

Wood Chemistry

# Wood Chemistry

## PSE 406/Chem E 470

### Lecture 14

### Fats/Waxes/Lignans

PSE 406 Lecture 14 1

Wood Chemistry

# Agenda


- Fats and Fatty Acids
  - » Chemistry
  - » Role in the tree
- Tall oil
- Waxes
- Lignans
  - » Chemistry
  - » Role in the tree
  - » Commercialization

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# What are Fats and Oils?

- Both you and I recognize fat when we see it. We also probably know that fat and oils are energy storage material.
- Fats and oils are similar chemically: the difference is that fats are solids at room temperature and oils are liquids.



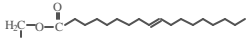
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# Chemical Composition of Fat/Oils

- Esters of long chain fatty acids
  - » Most often with glycerol
- Triglycerides, diglycerides, & monoglycerides
- Similar structures in all plants. What varies is the fatty acids attached to the glycerol and the percentage of tri, di, and monoglycerides




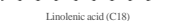

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Triglyceride	Diglyceride	Monoglyceride



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Wood Chemistry **Chemical Composition of Fatty Acids**

- Fatty acids are long chained carboxylic acids
  - » Mostly even numbered chains
    - 16-18 carbons most common
    - 20-22 less common
  - » 80% unsaturated: 1, 2 or 3 double bonds

Major Fatty Acids	Secondary Fatty Acids
 Oleic acid (C18)	 Palmitic acid (C16)
 Linoleic acid (C18)	 Linolenic acid (C18)
	 Eicosadienoic acid (C20)

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Wood Chemistry **Fat (Oil) Content**

- There are high levels of fats in seeds.
  - » Corn and soybeans contain 10-20% oils.
  - » Canola and sunflower contain up almost 50% oils.
  - » Nuts 50-70% oils
- In agricultural crops the majority of the oils are triglycerides.

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Wood Chemistry **Fats in Trees**

- Fats are found in living cells - parenchyma
  - » Very low content (1-2%) in oleoresin.
  - » More present in sapwood than heartwood.
  - » High content in many nuts.
- Function
  - » Fats role in trees is the same as in your waist line: serves as a storage material.
  - » The amount of fat in the tree is seasonally dependent.

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Wood Chemistry **Free Fatty Acids**

- Most fatty acids are linked as esters to other components (glycerol, sterols, etc) in the cells.
- A small amount of free fatty acids are present in plants. (not according to Encyclopedia Britannica)
- Roles of free acids:
  - » Disease resistance (messengers)
  - » Other?????????

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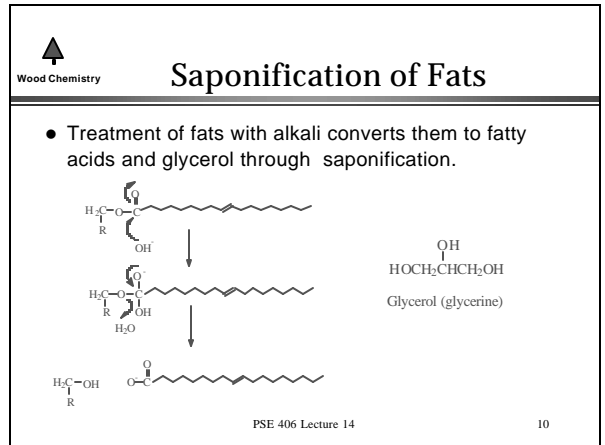
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## Fats & Fatty Acids Composition in Wood

	Picea abies <sup>a</sup> % of wood	Pinus Syv. <sup>b</sup> % of wood	Populus Tr. <sup>c</sup> % of wood
Fatty Acids	0.08 (29%) <sup>1</sup>	0.17 (24%)	0.11 (9%)
Fats			
- Triglycerides	0.12 (45%)	0.53 (72%)	0.98 (78%)
- Diglycerides	0.03 (13%)	0.02 (3%)	0.05 (4%)
- Monoglycerides	0.03 (13%)	0.01 (2%)	0.11 (9%)

a: Norway spruce  
b: Scotch pine  
c: European aspen  
1: % of total fatty material

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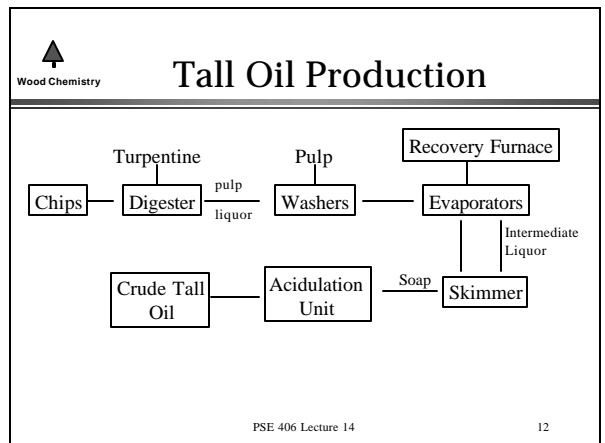


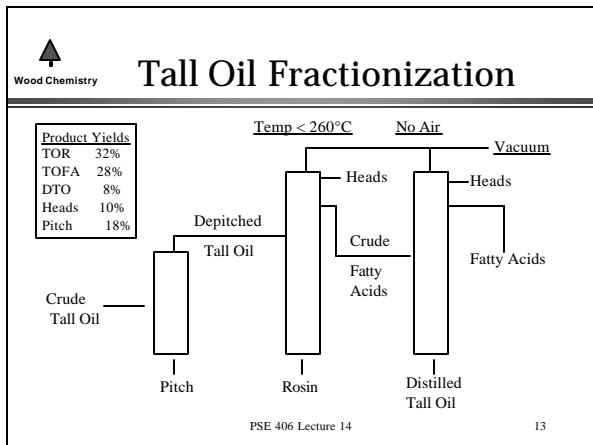
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## Fats & Fatty Acids Pulp and Paper Issues

- Fats and fatty acids are not water soluble and are therefore involved in the formation of stickies.
  - Remember that these chemicals are found in little parenchyma cells. Beating of pulp can release this material.
- Fatty acids are often recovered along with resin acids from kraft mills. This combination of chemicals is known as tall oil.

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## Waxes

- Wax is the water resistant protective coatings of leaves, fruits, and trees (bark). Wax is a mixture of a variety of different chemicals.
  - » Waxes consist mainly of very long chained (C12-38) fatty acid esters of long chained alcohols.

Waxes

$$\text{CH}_3-(\text{CH}_2)_n-\text{O}-\text{CO}-(\text{CH}_2)_m-\text{CH}_3$$

$\text{C}_{20}\text{H}_{41}\text{OH}$	Arachidic Alcohol
$\text{C}_{25}\text{H}_{50}\text{OH}$	Lignoceric Alcohol

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## Waxes

- Other components found in waxes include n-alkanes, ketones, primary and secondary alcohols, aldehydes, dicarboxylic acids, and hydroxy acids.
- Minor wood component
  - » 0.08-0.09%
  - » Much higher percentage in foliage, fruits and some barks.
- Physical Properties
  - » Soluble in organic solvents. Water insoluble
  - » mp/bp: think candles

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## Lignans

- Another class of extractive produced by the plant for protection. There are large numbers of different lignans.
- Lignans are found in the bark, fruit, heartwood, leaves, and roots of plants.
- Isolation is accomplished through solvent extraction.
- Yields of 0-30% are obtained.

$\alpha$ -Conidendrin

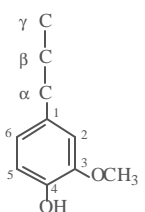
Example lignan found  
In heartwood of softwoods

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## Lignans Structural Information

- Two phenylpropane units (C9) linked  $\beta$ - $\beta$ 
  - Comes through same biosynthetic pathway as lignins
  - C9 units linked through enzymatic free radical coupling
  - Protein found which acts as template to force  $\beta$ - $\beta$  orientation
- Lignans differ in:
  - Ring substitution (3, 4, 5)
  - Nature of linked side chain
  - Nature of additional bonds between rings



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## Lignans: Role in the Plant

- Many lignans have fungicidal, insecticidal, and antioxidant properties.
  - Hydroxymatairesinol actually consumed by fungi accelerating degradation.
- In trees, lignans are laid down at the sapwood/heartwood boundary.
  - They are laid down when the tree is depositing chemicals to protect itself.

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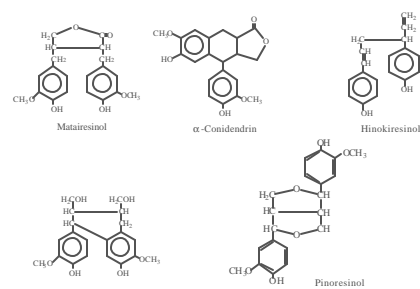
## Lignans: Location in Tree

- Widely distributed in softwoods and hardwoods
  - Typically amount: < 1% of heartwood
  - Can be as high as 30% of heartwood
- Found in Heartwood
  - Nearly non-existent in sapwood
  - In *Tsuga*, lignans were found lining the tracheid walls as surface coatings and encrusting bordered pits
  - Lignans deposited during heartwood formation
  - Greatly responsible for coloration of heartwood

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## Lignans Typical Softwood Species



Matairesinol       $\alpha$ -Condendrin      Hinokiresinol  
Isolaricresinol      Pinoresinol

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## Lignans Medicinal uses

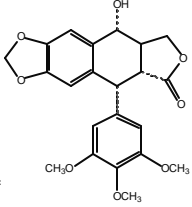
- Large amount of research devoted to investigating medicinal properties of lignans.
  - » Particularly from tropical hardwoods and grasses.
    - Example 1999 reference: 35 lignans isolated from the twigs of *Tazus mairei* (a shrub) for possible use as drugs.
- Studies have found certain medicinal properties:
  - » Antiviral, antitumor, antioxidant
- Lignans are phytoestrogens
  - » These are compounds produced by plants which are similar in structure to oestrogen and exhibit oestrogenicity.

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## Lignans Example Uses: Podophyllotoxin

- Extract of *Podophyllum emodi*
  - » Asian plant
  - » Material in root (rhizomes)
- Also found in mayapple common American weed
  - » Extracted from leaves
- Functions as cell poison: affects cells undergoing mitosis.
- Inhibits enzyme needed for cancer cell reproduction.
- Starting material for the manufacture of other cancer drugs.

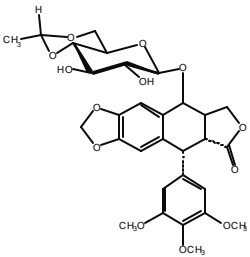


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## Lignans Example Uses: Etoposide

- Sold by Bristol-Myer Squibb as VePesid
- Treatment for testicular cancer and small lung cancers and others.
- Glycoside (sugar containing) of Podophyllotoxin

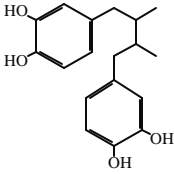


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## Lignans Nordihydroguaiaretic Acid

- Isolated from the leaves of *Larrea divaricata*
  - » 12% yield
- NDGA is a proven antioxidant
  - » Used in fats and oils in food.
- Produced synthetically from petroleum based starting material.



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- **Lignans found in water discharge from mechanical pulping operations**
  - » Toxic to fish but not as much as other extractive compounds
  - » Are readily handled through biological treatment systems
- Plicatic acid has been found to be the number one cause of respiratory problems in cedar saw mills