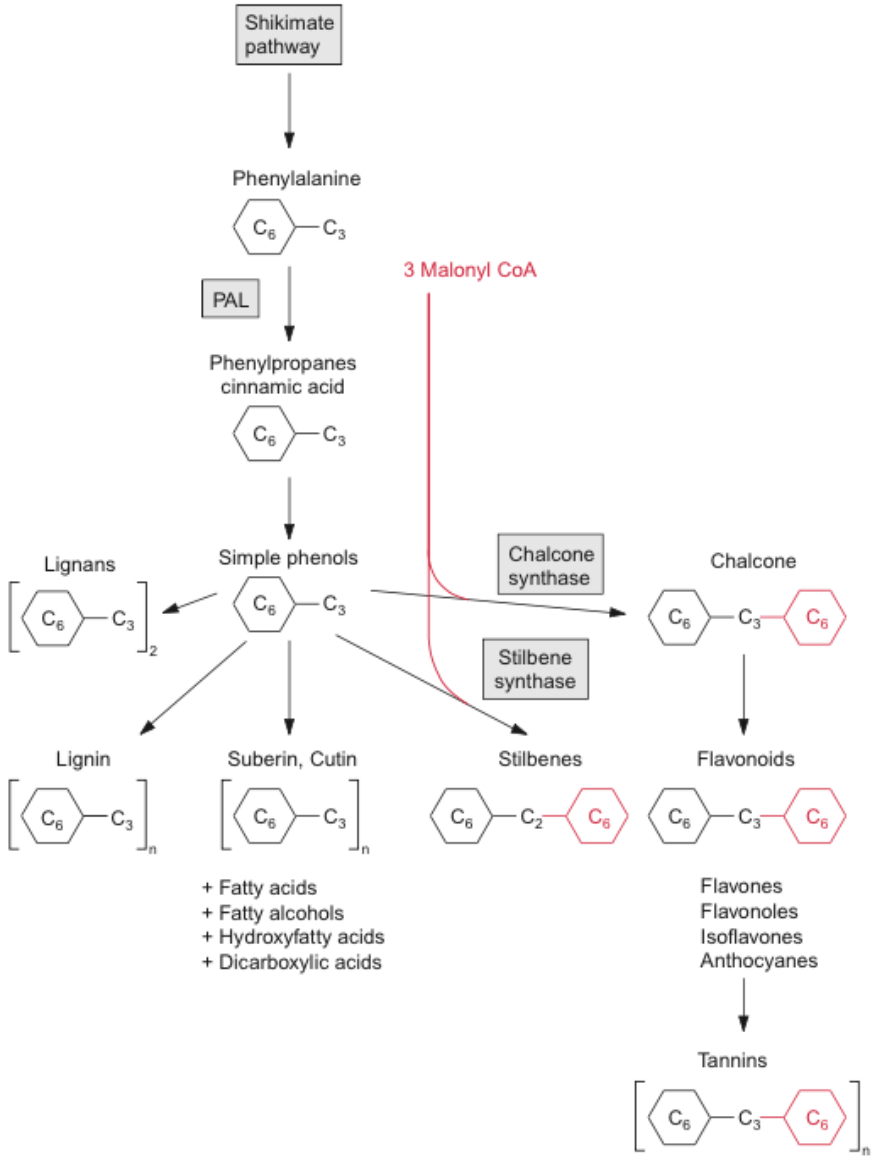
Roadmap of Phenylpropanoids (Fig 18.1)



Phenolics and Phenylpropanoids (non-lignin)

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

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

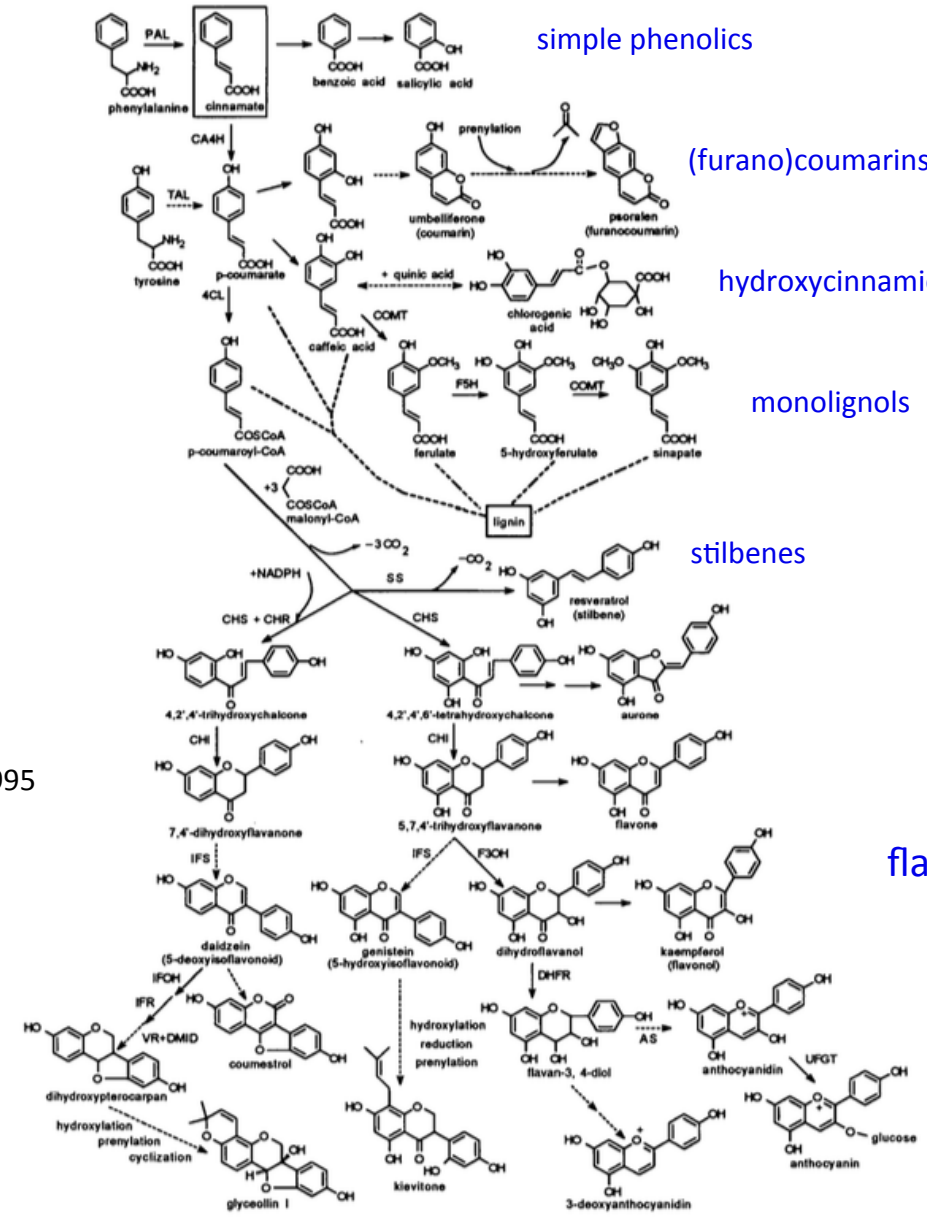
- many have an "ecological" function (as opposed to physiological functions)
- also called **natural products** or **phytochemicals**
- used by humans as drugs, pigments, spices, stimulants, toxins, etc.

Background

- phenolics are one of the three major groups of secondary plant metabolites (1000's)
- have biosynthetic unity: almost all are derived from shikimate and phenylalanine
- 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, etc)

-> use well-studied examples to illustrate the diverse functions of this class of SPMs

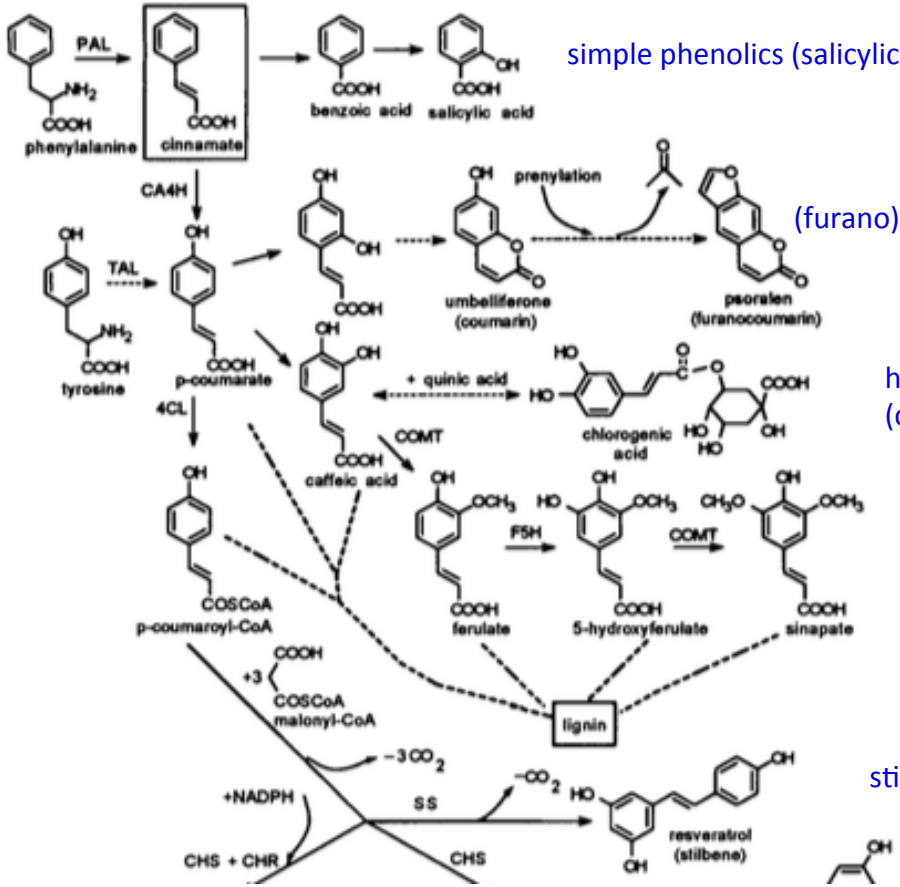
Roadmap of phenylpropanoids in plants



Paiva & Dixon, Plant Cell 1995

Figure 1. Biosynthetic Relationships among Stress-Induced Phenylpropanoids.

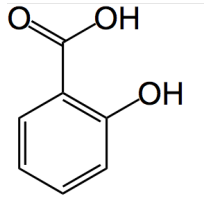
Roadmap of phenylpropanoids in plants – part 1



Paiva & Dixon, Plant Cell 1995

1. Simple Phenolics and Phenolic Acids

salicylic acid



skunk cabbage

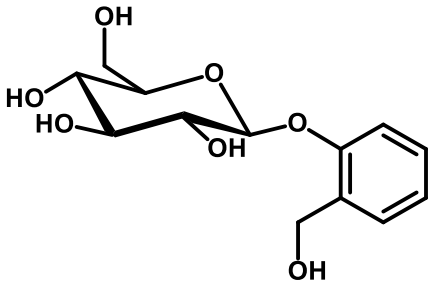
i) **salicylic acid**

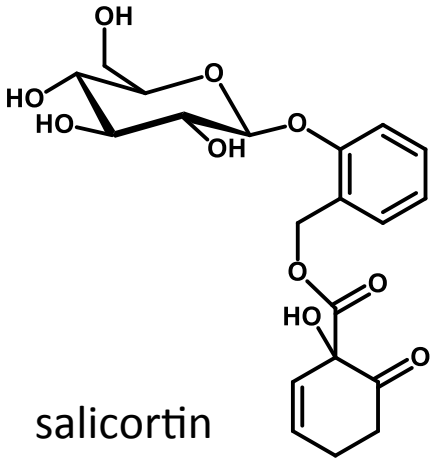
- signal in systemic acquired resistance – (SAR) - against pathogens

- signaling to create heat in thermogenic plants (skunk cabbage, others)

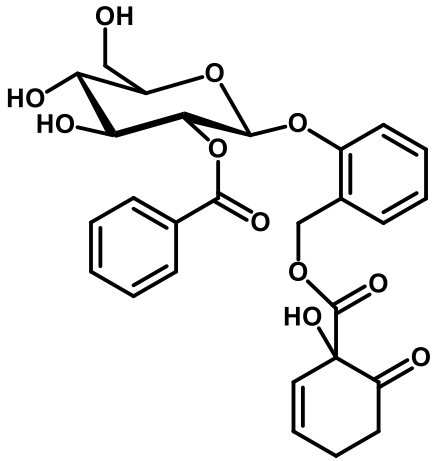
- Salix (willow) is the source of salicylic acid (first isolated 1828, synthesized in 1898,
-> aspirin (acetylsalicylic acid) birth of German chemical industry
(Bayer)

ii) Poplar and willow "salicinoids" (phenolic glycosides)



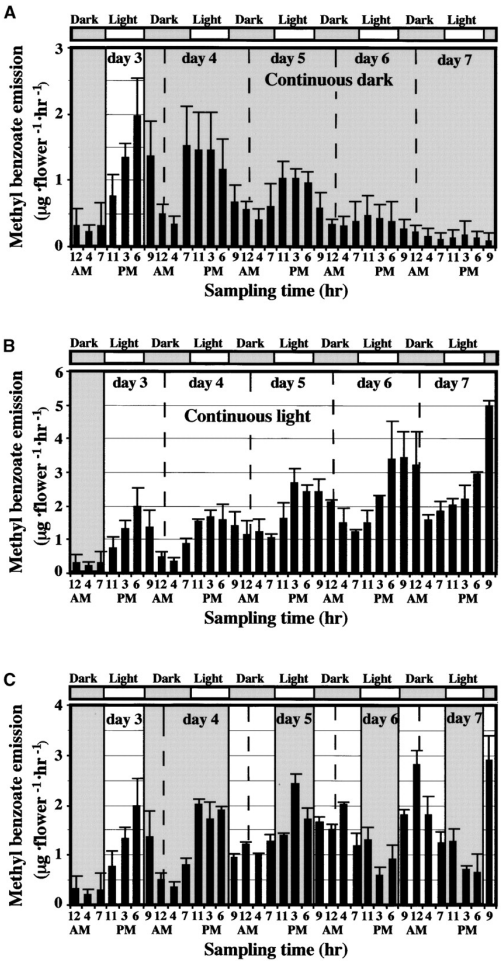


salicortin

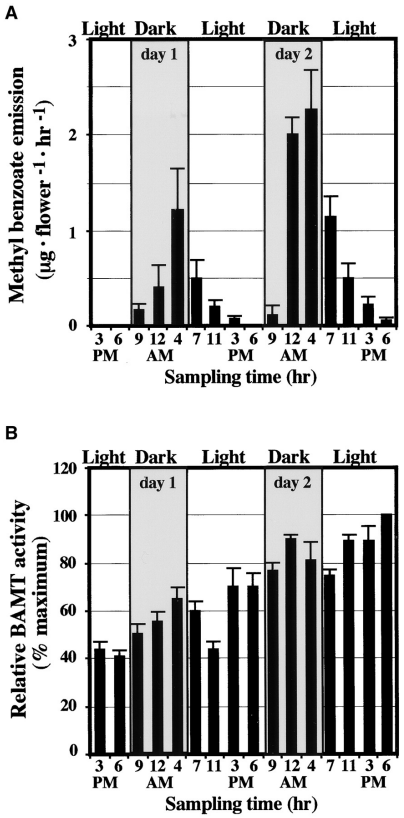


- structure vs. function of the series
- defense against insects (lepidopterans)
- structure-function: *cyclohexen-one* moiety is most active

iii) Emission of Methyl Benzoate from Snapdragon Flowers



Emission of Methyl Benzoate and BAMT Activity in Snapdragon Flowers during Two Normal Light/Dark Cycles



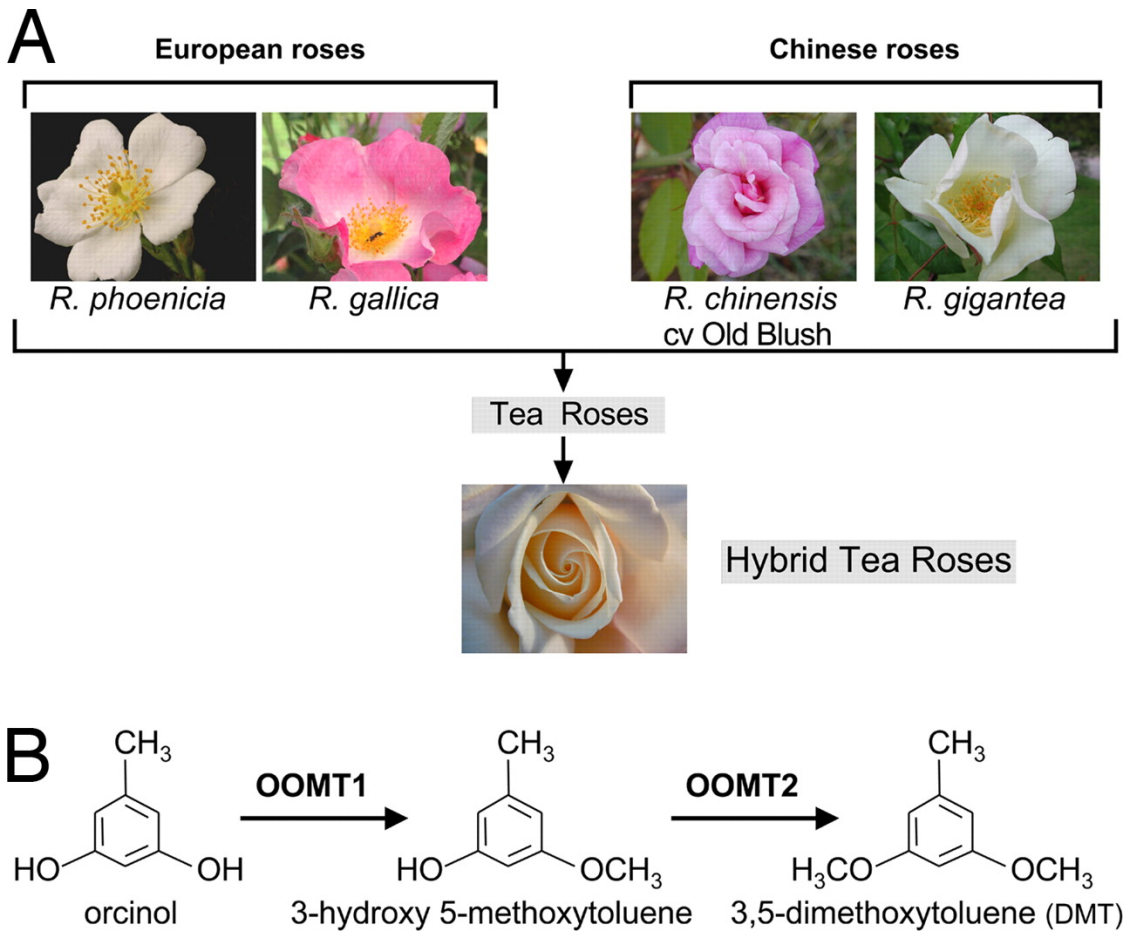
- daily rhythm, circadian clock controlled, coordinate with pollinators.

Natalia Kolosova et al. Plant Cell 2001;13:2333-2347

iv) **phenolic methyl ethers** (orcinol, dimethyl toluene)
- fragrance compounds in rose

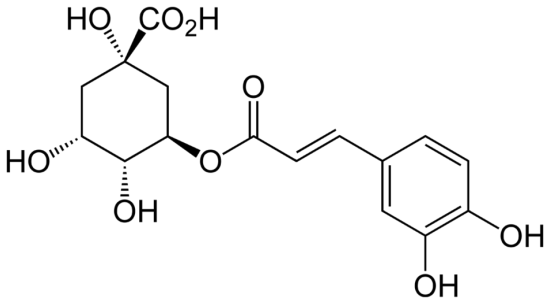
- 90% of rose fragrance is DMT, but found in Chinese rose

- breeding of this trait into modern hybrid tea roses is due to specific ***O*-methyl transferases**

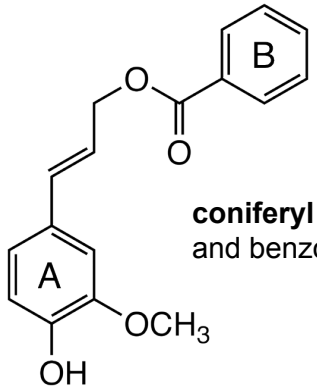


Scalliet G et al. PNAS 2008;105:5927-5932

2. Hydroxycinnamic acids & esters derived from these

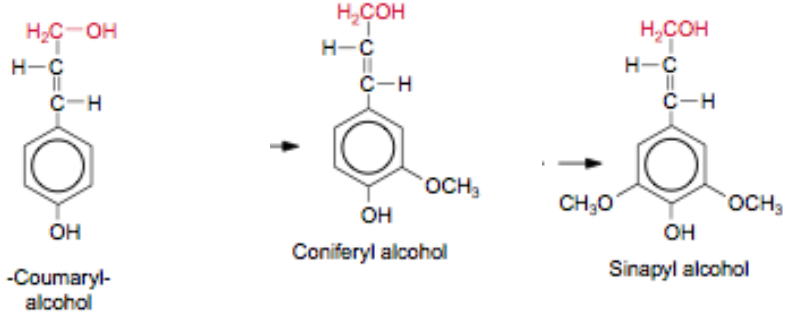


chlorogenic acid (ester of caffeic acid with quinic acid)

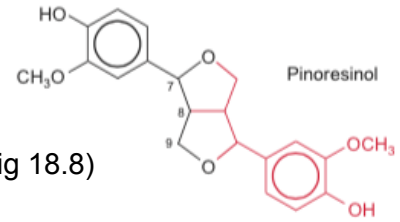


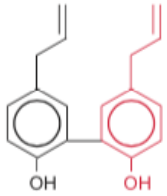
coniferyl benzoate (ester of coniferyl alcohol and benzoic acid)

For reference – three monolignols



3. Lignans: **two C6-C3** phenylpropanoid units**,** also derived from **coniferyl alcohol** (Fig 18.8)



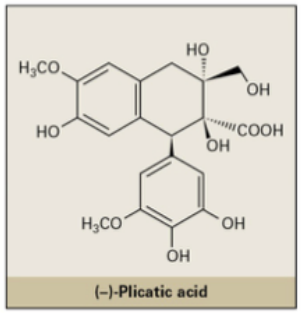


(Fig 18.8)

pinoresinol: found in **heartwood** of trees

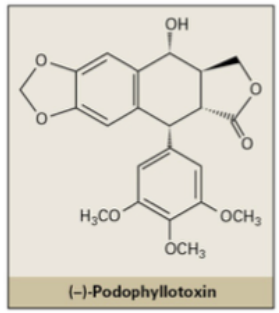
Thuja plicata

A



Podophyllum peltatum

B

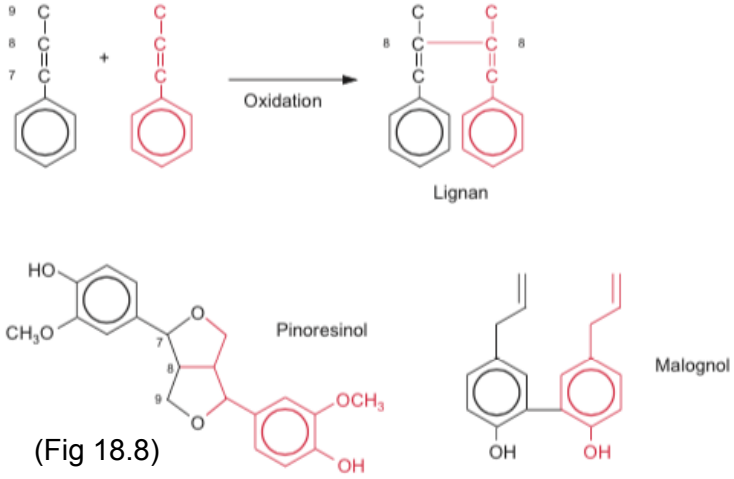


plicatic acid: heartwood of Western Redcedar

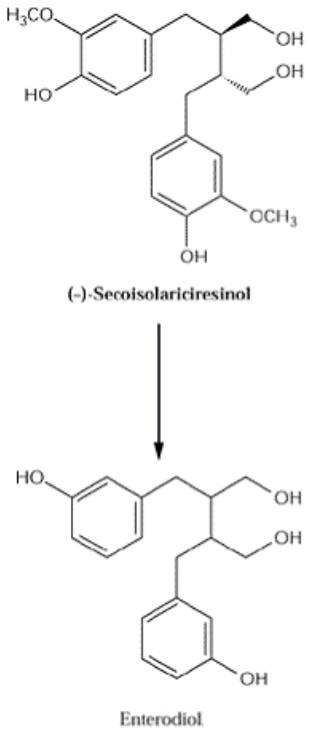
podophyllotoxin (Mayapple) -> mitotic toxin in humans

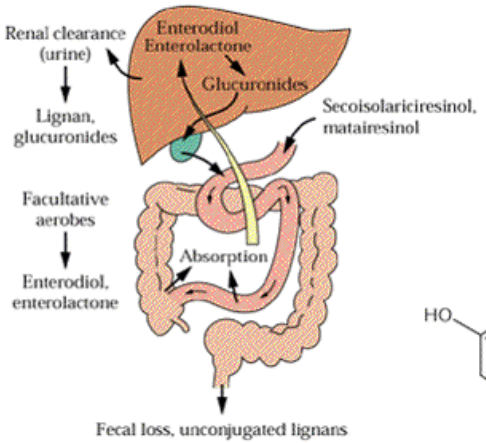
Buchanan, *Biochemistry and Molecular Biology of Plants*

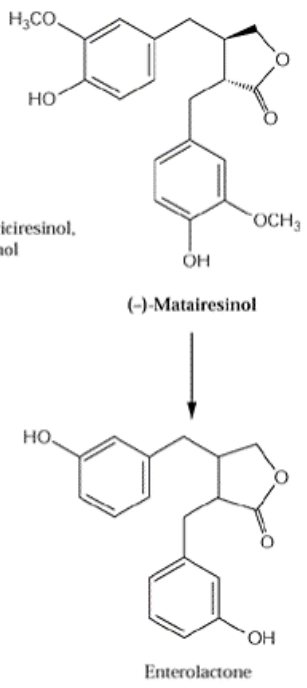
3. Lignans (Fig 18.8)



(Fig 18.8)







f**lax seed lignan** (*secoisolariciresinol*, *matiresinol*)

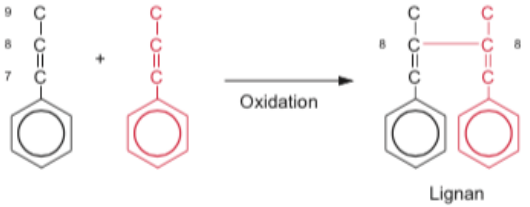
- estrogen mimics when in the diet

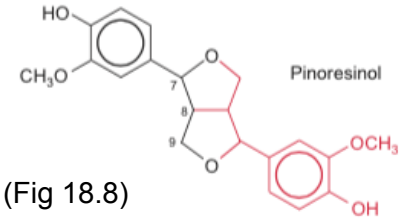
- complex bioconversion in digestive system involving both bacterial & human enzymes.

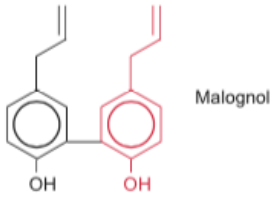
- converted to *enterodiol* and *enterolactone* by bacteria (active components)

Buchanan, *Biochemistry and Molecular Biology of Plants*

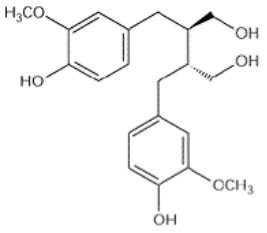
3. Lignans (Fig 18.8)

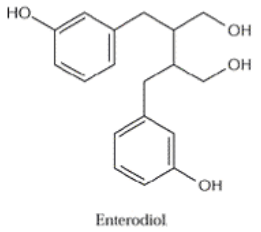


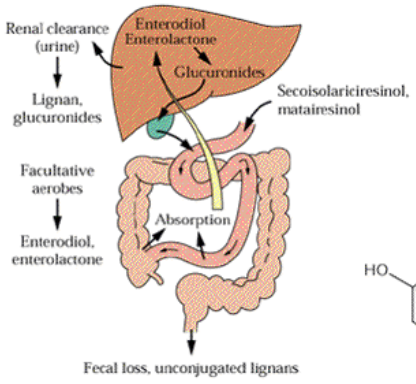


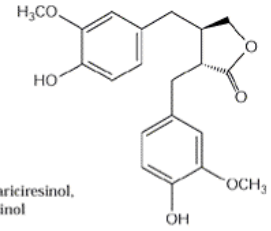


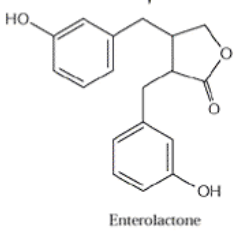
(Fig 18.8)

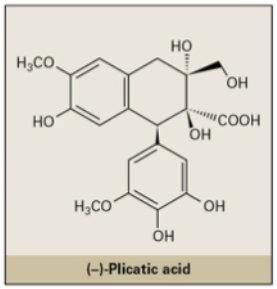


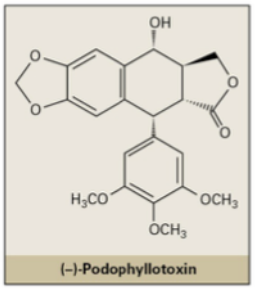






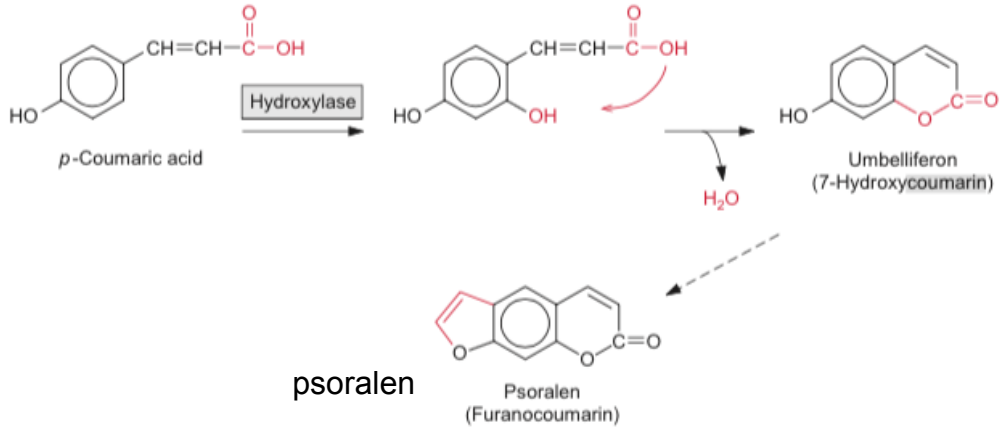






Buchanan, *Biochemistry and Molecular Biology of Plants*

4. Synthesis of coumarins (Fig 18.1)



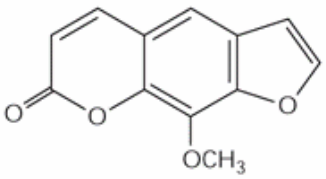
4. Coumarins - **intermolecular esters** of ***p*-coumaric acid**

- structure is characterized by the **lactone** ring.
- synthesis requires a specific hydroxylation, followed by ring closure
- angular and linear forms of **furanocoumarins**
- generally toxic compounds i.e. **xanthotoxin**
- found in Umbelliferae (parsley & carrot), Rutaceae (citrus)
- classic chemical ecology, specialist insects (detoxify) plant family

ii) human chemical ecology with coumarins:

- coumarins cause light-activated skin inflammations, blistering, sensitivity, and dermatitis

Heracleum



8-Methoxypsoralen
(a furanocoumarin)

photodermatitis caused by furanocoumarins in light

ii) human chemical ecology with coumarins:

- coumarins cause light- activated skin inflammations, blistering, sensitivity, and dermatitis

Heracleum mantegazzianum (Giant Hogweed)

- escaped ornamental from Eurasia, invasive weed here in BC)

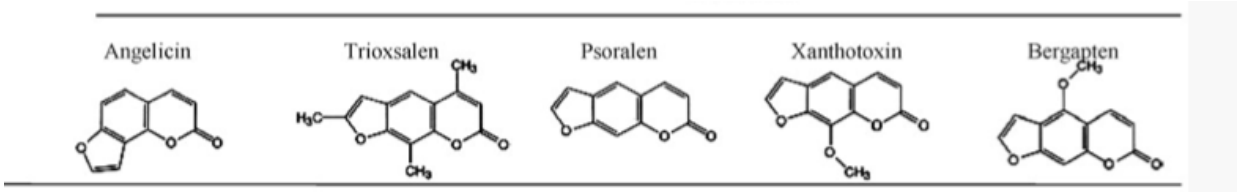
- ***Warning****: small hairs on stems and leaves contain a poisonous sap that can cause severe irritation, blistering and dermatitis*

www.agf.gov.bc.ca/cropprot/weedguid/

Furanocoumarins are UV-activated **phototoxins**: toxins that are enhanced by UV light!

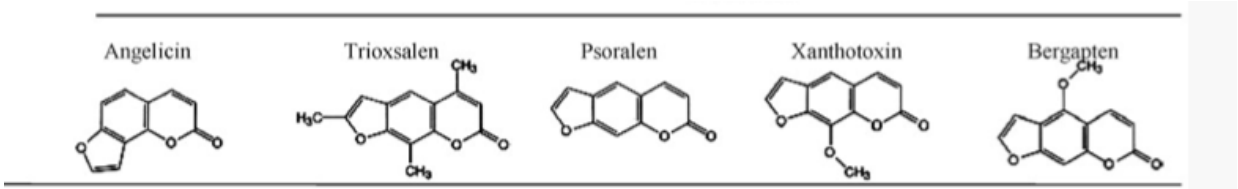
- highly effective as anti-insect defenses - toxic to **generalist insects**
- insects can evolve counteradaptations, biochemical or behavioral, leading to **specialist insects.**
- found as mixtures, and important for dynamics of plant-insect coevolution(?)
- detoxification by *Papilio* larvae of different levels of specialization

(see Berenbaum, PNAS 100: 14593)



Furanocoumarins are UV-activated **phototoxins**: toxins that are enhanced by UV light!

- highly effective as anti-insect defenses - toxic to **generalist insects**
- insects can evolve counteradaptations, biochemical or behavioral, leading to **specialist insects.**
- found as mixtures, and important for dynamics of plant-insect coevolution(?)
- detoxification by *Papilio* larvae of different levels of specialization (Berenbaum, PNAS 100: 14593)
    - specialists have specific **detoxification enzymes** *Cytochrome P450 oxygenases*
    - CYP enzymes from generalists have less specific and inefficient
    - *some compounds in mixture are not toxic, but interfere with detoxification*

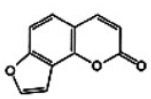
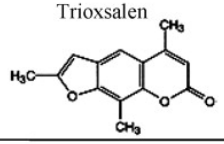
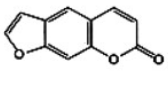
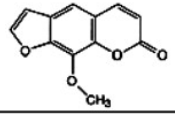
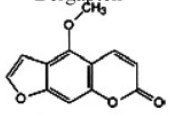


4. Coumarins / furanocoumarins

CYP furanocoumarin detoxification enzymes show specificities and activities that vary with 'substrate encouter rate' by Papilio species

Table 1.

Specific activities of CYP6B proteins coexpressed with house fly NADPH P450 reductase in baculovirus expression system

P450	CO-diff	Specific activity (nmol/min/nmol P450),* means ± SD				
		Angelicin 	Trioxsalen 	Psoralen 	Xanthotoxin 	Bergapten 
CYP6B4 (*Pg*)	450	1.906 ± 0.180[a]	1.412 ± 0.090[a]	2.208 ± 0.115[a]	3.214 ± 0.174[a]	3.541 ± 0.126[a]
CYP6B17 (*Pg*)	450	0.060 ± 0.023[c] (97%↓)	0.557 ± 0.081[b] (61%↓)	0.381 ± 0.150[b] (83%↓)	0.800 ± 0.251[d] (75%↓)	1.122 ± 0.141[d] (68%↓)
CYP6B21 (*Pg*)	450	0.518 ± 0.130[b] (73%↓)	0.773 ± 0.170[b] (45%↓)	1.800 ± 0.211[a] (18%↓)	2.547 ± 0.087[b] (21%↓)	2.150 ± 0.266[b] (39%↓)
CYP6B25 (*Pc*)	450/420	0.372 ± 0.210[b] (80%↓)	0.179 ± 0.190[d] (87%↓)	0.627 ± 0.346[b] (72%↓)	1.212 ± 0.160[c] (62%↓)	1.486 ± 0.124[c] (58%↓)
CYP6B26 (*Pc*)	420	ND (100%↓)	ND (100%↓)	ND (100%↓)	ND (100%↓)	ND (100%↓)
CYP6B1†	450	0.640	–‡	2.560	6.980	–‡

P. glaucus (occassional)

P. canadensis (never)

P. polyxenes (FC specialist)

Proc Natl Acad Sci U S A. 2003 November 25; 100(Suppl 2): 14593–14598.
doi: 10.1073/pnas.1934643100.

5. Stilbenes C6-C2-C6 structures

- structure: two aromatic rings plus a 2-carbon bridge**[C6-C2-C6]**
- synthesis: **p-coumaric a**. plus **3x malonyl-CoA** (enzyme: *stilbene synthase)*

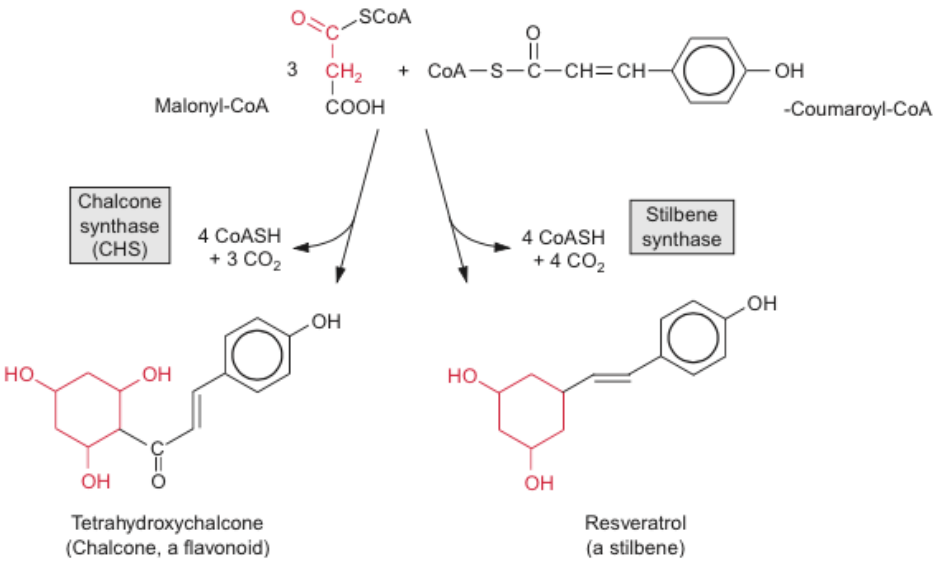
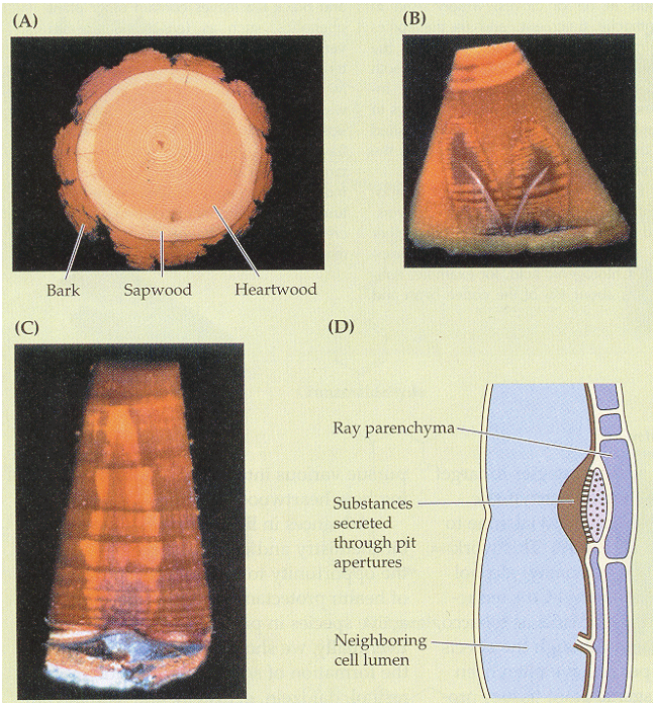


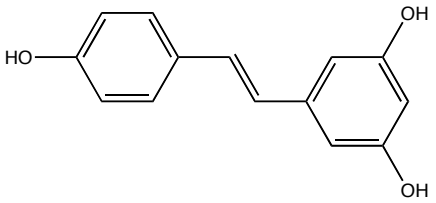
Figure 18.11 An additional aromatic ring is formed by chalcone synthase and stilbene synthase.

Biosynthesis: Fig. 18.1

5. Stilbenes

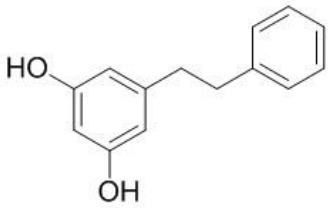
heartwood is impregnated with antifungal phenolics incl. stilbenes



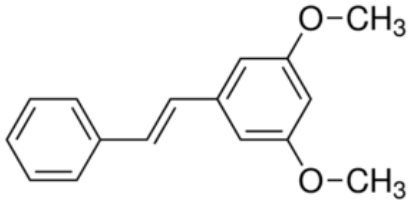


resveratrol - not the French paradox

pests and pathogens can cause localized phenolic deposition ("phytoalexins") in wood



pinosylvin –heartwood and stress-induced antifungal stilbenes



pinosylvin dimethyl ether – feeding deterrent for winter-feeding snowshoe hares

Roadmap of phenylpropanoids in plants

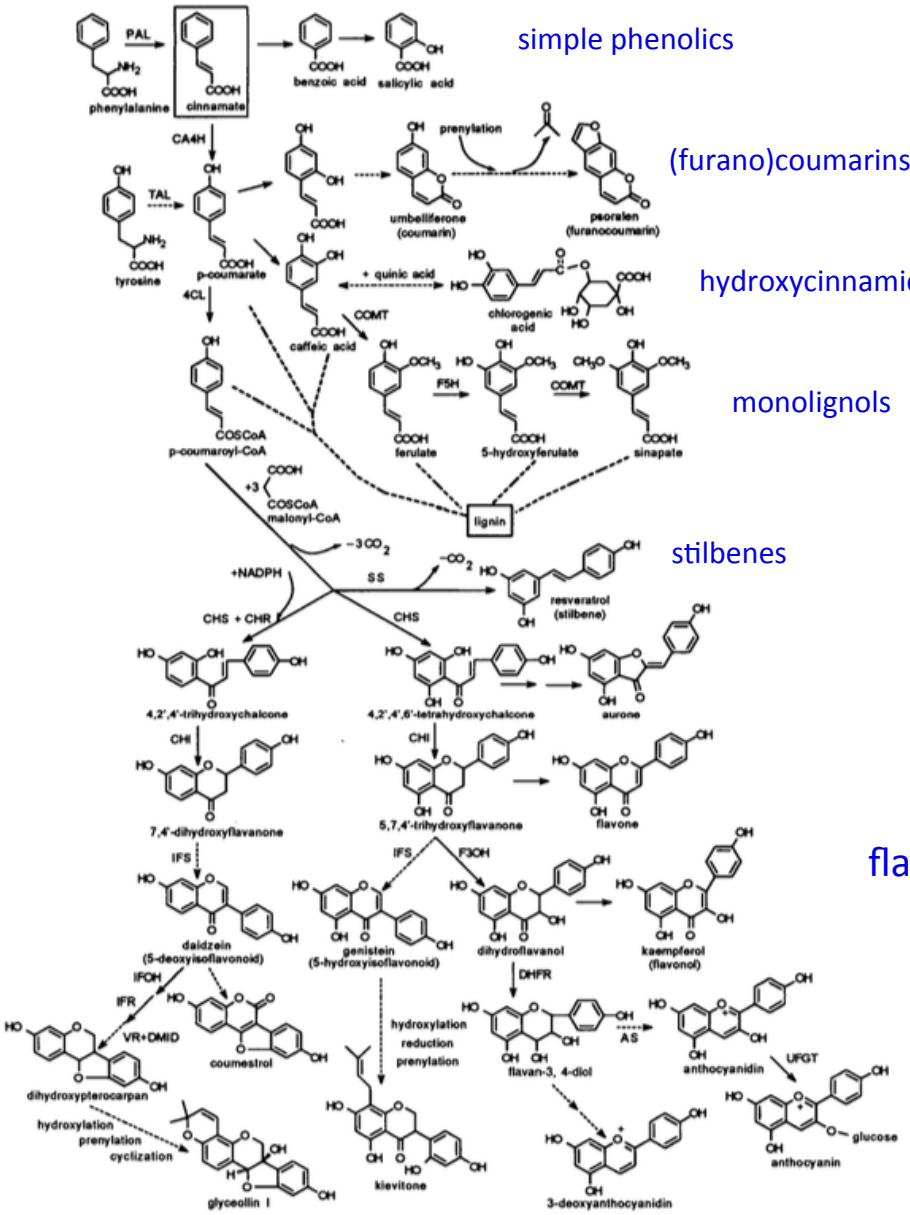


Figure 1. Biosynthetic Relationships among Stress-Induced Phenylpropanoids.

Paiva & Dixon, Plant Cell 1995

Roadmap of phenylpropanoids (fig 18.1)