By- Shailendra Shukla Sir

Biomolecules

Carbohydrates

"The optically active, polyhydroxy aldehydes or ketones or the compounds which produce these compounds on hydrolysis are called Carbohydrates".

The most common examples of carbohydrates are cane sugar ($C_{12}H_{22}O_{11}$), glucose ($C_6H_{12}O_6$), fructose ($C_6H_{12}O_6$), starch [$(C_6H_{10}O_5)_n$], cellulose etc. Most of the carbohydrates have the general formula, $C_x(H_2O)_y$. For example, the molecular formula of glucose ($C_6H_{12}O_6$) fits into this general formula, $C_6(H_2O)_6$. However, all the compounds which fit into this formula may not be essentially carbohydrates. For example, acetic acid (CH_3COOH) fits into this general formula, $C_2(H_2O)_2$, but it is not a carbohydrate. Similarly, rhamnose, ($C_6H_{12}O_5$) does not fit in this definition, but it is a carbohydrate. Since, the ratio hydrogen and oxygen atoms in carbohydrates is in general, the same as in water (2:1), they were considered as hydrates of carbon and named as carbohydrate. Now, it has been well established that, carbohydrates do not contain water and therefore, their name carbohydrate is erroneous, but because of being well established, it still persist.

Some of the carbohydrates, which are sweet in taste, are also called sugars. The most common sugar, used in our homes is sucrose, whereas the sugar present in milk is lactose. Carbohydrates are also called saccharides (Greek, *sakcharon* means sugar).

Classification of Carbohydrates

Carbohydrates are classified on the basis of their behaviour on hydrolysis. They have been broadly divided into following three groups-

(1)Monosaccharides- The simplest carbohydrates that cannot be hydrolysed further to give simpler unit of polyhydroxy aldehydes or

CHEMISTRYFORCOMPETITION.COM

ketones are called a monosaccharide. About 20 monosaccharides are known to found in nature. Some common examples are glucose ($C_6H_{12}O_6$), fructose ($C_6H_{12}O_6$), ribose ($C_5H_{10}O_5$), etc.

(2)Oligosaccharides- Such carbohydrates which yield two to ten monosaccharide units on hydrolysis, are called oligosaccharides. They are further classified as disaccharides, trisaccharides, tetrasaccharides, etc., depending upon the number of monosaccharides, they give on hydrolysis.

The most common oligosaccharides are disaccharides. The two monosaccharide units obtained on hydrolysis of a disaccharide may be same or different. For example, one molecule of sucrose ($C_{12}H_{22}O_{11}$), on hydrolysis gives one molecule each of glucose and fructose, whereas one molecule of maltose ($C_{12}H_{22}O_{11}$), on hydrolysis gives two molecules of glucose.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Glucose}}{C_6H_{12}O_6}$$

Monosaccharides and oligosaccharides are sweet in taste, hence they are collectively called sugars.

(3)Polysaccharides- Carbohydrates which yield a large number of monosaccharide units on hydrolysis are called polysaccharides. Some common examples are starch, cellulose, glycogen, gums, etc.

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow[298K,\ 2\text{-}3\ atm]{H^+} \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

Polysaccharides are not sweet in taste, hence they are also called non-sugars.

Reducing and Non-reducing Sugars- Such carbohydrates which reduce Fehling's solution and Tollens' reagent are called reducing sugars. All monosaccharides, whether aldose or ketose are

CHEMISTRYFORCOMPETITION.COM

reducing sugars. Amongst disaccharides, maltose and lactose are also reducing sugars.
On the other hand, those carbohydrates which do not reduce Fehling's solution and Tollens' reagent are called non-reducing sugars. For example, sucrose is a non- reducing sugars.

Aldoses and Ketoses- If a monosaccharide contains an aldehyde group, then it is called an aldose (e.g. glucose), but if it contains a keto group (e.g. fructose), then it is called a ketose.

Depending on the number of carbon atoms present in monosaccharides, they are further classified as trioses, tetrotes, pentoses, hexoses etc.

Monosaccharides

(1)Glucose ($C_6H_{12}O_6$)

Glucose is found in free as well as in combined form in nature. It is present in sweet fruits and honey. Ripe grapes also contain glucose in large amounts.

Preparation Methods

(1)By hydrolysis of sucrose (Cane sugar)

When sucrose is boiled with dilute HCl or H_2SO_4 in alcoholic solution, it gets hydrolyzed to give glucose and fructose in equal amounts.

$$\underset{}{C_{12}H_{22}O_{11}} + \underset{}{H_2O} \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

(2)By Hydrolysis of starch

Commercially glucose is obtained by hydrolysis of starch with dilute H_2SO_4 at 393 K temperature and 2-3 atm pressure.

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow[298K,\ 2\text{-}3\ atm]{H^+} \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

CHEMISTRYFORCOMPETITION.COM

Structure of Glucose

(A)Open Chain Structure of Glucose

Glucose is an aldohexose and is also known as dextrose. It is the monomer of many of the higher carbohydrates such as starch, cellulose etc. It is probably the most abundant organic compound on earth.

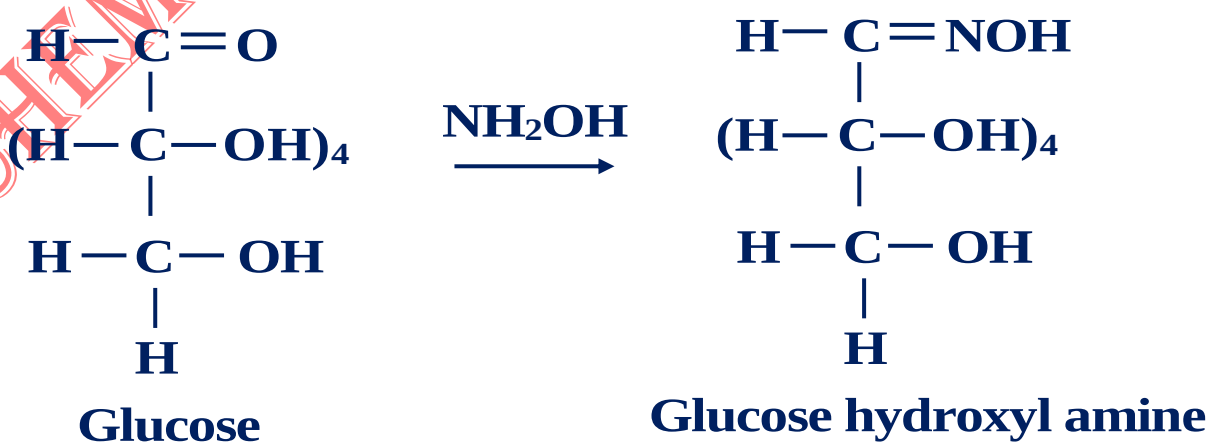
Glucose has been assigned the open chain structure on the basis of the following evidences-

(1) The molecular formula of glucose is found to be $C_6H_{12}O_6$.

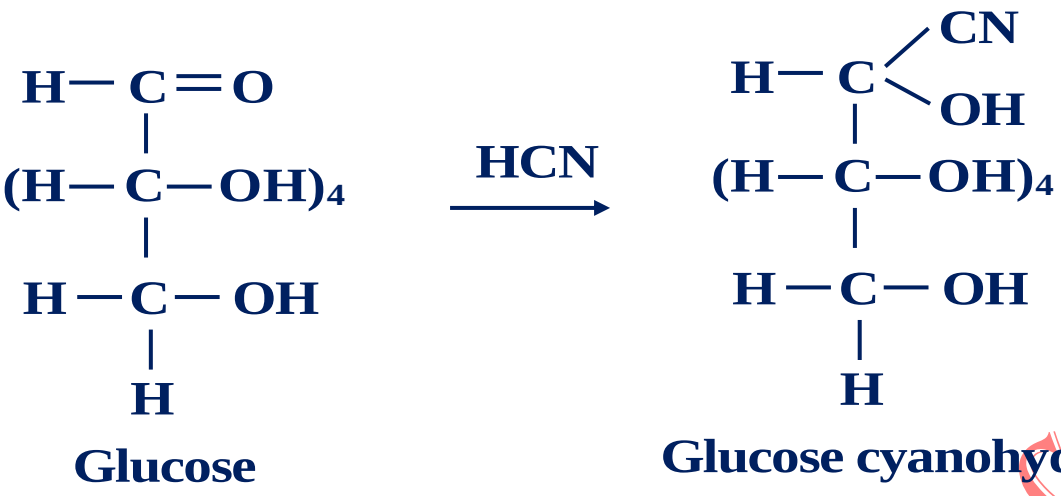
(2) On prolonged heating with HI, it forms n-hexane, suggesting that all the six carbon atoms are linked in a straight chain.



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



CHEMISTRYFORCOMPETITION.COM



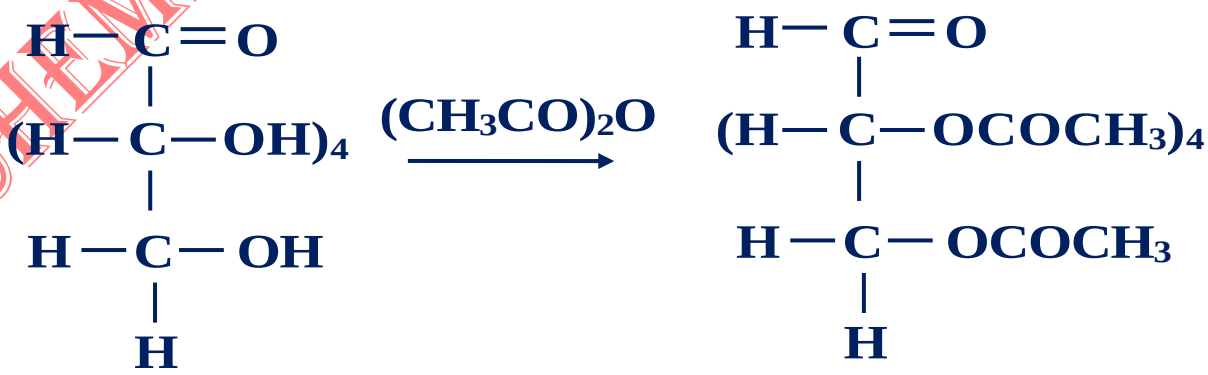
Glucose **Glucose cyanohydrin**

(4)Glucose on reaction with a mild oxidizing agents such as bromine water, gets oxidized into six carbon carboxylic acid i.e. gluconic acid. It indicates that, in glucose molecule, the carbonyl group is present as an aldehydic group.



Glucose **Gluconic acid**

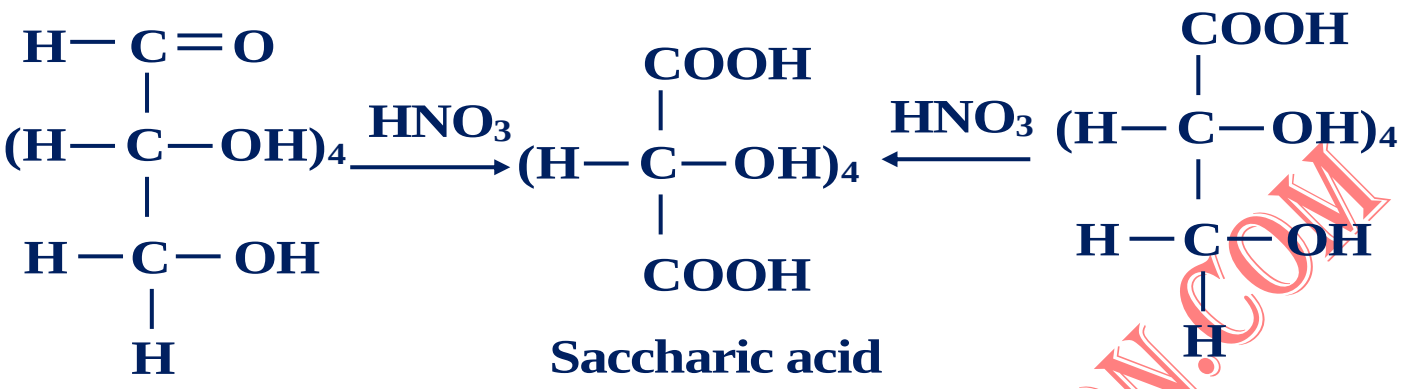
(5)Acetylation of glucose with acetic anhydride gives glucose pentaacetate. It confirms the presence of five -OH groups in glucose molecule. Since glucose exists as a stable compound, these five -OH groups must be attached to different carbon atoms.



Glucose **Glucose pentaacetate**

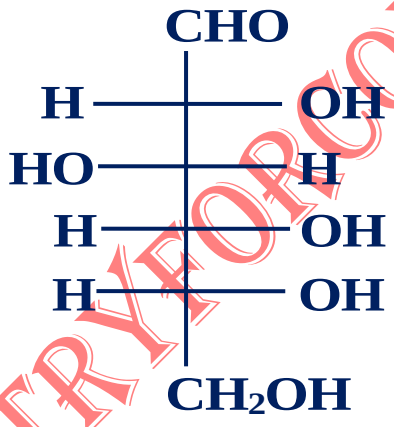
CHEMISTRYFORCOMPETITION.COM

(6)On oxidation with nitric acid, both glucose and gluconic acid give saccharic acid (a dicarboxylic acid). This indicates the presence of a primary alcoholic (-OH) group in glucose.



Glucose Saccharic acid Gluconic acid

Studying a number of properties, Fischer has given the exact spatial arrangement of different -OH groups in glucose molecule and assigned the following open chain structure for glucose-



Open Chain Structure of Glucose

(B)Cyclic Structure of Glucose

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

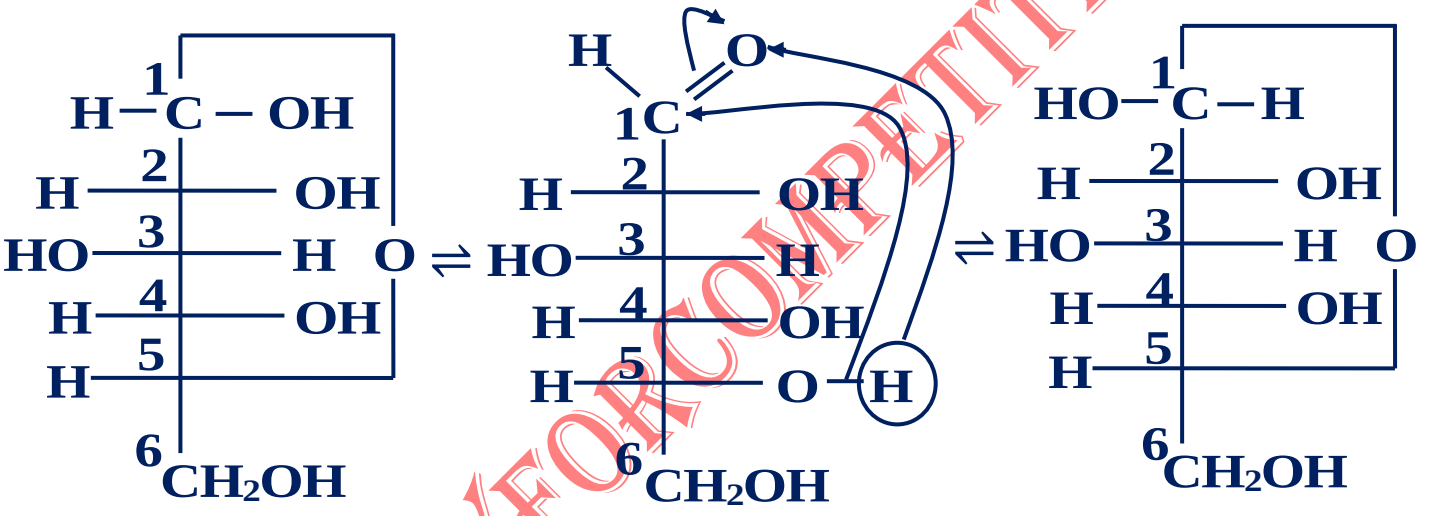
(1) Despite having the aldehyde group, glucose does not give Schiff's test and it does not form the hydrogensulphite addition product with $NaHSO_3$.

(2) The pentaacetate of glucose does not react with hydroxylamine indicating the absence of free -CHO group.

CHEMISTRYFORCOMPETITION.COM

(3) Glucose is found to exist in two different crystalline forms namely α and β -forms. The α-form of glucose (m.p. = 419K) is obtained by crystallization from concentrated solution of glucose at 303K, while the β -form (m.p. = 423K) is obtained by crystallisation from hot and saturated aqueous solution at 371K. This behaviour could not be explained by the open chain structure for glucose.

It fact, the -OH group of fifth carbon atom of glucose molecule adds to the -CHO group and form a cyclic hemiacetal structure. Thus, 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 the existence of glucose in two cyclic forms which exist in equilibrium with open chain structure.

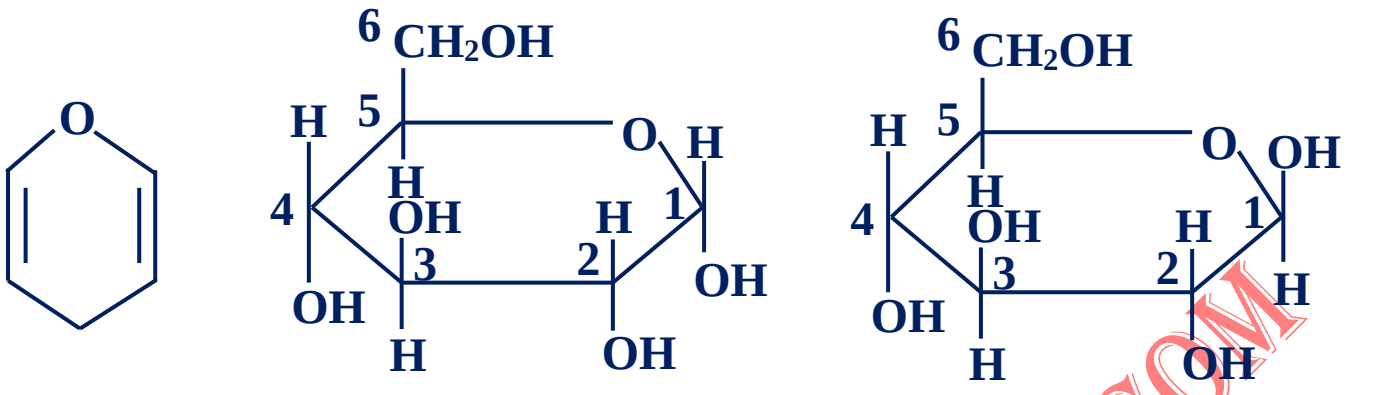


α-D-(+)-Glucose **Glucose (Open chain)** **β-D-(+)-Glucose**

The two cyclic hemiacetal forms of glucose differ only in the configuration of the hydroxyl group at first carbon atom i.e. C_1 called anomeric carbon (the aldehyde carbon before cyclisation). Such isomers, i.e., α and β -forms are called anomers. The six membered cyclic structure of glucose is called pyranose structure of glucose. (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 under-

CHEMISTRYFORCOMPETITION.COM



Pyran α - D - (+) - Glucopyranose β - D - (+) - Glucopyranose

Fig.- Cyclic Structure of Glucose

Cofiguration of Carbohydrates (D and L- System of Naming)

The spatial arrangement of different atoms and groups around the chiral centres of a compounds is called the configuration of the compounds.

The relative configuration of carbohydrates is expressed with respect to the configuration of glyceraldehyde. In fact, glyceraldehyde contains an asymmetric carbon atom and exists in following two enantiomeric forms-



d or (+)-Glyceraldehyde **l or (-)-Glyceraldehyde**

Here, d or (+) glyceraldehyde having hydrogen atom on left hand side and –OH group on right hand side has been arbitrarily assigned D-configuration. On the other hand, l or (-) glyceraldehyde having hydrogen atom on right hand side and –OH group on left hand side has been arbitrarily assigned L-configuration. All those compounds which can be chemically correlated to D-(+)-glyceraldehyde i.e. which have genetic relation with D-(+)-glyceraldehyde (can be obtained

CHEMISTRYFORCOMPETITION.COM

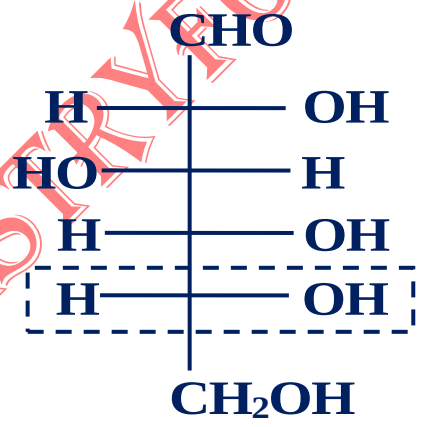
from or converted into D-(+)-glyceraldehyde are said to have D-configuration. On the other hand, those carbohydrates which can be correlated to L-(-)-glyceraldehyde i.e. which have genetic relation with L-(-)-glyceraldehyde (can be obtained from or converted into L-(-)-glyceraldehyde) are said to have L-configuration.

For example, Glucose is correctly named as D-(+)-glucose. Here, the letter D- represents its configuration while, (+) sign represents the dextrorotatory nature of the compound. It should be remembered that 'D' and 'L' have no relation with the optical activity of the compound and therefore, they are not related to letter d (dextrorotatory) and l (laevorotatory).

Thus, the letters D or L before the name of a compound indicates the relative configuration of respective stereoisomer of the compound.

For assigning the configuration to the monosaccharides, the configuration of the highest asymmetric carbon atom is compared. For example, in d or (+) glucose, -OH group on the highest asymmetric carbon (Lowest in position) is on the right hand side which is comparable to d or (+) glyceraldehyde. Hence, d or (+) glucose is assigned D-configuration. Here, other asymmetric carbon atoms of glucose are not considered for this comparison.

The structure of glucose and glyceraldehyde is written in such a way that most oxidised carbon (in this case -CHO group) lies at the top.



D-(+)-Glucose

CHEMISTRY FOR COMPETITION.COM

(2)Fructose ($C_6H_{12}O_6$)

Fructose is an important ketohexose. It is obtained by the hydrolysis of sucrose along with glucose. It is a natural monosaccharide found in fruits, honey and vegetables. In its pure form it is used as a

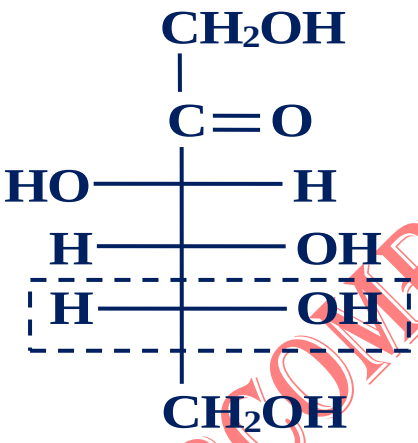
sweetner.

Structure f Fructose

Just like glucose, fructose also has the molecular formula $C_6H_{12}O_6$. On the basis of its reactions it has been found to contain a ketonic functional group at carbon number 2 and six carbons in straight chain as in the case of glucose.

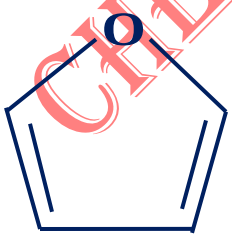
Like glucose natural fructose has D-configuration but it is a laevorotatory compound. Hence, it is appropriately written as D-(-)-fructose.

The open chain structure of fructose can be represented as under-

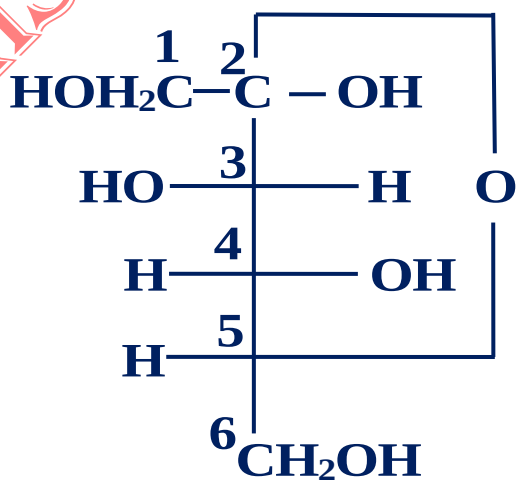


D-(-)-Fructose

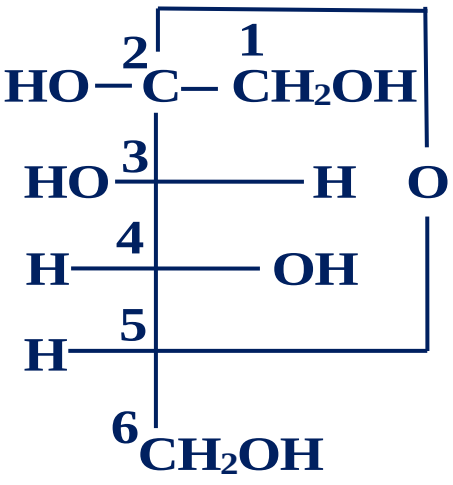
It also exists in two cyclic forms which are obtained by the addition of -OH at C5 to the (>C=O) group. The five membered ring, thus formed is named as furanose with analogy to the compound furan. Furan is a five membered cyclic compound with one oxygen and four carbon atoms in the ring.



Furan



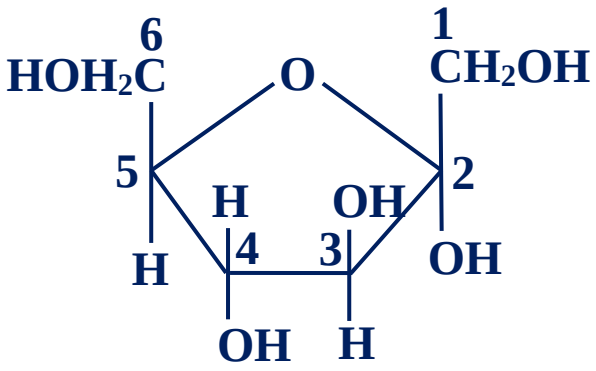
α-D-(-)-Fructose



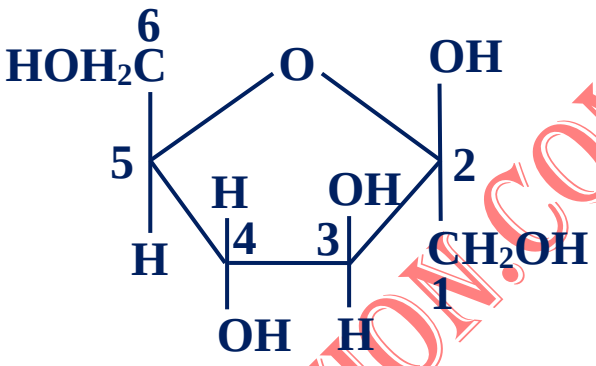
β-D-(-)-Fructose

CHEMISTRYFORCOMPETITION.COM

The Haworth structures of the cyclic structures of two anomers of fructose are represented as under-



α-D-(-)-Fructofuranose



β-D-(-)-Fructofuranose

Disaccharides

Such carbohydrates which yield two same or different monosaccharide units on hydrolysis with dilute acids or enzymes are called disaccharides.

In disaccharides the two monosaccharides are joined together by an oxide linkage formed by the loss of a water molecule. Such a linkage between two monosaccharide units through oxygen atom is called **glycosidic linkage.**

In disaccharides, if the reducing groups of both the monosaccharides i.e., aldehydic or ketonic groups are bonded, then they are not capable to reduce Fehling's solution and Tollens' reagent and are said to be non-reducing sugars, e.g., sucrose. On the other hand, such sugars which contain these functional groups in free state, are capable to reduce Fehling's solution and Tollen's reagent and therefore, they are called reducing sugars. For example, maltose and lactose.

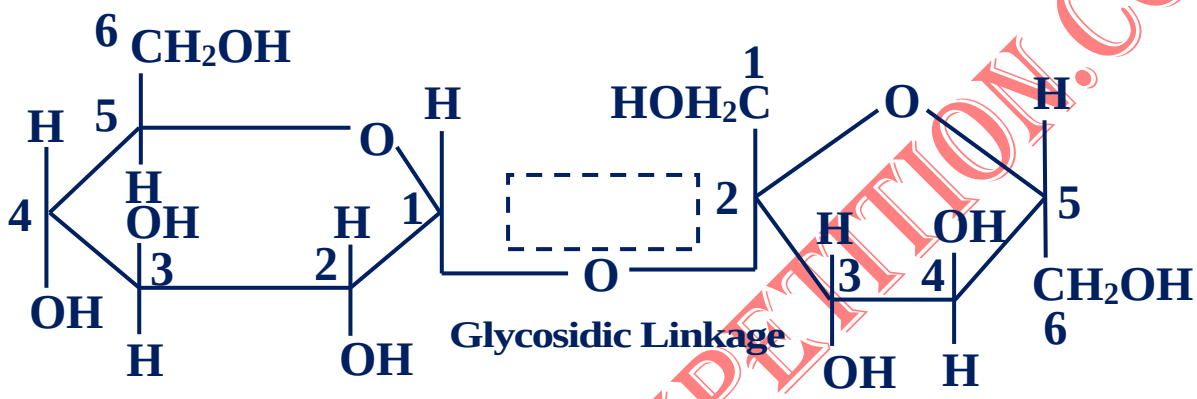
(1)Sucrose

It is one of the most common disaccharides which on hydrolysis gives equimolar mixture of D-(+)-glucose and D-(-) fructose.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{D-(+)-Glucose}}{C_6H_{12}O_6} + \underset{\text{D-(-)-Fructose}}{C_6H_{12}O_6}$$

CHEMISTRYFORCOMPETITION.COM

In sucrose molecule, these two monosaccharides are held together by a glycosidic linkage between C_1 of α-D-glucose and C_2 of β-D-fructose. Since the reducing groups of glucose and fructose are involved in glycosidic bond formation, sucrose is not capable to reduce Fehling's solution and Tollens' reagent and therefore, it is an example of a non reducing sugar.



α - D - (+) - Glucopyranose **β-D-(-)-Fructofuranose**

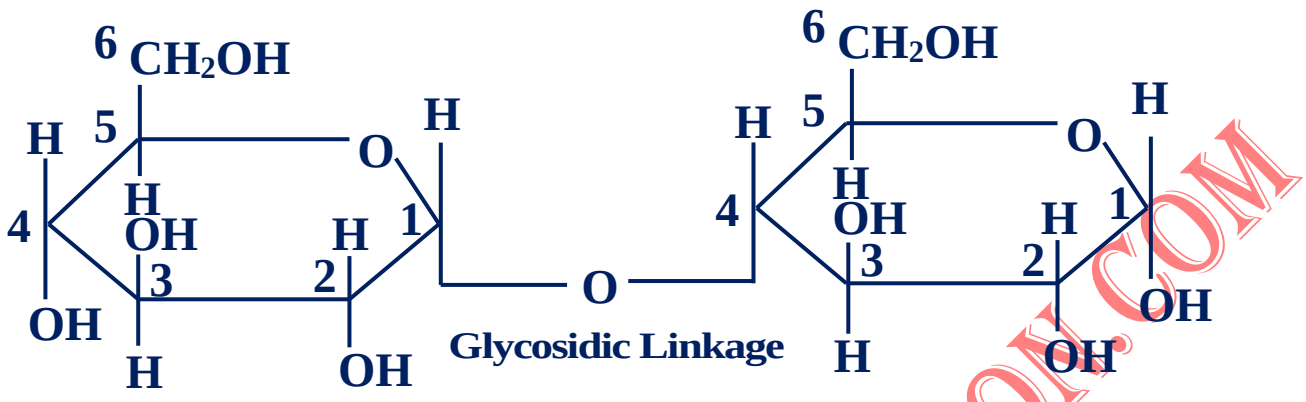
Structure of Sucrose

Sucrose is dextrorotatory, but after hydrolysis gives dextrorotatory glucose and laevorotatory fructose. Since the laevorotation of fructose (-92.4°) is more than dextrorotation of glucose (+52.5°), the mixture is laevorotatory. Thus, hydrolysis of sucrose brings about a change in the sign of rotation, from dextro (+) to laevo (-) and therefore, the product is named as **invert sugar**.

(2)Maltose

Maltose (disaccharide) is composed of two α-D-glucose units where C_1 of one glucose (I) is linked to C_4 of another glucose unit (II). Here, free aldehyde group can be produced at C_1 of second glucose in solution and therefore, it shows reducing properties and is an example of a reducing sugar.

CHEMISTRYFORCOMPETITION.COM

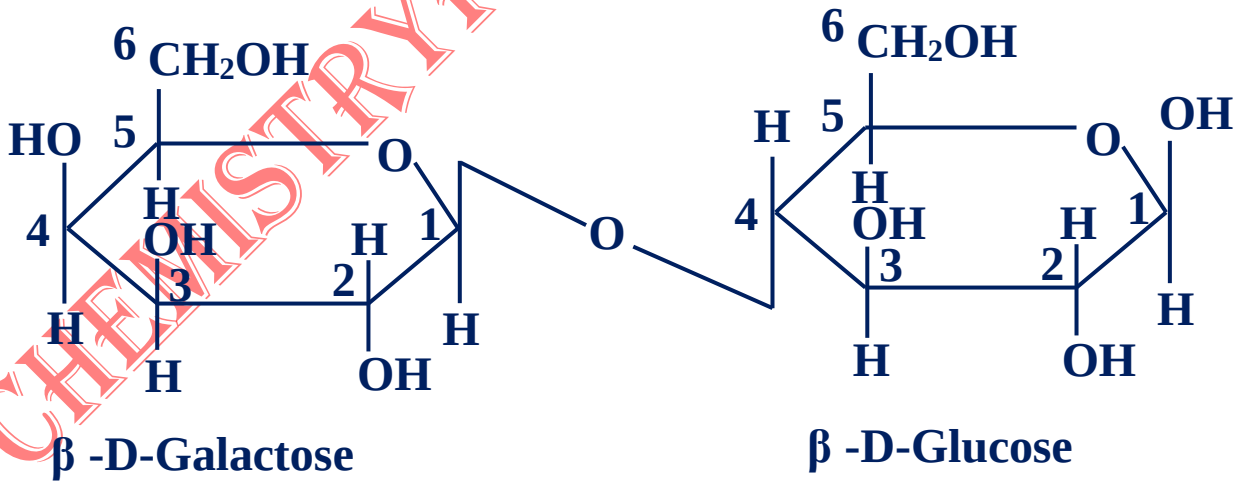


α - D - (+) - Glucopyranose α - D - (+) - Glucopyranose

Structure of Maltose

(3)Lactose

It is a disaccharide which is found in milk and therefore, it is more commonly known as milk sugar. It is composed of β-D-galactose and β-D-glucose. The linkage is between C_1 of galactose and C_4 of glucose. Free aldehyde group may be produced at C_1 of glucose unit, hence it is also a reducing sugar.



β -D-Galactose β -D-Glucose

Structure of Lactose

CHEMISTRYFORCOMPETITION.COM

Polysaccharides

Such carbohydrates which contain a large number of monosaccharide units joined together by glycosidic linkages, and therefore, give a large number of same or different monosaccharide units on hydrolysis are called Polysaccharides. These are the most commonly encountered carbohydrates in nature. They mainly act as the food storage or structural materials in living beings.

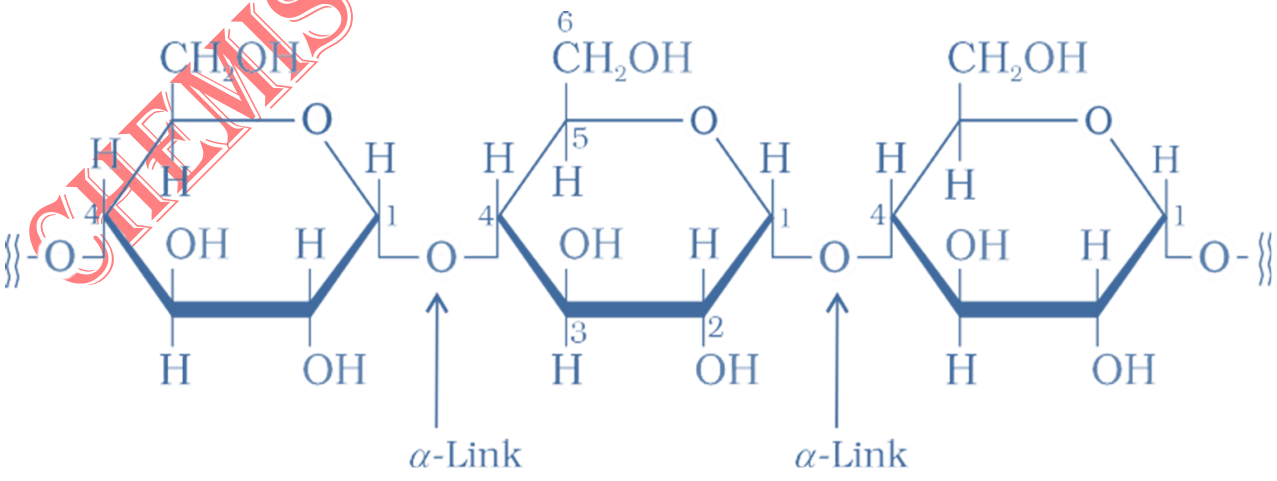
Some most common examples of polysaccharides are as under-

(1)Starch

Starch is the main storage polysaccharide of plants. It is the most important dietary source for human beings. High content of starch is found in cereals, roots, tubers and some vegetables. It is a polymer of α-glucose and consists of two components i.e. **Amylose** and **Amylopectin**.

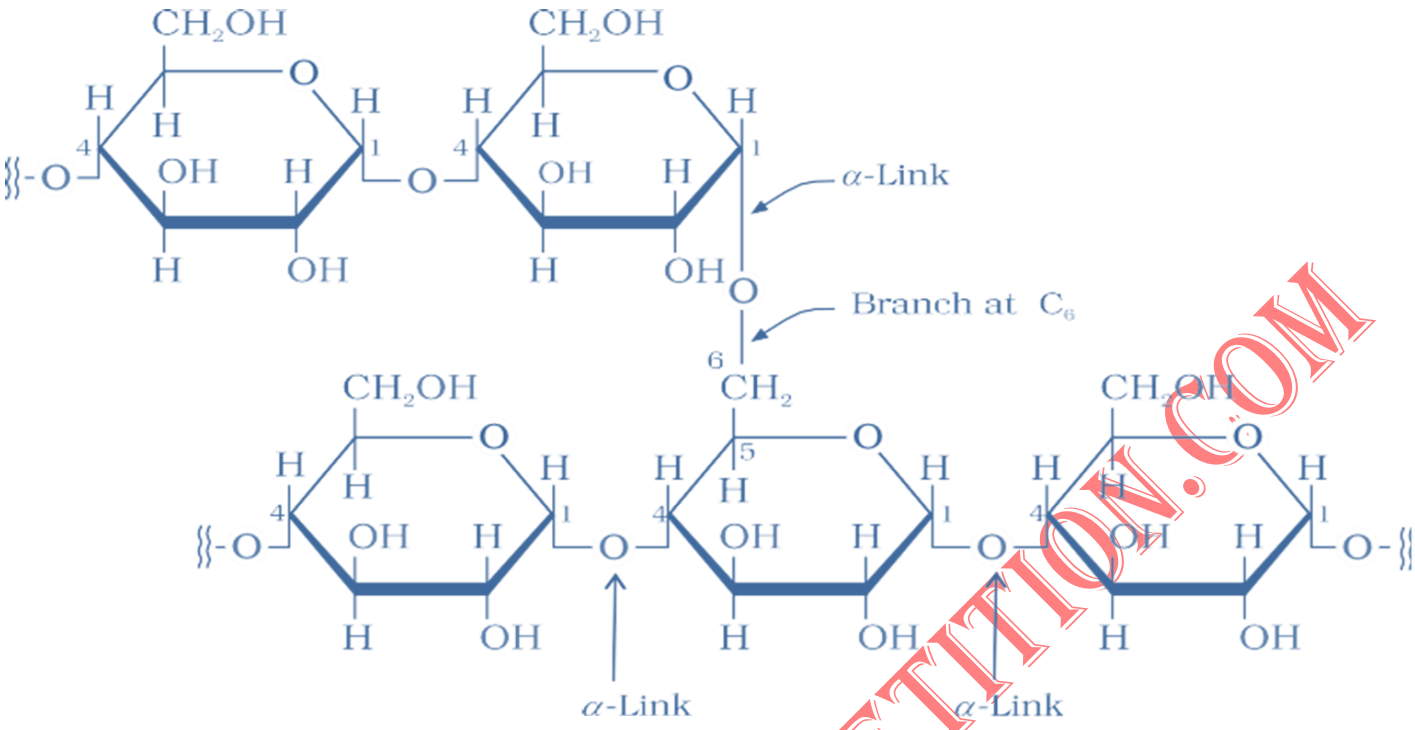
Amylose is water soluble component of starch which constitutes about 15-20% of starch. Chemically, it is a long unbranched chain with 200-1000 α-D-(+)-glucose units held together by C_1-C_4 glycosidic linkage.

Amylopectin is insoluble in water and constitutes about 80-85% of starch. It is a branched chain polymer of α-D-glucose units in which chain is formed by C_1–C_4 glycosidic linkage whereas branching occurs by C_1–C_6 glycosidic linkage.



Structure of Amylose

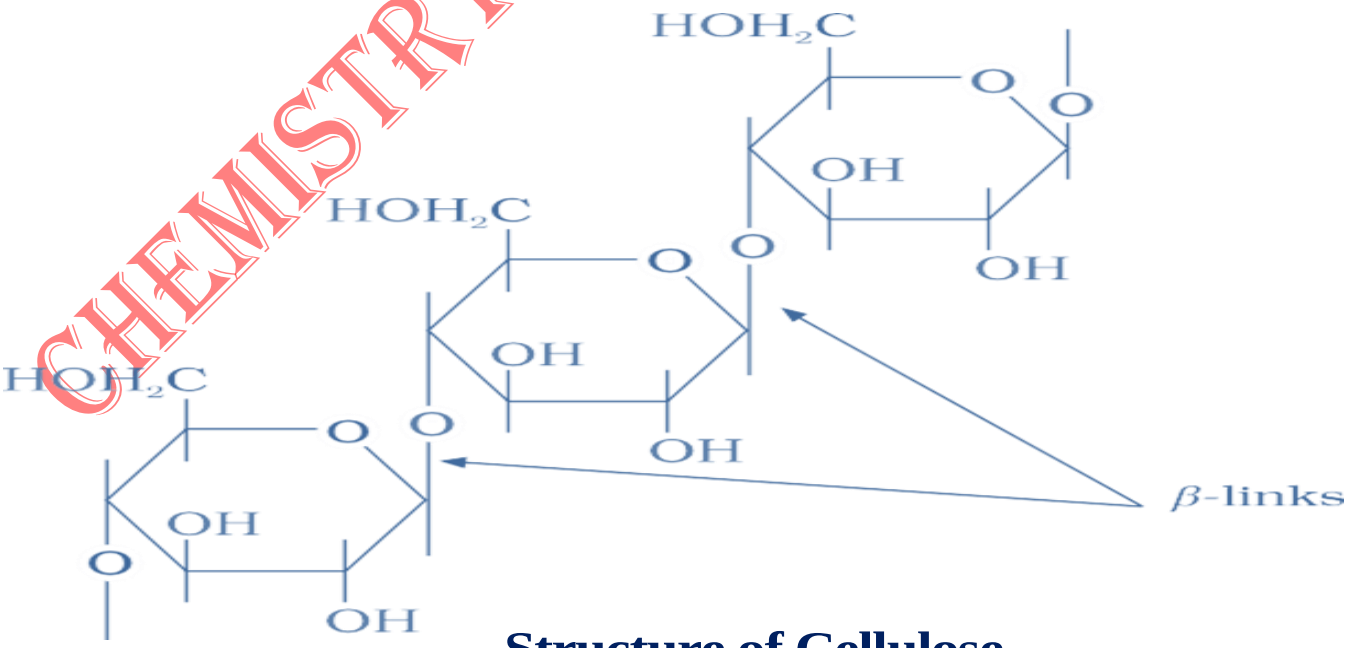
CHEMISTRYFORCOMPETITION.COM



Structure of Amylopectin

(2) Cellulose

Cellulose occurs exclusively in plants and it is the most abundant organic substance in plant kingdom. It is a predominant constituent of cell wall of plant cells. Cellulose is a straight chain polysaccharide composed only of β-D-glucose units which are joined by glycosidic linkage between C_1 of one glucose unit and C_4 of the next glucose unit.



Structure of Cellulose

CHEMISTRY FOR COMPETITION.COM

(3) Glycogen

The carbohydrates are stored in animal body as glycogen. It is also known as **animal starch.** Its structure is similar to amylopectin but it is relatively more highly branched. It is present in liver, muscles and brain. When the body needs glucose, enzymes break the glycogen down to glucose. Glycogen is also found in yeast and fungi.

Importance of Carbohydrates

Carbohydrates are essential for life in both plants and animals. They form a major portion of our food. Honey has been used for a long time as an instant source of energy by '**Vaidyas**' in ayurvedic system of medicine. Carbohydrates are used as storage molecules as starch in plants and **glycogen** in animals. Cell wall of bacteria and plants is made up of cellulose. Furniture are made up of cellulose in the form of wood. Similarly, clothe are made up of cellulose in the form of cotton fibre. Carbohydrates provide raw materials for many important industries like textiles, paper, lacquers and breweries.

Two aldopentoses namely D-ribose and 2-deoxy-D-ribose are present in nucleic acids. Carbohydrates are found in biosystem in combination with many proteins and lipids.

Intext Questions

(1)Glucose and sucrose are soluble in water but cyclohexane or benzene (simple six membered ring compounds) are insoluble in water. Explain.

(2)What are the expected products of hydrolysis of lactose?

(3)How do you explain the absence of aldehyde group in the pentaacetate of D-glucose?

- **For PPTs to take Online Classes Whats App at +91 7389757666**
- ***Download Mobile App - "Exacademy" from App Store***
- ***Download pdf at- https://chemistryforcompetition.com/***
- ***"Chemistry for Competitions" Telegram Channel***
- ***For Video Lectures Visit- "Exacademy"Youtube Channel***

CHEMISTRYFORCOMPETITION.COM