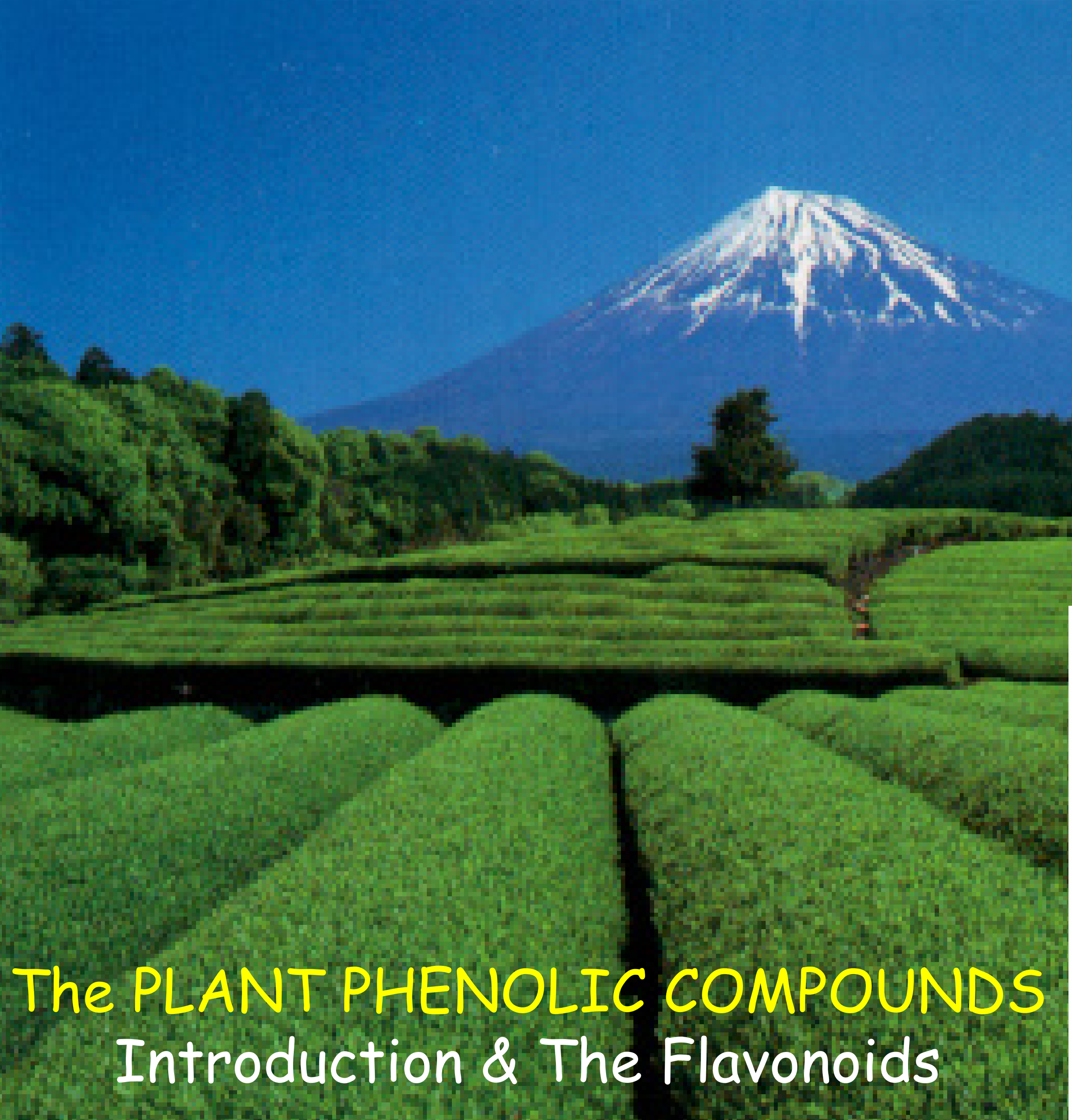
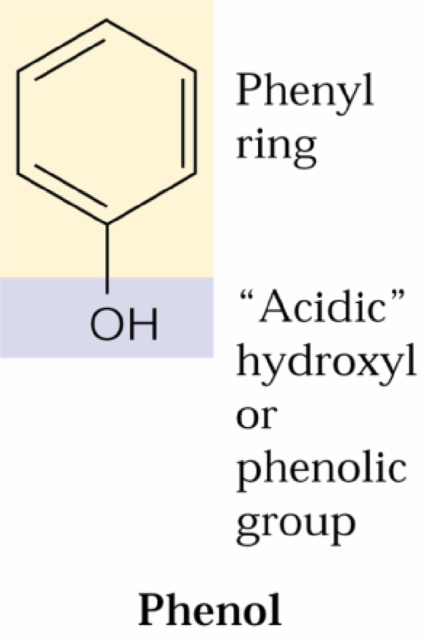


The PLANT PHENOLIC COMPOUNDS
Introduction & The Flavonoids



The plant phenolic compounds

- 8,000 Phenolic structures known

- Account for 40% of organic carbon circulating in the biosphere

- Evolution of vascular plants: in cell wall structures, plant defense, features of woods and barks, flower color, flavors

The plant phenolic compounds

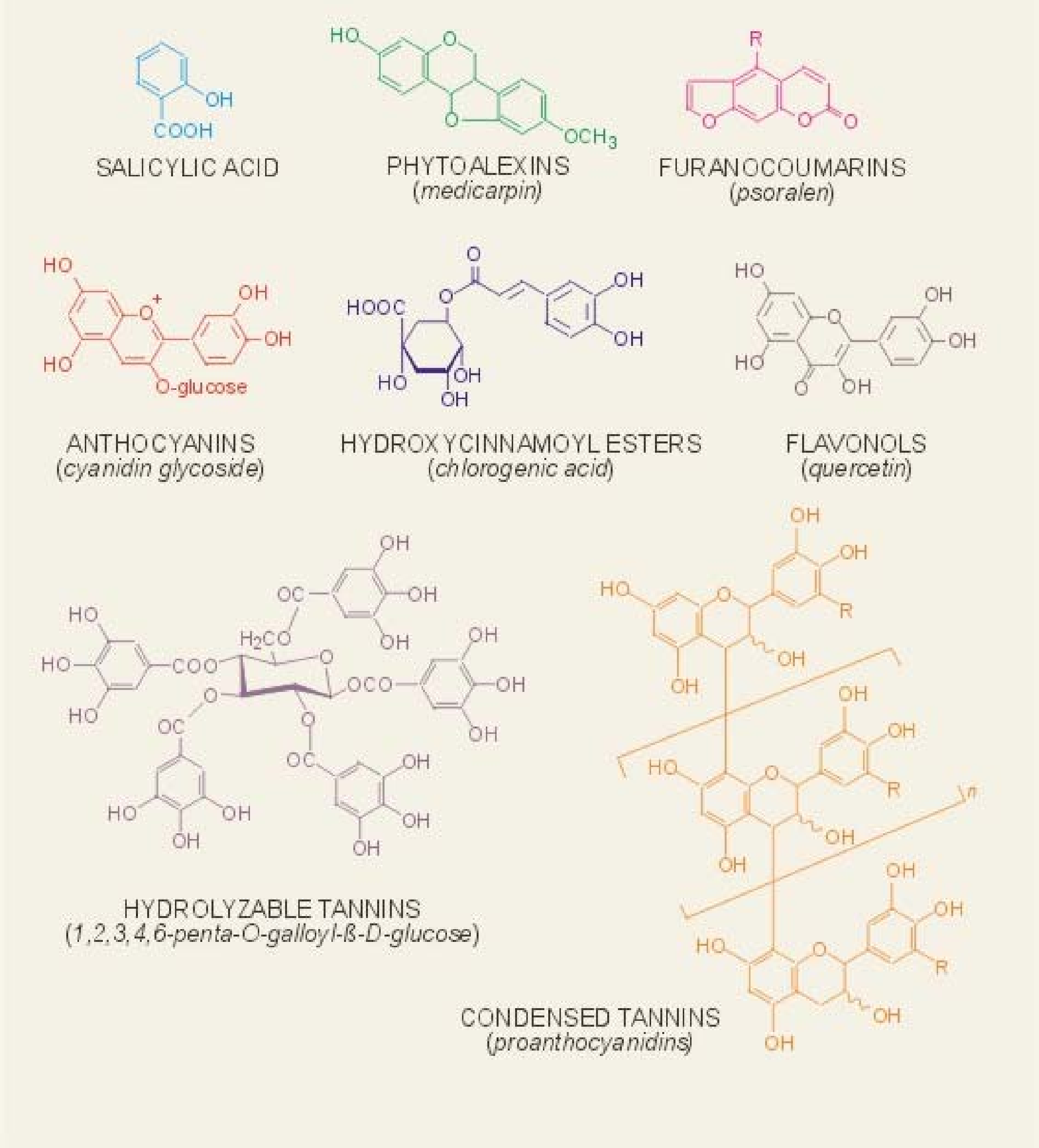
<u>They can be:</u>

Simple, low molecular weight, single aromatic ringed compounds

TO-

Large and complex-polyphenols

The Plant phenolic compounds



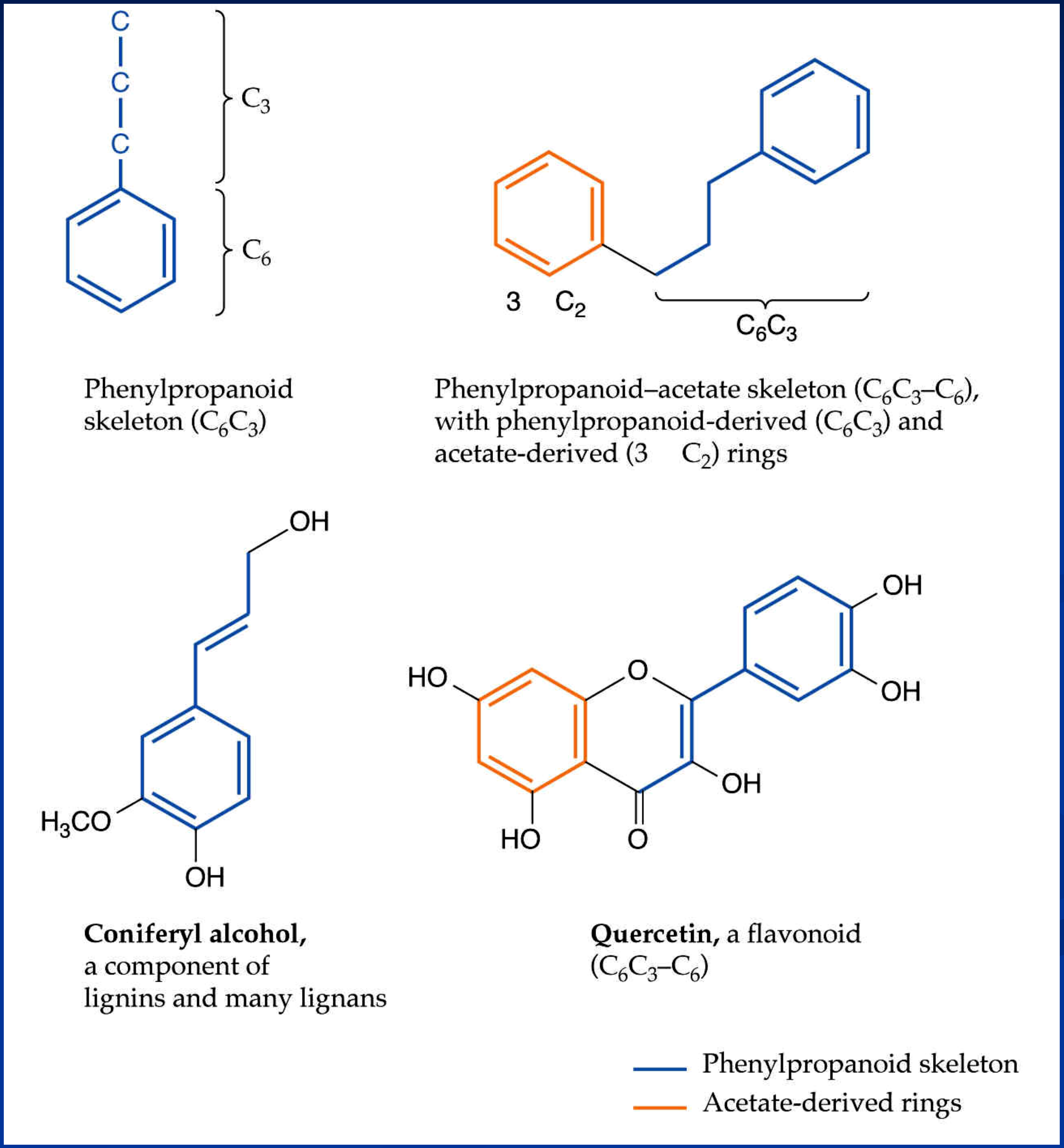
The plant phenolic compounds

- Primarily derived from the:

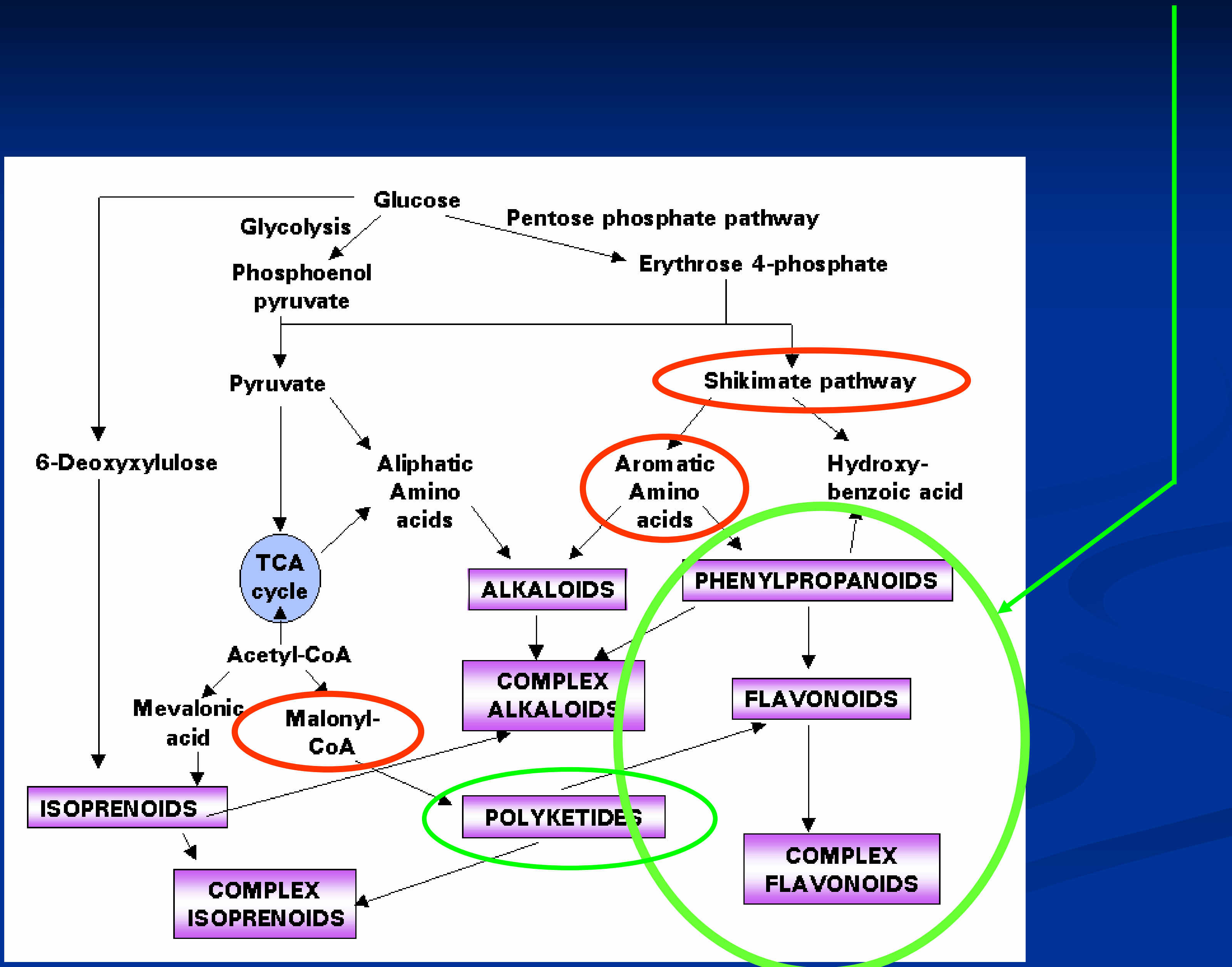
Phenylpropanoid pathway and acetate pathway

(and related pathways)

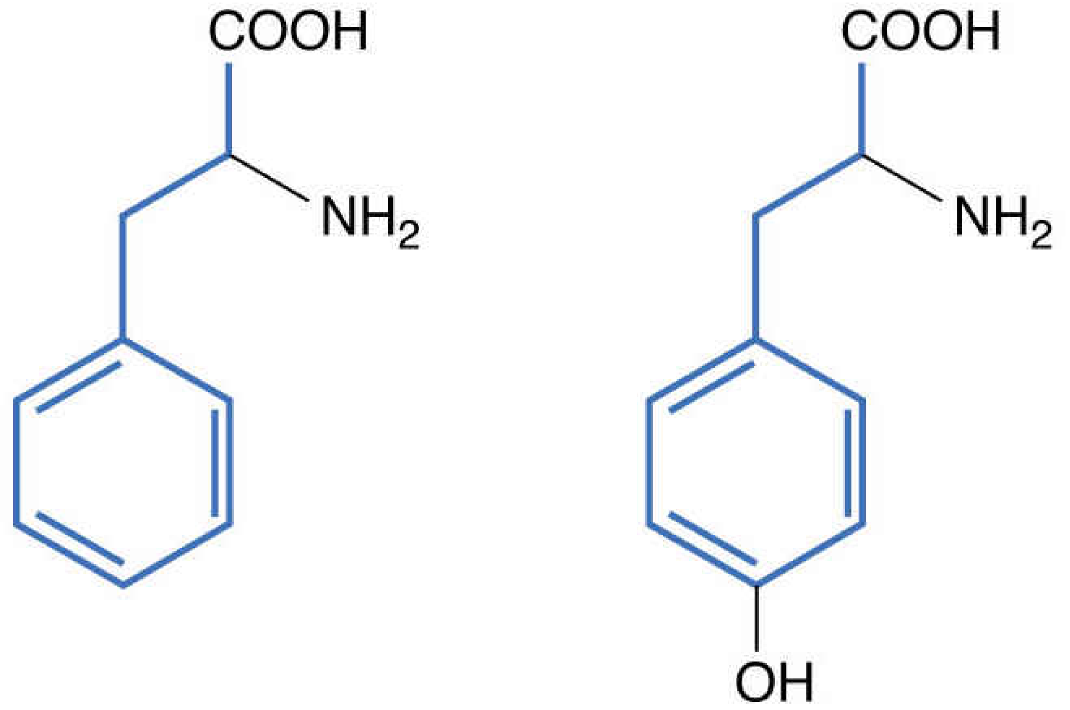
Phenylpropanoid pathway and phenylpropanoid-acetate pathway



Precursors for plant phenolic compounds

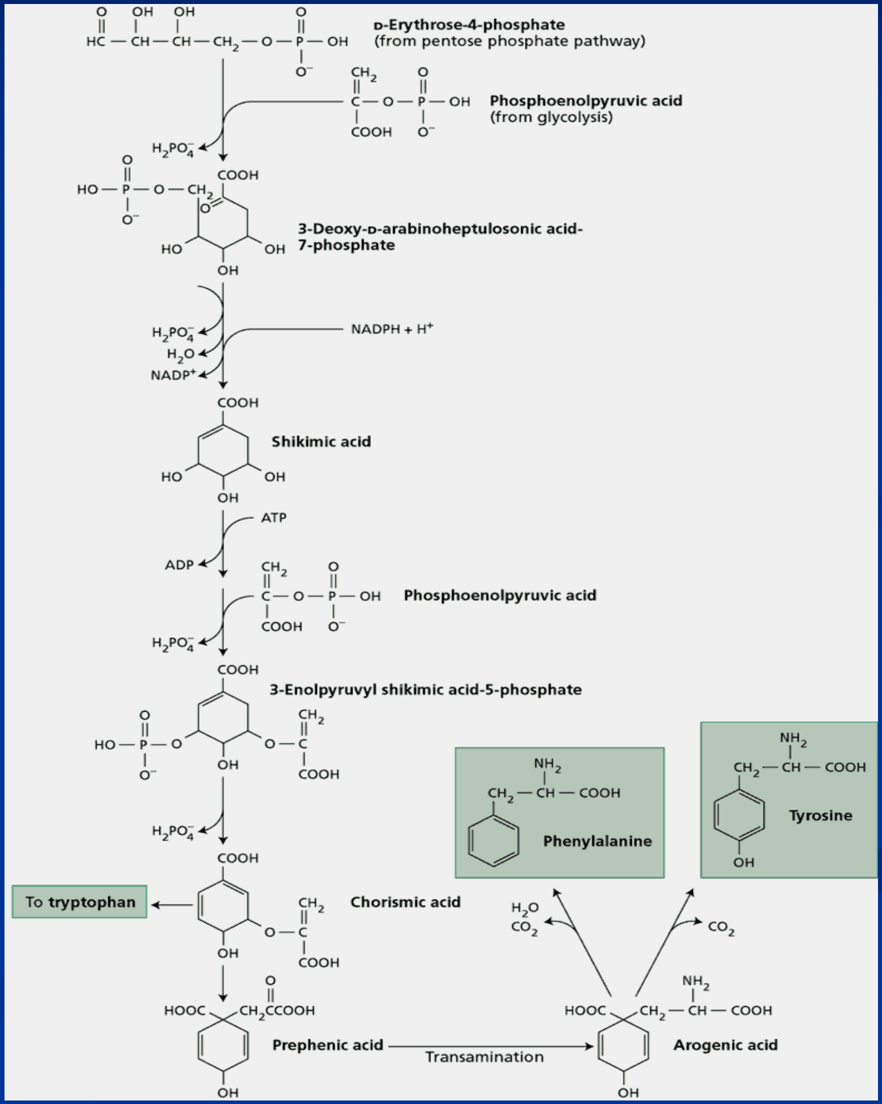


The phenylpropanoids: products of the shikimic acid pathway



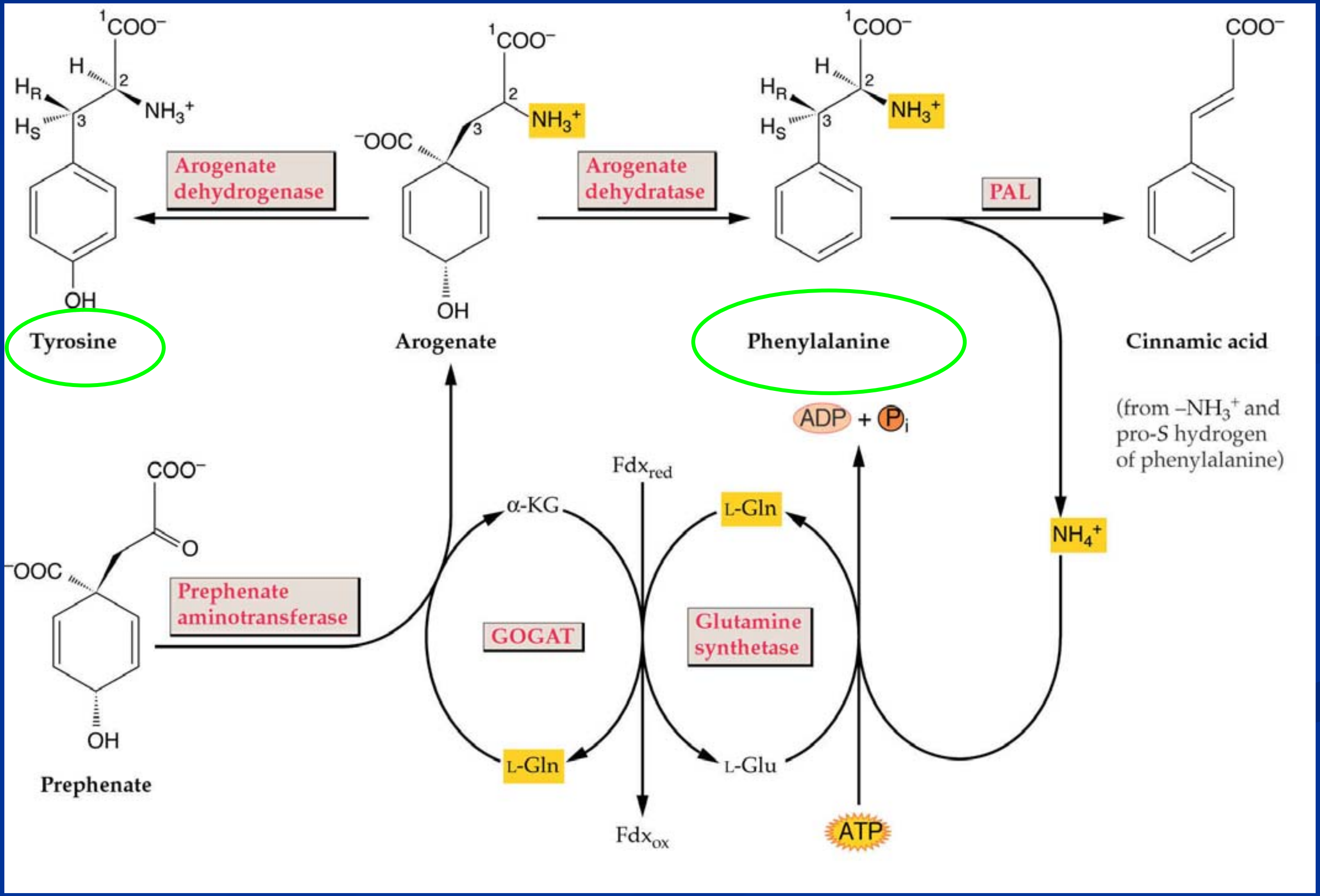
Phenylalanine **Tyrosine**

The phenylpropanoids: products of the shikimic acid pathway (phe and tyr)



THE PHENYLPROPANOIDS: PRODUCTS OF THE SHIKIMIC ACID PATHWAY (phe & tyr)

The shikimate pathway



The plant phenolic compounds

- As in other cases of SMs, branches of pathway leading to biosynthesis of phenols are found or amplified only in specific plant families

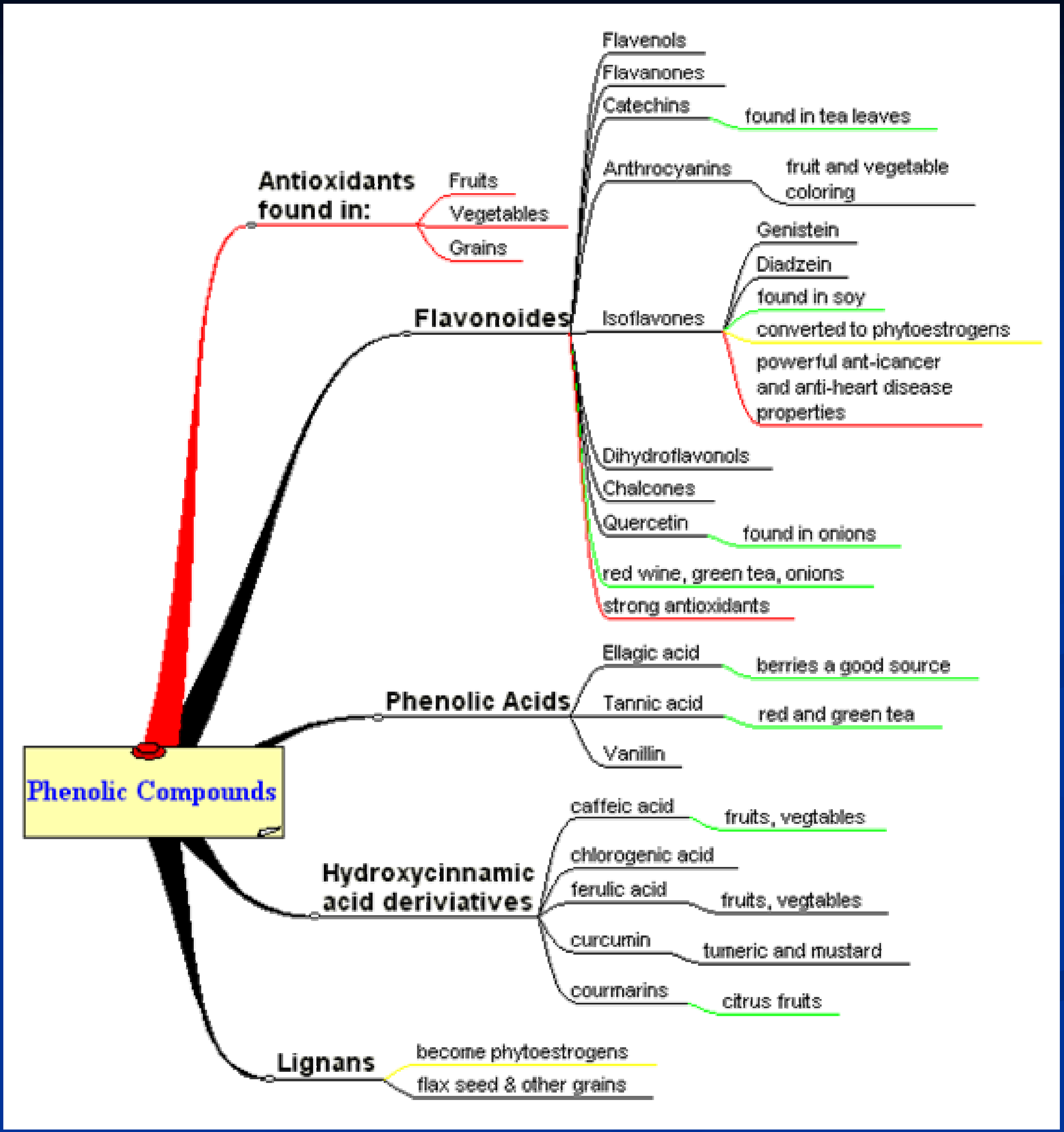
- Commonly found conjugated to sugars and organic acids

The plant phenolic compounds

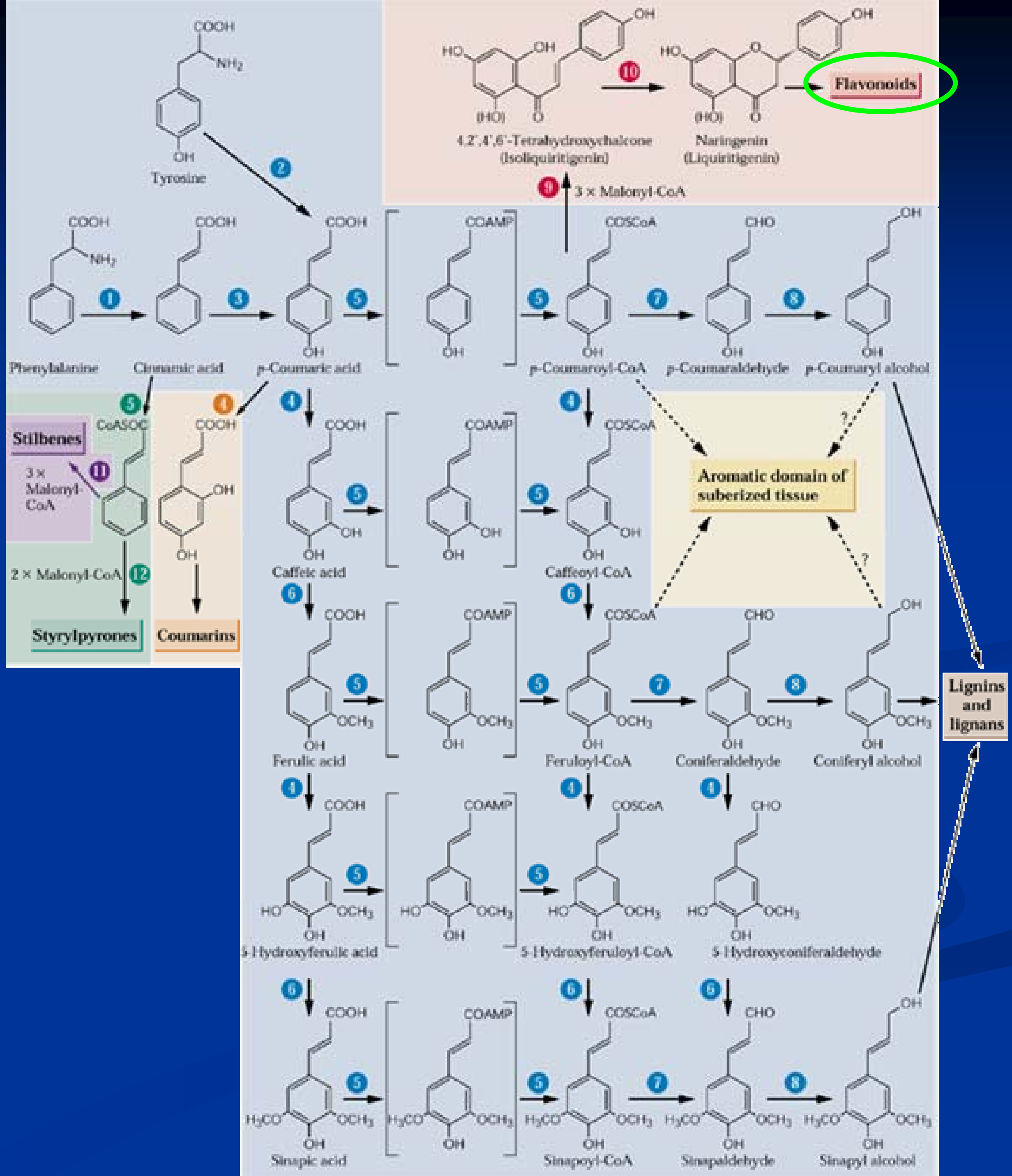
Phenolics can be classified into 2 groups:

1. The FLAVONOIDS

2. The NON-FLAVONOIDS


Phenolic Compounds
Antioxidants found in:
Fruits
Vegetables
Grains
Flavonoides
Flavenols
Flavanones
Catechins
found in tea leaves
Anthrocyanins
fruit and vegetable coloring
Isoflavones
Genistein
Diadzein
found in soy
converted to phytoestrogens
powerful ant-icancer and anti-heart disease properties
Dihydroflavonols
Chalcones
Quercetin
found in onions
red wine, green tea, onions
strong antioxidants
Phenolic Acids
Ellagic acid
berries a good source
Tannic acid
red and green tea
Vanillin
Hydroxycinnamic acid deriviatives
caffeic acid
fruits, vegtables
chlorogenic acid
ferulic acid
fruits, vegtables
curcumin
tumeric and mustard
coumarins
citrus fruits
Lignans
become phytoestrogens
flax seed & other grains

The plant phenolic compounds

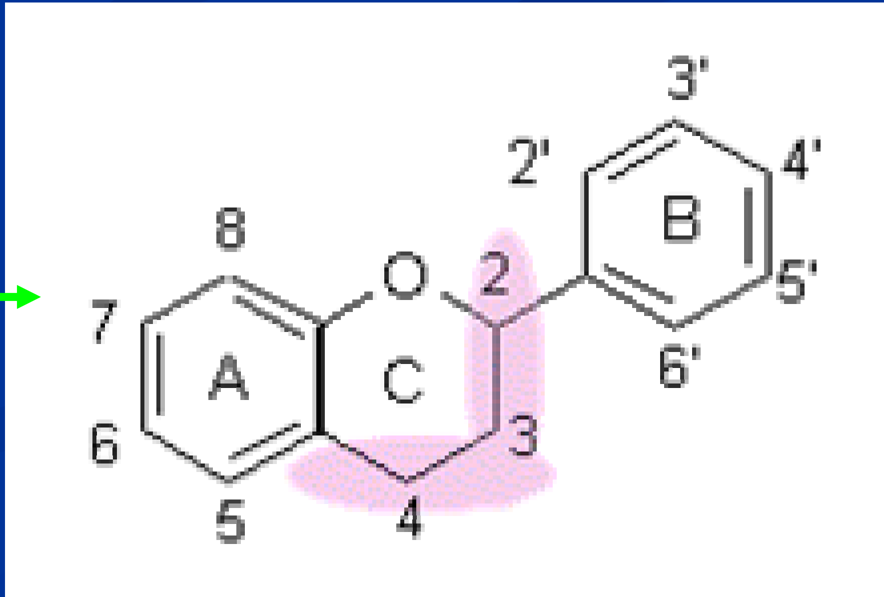


THE FLAVONOIDS

- Polyphenolic compounds
- Comprise:

15 carbons + 2 aromatic rings connected with a 3 carbon bridge

The Flavane Nucleus



THE FLAVONOIDS

- Largest group of phenols: 4500

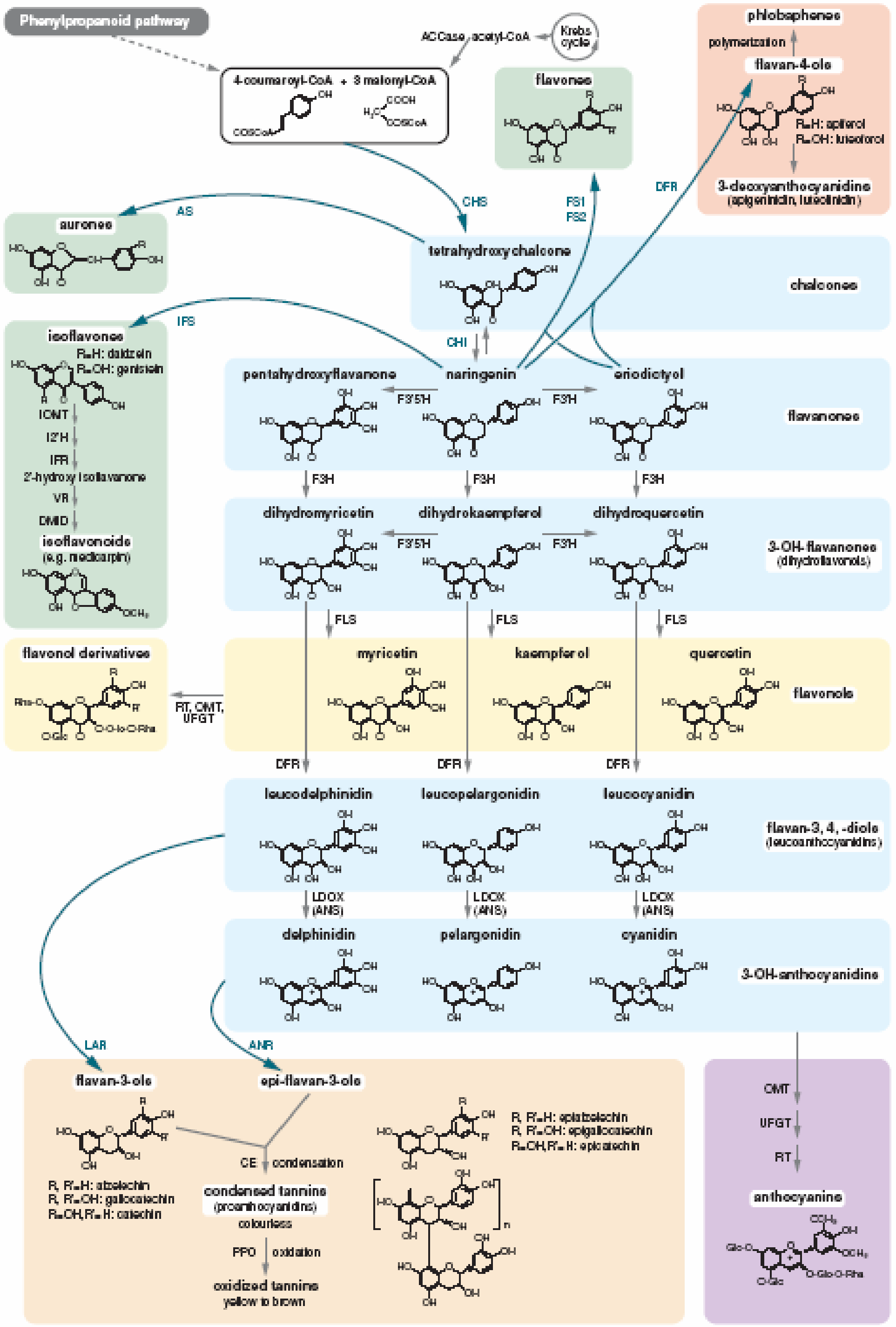
- Major role in plants: color, pathogens, light stress

- Very often in epidermis of leaves and fruit skin

- Potential health promoting compounds- antioxidants

- A large number of genes known

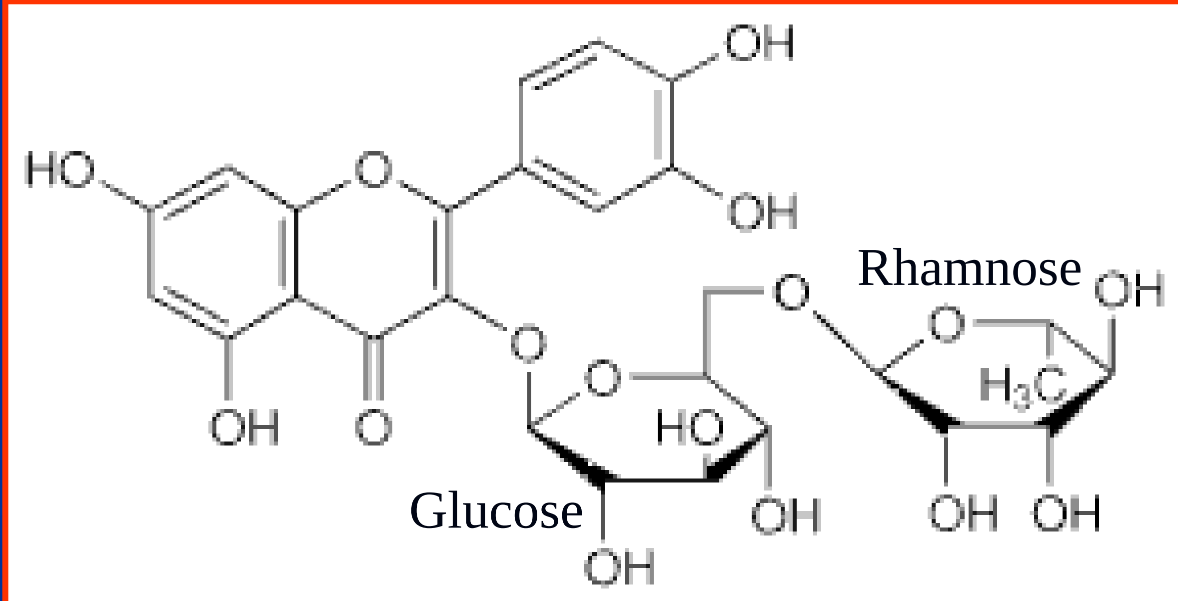
THE Flavonoids-classes



Lepiniec et al., 2006

THE Flavonoids

- The basic flavonoid skeleton can have a large number of substitutions on it:
- Hydroxyl groups
- Sugars - e.g. glucose, galactose, rhamnose. most structures are glycosylated
- Methylated
- Prenylated (farnesylated)
- Acylated



THE Flavonoids

- Sugars and hydroxyl groups increase the water solubility of flavonoids

- Methyl and isopentyl groups make flavonoids lipophilc

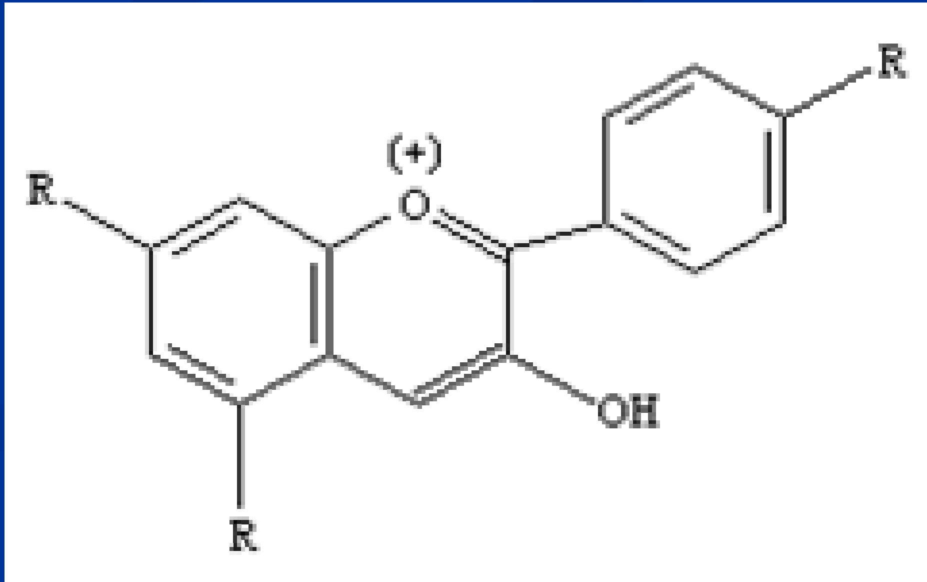
- If no sugar- AGLYCONE
- With sugar- GLYCOSIDE

Anthocyanins, Carotenoids, Chlorophylls

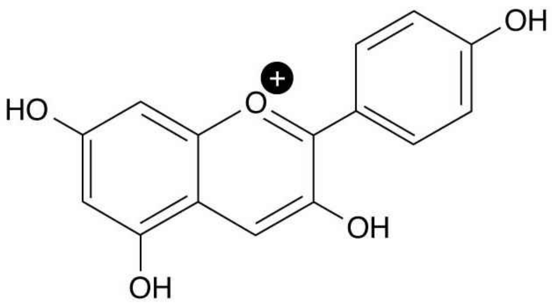
Anthocyanidins

- A positive charge the C ring

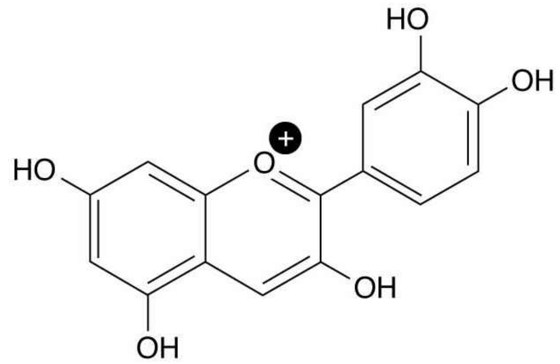
- Two double bonds in the C ring



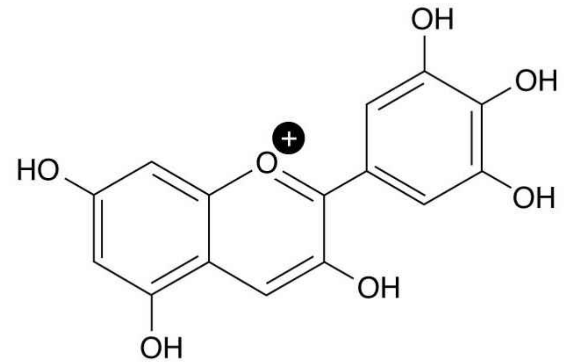
Anthocyanidins



Pelargonidin



Cyanidin



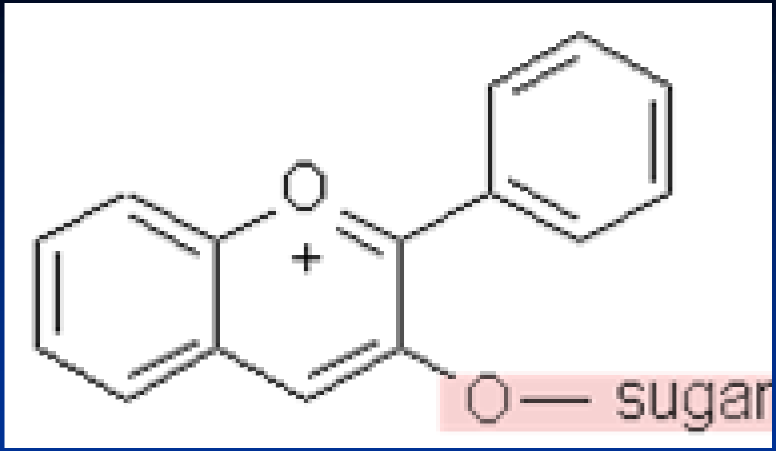
Delphinidin

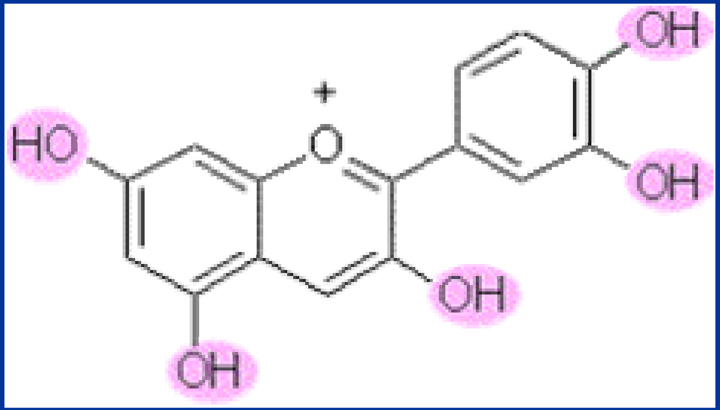
Pelargonium
(Geranium)

Rosa
(Rose)

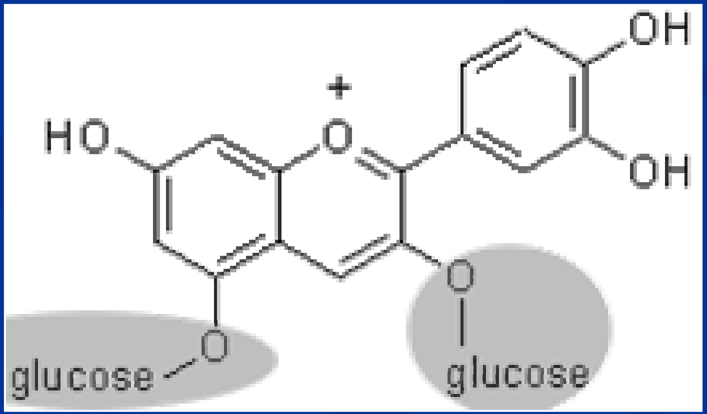
Delphinium
(Larkspur)

Anthocyanines





Cyanidin



Cyanin

Anthocyanidins

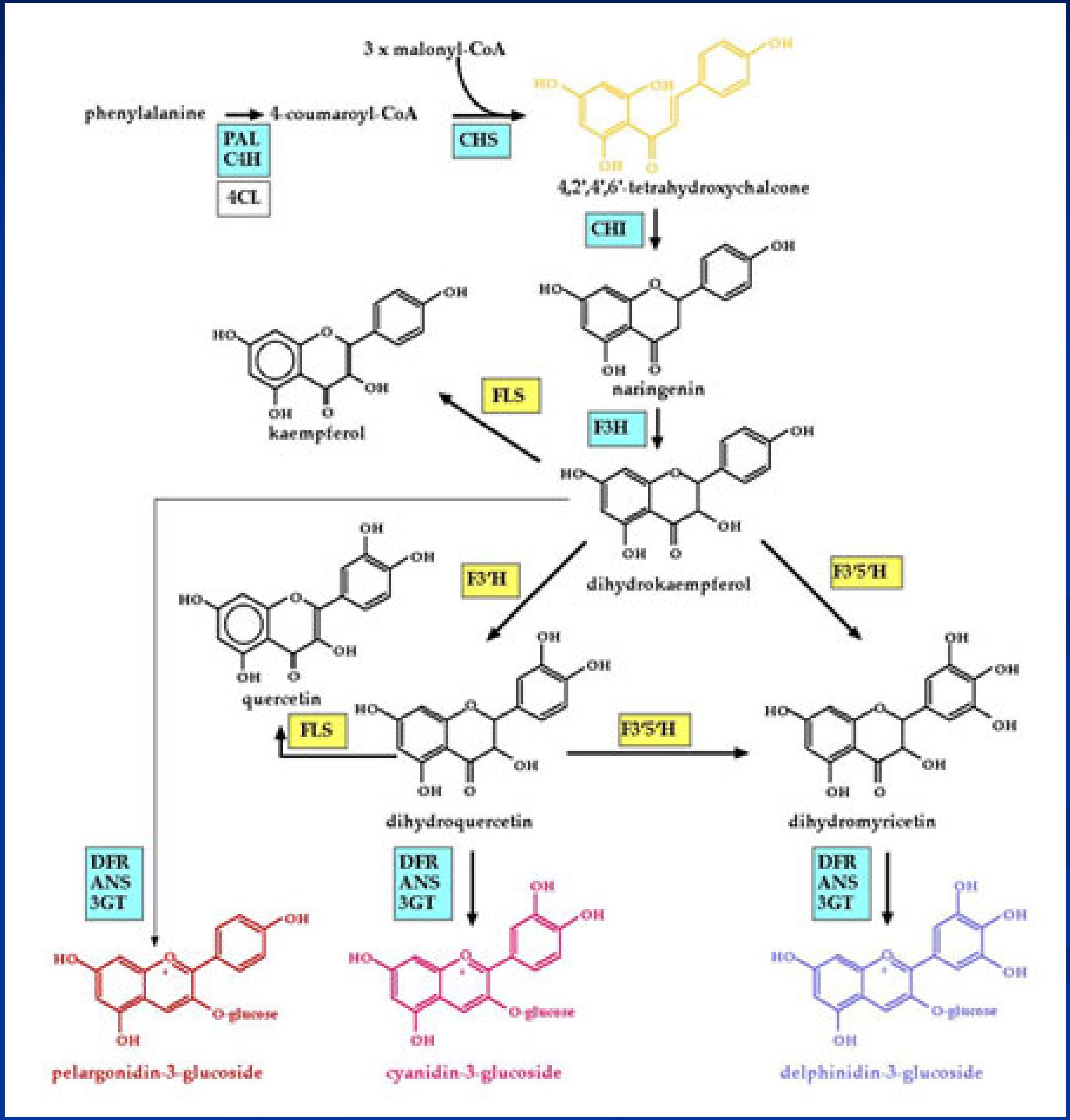
Anthocyanidin	R_1	R_2	R_3	R_4	R_5	R_6	R_7	main colour
Apigeninidin	-H	-OH	-H	-H	-OH	-H	-OH	orange
Aurantinidin	-H	-OH	-H	-OH	-OH	-OH	-OH	orange
Capensinidin	$-OCH_3$	-OH	$-OCH_3$	-OH	$-OCH_3$	-H	-OH	bluish-red
Cyanidin	-OH	-OH	-H	-OH	-OH	-H	-OH	magenta
Delphinidin	-OH	-OH	-OH	-OH	-OH	-H	-OH	purple, blue
Europinidin	$-OCH_3$	-OH	-OH	-OH	$-OCH_3$	-H	-OH	bluish red
Hirsutidin	$-OCH_3$	-OH	$-OCH_3$	-OH	-OH	-H	$-OCH_3$	bluish-red
Luteolinidin	-OH	-OH	-H	-H	-OH	-H	-OH	orange
Pelargonidin	-H	-OH	-H	-OH	-OH	-H	-OH	orange, salmon
Malvidin	$-OCH_3$	-OH	$-OCH_3$	-OH	-OH	-H	-OH	purple
Peonidin	$-OCH_3$	-OH	-H	-OH	-OH	-H	-OH	magenta
Petunidin	-OH	-OH	$-OCH_3$	-OH	-OH	-H	-OH	purple
Pulchellidin	-OH	-OH	-OH	-OH	$-OCH_3$	-H	-OH	bluish-red
Rosinidin	$-OCH_3$	-OH	-H	-OH	-OH	-H	$-OCH_3$	red
Triacetidin	-OH	-OH	-OH	-H	-OH	-H	-OH	red

Anthocyanins- Fruit color

Anthocyanins- Flower color

Anthocyanins- leaves and root color

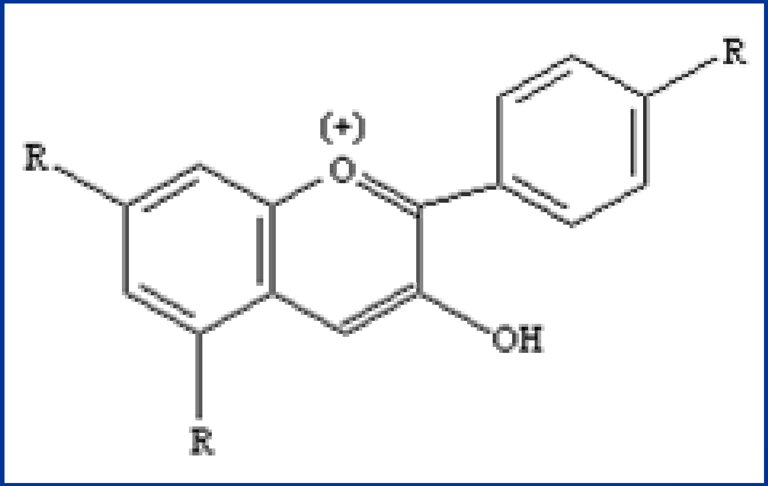
Anthocyanins biosynthesis



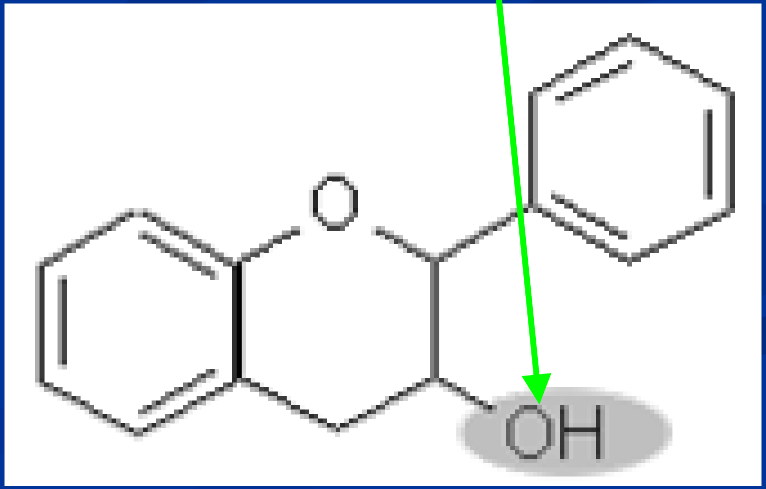
The flavAnols

- Structures are very similar to those of anthocyanidins: But no positive charge on the oxygen atom and no double bonds in the C ring.

Anthocyanidin



One type: Flavan-3-ol

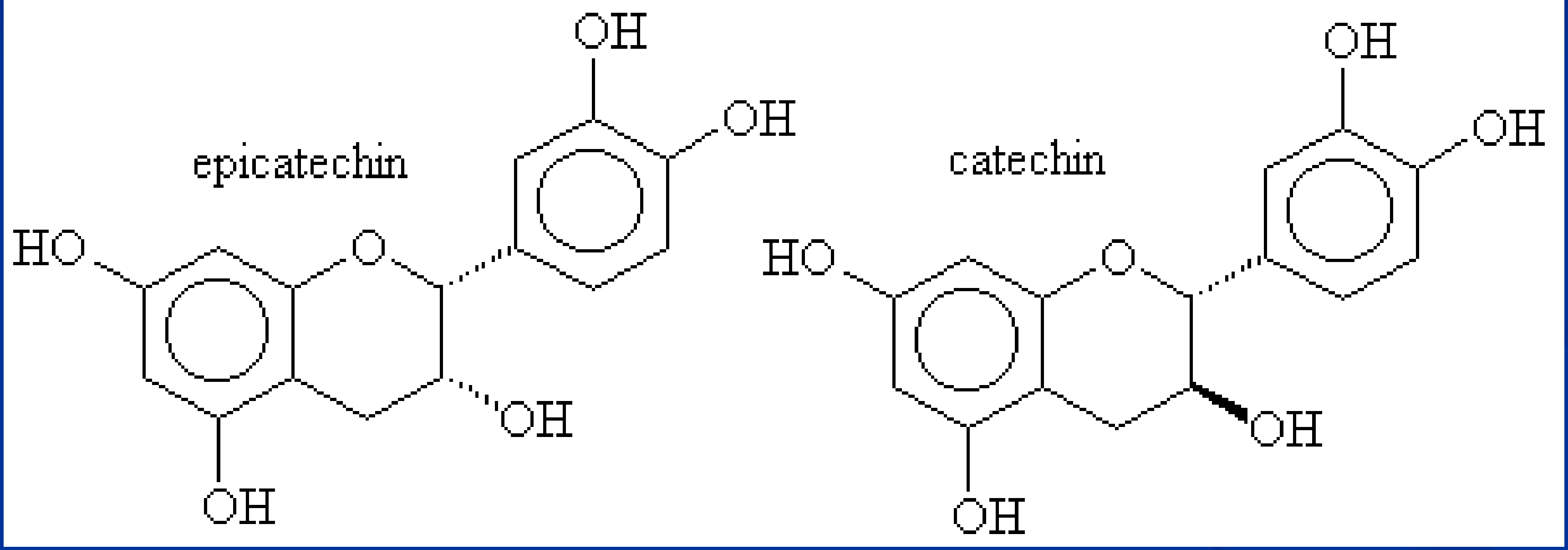


The flavAnols: Catechin & Epicatechin

Catechin-

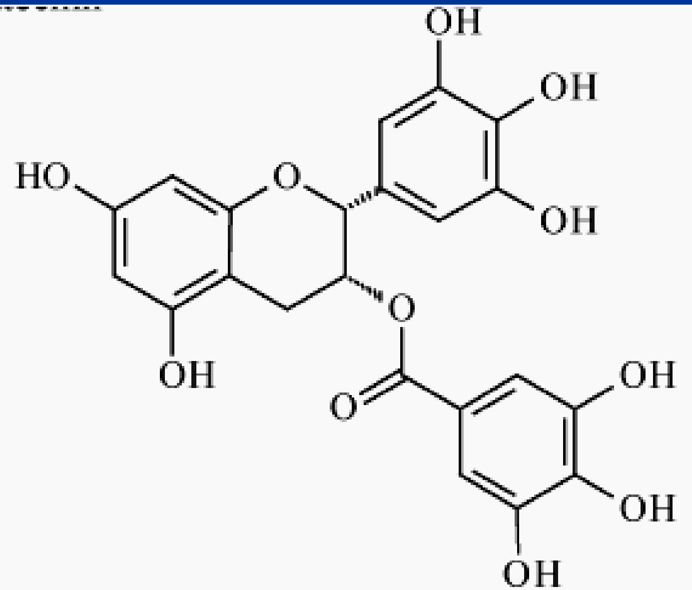
1. A common flavan-3-ol that occurs in many plants.
2. It's found in Green tea, Cocoa powder, Red wine
3. It is also a common subunit of proanthocyanidin polymers such as Procyanidin C2.
4. Epicatechin is another common example; it differs from Catechin only in the spatial orientation of its -OH group.

The flavAnols: Catechin & Epicatechin



The flavAnols in green tea

-Green tea contains high levels of flav-3-ols such as (-) Epigallocatechin gallate



(-) – Epigallocatechin gallate

The flavAnols in green tea

- Flav-3-ols, such as epicatechin, catechin and epigallocatechin (and procyandins their polymers) are:

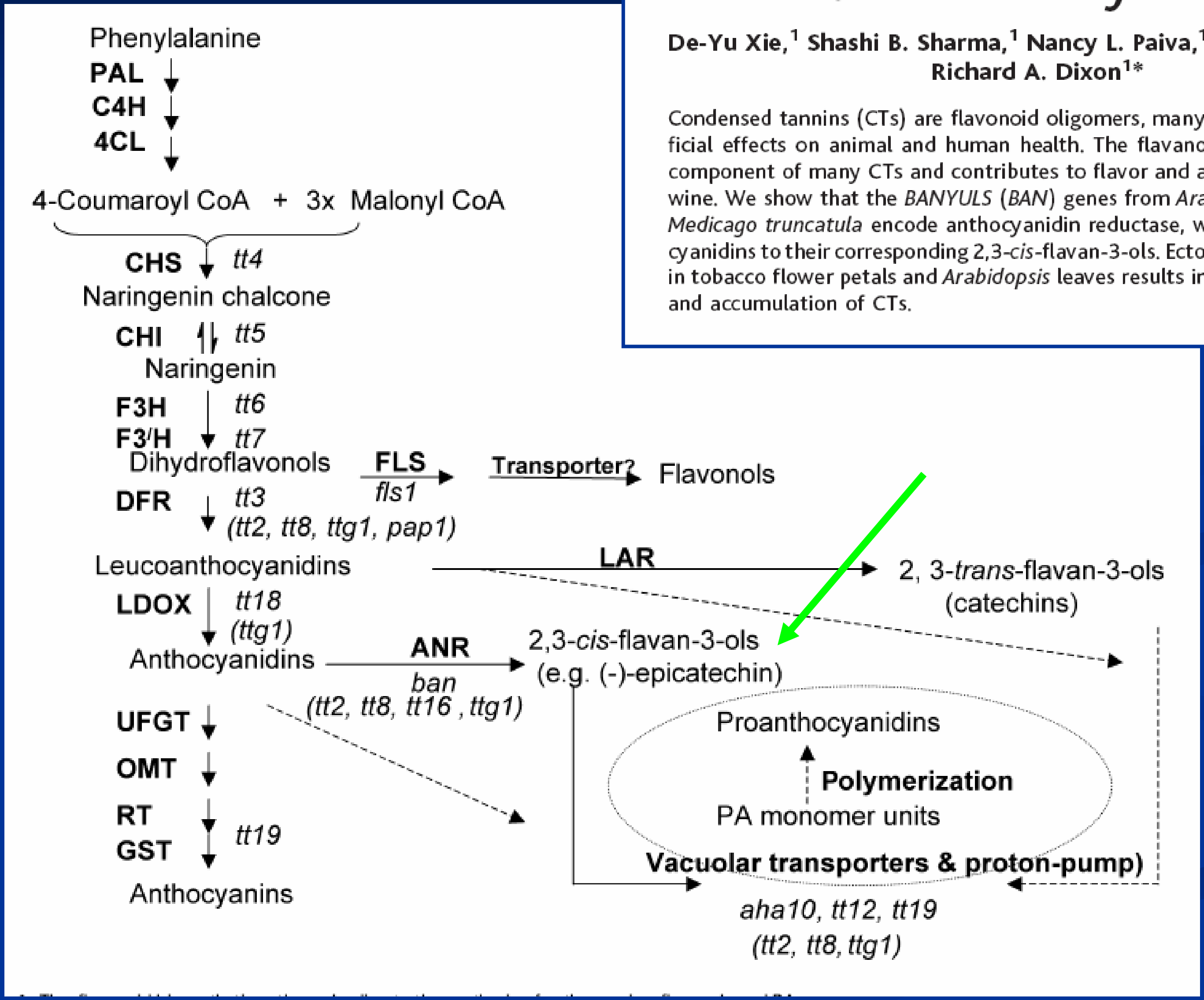
1. Powerful antioxidants
2. Have beneficial effects on cardiac health, immunity and longevity
3. Levels of flav-3-ols decline in roasting

FlavAnols Biosynthesis

Role of Anthocyanidin Reductase, Encoded by *BANYULS* in Plant Flavonoid Biosynthesis

De-Yu Xie,[1] Shashi B. Sharma,[1] Nancy L. Paiva,[1] Daneel Ferreira,[2] Richard A. Dixon[1]*

Condensed tannins (CTs) are flavonoid oligomers, many of which have beneficial effects on animal and human health. The flavanol (–)-epicatechin is a component of many CTs and contributes to flavor and astringency in tea and wine. We show that the *BANYULS* (*BAN*) genes from *Arabidopsis thaliana* and *Medicago truncatula* encode anthocyanidin reductase, which converts anthocyanidins to their corresponding 2,3-*cis*-flavan-3-ols. Ectopic expression of BAN in tobacco flower petals and *Arabidopsis* leaves results in loss of anthocyanins and accumulation of CTs.



(Sharma & Dixon, 2005)

Proanthocyanidines or Condensed Tannins

- Polymers made from multiple flavAnols

- They are called proanthocyanidins because, if broken apart with acid treatment, they yield anthocyanidins such as Cyanidin

- Proanthocyanidin polymers consisting of up to 50 subunits

- Oligomeric proanthocyanidins (OPCs) are the water-soluble, short-chain polymers

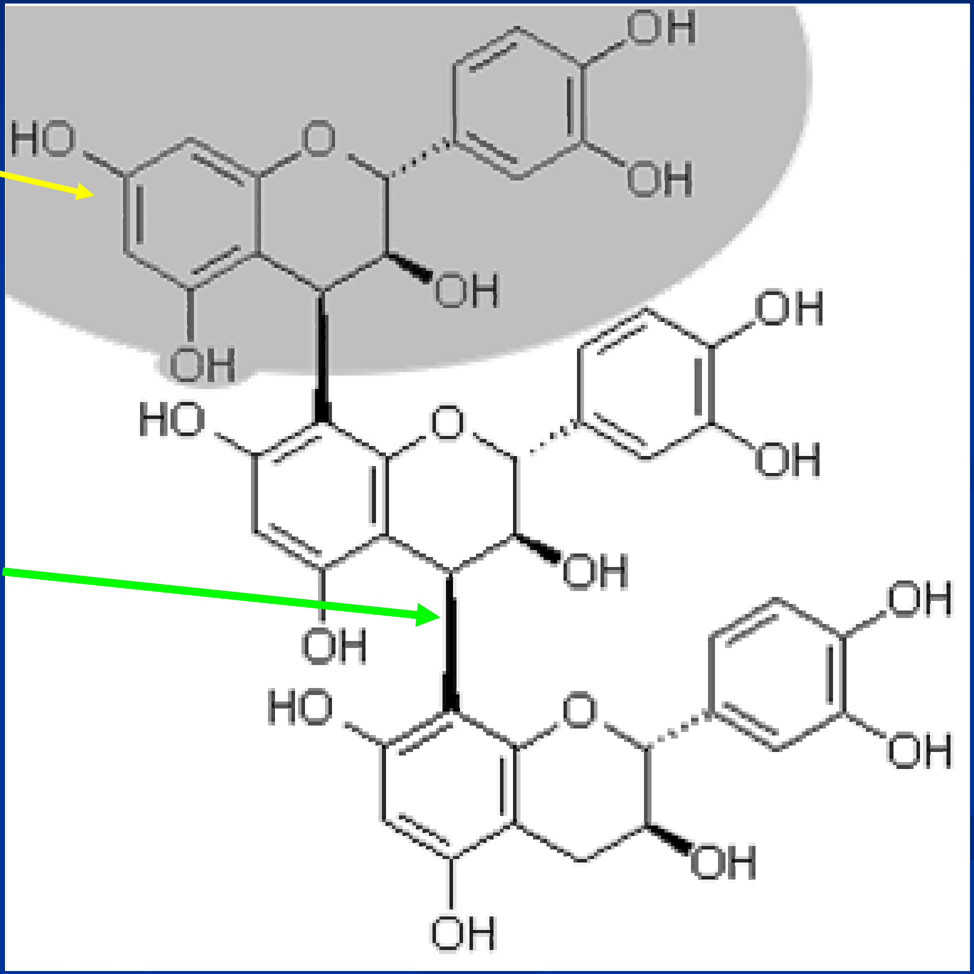
Proanthocyanidines or Condensed Tannins

- Sometimes referred to as "condensed tannins"
- Responsible for astringency in many foods and medicinal herbs
- Red wine contains many complex proanthocyanidins (extracted from grape skins and seeds); so do blueberries, blackberries, strawberries, elderberries, and other red/blue/purple colored plant parts

Type-B proanthocyanidins (formed from -epicatechin and + catechin)

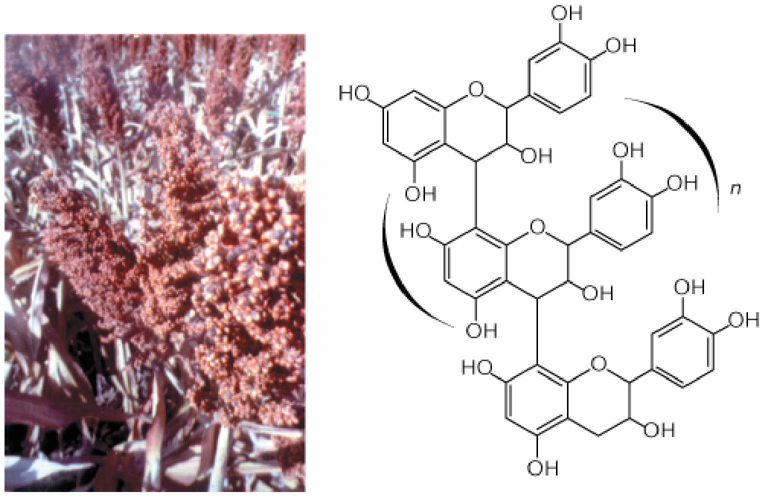
Catechin subunit

Oxidative coupling between C-4 of the heterocycle and the C-6 or C-8 positions of the adjacent unit



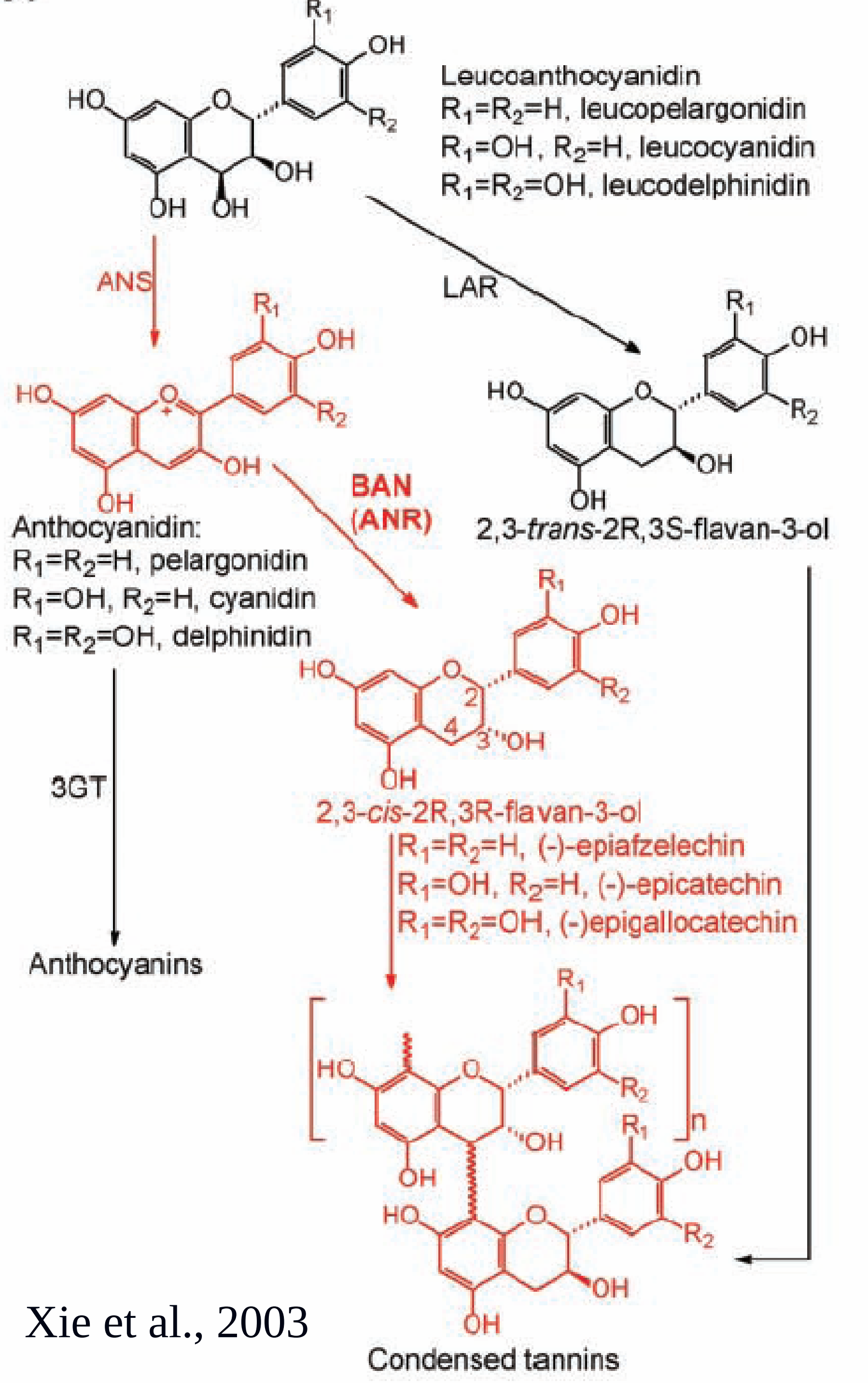
Type-B proanthocyanidins (formed from - epicatechin and + catechin)

- Antifeedant proanthocyanidin in red sorghum
- These condensed tannins deter birds from feeding on the seed
- White sorghum deficient in these compounds is eaten by birds



Red sorghum   Proanthocyanidin (n = 1–30)

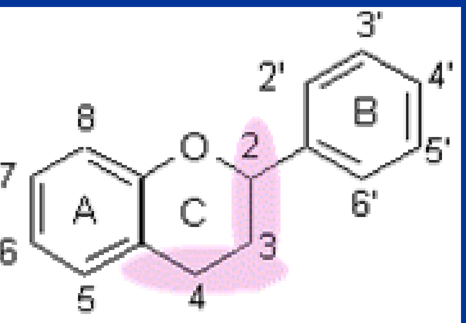
Proanthocyanidins (or condensed tannins) Biosynthesis

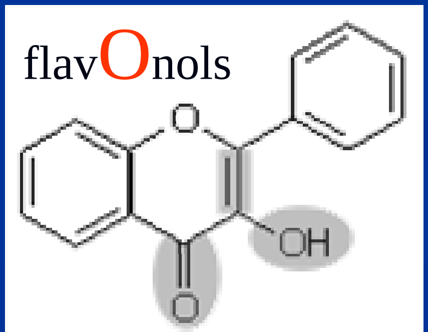


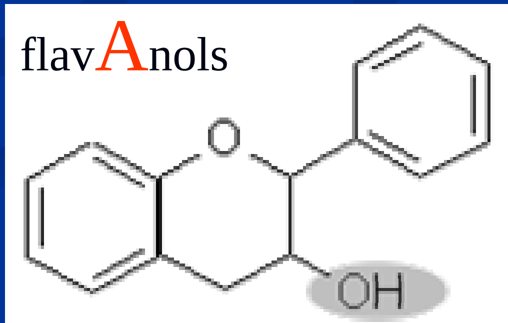
Xie et al., 2003

The FlavOnols

- The molecule has a double-bonded oxygen atom attached to position 4 (that’s why flavOnols).
- They're still "-ols" because they retain the -OH group at position 3 like the flavAnols
- The double-bonded oxygen atom, makes them like another class of flavonoids known as "flavones" (next)
- Double bond in between C2 and C3 (C ring)
- Involved in UV screening, due to their strong absorbance in UV-A (325-400nm) and UV-B (280-325 nm) wavelengths





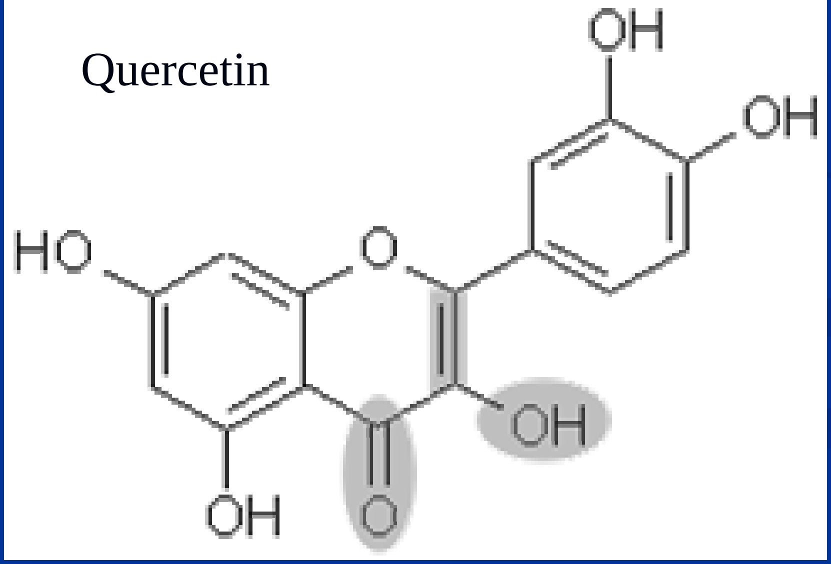


The FlavOnols- Quercetin

- The most abundant flavonol in the diet and is found in hundreds of herbs and foods.

- Onions are especially rich in *Quercetin*.

- It has proven antioxidant effects



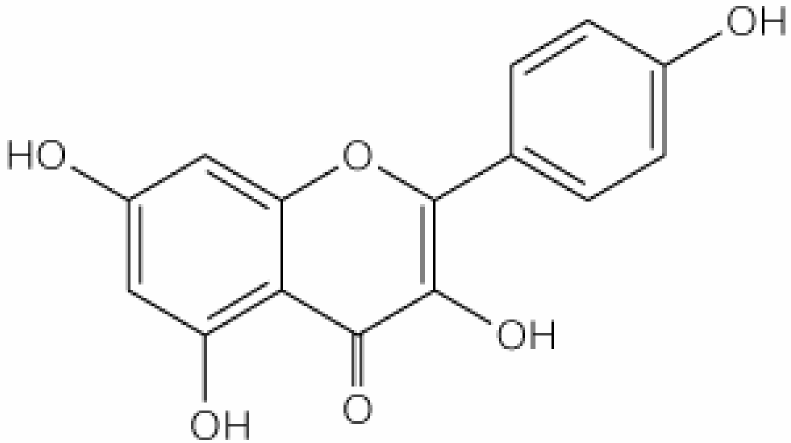
The FlavOnols- Quercetin

- FalvOnols are mostly found as *O*-glycosides

- Aglycons- 300

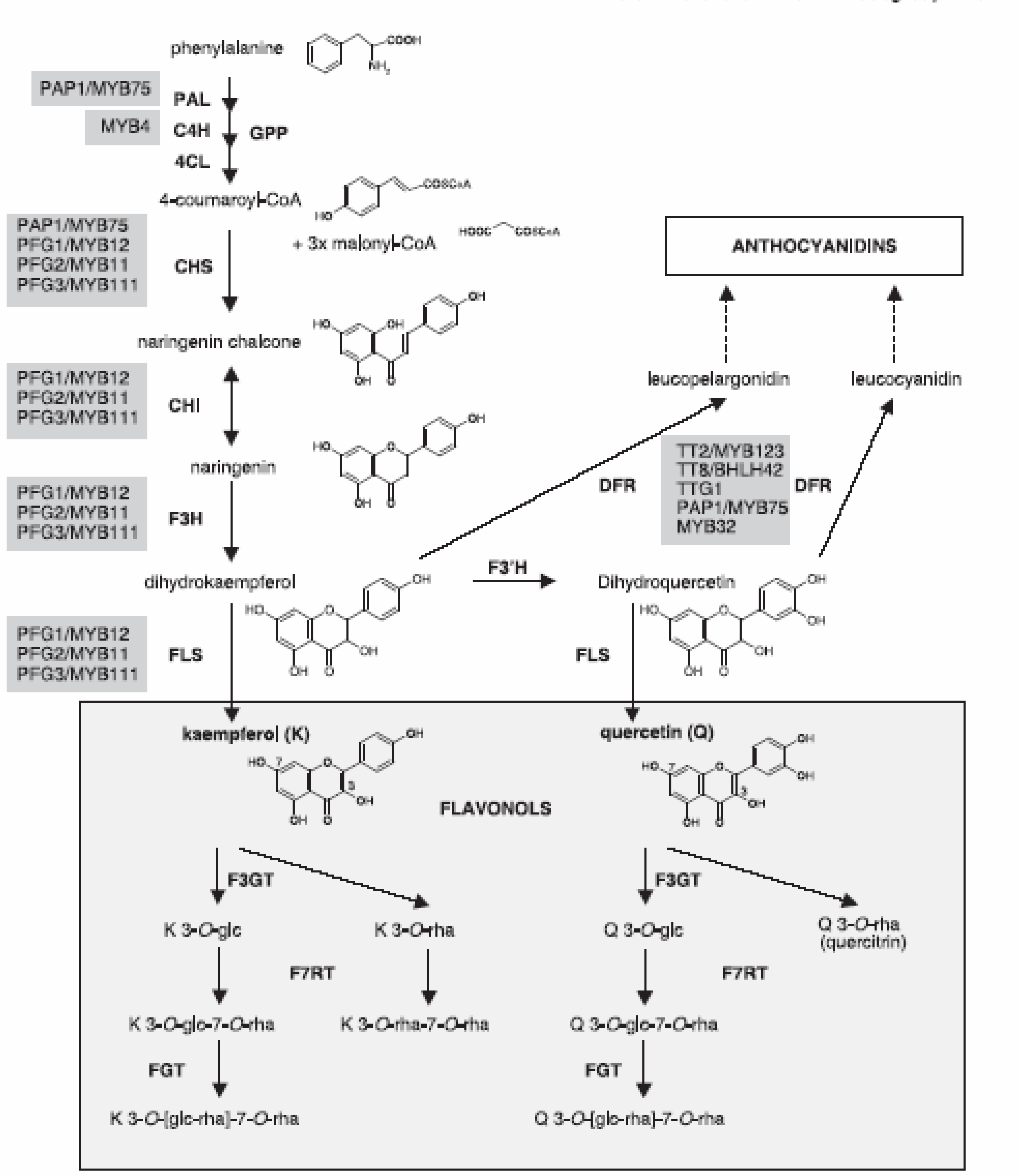
- Total- 1030

- More than 200 different sugar conjugates of Kaempferol !!



Kaempferol

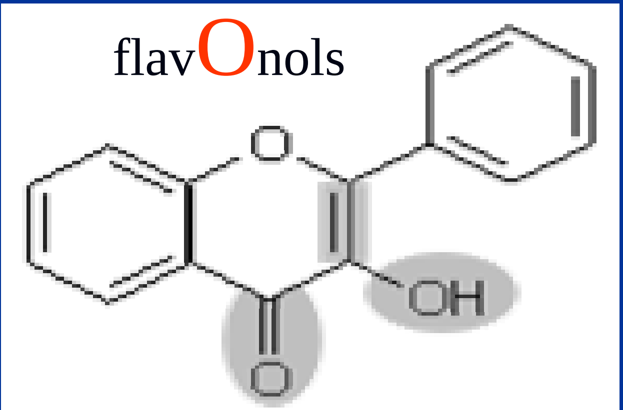
FlavOnols Biosynthesis

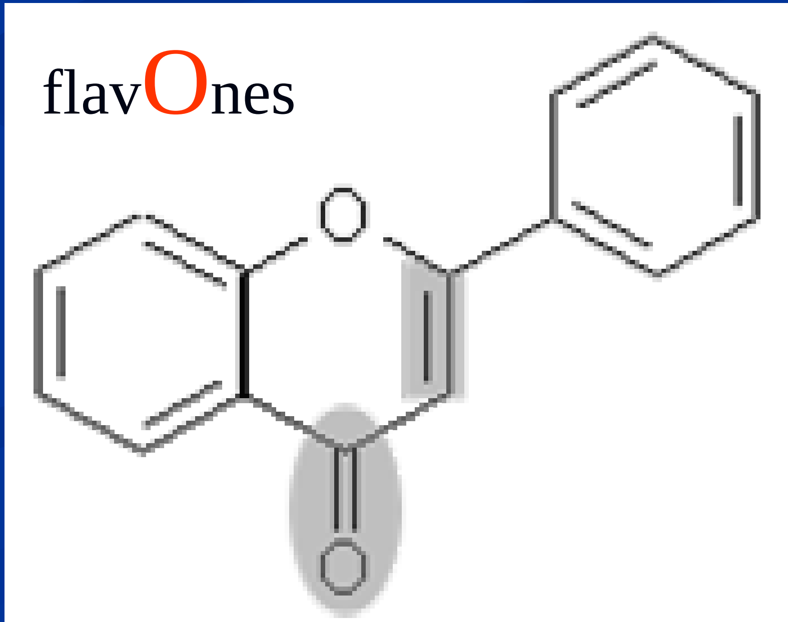


The Flavones

- Close to the flavOnols but not so widespread (celery, parsley and some herbs)

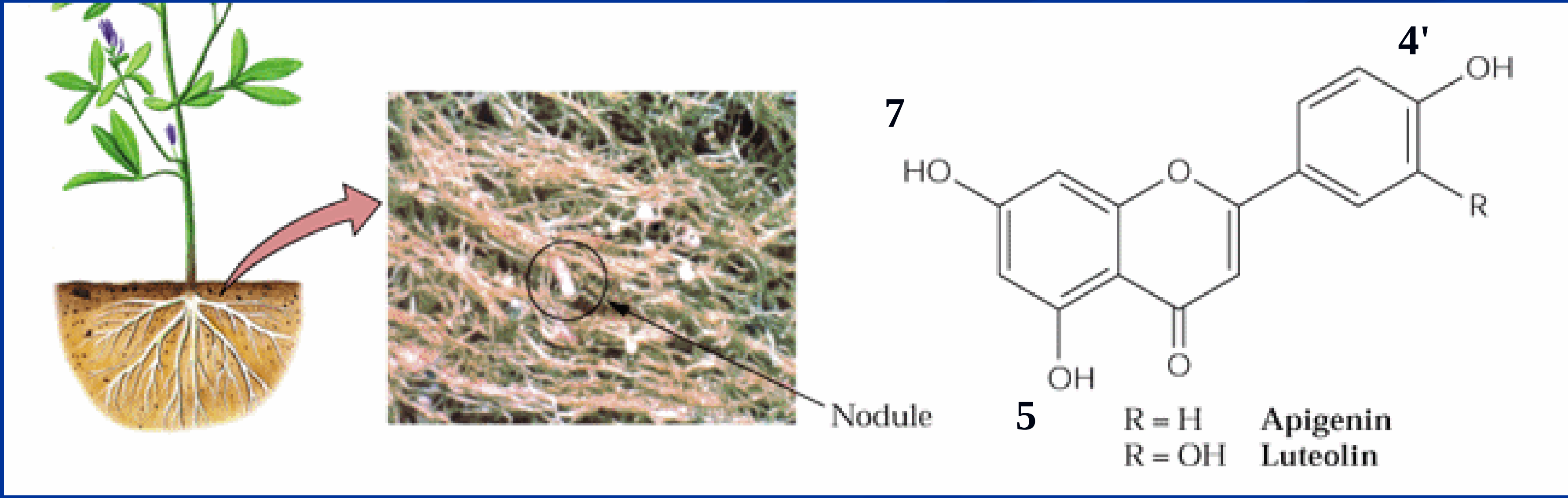
- BUT Without the "-ol." there is no longer an -OH group at position 3 on the central ring





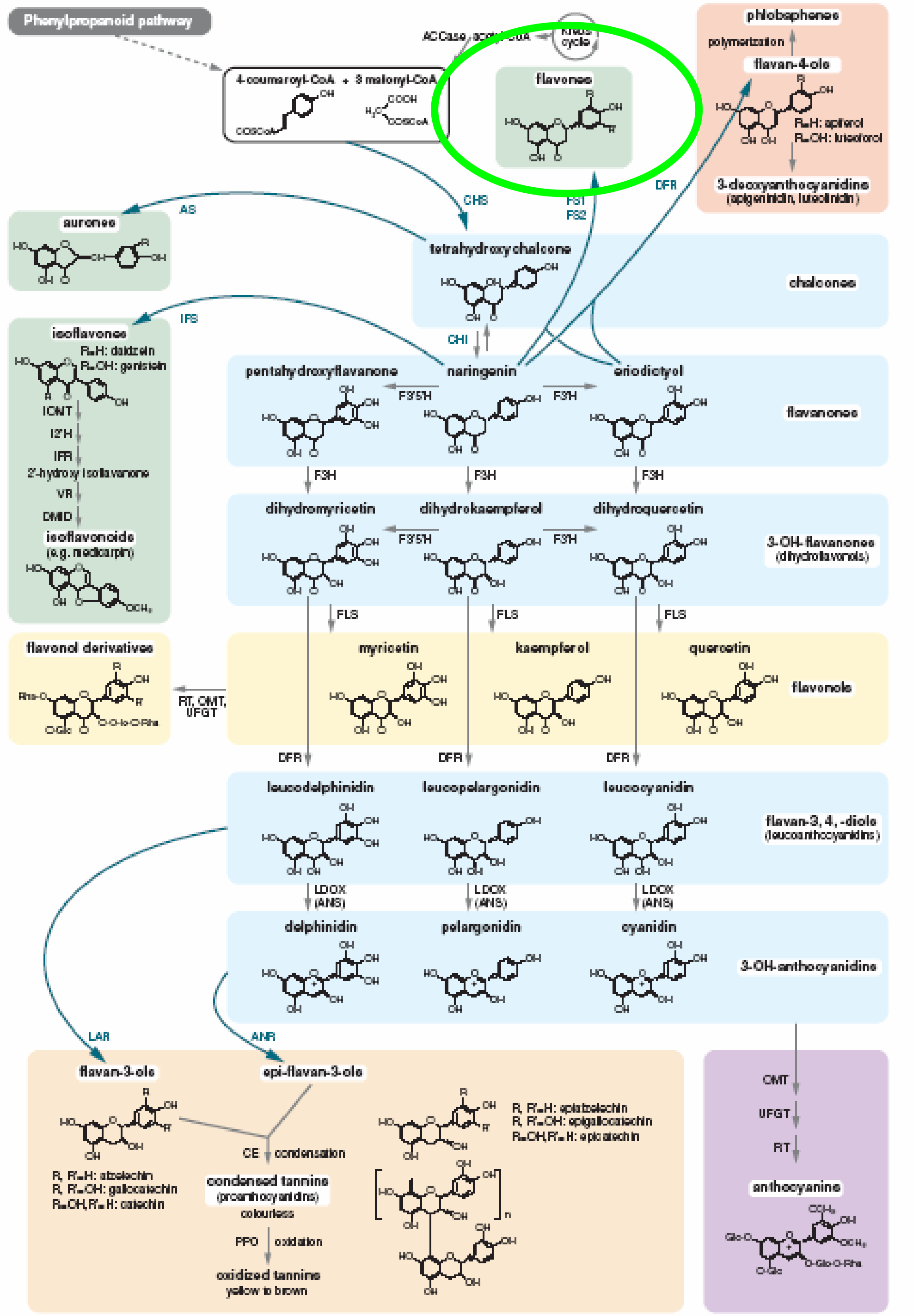
The Flavones- Apigenin

- Apigenin, a flavone with - OH groups added to positions 5, 7, and 4'
- Another flavone is luteolin, found in sweet red peppers
- Both act as signaling molecules that induce NOD factors in compatible interaction with Rhizobium bacteria (nitrogen fixing root nodules) in legumes (e.g. alfalfa)



THE Flavones

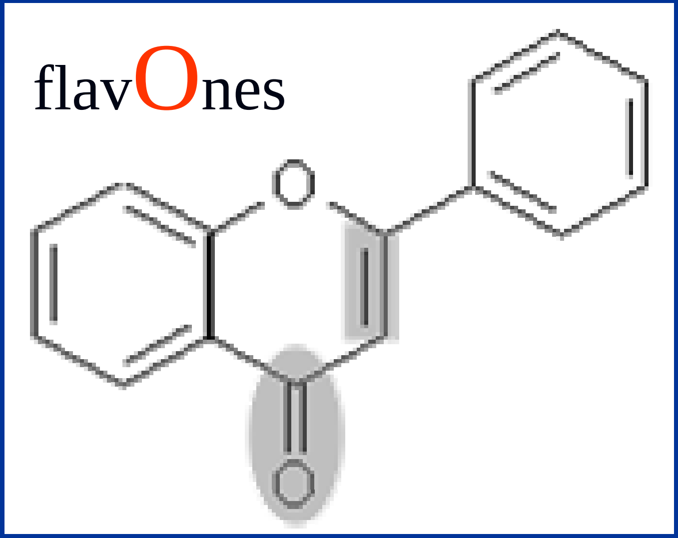
Origenate from the Flavanones (naringenin)

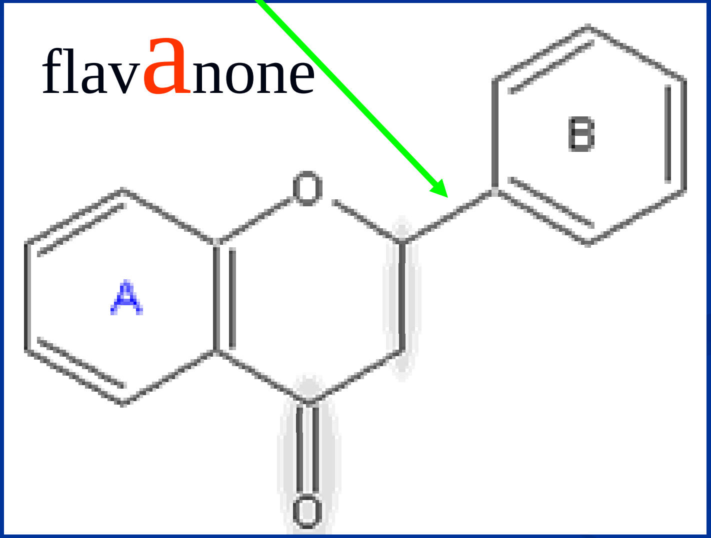


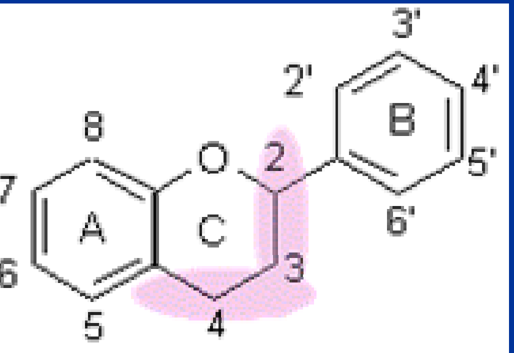
Lepiniec et al., 2006

The Flavanones

- No double bond between carbons 2 and 3 of the flavone structure, and chiral center (C2)
- A highly reactive structure (a lot of substitutions)





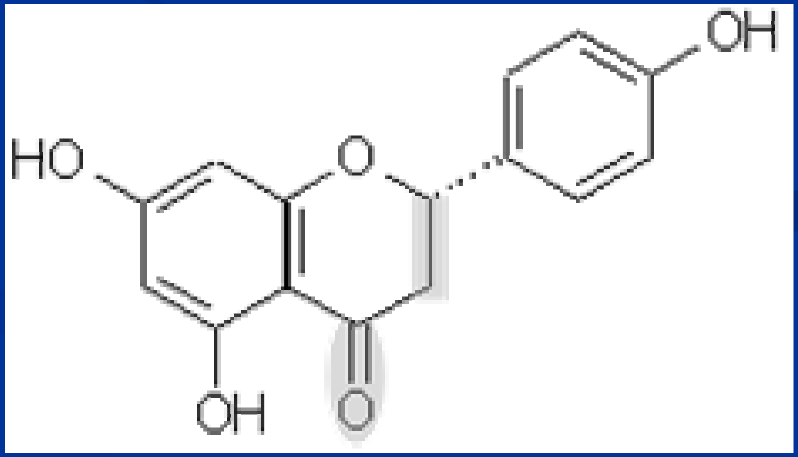


The Flavanones- Naringenin

- An antioxidant flavanone from citrus species

- Has - OH groups attached at positions 5, 7, and 4'

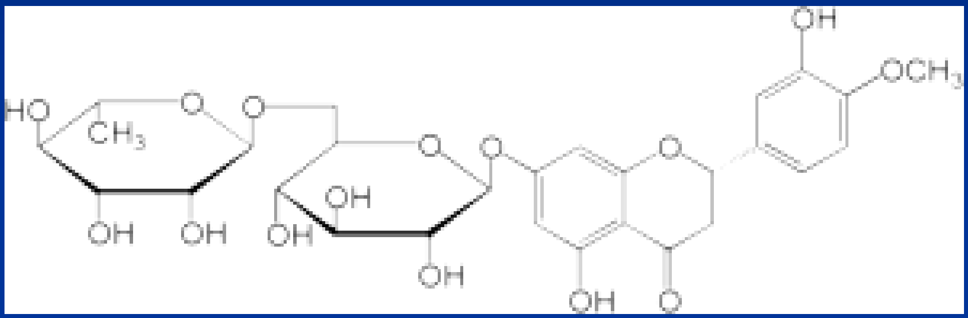
- Studies have indicated that it has anti-inflammatory, anti-cancer, and liver protective effects



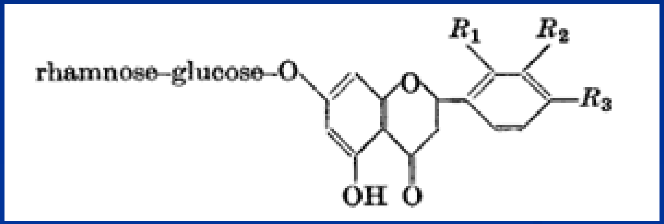

The Flavanones of citrus

The Flavanones- in citrus

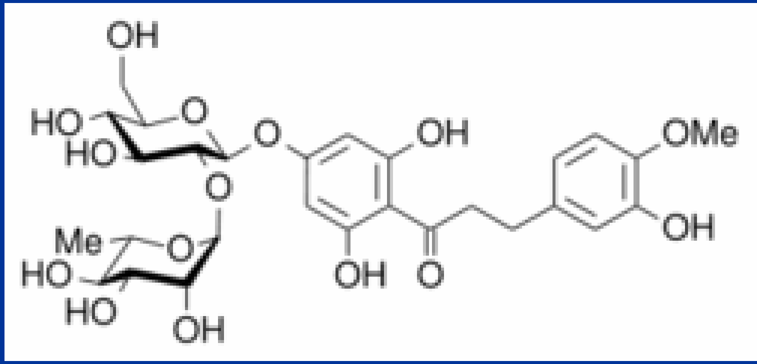
- High concentrations in citrus fruit



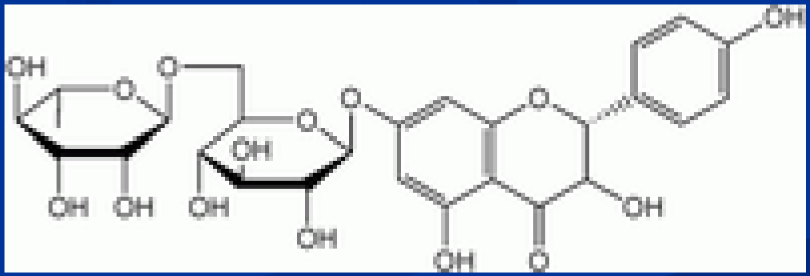
Hesperidin, citrus peel, tasteless



Neohesperidin, bitter orange, intense bitter taste

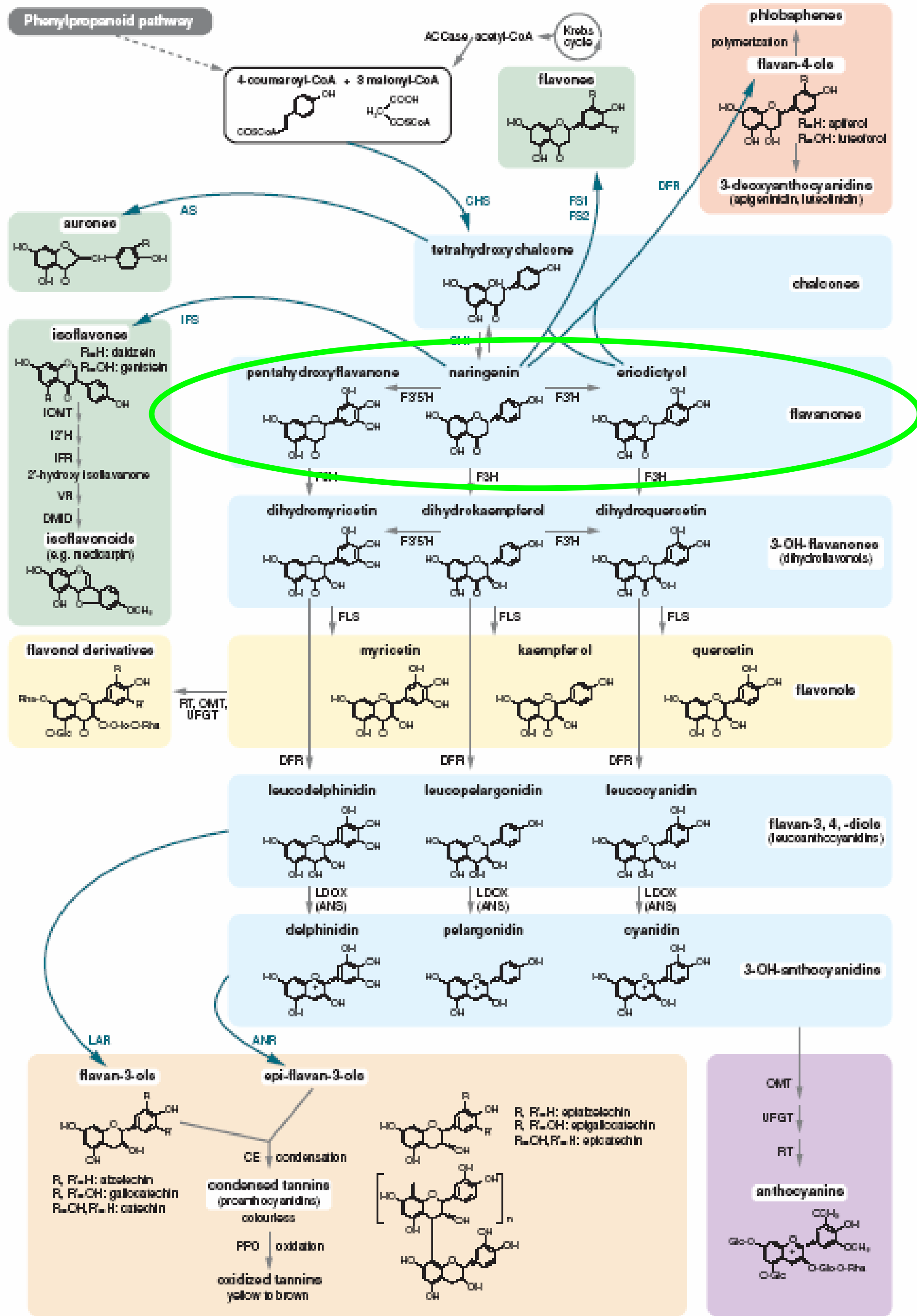


Neohesperidin dihydrochalcon, citrus, arteficial sweetner, in non-alcoholic beers



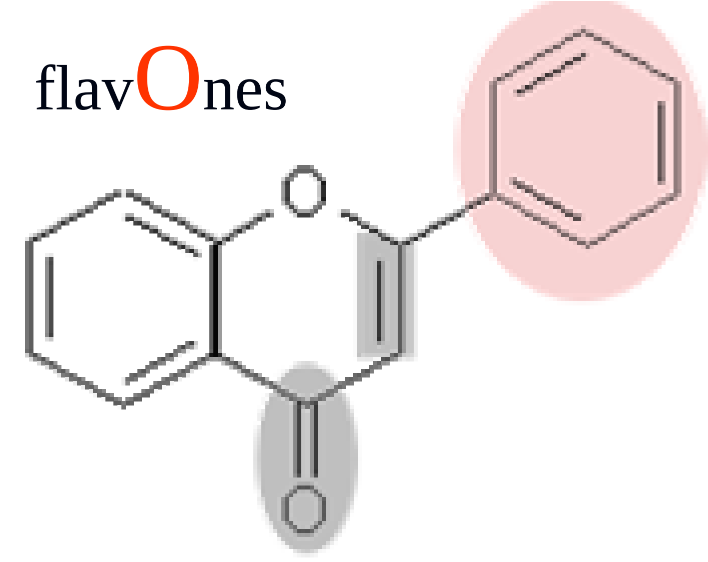
Naringin, grapefruit peel, intense bitter taste

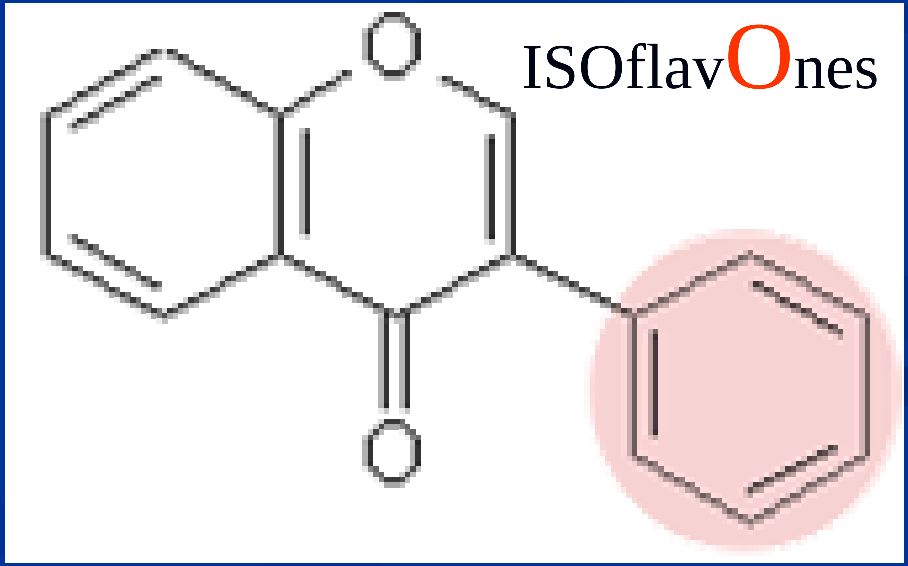
Flavanones Biosynthesis



The Isoflavones (Isoflavonoids)

- Isoflavones are also known as isoflavonoids
- Very similar to flavones, except that the B ring is attached to position 3 of the C ring, rather than to position 2 as in the flavones





The Isoflavones (Isoflavonoids)

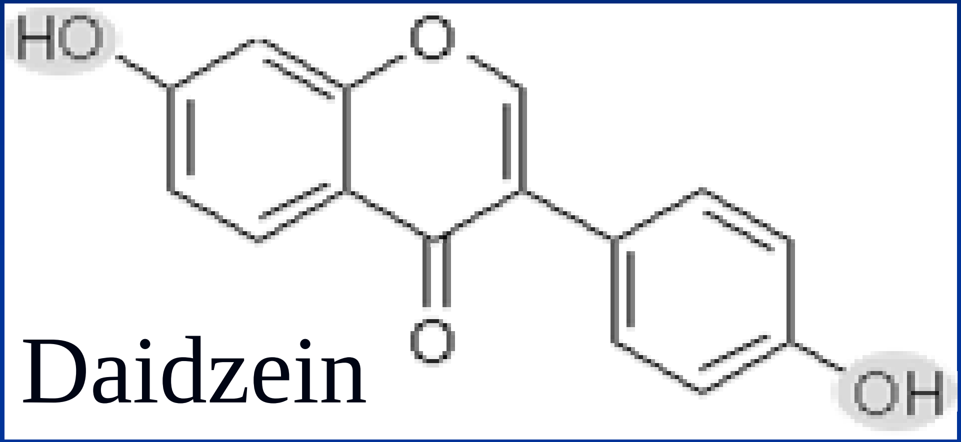
- Found almost exclusively in leguminous plants with highest concentrations in soybean

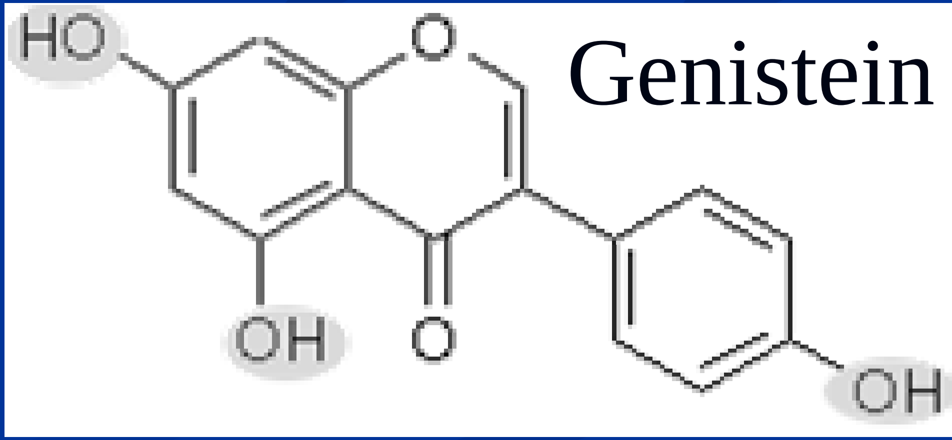
- Genistein, daidzein- phyto-oestrogens (can effect reproduction of grazing animals)

- Structure similar to the steroidal hormone oestradiol which blocks ovulation

- Low isoflavonoid producing varieties are being fed to animals

The Isoflavones (Isoflavonoids)





The Isoflavones (Isoflavonoids)

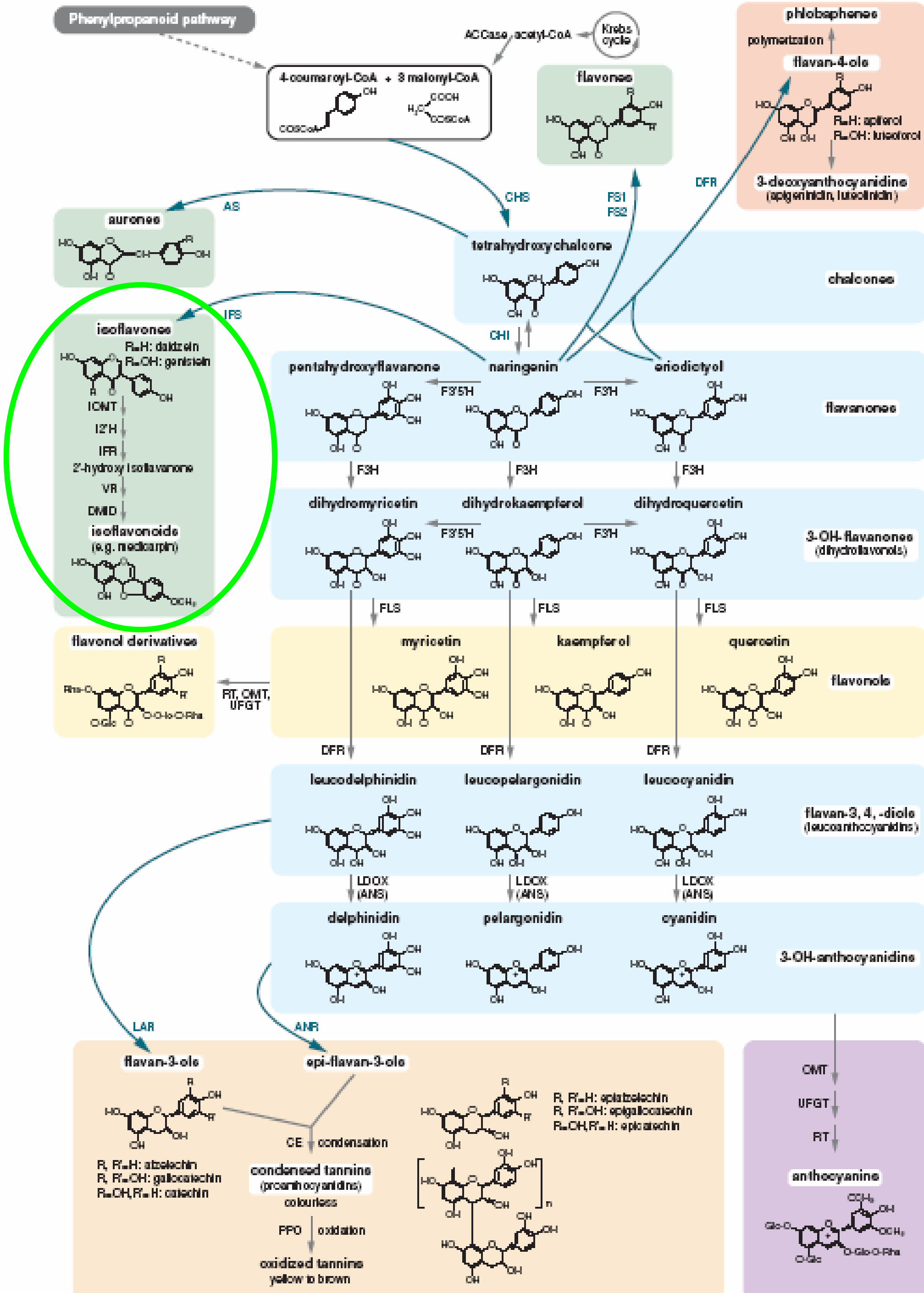
Important for human health:

- Reduce prostate and breast cancer

- In prostate cancer- growth of cancer cells by testosterone but suppressed by oestrradiol. - Isoflavonoids can suppress testosterone when oestradiol is not sufficient

- Anti-inflammatory and show cardioprotective

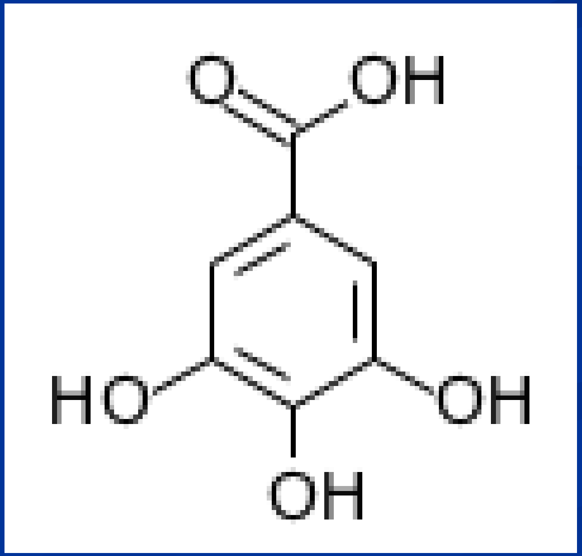
Isoflavones Biosynthesis



Non-Flavonoids- Phenolic acids

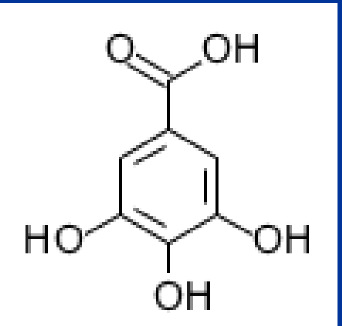
- Also known as hydroxybenzoates

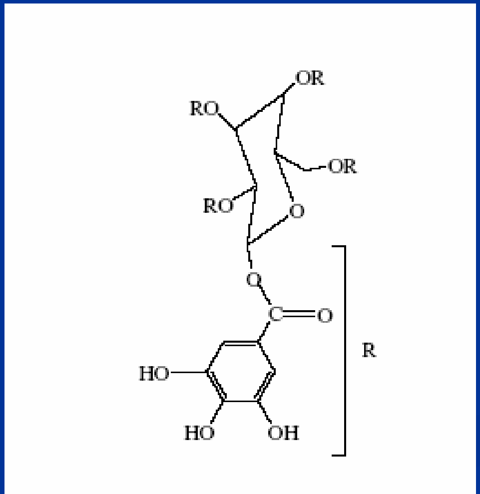
- Principle component is Gallic acid (derived from the shikimate pathway)



Non-Flavonoids- Gallotanines

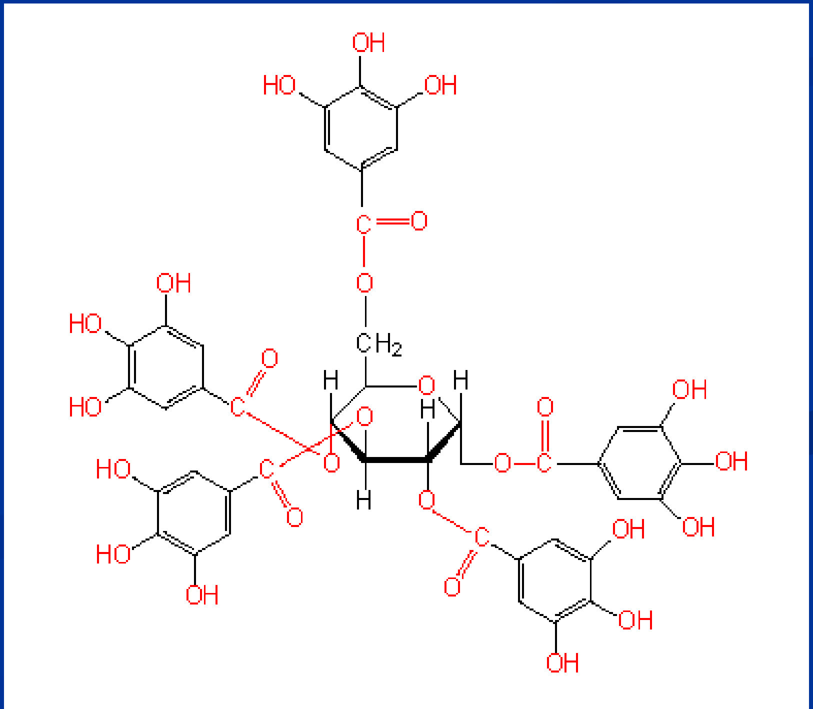
- Gallic acid is the base unit of Gallotanines
- Gallic acid residues linked to Glucose (often) via glycosidic bond (galloyl moiety)
- Gallotanines are hydrolysable tannins, treatment with dilute acids release gallic acid residues





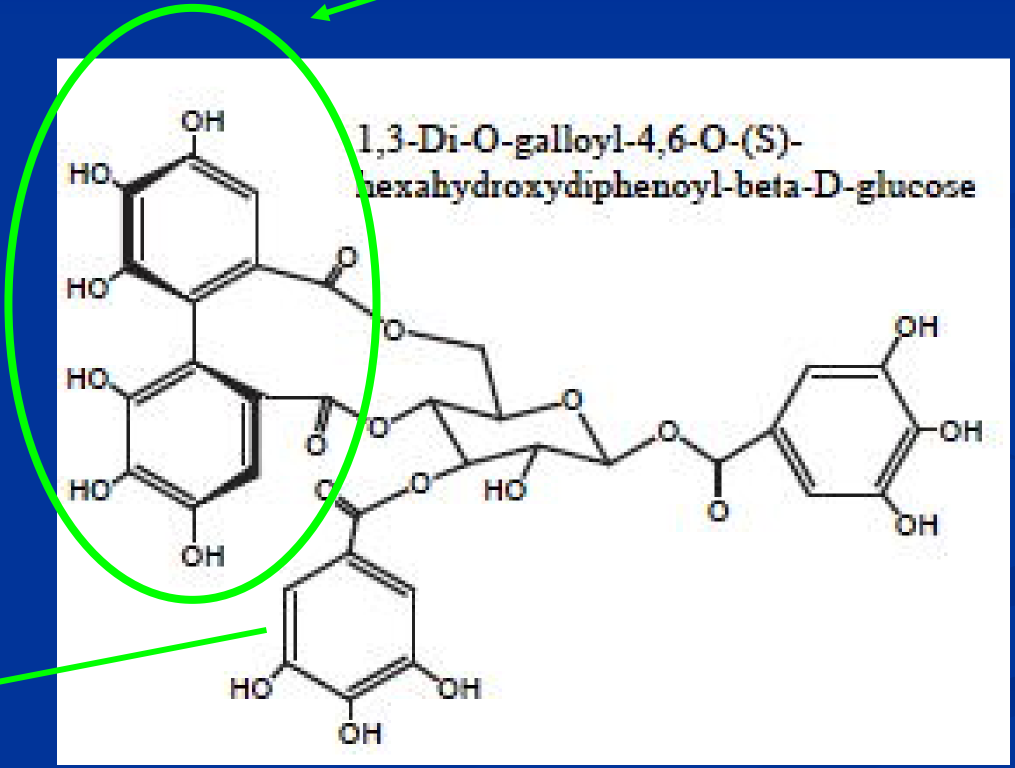
R=Galloyl moiety (G)

Gallotannins

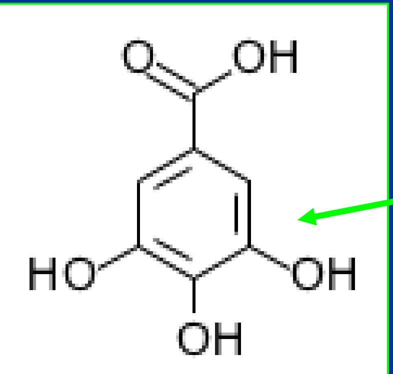


Non-Flavonoids- Ellagitanines

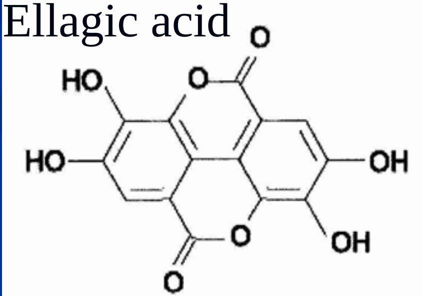
- Called ellagitannins since ellagic acid is released acid
- Composed of Gallic acid and hexahydroxydiphenoyl moieties



Gallic acid

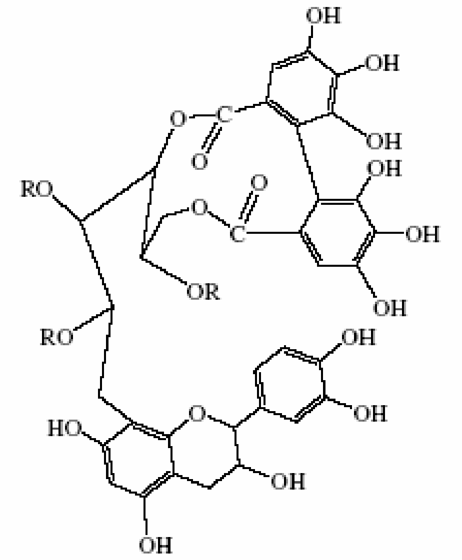


Ellagic acid



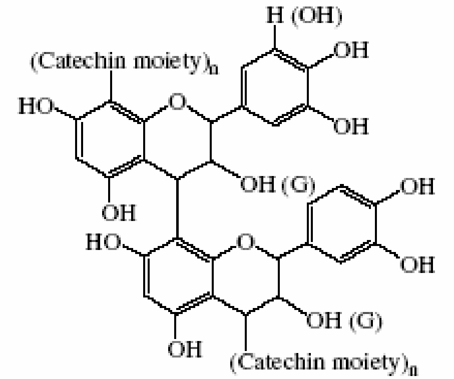
Non-Flavonoids- Type of Tannins

- Complex tannins- catechin or epicatechin bound bound to a galltannin or ellagitannin unit



R=Galloyl moiety (G) or other substituents

Complex Tannins



Condensed Tannins

Non-Flavonoids- General

Hydrolysable & Condensed Tannines

- Plant polyphenols that have the ability to precipitate protein- generally called tannins

- Used for a 1000 years to convert raw animal hides into leather

- In this process, tannin molecules cross-link the protein and make it more resistant to bacterial and fungal attack

Non-Flavonoids- Tannines

Occurrence of tannins in plants

Family	Species	Types of tannins
Anacardiaceae	*Rhus* sp.	Gallotannins, ellagitannins
	Schinopsis sp.	Condensed tannins
	Loxopterygium sp.	Condensed tannins
Leguminosae	*Caesalpinia* sp.	Gallotannins, ellagitannins
	Acacia sp.	Gallotannins, condensed tannins
Fagaceae	*Quercus* sp.	Gallotannins, ellagitannins
	Castanea sp.	Ellagitannins
	Myroxylon sp.	Gallotannins, ellagitannins
	Prosopis sp.	Gallotannins, ellagitannins
Combretaceae	*Terminalia* sp.	Ellagitannins
Myrtaceae	*Eucalyptus* sp.	Ellagitannins
Rosaceae	*Prunus* sp.	Ellagitannins
	Rubus sp.	Ellagitannins
Saxifragaceae	*Ribes* sp.	Ellagitannins
Theaceae	*Camelia* sp.	Ellagitannins, complex tannins
Vitaceae	*Vitis* sp.	Ellagitannins, complex tannins
Pinaceae	*Pinus* sp.	Condensed tannins

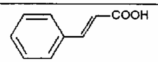
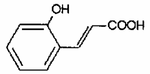
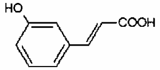
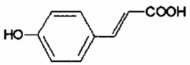
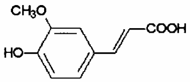
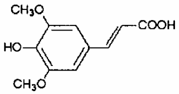
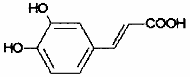
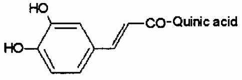
Non-Flavonoids- General

Hydrolysable & Condensed Tannines

- Tannins bind to salivary proteins and making the astringency taste
- In fruit- Astringency in Persimmon, strawberry (boser)
- Astringency (mild) enhances the taste of wine and tea
- Animals such as apes and dear will not eat fruit with high tannins
- In fruit- tannins decline in ripening-evolution for seed dispersal

Non-Flavonoids- Hydroxycinnamates or cinnamic acids

- Generated from cinnamic acid
- They are phenylpropanoids
- Most common: p-coumaric acid, caffeic and ferulic acids

Name	Structure	Source
cinnamic acid		oil of cinnamon, coca leaves
o-coumaric acid		cherry, plum
m-coumaric acid		cherry, plum
p-coumaric acid		most fruits (esp. blueberry, raspberry and pineapple) apple, tomato, grape, olive
ferulic acid		grains, nuts, tumeric, peppers, citrus fruit, tomato, cabbage, asparagus
sinapic acid		brussel sprouts, potatoes, rapeseed; trace amounts in citrus, pineapple, tomato
caffeic acid		grape, apple, plum, tomato, eggplant, cabbage, asparagus, endives, potatoes (the most abundant hydroxycinnamic acid)
chlorogenic acid		apple, pear, peach (and most fruits), tomato, coffee

Non-Flavonoids- Stilbens

- Members of the stilbene family have the C6-C2-C6 structure
- Polyphenolic like flavonoids

- They are phytoalexines, produced in response to fungal, bacterial, viral attack

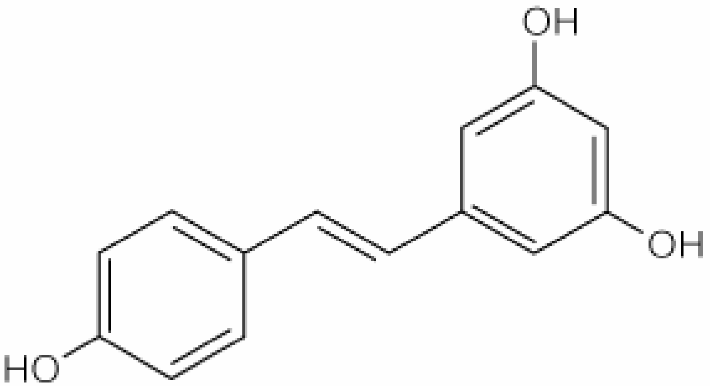
- Resveratrol, the most common stilbene

- Major source: grape, wine, peanut products and soya

- trans-resveratrol and its glucoside are the active agents in the famous Itadori root ("well being" in Japanese)

- Cardio protective effects of red wine, can inhibit LDL oxidation which is the initial stage of atherosclerosis

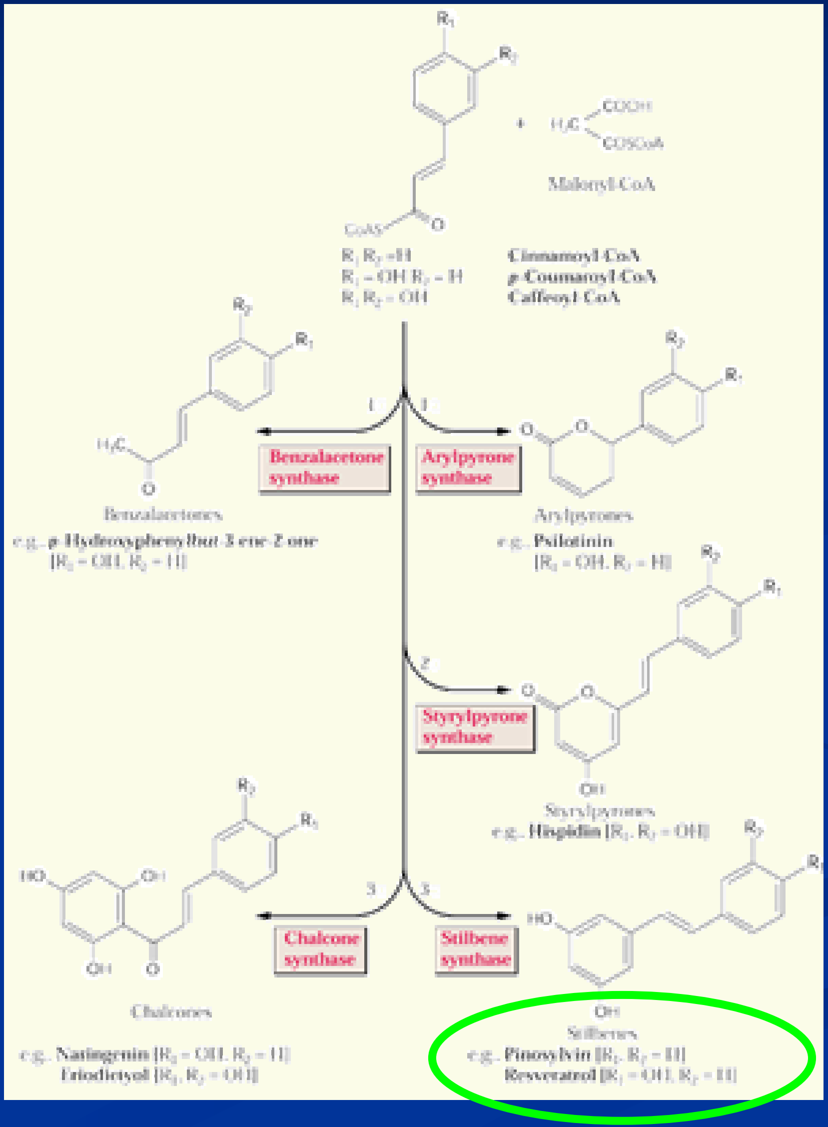
Non-Flavonoids- Stilbens- Resveratrol



Resveratrol
(a stilbene)

Also has potent anti-tumer activity

Non-Flavonoids- Stilbens- Resveratrol



Phenylypropanoids & flavour/fragrance