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Biochemistry

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Isomers and Epimers

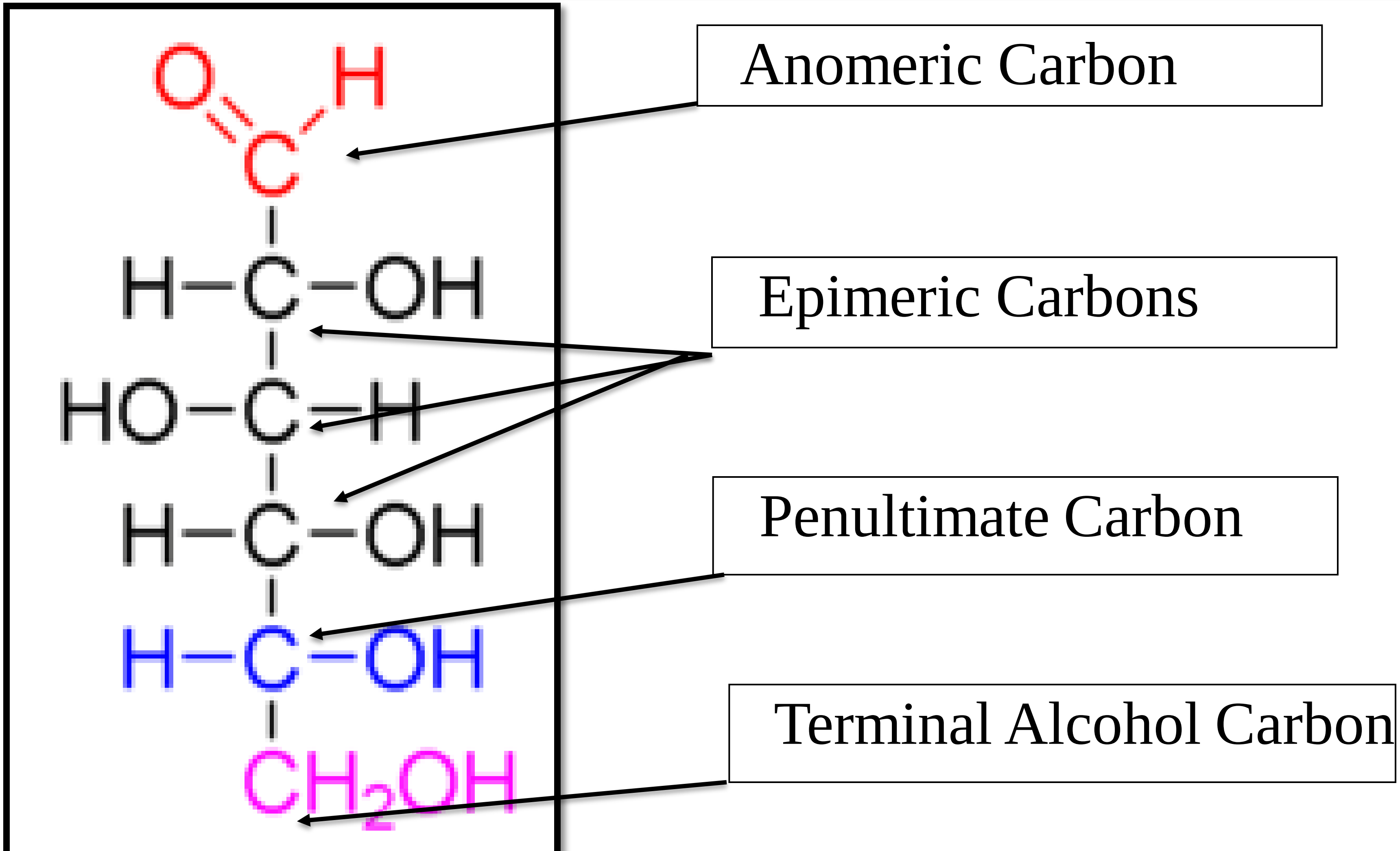
Epimers:

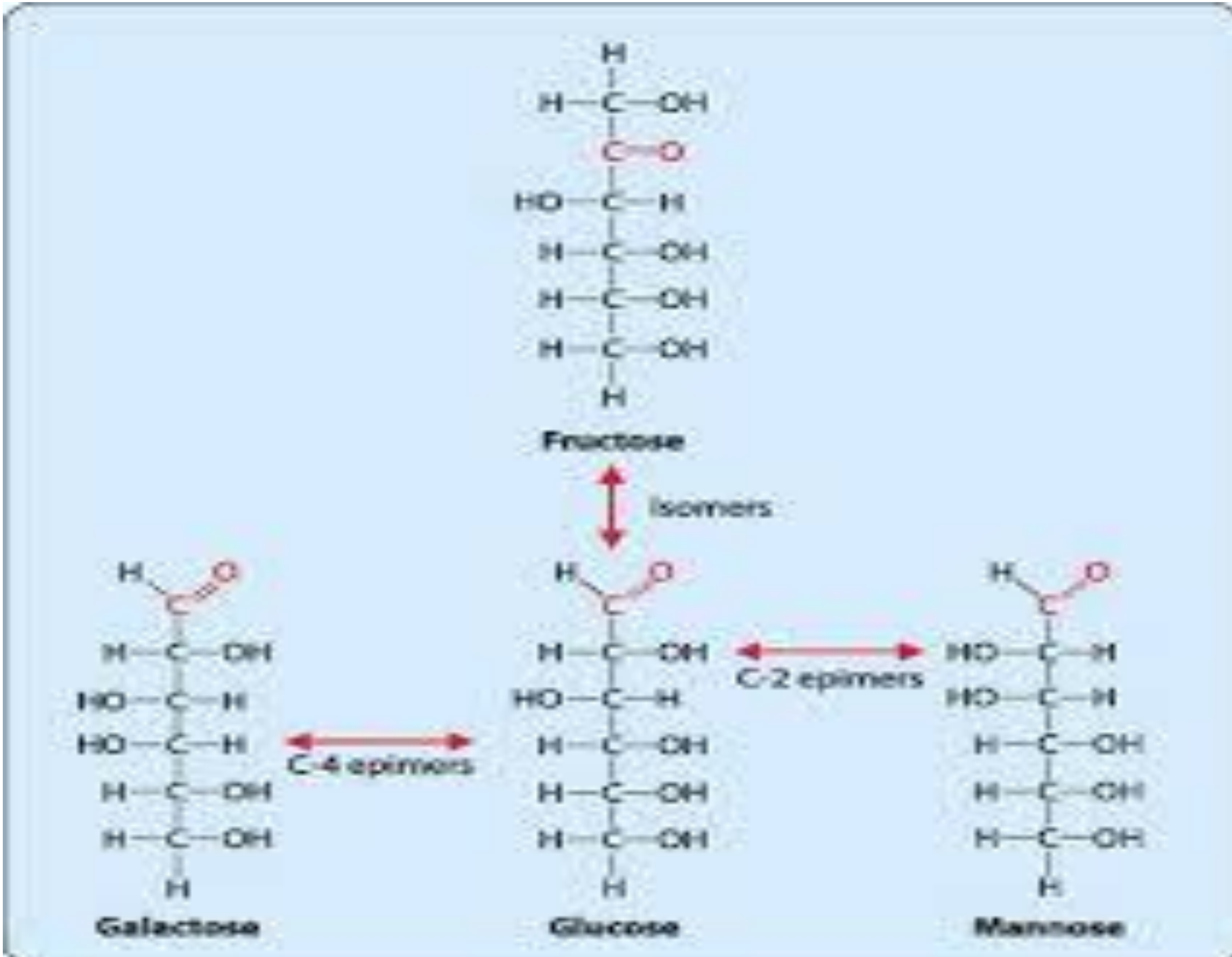
Carbohydrate isomers that differ in configuration around only one specific carbon atom (with the exception of the carbonyl carbon) are defined as epimers of each other. Example:

Glucose and galactose are C-4 epimers (their structures differ only in the position of the –OH group at carbon 4).

Glucose and mannose are C-2 epimers.

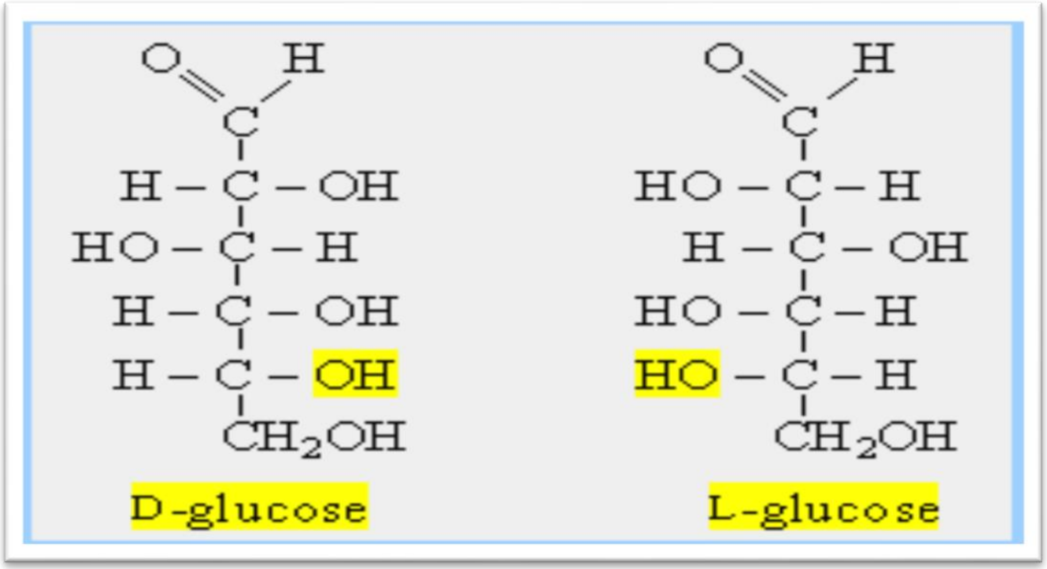
Straight Chain Structure of Typical Monosaccharide (Glucose)

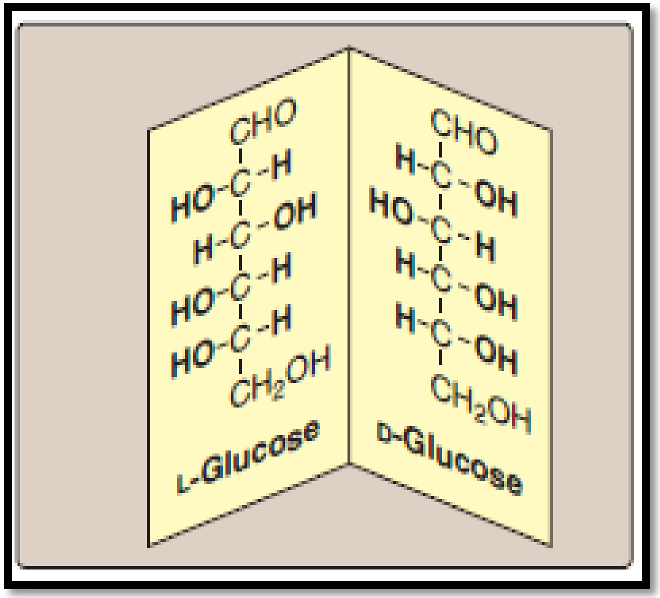



Fructose
Isomers
C-2 epimers
C-4 epimers
Galactose
Glucose
Mannose

Enantiomers

- A special type of isomerism is found in the pairs of structures that are mirror images of each other.
- These mirror images are called enantiomers, and the two members of the pair are designated as a D- and an L-sugar .
- The vast majority of the sugars in humans are D-sugars.
- In the **D isomeric** form, the –OH group on the asymmetric carbon (a carbon linked to four different atoms or groups) farthest from the carbonyl carbon is on the **right**, whereas in the **L-isomer** it is on the **left.**



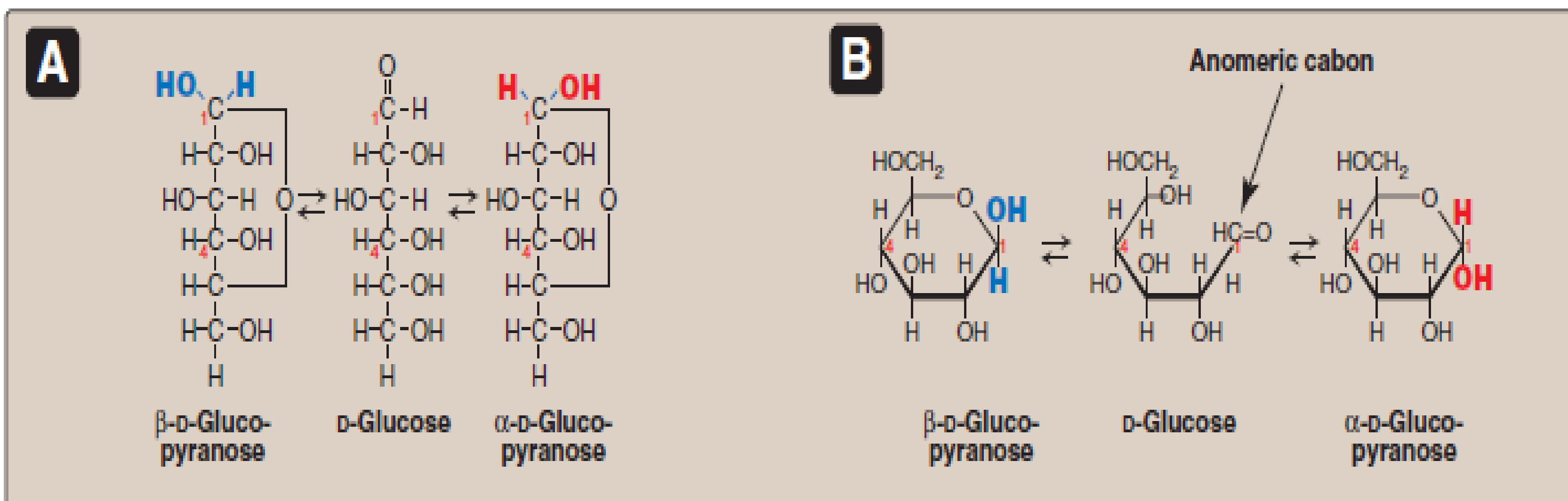


Cyclization of Monosaccharide

- Less than 1% of each of the monosaccharide with five or more carbons exists in the open-chain (acyclic) form.
- Rather, they are predominantly found in a ring (cyclic) form, in which **the aldehyde (or keto) group has reacted with an alcohol group on the same sugar, making the carbonyl carbon (carbon 1 for an aldose or carbon 2 for a ketose) asymmetric.**

<u>Note:</u>

- Pyranose refers to a six-membered ring consisting of five carbons and one oxygen, for example, glucopyranose whereas furanose denotes a five-membered ring with four carbons and one oxygen.



Anomeric carbon: Cyclization creates an anomeric carbon

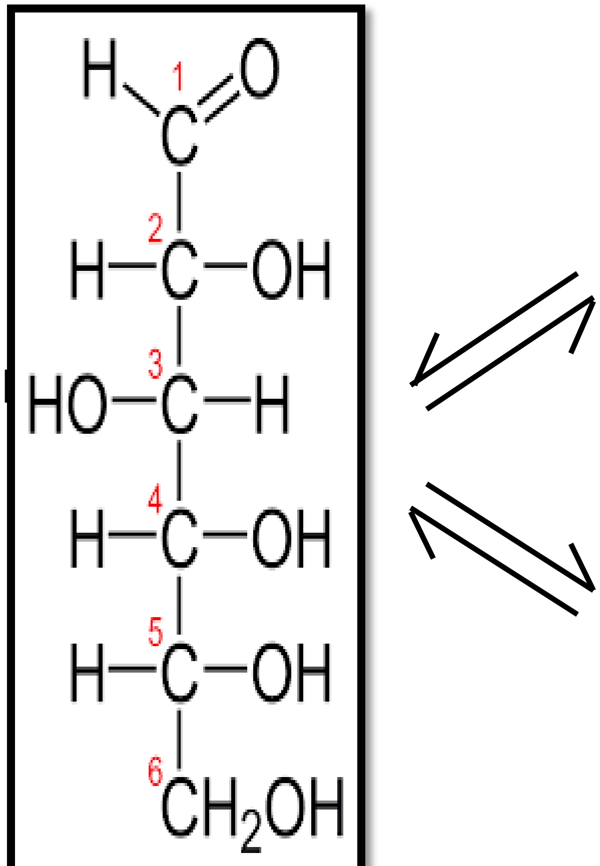
- Anomeric carbon: Cyclization creates an anomeric carbon (the former carbonyl carbon), generating the α and β configurations of the sugar, for example, α-D-glucopyranose and β-D-glucopryanose.
- These two sugars are both glucose but are anomers of each other.

Note:

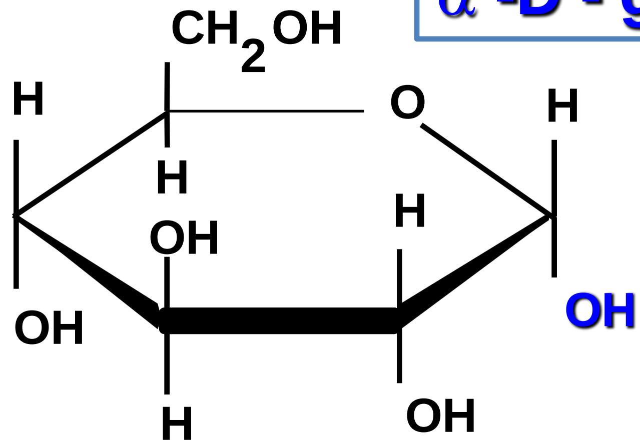
In the α configuration, the OH on the anomeric C projects to the same side as the ring in a modified Fischer projection formula and is trans to the CH2OH group in a Haworth projection formula.

- Enzymes are able to distinguish between these two structures and use one or the other preferentially. For example, glycogen is synthesized from α-D-glucopyranose, whereas cellulose is synthesized from β-D-glucopyranose.
- The cyclic α and β anomers of a sugar in solution are in equilibrium with each other, and can be spontaneously interconverted (a process called mutarotation).

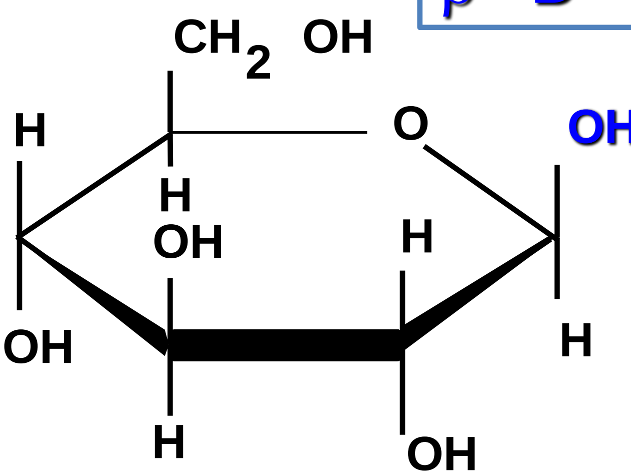
Cyclization of D-glucose
Fischer vs. Haworth projections



α -D - glucose

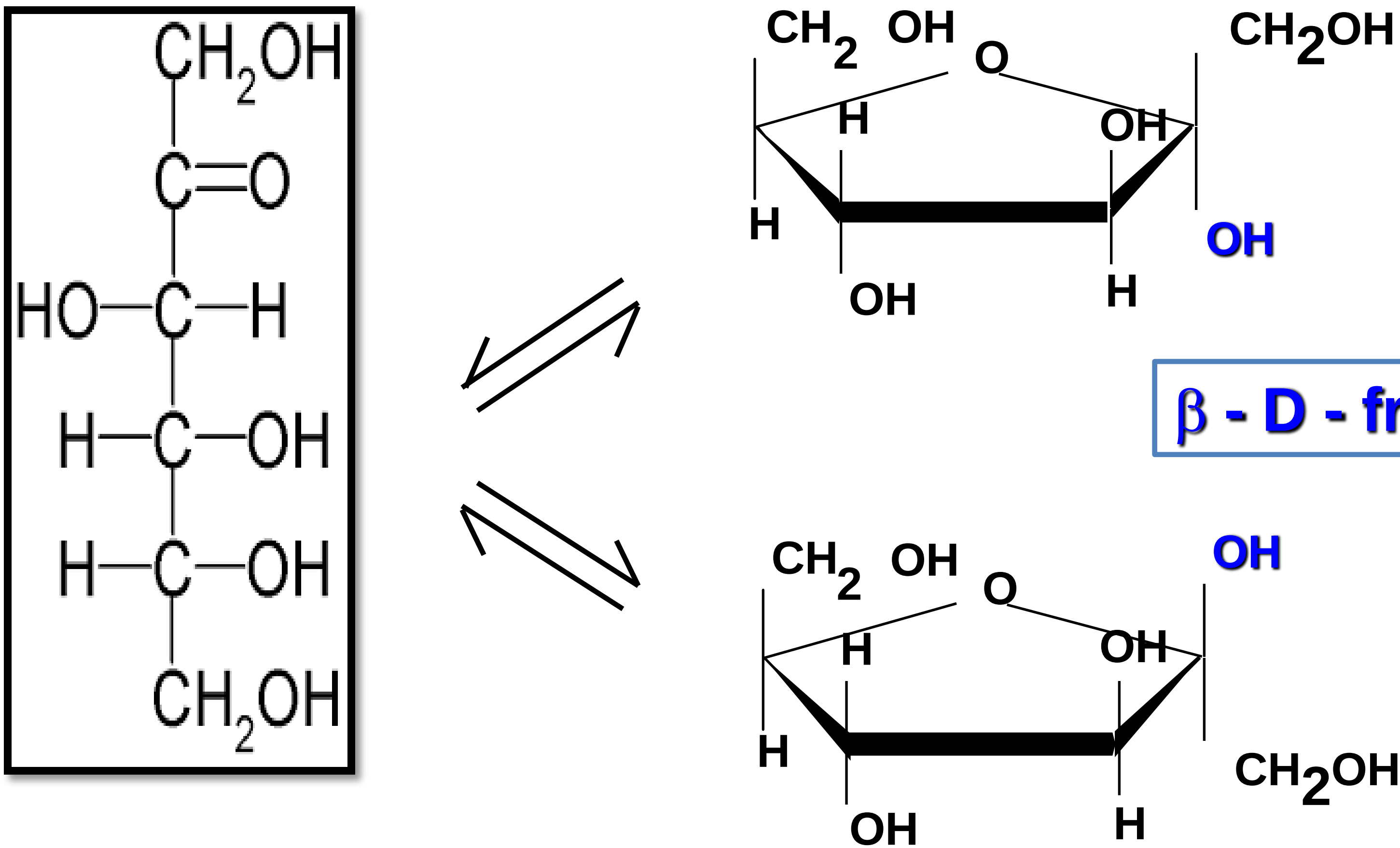


β - D - glucose



Cyclization of D-fructose

α - D - fructose



β - D - fructose

Joining of Monosaccharide

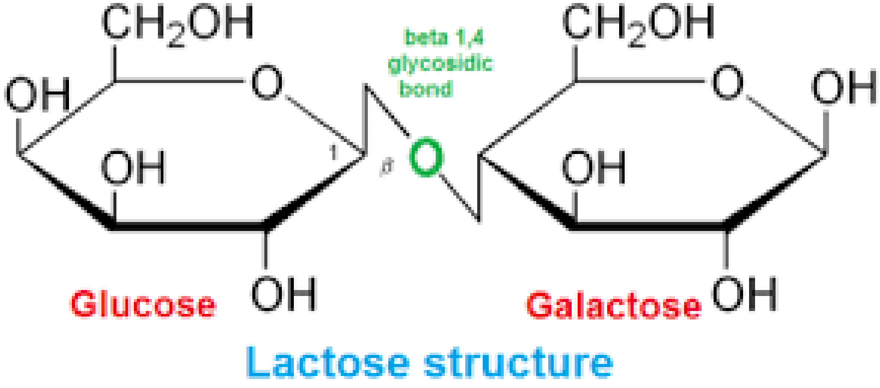
- Monosaccharide can be joined to form disaccharides, oligosaccharides, and polysaccharides.

- The bonds that link sugars are called glycosidic bonds. These are formed by enzymes known as **glycosyl transferase** that use nucleotide sugars such as UDP-glucose as substrates.

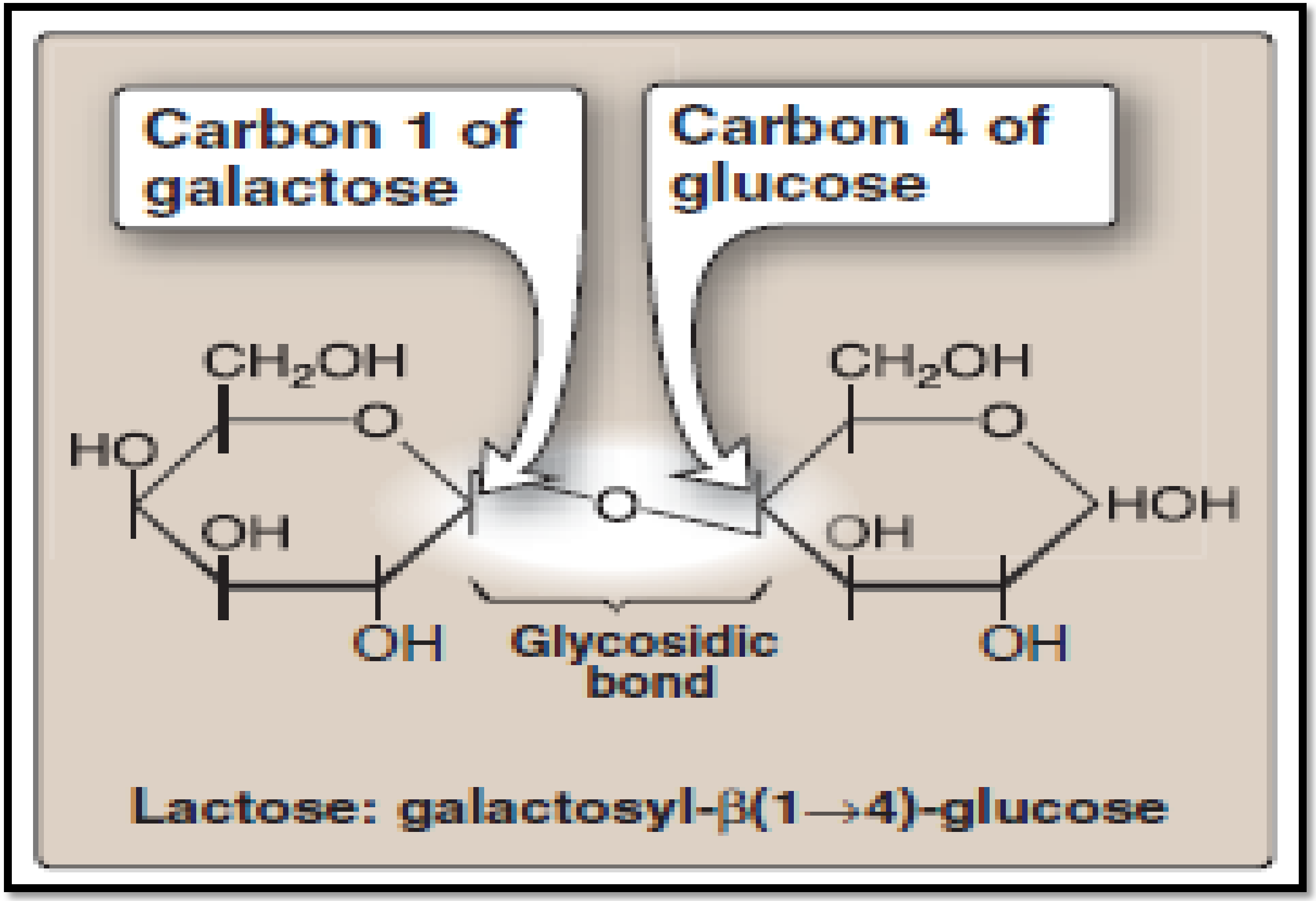
- Naming glycosidic bonds: Glycosidic bonds between sugars are named according to the numbers of the connected carbons, and with regard to the position of the **anomeric hydroxyl group** of the sugar involved in the bond.

- If this anomeric hydroxyl is in the **α configuration**, the linkage is an **α-bond**. If it is in the **β configuration**, the linkage is a **β-bond.**

- Lactose, for example, is synthesized by forming a glycosidic bond between carbon 1 of β-galactose and carbon 4 of glucose. The linkage is, therefore, a β(1→4) glycosidic bond



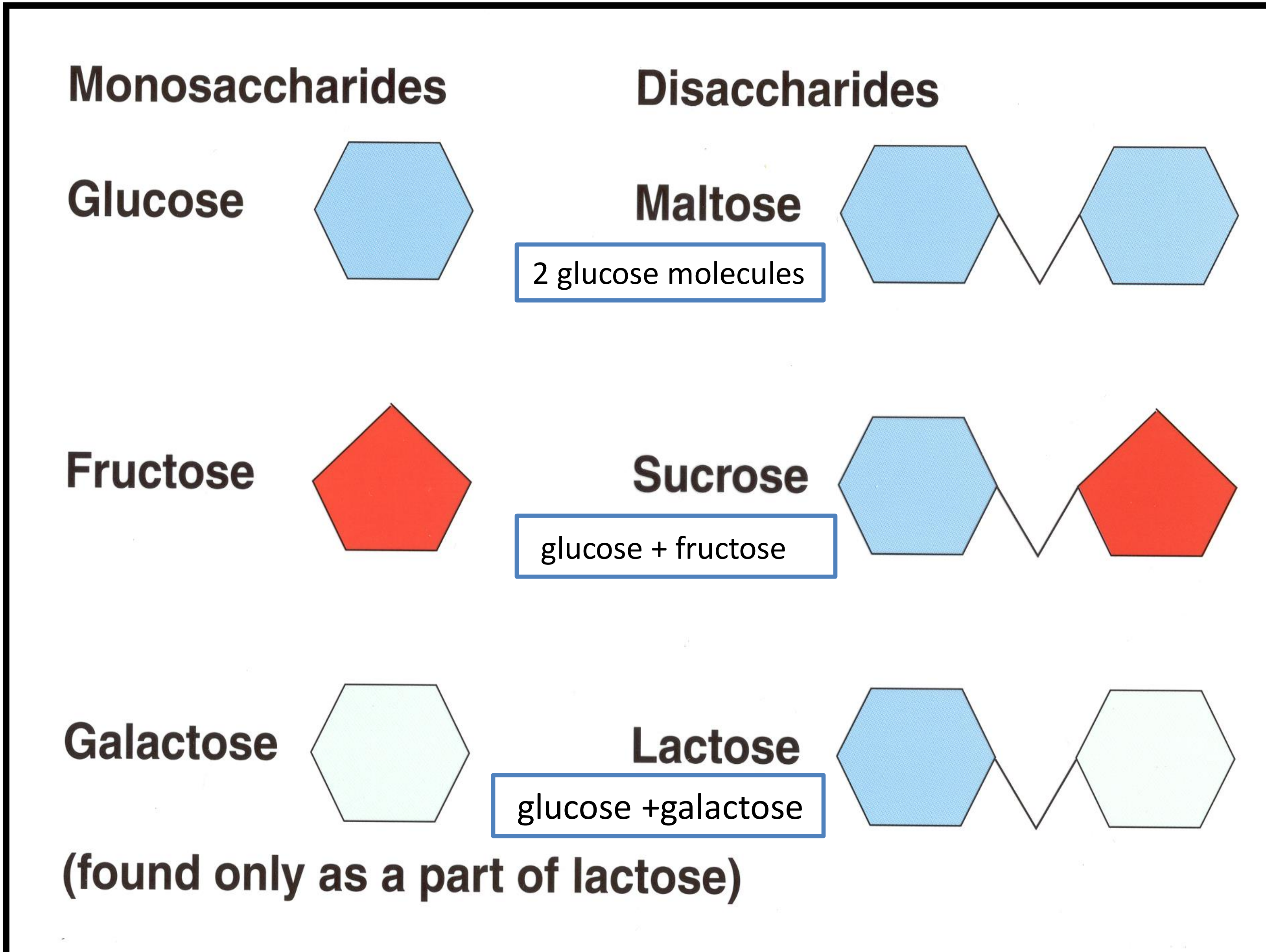
Glycosidic Bonds

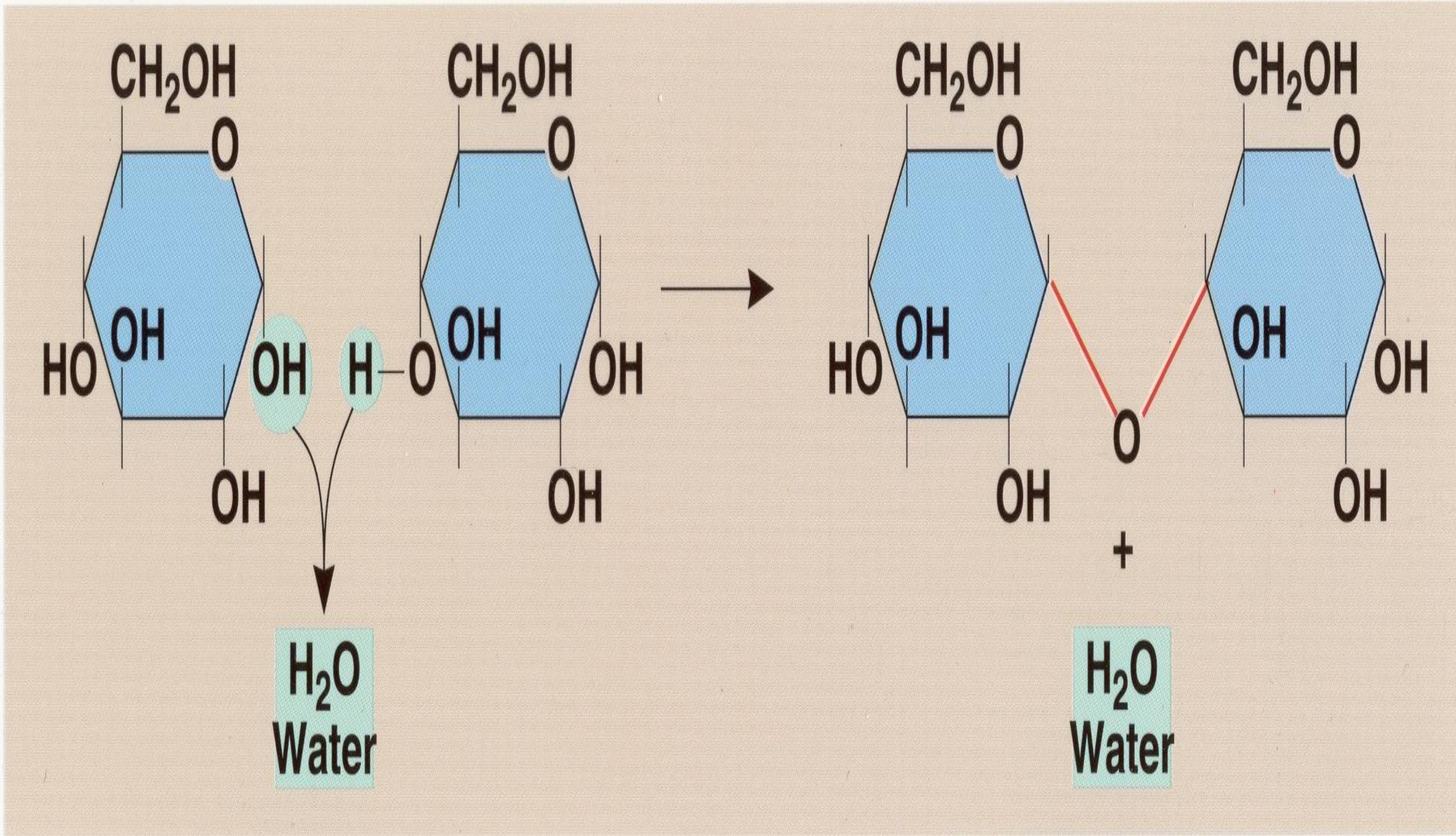


Disaccharides

- Two Joined Monosaccharides, examples:
  - Sucrose: Glucose + Fructose
  - Maltose: Glucose + Glucose
  - Lactose: Glucose + Galactose

The Most Important Disaccharides





Glucose + glucose → Maltose

Oligosaccharides

Composed of:

- Three to ten monosaccharide units.
- E.g. Fructooligosaccharides

Polysaccharides

- Larger than ten monosaccharide units.
- Can reach many thousands of units.
- Examples:
  - Glycogen
  - Starch
  - Fibres (Cellulose)


Thank you