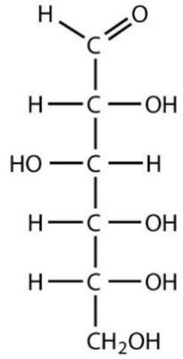
MONOSACCHARIDES STRUCTURE

1. Glucose-



- Glucose is a type of carbohydrate molecules which is a simple sugar with a structural formula $C_6H_{12}O_6$.
- It is made of six carbon atoms and an aldehyde group. Therefore, it is mentioned as an aldohexose group of molecules.

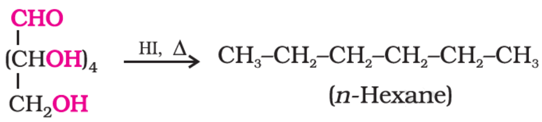
- The natural form of glucose, i.e., D- glucose is also known as dextrose.
- Glucose is the primary source of energy that is essential for living organisms.
- Plants and algae produce glucose during the process of photosynthesis with the help of water from the soil, sunlight, and carbon dioxide from the atmosphere.
- Glucose is naturally found in fruits, honey. Glucose in animals is formed by the process of glycogenolysis.
- Chemical formula of glucose, galactose and fructose is same $C_6H_{12}O_6$.
- Glucose is the monomer of many of the larger carbohydrates, namely starch, cellulose.
- It exists in two forms – 1. open-chain (acyclic) form & 2. ring (cyclic) form

➢ **Open chain structure of glucose-**

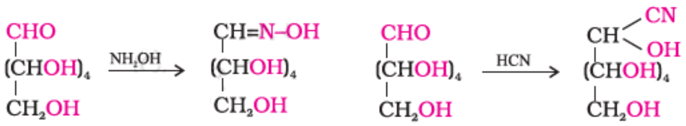
It was assigned the structure given below on the basis of the following evidences:

i) Its molecular formula was found to be $C_6H_{12}O_6$.

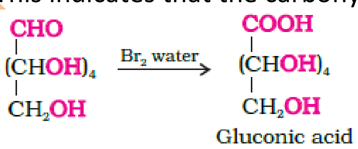
ii) On prolonged heating with HI, it forms n-hexane, suggesting that all the six carbon atoms are linked in a straight chain.



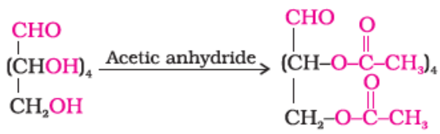
iii) Glucose reacts with hydroxylamine to form an oxime and adds a molecule of hydrogen cyanide to give cyanohydrin. These reactions confirm the presence of a carbonyl group (>C = O) in glucose.



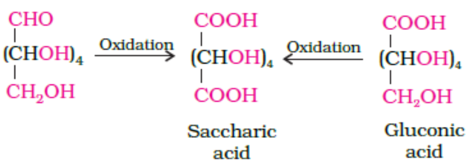
iv) Glucose gets oxidised to six carbon carboxylic acid (gluconic acid) on reaction with a mild oxidising agent like bromine water. This indicates that the carbonyl group is present as an aldehydic group.



v) Acetylation of glucose with acetic anhydride gives glucose pentaacetate which confirms the presence of five –OH groups. Since it exists as a stable compound, five –OH groups should be attached to different carbon atoms.



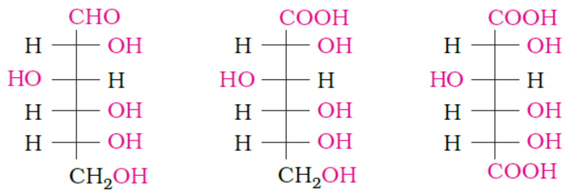
vi) On oxidation with nitric acid, glucose as well as gluconic acid both yield a dicarboxylic acid, saccharic acid. This indicates the presence of a primary alcoholic (–OH) group in glucose.



The exact spatial arrangement of different —OH groups was given by Fischer after studying many other properties

Fischer structure(Open chain structure).

- Structure I represent the glucose, II represent the gluconic acid and III represent saccharic acid



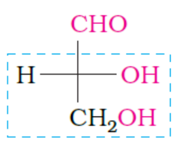
I II III

➢ D and L configuration

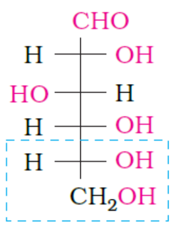
- Glucose is correctly named as D(+)-glucose. 'D' before the name of glucose represents the configuration whereas '(+)' represents dextrorotatory nature of the molecule. It should be remembered that 'D' and 'L' have no relation with the optical activity of the compound.
- **The meaning of D– and L– notations is as follows**
  - → The letters 'D' or 'L' before the name of any compound indicate the relative configuration of a particular stereoisomer of a compound with respect to configuration of some other compound, configuration of which is known. In the case of carbohydrates, this refers to their relation with a particular isomer of glyceraldehyde. Glyceraldehyde contains one asymmetric carbon atom and exists in two enantiomeric forms as shown below.

(+) – Glyceraldehyde (–) – Glyceraldehyde

- (+) Isomer of glyceraldehyde has 'D' configuration. It means that when its structural formula is written on paper, the –OH group lies on right hand side in the structure. All those compounds which can be chemically correlated to D (+) isomer of glyceraldehyde are said to have D-configuration whereas In L (–) isomer –OH group is on left hand side as you can see in the structure and those which can be correlated to 'L' (–) isomer of glyceraldehyde are said to have L—configuration.
- For assigning the configuration of monosaccharides, it is the lowest asymmetric carbon atom which is compared. As in (+) glucose, —OH on the lowest asymmetric carbon is on the right side which is comparable to (+) glyceraldehyde, so (+) glucose is assigned D-configuration.



D– (+) – Glyceraldehyde



D–(+) – Glucose

➢ Cyclic structure of Glucose-

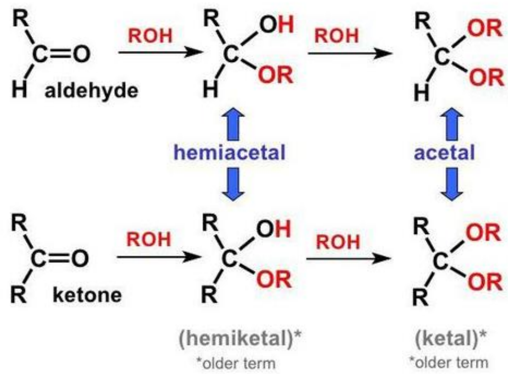
The open chain structure of glucose explained most of its properties but the following reactions and facts could not be explained by this structure.

i) Despite having the aldehyde group, glucose does not give Schiff's test and it does not form the hydrogen sulphite addition product with $NaHSO_3$.

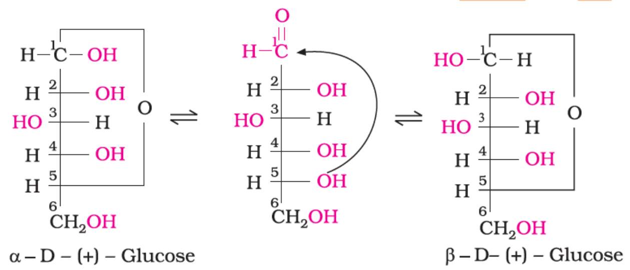
ii) The pentaacetate of glucose does not react with hydroxylamine indicating the absence of free —CHO group.

iii) **α and β form of Glucose**

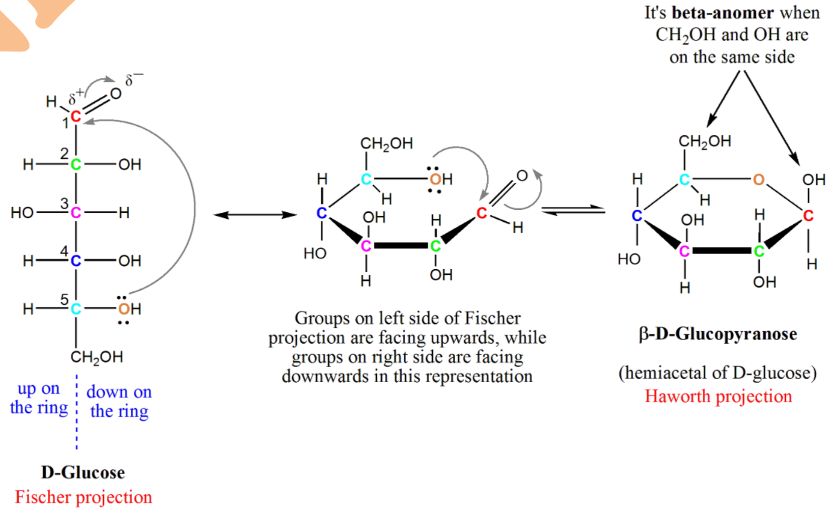
- It is found that glucose exist in two different crystalline forms which are named as α and β. The α-form of glucose (m.p. 419 K) is obtained by crystallisation from concentrated solution of glucose at 303 K while the β-form (m.p. 423 K) is obtained by crystallisation from hot and saturated aqueous solution at 371 K.
- This behaviour could not be explained by the open chain structure of glucose.
- It was proposed that one of the —OH groups may add to the —CHO group and form a cyclic hemiacetal structure.



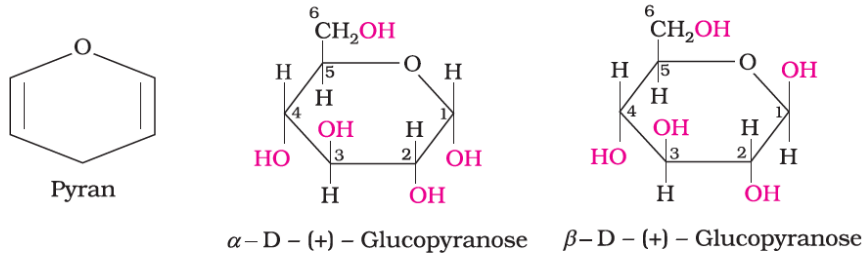
- It was found that glucose forms a six-membered ring in which —OH at C-5 is involved in ring formation.
- This explains the absence of —CHO group and also existence of glucose in two forms as shown below.
- These two cyclic forms exist in equilibrium with open chain structure.



- The two cyclic hemiacetal forms of glucose differ only in the configuration of the hydroxyl group at C_1, called *anomeric carbon* (An anomeric carbon can be identified as **the carbonyl carbon of the aldehyde or ketone functional group in the open-chain form of the sugar**.). Such isomers, i.e., α-form and β-form, are called anomers.
- The six membered cyclic structure of glucose is called pyranose structure because of their analogy with pyran.
- Pyran is a cyclic organic compound with one oxygen atom and five carbon atoms in the ring.
- The cyclic structure of glucose is more correctly represented by **Haworth structure** as given below.

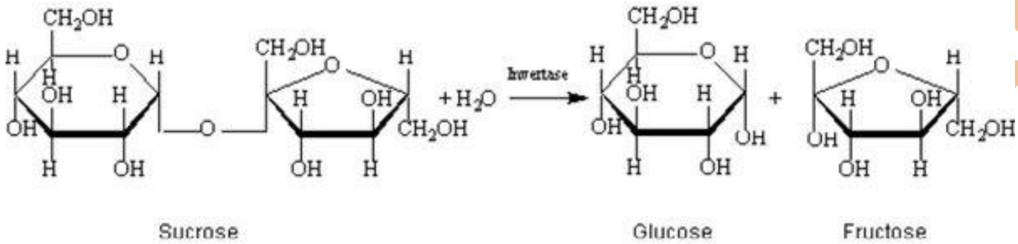


Haworth structure

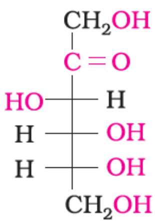


2. **FRUCTOSE**

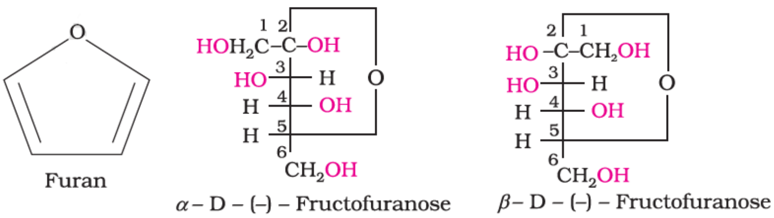
- Fructose is an important **ketohexose**. It is obtained along with glucose by the hydrolysis of disaccharide, sucrose.



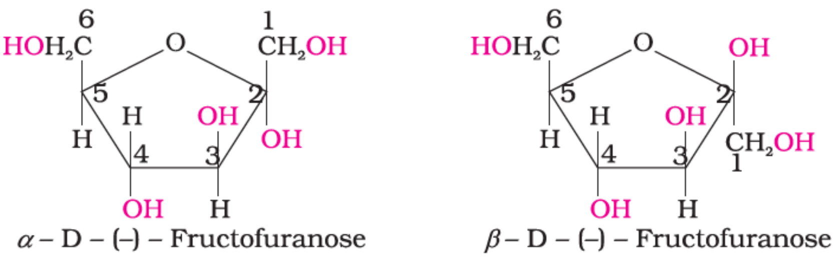
- It is a natural monosaccharide found in fruits, honey and vegetables
- Fructose also has the molecular formula $C_6H_{12}O_6$ and on the basis of its reactions it was found to contain a ketonic functional group at carbon number 2 and six carbons in straight chain as in the case of glucose. It belongs to D-series and is a laevorotatory compound. It is appropriately written as D-(–)-fructose. Its open chain structure is as shown below



- It also exists in two cyclic forms which are obtained by the addition of —OH at C_5 to the carbonyl group. The ring, thus formed is a five membered ring and is named as furanose with analogy to the compound furan. Furan is a five membered cyclic compound with one oxygen and four carbon atoms.

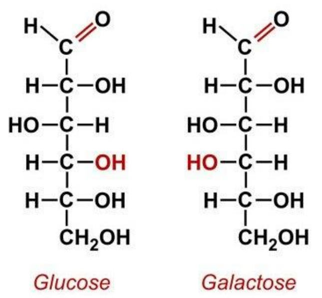


- The cyclic structures of two anomers of fructose are represented by **Haworth structures** as given.

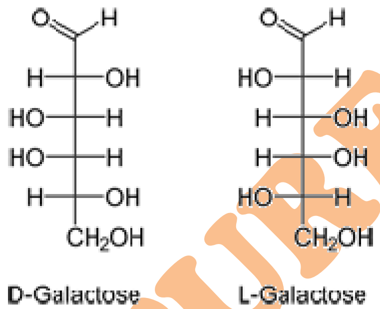


3. **GALACTOSE**

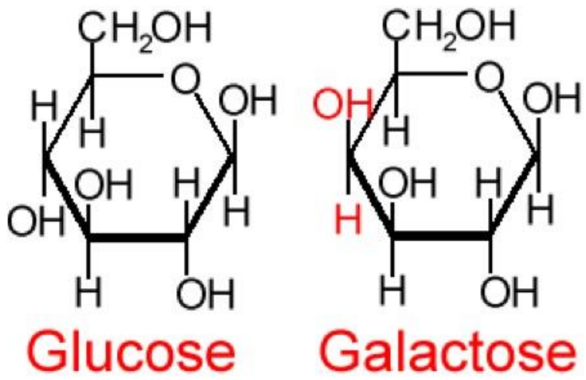
- **Galactose** is a six-carbon monosaccharide.
- Isolated for the first time by Louis Pasteur in 1855 from milk, therefore from the Greek *galaktos*, which means milk, followed by the suffix for sugars –*ose* its name become galctose
- The molecular formula of galactose is $C_6H_{12}O_6$.
- Galactose is a monosaccharide and epimer of glucose.
- Epimer- Epimers are **carbohydrates which vary in one position for the placement of the -OH group**.



- Like all aldohexoses, galactose has two **enantiomers**: D-galactose and L-galactose. The latter is not naturally occurring in higher organisms as it cannot be further metabolized. Therefore, the term galactose will be used to indicate D-galactose.



- The other interesting facts about galactose are:
  i) Most of the galactose ingested by humans gets converted to glucose.
  ii) Galactose binds to glucose to make lactose, to lipids to make glycolipids and to proteins to make glycoproteins.
- Galactose can exist in open-chain(Fischer Projection) as well as cyclic form.
- The open chain form has a carbonyl group at one end of the chain, which makes it an aldehyde derivative, therefore it is an aldohexose and a reducing sugar.
- The only cyclic form found in **mammals** is the **pyranose form**, which is a epimer of glucose as it differs only by the configuration of the hydroxyl group on the C_4. The furanose form is found in many lower organisms, both prokaryotes and eukaryotes, such as bacteria, green algae, fungi, protozoa, Furanose form is also found in pathogenic species where it may play an important role, for example for survival, while its biosynthetic pathway may be a target for the development of new drugs to treat infections caused by these pathogens



- In the cyclic form, it has four stereoisomers.
- In the cyclic form, galactose exists as four stereoisomers. Two have a five-member ring consisting of one oxygen atom and four carbon atoms, namely, a furanose ring, and two have a six-member ring consisting of one oxygen atom and five carbon atoms, namely, a pyranose ring. In solution, pyranose and furanose forms are in equilibrium with the open chain form but, since the furanose form is less stable than the pyranose form, the equilibrium is strongly shifted towards the latter.