II SEMESTER

PAPER – BIOMOLECULES AND ANALYTICAL TECHNIQUES

TOPIC – CARBOHYDRATES

SOURCE – INTERNET

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Carbohydrates are a class of naturally occurring organic compounds of carbon, hydrogen and oxygen which are primarily produced by plants. They are extremely widespread in plants comprising upto 80% of dry weight. These are ultimate source of our food. In higher animals the simple sugar glucose is an essential constituent of blood and occurs in a polymeric form as glycogen in the liver and muscle.

In the green plants, carbohydrates are produced by a process called photosynthesis. This process involves the conversion of simple compounds CO_2 and H_2O into glucose ($C_6H_{12}O_6$) and is catalysed by green colouring pigment chlorophyll present in the leaves of plants. The energy required for this conversion is supplied by sun in the form of sunlight.

Carbohydrates are very useful for human beings. They provide us all the three basic necessities of life i.e., foog (starch containing grain), clothes (cellulose in the form of cotton , linen and rayon) and shelter (cellulose in the form of wood used for making our houses and furniture etc.). Carbohydrates are also important to the economy of many nations. For example, sugar is one of the most important commercial commotidies.

The term carbohydrates arose because the general formula for most of them could be written as C_x $(H_2O)_y$ and thus they may be regarded as hydrates of carbon. However, this definition was not found to be correct e.g., rhamnose, a carbohydrate, is having the formula $C_6H_{12}O_5$ while acetic acid having formula $C_2H_4O_2$ is not a carbohydrate. Simple carbohydrates are also known as sugars or saccharides (Latin: Saccharum; Greek : Sakcharon, Sugar) and the ending of the names of most sungars is –ose. Examples: glucose, fructose, sucrose, maltose, arabinose, etc.

Chemically, carbohydrates contain mainly two functional groups, carbonyl group (aldehyde or or ketone) and a number of hydroxyl groups. Accordingly carbohydrates are now defined optically active polyhydroxy aldehydes or polyhydroxy ketones or the compound that can be hydrolysed to either of them.

7.3 CLASSIFICATION AND NOMENCLATURE

7.3.1 Classification

Carbohydrates, in general, may be classified into two classes:

(i) **Sugars.** These are crystalline substances which are sweet and water soluble. For examples, glucose, fructose and cane sugar.

(ii) **Non-sugars**. These are tasteless, insoluble in water and amorphous. For example. Starch, cellulose, etc.

However, these days Carbohydrates are systematically classified into three major group:

(a) Monosaccharides. The simplest carbohydrates that cannot be hydrolysed into simpler carbohydrates, are called monosaccharides.depending upon whether they contain an aldehyde or keto groups, they may be called aldoses or ketoses. For example, a five carbon monosaccharide having aldehyde group is called aldopentose and six carbon monosaccharide containing a keto group is called keto-hexose. A few examples of monosaccharides are given below:

Aldotetroses. Erythrose and Threose; $CH_2OH(CHOH)_2$ CHO.

Ketotetroses. Erythrulose, $CH_2OHCOCHOHCH_2OH$.

Aldopentoses. Ribose, arabinose, Xylose and Lyxose. $CH_2OH(CHOH)_3$ CHO.

All have a common molecular formula but different structures.

Ketopentoses. Ribulose and Xylulose; $CH_2OHCO(CHOH)_2$ CH_2OH.

Aldohexoses. Glucose, mannose, galactose; $CH_2OH(CHOH)_4$ CHO.

Ketohexoses. Fructose, Sorbose etc. $CH_2OHCO(CHOH)_3$ CH_2OH.

(b) Oligosaccharides. These are the carbohydrates which can be hydrolysed into a definite number of monosaccharide molecules. Depending upon the number of monosaccharides that are obtained from them on hydrolysis, they may be called di-, tri- or tetra-saccharides: For example:

Disaccharides: sucrose, lactose, maltose. All these have the same molecular formula $C_{12}H_{22}O_{11}$.

Trisaccharides: raffinmose ($C_{18}H_{32}O_{16}$).

Tetrasaccharides: stachyose ($C_{24}H_{42}O_{21}$).

(c) Polysaccharides. Carbohydrates that yield a large number of molecules (more than ten molecules) of monosaccharides on hydrolysis are called polysaccharides. The common examples are starch, cellulose, glycogen, etc.

7.3.2 Nomenclature

Carbohydrates contain hydroxy and aldehydic or ketonic groups. They are named according to IUPAC system of nomenclature

Compound	Common name	IUPAC name
$CH_2OHCHOHCHO$	Glyceraldehyde	2, 3-dihydroxy propanol
$CH_2OHCOCH_2OH$	Dihydroxyacetone	1,3-dihydroxy propanone
$CH_2OH(CHOH)_4CHO$	Glucose	2,3,4,5,6-pentahydroxyhexanal
$CH_2OH(CHOH)_3COCH_2OH$	Fructose	1,3,4,5,6-pentahydroxyhexan-2-one

7.4 MONOSACCHARIDES

The monosaccharides are again classified on the basis of two factors:

(1) By the carbonyl function. Those containing the aldehydic function,-CHO, are called aldoses. Others containing the keto group, -CO-, are called ketoses.

(2) By the number of Carbonyl atoms in the molecule. These monosaccharides containing 3,4,5,6 etc., carbon atoms are designated as trioses, tetroses, pentoses, hexoses, and so on.

Monosaccharides are polyhydric aldehydes and ketones which cannot be hydrolysed into simpler carbohydrates.

7.4.1 Structures of monosaccharides

The common monosaccharides are given in table.

Table. Monosaccharides

No of carbon atoms	**Class**	**Molecular formula aldoses**	**Structural formula**	**Examples**
3	aldotrioses	$C_3H_6O_3$	$CH_2OHCHOHCHO$	Glyceraldehyde
4	aldotetroses	$C_4H_8O_4$	$CH_2OH(CHOH)_2CHO$	Erythrose, Threose
5	Aldopentose	$C_5H_{10}O_5$	$CH_2OH(CHOH)_3CHO$	Arabinose, Ribose, Xylose, Lyxose
6	aldohexoses	$C_6H_{12}O_6$	$CH_2OH(CHOH)_4CHO$	Glucose, galactose, mannose, allose, talose, gulose, iodose, etc.
3	ketotrioses	$C_3H_6O_3$	$CH_2OHCOCH_2OH$	dihydroxyacetone
4	ketotetroses	$C_4H_8O_4$	$CH_2OHCOCHOHCH_2OH$	erythrulose
5	ketopentoses	$C_5H_{10}O_5$	$CH_2OHCO(CHOH)_2CH_2OH$	Ribulose, Xylulose
6	ketohexoses	$C_6H_{12}O_6$	$CH_2OHCO(CHOH)_3CH_2OH$	Fructose, Sorbose, Tagatose, Psicose

7.4.2 Glucose

Glucose is most common monosaccharide. It is known as Dextrose because it occurs in nature principally as optically dextrorotatory isomer. Glucose is found in most sweet fruits, especially grapes (20-30%), and honey. It is an essential constituent of human blood. The blood normally conatains 65 to 110 mg (0.06 to 0.1%) of glucose per 100 ml. In diabetic persons the

level may be much higher. In combined form glucose occurs in abundance in cane sugar and polysaccharides such as starch and cellulose.

Preparation of Glucose

1. **From sucrose (Cane sugar)**

When sucrose in boiled with dilute HCl or H2SO4 in alcoholic solution, glucose and fructose are obtained in equal amounts.

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

2. **From Starch**

Glucose is produced commercially by the hydrolysis of starch by boiling it with dilute H2SO4 at high temperature under pressure.

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{HCl} \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

in this process, an aqueous solution of starch obtained from corn is acidified with dilute H2SO4. It is then heated with high pressure steam in an autoclave. When the hydrolysis is complete, the liquid is neutralized with sodium carbonate to pH of 4-5. The resulting solution is concentrated under reduced pressure to get the crystals of glucose.

Physical properties of glucose

Some important physical properties of glucose are mentioned as under:

1. It is colourless sweet crystalline compound having m.p.419 K.
2. It is readily soluble in water, sparingly soluble in alcohol and insoluble in ether.
3. It forms a monohydrate having m.p. 391 K.
4. It is optically active and its solution is dextrorotatory. The specific rotation of fresh solution is + 112^0 C.
5. It is about three fourth as sweet as sugarcane i.e., sucrose.

Chemical properties of glucose

Chemical properties of glucose can be studied under the following headings:

(A) Reactions of aldehydic group

1. **Oxidation**. (a) Glucose gets oxidized to gluconic acid with mild oxiding agents like bromine water

$$\underset{\text{Glucose}}{CH_2OH\,(CHOH)_4CHO} \xrightarrow[Br_2,\ H_2O]{[O]} \underset{\text{Gluconic acid}}{CH_2OH\,(CHOH)_4COOH}$$

Only-CHO group is affected.

(b) A strong oxidizing agent like nitric acid oxidizes both the terminal groups viz. –CH2OH and –CHO groups and saccharic acid or glucaric acid is obtained.

$$\underset{\text{Glucose}}{CH_2OH\,(CHOH)_4CHO} \xrightarrow[[O]]{HNO_3} \underset{\text{Glucaric acid}}{COOH\,(CHOH)_4COOH}$$

(d) Glucose gets oxidized to gluconic acid with ammonical silver nitrate (Tollen's reagent) and alkaline copper sulphate (Fehling solution). Tollen's reagent is reduced to metallic silver (silver mirror) and Fehling solution to cuprous oxide which is a red precipitate.

(i) With Tollen's reagent

$$AgNO_3 + NH_4OH \longrightarrow AgOH + NH_4NO_3$$

$$2AgOH \longrightarrow Ag_2O + H_2O$$

$$\underset{\text{Glucose}}{CH_2OH(CHOH)_4CHO} + Ag_2O \longrightarrow \underset{\text{Gluconic acid}}{CH_2OH(CHOH)_4COOH} + 2Ag\downarrow \quad \text{Silver mirror}$$

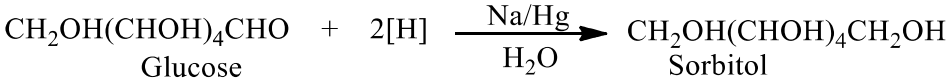
(ii) With Fehling solution

$$CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4$$

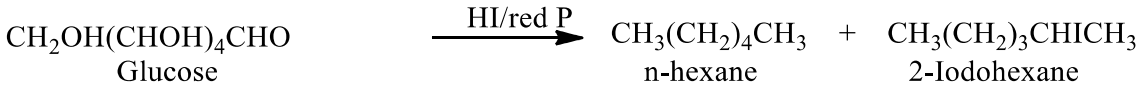
$$Cu(OH)_2 \longrightarrow CuO + H_2O$$

$$\underset{\text{Glucose}}{CH_2OH(CHOH)_4CHO} + 2CuO \longrightarrow \underset{\text{Gluconic acid}}{CH_2OH(CHOH)_4COOH} + \underset{\text{Red ppt.}}{Cu_2O}$$

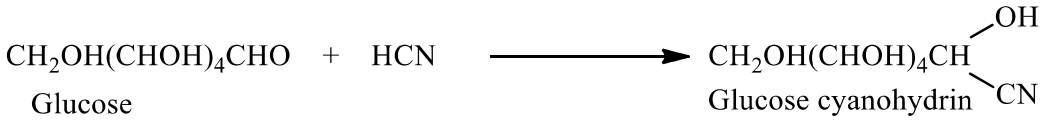
2. **Reduction** (a) glucose is reduced to sorbitol or Glucitol on treatment with sodium amalgam and water.



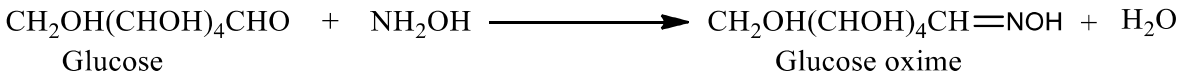
(b) On reduction with conc. HI and red P at 373 K glucose gives a mixture of n-hexane and 2-idohexane



3. **Reaction with HCN**. Like aldehydes, glucose reacts with HCN forming cyanohydrins.

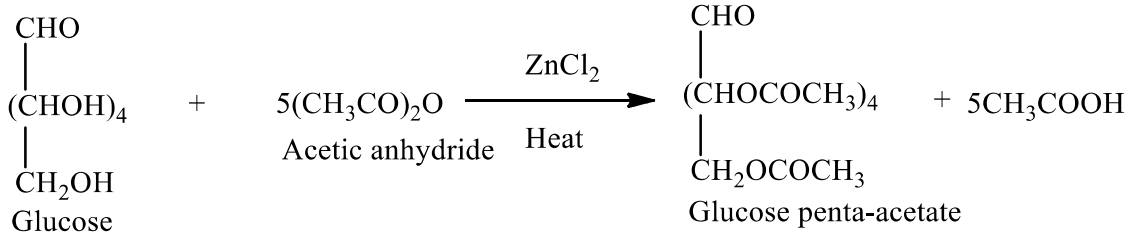


4. **Reaction with hydroxylamine**. Glucose forms glucose oxime.

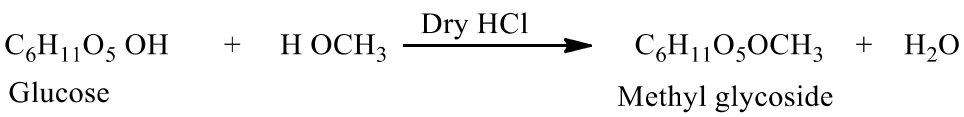


(B) Reactions of hydroxyl groups

1. **Reaction with acetic anhydride or acetyl chloride**. Glucose forms penta acetate with acetic anhydride of acetyl chloride.



2. **Reaction with methyl alcohol**. Glucose reacts with methy alcohol in the presence of dry HCl gas to form methyl glucoside.

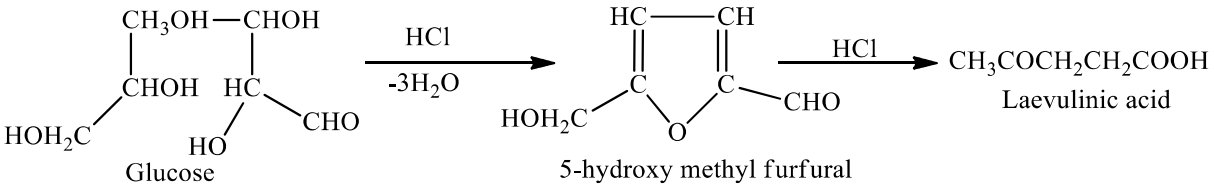


3. **Reaction with metallic hydroxides**. Glucose reacts with calcium hydroxide to form calcium glucosate which is water soluble.

$$\underset{\text{Glucose}}{C_6H_{11}O_5\,OH} + \underset{\text{calcium hydroxide}}{H\,OCaOH} \longrightarrow \underset{\text{calcium-glucosate}}{C_6H_{11}O_5OCaOH} + H_2O$$

(C) Miscellaneous reactions

1. Action of acids. On warming with conc.HCl, glucose forms 5-hydroxy methyl furfural, which on further reaction gives laevulinic acid.

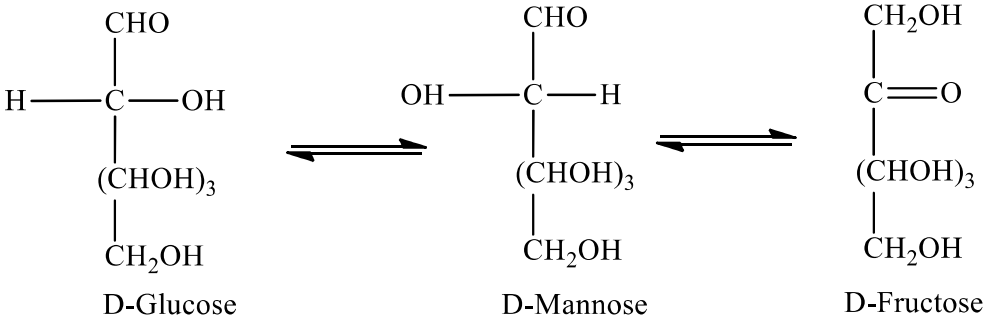


2. Fermentation. Glucose undergoes fermentation into ethyl alcohol in the presence of the enzyme zymase.

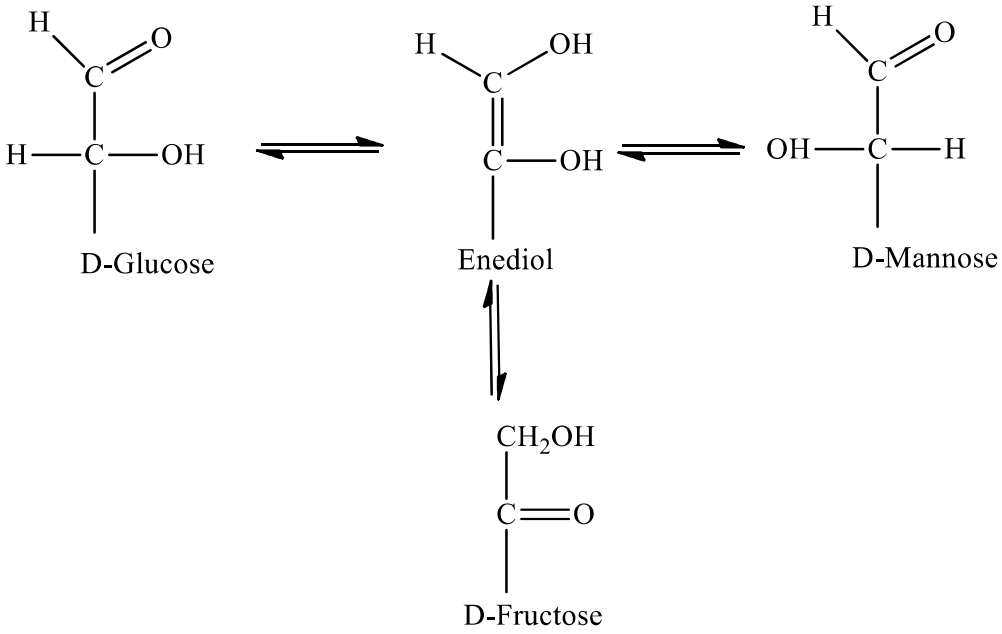
$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{Ethyl alcohol}}{2C_2H_5OH} + 2CO_2$$

This reaction called alcoholic fermentation is the basis of manufacture of wines and alcohol.

3. Reaction with Alkalies. When warmed with strong sodium hydroxide solution, glucose forms a brown resinous product. In dilute alkali solution, D-glucose rearranges to give a mixture of D- glucose, D-mannose and d-fructose.



The above equilibrium is established via the enediol starting from any of these three hexoses.



That is why D-Fructose, although it has a ketonic C=O group, reduces Fehling's solution or Tollen's reagent. The rearrangement reaction of a monosaccharides in weakly alkaline solutions to give a mixture of isomeric sugars, is named as Lobry de Bruyn Van Ekestein rearrangement.

Structure of glucose

1. On the basis of elemental analysis and molecular weight determination the molecular formula of glucose is $C_6H_{12}O_6$.
2. The reduction of glucose with red phosphorus and HI gives n-hexane.

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{HI/redP}} \underset{\text{n-hexane}}{CH_3CH_2CH_2CH_2CH_2CH_3}$$

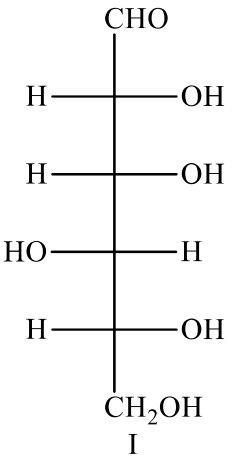
Therefore, the six carbon atoms of glucose form a straight chain.

3. It forms penta acetate on treatment with acetic anhydride which indicates the presence of five hydroxyl groups in the molecule.
4. Glucose reacts with hydroxyl amine to form an oxime and with hydrogen cyanide to form cyanohydrins. It indicates the presence of a carbonyl group. It also forms phenylhydrazone on treatment with phenylhydrazine.

5. The mild oxidation of glucose with bromine water or sodium hypobromide yields a monocarboxylic acid (gluconic acid) containing same number of carbon atoms as in glucose, i.e., six. This indicates that the carbonyl group must be aldehyde group.
6. The catalytic reduction of glucose gives a hexahydric alcohol (sorbitol) which gives hexaacetate on treatment with acetic anhydride. The sixth hydroxyl group must be obtained by the reduction of aldehyde group, thus further confirming the presence of an aldehyde group and five hydroxyl groups in glucose.
7. Oxidation of gluconic acid with nitric acid yields a dicarboxylic acid (glucaric acid) with the same number of carbon atoms as in glucose. Thus besides aldehyde group, glucose must contain a primary alcoholic group also, which generates the second carboxylic group on oxidation.
8. Glucose is a stable compound and does not undergo dehydration easily, indiacating that not more than one hydroxyl group is bonded to a single carbon atom. Thus all the hydroxyl groups are attached to different carbon atoms.

Open –chain structure of glucose

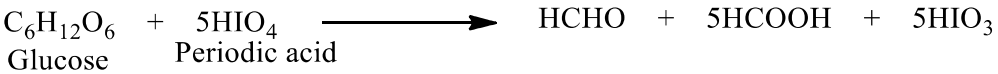
On the basis of above reactions, Fisher assigned an open chain structure of glucose shown below as structure I



I

D-(+)-Glucose

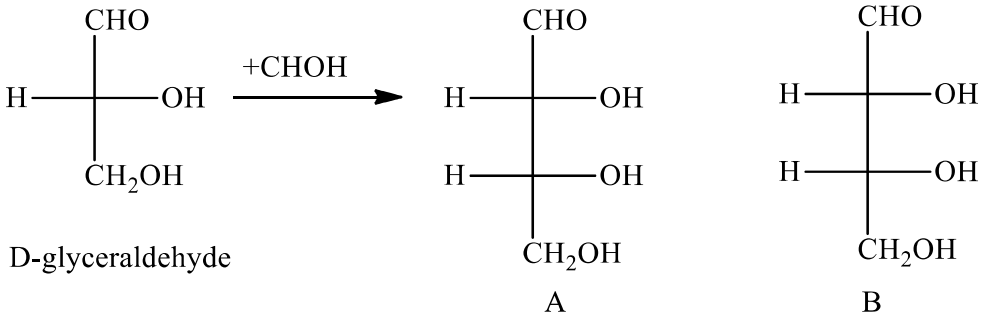
The above structure of glucose is also confirmed by the cleavage reaction of glucose with periodic acid. Five moles of periodic acid are consumed by one mole of glucose giving five moles of formic acid and one mole of formaldehyde.



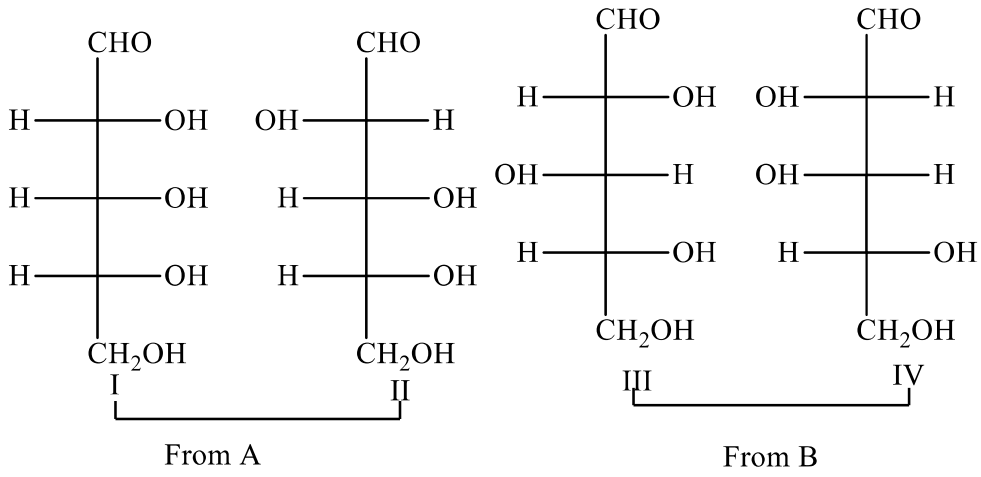
Configuration of D-Glucose

The configuration of D-glucose was proved by Emil Fisher by arguments similar to the ones stated below.

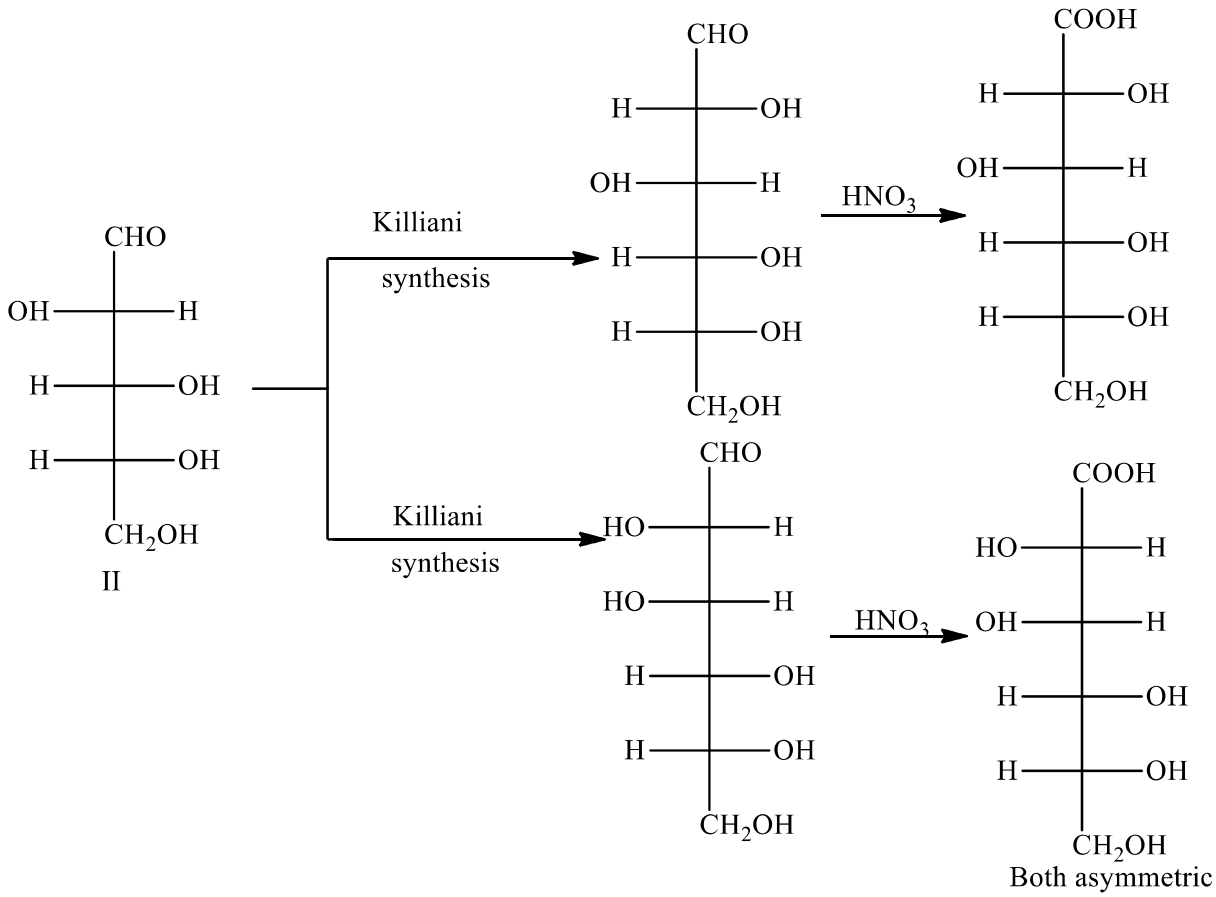
1. Construction of four possible D-pentoses. Taking the configuration of D-glyceraldehyde as the standard, two possible D-aldotetroses (A and B) may be constructed by adding a CHOH just below CHO, placing OH to the right and then to the left.



Similarily, each of the two D-tetroses (A and B) gives two D-aldopentoses. Thus four possible D-aldopentoses are:



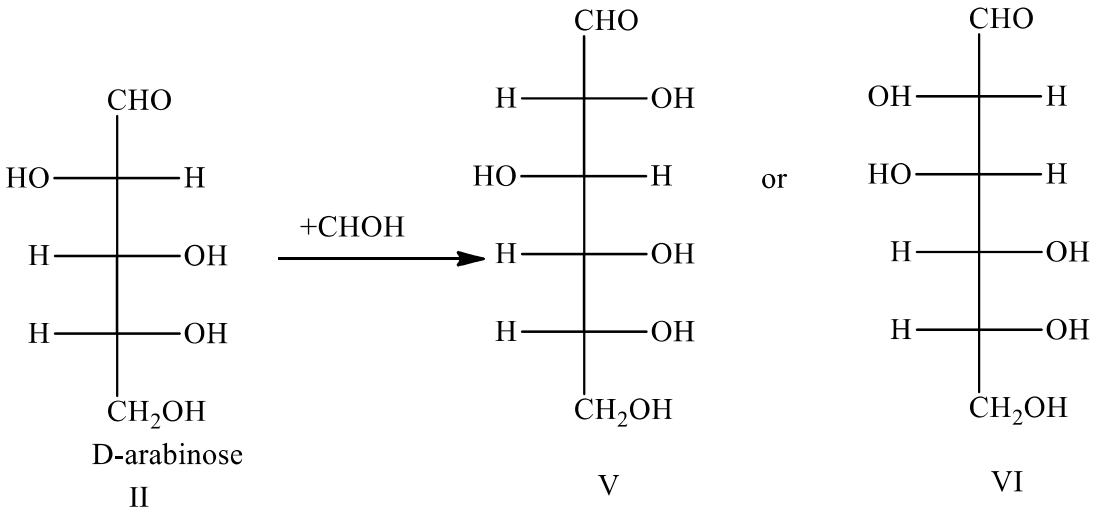
2. D-Arabinose has configuration II or IV. Oxidation of D-arabinose with nitric acid oxidizes the terminal CHO and CH_2OH groups yielding two optically active dicarboxylic acids. The forms II and IV can form two optically active diacids, while I and III can give meso acids only that have a plane of symmetry, therefore, D-arabinose is either II or IV.
3. Configyration II confirmed for D-arabinose. D-arabinose by Killiani-Fisher synthesis yields two epimeric aldohexoses, D-glucose and D-mannose. Thses of oxidation with nitric acid form two optically active dicarboxylic acids. This is theoretically possible only if D-arabinose has the configuration II and not IV.



Proceeding similarily, you will find that if D-arabinose had configuration IV, of the two dicarboxylic acids derived from it, one would be meso and one asymmetric. Hence D-arabinose has the configuration II.

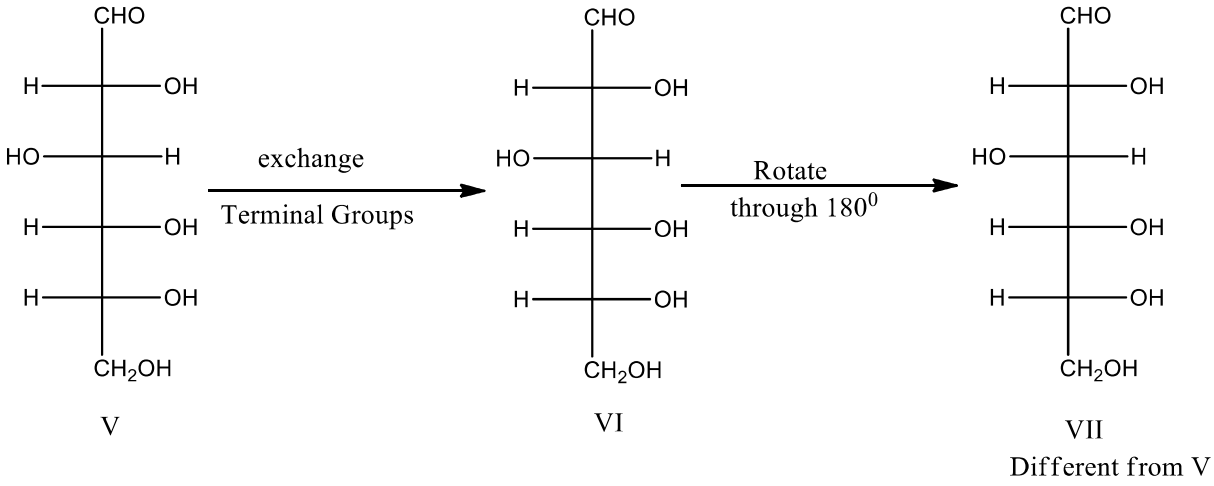
4. Ruff degradation of D-glucose and D-mannose produces D-arabinose in each case. In ruff degradation the CHOH below CHO is destroyed. Therefore , the configuration of the two

aldohexoses, D-glucose and D-mannose, can be derived by adding a new CHOH below CHO in form II of D-arabinose.



Hence D-glucose has configuration V or VI.

5. D-Glucose and L-Glucose yield the same dicarboxylic acid. This means thattwo sugars differ only in respect of the position of the terminal groups (CHO and CH_2OH). Therefore , the exchange of the terminal groups in D-glucose should be able to give a different aldohexose (L-glucose). Let us now examine configuration formula V and VI (one of which is D-glucose) from the angle.



If VII is rotated through 180^0 in the plane of paper, it gives an aldohexose VII, different from V. a similar procedure with formula VI does not give rise to a different sugar.

From the above arguments it is evident that D-glucose has the configuration as shown by the form V.

Cyclic structure of D-Glucose

The open chain structure of glucose explained most of its properties. However, it could not explain the following facts.

1. Despite having an aldehyde group, glucose does not undergo certain characteristic reactions of aldehyde,

(a) Glucose does not react with sodium bisulphate to form addition product.

(b) Glucose does not react with ammonia.

(c) Glucose does not give Schiff's test and 2, 4-DNP test like other aldehydes.

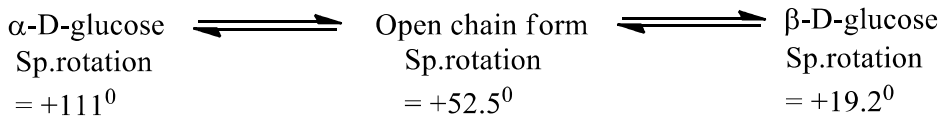
2. Glucose reacts with hydroxylamine to form an oxime but glucose pentaacetate does not react with hydroxylamine. This shows that –CHO group is not present in glucose pentaacetate.
3. **D (+)-Glucose exist in two stereoisomeric forms i.e., α- D (+)-Glucose and β- D (+)-Glucose.** These two forms are crystalline and have different m.p and optical rotations. When glucose was crystallized from a concentrated solution at 303 K, it gave α-form of glucose having m.p 419 K and $[\alpha]_D = +111^0$. On the other hand, the β-form of glucose is obtained on crystallization of glucose from a hot saturated solution of at a temperature above 371 K. The β-form of glucose has m.p 423 K and $[\alpha]_D = +19.2^0$.
4. **Mutarotation**. When either of two forms of glucose (α- D-glucose and β- D-glucose) are dissolved in water and allowed to stand, these get slowly converted into other form and a equilibrium mixture of both α- D-glucose (36 %) and β- D-glucose (about 64%) is formed.

The formation of equilibrium mixture can be explained as:

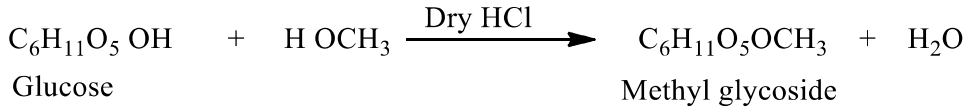
The α- D-glucose has a specific rotation of $+111^0$, while β- D-glucose has a specific rotation of $+19.2^0$. When α-form is dissolved in water, its specific rotation falls until a constant value of $+52.5^0$ is reached. On the other hand, when β-form is dissolved in water, its specific rotation increases and becomes constant at 52.5^0.

This spontaneous change in specific rotation of an optically active compound with time to an equilibrium value is called mutarotation.(Latin, muto means to change).

Thus, there is an equilibrium mixture of α- and β-forms in the solution



5. Glucose forms isomeric methyl glucosides. When glucose is heated with methanol in the presence of dry HCl, it gives two isomeric monomethyl derivatives known as α-D-glucoside (m.p. = 438 K) and β-D-glucoside (m.p. 380 K).



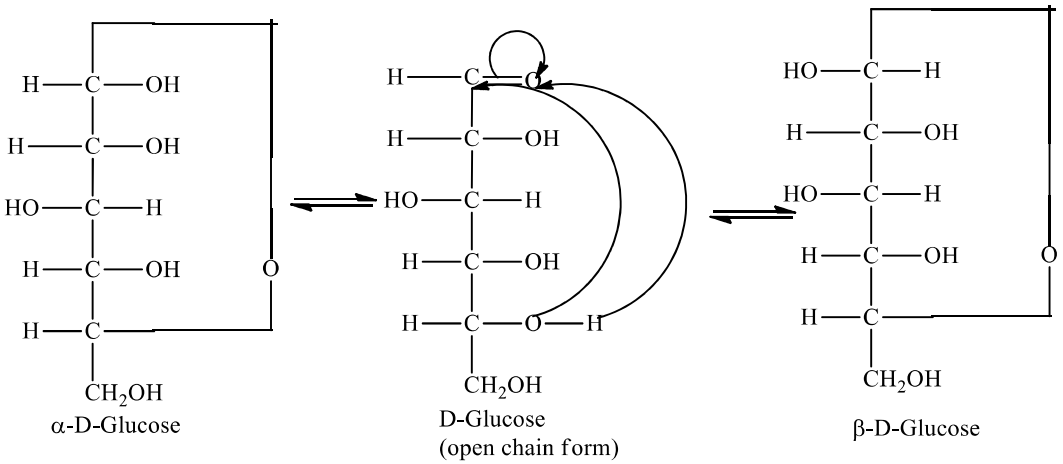
These two glucosides do not reduce Fehling's solution and also do not react with HCN or NH_2OH indicating that the free –CHO group is not present but it is converted to –COOH group.

Cyclic structure of Glucose

Anomers:

Glucose forms a hemiacetal between the –CHO group and the -OH group on the C_5 atom. As a result, of cyclisation, C_1 becomes asymmetric (chiral) and the newly formed –OH group may be either on the left or on the right in Fisher projection formulae. These results in the formation of two isomerswhich differ in the orientation of H and –OH groups around C1 atom. These isomers are known as α- D-glucose and β- D-glucose. The isomer having the –OH group on the right is called α- D-glucose and one having the –OH group on the left is called β- D-glucose. Such pairs of optical isomers which differ in the configuration only around C_1 atom are called anomers.

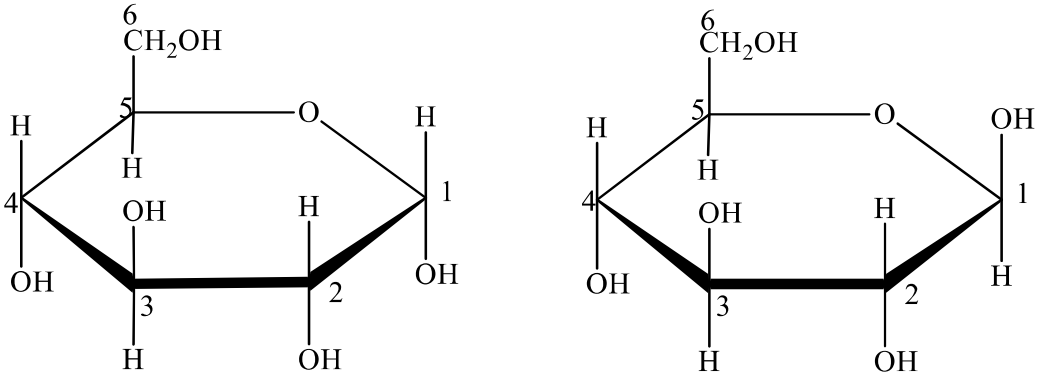
These two forms are not mirror image of each other, hence are not enantiomers. The C1 carbon is known as anomeric carbon or glycosidic carbon.



The above representations are called Fisher projection formulae.

Haworth projection formulae or pyranose structures of D-Glucose.

In Haworth structures drawn with the heterocyclic oxygen in the upper right corner, the α-form has the –OH group on C_1 pointing "down". The β-form has the same group pointing "up". For D-sugars, the free –CH2OH group of an aldohexose is drawn above the plane of ring when ring oxygen is in the upper right. The rest is the simple, the groups on the left of the Fisher projection are up and those on the right are down in the Haworth structure.



α-D-Glucose
or
α-D-Glucopyranose

β–D-Glucose
or
β-D-Glucopyranose

Fructose

Fructose is another commonly known monosaccharide having the same molecular formula as glucose. It is laevorotatory because it roatates plane polarized light towards the left. It is present abundantly in fruits. That is why it is called fruit-sugar also.

Physical properties

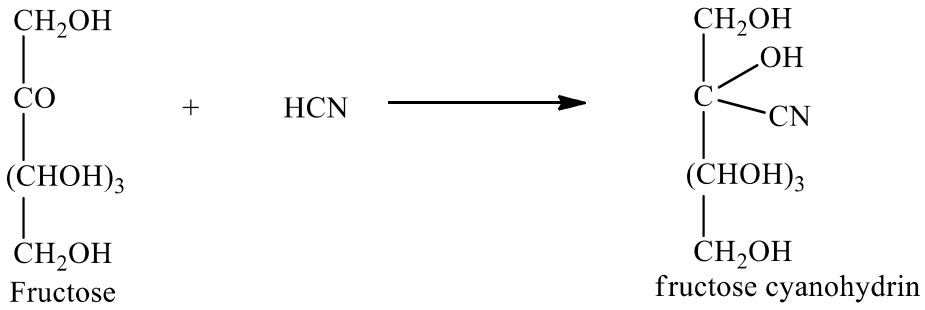
1. It is sweetest of all known sugars.
2. It is readily soluble in water, sparingly soluble in alcohol and insoluble in ether.
3. It is white crystalline solid with m.p. 375 K.
4. Fresh solution of fructose has a specific rotation -133^0.

Chemical properties of fructose

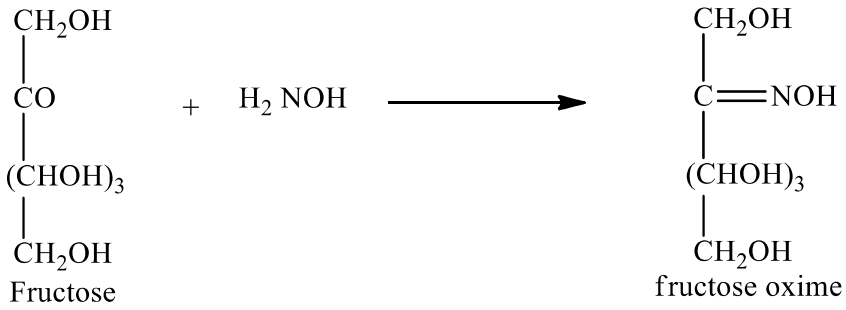
Chemical properties of fructose can be studied under the following heads:

(A) Reactions due to ketonic group

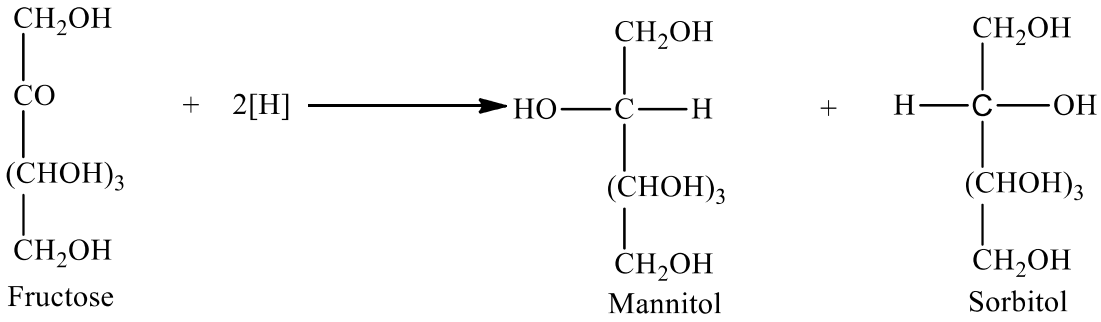
1. **Reaction with HCN**. Fructose reacts with HCN to form cyanohydrins.



2. **Reaction with hydroxylamine**. Fructose reacts with hydroxylamine to form an oxime.

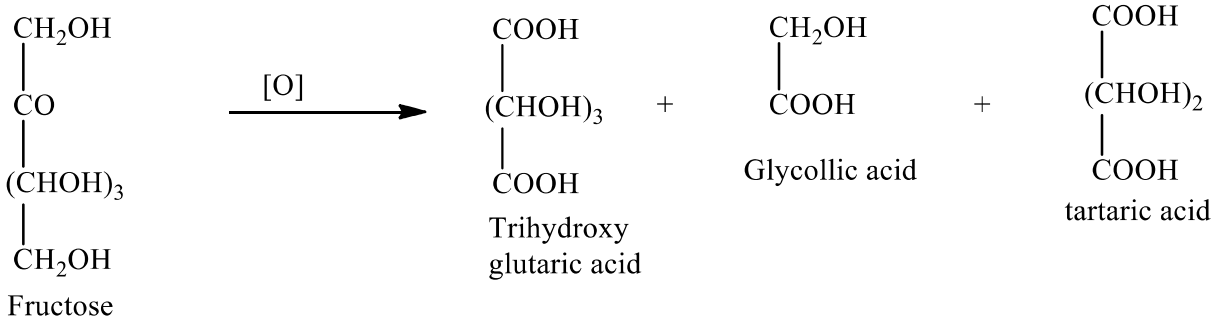


3. **Reduction**. Fructose gives a mixture of sorbitol and mannitol on reduction with Na-Hg and water or catalytic hydrogenation.



4. **Oxidation.** (i) there is no action of mild oxidizing agent like bromine water on fructose.

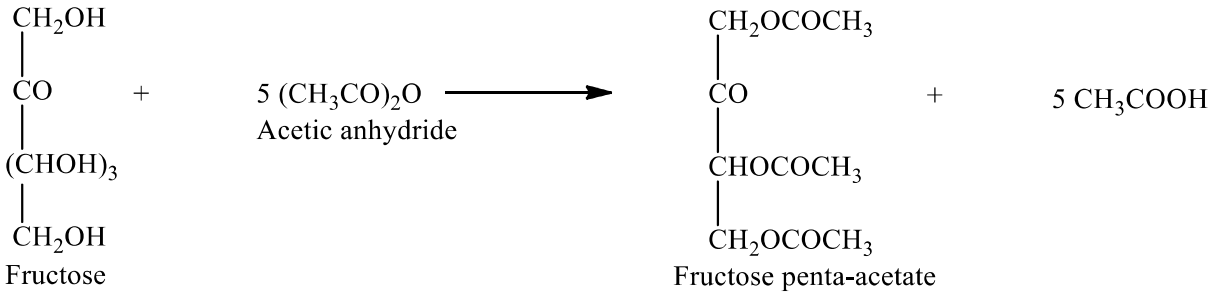
   (ii) Strong oxidizing agents like nitric acid oxidize fructose into a mixture of trihydroxy glutaric, glycolic and tartaric acids.



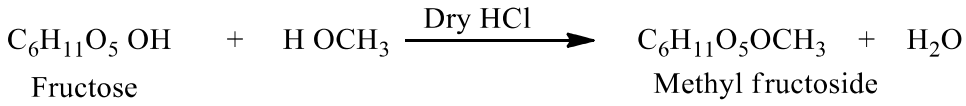
   (iii) Unlike other ketones, it reduces Tollen's reagent and Fehling solution. This is due to the presence of traces of glucose in alkaline medium.

[B] reactions of the alcoholic group

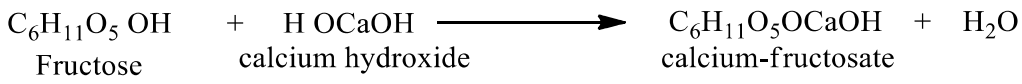
1. Acetylation . with acetic anhydride or acetyl chloride, fructose forms penta-acetate.



2. Reaction with methyl alcohol (glucoside formation). Fructose reacts with methyl alcohol in the presence of dry HCl gas forming methyl fructoside.



3. Reaction with metallic hydroxides (fructosate formation)



Structure of Fructose

1. elemental analysis and molecular weight determination of fructose show that it ahs the molecular formula $C_6H_{12}O_6$.

2. fructose on reduction gives sorbitol which on reduction with HI and red P gives a mixture of n-hexane and 2-Iodohexane. This reaction indicates that six carbon atoms in fructose are in a straight chain.

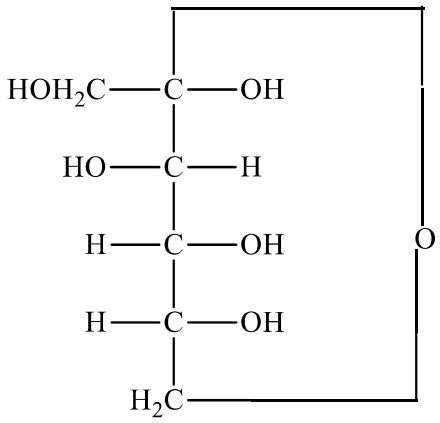
3. Fructose reacts with hydroxylamine, HCN and phenylhydrazine. It shows the presence of _CHO or C=O group in the molecule of fructose.

4. On treatment with bromine water , no reaction takes palce. This rules out the possibility of presence of –CHO group.

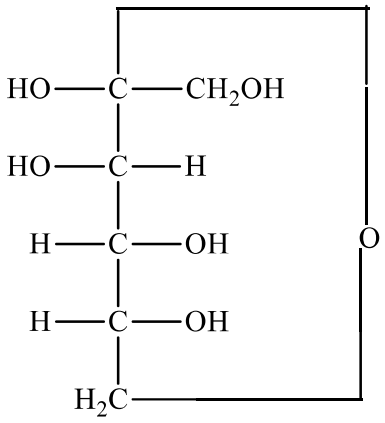
5. on oxidation with nitric acid, it gives glycollic acid and tartaric acids which contain smaller number of carbon atoms than fructose. This shows that a ketonic group is present at position 2. It is at this point that the molecule is broken.

Cyclic structure of D-Fructose

Fructose shows the property of mutarotation. This means that it exists in two forms α-fructose and β-fructose which are cyclic in structure and change into each other via the open chain structure. The cyclic and pyranose structures of α-D-fructose and β-D-fructose are represented below:

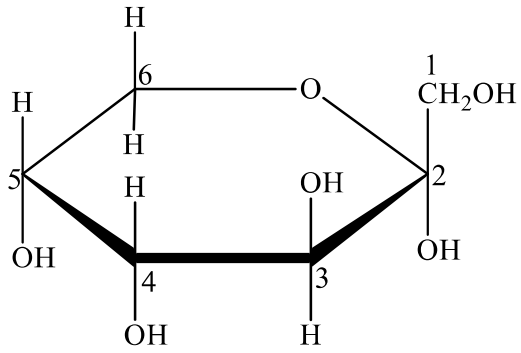


α-D-fructose

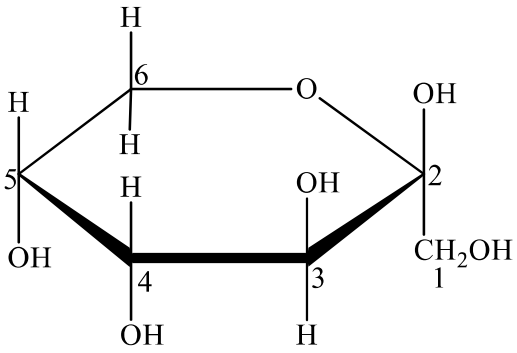


β-D-fructose

Haworth Pyranose structure

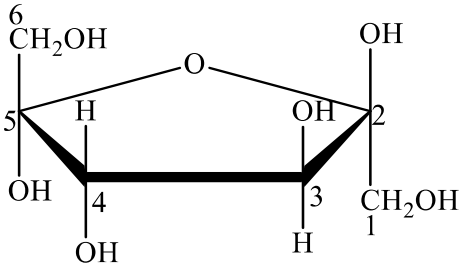


α-D-fructopyranose



β-D-fructopyranose

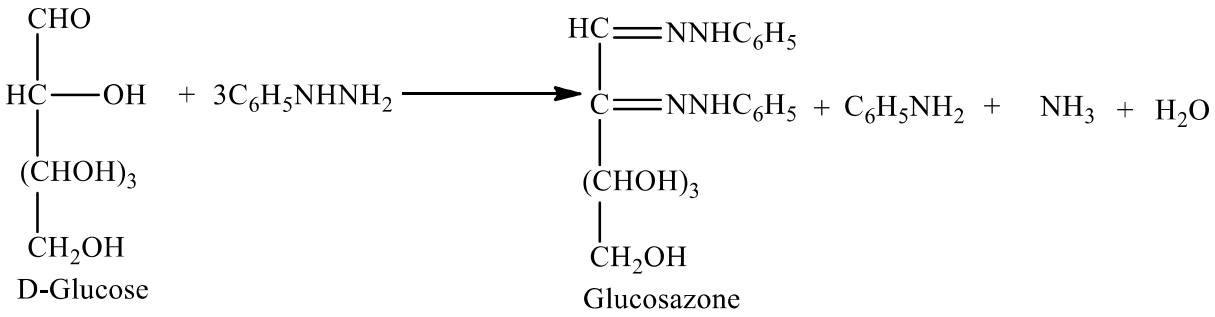
However, when fructose is linked to glucose in a sucrose molecule, it has the furanose structure as shown below:



β-D-fructofuranose

7.5 MECHANISM OF OSAZONE FORMATION

Glucose and fructose react with one equivalent of phenylhydrazine, forming phenylhydrazone. In contrast, α-hydroxy carbonyl compounds react with three equivalents of phenylhydrazine to form bis-phenylhydrazones, commonly called osazones.



Phenylosazones crystallize readily and are useful derivatives for identifying sugars.

Mechanism: the first equivalent of phenylhydrazine forms phenylhydrazone with the aldehyde or ketone group as expected. Phenylhydrazone the ungergoes the rearrangement , known as Amadori rearrangement, to give α-iminoketone (IV) with the loss of aniline.