Wood Chemistry
PSE 406/ Chem E 470

Lecture 18
Chemical Isolation and Analysis II
Hemicelluloses

Class Agenda

- How are hemicelluloses separated from cellulose and lignin?
- How are individual hemicelluloses separated?
- How is the composition of individual hemicelluloses determined?
- How are the linkages determined?

How are hemicelluloses separated from cellulose and lignin?

- Generate Holocellulose
- Remember….in this procedure lignin is removed through the action of sodium chlorite

How are the hemicelluloses separated from cellulose?

- Cellulose is not soluble in almost any solvents.
- What are hemicelluloses soluble in?
- NaOH or KOH!!!!!
  » OK……they are mostly soluble
- Quick question…what happens to acetyl groups?
  » Saponification
Wood Chemistry

Isolation Scheme: Softwoods

Wood
\[ \xrightarrow{\text{HClO}_2} \]
Holocellulose

Soluble
Insoluble

Hemicellulose Mixture
Residue

What is in the residue?

- Cellulose
  - It is not soluble in much of anything
- Galactoglucomannan (not the water soluble one)
  - It turns out that this hemicellulose is not all that alkali soluble at this level of KOH
  - It takes the addition of NaOH and borate to solubilize this material

What makes up the rest of the hemicellulose mixture?

- Xylans
- Galactoglucomannans (water soluble)
- Maybe some pectins, a little glucans, and who knows what else

We are mainly concerned with the top two….

- How do we separate the xylans from the galactoglucomannans?
Because of the orientation of the C2 and C3 hydroxyl groups in mannose, it will form an insoluble complex with barium ions. Therefore the addition of Ba(OH)$_2$ will cause gluomannans to precipitate out of solution.

**Isolation Scheme: Softwoods**

- Hemicellulose Mixture
- Ba(OH)$_2$
- Soluble
- Insoluble
- Mixture
- Ba(OH)$_2$
- Crude Galactoglucomannan
- Soluble
- Insoluble
- Galactoglucomann
- Ba(OH)$_2$
- Arabinoxylan
- Soluble
- Insoluble
- Discard
- Galactoglucomannan

**Hemicellulose Analysis**

- The individual sugars are quantified using gas or liquid chromatography.
  - Often the individual components require derivitization before analysis.
  - Other analytical techniques are used to positively identify components.

How is the composition of individual hemicelluloses determined?

- How can hemicelluloses be broken down into individual sugars.
- Acid hydrolysis of glycosidic linkages !!!!!!!
Chromatography

- Chromatography is the process in which chemicals are transported by liquid or gas past a stationary phase. The individual components are attracted by different degrees to the stationary phase and thus travel at different speeds and are separated.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Column</th>
<th>Packing material</th>
<th>Detector</th>
</tr>
</thead>
<tbody>
<tr>
<td>gas</td>
<td>UV, RI FID, MS, Etc.</td>
<td>Detector</td>
<td>UV, RI FID, MS, Etc.</td>
</tr>
<tr>
<td>liquid</td>
<td>Compounds separate through: adsorption, size exclusion, boiling points</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Time

Derivitization

- Gas Chromatography - Chemicals to be analyzed must be volatile: Sugars and uronic acids are not volatile.
- Blocking hydroxyl groups will make chemicals volatile.
- Derivitization procedures:
  - Methylation
  - Acetylation
  - Silylation

Once the components are separated, they are detected by a number of different types of systems.

- A chromatograph is produced in which the components are seen as peaks.
- Quantification is accomplished by measuring the peak area

Determination of Linkages

- How is it possible to determine how the individual sugars are linked?
- Methylation of the free hydroxyl groups
- Acid Hydrolysis
- Chromatographic determination of products
- Another method to determine linkages is the Smith degradation which involves periodate oxidation, borohydride reduction and very mild acid hydrolysis. We are not going to cover this reaction.
Mild hydrolysis of hemicellulose results in the presence of monomers, dimers, trimers, etc of the hemicelluloses. These materials can be separated by chromatography and compared to known dimers.