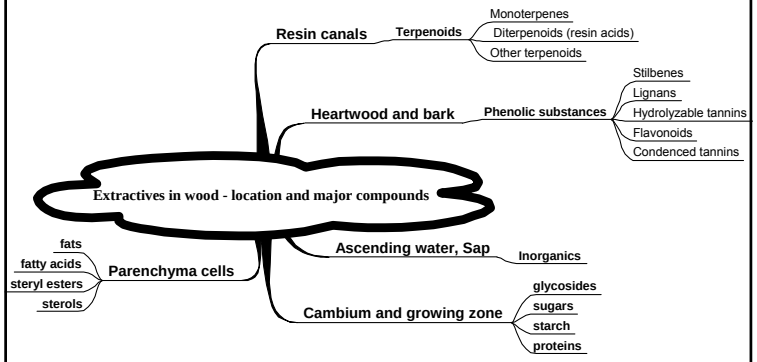
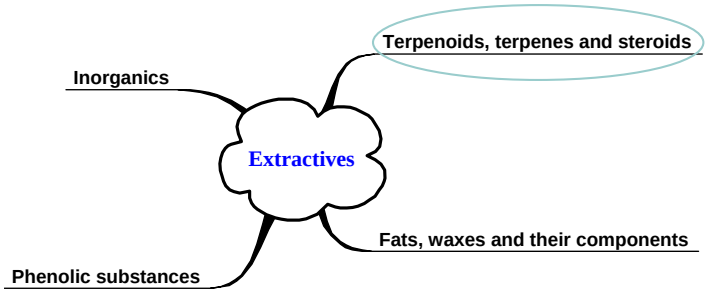
Extractives in wood and their behaviour in pulping

Extractives in wood



Extractives



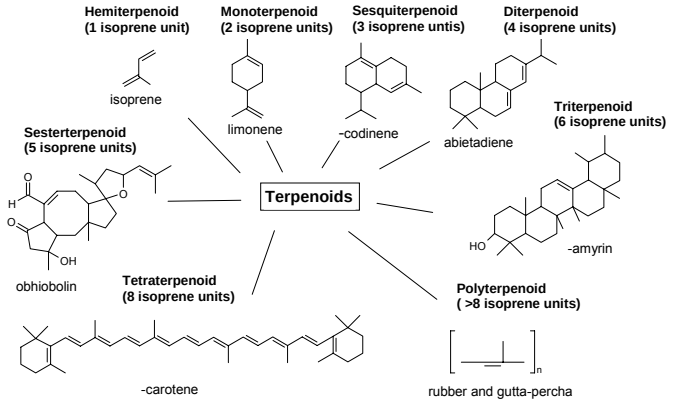
terpene=terpeeni, terpenoid=terpenoidi, steroid=steroidi, phenolic substance=fenolinen yhdiste

Terpenoids, terpenes and sterols

- Exist mainly in resin canals of conifers
- Terpenoid is a general name for terpenoids and terpenes, more strictly terpenoid is a terpene with a hydroxyl, carbonyl or carboxyl function

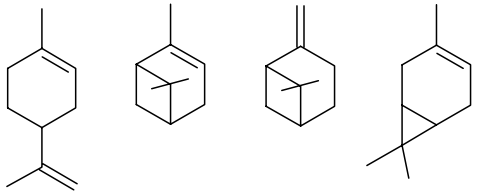
resin canal=pihkatiehyt, conifer=havupuu

General classification of terpenoids



Monoterpenes

- Consist of two isoprene units
- Exist mainly in softwood canal resin
- Relatively volatile compounds



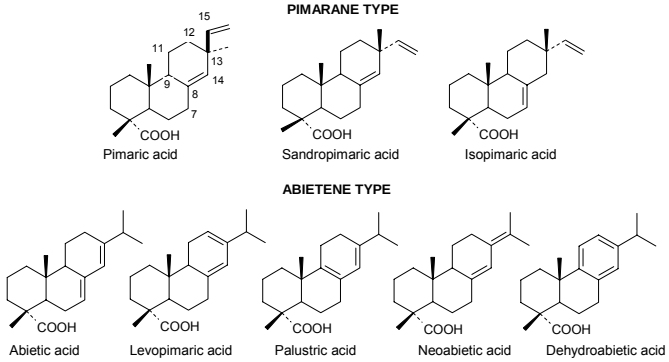
Limonene α-pinene β-pinene Δ^3-carene

Diterpenes and diterpenoids

- Consist of 4 isoprene units
- Diterpenoids, mainly resin acids, constitute a major part of softwood canal resin, i.e. oleoresin
- In softwood main types are pimarane or abietane types of tricyclic diterpenoids.

resin acid=hartsihappo, oleoresin=pihka

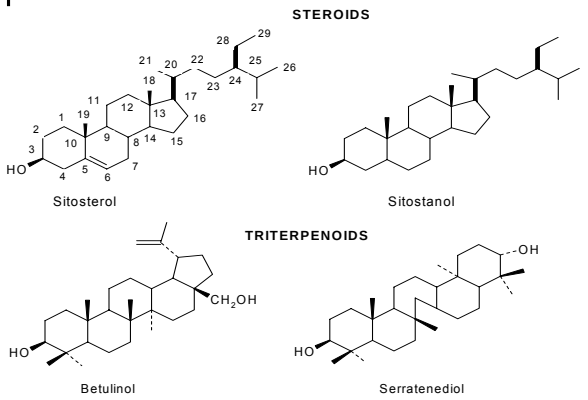
Diterpenoids from softwood



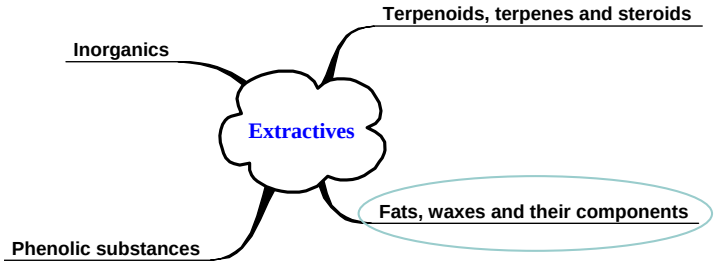
Triterpenoids and steroids

- Both consist of 6 isoprene units
- Structures are closely related
- Steroids in wood, for example:
  - β-sitosterol
  - sitostanol
- Triterpenoids in wood, for example:
  - betulinol, found in birch bark
  - serratenediol, found in pine bark

Triterpenoids and steroids

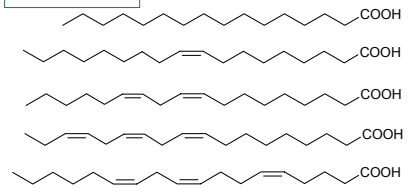


Extractives



Fats, waxes and their components

Fatty acids:



palmitic acid C16

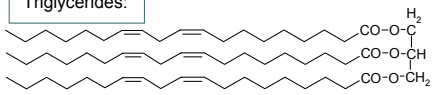
oleic acid C18

linoleic acid C18

linolenic acid C18

pinolenic acid C18

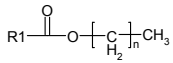
Triglycerides:



trilinolein

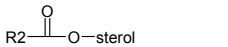
Fats, waxes and their components

Fatty acid esters:

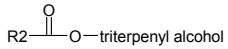


n=19-23

waxes



steryl esters

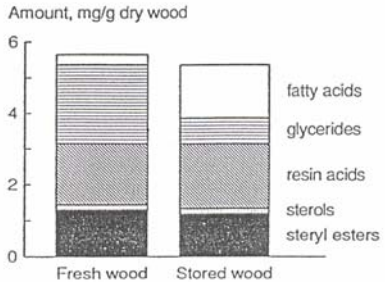


triterpenyl esters

R1= fatty acid chain, R2 = chains of saturated and unsaturated C14-C20 fatty acids

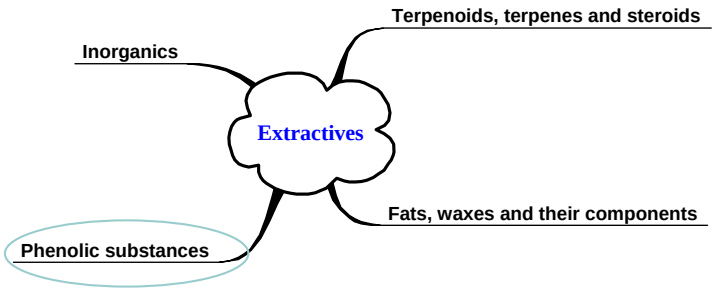
Fats and fatty acids

- In wood fats occur mainly as triglycerides
- Free fatty acids (FA) are present only in heartwood
  - The amount of free FAs decreases when logs are stored



Composition and amount of lipophilic extractives of fresh and water-stored logs of Norway spruce.

Extractives

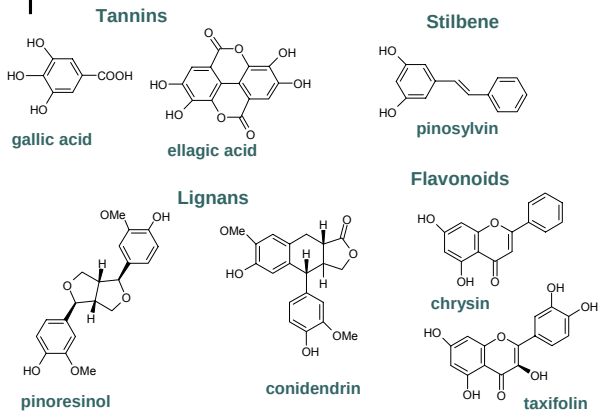


Phenolic substances

- Many structures derive from phenylpropanol structures
- Main groups are stilbenes, lignans, flavonoids and tannins
- to some extent these structures are hydrophilic
- Are usually also chromophores

stilbene=stilbeeni, lignan=lignaani, flavonoid=flavonoidi, tannin=tanniini, chromophore=kromofori

Phenolic substances



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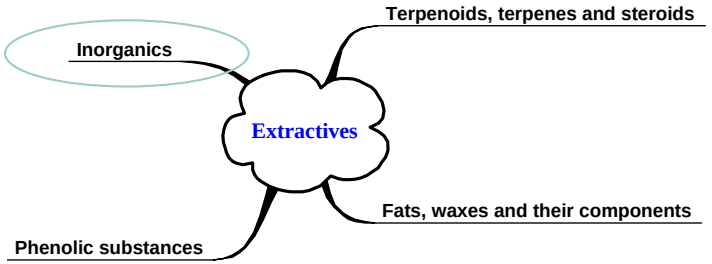
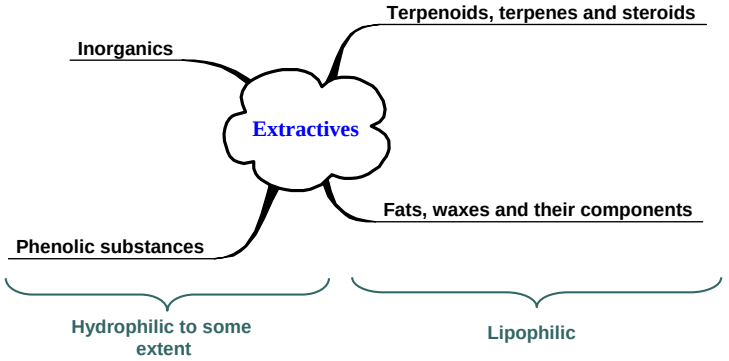


Inorganic compounds

- Wood contains also some metals
- Main compounds are:
  - Calcium (Ca), potassium (K), and magnesium (Mg)
- Also some heavy metals are present:
  - Iron (Fe), cobalt (Co), and manganese (Mn)

Properties of extractives



Wood resin and pitch

- Wood resin = lipophilic, i.e. water insoluble, wood extractive:
  - Fatty acids
  - Glycerides
  - Resin acids
  - Sterol and triterpenyl alcohols (i.e. triterpenoids) and
  - Their fatty acid esters
  - Variety of other compounds (i.e., volatile resin components like monoterpenes)
- Wood pitch = deposit that is rich with wood resin components

Reactions of extractives in pulping – volatile fraction

- During the initial delignification low molar mass terpenes (monoterpenes, sesquiterpenes) are distilled out of wood chips
- The volatile fraction, turpentine, is recovered from digester relief

Reactions of extractives in pulping – non-volatile fraction: saponifiable compounds

- A part of wood resin is saponifiable
- Consequently saponification of these saponifiable compounds occurs in alkaline media.
- Saponification is actually an alkaline hydrolysis of esters.
- The reaction products are soaps which may function as surface active agents
- After cooking the soap is removed
  - Tall oil soap

saponification=saponifikaatio, saippuoituminen;saponifiable=saippuoituva; tall oil=mäntyöljy; surface active agent=pinta-aktiivinen aine

Reactions of extractives in pulping – non-volatile fraction: saponification

I) Free (fatty and resin) acids → Sodium soaps

II) Fats (mainly triglycerides) → Sodium soaps and glycerol (soluble in water)

III) Steryl esters → Sodium soaps and sterols (insoluble in water)

Reactions of extractives in pulping – nonvolatile fraction: unsaponifiable compounds

- Part of the wood resin is unsaponifiable
  - Neutral components : hydrocarbons, fatty acids, sterols, triterpenyl alcohols
- These compounds may cause problems in pulping and bleaching
  - e.g. deposit build-up tendency
  - Means of deresination are needed

deresination=pihkanpoisto

Effects of extractives in pulping and papermaking

Effect	Major responsible component groups
Process disturbances	
Foaming	Resin and fatty acid soaps
Deposits in kraft mills	Ca soaps of fatty acids, steryl esters, hydrocarbons
Deposits from mechanical pulps	All resin groups, but especially triglycerides and fatty acids
Wet-end chemistry disturbance	Colloidal pitch droplets, mainly composed of triglycerides, fatty acids
Effluent toxicity	Resin acids, diterpene aldehydes and alcohols, sterols

Effects of extractives in pulping and papermaking

Effect	Major responsible component groups
Product quality impairment	
Lower sheet strength	Triglycerides, fatty acids
Lower water absorbance	All hydrophobic components
Lower friction	Fatty acids, triglycerides
Taste and odor	Unsaturated fatty acids (after oxidation)
Allergic reactions	Oxidized resin acid products

Some means of deresination

- Use of surfactants (e.g. soaps)
  - If concentration of surfactants is sufficiently high, micelles are formed
  - Micelles can dissolve water insoluble neutral components
- Use of talc

surfactant=pinta-aktiivinen aine; micelle=miselli; talc=talkki