Wood Chemistry

Wood Chemistry

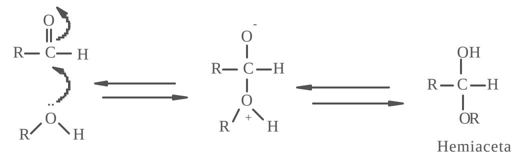
PSE 406 / Chem E 470

Lecture 4

More Sugars: Disaccharides and Rings

Wood Chemistry

Hemiacetal Formation



A hemiacetal is a compound having the C(OH)OR group that results from the reaction of an aldehyde with one mole of an alcohol.
Sugar molecules contain an aldehyde group and lots of alcohol groups.

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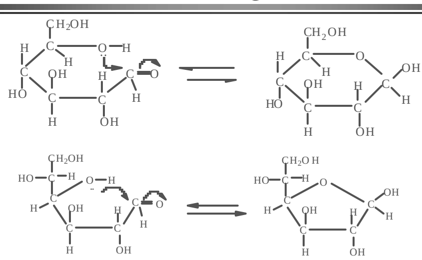
Hemiacetal Formation in Sugars



Notes

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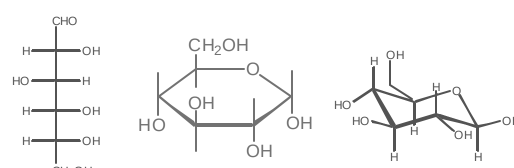
Important Monosaccharide Projections



Fischer Haworth Chair Configuration

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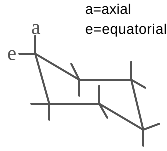
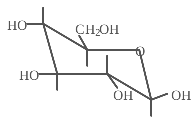
Conformation: The Chair

a=axial
e=equatorial



Chair



β-d-glucopyranose

The most stable form of a sugar in a six membered ring is in the chair formation. The substituent groups on the molecule are either in an axial or equatorial position depending on what gives the most stable molecule. Check out the 3D version of the above sugar on the notes page.

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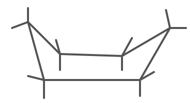
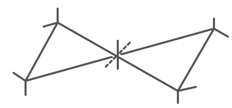
Conformation: Other Forms



Boat



Skew Boat

We won't be worrying about these forms.

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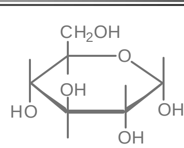
The Haworth Projection

- This is a very common way that wood chemists draw sugars in the ring form.
- In this projection, the thick bonds are perpendicular to the plane of the paper



- Substituents are parallel to the plane of the paper and lie either above or below the plane of the molecule

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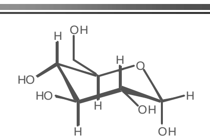
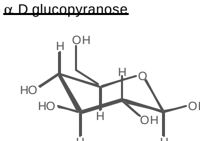
Formation of Anomers

- Ring closure creates new chiral center at C1; new pair C1 epimers termed anomers. For d sugars, the following is true:
  - » **alpha form: OH below the ring**
  - » **beta form: OH above the ring**
- For l sugars, the opposite is true.



α D glucopyranose



β D glucopyranose

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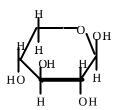
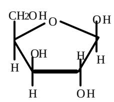
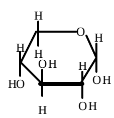
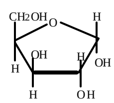
Nomenclature


β-d-xylopyranose


β-d-xylofuranose


α-d-xylopyranose


α-d-xylofuranose

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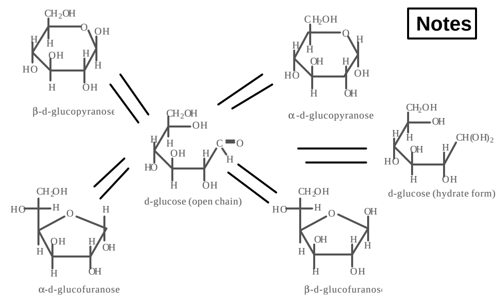
Mutarotation

Notes



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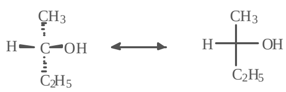
Fischer to Haworth

- In order to convert a Fischer projection of a sugar to a Haworth project, certain rules must be followed in order to maintain correct orientation of the molecule.
- Remember, the horizontal bonds in the Fischer projection (solid wedges) are out of the plane and the vertical wedges (broken wedges) are into the plane.



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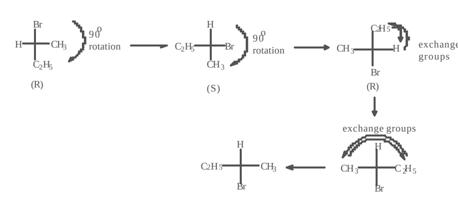
Fischer Formula Manipulation

- Manipulation of Fischer formulas will change conformation of structures so this must be done carefully as in the following example.



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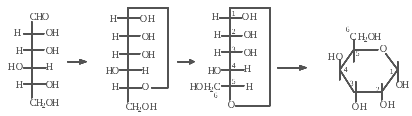
Fischer to Haworth



- Modify the Fischer formula so that all of the ring atoms lie along a vertical line. When rotating substituents around a chiral carbon, to keep the correct configuration, after a 90 rotation, the opposite substituents must be switched.
- Proceed around the Haworth formula placing the groups on the left above the hexagon and those on the right below the plane.

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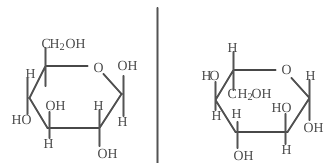
Monosaccharides
D Versus L, Part II



β-D-Glucopyranose β-L-Glucopyranose

Mirror Images

(Enantiomers)

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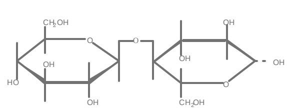
Linkages Between Sugars

- In the tree, monosaccharides are linked through enzymatic processes.
- Linkage proceeds through a dehydration process (loss of H_2O).
- The bond between the glucoses units in cellobiose is a glycosidic bond. Once linked, the glucose unit on the left is no longer a hemiacetal , it is now an acetal .



Cellobiose
4-O-(β-D-Glucopyranosyl)-D-Glucopyranose

- Cellobiose is disaccharide produced from the partial hydrolysis of cellulose. It is not naturally found in wood.
- The squiggly bond on C1 above means it can be either α or β.

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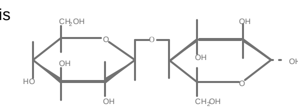
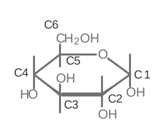
Linkages Between Sugars

- The glycosidic linkage between the glucose units is between the β C1 of one glucose to C4 of the other glucose. So this bond is a β(1→4) linkage.
- The glucose molecules in the drawing on the right are opposite to make drawing the β(1→4) linkage easy.



Cellobiose
4-O-(β-D-Glucopyranosyl)-D-Glucopyranose



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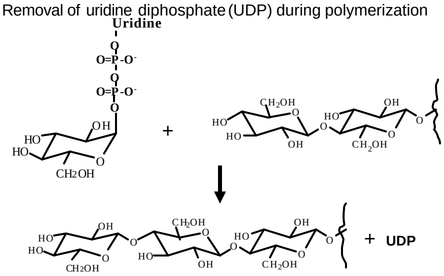
Cellulose polymerized by condensation reactions

- Removal of uridine diphosphate (UDP) during polymerization



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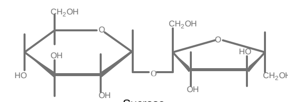
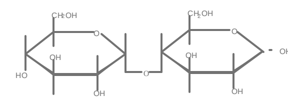
More Disaccharides

- Neither of these sugars are found in wood. Sucrose occurs naturally in sugarcane and in sugar beets. Maltose is formed through the degradation of starch.



Sucrose
α-D-Glucopyranosyl-β-D-Fructofuranoside



Maltose
4-O-(α-D-Glucopyranosyl)-D-Glucopyranose

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Reducing End Groups

- Sugars containing aldehydes and ketones are referred to as reducing sugars.
- These sugars will reduce copper in a specific reducing substances test. The aldehyde or ketone groups are oxidized by the copper.
- Sucrose is <u>not</u> a reducing substance

$$RCHO + Cu^{2+} \longrightarrow RCOOH + Cu^{1+}$$