

Biomolecules & Polymers

CARBOHYDRATES

Section - 1

Definition :

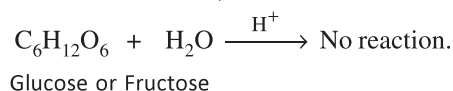
In olden times, carbohydrates were defined as hydrates of carbon, represented by general formula $C_x(H_2O)_y$, i.e., hydrogen and oxygen existed in the ratio of 2 : 1 as in water molecule, e.g., Glucose $[C_6(H_2O)_6]$, Sucrose $[C_{12}(H_2O)_{11}]$, etc. However, a number of compounds such as Rhamnose $[C_6H_{10}O_4]$, 2-Deoxyribose $[C_5H_{10}O_4]$ are known, which are carbohydrates by their chemical behaviour but cannot be represented as hydrates of carbon. It is also important to note that all compounds possessing the formula $C_x(H_2O)_y$ are not necessarily carbohydrates, e.g., Formaldehyde, $HCHO [C(H_2O)_1]$, Acetic acid $[C_2(H_2O)_2]$, etc.

Now, carbohydrates are defined as **polyhydroxy aldehydes** or **polyhydroxy ketones** or substances which give these on hydrolysis and contain atleast one **chiral carbon** atom. It may be noted here that aldehydic and ketonic groups in carbohydrates are not present as such but usually exist in combination with one of the hydroxyl groups of the molecule in the form of hemiacetals.

Classification of Carbohydrates :

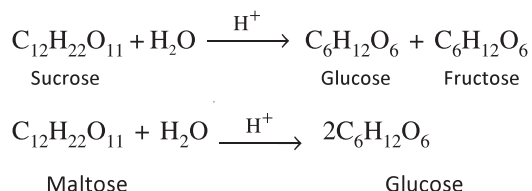
On the basis of hydrolysis, carbohydrates are divided into three major classes. These are :

- (i) **Monosaccharides** : These are polyhydroxy aldehydes or ketones which cannot be decomposed by hydrolysis to give simpler carbohydrates. With a few exceptions, they have general formula, $C_nH_{2n}O_n$. **Glucose** is the most important member in their class. These are crystalline in nature, readily dissolve in water and are sweet in taste (sugars).

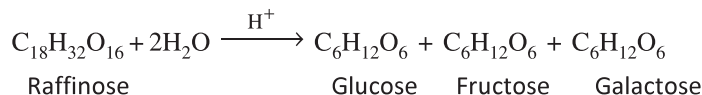


- (ii) **Oligosaccharides** : The oligosaccharides are carbohydrates which yield a definite number (2-10) of monosaccharides molecules on hydrolysis.

The oligosaccharides containing two monosaccharide units are called disaccharides, and those containing three, four or five units are termed as trisaccharides, tetrasaccharides or pentasaccharides respectively, e.g., **Sucrose** and **Maltose**, both disaccharides, yield two molecules of monosaccharides on hydrolysis.

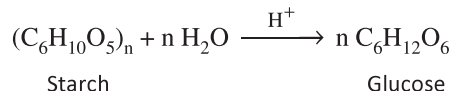


Rafinose, a trisaccharide, with molecular formula $C_{18}H_{32}O_{16}$, yields three monosaccharide units.



Majority of oligosaccharides are colourless crystalline solids, soluble in water and sweet in taste.

(iii) Polysaccharides : The polysaccharides are carbohydrates of high molecular weight which yield many monosaccharide molecules on hydrolysis. The general formula of polysaccharides is $(\text{C}_6\text{H}_{10}\text{O}_5)_n$. **Starch**, **cellulose**, **glycogen**, etc. are the examples of polysaccharides.



Polysaccharides are colourless, amorphous solids having no taste and insoluble in cold water. These are also called non-sugars.

Sugars and Non-Sugars :

All the mono and disaccharides are commonly known as sugar as they possess a sweet taste, while, higher carbohydrates than disaccharides are called non-sugars.

Reducing and Non-Reducing Carbohydrates :

Carbohydrates that reduce Fehling's solution or Tollen's reagent are termed reducing carbohydrates while the others are non-reducing carbohydrates. "All **monosaccharides** and most of the **disaccharides** except **sucrose** are reducing carbohydrates."

Monosaccharide :

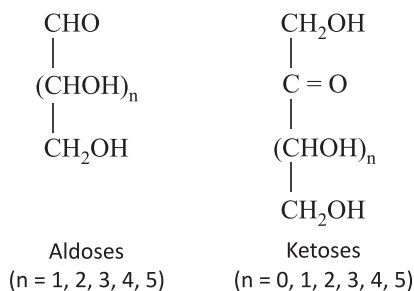
The monosaccharides are the basis of carbohydrate chemistry, since all carbohydrates are either monosaccharides or are converted into monosaccharides on hydrolysis. The monosaccharides are either polyhydroxy aldehydes or ketones.

These are, therefore, classified into two main groups, viz., **Aldoses** (containing $\text{—}\overset{\text{O}}{\parallel}\text{C—H}$ group), and **Ketoses**

(containing $\text{—}\overset{\text{O}}{\parallel}\text{C—}$ group).

The aldoses and ketoses are further divided into sub-groups, on the basis of the number of carbon atoms in their molecules as trioses, tetroses, etc. To classify a monosaccharide completely, it is necessary to specify both, the type of the carbonyl group and the number of carbon atom present in the molecule. Thus monosaccharides are generally referred to as aldotrioses, ketotrioses, aldotetroses, ketotetroses, etc.

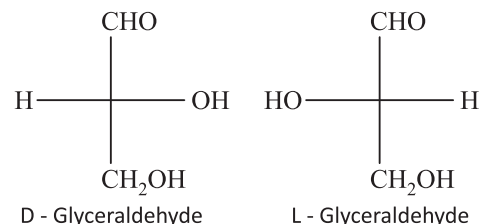
The aldoses and ketoses may be represented by the following general formulas.



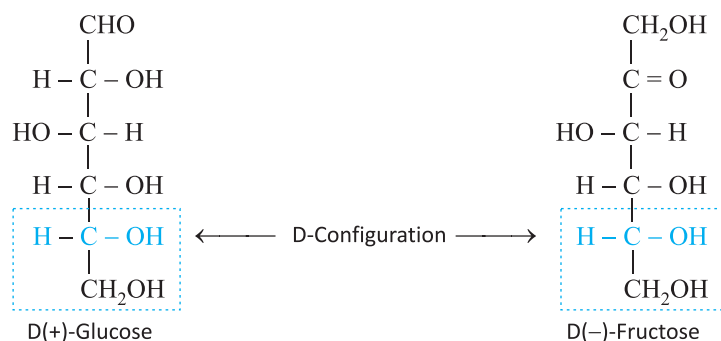
Except ketotriose (dihydroxy acetone), all aldoses and ketoses contain **asymmetric carbon** atoms and are **optically active**. The enantiomers which rotate the plane of plane polarised light to the right are written as (+), the others which rotate to the left are written as (–). The (+) and (–) signs only specify the direction of rotation of the plane polarised light by a particular enantiomer but it does not give any indication of the arrangement of OH and H around the asymmetric carbon atom. Maximum number of optical isomers is 2^n where n is the number of asymmetric carbon atoms in the molecule.

Note : Aldohexoses exist in sixteen optically active forms, i.e., Glucose, Mannose, Galactose, Allose, Altrose, Idose, Gulose and Talose and each existing in two forms.

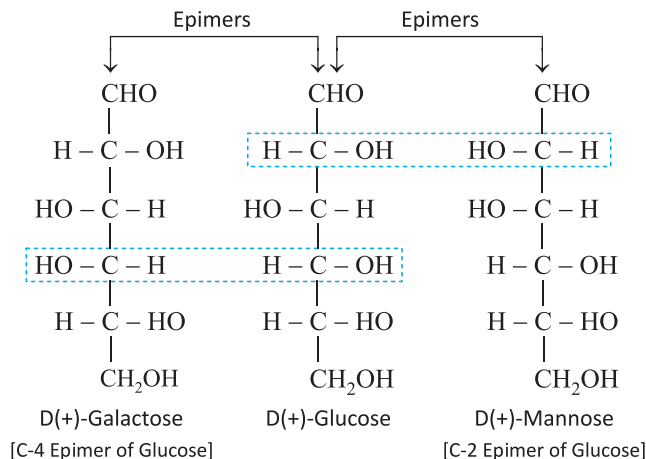
Glyceraldehyde contains one asymmetric carbon atom and can thus exist in two optically active forms, called the D-form (–OH group on the **right side** of lowest asymmetric carbon) and the L-form (–OH group on the **left side** of lowest asymmetric carbon).



The sugars having same configuration as of D-Glyceraldehyde are known as **D-sugars** while that of L-Glyceraldehyde as **L-sugars**. Glucose, an aldose, and Fructose, a ketose, are most important monosaccharides. The natural form of Glucose and Fructose are D-forms.



Note : Epimers: A pair of diastereomers that differ only in the configuration about a single carbon atom are said to be **epimers**, e.g., D(+)-Glucose is epimeric with D(+)-Mannose and D(+)-Galactose.

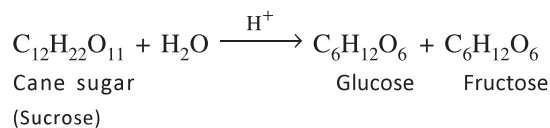


Glucose [C₆H₁₂O₆] (Aldo-Hexose) :

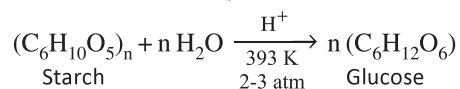
As glucose occurs in nature as the optically active dextro-rotatory isomer, it is known as **dextrose**. It is also called as **grape sugar**. In combined form, it occurs in cane sugar, polysaccharides such as starch and cellulose. It is also present in various glycosides like Amygdalin and Salicin.

Preparation :

- Laboratory Method :** It is prepared in laboratory by acid hydrolysis of cane sugar in presence of alcohol.



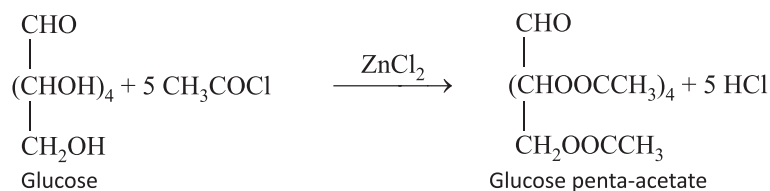
- Manufacture :** It is obtained on a large scale by the hydrolysis of starch (corn starch or potato starch) with dilute sulphuric acid or HCl.



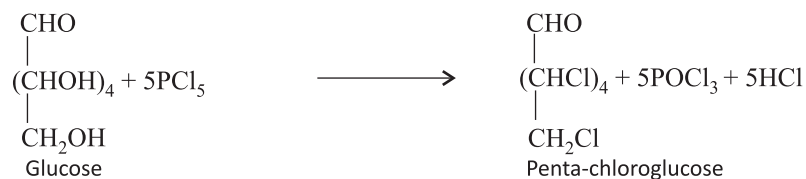
Property :

- It is a colourless crystalline solid, readily soluble in water, with melting point as 146°C.
- From aqueous solution, it separates out as a crystalline monohydrate (C₆H₁₂O₆·H₂O) which melts at 86°C.
- It is sparingly soluble in alcohol but insoluble in ether.
- It shows characteristic of hydroxyl and aldehydic group.
- Alcoholic Reaction: (Reactions due to -OH group) :**

(i) Reaction with acid chloride and acid anhydrides :



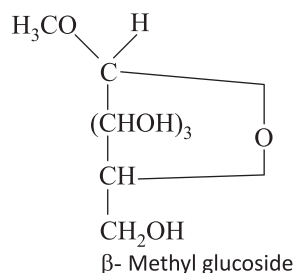
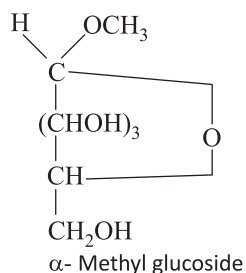
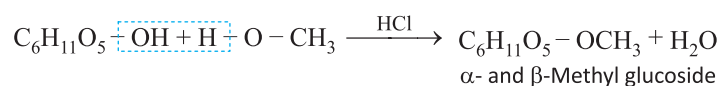
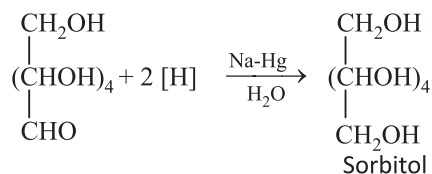
This shows that a molecules of glucose contains 5-OH groups.

(ii) Reaction with PCl_5 :

(iii) Reaction with metallic hydroxides : Glucose behaves as a weak acid. It reacts with certain metallic hydroxides like $\text{Ca}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$, etc. to form metallic glucosates, which are soluble in water.



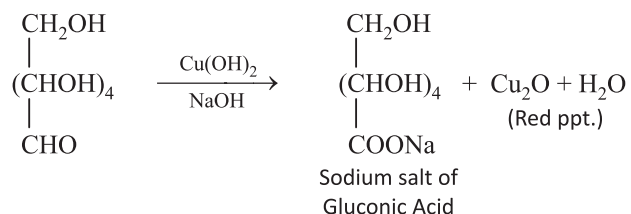
(iv) Formation of Glycosides : When treated with methyl alcohol in presence of dry HCl gas, glucose yields mono-methyl ether which is actually a mixture of α - and β -forms indicating that one of the $-\text{OH}$ group is different from others.

**6. Reactions of carbonyl Group (Aldehydic group) :****(i) Reduction :**

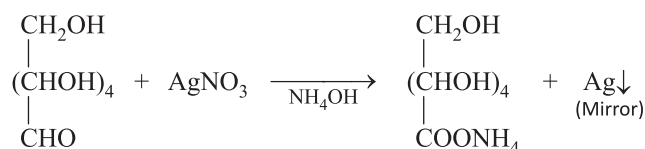
On prolonged heating with concentrated HI and red phosphorus at 110°C , glucose forms a mixture of 2-iodohexane and n-hexane.

(ii) Oxidation : Glucose undergoes oxidation with various oxidising agents readily, i.e., glucose acts as a **reducing agent**.

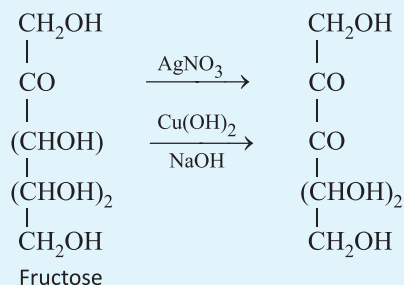
(a) **Reaction with Fehling's solution:** With Fehling's solution, a **red precipitate** of cuprous oxide is formed.



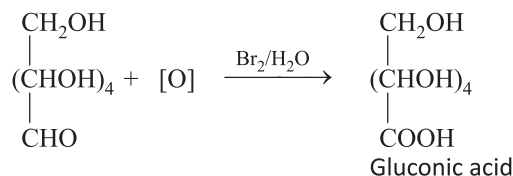
(b) **Reaction with Tollen's Reagent :** With ammonical AgNO_3 , a **silver mirror** or black precipitate is formed.



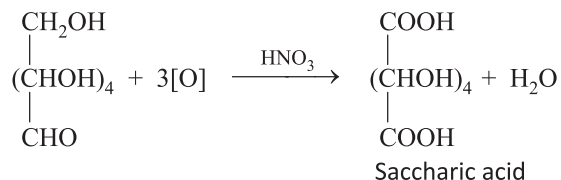
Note : Fructose being an α -hydroxyl ketone also gives positive result with Tollen's Reagent and Fehling's solution. Hence **fructose** is also a **reducing sugar**.



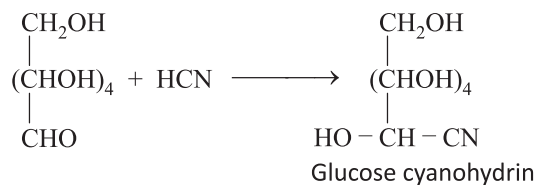
(c) **Reaction with Bromine Water :**



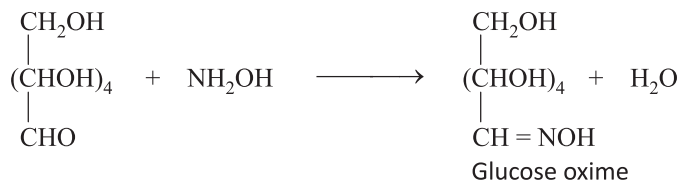
(d) **Reaction with Nitric acid :** Nitric acid or any other strong oxidising agent converts glucose to saccharic acid or **glucaric acid** containing same number of carbon atoms.



(iii) Reaction with HCN :

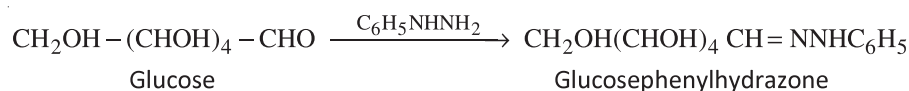


(iv) Reaction with Hydroxylamine :

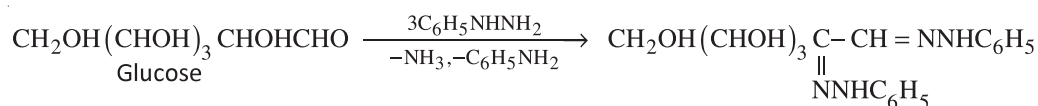


(v) Reaction with phenylhydrazine (Fischer's mechanism) :

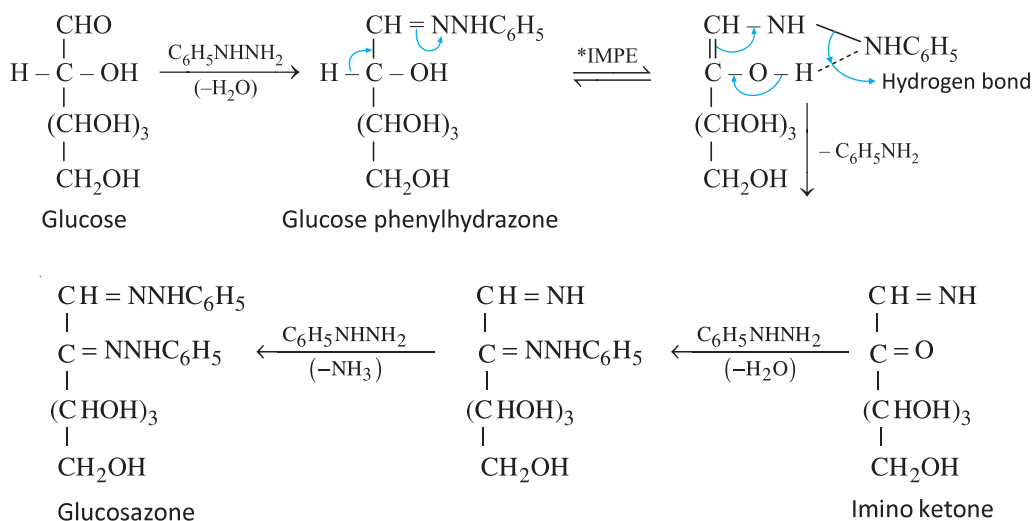
With limited amounts of phenylhydrazine, glucose forms a phenylhydrazone.



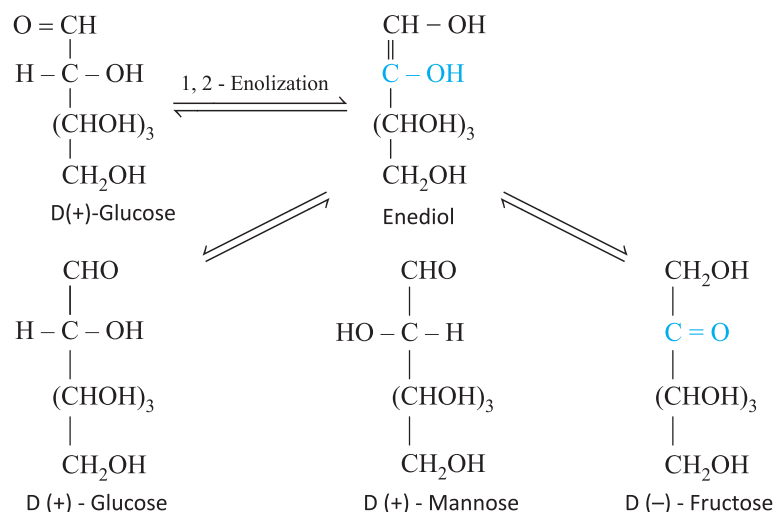
With an excess of phenylhydrazine, the reaction is some what more complicated. **Three moles** of phenylhydrazine are consumed for each mole of the glucose to form **glucosazone**, a yellow crystalline solid containing two phenylhydrazine residues per molecule.



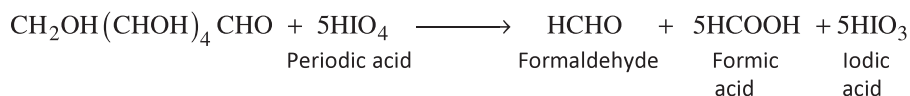
It was suggested that the second molecule of phenylhydrazine **oxidise** the hydroxyl group adjacent to the aldehyde group, followed by the reaction of the carbonyl group so generated with the third molecule of phenylhydrazine. (* IMPE is intramolecular proton exchange)



(vi) Action of Alkalies-Lobry de Bruyn van Ekenstein Rearrangement :

(vii) Reaction with HIO_4 :

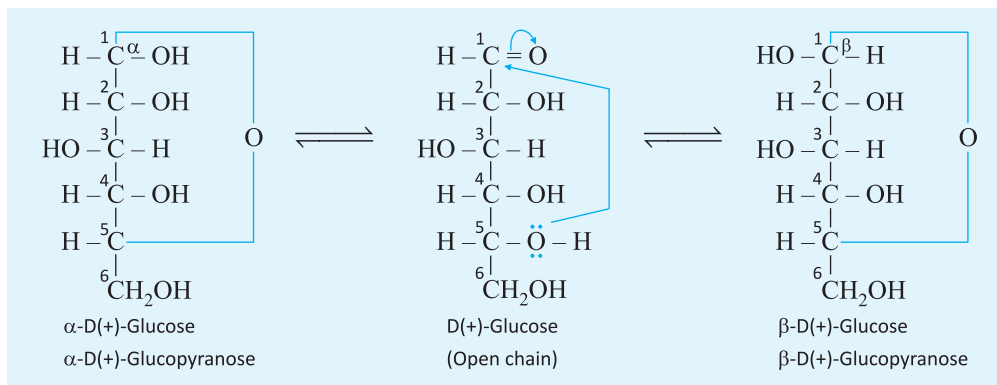
Being an α -hydroxy carbonyl compound containing a number of vic-hydroxyl groups, glucose undergoes oxidative cleavage with specific oxidising agents like periodic acid (Malaprade reagent) and lead tetra-acetate.



This reaction has a great potential for application to structure determination of glycols, and it has been extensively used in carbohydrate research for structure determination.

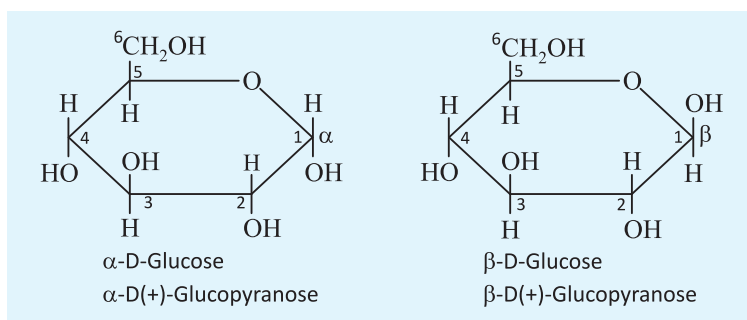
Note : Monosaccharides exist as **cyclic structures** in the form of **hemiacetals**. Thus glucose forms a six membered ring of five carbon atoms and one oxygen atom (**Pyranose form**).

Anomers : In the cyclic structures of monosaccharides, C_5-OH of glucose combines with C_1 aldehydic group. As a result C_1 becomes **chiral** or asymmetric and thus has two possible arrangements of $-\text{H}$ and $-\text{OH}$ groups around it, i.e. $-\text{OH}$ group may be on **right side** at C_1 (**α -D-Glucose**) or on the **left side** of C_1 (**β -D-Glucose**). Such pair of stereoisomers which differ in configuration only around C_1 are called **anomers**. C_1 carbon atom is called **anomeric carbon**.

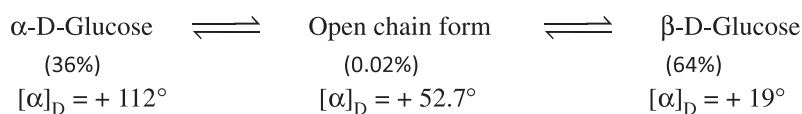


Fischer projection formula of cyclic form and open chain form.

Haworth projection formula of cyclic form



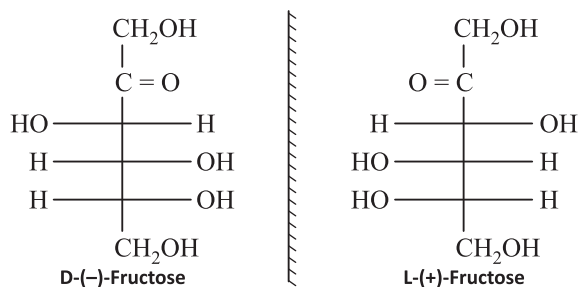
Mutarotation : The change in specific rotation of an optically active compound in solution with time to an equilibrium value is called as **mutarotation**, e.g., when either of the stereoisomeric forms of glucose, i.e., α -D-glucose and β -D-glucose, is dissolved in water and allowed to stand, it gets converted into equilibrium mixture through a small amount of an open chain form.



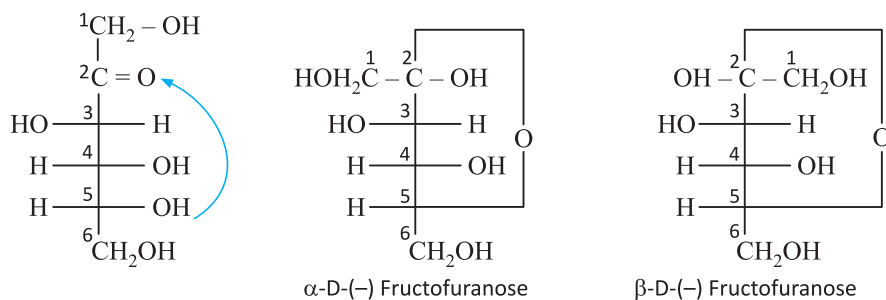
Fructose [$\text{C}_6\text{H}_{12}\text{O}_6$] (Keto-Hexose) :

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

Open Chain Structure of Fructose :



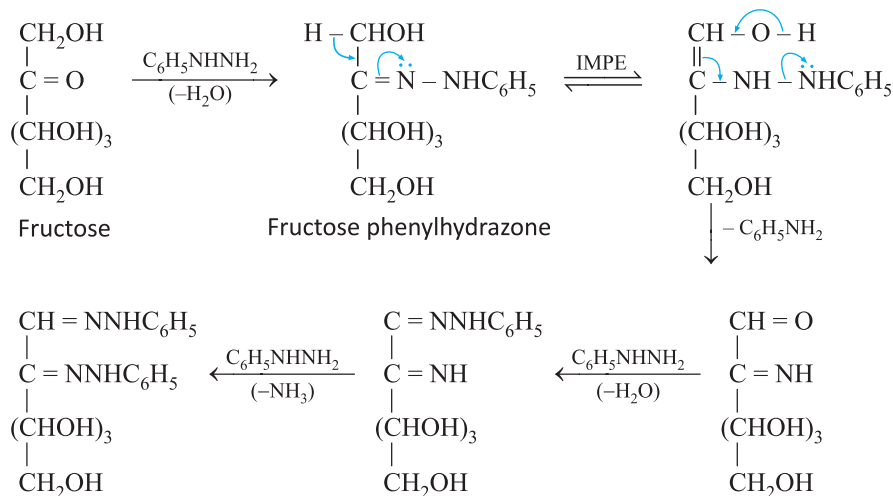
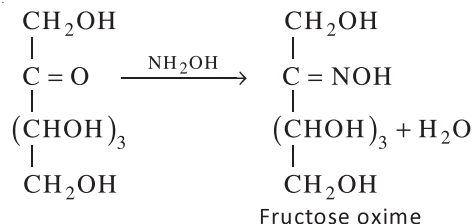
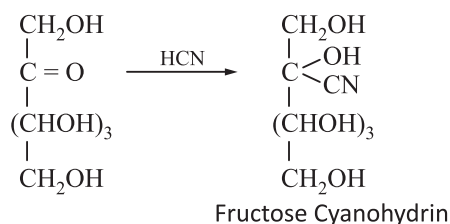
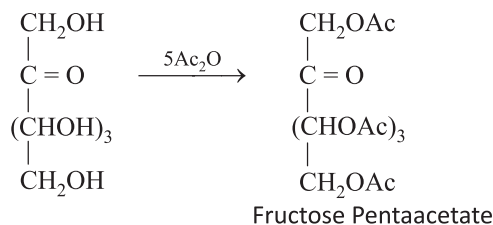
➤ Fructose also undergoes cyclisation process by **hemi-ketal** formation to result in a five-membered ring like **furan**.

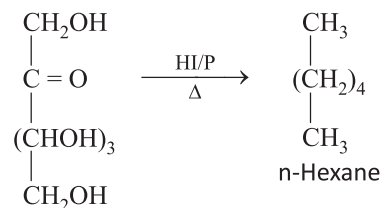


Reaction of Fructose :**(i) Reaction with Phenylhydrazine :**

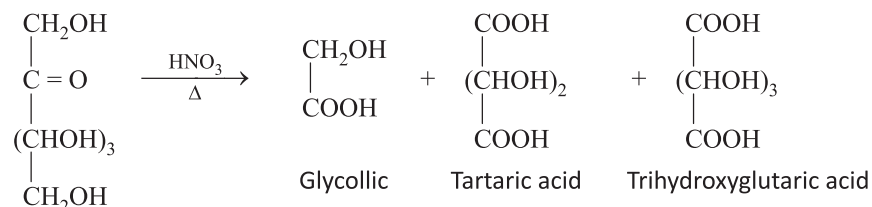
Equimolar amounts of fructose and phenylhydrazine react to form fructose phenylhydrazone, but with excess of phenylhydrazine, fructose yields the **same osazone** as that obtained from glucose.

As in the case of glucose, formation of glucosazone from fructose can be explained as follows:

**(ii) Reaction with NH_2OH :****(iii) Reaction with HCN :****(iv) Reaction with Acetic anhydride :**

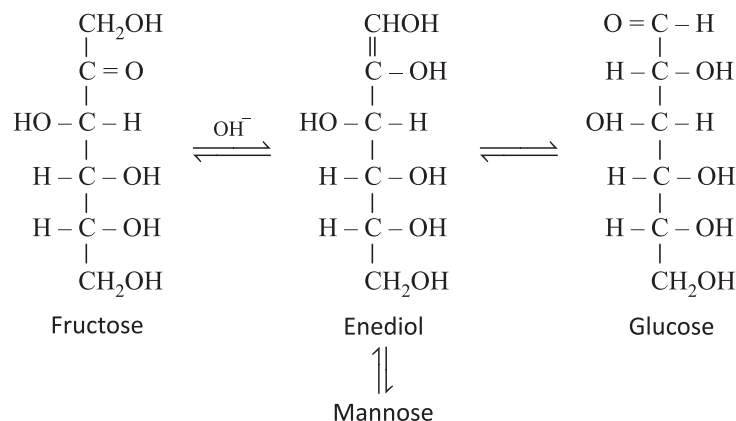
(v) Reaction with Red P and HI :**(vi) Oxidation by Nitric Acid :**

On oxidation with HNO_3 , fructose yields a mixture of acids, namely trihydroxyglutaric acid, tartaric acid and glycollic acid. Each of these acids contains a fewer number of carbon atoms than fructose, thereby suggesting that the carbonyl group in fructose is a keto group and not an aldehyde group.

**(vii) Action of Alkalies on Fructose :**

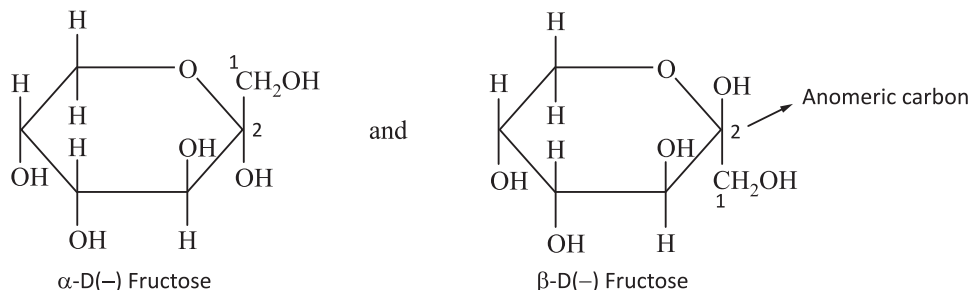
This reaction is known as Lobry de Bruyn and Alberda Van Elkenstein rearrangement or simply Elkenstein rearrangement.

On warming with dilute alkali fructose like glucose, gives rise to an equilibrium mixture of glucose, fructose and mannose. The ability of fructose (a ketose) to reduce [Fehling solution](#) and [Tollen's reagent](#) is possibly due to this initial isomerisation of fructose to glucose and mannose which are being aldoses are capable to reduce Fehling solution and Tollen's reagent.

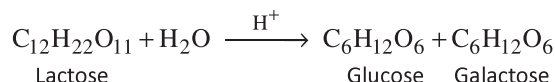
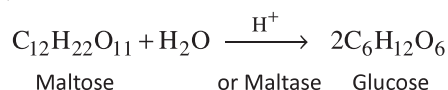
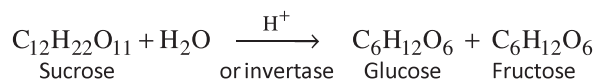


Haworth projection formula of Fructose :

Just like glucose, D (–) fructose also exists in two forms α and β forms, which exhibit **mutarotation**. By reasoning similar to that used earlier in the case of glucose D(–) fructose was assigned a six-membered structure or a **pyranose** ring structure and the α , and β -forms can be depicted as follows

**Disaccharides :**

Carbohydrates which upon hydrolysis give two molecules of the same or different monosaccharides are called disaccharides. Their general formula is $C_{12}H_{22}O_{11}$. The three most important disaccharides are **sucrose**, **maltose** and **lactose**.

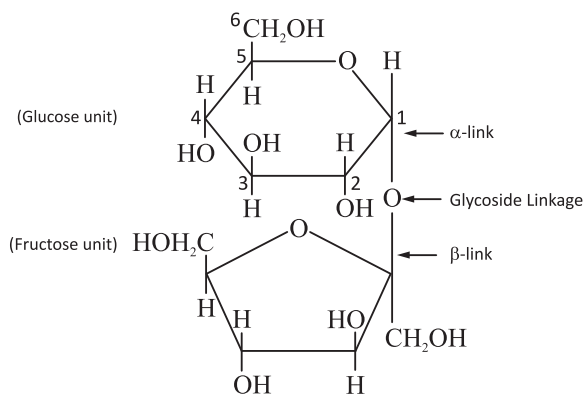


Disaccharides may also be considered to be formed by a condensation reaction between two molecules of the same or different monosaccharides with the elimination of a molecule of water. This reaction involves the formation of an acetal from a hemiacetal and alcohol - in which one of the monosaccharides acts as the hemiacetal while the other acts as the alcohol.

Sucrose [$C_{12}H_{22}O_{11}$] :

It is also called cane sugar. It is our common table sugar. It is obtained from cane-sugar and sugarbeets. It is actually found in all photosynthesis plants.

It is formed by condensation of one molecule of glucose and one molecule of fructose. Unlike maltose and Lactose, it is **non-reducing sugar** since both glucose ($C_1 - \alpha$) and fructose ($C_2 - \beta$) are connected to each other through their **reducing centres**.

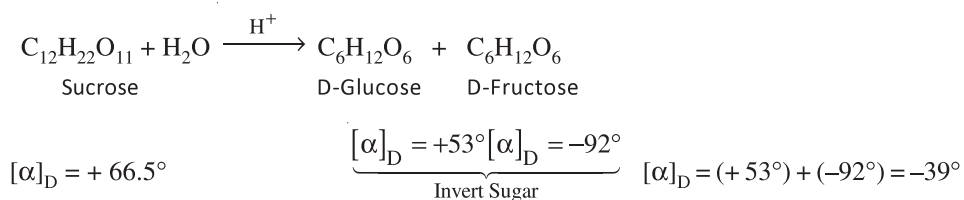


Properties :

1. It is a colourless, odourless crystalline compound, with melting point as 185°–186°C.
2. It is very soluble in water, slightly soluble in alcohol and insoluble in ether.
3. It is dextro-rotatory but does not show **mutarotation**.
4. It is a non-reducing sugar as it does not reduce Fehling's solution or Tollen's reagent.
5. On heating, slowly and carefully, it melts and then if allowed to cool, it solidifies to pale yellow glassy mass called 'Barley Sugar'. When heated at 200°C, it loses water to form brown amorphous mass called caramel. On strong heating, it chars to almost pure carbon giving smell of burnt sugar.

Inversion of Cane - Sugar :

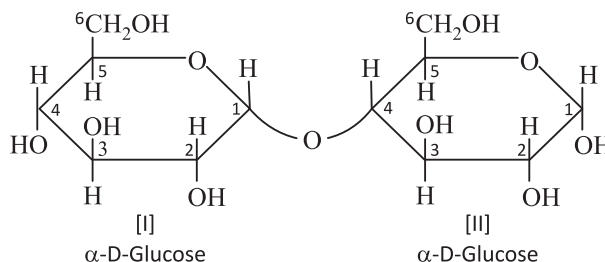
The hydrolysis of sucrose by boiling with HCl, produces a mixture of equal molecules of D-Glucose and D-Fructose.



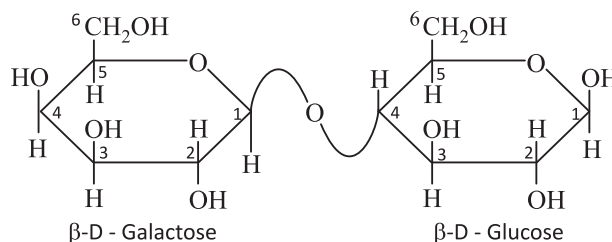
Sucrose solution is dextro-rotatory. Its specific rotation is + 66.5°. But on hydrolysis, it's solution become laevorotatory, because D-fructose has a greater specific rotation than D-glucose. Because of this, the hydrolysis of sucrose is known as the inversion of sucrose, and the equimolecular mixture of glucose and fructose is known as invert sugar or invertose.

Maltose :

- It is composed of 2 α-D-glucose units joined together by C₁ – C₄ **glycosidic linkage**.
- It is a reducing sugar as free-aldehydic group can be produced at the C₁ of 2nd glucose.

**Lactose :**

- It is formed by glycosidic linkage between C₁ of β-D-galactose and C₄ of β-D-glucose.
- It is also reducing in nature



- Note :**
- Galactose : 3 and 4 abnormal
 - Mannose : 2 and 3 abnormal
 - Sucrose : C1-C2 (α-D glucose and β-D fructose)
 - Lactose : C1-C4 (β-D galactose and β-D glucose)
 - Maltose : C1-C4 (α-D glucose and α-D glucose)
 - Amylose : Polymer of α Glucose
 - Cellulose : C1-C4 (Polysaccharide of β-D glucose).

Polysaccharides : They contain a large number of monosaccharide units joined together by glycosidic linkages.

I. Starch : It is a polymer of α -glucose and consists of two components :

(a) Amylose :

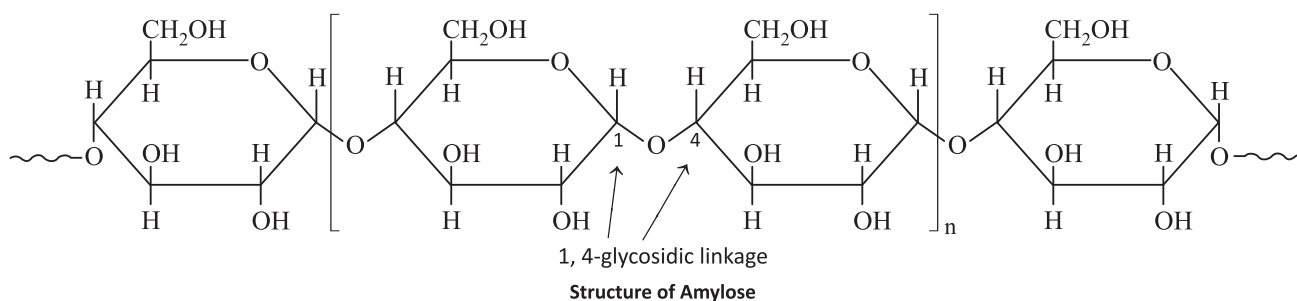
- It is a water soluble component.
- It constitutes about 15-20% of starch.
- It is a long unbranched chain with α -D-(+)-glucose units joined together by $C_1 - C_4$ glycosidic linkage.

(b) Amylopectin :

- It is insoluble in water.
- It constitutes about 80-85% of starch.
- It is a branched chain polymers 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.

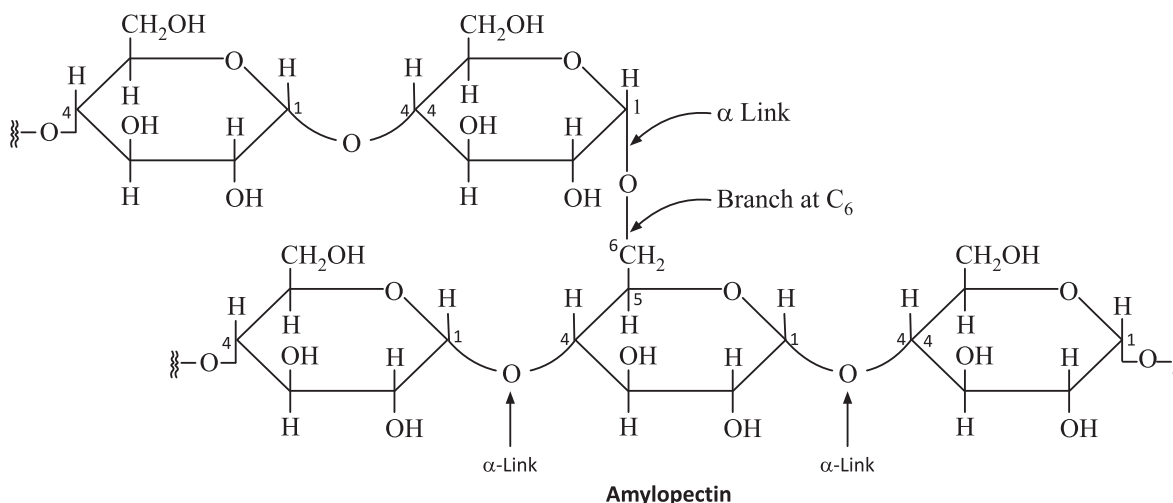
Structure of Starch :

Amylose and Amylopectin are both different carbohydrates of high molecular weight and formula $(C_6H_{10}O_5)_n$. The polysaccharide amylose is made up of long straight chains each containing about 200 or more D-glucose units joined together by a 1,4-linkage.



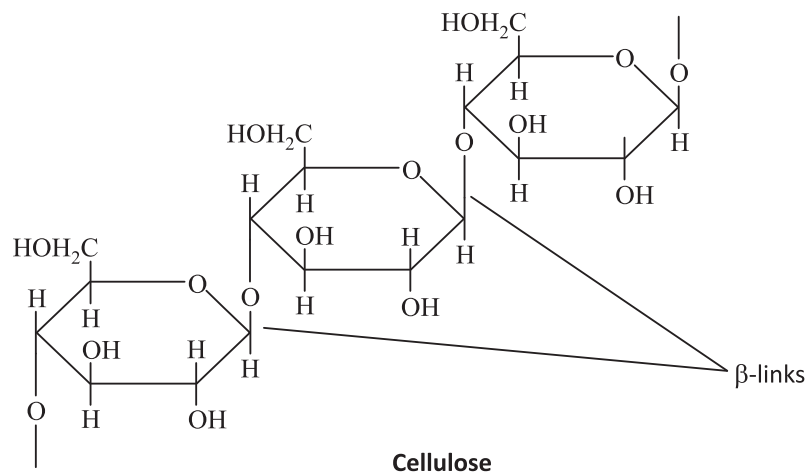
Molecular weight of amylose lies between 30,000 to 40,000.

The polysaccharide amylopectin consists of chains of D-Glucose units each unit joined by a glycosidic linkage to C-4 of the next unit. Further investigation reveals that amylopectin is **highly branched** structure consists of several short chains of about 20 glucose units each, one end of each of these chains being joined through C-1 to C-6 on the next chain.



II. Cellulose :

- It is a straight chain polysaccharide composed of β -D-glucose units held together by $C_1 - C_4$ glycosidic linkage.



- III. Glycogen :** Carbohydrates are stored in animal body as Glycogen. When Body needs glucose, enzymes break the glycogen down to glucose. It is found in liver, muscles brain, yeast and fungi. It is also known as animal starch because its structure is similar to amylopectin and is rather more highly branched.

Analysis of Carbohydrates :

The following reactions characterizes the carbohydrates as a class of organic compounds :

(i) Molisch Test :

For this test 2,3 drops of a 1% alcoholic solution of α -naphthol is added to a 5% aqueous solution of the organic compound (suspected to be a carbohydrate), followed by a careful addition of about 2 ml of conc. sulphuric acid.

“Formation of a deep **violet ring** at the junction of the liquids indicates the presence of a carbohydrate”.

The violet ring formed in this test is believed to be due to the formation of an unstable condensation product of α -naphthol with furfural formed presumably by the cyclodehydration of the carbohydrate with the acid.

(ii) Action of Heat :

When heated strongly in a dry test tube, carbohydrates generally char and give out the smell of burnt sugar.

(iii) Action of conc. H_2SO_4 :

When warmed with conc. H_2SO_4 carbohydrates show immediate blackening.

If a carbohydrate has been indicated by the above test, the following tests are used to distinguish reducing carbohydrates from non-reducing carbohydrates, only reducing carbohydrates respond to these tests.

(i) Fehling test

(ii) Tollen's test

These test are already described in an earlier chapter of Aldehyde and Ketones.