

Carbohydrates

BIOS 10016

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Objectives

- Know all definitions presented about Carbohydrates.
- Classify sugars and describe relationships between sugars based on chemical and structural differences.
- Use the nomenclature associated with sugar chirality and structure to name sugars in linear and hemiacetal/hemiketal forms.
- Number the positions in a sugar.
- Describe the differences between aldoses and ketoses.
- Describe the properties of the functional groups in sugars, and how it enables them to interact with other molecules, like water.
- Describe the formation, properties and prevalence of hemiacetal/hemiketal structures of sugars in solution.
- Interconvert between the Fischer, Projection and Haworth representations.
- Describe the reactions that sugars undergo:
 - Difference between reducing and non-reducing sugars
 - Isomerization, esterification, and glycoside formation
 - Identify and describe deoxy and amino sugars
- Describe the formation and naming of glycosidic linkages.
- Identify and name the glycosidic linkages that can exist between sugars.
- Describe the components, linkages and properties of disaccharides: lactose, maltose, and sucrose.
- Describe the properties of branched and linear polysaccharides and their dependence on the types of glycosidic linkages.
 - Differences between starch, amylose, amylopectin and cellulose

- Difference between amylose and heparin

Carbohydrates

Monosaccharides

- Monosaccharides are the simplest carbohydrates and are aldehydes or ketones containing two or more hydroxyl groups
- Aldehyde: aldoses; ketone: ketoses
- Smallest monosaccharides are composed of 3 carbons
- End carbon closest to the most oxidized carbon is 1
- Often represented in **Fischer** or **Haworth**
- Often named relative to glyceraldehyde: D, L (depends on where the hydroxyl group is)
- D sugars are the most common in nature

Chirality

D and L sugars are defined by the chiral carbon furthest from the most oxidized carbon and where the hydroxyl group is relative to that carbon.

3 carbons - **triose**

4 carbons - **tetrose**

5 carbons - **pentose**

6 carbons - **hexose**

Different forms of monosaccharides

constitutional isomers same formula, different attachment

stereoisomers same formula, different 3D orientation

enantiomers stereoisomers that are nonsuperimposable mirror images of each other (only look at the chiral carbons)

diastereoisomers stereoisomers that are not mirror images

epimers diastereoisomers that differ at only one asymmetric carbon atom

anomers diastereoisomers that differ at a new asymmetric carbon atom formed on ring closure (anomeric carbon (the carbon where the molecule attached differs): α is trans (CH₂OH and OH on opposite sides), β is cis (CH₂OH and OH on the same side)

Hemiacetal or **hemiketal** sugars

Aldehyde + alcohol \rightarrow hemiacetal

Ketone + alcohol \rightarrow hemiketal

Happens through **nucleophilic attack**

α and β designations based upon chirality at anomeric carbon

α and β conformations are in equilibrium in water. The linear conformation is the least dominant species in solution

Naming of cyclic sugars

Glucose forms a six-member ring: **pyranose** since it resembles pyran (most biologically relevant)

Fructose forms a five-member ring: **furanose** since it resembles furan (most stable)

α and β anomers result from carbonyl containing functional groups having two faces.

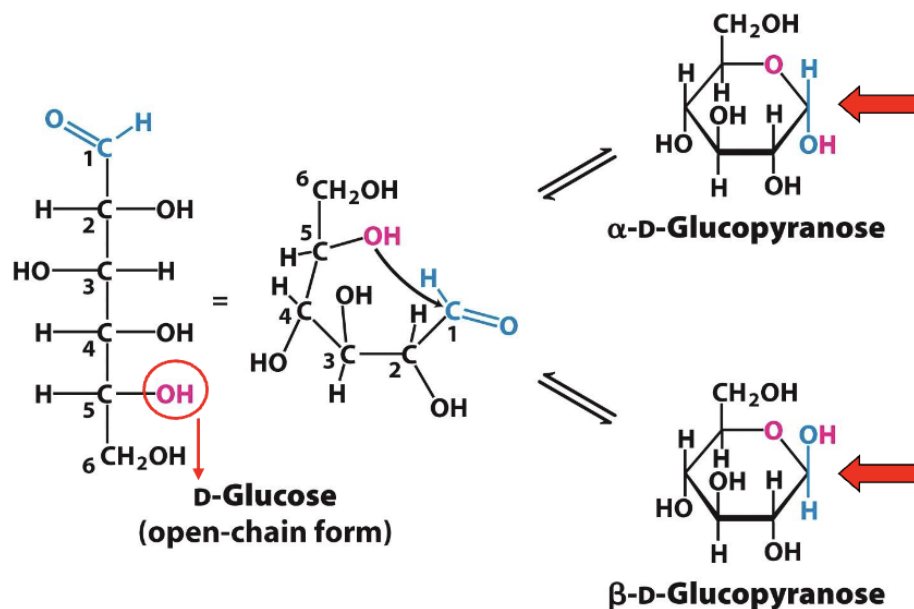
4 parts to the name:

1. Anomeric carbon - α or β ?
2. Chirality - D or L? (Last carbon pointing up = D, pointing down = L)
3. Sugar name
4. Number of atoms - furanose or pyranose?

Example: β -D-Ribofuranose

Fischer vs. Haworth Projection

- Carbon 1 from the planar structure (carbonyl carbon) becomes anomeric carbon in Haworth projection
- Last hydroxyl (OH) attacks ketone (C=O) group
- If O and OH are on same side = cis = β
- If O and OH are on opposite sides = trans = α



To convert from Fischer (open) to Haworth (ring):

1. Count the number of carbons - OH attacks C=O (6 membered ring = 5 carbons, 1 oxygen, 5 membered ring = 4 carbons, 1 oxygen)
2. If D, draw the last carbon pointing up; if L, draw the last carbon pointing down
3. Let the Fischer representation fall to the right by 90°
4. Anything on the original right side should point down
5. Anything on the original left side should point up

To convert from Haworth to Fischer:

1. Count the number of carbons (even the ones that stick out). Number them. The second carbon is anomeric.
2. Draw out the six-carbon chain.
3. Draw molecules pointing up on the right, and molecules pointing down on the left.
4. Fill in the gaps with hydrogens if the carbon has not fulfilled its octet.

Reducing sugars

Reducing sugars have an accessible functional group that can be oxidized (the sugar is a reducing agent). Non-reducing sugars cannot be oxidized. Any sugar that can undergo **ring opening** is a reducing sugar. (hemiacetal, hemiketal, **free OH group**)

Reaction with **Benedict's solution** or **Fehling's solution**

Benedict's test: adding 2+ copper ions to a solution containing a reducing sugar will result in a color change from blue to red, indicating the presence of reducing sugars. The sugar will reduce the copper to Cu_2O .

Reactions

Isomerization reactions

Fructose can convert to glucose and therefore is a reducing sugar.

Glucose \rightleftharpoons enediol intermediate \rightleftharpoons fructose \rightleftharpoons mannose

Esterification reactions

sugar + fatty acid \rightarrow ester

sugar + phosphate \rightarrow phosphoester

glucose-6-phosphate (glycolysis, glycogenesis, and pentose phosphate pathway)

Adding phosphate to modify glucose molecules

Sugar derivatives

deoxy sugars monosaccharides with one or more hydroxyl groups replaced by hydrogens (constituents of DNA, etc.)

amino sugars contain an amino group in place of a hydroxyl group, typically at the 2 position

Glycoside formation

A reaction of the anomeric carbon to form an **acetal** or **ketal**

aldehyde + alcohol \rightleftharpoons hemiacetal (OR and OH in the same molecule 2 R groups) \rightleftharpoons acetal (3 R groups and a hydrogen)

ketone + alcohol \rightleftharpoons hemiketal (OR and OH in the same molecule, 3 R groups) \rightleftharpoons ketal (4 R groups)

Under alkaline conditions, reverse reaction does not occur!

If a sugar is a hemiacetal or hemiketal, it is still able to undergo ring opening (a reducing sugar). If a sugar is involved in an acetal or ketal, *it will not be able to undergo ring opening* (not a reducing sugar).

Glycosidic linkages

Example: α -1 reacts with Carbon 6

Named based on the carbons involved ($\alpha 1 \rightarrow 6$)

Name from the sugar that has the lowest anomeric carbon

Types of sugars

Lactose (milk sugar)

Combination of **glucose** and **galactose** in a glycosidic $\beta 1 \rightarrow 4$ linkage

Is a reducing sugar

Maltose

An intermediate in starch metabolism

Combination of two glucose molecules in a $\alpha 1 \rightarrow 4$ glycosidic linkage

Amylose

Linear polymer of glucose molecules, in plants

Has a $\alpha 1 \rightarrow 4$ glycosidic linkage

Lack of branching enables formation of a helical structure stabilized by H-bonds between hydroxyl groups. Left-handed (**polysaccharides are usually left-handed**)

One of the components of **starch**

Cellulose

Polymer of **glucose**, synthesized by plants

Predominantly $\beta 1 \rightarrow 4$ linkages (not able to be broken down by humans)

Forms sheet-like structures stabilized by H-bonds between hydroxyl groups

Amylopectin and glycogen

Glucose polymer

Predominantly $\alpha 1 \rightarrow 4$ linkages

Highly branched - $\alpha 1 \rightarrow 6$ linkages

Technically reducing sugars

Non reducing end is the end of the chain that does not have a free anomeric carbon

Reducing end is the end of the chain that has a free anomeric carbon

Heteroglycans

Polymers of two or more different monosaccharides

Glycosaminoglycans: polymers of glucosamine or galactosamine derivatives that include a carboxylate or sulfate group