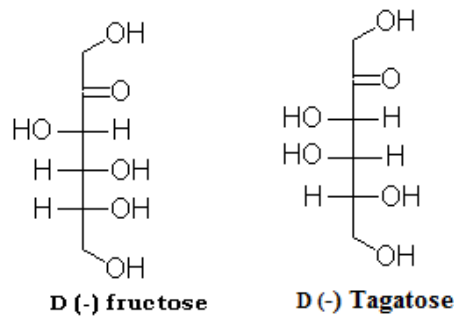


dextrorotatory (+); or to the left, levorotatory (-). The direction of rotation is independent of the stereochemistry of the sugar, so it may be designated D (-), D (+), L (-), or L (+). For example, the naturally occurring form of fructose is the D (-) isomer.



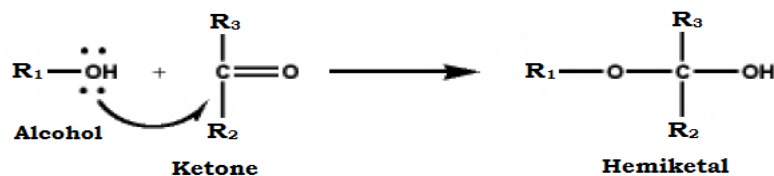
D-Tagatose is an epimer of D-fructose inverted at C-4

(iii) **Alpha and beta anomers**

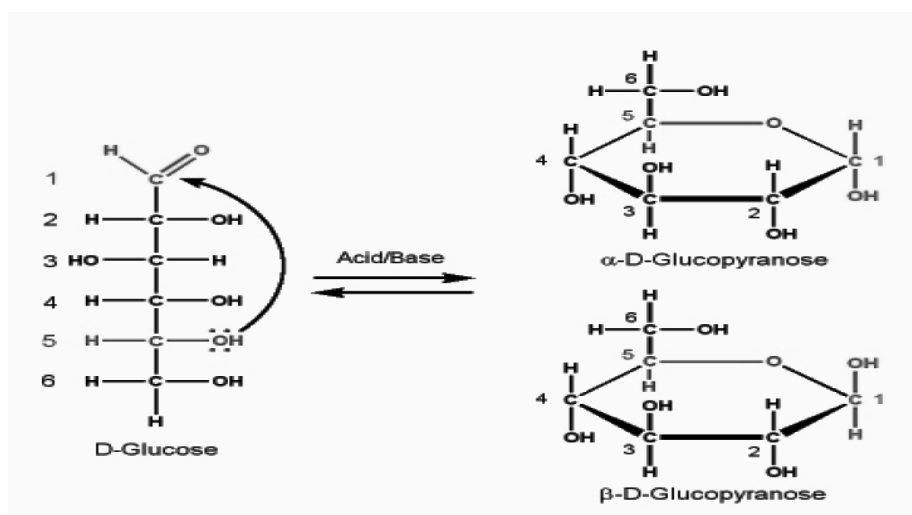
- The anomeric centre of a sugar is a stereocentre created from the intramolecular formation of an acetal (or ketal) of a sugar hydroxyl group and an aldehyde (or ketone) group. The two stereoisomers formed from the two possible stereochemistry at the anomeric centre are called anomers. They are diastereoisomers of one another.
- *Cyclic Structures and Anomeric Forms*
 - Alcohols react readily with **aldehydes** to form **hemiacetals**:
 - ✓ This reaction is promoted in the presence of either acid or base
 - ✓ One of the subtleties of this reaction involves the stereochemistry of the aldehyde and keto carbon it goes from being **achiral** to **ch**:



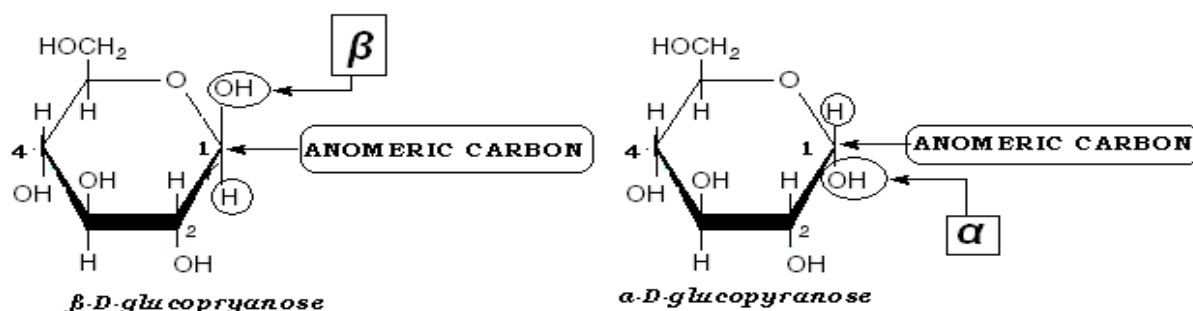
- Similarly alcohols react with **ketones** to produce **hemiketals**:



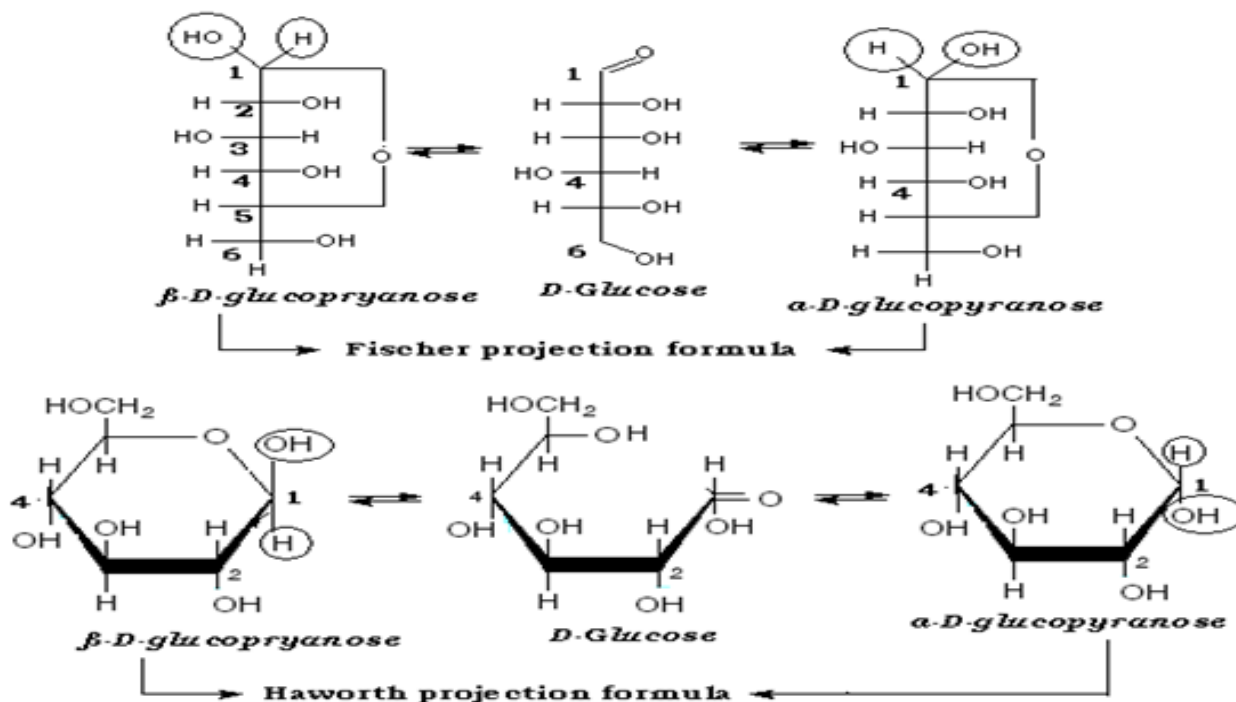
- Since **aldoses** and **ketoses** contain alcohol groups, in addition to their aldehyde or ketone groups, they have the potential to react to form **cyclic forms**.



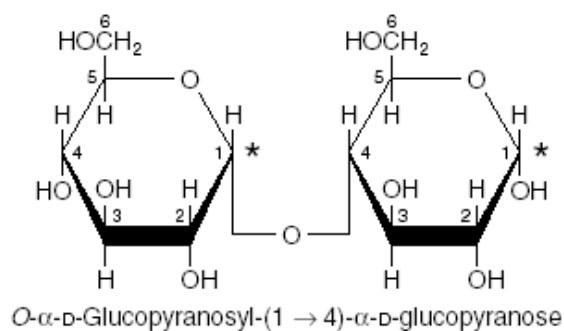
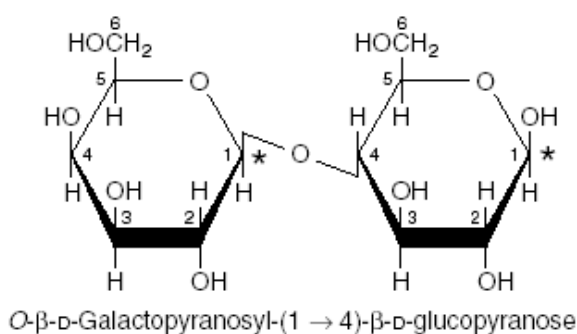
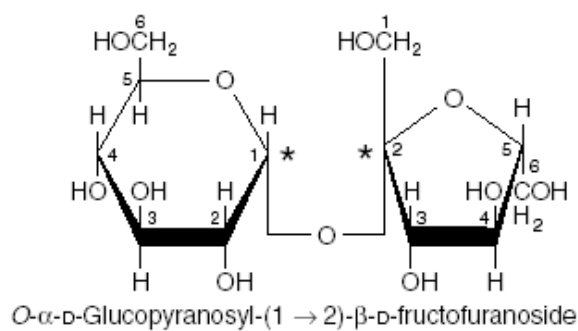
- Cyclization creates an anomeric carbon (the former carbonyl carbon), generating the α and β configurations of the sugar, for example, α -D-glucopyranose and β -D-glucopyranose.
- These two sugars are both glucose but are anomers of each other.
- In the α configuration, the OH on the anomeric C projects to the same side as the ring in a modified Fischer projection formula. In a Haworth projection formula of the α configuration, this OH is trans to the CH₂OH group.
- Since the α and β forms are not mirror images, they are referred to as **diastereomers**.
- 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 which is known as **mutarotation**.

**Note By:**

Structures of important disaccharides: The α and β refer to the configuration at the anomeric carbon atom (asterisk). When the anomeric carbon of the second residue takes part in the formation of the glycosidic bond, as in sucrose, the residue becomes a glycoside known as a furanoside or pyranoside. As the disaccharide no longer has an anomeric carbon with a free potential aldehyde or ketone group, it no longer exhibits reducing properties, whereas the anomeric end of the glucose residue is not involved in the glycosidic linkage it and, therefore, lactose remains a reducing sugar.

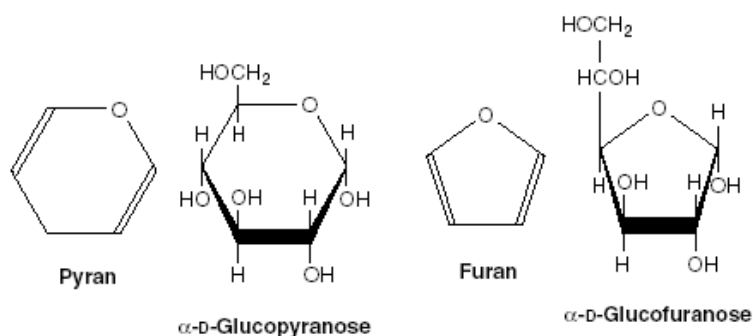


- **Reducing sugars:** If the oxygen on the anomeric carbon of a sugar is not attached to any other structure, that sugar can act as a reducing agent and is termed a reducing sugar. Such sugars can react with chromogenic agents (for example, Benedict's reagent or Fehling's solution) causing the reagent to be reduced and colored, with the anomeric carbon of the sugar becoming oxidized. [Note: Only the state of the oxygen on the anomeric carbon determines if the sugar is reducing or nonreducing—the other hydroxyl groups on the molecule are not involved.]

Maltose**Lactose****Sucrose**

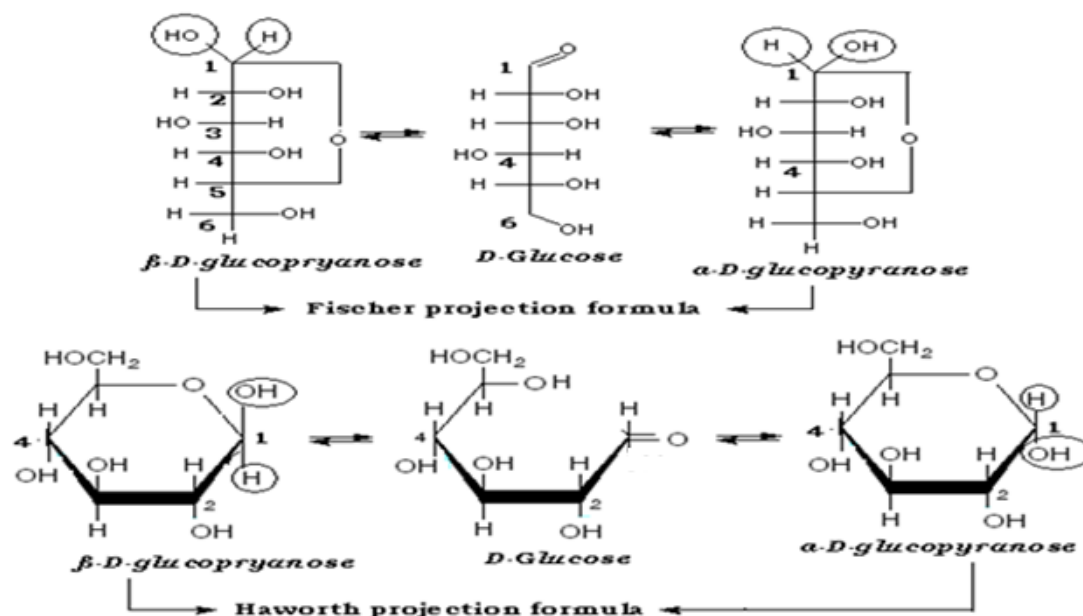
(iv) Pyranose and furanose ring structures

- The stable ring structures of monosaccharides are similar to the ring structures of either pyran (a six-membered ring) or furan (a five-membered ring). For glucose in solution, more than 99% is in the pyranose form.

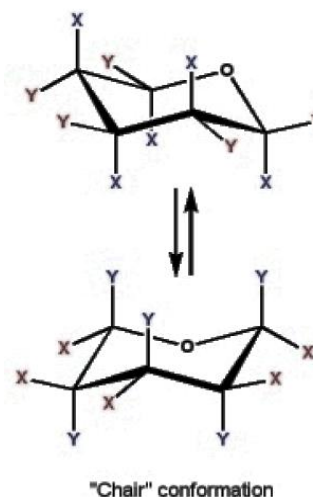
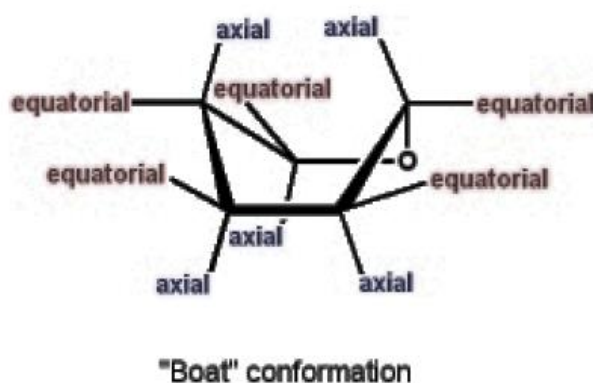
**Pyranose and furanose forms of glucose**

- "Pyranose" is used to refer to the pyran ring structure (6membered ring with 5 carbons and 1 oxygen)
- For five membered rings (four carbons and 1 oxygen) the structure is a furanose ring.
- Cyclization is reversible.
- The resulting chirality of the aldehyde carbon (or keto carbon in ketoses) in the cyclic structure can be either the α - or β -form. This carbon is termed the **anomeric** carbon, and the α - and β -forms are anomers.

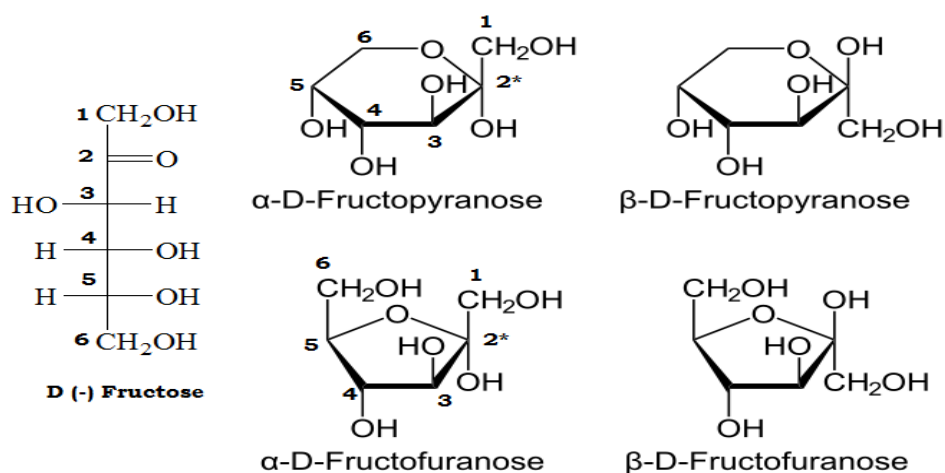
- The ring structure representations are termed "**Haworth Projections**".
- Cyclic structures can also be represented using Fischer diagrams



- Alternative ring structures**
 - Glucose has a variety of alcohol functional groups, and is able to form alternative hemiacetal ring structures.
 - The 5C-OH can react with the aldehyde forming the above pyranose ring
 - The 4C-OH can react with the aldehyde forming a five membered furanose ring
- Ring geometry**
 - The carbon atoms in the ring are sp^3 hybrid orbitals, and tetrahedral geometry.
 - The oxygen in the ring is also sp^3 , and tetrahedral.
 - Thus, the ring structures cannot be planar (that would require trigonal planar geometry, or sp^2 hybrid orbitals, for the atoms in the ring)
 - The rings actually look like



- There is a "boat" and a "chair" structure. There are two different orientations of the functional groups bonded to the ring carbons:
 - If they point in the general plane of the ring, they are said to be in the "equatorial" position
 - If they point in an orientation perpendicular to the general plane of the ring, they are said to be in the "axial" position
 - The chair can have two different conformations. *The principle effect of the alternative conformations is to change the axial versus equatorial orientations for the carbon functional groups.*
- Functional groups in the axial position are somewhat crowded together, whereas, the same functional groups in the equatorial position are separated from each other.



Fischer Projection	Haworth Projection	Configuration	Chair Conformation
Right	Down	α	Axial
Left	Up	β	Equatorial

