Flavonoids

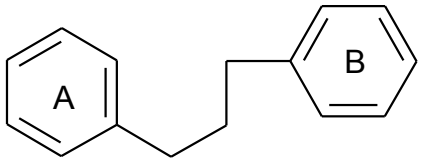
General characteristic

Plan

1. The general characteristic of flavonoids
2. Physical and chemical properties of flavonoids
3. Qualitative and quantitative determination of flavonoids

- Flavonoids are the largest group of naturally occurring phenols and occur in the plant both in the free state and as glycosides.

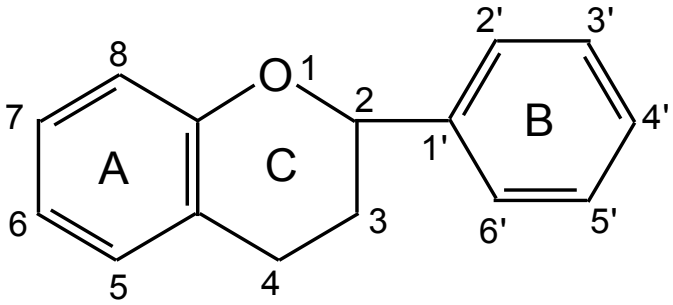
They may be described as a series of **C_6-C_3-C_6** compounds.



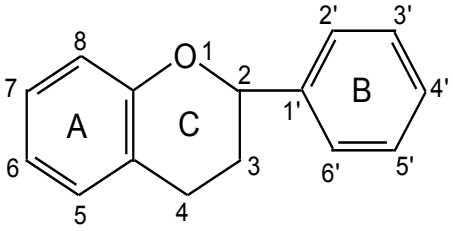
Classification

The largest group of flavonoids is characterized by the presence of a pyran ring linking the three carbon chain with one of the benzene rings.

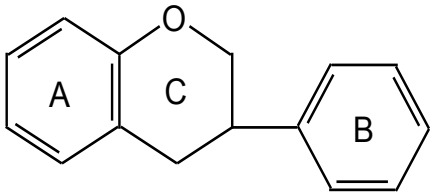
The numbering system for these flavonoid derivatives is as follows:



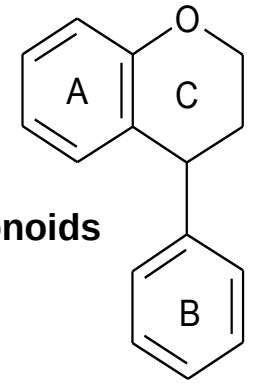
- ***Flavonoids are distinguished by the place of B-ring location*** :



True flavonoids

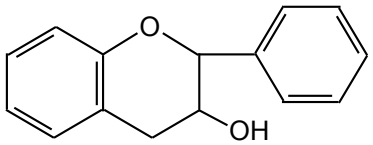


Isoflavonoids

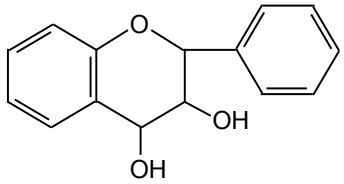


Neoflavonoids

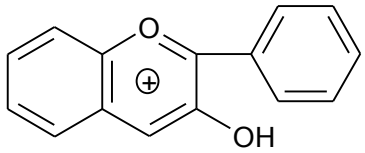
- **True flavonoids** are classified according to the oxidation level of the propane moiety of the molecule.



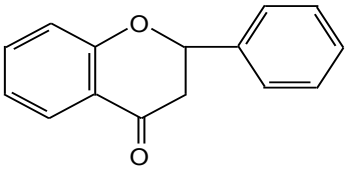
Catechins



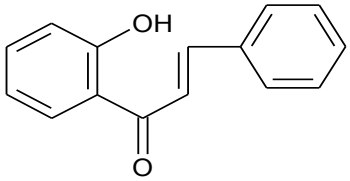
Leucoanthocyanidins



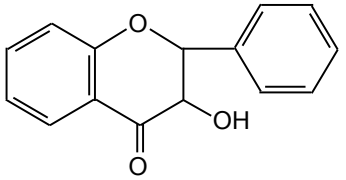
Anthocyanidins



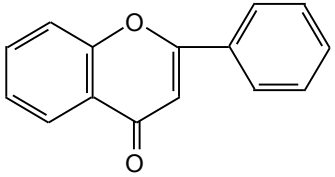
Flavanones



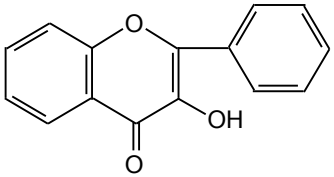
Chalcones



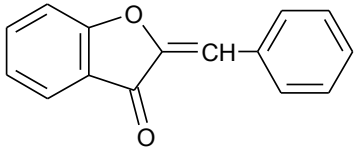
Flavanonoles



Flavones



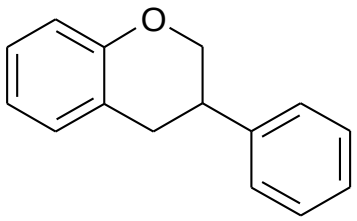
Flavonoles



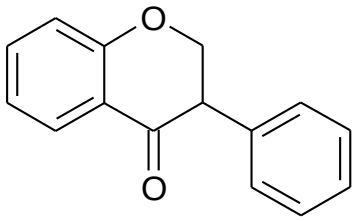
Aurones

ISOFLAVONOIDS

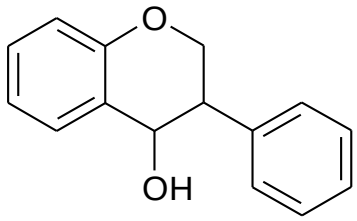
Simple isoflavonoids



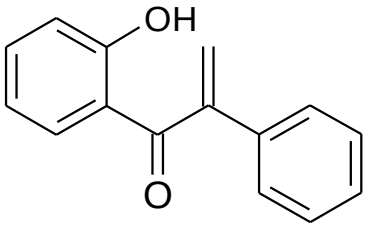
Isoflavan



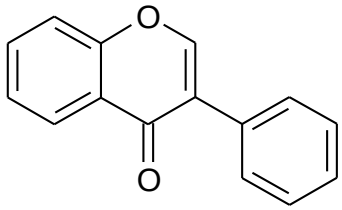
Isoflavanone



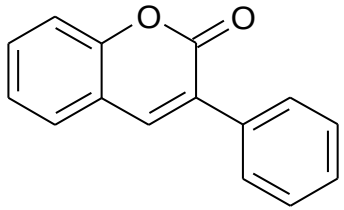
Isoflavanol



Isochalcone

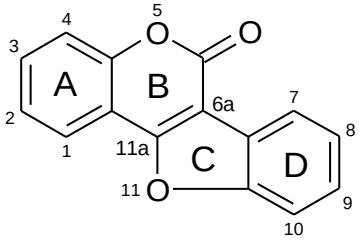


Isoflavone

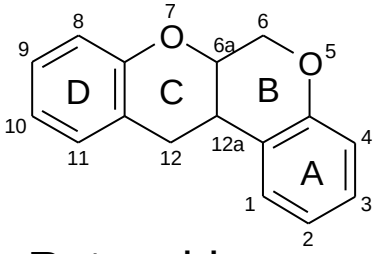


3-arylcoumarin

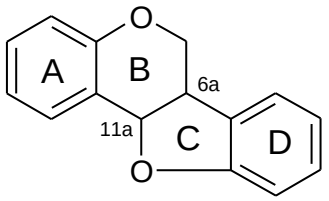
Condensed isoflavonoids



Coumestane



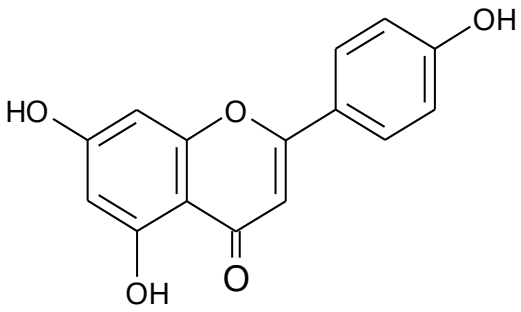
Rotenoid



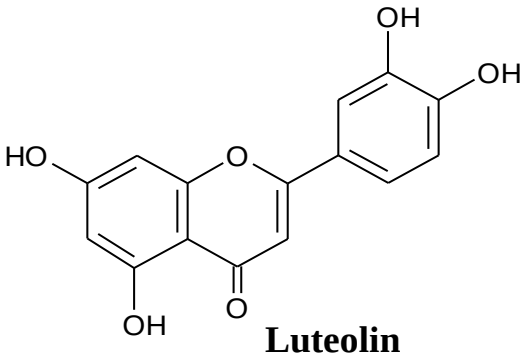
Pterocarpane

THE MOST WIDE-SPREAD COMPOUNDS

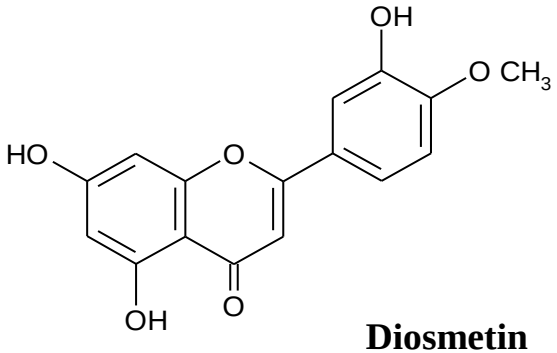
Flavones



Apigenin

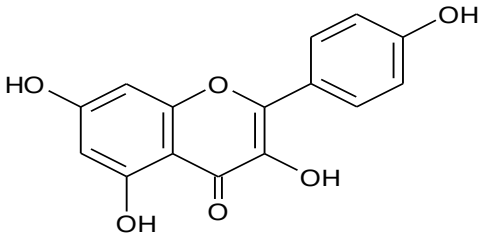


Luteolin

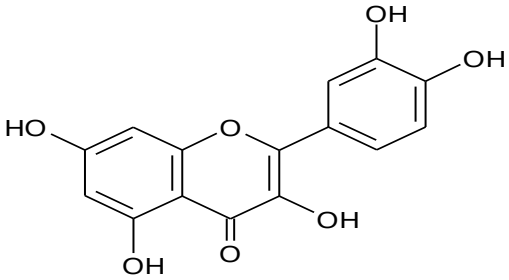


Diosmetin

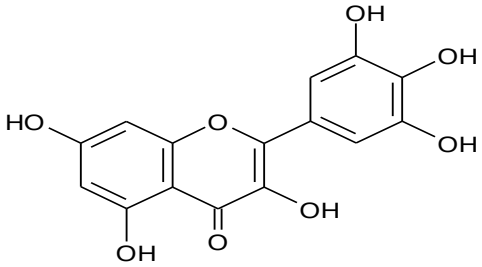
Flavonoles



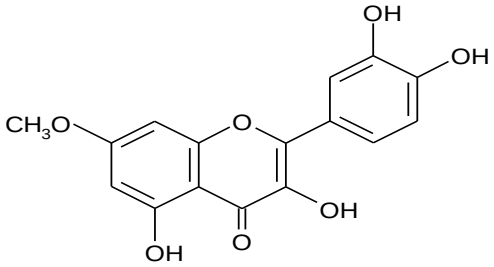
Kaempferol



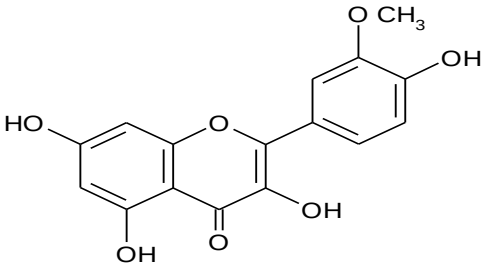
Quercetin



Myricetin



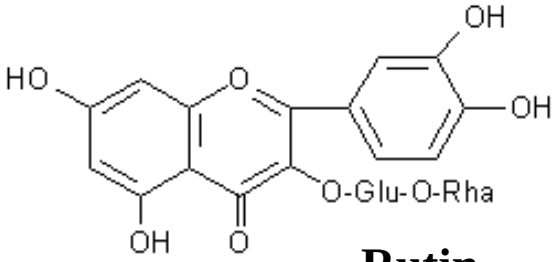
Rhamnetin



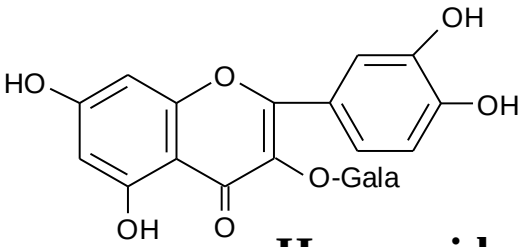
Isorhamnetin

Flavonoid glycosides

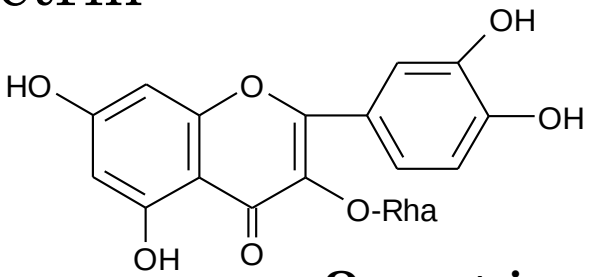
Rutin, Hyperoside, Quercetrin



Rutin



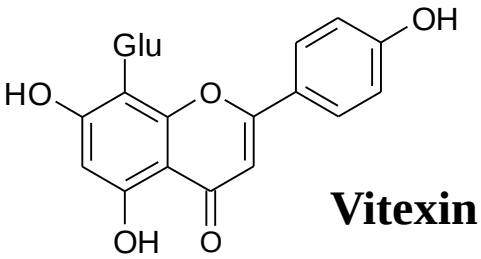
Hyperoside



Quercetrin

Flavonoids are widely distributed in nature either in a free state or linked to sugars, which are more common in higher plants and in young tissues, where they occur in the cell sap.

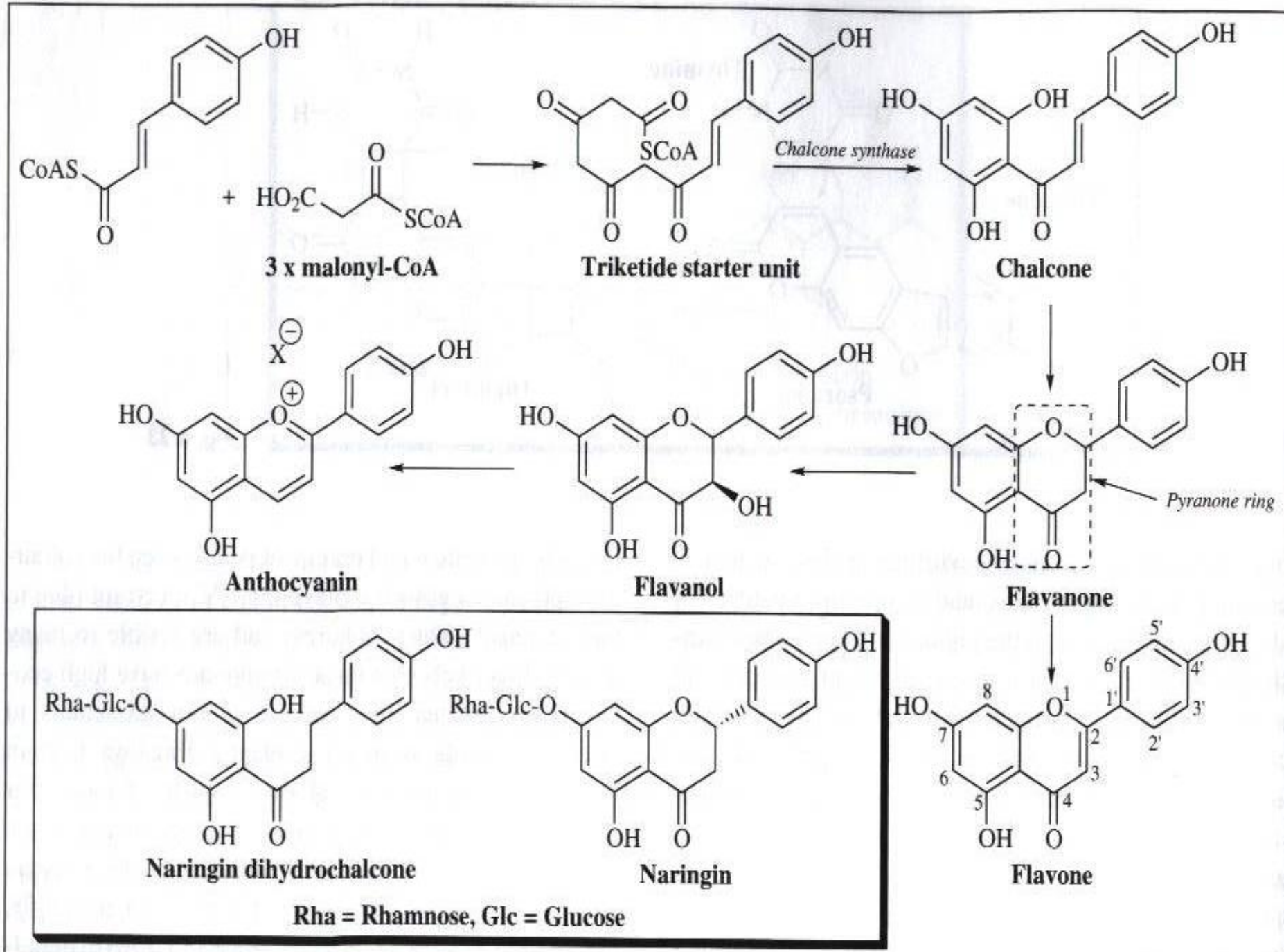
Flavonoids are of abundant in the *Polygonaceae, Rutaceae, Fabaceae, Rosaceae.*



Vitexin

BIOSYNTHESIS:

- Flavonoids are products from a cinnamoyl-CoA (C_6C_3, precursor from the shikimate pathway) starter unit, with chain extension using three molecules of malonyl-CoA.
- Flavonoids are therefore of mixed biosynthesis, consisting of units derived from both shikimate and acetate pathways.

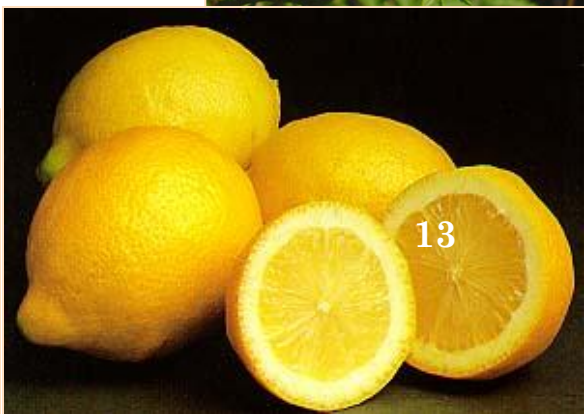

CoAS
O
OH
+ HO2C
SCoA
3 x malonyl-CoA
Triketide starter unit
Chalcone synthase
Chalcone
Pyranone ring
Flavanone
Flavanol
Anthocyanin
Rha-Glc-O
Naringin dihydrochalcone
Naringin
Rha = Rhamnose, Glc = Glucose
Flavone

- The triketide starter unit undergoes cyclization by the enzyme chalcone synthase to generate the **chalcone** group of flavonoids. Cyclization can then occur to give a pyranone ring containing **flavanone** nucleus, which can either have the C2-C3 bond oxidized (unsaturated) to give the **flavones** or be hydroxylated at position C3 of the pyranone ring to give the **flavanonol** group of flavonoids. The flavanonols may then be further oxidized to yield the **anthocyanins,** which contribute to the brilliant blues of flowers and the dark colour of red wine.

Functions in plants

- Control of the plant growth;
- Inhibiting and activating the enzymes;
- Having a role in the biochemistry of reproduction;
- Fungicidal properties;
- Protect the plant from parasites' attack;

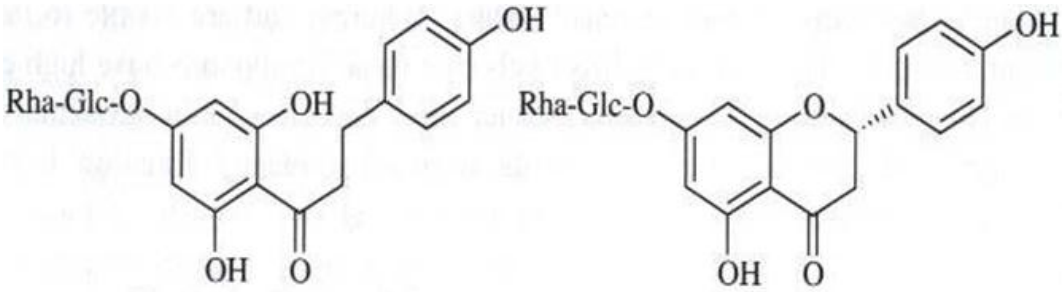
- These compounds have high ***ecological*** importance in nature as colour attractants to insects and birds as an aid to plant pollination.
- The flavonoids contribute to many other colors found in nature, particularly the yellow and orange of petals; even the colourless flavonoids absorb light in the UV spectrum (due to their extensive chromophores) and are visible to many insects. [A ***chromophore*** is the part (or moiety) of a molecule responsible for its color].



PHYSICAL AND CHEMICAL PROPERTIES

- Flavonoids are crystalline compounds;
- They are colored:
  - **yellow**: flavones, flavonoles, chalcones, aurones;
  - **red**: anthocyanidins in acidic media;
  - **blue**: anthocyanidins in alkaline media;
  - colorless: catechins, flavans, flavanones, leucoanthocyanidins, isoflavones.
- Flavonoid glycosides are generally soluble in water and alcohol but insoluble in organic solvents; the aglycones (genins) are only sparingly soluble in water but soluble in ether, chloroform.
- Under the UV light flavonoids show fluorescence ofdifferent colors (yellow, orange, brown, red).

- Certain flavonoids also markedly affect the taste of foods: for example, some are very bitter and astringent such as the flavanone glycoside **naringin**, which occurs in the peel of grapefruit *(Citrus paradisii)*. Interestingly. the closely related compound **naringin dihydrochalcone**, which lacks the pyranone ring of naringin, is exceptionally sweet, being some 1000 times sweeter than table sugar (sucrose).



Rha = Rhamnose, Glc = Glucose

IDENTIFICATION

1. Chromatographic identification

Fluorescence under filtered UV light is used to differentiate different groups of these compounds as follows:

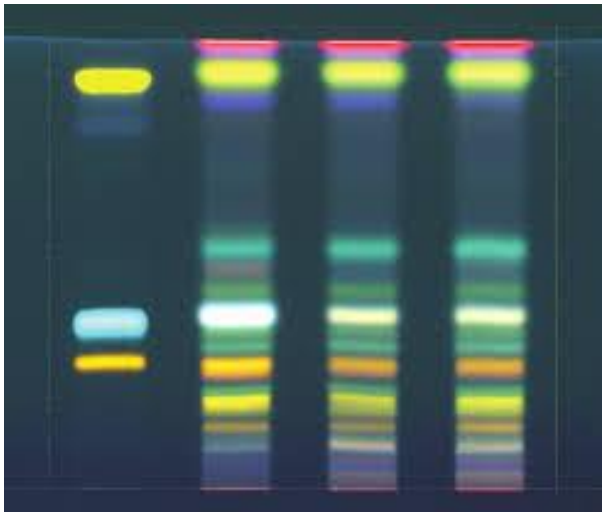
$AlCl_3$ gives yellow color (flavones, flavonoles, chalcones, aurones). Under the UV light these compounds show fluorescence of different colors, e.g.

flavones – green;

Flavonoles – yellowish to yellowish-green;

Chalcones – brown-pink;

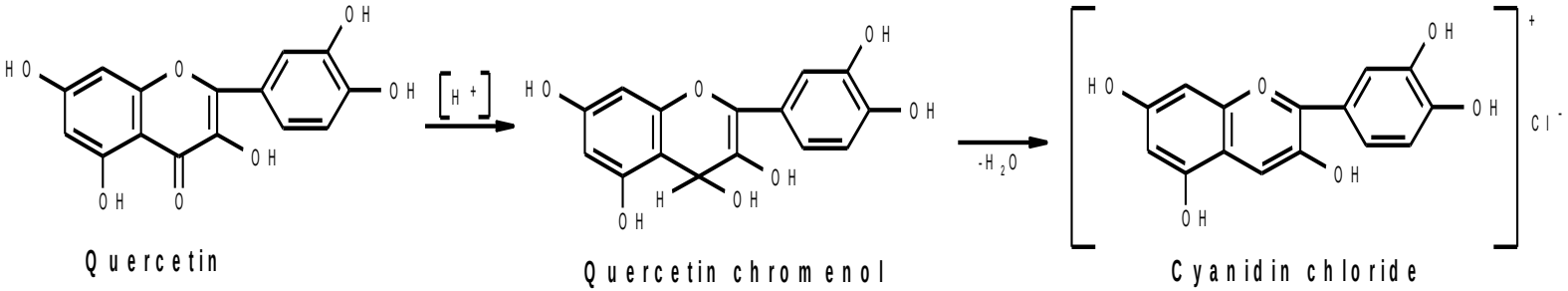
Aurones – pale-brown.



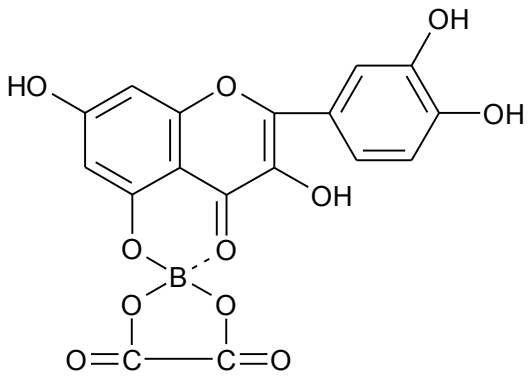
1 – rutin, 2 – chlorogenic acid, 3 – quercetin in ginkgo leaves samples and tinctures

2. Shinoda's test (cyanidin reaction)

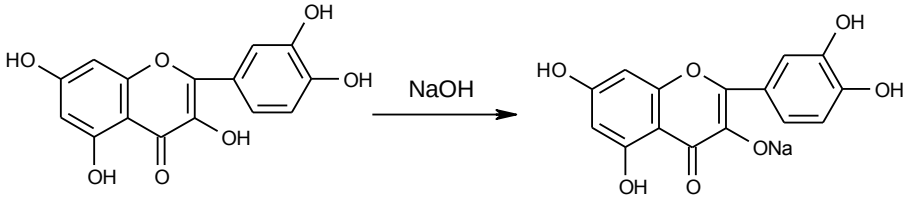
The alcoholic solution of flavone or flavonol when treated with metallic magnesium (or Zinc) and hydrochloric acid gives an orange, red or violet color



3. Wilson's reaction. Flavonoids form complexes with boric acid which is not destroyed by addition of citric acid alcoholic solution (or oxalic acid).

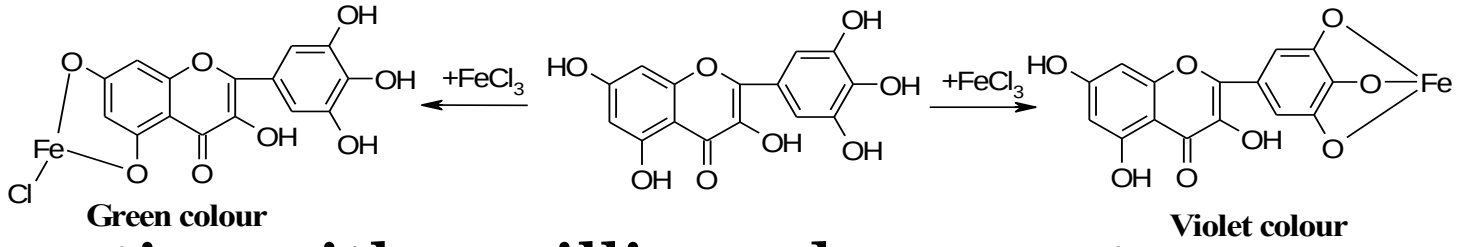


4. A reaction with alkal isolution. Flavonoids (flavones, flavonoles, chalcones, aurones) when treated with alkali solution give **yellow** or **orange** color.



5. Reaction with iron (III) chloride.

Flavonoids (flavones, flavonoles, chalcones, aurones) when treated with iron (III) chloride solution give **green** or **violet** color.



6. Reaction with vanillin and concentrated hydrochloric acid.

Catechins when treated with vanillin solution in hydrochloric acid give **red** color.

QUANTITATIVE DETERMINATION

- **Spectrophotometric**
- **High performance liquid chromatography**
- **Gravimetric**
- **Titration**
- **Fluorometric**
- **Polarographic**

USES

- Flavonoids have important dietary significance because, being phenolic compounds, they are potent antioxidants.

Many disease states are known to be exacerbated by the presence of *free radicals* such as superoxide and hydroxyl, and flavonoids have the ability to scavenge and effectively 'mop up' these damaging oxidizing species.

- Flavonoids contribute to the diuretic and diaphoretic action of such drugs as chamomile, elder flowers, linden blossoms, horsetail and others
- The isoflavone derivatives have a distinct estrogenic effect.

- Foods rich in this group of compounds have therefore been proposed to be important in ameliorating diseases such as cancer and heart disease (which can be worsened by oxidation of low-density lipoprotein); **quercetin**, a flavonoid present in many foodstuffs, is a strong antioxidant. Components of milk thistle *(Silybum marianum),* in particular **silybin**, are antihepatotoxins; extracts of milk thistle are generally known as **silymarin.**

Literature

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