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Nutritional phenolic compounds in red wines determined by HPLC-DAD-ESI-MS and MS/MS

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WINE

Wine is a complex mixture of different compounds:

- ✓ **Organic acids**
- ✓ **Alcohols**
- ✓ **Carbohydrates**
- ✓ **Aldehydes, esters**
- ✓ **Minerals**
- ✓ **Nitrogen compounds**
- ✓ **Phenolic compounds**
- ✓ **Varietal aroma**

PHENOLIC COMPONENTS

- ✓ Determine the colour, mouthfeel, astringency and bitterness of wine.
- ✓ Influenece the sensorial characteristics of grape and wine
- ✓ Antioxidant, antimicrobal, anticancerogenic effects, prevention of cardiovascular diseases.

Two groups of polyphenols:

Non-flavonoids

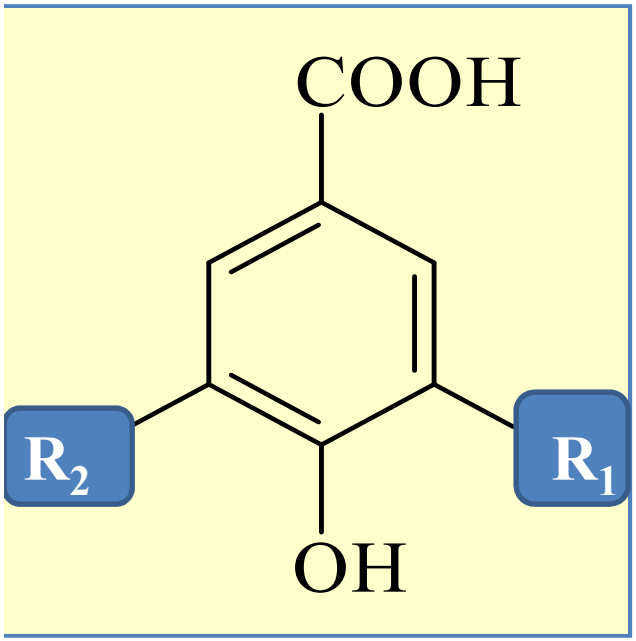
Flavonoids

NON - FLAVONOIDS

The main non-flavonoid phenols in grape and wine which contain only one aromatic ring are:

1. **Hydroxybenzoic acids**
2. **Hydroxycinnamic acids and derivatives**
3. **Stilbenes and stilbene glucosides**

NON-FLAVONOIDS – Hydroxybenzoic acids



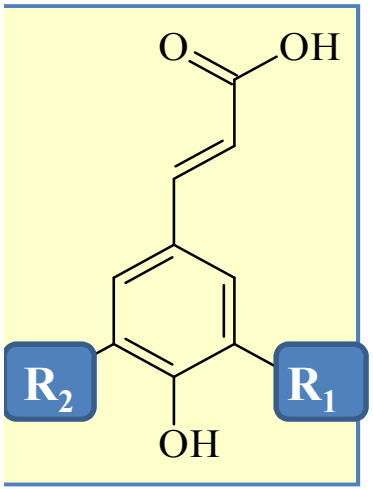
Hydroxybenzoic acids	R_1	R_2	M_r
Gallic acid	OH	OH	170
p-Hydroxybenzoic acid	H	H	138
Protocatechuic acid	OH	H	154
Syringic acid	OCH_3	OCH_3	198
Vanillic acid	H	OCH_3	168

✓**Gallic acid is present in the highest concentration in wine.**

✓**Gallic acid** originates from the grapes or from hydrolysis of hydrolyzable and condensed tannins

✓These acids are present in free forms in the wine (hydrolysis or heat breakdown reactions of the complex moleculs)

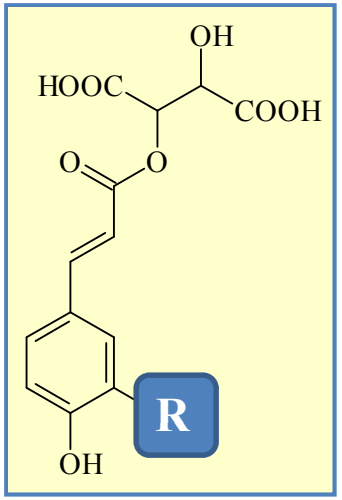
NON-FLAVONOIDS – Hydroxycinnamic acids and derivatives



Hydroxycinnamic acids

Hydroxycinnamic acids	R_1	R_2	M_r
Coumaric acid	H	H	164
Caffeic acid	OH	H	180
Ferulic acid	OCH_3	H	194
Sinapic acid	OCH_3	OCH_3	224

Derivatives	R_1	M_r
Coutaric acid	H	296
Caftaric acid	OH	312
Fertaric acid	OCH_3	326



Derivatives

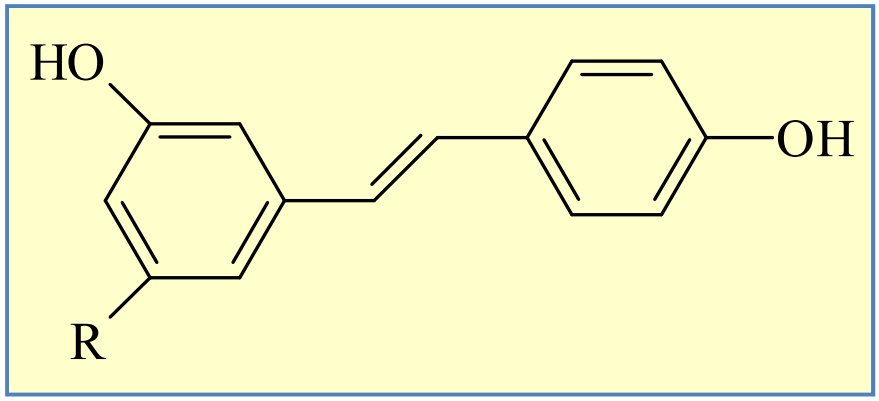
✓Present in *cis*- and *trans*-forms, *trans*-forms are more stable and prevalent.

✓Present in form of esters of l-(+)-tartaric acid (predominant).

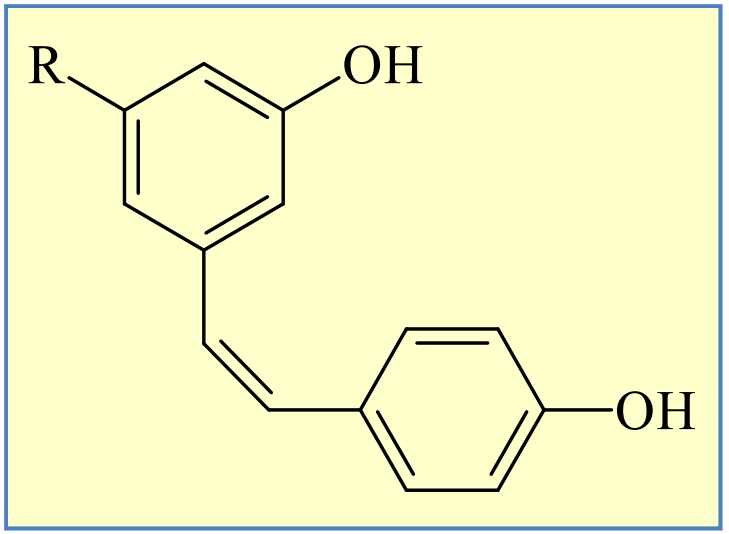
✓Caftaric and coutaric acids are the most abundant in the wine; highly oxidizible components causing the browning of white must.

NON-FLAVONOIDS – Stilbenes

3. Stilbenes



R=OH - *trans*-resveratrol
R=OGlc - *trans*- piceid



R=OH - *cis*- resveratrol
R=OGlc- *cis*-piceid

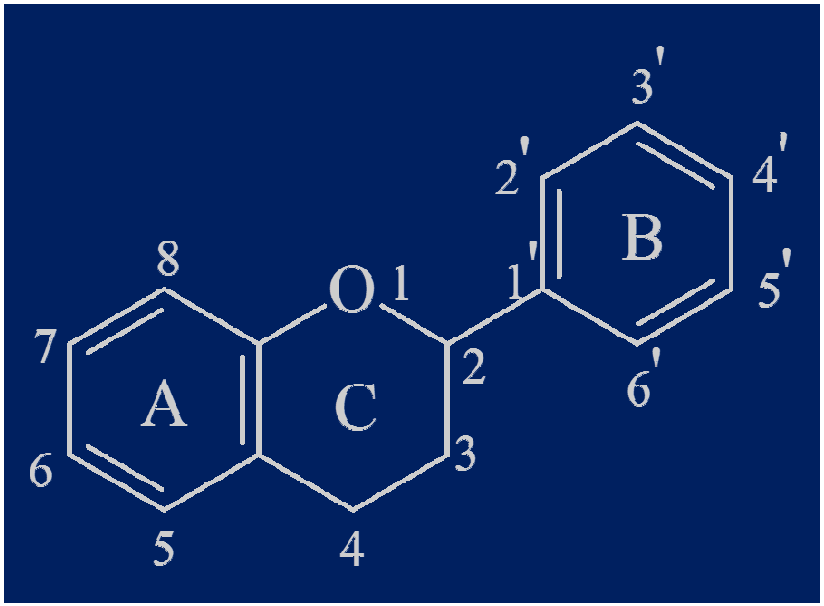
- **Resveratrol is considered to be a phytoalexin, t.e. Toxin produced in the grapes due to fungal infection (e.g. *Botrytis cinera Pers or Plasmopora viticola*) or a product produced from abiotic stress (UV radiation, heavy metal catalysis, etc).**
- **Wines resulting from longer maturation periods contain a higher content of resveratrol.**
- **The concentration of resveratrol is higher in red wines as compared to white wines.**

FLAVONOIDS

- free and polymerized to other flavonoids, sugars, nonflavonoids,

- esterified to sugars, organic acids, or various alcohols

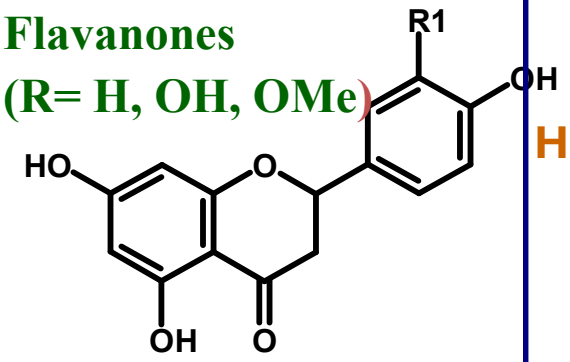
The FLAVONOIDS structure:



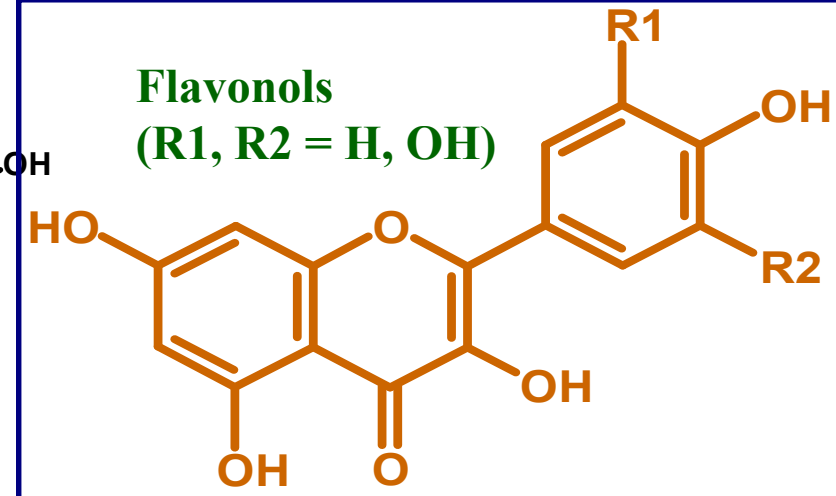
FLAVONOIDS

Flavonoids are divided into the following groups:

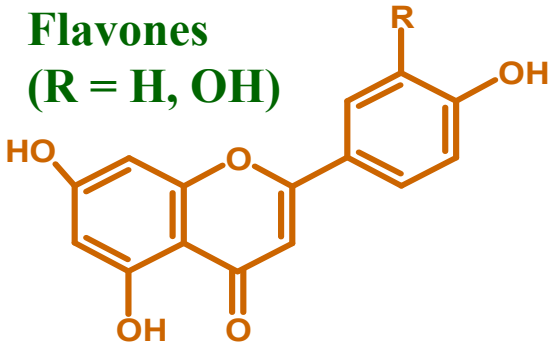
Flavanones
(R= H, OH, OMe)



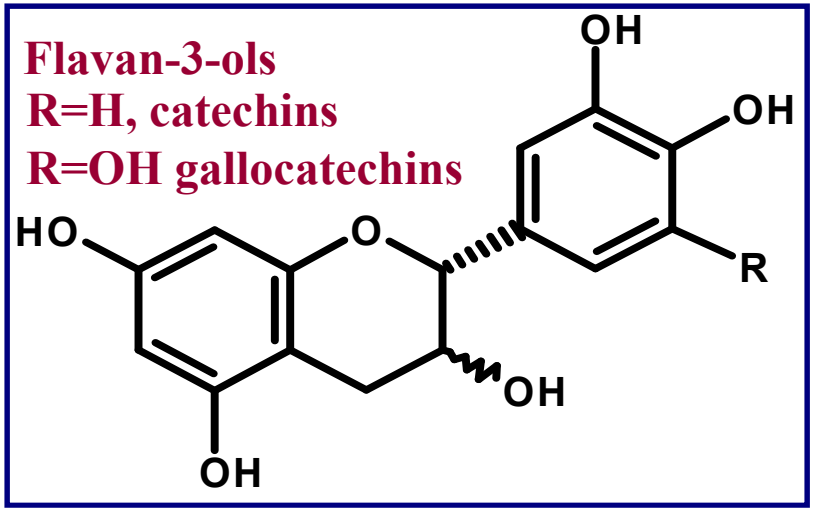
Flavonols
(R1, R2 = H, OH)

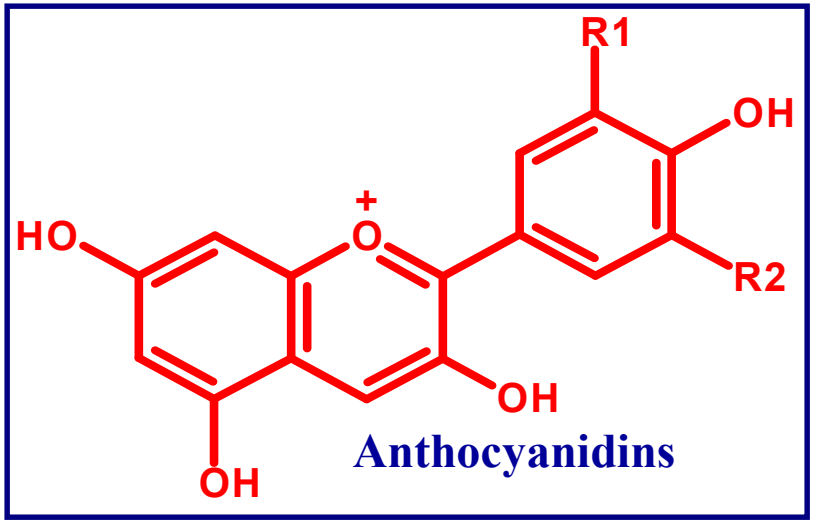


Flavones
(R = H, OH)



Flavan-3-ols
R=H, catechins
R=OH gallocatechins





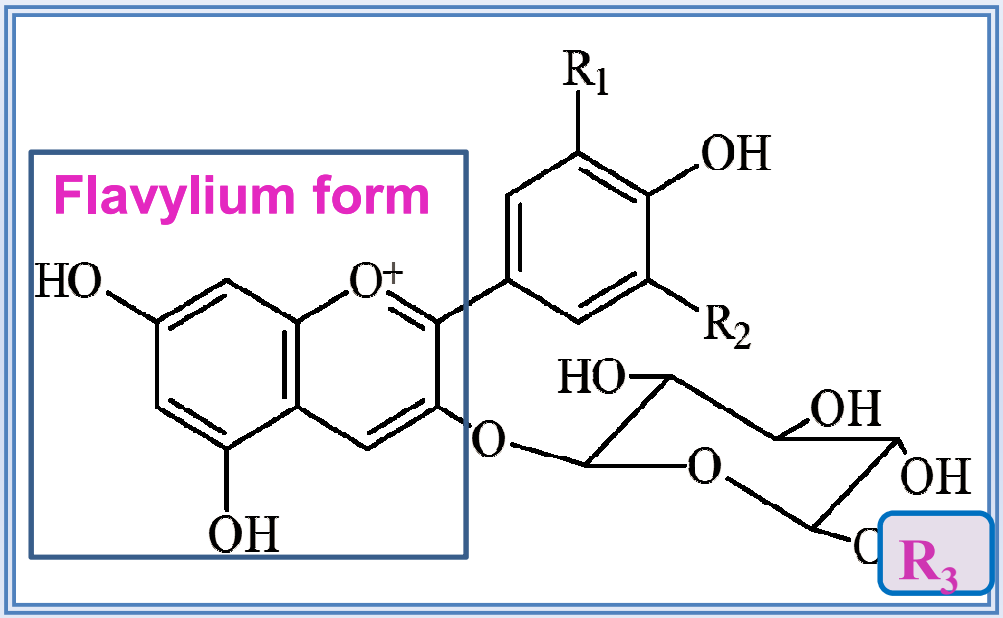
Anthocyanidins

ANTHOCYANINS

- Anthocyanins are **red compounds**, responsible for the colour of red grapes and wines.
- Mainly located in the **grape skins**, (exception are the teinturier varieties that contain anthocyanins in the pulp).

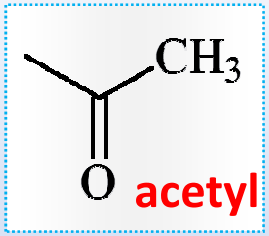
Anthocyanidins	R_1	R_2
Delphinidin	OH	OH
Cyanidin	OH	H
Petunidin	OCH_3	OH
Peonidin	OCH_3	H
Malvidin	OCH_3	OCH_3

ANTHOCYANINS

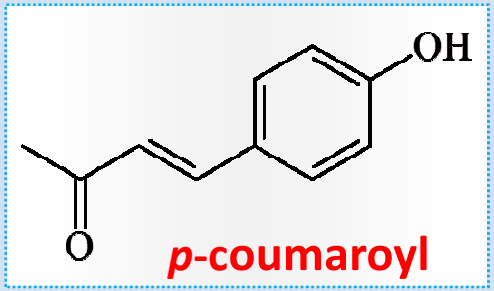


Flavylium form, 96 % at pH 1.5

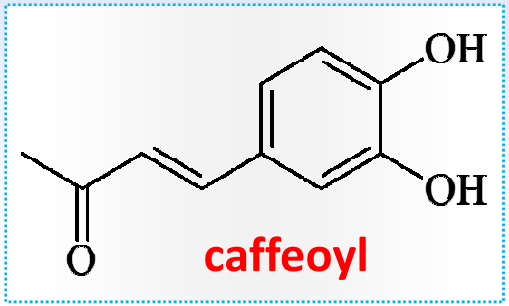
R_3 =



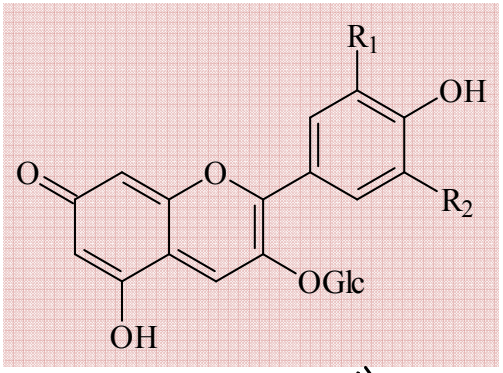
R_3 =



R_3 =



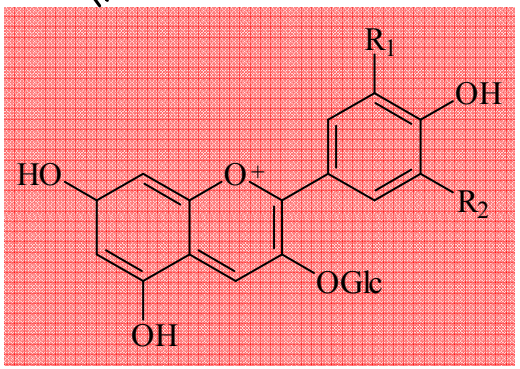
Anthocyanin transformations



Quinoidal anhydrobase (A)

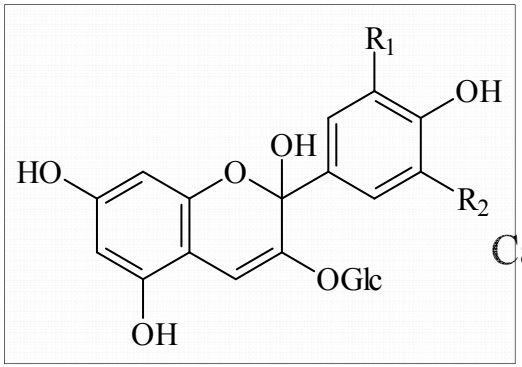
In neutral media

deprotonation ($-H^+$)



Flavylium cation (AH^+)

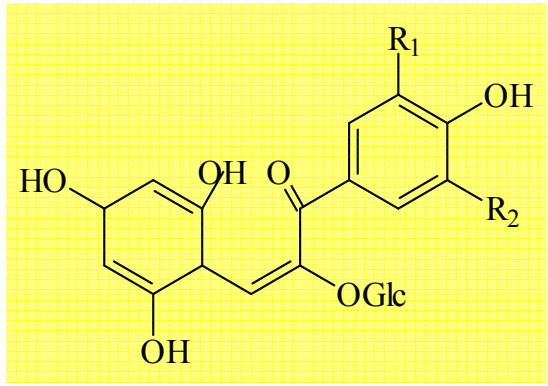
hydratation reaction ($+H_2O/-H^+$)



In highly acidic media

Carbinol pseudobase (B)

tautomeric reaction



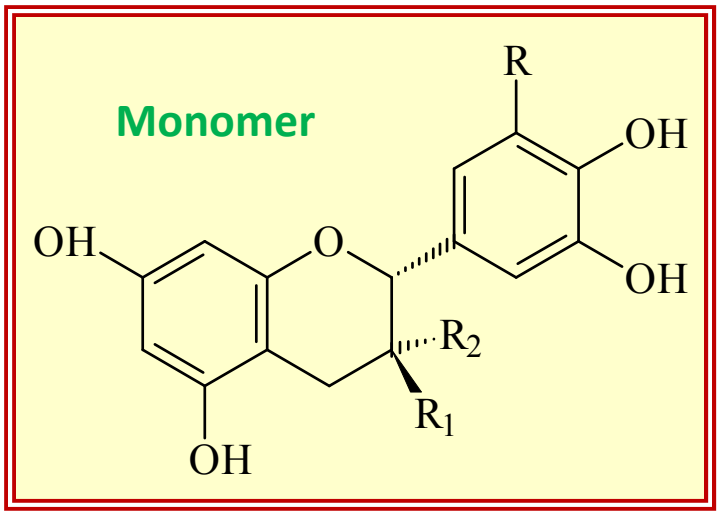
Chalcone (C)

FLAVAN-3-OLS

Flavan-3-ol monomers:

(+)-catechin

(–)-epicatechin



Flavan-3-ols	R	R1	R2	M_r
(+)-Catechin	H	OH	H	290
(-)-Epicatechin	H	H	OH	290
(+)-Gallocatechin	OH	OH	H	306
(-)-Epigallocatechin	OH	H	OH	306
(-)-Epicatechin-3-gallate	H	H	OGallate	442

FLAVAN-3-OLS

Flavan-3-ol dimers:

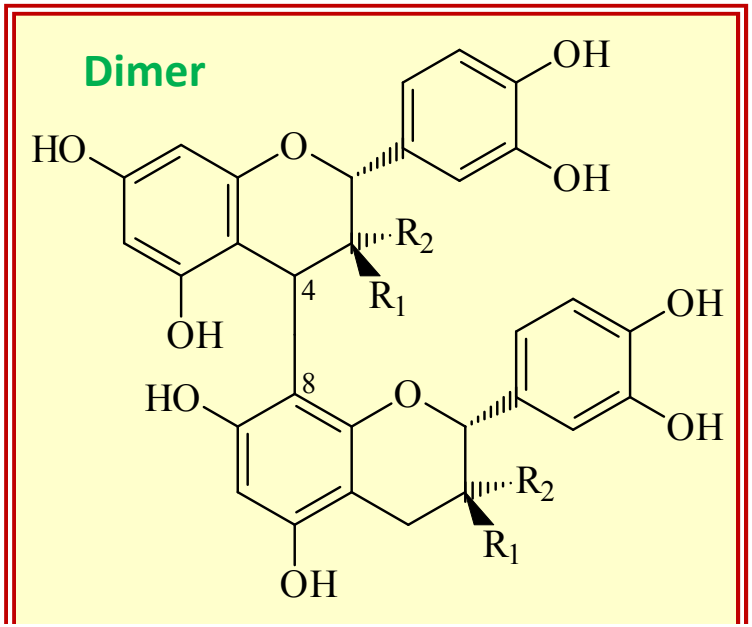
Procyanidin dimers:

B1: (-)-epicatechin-(4-8)-(+)-catechin

B2: (-)-epicatechin-(4-8)-(-)-epicatechin

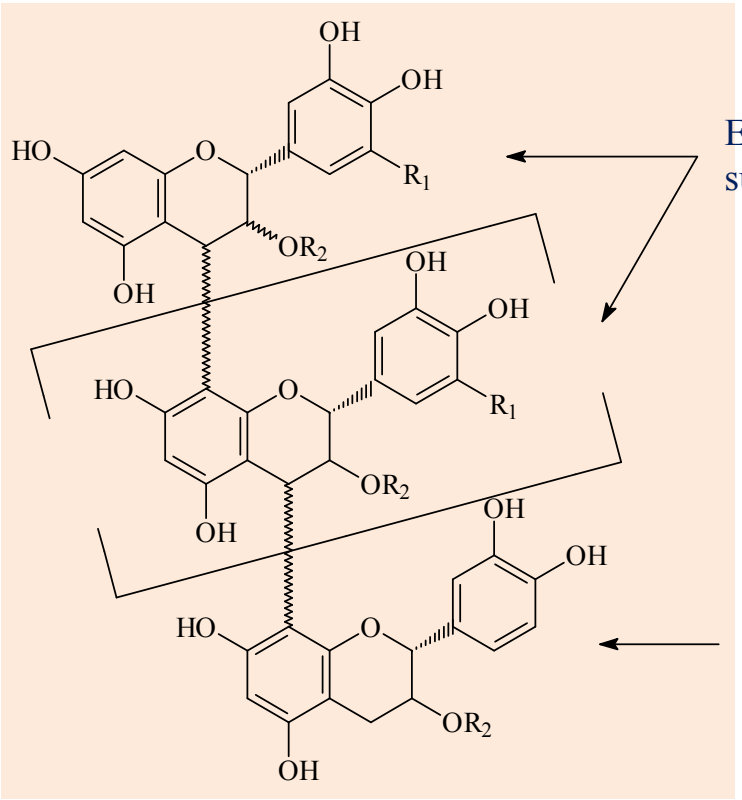
B3: (+)-catechin-(4-8)-(+)-catechin

B4: (+)-catechin-(4-8)-(-)-epicatechin



FLAVAN-3-OLS

Proanthocyanidins (Condensed tannins):



Flavanol oligomers and polymers are called **condensed tannins** or **proanthocyanidins.**

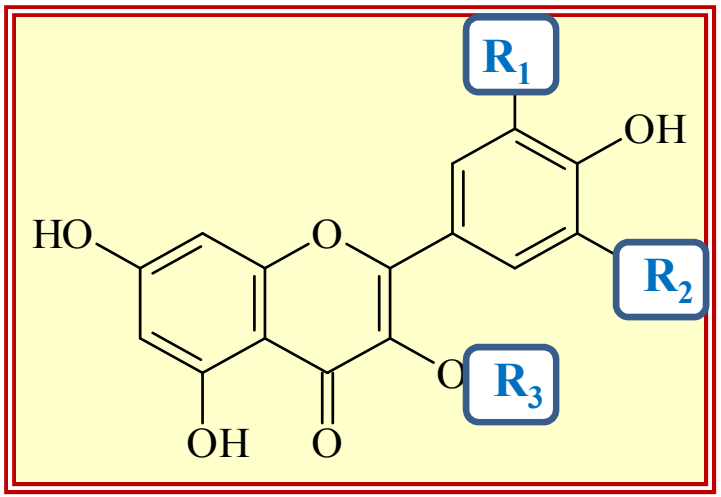
The most abundant condensed tannins in grape and wine

R_3=H, Procyanidins *(2 or more units of catechins)* **hydrolyze to cyanidin**

R_3=OH, Prodelphinidins *(2 or more units of gallocatechins)* **hydrolyze to delphinidin**

FLAVONOLS

Absorb the UV radiation and play a protective role in grapes



Flavonols	R_1	R_2	R_3	M_r
Myricetin	OH	OH	OH	318
Myricetin-3-glucoside	OH	OH	glucoside	480
Myricetin-3-glucuronide	OH	OH	glucuronide	494
Quercetin	OH	H	H	302
Quercetin-3-glucoside	OH	H	glucoside	464
Quercetin-3-glucuronide	OH	H	glucuronide	478
Kaempferol	H	H	H	286
Laricitrin-3-glucoside	OCH_3	OH	glucoside	494
Syringetin-3-glucoside	OCH_3	OCH_3	glucoside	508
Isorhamnetin	OCH_3	H	H	316
Isorhamnetin-3-glucoside	OCH_3	H	glucoside	498

ACKNOWLEDGEMENT

SOE-DAAD project

“From Molecules to Functionalized Materials”