

Wood Chemistry

Wood Chemistry

PSE 406/Chem E 470

Lecture 15

Stilbenes, Flavonoids, and Condensed Tannins

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Wood Chemistry

Agenda

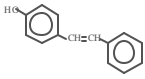
- Stilbenes
 - » Chemistry, biological significance, commercial uses, pulp and paper problems.
- Flavonoids
 - » Chemistry, biological significance, commercial uses, pulp and paper problems.
- Condensed Tannins
 - » Chemistry, biological significance, commercial uses, pulp and paper problems.

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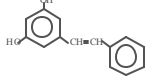
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Stilbenes

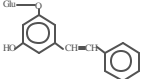
- Phenolic extractive found in the heartwood of softwoods
 - » Particularly prevalent in Pinus
- Cause light induced darkening in wood
- Most often 2 aromatic rings: occasionally more
- Presence of double bond linkage
 - » Naturally present most often in trans form



4-Hydroxystilbene



Pinosylvin



Piceid

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Stilbenes

Biological Significance

- Improves decay resistance
 - » Reduces fungal activity.
- Improves Insect resistance
 - » Stilbenes in leaves reduce insect feeding.
- Reduces animal damage
 - » Pinosylvin containing leaves have been shown to suffer less damage from Snowshoe hare consumption.

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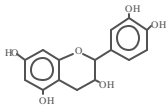
Wood Chemistry **Stilbenes**
Pulp and Paper Problems

- Effluent issues
 - » Chlorinated stilbene derivatives cause problems in effluents
 - Fish are affected at low levels
- Pulping problems
 - » Discovered in 1800's, that certain trees (pine and others) cannot be pulped by the acid sulfite process. Culprit turned out to be stilbenes which cause lignin crosslinking reactions (condensation).


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Wood Chemistry **Flavonoids**

- Referred to as the most ubiquitous monomeric natural product.
- Serve many roles in plants:
 - » Protection
 - » Coloration
 - » Other unique roles.



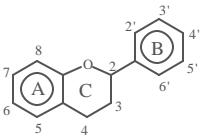
Catechin
(Western Hemlock)



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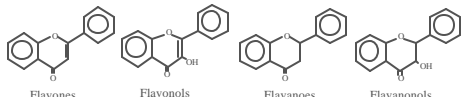
Wood Chemistry **Flavonoids**
General Structural Information

- Polyphenolic compounds found in softwoods and hardwoods
- Composed of diphenylpropane units $C_6-C_3-C_6$
- Eight structural classifications
- Flavonoids differ through substitution on the rings
 - » Typically OH or OCH_3 groups
 - » Typical to have OH on positions:
 - 5 and 7
 - 3', 4' and 5
- Are also present as glycosides

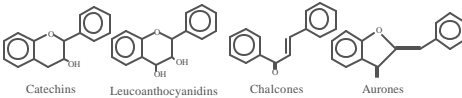


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Wood Chemistry **Flavonoids**
Classifications



Flavones Flavonols Flavanoes Flavanonols



Catechins Leucoanthocyanidins Chalcones Aurones

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Representative Structures of Flavonoid Classes

Chrysin

Taxifolin (Douglas Fir)

Pinocembrin

Pinobanksin

Catechin (Western Hemlock)

Quercetin (Oak)

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Flavonoids Biological Significance

- Not all flavonoids have same function in plants
- Anti-fungal
- Insects
 - » some feeding deterrents/some stimulants
- Antioxidant
- Color: bright colors in plants

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Flavonoids Location in Tree

- Found in the heartwood of most trees
 - » Referred to as most ubiquitous monomeric natural product
 - » Often responsible for coloration
- Found in lesser amounts in the sapwood
- Are found in large amounts in bark
- Roots
 - » Certain flavonoids play role in tree's interaction with beneficial organisms
- Leaves: Green tea can contain up to 30% flavonoids
- Flowers: Color is often due to flavonoids

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Flavonoids Medicinal Uses

- Higher flavonoid content in diet reduces chance of:
 - » Heart Disease
 - Strengthen capillaries
 - Dilates blood vessels
 - » Stroke
 - » Cancer: all types reduced
 - Finnish study = 1/2 rate of cancer

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Flavonoids Pulp and Paper Problems

- Flavonoids (flavanonols - taxifolin) also cause problems in sulfite pulping
 - Flavanonols are oxidized by bisulfite to flavanols producing thiosulfite
 - Thiosulfite causes lignin condensation reactions

Taxifolin $\xrightarrow{\text{HSO}_3^-}$ Quercetin + $\text{S}_2\text{O}_3^{2-}$

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Condensed Tannins

- Condensed tannins are formed through the polymerization of flavan-3-ol (catechin) and flavan-3,4-diols (leucoanthocyanidins)
 - In tree, polymerization through acidic enzymatic non-oxidative coupling
 - 2-50 units
 - Typically 2-8
 - Linkages can be through a variety of sites

Flavan-3,4-diols
(Leucoanthocyanidins)

Flavan-3-ols
(Catechins)

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Condensed Tannins

Catechins
(flavan-3-ols)

Leucoanthocyanidins

Typical Structure of Condensed Tannins

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Condensed Tannins Location in the Tree

- Western hemlock
 - Bark: 18% tannins
 - Wood: 2% tannins
- Quebracho
 - In wood, tannins found in heartwood
 - Majority (80%) located in vessel lumina
 - Tannins deposit in dead cell starting at CML and ending in secondary wall

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Condensed Tannins

Biological Significance

- Protection of plants against insects/animals
 - » Bad Taste/Astringency (bitter taste)
 - » Animals: tannins reduce digestion of food
- Toxic to bacteria
- Pine calluses: created by fungal invasion
 - » Tree forms calluses as protective tissue
 - » Calluses contain high levels of tannins (Chinese 50-80%)

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Uses of Condensed Tannins

- Wattle & Quebracho
- Leather tanning: 10,000+ year old industry
 - » Vegetable tannins & chrome
 - » Tannins interact with proteins in hides
- Adhesives
- Biocides
- Chelation: micronutrient fertilizers
- Mineral flotation

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