Wood Chemistry

Wood Chemistry
PSE 406 / Chem E 470

Lecture 7 - Hemicelluloses

Wood Chemistry

Class Agenda

- General Information
- Components
  - » Sugars
  - » Acids (Lactones)
  - » Acetyl/Methyl Groups
- Nomenclature/Classification
- Xylans
- Mannans

Wood Chemistry

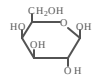
General Information

- Cell wall supporting components
- 27-30% of wood
  - » ~27% softwoods
  - » ~30% hardwoods
- Short branched polymers
  - » 50-300 DP
- In wood they are not crystalline
  - » Very accessible to chemicals
  - » Very reactive

Wood Chemistry

Major Components

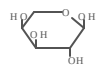
Hexoses


β-D-Galactopyranose

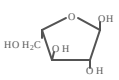

β-D-Glucopyranos


β-D-Mannopyranose

Pentoses


α-L-Arabinopyranose

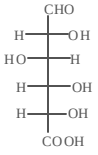

β-D-Xylopyranose


α-L-Arabinofuranose

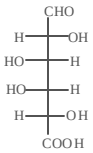
Wood Chemistry

Other Components

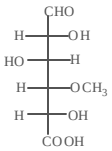
Hexuronic Acids: Minor Constituents



D-Glucuronic Acid



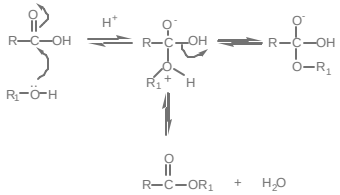
D-Galacturonic Acid



D-4-O-Me-Glucuronic Acid

Wood Chemistry

Ester Formation (Lactones)



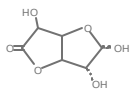
- Under acidic conditions, carboxylic acids and alcohols will react forming carboxylic acid esters.

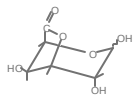
Notes

Wood Chemistry

Uronic Acid Lactones

- The uronic acids mutarotate as did the hexoses and pentoses Additionally, however, they will also form internal lactones (cyclic esters) under acidic conditions. Galacturonic acid prefers the pyranose form while glucuronic acid the furanose form.


D-Glucuronic Acid γ Lactone (furanose structure)


D-Galacturonic Acid γ Lactone (pyranose structure)

Notes

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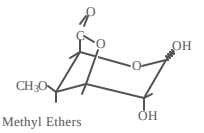
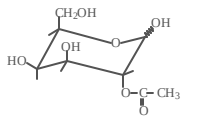
Acetyl and Methyl Groups

- Hemicellulose sugars can also contain methoxyl or acetyl groups. The percentage of these groups varies significantly between different hemicelluloses.


Methyl Ethers


Acetyl Grou

Notes

Wood Chemistry

Nomenclature

- Named after components in linear backbone
  - » Xylans (1-4 linked xylose chain)
  - » glucomannans (1-4 glucose/mannose backbone)
- Branching noted in first part of the name
  - » gluco, arabino, o-acetyl
- Branching linkage is also included
  - » 1→2, 1→6, or -O-
- In structural drawings, abbreviations for the components are used: Glc*r* = glucopyranose

Notes

Wood Chemistry

Hemicellulose Classifications

- Softwood Hemicelluloses
  - » Galactoglucomannan (Mannans)
  - » Arabinoglucuronoxylan (Xylans)
  - » Arabinogalactan
  - » Pectins
- Hardwood Hemicelluloses
  - » Glucuronxylan (Xylans)
  - » Glucomannan

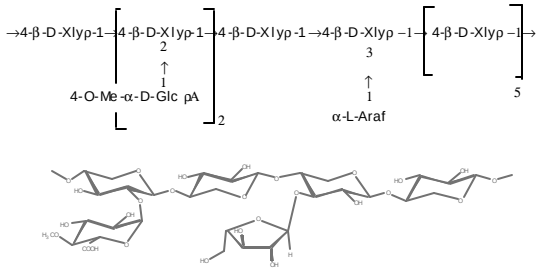
Wood Chemistry

Softwood Xylans

- 10-15% of wood
- Major xylan:
  - » Arabino-4-O-methylglucuronoxylan
- 1→4 linked β-D-xylopyranose linked backbone
- Arabinose furanose ring attached 1→3 α to about 1 in every 10 xylose units
- 2/10 xylose 1→2 α linked to 4-O-methylglucuronic acid
- DP ~ 120

Wood Chemistry

Softwood Xylans



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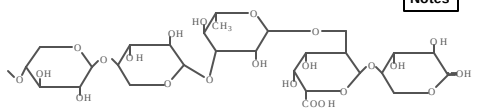
Xylan Reducing End

- Xylans have a very unusual reducing end which makes them mostly stable to alkaline degradation reactions. As you can see, there is a rhamnose molecule attached 1→2 to a galacturonic acid in the backbone.

Notes



-β-Xlyp-1→4--β-D-Xlyp–1→3-α-L-Rhap-1→2-α-D-GalpA-1→4-D-Xlyp

Wood Chemistry

Hardwood Xylans

- 15-30% of wood
- Major xylan:
  - » O-acetyl-4-O-methylglucurono-β–D-xylan
  - » Also called glucuronoxylan
- 1→4 linked β-D-xylopyranose linked backbone
- Most xylose (7/10) are actylated at C2 or C3
- 1/10 xylose 1→2 α linked to 4-O-methylglucuronic acid
- DP~ 150-200

Wood Chemistry

Hardwood Xylans

→4 - β - D - Xlyp -1→ 4 - β - D - Xlyp -1→4 - β - D - Xlyp -1→4 - β - D - Xlyp – 1→

2,3 ↑ R

2 ↑ 1

4 - O - Me - α - D - Glc pA

7

R = Acetyl

Wood Chemistry

Hardwood Mannans

- 3-5% of Hardwoods
- Simple unbranched polymer
- DP ~ 70
- Contains 1 to 2 parts Mannose per 1 part Glucose
- Linkage 1→4β

→4-β-D-Glcp-1→4-β-D-Manp-1→4-β-D-Glcp-1→4-β-D-Manp-1→4-β-D-Manp

Wood Chemistry

Softwood Mannans-Water Soluble

- Galactoglucomannans
- 5-10% of wood
- DP 100-150
- Glucose/Mannose backbone linked 1→4β
  - » Mannose/Glucose = 3/1
- Galactose side chain
  - » Galactose/Glucose = 1/1
  - » Galactose 1→6α
- Acetyl Groups 1 per every 3~4 backbone units - on C2 or C3

Wood Chemistry

Softwood Mannans-Alkali Soluble

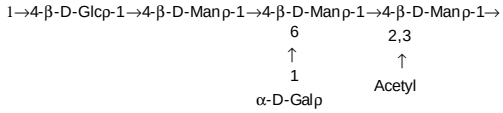
- Galactoglucomannans (glucomannans)
- 10-15% of wood
- DP 100-150
- Glucose/Mannose backbone linked 1→4β
  - » Mannose/Glucose = 4/1
- Galactose side chain
  - » Galactose/Glucose = 0.1/1
  - » Galactose 1→6α
- Acetyl Groups 1 per every 3~4 backbone units - on C2 or C3

Notes

Wood Chemistry

Softwood Mannans

Water Soluble Structure



- Alkali soluble mannans are similar in structure except there is much less branching (i.e. less galactose groups)