Lecture 24: Carbohydrates I

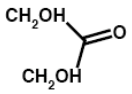
Reading in Campbell: Chapter 16.1-16.2

Key Terms:

- **Aldose, Ketose**
- **Monosaccharides**
- **Epimers**
- **Pyranose, Furanose**
- **Anomeric carbon**
- **Chair & boat conformations**
- **Equatorial & axial groups.**
- **Disaccharides**

Carbohydrates are:

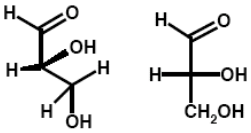
1. The primary energy reservoir in biosphere.
2. Biosynthetic precursors to amino acids and nucleic acids.
3. Structural and mechanical components of:
   - Cell walls in plants, bacteria & yeast
   - Extracellular matrix of animal cells (eg, connective tissue)



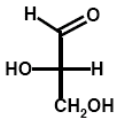
dihydroxyacetone
(no chiral center)

Structural Hierarchy:

1. Monosaccharides: cannot be hydrolyzed to simpler sugars.
2. Disaccharides: two covalently linked monosaccharides.
3. Oligosaccharides & Polysaccharides: 'a few' & 'many' covalently linked monosaccharides



D(R) glyceraldehyde



S(L) glyceraldehyde

Monosaccharides:
All carbons in monosaccharides are 'hydrated' - hence the name carbohydrate (general formula $(CH_2O)_n$)

1. The simplest monosaccharides contain three carbons.
2. Either polyhydroxyaldehydes or polyhydroxy ketones.
3. When the C=O group is at the very end it's an Aldose. When the C=O group is at the 2nd position it's called an Ketose.
4. Note that the aldose glyceraldehyde has a chiral center and therefore exists in D and L forms, or mirror images of each other. The D form predominates in nature.
5. Additional carbons (HO-C-H) are added just below the aldehyde or ketone group. Therefore, the chiral center of D-glyceraldehyde is preserved. The added carbon generates a new chiral center. The two different molecules generated by the addition of another carbon are called ***epimers*** because the differ in only *one* chiral center. For example, the addition of a CH_2OH unit to D-glyceraldehyde gives the following two epimers shown to the right, erythrose and threose.

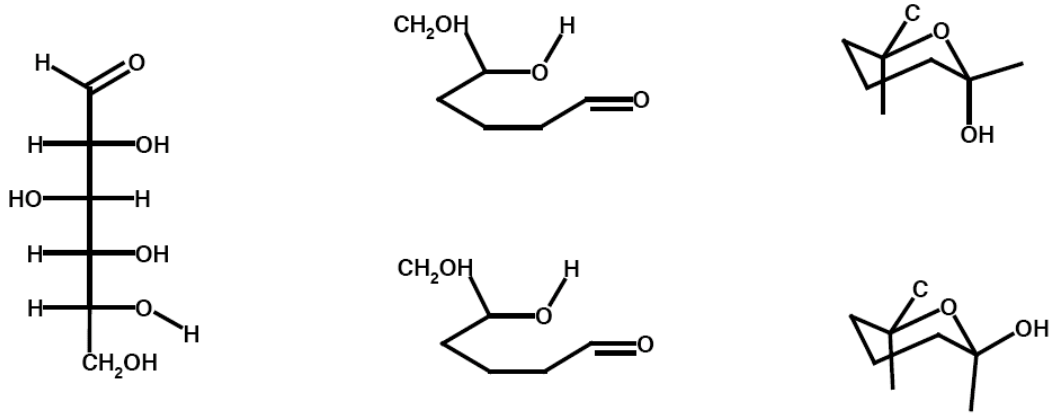
Important Sugars to Remember are:

Aldose	Ketose
Glyceraldehyde (C3) [Important in energy metabolism]	**Fructose** (C6) [Important in metabolism]
Ribose (C5) [Building block of DNA and RNA]	
Glucose (C6) [Energy metabolism and structural elements]	

Cyclization of monosaccharides in solution.
In general, alcohols can attack the C=O group in sugars to form *hemiacetals*. (or hemiketals). Since sugars have OH groups, they can form hemiacetals by an intramolecular reaction, forming closed rings. Only long (>C4) saccharides can form internal hemiacetals, giving closed rings (examples include Ribose, Glucose, Fructose)

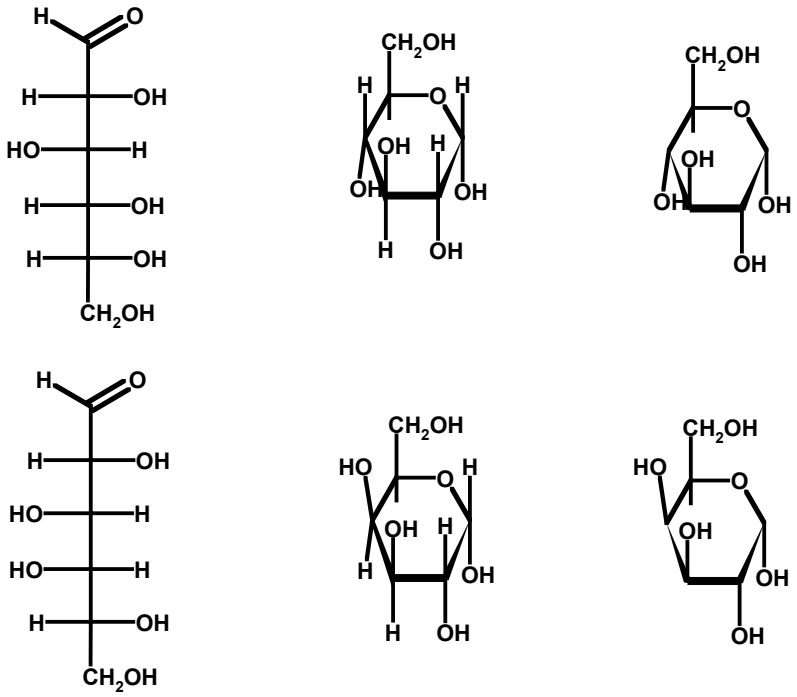
Ring Formation in Glucose

1. Six membered ring created by forming a bond between C1 and O5.
2. This form is called pyranose, *i.e.* glucopyranose after the organic compound, pyran.
3. The C1 carbon becomes chiral and is called the ***anomeric*** carbon
4. The new OH group (on C1) can exist in:
   -form, pointing 'down'.
   -form, pointing 'up'.
   The and forms can readily inter-convert via the linear intermediate.

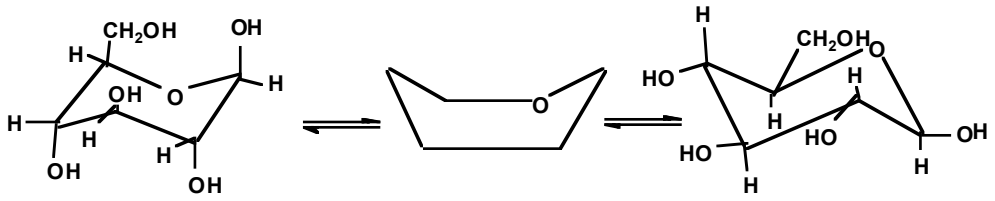


Presentation of structures

1. Fischer drawing - linear chain.
2. Haworth - Ring form, indicating chirality at each center. Both H and OH shown.
3. Reduced Haworth - only OH shown.



Conformational Dynamics of Pyranose Rings:
Monosaccharide rings are not actually planar. The ring can exist in three forms:



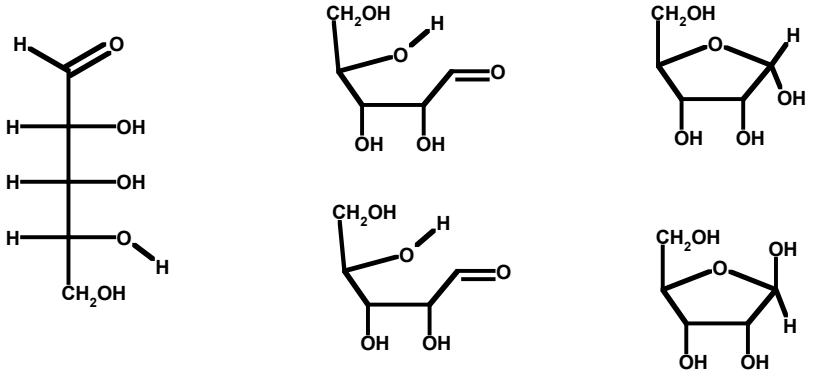
Chair - Form A Boat Chair-Form B

- The boat form is less stable than the chair form. Interchanging between the two chair forms interconverts axial and equatorial groups. Depending on the nature of the groups, one chair form is more stable than the other.
- Note that interconversion between the different chair forms does not affect the configuration of the anomeric carbon (although it may appear so).
- In the case of glucose, the chair form on the right presents all of the OH groups as equatorial. This conformation reduces steric crowding and provides ready access to the OH groups. This may explain, in part, why glucose is one of the more common C6 sugars.

C5 Aldose: Ribose

1. Formation of a 5 membered ring can occur by forming a bond between C1 and O4.

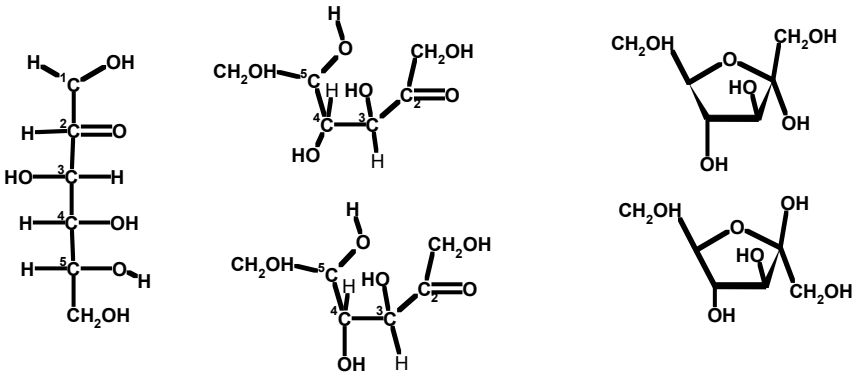
2. Because the ring is small, these sugars exist in 'twist' and envelope' conformations, instead of 'boat' and 'chair'.



C6 Ketose: Fructose

This is called a furanose (*i.e.* fructo-furanose) after the organic compound, furan.

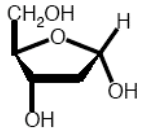
Although this is a 6-carbon sugar, it is a ketose, making the ring size five.



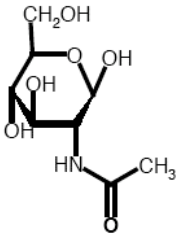
Modified Sugars:

1. Deoxy-sugars: loss of the 2'-OH group: *e.g.*DNA versus RNA

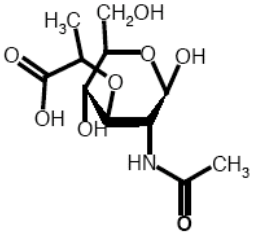
2. Amino-sugars:
- D-glucosamine
- N-acetyl glucosamine (NAG, found in cartilage and yeast cell walls)
- N-acetylmuramic acid (NAM, found in bacterial cell walls



2' Deoxyribose



N-acetyl glucosamine (NAG)

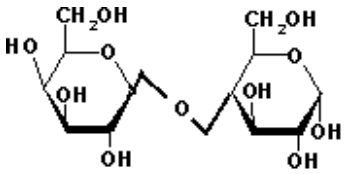


N-acetylmuramic acid (NAM)

Disaccharides

Linkage of the anomeric carbon of one monosaccharide to the OH of another monosaccharide via a *condensation* reaction. The bond is termed a ***glycosidic bond.***

Nomenclature: The Six Simple Rules for Naming Disaccharides are as follows:



1. Type of atom involved in linkage (oxygen or nitrogen)
2. Configuration of the anomeric hydroxyl of the 1st sugar (α or β)
3. Name of 1st monosaccharide, root name followed by pyrano**syl** (6-ring) or furano**syl** (5-ring)
4. Atoms that are linked together, 1st sugar then 2nd sugar.
5. Configuration of the anomeric hydroxyl of the second sugar (α or β) (often omitted)
6. Name of 2nd monosaccharide, root name followed by pyran**ose** (6-ring) or furan**os**e (5-ring)

_____ ____ _____ _____ _____ _____

1 2 3 4 5 6

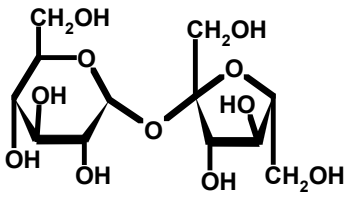
Lactose: β (1-4) linkage between galactose and glucose:

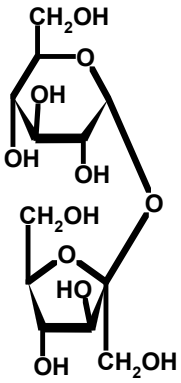
O-β-galactopyranosyl-(1-4)-β-glucopyranose

The anomeric carbon of galactose is bonded to O4 of glucose.

Lactose is the major sugar in mammalian milk.

- Infants produce lactase to hydrolyze the disaccharide to monosaccharides.
- Some adults have low levels of lactase. This leads to *lactose intolerance*. The ingested lactose is not absorbed in the small intestine, but instead is fermented by bacteria in the large intestine, producing uncomfortable volumes of CO_2.





Sucrose: O-α-glucopyranosyl-(1-2)-fructofuranoside (a.k.a. table sugar).
The anomeric carbon of glucose forms a bridge to the anomeric carbon of fructose.