FOOD POLYPHENOLS

Characteristic and food sources

Polyphenols - primary role in plants

- Polyphenols are important secondary metabolites of plants.
- Up to now there is about 8000 of polyphenolic structures which were found in plants and described.
- **Main functions of polyphenols in plants:**

- giving color to flowers and fruits (mainly by anthocyanins) → attractions of insects necessary for pollination or animals that contribute to the distribution of fruits and seeds contained in them
- giving fruits and vegetables a tart taste (astringent polyphenols causes an unpleasant sensory perception),
- protecting plant tissues against herbivores and - thanks to their antimicrobial activity - limiting the spread of pathogens in plants

Additional functions involve the energy transfer, sex determination, regulation of growth factors, photosynthesis and morphogenesis, the plant protection against other abiotic stressors, such as UV radiation, cold, heat or salinity.

Polyphenols as antioxidants

Polyphenols, which their numerous functional groups, double bonds and aromatic rings, have an ideal structure to act as effective antioxidants. Therefore, polyphenols:

- **scavenge** already formed **free radicals**, such as a hydroxyl radical ($^{\bullet}OH$) or the superoxide anion radical ($O_2^{-\bullet}$), as well as **quench the reactive oxygens species** like hydrogen peroxide (H_2O_2) or singlet oxygen ($^1O_2$) by donating a single electron /SET/ or by hydrogen atom transfer /HAT/;
- might **prevent initiation and interrupt** of yet initiated **radical reactions**, like the peroxidation of lipids, the oxidation of proteins and sugars, and oxidative damage to nucleic acids;
- are able to **chelate the ions of transition metals** (e.g., Fe and Cu), thus **preventing** the formation of free radicals in the Fenton and Haber-Weiss reactions;
- function as a co-antioxidant and thus they are involved in the **regeneration** of essential vitamins;
- are involved in the regulation of numerous signalling pathways responsible, among others, for energy metabolism, adipogenesis, antioxidant and anti-inflammatory reactions in cells.

Polyphenols in disease prevention

Polyphenols can also:

- **prevent or reduce the symptoms of various metabolic diseases**, such as: **metabolic syndrome** (which includes type 2 diabetes mellitus, central and abdominal obesity, systemic hypertension, atherogenic dyslipidemia), as well as **cardiovascular diseases** (e.g., atherosclerosis, myocardial infarction, heart failure, stroke);
- **inhibit LDL oxidation** and increase HDL improving endothelial function;
- **reduce blood pressure**;
- **improve the glucose homeostasis**; relax smooth muscle contraction, enhancing endothelial nitric oxide synthase activity, reducing vascular inflammation, inhibiting rennin activity, and anti-vascular oxidative stress;
- exert **beneficial effects in systemic and neurodegenerative diseases**, amyloid diseases, particularly Alzheimer's disease and Parkinson's disease, as well as on cognitive function;

Polyphenols in disease prevention

- act as **anti-cancer agents:**

- prevent the development of various cancers (e.g., ovarian, breast, pancreas, colorectal cancer, esophagus, liver, lung, kidney), mainly by **the growth inhibition** or **apoptosis stimulation in various cancer cells**, antioxidant/prooxidant activity, inhibition of specific protein kinases and other enzymes and the resulting changes in cellular signaling, estrogenic/antiestrogenic activity, antiproliferation, induction of detoxification enzymes, regulation of the host immune system, anti-inflammatory activity;

- **inhibit the angiogenesis;**

- some polyphenols (e.g., quercetin, kaempferol, curcumin, resveratrol, EGCG) **downregulate the expression of histone deacetylases**; it means that these compounds exert anticancer action by restoring epigenetic alterations in cancer cells and by DNA methylation and histone modifications which may prevent normal cells from turning into tumors;

Polyphenols in disease prevention

- **alleviate the undesirable menopausal symptoms** (e.g., soya isoflavones such as daidzein and genistein)
- **exert bacteriostatic or bactericidal effect** against various pathogens, e.g., *Helicobacter pylori, Pseudomonas aeruginosa, Escherichia coli, Streptococcus mutans, S. aureus*, *Salmonella enteritidis, Vibrio cholerae, Klebsiella pneumoniae, Yersinia enterocolitica, Listeria monocytogenes, Candida albicans, Bacteroides fragilis, Clostridium perfringens and Clostridium difficile;*
- **stimulate the growth of beneficial bacteria,** enhanced the growth of *Akkermansia muciniphila Lactobacillus* and *Bifidobacterium;*

Polyphenols - sources

In a human diet, polyphenols are provided mainly by plant food such as fruit and vegetables.

Among **the richest food sources** of polyphenols are:

- seasonings and dried herbs (e.g., cloves, peppermint, anise, oregano, rosemary),
- cocoa,
- dark coloured berries,
- some seeds and nuts (e.g., flaxseed, soybean, chestnut, hazelnut),
- some vegetables (e.g., black ol-ives, globe artichoke heads, red chicory).

Polyphenols - classification

Polyphenols are a large group of non-enzymatic antioxidants that comprise:

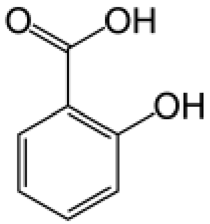
- phenolic acids,
- flavonoids (these include flavonols, flavanones, flavanols, flavones, anthocyanins and isoflavones),
- tannins,
- lignans,
- stilbens,
- coumarins.

Phenolic acids

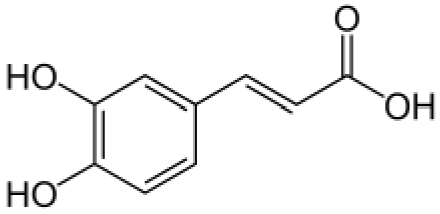
Two subclasses of phenolic acids are distinguished:

1) **hydroxybenzoic acids**, contain a phenolic ring and an organic carboxylic acid function (C6-C1 skeleton), e.g. salicilic acid

salicilic acid



caffeic acid

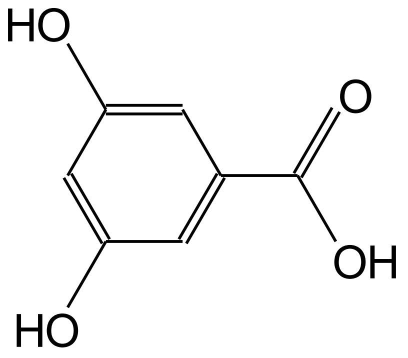


2) **hydroxycinnamic acids,** aromatic acids or phenylpropanoids having a C6–C3 skeleton, e.g. caffeic acid.

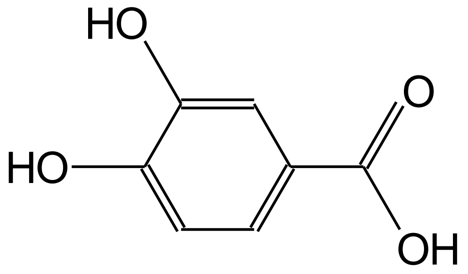
- The antioxidant activity of phenolic acids and their esters **depends on the number of hydroxyl groups in their localisation (can be enhanced by spherical effects.**
- The ability of the carboxyl group to withdraw an electron has an adverse effect on the donor properties of hydroxybenzoate, which is why **cinnamic acid derivatives are much more effective antioxidants than benzoic acid derivatives**.

Hydroxybenzoic acids

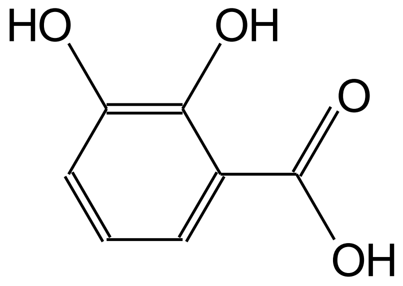
- **No antioxidant activity** was found in ortho- and para-monohydroxy derivatives of benzoic acid, unlike meta-derivatives. This is related to the ability to withdraw electrons by a single carboxyl group affecting the ortho- and para- position.
- **Dihydroxy derivatives show antioxidant properties** depending on the position of the OH groups in the ring, for example, 3,5-dihydroxybenzoic acid has twice as much antioxidant capacity as 2,3-dihydroxybenzoic acid and 3,4-dihydroxybenzoic acid (protocatechuic acid)



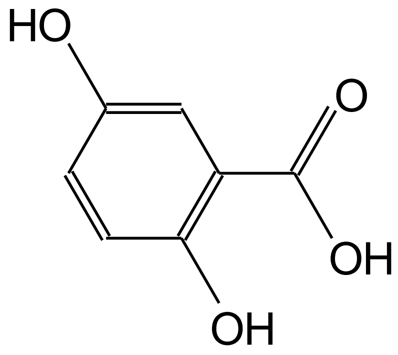
3,5-dihydroxybenzoic acid



protocatechuic acid



2,3-dihydroxybenzoic acid



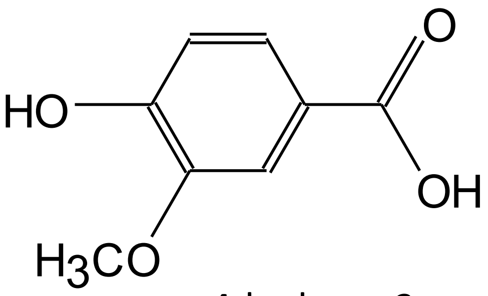
gentisic acid

Hydroxybenzoic acids

- Generally, the hydroxybenzoic acid content of edible plants is very low, with the exception of some red fruits (strawberries, raspberries and blackberries) and onions

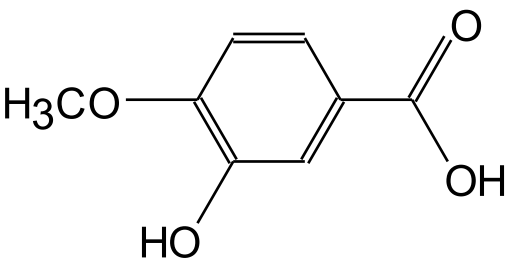
Food	***Total hydroxybenzoic acid content* (mg per 100 g fresh weight)**
Blackberry	8–27
Blackcurrant	4–12
Raspberry	6–10
Strawberry	2–8

Hydroxybenzoic acids

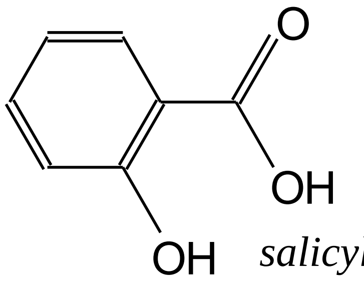


The primary component of the extract of the vanilla bean.

4-hydroxy-3-methoxybenzaldehyde
(vanilline)

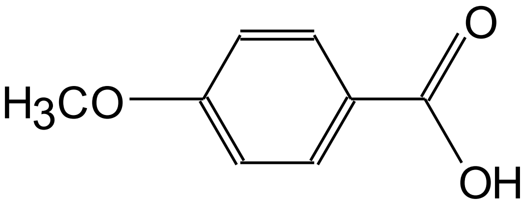


3-Hydroxy-4-methoxybenzaldehyde
(isovanilline*)*



salicylic acid

extracted for the first time from willow bark (Latin *Salix*, hence the name), precursor of aspirin (acetylsalicylic acid)

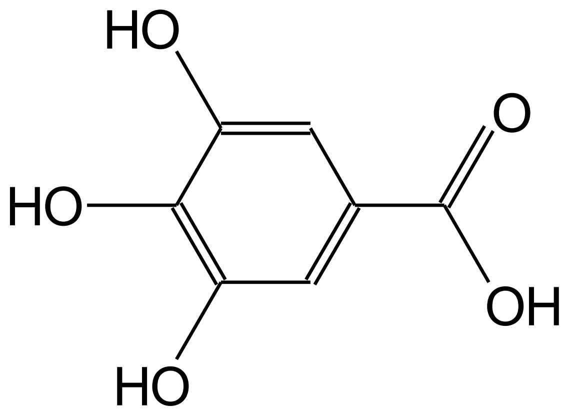


4-methoxybenzoic acid
(*p*-anisic acid)

It is found in the essential oils obtained from the star anise

Hydroxybenzoic acids

- A very strong antioxidant is **gallic acid**, which has three hydroxyl groups in position 3,4,5.
- It is worth emphasizing that the esterification of the carboxyl group reduces its activity. An even stronger effect is caused by replacing the 3-OH and 5-OH groups with methoxy substituents

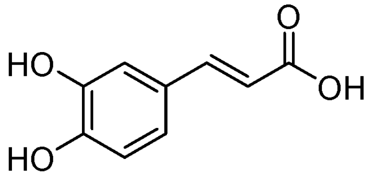


3,4,5-trihydroxybenzoic acid
(gallic acid)

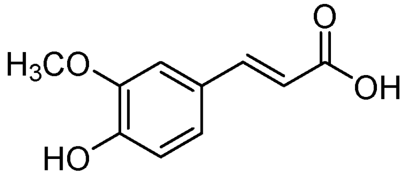
found in gallnuts, sumac, witch hazel, tea leaves, oak bark, and other plants

Hydroxycinnamic acids

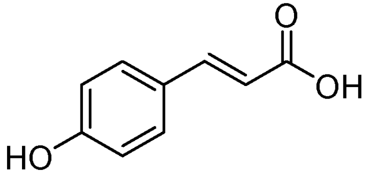
- They belong to plant phenylpropanoids much more common in nature.
- The most important in this group include four acids: **caffeic, p-coumaric, ferulic and sinapic,** which are produced in the shikimic acid cycle.
- These compounds are rarely found in free form, usually in the form of **glycosyl derivatives** or **esters with quinic, shikimic and tartaric acids**.
- Hydroxycinnamic acids are abundant in fruits, vegetables, cereals and seeds of fruits.



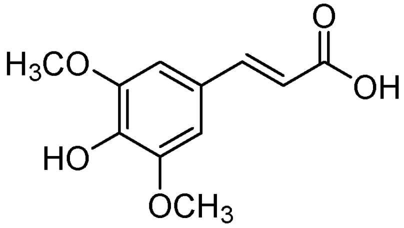
Caffeic acid



Ferulic acid



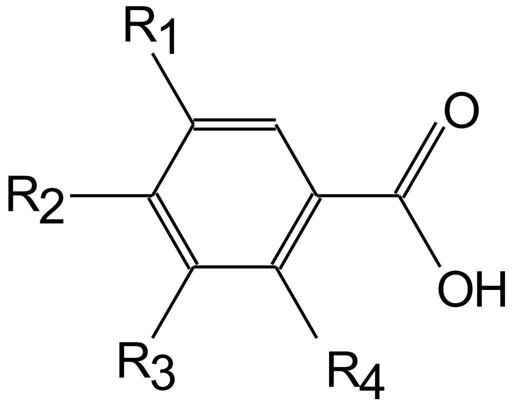
p-Coumaric acid



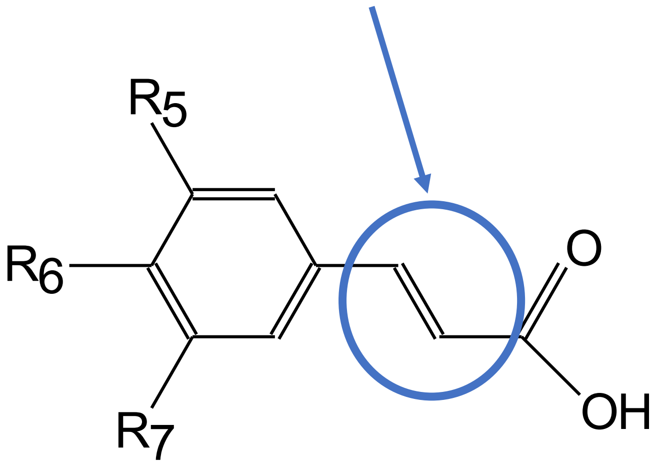
Sinapic acid

Hydroxycinnamic acids

- The introduction of an ethylene group (-CH=CH-) between the phenyl ring and the carboxyl group **significantly strengthens the antioxidant properties** of the molecule, among others through greater ability to donate hydrogen and stabilization of the emerging radical

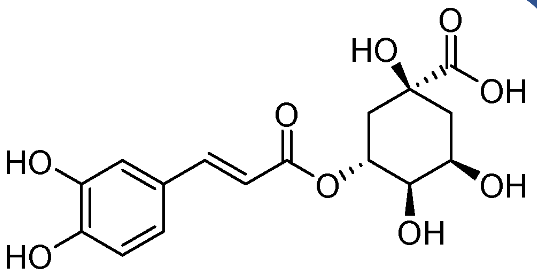


ethylene group (-CH=CH-)

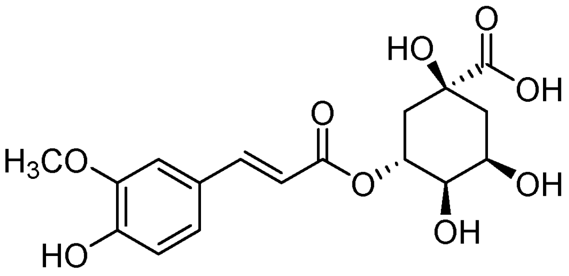


Esters of hydroxycinnamic acids

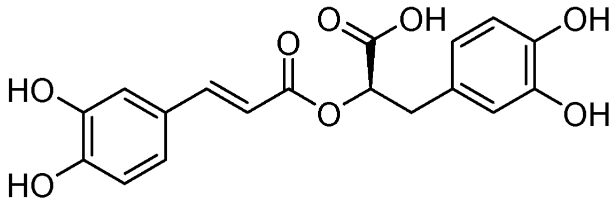
Esters of main HCAs



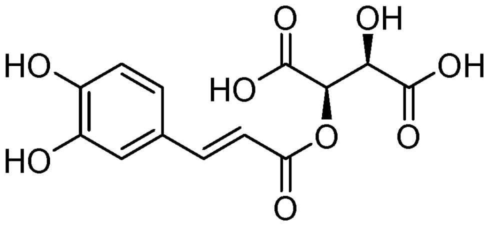
5-O-Caffeoylquinic acid
(chlorogenic acid)



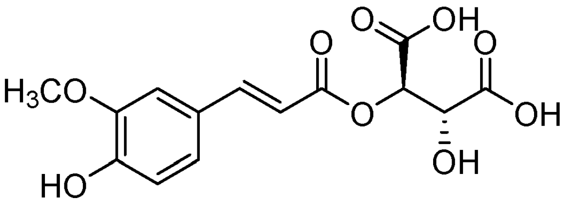
5-O-Feruoylquinic acid



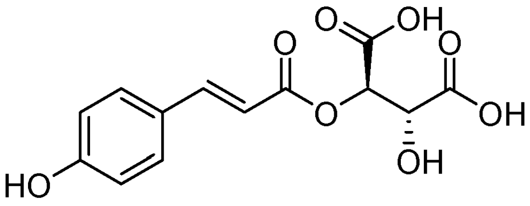
Rosmarinic acid



Caftaric acid



Fertaric acid



Coutaric acid

Chlorogenic acid

- Abundant in yerba mate, green leaves and fruits of the coffee tree (raw grain has 60,000 mg/kg; coffee infusion - 500 mg/dm³), hawthorn, artichokes, nettle, blueberries, raw potatoes and in smaller amounts m among others in common ivy, plums, cherries, apples, peaches, apricots

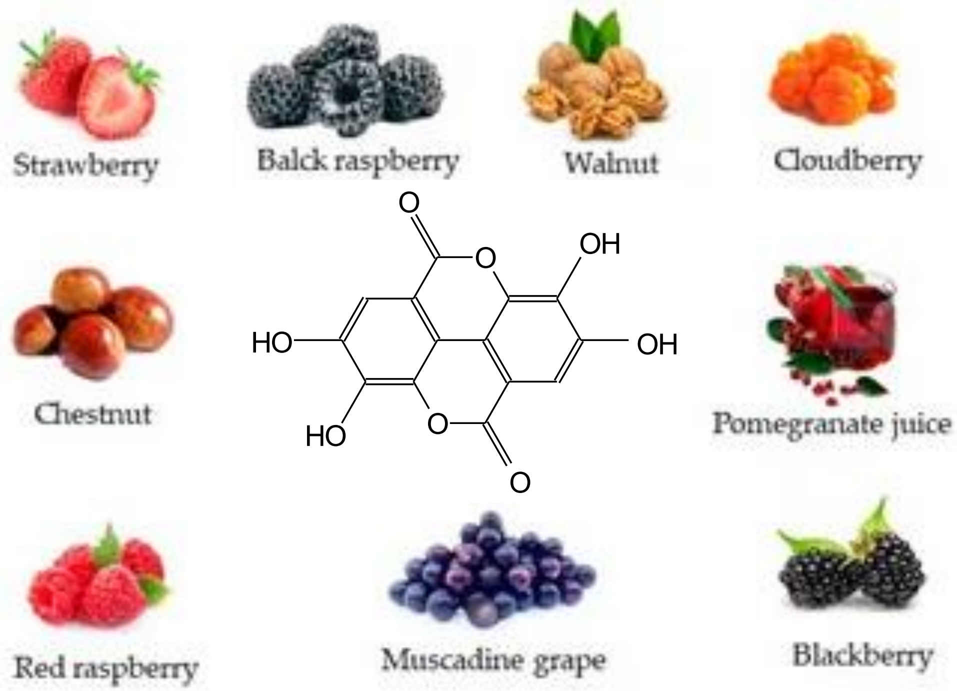






Ellagic acid

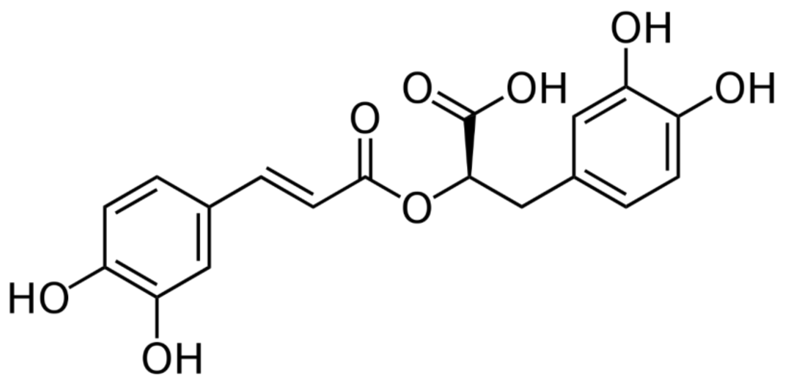
- **Ellagic acid** - the highest levels found in raw chestnuts, walnuts, pomengranate, clouberries, raspberries, strawberries, as well as in some distilled beverages (Cognac, oak-aged red wine)



Dietary source	Ellagic acid (mg/100g fresh weight)
Blackberries	150
Pomegranate juice	811.1
Cognac	31–55
Cloudberries	315.1
Pomegranate	269.9
Raspberries	270
Rose hip	109.6
Strawberries	77.6
Walnuts	59
Yellow raspberries	1900

Depsides – esters of phenolis acids

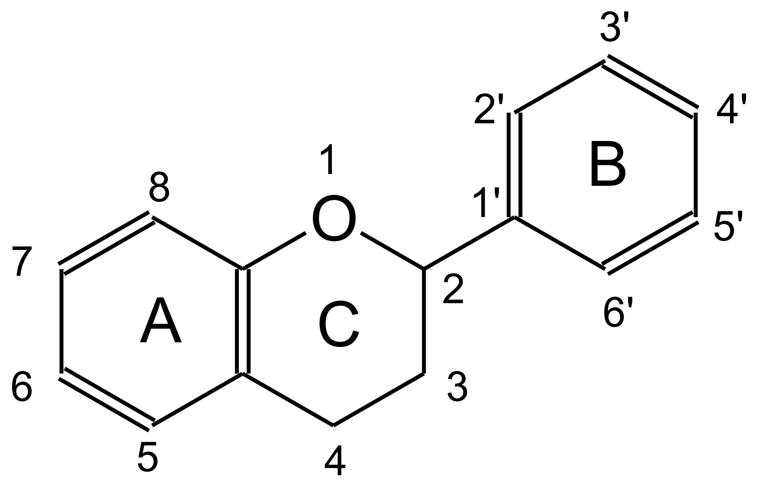
- **Rosmarinic acid** - is a caffeic acid ester, with tyrosine providing another phenolic ring via dihydroxyphenyl-lactic acid, polyphenol found in many culinary herbs, including rosemary, perilla, sage, mint, and basil



Has anti-cancer and antioxidant properties, stabilizes biological membranes, protects against the harmful effects of UV radiation and reactive oxygen species, including free radicals, has anti-inflammatory, anti-proliferative, anti-bacterial, anti-viral, anti-hormonal and most likely sedative effects on the central nervous system. It also has slight anti-allergic properties and immunomodulatory activity; stimulates the production of prostaglandin E2 and reduces the synthesis of leukotrienes B4 in human polymorphonuclear leukocytes

Flavonoids

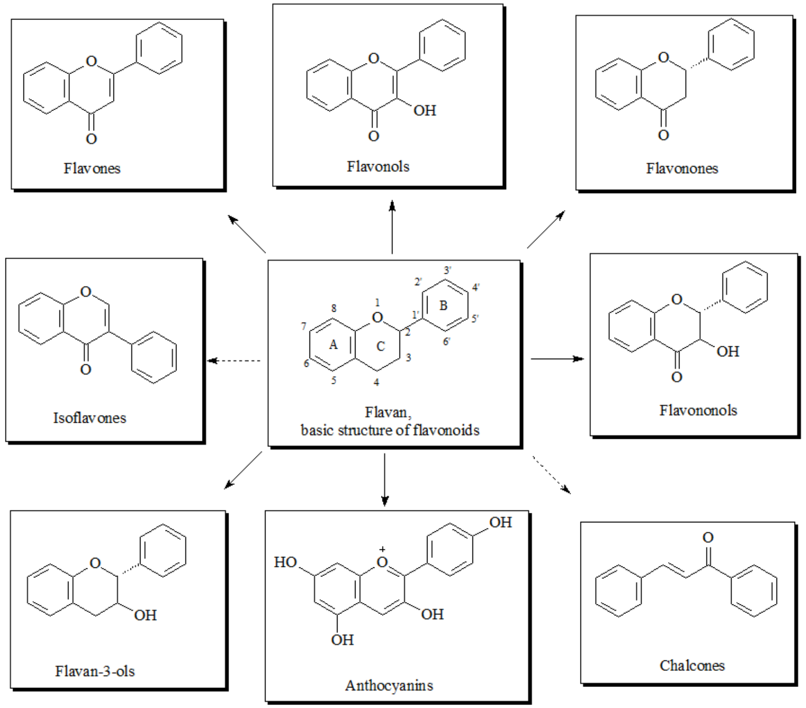
An extensive group of compounds characterized by the presence of a diphenylpropane system in the molecule, consisting of two benzene rings, which are connected by a three-carbon chain or a heterocyclic ring (C6-C3-C6).



Structure and determination of carbons in the flavone basic skeleton

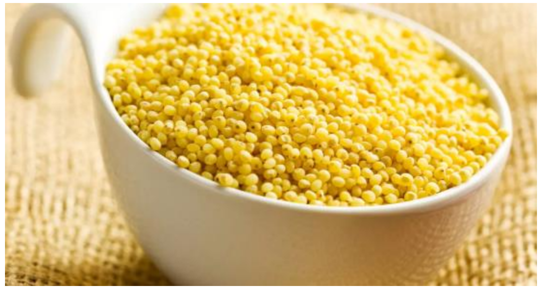
Flavonoids

- Several subclasses of flavonoids are distinguished. Within tchem there is a **large diversity both in terms of structure and the resulting antioxidant activity.**
- Flavonoids include:
  - flavans,
  - flavones,
  - flavonols,
  - flavan-3-ols (catechins and proanthocyanidins),
  - flavanones,
  - anthocyanins,
  - isoflavones,
  - chalcones, as an intermediate form

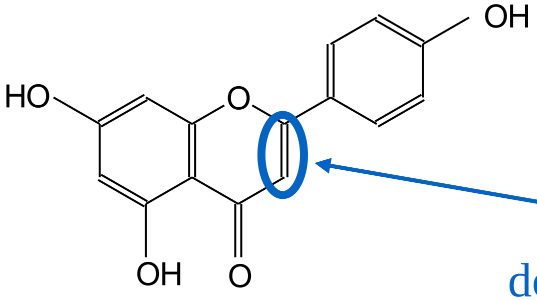


Flavones

- The flavone backbone contains a **double bond between C2 and C3.**
- **The main representatives** of this group **are apigenin and luteolin glycosides**, and their abundant source is **parsley and celery**, as well as some **cereals, especially millet and wheat.**
- Flavones are characterized by **a flat ring structure**, a **yellow colour** that deepens as the number of hydroxyl groups in the molecule increases, **poor solubility in water, but good solubility in alkaline solutions and in alcohol.**

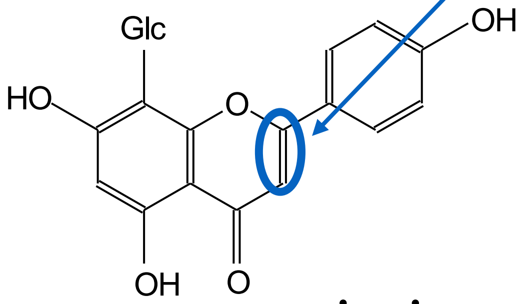



Flavones - apigenin



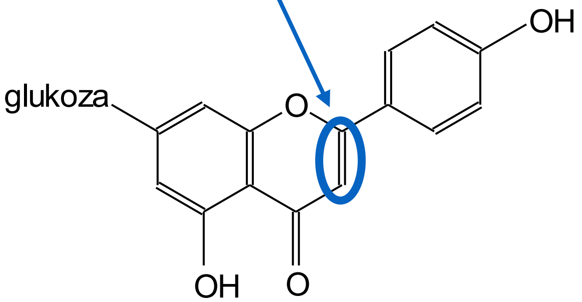
apigenin

double bond between C2 and C3



vitexin

(apigenin 8-C-glucoside)



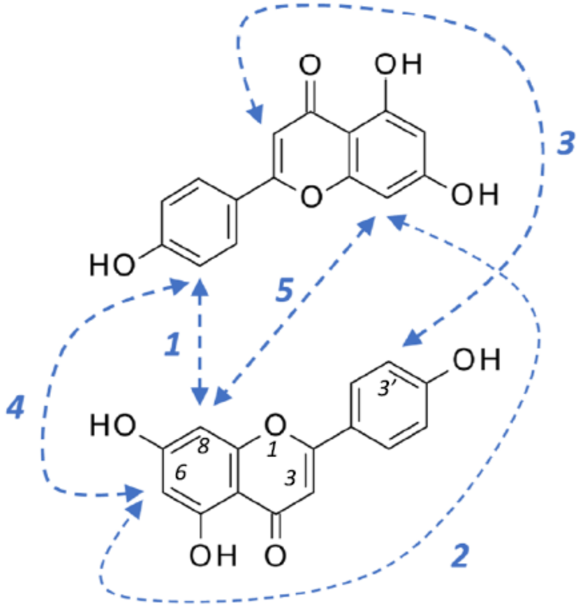
apigenin 7-monoglucoside

Apigenin - a bioflavonoid derived from **grapefruit,** But is also detected in other fruits, chamomile. It counteracts angiogenesis, strengthens blood vessels, has anti-inflammatory, antioxidant and anti-radical properties, lowers cholesterol, absorbs UV radiation.

Biflavonoids – apigenin dimers

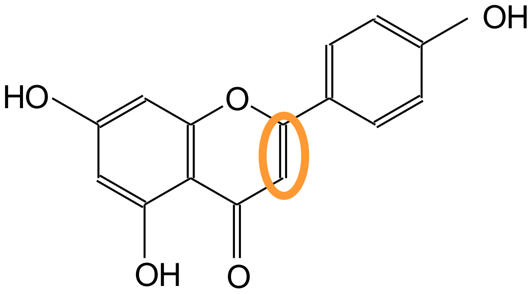
Apigenin derivatives are of various types. Amon C-C-type bifavonoids are:

1) C3' - C8 amentoflavone type
2) C6 – C8” agathisflavone type
3) C3 – C3” Taiwanese type
4) C3' - C6" robustaflavone type
5) C8 - C8 cupressuflavone type



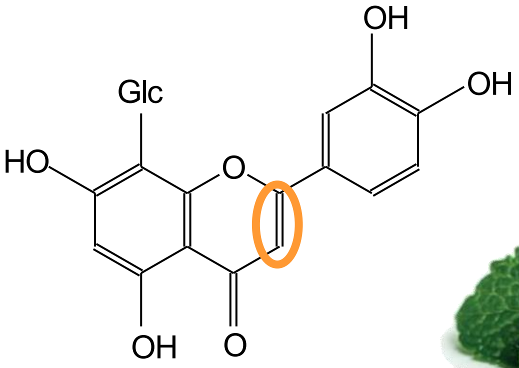
Detected in large quantities in the bark of various varieties of willow, ginkgo or aloe

Flavones - luteolin



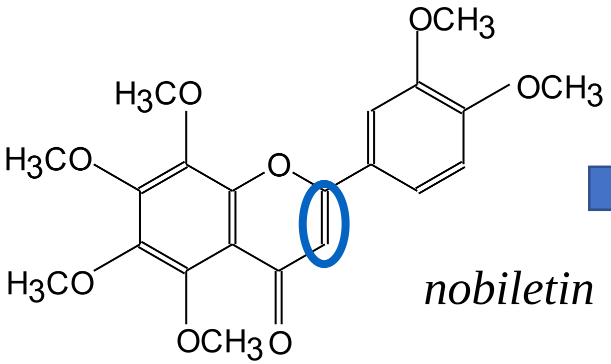
luteolin

Luteolin is found in parsley, thyme, celery, basil, mint and artichokes.

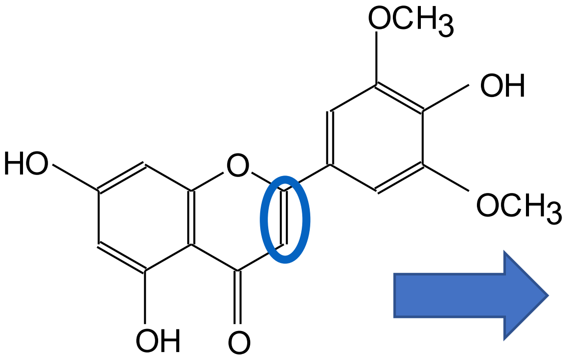


orientin
(luteolin 8-C-glucoside)

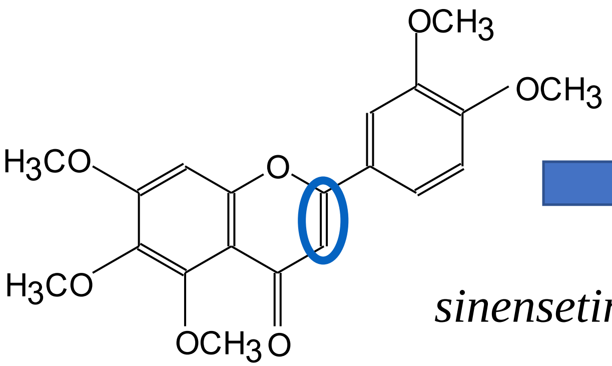
Other flavones



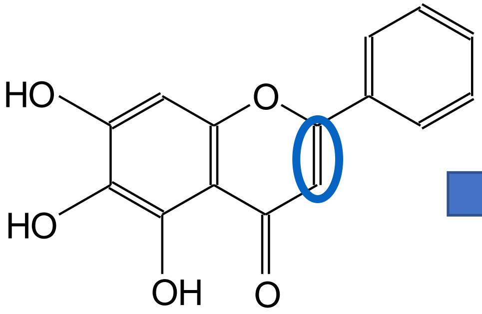
nobiletin



tricin

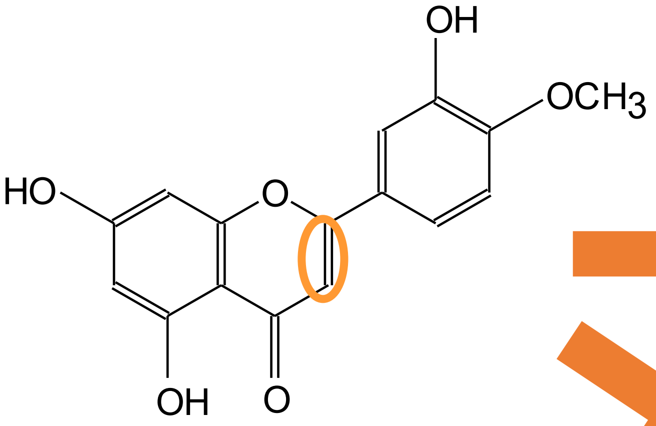


sinensetin

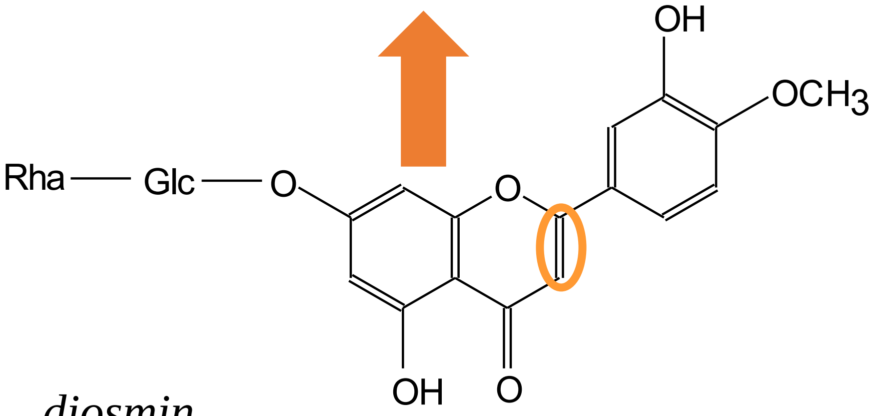


baicalein

Other flavones



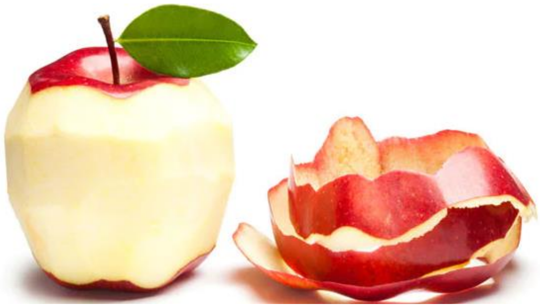
diosmetin



diosmin
(diosmetin 7-O-rutinoside)

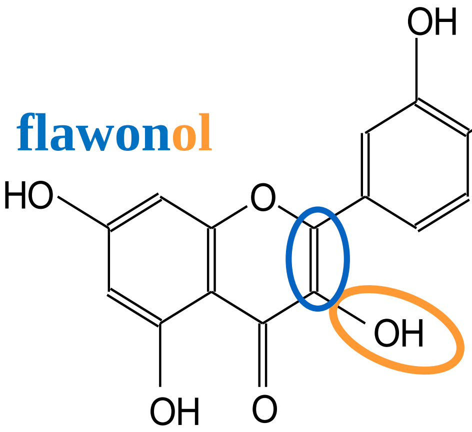
Flavonoles

- They differ from flavones by the **presence of an OH group at the C3 carbon.**
- They are the most common flavonoids found in food, represented mainly by **kaempferol** and **quercetin**, and **more specifically their glycosyl derivatives.**
- Since the synthesis of flavonols is dependent on light, they are mainly accumulated in **the outer parts of the leaf tissues and in the skin of the fruit.**
- A rich source of flavonols is **onion, apple peel, broccoli and tea.**

Flavonoles - quercetin

flawonol



quercetin

Dietary source	Quercetin [mg/100g]
Chilli pepper	32.6
Kale	22.6
Broccoli	13.7
Spinach	27.2
Onion	45.0
Cranberry	25.0
Oregano	42.0
Fennel leaves	46.8
Dill	79.0

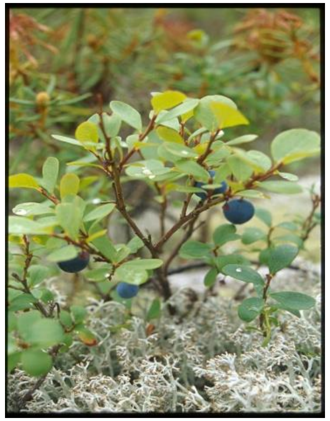








Quercetin level in berries



European blueberry
(158 mg/kg)

Cranberry
(83 - 121 mg/kg)

Chokeberry
(89 mg/kg)

Rowan
(63 mg/kg)

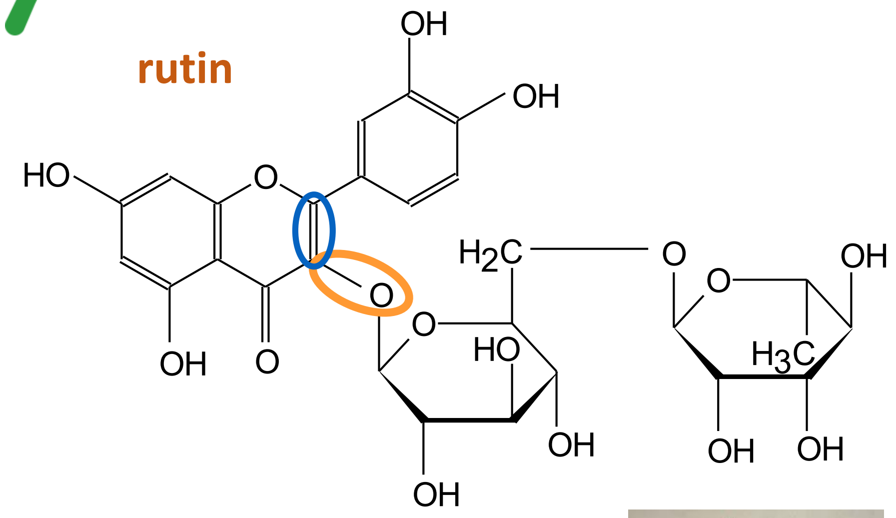
Crowberry
(53-56 mg/kg)

Sea-buckthorn
(62 mg/kg)

Lingonberry
(74-146 mg/kg)

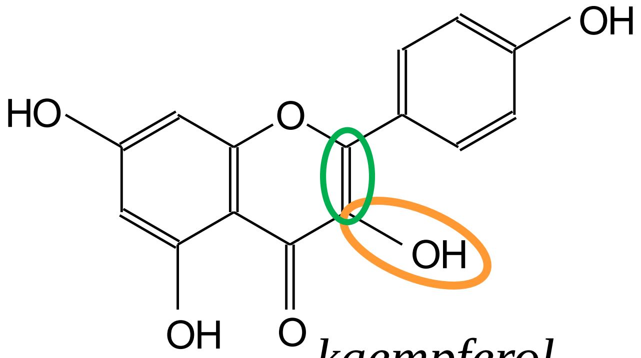
Quercetin glycosides

rutin



Food source	Quercetin glycosides
Red wine	Quercetin 3-O-glucoside (isoquercitrin) quercetin 3-O-rutinoside (rutin)
Onion	Quercetin 4′-glucoside (spiraeoside) Quercetin 3,4′-diglucoside
Tea	Rutin
Apple	Rutin, isoquercitrin Quercetin 3-O-galactoside (hyperoside) Quercetin 3-O-rhamnoside (quercitrin)
Wild leek *Allium tricoccum*	Isoquercetin Quercetin-sophoroside Quercetin 3-sophoroside-7-glucuronide Quercetin 3-O-glucuronide (miquelianin)

Flavonoles - kaempferol

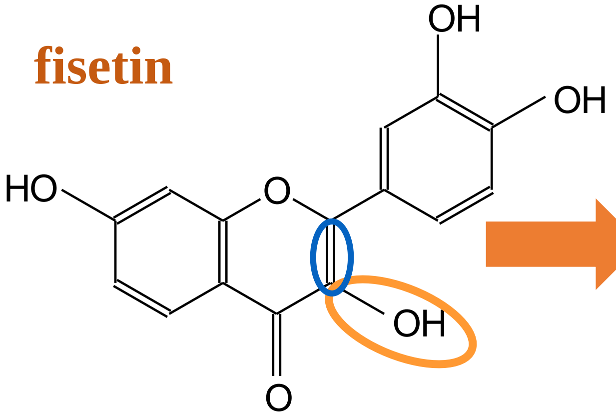


kaempferol

Dietary source	Kaempferol [mg/100g]
Spinach	55.0
Kale	47.0
Broccoli	7.2
Onion	4.5
Blueberry	3.17
Cappers	104.29
Cumin	38.6
Cloves	23.8

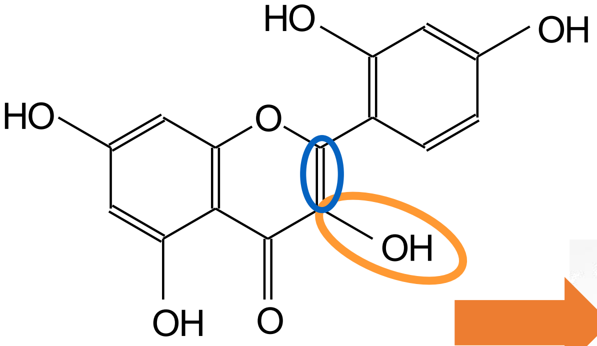
Flavonoles - other

fisetin



Chinese Lacquer *(Toxicodendron vernicifluum)*

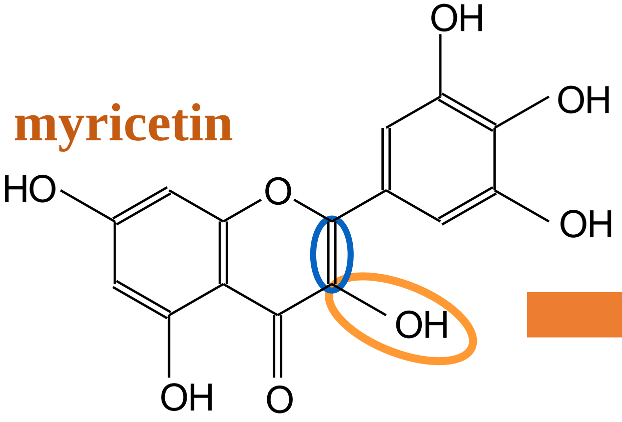
strawberries



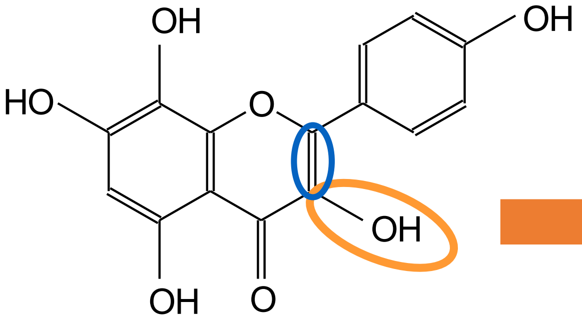
morin

guava

myricetin



carob



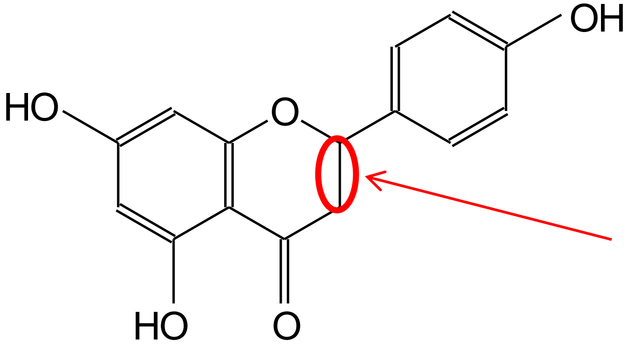
herbacetin

Flavanones

- Unlike flavonols, flavanones **do not have a double bond between C2 and C3.**
- In high concentrations, they are detected mainly in **tomatoes** and **aromatic herbs** (such as mint) and in **citrus fruits**, where they occur in the form of **aglycones: naringenin in grapefruit, hesperetin in oranges.** More often, however, they are **are glycosylated with disaccharides in the C7 position: hesperidin, narirutin or naringin.**
- Since **albedo and skins contain significant amounts of flavanones**, whole fruits are several times richer in these compounds than the juice produced from them.

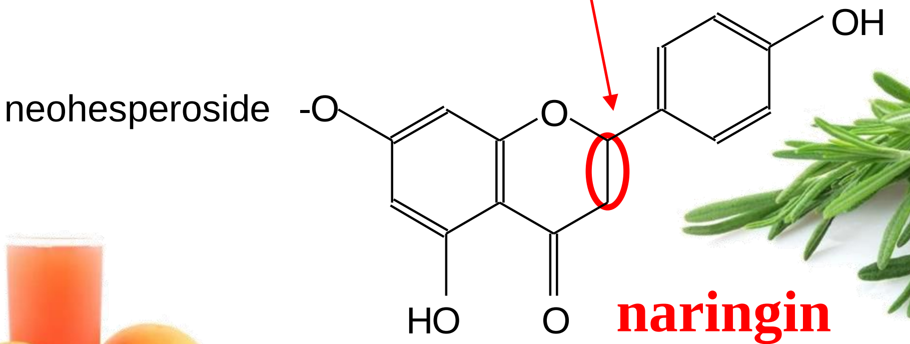
Naringenin (NR) and naringin (N)

Dietary source	Naringenin [mg/100 ml or mg/100 g]
Rosmary (N)	55.1
Grapefruit, pure juice (N)	37.8
Grapefruit, pure juice (NR)	1.6
Mexican oreano (NR)	372



no double bond!

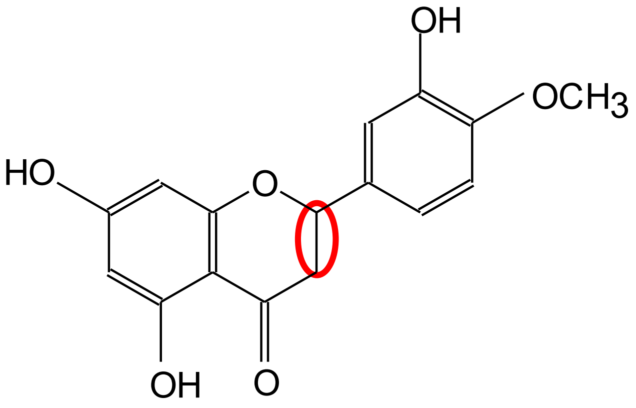
naringenin



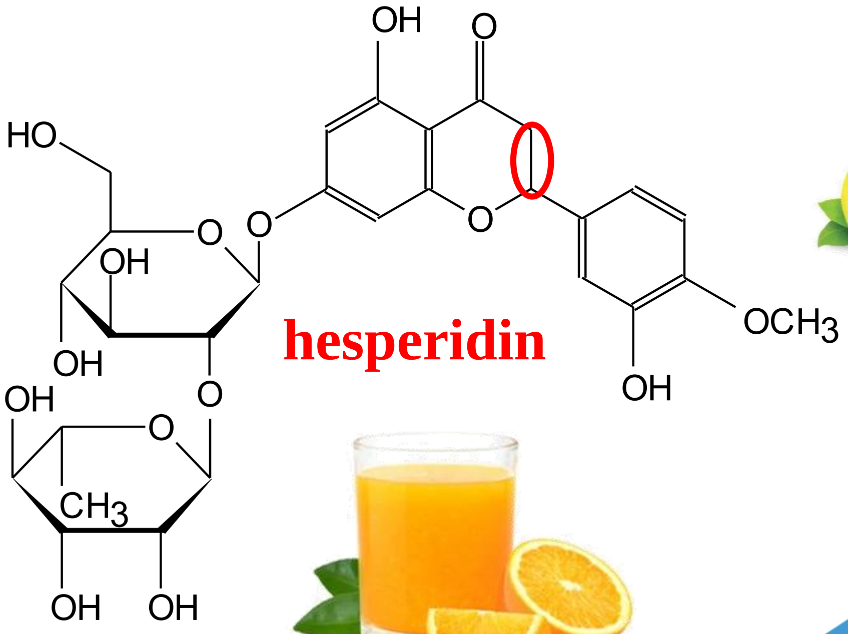
naringin

Hesperetin (HR) and hesperidin (H)

Dietary source	Naringenin [mg/100 ml or mg/100 g]
Peppermint (H)	480
Orange juice (H)	25.9 - 43.6
Tangerin juice (H)	36.1
Lemon juice (H)	17.8
Red wine (HR)	0.05



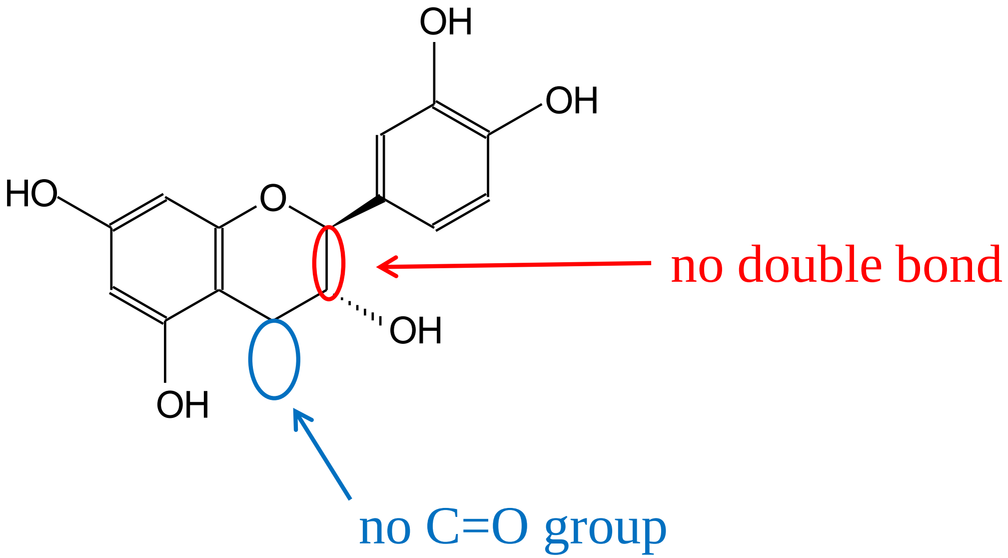
hesperetin



hesperidin

Flavanols

- Also, flavanols **do not contain a double bond between C2 and C3,** but they **do not have a carbonyl group at C4**. They have the highest degree of hydrogenation of the heterocyclic ring.



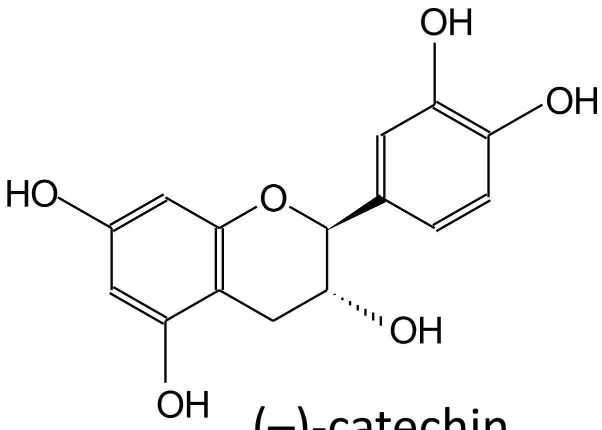
Flavanols

- They are **characterized by a spatial ring structure** and **good solubility in water**, which, however, decreases with the degree of their polymerization.
- They **occur both in the monomeric form as catechins** and in **the polymerized form (tannins)**, but **always in the form of aglycones.**
- **Catechin and epicatechin** are the basic flavanols of **fruits** (especially apricots, cherries, grapes)
- **Gallocatechin, epigallocatechin and epigallocatechin gallate** are found mainly in **tea, legumes and grapes**.

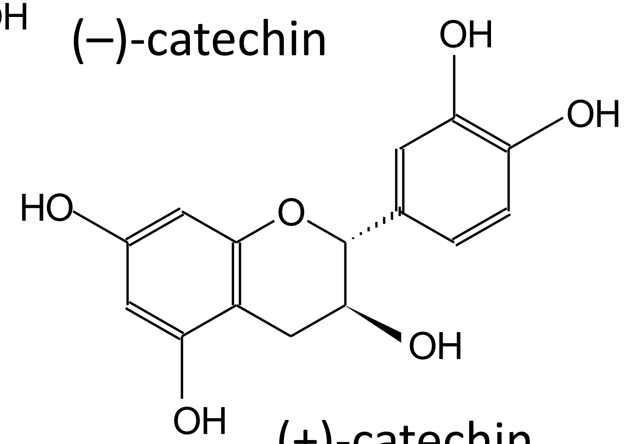
Flavanols

- The presence of **large amounts of hydroxyl groups** in the molecule enables them to form **complexes with polysaccharides, proteins and anthocyanins,** which affects the organoleptic and sensory characteristics of fruits and vegetables (smell, color, astringency).
- **Proanthocyanidins** and **catechins** are easily oxidized and condensed, forming brown-colored compounds, which give **an unattractive appearance to fruit and fruit preserves**, however, the phenomenon of co-pigmentation between condensed tannins and anthocyanins increases the durability of the color of fruit products.

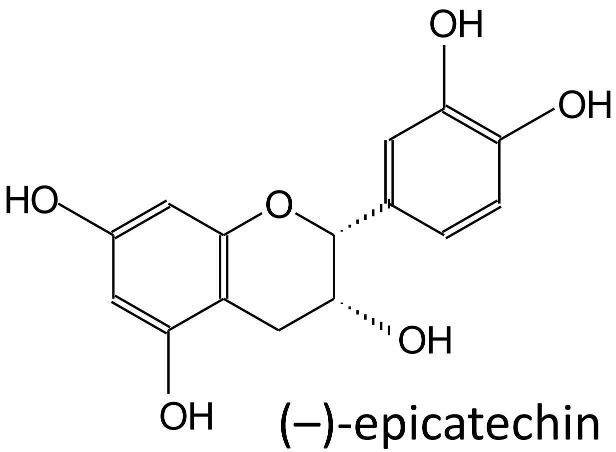
Catechins



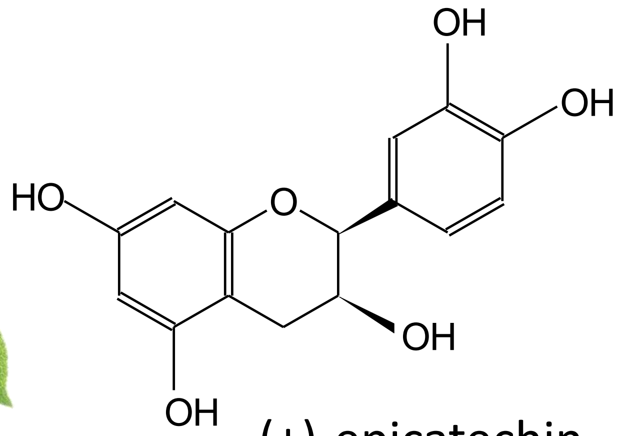
(–)-catechin



(+)-catechin

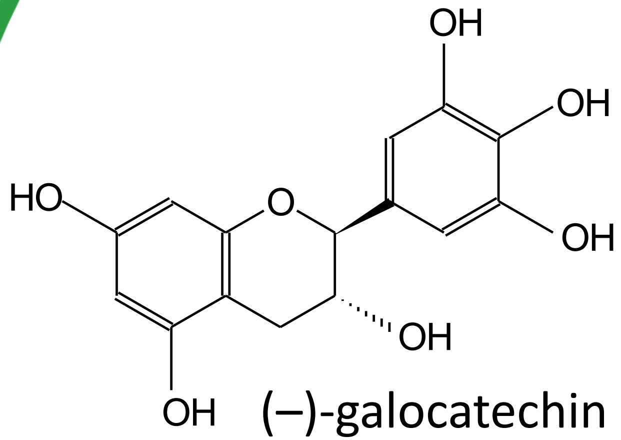


(–)-epicatechin

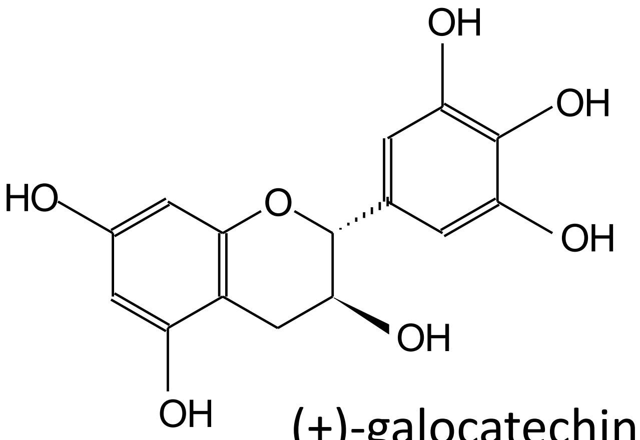


(+)-epicatechin

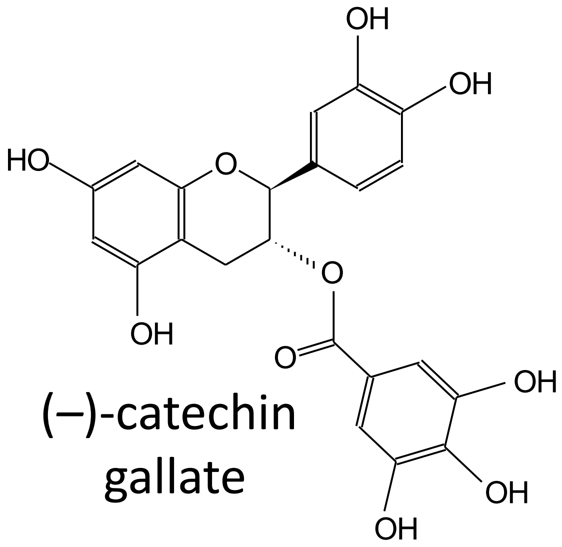
Catechins



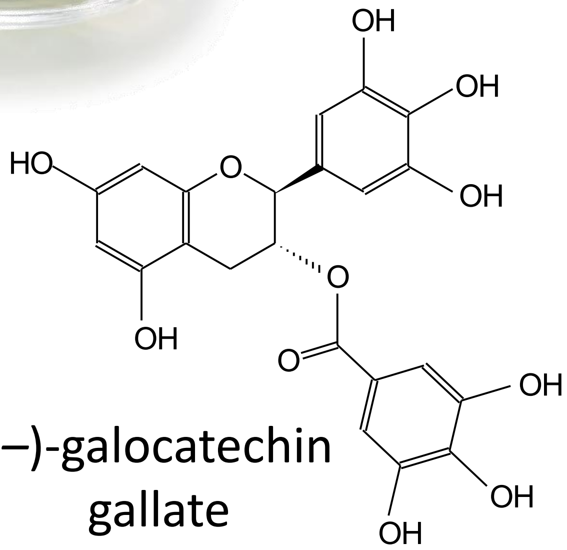
(–)-galocatechin



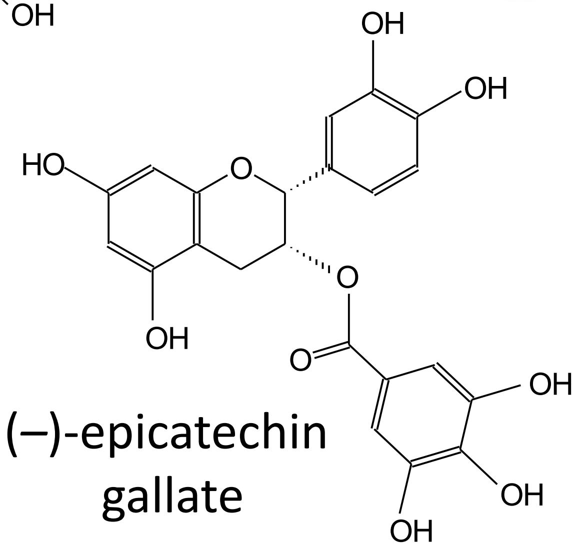
(+)-galocatechin



(–)-catechin gallate



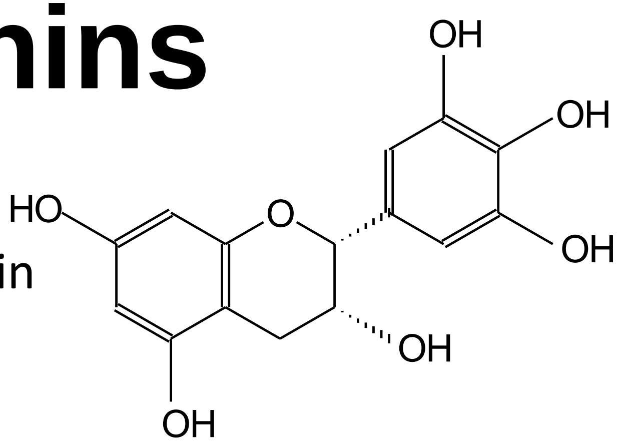
(–)-galocatechin gallate

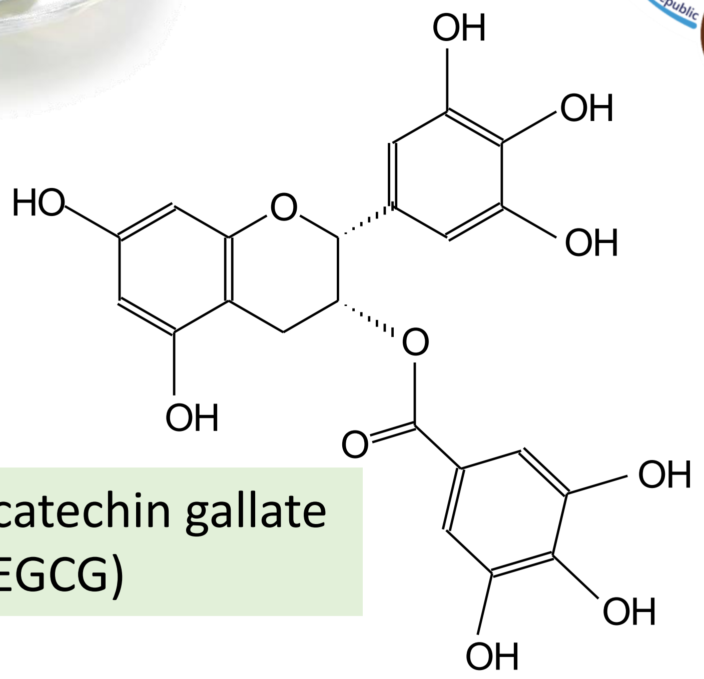


(–)-epicatechin gallate

Catechins

(–)-epigalocatechin





(–)-epigalocatechin gallate (EGCG)

EGCG is the most active! In vitro, it **inhibits the development of cancer cells**, the formation of new blood vessels (angiogenesis) and the ability to metastasis (i.e. to form metastases).

EGCG has the ability to block the CD4 receptor of lymphocytes, which **prevents the attachment of glycoproteins in the HIV virus envelope**, and thus protects the cells of our body against invasion.

Catechins

Green tea extracts have been used for many years as **a component of functional foods** and **pharmaceutical preparations** that are dietary supplements. These preparations are intended to **prevent many diseases**, **support the treatment of cancer**, support the body in people who smoke or **lose weight**. They are also widely used **in cosmetics**.

Tannins

- Many flavonoids in food polymerize into large molecules, either still within the plant or as a result of food processing. These polymers are called **tannins**.

One of the tannins definitions is: „Any phenolic component of sufficiently high molecular weight containing enough hydroxyl or other appropriate groups (e.g. carboxyl) to efficiently form strong complexes with proteins and other macromolecules under specified environmental conditions"

- Tannins form complexes with proteins, starch, cellulose and minerals.

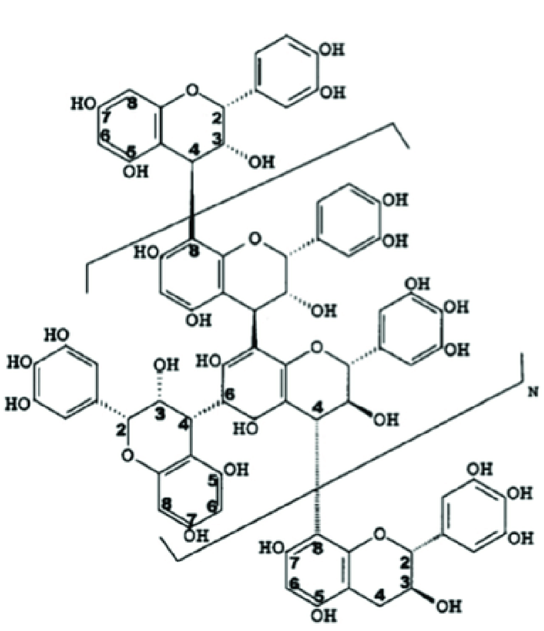
- **Tannins are found in tea, wine, nuts, fruits and vegetables, among others.**

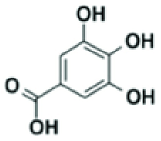
- They include polyphenols with a **molecular weight of 3,000 to 20,000,** i.e. compounds composed of 5 to 7 aromatic rings and containing 12-16 phenolic groups in the molecule.

Tannins

Tannins are divided into:

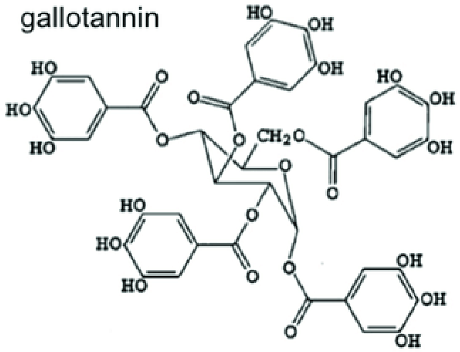
1. **hydrolysable tannins** – esters of gallic or ellagic acid and non-aromatic polyols,
2. **proanthocyanidins** (condensed tannins, non-hydrolyzing tannins) – polymers of flavanols, linked by 4→8 or 4→6 bond





gallic acid

gallotannin



condensed tannins (proanthocyanidins)

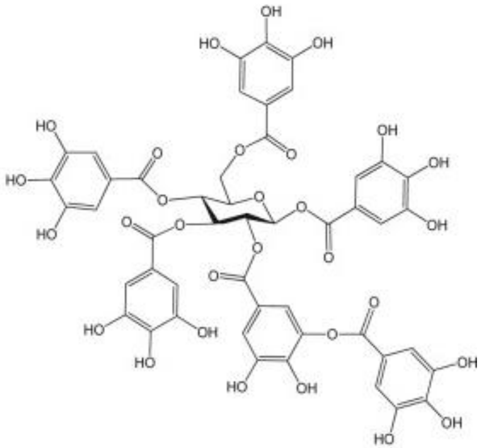
hydrolysable tannins

Hydrolysable tannins

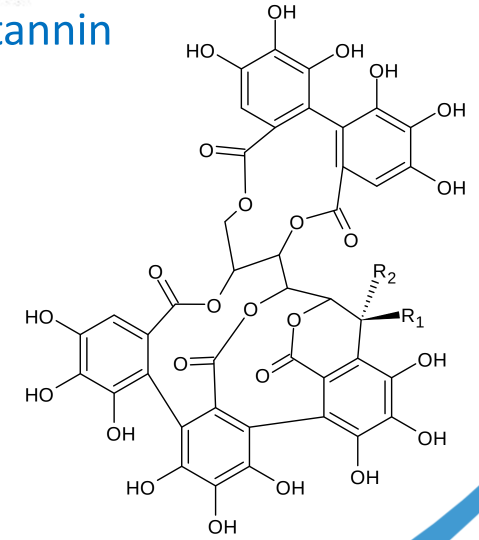
Hydrolysable tannins (HT) are molecules having non-aromatic polyols (usually D-glucose or quinic acid) as a central core. The hydroxyl groups of these carbohydrates **are partially or fully esterified with phenolic groups such as gallic acid** (→ gallotannins) or **ellagic acid** (→ ellagitannins).

The name „hydrolysable tannins" comes from the ease with which the ester bond breaks down. However, numerous other bonds (C-C, C-O-C) can form, resulting in the formation of dimers or higher complexes that differ in their degree of resistance to chemical degradation.

Hydrolysable tannins are widespread in plant foods, contributing to their taste.

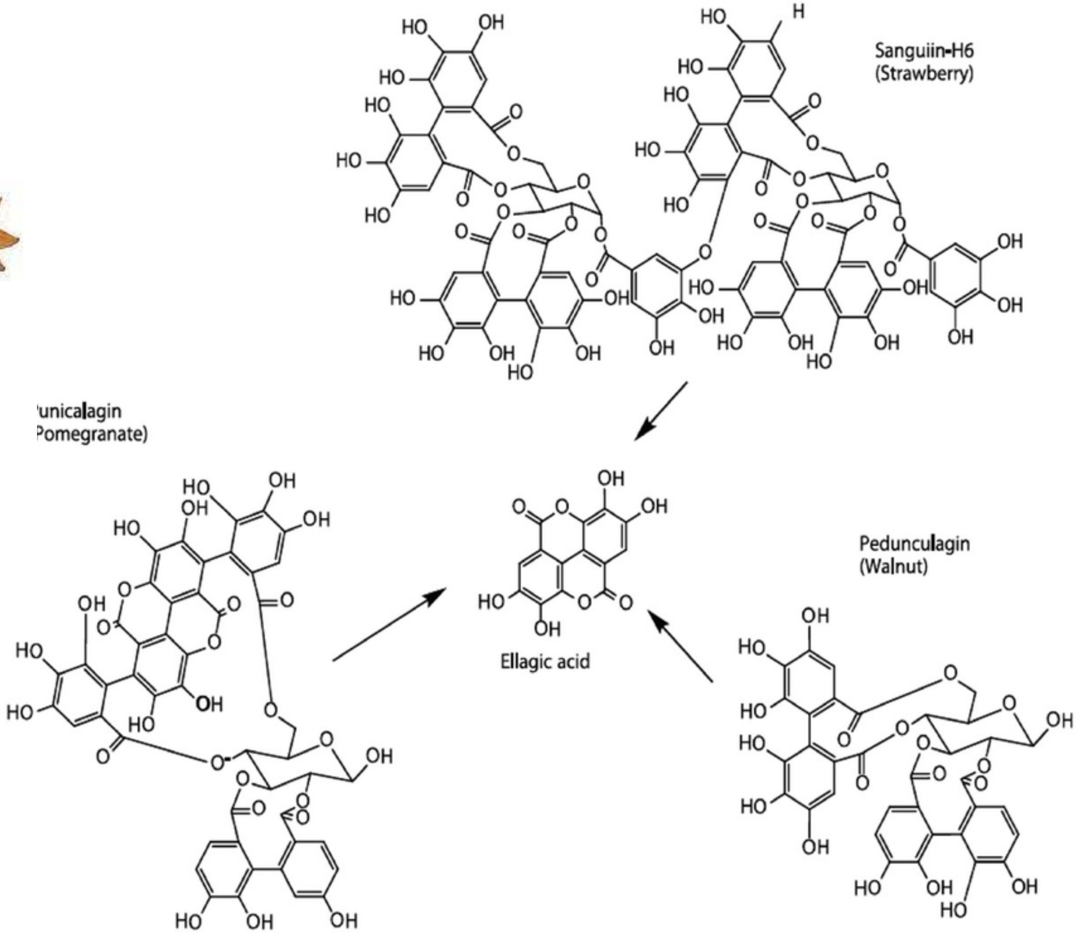


example of gallotannin



example of ellagitannin

Elagitannins



Condensed tannins

Condensed tannins = proanthocyanidins = non-hydrolyzing tannins

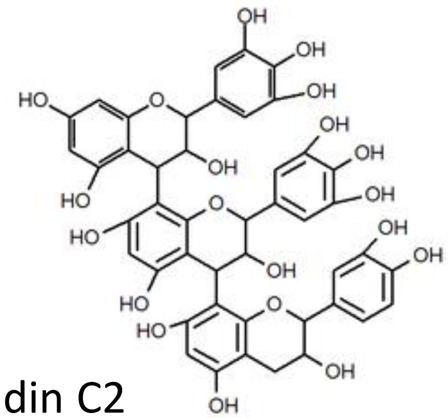
- They are much more widely distributed than hydrolysable tannins.
- They are **oligomers or polymers of flavan-3-ols linked by C-C bonds** that are not sensitive to hydrolytic degradation.
- In food, the monomers are most often linked via 4→6 or 4→8 (C-C) or 4→8 (C-C) and 2→7 (ether) bonds.
- They are called condensed tannins because **they have a packed (condensed) structure.**

Proanthocyanidins

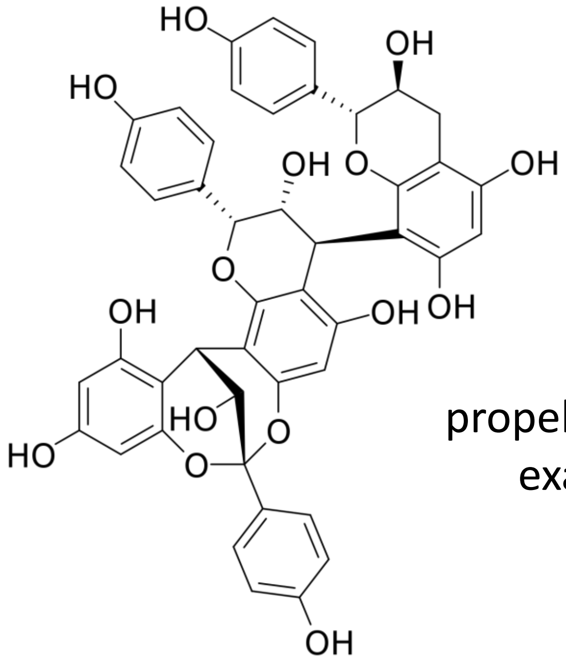
- Proanthocyanidins contain from 2 to 50 flavonoid subunits.
- Their complexes have a complex structure due to the structure of their flavonoid units and due to various bonds between them.

There are 15 subclasses known, but 3 are especially important in food:

- procyanidins (epicatechin polymers)
- prodelphinidins (epigallocatechin polymers)
- propelargonidins (epiafzelechin polymers)

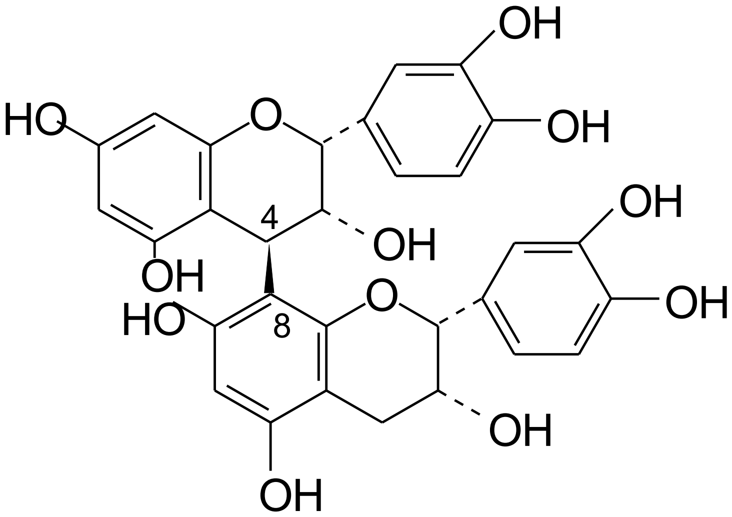


prodelphinidin C2

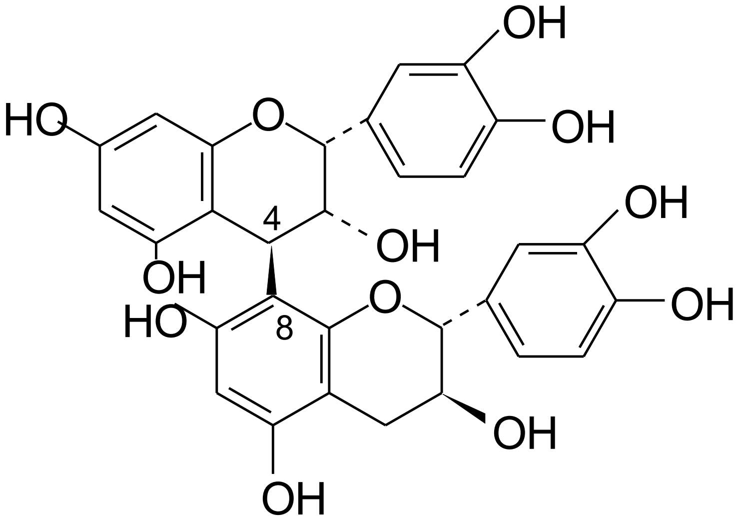


propelargonidin example

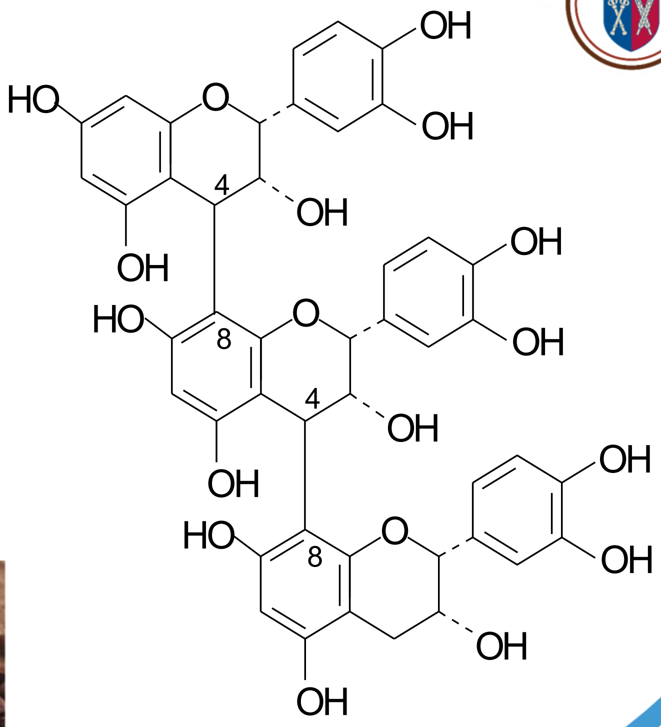
Proanthocyanidins



procyanidin B_2



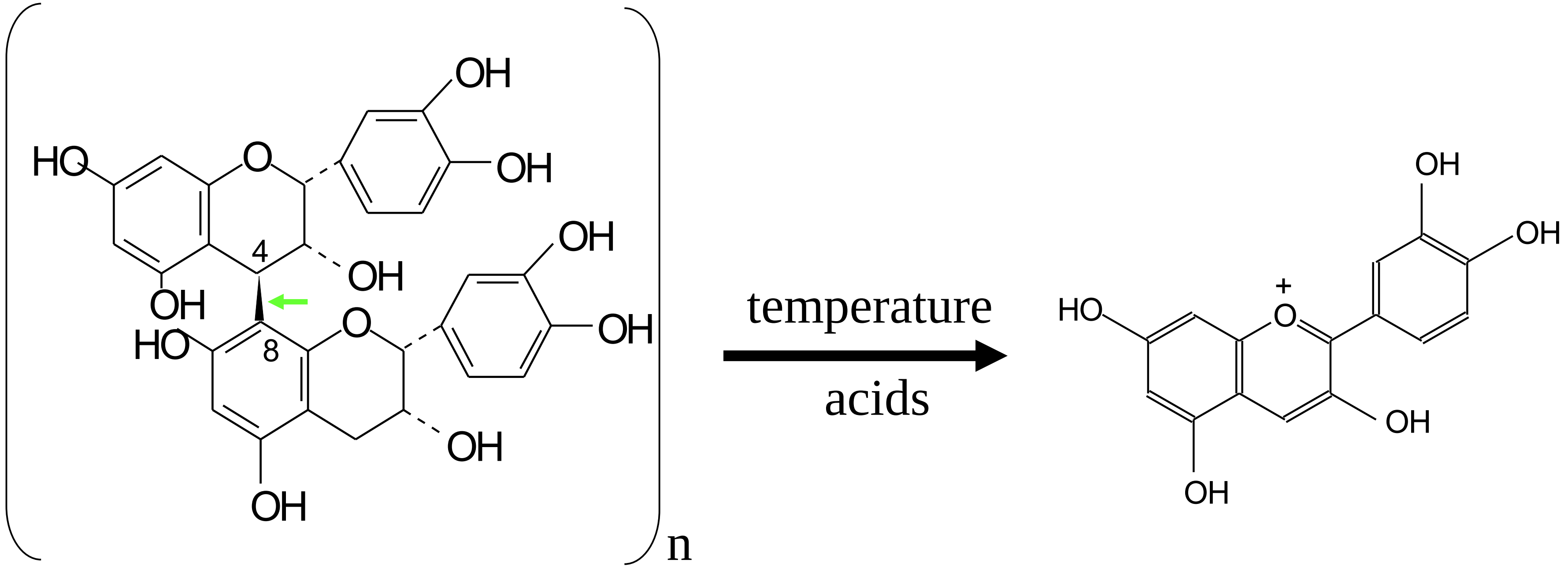
procyanidin B_1



procyanidin C_1

Why proanthocyanidins?

- The name **proanthocyanidins** is derived from the acid-catalysed oxidation reaction that **produces coloured anthocyanidins** from proanthocyanidins heated in acidic alcohol solutions.



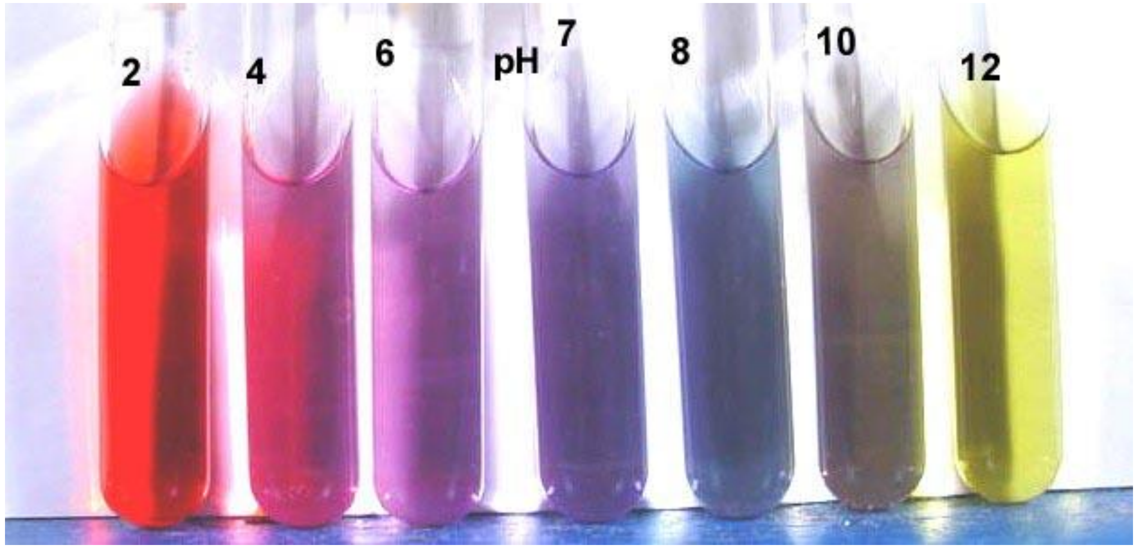
proanthocyanidin

anthocyanidin

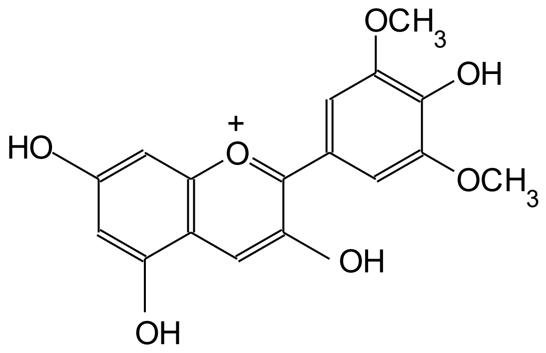
Anthocyanidin pigments are responsible for a wide range of shades of **pink, red, purple and purple** in flowers, leaves, fruits, fruit juices and wines.

Anthocyanins

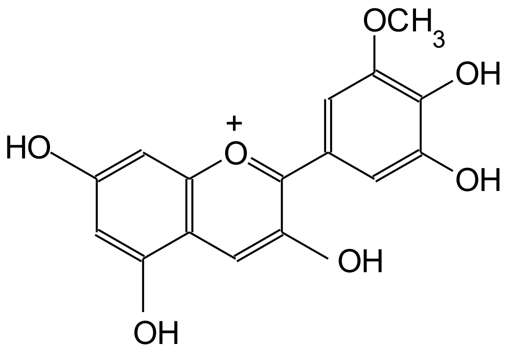
- **Anthocyanins are glycosides of anthocyanidins.**
- They **do not have a carbonyl group at C4**, which causes a positive charge to appear on the C ring.
- These are pink, blue and purple dyes dissolved in the vacuole of the skin cells of flowers and fruits.
- **Depending on the pH, they exist in various chemical forms, coloured or colourless.**



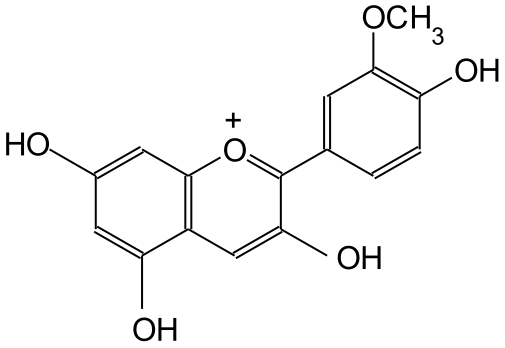
Anthocyanidins



malvidin

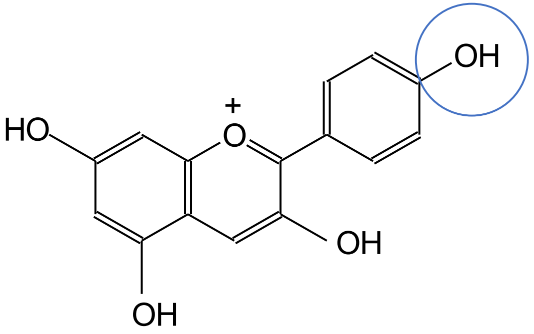


petunidin

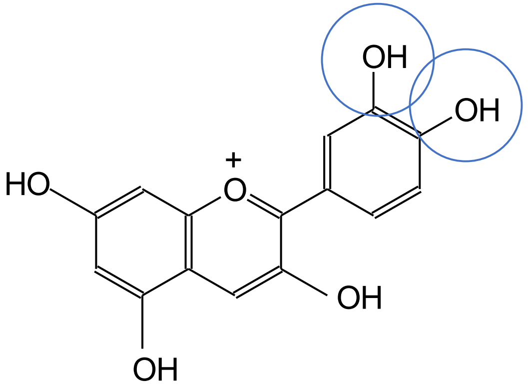


peonidin

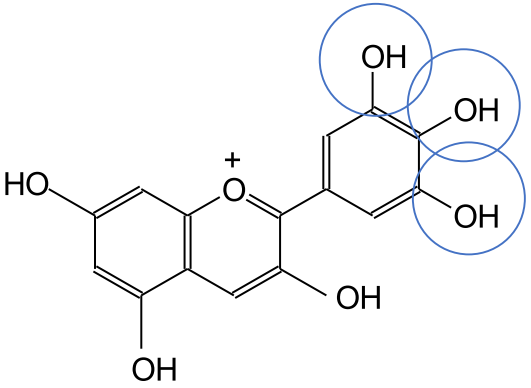
Anthocyanidins



pelargonidin



cyanidin

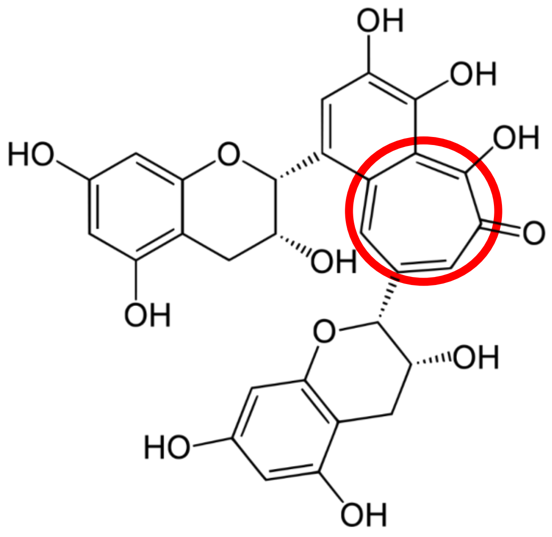


delphinidin

Theaflavins and thearubigins

The most important tannin derivatives in food are **theaflavins** and **thearubigins** found in **fermented teas (black tea and oolongs)**, where they are responsible for their characteristic astringent taste and color of tea.

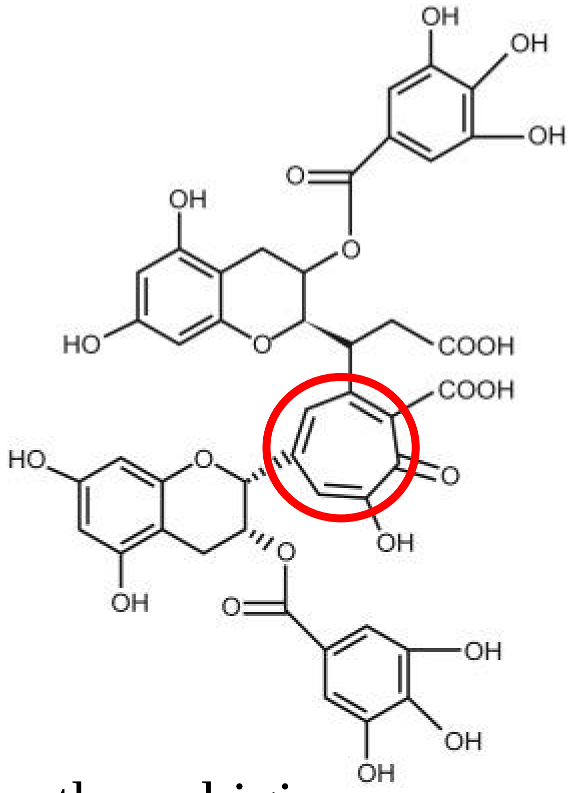
Theaflavins are dimer derivatives of tannins.
Their unique feature is **the 7-carbon benzotropolone ring**, formed by the oxidation of the B ring either in (-)-epigallocatechin or in (-)-epigallocatechin gallate, loss of CO_2 and simultaneous fusion with the B ring of a second molecule of (-)-epigallocatechin or (-)-epigallocatechin gallate. As a result, different 4 components can be formed: theaflavin, theaflavin 3-galate, theaflavin 3’-galate, and theaflavin 3,3’-digalate.



theaflavin

Theaflavins and thearubigins

Under conditions that favor to the condensation of flavanols, heterogeneous high-molecular components (1-10 kDa) are also formed. They are called **thearubigins**.

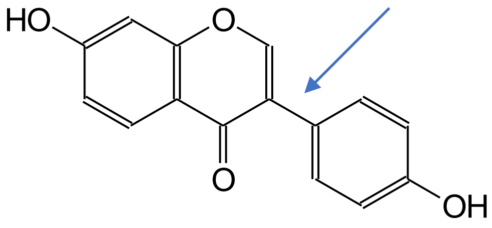


thearubigin

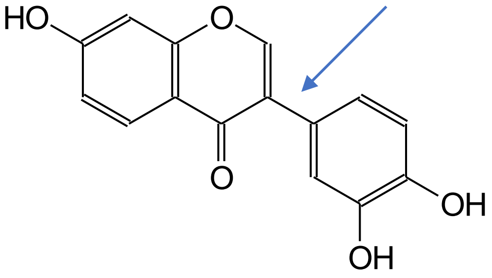
Isoflavones

- The characteristic feature of this group is **the B ring attached to the C carbon at the C3 position instead of the C2 position.**
- Isoflavones have estrogen-like effects, which is why they are often classified as **phytoestrogens** together with lignans.
- Although they are not steroids, **they can bind to estrogen receptors** because their hydroxyl groups arranged in the 4'- and 7- position simulate the configuration of estradiol.
- Isoflavones (**genistein, daidzein, glycitein**) are present in large amounts in **soybeans and legumes**.
- They have been shown to be protective against LDL and can alleviate the symptoms of menopause, however only after microbial conversion to active metabolites like S-equol or O-desmethylangolensin.

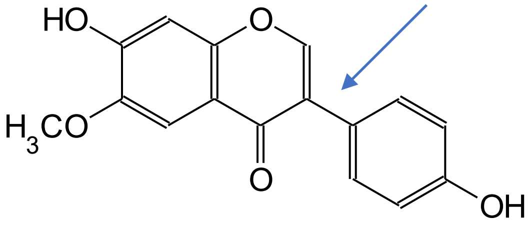
Isoflavones



daidzein



genistein

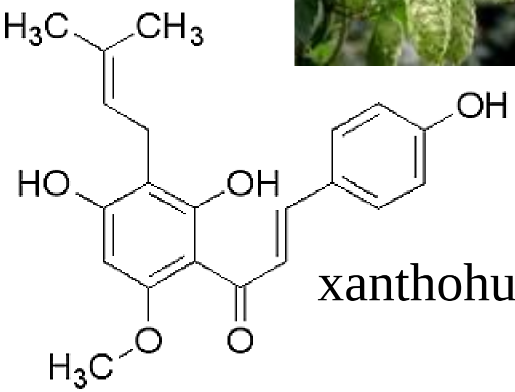


glycitein

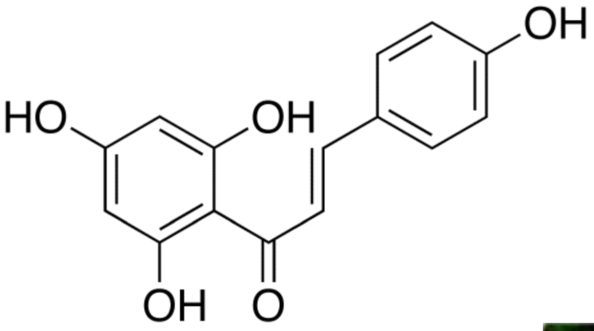
Chalcones

- Chalcones are an **unstable form** resulting from the enzymatic activity of two different metabolic pathways (shikimic acid and malonic acid).
- The precursors of chalcone synthesis are malonyl-S-CoA and p-coumaryl-S-CoA, which are biochemical precursors of flavonoids, mainly flavanones, flavones and isoflavones, **constituting an intermediate stage preceding the closure of the pyrone ring.**
- The basic **backbone of chalcones lacks a central heterocyclic system**, which results in different numbering of individual atoms.
- **Chalcones are lipophilic compounds**, yellow in color and, depending on the structure, are extracted with more or less polar organic solvents.
- The most important compounds in this group include **xanthohumol** present in hops and **isosalipurpol** and its glucoside - **isosalipurposide** found in *Helichrysum* inflorescences.
- **Phloridzin**, one of the dihydro-derivatives of glycosylated chalcones, is the dominant polyphenolic compound in apple seeds.

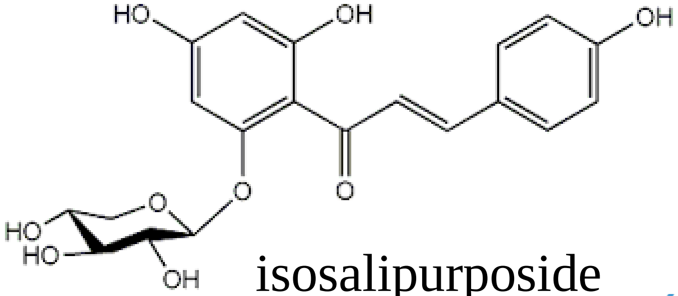
Chalcones



xanthohumol



isosalipurpol



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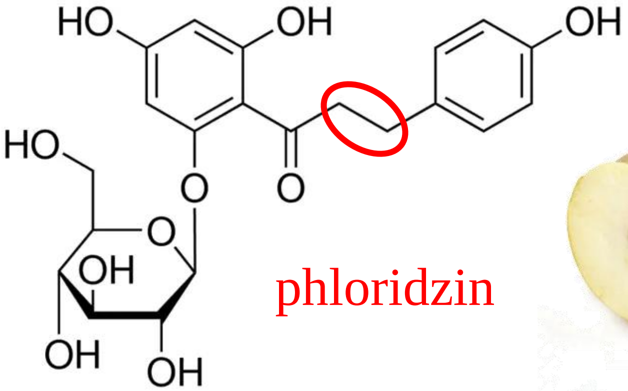


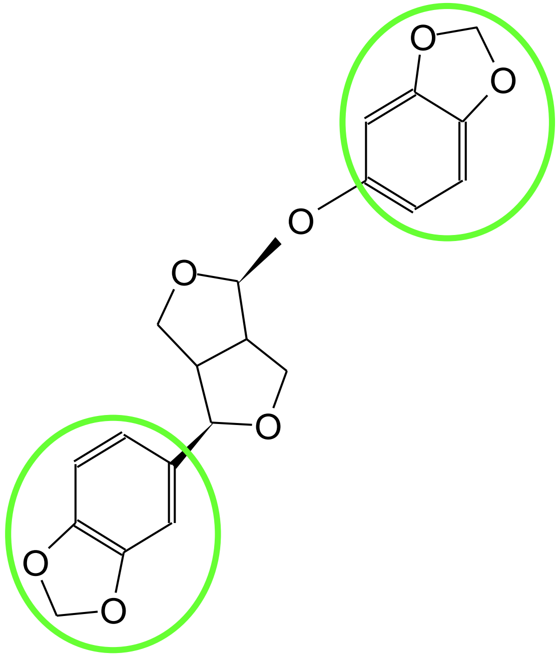
phloridzin

Lignans

A characteristic feature of their structure is the presence of two p-hydroxyphenyl propane (C_6C_3) units.

The most important lignans include:

- sesamin,
- sesaminol,
- sesamolin,
- enterodiol,
- enterolactone,
- matairesinol,
- pinoresinol,
- secoisolariciresinol,
- schizandrine,
- schizandrol.



Lignans

Lignans are widely distributed in seeds (lentils), vegetables (garlic, asparagus, carrots) and fruits (pears, plums), and the **richest sources are linseed and whole cereal grains**.

They are a component of cell walls and can be released by intestinal bacteria.

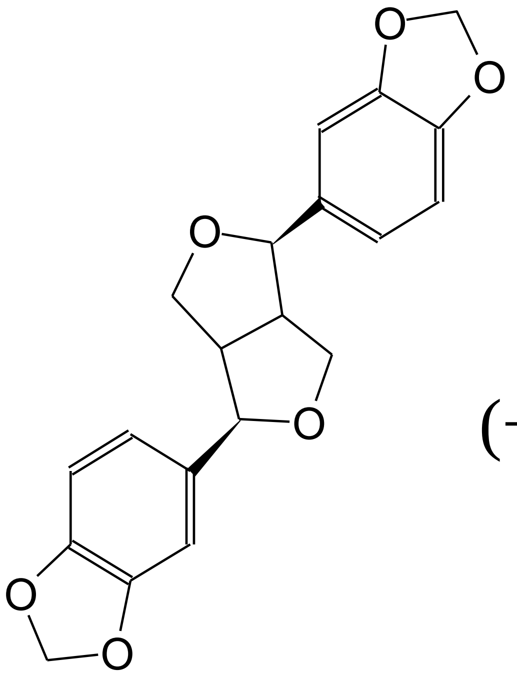






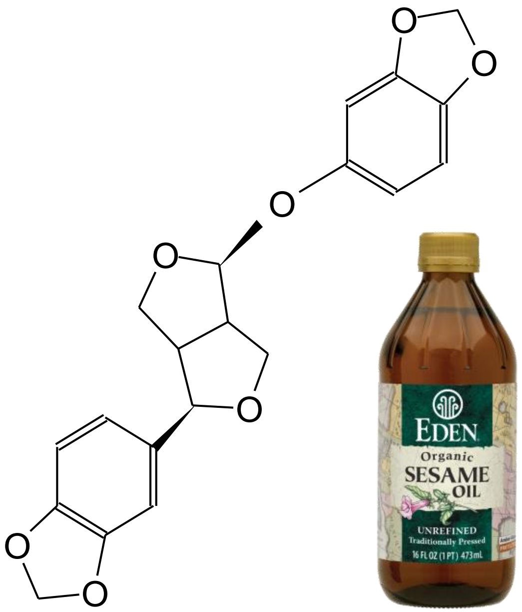

Lignans – sesamin

Sesamin acts as an antioxidant, lowers LDL levels, activates anti-inflammatory processes, but also **takes part in beta-oxidation of fatty acids**, while **slowing down lipogenesis** (creation of new fatty acids) → **accelerating fat burning in muscle tissue**

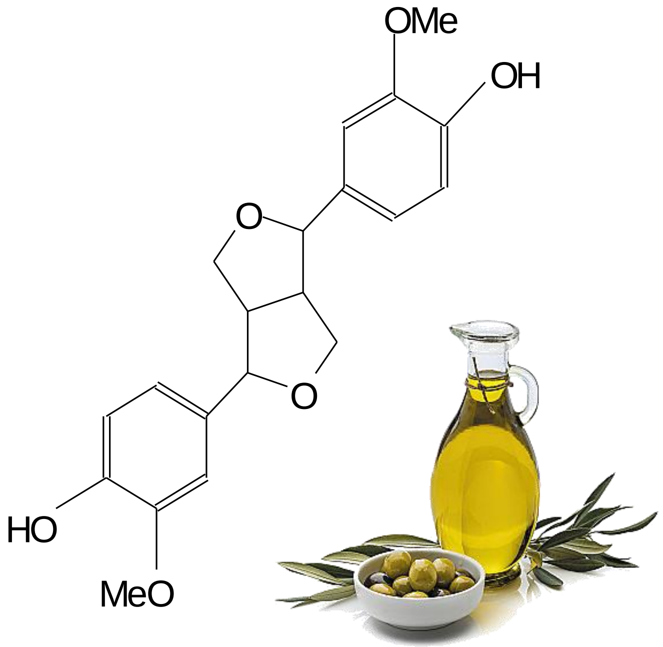


(+)-sesamin

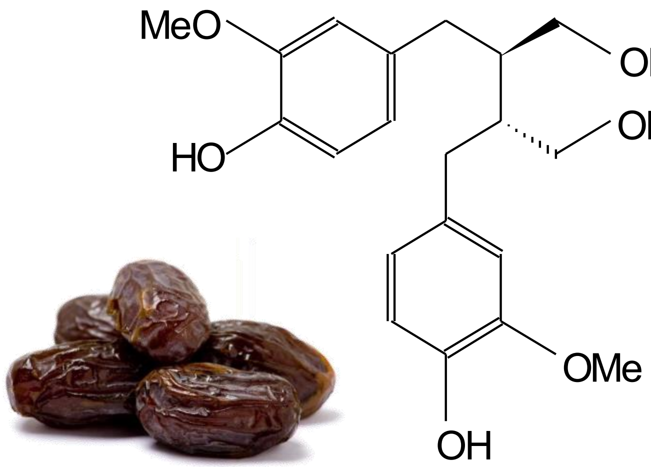
Lignans



sesamolin



pinoresinol

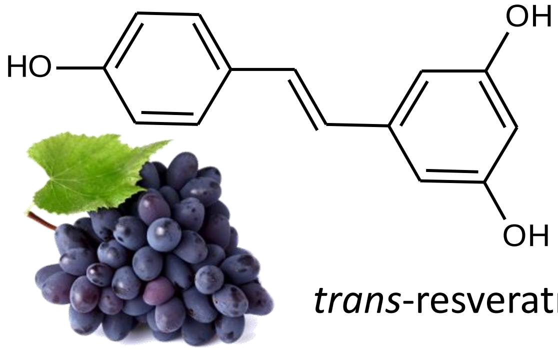


secoisolariciresinol

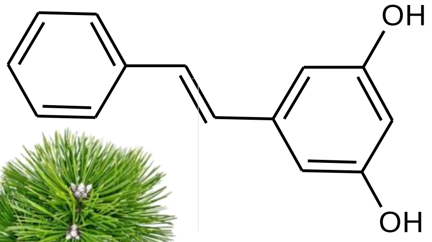
Stilbenes

Stilbenes are compounds belonging to phytoalexins, the low-molecular cell components with **antibacterial properties**.
Stilbenes are synthesized via the phenylalanine/polymalonate pathway, and the key enzyme in this process is stilbene synthase (E.C. 2.3.1.95), which catalyzes the condensation reaction of *p*-coumaryl-S-CoA and 3 malonyl-S-CoA molecules, resulting in resveratrol production.
Resveratrol is one of **the best-studied antioxidant components of wine** and at the same time the first synthesized compound belonging to the stilbenes derivatives - **stilbenoids**. Under the influence of the activity of plant pathogens (*Botrytis cinerea*), the vine is infected, which results in increased production of resveratrol, which then appears in the wine. It has been shown that this compound **inhibits the development of cancer cells** by blocking proliferation and inducing apoptosis by regulating the expression of the bcl-2 and bax genes. In addition, it protects protein thiol groups from oxidative damage. However, the resveratrol level in red wines is too low to exert beneficial impact.

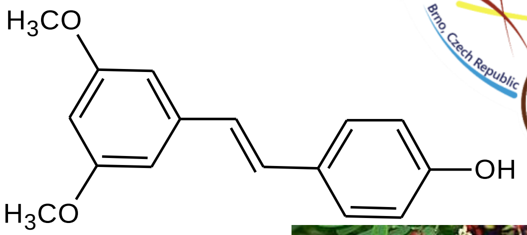
Stilbenoids - hydroxylated stilbenes



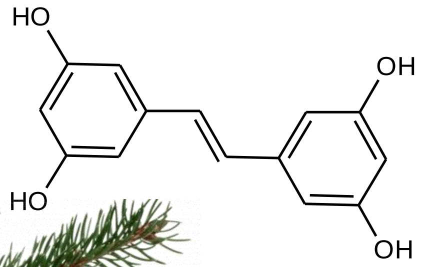
trans-resveratrol

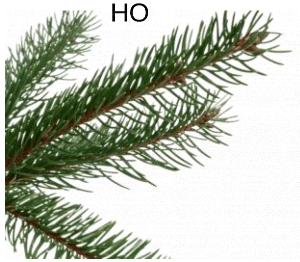


pinosylvin

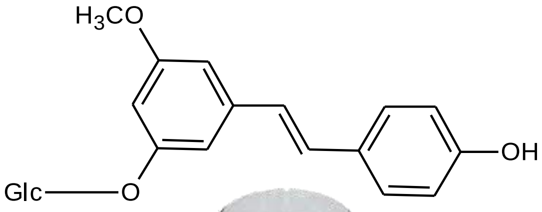


pterostilbene





piceatannol



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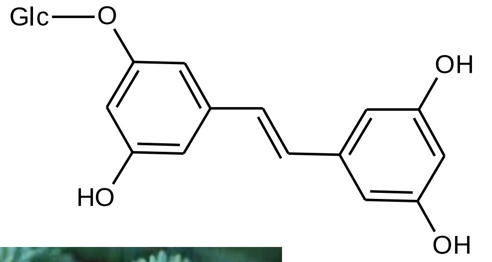
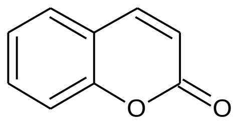


astringin

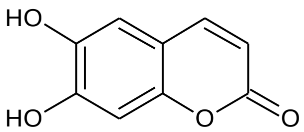
Coumarins

Coumarin has analgesic, anti-swelling, sedative, antispasmodic, anti-allergic and antioxidant properties, while esculin has a sealing and elasticizing effect on small blood vessels (which can be useful in the treatment of varicose veins and hemorrhoids). Natural coumarins play also a significant role in cancer prevention and treatment. Among important coumarin derivatives are drugs used in anticoagulant therapy – dicoumarol, acenocoumarol and warfarin.

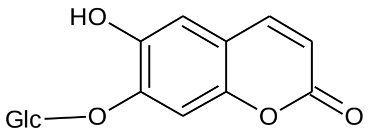
Coumarins are accountable for the specific odour of food (coumarin has a smell of hay).



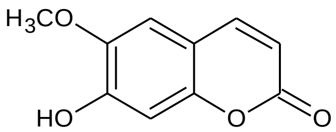
coumarin



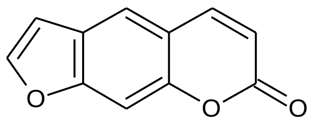
esculetin



esculin



scopoletin



psolaren

Cinnamon is the main source of the coumarin from food, but also peels of bergamot, grapefruit and pummelo contais high amounts. Large amounts of coumarin can be hepatotoxic!

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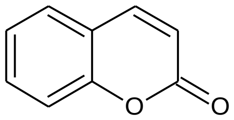
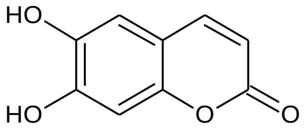
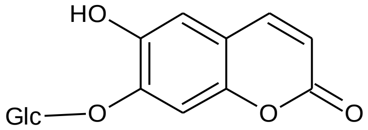


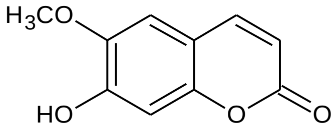
coumarin



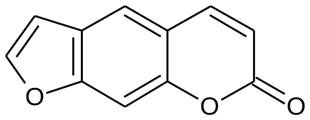
esculetin



esculin



scopoletin



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Innovation of the structure and content of study programs profiling food study fields with a view to digitizing teaching

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