

Wood Chemistry

Wood Chemistry

PSE 406/Chem E 470

Lecture 16

Wood Extractives, Components and Analysis

PSE 406: Lecture 16 1

Wood Chemistry

Wood Extractives II

Agenda

- Hydrolyzable Tannins
 - » Chemistry, biological significance, commercial uses, pulp and paper problems.
- Miscellaneous Extractives
 - » Tetraterpenes, Phenolics, Alkaloids, Etc.
- Extractive Procedures
- Extractive Contents
- Wood Analysis Procedures
- General Wood Compositions


PSE 406: Lecture 16 2

Wood Chemistry

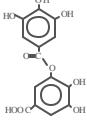
Hydrolyzable Tannins

Structure

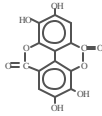
- Polymers (esters) of a sugar (usually glucose) with one or more polyphenolic carboxylic acids.
- Gallotannins: Gallic acid polymer
- Ellagitannins: Ellagic Acid polymer



Gallic Acid



Digallic Acid



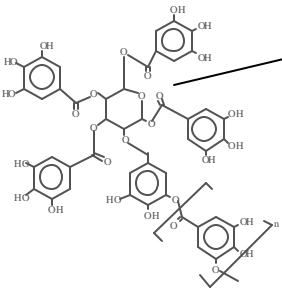
Ellagic Acid

PSE 406: Lecture 16 3

Wood Chemistry

Hydrolyzable Tannins

Polymer Structure Example



PSE 406: Lecture 16 4

Wood Chemistry

Hydrolyzable Tannins General Information

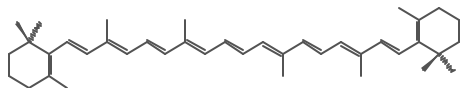
- Rare to nonexistent in softwoods.
- Hardwoods which contain large amounts:
 - » Oak (gallic and ellagic tannins)
 - » Eucalyptus (Ellagitannins)
 - » Chestnut (gallic tannins)
- Hydrolyzable tannins located in heartwood.
- Pulp and paper problems:
 - » Increased consumption of bleaching chemicals.
 - » Coloration problems.

PSE 406: Lecture 16 5

Wood Chemistry

Tetraterpenes

- Polymers of isoprene containing 40 carbons (8 isoprene units)
- Most common are the carotenoids
 - » Generally derivatives of lycopene
 - This is a carotenoid which is in high concentration in red fruits (gives color): tomatoes, watermelon, guava, etc.

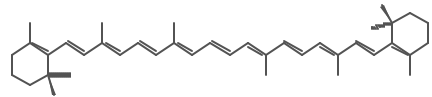


PSE 406: Lecture 16 6

Wood Chemistry

β Carotene

- Tetraterpene carotenoid found in dark green and orange yellow vegetables.
- In the human body, it is converted to vitamin A
- Has been shown to have many health related benefits.

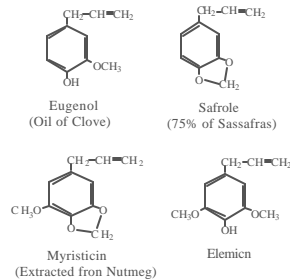


PSE 406: Lecture 16 7

Wood Chemistry

Phenolics

- Aromatic odor
 - » Balsam odor
 - » Foliage, bark, fruits
 - Sometimes in heartwood
 - » Variety of aromatic compounds
 - » Typically in small amounts (1%<)



Eugenol (Oil of Clove)

Safrole (75% of Sassafras)


Myristicin (Extracted from Nutmeg)

Elemicin


PSE 406: Lecture 16 8

Wood Chemistry

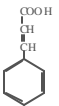
Phenolics




Vanillin




Veratraldehyde
(Smells like vanilla)




Cinnamic Acid
(Cinnamon - Bark)




Methyl Chavicol
(Pine turpentine)




Salicylic Acid
(aspirin - close)



Salicyl Alcohol



Vanillic Acid



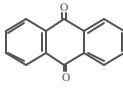
Acetovanillone

PSE 406: Lecture 16 9

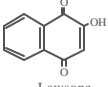
Wood Chemistry

Highly Colored Compounds

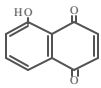
- Anthraquinone
 - » Found in Teak
 - » Used as pulping catalyst*
- Naphthaquinones
 - » Used as UV absorbers
 - » Used in polymer products*
- Benzoquinones



Anthraquinone



Lawsone
(Naphthaquinone)



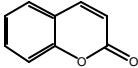
Juglone
(Pigment in walnuts)

* Produced from other sources PSE 406: Lecture 16 10

Wood Chemistry

Coumarin

- Chemical which has the aroma of fresh mowed hay (or vanilla).
 - » Produced by white clover.
 - » When clover is cut, a glycosylated cinnamic acid is enzymatically cleaved releasing glucose and a hydroxy cinnamic acid which esterifies.
- Coumarin produced in the fruit and nuts of certain trees (tonka trees for example)
- Coumarin is used as a rat poison.



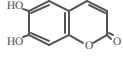
Coumarin

PSE 406: Lecture 16 11

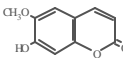
Wood Chemistry

Other Coumarin Facts

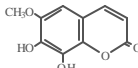
- Phytoalexins
 - » Anti-microbial agents
- Often exist as glycosides
- Can cause health problems
 - » Coumarin substituted for vanillin by shady individuals.
 - » FDA banned coumarin for human consumption in 1954.
- Some coumarins are commercially used as UV absorbers. (These are typically synthetic products from petroleum)



Esculetin



Scopoletin



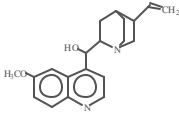
Fraxetin

PSE 406: Lecture 16 12

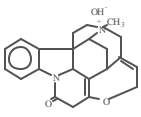
Wood Chemistry

Alkaloids

- These nitrogen containing compounds are found in a variety of different plants.
 - » Located in the leaves, fruits, and bark.
- Quinine
 - » Used to treat malaria
 - » Isolated from bark of cinchonas (South American Hardwood)
 - some eucalyptus species
 - » Causes pulping problems
- Strychnine
 - » Found in seeds of tree *Strychnos nux-vomica* (Tropical hardwood)



Quinine



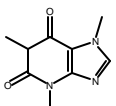
Strychnine

PSE 406: Lecture 16 13

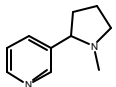
Wood Chemistry

Alkaloids

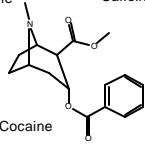
- You are all aware of the alkaloids shown on this page you probably have never seen their structures. These are typically found in small amounts in plants but are worth large sums of cash.



Nicotine



Caffeine



Cocaine

PSE 406: Lecture 16 14

Wood Chemistry

Miscellaneous

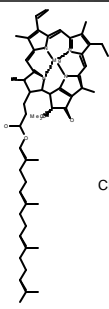
- Proteins & Amino acids
 - » Enzymes used by living organisms are proteins made of amino acids.
 - » Plant contain small amounts (~0.5%) of proteins.
 - » Chlorophyll (need the structure)
- Sugars
 - » Glycosides or free sugars.
 - Many extractives in plants have sugars attached which are often freed in enzymatic processes.
 - There are typically low levels of free sugars in plants with some notable exceptions: sugar cane and sugar beets.
 - These plants have high levels of free sucrose.
 - » Some of the water soluble hemicelluloses
 - Pectins are often called extractives.

PSE 406: Lecture 16 15

Wood Chemistry


Chlorophylls

- Probably the most well known chemicals in plants are the chlorophylls. These are tetrapyrroles that are located in the chloroplasts of most all photosynthetic plant tissues.
- As we all know, chlorophylls give leaves their green color.




Chlorophyll a

PSE 406: Lecture 16 16

Wood Chemistry  **Inorganic Materials**


- Inorganic materials
 - » Plants contains small amounts of most metals.
 - Some are used by living cells
 - Some present as contaminants
- Ash content gives a rough idea of the amounts of metals present.
 - » Sugar cane: 1.7-3.8% ash
 - » Corn Cobs: 2% ash
- Temperate woods contain 0.1-1% ash while tropical and subtropical species contain up to 5% ash.
 - » Main components Ca (50%), potassium and magnesium.

PSE 406: Lecture 16 17

Wood Chemistry  **Inorganics in Grasses**


- Grasses contain high levels of inorganics particularly silica.
- Wheat straw: Reported values 4-12+% ash
 - » Leaves: 14-19% ash, 10-14% silica
 - » Nodes: 8-14% ash, 5-7% silica
 - » Internodes: 3+% ash, 2+% silica
 - » Potassium: 1%

PSE 406: Lecture 16 18

Wood Chemistry  **Extraction Procedures**

<u>Extraction Technique</u>	<u>Products</u>
Steam Distillation →	Terpenes Phenols Hydrocarbons Lignans
Ether Extraction →	Fats/Waxes Resin Acids Sterols
Alcohol Extraction →	Flavonoids Phlobaphenes Tannins Stilbenes
Water Extraction →	Carbohydrates Protein/Alkaloids Inorganics

PSE 406: Lecture 16 19

Wood Chemistry  **Western Hemlock Extractives**

<u>Extractive</u>	<u>% on Wood</u>
Wax	0.3%
Flavonoids/Lignans	1.7%
Condensed Tannin	1.7%
Water sol. Carbohydrates	0.8%
Total	4.5%

* Western Hemlock contains only minimal tall oil type compounds (resin acids, fatty acids, sterols, terpenes, etc)

PSE 406: Lecture 16 20

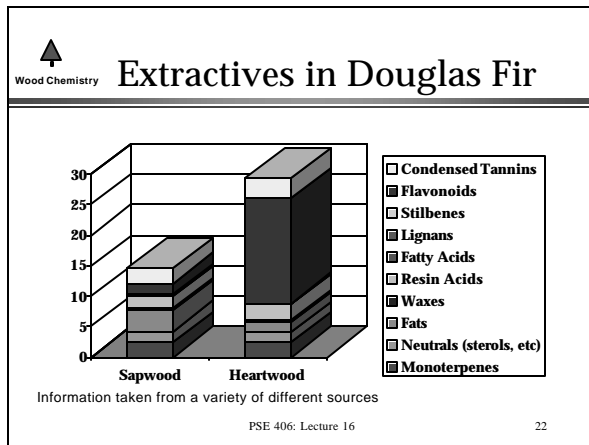
Wood Chemistry

Non-Volatile Resin Composition (1960 data for reference)

	Spruce	Pine	Aspen	Birch
Wood Ether Extractives	0.6-1.0%	2.1-9.2%	1-2.7%	1.5-3.5%
- Resin Acids	31%	30-41%	0%	31%
- Free Fatty Acids	0%	3-8%	35%	6%
- Fatty Acid Esters	42%	40-60%	50%	25%
- Unsaponifiables	21%	7-11%	14%	30%

Use this information as a relative comparison only

PSE 406: Lecture 16 21



- Wood Chemistry
- ### Quantification of Major Wood Components
- Wood Meal Preparation
Wood Chips, etc. $\xrightarrow{\text{Wiley Mill}}$ Wood Meal (40-60 mesh)
 - Extraction Using Soxhlet Apparatus (to remove extractives)
 - Alcohol: Benzene (2:1)
 - Acetone
 - Water
 - Lignin
 - Swell with 72% H_2SO_4 for several hours
 - Reflux in 3% H_2SO_4
 - Weigh residue = Klason Lignin
 - Hardwood Lignin Soluble Lignin by UV
- PSE 406: Lecture 16 23

- Wood Chemistry
- ### Quantification of Major Wood Components
- Holocellulose (Total Polysaccharides)
Extractive Free Wood Meal $\xrightarrow{\text{ClO}_2}$ Holocellulose
Procedure dissolves lignin
 - Alpha Cellulose
Holocellulose $\xrightarrow{\text{17.5\% NaOH Macerate}}$ Cellulose (Insoluble Fraction)
 - Hemicellulose
Hemicellulose = Holocellulose - Alpha Cellulose
- PSE 406: Lecture 16 24

