BIOMOLECULES

TOPIC-1

Carbohydrates

VERY SHORT ANSWER QUESTIONS

1. Define carbohydrates.

Ans: **Old Definition**: The group of compounds known as carbohydrates received their general name because of early observations that they often have the formula $C_x(H_2O)_y$ - that is, they appear to be hydrates of carbon.

New definition: Carbohydrates are defined as polyhydroxy aldehydes or polyhydroxy ketones or substances which give these on hydrolysis and contain at least 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 group of the molecule in the form of hemiacetals and hemiketals respectively.

2. **What are the limitations of old definition?**

Ans: Limitations of the old definition: The above definition could not survive long due to the following reasons:

(i) A number of compounds such as rhamnose, ($C_6H_{12}O_5$) and 2-deoxyribose ($C_5H_{10}O_4$) are known which are carbohydrates by their chemical behaviour but cannot be represented as hydrates of carbon.

(ii) There are other substances like formaldehyde (HCHO, CH_2O) and acetic acid [CH_3COOH, $C_2(H_2O)_2$] which do not behave like carbohydrates but can be represented by the general formula, $C_x(H_2O)_y$.

3. What are monosachharides?

Ans: **Monosaccharides**: The monosaccharides are polyhydroxy aldehydes or polyhydroxy ketones which cannot be decomposed by hydrolysis to give simpler carbohydrates. Examples are glucose and fructose, both of which have molecular formula, $C_6H_{12}O_6$.

$$\underset{\text{glucose or fructose}}{C_6H_{12}O_6} + H_2O \xrightarrow{H^+} \text{No reaction}$$

4. What are oligo sachharides?

Ans: **Oligosaccharides**: The oligosaccharides (Greek, oligo, few) are carbohydrates which yield a definite number (2-9) of monosaccharide molecules on hydrolysis. They include,

(a) Disaccharides, which yield two monosaccharide molecules on hydrolysis. Examples are sucrose and maltose, both of which have molecular formula, $C_{12}H_{22}O_{11}$.

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{glucose}}{2C_6H_{12}O_6}$$

5. What are tri-sachharides?

Ans: **Trisaccharides,** which yield three monosaccharide molecules on hydrolysis. Example is raffinose, which has molecular formula, $C_{18}H_{32}O_{16}$.

$$\underset{\text{raffinose}}{C_{18}H_{32}O_{16}} + 2H_2O \xrightarrow{H^+} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6} + \underset{\text{galactose}}{C_6H_{22}O_6}$$

6. What are poly-sachharides?

Ans: Polysaccharides: The polysaccahrides are carbohydrates of high molecular weight which yield many monosaccharide molecules on hydrolysis. Examples are starch and cellulose, both of which have molecular formula, $(C_6H_{10}O5)_n$.

$$\underset{\text{starch}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{H^+} \underset{\text{glucose}}{nC_6H_{12}O_6}$$

In general, the monosaccharides and oligosaccharides are crystalline solids, soluble in water and sweet to taste. They are collectively known as sugars. The polysaccharides, on the other hand, are amorphous, insoluble in water and tasteless. They are called non-sugars. The carbohydrates may also be classified as either reducing or non-reducing sugars. All those carbohydrates which have the ability to reduce Fehling's solution and Tollen's reagent are referred to as reducing sugars, while others are non-reducing sugars. All monosaccharides and the disaccharides other than sucrose are reducing sugars.

7. Explain mutarotation.

Ans: **<u>MUTAROTATION</u>**

The two stereoisomeric forms of glucose, i.e., α-D-glucose and β-D-glucose exist in separate crystalline forms and thus have different melting points and specific roations. For example α-D-glucose has a m.p. of 419 K with a specific rotation of +112° while β-D-glucose has a m.p. of 424 K and has a specific rotation of +19°. However, when either of these two forms is dissolved in water and allowed to stand, it gets converted into an equilibrium mixture of α-and β-forms through a small amount of the open chain form.

$$\alpha\text{-D-Glucose (36\%)} \rightleftharpoons \text{Open chain form (0.02\%)} \rightleftharpoons \beta\text{-D-Glucose (64\%)}$$

As a result of this equilibrium, the specific rotation of a freshly prepared solution of α-D-glucose gradually decreases from of +112° to +52.7° and that of β-D-glucose gradually increases from +19° to +52.7°.

$$\underset{[\alpha]_D = +112^\circ}{\alpha\text{-D-Glucose}} \rightleftharpoons \underset{[\alpha]_D = +52.7^\circ}{\text{Equilibrium mixture}} \rightleftharpoons \underset{[\alpha]_D = +19^\circ}{\beta\text{-D-Glucose}}$$

Where $[\alpha]_D$ = specific rotation

This change in specific rotation of an optically active compound in solution with time, to an equilibrium value, is called mutarotation. During mutarotation, the ring opens and then recloses either in the inverted position or in the original position giving a mixture of α-and-β-forms. All reducing carbohydrates, i.e., monosaccharides and disacchardies (maltose, lactose etc.) undergo mutarotation in aqueous solution.

8. **Explain the classificatio of carbohydrates based on taste.**

Ans: Sugars: Sugars are monosaccharides and oligosaccharides are crystalline solids soluble in water and sweet in taste are called sugars.

Nonsugars : These are polysaccharides which are amorphous solids insoluble in water and taste less called reducing sugars while others which do not reduced.

SHORT ANSWER QUESTIONS

1. Explain the classification of Carbohydrates.

Ans: <u>Classification Of Carbohydrates</u>

The carbohydrates are divided into three major classes depending upon whether or not they undergo hydrolysis, and if they do, on the number of products formed.

(i) **Monosaccharides**: The monosaccharides are polyhydroxy aldehydes or polyhydroxy ketones which cannot be decomposed by hydrolysis to give simpler carbohydrates. Examples are glucose and fructose, both of which have molecular formula, $C_6H_{12}O_6$.

$$\underset{\text{glucose or fructose}}{C_6H_{12}O_6} + H_2O \xrightarrow{H^+} \text{No reaction}$$

ii) **Oligosaccharides**: The oligosaccharides (Greek, oligo, few) are carbohydrates which yield a definite number (2-9) of monosaccharide molecules on hydrolysis. They include,

(a) Disaccharides, which yield two monosaccharide molecules on hydrolysis. Examples are sucrose and maltose, both of which have molecular formula, $C_{12}H_{22}O_{11}$.

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$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{glucose}}{2C_6H_{12}O_6}$$

(b) **Trisaccharides**, which yield three monosaccharide molecules on hydrolysis. Example is raffinose, which has molecular formula, $C_{18}H_{32}O_{16}$.

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(c) **Tetrasaccharides**, etc.

(iii) Polysaccharides: The polysaccahrides are carbohydrates of high molecular weight which yield many monosaccharide molecules on hydrolysis. Examples are starch and cellulose, both of which have molecular formula, $(C_6H_{10}O5)_n$.

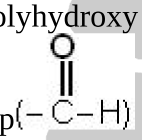
$$\underset{\text{starch}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{H^+} \underset{\text{glucose}}{nC_6H_{12}O_6}$$

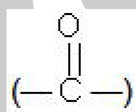
In general, the monosaccharides and oligosaccharides are crystalline solids, soluble in water and sweet to taste. They are collectively known as sugars. The polysaccharides, on the other hand, are amorphous, insoluble in water and tasteless. They are called non-sugars. The carbohydrates may also be classified as either reducing or non-reducing sugars. All those carbohydrates which have the ability to reduce Fehling's solution and Tollen's reagent are referred to as reducing sugars, while others are non-reducing sugars. All monosaccharides and the disaccharides other than sucrose are reducing sugars.

2. Explain how mono-sachharideas are classified.

Ans: MONOSACCHARIDES

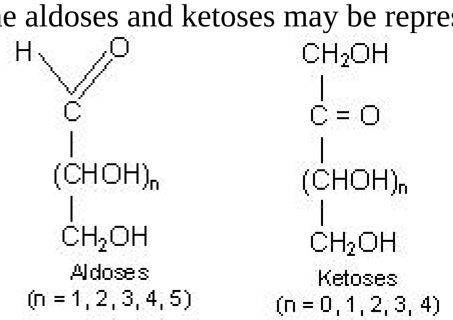
The monosaccharides are the basis of carbohydrate chemistry since all carbohydrates are either monosaccharides or are converted into monosaccharides on hydrolysis. The monosaccharides are polyhydroxy aldehydes or polyhydroxy ketones. There are,

1. The Aldoses, which contain an aldehyde group 

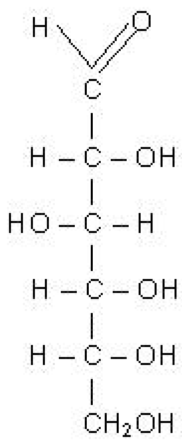
2. The Ketoses, which contain a ketone group 

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, pentoses, hexoses, etc. To classify a monosaccharide completely, it is necessary to specify both, the type of the carbonyl group and the number of carbon atoms present in the molecule. Thus monosaccharides are generally referred to as aldotrioses, aldotetroses, aldopentoses, aldohexoses, ketohexoses, etc.

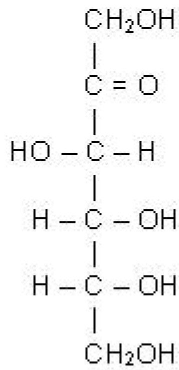
The aldoses and ketoses may be represented by the following general formulas.



Glucose and fructose are specific examples of an aldose and a ketose.



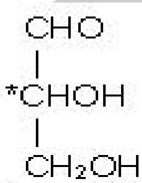
Glucose (an aldohexose)



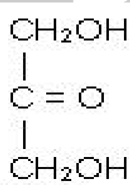
fructose
(a ketohexose)

3. **Explain what are trioses?**

Ans: **<u>Trioses</u> :** D and L Terminology: The simplest of all carbohydrates that fit the definition we have given for carbohydrates are the trioses, glyceraldehyde and dihydroxyacetone. Glyceraldehyde is aldotriose, and dihydroxyacetone is a ketotriose.

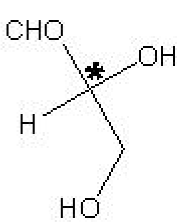


Glyceraldehyde
(an aldotriose)

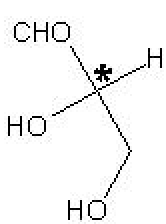


Dihydroxyacetone
(a ketotriose)

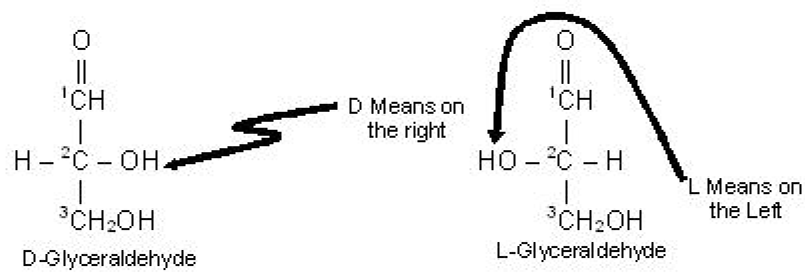
Glyceraldehyde cont¬ains one asymmetric carbon atom (marked by an asterisk) and can thus exist in two optically active forms, called the D-form and the L-form. Clearly, the two forms are mirror images that cannot be superimposed, that is they are enantiomers.



D-Glyceraldehyde

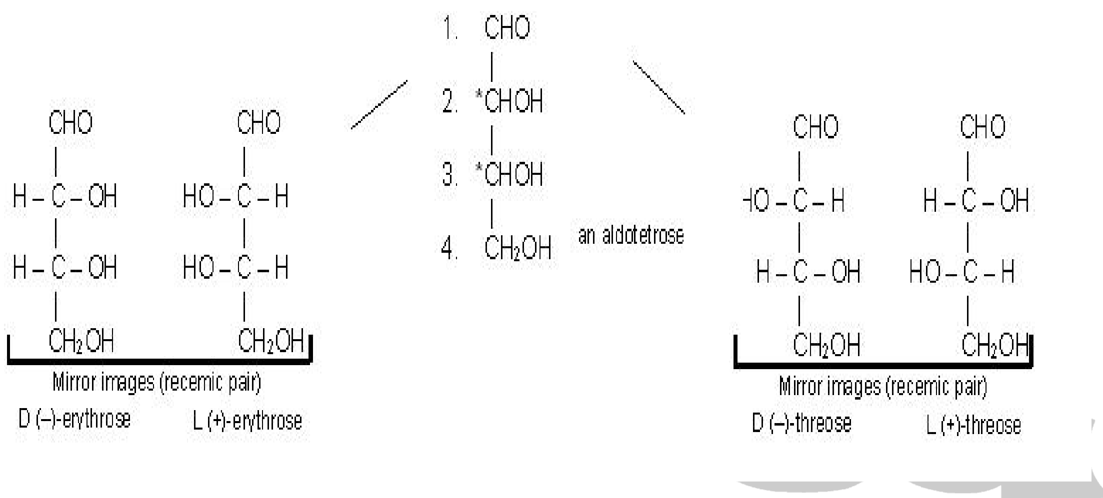


L-Glyceraldehyde



4. **Explain what are aldotetroses?**

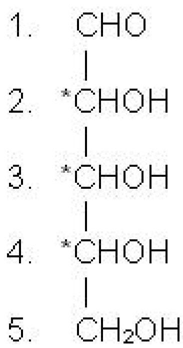
Ans: **<u>Aldotetroses</u>:** If we examine the general formula of an aldotetrose, we see that they contain two asymmetric carbon atoms (marked by asterisks).
This means that 2^2 or 4 optical isomers are possible. They may be represented as the following two pairs:



All four isomers have been prepared synthetically. The D- and L-erythrose are mirror images, that is, they are enantiomers. They have exactly the same degree of rotation but in opposite directions. Equal amounts of the two would constitute a racemic mixture, that is, a mixture that would allow a plane-polarised light to pass through the solution unchanged but could be separated into detrorotatory and laevorotatory isomers. The same comments hold for D- and L-threose. However, D-erythrose and L-threose are not images, that is, they are diastereomers (optical isomers that are not mirror images are called diastereomers), and the degree of rotation of each would probably differ.

5. **Explain what are aldopentoses?**

Ans: **<u>Aldopentoses</u> :** If we examine the general formula of an aldopentose, we see that they contain three asymmetric carbon atoms.
This means that 2^3 or 8 optical isomers are possible. These are:
- D(–) xylose, L(+)-xylose, D(–) xylose, L(–)xylose, D(–) arabinose, L(+)-arabinose, D(–)-ribose, L(+)-ribose

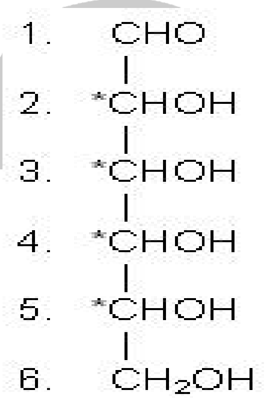


an aldopentose

6. Explain what are aldohexoses?

Ans: Aldohexoses: If we examine the general formula of aldohexose, we see that it contains four asymmetric carbon atoms. This means that 2^4 or 16 optical isomers are possible. D and L forms of altrose, allose glucose, mannose, galactose, talose, arabinose and idose

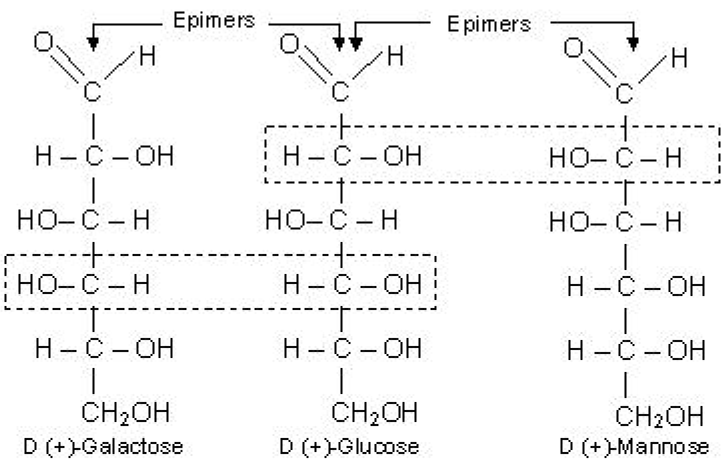
Only three of the sixteen possible aldohexoses are found in nature (all sixteen isomers have been prepared synthetically). They are D-glucose, D- mannose, and D-galactose. No one of these three optical iosmers is a mirror image of any of the others, so all three are diastereomers of each other.



an aldohexose

7. **Explain what are epimers?**

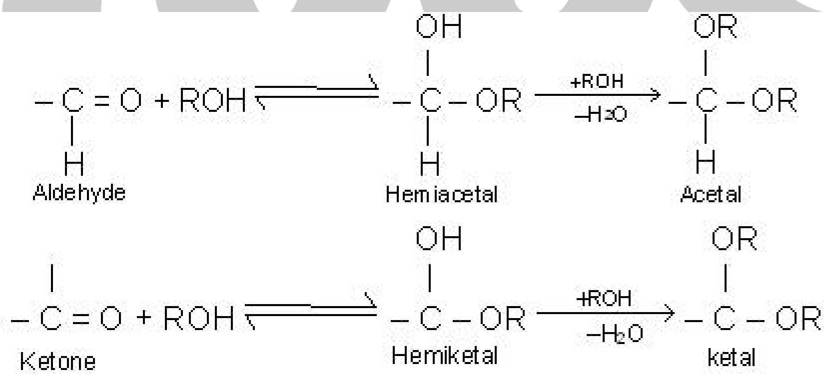
Ans: Epimers : A pair of diastereomers that differ only in the configuration about of a single carbon atom are said to be epimers. e.g D(+)- glucose is epimeric with D(+) -mannose and D(+) -galactose as shown below:



LONG ANSWER QUESTIONS

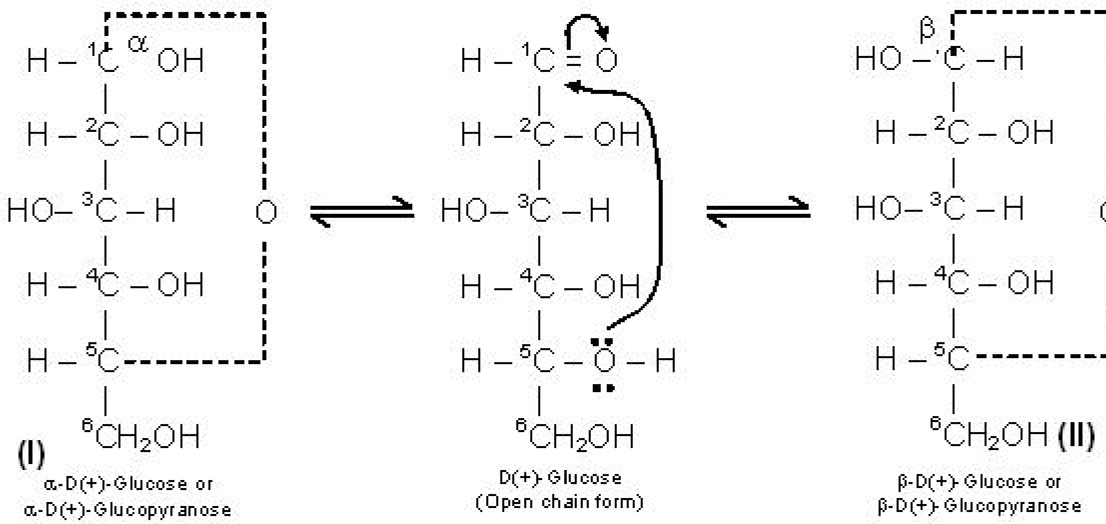
1. Explain the structure of Glucose.

Ans: Cyclic structure of Monosaccharides
We know that aldoses (and ketoses) react with alcohols to give first hemiacetals (and hemiketals) and then acetals (and ketals), i.e.



Since monosaccharides contain a number of hydroxyl groups and an aldehyde or a keto group, therefore, any one of the –OH groups (usually C4 or C5 in aldohexoses and C5 or C6 in ketohexoses) may combine with the aldehyde or the keto group to form intramolecular hemiacetal or hemiketal.

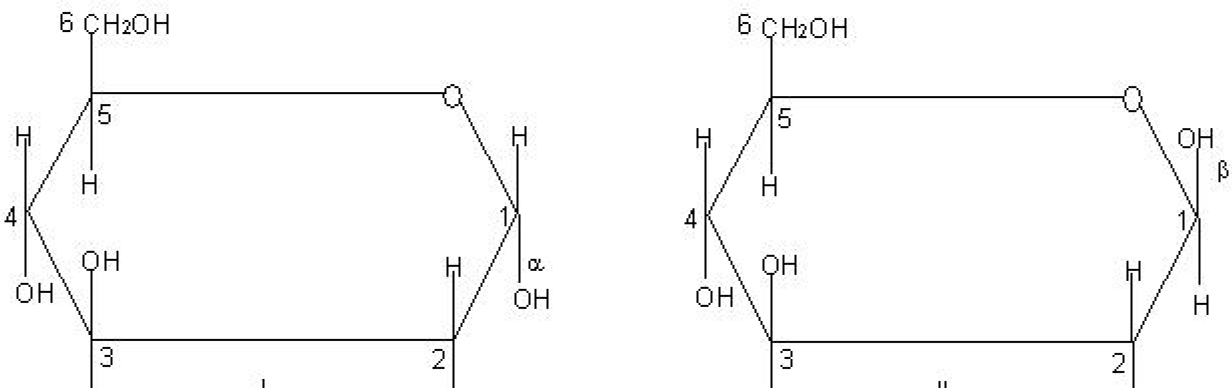
Cyclic Structure of Glucose – Anomers



We know monosaccharides have cyclic hemiacetal or hemiketal structures. To illustrate, let us first consider the example of D-glucose. During hemiacetal formation C_5 – OH of glucose combines with the C_1 – aldehydic group. As a result, C_1 becomes chiral or asymmetric and thus has two possible arrangements of H and OH groups around it. In other words, D-glucose exists in two stereoisomeric forms, i.e., α-D-glucose and β-D-glucose as shown below:

In α-D-glucose, the OH group at C_1 is towards right while in β-D-glucose, the OH group at C_1 is towards left. Such pair of stereoisomers which differ in configuration only around C_1 are called anomers and the C_1 carbon is called Anomeric carbon (or glycosidic carbon. The cyclic structures of monosaccharides can be better represented by Haworth Projection formulae. To get such a formula for any monosaccharide (say α-and β-D-glucose), draw a hexagon with its oxygen atom at the upper right hand corner. Place all the groups (on C_1, C_2, C_3 and C_4) which are present on left hand side in structures I and II, above the plane of the ring and all those groups on the right hand side below the plane of the ring.

The terminal – CH_2OH group is always placed above the plane of the hexagon ring (in D-series). Following the above procedure, Haworth Projection Formulae for α-D-glucose (I) and β-D-glucose (II) are obtained as shown below:

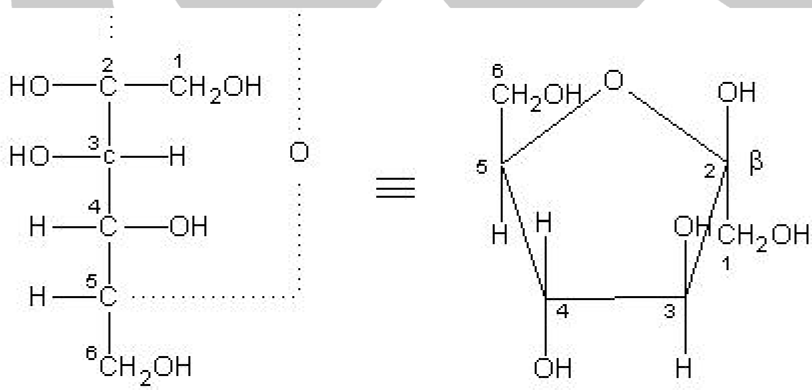


I
α-D-Glucose
or α-D(+)-Glucopyranose

II
β-D-Glucose
or β-D(+)-Glucopyranose

2. **Explain the structure of Fructose.**

Ans: <u>**Cyclic structure of Fructose:**</u> Like glucose, fructose also has a cyclic structure. Since fructose contains a keto group, it forms an intra molecular hemiketal. In the hemiketal formation, C_5– OH of the fructose combines with C_2-keto group. As a result, C_2 becomes chiral and thus has two possible arrangements of CH_2OH and OH group around it. Thus, D-fructose exists in two stereoisomeric forms, i.e., α-D-fructopyranose and β-D fructopyranose. However in the combined state (such as sucrose), fructose exists in furanose form as shown below:



β – D – Fructofuranose

MUTAROTATION

The two stereoisomeric forms of glucose, i.e., α-D-glucose and β-D-glucose exist in separate crystalline forms and thus have different melting points and specific roations. For example α-D-glucose has a m.p. of 419 K with a specific rotation of +112° while β-D-glucose has a m.p. of 424 K and has a specific rotation of +19°. However, when either of these two forms is dissolved in water and allowed to stand, it gets converted into an equilibrium mixture of α-and β-forms through a small amount of the open chain form.

$$\alpha\text{-D-Glucose}\ (36\%) \rightleftharpoons \text{Open chain form}\ (0.02\%) \rightleftharpoons \beta\text{-D-Glucose}\ (64\%)$$

As a result of this equilibrium, the specific rotation of a freshly prepared solution of α-D-glucose gradually decreases from of +112° to +52.7° and that of β-D-glucose gradually increases from +19° to +52.7°.

$$\underset{[\alpha]_D = +112^\circ}{\alpha\text{-D-Glucose}} \rightleftharpoons \underset{[\alpha]_D = +52.7^\circ}{\text{Equilibrium mixture}} \rightleftharpoons \underset{[\alpha]_D = +19^\circ}{\beta\text{-D-Glucose}}$$

Where $[\alpha]_D$ = specific rotation

This change in specific rotation of an optically active compound in solution with time, to an equilibrium value, is called mutarotation. During mutarotation, the ring opens and then recloses either in the inverted position or in the original position giving a mixture of α- and-β-forms. All reducing carbohydrates, i.e., monosaccharides and disacchardies (maltose, lactose etc.) undergo mutarotation in aqueous solution.

3. **Explain the reactions of Glucose.**

Ans: <u>REACTIONS OF GLUCOSE</u>

(a) **With HI/P**: It undergoes reduction to form n-hexane while with sodium amalgam it forms sorbitol.

$$\text{Glucose} \xrightarrow{HI/P} \underset{\text{n-hexane}}{CH_3 - (CH_2)_4 - CH_3}$$

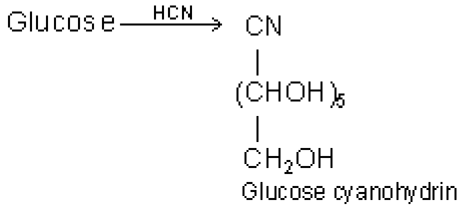
$$\text{Glucose} \xrightarrow{Na/Hg} \underset{\text{sorbitol}}{CH_2OH - (CHOH)_4 - CH_2OH}$$

(b) **With H_2O**: It forms neutral solution

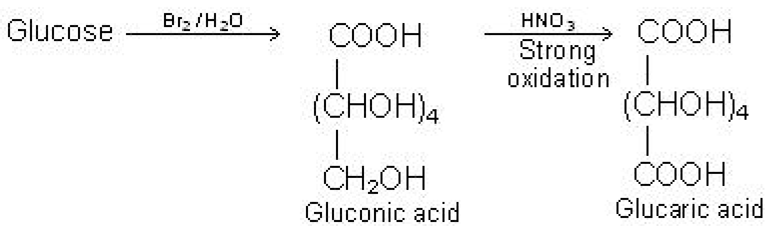
(c) **With Hydroxylamine (NH_2OH)**

$$\text{Glucose} \xrightarrow{NH_2OH} \underset{\text{Glucose oxime}}{HC{=}NOH - (CHOH)_4 - CH_2OH}$$

(d) **With HCN**: It forms addition product cyanohydrin

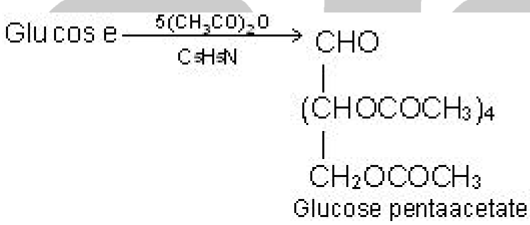


(e) **Oxidation**: Glucose on oxidation with Br_2 gives gluconic acid which on further oxidation with HNO_3 gives glucaric acid

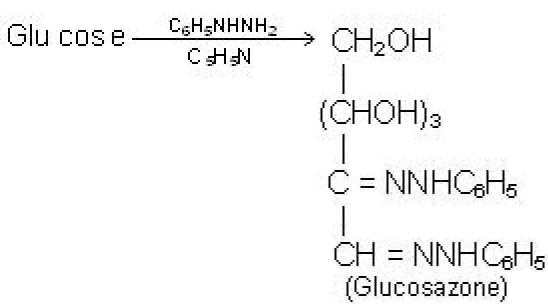


(f) With Tollen reagent and Fehling solution. Glucose forms silver mirror and red ppt. of Cu_2O respectively.

(g) With acetic anhydride. In presence of pyridine glucose forms pentaacetate.



(h) **With phenylhydrazine**: it forms glucosazone

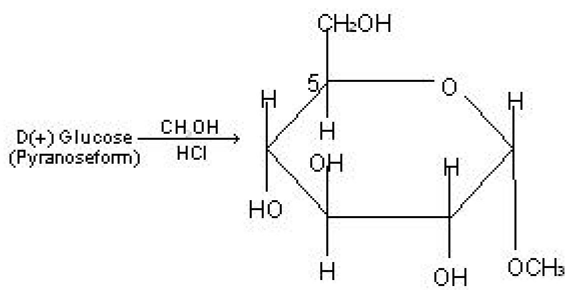


(j) **Glycoside formation**: When a small amount of gaseous HCl is passed into a solution of D (+) glucose in methanol, a reaction takes place that results in the formation of anomeric methyl acetals.

(i) **With conc. HCl acid**: Glucose gives laevulinic acid

$$\text{Glucose} \xrightarrow{\text{Conc. HCl}} \underset{\text{Laevulinic acid}}{CH_3CO \cdot CH_2CH_2 \cdot COOH} + HCOOH + H_2O$$

(j) **Glycoside formation**: When a small amount of gaseous HCl is passed into a solution of D (+) glucose in methanol , a reaction takes place that results in the formation of anomeric methyl acetals.



Methyl α-D-glucopyranoside
+
Methyl β-D-glucopyranoside

4. **Explain Disachharides.**

Ans: **<u>DISACCHARIDES</u>:** 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. Each one of these on hydrolysis with either an acid or an enzyme gives two molecules of the same or different monosaccharides as shown below:

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

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{or Maltase}]{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Glucose}}{C_6H_{12}O_6}$$

$$\underset{\text{Lactose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{or Lactase}]{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Galactose}}{C_6H_{12}O_6}$$

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

Sucrose

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 - α) and fructose (C_2 -β) are connected to each other through their reducing centres. Its structure is shown below:

Hydrolysis: (Invert Sugar or Invertose). Hydrolysis of sucrose with hot dilute acid yields D-glucose and D-fructose.

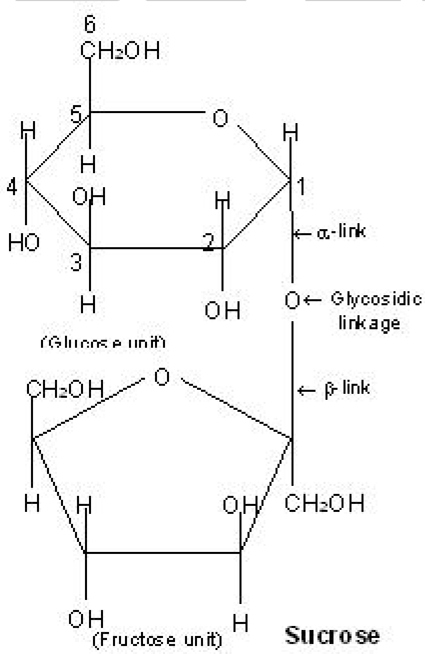
$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{D-glucose}}{C_6H_{12}O_6} + \underset{\text{D-fructose}}{C_6H_{12}O_6}$$

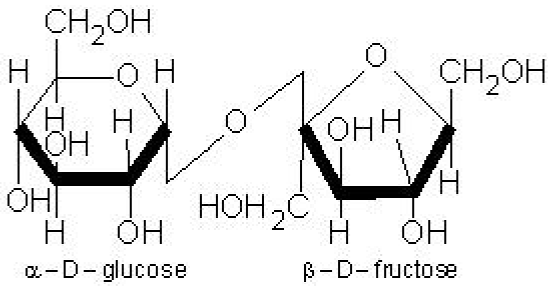
$$\text{Sucrose: } [\alpha]_D = +66.5^\circ \qquad \text{D-glucose: } [\alpha]_D = +53^\circ \qquad \text{D-fructose: } [\alpha]_D = -92^\circ$$

Invert Sugar

$$[\alpha]_D = (+53^\circ) - (-92^\circ) = -39^\circ$$

Sucrose is dextrorotatory, its specific rotation being +66.5%, D-glucose is also dextrorotatory, $[\alpha]_D = +53^\circ$, but D-fructose has a large negative rotation, $[\alpha]_D = -92^\circ$. Since D-fructose has a greater specific rotation than D-glucose, the resulting mixture is laevorotatory. Because of this the hydrolysis of sucrose is known as the inversion of sucrose, and the equimolecular mixture of glucose and fructose is known is invert sugar or invertose.





5. **Explain poly-sachharides.**

Ans: POLYSACCHARIDES: Polysaccharides are formed when a large number (hundreds to even thousands) of monosaccharide molecules join together with the elimination of water molecule. Thus, polysaccharides may be regarded as condensation polymers in which the monosaccharides are joined together by glycosidic linkages. Some important polysaccharides are:

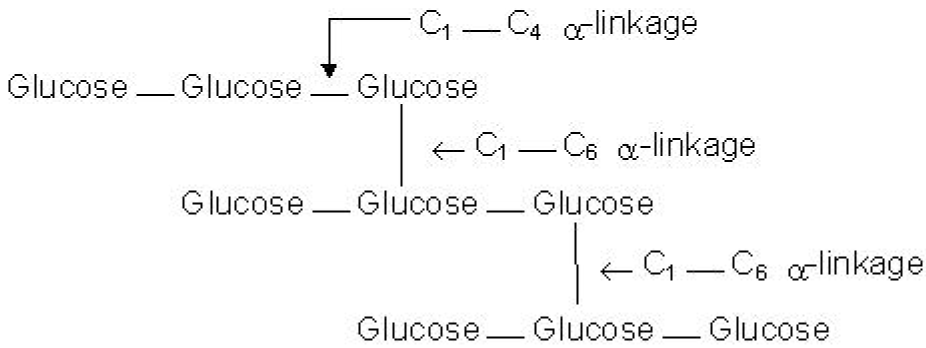
1. Cellulose
2. Starch
3. Glycogen
4. Gums and
5. Pectins

Starch: It is a polymer of glucose. Its molecular formula is $(C_6H_{10}O_5)n$ where the value of n (200 – 1000) varies from source to source. It is the chief food reserve material or storage polysaccharide of plants and is found mainly in seeds, roots, tubers, etc. Wheat, rice, potatoes, corn, bananas etc., are rich sources of starch. Starch is not a single compound but is a mixture of two components – amylose (10 to 20%) and amylopectin (20 to 80%). Both amylose and amylopectin are polymers of α-D-glucose.

Amylose is a linear polymer of α-D-glucose. It contains about 200 glucose units which are linked to one another through α-linkage involving C_1 of one glucose unit with C_4 of the other as shown below:

Linear Polymer

Amylopectin, on the other hand, is a highly branched polymer. It consists of a large number (several branches) of short chains each containing 20-25 glucose units which are joined together through α-linkages involving C_1 of one glucose unit with C_4 of the other. The C_1 of terminal glucose unit in each chain is further linked to C_6 of the other glucose unit in the next chain through $C_1 – C_6$ α-linkage. This gives amylopectin a highly branched structure as shown below.-



Hydrolysis: Hydrolysis of starch with hot dilute acids or by enzymes gives dextrins of varying complexity, maltose and finally D-glucose. Starch does not reduce Tollen's reagent and Fehling's solution.

Uses: It is used as a food. It is encountered daily in the form of potatoes, bread, cakes, rice etc. It is used in coating and sizing paper to improve the writing qualities. Starch is used to treat textile fibres before they are woven into cloth so that they can be woven without breaking. It is used in manufacture of dextrins, glucose and ethyl alcohol. Starch is also used in manufacture of starch nitrate, which is used as an explosive.

Amylopectin is a branched chain saccharides consist of α - D – glucose unit join straight chain by α, 1, 4 linkage & both the straight chain are ionized α - 1, 6 linkage.

Solved example: