# **Phenolics and Phenylpropanoi**ds (non-lignin)

These are considered **secondary plant metabolites (SPMs):**

**=** ***"small organic plant constituents, not required for day-to-day activities of plant"***

- many have an "ecological" function (as opposed to physiological functions)
- also called **natural products** or **phytochemicals**
- used by humans as drugs, pigments, spices, stimulants, toxins, etc.

**Background**

- phenolics are one of the three major groups of secondary plant metabolites (1000's)
- have biosynthetic unity and almost all are derived from shikimate and phenylalanine, and can be grouped into types or structural families (see "Roadmap" figure)
- widespread in the plant kingdom - examples are found in all plant families
- many have **stress-related functions** (UV screens, pest or pathogen defense, and others)
  *-> use interesting examples to illustrate the diverse functions of this class of SPMs*

## 1. Simple phenolic acids

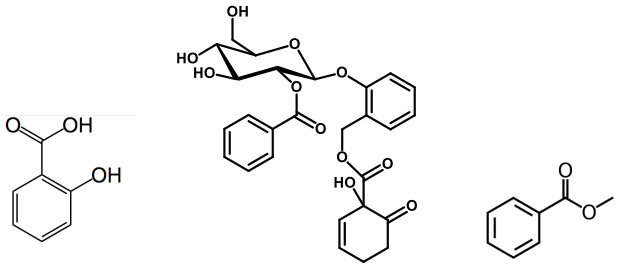
- general structure: benzoic acid derivatives **(C6 + COOH)**

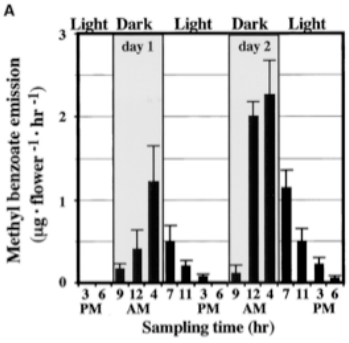
i) **salicylic acid** (signaling in thermogenic plants (skunk cabbage)
- signal in systemic acquired resistance - SAR - against pathogens)

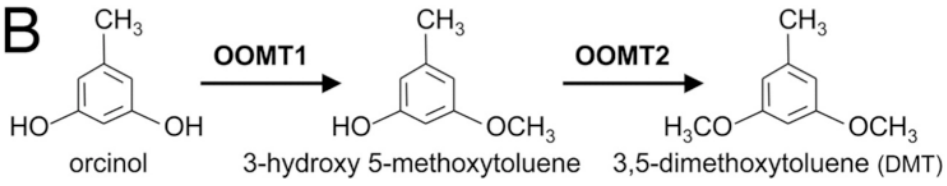
ii) **salicylate phenolic glycosides** in willow, poplar
- insect herbivory protection. (The variety of compounds makes for a nice functional series, where structure-function relationships can be tested. Cyclohexen-one is the most important component.
- Salix (willow) is the source of **aspirin** - acetyl-salicylic acid (first isolated 1828, synthesized in 1898, -> birth of German chemical industry (Bayer)

iii) **methyl benzoate** in snapdragon flowers (timed release of volatile & strict biosynthetic control)
- daily rhythm, circadian clock controlled, coordinate with pollinators.

iv) **phenolic methyl ethers** (orcinol, dimethyl toluene) are major fragrance compounds in rose, synthesized by specific *O-methyl transferases* found in Chinese roses. These have been crossed into modern hybrids. 90% of rose fragrance is DMT.





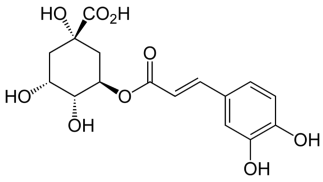
## 2. Hydroxycinnamic acids: **C6-C3** phenylpropanoid

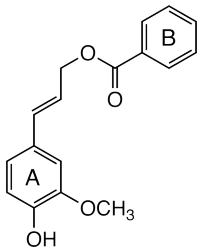
- structure is a modified cinnamic acid - see monolignol pathway, branch off this pathway.
- ubiquitous, lots of function including defense against pests and pathogens.
- typically conjugated

i) **coniferoyl benzoate**, a different type of ester. Can function as a feeding deterrent for wintering grouse (in aspen/poplar buds)

ii) **chlorogenic acid** (ester of caffeic acid) is very common in plants. It's found in particularly high levels in coffee. Acts as a feeding deterrent (thrips on Chrysanthemums), likely others.

iii) **sinapine** (*sinapoyl choline*) in canola. Found in different plant parts including seeds.
- acts as a UV-screen and protectant.
- when found in canola meal.....makes eggs taste fishy...



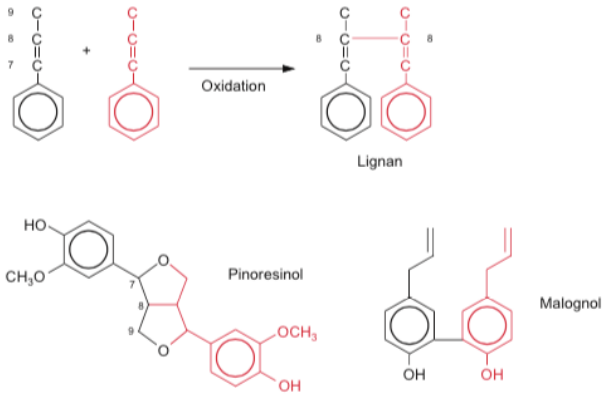

## 3. Lignans: **two C6-C3** phenylpropanoid units, also derived from **coniferyl alcohol**

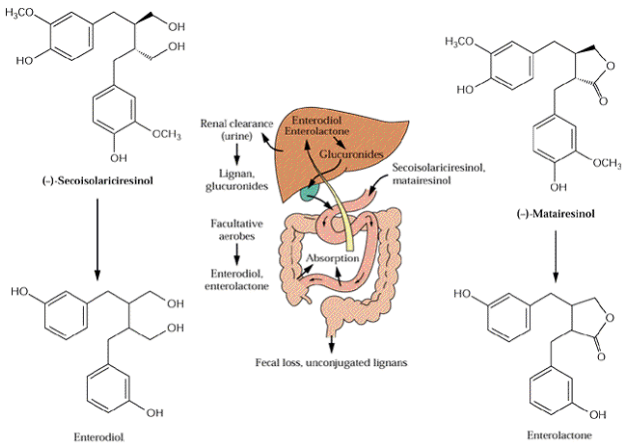
i) **pinoresinol**: found in **heartwood** of trees (functionally dead internal wood).
- antimicrobial

ii) f**lax seed lignan** (*secoisolariciresinol*, *matiresinol*)
- observed to act as an **estrogen mimics** when in the diet
- see complex bioconversion in digestive system involving both bacterial & human enzymes. Converted to *enterodiol* and *enterolactone* by bacteria, circulates between liver and intestine, and is absorbed.
--> these are associated with a reduced risk of breast/prostate cancer.
(NB seeds are tough - need to be ground for absorption)

iii) **plicatic acid** (in western Redcedar heartwood)- > rotting resistant! (=antimicrobial activity).
*Note: Other compounds called tropolones (modified isoprenoid), are also important.*

iv) **podophyllotoxin** (Mayapple) -> mitotic toxin in humans, used in cancer treatment



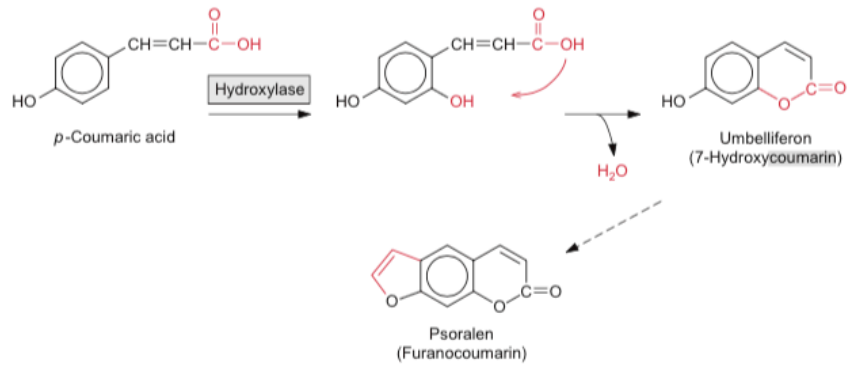



**4. Coumarins** - **intermolecular esters** of ***p*-coumaric acid**

- structure is characterized by the **lactone** ring.
- synthesis requires a specific hydroxylation, followed by ring closure, and additiona ring
  -> **psoralen**
- angular and linear forms, depending on position of the ring
- generally toxic compounds, in particular **xanthotoxin** (8-methoxypsoralen)
- found in Umbelliferae (parsley & carrot), Rutaceae (citrus) plant families
- classic studies in chemical ecology carried out on this system. For example, many specialist insects can detoxify these compounds using specific **CYP P450 oxygenases**

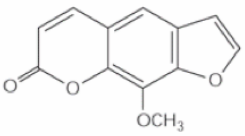
i) **psoralen**, xanthotoxin are examples of linear **furanocoumarins**
  -> UV phototoxins: toxins that are enhanced by UV light!
- effective as anti-insect defenses - highly toxic to **generalist insects**
- insects can evolve counteradaptations, biochemical or behavioral, leading to **specialist insects.**
- found as mixtures, and important for plant-insect coevolution?
- detoxification by *Papilio* larvae of different levels of specialization (Berenbaum, PNAS 100: 14593)

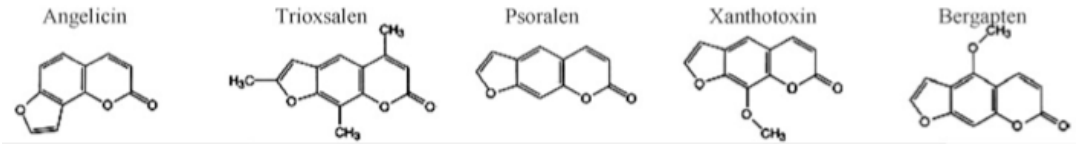
ii) human chemical ecology with coumarins:
- coumarins cause light- activated skin inflammations, blistering, sensitivity, and dermatitis
- symptoms known as "celery burn" and "Margarita dermatitis"





*Heracleum*


8-Methoxypsoralen
(a furanocoumarin)




**5. Stilbenes**

- structure: 2 aromatic rings, 2C bridge **[C6-C2-C6]**
- synthesis: **p-coumaric a**. plus **3x malonyl-CoA** (enzyme: *stilbene synthase)*
- prevalent in woody plants and trees, often in **heartwood**, which is commonly impregnated with phenolics, leading to a darker color

- can also be damage-induced in bark and sapwood (living region of trunk), by insects and fungi

i) **pinosylvin** in *Pinus sylvestris* heartwood and induced pathogen defense [**phytoalexin**]
(= *pathogen-induced secondary metabolites with antibacterial and anti-fungal activity*)

ii) **pinosylvin methyl ether**
- in alder twigs (snowshoe hare & winter diet)
- high concentrations avoided by browsers
- shown via **choice tests** (cafeteria experiments)

iii) **resveratrol**
- acts as a phytoalexin in grape leaves (antifungal compound)
- found in **red** wine (along with many other phenolics)
- became well known as it was thought to underlie the "French Paradox" (= *low levels of cardiovascular disease despite a fat-rich diet*...), but actually more likely tannins (proanthocyanidins) are more effective

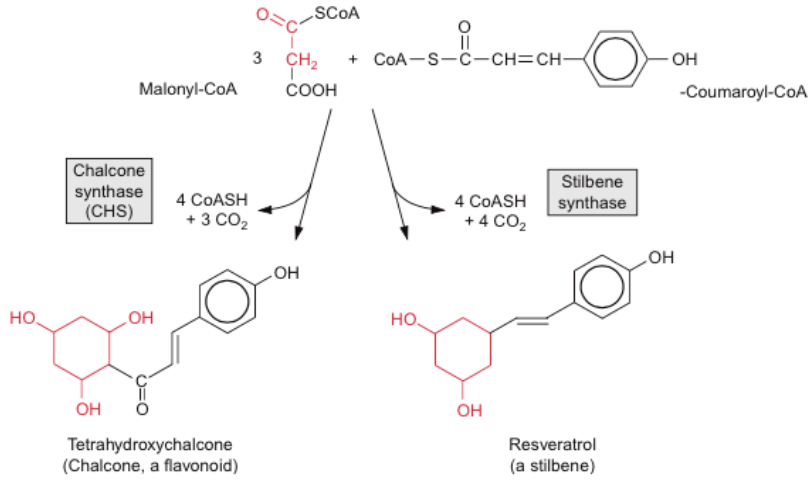
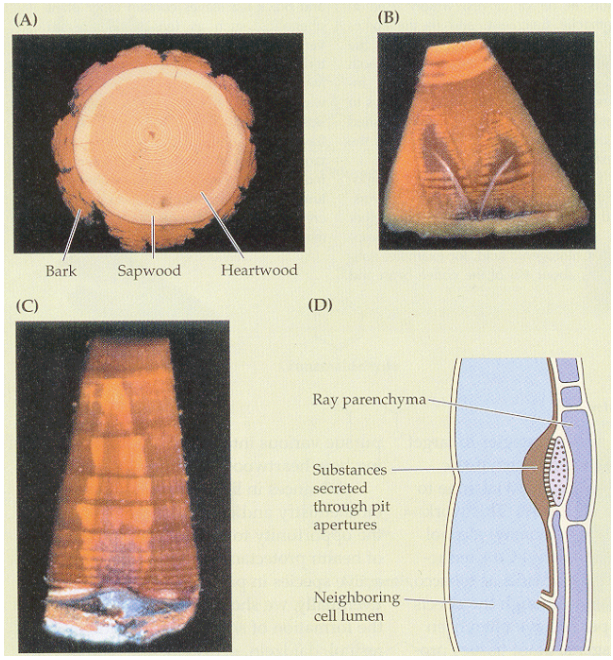



**Figure 18.11** An additional aromatic ring is formed by chalcone synthase and stilbene synthase.



# Roadmap of phenylpropanoids in plants

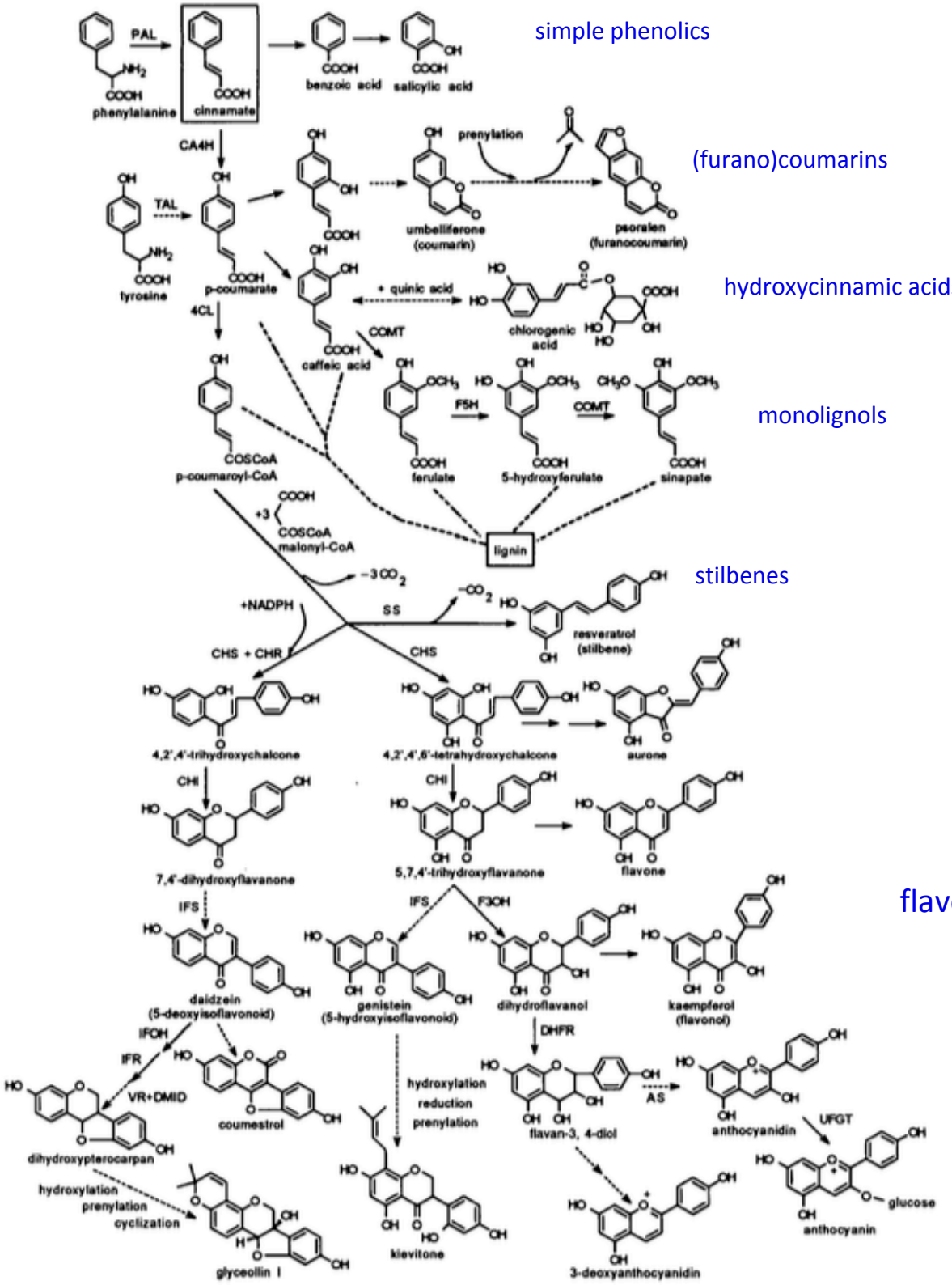



**Figure 1.** Biosynthetic Relationships among Stress-Induced Phenylpropanoids.

Paiva & Dixon, Plant Cell 1995