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CHEMISTRY

Target : JEE (Main)

BIOMOLECULES & POLYMERS

BIOMOLECULES & POLYMERS

Contents

Biomolecules

CARBOHYDRATE

1. Concept

Generally, carbohydrates are substances with the general formula $C_x(H_2O)_y$. They are called carbohydrates (hydrates of carbon) because they contain hydrogen and oxygen in the same proportion as in water. However, a number of compounds have been found, which are carbohydrates by chemical behaviour but do not conform to the formula $C_x(H_2O)_y$. E.g : 2-deoxyribose.

(i) carbohydrates are biopolymers of polyhydroxy aldehyde or polyhydroxy ketones.

(ii) monomeric polyhydroxy aldehydes or ketones can also exist in hemiacetal and acetal forms in cyclic structures.

(iii) Almost all of these compounds are chiral and optically active. An exception of this is 1,3-dihydroxypropanone.

2. Classification of Carbohydrate

(A) Classification on the basis of number of hydrolysed products

S.No.	Carbohydrate	No. of units (on hydrolysis)	Examples
1	Monosaccharides	1 or single unit (cannot be hydrolysed)	Glucose, Fructose, Galactose
2	Oligosaccharides	2 to 10 units	Sucrose, Maltose, Lactose
3	Polysaccharides	Many units	Starch, Cellulose, Gums, Resins etc

(B) Classification on the basic of functional groups

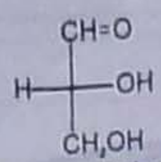
S.No.	Carbohydrate	No. of functional group	Examples
1	Aldose	Aldehyde CH = O | $(CHOH)_n$ | CH_2OH	Glyceraldehyde, Erythrose, Threose, Ribose & 2-Deoxyribose Glucose, Mannose, Allose.
2	Ketose	Ketone CH_2OH | C = O | $(CHOH)_n$ | CH_2OH	n=0; Ketotriose, n = 1; Ketotetroses, n = 2; Ketopentoses, n = 3; Ketohexoses

(C) Classification of monosaccharides on basis of carbon atoms in hydrolysed product.

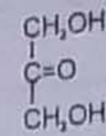
S.No.	Carbon atoms	General term	Aldehyde	Ketone
1	3	Triose	Aldotriose	Ketotriose
2	4	Tetrose	Aldotetrose	Ketotetrose
3	5	Pentose	Aldopentose	Ketopentose
4	6	Hexose	Aldohexose	Ketohexose
5	7	Heptose	Aldoheptose	Ketoheptose

Some facts :

1. Number of carbons in monosaccharides are generally 3 to 7.
2. Simplest aldose is Glyceraldehyde and simplest Ketose is Dihydroxyacetone.

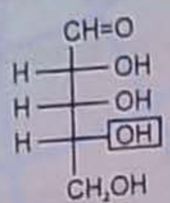


(D-Glyceraldehyde)

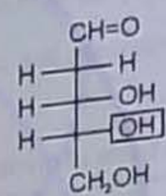


(Dihydroxyacetone)

3. Most naturally occuring monosacharides are :
   (a) Pentoses E.g. D-Ribose (present in RNA) and 2-Deoxyribose (present in DNA)
   (b) Hexoses E.g. D-Glucose, D-Mannose, D-Allose, D-Galactose and D-Fructose



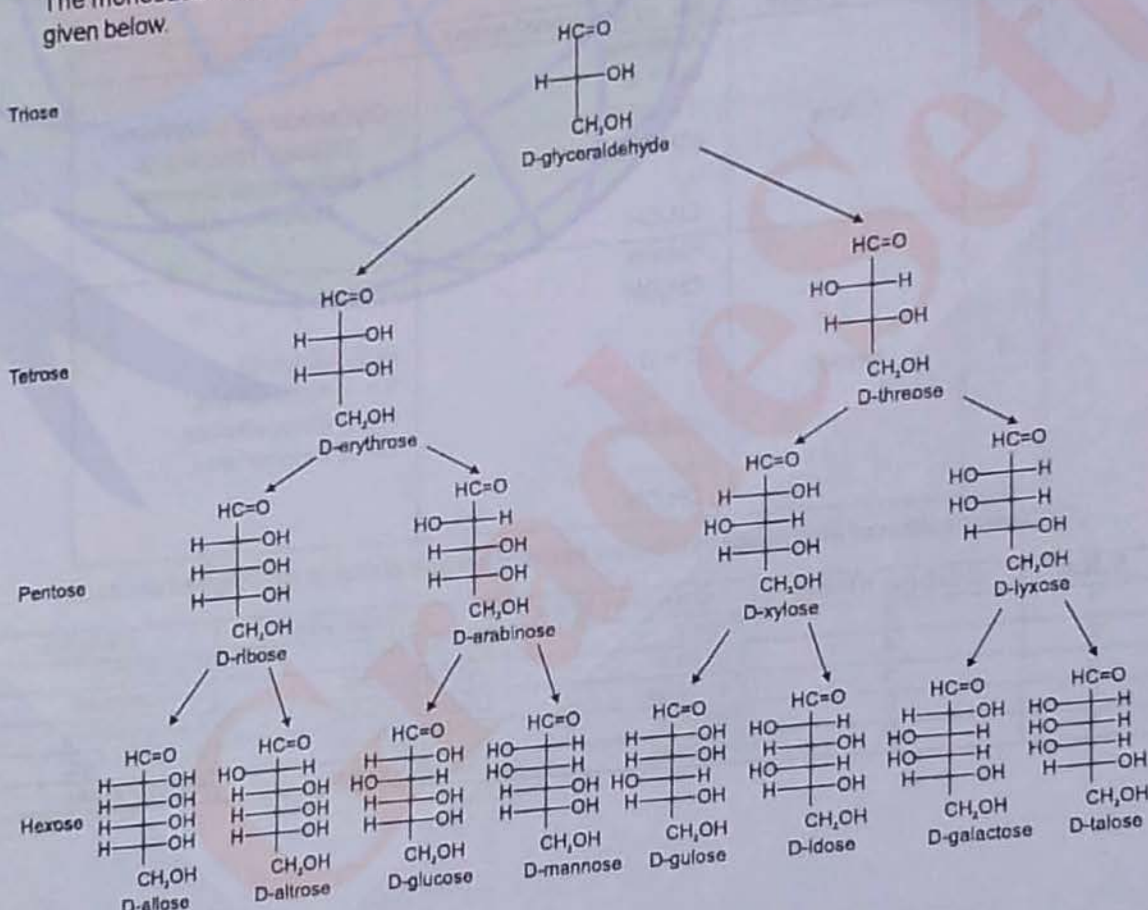
(D-Ribose)



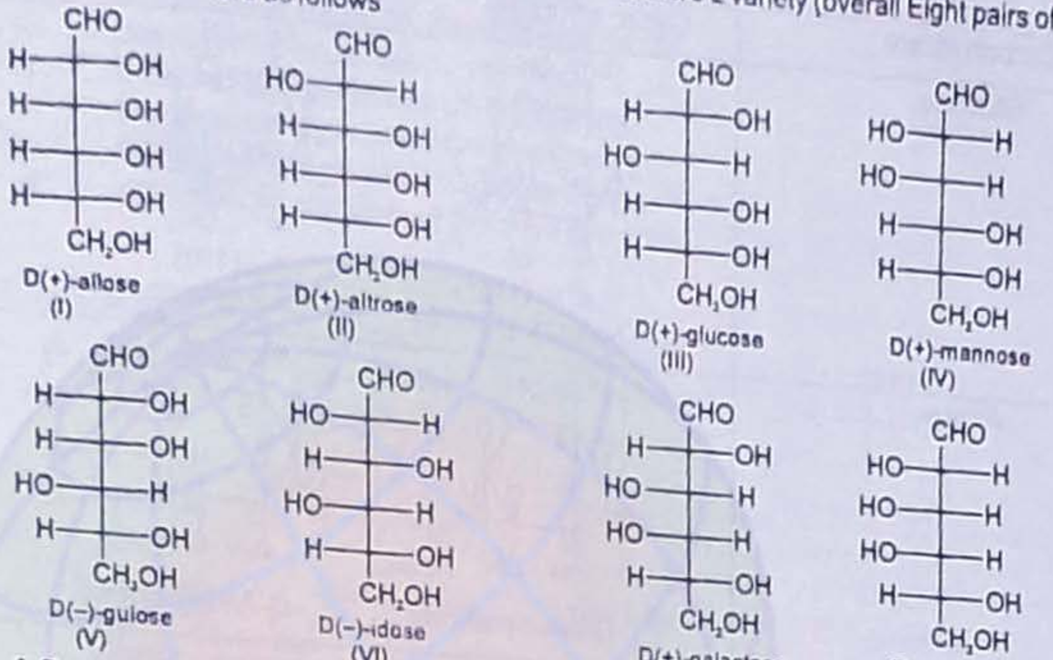
(D-2-Deoxyribose)

3. Stereochemistry of Aldoses :

The monosaccharides are chiral and may have D or L configuration. A simple illustration of all 'D' forms is given below.



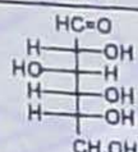
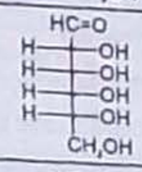
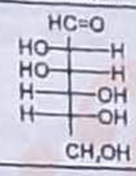
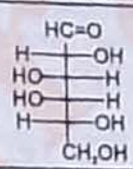
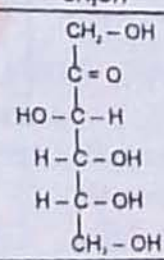
Optical isomers of Aldohexoses : Aldohexoses have four asymmetric carbon atoms, therefore they have sixteen optical isomers out of which 8 are D and 8 are L variety (overall Eight pairs of enantiomers). D-variety of them are as follows



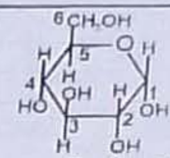
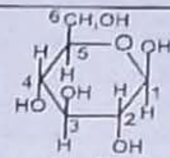
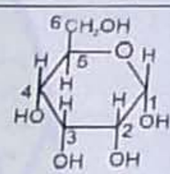
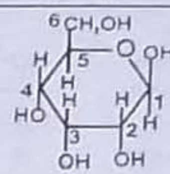
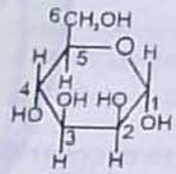
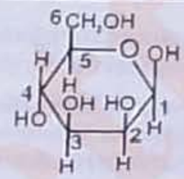
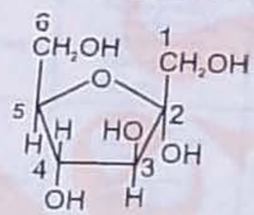
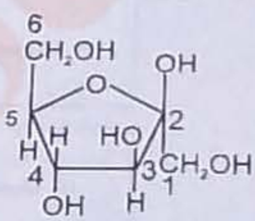
Note : 1. D-aldohexoses shown above have epimeric / diastereomeric relationship with each other
2. D-aldohexoses can be either dextro (+) or laevo (-).

4. Structure of aldohexoses : All form of Aldose or ketose may exist in open chain form as well as in cyclic pyranose or furanose form.

(i) **Open chain structure of mono saccharide**

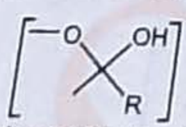
Carbohydrate	Structure	Functional Group	Typical nature
D - Glucose		aldehyde	3rd (L)
D - Allose		aldehyde	No (L)
D - Mannose		aldehyde	2, 3 (L)
D - Galatose		aldehyde	3, 4 (L)
D - Fructose		Ketone	3 (L)

(ii) **Cyclic structure of monosaccharide**

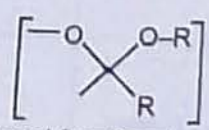
Carbohydrate	Cyclic structure	
Glucose	 $\alpha^o = (112^o)$ D-glucopyranose	 $\alpha^o = (19^o)$ β-D-glucopyranose
Allose	 -D-Allopyranose	 -D-Allopyranose
Mannose	 -D-Mannopyranose	 -D-Mannopyranose
Fructose	 α-fructofuranose	 β-fructofuranose

• ***Anomers :***

Anomers are diastereomers that differ in the configuration at the acetal or hemiacetal C atom of a sugar in its cyclic form or Anomers are epimers whose conformations differ only at anomeric carbon. (Anomeric carbon: A carbon bonded with two 'O' atoms). For example, α D(+) and β -D(+) glucose are anomers. α-D(–) and β-D(–) fructose are anomers.

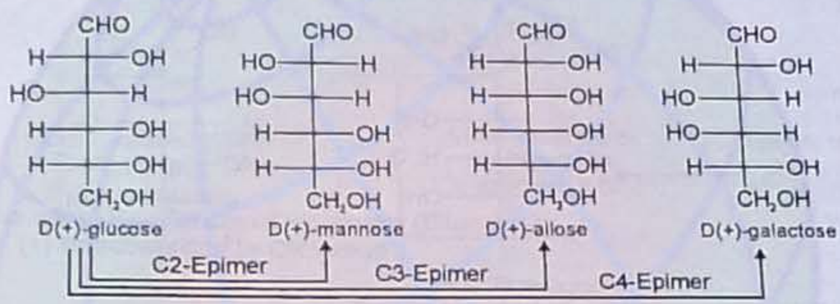


Hemiacetal functional group



Acetal functional group

- **Epimers :** Diastereomers with more than one stereocentre that differ in the configuration about only one stereocentre are called epimers.
  i. D-Erythrose and L-threose are epimers.
  ii. D-glucose and D-galactose are C-4 epimers and
  iii. D-idose and D-talose are C-3 epimers.
  iv. D-glucose and D-mannose are C-2 epimers.
  v. Epimerisation of glucose at C-2 gives mannose.
  vi. Epimerisation of glucose at C-3 gives allose.
  vii. Epimerisation of glucose at C-4 gives galactose.



Reducing and non Reducing properties of (Sugars) :

(I) Reducing sugars
1. Reduces Tollen's reagent, Fehling's solution & Benedicts's solution.
2. Should have atleast one hemiacetal or hemiketal functional group.
   Ex. All Mono and Oligosaccharides except Sucrose

(II) Non Reducing sugars
Don't reduce Tollen's, Fehling's & Benedict's solution.
Should have acetal linkage.
Ex. All Polysaccharides and few Oligosaccharides (Ex. Sucrose)

MONOSACCHARIDES

(a) Glucose : Glucose is the most common monosaccharide. It is known as Dextrose because it occurs in nature principally as the optically active dextrorotatory isomers. It is act as a reducing agent (reduces both Fehling's solution and ammonical silver nitrate solution ; **Tollen's reagent**). It is known as **dextrose** and found as grapes, honey, cane sugar, starch and cellulose.

(b) Preparation :

(i) By acid hydrolysis of canes sugar (a disaccharide) :
If sucrose is boiled with dil. HCl or H_2SO_4 in alcoholic solution. Glucose & fructose are obtained in equal amount.

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

(ii) By enzymatic action over starch : Glucose is obtained by hydrolysis of starch by boiling it with dil. H_2SO_4 at 393 K under pressure.

$$\underset{\substack{\text{Polysaccharides}\\(C_6H_{10}O_5)_n}}{\text{Starch}} \xrightarrow{\text{Diastase}} \underset{\substack{\text{Disaccharides}\\(C_{12}H_{22}O_{11})}}{\text{Maltose}} \xrightarrow{\text{Maltase}} \underset{\substack{\text{Monosaccharides}\\(C_6H_{12}O_6)}}{\text{Glucose}}$$

(c) Structure of Monosaccharides :

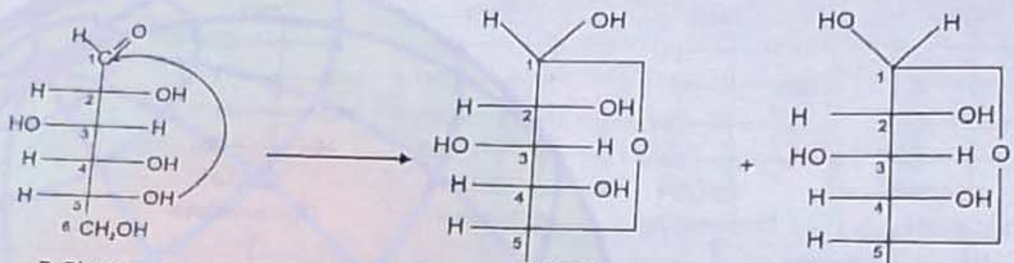
Open chain structure (Fisher projection) and Cyclic structure (Haworth projection) :

(1) Despite having aldehyde group , glucose does not give schiff's test & does not form hydrogen sulphite (bisulphite) addition product with $NaHSO_3$.

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

This behaviour could not be explained by open chain structure. It was proposed that one of –OH group add to CHO group , forms a cyclic structure.

These two cyclic hemiacetal form of glucose differe only in configuration of the hydroxyl group at C_1, called anomeric carbon. Such isomers i.e. α-form & β-form, are called anomers.



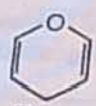
D-Glucose
Specific rotation (+52.7°)

α-D-glucose
Specific rotation (+112°)

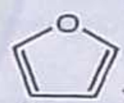
β-D-glucose
Specific rotation (+19°)

Haworth projection

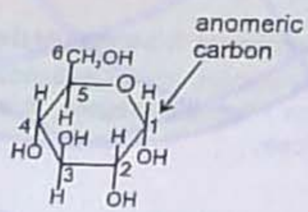
The six membered cyclic structure of glucose is called pyranose structure (α- or β-), in analogy with pyran. and five membered cyclic structure of monosaccharides is called pyranose structure (α or β) in analogy with furan



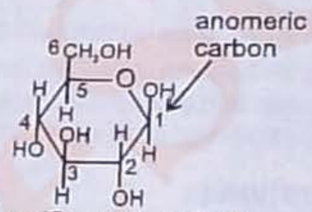
Pyran



Furan

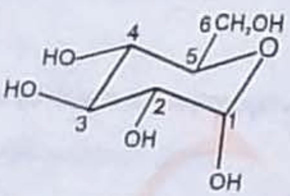


Specific rotation (112°)
α-D-glucose
α-D-glucopyronose

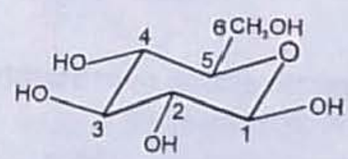


Specific rotation (19°)
β-D-glucose
β-D-glucopyranose

α and β-Glucose are anomer's of each other (i.e change in configuration of 1[st] carbon atom only)



α-D Glucose

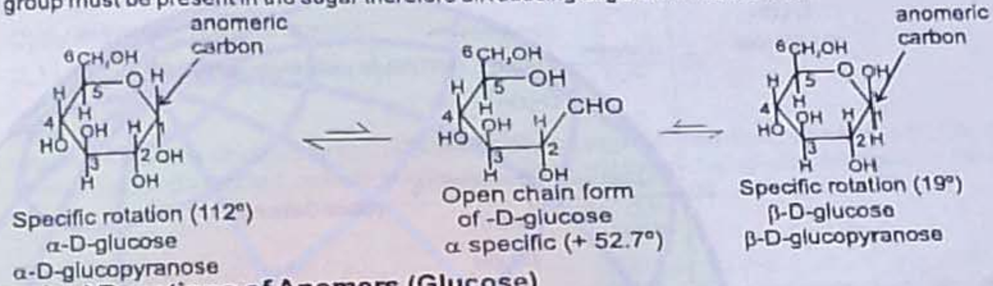


β-D-Glucose

4.1 Properties of Anomers : Mutarotation

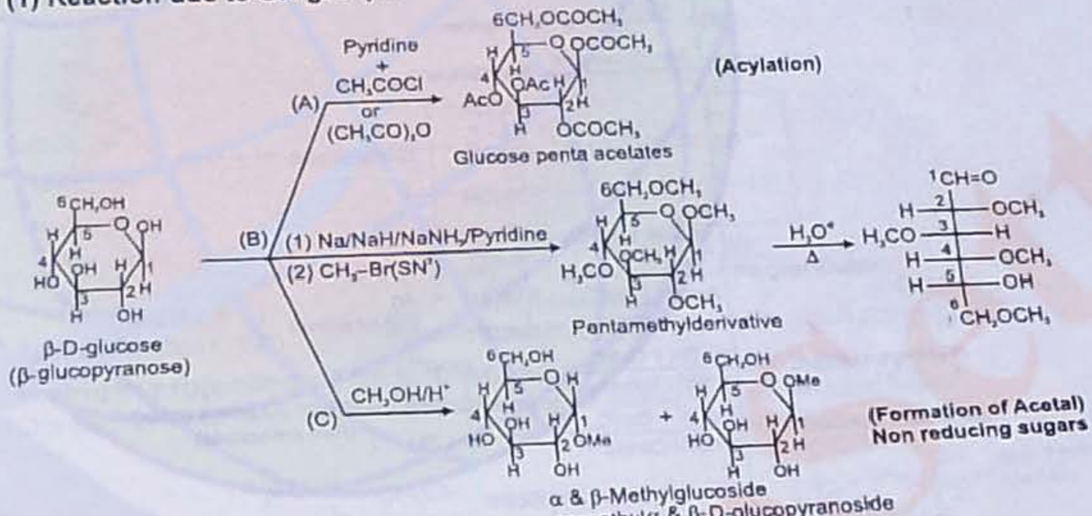
When one of the pure glucose anomers dissolve in water, an intersting change in the specific rotation is observed. When the α-anomer dissolves, its specific rotation gradually decreases from an initial value of +112° to +52.7°. When the pure β anomer dissolves, its specific rotation gradually increases from +19° to the same value of +52.7°. **This change (mutation) in the specific rotation is called mutarotation.** What is happening to each solution ?

Initially solution with only one anomeric form, undergoes equilibrium to the same mixture of α-and β-forms. The open chain forms is in intermediate in the process of equilibrium. For mutarotation atleast one hemiacetal group must be present in the sugar therefore all reducing sugars will mutarotate.



5. Chemical Reactions of Anomers (Glucose)

(1) Reaction due to OH group :



Note : (A) Acylation with acid halide or acetic anhydride gives pentaacetates which confirms the presence of five –OH groups.

(B) After Hydrolysis product of pentamethyle derivatives, aldehyde group and hydroxy of C_5 regenerated hence hydroxy of C_5 is involved in the hemiacetal formation.

(C) (i) Sugars in the form of **acetals** are called **glycosides**. (glucose → glucoside, mannose → mannoside, ribose → riboside, fructose → fructoside etc).

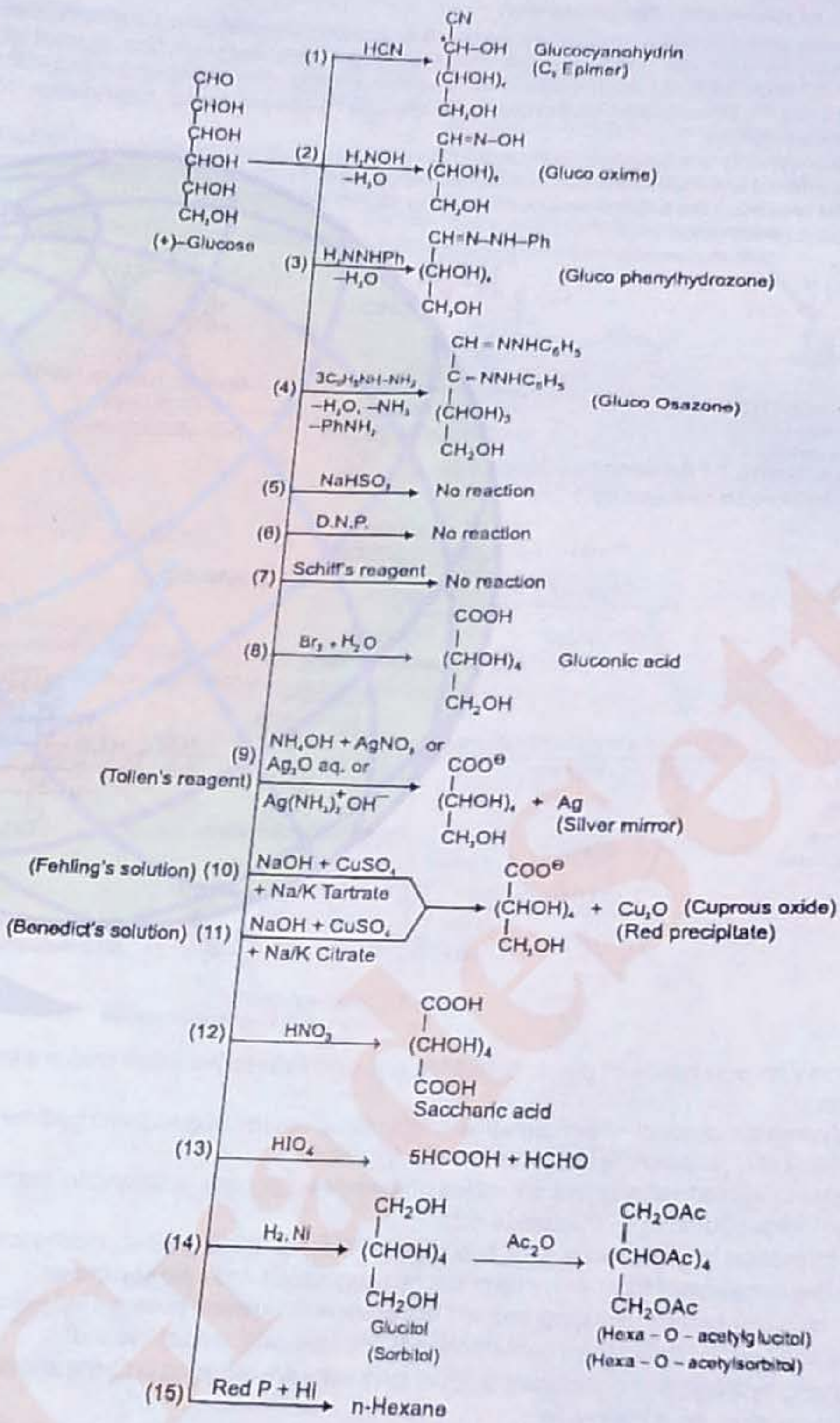
(ii) In the formation of glycosides only one mole of alcohol is required so monosacchardies are already present in the hemiacetal form with one of the hydroxyl group and carbonyl group.

(iii) Glycosides are known reducing and will not show mutarotation because in neutral are basic condition glycosides are stable (cyclic form cannot open to the free carbonyl compound).

(iv) After acidic hydrolysis of glycosides product form will have reducing property and also show mutarotation.

(2) Reaction due to aldehyde :

In aqueous solution, α-Anomer or β-Anomer remains in the equilibrium with each other by small amount of open chain forms (0.02%), in which carbonyl group is regenerated and gives various reactions.


CHO
CHOH
CHOH
CHOH
CHOH
CH2OH
(+)-Glucose
(1) HCN
CN
CH–OH
(CHOH)4
CH2OH
Glucocyanohydrin
(C2 Epimer)
(2) H2NOH
–H2O
CH=N–OH
(CHOH)4
CH2OH
(Gluco oxime)
(3) H2NNHPh
–H2O
CH=N–NH–Ph
(CHOH)4
CH2OH
(Gluco phenylhydrazone)
(4) 3C6H5NH-NH2
–H2O, –NH3
–PhNH2
CH = NNHC6H5
C – NNHC6H5
(CHOH)3
CH2OH
(Gluco Osazone)
(5) NaHSO3
No reaction
(6) D.N.P.
No reaction
(7) Schiff's reagent
No reaction
(8) Br2 + H2O
COOH
(CHOH)4
CH2OH
Gluconic acid
(9) NH4OH + AgNO3 or
Ag2O aq. or
Ag(NH3)2+OH–
(Tollen's reagent)
COO⊖
(CHOH)4
CH2OH
+ Ag
(Silver mirror)
(Fehling's solution) (10)
NaOH + CuSO4
+ Na/K Tartrate
(Benedict's solution) (11)
NaOH + CuSO4
+ Na/K Citrate
COO⊖
(CHOH)4
CH2OH
+ Cu2O (Cuprous oxide)
(Red precipitate)
(12) HNO3
COOH
(CHOH)4
COOH
Saccharic acid
(13) HIO4
5HCOOH + HCHO
(14) H2, Ni
CH2OH
(CHOH)4
CH2OH
Glucitol
(Sorbitol)
Ac2O
CH2OAc
(CHOAc)4
CH2OAc
(Hexa – O – acetylglucitol)
(Hexa – O – acetylsorbitol)
(15) Red P + HI
n-Hexane

FRUCTOSE

Fructose preparation :

(1) By acid hydrolysis of cane sugar.

$$\underset{\substack{\text{Sucrose} \\ \text{Disacchandes}}}{C_{12}H_{22}O_{11}} \xrightarrow{H_2O/H^+} \underset{\alpha\text{-glucose}}{C_6H_{12}O_6} + \underset{\beta\text{-fructose}}{C_6H_{12}O_6}$$

(2) By enzymatic action of sucrose.

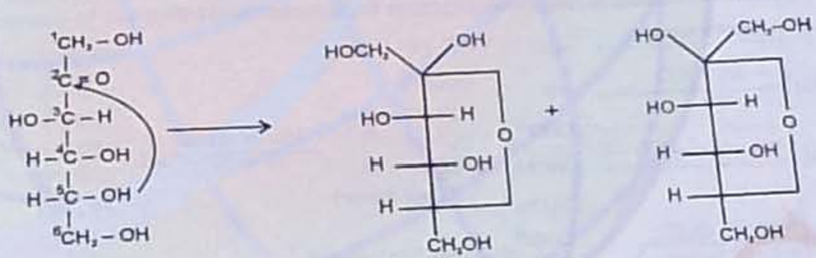
$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} \xrightarrow{\text{Invertase}} \text{Glucose} + \text{Fructose}$$

Note :

Glucose & fructose obtained by acid hydrolysis of sucrose can be separated by treating with $Ca(OH)_2$ which forms calcium glucosate & calcium fructosate. Calcium fructosate, being water insoluble, is seperated out easily.

Structure of fructose :

It also exist in two cyclic forms which are obtained by the addition of –OH at C5 to the (>C=O) group.



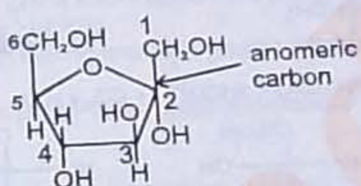
D-fructose
Specific Rotation (– 92°)

α-D-fructose
Specific Rotation (– 21°)

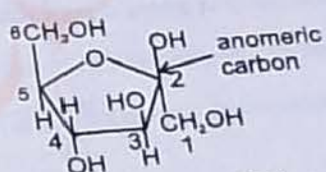
β-D-fructose
Specific Rotation (– 133°)

Haworth projection : Fructofuranose

The five membered ring & is named as furanose with analogy to the compound furan.



Specific rotation (-21°)
α-fructose
α-fructofuranose

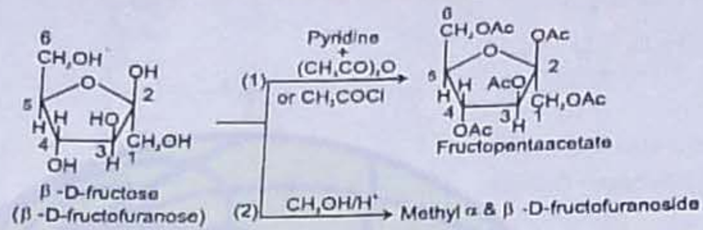


Specific rotation (-133°)
β-fructose
β-fructofuranose

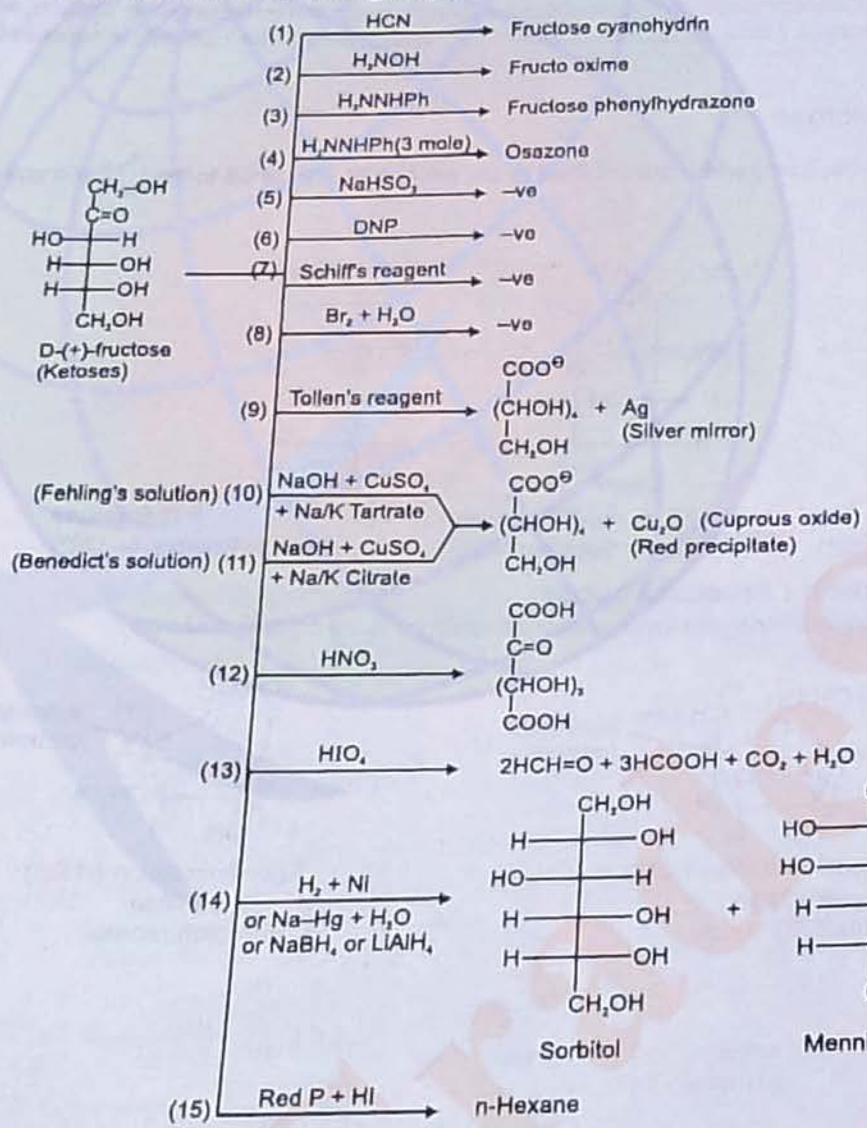
Chemical Reactions of Fructose :

Reaction due to OH group at 2nd carbon :

(1) It forms fructose pentaacetate with acetyl chloride :



(2) Reaction due to keto group :



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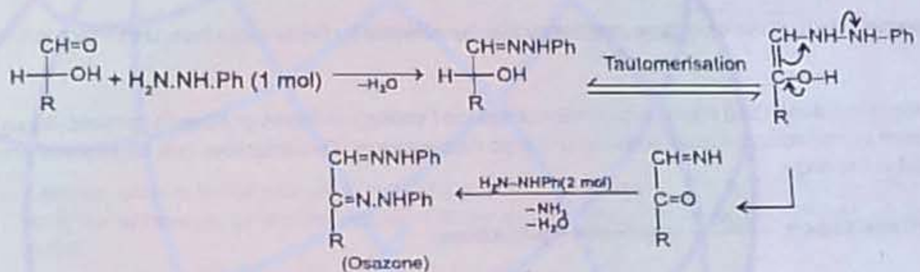
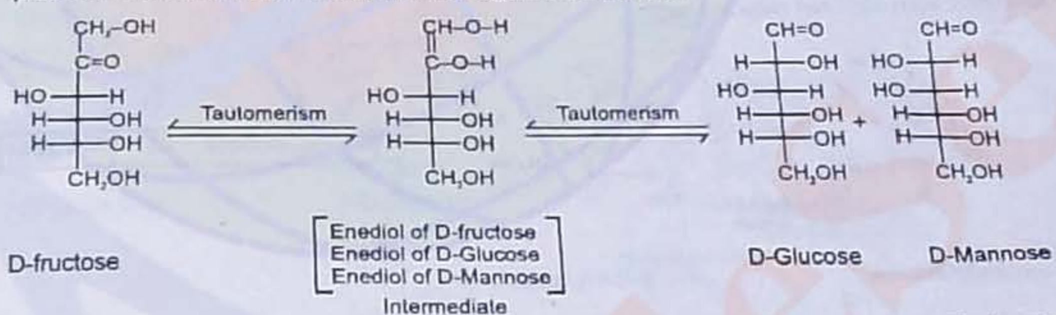
Some highlights :

1. Since glucose & fructose (Aldoses/Ketoses) reacts with HCN, H_2NOH, H_2NNHPh which indicates the presence of carbonyl group but they don't react with DNP, $NaHSO_3$ & Schiff's reagent (weak reagents) therefore we can conclude that carbonyl group is not free, but remains in the form of cyclic structures.
2. In the formation of osazone, C_1 & C_2 are only involved so glucose, fructose and C-2 epimers (Glucose & Mannose, Threose and Erythrose) give same osazone.
3. Osazone are crystalline solid having sharp melting point so used for identifying the carbohydrates. In the osazone formation three molecules of NH_2NHPh is overall consumed out of which two mole react with nucleophilic addition/elimination reaction forming hydrazone whereas one molecule undergoes redox reaction.



3. Both glucose and fructose gives test with Tollen's reagent, Fehling's solution and Benedict's solution because in basic medium, ketoses remains in the form of dynamic equilibrium with Aldoses (C-2 epimers) by the process of **tautomerisation/enediol rearrangement as below.**



4. Only Br_2/H_2O is used for the identification of Aldoses & Ketoses. (Mild oxidising agent like bromine water (Neutral) Oxidises only aldehydic group).
5. Oxidation with HNO_3, gives information that one primary alcohol is present in aldoses and two primary alcohols are present in ketoses.
6. Reduction product with Na/Hg and H_2O gives only one alcohol with aldoses and two alcohols with ketoses (C-2 epimers)
7. Reduction product with Red P & HI, gives n-Hexane which indicates that all the six carbon atoms are linearly arranged.

Disaccharides

Condensation of two monosacharides after loss of water molecule (Glycosidic bond), gives disacharides. Common examples are sucrose, maltose, lactose, cellubiose.

Sucrose :

(i) Sucrose is a white crystalline solid, soluble in water.
(ii) When heated above its melting point, it forms a brown substance known as caramel.
(iii) Sucrose is dextrorotatory, its specific rotation being + 66.5°.
(iv) On hydrolysis with dilute acids sucrose yields an equimolecular mixture of D(+)-glucose and D(–)-fructose :

$$\underset{[\alpha] = +66.5^\circ}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{HCl} \underset{\substack{D - glucose \\ [\alpha] = +52.7^\circ}}{C_6H_{12}O_6} + \underset{\substack{D - fructose \\ [\alpha] = -92.4^\circ}}{C_6H_{12}O_6}$$

Since D(–)-fructose has a greater specific rotation than D(+)-glucose, the resulting mixture is laevorotatory

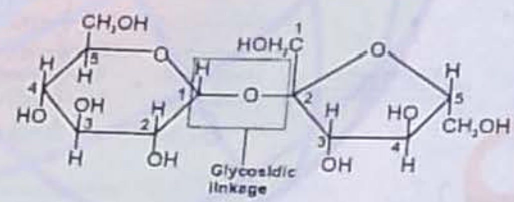
Since the hydrolysis of cane-sugar (sucrose) gives laevorotatory solution in place of original dextrorotatory solution therefore hydrolysis of cane-sugar is also known as the **inversion of cane-sugar or inversion of sucrose** and the mixture of sugars are known as **invert sugar Ex. D - Glucose & D-Fructose.**

The inversion (i.e., hydrolysis) of cane-sugar may also be effected by the enzyme invertase which is found in yeast.

(v) Sucrose is not a reducing sugar, e.g., it will not reduce Fehling's solution or Tollen's reagnet. It does not form an oxime or an osazone, and does not undergo mutarotation. This indicates that hemiacetal group is not present in the rings.

Sucrose (Cane sugar) $\xrightarrow{H_3O^{\oplus}}$ **α-glucose + β-fructose**

In sucrose two monosaccharides are joined together by an oxide linkage formed by loss of water molecule. Such linkage through oxygen atom is called glycosidic linkage. In sucrose linkage in between C1 of α-glucose and C2 of β-fructose. Since the reducing group of glucose & fructose are involved in glycosidic bond formation, sucrose is non reducing sugar.



C_1 –D-glucose + C_2 -D-fructose

α-D-Glucose β-D-Fructose.

Maltose :

Maltose (malt sugar), $C_{12}H_{22}O_{11}$, is produced by the action of malt (which contains the enzyme diastase) on starch :

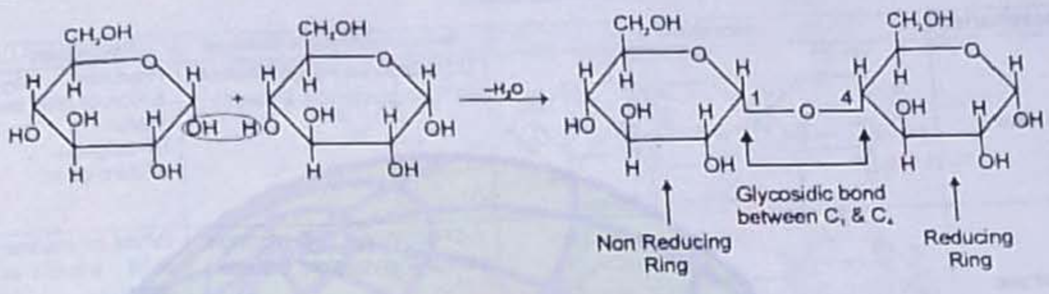
$$C_{12}H_{22}O_{11} \xrightarrow{H_3O^{\oplus}} 2C_6H_{12}O_6 \text{ α-D-Glucose}$$

When it is hydrolysed with dilute acids or by the enzyme maltase, maltose yields two molecules of D (+)-glucose. Maltose is a reducing sugar, e.g., it reduces Fehling's solution or Tollen's reagent; it forms an oxime and an osazone, and undergoes mutarotation. This indicates that at least one hemiacetal group (of the two glucose molecules) is free in maltose.

Maltose (Malt sugar) $\xrightarrow{H_3O^{\oplus}}$ **α-glucose + α-glucose**

Formation of Maltose ($C_{12}H_{22}O_{11}$)

C_1 α–D-Glucose + C_4 α-D-Glucose

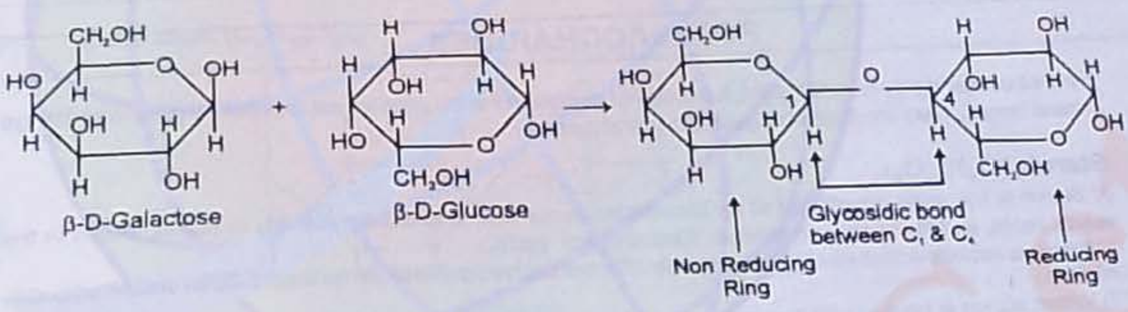


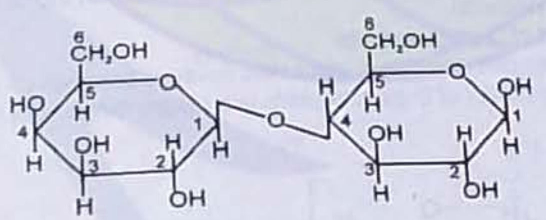
Lactose :

Lactose occurs in the milk of all animals and is dextrorotatory. It is hydrolysed by dilute acids or by the enzyme lactase, to an equimolecular mixture of D(+)-glucose and D(+)-galactose. Lactose is a reducing sugar.

Lactose (Milk sugar) $\xrightarrow{H_3O^{\oplus}}$ β-galactose + β-glucose

Formation of Lactose ($C_{12}H_{22}O_{11}$)





C_1 –D-Galactose + C_4 -D-Glucose

The linkage is between C-1 of Galactose and C-4 of Glucose.

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