Natural coloring agents

Biologically Active Natural Compounds
Colorants are characterized by their ability to absorb visible part of the electromagnetic spectrum [380-780 nm]. For good colouring property it has to have high enough absorption coefficient (10 000 to 40 000 l.mol⁻¹.cm⁻¹). Further it must have properties enabling it to keep with coloured material and stability (fotocemical, chemical, oxidation ...). As a rule, colorants nowadays have to be harmless.

Sometimes we also distinguish [i.a.]:
onedimensional pigments (they absorb certain wavelength and reflect the rest)
twodimensional (they reflect the light mirror-like)
threedimensional (they reflect with pearl effect)
Natural Dyestuffs

The most important dyes extracted from animal sources are natural sepia (from the ink sac of the cuttlefish), crimson (from the kermes louse) and Tyrian purple (the Imperial purple of the ancient world, from the murex shellfish). Very many dyes have been extracted traditionally from roots, berries, flowerheads, barks and leaves. Red dyes include madder (from 'dyer's root', the madder plant), brazilwood, beetroot, cranberry, safflower ('dyer's thistle'), and orchil ('dyer's moss'). Orange dye is obtained from stigmas of the saffron flower, yellows from camomile and milkwort flowers, plus weld ('dyer's herb'). Greens are obtainable from ripe buckthorn berries and ragweed; and blue from the woad plant (also called 'dyer's weed') and indigo.

As a rule, vegetable dyes are extracted by pounding or cutting up the colouring material. This is immersed in water, heated to just below boiling point and simmered until the colour has been transferred from the dye solution.

Colorants could be divided by their
da/ colour,
b/ chemical composition or structure,
c/ biological function in plant/organism (chlorophyll, haemoglobin …),
d/ physical properties (solubility),
e/ etc.
For most natural dyestuffs to be effective, the article to be coloured must first be saturated with a fixer or mordant, a mineral compound which 'bites' the fibres of the cloth in order to permit the insoluble adhesion of the colouring agent. (A typical mordant consists of a 4:1 mixture of alum [aluminum sulfate Al$_2$(SO$_4$)] and cream of tartar [potassium hydrogen tartrate, KC$_4$H$_5$O$_6$].) The use of other metallic salts, as those containing chromium, copper, tin or iron, make it possible to obtain a considerable range of colours from a single dye source.

What is the function of a mordant?
## Categories of Natural Colorants, examples

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Natural Colorants, some typical examples

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<tr>
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<td></td>
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<tr>
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<td>annato <em>Bixa orellana</em></td>
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<tr>
<td></td>
<td>saffron red stigmas <em>Crocus sativus</em></td>
</tr>
<tr>
<td></td>
<td>bloodroot <em>Sanguinaria canadensis</em></td>
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<tr>
<td>Green</td>
<td>chlorophyll</td>
</tr>
<tr>
<td>Brown</td>
<td>cocoa <em>Theobroma cacao</em></td>
</tr>
<tr>
<td></td>
<td>fermented tea <em>Camellia thea</em></td>
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<td>henna <em>Lawsonia inermis</em></td>
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<td>alkanet root <em>Alkanna tinctoria</em></td>
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<td>butternuts <em>Juglans cinerea</em></td>
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<tr>
<td>White</td>
<td>titanium oxide</td>
</tr>
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[boryt barviřský] [indigovník barviřský] [květy chrpy modré] [plody borůvek] [plody černého bezu] [kůra jasanu ztepilého]
[oddének kurkumy] [světlice barviřská] [kořen mrkve] [aksamitník vzpřímený]
[paprika] [anato] [šafrán] [krvavěnka]
[chlorofyl] [kakao] [čaj] [henna pravá]
[kamejník barviřský] [uhel a karamel] [ořešák popelavý] [oxid titaničitý]
Natural colorants, some typical examples

**Red**
Red could have been dyed with madder (*Rubia tinctoria*) which was used in central Europe since 800 A.D. Red can also be produced from native plants and sources such as:

- Northern Bedstraw *Galium boreale*,
- Hedge Bedstraw *Galium album mollugo*,
- Lady's Bedstraw *Galium verum*,
- Dyers Woodruff ' *Asperula tinctoria*,
- St. John's Wort *Hypericum perforatum*,
- paprika (may be irritating),
- grapes *Vitaceae*, red cabbage *Brassica oleracea capitata*, black currants *Ribes* (cyanins)
- cochineal. carmina *Coccus cacti* or *Dactylopius coccus*
- red beet, *Beta vulgaris* (betanin)

**Reds from Mushrooms**
The Dermocybe family of mushrooms produces oranges and reds. Addition of an iron mordant gives darker shades and almost black. With older mushrooms, longer cooking times or the addition of ammonia can give lilac shades. Low heat or the addition of acid or vinegar gives warm reds.

*Dictyophora cinnabarina*
*Cortinarius semisanguineus*
Blue

Blue was the most used colour in many of the fabrics from the gravesites. Blue may have come from Dyers Woad, *Isatis tinctoria*.

**Blue from Mushrooms**

*Thelephora*

With iron or tin mordants, yields greens and blues.

*Hydnellum suaveolens,*

*Sarcodon imbricatus,*

Yields blues if it is old and its top has darkened.

*Hapalopilus rutilans,*

With ammonia, yields strong, colourfast violet blue shades.

*Cortinarius violaceus*

Produces violet blue shades, and with an iron mordant, dark greys.
Biologically Active Natural Compounds

**mineral dyes**

**ocher**
mixture of varying proportions of iron oxide and clay, used as a pigment. It occurs naturally as yellow ocher (yellow or yellow-brown in color), the iron oxide being limonite, or as red ocher, the iron oxide being hematite. Ocher grades into sienna, a yellow-brown pigment containing a higher percentage of iron ore than ocher as well as some manganese dioxide; sienna grades into umber, which is darker brown and contains a higher percentage of manganese dioxide. Burnt sienna is brown or bright red; burnt umber is a darker brown than umber.

![ocher samples](image)

**white**, titanium oxide, limestone  
**black**, carbon, sooth  
**green**, malachite  
**blue**, azurite, turquoise  
**red**, zinober, iron oxides and hydroxides
The principle of the fact that something has a colour is in the interaction of the substance with a light which is then reflected or passed through. The substance could be also involved in the process of light generation (electric arch, burning ...). The interaction influences different wavelength intensity of the light.

Most common is the interaction of photons with electron orbitals of molecules. This effect is discussed with electron spectra (UV-VIS).

To see the colours we need a detector which is commonly a spectrophotometer (or for the wavelengths between 400 and 800 nm also human eye) which is capable of distinguishing the changes.

**chromophore**

From the Greek from Greek *chromophorus* (*chromos* colour), or „colour carrier“, a chromophore is generally a groups of atoms in a molecule responsible for the interaction with the radiation at certain wavelength; example of common chromophore is conjugated multiple bond, rich in electrons.
Biologically Active Natural Compounds

light irradiates the surface (white, polychromatic)

orange part is absorbed (610 nm)

reflected light is seen in complementary colour and we see it as blue-green

Through light is seen in complementary colour and we see it as blue-green
Biologically Active Natural Compounds

---

observed colour | absorbed colour | absorbed wavelength
---|---|---
green | red | 700 nm
blue-green | orange red | 600 nm
violet | yellow | 550 nm
violet-red | yellow green | 530 nm
red | blue green | 500 nm
orange | blue | 450 nm
yellow | violet | 400 nm
how photons can interact with the electron orbitals:

A typical molecular orbital is as follows:
energy of the light which passes through the sample is absorbed by some electrons and they are in that way “excited” to a higher energetic level (state).

let us see this situation in butadiene, e.g.

four basic p atomic orbitals

normal state of molecule orbitals of butadiene

excited state

LUMO – Lowest Unoccupied Molecular Orbital
HOMO – Highest Occupied Molecular Orbital
non-conjugated alkene is not “rich in electrons”

in common non-conjugated alkene the situation is simple:

two basic p atomic orbitals

ground state of a molecular orbital of butadiene

excited state

165 nm

ε 15,000
there are “allowed” and “forbidden” energy transitions in carbonyl we observe also the forbidden transition n->π*
electron transition $\pi \rightarrow \pi^*$ matches in butadiene the change of energy seen in the spectrum as absorption at 217 nm

these wavelengths are not yet in visible region, we need more electrons to be involved
Influence of pH (protonation state) on colour properties of colorants

pH affects the change in electron density in some parts of the molecule.

Thymolphthaleine

- pH 10, both OH deprotonated
- $\lambda_{\text{max}} : 590$ nm
- Blue

pH 8

- Colourless
- $\text{pH } 8.8 - \text{Colourless}$
- $\text{pH } 9.4 - \text{Pale grayish blue}$
- $\text{pH } 9.9 - \text{Blue}$

pH 9.91 dissociates

pH 10.51 dissociates
influence of pH (protonation state) on colour properties of colorants

simple example, influence of pH to aromatic absorption

\[
\text{Phenoxide ion: } \begin{align*}
\text{OH} & \quad \rightarrow \quad \text{O}^- \\
\lambda = 270 \text{ nm} & \quad (\varepsilon = 1450) \quad & \lambda = 287 \text{ nm} & \quad (\varepsilon = 2600)
\end{align*}
\]

\[
\text{Anilinium ion: } \begin{align*}
\text{NH}_2 & \quad \rightarrow \quad \text{NH}_3^+ \\
\lambda = 280 \text{ nm} & \quad (\varepsilon = 1450) \quad & \lambda = 254 \text{ nm} & \quad (\varepsilon = 160)
\end{align*}
\]
electron transition $\pi \rightarrow \pi^*$ matches in butadiene the change of energy seen in the spectrum as absorption at 425 nm and more

eleven conjugated double bonds with 22 $\pi$ electrons delocalized along the chain is seen in the spectrum as the absorption of blue part at $\lambda_{\text{max}}$ 497 nm ($\varepsilon$ 133,000), giving the compound orange colour
Chamomile, lat. *Matricaria recuitila* (*M. chamomilla)*

Azulene

UV/VIS SPECTRUM

Azulene, whose name is derived from the Spanish word *azul*, meaning "blue", is a dark blue powder.

not necessarily the double bonds have to be acyclic
difference in the size of molecule and amount of electrons and their conjugation in coloured molecules influences the observed effect

lawson yellow colorant from henna *Lawsonia alba* (LANK.);
chinone molecule

orange β-carotene from carrots

blue azulene from Chamomile, lat. *Matricaria recutita* (i)

green billiverdin bile colorant
POLYENE COLORANTS

Polyenes are hydrocarbons with more conjugated double bonds in the chain mostly in “trans” configuration.
POLYENE COLORANTS

yellow lutein in egg yolks, fat cells and green leaves principally in marigold

"Marigold meal" and "Aztec marigold" for the dried, powdered flowers; and „Marigold extract” for the solvent extract of the flowers.

**World production and trade: 6,000 tonnes of meal.**

Mexican tarragon (*Tagetes lucida* Cav.)
POLYENE COLORANTS

Paprika
"sweet peppers", Capsicum annuum L.

As a spice and as an orange-red food colourant.

World production: Paprika - 45,000 tonnes (estimate)

The pigments present in paprika are a mixture of carotenoids, in which capsanthin and capsorubin dominate. These are oil-soluble, stable to heat and pH variation but deteriorate in light.
**POLYENE COLORANTS**

zeaxanthin from corn (maize) *Zea mays*  
$\lambda_{\text{max}}$ 483, 451 nm, insoluble in water

rubixanthin from hips (fruits) of dog rose *Rosa canina*  
$\lambda_{\text{max}}$ 509, 474, 439 nm, insoluble in water

cryptoxanthin from eggyolk, corn or strawberries  
$\lambda_{\text{max}}$ 480, 452 nm

astacin from shells of crabs and lobsters *Homarus,*  
algae, sponges, fish  
$\lambda_{\text{max}}$ 500 nm  
pract. insoluble in water
POLYENE COLORANTS

orange β-carotene from carrots *Daucus carota*
yellow food colorant $\lambda_{\text{max}}$ 497, 466 nm

α-carotene $\lambda_{\text{max}}$ 485, 454 nm

δ-carotene

γ-carotene $\lambda_{\text{max}}$ 508, 575, 446 nm

ψ-carotene
Biologically Active Natural Compounds

POLYENE COLORANTS

orange-yellow rhodoxanthin from autumn leaves and in the seeds of the poisonous yew tree (*Taxus baccata*) or feathers of the downy legged pigeon

red lycopene from tomato *Lycopersicon*  
$\lambda_{\text{max}}$ 505, 472, 446 nm insoluble in water
Biologically Active Natural Compounds

**Annatto** is a red to orange natural (golden yellow) pigment derived from the seed of the tropical bush *Bixa orellana*. The major colour present is *cis*-bixin, the monomethyl ester of the diapocarotenoic acid norbixin, which is found as a resinous coating surrounding the seed itself. Also present, as minor constituents, are *trans*-bixin and *cis*-norbixin. The annatto bush is native to Central and South America where its seeds are used as a spice in traditional cooking.

World production: (estimated)
10,000 tonnes annually.

**POLYENE COLORANTS**

\[ \text{CH}_3 \]
\[ \text{H}_3 \text{C} - \text{O} \]
\[ \text{OH} \]
\[ \text{O} \]
\[ \text{OH} \]

\[ \lambda_{\text{max}} \ 509, 475, 443 \text{ nm} \]
Biologically Active Natural Compounds

POLYENE (POLYUNSATURATED) COLORANTS

Arctium Lappa
Burdock

Root produces a yellow dye when used with alum mordant.

burdock contains several compounds of the type as:

\[
\text{(4E,6E)-4,6-tetradecadien-8,10,12-triyn-1,3-diol diacetate}
\]

\[
1,11\text{-tridecadiene-3,5,7,9-tetrayne}
\]
Biologically Active Natural Compounds

POLYENE COLORANTS

crocin (bis gentiobioside) $\lambda_{\text{max}}$ 464, 434 nm

orange crocetin from saffron $\lambda_{\text{max}}$ 464, 436, 411 nm

Crocin extract is the trade term for the yellow, water-soluble food colourant obtained from cape jasmine (*Gardenia jasminoides* L.) and from red stigmas of saffron (*Crocus sativus* L.). However, the extracts are not used interchangeably in all applications since saffron is valued as much for its aroma and flavour as for its colouring properties and, moreover, it is the world's most expensive spice/colourant.

International Trade: Possibly 50 tonnes/annum of saffron.

*Gardenia jasminoides* L.
POLYENE COLORANTS

β-citraurin from *Citrus sinensis*  \( \lambda_{\text{max}} 497, 467 \text{ nm} \)
sweet orange, navel orange
carotenoid pigment found only in orange peel

violaxanthin from *Citrus sinensis*  \( \lambda_{\text{max}} 471, 442, 417 \text{ nm} \)
Curcumin is the principal colour present in the rhizome of the turmeric plant (Curcuma longa). Turmeric has been used as a spice for many thousands of years and is today still one of the principal ingredients of curry powder. Turmeric is cultivated in many tropical countries including India, China and Pakistan and is usually marketed as the dried rhizome, which is subsequently milled to a fine powder. This imparts both flavour and colour to a food product.

International trade: 15,000-20,000 tonnes per annum for the spice
**CHALCONE COLORANTS**

Safflower (*Carthamus tinctorius* L.)
Formerly as a red dyestuff for textiles; and currently as a minor colourant by the food industry.

The florets contain three major pigments, all of which are present as chalcone glucosides: the water-insoluble scarlet-red *carthamin* and the water-soluble "safflor yellow" A and B or *safflomin(e)* A and B.

The term "red tape" originates from the use of safflower to impart a pink-red colour to the tape employed to bind legal documents.
CHINONE AND ANTRACHINONE COLORANTS

Polyporic acid
Atromentin
Bovichinon-3
Grevillin A

p-Chinon
gold-yellow

Grevillin B
Grevillin D

names of typical structures
CHINONE AND ANTRACHINONE COLORANTS

- Naphthochinon yellow
- Lawson
- Juglon
- Lapachol
- Alkannin
- Shikonin
- Fumigatin
- Spinulosin

Names of typical structures
CHINONE AND ANTRACHINONE COLORANTS

- Alizarin
- Purpurin
- Pseudopurpurin
- Purpuroxanthin
- Rubiadin
- Munjistin
- Chinizarin
- Morindon
- Emodin
- Aloe-Emodin
- Rhein
- Chrysophanol
- Kermesic acid
- Flavokermesic acid, Laccainic acid

Biologically Active Natural Compounds

9,10-Anthrachinon deep yellow
	names of typical structures
CHINONE AND ANTRACHINONE COLORANTS

The major pigments obtained from European madder are the anthraquinones **alizarin and purpurin**, but isolation requires the prior hydrolysis of the glucoside precursor in the roots. Indian madder mainly yields purpurin. Alizarin gives an intense red colour on conversion to an insoluble lake by the addition of alum and alkali. Depending on the mordant used, the colour shade can be modified through red, pink, orange, lilac and brown. The importance of madder as a red dyestuff for textiles, especially with cotton and linen, expanded upon the adoption of the "Turkey red" process in which calcium is incorporated in the pigment complex. However, alizarin was amongst the first dyes to be synthesised in the second half of the nineteenth century and the natural material was rapidly displaced from the market.
Biologically Active Natural Compounds

CHINONE AND ANTRACHINONE COLORANTS
CHINONE AND ANTRACHINONE COLORANTS

alizarin red from madder, *Rubia tinctorum* occurs in nature as (glycoside) called **ruberythrinic or ruberythic acid**

it is its 6-\(O-\beta-D\)-xylopyranosyl-\(\beta-D\)-glucopyranoside
**Biologically Active Natural Compounds**

**Galium mollugo, White Bedstraw**
Bedstraw roots were used by native Indians to obtain a red colour, The root of this plant, were an important source of the dye alizarin.

![Galium mollugo](image1)

**Galium Odoratum, Sweet Woodruff**
The Sweet Woodruff is similar to the White Bedstraw. It's roots can be used to produce a red/pink dye, and is also part of the same family as madder.

![Galium odoratum](image2)
CHINONE AND ANTRACHINONE COLORANTS

Fumigatin

brown fungal toxin with antibiotic properties fumigatin isolated from Aspergillus fumigatus

Spinulosin

bronze purple spinulosin is a metabolic product of Penicillium spinulosum
CHINONE AND ANTRACHINONE COLORANTS

naphtoquinone

*Juglans cinerea, J. regia, J. nigra* (Butternut, P. walnut, Black walnut), hulls of the nut contain dark colorant which is used as pink, brown to dark brown

Naphthoquinones, including juglone, juglandin.

In the bark of *Juglans cinerea*, (Butternut tree), is a bitter extractive, much oil, crystallizable, orange-yellow juglandic acid, soluble in benzoïl, alcohol, and ether, but hardly soluble in water, orange-red crystals from the alcohol extract when this was treated with water and the solution abstracted with ether. The crystals turn deep-violet with alkalies, and decompose very readily.

juglandic acid is identical with nucin or juglon
Cochineal can be used with or without mordants and produces reds, pinks and purples. Cochineal is a natural dye substance that comes from dried crushed bodies of female insects, *Coccus cacti* or *Dactylopius coccus*, found on prickly pear cacti (Mexico, Central America).

Kermes (dye), kermesic acid
red ($\lambda_{\text{max}}$ 498 nm)
violet-red in $\text{H}_2\text{SO}_4$,
blue in boric acid
violet on alkali

carminic acid
black red in water
yellow to violet in acids
CHINONE AND ANTRACHINONE COLORANTS

For centuries, the magenta pigment extracted from the female cochineal insect has been an important natural dye. Archaeologists have identified 1,800-year-old cloth dyed with cochineal in caves in the Judean desert. The Mayan and Incan Indians are believed to have used cochineal extracts for centuries before actively cultivating the bug for its coloring value.

World production and trade: Approx. 300-350 tonnes of dried insects per annum.

The red colour is sometimes called carmine from Coccus cacti L., Homoptera
CHINONE AND ANTRACHINONE COLORANTS

Lac, yellow-red colorant, is obtained from the secretions of an insect found in India (*Coccus laccae*).

Laccaic acids A, B, C and D, laccaic acid A being the most abundant. Crimson dye.

Laccaic acids A, B and C are very similar, differing at a single point.

Laccaic acid D is also called *xanthokermesic acid*, and closely resembles kermesic acid in structure.

International trade: Small; possibly 10 tonnes annually.
CHINONE AND ANTRACHINONE COLORANTS

bronze-purple spinulosin from Penicillium spinulosum IMI 091950
Aspergillus fumigatus IMI 089354

brown fumigatin from Aspergillus fumigatus IMI 045338

dark violet polyporic acid from Polyporus vidulans parasitic mushroom
from oak trees
Biologically Active Natural Compounds

CHINONE AND ANTRACHINONE COLORANTS

spinochromes ('spino' for spine and 'chrome' for color)

from sea urchins
Biologically Active Natural Compounds

CHINONE AND ANTRACHINONE COLORANTS

spinochromes ('spino' for spine and 'chrome' for color)

from sea urchins

Pigments from the sea urchin Strongylocentrotus droebachiensis
Biologically Active Natural Compounds

CHINONE AND ANTRACHINONE COLORANTS

spinochromes ('spino' for spine and 'chrome' for color)

from sea urchins

Sea urchin
*Eucidaris tribuloides*

\[ \lambda_{\text{max}} \text{533, 497, 462 nm} \]
What is henna (hena)?

It is a powder from grinded dry leaves and sprouts of henna brush Lawsonia inermis. It grows 6 m, has white or yellow flowers and sweet smell.

Colorants from henna are capable to absorb 100 % UV light from the sun.

used by Prophet Muhammad for dyeing of his hair

Used for painting on human skin (tatoo) together with malachite - green, azurite - blue, zinober - red, limestone - white clay - ochre, brown.

Henna world trade: At least 9,000 tonnes annually.
CHINONE AND ANTRACHINONE COLORANTS

Alkanet root contains the red coloring matter – anchusin (alkannin or alkanet-red). Alkanet is an ancient dyestuff known throughout Europe.

\[
\text{red alkannin} \\
\text{colorant for cosmetics and food}
\]

*Alkanna tinctoria* (TAUSCH.), *Lithospermum tinctorium* (VAH L.)
**CHINONE AND ANTRACHINONE COLORANTS**

**hypericin**
red, fluorescent pigment from St. John's Wort
*Hypericum*
causes sensitivity to light of cattle

**lapachol**
yellow from tropic wood
*Tabebuia avellanedae* (antineoplastic)

lapachol is a yellow crystalline material from heartwood with $\lambda_{max}$ 331, 278, 251 nm
Shepherdia canadensis
Russet Buffalo berry (Soapberry) fruit produces a red dye, it contains ericolin glucoside, bitter, yellow
Arbutin = Ursin = Ericolin and chimaphilin is a yellow naphthoquinone

Arbutin
4-Hydroxyphenyl-β-D-glucopyranoside, přirodě se vyskytující glykosid hydrochinonu, obvykle s methylarbutinem. Antibakteriální součást přípravků tradiční medicíny, jako např. z Arctostaphylos uva ursi. (Mountain cranberry, medvědice lékařská) also red colorant and stabiliser in color photography

Arbutin can be found also in common carnberry Rhodococcus vitis-idaea (brusinka) in 4-9 % or in Saxifraga granulata (10-22 %)
Biologically Active Natural Compounds

CHINONE AND ANTRACHINONE COLORANTS

Rhubarb Root Dye

*Rheum rhaponticum*

rhubarb roots makes yellow, orange or red shades.

Sometimes used for dyeing of hair.

Rhubarb root has chrysophanic acid, a yellow dye, which will bind to keratin.

\[
\text{chrysophanic acid} \\
\lambda_{\text{max}} 436, 288, 278, 256 \text{ nm}
\]
This picture depicts and labels the essential components of a plantation producing indigo, a blue dye used for coloring cloth. Slaves are shown here working at different parts of the production process.

from *Indigofera tinctoria*

World trade: Small, possibly 50 tonnes/year. It is now mostly synthesized.
Indigo, the deep blue dye used to be most commonly applied to jeans, was first derived from plants such as woad and dyer's knotweed. Levi Strauss used the dye in the 19th century.

It seems to be the oldest known colorant.

Indigo - Saxon Blue

Indigo has been made from several different dye plants, such as Indigofera tinctoria and Indigo suffraticosa. The plants are cut and soaked in warm water and mixed with oxygen to release the dyestuff. The resulting mixture is then dried to produce chunks of indigo pigment.

To use the Indigo in dyeing it must be mixed with calcium carbonate and sulphuric acid. Because sulphuric acid is very corrosive, the use a pre-mixed solution called Saxon Blue is preferred.
INDOLE COLORANTS

indigo (trans)

indican (colorless)

indoxyl (light yellow)

indigowhite (vat) colorless water soluble

indigo (blue) water insoluble

“BROMINATED INDIGO”

punicin antic (tyrian purple) from Murex molluscs
INDOLE COLORANTS
- BETANINS

basic structure

Betanidin

Isobetanidin

Vulgaxanthin I and II
R = -OH and -NH₂

colorants of red beet and some mushrooms
Betanin from beets – *Beta vulgaris*

Beets will give rust/red or pink colours, but fade with time. The colour is hardly affected by pH changes in the range normally encountered in foodstuffs.

Below pH 3.5 the absorption maximum of betanine solutions is 535 nm, between pH 3.5 and 7.0 it is 538 nm and at pH 9.0 rises to 544 nm. Figure 11.3 shows the visible spectra of betanin at pH 2.0, 5.0 and 9.0.

- carbohydrate changes protonation between pH 12-14
- phenol changes protonation at cca pH 8
- acids change protonation between pH 1.5 and 3
- amine changes protonation at ca pH 10
melanins (Allomelans from plants eumelaninys and phaeomelanins are formed by oxidative polymerization of 5,6-dihydroxyindoles derived enzymatically from tyrosine with assistance of 3-hydroxytyrosine [dopa])

dark colorants of skin, feathers, scales, eyes, and some internal membranes (albinos do not have it)
colorant of insect cuticula, soil and some mushrooms

phaeomelanins contain sulphur, are formed from cysteinyldopa
PYRAN COLORANTS
xanthons and flavonoids (flavones, isoflavones, flavonols, anthocyanins ia.)

general flavonoid structure, the most important of a lot
and its numbering system

it belongs to the chroman family, which is then
substituted on the ring C by another ring [B]
in position 2 (or 3)
**PYRAN COLORANTS**

xanthons and flavonoids (flavones, isoflavones, flavonols, anthokyanins ia.)

<table>
<thead>
<tr>
<th>anthocyanins</th>
<th>flavonoids</th>
<th>flavones</th>
</tr>
</thead>
<tbody>
<tr>
<td>pelargonidin cyanidin delphinidin peonidin petunidin malvidin</td>
<td>fisetin galangin kaempferide kaempferol morin myricetin spirenoside</td>
<td>myricitrin quercetin quercetin rhamnetin robinin rutin</td>
</tr>
<tr>
<td></td>
<td></td>
<td>red, blue, violet</td>
</tr>
<tr>
<td></td>
<td></td>
<td>yellow</td>
</tr>
</tbody>
</table>

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>apigenin biacalein chrysin diosmetin diosmin</td>
<td>techtochrysin tangeretin rpoifolin luteolin flavone</td>
<td>yellow</td>
</tr>
</tbody>
</table>
PYRAN COLORANTS
xanthons and flavonoids (flavones, isoflavones, flavonols, anthocyanins ia.)

Flavan

Flavan
Flavan-3-ol (catechin)
Flavanon

Flavon

Flavon
Flavonol

Anthocyanidin

Anthocyanidin

Chalkone

Chalkone

chromen(e)
pyran

typical structures
PYRAN COLORANTS
Flavan-3-ols (Catechines), Flavan-3,4-diola and Flavanones, mostly colorless, yellowish in some conjugates

-Catechin
-Epicatechin
-Gallocatechin

-Naringenin
-Hesperitin
-Eriodictyol

typical structures
PYRAN COLORANTS

anthocyanins, violet-blue

Pelargonidin

Cyanidin

Delphinidin

Paeonidin

Petunidin

Malvidin

they occur mostly as glycosides (3-gal, 3-glc)

typical structures
PYRAN COLORANTS

anthocyanins

are commonly as glycosides, however, as the aglycone contains at least four OH-groups suitable for glycosylation (mostly in position 3, often 5, rarely 7, 3’ and 4’)

D-glucose
L-rhamnose
D-arabinose
rutinose (α-L-rhamnosyl-(1→6)-D-glucose)
sophorose (β-D-glucosyl-(1→2)-D-glucose)
yellow apigenin from parsley *Petroselinum crispum*,
celery *Apium graveolens* and
chamomile, lat. *Matricaria recutita* (*M. chamomilla*)
yellow hesperidin from citruses
yellow hesperetin is his aglycon
yellow genistein (important phytoestrogen)!!) contained as glucoside genistin in common woadwaxen;
dyer's Greenwood, *Genista tinctoria*
PYRAN COLORANTS

quercetin
tetrahydroxyflavonol, orange-brown
in hops, oak bark, tea, horse chestnuts ia.

aglycon of rutin (ruta) which influences permeability of
cell walls

delphinidin from red
wine, brown

his glucoside myrtillin-A
deep purple from
*Viola tricolor*

pelargonidin
from pelargonia
*Pelargonium* (red)
PYRAN COLORANTS

cyanidin
in acidic media red (roses, cherries, carnberries ...)
in alkali blue (Cornflower - bluebottle)

3-\(O-\beta-D\)-glucopyranosyl cyanidin

\[ pH < 3, \text{ red} \]

\[ pH = 7-8, \text{ violet} \]

\[ pH > 11, \text{ blue} \]

Hollyhock  
\textit{Alcea rosea} L.

cyanin, 3,5-di-\(O-\beta-D\)-glucopyranosyl cyanidin
Flavones and flavonols contribute to yellow colours in many plants
Que-3-gal  aple
Que-3-glc  aple, pear, apricot, peach, plum, cherry, currants, grapes
Que-3-rha  apple, plum, grapes
Myr-3-glc  currants
Kam-3-glc  currants, peach
**PYRAN COLORANTS**

**Jackfruit**  
*Artocarpus heterophyllus*

Heart of the wood contains morin as well as  
*Maclura pomifera* tree heart of wood

Morin

**Quercus velutina**, oak tree contains in inner bark quercetin

Quercetin
Biologically Active Natural Compounds

PYRAN COLORANTS

quercitrin is a yellow-orange colorant isolated from *Ginkgo biloba* (jinan)

The ginkgo is the oldest living tree species, geological records indicate this plant has been growing on earth for 150 - 200 million years. Chinese monks re credited with keeping the tree in existence, as a sacred herb. It was first brought to Europe in the 1700's and it is now a commonly prescribed drug in France and Germany. It is one of the most well-researched herbs in the world.

<table>
<thead>
<tr>
<th>Flavonol</th>
<th>R&lt;sub&gt;1&lt;/sub&gt;</th>
<th>R&lt;sub&gt;2&lt;/sub&gt;</th>
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<tbody>
<tr>
<td>Rutin</td>
<td>OH</td>
<td>Rutinose</td>
</tr>
<tr>
<td>Quercitrin</td>
<td>OH</td>
<td>Rhamnose</td>
</tr>
<tr>
<td>Quercetin</td>
<td>OH</td>
<td>H</td>
</tr>
<tr>
<td>Kaempferol</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>Isorhamnetin</td>
<td>OCH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>H</td>
</tr>
</tbody>
</table>
Wood from *Chlorophora tinctoria* from the Americas and "Indian mulberry" *Morinda citrifolia* of Asia, whose pigments are mixtures of yellow to orange flavones related in structure to fustin and morin.

These commodities are rare in current days.
Galium verum
Lady's Bedstraw

In addition to being a dye source for red and **yellow** colours, Lady's Bedstraw has been used for curdling milk and is used as a cheese rennet. Coloured compounds in the dye are flavonoids.

asperuloside
found also in *Asperula odorata* (Sweet Woodruff)
up to 80% of the phenolic compounds in the tea (Camellia thea) leaves are flavanols, they are responsible for tea flavor and colour.
Biologically Active Natural Compounds

Logwood (*Haematoxylum campechianum* L.)

The heartwood contains about 10% of a colourless compound, haematoxylin, which on oxidation transforms to a red to violet-blue substance, haematoxein (commercial synonym, haematein).

**World production and international trade:** Estimated at 600 tonnes annually.

An alcoholic solution of haematoxylin (0.2 percent.) is used as an indicator. It is yellow to orange in acid solution and purple in alkaline solution. Solutions of haematoxylin are much used in microscopy to stain tissues in sections or in bulk. Freshly prepared solutions have no staining powers; on keeping, however, the haematoxylin is oxidised to haematein, which is the actual colouring agent. Haematoxylin solutions for this purpose are prepared with ammonia alum, which appears to hasten the process of "ripening." The tissues, after being stained red with haematoxylin, are washed in tap water, to change the colour to blue.
The American **brazilwood** *Caesalpinia echinata* contain a water-soluble compound, brazilin, in their pale yellow heartwoods and this transforms on oxidation to the red dyestuff, brazilein. Shades of purple to bright red are obtained according to the mordant used in the dyeing process. East Indian sappanwood contains brazilin and another pigment, sappanin (2,3',4,4'-tetrahydroxybiphenyl).

"Brazilwood" held the role as one of the most important red dyestuffs for textiles from the Middle Ages to the end of the nineteenth century. **Today, the production is negligible**
**Biologically Active Natural Compounds**

**Mallotus philippensis**
Kamala "Monkey face tree"
Excrescence from the fruit pods of an evergreen shrub. Root can also be used.
Yellow orange red
Red rottlerin

*World production: Unknown.*

**Acacia catechu** Willd., cutch, cheap brown dye containing catechin (catechol) a falvan

*World production: Possibly between 6,000-9,000 tonnes per annum.*

*Found genetically in higher woody plants*

(+)-catechin is *trans*
(−)-catechin is *cis*
The principal red pigments in red sandal heartwood are santalin A and B, and these are soluble in organic solvents and alkalis but not in water. A yellow isoflavone pigment, santal, is present also.

World production and trade:
Around 50 tonnes a year of heartwood.
Yarrow - Achillea is used for yellow, tan and green dye colours. Use the flowering heads or the whole plant for the dyestuff. The plant yields yellows, tans and green colours.

**Rutin** is pale yellow, slightly soluble in water.
PYRAN COLORANTS
(XANTHONE)
pale yellow, depending on conjugation

Xanthen

9H-Xanthone

Euxanthon

Gentisin

Euxanthinic acid

Isogentisin

Gentisein

Mangiferin

Homomangiferin

typical structures
PYRAN COLORANTS
(XANTHONE)
pale yellow, depending on conjugation

yellow gentisin from *Gentiana* root
xanthone colorant

\[ \lambda_{\text{max}} \approx 410, 315, 275, 260 \text{ nm} \]
OLIGOPYRROL COLORANTS

pyrrol

porphyrin

open oligopyrrol
OLIGOPYRROL COLORANTS

porphin(e) porphyrin

heme - red
in organism is bonded to proteins via histidin and globin then to oxygen which carries

chlorophyll - green
takes part in photosynthesis

Chlorophyll a
Chlorophyll b

x = propionic acid
fytyl

Biologically Active Natural Compounds

OLIGOPYRROL COLORANTS
billirubin
main colorant of bile (orange red)
originated by oxidation of heme
occurs as glucuronide

green billiverdin
bile colorant

(−)-stercobillin
one of orange yellow urobilins
formed in intestins from heme metabolites
phycocyanobilin and phycoerythrobilin (right)
bilins are attached to a cystine residue in apoprotein by thioether linkage

Phycobiliproteins are **red or blue pigments** that are characteristic of three types of algae: the *Rhodophyta*, the *Cyanophyta* and the *Cryptophyta*. They are built up of bilins, which are open-chain tetrapyrroles they are classified according to UV-vis absorption as blue phycocyanins, red phycoerythrins and pale blue allophycocyanins

these algal pigments have potential as natural colorants for use in food, cosmetics and pharmaceuticals
Myoglobin is part of the sarcoplasmic protein of muscle and is responsible for more than 90% of the pigmentation in meat. The amount of myoglobin varies among muscle tissues. It is soluble in water and in dilute salt solutions. Myoglobin is a complex of globin and heme. Globin is the protein portion of the molecule and heme is the chromophore component responsible for light absorption and color. Within the porphyrin ring, a centrally located iron atom possesses six coordination sites. Four of these sites are occupied by the nitrogen atoms within the tetrapyrrole ring. The fifth coordination site is bound by the histidine residue of globin, leaving the sixth site available to complex with electronegative atoms donated by various ligands.
Biologically Active Natural Compounds

**PTERIDINE COLORANTS**

- **red erythropterin** from butterfly wings
  ![Red Erythropterin](image)

- **yellow leukopterin** from butterfly wings
  ![Yellow Leukopterin](image)

- **orange xanthopterin** from butterfly wings, crabs, and urine
  lsdo from insects
  ![Orange Xanthopterin](image)

- **pteridine**
  ![Pteridine](image)
PTERIDINE COLORANTS

riboflavin yellow, Vitamin B-2

fluorescent yellow colorant (flavus is Latin for yellow) occurs free in the eye retina only

contained in liver, veal, lamb, fatty fish (like salmon), whole milk, yogurt, cheese, egg yolks, avocados, oysters, nuts, legumes, whole grains, broccoli, dark leafy green vegetables (like spinach), asparagus, and green peas, whey

bioactive forms occurring in nature are riboflavin monophosphate and FAD (flavin adenine dinucleotide)
The root of the Bloodroot *Sanguinaria canadensis* plant has been used by the First Nations peoples for producing oranges, pinks and reds. A blood red juice can be extracted from the reddish orange root, actually a rhizome. Bloodroot contains isoquinoline alkaloids, notably sanguinarine (1 %, colorless alkaloid yielding red salts), and many others, including berberine. Berberine, imparts the yellow color.

ISOQUINOLINE COLORANTS

also in common barberry, *Berberis vulgaris*
Biologically Active Natural Compounds

LICHEN DYES
(phenoxazine)

Orchil, archil, orseille (French) and cudbear;
generic terms used for red/purple/violet dyes obtained by treatment of certain lichen species with ammonia.

Orchil/cudbear types: *Rocella tinctoria, Ochrolechia tartarea* (syn. *Lecanora tartarea*), *Evarina prunastri* (Stag's horn), plus some species of *Parmelia, Umbilicaria* and *Lasallia*.

Orcein and orchil are colourings derived from archil, the lichen *Rocella tinctoria*
orcein is a mixture of compounds with a phenoxazine structure, composed of hydroxy-orceins, amino-orceins and amino-orceinimines

*Ochrolechia tartarea*
CARAMEL COLOR

One of the most widely used colors is *caramel*, the color of burnt sugar. There are many different types of caramel color, each engineered to serve a particular purpose in food chemistry. Caramel color is a *colloid*, a mixture in which solid particles are suspended in water. The particles in colloids have electric charges that keep the particles from clumping together and settling out of solution. The charges can be positive or negative. If a negative colloid is added to a product that has positive colloidal particles in it, the two will attract one another and clump up, making the product cloudy. Caramel color can be made with either positively or negatively charged particles. This allows manufacturers to use negative colloidal caramel in acidic soft drinks, and positive in beers and soy sauces. Beer has positively charged proteins suspended in it, and soy sauce has a high salt content that requires the more salt-tolerant positive caramel color. Caramel color is an emulsifying agent as well as a colorant. In soft drinks, it helps keep the flavor oils suspended in the solution.
MUSHROOMS DYES

Boletopsis grisea
The mushroom gives lovely green and olive colours.

Cortinarius semisanguineus
The mushroom produces orange and red dyes with an alum mordant.

Hapalopilus rutilans
The mushroom yields violet and red colours in an alkali dyebath.

Phaeolus schweinitzii
The fungus gives lovely gold yellow shades of colour.

Pisolithus arhizus
The mushroom yields browns and gold colours.
MAILLARD REACTION COLOURANTS

Maillard reaction is a type of non-enzymatic browning which involves the rather complex reaction of simple sugars (carbonyl groups) and amino acids (free amino groups). They begin to occur at lower temperatures and at higher dilutions than caramelization.
Maillard Reaction colourants

Figure 1: An outline of the Maillard reaction
An outline of the Maillard reaction is given in Figure 1. Maillard reactions have three basic phases. The initial reaction is the condensation of the carbonyl group of a reducing sugar (aldose) with a free amino group of a protein or an amino acid, which loses a molecule of water to form $N$-substituted glycosylamine (Step A). This is unstable and undergoes the "Amadori rearrangement" to form "1-amino-1-deoxy-2-ketoses" (known as "ketosamines") (step B). The ketosamine products of the Amadori rearrangement can then react three ways in the second phase. One is simply further dehydration (loss of two water molecules) into reductones & dehydro reductones (step C). These are essentially "caramel" products and in their reduced state are powerful antioxidants. A second is the production of short chain hydrolytic fission products such as diacetyl, acetol, pyruvaldehyde, etc (step D). These then undergo "Strecker degradation" with amino acids to aldehydes (step E) and by condensation to aldols, or they may react in the absence of amino compounds, to give aldols and high molecular weight, nitrogen-free polymers (step F). A third path is the Schiff's base/furfural path. This involves the loss of 3 water molecules (step C), then a reaction with amino acids and water. All these products react further with amino acids in the third phase to form the brown nitrogenous polymers and copolymers called melanoidins (step G). These can be off flavours (bitter), off aromas (burnt, onion, solvent, rancid, sweaty, cabbage) or positive aromas (malty, bread crust-like, caramel, coffee, roasted). Step H in Figure 1 illustrates a direct route to fission products from $N$-substituted glycosylamines, without the formation of an ARP (Amadori rearrangement product).
### Permitted Food Colours (Natural and synthetic)

<table>
<thead>
<tr>
<th>Code</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>E100</td>
<td>Curcumin</td>
</tr>
<tr>
<td>E101</td>
<td>(i) Riboflavin, (ii) Riboflavin-5'-phosphate</td>
</tr>
<tr>
<td>E102</td>
<td>Tartrazine</td>
</tr>
<tr>
<td>E104</td>
<td>Quinoline yellow</td>
</tr>
<tr>
<td>E110</td>
<td>Sunset Yellow FCF; Orange Yellow S</td>
</tr>
<tr>
<td>E120</td>
<td>Cochineal; Carminic acid; Carmines</td>
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<td>E122</td>
<td>Azorubine; Carmoisine</td>
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<tr>
<td>E123</td>
<td>Amaranth</td>
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<td>E124</td>
<td>Ponceau 4R; Cochineal Red A</td>
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<td>E127</td>
<td>Erythrosine</td>
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<td>E128</td>
<td>Red 2G</td>
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<td>Allura Red AC</td>
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<td>E131</td>
<td>Patent Blue V</td>
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<td>E132</td>
<td>Indigotine; Indigo Carmine</td>
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<td>E133</td>
<td>Brilliant Blue FCF</td>
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<td>E140</td>
<td>Chlorophylls and chlorophyllins</td>
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<td>Brilliant Black BN; Black PN</td>
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<td>Vegetable carbon</td>
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<td>E160b</td>
<td>Annatto; Bixin; Norbixin</td>
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<td>E160c</td>
<td>Paprika extract; Capsanthian; Capsorubin</td>
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<td>E160d</td>
<td>Lycopene</td>
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<tr>
<td>E160e</td>
<td>Beta-apo-8'-carotenal (C30)</td>
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<td>E160f</td>
<td>Ethyl ester of beta-apo-8'-carotenoic acid (C30)</td>
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<td>E162</td>
<td>Beetroot Red; Betanin</td>
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<td>E164</td>
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<td>E173</td>
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<td>E175</td>
<td>Gold</td>
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<tr>
<td>E180</td>
<td>Litholrubine BK</td>
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</tbody>
</table>
Biologically Active Natural Compounds

Presented material is aimed mainly at the students of the Institute of Chemical Technology, Prague. Some of its data stems from public sources and for reasons of simplicity and clarity not all quotations are properly cited as it is common in technical literature. With possible objections please turn directly to the authors.

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