

# **Classification of Natural dyes and Synthetic dyes – By structure and by color**

# Natural dyes

One can get coloring matter from almost all-vegetable matter. However, only a few of these sources yield colorants which can be extracted and work out to be commercially viable. Similar is the case of colorants obtained from animal origin.

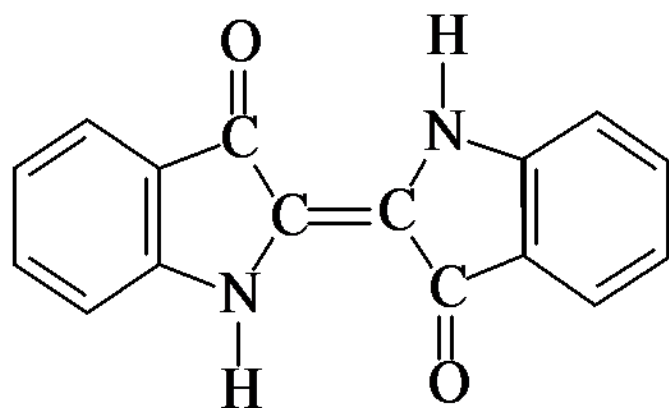
Basically, three primary colors are required to get any given hue (or color). This type of approach has been worked out for synthetic dyes. However in the case of natural dyes, the dyeing procedures are different for different dyes and they cannot be blended to get required color easily

# Why and how natural dyes are different

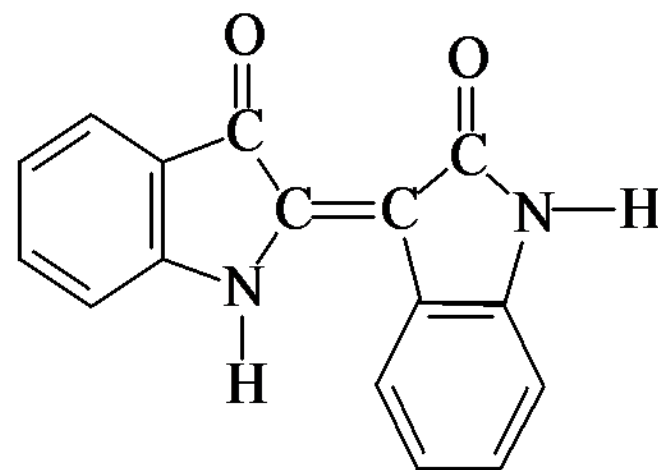
- Never-the-less, while looking for different colors one finds that it is better to have a limited number of dyes with good fastness properties, rather than having too many colors (sources) with limited fastness properties.
- While selecting the proper palette of colors one would like to have at least one blue, one red and a yellow to start with. Due to the limited number of natural dyes available, the correct choice of the dyes is very important. Information of some important natural dyes is given below.

## Blue dyes

- The color index lists only four natural dyes, that is Natural Indigo, sulphonated Natural Indigo, Kumbh (Manipur) and the flowers of Japanese 'Tsuykusa' used mainly for making awobana paper.
- The only viable choice among the blue natural dyes is Indigo. Natural indigo is obtained by fermenting the leaves of various species of Indigofera, running off the liquor and oxidizing it to precipitate the dye. Woad (*Isatis tinctoria* L.) is another important source of indigo. The plant is grown mostly in North Europe and British Isles.
- With the synthesis of indigo in 1880 and its successful commercial exploitation in 1897 by BASF, the production of natural Indigo decreased. The king of natural dyes went into oblivion. There are some signs of its revival. The current demand of Indigo in US is estimated to be around 800 tonnes per year, priced at around \$ 20 million. The main ingredients of natural indigo are indigotin (I) and indirubin (II)



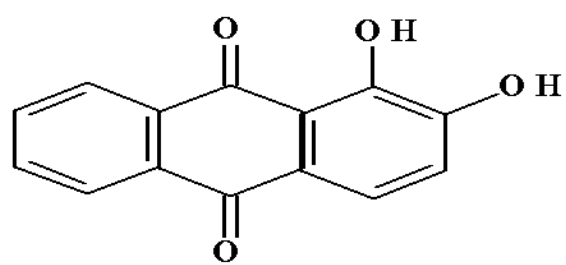
(I)



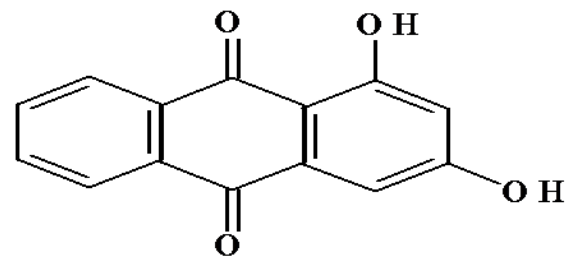
(II)

## Red Dyes

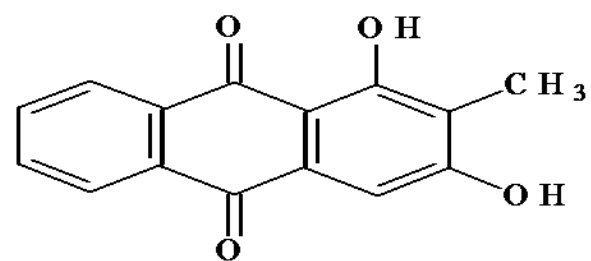
- The color index lists 32 red natural dyes. The prominent among them are madder (*Rubia tinctorum* L.), manjistha (*Rubia cordifolia* L.), brazil wood/ sappan wood (*Caesalpina sappan* L.), Al or morinda (*Morinda citrifolia* L.) cochineal (*Coccus cacti* L.) and lac dye (*Coccus laccae*).
- Manjistha or Indian madder is anthraquinone based red dye. The most important colorants in madder are the anthraquinones, alizarin (III), purpuroxanthin (IV), rubiadin (V), manjistin (VI), purpurin (VII) and pseudopurpurin (VIII).



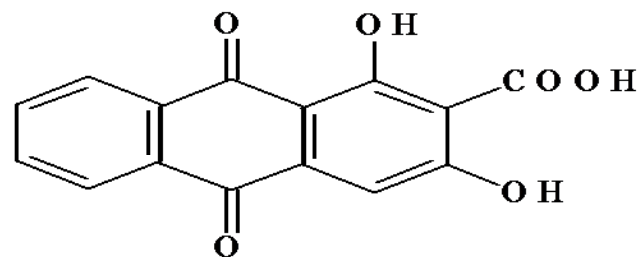
(III)



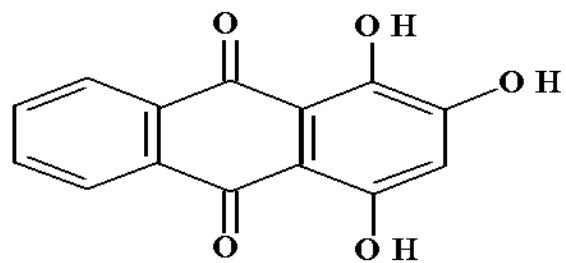
(IV)



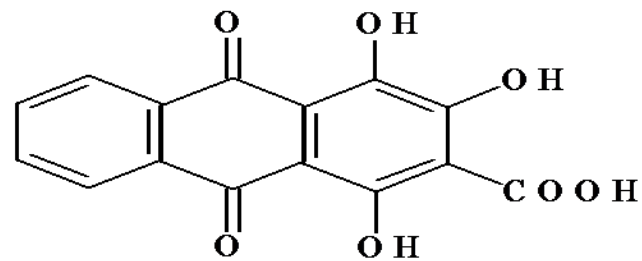
(V)



(VI)



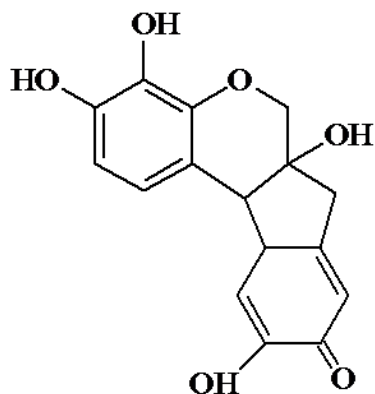
(VII)



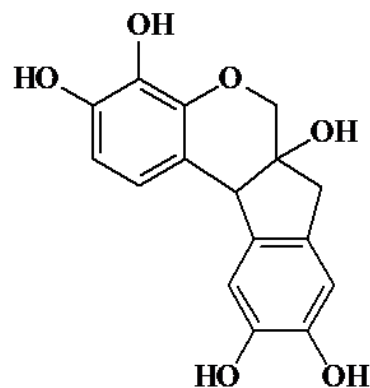
(VIII)

## More red Dyes

- Brazilin (C.I. Natural Red 24) is the main coloring component of *Ceasalpinia echinata* Lam (*Brazil wood*) and *Ceasapinia sapan* L. (*Sappan wood*). Brazilin (IX) gets oxidized to form the red Brasilein (X) as indicated below.



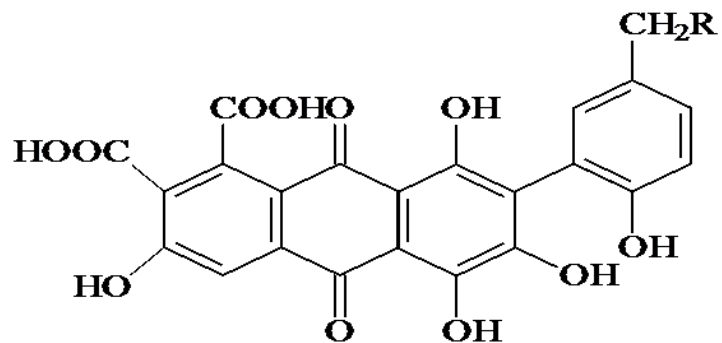
(IX)



(X)

## Red dye- lac dye

- Lac is perhaps one of the oldest of all known red dyes. However, cochineal and kermes were widely used in the western world for the production of bright purple and red colors.
- The lac dye is extracted from lac, the resinous protective secretion of tiny insect, *Laccifer lacca*, which is a pest on a number of plants both wild and cultivated. It secretes a thick resinous fluid which envelopes their bodies: and secretion from a hard continuous encrustation over the twigs. They contain only 1-2 % dye. There are four coloring compounds in lac, designated as laccaic acid A, B, C and E (XI). Laccaic acid (A) being the most abundant. Laccaic acid is also called Xanthokermesic acid, and it closely resembles Kermesic acid in structure. Lac dye being an acid dye can be directly dyed on protein fiber such as wool and silk. It also produces very dark shades on nylon. The hues can be modified by post mordanting treatment with metal salts. The dye has very good light and washing fastness.



(XI)

Laccaic acid- A

$\text{R}=\text{CH}_2\text{NHCOCH}_3$ )

B

$\text{R}=\text{CH}_2\text{OH}$ )

C

$\text{R}=\text{CH}(\text{NH}_2)\text{COOH}$ )

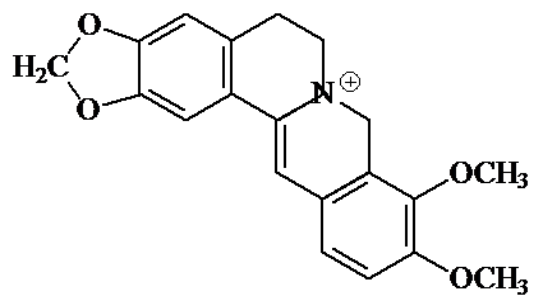
E

$(\text{R}=\text{CH}_2\text{NH}_2)$

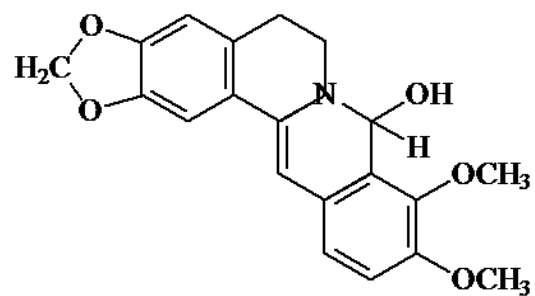
# Yellow Dyes

Yellow [Mayer and cook, 1943; Goodwin, 1976; Cardon and Chatenet, 1990 and Singh et al., 2001] is the most common color in the natural dyes. However most of the yellow colorants are fugitive. The color index lists 28 yellow dyes. Some of the important yellow dyes are obtained from berberry (*Berberis aristata*), tessu flowers (*Butea frondosa, monosperma*) and kamala (*Mallotus philippensis*).

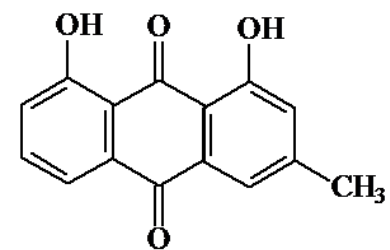
- Other sources of yellow dye are black oak (*Quercus velutina*), turmeric (*Curcuma longa*), weld (*Reseda luteola*) and himalalayan rhubarb (*Rheum emodi*).
- Some coloring matters are berberine (XII), its derivatives (XIII), chrysophanic acid (XIV) and luteolin (XV).



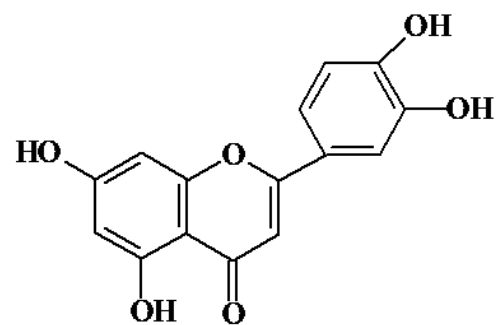
(XII)



(XIII)



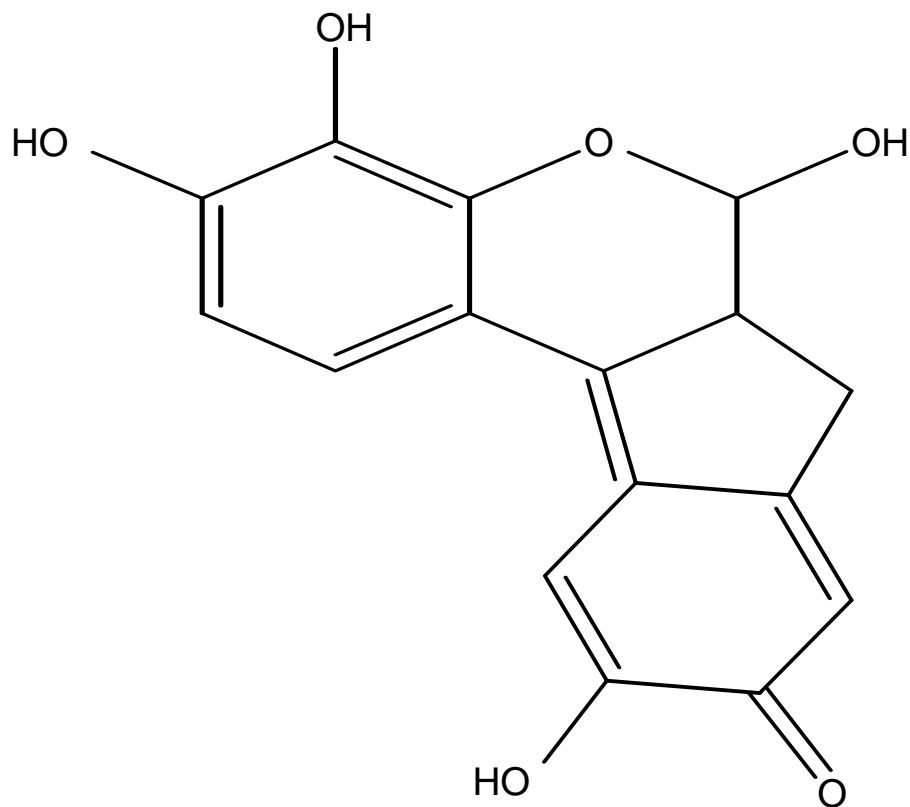
(XIV)



(XV)

## Dihydropyran

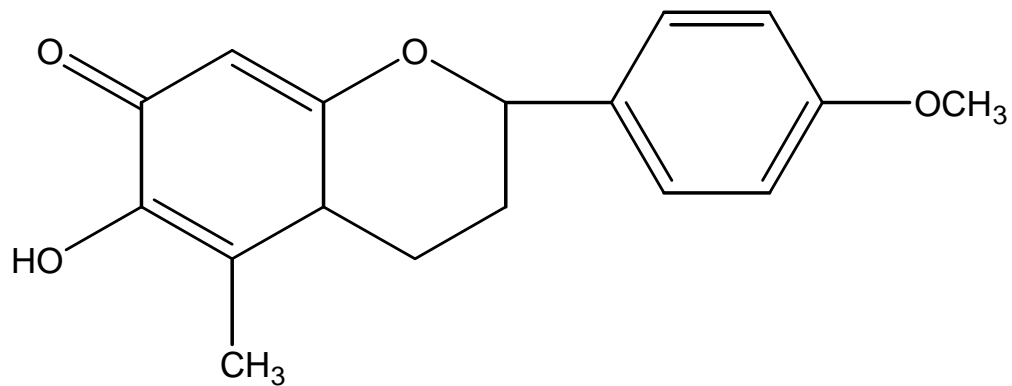
**Dihydropyran** : Closely related to flavones in chemical structure are substituted dihydropyrans like the one shown here.



Dihydrpyran

# Anthracyanidines

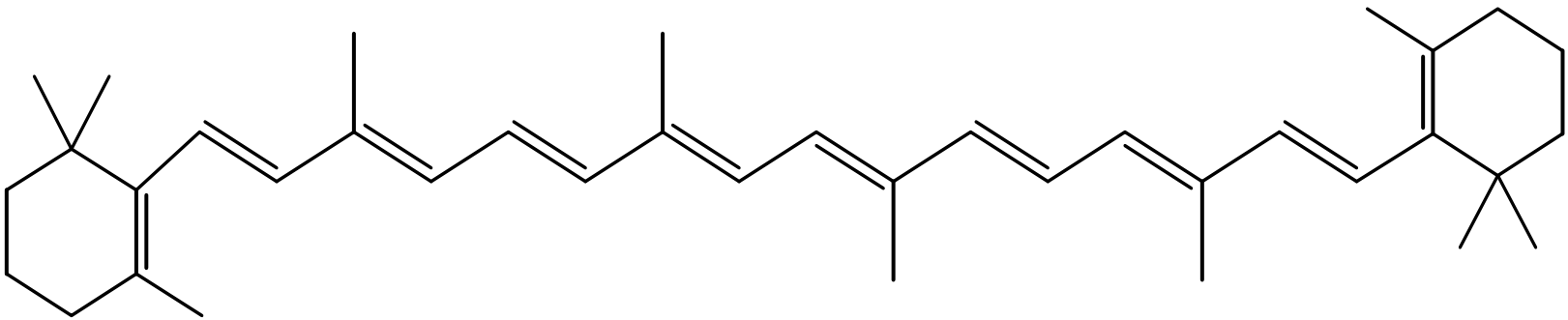
**Anthracyanidines** : Carajurin obtained from bignonia Chica



Anthocyanidine

## Carotinoids

**Carotinoids** : In these the color is due to the presence of the long conjugated double bond. Annato and Saffron are examples of this.



$\beta$ - Carotene

## Triaryl methane dyes- Synthetic dyes

- Triaryl methane dyes. These include the quinonoid arrangement as the actual chromophore. The quinonoid ring but since all three benzene rings are equivalent there can be rearrangement of the bonds and any of the benzene rings could take up this arrangement.
- There are a large number of dyes used in histology that fall into this category; a few examples are fuchsins, methyl violet, methyl blue and aniline blue

## Other dye- Synthetic dyes

- Anthraquinone. Here the quinonoid ring is seen as the middle of the three fused rings. Examples are alizarin and carmine.
- Xanthene. Here the quinonoid ring is the right hand one of the three fused rings and the ring is tilted compared with the previous example. Examples include eosin and xanthene.
- Thiazine. This is very similar to the previous example in overall structure, but the middle ring now has S and N as constituent atoms. This group contains many important metachromatic dyes, such as toluidine blue, methylene blue and azure A.

## Basic Dyes

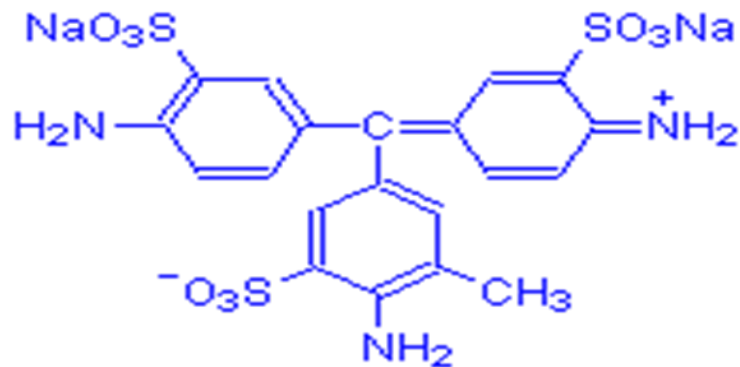
Basic dyes are cationic and will stain/ color anionic or acidic materials such as carboxylates, sulphates (many complex carbohydrates are sulphated) and phosphates (particularly the phosphates in nucleic acids). Most are used as nuclear stains and staining of cytoplasmic carboxyl groups is deliberately suppressed by using a slightly acid pH. Acidic substances that stain with basic dyes are termed basophilic.

## Acidic and Neutral dyes

- Acidic dyes are anionic and will color cationic or basic groups such as amino groups. Most are used to stain proteins in the cytoplasm and connective tissues. Substances that stain with acid dyes are called acidophilic.
- Neutral dyes are simply compounds of basic and acid dyes. In this case, both ions are coloured. Such dye complexes will stain both nucleus and cytoplasm from a single dye bath. Romanowsky stains are neutral dyes made from more complex mixtures. These are the commonest dyes used in haematology. They are less common in histology but still very useful and include Giemsa, Leishman and Wright's stains.

# Amphoteric dyes

- Amphoteric dyes also have both anionic and cationic groups, but these are on the same ion.
- Amphoteric dyes have both positively chargeable groups and negatively chargeable groups present on the molecule. Depending on the charge actually present, these dyes may interact as either positively charged ions basic dyes or negatively charged ions acid dyes



## Natural dyes

Natural dyes are simply dye substances extracted from natural sources. Although the main source of dyes for early times, they have largely been replaced by synthetic dyes, which are usually more reliable, cheaper and can be supplied more readily. Natural dyes still in use include haematoxylin, carmine, orcein and litmus, although synthetic varieties are also available for some of these.

