

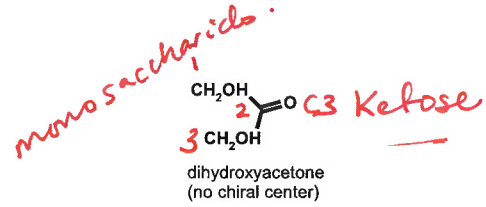
# Lecture 23 – Carbohydrates I.

## Goals

- Distinguish between aldose & ketose.
- Number the carbons in a monosaccharide
- Explain ring formation
- Identify the anomeric carbon
- Correctly name cyclic sugars

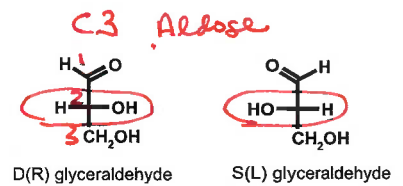
## Carbohydrates are:

1. The primary energy reservoir in biosphere.
2. Biosynthetic precursors to amino acids and nucleic acids.
3. Targeting of proteins for trafficking within the cell.
4. Structural and mechanical components.
  - Cell walls in plants & bacteria



## Structural Hierarchy:

1. Monosaccharides: cannot be hydrolyzed to simpler sugars (= amino acid)
2. Oligosaccharides: 'a few' covalently linked monosaccharides (= peptide)
3. Polysaccharides: 'many' covalently linked monosaccharides (= protein)



## Proteins versus carbohydrates:

20 Amino Acids	>>20 monosaccharides
Unique linkage (peptide bond)	Multiple ways to link
Linear chains	Branched chains
Few chiral centers/residue	Many chiral centers

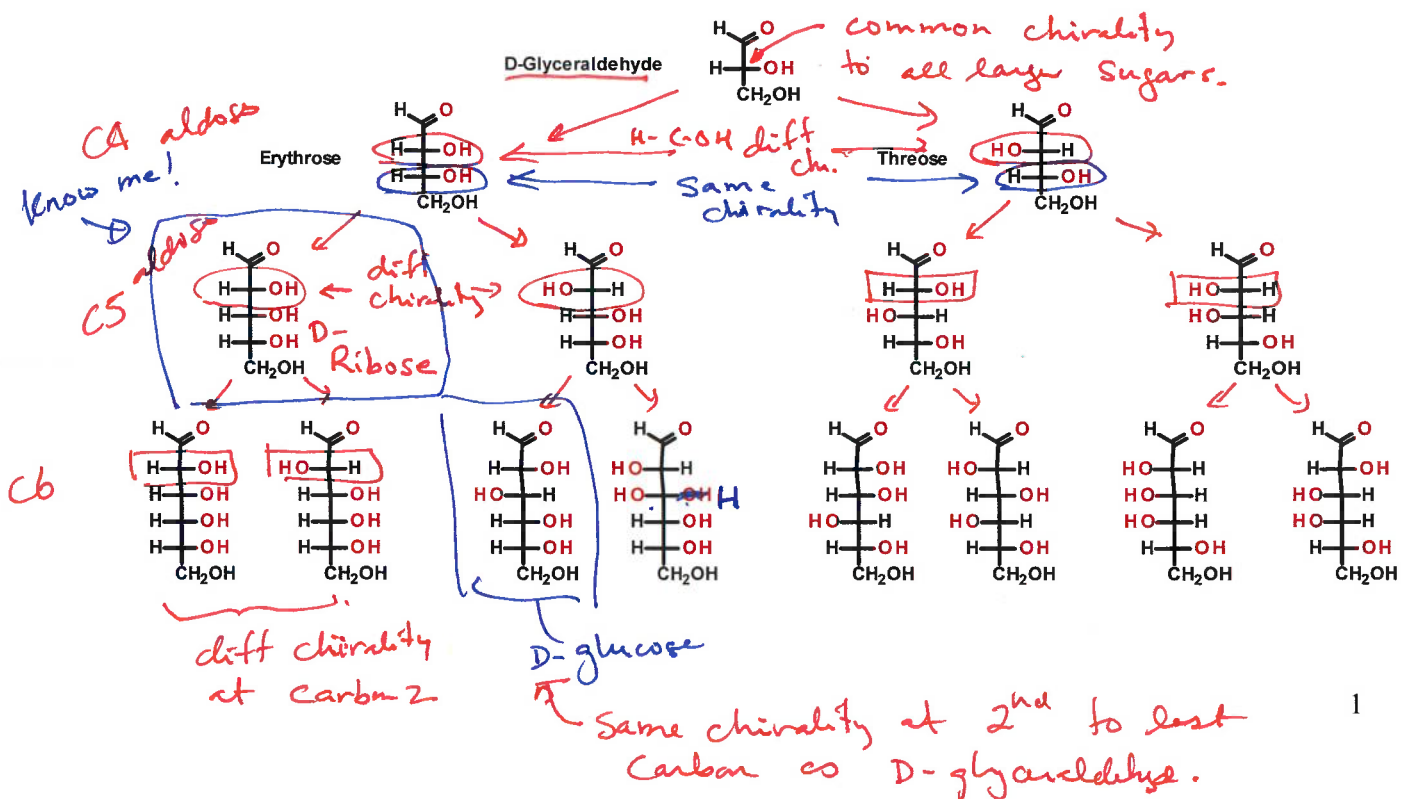
**Monosaccharides:** All carbons in monosaccharides are 'hydrated' -hence the name *carbohydrate* (general formula  $(CH_2O)_N$ )

The simplest monosaccharides contain three carbons:

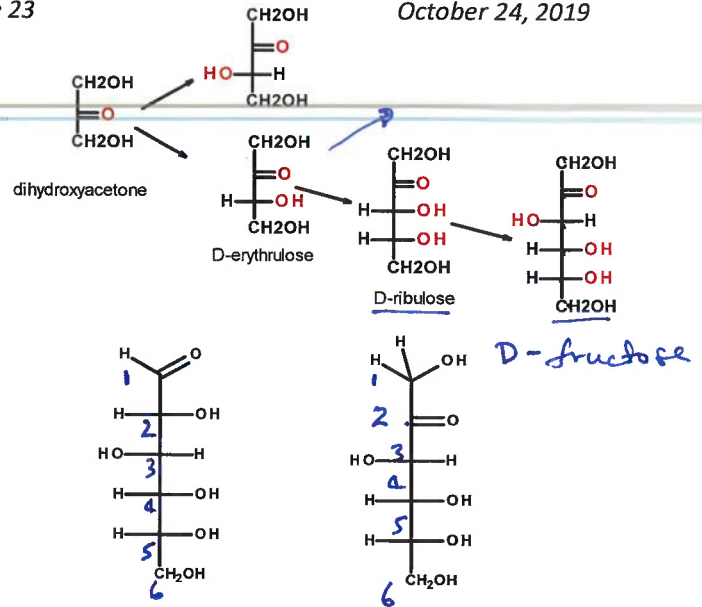
- When the C=O group is at the 2nd position it's called a **ketose**.
- When the C=O group is at the very end it's an **aldose**.

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 is the "root" compound for all other naturally occurring aldoses, this is why all natural sugars are "D", e.g. D-glucose.

**Aldose Series:** Additional hydrated carbons (HO-C-H) are added just below the aldehyde 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 they differ in only *one* chiral center. For example, erythrose and threose are epimers.



**Ketose Series:** These are formed in the same way, the addition of a hydrated carbon below the keto group, with each addition forming a new chiral center.



**Carbon numbering:** Begin at the end closest to the C=O group.

- Aldoses – C1 is the aldehyde carbon
- Ketoses – C2 is the ketone carbon

**Important sugars to remember:**

- Glyceraldehyde (C3 aldose) - metabolism
- Ribose (C5 aldose) DNA & RNA
- Glucose (C6 aldose) - met
- Fructose (C6 ketose) - met.

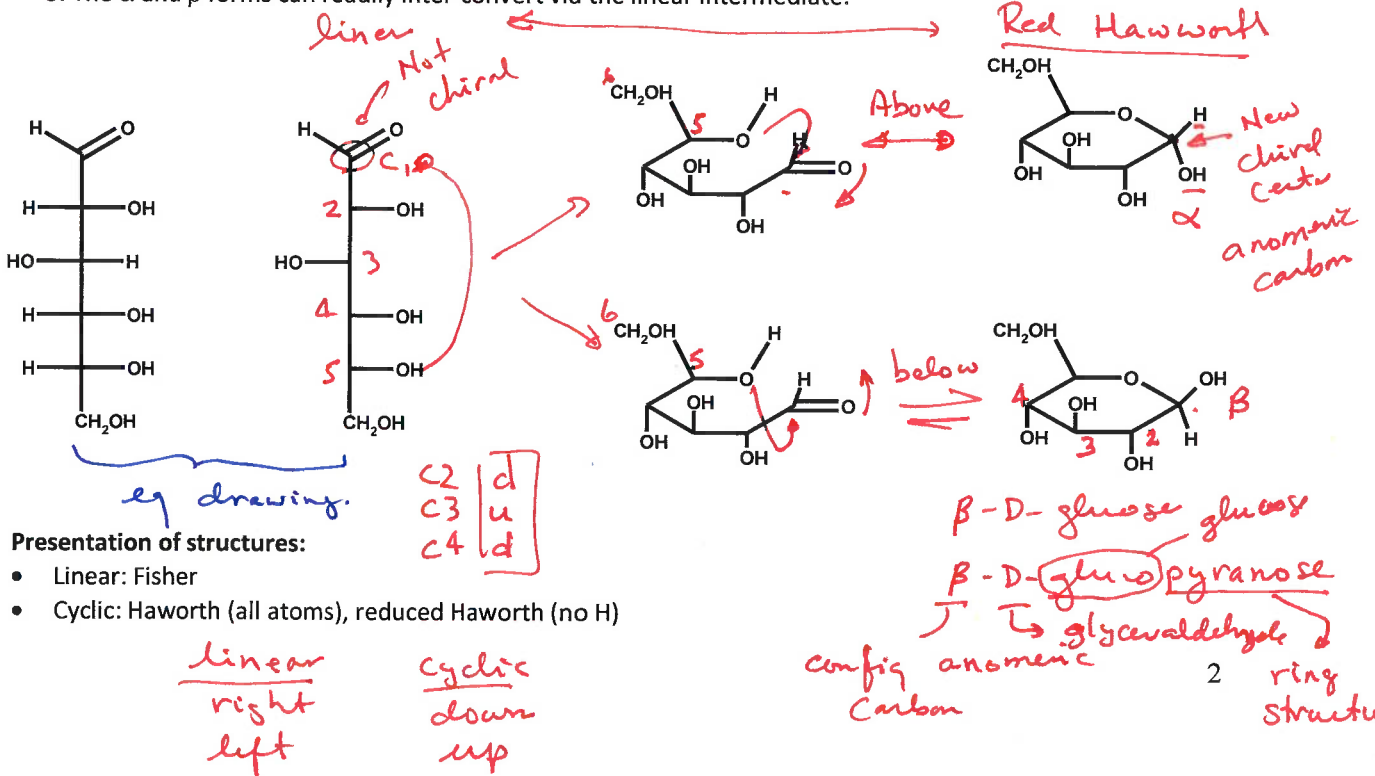
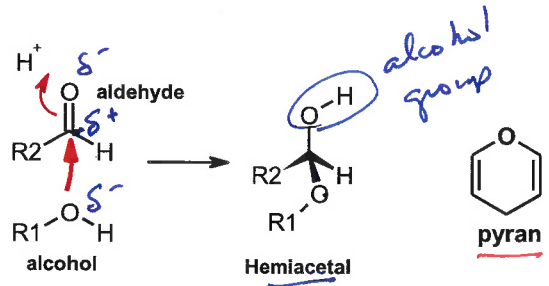
**Ring formation:**

In general, alcohols can attack the C=O group in sugars to form *hemiacetals*. 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 (Includes ribose, glucose, fructose). **No atoms are lost or gained in this reaction!**

**Ring Formation in Glucose**

1. Six membered ring created by forming a bond between C1 and O5 (most stable ring size).
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 either the  $\alpha$  or  $\beta$  form.
5. The  $\alpha$  and  $\beta$  forms can readily inter-convert via the linear intermediate.



**Presentation of structures:**

- Linear: Fisher
- Cyclic: Haworth (all atoms), reduced Haworth (no H)

linear  
right  
left

cyclic  
down  
up

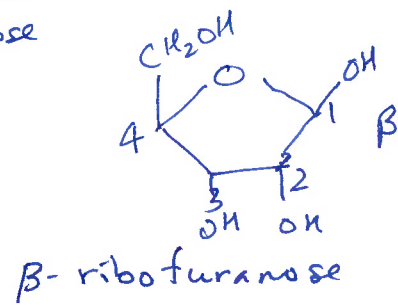
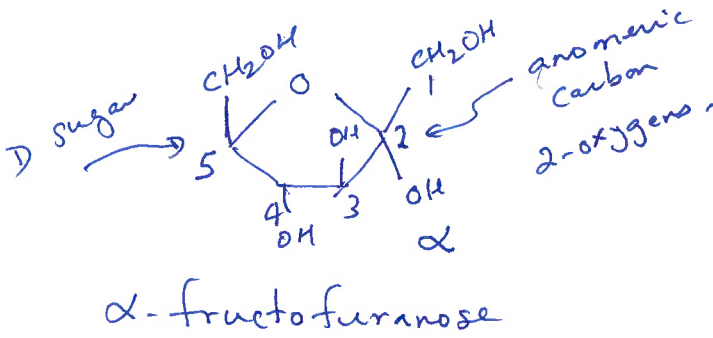
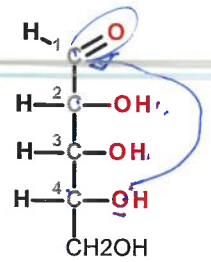
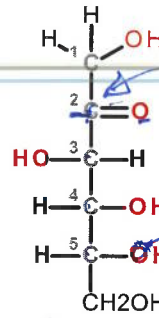
$\beta$ -D-glucose glucos  
 $\beta$ -D-glucopyranose  
glyceraldehyde  
config anomeric carbon  
2 ring structure

**Carbohydrate Worksheet.**

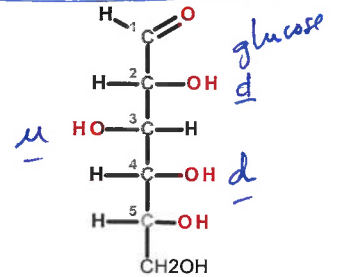
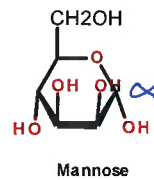
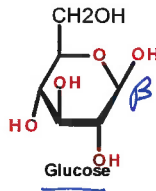
1. Draw the cyclic form of fructose and ribose.

Hints:

- i) the 2<sup>nd</sup> to last carbon attacks the C=O.
- ii) Draw the ring first, and then add the -OH groups with the correct stereochemistry.



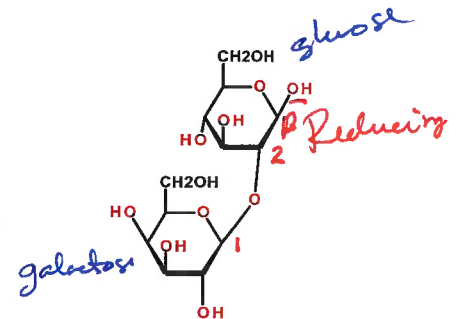
- 2.i) Identify the configuration of the anomeric carbon on both sugars.
- ii) Which one corresponds to the linear sugar on the far right?



3. Name the following disaccharide (one monosaccharide is glucose, the other is galactose).

The six simple rules for naming disaccharides are:

1. The **non-reducing** end defines the first sugar.
2. Configuration of the anomeric carbon of the 1<sup>st</sup> sugar ( $\alpha, \beta$ )
3. Name of 1<sup>st</sup> monosaccharide, root name followed by **pyranosyl** (6-ring) or **furanosyl** (5-ring)
4. Atoms which are linked together, 1st sugar then 2nd sugar.
5. Configuration of the anomeric carbon of the second sugar ( $\alpha, \beta$ ) (omitted if the anomeric carbon is free since  $\alpha$  &  $\beta$  forms are in equilibrium.)
6. Name of 2<sup>nd</sup> monosaccharide, root name followed by **pyranose** (6-ring) or **furanose** (5-ring) (If **both** anomeric carbons are linked, then the name ends in 'oside', not 'ose')



$\beta$  galactopyranosyl (1-2)  $\beta$  glucopyranose

4. What is wrong with this disaccharide?

No anomeric carbon used for bond formation.

