Wood Chemistry

PSE 406 / Chem E 470

Lecture 13

Diterpenes and Triterpenes

Pitch Chemicals

- When you grab a softwood tree and your hand sticks to the tree, you have discovered pitch.
- Pitch consists of about 50/50 terpenes and resin acids. Resin acids are glassy like chemicals also made of isoprene units.
- The Christmas tree I'm holding didn't have any pitch left.

Pitch as a Bandage

- When a softwood tree is wounded, it releases pitch to "seal" the wound.
  - » Terpenes serve as the antiseptic and then evaporate.
  - » Resin acids serve as the bandage (and also as an antiseptic).

Rosin

- The term rosin refers to a mixture of resin acids produced through the distillation of pitch.
- Gum rosin: distillation of gum resins (wound resin)
  - » US 197 metric tons (1998)
- Tall oil rosin: from the Swedish word talloja which means pine oil. Produced during the kraft pulping process.
  - » US 247,000 metric tons (1998)
- Wood rosin: Distillation of old stumps.
  - » US 30,000 metric tons (1998)

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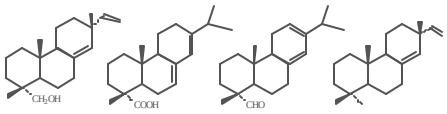
Diterpenes: Structure

- 4 isoprene units linked head to tail
- Neutrals:
  - » Hydrocarbons, phenolics, alcohols, ketones and aldehydes
- Acids: Typically referred to as resin acids
- Acid content much higher in heartwood than sapwood



Pimarinol Abietic Acid Levopimaral Pimaradiene

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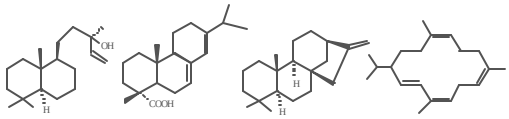
Diterpenes: Structure

- Ring structures
  - » Acyclic, mono, di, tri and tetracyclic
  - » Macrocylcic (10-15 carbons)



Bicyclic Tricylcic Tetracyclic Macrocyclic

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Diterpenes: Location in Tree

- Composition is very species dependent
- Mainly found in conifers (0.2-0.8%)
  - » Oleoresin: ~70% resin acids (tricyclic/COOH)
  - » Heartwood: Large amount of neutral diterpenoids that have been modified through various reactions:
    - – Aromatization, hydroxylation, oxidation, & rearrangements (often losing C atom)
- Tropical Hardwoods:
  - » Sandalwood: 12-14% resin

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Diterpenes Physical Properties

- Rosin (mixture of diterpenoids) is glass like: it slowly softens when heated – does not have a melting point
- Pure resin acids are crystalline
  - » Pimaric acid mp = 217-219°C
- Tricylcic structure quite stable: Amber
- Volatilization
  - » Some diterpenoids can be volatilized with steam
  - » Problem in TMP plants (health reasons)
- Solubility: Abietic acid
  - – Insoluble in water
  - – Some solubility in base

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Diterpenes
Pulp and Paper Problems

- Toxicity
  - » Diterpenoids are primary pollutants in pulp mill effluents
  - » Very toxic to fish
  - » Difficult to remove in treatment systems
  - » LD_{50} not particularly high (abietic 180mg/kg)
  - » Inhalation problems in saw mills
- Stickies

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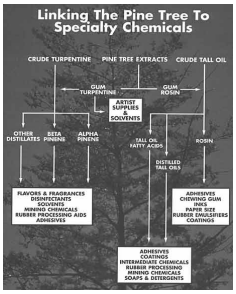
Uses of Diterpenes

- Rosin: Mixture of resin acids
  - » Gum Rosin
  - » Tall Oil Rosin
- Uses of Rosin
  - » Printing Inks, Paper Size, Rubber, Adhesives, Miscellaneous



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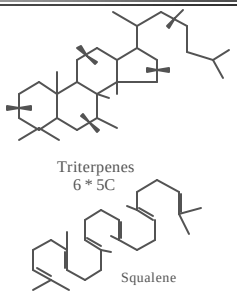
Triterpenes & Sterols
Chemical Composition

- 6 isoprene units linked head to tail
- Many are classified as steroids (sterane structure)
  - » Triterpenoids and sterols have same synthetic pathway so they should not be separated
  - » Both start from squalene and then branch off



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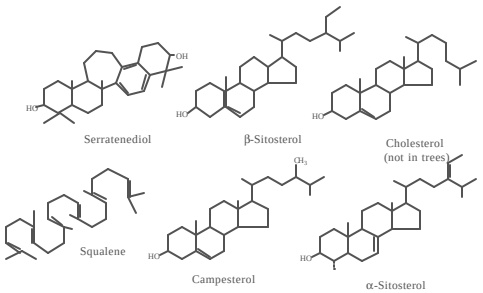
Triterpenes & Sterols
Chemical Composition



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Triterpenes & Sterols Chemical Composition

- Triterpenoids exist in three forms
  - » Free form
  - » Esters of fatty acids
  - » Glycosides
- Can contain a large variety of functional groups
  - » Carboxyl
  - » Ethers
  - » Acetyl
  - » Alcohols
  - » Ketones

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Triterpenes& Sterols Physical Properties

b**-sitosterol**

- Crystalline
  - » mp 140°C
- Solubility
  - » Organic solvents: ether, alcohols, etc
- Boiling Point
  - » Merck index: no boiling point listed. Found in tall oil pitch - does not distill

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Triterpenes & Sterols Role in Nature

- Sterols are found in plants as both free sterols, as sterol esters (of fatty acids) and as sterol glycosides
- Serve as components of membranes
  - » Work with phospolipids to create membranes which are only permeable to certain chemicals
- Sterol esters
  - » Believed to serve as transport agent to get sterols from site of biosynthesis to membrane
- Sterol glycosides ?????????

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Sterol levels in plants

- Levels of sterols variable depending on plant.
  - » Broccoli: 3.4g/kg
  - » Banana: 0.5g/kg
  - » Alfalfa 2.1 g/kg
  - » Aspen (wood): 5 g/kg
- Free sterols are found in vegetable oils.
  - » Peanut oil: 1-2 mg/kg oil
  - » Corn oil: 2-4 mg/kg

•1. J Food Comp Anal 2002 15, 123
•2. TAPPI, 1999 83(5)

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Triterpenes & Sterols
Tree Information

- Found in both hardwoods and softwoods
  - » Not a very large component in softwoods
  - » β-sitosterol major component
  - » Larger amounts in tropical hardwoods
- Not found to any extent in oleoresin
- Found throughout the tree
  - » Concentration actually higher as go from bark to pith
    - – Not involved in heartwood formation
    - – Higher concentration of sterols in younger trees

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Triterpenes & Sterols
Pulp and Paper Problems

- Sterol esters are difficult to saponify: known as nonsaponifiables
  - » Some chemical conversions during pulping but mostly stable.
  - » Large number of reactions during bleaching
    - – saponification
- Hydrophobic nature of sterol esters cause them to be a major pitch problem in papermaking
  - » Major components of pitch deposits

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Sterols from Trees
Benecol (1)

- Benecol: cholesterol reducing product.
  - » Known since 1950s that vegetable sterols can reduce blood cholesterol.
    - – High levels of sterols can cause other problems
  - » 1970s shown that plant stanols were effective at lowering cholesterol without negative effects.
    - – Stanols not fat soluble so difficult to use.
    - – Finnish company (Rasio) developed a procedure in late 1980s early 1990s to produce stable fat soluble stanol esters from plant derived sterols.

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Sterols from Trees:
Benecol (2)

- Sitostanol
  - » Similar structure to sitosterol
  - » Saturated sterol
  - » Found in Nordic Pine
- In Benecol the sitostanol is in the form of a fatty acid ester.