction center chlorophyll–protein complexes are capable of directly absorbing light and performing charge separation events without other chlorophyll pigments, but the absorption cross section (the likelihood of absorbing a photon under a given light intensity) is small. Thus, the remaining chlorophylls in the photosystem and antenna pigment protein complexes associated with the photosystems all cooperatively absorb and funnel light energy to the reaction center. Besides chlorophyll a, there are other pigments, called accessory pigments, which occur in these pigment–protein antenna complexes.

A green sea slug, *Elysia chlorotica*, has been found to use the chlorophyll it has eaten to perform photosynthesis for itself. This process is known as kleptoplasty, and no other animal has been found to have this ability.

### 1 – 1 - Why green and not black :



*Black plants can absorb more radiation,  
and yet most plants are green*

It is as of yet unclear exactly why plants (or rather, their light absorbing molecule, chlorophyll) have mostly evolved to be green. Green plants reflect mostly green and near-green light to viewers rather than absorbing it. Other parts of the system of photosynthesis still allow green plants to use the green light spectrum (e.g. through a light-trapping leaf structure, carotenoids, etc). Green plants do not use a large part of the visible spectrum as efficiently as possible. A black plant can

absorb more radiation, and this could be very useful, notwithstanding the problems of disposing of this extra heat (e.g. some plants must close their openings, called stoma, on hot days to avoid losing too much water). More precisely, the question becomes why the only light absorbing molecule used for power in plants is green and not simply black.

The biologist John Berman has offered the opinion that evolution is not an engineering process, and so it is often subject to various limitations that an engineer or other designer is not. Even if black leaves were better, evolution's limitations can prevent species from climbing to the absolute highest peak on the fitness landscape. Berman wrote that achieving pigments that work better than chlorophyll could be very difficult. In fact, all higher plants (embryophytes) are believed to have evolved from a common ancestor that is a sort of green algae - with the idea being that chlorophyll has evolved only once.

Shil DasSarma, a microbial geneticist at the University of Maryland, has pointed out that species of archae do use another light-absorbing molecule, retinal, to extract power from the green spectrum. He described the view of some scientists that such green-light-absorbing archae once dominated the earth environment. This could have left open a "niche" for green organisms which would absorb the other wavelengths of sunlight. This is just a possibility, and Berman wrote that scientists are still not convinced of any one explanation.

## **2 - Chemical structure :**

Chlorophyll is a chlorin pigment, which is structurally similar to and produced through the same metabolic pathway as other porphyrin pigments such as heme. At the center of the chlorin ring is a magnesium ion. For the structures depicted in this article, some of the ligands attached to the  $Mg^{2+}$  center are

omitted for clarity. The chlorin ring can have several different side chains, usually including a long phytol chain. There are a few different forms that occur naturally, but the most widely distributed form in terrestrial plants is chlorophyll a. The general structure of chlorophyll a was elucidated by Hans Fischer in 1940, and by 1960, when most of the stereochemistry of chlorophyll a was known, Robert Burns Woodward published a total synthesis of the molecule. In 1967, the last remaining stereochemical elucidation was completed by Ian Fleming, and in 1990 Woodward and co-authors published an updated synthesis. In 2010, a near-infrared-light photosynthetic pigment called chlorophyll f might have been discovered in cyanobacteria and other oxygenic microorganisms that form stromatolites. Based on NMR data, optical and mass spectra, it is thought to have a structure of C<sub>55</sub>H<sub>70</sub>O<sub>6</sub>N<sub>4</sub>Mg or [2-formyl]-chlorophyll a.

**The different structures of chlorophyll are summarized below :**

	Chlorophyll a	Chlorophyll b	Chlorophyll c1	Chlorophyll c2	Chlorophyll d	Chlorophyll f
<b>Molecular formula</b>	C <sub>55</sub> H <sub>72</sub> O <sub>5</sub> N <sub>4</sub> Mg	C <sub>55</sub> H <sub>70</sub> O <sub>6</sub> N <sub>4</sub> Mg	C <sub>35</sub> H <sub>30</sub> O <sub>5</sub> N <sub>4</sub> Mg	C <sub>35</sub> H <sub>28</sub> O <sub>5</sub> N <sub>4</sub> Mg	C <sub>54</sub> H <sub>70</sub> O <sub>6</sub> N <sub>4</sub> Mg	C <sub>55</sub> H <sub>70</sub> O <sub>6</sub> N <sub>4</sub> Mg
<b>C2 group</b>	-CH <sub>3</sub>	-CHO				
<b>C3 group</b>	-CH=CH <sub>2</sub>	-CH=CH <sub>2</sub>	-CH=CH <sub>2</sub>	-CH=CH <sub>2</sub>	-CHO	-CH=CH <sub>2</sub>
<b>C7 group</b>	-CH <sub>3</sub>	-CHO	-CH <sub>3</sub>	-CH <sub>3</sub>	-CH <sub>3</sub>	-CH <sub>3</sub>
<b>C8 group</b>	-CH <sub>2</sub> CH <sub>3</sub>	-CH <sub>2</sub> CH <sub>3</sub>	-CH <sub>2</sub> CH <sub>3</sub>	-CH=CH <sub>2</sub>	-CH <sub>2</sub> CH <sub>3</sub>	-CH <sub>2</sub> CH <sub>3</sub>
<b>C17 group</b>	- CH <sub>2</sub> CH <sub>2</sub> CO O-Phytol	- CH <sub>2</sub> CH <sub>2</sub> COO -Phytol	- CH=CHCOO H	- CH=CHCOO H	- CH <sub>2</sub> CH <sub>2</sub> COO -Phytol	- CH <sub>2</sub> CH <sub>2</sub> COO -Phytol
<b>C17-C18 bond</b>	Single (chlorin)	Single (chlorin)	Double (porphyrin)	Double (porphyrin)	Single (chlorin)	Single (chlorin)
<b>Occurrence</b>	Universal	Mostly plants	Various algae	Various algae	Cyanobacteria	Cyanobacteria



The absorption peaks of chlorophyll a are at 665 nm and 465 nm. Chlorophyll a fluoresces at 673 nm (maximum) and 726 nm. The peak molar absorption coefficient of chlorophyll a exceeds  $10^5 \text{ M}^{-1} \text{ cm}^{-1}$ , which is among the highest for small-molecule organic compounds.

In 90 % acetone-water, the peak absorption wavelengths of chlorophyll a are 430 nm and 664 nm; peaks for chlorophyll b are 460 nm and 647 nm; peaks for chlorophyll c1 are 442 nm and 630 nm; peaks for chlorophyll c2 are 444 nm and 630 nm; peaks for chlorophyll d are 401 nm, 455 nm and 696 nm.

By measuring chlorophyll fluorescence, plant ecophysiology can be investigated. Chlorophyll fluorometers are used by plant researchers to assess plant stress.

#### **4 - Biosynthesis :**

In plants, chlorophyll may be synthesized from succinyl-CoA and glycine, although the immediate precursor to chlorophyll a and b is protochlorophyllide. In Angiosperm plants, the last step, conversion of protochlorophyllide to chlorophyll, is light-dependent and such plants are pale (etiolated) if grown in the darkness. Non-vascular plants and green algae have an additional light-independent enzyme and grow green in the darkness as well.

Chlorophyll itself is bound to proteins and can transfer the absorbed energy in the required direction. Protochlorophyllide occurs mostly in the free form and, under light conditions, acts as a photosensitizer, forming highly toxic free radicals. Hence, plants need an efficient mechanism of regulating the amount of chlorophyll precursor. In angiosperms, this is done at the step of aminolevulinic acid (ALA), one of the intermediate compounds in the biosynthesis pathway. Plants that are fed by ALA

accumulate high and toxic levels of protochlorophyllide; so do the mutants with the damaged regulatory system.

Chlorosis is a condition in which leaves produce insufficient chlorophyll, turning them yellow. Chlorosis can be caused by a nutrient deficiency of iron -- called iron chlorosis — or by a shortage of magnesium or nitrogen. Soil pH sometimes plays a role in nutrient-caused chlorosis; many plants are adapted to grow in soils with specific pH levels and their ability to absorb nutrients from the soil can be dependent on this. Chlorosis can also be caused by pathogens including viruses, bacteria and fungal infections, or sap - sucking insects.

### **5 - Measuring chlorophyll :**

The chlorophyll content of leaves can be non-destructively measured using hand - held, battery-powered meters.

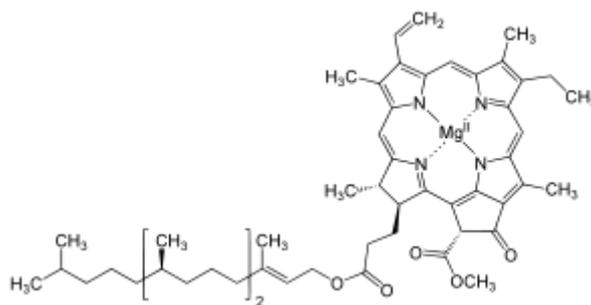
Chlorophyll Content meters measure the optical absorption of a leaf to estimate its chlorophyll content. Chlorophyll molecules absorb in the blue and red bands, but not the green and infra-red bands. Chlorophyll content meters measure the amount of absorption at the red band to estimate the amount of chlorophyll present in the leaf. To compensate for varying leaf thickness, Chlorophyll Meters also measure absorption at the infrared band which is not significantly affected by chlorophyll. For instance, the CCM 200 plus Chlorophyll Meter measures the transmittance at 653 nm (in the red band) and transmittance at 931 nm (in the infrared band). The percentage of transmittance at 931 nm, relative to the percentage of transmittance at 653 nm, estimates the relative chlorophyll content of the leaf.

The measurements made by these devices are simple, quick and relatively inexpensive. They now, typically, have large data storage capacity, averaging and graphical displays .

## **6 - Culinary use :**

Chlorophyll is registered as a food additive (colorant), and its E number is E140. Chefs use chlorophyll to color a variety of foods and beverages green, such as pasta and absinthe. Chlorophyll is not soluble in water, and it is first mixed with a small quantity of vegetable oil to obtain the desired solution. Extracted liquid chlorophyll was considered to be unstable and always denatured until 1997, when Frank S. & Lisa Sagliano used freeze-drying of liquid chlorophyll at the University of Florida and stabilized it as a powder, preserving it for future use.

# Chlorophyll a



## Properties

Molecular formula	C <sub>55</sub> H <sub>72</sub> Mg N <sub>4</sub> O <sub>5</sub>
Molar mass	893.5 g mol <sup>-1</sup>
Melting point	117-120 °C
Boiling point	decomposes

## Contents :

- 1 Distribution of Chlorophyll a
- 2 Molecular Structure
  - 2.1 Chlorin Ring
  - 2.2 Side Chains
  - 2.3 Hydrocarbon Tail
- 3 Biosynthesis
- 4 Reactions of Photosynthesis
  - 4.1 Absorbance of Light
  - 4.2 Primary Electron Donation

## Introduction :

Chlorophyll a is a specific form of chlorophyll used in oxygenic photosynthesis. It absorbs most energy from wavelengths of violet-blue and orange-red light. This photosynthetic pigment is essential for photosynthesis in eukaryotes, cyanobacteria and prochlorophytes because of its role as primary electron donor in the electron transport chain.

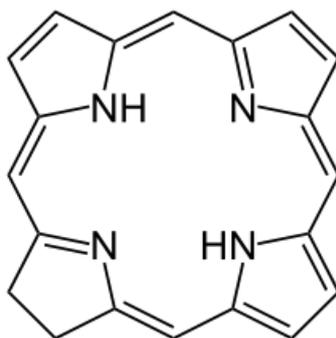
Chlorophyll a also transfers resonance energy in the antenna complex, ending in the reaction center where specific chlorophyll's P680 and P700 are located.

## 1 - Distribution of Chlorophyll a

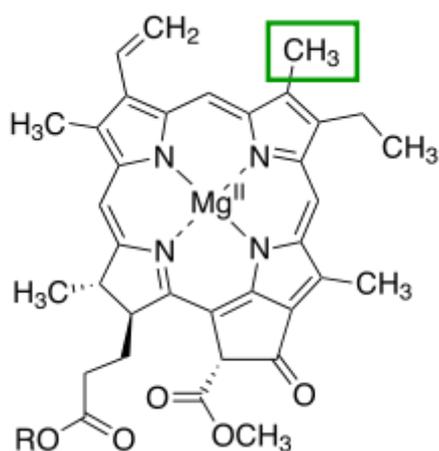
Organism	Photosynthetic pigments	Habitat
Dinoflagellates	Chlorophyll a & c, carotenoids	Marine, freshwater
Euglenoids	Chlorophyll a & b, carotenoids	Mostly freshwater, some marine
Cryptomonads	Chlorophyll a & c, Phycobilins	Cold marine & freshwater
Haptophyte algae	Chlorophyll a & c, carotenoids	Most marine, few freshwater
Diatoms	Chlorophyll a & c, carotenoids	Marine & freshwater
Brown algae	Chlorophyll a & c, carotenoids	Almost all marine
Red algae	Chlorophyll a, Phycobilins	Mostly marine, few freshwater
Green Algae	Chlorophyll a & b, carotenoids	Mostly aquatic (freshwater or marine)
Plants	Chlorophyll a & b, carotenoids	Land & some aquatic

*This table shows the distribution of different photosynthetic pigments among many different organisms. Chlorophyll a (red) is produced by all oxygenic, photosynthetic organisms (modified from 2).*

Chlorophyll a is essential for most photosynthetic organisms to release chemical energy but is not the only pigment that can be used for photosynthesis. All oxygenic photosynthetic organisms use chlorophyll a, but differ in accessory pigments like chlorophylls b and c.[2] Chlorophyll a can also be found in very small quantities in the green sulfur bacteria, an anaerobic photoautotroph.[4] These organisms use bacteriochlorophyll and some chlorophyll a but do not produce oxygen.[4] Anoxygenic photosynthesis is the term applied to this process, unlike oxygenic photosynthesis where oxygen is produced during the light reactions of photosynthesis.



*This is the structure of a chlorin ring without the central Mg center of the chlorophyll a structure.*



*The chlorophyll a central molecular structure. The green box identifies the C-3 position on the ring indicating the important methyl group on the structure.*

## Common Madder ( *Rubia tinctorum* )



Common Madder (*Rubia tinctorum*)

### Scientific classification

Kingdom :	Plantae
(unranked) :	Angiosperms
(unranked) :	Eudicots
(unranked) :	Asterids
Order :	Gentianales
Family :	Rubiaceae
Subfamily :	Rubioideae
Tribe :	Rubieae
Genus :	<i>Rubia</i> L.

### I - Introduction :

*Rubia* is a genus of the madder family Rubiaceae, which contains about 60 species of perennial scrambling or climbing herbs and sub-shrubs native to the Old World, Africa, temperate Asia and America. The genus and its best known species are also known as **Madder**, *Rubia tinctorum* ( Common Madder ), *Rubia peregrina* ( Wild Madder ) , and *Rubia cordifolia* (Munjeet or Indian Madder ) .

The Common Madder can grow to 1.5 m in height. The evergreen leaves are 5–10 cm long and 2–3 cm broad, produced in whorls of 4 –7 starlike around the central stem. It climbs with

tiny hooks at the leaves and stems . The flowers are small ( 3 – 5 mm across ) , with five pale yellow petals, in dense racemes, and appear from June to August, followed by small (4–6 mm diameter) red to black berries. The roots can be over a metre long, up to 12 mm thick and the source of red dyes known as rose madder and **Turkey red**. It prefers loamy soils with a constant level of moisture. Madders are used as food plants for the larvae of some Lepidoptera species including Hummingbird hawk moth.

## 2 - Species :

- *Rubia akane*
- *Rubia alaica* Pachom.
- *Rubia angustifolia* L.
- *Rubia chinensis* Regel & Maack
- *Rubia chitralensis* Ehrend.
- *Rubia cordata* Thunb
- *Rubia cordifolia* L. : Indian Madder
- *Rubia cretacea* Pojark.
- *Rubia deserticola* Pojark.
- *Rubia dolichophylla* Schrenk
- *Rubia florida* Boiss.
- *Rubia fruticosa*
- *Rubia jesoensis* (Miq.) Miyabe & Miyake
- *Rubia komarovii* Pojark.
- *Rubia krascheninnikovii* Pojark.
- *Rubia laevissima* Tscherneva
- *Rubia laxiflora* Gontsch.
- *Rubia pavlovii* Bajtenov & Myrz.
- *Rubia peregrina* L. : Wild Madder
- *Rubia rechingeri* Ehrend.
- *Rubia regelii* Pojark.
- *Rubia reznitzenkoana* Litv.
- *Rubia rigidifolia* Pojark.
- *Rubia schugnanica* B.Fedtsch. ex Pojark.
- *Rubia sikkimensis* Kurz
- *Rubia syrticola* Miq.

- *Rubia tatarica* (Trevir.) F.Schmidt
- *Rubia tibetica* Hook.f.
- *Rubia tinctorum* L. : Common Madder
- *Rubia transcaucasica* Grossh.
- *Rubia yunnanensis* (Franch. ex Diels) Diels

### 3 - Uses :

It has been used since ancient times as a vegetable red dye for leather, wool, cotton and silk. For dye production, the roots are harvested in the first year. The outer brown layer gives the common variety of the dye, the lower yellow layer the refined variety. The dye is fixed to the cloth with help of a mordant, most commonly alum. Madder can be fermented for dyeing as well (Fleurs de garance). In France, the remains were used to produce a spirit as well.

The roots contain the acid ruberthyrin. By drying, fermenting or a treatment with acids, this is changed to sugar, alizarin and purpurin, which were first isolated by the French chemist Pierre Jean Robiquet in 1826. Purpurin is normally not coloured, but is red when dissolved in alcalic solutions. Mixed with clay and treated with alum and ammonia, it gives a brilliant red colourant (madder lake).



Common Madder (*Rubia tinctorum*), from Thomé, *Flora von Deutschland, Österreich und der Schweiz* 1885.

The pulverised roots can be dissolved in sulfuric acid, which leaves a dye called garance (the French name for madder) after drying. Another method of increasing the yield consisted of dissolving the roots in sulfuric acid after they had been used for dyeing. This produces a dye called garanceux. By treating the pulverized roots with alcohol, colorin was produced. It contained 40–50 times the amount of alizarin of the roots.

The chemical name for the pigment is alizarin, of the anthraquinone-group. In 1869, the German chemists Graebe and Liebermann synthesised artificial alizarin, which was produced industrially from 1871 onwards, which effectively put an end to the cultivation of madder. In the 20th century, madder was only grown in some areas of France.

#### **4 - History :**

Early evidence of dyeing comes from India where a piece of cotton dyed with madder has been recovered from the archaeological site at Mohenjo-daro ( 3rd millennium BCE ). In Sanskrit, this plant is known by the name Manjishtha. It was used by hermits to dye their clothes saffron. Dioscorides and Pliny the Elder (*De Re Natura*) mention the plant (*Rubia passiva*). In Viking age levels of York, remains of both woad and madder have been excavated. The oldest European textiles dyed with madder come from the grave of the Merovingian queen Arnegundis in St. Denis near Paris (between 565 and 570 AD). In the "Capitulare de villis" of Charlemagne, madder is mentioned as "warentiam". The herbal of Hildegard of Bingen mentions the plant as well. The red coats of the British Redcoats were dyed with madder, after earlier being dyed with cochineal.

Turkey red was a strong, very fast red dye for cotton obtained from madder root via a complicated multistep process involving "sumac and oak galls, calf's blood, sheep's dung, oil, soda, alum, and a solution of tin." Turkey red was developed in India and spread to Turkey. Greek workers familiar with the methods of its production were brought to France in 1747, and

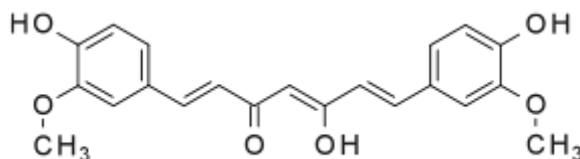
Dutch and English spies soon discovered the secret. A sanitized version of Turkey red was being produced in Manchester by 1784, and roller-printed dress cottons with a Turkey red ground were fashionable in England by the 1820s.

According to Culpeper's herbal, the plant is ruled by Mars and has an opening quality, and will bind and strengthen afterwards. It was used in the treatment of jaundice, obstruction of the spleen, melancholy, palsy, haemorrhoids, sciatica, and of bruises. The root should be boiled in wine, and sugar or honey added. The seed of madder, drunk with vinegar and honey is used for the swelling of the spleen. Leaves and stems are used when the monthly female menstrual bleeding is late. Leaves and roots are squashed and put on freckles and other discolorations of the skin.

### **External links**

- World Checklist of Rubiaceae
- Picture showing shades of red obtained on wool with Madder
- Article showing the results of cold dyeing wool with madder
- Data sheet with pictures of madder (German)

# Curcumin



## Contents

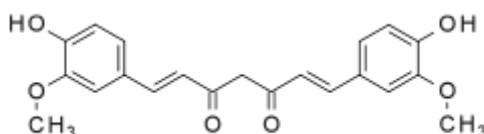
- 1 Introduction
- 2 Chemistry
- 3 Biosynthesis
- 4 Potential medical uses
  - 4.1 Anticarcinogenic effects
- 5 Bioavailability
- 6 Potential risks and side effects

### 1 – Introduction :

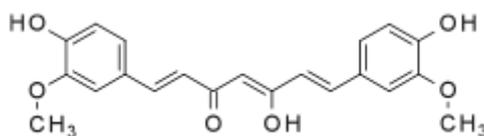
**Curcumin** is the principal curcuminoid of the popular Indian spice turmeric, which is a member of the ginger family (Zingiberaceae). The other two curcuminoids are desmethoxycurcumin and bis-desmethoxycurcumin. The curcuminoids are natural phenols and are responsible for the yellow color of turmeric. Curcumin can exist in at least two tautomeric forms, keto and enol. The enol form is more energetically stable in the solid phase and in solution.

Curcumin can be used for boron quantification in the curcumin method. It reacts with boric acid forming a red colored compound, known as rosocyanine.

Curcumin is brightly yellow colored and may be used as a food coloring. As a food additive, its E number is E100.



*Curcumin Keto form*



*Curcumin Enol form*



*Curcumin*

**IUPAC name :**

( 1*E* , 6*E* ) -1,7- bis ( 4 - hydroxy- 3 - methoxyphenyl) -  
1,6 – heptadiene - 3 , 5- dione

**Other names :**

curcumin  
diferuloylmethane  
C.I. 75300  
Natural Yellow 3

**Properties**

Molecular formula	$C_{21}H_{20}O_6$
Molar mass	368 g / mol
Appearance	Bright yellow - orange powder
Melting point	183 °C

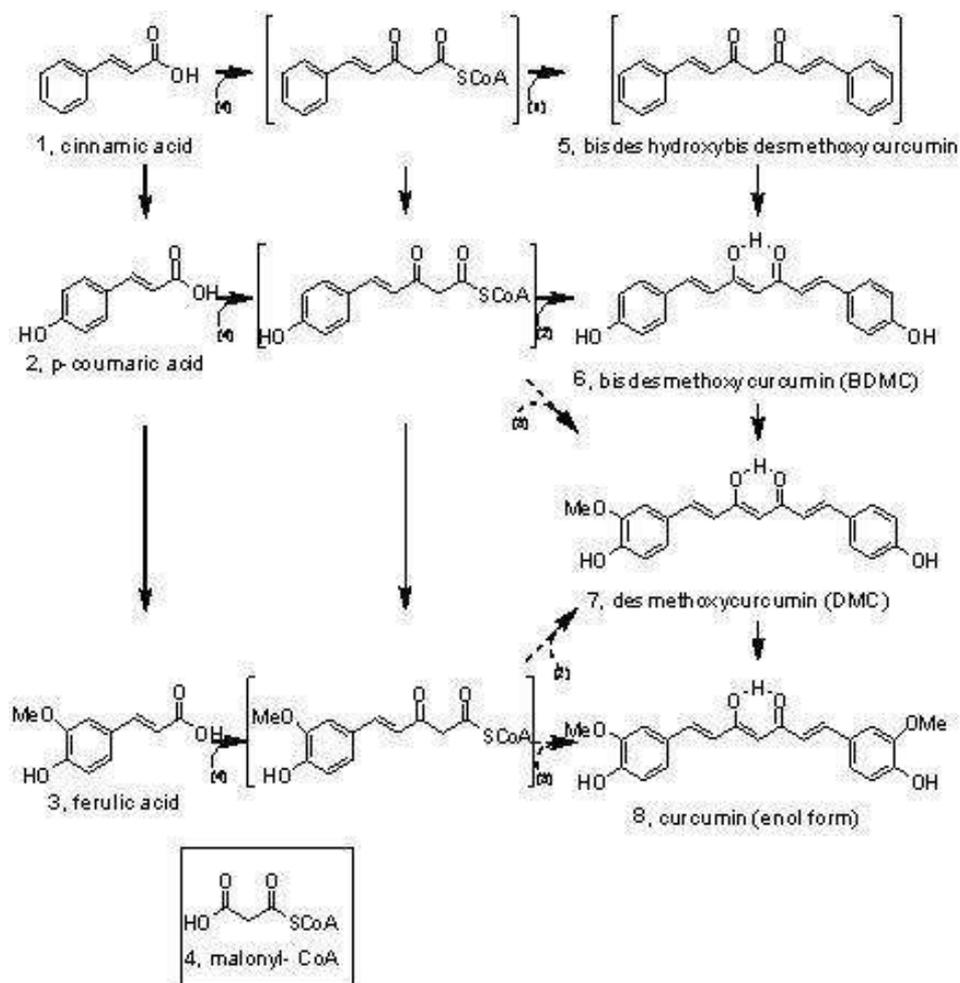
**2 - Chemistry :**

Curcumin incorporates several functional groups. The aromatic ring systems, which are polyphenols are connected by two  $\alpha,\beta$ -unsaturated carbonyl groups. The diketones form stable enols or are easily deprotonated and form enolates, while the  $\alpha$  ,  $\beta$  - unsaturated carbonyl is a good Michael acceptor and undergoes nucleophilic addition. The structure was first identified in 1910 by J. Miłobędzka, Stanisław Kostanecki and Wiktor Lampe .

Curcumin is used as a reagent for boron in EPA Method 212.3.

### **3 - Biosynthesis :**

The biosynthetic route of curcumin has proven to be very difficult for researchers to determine. In 1973 Roughly and Whiting proposed two mechanisms for curcumin biosynthesis. The first mechanism involved a chain extension reaction by cinnamic acid and 5 malonyl-CoA molecules that eventually arylized into a curcuminoid. The second mechanism involved two cinnamate units being coupled together by malonyl - CoA. Both mechanisms use cinnamic acid as their starting point, which is derived from the amino acid phenylalanine . This is noteworthy because plant biosyntheses employing cinnamic acid as a starting point are rare compared to the more common use of p-coumaric acid . Only a few identified compounds, such as anigorufone and pinosylvin , use cinnamic acid as their start molecule. An experimentally backed route was not presented until 2008. This proposed biosynthetic route follows both the first and second mechanisms suggested by Roughley and Whiting. However, the labeling data supported the first mechanism model in which 5 malonyl-CoA molecules react with cinnamic acid to form curcumin . However, the sequencing in which the functional groups, the alcohol and the methoxy, introduce them selves on to the curcuminoid seems to support more strongly the second proposed mechanism. There fore, it was concluded the second pathway proposed by Roughly and Whiting was correct.



#### 4 - Potential medical uses :

Turmeric has been used historically as a component of Indian Ayurvedic medicine since 1900 BC to treat a wide variety of ailments. Research in the latter half of the 20th century has identified curcumin as responsible for most of the biological activity of turmeric. *In vitro* and animal studies have suggested a wide range of potential therapeutic or preventive effects associated with curcumin. At present, these effects have not been confirmed in humans. However, as of 2008, numerous clinical trials in humans were underway, studying the effect of curcumin on various diseases, including multiple myeloma, pancreatic cancer, myelodysplastic syndromes, colon cancer, psoriasis, and Alzheimer's disease.

*In vitro* and animal studies have suggested curcumin may have antitumor , antioxidant, antiarthritic , anti-amyloid, anti-ischemic , and anti-inflammatory properties . Anti-inflammatory properties may be due to inhibition of eicosanoid biosynthesis . In addition it may be effective in treating malaria , prevention of cervical cancer, and may interfere with the replication of the human immunodeficiency virus ( HIV ) . In HIV, it appears to act by interfering with P300 / CREB -binding protein ( CBP ) . It is also hepatoprotective . A 2008 study at Michigan State University showed low concentrations of curcumin interfere with Herpes simplex virus - 1 ( HSV-1 ) replication . The same study showed curcumin inhibited the recruitment of RNA polymerase II to viral DNA, thus inhibiting its transcription . This effect was shown to be independent of effect on histone acetyltransferase activities of p300 / CBP . A previous ( 1999 ) study performed at University of Cincinnati indicated curcumin is significantly associated with protection from infection by HSV - 2 in animal models of intravaginal infections .

Curcumin acts as a free radical scavenger and antioxidant, inhibiting lipid peroxidation and oxidative DNA damage. Curcuminoids induce glutathione S - transferase and are potent inhibitors of cytochrome P450 .

The Siegel Life Project funded an initial study on curcumin for Alzheimer's in 1997-1998 through the UCLA Center on Aging. UCLA/VA researchers Drs. Cole and Frautschy presented potent anti -Alzheimer's effects in 1997 and 2000 at the Society for Neuroscience . These data were then published in 2001, demonstrating that curcumin was particularly effective in reducing neurodegeneration, oxidative damage, diffuse plaque deposition, aberrant inflammation and impaired inflammatory clearance following beta-amyloid infusion, which was published in 2001 . This led to testing in a transgenic animal model where it was shown to dramatically diminish plaque burden and overall inflammation, but also increase plaque associated inflammatory cells suggesting clearance . In

2004 this UCLA / Veterans group demonstrated that the effect was in part to the highly specific binding effects to beta-amyloid, whereby it could break apart amyloid aggregates in vitro, bind to plaques in vivo, and because of its fluorescent properties, it could be determined that plaques of transgenic mice ingesting curcumin fluoresced green, demonstrating brain penetration . A Harvard group showed that 7 days of tail vein injections of curcumin shrunk plaque size and reduced dystrophic neurites . The UCLA group also showed curcumin synergizing with fish oil working to protect against cognitive deficits in another transgenic model . However humans show much more glucuronidation than rodents , and glucuronidated curcumin does not pass the blood brain barrier ( See section on curcumin formulations ) . Free curcumin but not glucuronidated curcumin readily passes through the barrier. But extensive glucuronidation in humans is the major barrier to translation in neurodegenerative diseases. Human intestinal cells glucuronidate more than rodent intestine ( Ireson ) .

There is also circumstantial evidence curcumin improves mental functions; a survey of 1010 Asian people who ate yellow curry and were between the ages of 60 and 93 showed those who ate the sauce "once every six months" or more had higher MMSE results than those who did not . From a scientific standpoint, though, this does not show whether the curry caused it, or people who had healthy habits also tended to eat the curry, or some completely different relationship.

Numerous studies have demonstrated curcumin, amongst only a few other things, such as high impact exercise, learning, bright light, and antidepressant usage, has a positive effect on neurogenesis in the hippocampus and concentrations of brain - derived neurotrophic factor ( BDNF ) , reductions in both of which are associated with stress, depression, and anxiety . Curcumin has also been demonstrated to be a selective monoamine oxidase inhibitor ( MAOI ) of type MAO - A . Fluorescent imaging in a mouse model of Alzheimer's disease showed that curcumin crosses the blood - brain barrier . Several

studies have demonstrated that unlike glucuronidated curcumin, free curcumin, which is lipophilic, readily passes the blood brain barrier .

In 2009, an Iranian group demonstrated the combination effect of curcumin with 24 antibiotics against *Staphylococcus aureus*. In that study, in the presence of a subinhibitory concentration of curcumin, the antibacterial activities of cefixime, cefotaxime, vancomycin and tetracycline were increased against test strain. The increase in inhibition zone surface area for these antibiotics were 52.6 % ( cefixime ) , 24.9 % ( cephotaxime ) , 26.5 % ( vancomycin ) and 24.4 % (tetracycline). Also it showed curcumin has an antagonist effect on the antibacterial effect of nalidixic acid against the test strain

Although many preclinical studies suggest curcumin may be useful for the prevention and treatment of several diseases, the effectiveness of curcumin has not yet been demonstrated in randomized, placebo - controlled, double - blind clinical trials .

In 2008 scientists at the Salk Institute ( Drs. Dave Schubert and Pam Maher ) performed high throughput screening, identifying a curcumin pyrazole derivative, which improved memory , is broadly neuroprotective , stimulates BDNF in vitro and in vivo. This group showed in collaboration with UCLA that it was protective in brain trauma and in collaboration with Cedars Sinai / UCSD groups that it was protective in stroke .

#### **4 – 1 - Anti carcinogenic effects :**

Its potential anticancer effects stem from its ability to induce apoptosis in cancer cells without cytotoxic effects on healthy cells. Curcumin can interfere with the activity of the transcription factor NF- $\kappa$ B , which has been linked to a number of inflammatory diseases such as cancer.

A 2009 study suggested curcumin may inhibit mTOR complex I via a novel mechanism .

Another 2009 study on curcumin effects on cancer states it "modulates growth of tumor cells through regulation of multiple cell signaling pathways including cell proliferation pathway ( cyclin D1, c-myc), cell survival pathway ( Bcl - 2, Bcl - xL, cFLIP, XIAP, c-IAP1), caspase activation pathway ( caspase - 8, 3, 9 ) , tumor suppressor pathway ( p53, p21 ) death receptor pathway ( DR4, DR5), mitochondrial pathways, and protein kinase pathway ( JNK , Akt , and AMPK )" .

A 2010 study in malignant brain tumors showed curcumin effectively inhibits tumor cell proliferation, as well as migration and invasion, and these effects may be mediated through interference with the STAT3 signaling pathway .

When 0.2 % curcumin is added to diet given to rats or mice previously given a carcinogen, it significantly reduces colon carcinogenesis .

Curcumin has recently been shown to have phyto-estrogenic activity that might contribute to activity against breast cancer . In the murine model of breast cancer metastasis, curcumin inhibits the formation of lung metastases probably through the NF-kappa-B dependent regulation of protumorigenic inflammatory cytokines .

## **5 - Bio availability :**

There have been several commercial products developed to provide an alternate route to curcumin. Several trials with unformulated curcumin show extensive glucuronidation and sulfation and typically undetectable levels of free curcumin : For example, trials show that ingestion from 2 to 10 grams of unformulated curcumin lead to undetectable or very low serum levels of free curcumin . For neurodegenerative diseases, it is important that curcumin is absorbed predominantly as 'free" as opposed to glucuronidated, since glucuronidated curcumin does not penetrate the blood brain barrier, while free curcumin is readily brain penetrant .

The first formulation to improve bioavailability was curcumin supplements with piperine ( "bioperine", manufactured by Sabinsa Corp , New Jersey ) and distributed by several companies. Co-supplementation with 20 mg of piperine ( extracted from black pepper) significantly increased the absorption of curcumin by 2000 % in a study funded by the manufacturer of piperine . How ever, the increase in absorption in plasma only occurred during the first hour, after which the difference between the piperine curcumin and the regular curcumin was almost the same as far as absorption. It is important to recognize that rapid clearance from plasma after acute administration does not necessarily represent levels in tissues such as adipose, breast or brain . Glucuronidation inhibitors should be taken cautiously ( if at all ) by individuals taking other medications, but whether the doses of piperine used can dramatically alter pharmacokinetics of other drugs is unclear .

The second major commercial innovation of curcumin bioavailability was made in 2006, when UC Regents and the Veterans Administration filed a provisional patent, which led to Longvida Optimized Curcumin. In July 2008, the inventors described a new form of "lipidated curcumin" from Verdure Sciences as "Longvida" that was noted to achieve more than 5 micromolar in the brain in vivo.<sup>[33]</sup> Pharmacokinetics of Longvida in humans shows superior absorption of free curcumin.<sup>[52]</sup> Extensive toxicity studies have been performed showing Longvida to have an excellent safety profile . as was found in the NIH cancer toxicity studies with tumeric oleoresin leading it to be placed on the FDA's GRAS ( generally recognized as safe ) list .

Another method to increase the bioavailability of curcumin was later developed as Meriva, patent pending since 2006 and involves a simple procedure creating a complex with soy phospholipids. However, there was no plasma concentration of free curcumin found in humans. In animals, free curcumin reaching 33.4 nanomolar while in humans, none was detected .

Another curcumin proprietary formulation was introduced in 2008 ( BCM-95®, Bio curcumax , Arjuna ) mixed with turmeric oils, was shown in human cross-over bioavailability comparison tests to have 8 times the bioavailability and greater blood retention time than standard 95 % and up to 5 times more than curcumin combined with lecithin and piperine . This same formula was also shown to remain above 200 ng / g for 12 hours in a human clinical study. Plain curcumin remained above 200 ng / g for less than 2 hours. Two hours after ingestion, BCM-95 levels of free curcumin were 10 - fold over that of plain curcumin . How ever these data were in contrast to a six-month placebo-controlled, double - blind clinical trial for Alzheimer's disease, individuals in the BCM-95 groups even doses as high as 4 g failed to yield any significant free curcumin in the plasma. Interestingly there was a non - significant increase in serum amyloid beta with the high dose, which may relate to some effect on amyloid clearance from the brain. ”.

There are other formulations for curcumin in the pipeline, that have not yet become commercial. In 2007, a polymeric nano particle-encapsulated formulation of curcumin ( "nanocurcumin" ) . Nanocurcumin particles have a size of less than 100 nanometers on average, and demonstrate comparable to superior efficacy compared to free curcumin in human cancer cell line models . How ever, actual *in vivo* absorption ( injected or oral ) should be tested with this nanoparticle.

In the year of 2010, a food - grade polymer micellar encapsulation system was shown to increase curcumin's water solubility and *in vitro* anti - cancer activity. It was found that hydrophobically modified starch , usually used to encapsulate flavors, was able to form polymer micelles. Using a simple high - speed homogenization method, it can load curcumin into its hydrophobic core, and thus solubilize curcumin. Cell culture experiments revealed an enhanced anti-cancer activity on HepG2 cell line. However, more *in vivo* studies are needed to further prove its efficacy in the aspect of bioavailability.

Populations ingesting high amounts of curcumin in foods may have reduced risk for some diseases ( Parkinson's ), which may be due to an effect of cooking or dissolution in oil. Some benefits of curcumin, such as the potential protection from colon cancer, may not require systemic absorption. Alternatively, dissolving curcumin in warm oils prior to ingestion increases bioavailability; however, other than abstracts presented at Society for Neuroscience in 2009 "Efficacy of curcumin formulations in relation to systemic availability in the brain and different blood compartments in neuroinflammatory and AD models. Society for Neuroscience, Oct 18. 2009, #211.7, Chicago Ill 36:2009", no manuscripts to date have documented this. The poor stability in aqueous solution as opposed to high stability in lipid solutions argues that cooking with curcumin and oil may increase absorption. Curcumin is not stable in water because it is prone to hydrolysis, that convert it to vanillin and ferulic acid . In addition to curries, one can purchase food products containing turmeric ( ~5 % curcumin ) such as Nutmeric , which provide turmeric in an oil-solubilized form similar to Indian curry preparations. But the exact amount of curcumin may be far less than 1 % curcumin, questioning health relevance.

## **6 - Potential risks and side effects :**

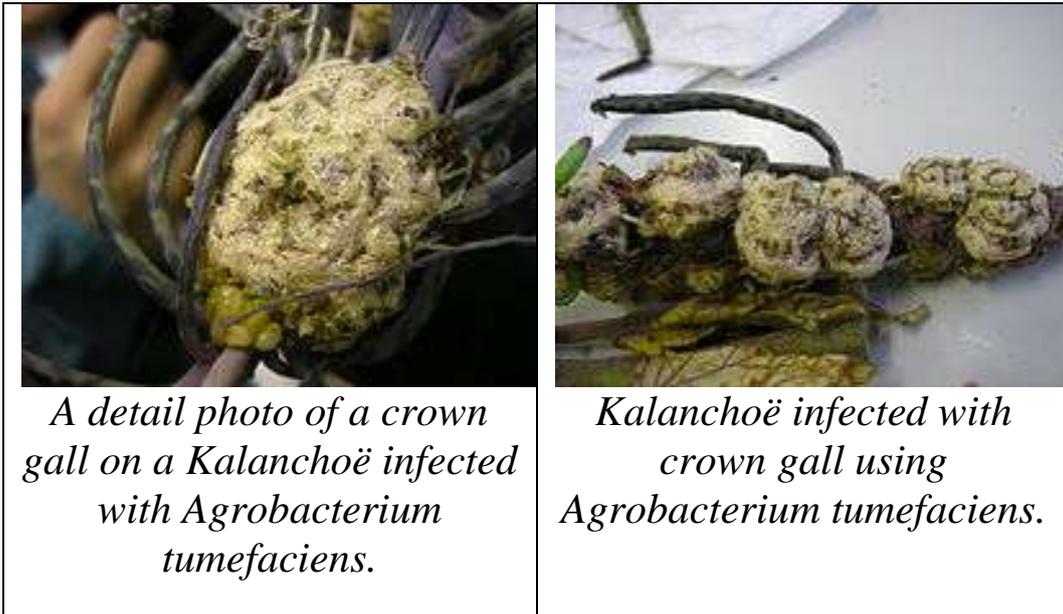
Extensive in vivo toxicity studies have been performed with turmeric Oleoresin ( 85 % curcumin ) which led to it being placed on the FDA's GRAS ( generally recognized as safe ) list [54] . Kawanishi et al. (2005) remarked that curcumin, like many antioxidants, can be a "double-edged sword" where, in the test tube, anticancer and antioxidant effects may be seen in addition to pro-oxidant effects . Carcinogenic effects are inferred from interference with the p53 tumor suppressor pathway, an important factor in human colon cancer. Carcinogenic and LD<sub>50</sub> tests in mice and rats, however, have failed to establish a clear relationship between tumorigenesis and administration of curcumin in turmeric oleoresin at > 98 % concentrations . Other in vitro and in vivo studies suggest that

curcumin may cause carcinogenic effects under specific conditions .

Clinical studies in humans with high doses ( 2–12 grams ) of curcumin have shown few side effects, with some subjects reporting mild nausea or diarrhea . More recently, curcumin was found to alter iron metabolism by chelating iron and suppressing the protein hepcidin , potentially causing iron deficiency in susceptible patients.

There is no or little evidence to suggest curcumin is either safe or unsafe for pregnant women. How ever, there is still some concern medicinal use of products containing curcumin could stimulate the uterus, which may lead to a miscarriage, although there is not much evidence to support this claim. According to experiments done on rats and guinea pigs, there is no obvious effect (neither positive, nor negative) on the pregnancy rate or number of live or dead embryos . Curcumin has embryotoxic and teratogenic effects on zebrafishes (*Danio rerio*) embryos.

## Gall



### Contents :

- 1 Causes of plant galls
  - 1.1 Insects
  - 1.2 Fungi
  - 1.3 Bacteria and viruses
  - 1.4 Other plants
- 2 Uses
- 3 Gallery

### Introduction :

**Galls** or *cecidia* are outgrowths on the surface of lifeforms caused by invasion by other lifeforms, such as parasites or bacterial infection. Plant galls are abnormal outgrowths of plant tissues and can be caused by various parasites, from fungi and bacteria, to insects and mites. Plant galls are often highly organised structures and because of this the cause of the gall can often be determined without the actual agent being identified. This applies particularly to some insect and mite plant galls. In pathology, a gall is a raised sore on the skin, usually caused by chafing or rubbing.

## **1 - Causes of plant galls :**

### **1 – 1 – Insects :**

Insect galls are the highly distinctive plant structures formed by some herbivorous insects as their own microhabitats. They are plant tissue which is controlled by the insect. Galls act as both the habitat and food source for the maker of the gall. The interior of a gall can contain edible nutritious starch and other tissues. Some galls act as "physiologic sinks", concentrating resources in the gall from the surrounding plant parts . Galls may also provide the insect with physical protection from predators .

Insect galls are usually induced by chemicals injected by the larvae or the adults of the insects into the plants, and possibly mechanical damage. After the galls are formed, the larvae develop inside until fully grown, when they leave. In order to form galls, the insects must seize the time when plant cell division occurs quickly: the growing season, usually spring in temperate climates, but which is extended in the tropics.

The meristems, where plant cell division occurs, are the usual sites of galls, though insect galls can be found on other parts of the plant, such as the leaves, stalks, branches, buds, roots, and even flowers and fruits. Gall-inducing insects are usually species-specific and sometimes tissue-specific on the plants they gall.

Gall-inducing insects include gall wasps, gall midges, gall flies, aphids (such as *Melaphis chinensis*), and psyllids.

### **1 – 2 – Fungi :**

One gall-inducing fungus is Cedar-apple rust. Galls are often seen in *Millettia pinnata* leaves and fruits. Leaf galls appear like tiny clubs; however, flower galls are globose.

It is worth noting that the fungus *Ustilago esculenta* associated with *Zizania latifolia*, a wild rice, produces an edible gall highly valued as a food source in the Zhejiang and Jiangsu provinces of China.

### **1 – 3 - Bacteria and viruses :**

*Agrobacterium tumefaciens* is an example of a gall-causing bacterium.

### **1 – 4 - Other plants :**

Mistletoe can form galls on its hosts

### **2 – Uses :**

Galls are rich in resins and tannic acid and have been used in the manufacture of permanent inks (such as iron gall ink) and astringent ointments, in dyeing, and in tanning. A high-quality ink has long been made from the Aleppo gall, found on oaks in the Middle East; it is one of a number of galls resembling nuts and called "gallnuts" or "nutgalls". The larvae in galls are useful for a survival food and fishing bait; see the Indigenous Australian foods Bush coconut and Mulga apple. Nutgalls also produce purpurogallin.

### **3 – Gallery :**





*Knopper gall (Andricus quercuscalicis)*



*Oak artichoke gall (Andricus fecundator)*



*Neuroterus albipes forma laeviusculus*



*Knopper gall (Andricus quercuscalicis)*



*Andricus kollari oak gall*



*Eucalyptus leaf gall*



*Gymnosporangium*



*Cola-nut galls (Andricus lignicola) on Pedunculate Oak*



*Sectioned gall showing central 'cell' and inquiline chamber; exit-hole and a possibly parasitised stunted gall specimen.*



*Oak marble galls, one with a Gall fly exit hole and another with Phoma gallorum fungal attack.*



*Pineapple gall on Sitka Spruce caused by Adelges abietis.*



*Red-pea gall (Cynips divisa) on Pedunculate oak*



*Goldenrod Gall*



*Developing Pineapple pseudocone galls on Norway Spruce*



*Oak Apples on an oak tree.*



*An Oak tree with multiple Oak apples.*



*Gall of peach tree leaves, found at Beijing*



*Lime nail galls (*Eriophyes tiliae tiliae*)*

**See also :**

- Bush coconut
- Mulga apple

- Oak apple
- Oak Marble gall
- Knopper gall
- Oak artichoke gall
- Rose bedeguar gall
- Pineapple gall
- Cola-nut gall

# Hair coloring



*A hair dresser colors a client's hair.*

## Contents :

- 1 Introduction
- 2\_Types of hair coloring
  - 2.1\_Permanent hair color
  - 2.2\_Semi - permanent hair dye
  - 2.3\_Demi - permanent hair color
  - 2.4\_Temporary hair color
- 3\_Application techniques
- 4\_Alternative hair colorants
- 5\_Adverse effects of hair coloring
  - 5.1\_Skin irritation and allergy
  - 5.2\_Hair breakage
  - 5.3\_Skin discoloration
  - 5.4\_Unpredictable color results
  - 5.5\_Health concerns
- 6\_Alternatives to industrial tints

## 1 - Introduction :

**Hair coloring** is the practice of changing the color of hair. Common reasons are to cover gray hair, to change to a color regarded as more fashionable or desirable, and to restore the original hair color after it has been discolored by hairdressing processes or sun bleaching. In the 1661 book *Eighteen Books of the Secrets of Art & Nature*, various methods of coloring hair black , gold , green , red, yellow , and white are explained .

## 2 - Types of hair coloring :

The four most common classifications are *permanent*, *demi-permanent* ( some times called *deposit only* ) , *semi – permanent* , and *temporary* .

### 2 – 1 - Permanent hair color :

The most popular way to achieve permanent hair coloring is through the use of oxidation dyes. The ingredients include 1,4-diaminobenzene (historically) or 2,5- diaminotoluene (currently), a coupling agent, and an oxidant. The process is typically performed under basic conditions.

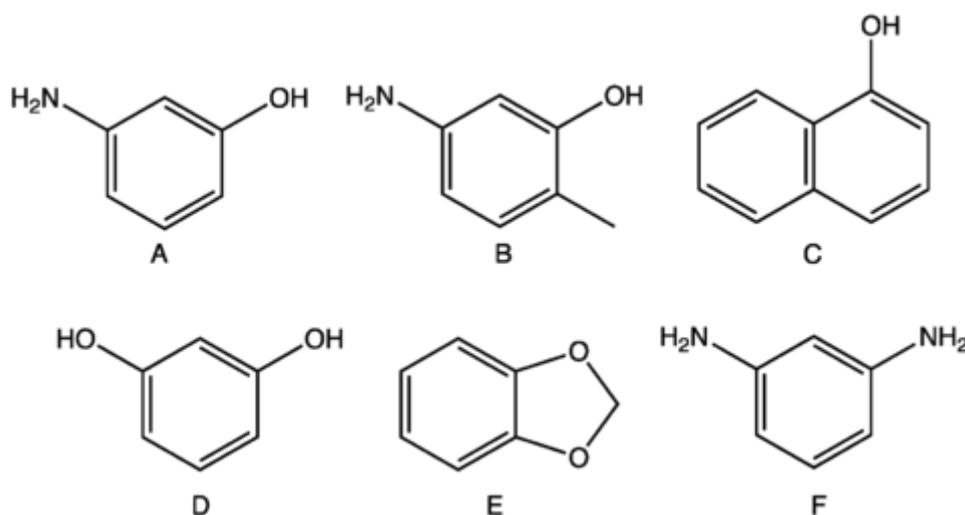
The mechanism of oxidation dyes involves three steps: 1) Oxidation of 1,4- diaminobenzene derivative to the quinone state. 2) Reaction of this diimine with a coupler (more detail below). 3) Oxidation of the resulting compound to give the final dye.

The preparation (dye precursors) is in the leuco (colorless) form. Oxidizing agents are usually hydrogen peroxide, and the alkaline environment is usually provided by ammonia. The combination of hydrogen peroxide and the primary intermediate causes the natural hair to be lightened, which provides a blank canvas for the dye. Ammonia opens the hair shaft so that the dye can actually bond with the hair, and ammonia speeds up the reaction of the dye with the hair.

Various combinations of primary intermediates and couplers provide a spectrum of shades of hair colors. The primary intermediates are aromatic para compounds, such as 1,4-diaminobenzene or 4- aminophenol. The couplers are meta-substituted derivatives of aniline. They come in three major classes based on the color that they produce when they react with the primary intermediate.

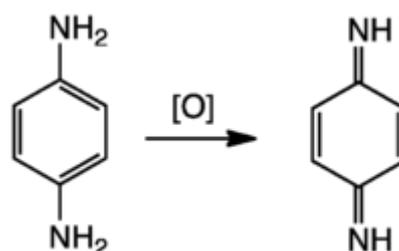
- Blue couplers include 1,3-diaminobenzene and its derivatives.

- Red couplers include phenols and naphthols, such as 3-aminophenol, 5-amino-2-methylphenol and 1-naphthol. The combination of 2,5-diaminotoluene with the coupler 3-aminophenol gives a magenta-brown dye, while the combination of 2,5-diaminotoluene with the coupler 1-naphthol gives a purple dye.
- Yellow-green couplers include resorcinol, 4-chlororesorcinol, and benzodioxoles. These compounds produce broad-band absorption when they react to form dyes, allowing for more natural-looking hair colors. The combination of 2,5-diaminotoluene with the coupler resorcinol gives a greenish brown dye.

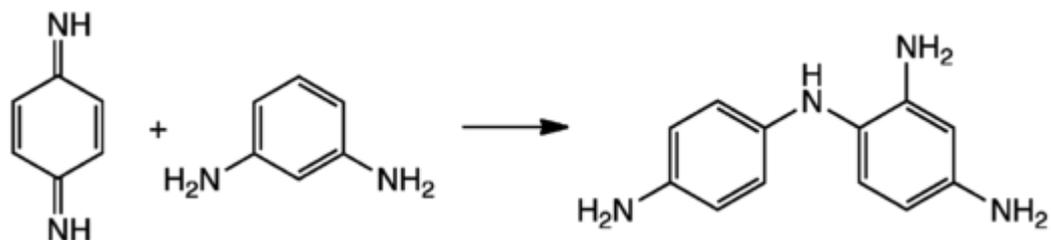


*Couplers are chemical compounds that define the color of the hair dye. Shown here are three red couplers (A,B,C), two yellow-green couplers (D,E) and a blue coupler (F).*

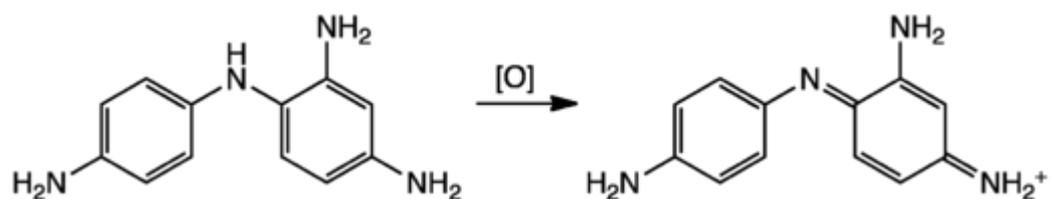
The first step shows the oxidation of p-phenylenediamine to the quinonediimine ( $C_6H_4(NH)_2$ ):



This species exists in equilibrium with the monoprotonated form ( $C_6H_4(NH)(NH_2)^+$ ). The second step involves the attack of this quinonediimine on the coupler. In organic chemistry, this reaction is called electrophilic aromatic substitution:



In the third and final step, the product from the quinonediimine-coupler reaction oxidizes to the final hair dye.



The resulting hair dye is also much larger than the precursor molecules, which causes the dye to bond to the hair.

## 2 – 2 – Semi - permanent hair dye :

Semi-permanent hair dye has smaller molecules than temporary dyes, and is therefore able to partially penetrate the hair shaft. For this reason, the color will survive repeated washing, typically 4–5 shampoos or a few weeks. Semi-permanents contain no, or very low levels of developer, peroxide or ammonia, and are therefore safer for damaged or fragile hair. However, semi-permanents may still contain the toxic compound p-phenylenediamine or other such ingredients. The U.S. Environmental Protection Agency reported that in rats and mice chronically exposed to PPD in their diet, it simply depressed body weights, and no other clinical signs of toxicity were observed in several studies.

The final color of each strand of hair will depend on its original color and porosity, so there will be subtle variations in

shade across the whole head. This gives a more natural result than the solid, all over color of a permanent dye. However, it also means that gray or white hairs will not dye to the same shade as the rest of the hair. If there are only a few grey / white hairs, the effect will usually be enough for them to blend in, but as the gray spreads, there will come a point where it will not be disguised as well. In this case, the move to permanent color can sometimes be delayed by using the semi-permanent as a base and adding highlights.

Semi - permanent color cannot lighten the hair.

### **2 – 3 - Demi - permanent hair color :**

Demi - permanent hair color is permanent hair color that contains an alkaline agent other than ammonia (e.g., ethanolamine, sodium carbonate) and, while always employed with a developer, the concentration of hydrogen peroxide in that developer may be lower than used with a permanent hair color. Since the alkaline agents employed in demi-permanent colors are less effective in removing the natural pigment of hair than ammonia these products provide no lightening of hair's color during dyeing. As the result, they cannot color hair to a lighter shade than it was before dyeing and are less damaging to hair than their permanent counterpart.

Demi-permanents are much more effective at covering gray hair than semi-permanents, but less so than permanents.

Demi-permanents have several advantages as compared with permanent color. Because there is essentially no lifting ( i.e. removal ) of natural hair color, the final color is less uniform / homogeneous than a permanent and therefore more natural looking; they are gentler on hair and therefore safer, especially for damaged hair; and they wash out over time ( typically 20 to 28 shampoos ) , so root regrowth is less noticeable and if a change of color is desired, it is easier to achieve. Demi-permanent hair colors are, in essence, permanent color and the

darker shades in particular may persist longer than indicated on the packet.

## **2 – 4 - Temporary hair color :**

Temporary hair color is available in various forms including rinses, shampoos, gels, sprays, and foams. Temporary hair color is typically brighter and more vibrant than semi-permanent and permanent hair color. It is most often used to color hair for special occasions such as costume parties and Halloween.

The pigment molecules in temporary hair color are large and cannot penetrate the cuticle layer. The color particles remain adsorbed (closely adherent ) to the hair shaft and are easily removed with a single shampooing. Temporary hair color can persist on hair that is excessively dry or damaged in a way that allows for migration of the pigment to the interior of the hair shaft. It lasts for about a few hours to 1 day.

## **3 - Application techniques**



*Hair with blonde highlights*

Hair color was traditionally applied to the hair as one overall color. The modern trend is to use several colors to

produce streaks or gradations, either on top of the natural color or on top of a single base color. These are referred to as :

- Highlighting, where sections of hair are treated with lighteners, usually to create blond streaks.
- Lowlighting, where sections of hair are treated with darker hair color.

These can be applied by the following methods :

- Foiling, where pieces of foil or plastic film are used to separate off the hair to be colored; especially when applying more than one color.
- Cap, when a plastic cap is placed tight on the head and strands are pulled through with a hook.
- Balayage, where hair color is painted directly onto sections of the hair with no foils used to keep the color contained.

All application techniques can be used with any type of color. For highlights, the hair will usually have to be bleached before coloring.

#### **4 - Alternative hair colorants :**



*Hair and beard colored blue.*

A minority of hair coloring products are designed to create hair colors not typically found in nature. These are available in almost any color imaginable, including green and fuchsia.

These dyes are typically sold in punk - themed stores (such as comic book and music stores), with brand names like "Beyond The Zone", "Splat", "Clairol Jazzing", "Manic Panic", "Special Effects", "Punky Colour", "Stargazer", "La Riche Directions". A permanent alternative in some colors (such as bold red and dark, inky purples and blues) are available from big haircare brands. Some alternative color shades are blacklight reactive, to show up under nightclub lighting.

The chemical formula of alternative color dyes typically contain only tint and have no developer. This means that they will only create the bright color of the packet if they are applied to light blond hair. People with darker hair (medium brown to black) will need to use a bleaching kit prior to tint application. Some people with fair hair may benefit from prior bleaching as well. Gold, yellow and orange undertones in hair that has not been lightened enough can adversely affect results, especially with pinks, blues and greens. Although alternative colors are semi - permanent in the cases of some colors, such as blue and purple, it could take several months to fully wash the color from bleached or pre - lightened hair.

## **5 - Adverse effects of hair coloring :**

Hair coloring involves the use of chemicals capable of removing, replacing and/or covering up pigments naturally found inside the hair shaft. Use of these chemicals can result in a range of adverse effects, including temporary skin irritation and allergy, hair breakage, skin discoloration and unexpected hair color results.

Additionally, there is ongoing debate regarding more serious health consequences of hair color usage, including lead poisoning.

### **5 – 1 - Skin irritation and allergy :**

In certain individuals, the use of hair coloring can result in allergic reaction and/or skin irritation. Symptoms of these

reactions can include redness, sores, itching, burning sensation and discomfort. If any of these symptoms occur, alert your hair colorist immediately so that they can remove the color. Symptoms will sometimes not be apparent immediately following the application and processing of the tint, but can also arise after hours or even a day later. To help prevent or limit allergic reactions, the majority of hair color products recommend that the client conduct a patch test before using the product. This involves mixing a small quantity of tint preparation and applying it directly to the skin for a period of 48 hours. If irritation develops, manufacturers recommend that the client not use the product. A skin patch test is advised before the use of every coloring process, since allergies can develop even after years of use with no reaction.

### **5 – 2 - Hair breakage :**

Hair that has been damaged by excessive exposure to chemicals is considered *over-processed*. This results in dry, rough and fragile hair. In extreme cases, the hair can be so damaged that it breaks off entirely. This is especially true for Afro - Caribbean hair, especially if used in combination with relaxers. Treatments are available but the only real solution is to stop the use of chemicals until new hair grows and the damaged hair is cut off . It is advised that colored hair be deep conditioned regularly, and washed and conditioned with gentle products specifically designed for color-treated hair. This will help keep the hair intact and minimize color fading.

### **5 – 3 - Skin discoloration :**

Skin and fingernails are made of the same type of keratinized protein as hair. That means that drips, slips and extra hair tint around the hairline can result in patches of discolored skin. This is more common with darker hair colors and persons with dry absorbent skin.

This discoloration will disappear as the skin naturally renews itself and the top layer of skin is removed ( typically

takes a few days or at most a week ) . A good way to prevent dye discoloration is to put a thin layer of Vaseline or any oil-based preparation around the hairline. It is recommended that latex or nitrile gloves be worn to protect the hands.

#### **5 – 4 - Unpredictable color results :**

Several factors influence the final color of the hair following the coloring process.

- For semi - permanent and demi - permanent color, the final color is a blend of the natural color of the hair and the dye color.
- Bleached hair will often require pre-pigmentation before a color application. Dyeing bleached hair brown can result in grey or very ashy ( grey sheen ) hair.
- Previously color treated hair can react unpredictably with subsequent color treatments.
- Previous use of shampoos which deposit a layer of plastic on the hair can block the action of the dye.
- Presence of minerals, salts, chlorine or other contaminants in the water used in the coloring process
- Certain prescription drugs can alter hair chemistry
- Coloring dark hair to achieve a desirable shade of blond requires bleaching, followed by a secondary color treatment. Bleached hair can still have a yellow or coppery shade. A violet-based color can cancel out yellow tones, and a blue-based shade will cancel out coppery orange.

Professional hair colorists have a number of products to correct or deemphasize unintended hair coloring outcomes.

## 5 – 5 - Health concerns :

An FDA study that found lead acetate ( the active ingredient in gradual darkening products such as Grecian formula ) is toxic if ingested .

- Articles that link the development of some forms of cancer ( including leukemia , non - Hodgkin's lymphoma, bladder cancer, blood cancer, and multiple myeloma ) with use of hair color . More specifically , prolonged use of permanent dark hair dyes can double a person's risk of getting various types of blood cancer .
- Recently a known human carcinogen , 4 - aminobiphenyl or 4 - ABP, was found in some hair dyes that you can get off the shelf . How ever , evidence is limited and inconsistent for the link between cancer from hair dye .

## 6 - Alternatives to industrial tints :

Ancient civilizations dyed their hair using plants. Some of the most well known are henna, indigo, *Cassia obovata*, senna, turmeric and amla. Others include katam, black walnut hulls, red ochre and leeks .

Alternate based dyes are available for people sensitive to PPD, a chemical found in most hair colors.

Products that avoid the side effects of most industrial tints are available. The safer alternatives generally contain fewer potentially toxic compounds or are plant based. Temporary, semi-permanent and permanent exist with the same persistence as the industrial versions. In practice the results produced by these products often do not last as long as industrial tints . Allergic reactions are possible even from natural vegetable dyes.

Henna is a plant ( *Lawsonia inermis* ) used for Ayurvedic hair coloring. The orange dye is commonly used as a deposit -

only hair color whose active component, lawsone, binds to keratin. It is therefore considered semi-permanent to permanent, depending on a person's hair type. Most people will achieve a permanent color from henna, especially after the second dye. With repeated use the orange color builds up into red and then auburn. While "natural" henna is generally a red color, variations exist. These variations usually contain ingredients from other plants and even synthetic dyes.

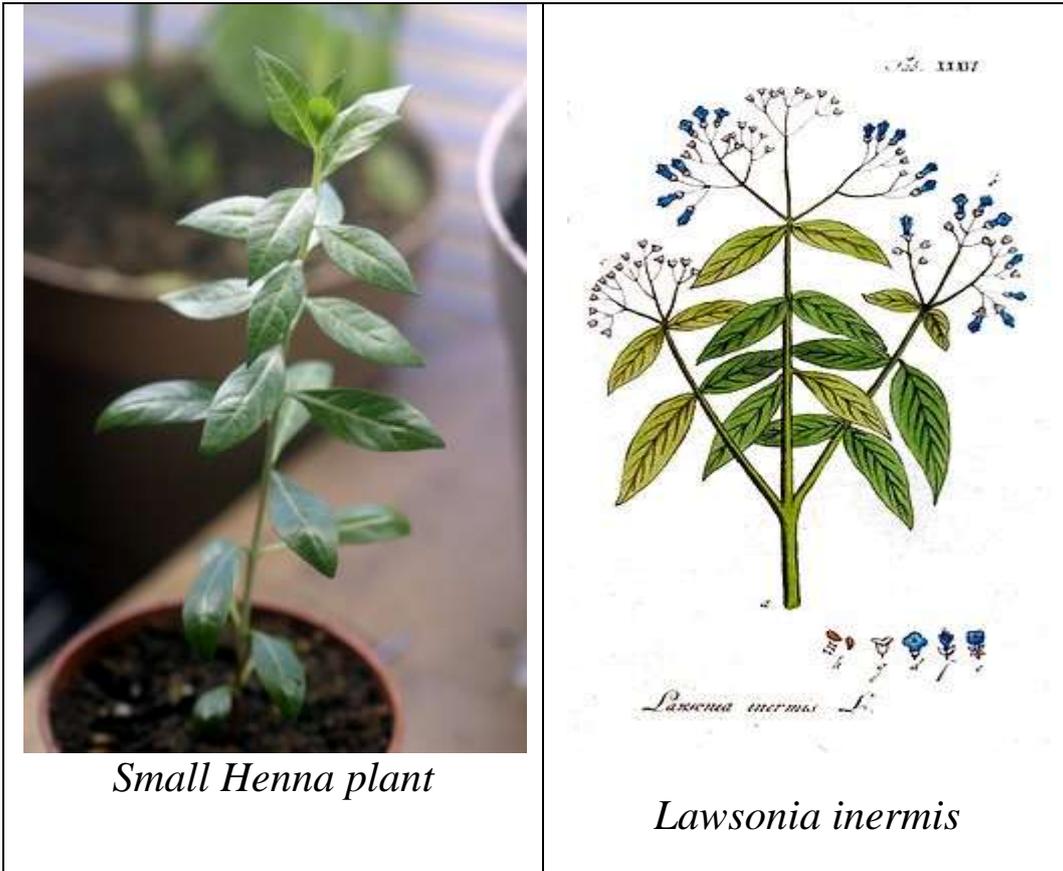
Indigo is natural dye from a plant (*Indigofera tinctoria*, *suffruticosa*, or *arrecta*) that can be added to henna or layered on top of it to create brown to black colors in the hair. On the color wheel, henna is orange, and indigo is blue, so the two colors work together to create brown tones. Like henna, indigo may fade after one application, but it becomes permanent on the hair with repeated use.

Using a plant-based color such as henna can cause problems later when trying to do a perm or permanent hair color. Pure imported body art quality henna is claimed not to cause such problems, but most store-bought henna is mixed with additives which can lead to unpredictable results if the hair is later colored. Although it may not be visible on darker hair, the staining from henna will remain for several months and this may only be realized when dyeing is attempted and an unpleasant, permanent orange color results.

### **External links**

- [Hair dye for men](#)
- [How to Dye Your Hair Unnatural Colours](#)
- [How Stuff Works "How Hair Coloring Works"](#)
- [Hair Colour Decoder – marie claire magazine Australia](#)

# Henna



*Small Henna plant*

*Lawsonia inermis*

## Contents

- 1 Description
- 2 Cultivation
- 3 Uses
- 4 Preparation and application
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## Introduction :

**Henna** (*Lawsonia inermis*, also called **mignonette tree**) is a flowering plant used since antiquity to dye skin, hair, fingernails, leather and wool. The name is also used for dye preparations derived from the plant, and for the art of temporary tattooing based on those dyes. Additionally, the name is misused for other skin and hair dyes, such as **black henna** or **neutral henna**, which do not derive from the plant . The English name "henna" comes from the Arabic حِنَّاء,

### Scientific classification

Kingdom: Plantae  
 Division: Magnoliophyta  
 Class: Magnoliopsida  
 Order: Myrtales  
 Family: Lythraceae  
 Genus: *Lawsonia*  
 Species: *L. inermis*

### Binomial name

*Lawsonia inermis* L.

## 1 – Description :

Henna is a tall shrub or small tree, 2.6 m high. It is glabrous, multibranched with spine tipped branchlets. Leaves are opposite, entire, glabrous, sub-sessile, elliptical, and broadly lanceolate (1.5–5.0 cm x 0.5–2 cm ) , acuminate, having depressed veins on the dorsal surface. Henna flowers have four sepals and a 2 mm calyx tube with 3 mm spread lobes. Petals are obvate, white or red stamens inserted in pairs on the rim of the calyx tube. Ovary is four celled, style up to 5 mm long and erect. Fruits are small, brownish capsules, 4 – 8 mm in diameter, with 32– 49 seeds per fruit, and open irregularly into four splits.

## **2 – Cultivation :**

The henna plant is native to tropical and subtropical regions of Africa, southern Asia, and northern Australasia in semi-arid zones. Henna's indigenous zone is the tropical savannah and tropical arid zone, in latitudes between 15° and 25° N and S from Africa to the western Pacific rim, and produces highest dye content in temperatures between 35 °C and 45 °C. During the onset of precipitation intervals, the plant grows rapidly; putting out new shoots, then growth slows. The leaves gradually yellow and fall during prolonged dry or cool intervals. It does not thrive where minimum temperatures are below 11 °C. Temperatures below 5 °C will kill the henna plant. Henna is commercially cultivated in UAE, Morocco, Yemen, Tunisia, Libya, Saudi Arabia, Egypt, western India, Iran, Pakistan, Bangladesh, Afghanistan, Turkey, Somalia and Sudan. Presently the Pali district of Rajasthan is the most heavily cultivated henna production area in India, with over 100 henna processors operating in Sojat City.

## **3 – Uses :**

Henna has been used since the Bronze Age to dye skin (including body art), hair, fingernails, leather, silk and wool. In several parts of the world it is traditionally used in various festivals and celebrations. There is mention of henna as a hair dye in Indian court records around 400 CE, in Rome during the Roman Empire, and in Spain during Convivencia. It was listed in the medical texts of the Ebers Papyrus (16th c BCE Egypt) and by Ibn Qayyim al-Jawziyya (14th c CE (Syria and Egypt) as a medicinal herb. In Morocco, wool is dyed and ornamented with henna, as are drumheads and other leather goods.

Use of henna for body art has enjoyed a recent renaissance due to improvements in cultivation, processing, and the emigration of people from traditional henna-using regions. For skin dyeing, a paste of ground henna (either prepared from a dried powder or from fresh ground leaves) is placed in contact

with the skin from a few hours to overnight. Henna stains can last a few days to a month depending on the quality of the paste, individual skin type, and how long the paste is allowed to stay on the skin.

Henna also acts as an anti - fungal and a preservative for leather and cloth.

Henna flowers have been used to create perfume since ancient times, and henna perfume is experiencing a resurgence. Henna repels some insect pests and mildew.

Henna's coloring properties are due to lawsone, a burgundy organic compound that has an affinity for bonding with protein. Lawsone is primarily concentrated in the leaves, especially in the petioles of the leaf. Lawsone content in leaves is negatively correlated with the number of seeds in the fruits.

#### **4 - Preparation and application :**



*Henna powder*

Whole, unbroken henna leaves will not stain the skin. Henna will not stain skin until the lawsone molecules are made available (released) from the henna leaf. Fresh henna leaves will stain the skin if they are smashed with a mildly acidic liquid. The lawsone will gradually migrate from the henna paste into the outer layer of the skin and bind to the proteins in it, creating a fast stain.

Since it is difficult to form intricate patterns from coarse crushed leaves, henna is commonly traded as a powder made by drying, milling and sifting the leaves. The dry powder is mixed

with lemon juice, strong tea, or other mildly acidic liquids to make a preparation with toothpaste-like consistency, which can be used to make finely detailed body art. The henna mix must rest for 6 to 12 hours before use, to release the lawsone from the leaf matter. Essential oils with high levels of monoterpene alcohols such as tea tree, eucalyptus, cajeput, or lavender will improve skin stain characteristics.

The paste can be applied with many traditional and innovative tools, including resist, shading, thick-paste, and cellowrap techniques. A satisfactory stain may be achieved within minutes, but the longer the paste is left on the skin, the stronger the stain will be, and it may be left for several hours. To prevent it from drying or falling off the skin, the paste is often sealed down by dabbing a sugar/lemon mix over the dried paste, or simply adding some form of sugar to the paste. This also adds to the colour of the end result, increasing the intensity of the shade. At the end of the procedure, the dry paste is simply brushed or scraped away.

Henna stains are orange soon after application, but darken over the following three days to a reddish brown. Soles and palms have the thickest layer of skin and so take up the most lawsone, and take it to the greatest depth, so that hands and feet will have the darkest and most long-lasting stains. Steaming or warming the henna pattern will darken the stain, either during the time the paste is still on the skin, or after the paste has been removed. Chlorinated water and soaps may spoil the darkening process: alkaline products may hasten the darkening process. After the stain reaches its peak color it will appear to fade, as the stained dead cells exfoliate.

## **5 -Traditions of henna as body art :**

The different words for henna in ancient languages imply that it had more than one point of discovery and origin, as well as different pathways of daily and ceremonial use.



*Mehndi on a hand*

Henna has been used to adorn young women's bodies as part of social and holiday celebrations since the late Bronze Age in the eastern Mediterranean. The earliest text mentioning henna in the context of marriage and fertility celebrations comes from the Ugaritic legend of Baal and Anath,<sup>[10]</sup> which has references to women marking themselves with henna in preparation to meet their husbands, and Anath adorning herself with henna to celebrate a victory over the enemies of Baal. Wall paintings excavated at Akrotiri (dating prior to the eruption of Thera in 1680 BCE) show women with markings consistent with henna on their nails, palms and soles, in a tableau consistent with the henna bridal description from Ugarit. Many statuettes of young women dating between 1500 and 500 BCE along the Mediterranean coastline have raised hands with markings consistent with henna. This early connection between young, fertile women and henna seems to be the origin of the Night of the Henna, which is now celebrated worldwide.

The Night of the Henna was celebrated by most groups in the areas where henna grew naturally: Jews, Muslims, Hindus, Christians and Zoroastrians, among others, all celebrated marriages by adorning the bride, and often the groom, with henna.

Across the henna-growing region, Purim, Eid, Diwali, Karva Chauth, Passover, Nowruz, Mawlid, and most saints' days were celebrated with some henna. Favorite horses, donkeys, and salukis had their hooves, paws, and tails hennaed. Battle victories, births, circumcision, birthdays, Zār, as well as

weddings, usually included some henna as part of the celebration. When there was joy, there was henna, as long as henna was available.

Henna was regarded as having "Barakah," blessings, and was applied for luck as well as joy and beauty. Brides typically had the most henna, and the most complex patterns, to support their greatest joy, and wishes for luck. Some bridal traditions were very complex, such as those in Yemen, where the Jewish bridal henna process took four or five days to complete, with multiple applications and resist work.

The fashion of "Bridal Mehndi" in Pakistan, Northern Libya and in North Indian diasporas is currently growing in complexity and elaboration, with new innovations in glitter, gilding, and fine-line work. Recent technological innovations in grinding, sifting, temperature control, and packaging henna, as well as government encouragement for henna cultivation, have improved dye content and artistic potential for henna.

Though traditional henna artists were Nai caste in India, and barbering castes in other countries (lower social classes), talented contemporary henna artists can command high fees for their work. Women in countries where women are discouraged from working outside the home can find socially acceptable, lucrative work doing henna. Morocco, Mauritania, Yemen, Libya, Somalia, Sudan, as well as India and many other countries have thriving women's henna businesses. These businesses are often open all night for Eids, Diwali and Karva Chauth, and many women may work as a team for a large wedding where hundreds of guests will be hennaed as well as the bride and groom.

## **6 - Health effects :**

Though user accounts cite few, if any, negative effects of natural henna paste, pre-mixed henna body art pastes may have ingredients added to darken stain, or to alter stain color. The health risks involved in pre-mixed paste can be significant. The

United States Food and Drug Administration (FDA) does consider these risks to be adulterants and therefore illegal for use on skin. Some pastes have been noted to include : silver nitrate, carmine, pyrogallol, disperse orange dye, and chromium. These have been found to cause allergic reactions, chronic inflammatory reactions, or late-onset allergic reactions to hairdressing products and textile dyes.

### **6 – 1 – Regulation :**

The FDA has not approved henna for direct application to the skin. It is unconditionally approved as a hair dye, and can only be imported for that purpose . Henna imported into the U.S. which appears to be for use as body art is subject to seizure, though prosecution is rare.

### **7 - "Neutral henna" and "black henna" :**

Natural henna stains only a rich red brown. Products sold as "black henna" or "neutral henna" do not contain henna, but are instead made from other plants, or from other substances altogether.

#### **7 – 1 - "Neutral henna" :**

So - called "neutral henna" does not change the color of hair. This is not henna powder; it is usually the powder of the plant *Senna italica* also known as *Cassia obovata* or a closely related *Cassia* species.

#### **7 – 2 - "Black henna" :**

So - called "black henna" powder may be derived from indigo (from the plant *Indigofera tinctoria*). It may also contain unlisted dyes and chemicals. "Black henna" may contain *p*-phenylene diamine (PPD), which can stain skin black quickly, but can cause severe allergic reactions and permanent scarring. The FDA specifically forbids PPD to be used for that purpose, and may prosecute those who produce "black henna".<sup>[25]</sup> Artists

who injure clients with "Black Henna" in the U.S. may be sued for damages.

"Black Henna" is a misnomer arising from imports of plant-based hair dyes into the West in the late 19th century. Partly fermented, dried indigo was called "black henna" because it could be used in combination with henna to dye hair black. This gave rise to the belief that there was such a thing as "black henna" which could dye skin black. Indigo will not dye skin black. Pictures of indigenous people with black body art (either alkalized henna or from some other source) also fed the belief that there was such a thing as "black henna."

In the 1990s, henna artists in Africa, India, Bali, the Arabian Peninsula and the West began to experiment with para-phenylene diamine (PPD) based black hair dye, applying it as a thick paste as they would apply henna, in an effort to find something that would quickly make jet black temporary body art. PPD can cause severe allergic reactions, with blistering, intense itching, permanent scarring, and permanent chemical sensitivities. Estimates of allergic reactions range between 3 % and 15 %. Henna does not cause these injuries. "Black henna" made with PPD can cause lifelong sensitization to coal tar derivatives. "Black henna" made with gasoline, kerosene, lighter fluid, paint thinner, and benzene has been linked to adult leukemia.

The most frequent serious health consequence of having a "black henna temporary tattoo" is sensitization to hair dye and related chemicals. If a person has had a "black henna tattoo", and later dyes their hair with chemical hair dye, the allergic reaction may be life threatening and require hospitalization. Because of the epidemic of para-phenylenediamine allergic reactions, chemical hair dye products now post warnings on the labels: "Temporary 'black henna' tattoos may increase your risk of allergy. Do not colour your hair if: ... - you have experienced a reaction to a temporary 'black henna' tattoo in the past."

Para-phenylenediamine is illegal for use on skin in western countries, though enforcement is difficult. Physicians have urged governments to legislate against "black henna" because of the frequency and severity of injuries, especially to children.<sup>[34]</sup> To assist prosecution of vendors, government agencies encourage citizens to report injuries and illegal use of "PPD black henna". When used in hair dye, the PPD amount must be below 6 %, and application instructions warn that the dye not touch the scalp and the dye must be quickly rinsed away. "Black henna" pastes have PPD percentages from 10% to 80%, and are left on the skin for half an hour.

Para-phenylenediamine "black henna" use is widespread , particularly in tourist areas. Because the blistering reaction appears 3 to 12 days after the application, most

tourists have left and do not return to show how much damage the artist has done. This permits the artists to continue injuring others, unaware they are causing severe injuries. The high profit margins of "black henna" and the demand for body art that emulates "tribal tattoos" further encourage artists to deny the dangers.

It is not difficult to recognize and avoid para-phenylenediamine "black henna":

- if a paste stains torso skin black in less than ½ hour, it has PPD in it.
- if the paste is mixed with peroxide, or if peroxide is wiped over the design to bring out the color, it has PPD in it.

Anyone who has an itching and blistering reaction to a black body stain should go to a doctor, and report that they have had an application of para-phenylenediamine to their skin.

PPD sensitivity is lifelong. A person who has become sensitized through "black henna tattoos" may have future allergic reactions to perfumes, printer ink, chemical hair dyes, textile dye, photographic developer, sunscreen and some

medications. A person who has had a "black henna tattoo" should consult their physician about health consequences of para-phenylenediamine sensitization.

### 8 – Gallery :



*in Hyderabad, India.*



*in Hyderabad, India.*

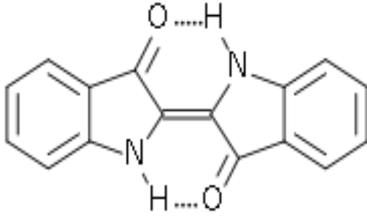


*in Hyderabad, India.*



*in Hyderabad, India.*

## Indigo dye

		
<p><i>Indigo Formola</i></p>	<p><i>Indigo dye</i></p>	<p><i>Indigo</i></p>

### Other Names :

2,2'- Bis ( 2,3- dihydro -3- oxoindolylden ) , Indigotin

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### Introduction :

**Indigo dye** is an organic compound with a distinctive blue color . Historically, indigo was a natural dye extracted from plants, and this process was important economically because blue dyes were once rare. Nearly all indigo dye produced today

— several thousand tons each year — is synthetic. It is the blue of blue jeans.

## 1 - Uses

The primary use for indigo is as a dye for cotton yarn, which is mainly for the production of denim cloth for blue jeans. On average, a pair of blue jean trousers requires 3 – 12 g of indigo. Small amounts are used for dyeing wool and silk.

Indigo carmine, or indigotine, is an indigo derivative which is also used as a colorant. Approximately 20M kilograms are produced annually, again mainly for blue jeans. It is also used as a food colorant, and is listed in the USA as FD&C Blue No. 2, and in the European Union as E Number **E132**.

## 2 - Natural indigo :

### 2 – 1 - Plant sources :

A variety of plants have provided indigo throughout history, but most natural indigo was obtained from those in the genus *Indigofera*, which are native to the tropics. The primary commercial indigo species in Asia was true indigo (*Indigofera tinctoria*, also known as *Indigofera sumatrana*). A common alternative used in the relatively colder subtropical locations such as Japan's Ryukyu Islands and Taiwan is *Strobilanthes cusia*. In Central and South America the two species *Indigofera suffruticosa* (Añil) and *Indigofera arrecta* (Natal indigo) were the most important. In temperate climates indigo can also be obtained from woad (*Isatis tinctoria*) and dyer's knotweed (*Polygonum tinctorum*), although the *Indigofera* species yield more dye.

### 2 – 2 – Extraction :

The precursor to indigo is indican, a colorless, water-soluble derivative of the amino acid tryptophan. Indican readily hydrolyzes to release  $\beta$ -D-glucose and indoxyl. Oxidation by

exposure to air converts indoxyl to indigo. Indican was obtained from the processing of the plant's leaves, which contain as much as 0.2 – 0.8 % of this compound. The leaves were soaked in water and fermented in order to convert the glycoside indican present in the plant to the blue dye indigotin.<sup>[2]</sup> The precipitate from the fermented leaf solution was mixed with a strong base such as lye, pressed into cakes, dried, and powdered. The powder was then mixed with various other substances to produce different shades of blue and purple.

### **2 – 3 – Cultivation :**

The demand for indigo in the 19th century is indicated by the fact that in 1897, 7000 square kilometers were dedicated to the cultivation of indican - producing plants, mainly in India. By comparison, the country of Luxembourg consists of 2,586 square kilometers.<sup>[1]</sup>

In literature, the play *Nildarpan* by Dinabandhu Mitra is based on the indigo slavery and forceful cultivation of indigo in India. It played an essential part in the Bengali indigo revolt of 1858 called *Nilbidraha*.

### **2 – 4 - History of natural indigo :**

Indigo was used in India, which was also the earliest major center for its production and processing . The *Indigofera tinctoria* variety of Indigo was domesticated in India . Indigo, used as a dye, made its way to the Greeks and the Romans, where it was valued as a luxury product.

Indigo is among the oldest dyes to be used for textile dyeing and printing. Many Asian countries, such as India, China, Japan and South East Asian nations have used indigo as a dye (particularly silk dye) for centuries. The dye was also known to ancient civilizations in Mesopotamia, Egypt, Greece, Rome, Britain, Mesoamerica, Peru, Iran, and Africa.

India is believed to be the oldest center of indigo dyeing in the Old World. It was a primary supplier of indigo to Europe as early as the Greco-Roman era. The association of India with indigo is reflected in the Greek word for the dye, *indikón* (ινδικόν, Indian). The Romans latinized the term to *indicum*, which passed into Italian dialect and eventually into English as the word *indigo*.

In Mesopotamia, a Neo-Babylonian cuneiform tablet of the 7th century BC gives a recipe for the dyeing of wool, where lapis-colored wool (uqnatu) is produced by repeated immersion and airing of the cloth. Indigo was most probably imported from India. The Romans used indigo as a pigment for painting and for medicinal and cosmetic purposes. It was a luxury item imported to the Mediterranean from India by Arab merchants.

Indigo remained a rare commodity in Europe throughout the Middle Ages. Woad, a chemically identical dye derived from the plant *Isatis tinctoria* (Brassicaceae), was used instead. In the late 15th century, the Portuguese explorer Vasco da Gama discovered a sea route to India. This led to the establishment of direct trade with India, the Spice Islands, China, and Japan. Importers could now avoid the heavy duties imposed by Persian, Levantine, and Greek middlemen and the lengthy and dangerous land routes which had previously been used. Consequently, the importation and use of indigo in Europe rose significantly. Much European indigo from Asia arrived through ports in Portugal, the Netherlands, and England. Spain imported the dye from its colonies in South America. Many indigo plantations were established by European powers in tropical climates; it was a major crop in Jamaica and South Carolina, with much or all of the labor performed by enslaved Africans and African-Americans. Indigo plantations also thrived in the Virgin Islands. However, France and Germany outlawed imported indigo in the 16th century to protect the local woad dye industry.

Indigo was the foundation of centuries-old textile traditions throughout West Africa. From the Tuareg nomads of

the Sahara to Cameroon, clothes dyed with indigo signified wealth. Women dyed the cloth in most areas, with the Yoruba of Nigeria and the Manding of Mali particularly well known for their expertise. Among the Hausa male dyers, working at communal dye pits was the basis of the wealth of the ancient city of Kano, and they can still be seen plying their trade today at the same pits .

In Japan, indigo became especially important in the Edo period when it was forbidden to use silk, so the Japanese began to import and plant cotton. It was difficult to dye the cotton fiber except with indigo. Even today indigo is very much appreciated as a color for the summer Kimono Yukata, as this traditional clothing recalls Nature and the blue sea. In colonial North America there were three commercially important species: the native *Indigofera caroliniana*, and the introduced *Indigofera tinctoria* and *Indigofera suffruticosa*.

Newton used "indigo" to describe one of the two new primary colors he added to the five he had originally named, in his revised account of the rainbow in *Lectiones Opticae* of 1675.

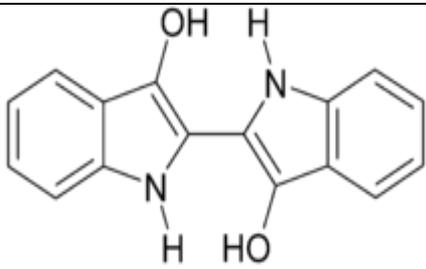
Because of its high value as a trading commodity, indigo was often referred to as Blue Gold.

### **3 - Era of synthetic indigo :**

In 1897, 19,000 tons of indigo were produced from plant sources. Largely due to advances in organic chemistry, production by natural sources dropped to 1000 tons by 1914 and continued to contract. These advances can be traced to 1865 when the German chemist Adolf von Baeyer began working on the synthesis of indigo. He described his first synthesis of indigo in 1878 (from isatin) and a second synthesis in 1880 (from 2-nitrobenzaldehyde). The synthesis of indigo remained impractical, so the search for alternative starting materials at BASF and Hoechst continued. The synthesis of N-(2-carboxyphenyl)glycine from the easy to obtain aniline provided a new and economically attractive route. BASF developed a

commercially feasible manufacturing process that was in use by 1897. As of 2002, 17,000 tons of synthetic indigo were produced world wide.

### 3 – 1 - Developments in dyeing technology :

	
<p><i>Yarn dyed with indigo dye</i></p>	<p><i>Indigo white (leuco-indigo)</i></p>

#### 3 – 1 - 1 - Indigo white :

Indigo is a challenging dye because it is not soluble in water. To be dissolved, it must undergo a chemical change (reduction). Reduction converts indigo into "white indigo" (leuco-indigo). When a submerged fabric is removed from the dye bath, the white indigo quickly combines with oxygen in the air and reverts to the insoluble, intensely colored indigo. When it first became widely available in Europe in the 16th century, European dyers and printers struggled with indigo because of this distinctive property. It also required several chemical manipulations, some involving toxic materials, and had many opportunities to injure workers. In the 19th century, English poet William Wordsworth referred to the plight of indigo dye workers of his hometown of Cockermouth in his autobiographical poem "The Prelude".

Speaking of their dire working conditions and the empathy that he feels for them, he wrote :

*Doubt less, I should have then made common cause  
With some who perished ; haply perished too*

*A poor mistaken and bewildered offering  
Unknown to those bare souls of miller blue*

A preindustrial process for production of indigo white, used in Europe, was to dissolve the indigo in stale urine. A more convenient reductive agent is zinc. Another preindustrial method, used in Japan, was to dissolve the indigo in a heated vat in which a culture of thermophilic, anaerobic bacteria was maintained. Some species of such bacteria generate hydrogen as a metabolic product, which convert insoluble indigo into soluble indigo white. Cloth dyed in such a vat was decorated with the techniques of shibori (tie-dye), kasuri, katazome, and tsutsugaki. Examples of clothing and banners dyed with these techniques can be seen in the works of Hokusai and other artists.

### **3 – 1 - 2 - Direct printing :**

Two different methods for the direct application of indigo were developed in England in the 18th century and remained in use well into the 19th century. The first method, known as *pencil blue* because it was most often applied by pencil or brush, could be used to achieve dark hues. Arsenic trisulfide and a thickener were added to the indigo vat. The arsenic compound delayed the oxidation of the indigo long enough to paint the dye onto fabrics.



*Freeze-dried indigo dye pot*

The second method was known as *china blue* due to its resemblance to Chinese blue-and-white porcelain. Instead of using an indigo solution directly, the process involved printing the insoluble form of indigo onto the fabric. The indigo was then

reduced in a sequence of baths of iron (II) sulfate, with air-oxidation between each immersion. The china blue process could make sharp designs, but it could not produce the dark hues possible with the pencil blue method.

Around 1880 the *glucose process* was developed. It finally enabled the direct printing of indigo onto fabric and could produce inexpensive dark indigo prints unattainable with the china blue method.

Since 2004 freeze-dried indigo, or instant indigo, has become available. In this method the indigo has already been reduced, and then freeze-dried into a crystal. The crystals are added to warm water to create the dye pot. As in a standard indigo dye pot, care has to be taken to avoid mixing in oxygen. Freeze-dried indigo is simple to use, and the crystals can be stored indefinitely as long as they are not exposed to moisture.

### **3 – 2 - Chemical properties :**

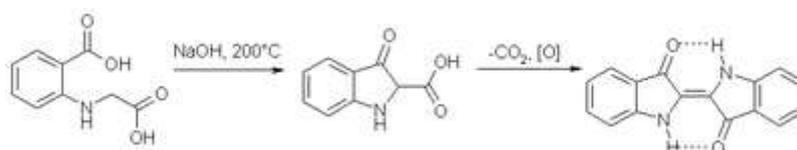
Indigo is a dark blue crystalline powder that sublimates at 390–392 °C. It is insoluble in water, alcohol, or ether but soluble in DMSO, chloroform, nitrobenzene, and concentrated sulfuric acid. The chemical formula of indigo is  $C_{16}H_{10}N_2O_2$ .

The molecule absorbs light in the orange part of the spectrum ( $\lambda_{\max} = 613 \text{ nm}$ ). The compound owes its deep colour to the conjugation of the double bonds, i.e. the double bonds within the molecule are adjacent and the molecule is planar. In indigo white, the conjugation is interrupted because the molecule is nonplanar.

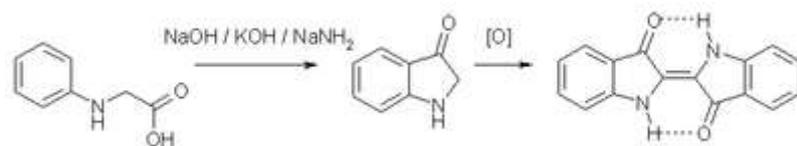
#### **3 – 2 - 1 - Chemical synthesis :**

Given its economic importance, indigo has been prepared by many methods. The Baeyer - Drewson indigo synthesis dates back to 1882 but was impractical. The first practical route is credited to Pflieger in 1901. In this process, *N*-phenylglycine is treated with a molten mixture of sodium hydroxide, potassium

hydroxide, and sodamide. This highly sensitive melt produces indoxyl, which is subsequently oxidized in air to form indigo. Variations of this method are still in use today. An alternative and also viable route to indigo is credited to Heumann in 1897. It involves heating *N*-(2-carboxyphenyl) glycine to 200 °C in an inert atmosphere with sodium hydroxide. The process is easier than the Pflieger method but the precursors are more expensive. Indoxyl-2-carboxylic acid is generated. This material readily decarboxylates to give indoxyl, which oxidizes in air to form indigo. The preparation of indigo dye is practiced in college laboratory classes.



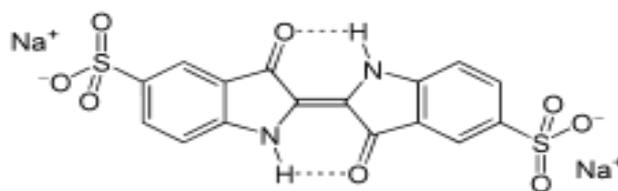
*Heumann's original synthesis of indigo*



*Pflieger's synthesis of indigo.*

### 3 – 2 - 2 - Indigo derivatives :

The benzene rings in indigo can be modified to give a variety of related dyestuffs. Thioindigo, where the two NH groups are replaced by S atoms, is deep red. Tyrian purple is a dull purple dye that is secreted by a common Mediterranean Sea snail. It was highly prized in antiquity. In 1909 its structure was shown to be 6,6'-dibromoindigo. It has never been produced on a commercial basis. The related Ciba blue (5,7,5',7'-tetra bromo indigo) is, however, of commercial value.



*Structure of indigo carmine*

Treatment with sulfuric acid converts indigo into a blue-green derivative called sulfonated indigo ( CAS # 860-22-0 ). It became available in the mid-18th century. Sulfonated indigo is also referred to as *Saxon blue* or *indigo carmine*. It is used as a colorant for food, pharmaceuticals, and cosmetics . specification Indigo tindisulfonate.

#### **4 - Safety and the environment :**

Indigo has a low oral toxicity, with an LD<sub>50</sub> of 5000 mg / kg in mammals . In 2009, large spills of blue dyes had been reported downstream of a blue jeans manufacturer in Lesotho.

#### **External links**

- [Plant Cultures: botany, history and uses of indigo](#)
- [Pubchem page for indigotine](#)
- [FD&C regulation on indigotine](#)
- [Indigo dye at the Open Directory Project](#)

## Isatis Tinctoria Woad



*The Hunt of the Unicorn  
Tapestry, dyed with weld  
(yellow), madder (red), and  
woad (blue).*



*Woad flowers*  
أزهار نبات الوسمة

### Contents

- 1 History of woad cultivation
  - 1.1 Ancient use
  - 1.2 The medieval period onwards
- 2 Woad and indigo
- 3 Woad and health
- 4 Invasive and noxious weed
- 5 - External links
- 

### Introduction :

**Isatis Tinctoria** , with **Woad** ( or **glastum** ) as the common name, is a flowering plant in the family Brassicaceae. It is commonly called dyer's woad , and sometimes incorrectly listed as *Isatis indigotica* (a newer and invalid name for the same plant ) . It is occasionally known as Asp of Jerusalem. Woad is also the name of a blue dyestuff produced from the leaves of the plant.

Woad is native to the steppe and desert zones of the Caucasus, Central Asia to eastern Siberia and Western Asia (Hegi), but is now found in southeastern and some parts of Central Europe as well. Long important as a source of blue dye, it has been cultivated throughout Europe, especially in Western and southern Europe, since ancient times. In medieval times there were important woad growing regions in England, Germany and France, and towns such as Toulouse became prosperous on the woad trade. Woad was eventually replaced by the stronger indigo and then by synthetic indigos.

### Scientific classification

Kingdom: Plantae  
 (unranked): Angiosperms  
 (unranked): Eudicots  
 (unranked): Rosids  
 Order: Brassicales  
 Family: Brassicaceae  
 Genus: *Isatis*  
 Species: *I. tinctoria*

### Binomial name

*Isatis tinctoria* L.

### Synonyms

*Isatis indigotica* Fortune

## 1 - History of woad cultivation :

### 1 – 1 - Ancient use :

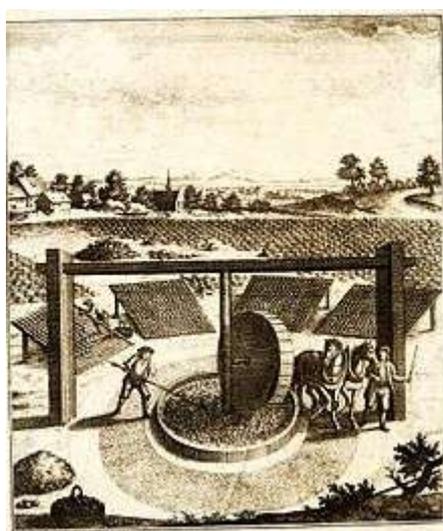
The first archaeological finds of woad seeds date to the Neolithic and have been found in the French cave of l'Audoste, Bouches-du-Rhône (France). Named *Färberwaid* (*Isatis tinctoria* L.) or German Indigo, of the plant family (Brassicaceae), in the Iron Age settlement of the Heuneburg, Germany, impressions of the seeds have been found on pottery.

The Hallstatt burials of Hochdorf and Hohmichele contained textiles dyed with Färberwaid (woad dye).

Melo and Rondão write that woad was known "as far back as the time of the ancient Egyptians, who used it to dye the cloth wrappings applied for the mummies." Skelton informs us that one of the early dyes discovered by the ancient Egyptians was "blue woad (*Isatis tinctoria*)."<sup>[4]</sup> Lucas writes, "What has been assumed to have been Indian Indigo on ancient Egyptian fabrics may have been woad."<sup>[5]</sup> Hall states that the ancient Egyptians created their blue dye "by using indigotin, otherwise known as woad."

Julius Caesar tells us (in *De Bello Gallico*) that the Britanni used to colour their bodies blue with *vitrum*, a word that roughly translates to "glass". While many have assumed *vitrum* or *vitro* refers to woad, and this misconception was probably repeated for political reasons,<sup>[7]</sup> it is probable that Caesar was describing some form of copper- or iron-based pigment. The northern inhabitants of Britain came to be known as Picts (*Picti*), which means "painted ones" in Latin, and may have been due to these accounts of them painting or tattooing their bodies.

## 1 – 2 - The medieval period onwards :



*Illustration of German woad mill in Thuringia, 1752*

Woad was one of the three staples of the European dying industry, along with weld (yellow) and madder (red). Chaucer, mentions them, lamenting their use by the dyer ("litestere") in his poem *The Former Age* :

*No mader, welde, or wood no litestere.  
Ne knew; the flees was of his former hewe*

The three can be seen together in tapestries such as The Hunt of the Unicorn ( 1495 – 1505 ) , though typically it is the dark blue of the woad that has lasted best.

In Viking age levels at York, a dye shop with remains of both woad and madder dating from the tenth century have been excavated. In Medieval times, centres of woad-cultivation lay in Lincolnshire and Somerset in England, Jülich and the Erfurt area in Thuringia in Germany, Piedmont and Tuscany in Italy, and Gascogne, Normandy, the Somme Basin (from Amiens to Saint-Quentin), Britany and above all Languedoc in France. This last region, in the triangle between Toulouse, Albi and Carcassonne, was for long the most productive of woad, or "pastel" as it was known there, one writer commenting that 'woad... hath made that country the happiest and richest in Europe .' The prosperous woad merchants of Toulouse displayed their affluence in splendid mansions, many of which are still standing. One, Jean de Bernuy, Spanish Jew who had fled the inquisition, was credit-worthy enough to be the main guarantor of the ransom King Francis I after his capture at the Battle of Pavia by Charles V of Spain. Much of the woad produced here was used for the cloth industry in southern France , but it was also exported via Bayonne, Narbonne and Bordeaux to Flanders, the Low Countries, Italy, and above all Britain and Spain.

A major market for woad was at Görlitz in Silesia . The citizens of the five Thuringian Färberwaid (dye woad) towns of Erfurt, Gotha, Tennstedt, Arnstadt and Langensalza had

their own charters. In Erfurt, the woad-traders gave the funds to found the University of Erfurt. Traditional fabric is still printed with woad in Thuringia, Saxony and Lusatia today: it is known as *Blaudruck* (literally, 'blue print(ing)').

Medieval uses of the dye were not limited to textiles. For example, the illustrator of the Lindisfarne Gospels used a woad-based pigment for blue paint.

## 2 - Woad and indigo :



*Woad plants in their first year*

The dye chemical extracted from woad is indigo, the same dye extracted from "true indigo", *Indigofera tinctoria*, but in a lower concentration. With the European discovery of the seaway to India, great amounts of indigo were imported. Laws were passed in some parts of Europe to protect the woad industry from the competition of the indigo trade. Indigo was proclaimed to rot the yarns as well. "In 1577 the German government officially prohibited the use of indigo, denouncing it as that pernicious, deceitful and corrosive substance, the Devil's dye." "... a recess of the Diet held in 1577 prohibited the use of 'the newly-invented, deceitful, eating and corrosive dye called the devil's dye.' This prohibition was repeated in 1594 and again in 1603. In France, Henry IV, in an edict of 1609, forbade under pain of death the use of "the false and pernicious Indian drug".

With the development of a chemical process to synthesize the pigment, both the woad and natural indigo industries collapsed in the first years of the twentieth century.

The last commercial harvest of woad until recent times occurred in 1932, in Lincolnshire, Britain. Small amounts of woad are now grown in UK and France to supply craft dyers . The classic book about woad is "The Woad Plant and its Dye" by J B Hurry, Oxford University Press, 1930, which contains an extensive bibliography.

A method for producing indigo dye from woad is described in the book *The History of Woad and the Medieval Woad Vat* (1998) ISBN 0 9534133 0 6 .

In Germany, there are attempts to use woad to protect wood against decay without dangerous chemicals. Production is also increasing again in the UK for use in inks, particularly for inkjet printers, and dyes, as woad is biodegradable and safe in the environment, unlike many synthetic inks. *Isatis tinctoria* is viewed as an invasive species in parts of the United States.

### 3 - Woad and health :

Chemicals from woad might be used to prevent cancer, as it can produce high levels of glucobrassicin . Young leaves when damaged can produce more glucobrassicin, up to 65 times as much.

**Indigowoad Root** ( Chinese : pinyin: *bǎn lán gēn*) is a traditional Chinese medicine herb that comes from the roots of woad, but often incorrectly listed under the synonymic name, *Isatis indigotica*. It is also known as *Radix isatidis*. The herb is cultivated in various regions of northern China, namely Hebei, Beijing, Heilongjiang, Henan, Jiangsu, and Gansu. The roots are harvested during the autumn and dried. The dried root is then processed into granules, which are most commonly consumed dissolved in hot water or tea. The product, called Banlangen Keli, is very popular throughout China, and used to remove toxic heat, soothe sore throat and to treat influenza, measles, mumps, syphilis, or scarlet fever. It is also used for pharyngitis, laryngitis, erysipelas, and

carbuncle, and to prevent hepatitis A, epidemic meningitis, cancer and inflammation. Possible minor side effects include allergic reactions and dizziness; only large dosages or long term usage can be toxic to the kidneys. These treatments have not generally been evaluated clinically.

#### **4 - Invasive and noxious weed :**

In certain locations the plant is classified as non-native and invasive weed. It is listed as a noxious weed by the agriculture departments of several states in the western United States . In Montana, it has been the target of an extensive, and largely successful, eradication attempt .

#### **5 - External links**

- [Woad.org.uk](http://Woad.org.uk) - All About Woad - Cultivation, Extraction, Dyeing with Woad, History and facts about woad
- [The Former Woad Industry](#)
- [From woad warriors to cancer-buster - Woad anticancer properties, New Scientist.](#)
- [IndigoPage.com](http://IndigoPage.com): Information, discussion, pictures on artistic uses of indigo dye.
- [The preparation of Woad - excerpt from paper by H. O. Clarke and Rex Wailes in Transactions of the Newcomen Society, 1935-36 Vol 16.](#)
- [The Problem of the Woad - Use of Woad in Body Art](#)
- [USDA information on \*Isatis tinctoria\*](#)
- [Woad is me: botany page at UCLA](#)
- [Data sheet with pictures of woad \(in German\)](#)
- [Wonder Woad - Stories with quintessences on the meaning of the woad](#)

#### **Techniques :**

Batik • Dyeing • Kalamkari • Katazome • Leheria • Mordant • Reactive dye printing • Resist • Ring dyeing • Rōketsuzome • Shibori • Tie-dye • Tsutsugaki

**Types of dyes :**

Dyes • Natural • Acid • Reactive • Solvent • Substantive • Sulfur • Vat • Disperse

**Traditional textile dyes:**

Black walnut • Bloodroot • Brazilin • Cochineal (Polish cochineal) • Cudbear • Cutch • Dyewoods • Fustic • Henna • Indigo • Kermes • Logwood • Madder • Saffron • Turmeric • Tyrian purple • Weld • **Woad**

**History:**

Trade and use of saffron • Traditional dyes of the Scottish Highlands

**Craft dyes :**

Dylon • Procion

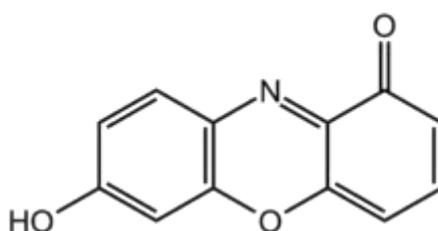
**Reference**

Glossary of dyeing terms • List of dyes

# Litmus



*Litmus powder*



*Chemical structure of 7-hydroxyphenoxazone,  
the chromophore of litmus components*

## 1 – Introduction :

**Litmus** is a water - soluble mixture of different dyes extracted from lichens , especially *Rocella tinctoria* . It is often absorbed onto filter paper to produce one of the oldest forms of pH indicator, used to test materials for acidity. Blue litmus paper turns red under acidic conditions and red litmus paper turns blue under basic (i.e. alkaline) conditions, with the color change occurring over the pH range 4.5-8.3 at 25 °C. Neutral litmus paper is purple . Litmus can also be prepared as an aqueous solution that functions similarly. Under acidic conditions the solution is red, and under basic conditions the solution is blue.

The litmus mixture has the CAS number 1393-92-6 and contains 10 to 15 different dyes. Most of the chemical components of litmus are likely to be the same as those of the related mixture known as orcein, but in different proportions. In contrast with orcein, the principal constituent of litmus has average molecular weight of 3300. Acid-base indicators on

litmus owe their properties to a 7-hydroxyphenoxazone chromophore . Some fractions of litmus were given specific names including erythrolitmin ( or erythrolein ) , azolitmin, spaniolitmin, leucoorcein and leucazolitin. Azolitmin shows nearly the same effect as litmus.

## 2 - History :

Litmus was used for the first time about 1300 AD by Spanish alchemist Arnaldus de Villa Nova. From the 16th century on , the blue dye was extracted from some lichens , especially in the Netherlands.

## 3 - Natural sources

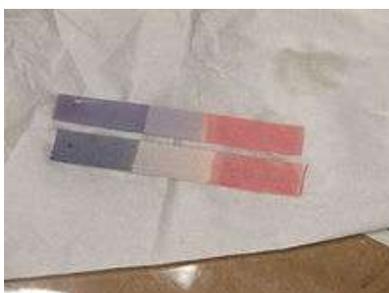


*Parmelia sulcata*

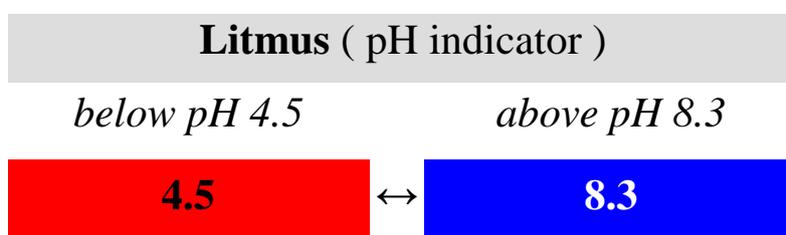
Litmus can be found in different species of lichens .The dyes would be extracted from such species as *Roccella tinctoria* ( South America ) , *Roccella fuciformis* ( Angola and Madagascar ) , *Roccella pygmaea* ( Algeria ) , *Roccella phycopsis*, *Lecanora tartarea* ( Norway , Sweden ) , *Variolaria dealbata*, *Ochrolechia parella*, *Parmotrema tinctorum* and *Parmelia*. Currently, the main sources are *Roccella montagnei* ( Mozambique ) and *Dendrographa leucophoea* (California) .

#### 4 - Uses :

The main use of litmus is to test whether a solution is acidic or alkaline. Wet litmus paper can also be used to test water-soluble gases; the gas dissolves in the water and the resulting solution colors the litmus paper. For instance, ammonia gas, which is alkaline, colors the red litmus paper blue. Chemical reactions other than acid-base reaction can also cause a color - change to litmus paper. For instance, chlorine gas turns blue litmus paper white – the litmus paper is bleached. This reaction is irreversible and therefore the litmus is not acting as an indicator in this situation.



*Litmus paper being used*



#### See also

- Dipstick
- Nitrazine strips - Measures pH about 4.5 to 7.5 with more precision
- pH indicator
- Phenol phthalein
- Bromo thymol blue
- Methyl orange

- Universal indicator - Modern paper measures pH 1 to 14 with distinct colors for each. The color chart is usually included with the strips.

## Mignonette ( Reseda )



*Reseda lutea* ( Wild Mignonette )

### Scientific classification

Kingdom :	Plantae
(unranked) :	Angiosperms
(unranked) :	Eudicots
(unranked) :	Rosids
Order :	Brassicales
Family :	Resedaceae
Genus :	<i>Reseda</i> L.

### Species

About 50-70 species, including :  
*Reseda alba* - White Mignonette  
*Reseda complicata* Glaucous Mignonette  
*Reseda lutea* - Wild Mignonette  
*Reseda luteola* - Weld  
*Reseda odorata* - Common Mignonette  
*Reseda phyteuma* - Corn Mignonette  
*Reseda scoparia* - Canaries Mignonette

### 1 – Introduction :

**Mignonette** (*Reseda*) is a genus of fragrant herbaceous plants native to the Mediterranean region and southwest Asia, from the Canary Islands and Iberia east to northwest India. The species include annuals, biennials and perennials, and grow to 40-130 cm tall. The leaves form a basal rosette at ground level,

and then spirally arranged up the stem; they can be entire, toothed or pinnate, and range from 1-15 cm long. The flowers are produced in a slender spike, each flower small (4-6 mm diameter), white, yellow, orange, or green, with four to six petals. The fruit is a small dry capsule containing several seeds.

Other common names include **Weld** (*R. luteola*), **Dyer's Rocket**, **Bastard Rocket** and **Sweet Reseda**.

## 2 - Cultivation and uses

Propagation is by seed, which is surface-sown directly into the garden or grass verge. The plant does not take well to transplanting and should not be moved after sowing.

Mignonette flowers are extremely fragrant. It is grown for the sweet ambrosial scent of its flowers. It is used in flower arrangements, perfumes and potpourri. A Victorian favourite, it was commonly grown in pots and in window-boxes to scent the city air. It was used as a sedative and a treatment for bruises in Roman times. The volatile oil is used in perfumery. The yellow dye was obtained from the roots of *R. luteola* by the first millennium BC, and perhaps earlier than either woad or madder. Use of this dye came to an end at the beginning of the twentieth century, when cheaper synthetic yellow dyes came into use.

Charles Darwin used *R. odorata* in his studies of self-fertilised plants, which he documented in *The Effects of Cross and Self-Fertilisation in the Vegetable Kingdom*.

### External links

- Mignonette - Offers more information about mignonette.
- Data sheet with pictures of weld (*Reseda luteola* L.)

# Oak



Foliage and acorns of *Quercus robur*

## Contents

- 1 Classification
  - 1.1 Subgenus *Quercus*
  - 1.2 Subgenus *Cyclobalanopsis*
- 2 Hybridisation
- 3 Uses
- 4 Biodiversity and ecology
- 5 Diseases and pests
- 6 Toxicity
- 7 Cultural significance
  - 7.1 National symbol
    - 7.1.1 Oaks as regional and state symbols
    - 7.1.2 Military use
    - 7.1.3 Political use
  - 7.2 Religious
  - 7.3 Historical
- 8 Historical note on Linnaean species
- 9 See also

## Introduction :

An **oak** is a tree or shrub in the genus *Quercus* Latin "oak tree" , of which about 600 species exist on earth. "Oak" may also appear in the names of species in related genera, notably *Lithocarpus*. The genus is native to the northern hemisphere, and includes deciduous and ever green species extending from cold latitudes to tropical Asia and the Americas.

Oaks have spirally arranged leaves, with a lobed margin in many species; some have serrated leaves or entire leaves with a smooth margin. The flowers are catkins, produced in spring. The fruit is a nut called an acorn, borne in a cup - like structure known as a cupule; each acorn contains one seed ( rarely two or three ) and takes 6 –18 months to mature, depending on species. The live oaks are distinguished for being evergreen, but are not actually a distinct group and instead are dispersed across the genus.

### Scientific classification

Kingdom :	Plantae
(unranked) :	Angiosperms
(unranked) :	Eudicots
(unranked) :	Rosids
Order :	Fagales
Family :	Fagaceae
Genus :	<i>Quercus</i> L.

## 2 – Classification :

Oak trees are *flowering plants*. The genus is divided into two subgenera and a number of sections:

### 1 - 2 - Subgenus *Quercus* :

See also: List of *Quercus* species

The Subgenus *Quercus* is divided into the following sections :

- Sect. *Quercus* ( synonyms *Lepidobalanus* and *Leucobalanus* ) , the white oaks of Europe , Asia and North America. Styles are short; acorns mature in 6 months and taste sweet or slightly bitter; the inside of an acorn shell is hairless. The leaves mostly lack a bristle on their lobe tips, which are usually rounded.
- Sect. *Mesobalanus*, Hungarian oak and its relatives of Europe and Asia. Styles long; acorns mature in about 6 months and taste bitter; the inside of this acorn's shell is hairless. The section *Mesobalanus* is closely related to section *Quercus* and sometimes included in it.
- Sect. *Cerris*, the Turkey oak and its relatives of Europe and Asia. Styles long; acorns mature in 18 months and taste very bitter. The inside of the acorn's shell is hairless. Its leaves typically have sharp lobe tips, with bristles at the lobe tip.
- Sect. *Protobalanus*, the Canyon live oak and its relatives, in southwest United States and northwest Mexico. Styles short, acorns mature in 18 months and taste very bitter. The inside of the acorn shell appears woolly. Leaves typically have sharp lobe tips, with bristles at the lobe tip.
- Sect. *Lobatae* (synonym *Erythrobalanus*), the red oaks of North America, Central America and northern South America. Styles long; acorns mature in 18 months and taste very bitter. The inside of the acorn shell appears woolly. The actual nut is encased in a thin, clinging, papery skin. Leaves typically have sharp lobe tips, with spiny bristles at the lobe.

### **1 - 2 - Subgenus *Cyclobalanopsis* :**

- The ring-cupped oaks of eastern and southeastern Asia. Evergreen trees growing 10 – 40 m tall. They are distinct from subgenus *Quercus* in that they have acorns with distinctive cups bearing concrescent rings of scales; they commonly also have densely clustered acorns, though this

does not apply to all of the species. The *Flora of China* treats *Cyclobalanopsis* as a distinct genus, but most taxonomists consider it a subgenus of *Quercus*. It contains about 150 species. Species of *Cyclobalanopsis* are common in the evergreen subtropical laurel forests which extend from southern Japan, southern Korea, and Taiwan across southern China and northern Indochina to the eastern Himalayas, in association with trees of genus *Castanopsis* and the laurel family (Lauraceae).



*A hybrid white oak, possibly Quercus stellata × Q. muhlenbergii*

## 2 - Hybridisation

Interspecific hybridisation is quite common among oaks, but usually between species within the same section only, and most common in the white oak group (subgenus *Quercus*, section *Quercus*; see **List of *Quercus* species**). Inter-section hybrids, except between species of sections *Quercus* and *Mesobalanus*, are unknown. Recent systematic studies appear to confirm a high tendency of *Quercus* species to hybridize because of a combination of factors. White oaks are unable to discriminate against pollination by other species in the same section. Because they are wind pollinated and they have weak internal barriers to hybridisation, hybridization produces functional seeds and fertile hybrid offspring. Ecological stresses, especially near habitat margins, can also cause a breakdown of mate recognition as well as a reduction of male function (pollen quantity and quality) in one parent species.

Frequent hybridisation among oaks has consequences for oak populations around the world; most notably, hybridization has produced large populations of hybrids with copious amounts of introgression, and the evolution of new species . Frequent hybridisation and high levels of introgression have caused different species in the same populations to share up to 50% of their genetic information. Having high rates of hybridisation and introgression produces genetic data that often does not differentiate between two clearly morphologically distinct species, but instead differentiates populations.<sup>[6]</sup> Numerous hypotheses have been proposed to explain how oak species are able to remain morphologically and ecologically distinct with such high levels of gene flow, but the problem is still largely a mystery to botanists.

The Fagaceae, or oak family, is a very slowly evolving clade compared to other angiosperms,<sup>[7][8]</sup> and the hybridisation patterns in *Quercus* pose a great challenge to the concept of a species . A species is often defined as a group of “actually or potentially interbreeding populations which are reproductively isolated from other such groups.” By this definition, many species of *Quercus* would be lumped together according to their geographic and ecological habitat, despite clear distinctions in morphology and, to a large extent, genetic data.

### 3 - Uses :



*Heart of oak beams of the frame of Saint-Girons church  
in Monein, France*

Oak wood has a density of about 0.75 g/cm<sup>3</sup>, great strength and hardness, and is very resistant to insect and fungal attack because of its high tannin content. It also has very attractive grain markings, particularly when quartersawn. Wide, quarter-sawn boards of oak have been prized since the Middle Ages for use in interior paneling of prestigious buildings such as the debating chamber of the House of Commons in London, England, and in the construction of fine furniture. Oak wood, from *Quercus robur* and *Quercus petraea*, was used in Europe for the construction of ships, especially naval men of war, until the 19th century, and was the principal timber used in the construction of European timber-framed buildings. Today oak wood is still commonly used for furniture making and flooring, timber frame buildings, and for veneer production. Barrels in which red wines, sherry, and spirits such as brandy, Scotch whisky and Bourbon whiskey are aged are made from European and American oak. The use of oak in wine can add many different dimensions to wine based on the type and style of the oak. Oak barrels, which may be charred before use, contribute to the colour, taste, and aroma of the contents, imparting a desirable oaky vanillin flavour to these drinks. The great dilemma for wine producers is to choose between French and American oakwoods. French oaks (*Quercus robur*, *Q. petraea*) give the wine greater refinement and are chosen for the best wines since they increase the price compared to those aged in American oak wood . American oak contributes greater texture and resistance to ageing, but produces more violent wine bouquets. Oak wood chips are used for smoking fish, meat, cheeses and other foods.



*Sherry maturing in oak barrels*

Japanese oak is used in the making of professional drums from manufacturer Yamaha Drums. The higher density of oak gives the drum a brighter and louder tone compared to traditional drum materials such as maple and birch.

The bark of *Quercus suber*, or Cork oak, is used to produce wine stoppers (corks). This species grows in the Mediterranean Sea region, with Portugal, Spain, Algeria and Morocco producing most of the world's supply. Of the North American oaks, the Northern red oak *Quercus rubra* is the most prized of the red oak group for lumber, all of which is marketed as red oak regardless of the species of origin. It is not good for outdoor use due to its open capillaries. One can blow air through an end grain piece 10 inches long to make bubbles come out in a glass of water. These openings give fungus easy access when the finish deteriorates. The standard for the lumber of the white oak group – all of which is marketed as white oak – is the White Oak *Quercus alba*. White Oak is often used to make wine barrels. The wood of the deciduous Pedunculate Oak *Quercus robur* and Sessile Oak *Quercus petraea* accounts for most of the European oak production, but evergreen species, such as Holm oak *Quercus ilex*, and Cork oak *Quercus suber* also produce valuable timber.



*A cross section of the trunk of a cork oak, Quercus suber*

The bark of the White Oak is dried and used in medical preparations. Oak bark is also rich in tannin, and is used by tanners for tanning leather. In Korea, oak bark ( Goolpy ) is used for traditional roof construction . Acorns are used for making flour or roasted for acorn coffee.

Oak galls were used for centuries as the main ingredient in manuscript ink, harvested at a specific time of year .

#### **4 - Biodiversity and ecology :**

Oaks are keystone species in a wide range of habitats from Mediterranean semi-desert to subtropical rainforest. For example, oak trees are important components of hardwood forests, and certain species are particularly known to grow in associations with members of the Ericaceae in oak - heath forests . A number of kinds of truffles, including the two well known varieties, the black Périgord truffle and the white Piedmont truffle , have symbiotic relationships with oak trees .

Many species of oaks are under threat of extinction in the wild, largely due to land use changes, livestock grazing and unsustainable harvesting. For example, over the past 200 years, large areas of oak forest in the highlands of Mexico, Central America and the northern Andes have been cleared for coffee plantations and cattle ranching. There is a continuing threat to these forests from exploitation for timber, fuelwood and charcoal . In the USA, entire oak ecosystems have declined due to a combination of factors still imperfectly known, but thought to include fire suppression, increased consumption of acorns by growing mammal populations, herbivory of seedlings, and introduced pests . In a recent survey, 78 wild oak species have been identified as being in danger of extinction, from a global total of over 500 species . The proportion under threat may be much higher in reality, as there is insufficient information about over 300 species, making it is near impossible to form any judgement of their status.

#### **5 - Diseases and pests :**

See also : List of Lepidoptera that feed on oaks

Sudden Oak Death (*Phytophthora ramorum*) is a water mould that can kill oaks within just a few weeks. Oak Wilt,

caused by the fungus *Ceratocystis fagacearum* (a fungus closely related to Dutch Elm Disease), is also a lethal disease of some oaks, particularly the red oaks (the white oaks can be infected but generally live longer). Other dangers include wood-boring beetles, as well as root rot in older trees which may not be apparent on the outside, often being discovered only when the trees come down in a strong gale. Oak apples are galls on oaks made by the gall wasp. The female kermes scale causes galls to grow on kermes oak. Oaks are used as food plants by the larvae of Lepidoptera (butter fly and moth) species such as the Gypsy Moth, *Lymantria dispar*, which can defoliate oak and other broadleaved tree species in North America. A considerable number of galls are found on oak leaves, buds, flowers, roots, etc. Examples are Oak artichoke gall, Oak Marble gall, Oak apple gall, Knopper gall, and Spangle gall.



*Oak powdery mildew on pedunculate oak*

A number of species of fungus cause powdery mildew on oak species. In Europe the species *Erysiphe alphitoides* is the most common cause. A new and as yet little understood disease of mature oaks, Acute oak decline, has been reported in parts of the UK since 2009.

Additionally, the Oak Processionary Moth ( *Thaumetopoea processionea* ) has become a serious threat in the UK since 2006. It defoliates the trees, and is hazardous to human health.

## **6 – Toxicity :**

The leaves and acorns of the oak tree are poisonous to cattle, horses, sheep, and goats in large amounts due to the toxin

tannic acid, and cause kidney damage and gastroenteritis. Additionally, once livestock have a taste for the leaves and acorns, they may seek them out. Symptoms of poisoning include lack of appetite, depression, constipation, diarrhea (which may contain blood), blood in urine, and colic. The exception to livestock and oak toxicity is the domestic pig, which may be fed entirely on acorns in the right conditions, and has traditionally been pastured in oak woodlands (such as the Spanish *dehesa* and the English system of pannage) for hundreds of years. Acorns are also edible to humans in processed form, after leaching of the tanins. They are a staple part of the forage consumed by wildlife, including squirrels and jays.

## **7 - Cultural significance :**

### **7 - 1 - National symbol :**

The oak is a common symbol of strength and endurance and has been chosen as the national tree of many countries. Already an ancient Germanic symbol (in the form of the Donar Oak, for instance), certainly since the early nineteenth century, it stands for the nation of Germany. In 2004 the Arbor Day Foundation held a vote for the official National Tree of the United States of America. In November 2004, Congress passed legislation designating the oak as America's National Tree.

Other countries have also designated the oak as their national tree including England, Estonia, France, Germany, Moldova, Latvia, Lithuania, Poland, the United States, Basque Country, Wales, Galicia, Bulgaria, and Serbia .

### **7 - 1 – 1 - Oaks as regional and state symbols :**

The oak is the emblem of County Londonderry in Northern Ireland, as a vast amount of the county was covered in forests of the tree until relatively recently. The name of the county comes from the city of Derry, which originally in Irish was known as *Doire* meaning *oak*.

The Irish County Kildare derives its name from the town of Kildare which originally in Irish was *Cill Dara* meaning the Church of the Oak or Oak Church.

Iowa designated the oak as its official state tree in 1961; and the White Oak is the state tree of Connecticut, Illinois and Maryland. The Northern Red Oak is the provincial tree of Prince Edward Island, as well as the state tree of New Jersey. The Live Oak is the state tree of Georgia, USA.

### **7 - 1 – 2 - Military use :**

Oak leaves are traditionally an important part of German Army regalia. They also symbolize rank in the United States Armed Forces. A gold oak leaf indicates an O - 4 ( Major or Lt. Commander ), where as a silver oak leaf indicates an O -5 ( Lt. Colonel or Commander ). Arrangements of oak leaves, acorns and sprigs indicate different branches of the United States Navy Staff corps officers. Oak leaves are embroidered onto the covers ( hats ) worn by field grade officers and flag officers in the United States armed services . If a service member earns multiple awards of the same medal, then instead of wearing a ribbon or medal for each award, he or she wears one metal representation of an "oak leaf cluster" attached to the appropriate ribbon for each subsequent award.

### **7 - 1 – 3 - Political use :**

The oak tree is used as a symbol by a number of political parties. It is the symbol of the Conservative Party in the United Kingdom, and formerly of the Progressive Democrats in Ireland. In the cultural arena, the oakleaf is the symbol of the National Trust (UK) and The Royal Oak Foundation .

### **7 - 2 – Religous :**

In Baltic mythology, the oak is the sacred tree of Latvian Pērkons, Lithuanian Perkūnas and Prussian Perkūns. Pērkons is

the god of thunder and one of the most important deities in the Baltic pantheon.

In Celtic mythology, it is the tree of doors, believed to be a gateway between worlds, or a place where portals could be erected .

In Norse mythology, the oak was sacred to the thunder god, Thor. Some scholars speculate that the reason for this is that the oak – the largest tree in northern Europe – was the one most often struck by lightning. Thor's Oak was a sacred tree of the Germanic Chatti tribe. According to legend, the Christianisation of the heathen tribes by Saint Boniface was marked by the oak's being replaced by the fir ( whose triangular shape symbolizes the Trinity ) as a "sacred" tree.

In the Bible, the oak tree at Shechem is the site where Jacob buries the foreign gods of his people ( Gen. 35:4 ) . In addition, Joshua erects a stone under an oak tree as the first covenant of the Lord (Josh. 24.25-7). In Isaiah 61, the prophet refers to the Israelites as "Oaks of Righteousness".

In Slavonic mythology, the oak was the most important tree of the god Perun.

### **7 - 3 – Historical :**

Several individual oak trees, such as the Royal Oak in Britain and the Charter Oak in the United States, are of great historical or cultural importance; for a list of important oaks, see Individual oak trees.

"The Proscribed Royalist, 1651", a famous painting by John Everett Millais, depicted a Royalist fleeing from Cromwell's forces and hidden in an oak. Millais painted the picture in Hayes, Kent, from a local oak tree that became known as the Millais Oak.

Approximately 50km west of Toronto, Canada is the town of Oakville, ON, famous for its history as a shipbuilding port on Lake Ontario.

The city of Raleigh, N.C., is known as "The City of Oaks."

The Jurupa Oak tree — a clonal colony of *Quercus palmeria* or Palmer's Oak found in Riverside County, California — is believed to be the world's oldest organism at 13,000 years.

## 8 - Historical note on Linnaean species

Linnaeus described only five species of oak from eastern North America, based on general leaf form. These were White oak, *Quercus alba*; Chestnut oak, *Q. montana*; Red oak, *Q. rubra*; Willow oak *Q. phellos*; and Water oak, *Q. nigra*. Because he was dealing with confusing leaf forms, the *Q. prinus* and *Q. rubra* specimens actually included mixed foliage of more than one species. For that reason, some taxonomists in the past proposed different names for these two species (*Q. montana* and *Q. borealis*, respectively), but the original Linnaean names have now been lectotypified by removing some of the specimens in Linnaeus' herbarium.

### See also

- List of plants poisonous to equines
- Thousand Oaks, California
- Foloji oak forest

### External links

- *Flora of China – Cyclobalanopsis*
- Flora Europaea: *Quercus*
- Oaks from Bialowieza Forest
- Common Oaks of Florida
- Oaks of the world
- The Global Trees Campaign
- Janka Hardness Scale for Oak

# pH indicator

## Acids and Bases :

Acid dissociation constant • Acid-base extraction • Acid-base reaction • Dissociation constant • Acidity function • Buffer solutions • pH • Proton affinity • Self - ionization of water •

## Acid types :

Brønsted • Lewis • Mineral • Organic • Strong • Superacids • Weak .

## Base types :

Brønsted • Lewis • Organic • Strong • Superbases • Non -nucleophilic • Weak .

## Contents :

- 1 Introduction
- 2 Theory
- 3 Application
- 4 Commercial preparations
- 5 Naturally occurring pH indicators

## 1 – Introduction :

A **pH indicator** is a halochromic chemical compound that is added in small amounts to a solution so that the pH ( acidity or basicity ) of the solution can be determined visually. Hence a pH indicator is a chemical detector for hydronium ions (  $\text{H}_3\text{O}^+$  ) or hydrogen ions (  $\text{H}^+$  ) in the Arrhenius model. Normally, the indicator causes the color of the solution to change depending on the pH. At 25° Celsius, considered the standard temperature, the pH value of a neutral solution is 7.0. Solutions with a pH value below 7.0 are considered acidic, whereas solutions with pH value above 7.0 are basic . As most naturally occurring

organic compounds are weak protolytes, carboxylic acids and amines, pH indicators find many applications in biology and analytical chemistry. Moreover, pH indicators form one of the three main types of indicator compounds used in chemical analysis. For the quantitative analysis of metal cations, the use of complexometric indicators is preferred, whereas the third compound class, the redox indicators, are used in titrations involving a redox reaction as the basis of the analysis.

## 2 - Theory :

In and of themselves, pH indicators are frequently weak acids or bases. The general reaction scheme of a pH indicator can be formulated as follows:



Here HInd stands for the acid form and Ind<sup>-</sup> for the conjugate base of the indicator. It is the ratio of these that determines the color of the solution and that connects the color to the pH value. For pH indicators that are weak protolytes, we can write the Henderson -Hasselbalch equation for them:

$$\text{pH} = \text{pK}_a + \log \frac{[\text{Ind}^-]}{[\text{HInd}]}$$

The equation, derived from the acidity constant, states that when pH equals the pKa value of the indicator, both species are present in 1:1 ratio. If pH is above the pKa value, the concentration of the conjugate base is greater than the concentration of the acid, and the color associated with the conjugate base dominates. If pH is below the pKa value, the converse is true.

Usually, the color change is not instantaneous at the pKa value, but there is a pH range where a mixture of colors is present. This pH range varies between indicators, but as a rule of thumb, it falls between the pKa value plus or minus one. This assumes that solutions retain their color as long as at least 10 %

of the other species persists. For example, if the concentration of the conjugate base is ten times greater than the concentration of the acid, their ratio is 10:1, and consequently the pH is  $pK_a + 1$ . Conversely, if there is a tenfold excess of the acid with respect to the base, the ratio is 1:10 and the pH is  $pK_a - 1$ .

For optimal accuracy, the color difference between the two species should be as clear as possible, and the narrower the pH range of the color change the better. In some indicators, such as phenolphthalein, one of the species is colorless, whereas in other indicators, such as methyl red, both species confer a color. While pH indicators work efficiently at their designated pH range, they are usually destroyed at the extreme ends of the pH scale due to undesired side-reactions.

### 3 – Application :

pH indicators are frequently employed in titrations in analytic chemistry and biology experiments to determine the extent of a chemical reaction. Because of the subjective determination of color, pH indicators are susceptible to imprecise readings. For applications requiring precise measurement of pH, a pH meter is frequently used.

Tabulated below are several common laboratory pH indicators. Indicators usually exhibit intermediate colors at pH values inside the listed transition range. For example, phenol red exhibits an orange color between pH 6.8 and pH 8.4. The transition range may shift slightly depending on the concentration of the indicator in the solution and on the temperature at which it is used.

Indicator	Low pH color	Transition pH range	High pH color
Gentian violet ( Methyl violet 10B )	yellow	0.0 – 2.0	blue-violet
Leucomalachite green (first transition)	yellow	0.0 – 2.0	green

Leucomalachite green (second transition )	green	11.6 – 14	colorless
Thymol blue ( first transition)	red	1.2 – 2.8	yellow
Thymol blue (second transition)	yellow	8.0 – 9.6	blue
Methyl yellow	red	2.9 – 4.0	yellow
Bromophenol blue	yellow	3.0 – 4.6	purple
Congo red	blue-violet	3.0 – 5.0	red
Methyl orange	red	3.1– 4.4	orange
Bromocresol green	yellow	3.8 – 5.4	blue
Methyl red	red	4.4 – 6.2	yellow
Methyl red	red	4.5 – 5.2	green
Azolitmin	red	4.5 – 8.3	blue
Bromocresol purple	yellow	5.2 – 6.8	purple
Bromothymol blue	yellow	6.0 – 7.6	blue
Phenol red	yellow	6.8 – 8.4	red
Neutral red	red	6.8 – 8.0	yellow
Naphtholphthalein	colorless to reddish	7.3 – 8.7	greenish to blue
Cresol Red	yellow	7.2 – 8.8	reddish- purple
Phenolphthalein	colorless	8.3 – 10.0	fuchsia
Thymolphthalein	colorless	9.3 – 10.5	blue
Alizarine Yellow R	yellow	10.2 – 12.0	red

#### 4 - Commercial preparations :

Universal indicator and Hydrion papers are blends of different indicators that exhibits several smooth color changes over a very wide range of pH values.



*pH measurement with indicator paper.*

## **5 - Naturally occurring pH indicators :**

Many plants or plant parts contain chemicals from the naturally-colored anthocyanin family of compounds. They are red in acidic solutions and blue in basic. Extracting anthocyanins from red cabbage leaves or the skin of a lemon to form a crude acid - base indicator is a popular introductory chemistry demonstration.

Anthocyanins can be extracted from a multitude of colored plants or plant parts , including from leaves ( red cabbage ) ; flowers ( geranium , poppy , or rose petals ) ; berries ( blueberries , black currant ) ; and stems ( rhubarb ) .

Litmus , used by alchemists in the Middle Ages and still readily available, is a naturally occurring pH indicator made from a mixture of lichen species, particularly *Rocella tinctoria*. The word 'litmus' derives from 'coloured moss' in Old Norse. The color changes between red in acid solutions and blue in alkalis. The term 'litmus test' has become a widely used metaphor for any test that purports to distinguish authoritatively between alternatives.

*Hydrangea macrophylla* flowers can change color depending on soil acidity. In acid soils, chemical reactions occur in the soil that make aluminum available to these plants, turning the flowers blue. In alkaline soils, these reactions cannot occur

and therefore aluminum is not taken up by the plant. As a result, the flowers remain pink.

Indicator	Low pH color	High pH color
Hydrangea flowers	blue	pink to purple
Anthocyanins	red	blue
Litmus	Red	blue



### See also

- Universal indicator
- Disappearing rainbow indicator
- Nitrazine
- Fecal pH test

# Rose madder

## 1 – Introduction :

**Rose Madder** is the commercial name sometimes used to designate a paint made from the pigment **Madder Lake** - a traditional lake pigment, extracted from the common madder plant (*Rubia tinctorum*).

Madder Lake contains two organic red dyes: alizarin and purpurin. As a paint, it has been described as "a fugitive, transparent, nonstaining, mid valued, moderately dull violet red pigment in tints and medum solutions, darkening to an impermanent, dull magenta red in masstone."

## 2 - History :

Madder has been cultivated as a dyestuff since antiquity in central Asia and Egypt, where it was grown as early as 1500 BC. Cloth dyed with madder root dye was found in the tomb of the Pharaoh Tutankhamun, in the ruins of Pompeii and ancient Corinth. It was included in the Talmud as well as mentioned in writings by Pliny the Elder, and other literary figures, as 'rubio', used in paintings by J. M. W. Turner, and as a color for ceramics remnants of its use have been found at the Baths of Titus. Madder was introduced and then cultivated in Spain by the Moors. It has been found on an Egyptian tomb painting from the Graeco-Roman period, diluted with gypsum to produce a pink color.

The production of a lake pigment from madder was first discovered by the ancient Egyptians. Several techniques and recipes developed. Ideal color was said to come from plants 18 to 28 months old that had been grown in calcareous soil, which is full of lime and typically chalky. Most were considered relatively weak and extremely fugitive until 1804 when the English dye maker George Field refined the technique of making a lake from madder by treating it with alum and an

alkali. The resulting Madder Lake had a less fugitive color and could be used more efficaciously, for example by blending it into a paint. Over the following years, it was found that other metal salts, including those containing iron, tin, and chromium, could be used in place of alum to give madder - based pigments of various other colors.

In 1827, the French chemists Pierre-Jean Robiquet and Colin began producing Garancine, the concentrated version of natural madder. They then found that Madder Lake contained two colorants, the red alizarin and the more rapidly fading purpurin. Purpurin is only present in the natural form of madder, and gives a distinctive orange/red generally warmer tone that pure synthetic alizarin does not. Purpurin fluoresces yellow to red under UV light, while synthetic alizarin slightly shows violet.<sup>[9]</sup> Alizarin was discovered before Purpurin, by heating the ground madder with acid and potash. A yellow vapor crystallized into bright red needles : Alizarin. This alizarin concentrate, makes only 1 % of the madder root.

Natural rose madder supplied half the world with red, up until 1868, when its alizarin component became the first natural dye to be synthetically duplicated by Carl Graebe and Carl Liebermann.<sup>[10]</sup> Advances in the understanding of chemistry: chemical structures, chemical formulas, and elemental formulas, aided these Berlin based scientists in discovering that Alizarin had a anthracene base. However, their recipe was not feasible for large scale production; it required expensive and volatile substances, specifically bromine. William Perkins, the inventor of mauve, filed a patent in June 1869, for a new way to produce alizarin without bromine. Graebe, Liebermann and Heinrich Caro filed a patent for a similar process just one day before Perkins did- yet both patents were granted, as Perkins had been sealed first. They divided the market in half: Perkins sold to the English market, and the scientists from Berlin to the United States and mainland Europe.

Because this synthetic alizarin dye could be produced for a fraction of the cost of the natural madder dye, it quickly replaced all madder-based colorants then in use (in, for instance, British army red coats that had been a shade of madder from the late 17th century to 1870 & French military cloth, often called 'Turkey Red'). In turn, alizarin itself has now been largely replaced by the more light - resistant quinacridone pigments originally developed at DuPont in 1958. It is still manufactured in traditional ways to meet the demands of the fine art market.

### 3 - Other names

Color Index name : **Natural Red 9** abbreviated **NR9**.

French name : *laque de garance*.

Italian name : *lacca di robbia*.

**Rose Madder Genuine** is some times used to specify a paint derived from the root of the madder plant in the traditional manner.<sup>[12]</sup> It is still manufactured and used by some but is too fugitive for professional artistic use.

**Alizarin Crimson** is a paint very similar in color to Rose Madder Genuine but derived from synthetic Alizarin.

**Rose Madder Hue** is some times used to specify a paint made from other pigments but meant to approximate the color of Rose Madder.

Rose Madder, the pigment, is derived from a herbaceous perennial called *Rubia Tinctorum* L.

Turkey Red

Alizarin's Chemical Composition : 1,2 dihydroxy anthraquinone (  $C_{14}H_8O_4$  )

Purpurin's Chemical Composition: 1,2,4 tri hydroxy anthraquinone (  $C_{14}H_8O_5$  )

#### **4 - Substitutes :**

As all madder-based pigments are notoriously fugitive, artists have long sought a more permanent and lightfast replacement for Rose Madder and Alizarin. Recommended alternative pigments include:

- Benzamida Carmine (PR176)
- Quinacridone Pyrrolodone
- Pyrrole Rubine (PR264)
- Anthraquinone red (PR177), a chemical cousin of Alizarin
- Quinacridone Violet (PV19), particularly dark and reddish varieties
- Quinacridone Magenta (PR122), for a brighter violet
- Quinacridone Rose (PV19), for a brighter violet
- Perylene Maroon (PR179], for mixing dull violets

# Saffron



( *Saffron crocus* ) *C. sativus* flower with red stigmas

## Contents

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- 9 Grade

## Introduction :

**Saffron** is a spice derived from the flower of the **saffron crocus** (*Crocus sativus*). *Crocus* is a genus in the family Iridaceae. A *C. sativus* flower bears three stigmas, each the distal end of a carpel. Together with the styles — stalks that connect the stigmas to their host plant — the dried stigmas are used in cooking as a seasoning and colouring agent. Saffron,

long the world's most expensive spice by weight, is native to Southwest Asia.

Saffron's bitter taste and iodoform - or hay - like fragrance result from the chemicals picrocrocin and safranal . Saffron also contains a carotenoid dye , crocin , which imparts a rich golden-yellow hue to dishes and textiles.

### Scientific classification

Kingdom: Plantae  
 (unranked): Angiosperms  
 (unranked): Monocots  
 Order: Asparagales  
 Family: Iridaceae  
 Subfamily: Crocoideae  
 Genus: *Crocus*  
 Species: *C. sativus*

### Binomial name

*Crocus sativus* L.

## 1 - Etymology :

The English word *saffron* stems from the Latin word *safranum* via the 13th- century Old French term *safran*. *Safranum* in turn derives from Persian زعفران (za'ferân). Some argue that it ultimately came from the Arabic word زَعْفَرَان (za'farān), which itself derives from the adjective أَصْفَر (aṣfar, "yellow"). However, some etymologists argue that زَعْفَرَان (za'farān) is the arabicized form of the Persian word زرپرآن (zarparān) — "having golden stigmas".<sup>[7]</sup> Latin *safranum* is also the source of the Italian *zafferano*, Portuguese *açafrão* and Spanish *azafrán* etc. *Crocum* in Latin is a Semitic loan word derived from Aramaic *kurkema* via Arabic *kurkum*, and Greek *krokos*.

## 2 – Biology :

The domesticated saffron crocus (*Crocus sativus*) is an autumn-flowering perennial plant unknown in the wild. It is often mistaken for the more plentiful common autumn crocus, which is also known as meadow saffron or naked ladies (*Colchicum autumnale*) and has been the cause of deaths due to mistaken identity. However, saffron in high dosage can also be poisonous. It is a sterile triploid form, possibly of the eastern Mediterranean autumn-flowering *Crocus cartwrightianus* that originated in Central Asia . The saffron crocus resulted when *Crocus cartwrightianus* was subjected to extensive artificial selection by growers seeking longer stigmas. Being sterile, the purple flowers of *Crocus sativus* fail to produce viable seeds; reproduction depends on human assistance : corms, underground bulb-like starch-storing organs, must be dug up, broken apart, and replanted. A corm survives for one season, producing via this division up to ten "cormlets" that grow into new plants . Corms are small brown globules up to 4.5 centimetres (1.8 in) in diameter and are shrouded in a dense mat of parallel fibers.

After aestivating in spring, the plant sends up five to eleven narrow and nearly vertical green leaves, each up to 40 cm (16 in) in length. In autumn, purple buds appear. Only in October, after most other flowering plants have released their seeds, do its brilliantly hued flowers develop; they range from a light pastel shade of lilac to a darker and more striated mauve. Upon flowering, plants average less than 30 cm (12 in) in height. A three - pronged style emerges from each flower. Each prong terminates with a vivid crimson stigma 25 – 30 mm ( 0.98 –1.2 in ) in length.

## 3 – Cultivation :

*Crocus sativus* thrives in the Mediterranean maquis (an ecotype superficially resembling the North American chaparral) and similar climates where hot, dry summer breezes sweep semi-arid lands. It can nonetheless survive cold winters,

tolerating frosts as low as  $-10\text{ }^{\circ}\text{C}$  ( $14\text{ }^{\circ}\text{F}$ ) and short periods of snow cover.

Irrigation is required if not grown in moist environments such as Kashmir, where annual rainfall averages 1,000–1,500 mm (39–59 in); saffron-growing regions in Greece (500 mm or 20 in annually) and Spain (400 mm or 16 in) are far drier than where *Crocus* is cultivated in Iran, for example. What makes this possible is the timing of the local wet seasons; generous spring rains and drier summers are optimal. Rain immediately preceding flowering boosts saffron yields; rainy or cold weather *during* flowering promotes disease and reduces yields. Persistently damp and hot conditions harm the crops, and rabbits, rats, and birds cause damage by digging out the corms. Nematodes, leaf rusts, and corm rot pose added threats.

The plants fare poorly in shady conditions; they grow best in full sunlight. Fields that slope towards the sunlight are optimal (i.e., south-sloping in the Northern Hemisphere). Planting is mostly done in June in the Northern Hemisphere, where corms are lodged 7 to 15 centimetres (2.8–5.9 in) deep. Planting depth and corm spacing, in concert with climate, are critical factors in determining yields. Mother corms planted deeper yield higher-quality saffron, though form fewer flower buds and daughter corms. Italian growers optimize thread yield by planting 15 centimetres (5.9 in) deep and in rows 2–3 cm apart; depths of 8–10 cm optimizes flower and corm production. Greek, Moroccan, and Spanish growers have devised distinct depths and spacings to suit their locales.

*C. sativus* prefers friable, loose, low-density, well-watered, and well-drained clay- calcareous soils with high organic content. Traditional raised beds promote good drainage. Soil organic content was historically boosted via application of some 20–30 tonnes of manure per hectare. After wards—and with no further manure application — corms were planted. After a period of dormancy through the summer, the corms send up their narrow leaves and begin to bud in early autumn. Only in

mid-autumn do they flower. Harvests are by necessity a speedy affair: after blossoming at dawn, flowers quickly wilt as the day passes. All plants bloom within a window of one or two weeks. Roughly 150 flowers yield 1 gram (0.035 oz) of dry saffron threads; to produce 12 g of dried saffron (72 g freshly harvested), 1 kg of flowers are needed (1 lb for 0.2 oz of dried saffron). One fresh-picked flower yields an average 30mg (0.03g) of fresh saffron or 7mg ( 0.007g ) of dried saffron.

#### 4 – Chemistry :

Saffron contains more than 150 volatile and aroma-yielding compounds. It also has many nonvolatile active components, many of which are carotenoids, including zeaxanthin, lycopene, and various  $\alpha$ - and  $\beta$ -carotenes. However, saffron's golden yellow-orange colour is primarily the result of  $\alpha$ -crocin. This crocin is trans-crocetin di-( $\beta$ -D-gentiobiosyl) ester (systematic (IUPAC) name: 8,8-diapo-8,8-carotenoic acid). This means that the crocin underlying saffron's aroma is a digentiobiose ester of the carotenoid crocetin. Crocins themselves are a series of hydrophilic carotenoids that are either monoglycosyl or diglycosyl polyene esters of crocetin.<sup>[21]</sup> Meanwhile, crocetin is a conjugated polyene dicarboxylic acid that is hydrophobic, and thus oil-soluble. When crocetin is esterified with two water-soluble gentiobioses (which are sugars), a product results that is itself water-soluble. The resultant  $\alpha$ -crocin is a carotenoid pigment that may comprise more than 10 % of dry saffron's mass. The two esterified gentiobioses make  $\alpha$ -crocin ideal for colouring water-based (non-fatty) foods such as rice dishes.

Chemical composition	
Component	Mass %
carbohydrates	12.0–15.0
water	9.0–14.0
polypeptides	11.0–13.0
cellulose	4.0–7.0
lipids	3.0–8.0

minerals	1.0–1.5
miscellaneous non-nitrogenous	40.0

<b>Proximate analysis</b>	
<b>Component</b>	<b>Mass %</b>
Water- soluble components	53.0
→ Gums	10.0
→ Pentosans	8.0
→ Pectins	6.0
→ Starch	6.0
→ $\alpha$ -Crocin	2.0
→ Other carotenoids	1.0
Lipids	12.0
→ Non-volatile oils	6.0
→ Volatile oils	1.0
Protein	12.0
Inorganic matter ("ash")	6.0
→ HCl-soluble ash	0.5
Water	10.0
Fiber (crude)	5.0

The bitter glucoside picrocrocin is responsible for saffron's flavour. Picrocrocin ( chemical formula :  $C_{16}H_{26}O_7$  ; systematic name : 4 - (  $\beta$  - D - gluco pyrano syloxy ) - 2,6,6 - tri methyl cyclohex -1- ene -1- carboxaldehyde ) is a union of an aldehyde sub-element known as safranal (systematic name: 2,6,6-trimethylcyclohexa-1,3-diene-1- carboxaldehyde) and a carbohydrate. It has insecticidal and pesticidal properties, and may comprise up to 4 % of dry saffron. Significantly, picrocrocin is a truncated version (produced via oxidative cleavage) of the carotenoid zeaxanthin and is the glycoside of the terpene aldehyde safranal. The reddish-coloured zeaxanthin is, incidentally, one of the carotenoids naturally present within the retina of the human eye.

When saffron is dried after its harvest, the heat, combined with enzymatic action, splits picrocrocin to yield D-glucose and a free safranal molecule . Safranal, a volatile oil, gives saffron much of its distinctive aroma . Safranal is less bitter than picrocrocin and may comprise up to 70 % of dry saffron's volatile fraction in some samples . A second element underlying saffron's aroma is 2-hydroxy-4,4,6-trimethyl-2,5-cyclohexadien-1-one, the scent of which has been described as "saffron, dried hay like". Chemists found this to be the most powerful contributor to saffron's fragrance despite its being present in a lesser quantity than safranal. Dry saffron is highly sensitive to fluctuating pH levels, and rapidly breaks down chemically in the presence of light and oxidizing agents. It must therefore be stored away in air - tight containers in order to minimise contact with atmospheric oxygen. Saffron is somewhat more resistant to heat.

## **5 - Medicinal uses :**

Saffron has many medicinal uses A 2010 double-blind, placebo - controlled study found saffron helped mild to moderate Alzheimer's disease. Crocetin, an important carotenoid constituent of saffron, has shown significant potential as an anti-tumor agent in animal models and cell culture systems. Saffron inhibits DMBA-induced skin carcinoma in mice when treated early. Both saffron stigma and petals are said to be helpful for depression. Satiereal (Inoreal Ltd, Plerin, France), a novel extract of saffron stigma, may reduce snacking and enhance satiety through its suggested mood-improving effect, and thus contribute to weight loss. Saffron was found to be effective in relieving symptoms of PMS. Saffron, crocins and crocetin inhibit breast cancer cell proliferation. *Crocus sativus* (most saffron research refers to the stigmas but often this is not made clear in research papers) inhibits histamine H1 receptors in animals, suggesting a potential use in allergic disorders. Histamine is a biological amine that plays an important role in allergic responses. Saffron may have a protective effect on the heart.

A recent ( 2011 ) double blind, human trial found use of 100 mg of saffron daily has temporary immunomodulatory activities.

## **6 - History of saffron :**

The history of saffron cultivation reaches back more than 3,000 years . The wild precursor of domesticated saffron crocus was *Crocus cartwrightianus*. Human cultivators bred wild specimens by selecting for unusually long stigmas. Thus, a sterile mutant form of *C. cartwrightianus*, *C. sativus*, emerged in late Bronze Age Crete.

### **6 – 1 - Asia :**

Experts believe saffron was first documented in a 7th century BC Assyrian botanical reference compiled under Ashurbanipal.

Documentation of saffron's use over the span of 4,000 years in the treatment of some 90 illnesses has been uncovered.

Saffron-based pigments have been found in 50,000 year-old depictions of prehistoric places in northwest Iran . Later, the Sumerians used wild-growing saffron in their remedies and magical potions . Saffron was an article of long-distance trade before the Minoan palace culture's 2nd millennium BC peak. Ancient Persians cultivated Persian saffron (*Crocus sativus* 'Hausknechtii') in Derbena, Isfahan, and Khorasan by the 10th century BC. At such sites, saffron threads were woven into textiles , ritually offered to divinities, and used in dyes, perfumes, medicines, and body washes. Thus, saffron threads would be scattered across beds and mixed into hot teas as a curative for bouts of melancholy. Non-Persians also feared the Persians' usage of saffron as a drugging agent and aphrodisiac. During his Asian campaigns, Alexander the Great used Persian saffron in his infusions, rice, and baths as a curative for battle wounds. Alexander's troops imitated the practice from the Persians and brought saffron-bathing to Greece.

Conflicting theories explain saffron's arrival in South Asia. Kashmiri and Chinese accounts date its arrival anywhere between 900 – 2500 years ago. Historians studying ancient Persian records date the arrival to sometime prior to 500 BC , attributing it to either Persian transplantation of saffron corms to stock new gardens and parks or to a Persian invasion and colonization of Kashmir. Phoenicians then marketed Kashmiri saffron as a dye and a treatment for melancholy. From there, saffron use in foods and dyes spread throughout South Asia. Buddhist monks in India adopted saffron-coloured robes after the Gautama Buddha's death. This color is now used widely in all Buddhist countries. However, the robes were not dyed with costly saffron but turmeric, a less expensive dye, or jackfruit . The Tamils have been using saffron for more than 2000 years. In Tamil it is called "gnaazhal poo" It is used to cure head ache, for painless labor etc.

Some historians believe that saffron came to China with Mongol invaders from Persia. On the other hand, saffron is mentioned in ancient Chinese medical texts, including the forty-volume *Shennong Bencaojing* ( *Shennong's Great Herbal*", also known as *Pen Ts'ao* or *Pun Tsao*) pharmacopoeia, a tome dating from 200–300 BC. Traditionally attributed to the legendary *Yan* ("Fire") Emperor Shennong, it documents 252 phytochemical-based medical treatments for various disorders. Yet around the 3rd century AD, the Chinese were referring to saffron as having a Kashmiri provenance. For example, Wan Zhen, a Chinese medical expert, reported that "[t]he habitat of saffron is in Kashmir, where people grow it principally to offer it to the Buddha." Wan also reflected on how saffron was used in his time: "The [saffron crocus] flower withers after a few days, and then the saffron is obtained. It is valued for its uniform yellow colour. It can be used to aromatise wine " .

## **6 – 2 – Europe / Mediterranean / America :**

Minoans portrayed saffron in their palace frescoes by 1500–1600 BC, showing saffron's use as a therapeutic drug.

Later, Greek legends told of sea voyages to Cilicia. There, adventurers hoped to procure what they believed was the world's most valuable saffron. Another legend tells of Crocus and Smilax, whereby Crocus is bewitched and transformed into the original saffron crocus. Ancient Mediterranean peoples—including perfumers in Egypt, physicians in Gaza, townspeople in Rhodes, and the Greek *hetaerae* courtesans—used saffron in their scented waters, perfumes, ointments, potpourris, mascaras, divine offerings, and medical treatments.

In late Hellenistic Egypt, Cleopatra used saffron in her baths so that lovemaking would be more pleasurable. Egyptian healers used saffron as a treatment for all varieties of gastrointestinal ailments. Saffron was also used as a fabric dye in such Levant cities as Sidon and Tyre. Aulus Cornelius Celsus prescribes saffron in medicines for wounds, cough, colic, and scabies, and in the mithridatium. Such was the Romans' love of saffron that Roman colonists took their saffron with them when they settled in southern Gaul, where it was extensively cultivated until Rome's fall. Competing theories state that saffron only returned to France with 8th century AD Moors or with the Avignon papacy in the 14th century AD.

European saffron cultivation plummeted following the Roman Empire's fall. The spread of Islamic civilization allowed saffron's reintroduction to Spain, France, and Italy. During the 14th century Black Death, demand for saffron-based medicine skyrocketed, and much saffron had to be imported via Venetian and Genoan ships from southern and Mediterranean lands such as Rhodes. The theft of one such shipment by noblemen sparked the fourteen-week long "Saffron War". The conflict and resulting fear of rampant saffron piracy spurred significant saffron cultivation in Basel, which grew prosperous. Cultivation and trade then spread to Nuremberg, where epidemic levels of saffron adulteration brought on the *Safranschou* code, under which saffron adulterators were fined, imprisoned, and executed. Soon after, saffron cultivation spread throughout England, especially Norfolk and Suffolk. The Essex town of

Saffron Walden, named for its new specialty crop, emerged as England's prime saffron growing and trading center. However, an influx of more exotic spices such as chocolate, coffee, tea, and vanilla from newly contacted Eastern and overseas countries caused European cultivation and usage of saffron to decline. Only in southern France, Italy, and Spain, did significant cultivation endure.

Europeans introduced saffron to the Americas when immigrant members of the Schwenkfelder Church left Europe with a trunk containing saffron corms; indeed, many Schwenkfelders had widely grown saffron in Europe. By 1730, the Pennsylvania Dutch were cultivating saffron throughout eastern Pennsylvania. Spanish colonies in the Caribbean bought large amounts of this new American saffron, and high demand ensured that saffron's list price on the Philadelphia commodities exchange was set equal to that of gold. The trade with the Caribbean later collapsed in the aftermath of the War of 1812, when many saffron - transporting merchant vessels were destroyed. Yet the Pennsylvania Dutch continued to grow lesser amounts of saffron for local trade and use in their cakes, noodles, and chicken or trout dishes. American saffron cultivation survived into modern times mainly in Lancaster County, Pennsylvania.

## **7 - Trade and use of Saffron :**

Saffron's aroma is often described by connoisseurs as reminiscent of metallic honey with grassy or hay-like notes, while its taste has also been noted as hay-like and sweet. Saffron also contributes a luminous yellow-orange colouring to foods. Saffron is widely used in Iranian (Persian), Arab, Central Asian, European, Pakistani, Indian, and Turkish cuisines. Confectioneries and liquors also often include saffron . Common saffron substitutes include safflower (*Carthamus tinctorius*, which is often sold as "Portuguese saffron" or "açafraão"), annatto, and turmeric (*Curcuma longa*). Medicinally, saffron has a long history as part of traditional healing; modern

medicine has also discovered saffron as having anticarcinogenic ( cancer-suppressing ) , anti - mutagenic ( mutation –preventing ) , immunomodulating , and antioxidant - like properties. Early studies show that saffron may protect the eyes from the direct effects of bright light and retinal stress apart from slowing down macular degeneration and retinitis pigmentosa . Saffron has also been used as a fabric dye, particularly in China and India, and in perfumery. It is widely used in religion in India. It is widely used in cooking in many ethnic cuisines, for example, Milanese risotto in Italy, Bouillabaise in France, to biryani with various meats in the subcontinent, and paella in Spain.

Most saffron is grown in a belt of land ranging from the Mediterranean in the west to Kashmir in the east. Annually, around 300 tonnes of saffron are produced worldwide.<sup>[5]</sup> Iran, Spain, India, Greece, Azerbaijan, Morocco, and Italy, in decreasing order of production, are the major producers of saffron. Iran with its cultivation of different varieties, is the largest producer of saffron with 93.7% of the world's total production. The main cultivation areas in the country are in eastern and southeastern parts. The Khorassan zone has managed to achieve an excellent yield on the production and export of saffron over time, so much so that 90 % of saffron production in Iran is obtained from there. Other famous regions are Fars Province, Estahbanat mainly and Kerman Province whose output is now on the up. Qayen region here is famous for its quality saffron. Kashmir's share has declined due to poor quality, caused by war.

A pound (454 grams) of dry saffron requires 50,000–75,000 flowers, the equivalent of a football field's area of cultivation ( 110,000 - 170,000 flowers or two football fields for a kilogram ) . Forty hours of labour are needed to pick 150,000 flowers. Stigmas are dried quickly upon extraction and (preferably) sealed in airtight containers. Saffron prices at wholesale and retail rates range from US \$ 500 to US \$ 5,000 per pound ( US \$ 1,100 –11,000 / kg ) — equivalent to £ 2,500 / € 3,500 per pound or £ 5,500 / € 7,500 per kilogram. The price

in Canada recently rose to CAN \$ 18,000 per kilogram. In Western countries, the average retail price is \$ 1,000 / £500 / €700 per pound ( US \$ 2,200 / £ 1 ,100 / € 1,550 per kilogram ) . A pound comprises between 70,000 and 200,000 threads. Vivid crimson colouring, slight moistness, elasticity, and lack of broken-off thread debris are all traits of fresh saffron.

## 8 - Cultivars :

Several saffron cultivars are grown worldwide. Spain's varieties, including the tradenames 'Spanish Superior' and 'Creme', are generally mellower in colour, flavour, and aroma; they are graded by government-imposed standards. Italian varieties are slightly more potent than Spanish, while the most intense varieties tend to be Iranian in origin. Aside from these, various "boutique" crops are available from New Zealand, France, Switzerland, England, the United States, and other countries, some organically grown. In the U.S., Pennsylvania Dutch saffron — known for its earthy notes—is marketed in small quantities.

Consumers regard certain cultivars as "premium" quality. The "Aquila" saffron ( *zafferano dell'Aquila* ) — defined by high safranal and crocin content, shape, unusually pungent aroma, and intense colour—is grown exclusively on eight hectares in the Navelli Valley of Italy's Abruzzo region, near L'Aquila. It was first introduced to Italy by a Dominican monk from Inquisition-era Spain. But in Italy the biggest saffron cultivation is in San Gavino Monreale, Sardinia. There, saffron is grown on 40 hectares ( 60 % of Italian production ) ; it also has very high crocin, picrocrocin, and safranal content. Another is the Kashmiri "Mongra" or "Lacha" saffron ( *Crocus sativus* 'Cashmirianus' ) , which is among the most difficult for consumers to obtain. Repeated droughts, blights, and crop failures in Kashmir, combined with an Indian export ban, contribute to its high prices. Kashmiri saffron is recognisable by its extremely dark maroon-purple hue, among the world's

darkest, which suggests the saffron's strong flavour, aroma, and colourative effect.

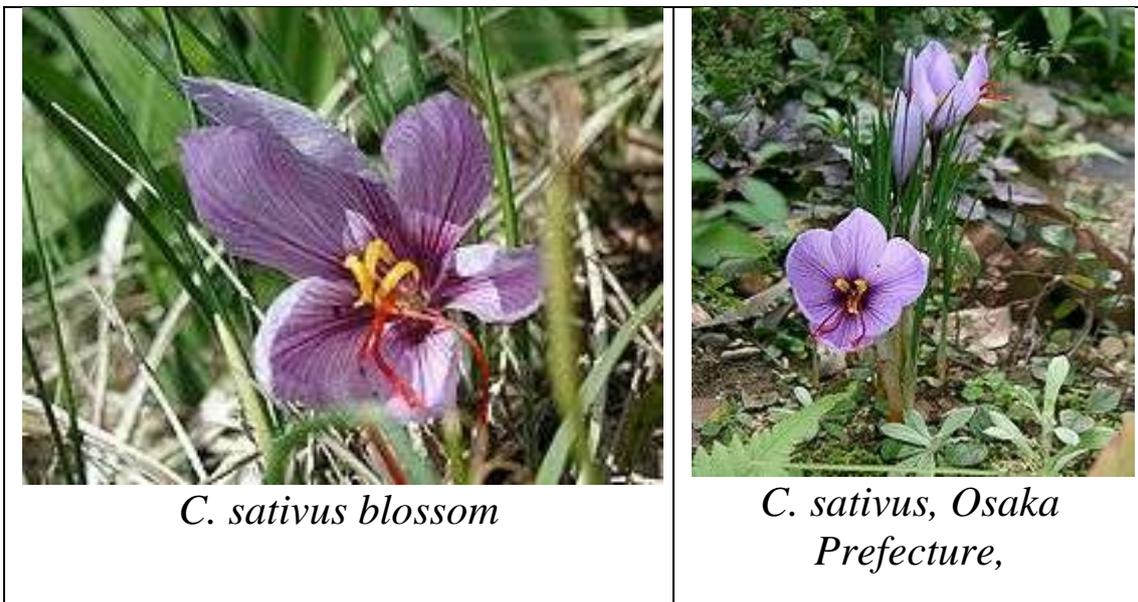
## 9 – Grade :

Saffron is graded via laboratory measurement of crocin (colour), picrocrocin (taste), and safranal (fragrance) content. Determination of non-stigma content ("floral waste content") and other extraneous matter such as inorganic material ("ash") are also key. Grading standards are set by the International Organization for Standardization, a federation of national standards bodies. ISO 3632 deals exclusively with saffron and establishes four empirical colour intensity grades: IV (poorest), III, II, and I (finest quality). Samples are assigned grades by gauging the spice's crocin content, revealed by measurements of crocin-specific spectroscopic absorbance. Absorbance is defined as  $A_\lambda = -\log(I/I_0)$ , with  $A_\lambda$  as absorbance (Beer-Lambert law) and indicates degree of transparency ( $I/I_0$ , the ratio of light intensity exiting the sample to that of the incident light) to a given wavelength of light.

Graders measure absorbances of 440-nm light by dry saffron samples. Higher absorbances imply greater crocin concentration, and thus a greater colourative intensity. These data are measured through spectrophotometry reports at certified testing laboratories worldwide. These colour grades proceed from grades with absorbances lower than 80 (for all category IV saffron) up to 190 or greater (for category I). The world's finest samples (the selected most red-maroon tips of stigmas picked from the finest flowers) receive absorbance scores in excess of 250. Market prices for saffron types follow directly from these ISO scores. However, many growers, traders, and consumers reject such lab test numbers. They prefer a more holistic method of sampling batches of thread for taste, aroma, pliability, and other traits in a fashion similar to that practiced by practised wine tasters.

Despite such attempts at quality control and standardisation, an extensive history of saffron adulteration — particularly among the cheapest grades — continues into modern times. Adulteration was first documented in Europe's Middle Ages, when those found selling adulterated saffron were executed under the *Safranschou* code. Typical methods include mixing in extraneous substances like beets, pomegranate fibers, red - dyed silk fibers, or the saffron crocus's tasteless and odorless yellow stamens. Other methods included dousing saffron fibers with viscid substances like honey or vegetable oil. However, powdered saffron is more prone to adulteration, with turmeric, paprika, and other powders used as diluting fillers. Adulteration can also consist of selling mislabeled mixes of different saffron grades. Thus, in India, high - grade Kashmiri saffron is often sold and mixed with cheaper Iranian imports; these mixes are then marketed as pure Kashmiri saffron, a development that has cost Kashmiri growers much of their income.

## Saffron trade and use



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### Introduction :

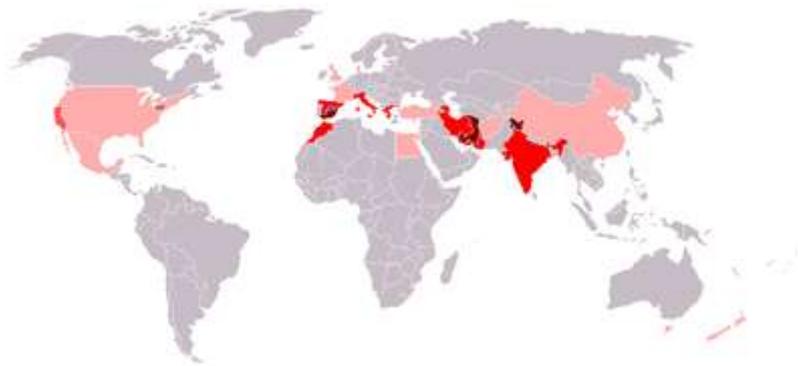
Saffron has been used as a seasoning, fragrance, dye, and medicine for more than 3,000 years . The world's most expensive spice by weight , saffron consists of stigmas plucked from the saffron crocus (*Crocus sativus*). The resulting dried "threads" are distinguished by their bitter taste, hay-like fragrance, and slight metallic notes. Saffron is native to Southwest Asia , but was first cultivated in Greece . Iran is the world's largest producer of saffron, accounting for over half the total harvest.

In both antiquity and modern times, most saffron was and is used in the preparation of food and drink: cultures spread across Africa, Asia, Europe, and the Americas value the red threads for use in such items as baked foods, curries, and liquor.

Medicinally, saffron was used in ancient times to treat a wide range of ailments, including stomach upsets, bubonic plague, and smallpox ; clinical trials have shown saffron's potential as an anticancer and anti-aging agent. Saffron has been used to colour textiles and other items, many of which carry a religious or hierarchical significance.

Saffron cultivation has long centred on a broad belt of Eurasia bounded by the Mediterranean Sea in the southwest to Kashmir and China in the northeast. The major saffron producers of antiquity—Iran, Spain, India, and Greece — continue to dominate the world trade. The cultivation of saffron in the Americas was begun by members of the Schwenkfelder Church in Pennsylvania. In recent decades cultivation has spread to New Zealand, Tasmania, and California.

### 1 - Modern trade :



World saffron cultivation patterns :

- Major producing regions
- Major producing nations
- Minor producing regions
- Minor producing nations
- Major trading centres (current)
- Major trading centres (historical)

Virtually all saffron is produced in a wide geographical belt extending from the Mediterranean in the west to Kashmir in the east. All continents outside this zone — except Antarctica — produce smaller amounts. Annual worldwide production

amounts to some 300 tonnes, including whole threads and powder This includes 50 tonnes of annual production of top - grade "coupe" saffron in 1991. Iran, Spain, India, Greece, Azerbaijan, Morocco, and Italy (in decreasing order of production) dominate the world saffron harvest, with Iran and Spain alone producing 80 % of the world crop. Afghanistan has resumed cultivation in recent decades. Iran with its cultivation of different varieties, is the largest producer of saffron with 93.7 % of the world's total production. The main cultivation areas in the country are in eastern and southeastern parts. The Khorassan zone has managed to achieve an excellent yield on the production and export of saffron over time, so much so that 90% of saffron production in Iran is obtained from there. Other famous regions are Fars Province, Estahbanat mainly and Kerman Province whose output is now on the up. Qayen region here is famous for its quality saffron. Kashmir's share has declined due to poor quality, caused by war

Despite numerous cultivation efforts in such countries as Austria, England, Germany, and Switzerland, only select locales continue the harvest in Northern and Central Europe. Among these is the small Swiss village of Mund, in the Valais canton, whose annual saffron output comes to several kilograms . Micro-scale cultivation also occurs in Tasmania , China, Egypt, France, Israel, Mexico, New Zealand, Turkey ( especially Safranbolu ) , California, and Central Africa .

The high cost of saffron is due to the difficulty of manually extracting large numbers of minute stigmas; the only part of the crocus with the desired properties of aroma and flavour. In addition, a large number of flowers need to be processed in order to yield marketable amounts of saffron. A pound of dry saffron (0.45 kg) requires the harvesting of some 50,000 flowers, the equivalent of a football pitch's area of cultivation . By another estimate some 75,000 flowers are needed to produce one pound of dry saffron . This too depends on the average size of each saffron cultivar's stigmas. Another complication arises in the flowers' simultaneous and transient blooming. Since so

many crocus flowers are needed to produce just one kilogram of dry saffron, about forty hours of intense labour, harvesting is often a frenetic affair. In Kashmir, for example, the thousands of growers must work continuously in relays over the span of one or two weeks throughout both day and night . However, the quality has decreased in recent years. Production is in small area surrounding the village Pampore close to Srinagar. The fields are divided into sections one or two square meters and are kept devoid of vegetation all 12 months. Flowers show up for a about two weeks in the end of October or the beginning of November. They are picked from the plants and separated into styles are waste afterwards. Including the final drying of the styles, all the work is done by families that use little or no mechanical aid.



*Saffron threads ( red-coloured stigmas ) mixed with styles (yellow) from Iran.*

Once extracted, the stigmas must be dried quickly, lest decomposition or mold ruin the batch's marketability. The traditional method of drying involves spreading the fresh stigmas over screens of fine mesh, which are then baked over hot coals or wood or in oven-heated rooms with temperatures reaching 30 – 35 °C for 10 – 12 hours. Afterwards, the dried spice is preferably sealed in airtight glass containers . Bulk quantities of relatively lower-grade saffron can reach up wards of US \$ 500 / pound, while retail costs for small amounts may exceed 10 times that rate. In Western countries the average retail price is approximately \$ 1,000 per pound, however . The high price is somewhat offset by the small quantities needed: a few

grams at most in medicinal use and a few strands, at most, in culinary applications; there are between 70,000 and 200,000 strands in a pound.

Experienced saffron buyers often have rules of thumb when deliberating on their purchases. They may look for threads exhibiting a vivid crimson colouring, slight moistness, and elasticity. Meanwhile, they reject threads displaying telltale dull brick red colouring (indicative of age) and broken-off debris collected at the container's bottom (indicative of age-related brittle dryness). Such aged samples are most likely encountered around the main June harvest season, when retailers attempt to clear out the previous season's old inventory and make room for the new season's crop. Indeed, experienced buyers recommend that only the current season's threads should be used at all. Thus, reputable saffron wholesalers and retailers will indicate the year of harvest or the two years that bracket the harvest date ; a late 2002 harvest would be shown as " 2002 / 2003 .

## **2 - Culinary use :**

Saffron is used extensively in European, North African, and Asian cuisines. Its aroma is described by experts as resembling that of honey, with grassy, hay-like, and metallic notes. Saffron's taste is like that of hay, but with hints of bitter. Saffron also contributes a luminous yellow-orange colouring to items it is soaked with. For these traits saffron is used in baked goods, cheeses, confectioneries, curries, liquors, meat dishes, and soups. Saffron is used in India, Iran, Spain, and other countries as a condiment for rice, along with sultanas and bay leaves. Saffron rice is used in many cuisines. It is used in many famous dishes such as *paella valenciana*, which is a spicy rice-meat preparation, and the *zarzuela* fish stews. They are also popular for spicing up subcontinental beef and chicken foods. It is also used in many Indian sweets, particularly among Muslims and Rajasthanis. Saffron ice cream is one such delicacy. In previous times, many dishes used copious amounts not for taste but to parade their wealth . It is also used in *fabada asturiana*.

Saffron is essential in making the French *bouillabaisse*, which is a spicy fish stew from Marseilles, the Italian *risotto alla milanese*, and the Swedish and Cornish varieties of saffron bun. Saffron-flavoured butter lassi is a symbol of visiting Jodhpur, an ancient center of Rajasthan. Saffron-flavoured ice cream, is also widespread.

A saffron bun, in Swedish *lussekatt* (literally "Lucy cat", after Saint Lucy) or *lussebulle*, is a rich yeast dough bun that is flavoured with saffron and cinnamon or nutmeg and contains currants. In Sweden, no cinnamon or nutmeg is used in the bun, and raisins are used instead of currants. The buns are baked into many traditional shapes, of which the simplest is a reversed S-shape. They are traditionally eaten during Advent, and especially on Saint Lucy's Day, December 13. In England, the buns were traditionally baked on sycamore leaves and dusted with powdered sugar. This "revel bun" from Cornwall is baked for special occasions, such as anniversary feasts (revels), or the dedication of a church. In the West of Cornwall large saffron buns are also known as "tea treat buns" and are associated with Methodist Sunday School outings or activities.



*Saffron is one of the three essential ingredients in the Spanish paella valenciana, and is responsible for its yellow colouring.*



*A Swedish-style saffron bun, traditionally consumed before Christmas*

Iranians use saffron in their national dish, *chelow kabab*, while Uzbeks use it in a special rice dish known as a "wedding

*plov*" (cf. pilaf). Moroccans use it in their *tajine*-prepared dishes, including *kefta* (meatballs with tomato), *mqualli* (a citron-chicken dish), and *mrouzia* (succulent lamb dressed with plums and almonds). Saffron is also central in chermoula herb mixture, which flavours many Moroccan dishes. Indian cuisine uses saffron in its *biryanis*, which are spicy rice-vegetable dishes. (An example is the *Pakki* variety of *Hyderabadi biryani*.) It is also used in Indian milk-based sweets:<sup>[5]</sup> *gulab jamun*, *kulfi*, *double ka meetha*, and "saffron *lassi*", the last a spicy Jodhpuri drink with a yogurt base.



*Basic Saffron rice, made with bouillon cubes and saffron*

Because of its high cost, saffron was often replaced by or diluted with safflower (*Carthamus tinctorius*) or turmeric (*Curcuma longa*) in cuisine. Both mimic saffron's colour well, but have flavours very different from that of saffron. Saffron is also used in the confectionery and liquor industries; this is its most common use in Italy. Chartreuse, izarra, and strega are types of alcoholic beverages that rely on saffron to provide a flourish of colour and flavour.

Experienced saffron users often crumble and pre-soak threads for several minutes prior to adding them to their dishes. For example, they may toss threads into water or sherry and leave them to soak for approximately ten minutes. This process extracts the threads' colour and flavour into the liquid phase; powdered saffron does not require this step.<sup>[18]</sup> Afterward, the soaking solution is added to the hot and cooking dish. This allows even distribution of saffron's colour and flavour throughout a dish, and is important when preparing baked goods

or thick sauces.<sup>[16]</sup> It can also be toasted or drenched in alcohol. Only a small pinch is needed and saffron can be stroed safely for great legnth.

### **3 - Medicinal use :**

Saffron's folkloric uses as an herbal medicine are legendary. It was used for its carminative (suppressing cramps and flatulence) and emmenagogic (enhancing pelvic blood flow) properties. Medieval Europeans used saffron to treat respiratory infections and disorders such as coughs and colds, scarlet fever, smallpox, cancer, hypoxia, and asthma. Other targets included blood disorders, insomnia, paralysis, heart diseases, stomach upsets, gout, chronic uterine haemorrhage, dysmorrhea, amenorrhea, baby colic, and eye disorders. For ancient Persians and Egyptians, saffron was also an aphrodisiac, a general-use antidote against poisoning, a digestive stimulant, and a tonic for dysentery and measles. In Europe practitioners of the archaic "Doctrine of Signatures" took saffron's yellowish hue as a sign of its supposed curative properties against jaundice.

Initial research suggests that carotenoids present in saffron are anticarcinogenic ( cancer - suppressing ) , anti-mutagenic ( mutation –preventing ) , and immunomodulatory properties. Dimethylcroctin, the compound responsible for these effects, counters a wide range of murine ( rodent ) tumours and human leukaemia cell lines. Saffron extract also delays ascites tumour growth, delays papilloma carcinogenesis, inhibits squamous cell carcinoma, and decreases soft tissue sarcoma incidence in treated mice. Researchers theorise that, based on the results of thymidine-uptake studies, such anticancer activity is best attributed to dimethylcroctin's disruption of the DNA-binding ability of a class of enzymes known as type II topoisomerases. As topoisomerases play a key role in managing DNA topology, the malignant cells are less successful in synthesizing or replicating their own DNA.

Saffron's pharmacological effects on malignant tumours have been documented in studies done both *in vitro* and *in vivo*. It extends the lives of mice that are intraperitoneally impregnated with transplanted sarcomas, namely, samples of S-180, Dalton's lymphoma ascites (DLA), and Ehrlich ascites carcinoma (EAC) tumours. Researchers followed this by orally administering 200 mg of saffron extract per each kg of mouse body weight. As a result the life spans of the tumour - bearing mice were extended to 111.0 %, 83.5 %, and 112.5 %, respectively, in relation to baseline spans. Researchers also discovered that saffron extract exhibits cytotoxicity in relation to DLA , EAC , P38B , and S -180 tumour cell lines cultured *in vitro*. Thus, saffron has shown promise as a new and alternative treatment for a variety of cancers.

Besides wound - healing and anticancer properties, saffron is also an antioxidant. This means that, as an "anti - aging" agent, it neutralises free radicals. Specifically, methanol extractions of saffron neutralise at high rates the DPPH ( IUPAC nomenclature: 1,1-diphenyl-2-picrylhydrazyl ) radicals. This occurred via vigorous proton donation to DPPH by two of saffron's active agents, safranal and crocin. Thus, at concentrations of 500 and 1000 ppm, crocin studies showed neutralisation of 50 % and 65 % of radicals, respectively. Safranal displayed a lesser rate of radical neutralisation than crocin, however. Such properties give saffron extracts promise as an ingredient for use as an antioxidant in pharmaceuticals, cosmetics, and as a food supplement . Ingested at high enough doses, however, saffron is lethal. Several studies done on lab animals have shown that saffron's LD<sub>50</sub> ( median lethal dose, or the dose at which 50% of test animals die from overdose) is 20.7 g / kg when delivered via a decoction . *C. sativus* has demonstrated antidepressant effects.

It is used greatly in Indian Ayurveda treatment. This has been known since 25 centuries , and are written in the great Indian texts. Also known as Kashmiran, Bahleeka, Rudhira and Sankocha. It can soothe all sorts of aches and pains across the

body, and also solves eyesight decay . It can also cure alcoholism.

#### 4 - Colouring and perfumery :

Despite its high cost, saffron has been used as a fabric dye, particularly in China and India. It is an unstable colouring agent; the imparted vibrant orange - yellow hue quickly fades to a pale and creamy yellow . The saffron stamens, even in minute amounts, yield a luminous yellow-orange colour. Increasing the amount of saffron applied will turn the fabric's imparted colour an increasingly rich shade of red. Traditionally, clothing dyed with saffron was reserved for the noble classes, implying that saffron played a ritualised and caste-representative role. Saffron dye is responsible for the saffron, vermilion, and ochre hues of the distinctive mantles and robes worn by Hindu and Buddhist monks. In medieval Ireland and Scotland, well-to-do monks wore a long linen undershirt known as a *léine*; it was traditionally dyed with saffron . In histology, the hematoxylin-phloxine-saffron (HPS) stain is used as a tissue stain to make biological structures more visible under a microscope.

There have been many attempts to replace costly saffron with a cheaper dye. Saffron's usual substitutes in food—turmeric, safflower, and other spices—yield a bright yellowish hue that does not precisely match that of saffron. Nevertheless, saffron's main colour-yielding constituent, the flavonoid crocin, has been discovered in the gardenia fruit. Because gardenia is much less expensive to cultivate than saffron, it is currently being researched in China as an economical saffron-dye substitute. In Europe, saffron threads were a key component of an aromatic oil known as *crocinum*, which comprised such ingredients as alkanet, dragon's blood (for colour), and wine (for colour). *Crocinum* was applied as a perfume to hair. Another preparation involved mixing saffron with wine to produce a viscous yellow spray that was copiously applied to Roman theatres as an air freshener.

## Sumac



*Sumac fruit in fall*

### Contents :

- 1 Cultivation and uses
- 2 Toxicity and control
- 3 Taxonomy
  - 3.1 Selected species

### Introduction :

**Sumac** also spelled **sumach** is any one of approximately 250 species of flowering plants in the genus ***Rhus*** and related genera, in the family Anacardiaceae. Sumacs grow in subtropical and temperate regions throughout the world, especially in Africa and North America.

Sumacs are shrubs and small trees that can reach a height of 1–10 metres .The leaves are spirally arranged; they are usually pinnately compound, though some species have trifoliate or simple leaves. The flowers are in dense panicles or spikes 5–30 centimetres long , each flower very small, greenish, creamy white or red, with five petals. The fruits form dense clusters of

reddish drupes called sumac bobs. The dried drupes of some species are ground to produce a tangy purple spice .

Sumacs propagate both by seed ( spread by birds and other animals through their droppings ), and by new shoots from rhizomes, forming large clonal colonies.

The word *sumac* traces its etymology from Old French *sumac* (13th century), from Medieval Latin *sumach*, from Arabic *summāq* (سماق), from Syriac *summāq* (ܣܡܩܐ) - meaning "red " .

### 1 - Cultivation and uses :



*Sumac spice*

The fruits ( drupes ) of the genus *Rhus* are ground into a deep-red or purple powder used as a spice in Middle Eastern cuisine to add a lemony taste to salads or meat. In Arab cuisine, it is used as a garnish on meze dishes such as hummus and is added to salads in the Levant. In Iranian (Persian and Kurdish) cuisine, sumac is added to rice or kebab. In Turkish cuisine, it is added to salad-servings of kebabs and lahmacun. *Rhus coriaria* is used in the spice mixture za'atar.

In North America, the Smooth Sumac (*R. glabra*) and the Staghorn Sumac (*R. typhina*) are sometimes used to make a beverage termed "sumac-ade," "Indian lemonade" or "rhus juice". This drink is made by soaking the drupes in cool water, rubbing them to extract the essence, straining the liquid through a cotton cloth and sweetening it. Native Americans also used the leaves and drupes of the Smooth and Staghorn Sumacs combined with tobacco in traditional smoking mixtures.

Species including the Fragrant Sumac (*R. aromatica*), the Littleleaf Sumac (*R. microphylla*), the Skunkbush Sumac (*R. trilobata*), the Smooth Sumac and the Staghorn Sumac are grown for ornament, either as the wild types or as cultivars.

The leaves of certain sumacs yield tannin (mostly pyrogallol-type), a substance used in vegetable tanning. Notable sources include the leaves of *R. coriaria*, Chinese gall on *R. chinensis*, and wood and roots of *R. pentaphylla*. Leather tanned with sumac is flexible, light in weight, and light in color. One type of leather made with sumac tannins is morocco leather.

Sumac was used as a treatment for half a dozen different ailments in medieval medicine, primarily in Islamic countries (where sumac was more readily available than in Europe). An 11th-century shipwreck off the coast of Rhodes, excavated by archeologists in the 1970s, contained commercial quantities of sumac drupes. These could have been intended for use as medicine, or as a culinary spice, or as a dye.

Some beekeepers use dried sumac bobs as a source of fuel for their smokers.

Dried sumac wood fluoresces under long-wave ultraviolet radiation, commonly known as black light.

## **2 - Toxicity and control :**

Some species, such as Poison ivy ( *Rhus toxicodendron*, syn. *Toxicodendron radicans* ), Poison oak ( *Rhus diversiloba*, syn. *Toxicodendron diversilobum* ) and Poison sumac (*Rhus vernix*, syn. *Toxicodendron vernix*), have the allergen urushiol and can cause severe allergic reactions. Poison sumac may be identified by its white drupes.

Mowing of sumac is not a good control measure, since the wood is springy, resulting in jagged, sharp pointed stumps when mowed. The plant will quickly recover with new growth after mowing. Goats have long been considered an efficient and

quick removal method as they eat the bark, which helps prevent new shoots.

### 3 - Taxonomy :



*A young branch of Staghorn Sumac*



*Drupes of a Staghorn Sumac in Coudersport, PA*



*Staghorn Sumac bob, Hamilton, Ontario*



*Rhus lancea fruit*



*Rhus malloryi fossil*



*Winged Sumac leaves and flowers*

At times *Rhus* has held over 250 species. Recent molecular phylogeny research suggests breaking *Rhus* sensu lato into

*Actinocheita*, *Baronia*, *Cotinus*, *Malosma*, *Searsia*, *Toxicodendron*, and *Rhus* sensu stricto. If this is done, about 35 species would remain in *Rhus*. However, the data are not yet clear enough to settle the proper placement of all species into these genera.

### 3 – 1 - Selected species :

#### Africa :

- *Rhus acocksii* Moffett
- *Rhus albomarginata* Sond.
- *Rhus angustifolia* L.
- *Rhus batophylla* Codd
- *Rhus baurii* Schönl.
- *Rhus bolusii* Sond. ex Engl.
- *Rhus burchellii* Sond. ex Engl.
- *Rhus carnosula* Schönl.
- *Rhus chirindensis* Bakh.f.
- *Rhus ciliata* Licht. ex Schult.
- *Rhus crenata* Thunb.
- *Rhus cuneifolia* L.
- *Rhus dentata* Thunb.
- *Rhus discolor* E.Mey. ex Sond.
- *Rhus dissecta* Thunb.
- *Rhus divaricata* Eckl. & Zeyh.
- *Rhus dracomontana* Moffett
- *Rhus dregeana* Sond.
- *Rhus dura* Schönl.
- *Rhus engleri* Britt.
- *Rhus erosa* Thunb.
- *Rhus fastigiata* Eckl. & Zeyh.
- *Rhus gerrardii* (Harv. ex Engl.) Diels.
- *Rhus glauca* Thunb.
- *Rhus gracillima* Engl.
- *Rhus grandidens* Harv. ex Engl.
- *Rhus gueinzii* Sond.
- *Rhus harveyi* Moffett

- *Rhus horrida* Eckl. & Zeyh.
- *Rhus incisa* L.f.
- *Rhus kirkii* Oliv.
- *Rhus keetii* Schönl.
- *Rhus krebsiana* Presl ex Engl.
- *Rhus laevigata* L.
- *Rhus lancea* L.f. □ (syn. *Searsia lancea*)
- *Rhus leptodictya* Diels.
- *Rhus loemnodia* Ruckt.
- *Rhus longispina* Eckl. & Zeyh.
- *Rhus lucens* Hutch.
- *Rhus lucida* L.
- *Rhus macowanii* Schönl.
- *Rhus magalismontana* Sond.
- *Rhus maricoana* Moffett
- *Rhus marlothii* Engl.
- *Rhus microcarpa* Schönl.
- *Rhus montana* Diels
- *Rhus natalensis* Bernh. ex Krauss
- *Rhus nebulosa* Schönl.
- *Rhus pallens* Eckl. & Zeyh.
- *Rhus pendulina* Jacq.
- *Rhus pentheri* Zahlbr.
- *Rhus pondoensis* Schönl.
- *Rhus populifolia* E.Mey. ex Sond.
- *Rhus problematodes* Merxm. & Roessl.
- *Rhus pterota* Presl
- *Rhus pygmaea* Moffett
- *Rhus pyroides* Burch.
- *Rhus quartiniana* A.Rich.
- *Rhus refracta* Eckl. & Zeyh.
- *Rhus rehmanniana* Engl.
- *Rhus rigida* Mill.
- *Rhus rimosa* Eckl. & Zeyh.
- *Rhus rogersii* Schönl.
- *Rhus rosmarinifolia* Vahl
- *Rhus rudatisii* Engl.

- *Rhus scytophylla* Eckl. & Zeyh.
- *Rhus sekhukhuniensis* Moffett
- *Rhus stenophylla* Eckl. & Zeyh.
- *Rhus tenuinervis* Engl.
- *Rhus tomentosa* L.
- *Rhus transvaalensis* Engl.
- *Rhus tridactyla* Burch.
- *Rhus tumulicola* S.Moore
- *Rhus undulata* Jacq.
- *Rhus volkii* Suesseng.
- *Rhus wilmsii* Diels.
  
- *Rhus zeyheri* Sond.*Rhus chinensis*  
• Mill. - Chinese Sumac
- *Rhus hypoleuca*
- *Rhus javanica*
- *Rhus punjabensis* - Punjab Sumac
- *Rhus verniciflua* (syn. *Toxicodendron vernicifluum*,  
Lacquer Tree)
- *Rhus succedanea* (syn. *Toxicodendron succedaneum*)

### **Australia , Pacific :**

- *Rhus taitensis* Guill. ( Northeast Australia, Malesia,  
Micronesia, French Polynesia )
- *Rhus sandwicensis* A.Gray - *Neneleau* ( Hawaii )

### **Mediterranean Basin**

- *Rhus coriaria* - Tanner's Sumac
- *Rhus pentaphylla*
- *Rhus tripartita*

### **Eastern North America**

- *Rhus aromatica* - Fragrant Sumac
- *Rhus copallina* - Winged or Shining Sumac
- *Rhus glabra* - Smooth Sumac
- *Rhus lanceolata* - Prairie Sumac

- *Rhus michauxii* - Michaux's Sumac
- *Rhus typhina* - Staghorn Sumac
- *Rhus toxicodendron* (syn. *Toxicodendron radicans*, poison ivy)
- *Rhus vernix* (syn. *Toxicodendron vernix*, poison sumac)

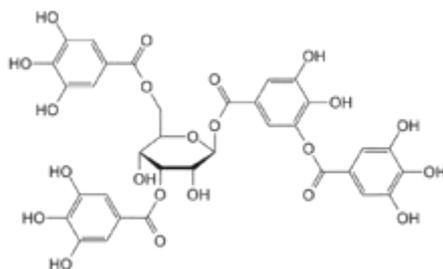
### **Western North America :**

- *Rhus choriophylla* - Mearn's Sumac (Arizona, New Mexico)
- *Rhus laurina* (syn. *Malosma laurina*) - Laurel Sumac
- *Rhus integrifolia* - Lemonade Sumac
- *Rhus glabra* - Smooth sumac
- †*Rhus malloryi* Wolfe & Wehr Eocene
- *Rhus microphylla* - Desert Sumac, Littleleaf Sumac
- *Rhus ovata* - Sugar Sumac
- *Rhus trilobata* Nutt. - Skunkbush Sumac
- *Rhus virens* - Evergreen Sumac

### **Mexico and Central America :**

- \* *Rhus muelleri* - Müller's Sumac (northeast Mexico)

# Tannin



*Tannic acid*

<p><i>Tannin powder ( mixture of compounds ).</i></p>	<p><i>A bottle of tannic acid solution in water.</i></p>

## Contents :

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### **Introduction :**

A **tannin** (a.k.a. vegetable tannin, i.e. a type of biomolecule, as opposed to modern synthetic tannin) is an astringent, bitter plant polyphenolic compound that binds to and precipitates proteins and various other organic compounds including amino acids and alkaloids. The astringency from the tannins is what causes the dry and puckery feeling in the mouth following the consumption of unripened fruit or red wine . Likewise, the destruction or modification of tannins with time plays an important role in the ripening of fruit and the aging of wine.

The term tannin (from *tanna*, an Old High German word for oak or fir tree, as in Tannenbaum) refers to the use of wood tannins from oak in tanning animal hides into leather; hence the words "tan" and "tanning" for the treatment of leather. However, the term "tannin" by extension is widely applied to any large polyphenolic compound containing sufficient hydroxyls and other suitable groups (such as carboxyls) to form strong complexes with proteins and other macromolecules. The compounds are widely distributed in many species of plants,

where they play a role in protection from predation, and perhaps also in growth regulation.

Tannins have molecular weights ranging from 500 to over 3,000 (gallic acid esters) and up to 20,000 (proanthocyanidins). Tannins are incompatible with alkalis, gelatin, heavy metals, iron, lime water, metallic salts, strong oxidizing agents and zinc sulfate, since they form complexes and precipitate in aqueous solution.

### **1 – Occurrence :**

Tannins are distributed in species throughout the plant kingdom. They are commonly found in both gymnosperms as well as angiosperms. Botanically, tannins are mainly physically located in the vacuoles or surface wax of plants. These storage sites keep tannins active against plant predators, but also keep some tannins from affecting plant metabolism while the plant tissue is alive; it is only after cell breakdown and death that the tannins are active in metabolic effects. Tannins are classified as ergastic substances i.e. non-protoplasm materials found in cells.

Tannins are found in leaf, bud, seed, root, and stem tissues. An example of the location of the tannins in stem tissue is that they are often found in the growth areas of trees, such as the secondary phloem and xylem and the layer between the cortex and epidermis. Tannins may help regulate the growth of these tissues. There may be a loss in the bio-availability of still other tannins in plants due to birds, pests, and other pathogens.

The most abundant polyphenols are the condensed tannins, found in virtually all families of plants, and comprising up to 50% of the dry weight of leaves.

### **1 – 1 - Presence in soils :**

The convergent evolution of tannin-rich plant communities has occurred on nutrient-poor acidic soils throughout the world. Tannins were once believed to function as anti-herbivore

defenses, but more and more ecologists now recognize them as important controllers of decomposition and nitrogen cycling processes. As concern grows about global warming, there is great interest to better understand the role of polyphenols as regulators of carbon cycling, particularly in northern boreal forests.

## 1 – 2 - Presence in water and wood :



*Bog - wood ( similar to, but not , driftwood )  
in an aquarium, turning the water a tea-like brown*

The leaching of highly water soluble tannins from decaying vegetation and leaves along a stream may produce what is known as a blackwater river. Water flowing out of bogs has a characteristic brown color from dissolved peat tannins. The presence of tannins (and / or humic acid) in well water can make it smell bad or taste bitter, but not be unsafe to drink.

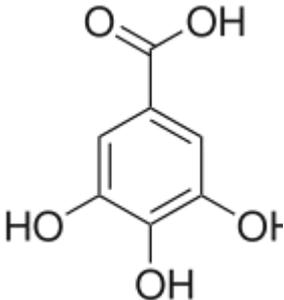
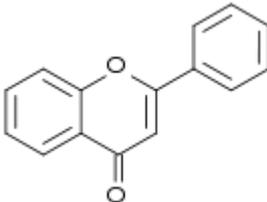
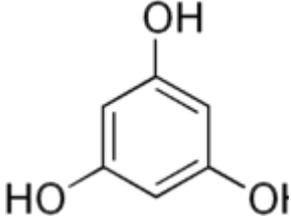
Tannins leaching from an unprepared driftwood decoration in an aquarium can cause pH lowering and coloring of the water to a tea-like tinge. A remedy is to boil the wood in water several times (which will also darken and water log the wood, i.e., make it sink), discarding the water each time. Using peat as an aquarium substrate can lead to the same problem.

Many hours of boiling the driftwood may need to be followed by many weeks or months of constant soaking and many water changes before the water will stay clear. Adding baking soda to the water to raise its pH level will accelerate the process of leaching, as the more alkaline solution can draw out tannic acid from the wood faster than the pH-neutral water.

Soft woods, while generally much lower in tannins than hardwoods, are usually not recommended for use in an aquarium so using a hard wood with a very light color, indicating a low tannin content, can be an easy way to avoid tannins. Tannic acid is brown in color, so generally white woods have a low tannin content. Woods with a lot of yellow, red or brown coloration to them (like southern yellow pine, cedar, redwood, red oak, etc.) tend to contain a lot of tannin. Finnish hardwoods, like birch and aspen, do not contain tannins.

## 2 - Classes of tannins :

There are three major classes of tannins:

<i>Base Unit:</i>			
	<i>Gallic acid</i>	<i>Flavone</i>	<i>Phloroglucinol</i>
<i>Class/Polyme r:</i>	<i>Hydrolyzable tannins</i>	<i>Non-Hydrolyzable or condensed tannins</i>	<i>Phlorotannins</i>
<i>Sources</i>	<i>Plants</i>	<i>Plants</i>	<i>Brown algae</i>

### 2 – 1 - Pseudo tannins :

Pseudo tannins are low molecular weight compounds associated with other compounds. They do not answer gold beater skin test unlike hydrolysable and condensed tannins. (When gold beater skin or ox skin is dipped in HCl & treated with 1 % Fe SO<sub>4</sub> solution, after washing with water it gives a blue / black colour). They are found in tea or coffee or in :

- Gallic acid : rhubarb
- Catechins : Acacia, catechu, cocoa, guarana

- Chlorogenic acid: Nux- vomica , coffee , mate
- Ipecacuanhic acid: Ipecacuanha .
- 

### 3 - Nutrition :

Tannins have traditionally been considered antinutritional but it is now known that their beneficial or antinutritional properties depend upon their chemical structure and dosage. The new technologies used to analyze molecular and chemical structures have shown that a division into condensed and hydrolyzable tannins is far too simplistic. Recent studies have demonstrated that products containing chestnut tannins included at low dosages (0.15 – 0.2 %) in the diet can be beneficial. Some studies suggest that chestnut tannins have been shown to have positive effects on silage quality in the round bale silages, in particular reducing NPNs (non protein nitrogen) in the lowest wilting level. Improved fermentability of soya meal nitrogen in the rumen has also been reported by F. Mathieu and J.P. Jouany (1993). Studies by S. Gonzalez et al. (2002)<sup>[18]</sup> on *in vitro* ammonia release and dry matter degradation of soybean meal comparing three different types of tannins (quebracho, acacia and chestnut) demonstrated that chestnut tannins are more efficient in protecting soybean meal from *in vitro* degradation by rumen bacteria.

Condensed tannins inhibit herbivore digestion by binding to consumed plant proteins and making them more difficult for animals to digest, and by interfering with protein absorption and digestive enzymes (for more on that topic, see plant defense against herbivory). Many tannin-consuming animals secrete a tannin-binding protein (mucin) in their saliva. Tannin-binding capacity of salivary mucin is directly related to its proline content. Advantages in using salivary proline-rich proteins (PRPs) to inactivate tannins are:

- PRPs inactivate tannins to a greater extent than do dietary proteins; this results in reduced fecal nitrogen losses
- PRPs contain non specific nitrogen and nonessential amino acids; this makes them more convenient for an animal to exploit rather than using up valuable dietary protein

### **3 – 1 - Drinks with tannins :**

Main articles : Tannins in tea and Tannins in wine

#### **3 – 1 – 1 – Coffee :**

Tannins were not found in any bean sample, and in contrast to previous reports, hydrolysable tannins *sensu stricto* were not detected in pulp. The presence of soluble condensed tannins in *Coffea arabica* pulp was confirmed at approximately 1% .

#### **3 – 1 – 2 – Beer :**

In addition to the alpha acids extracted from hops to provide bitterness in beer, condensed tannins are also present. These originate both from the malt and hops. Especially in Germany, trained brewmasters consider the presence of tannins as a flaw. However, in some styles, the presence of this astringency is acceptable or even desired, as, for example, in a Flanders red ale.

In lager type beers, the tannins can form a precipitate with specific haze forming proteins in the beer resulting in turbidity at low temperature. This chill haze can be prevented by removing part of the tannins or part of the haze forming proteins. Tannins are removed using PVPP, haze forming proteins by using silica or tannic acid.

#### **3 – 1 – 3 – Fruit juices :**

Although citrus fruits do not themselves contain tannins, orange-colored juices often contain food dyes with tannins. Apple juice, grape juices and berry juices are all high in tannins.

Sometimes tannins are even added to juices and ciders to create a more astringent feel to the taste.

### **3 – 2 – Food items with tannins :**

#### **3 – 2 – 1 – Fruits :**

#### **3 – 2 – 1 – 1 – Pomegranates :**

Pomegranates contain a diverse array of tannins, particularly hydrolysable tannins. The most abundant of pomegranate tannins are called punicalagins. Punicalagins have a molecular weight of 1038 and are the largest molecule found intact in rat plasma after oral ingestion and were found to show no toxic effects in rats who were given a 6% diet of punicalagins for 37 days . Punicalagins are also found to be the major component responsible for pomegranate juice's antioxidant and health benefits .



*Strawberries in a bowl*



*Pomegranate fruit, opened.*



*A persimmon fruit.*

Several dietary supplements and nutritional ingredients are available that contain extracts of whole pomegranate and/or are standardized to punicalagins, the marker compound of pomegranate. Extracts of pomegranate are also Generally Recognized as Safe (GRAS) by the United States Food and Drug Administration. It has been recommended to look for pomegranate ingredients that mimic the polyphenol ratio of the fruit, as potent synergistic effects have been observed in 'natural spectrum' extracts, especially pomegranate concentrate normalized to punicalagins.

### **3 – 2 – 1 – 2 – Persimmons :**

Some persimmons are highly astringent and therefore inedible when they are not extremely ripe ( specifically the Korean , American, and Hachiya or Japanese ). This is due to the high level of tannins, and if eaten by humans (and many other animals), the mouth will become completely dry, yet the saliva glands will continue to secrete saliva which cannot affect the tannin-laced food.

### **3 – 2 – 1 – 3 – Berries :**

Most berries, such as cranberries , strawberries and blueberries, contain both hydrolyzable and condensed tannins.

### **3 – 2 – 1 – 4 – Nuts :**

Nuts that can be consumed raw such as hazel nuts, wal nuts and pecans, contain high amounts of tannins. Almonds feature a lower content. Tannin concentration in the crude extract of these nuts did not directly translate to the same relationships for the condensed fraction. Acorns contain such high concentrations of tannins that they need to be processed before they can be consumed safely.

The areca nut also contains tannin which contributes to its antibacterial properties.

### **3 – 2 – 2 – Smoked foods :**

Tannins from the wood of mesquite, cherry, oak and other woods used in smoking are present on the surface of smoked fish and meat (although smoke from cherry wood can be toxic to humans.)

### **3 – 2 – 3 – Herbs and spices :**

Cloves , tarragon , cumin , thyme , vanilla , and cinnamon all contain tannins .

### **3 – 2 – 4 – Legumes :**

Most legumes contain tannins. Red- colored beans contain the most tannins, and white-colored beans have the least. Peanuts without shells have a very low tannin content. Chickpeas (garbanzo beans) have a smaller amount of tannins.

### **3 – 2 – 5 – Chocolate :**

Chocolate liquor contains about 6 % tannins.

### **3 – 3 – Toxicity :**

Tannins have been shown to precipitate proteins , which in some ruminant animals inhibits the absorption of nutrients from high-tannin grains such as sorghum.

In sensitive individuals, a large intake of tannins may cause bowel irritation, kidney irritation, liver damage, irritation of the stomach and gastrointestinal pain. With the exception of tea, long-term and/or excessive use of herbs containing high concentrations of tannins is not recommended. A correlation has been made between esophageal or nasal cancer in humans and regular consumption of certain herbs with high tannin concentrations.

Many plants employ tannins to deter animals. It has not been determined whether tannin was produced for another purpose, e.g. as pesticide, or whether it evolved specifically for the purpose of inhibiting predation . Animals that consume excessive amounts of these plants fall ill or die. Acorns are a well known problem in cattle breeding. The lethal dose is said to be around 6 % of the animal's body weight. This is only an approximate figure since acorns from red oak were shown to contain on average two to four times the tannins of those from white oak . Some deer and moose were found to have perished due to ingesting acorns. Symptoms include ataxia and shortness of breath. Some animals, like squirrels and mule deer have developed the ability to consume high concentrations of tannins

without ill effects. Humans would usually find the bitter taste of foods containing high amounts of tannins unpalatable. (Some humans were found to be unable to taste bitter foods.) Tannins are leached from acorns before they are used for human consumption .

### **3 – 4 - Metal chelation :**

If ingested in excessive quantities, tannins inhibit the absorption of minerals such as iron which may, if prolonged, lead to anemia. This is because tannins are metal ion chelators and tannin-chelated metal ions are not bioavailable. Tannins only reduce the bioavailability of plant sources of iron, also known as non-heme. Animal sources, or heme iron absorption will not be affected by tannins. Tannic acid does not affect absorption of other trace minerals such as zinc , copper , and manganese in rats.

Tannins interfere with iron absorption through a complex formation with iron when it is in the gastrointestinal lumen which decreases the bioavailability of iron. There is an important difference in the way in which the phenolic compounds interact with different hydroxylation patterns ( gallic acid , catechin , chlorogenic acid ) and the effect on iron absorption. The content of the iron-binding galloyl groups may be the major determinant of the inhibitory effect of phenolic compounds. However, condensed tannins do not interfere with iron absorption .

In order to prevent these problems, it is advised to drink tea and coffee between meals, not during. Foods rich in vitamin C help neutralize tannin's effects on iron absorption. Adding lemon juice to tea will reduce the negative effect of tannins in iron absorption as well. Adding milk to coffee and tea has very little to no influence on the inhibitory effect of tannins.

## 4 - Tannin market :



*Tannin in a plastic container*

Tannin production began at the beginning of the 19th century with the industrial revolution, to produce tanning material for the need for more leather. Before that time, processes used plant material and were long (up to six months).

There has been a collapse in the vegetable tannin market in the 1950s-1960s, due to the appearance of synthetic tannins, due the scarcity of vegetable tannins during World War II. At that time, many small tannin industry sites closed. Vegetable tannins are estimated to be used for the production of 10 - 20 % of the global leather production .

The cost of the final product depends on the method used to extract the tannins, in particular the use of solvents, alkali and other chemicals used ( for instance glycerin ) . For large quantities, the most cost-effective method is hot water extraction

Tannic acid is used worldwide as clarifying agent in alcoholic drinks and as aroma ingredient in both alcoholic and soft drinks or juices. Tannins from different botanical origins also find extensive uses in the wine industry.

### 4 – 1 - Uses :

Tannins are an important ingredient in the process of tanning leather. Oak bark, mimosa and quebracho tree have traditionally been the primary source of tannery tannin, though inorganic tanning agents are also in use today and account for 90 % of the world's leather production.

Tannins produce different colors with ferric chloride (either blue, blue black, or green to greenish black) according to the type of tannin. Iron gall ink is produced by treating a solution of tannins with iron (II) sulfate .

Tannin is a component in a type of industrial particleboard adhesive developed jointly by the Tanzania Industrial Research and Development Organization and Forintek Labs Canada . *Pinus radiata* tannins has been investigated for the production of wood adhesives.<sup>[41]</sup>

Tannins can be used for production of anti- corrosive primer, sold under brand name-Nox Primer for treatment of rusted steel surfaces prior to painting, rust converter to transform oxidized steel into a smooth sealed surface and rust inhibitor.

The use of resins made of tannins has been investigated to remove mercury and methylmercury from solution . Immobilized tannins have been tested to recover uranium from seawater.

#### **4 – 2 - Medical uses and potential :**

Tannins can also be effective in protecting the kidneys. When incubated with red grape juice and red wines with a high content of condensed tannins, the poliovirus, herpes simplex virus, and various enteric viruses are inactivated.

Tannins have shown potential antiviral , antibacterial and antiparasitic effects.

It is believed that tannins isolated from the stem bark of *Myracrodruon urundeuva* are of neuroprotective functions capable of reversing 6-hydroxydopamine induced toxicity. The plant has shown promising futures for therapeutic use, which may be of benefit to neuro disease patients . Souza *et al.* discovered that the tannins isolated from the stem bark also has the antiinflammatory and antiulcer potency on rodents, showing

a strong antioxidant property for possible therapeutic applications .

Foods rich in tannins can be used in the treatment of HFE hereditary hemochromatosis, a hereditary disease characterized by excessive absorption of dietary iron resulting in a pathological increase in total body iron stores.

#### **4 – 3 - Producers :**

There are three main producers of tannins in the world :

- Ajinomoto OmniChem NaturalSpecialities, a subsidiary of the Ajinomoto group, is specializing in the tannin production
- Silva Team produces tannins for leather tanning, oenology or other uses
- Unitán , an Argentine company, produces quebracho tannins.

Following companies are not producers but blenders of tannins for specific applications:

- AEB group, an Italian company based in Brescia, blends & markets tannins for oenology applications .
- Enartis, an Italian company based in San Martino, develops and sells oenological tannins .

## Tannins Sources of

### Sources of condensed tannins :

*Areca catechu* seed (arecatannins) | Broad bean (*Vicia faba*) | Grape (*Vitis vinifera*) | Quebracho wood | Mimosa bark (*Acacia mollissima*) | Myrtan or black marlock (*Eucalyptus redunca*)

### Sources of hydrolysable tannins :

Chestnut wood | Dhawa (*Anogeissus latifolia*) | Myrobalan fruit (*Terminalia chebula*) | **Oak** wood, bark or acorn cup (*Valonea Quercus macrolepis*) | Sumac (Tanner's sumach leaves - *Rhus coriaria* or Chinese gall on *Rhus chinensis*) | Tara pod (*Caesalpinia spinosa*)

### Other sources

#### Barks

Alder (*Alnus sp*) | Avaram (*Senna auriculata*) | Babul (*Acacia nilotica*) | Birch (*Betula sp*) | Larch (*Larix sp*) | Hemlock (*Tsuga sp*) | mangrove | Pine (*Pinus sp*) | Spruce (*Picea sp*) | Urunday (*Myracrodruon urundeuva*) | Willow (*Salix caprea*)

#### Leaves

Badan (*Bergenia crassifolia*) | Gambier (*Uncaria gambir*) | Redoul (*Coriaria myrtifolia*)

#### Roots

Canaigre (*Rumex hymenosepalus*) | Garouille (*Quercus coccifera*) | Sea lavender (*Limonium sp*)

#### Woods

Cutch (*Acacia catechu*)

#### Fruit

Divi-divi pod (*Caesalpinia coriaria*) | Sant pod (*Acacia nilotica*) | Teri pod (*Caesalpinia digyna*)

## **Galls**

Gall oak (*Quercus lusitanica*)

## **Whole plant**

*Prosopis* sp. bark and wood (eg *Prosopis humilis* or Algarrobilla) | Tanoak (*Lithocarpus densiflorus*) | Tizra heartwood and root (*Rhus pentaphylla*)

## **Misc**

Tanbark

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