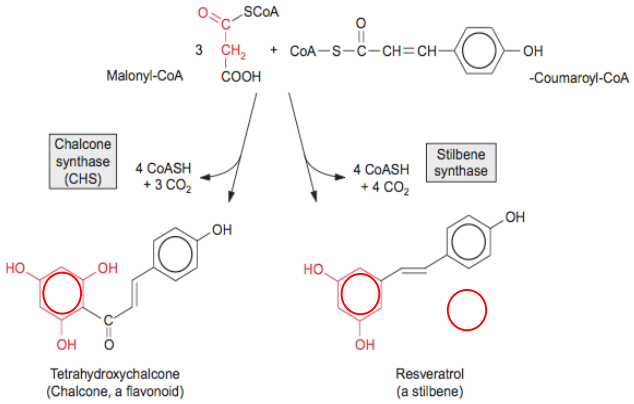
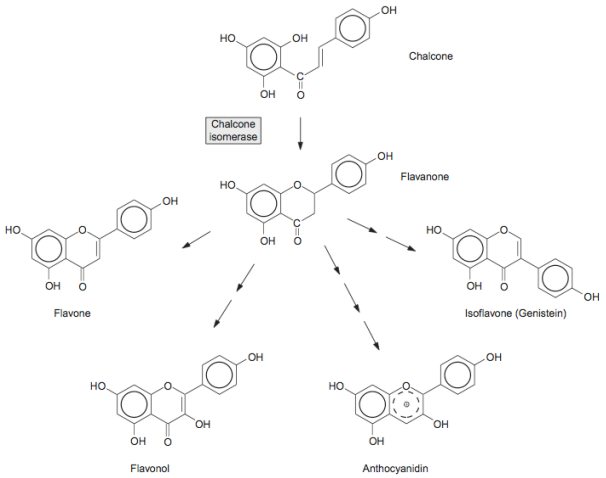
Phenolics and Phenylpropanoids (non-lignin) II

6. Flavonoids

- C6-C3-C6 structure: two aromatic rings, oxygen-containing heterocycle
- key enzymes: *chalcone synthase (CSH), chalcone isomerase (CHI)*
- CHS is similar to stilbene synthase, and the two pathways are similar
- thousands of flavonoids known, several classes
- structures can be used to help classify plants ("**chemotaxonomy**")





Classification:

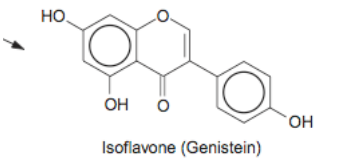
- by C skeleton & degree of **oxidation of C3 heterocycle**
- modified and decorated with substitutions (**hydroxylation**, **methoxylation**, **glycosylation**).
- **glycosylation** is common (mostly at C3 position), common sugars - rhamnose, galactose, glucose

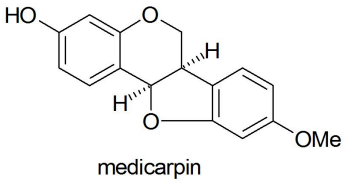
i) Flavones

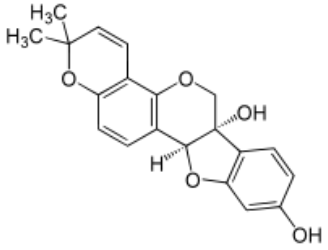
- defined by **C4 carbony**l group (and no hydroxyls on C3)
- signaling of plant with Rhizobia for symbiotic nodule formation (i.e. luteolin)
- also function in UV protection (see *flavonols*, which have similar activity)

ii) **Isoflavones** and **pterocarpans** (mostly in Legume family)

- structure: **B-ring** moved down on heterocycle (**isoflavone**)
- additional rings in structure lead to a subclass called **pterocarpan**s
- function: **phytoalexins** (antimicrobial and inducible secondary metabolites) in legumes
  (i.e. **genistein**, **medicarpin** **glyceollin**, led to discovery of phytoalexin response)
- also act as **estrogen mimics**, effecting on reproductive cycle in humans and vertebrates (sheep)
  - can cause lamb losses in sheep eating clover (sheep prefer low isoflavonoid plants)
  - reduce menopausal symptoms in humans (Asian diets), reduce hormone-dependent cancers







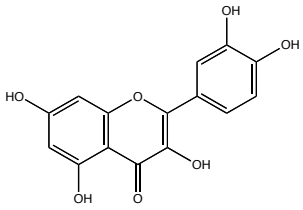
iii) Flavonols

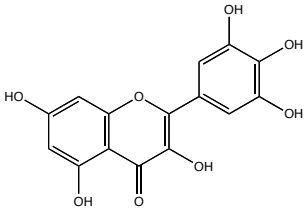
- structure: **4-carbonyl** group + **3-hydroxyl** or glycosylation

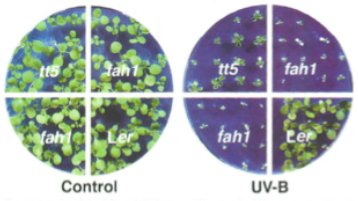
Typical functions:

- UV-protection (sun screen for plants) (ring structures)
  - -> flavonols are often **induced** by UV- irradiation
  - -> sensitivity of tt5 mutant (*chalcone isomerase* mutation) demonstrates UV protective function (see also the **sinapine** mutant (F5H mutant), does not make *sinapoyl choline*)
- Pigment / flower guide for insects with UV vision, and co-pigment for anthocyanins (see below)
- Human health: ubiquitous as dietary **antioxidants** ("bioflavonoids")

quercetin *myricetin*

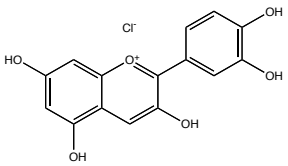






iv) Anthocyanins

- structure: flavynium **ion**, stabilized by presence of sugar
- terms: the **aglycone**, ie without glycosylation, is called **anthocyanidin**
- the flavynium ion structure allows for light absorption in the visisble spectrum
  - -> function as pigments for flower, fruit and leaf **coloration** (attract pollinators, seed dispersors)
  - -> also functions light protection of photosynthetic apparatus in young shoots and senescence (during N remobilization, and when Photosystems are not fully functional)



Modulation of anthocyanin flower color:

- B-ring **hydroxylation** --> blueing
- B-ring **methoxylation** --> reddening
- **metal** ions cause blue shift (importance of iron transporter)
- **pH** of vacuole [high pH shifts towards blue]
- **co-pigmentation** with colorless flavonoids

7. Tannins (condensed/flavonoid-derived and hydrolyzable)

Definition: ***water-soluble high MW polyphenols which precipitate proteins.***

Two basic structural types:

- **hydrolysable** tannins (**gallic acid**-glucose esters) (also give rise to **elagitannins**)
- **condensed tannins** (= **proanthocyanidins** - flavonoid polymers (MW 2000-7000)

Characteristics:

- large polymeric polyphenols
- **protein-binding** (& precipitating) ability via aromatic rings (hydrophobic interactions) and hydroxyls (H-bond with amino groups)
- astringency in wine and drinks: 'mouth-puckering', 'dry mouth' due to taste receptor interactions
- historically, used for leather -"tanning" ability, based on antimicrobial activity & protein binding
- generally antimicrobial compounds (see below)
- health foods (berries, apple, whole grains, nuts) and drinks (beer, wine) contain beneficial tannins (reduce risk of cardiovascular disease, metabolic syndromes, neurodegenerative disease)

Functions:

i) Herbivore defense against mammals (high levels, needs acidic gut)

- mechanism of tannin toxicity: bind gut proteins and prevent digestion / absorption
- many mammals have counter-adaptations: **proline-rich proteins** that bind tannins
- work with forest tent caterpillars on aspen showed no effect (!)

ii) *Antimicrobial (pathogen defense)*

- poplar tannins reduce poplar rust infection or growth

iii) Modulate soil nutrient dynamics

- tannins act as microbial inhibitors in soil -> slow **decomposition** and **mineralization**
- favor **mycorrhizae** and plant assimilation or amino acids (organic N)