Wood Chemistry

Wood Chemistry
PSE 406 / Chem E 470

Lecture 12

Wood Extractives Introduction

Terpenes and Sesquiterpenes

Wood Chemistry

Agenda

- General Extractives Information
- Terpenes
  - » Monoterpenes
    - – Chemistry
    - – Occurrence
    - – Uses
  - » Sesquiterpenes

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Tree Extractives (1)

- Besides the big three wood compounds, trees contain other compounds that serve a variety of functions including:
  - » Protection (from insects, animals, and rot).
  - » Attractants (flowers, fruits)
  - » Food storage
  - » Membranes
  - » Enzymes

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Tree Extractives (2)

- Extractives add significant properties to wood:
  - » Color
  - » Odor
  - » Density
- These compounds are typically present in very limited amounts but still affect the wood properties greatly.

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Protection Chemicals

- Here is a list of the classes of extractives that can serve to protect the tree. We will look at most of these.
  - » Terpenes
  - » Resin Acids
  - » Flavonoids
  - » Lignans
  - » Stilbenes
  - » Tannins
  - » Phenolics and others

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"Other Extractives"

- These extractives are in the tree typically for reasons other than protection.
  - » Fats and fatty acids
  - » Proteins
  - » Flavonoids (I know they are involved in protection).
  - » Sterols

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The Fragrance of a Tree

- Each tree has a unique fragrance.
  - » Some have strong fragrances. than others like Cedar.
  - » Some have only light odor
- The aroma is due to volatile compounds produced by the tree. (the odor chemicals become gases easily)
- These chemicals can be isolated and sold.

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Softwood Fragrance Chemicals

- The fragrance of softwood trees are typically from a class of chemicals named terpenes.
- Terpenes are hydrocarbon derivatives of isoprene; a chemical that can be produced from petroleum.

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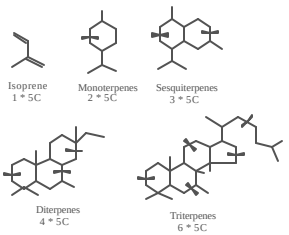
Terpenes / Terpenoids General Structures

- Polymers of Isoprene.
- Over 4000 have been identified in trees.
- Isoprene linked according to “isoprene rule”.
- Terpene: hydrocarbons
- Terpenoid: contains oxygen containing functional group.



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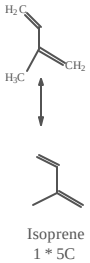
Monoterpene Structures

- Hydrocarbon derivatives of isoprene (2-methyl butadiene)
  - » Butadienes linked head to tail
- Can posses oxygen containing functional group(s) such as alcohols, carboxylic acids, and aldehydes
- Stereospecific (±)
- Acyclic, monocyclic, bicyclic, and trycyclic compounds



Isoprene
1 * 5C

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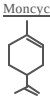
Monoterpene Structures

Acyclic

myrcene

Moncyclic



limonene

Tricyclic

tricylene

Bicylic Class

Carane Type

3-carene

Thujane Type

α-thujene

Pinane Type

α-Pinene

Bornane Type

Camphene

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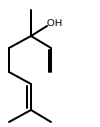
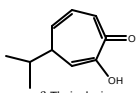
Monoterpenoids

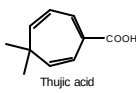
- Monoterpenes which consist of only carbon and hydrogen are hydrocarbons.
- Addition of functional groups such as OH, COOH, Aldehydes, etc. turn these monoterpenes into monoterpenoids.



Linalool



β Thujaplacin

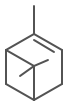


Thujic acid

Safranal

Monoterpenes (oids) Physical Properties

- Form
  - » Mostly liquids, some solids
- Melting Points
  - ≈ α-pinene: - 50°C
  - » camphor: 179°C (solid at room temp)
- Boiling Points
  - ≈ α-pinene: 156 °C @ 101.3 kPa
  - » nerolidol: 276°C @ 101.3 kPa
- Solubility
  - » Monoterpenes: organic solvents, insoluble in water
  - » Monoterpenoids: organic solvents with some limited water solubility



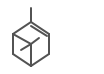
α-Pinene

Camphor

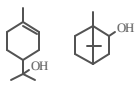
Monoterpenes Occurrence

- Found both in vegetative and animal kingdoms: both terrestrial and marine.
- Vegetable kingdom
  - » Widely distributed in higher plants: roots, stem, foliage, seeds.
  - » Trees: exist mainly in softwoods, some tropical hardwoods. Often responsible for the characteristic odor of wood.
  - » Typically found in oleoresin.
- Animal Kingdom
  - » Insects (warning compounds, attractants)/Alligators
- Volatile compounds released during pulping.
- Monoterpenoids widely used commercially:
  - » Turpentine/Pine Oil

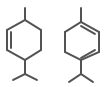
Composition of Douglas Fir Terpenes



α-Pinene
58.4%



α-Terineol/Borneol
6.6%



β-Phellandrene/ α-terpinene
6.3%

β-Pinene
4.2%

Terpinene-4-ol
2.5%

Camphene
2.4%

3-carene
1.5%

Monoterpenes (oids) Environmental Issues (1)

- Trees naturally release terpenes so there is a certain level of terpenes in the atmosphere
  - » Typical conifer forest (~100 ug/m^3)
- Terpenes as hydrocarbons react in the atmosphere with oxygen and sunlight to form photooxidants (O_3, H_2O_2, HO•, HOO•, $RONO_2$, etc.)
  - » These species cause damage to forest.

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Monoterpenes (oids)
Environmental Issues (2)

- Logging and wood processing operations significantly increases the level of terpenes in the atmosphere (10 – 1000 times higher than natural forests.
- Increased levels of terpenes can cause damage to the forest and to humans.
  - » Inhalation of terpenes can also cause certain health problems.
  - » Mill sites can have very high levels of terpenes.

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Monoterpenes (oids)
Chemical Sources: Turpentine

- Trees of the species *Pinus* are the source of nearly all turpentine
- Four classifications of turpentine:
  - » Gum - from wounds on tree
  - » Steam distilled wood - steaming of old stumps
  - » Sulfate wood turpentine - vented from kraft pulping
  - » Destructive distillation - not commercially significant

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Monoterpenes (oids)
Chemical Sources: Turpentine

Country	Tons	Country	Tons
USA/Canada	108,00 99% CST, 1% Gum	Mexico/ Central Am.	10,000 60% Gum, 40% CST
South Am.	17,000 90% Gum, 10% CST	Scandinavia	22,000 100% CST
Russia	91,000 90% CST, 10% Gum	Southern Europe	6,800 95% Gum, 5% CST
China	47,000 100% Gum	New Zealand	3,900 100% CST
Indonesia	8,400 Mostly gum	India	4,800 100% Gum
Miscellaneous	17,500	Total World	335,000 Tons (metric)

Source: Amazing Terpenes 1993

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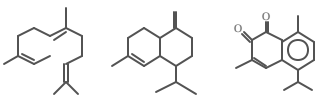
Sesquiterpenes

- Volatile compounds: isolated by steam distillation
  - » Components of turpentine
- 3 isoprene units linked head to tail
- Found in most plants and fungi. Typically very minor components.



Farnesene γ-Muurolene Mansonone

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Role of Sesquiterpenes

- Used to control other plants in a deleterious fashion. (Allelopathy)
- Anti bacterial compounds (Phytoalexins)
- Used by fungi to break down plants (Phytotoxins)
- Defensive chemicals used by plants against insects and fungi