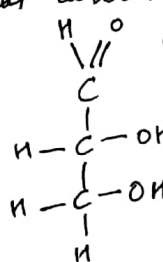


## Mutarotation - (Presence in carbohydrates)

Pg ①

Mutarotation is caused by a type of stereoisomerism involving formation of an asymmetrical centre at the first carbon atom (aldehyde carbon) in aldoses and the second one (Keto carbon) in ketoses.

Configuration - molecules such as the isomers of glyceraldehyde - the atoms of which can have different structural arrangements are known as asymmetrical molecules. The no. of possible structural arrangements for an asymmetrical molecule depends on the no. of centres of asymmetry; i.e., for  $n$  (any given no. of) centres of asymmetry,  $2^n$  different isomers of a molecule are possible. An asymmetrical centre in the case of carbon is defined as a carbon atom to which four diff't groups are attached. In the 3 carbon aldose sugar, glyceraldehyde, the asymmetrical centre is located at the central carbon atom. i.e., whether -OH projects from the left or the right - determines whether the molecule rotates the plane of polarized light to the left or to the right. Since, glyceraldehyde has one asymmetrical centre,  $n$  is 1 in the relationship  $2^n$ , and there thus are 2 possible glyceraldehyde isomers.



Sugars containing 4 carbon atoms have 2 asymmetrical centres; hence, there are four possible isomers ( $2^2$ ).

Similarly, sugars with 5 carbon atoms have 3 asymmetrical centres and thus have eight possible isomers ( $2^3$ ). Keto sugars have one less asymmetrical centre for a given no. of carbon atoms than do aldehyde sugars.

A convention of nomenclature, devised in 1906, states that the form of glyceraldehyde whose asymmetrical carbon atom has a hydroxyl group projecting to the right is designated as of the D-configuration, that form, whose asymmetrical carbon atom has a hydroxyl group projecting to the left, is designated as L. All sugars that can be derived from D-glyceraldehyde - i.e., hydroxyl group attached to the asymmetrical carbon atom most remote from the aldehyde or keto end of the molecule projects to the right - are said to be of the D-configuration, those sugars derived from L-glyceraldehyde are said to be of the L-configuration.

The configurational notation D or L is independent of the sign of the optical rotation of a sugar in solution. It is common, therefore, to designate both, as for example

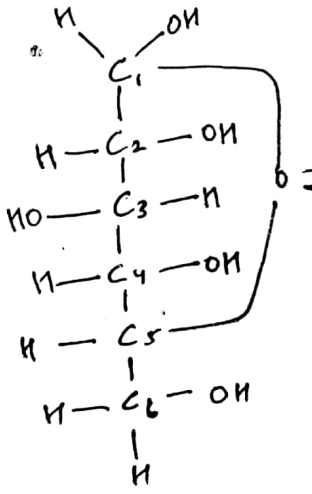
D-(+)-fructose or D-(d)-glucose i.e., both have a D-configuration at the centre of a symmetry most remote from the aldehyde end (in glucose) or keto end (in fructose) of the molecule, but fructose is laevorotatory and glucose is dextrorotatory - hence the latter has been given the alternative name dextrose.

When more than 1 asymmetrical centre is present in a molecule, as is the case with sugars having four or more carbon atoms, a series of DL pairs exists and they are functionally, physically, and chemically distinct.

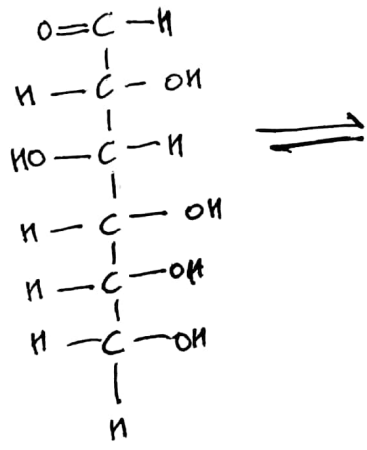
Thus, although D-xylose and D-lyxose both have five carbon atoms and are of the D-configuration, the spatial arrangement of the asymmetrical centres (at carbon atoms 2, 3 and 4) is such that they are not mirror images.

Pg-2) Hemiacetal and Hemiketal forms

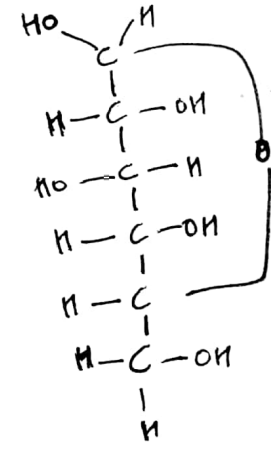
Although optical rotation has been one of the most frequently determined characteristics of carbohydrates since its recognition in the late 19<sup>th</sup> century, the rotational behaviours of freshly prepared solutions of many sugars differs from that of solutions that have been allowed to stand. This phenomenon, known as mutarotation, is demonstrable even with apparently identical sugars and is caused by a type of stereoisomerism involving formation of an asymmetrical centre at the first carbon atom (aldehyde carbon) in aldoses and the 2nd one (keto carbon) in ketoses.



$\alpha$ -D-glucose (hemiacetal form)

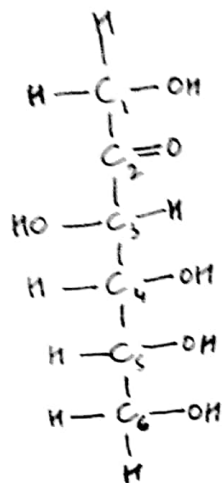


D-glucose (linear, open chain, or free form)

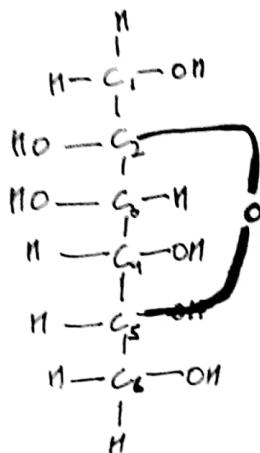


$\beta$ -D-glucose (hemiacetal form)

Fig 3



D-fructose  
(linear, open-chain or free form)



α-D-fructose  
(hemiketal form)

Most pentose and hexose sugars, therefore, do not exist as linear, or open-chain, structures in soln. but form cyclic, or ring, structures in hemiacetal or hemiketal forms, respectively. As illustrated for glucose and fructose, the cyclic structures are formed by the addition of the hydroxyl group (-OH) from either the fourth, fifth, or sixth carbon atom to the carbonyl group ( $>\text{C}=\text{O}$ ) at position 1 in glucose or 2 in fructose.

\* The carbon atom containing the aldehyde or ketogroup is called the anomeric carbon. Similarly, carbohydrate stereoisomers that differ in configuration only at this carbon atom are called anomers.

NOTE - The large no. of asymmetrical carbon atoms and the consequent no. of possible isomers considerably complicates the structural chemistry of carbohydrates.