CARBOHYDRATES

Carbohydrates are a biomolecule consisting of carbon (C), hydrogen (H) and oxygen (O) atoms ,These are compounds of tremendous biological importance .Carbohydrates are based upon the general formula $C_n(H_2O)_n$ .As if they were hydrates of carbon (most abundant organic molecules in our biosphere)n

Functions of Carbohydrates :

1- Energy source (glucose).

2- Energy storage (glycogen, starch) .

3- Carbon source (pyruvate used to make Ile, Leu, Val, Ala).

4- They form part of the structures of some cells and tissues.

5- Can be **attached** to other **macromolecules** (glycoprotein and glycolipids).

Classes of carbohydrates :

1- Monosaccharide (simple sugars like glucose)

2- Disaccharides (sucrose)

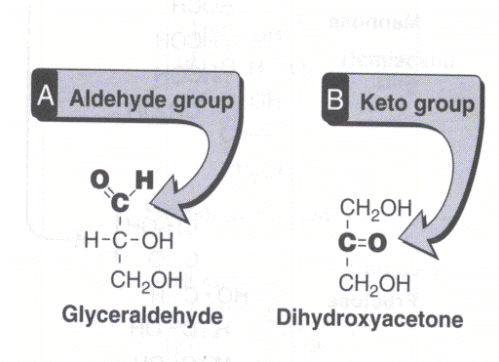
3- polysaccharides (oligosaccharides) (starch, cellulose, glycogen) long chains of monosaccharide; are the simplest of the carbohydrates, since they contain only one polyhydroxy aldehyde or ketone unit. chains of monosaccharide bridged through oxygen atoms can be thousands long and can be branched.

One H_2O is eliminated when sugars are linked together to form disaccharides or higher polymers . Common monosaccharide contain from 3 to 6 carbon atoms these sugars are called trioses, tetroses, pentoses, hexoses . **Monosaccharide** are either **aldehydes** or **ketones,** aldoses or ketoses

– glyceraldehyde is an aldotriose

– glucose is an aldohexose

– fructose is a ketohexose

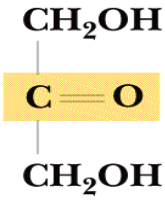


• For Aldoses and Ketoses – the name is based on the location of the carbonyl (C = O)

• The simplest **KETOSE** is **DIHYDROXYACETONE**

- Contains a **KETONE.**

- Does **NOT** contain a **chiral** center .



Dihydroxy-acetone

• The simplest **ALDOSE** is **GLYCERALDEHYDE**

- Contains an **ALDEHYDE**

- Contains a **CHIRAL** center: Carbon with 4 different groups bonded to it.

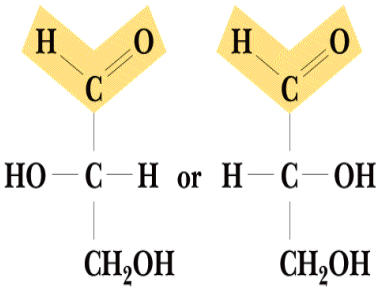
Isomer of carbohydrate :

• **Isomers :** same chemical formula, different structure.

• **Epimers :** isomers that differ at only one Carbon.

• **Enantiomers:** isomers that are mirror images (D and L).

• **Anomers :** isomers that differ only at keto-/aldo carbon.



L-isomer D-isomer

Glyceraldehyde

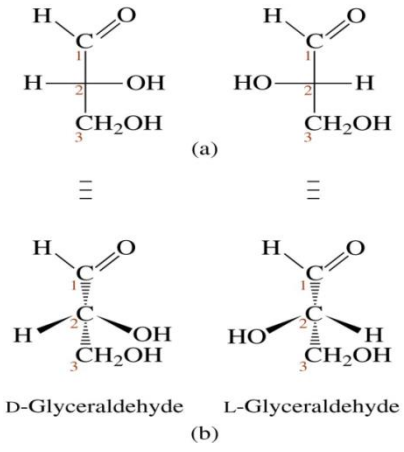
• These are the **Fischer Projections** for the two isomers of glyceraldehydes: Tell us stereochemistry.

Rules: -

1- Carbons are numbered from the top.

2- Last carbon will always be part of a CH_2OH group **(Not CHIRAL).**

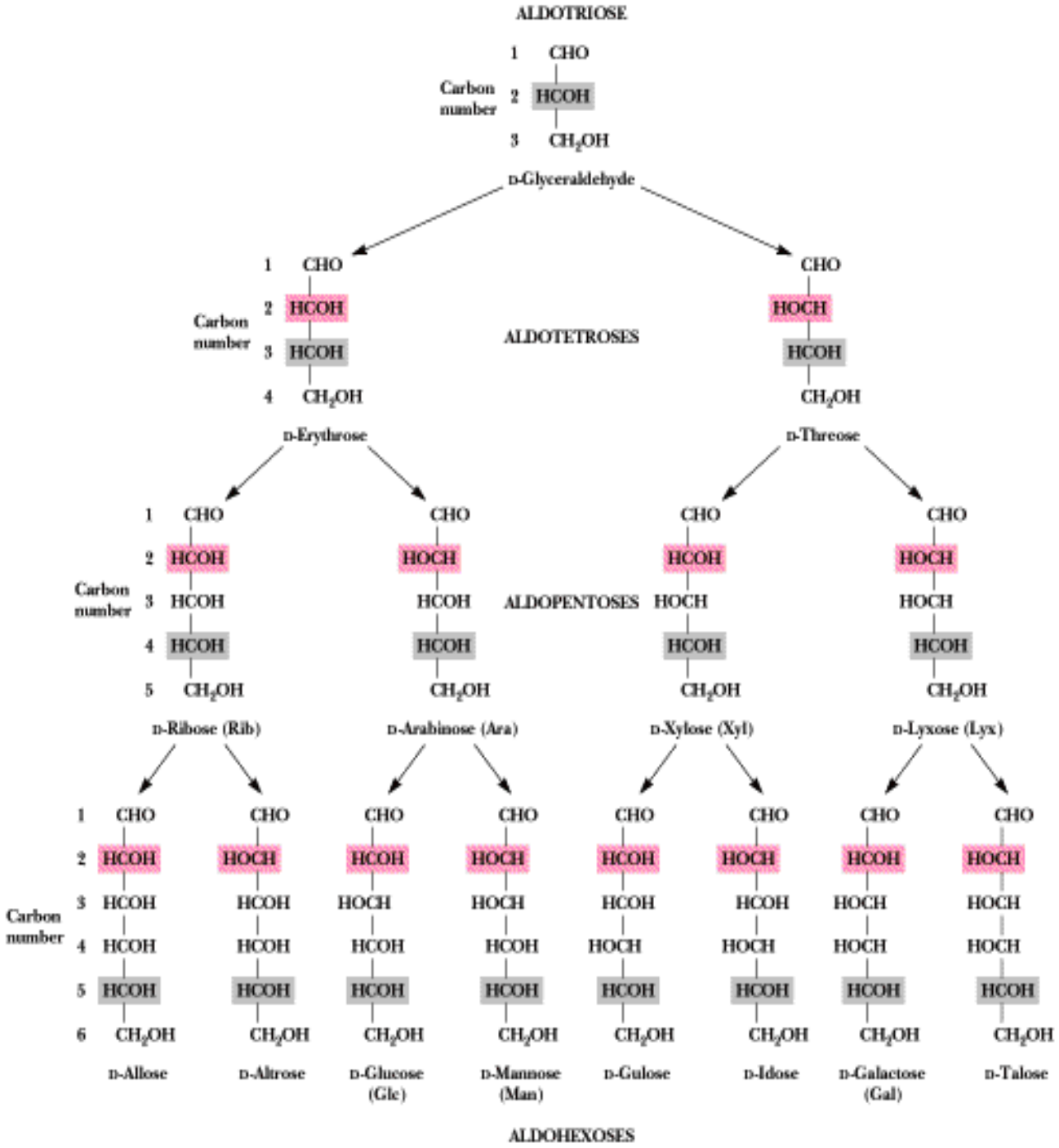
- Stereochemistry of the last CHIRAL carbon determines the stereochemistry of the sugar.



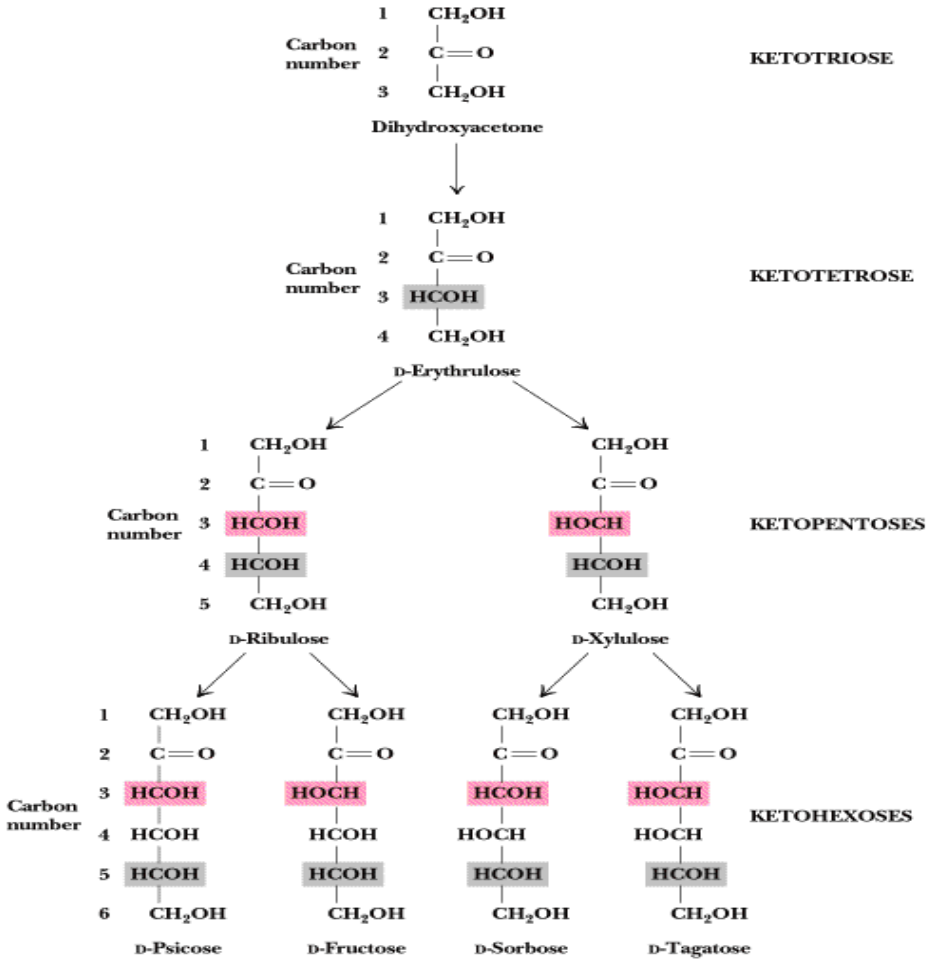
D-Glyceraldehyde L-Glyceraldehyde

(b)

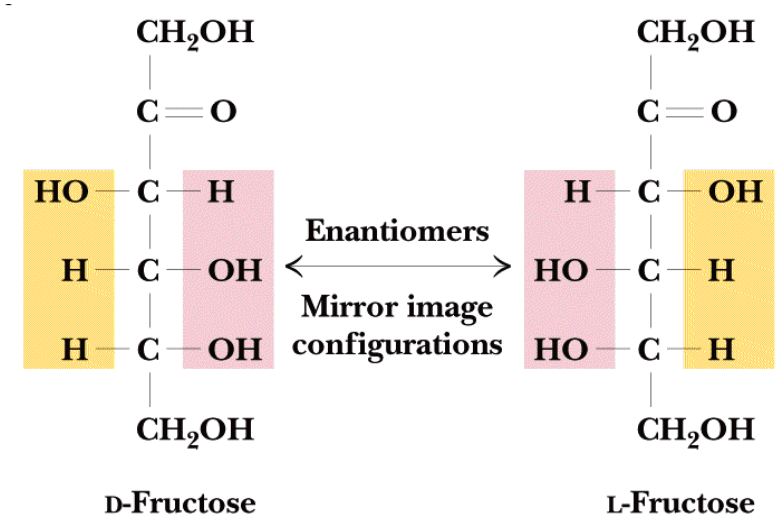
- **If –OH is to the RIGHT → D-isomer**
- **If –OH is to the LEFT → L-isomer**



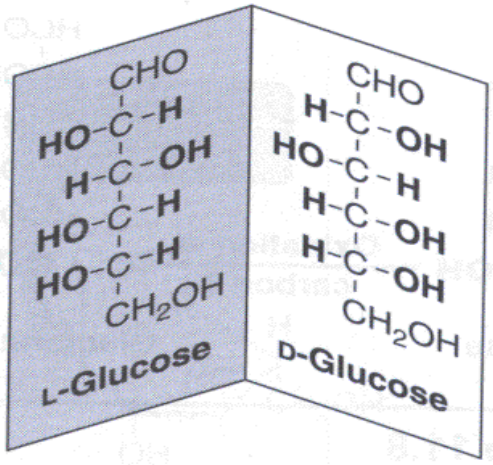
Same rules apply for **KETOSES**:



Enantiomers = isomers that are mirror images (D and L).



Enantionmers of Fructose: Note, in enantionmers the positions of ALL –OH change, not just the 2nd to last



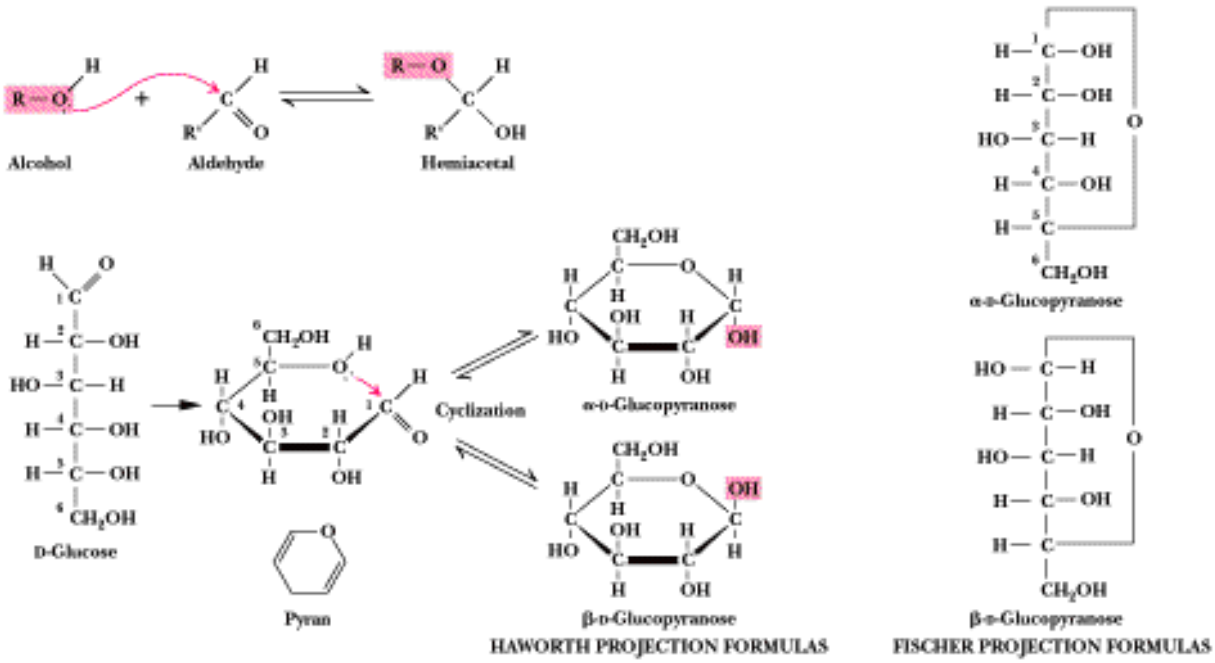
CYCLIZATION OF MONOSACCHARIDES

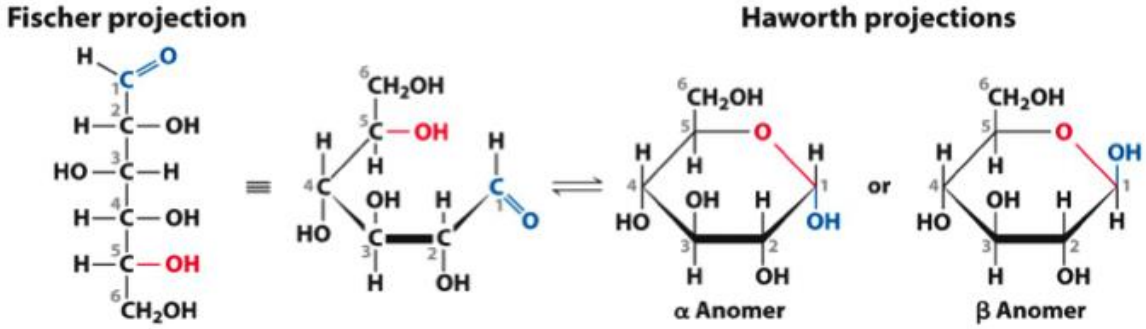
In solution, monosaccharides are cyclic especially C5 and C6 sugars.

TWO CASES OF CYCLIZATION:

1- **HEMIACETALS**:

Carbonyl reacting with hydroxyl group addition product called hemiacetal.





In this example, C1 carbonyl group (aldehyde) interacts with alcohol on C5 to form a six ring, with C6 above the ring structure.

- Reaction called an **ALDOL CONDENSATION.**
- Form a 5 or 6 ring.
- The C1 carbonyl carbon becomes a new chiral center – a new C1 hydroxyl.
- **New C1 hydroxyl = anomeric carbon.**

• The carbonyl carbon in the straight chain form Carbon bonded to both the ring oxygen and a hydroxyl group in the cyclic form.

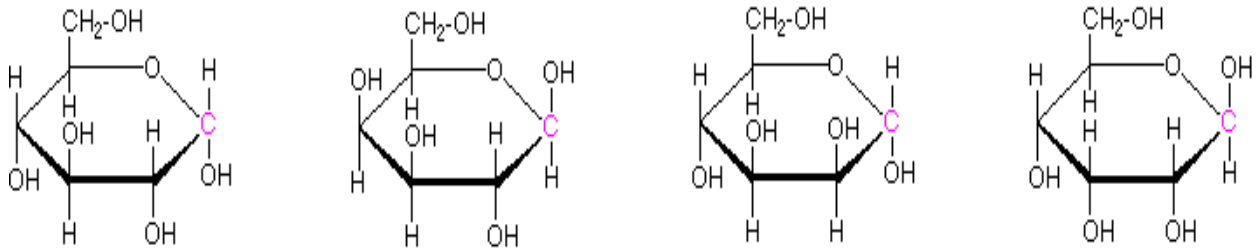
Hydroxyl group is either above or below the ring – **two forms α (alpha) and β (beta).**

• **α-anomer**: hydroxyl group **BELOW** ring (down)

• **β-anomer**: hydroxyl group **ABOVE** ring (up)

- **If –OH is on the right → points DOWN in Haworth**
- **If –OH is on the left → points UP in Haworth**

Examples of Some Pyranose Forms of Hexoses

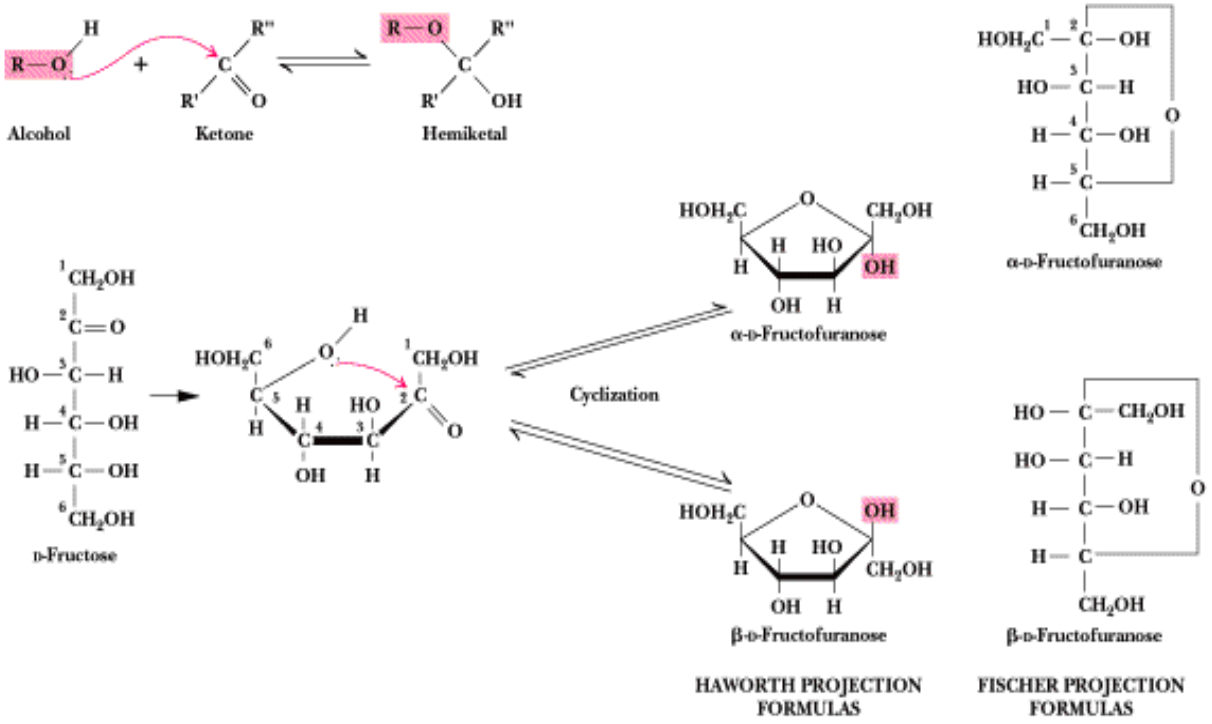


α-D-glucopyranose | β-D-galactopyranose | α-D-mannopyranose | β-D-allopyranose

2. HEMIKETALS:

functional group includes a carbon center with 2 R-groups, an –OH and OR group. Formed when C5 hydroxyl interacts with C2 carbonyl of a ketose.

Example: **D-fructose cyclization:**



- Lone pair of electrons on –OH at position C5 attacks carbonyl at C2 forming the ring.
- **Anomeric carbon is C2.**
- Hemiketals also have α **and** β **anomers.**
- Depends on stereochemistry of –OH at **C2.**
  - **Down = alpha.**
  - **Up = beta.**

MUTAROTATION

Mutarotation = inter conversion between the α and β anomers

[Almost all monosaccharide in solution are in cyclized form]