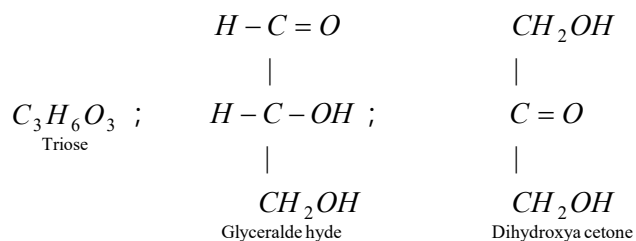## Monosaccharides.

These are the simplest one unit non-hydrolysable sugars. They have the general formula $C_nH_{2n}O_n$ where n varies from 3 to 9 carbon atoms. About 20 monosaccharides occur in nature. The simplest are trioses (n=3)

$$C_3H_6O_3 \; ; \qquad
\begin{array}{c}
H - C = O \\
| \\
H - C - OH \; ; \\
| \\
CH_2OH
\end{array}
\qquad
\begin{array}{c}
CH_2OH \\
| \\
C = O \\
| \\
CH_2OH
\end{array}$$

Triose   Glyceralde hyde   Dihydroxya cetone

The most important naturally occurring monosaccharides are pentoses and hexoses. A common pentose is ribose and two common hexoses are glucose and fructose.

Except ketotriose {dihydroxyacetone}, all aldose and ketoses {monosaccharides} contain asymmetric carbon atoms and are optically active. Number of isomers depend upon the number of asymmetric carbon atom in the molecules of monosaccharide and is derived by the formula 2^n where n is the number of asymmetric carbon atoms in the molecules.

Number of carbon atoms		No. of asymmetric carbon atoms	No. of isomers
Trioses 3	CH₂OHCHOHCHO	1	2
	CH₂OHCOCH₂OH	–	–
Tetroses 4	CH₂OH(CHOH)₂CHO	2	4
	CH₂OHCHOHCOCH₂OH	1	2
Pentoses 5	CH₂OH(CHOH)₃CHO	3	8
	CH₂OH(CHOH)₂COCH₂OH	2	4
Hexoses 6	CH₂OH(CHOH)₄CHO	4	16
	CH₂OH(CHOH)₃COCH₂OH	3	8

Class	Molecular formula	Structural formula	Examples
		Aldoses	
Aldotrioses	C₃H₆O₃	CH₂OHCHOHCHO	Glyceraldehyde
Aldotetroses	C₄H₈O₄	CH₂OH(CHOH)₂CHO	Erythrose, Threose
Aldopentoses	C₅H₁₀O₅	CH₂OH(CHOH)₃CHO	Arabinose, Ribose, Xylose, Lyxose
Aldohexoses	C₆H₁₂O₆	CH₂OH(CHOH)₄CHO	Glucose, Galactose, Mannose, Allose, Talose, Gulose, Idose, etc.
		Ketoses	
Ketotrioses	C₃H₆O₃	CH₂OHCO.CH₂OH	Dihydroxyacetone
Ketotetroses	C₄H₈O₄	CH₂OH.CO.CHOH.CH₂OH	Erythrulose

Ketopentoses	$C_5H_{10}O_5$	$CH_2OH.CO.(CHOH)_2CH_2OH$	Ribulose, Xylulose
Ketohexoses	$C_6H_{12}O_6$	$CH_2OH.CO(CHOH)_3CH_2OH$	Fructose, Sorbose, Tangatose, Psicose

(1) **D and L-designation:** By **convention,** a molecule is assigned D-configuration if the –OH group attached to the carbon adjacent to the –CH_2OH group (last chiral carbon) is on the right hand side irrespective of the position of other groups. On the other hand, the molecule is assigned L-configuration if the –OH group attached to the carbon adjacent to the –CH_2OH group is on the left.
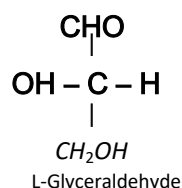
However, it may be noted that D- and L- do not represent dextrorotatory or laevorotatory. The optical activity of the molecule is represented by (+) and (–) which represent the direction of rotation of plane polarized light whether dextrorotatory or laevorotatory.

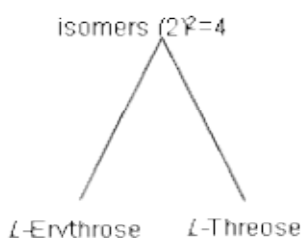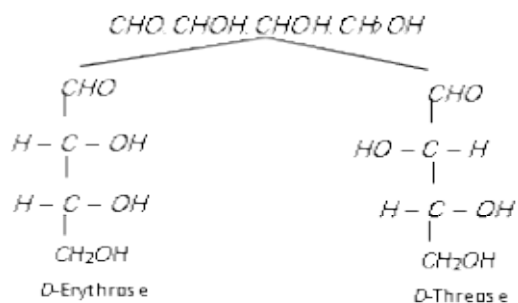(2) **Configuration:** Configuration of Monosaccharides

(i) **Aldotriose:**

$CHO.CHOHCH_2OH$ isomers $(2)^1 = 2$

$$\begin{array}{c} CHO \\ | \\ H - C - OH \\ | \\ CH_2OH \end{array}$$

D-Glyceraldehyde

$$\begin{array}{c} CHO \\ | \\ OH - C - H \\ | \\ CH_2OH \end{array}$$

L-Glyceraldehyde

(ii) **Aldotetrose :**

$CHO.CHOH.CHOH.CH_2OH$ isomers $(2)^2 = 4$

$$\begin{array}{c} CHO \\ | \\ H - C - OH \\ | \\ H - C - OH \\ | \\ CH_2OH \end{array}$$

D-Erythrose

$$\begin{array}{c} CHO \\ | \\ HO - C - H \\ | \\ H - C - OH \\ | \\ CH_2OH \end{array}$$
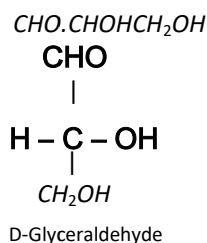
D-Threose

L-Erythrose   L-Threose
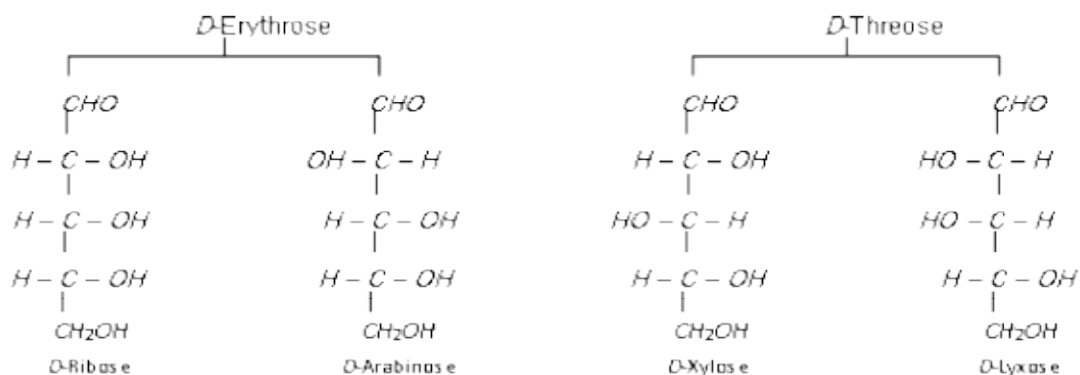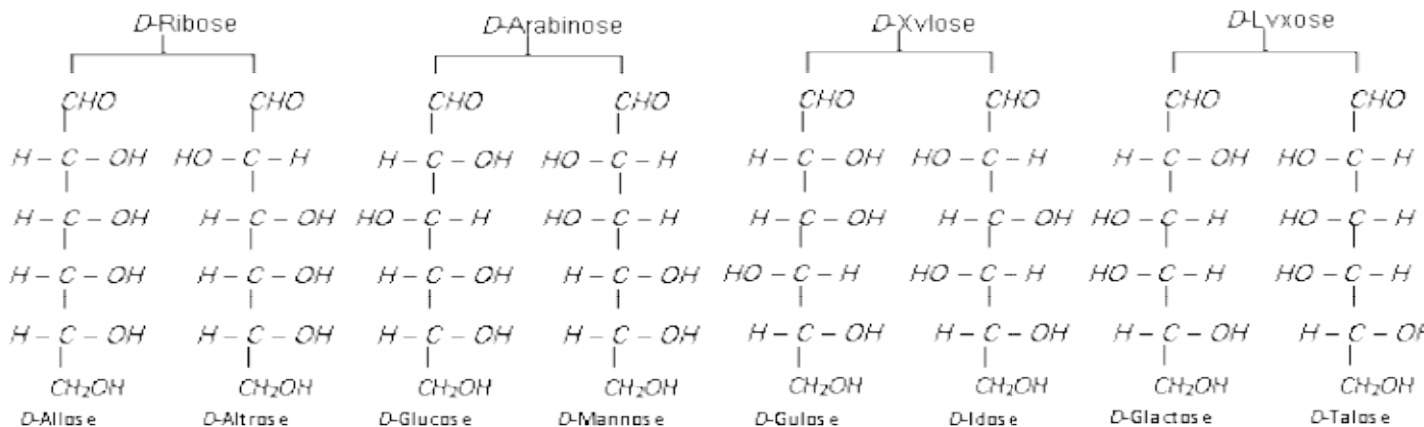
So it has four isomers, i.e., D, L-Erythrose and D, L-Threose.

(iii) Aldopentose: $CHO.CHOH.CHOH.CHOH.CH_2OH$, isomers $(2)^3 = 8$

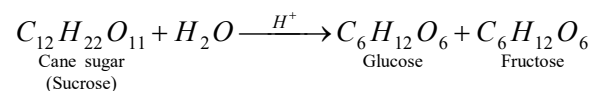So aldopentoses has eight isomers, i.e., D- and L-Ribose, D- and L-Arabinose, D- and L-Xylose and D, L-Lyxose

(iv) Aldohexose: $CHO.(CHOH)_4CH_2OH$,   isomers $(2)^4 = 16$

(3) **Glucose; C₆H₁₂O₆; Aldo-hexose:** Glucose is known as **dextrose** because it occurs in nature as the optically active dextrorotatory isomer. It is also called grape sugar as it is found in most sweet fruits especially grapes. It is present in honey also. It is essential constituent of human blood. The blood normally contains 65 to 110 mg of glucose per 100 mL (hence named Blood sugar). In combined form, it occurs in cane sugar and polysaccharides such as starch and cellulose. It is also present in various glycosides like **amygdalin** and **salicin.**

(i) **Preparation**

(a) Laboratory method

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

Note: HCl (dil.) is used for hydrolysis. Glucose being much less soluble in alcohol than fructose separates out by crystallising on cooling.

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

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{H^+} \underset{\text{Glucose}}{nC_6H_{12}O_6}$$
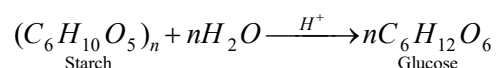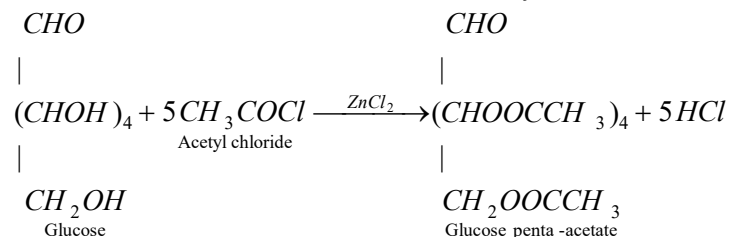
A thin paste of starch is boiled with dilute acid till the hydrolysis is complete. The excess of acid is neutralised with chalk (calcium carbonate) and the filtrate containing glucose is decolourised with animal charcoal. The solution is concentrated and evaporated under reduced pressure. Glucose is obtained in crystalline form.

(ii) **Physical properties:** It is a colourless crystalline solid, melts at $146\,^oC$. It is readily soluble in water. From aqueous solution, it separates as a crystalline monohydrate $(C_6H_{12}O_6.H_2O)$ which melts at $86\,^oC$. It is sparingly soluble in alcohol but insoluble in ether. It is less sweet (three-fourth) than cane sugar. It is optically active and the ordinary naturally occuring form is (+) glucose or dextro form. It shows **mutarotation.**

(iii) **Chemical properties:** Glucose is a polyhydroxy aldehyde i.e. aldohexose. It has five – OH groups and one aldehydic group. It shows characteristics of hydroxyl and aldehydic group. Important chemical reaction of the glucose are the following:
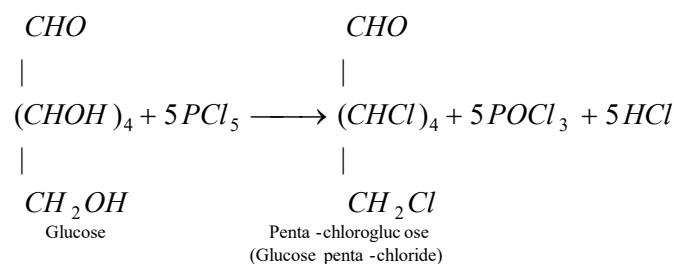
(a) Alcoholic reaction (Reaction due to –OH group)

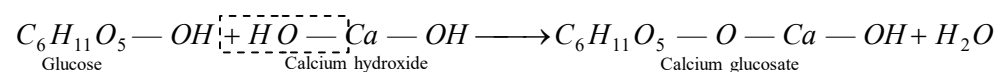• Reaction with acid chlorides and acid anhydride

$$
\begin{array}{c}
CHO \\
| \\
(CHOH)_4 + 5\,CH_3COCl \xrightarrow{\;ZnCl_2\;} (CHOOCCH_3)_4 + 5\,HCl \\
| \\
CH_2OH
\end{array}
\qquad
\begin{array}{c}
CHO \\
| \\
\\
| \\
CH_2OOCCH_3
\end{array}
$$

Glucose   Acetyl chloride   Glucose penta-acetate

This shows that a molecule of glucose contains 5 – OH groups.

• Reaction with PCl_5

$$
\begin{array}{c}
CHO \\
| \\
(CHOH)_4 + 5\,PCl_5 \longrightarrow (CHCl)_4 + 5\,POCl_3 + 5\,HCl \\
| \\
CH_2OH
\end{array}
$$

Glucose   Penta-chloroglucose
(Glucose penta-chloride)

• Reaction with metallic hydroxides:

$$
\underset{\text{Glucose}}{C_6H_{11}O_5 - OH} + \underset{\text{Calcium hydroxide}}{HO - Ca - OH} \longrightarrow \underset{\text{Calcium glucosate}}{C_6H_{11}O_5 - O - Ca - OH} + H_2O
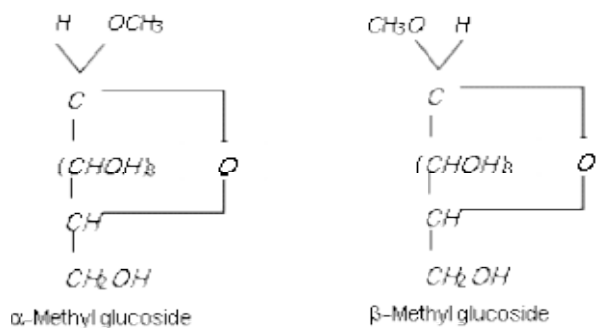$$

Note: Glucose behaves as a weak acid. Instead of $Ca(OH)_2$ we can take other metallic hydroxide like $Ba(OH)_2, Sr(OH)_2, Cu(OH)_2$ etc to form glucosate which is soluble in water.

• Formation of glycosides: $C_6H_{11}O_5 - OH + H\,OCH_3 \xrightarrow{\;HCl\;} C_6H_{11}O_5OCH_3 + H_2O$

α- and β-Methyl glucoside

α-Methyl glucoside   β–Methyl glucoside

This reaction shows the presence of ring structure in glucose.

(b) Reactions of carbonyl group (Aldehydic group)

• Reduction: $CH_2OH(CHOH)_4 CHO + 2H \xrightarrow[H_2O]{Na-Hg} CH_2OH(CHOH)_4 CH_2OH$

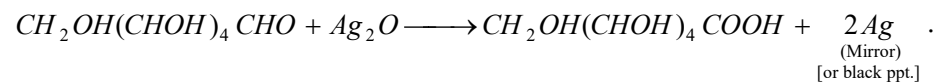   Glucose   Sorbitol
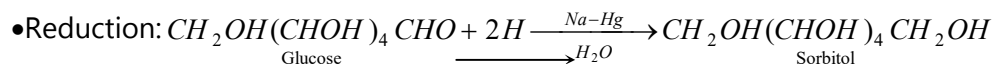
On prolonged heating with concentrated HI and red phosphorus at $110\,^oC$, glucose forms a mixture of 2-iodohexane and n-hexane.
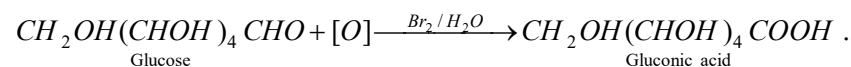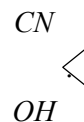
• Oxidation

❑ Reaction with Fehling solution:

$CH_2OH(CHOH)_4 CHO + 2CuO \longrightarrow CH_2OH(CHOH)_4 COOH + Cu_2O$.

         Glucose   Gluconic acid   (red ppt.)
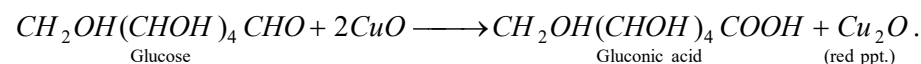
❑ Reaction with Tollen's reagent:

$CH_2OH(CHOH)_4 CHO + Ag_2O \longrightarrow CH_2OH(CHOH)_4 COOH + \underset{\substack{(Mirror) \\ [or\ black\ ppt.]}}{2Ag}$.

❑ Reaction with Bromine water:

$CH_2OH(CHOH)_4 CHO + [O] \xrightarrow{Br_2/H_2O} CH_2OH(CHOH)_4 COOH$.

         Glucose   Gluconic acid

❑ Reaction with Nitric acid:

$CH_2OH(CHOH)_4 CHO + 3[O] \xrightarrow{HNO_3} COOH(CHOH)_4 COOH + H_2O$.

     Glucose (C_6) Saccharic acid (C_6)

• Reaction with HCN: $CH_2OH(CHOH)_4 CHO + HCN \longrightarrow CH_2OH(CHOH)_4 CH \overset{CN}{\underset{OH}{\diagup}}$

                                                           Glucose cyanohydri n
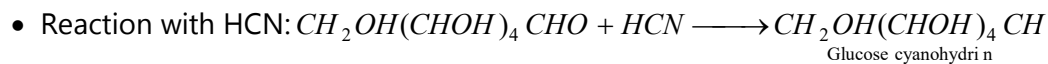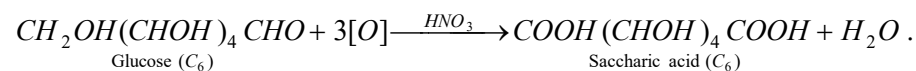
• Reaction with hydroxyl amine

$CH_2OH(CHOH)_4 CHO + NH_2OH \rightarrow CH_2OH(CHOH)_4 CH = NOH + H_2O$.

                                     Glucose oxime
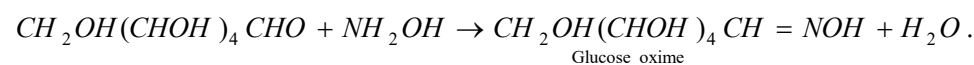
• Reaction with Phenyl hydrazine (Fischer's mechanism): When warmed with excess of phenyl hydrazine, glucose first forms phenylhydrazone by condensation with – CHO group.

CHO + H₂NNHC₆H₅ → CH = NNHC₆H₅

Glucose / Phenyl hydrazine / Warm / Glucose phenyl hydrazone
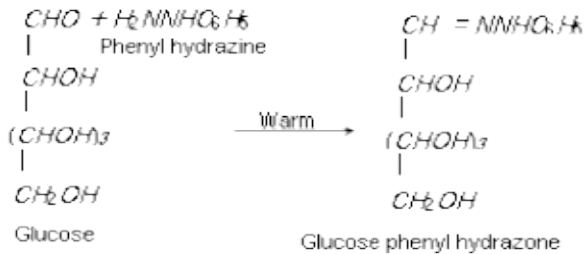
The adjacent – CHOH group is then oxidized by a second molecule of phenyl hydrazine.

The resulting carbonyl compounds reacts with a third molecule of phenyl hydrazine to yield glucosazone.

Glucosazone

(c) Miscellaneous reactions

• Fermentation: $C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$

Glucose / Ethanol

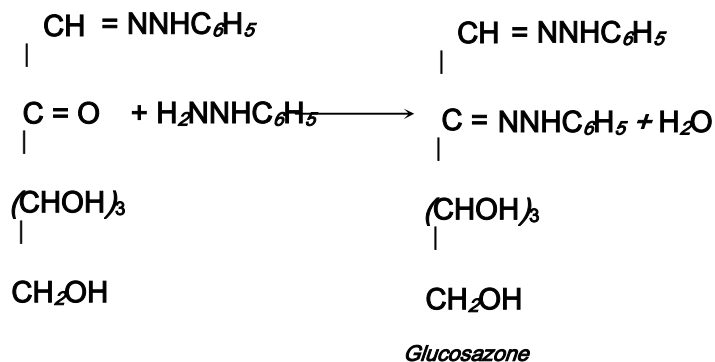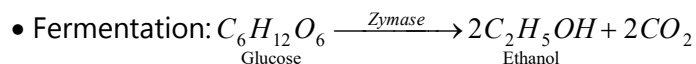• Dehydration: When heated strongly or when treated with warn concentrated sulphuric acid, glucose is dehydrated to give a black mass (sugar carbon).

• Reaction with alkalies: When warmed with concentrated alkali, glucose first turns yellow; then brown and finally gives a resinous mass.
A dilute solution of glucose, when warmed with dilute solution of alkali, some glucose is converted into fructose and mannose. **D-glucose** and **D-mannose** are **epimers**.

Glucose / Enol / Fructose / Enol / Mannose

D(+) Glucose   D(+) Mannose

Epimers
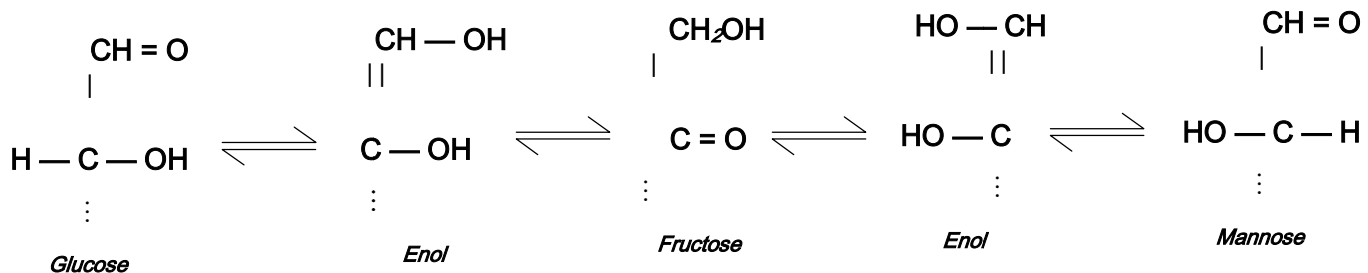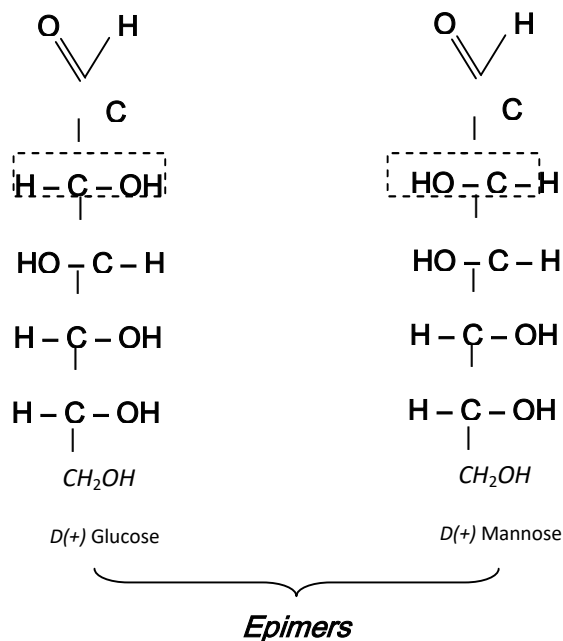
• Action of concentrated hydrochloric acid

$$C_6H_{12}O_6 \xrightarrow{Conc.HCl} \underset{\text{Laevulic acid}}{CH_3COCH_2CH_2COOH} + HCOOH + H_2O$$

On treatment with conc. HCl, glucose can also form hydroxymethyl furfural.

Hydroxymethyl

furfural
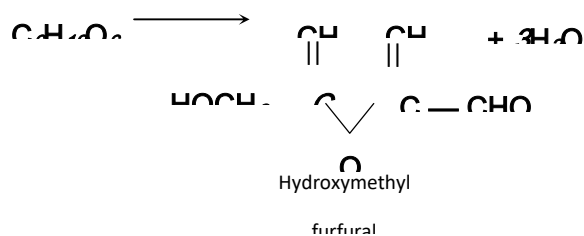
This on acid treatment gives laevulic acid

(iv) **Uses**

(a) In the preservation of fruits and preparation of jams and jellies.
(b) In the preparation of confectionary and as a sweetening agent.
(c) As a food for patients, invalids and children.
(d) In the form of calcium glucosate as medicine in treatment of calcium deficiency.

(e) As a reducing agent in silvering of mirrors.

(f) As a raw material for alcoholic preparations.

(g) In industrial preparation of vitamin-C.

(h) In the processing of tobacco.

(i) As an intravenous injection to the patients with lower glucose content in blood.

(v) **Test of glucose**

(a) When heated in a dry test tube, it melts, turns brown and finally black, giving a characteristic smell of burnt sugar.

(b) When warmed with a little conc. H_2SO_4, it leaves a charred residue of carbon.

(c) When it is boiled with dilute $NaOH$ solution, it first turns yellow and then brown.

(d) Molisch's test: This is a general test for carbohydrates. A drop or two of alcoholic solution of α-naphthol is added to 2mL of glucose solution. 1 mL of concentrated H_2SO_4 is added carefully along the sides of the test tube. The formation of a violet ring, at the junction of two liquids confirms the presence of a carbohydrate.

(e) Silver mirror test: A mixture of glucose and ammonical silver nitrate is warmed in a test tube. Appearance of silver mirror on the inner walls confirms glucose.

(f) Fehling's solution test: A little glucose is warmed with Fehling's solution. A red precipitate of cuprous oxide is formed.

(g) Osazone formation: Glucose on heating with excess of phenyl hydrazine in acetic acid gives a yellow crystalline compound, m.pt. $205^o C$.

(vi) **Structure of glucose**: The structure of glucose has been established as follows

(a) Open chain structure: It is based on the following points:

• Elemental analysis and molecular mass determination show that the molecular formula of glucose is $C_6H_{12}O_6$.

• Glucose on complete reduction with HI and red phosphorus finally gives n-hexane. This indicates that it contains a straight chain of six carbon atoms.

• It reacts with acetic anhydride and forms penta-acetate derivative. This shows the presence of five hydroxyl groups each linked to a separate carbon atom as the molecule is stable.

• Glucose combines with hydroxyl amine to form a monoxime. It also combines with one mole of HCN to form a cyanohydrin. These reactions indicate the presence of a carbonyl group, $>C=O$, in the molecule.

• Mild oxidation of glucose with bromine water gives gluconic acid. This shows the presence of an aldehyde group.

On the basis of above observations, the following open chain structure can be written for glucose.

$$\underset{\underset{H}{|}}{H-C}-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{\overset{*}{C}}}-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{\overset{*}{C}}}-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{\overset{*}{C}}}-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{\overset{*}{C}}}-\overset{\overset{H}{|}}{C}=O$$
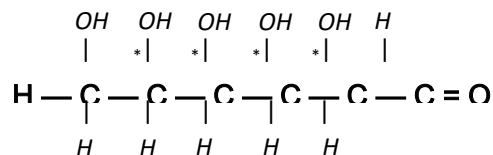
There are four asymmetric carbon atoms marked by asterisks (*) in the molecule. This representation is incomplete, because a definite configuration to these asymmetric centres has not been assigned. The configuration of D-glucose was proved by **Emil Fischer**. The structure of D-glucose as elucidated by Emil Fischer is,
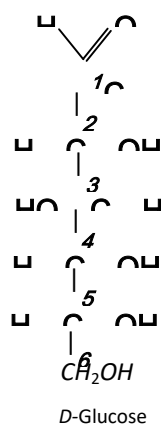
D-Glucose

Evidence against open chain structure: The open chain formula of glucose accounts for most of the reactions satisfactorily but fails to explain the following

❒ Even though an aldehyde group is present, the glucose does not react with $NaHSO_3$ and NH_3 .

❒ Glucose does not give the Schiff's test for aldehydes.

❒ Glucose does not react with Grignard reagents.

❒ Glucose penta-acetate does not react with hydroxyl-amine.

❒ Two isomeric methyl glucosides (αand β) are obtained by heating glucose with methyl alcohol in presence of dry HCl gas.
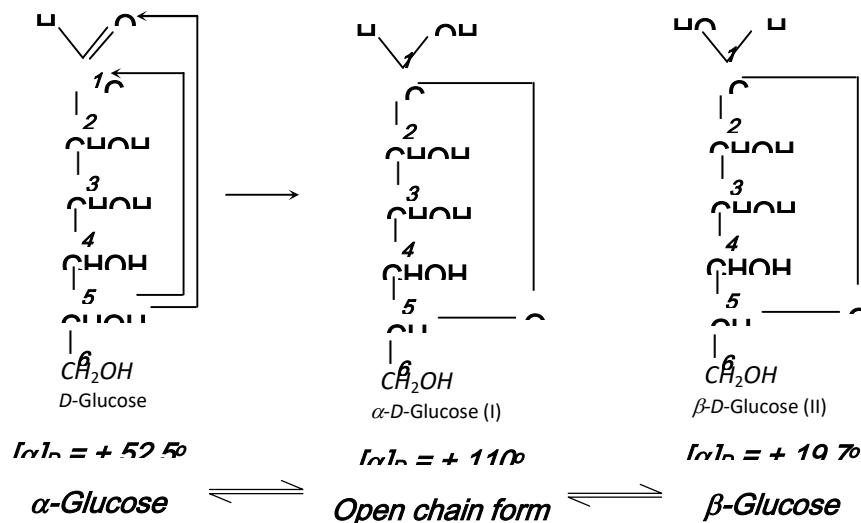
❏ Glucose exists in two stereoisomeric forms (α and β). α- glucose with specific rotation $+110^o$ is obtained by crystallizing glucose from alcohol or acetic acid solution, whereas β-glucose with specific rotation $+19.7^o$ is obtained by crystallizing glucose from pyridine solution.

❏ An aqueous solution of glucose shows **mutarotation,** i.e., its specific rotation gradually decreases from $+110^o$ to $+52.5^o$ in case of α-glucose and increases from $+19.7^o$ to $+52.5^o$ in case of β-glucose.

All these observation indicate that free aldehydic group is not present in the molecule.

(b) Cyclic structure of glucose: D-glucose exists in two optically active forms known as α-D-glucose and   β-D-glucose.

α-D-glucose has specific rotation of $+110^o$ and β-D-glucose has specific rotation of $+19.7^o$. The two isomers are interconvertible in aqueous solution. The equilibrium rotation is $+52^o$. The equilibrium mixture has 36% α-glucose, 64% β-glucose. Glucose forms a stable cyclic hemiacetal (according to Fischer) between $-CHO$ group and the $-OH$ group of the fifth carbon atom in pyranose structure. In this process first carbon atom becomes asymmetric giving two isomers (I) and (II) which differ only in the configuration of the first asymmetric carbon.

D-Glucose

α-D-Glucose (I)

β-D-Glucose (II)

$[\alpha]_D = +52.5^o$

$[\alpha]_D = +110^o$

$[\alpha]_D = +19.7^o$

α-Glucose ⇌ Open chain form ⇌ β-Glucose

Carbon-1 in both configuration (I) and (II) is called an anomeric carbon atom. Due to anomeric carbon, glucose exists in two forms. Both the forms have different physical properties and are called anomers.

The ring structure explains all the reactions of glucose. The objections against the open chain structure of glucose have also been satisfactory explained, e.g.,

•α- andβ-glucose on treatment with CH_3OH in presence of dry HCl gas forms α- and β-methyl glucosides respectively.

H – C – OH
H – C – OH
HO – C – H
H – C – OH
H – C
  |
 CH_2OH

α-D-Glucose (I)

$\xrightarrow[\text{(Dry } HCl \text{ gas)}]{+ CH_3OH}$

H – C – OCH₃
H – C – OH
HO – C – H
H – C – OH
H – C
  |
 CH_2OH

α-D-Methyl glucoside

HO – C – H
H – C – OH
HO – C – H
H – C – OH
H – C
  |
 CH_2OH

β-D-Glucose (II)

$\xrightarrow[\text{(Dry } HCl \text{ gas)}]{+ CH_3OH}$

CH₃O – C – H
H – C – OH
HO – C – H
H – C – OH
H – C
  |
 CH_2OH

β-D-Methyl glucoside
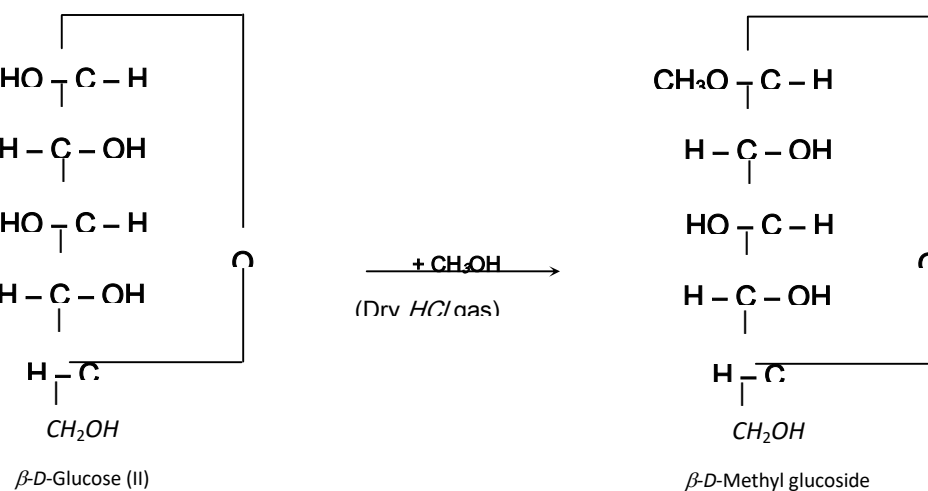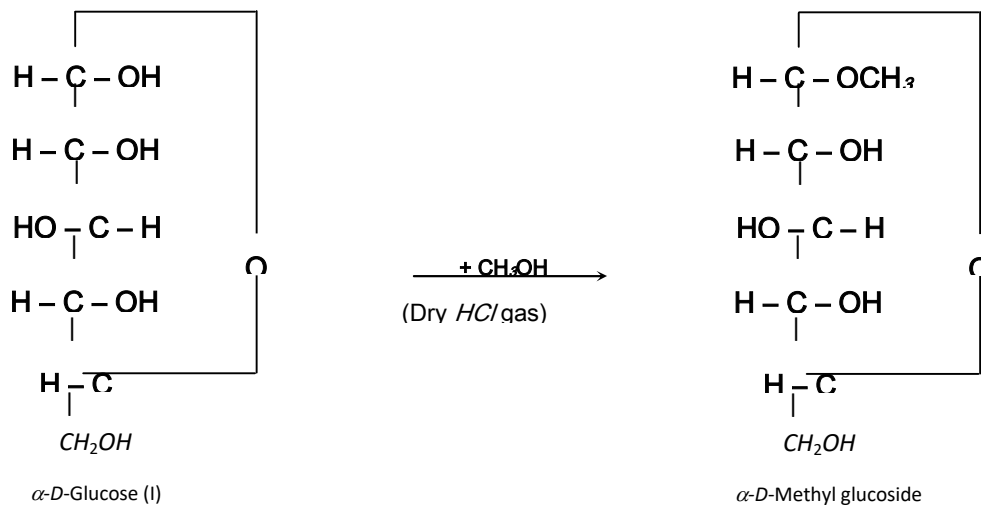
•**No reaction with NH₃ and NaHSO₃:** The glucose ring is not very stable. It is easily broken up by **strong reagents** like HCN, NH₂OH and C₆H₅NHNH₂, etc., to give the intermediate aldehyde form, which reacts with them just like an aldehyde.
But weak reagents like NH₃ and NaHSO₃ are unable to open the chain and cannot react with it. This explains the inability of glucose to form aldehyde ammonia and bisulphite compound.

•**It explains mutarotation :** Ordinary glucose is α-glucose, with a fresh aqueous solution has specific rotation, $[\alpha]_D +110^o$. On keeping the solution for some time; α-glucose slowly changes into an equilibrium mixutre of α-glucose (36%) and β-glucose (64%) and the mixture has specific rotation + 52.5°.

Similarly a fresh aqueous solution of β-glucose having specific rotation, $[\alpha]_D +19.7^o$, on keeping (standing) gradually changes into the same equilibrium mixutre (having, specific rotation $+52.7^o$). So an aqueous solution of glucose shows a physical property, known as **mutarotation**, i.e., a change in the value of specific rotation (muta=change; rotation = specific rotation) is called **mutarotation.**

•**Methods for determining the size of rings:** Fischer and Tollen's proposed that the ring or the internal hemiacetal is formed between C^1 and C^4. It means the ring is **Furan type** or 5-membered ring; this is called **Furanosestrucutre,**

Furan
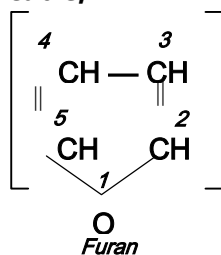
However according to Haworth and Hirst the ring is formed between C^1 and C^5. It means the ring is **Pyran type** or 6-membered ring, this is called **Pyranose structure.**

Pyran
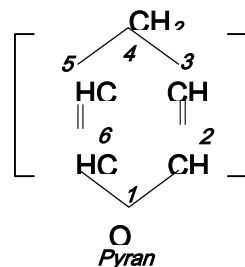
The two forms of D-glucose are also shown by **Haworth** projection formula which are given below;

α-D *glucose*

β-D *glucose*
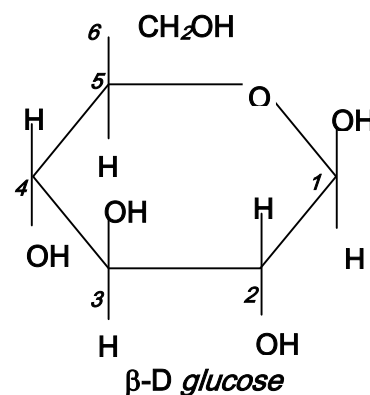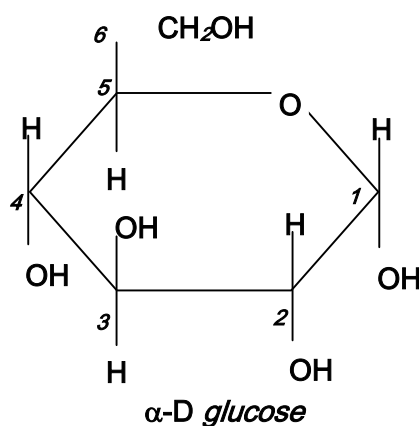
The above projection formulae show that the six membered ring is planar but actually the ring has a chain structure similar to cyclohexane.

In Haworth formula all the OH groups on the right in Fischer's formula are directed below the plane of the ring while those on the left go above the plane. The terminal CH_2OH projects above the plane of the ring.

(4) **Fructose, fruit sugar C₆H₁₂O₆, Ketohexose:** It is present in abundance in fruits and hence is called **fruit sugar.** It is also present in cane sugar and honey alongwith glucose in combined form. The polysaccharide **inulin** is a polymer of fructose and gives only fructose on hydrolysis. Since naturally occurring fructose is laevorotatory, it is also known as **laevulose**.

(i) **Preparation**

(a) Hydrolysis of cane sugar: $\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{Warm}]{H_2SO_4(\text{dil.})} \underset{\text{D-Glucose}}{C_6H_{12}O_6} + \underset{\text{D-Fructose}}{C_6H_{12}O_6}$
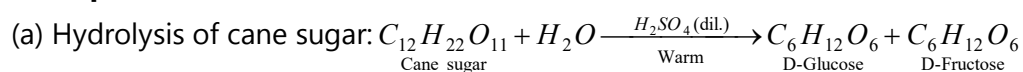
The solution having equal molecules of D-glucose and D-fructose is termed **invert sugar** and the process is known **as inversion**.

$\underset{\text{Calcium fructose}}{C_6H_{11}O_5 - O - CaOH} + CO_2 \longrightarrow \underset{\text{Fructose}}{C_6H_{12}O_6} + CaCO_3$

(b) Hydrolysis of Inulin with dilute sulphuric acid: $\underset{\text{Inulin}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{H_2SO_4(\text{dil.})} \underset{\text{Fructose}}{nC_6H_{12}O_6}$
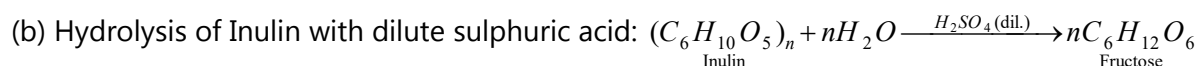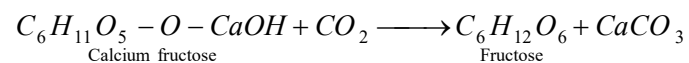
(ii) **Properties:** The anhydrous fructose is a colorless crystalline compounds. It melts at $102^{\circ}C$. It is soluble in water but insoluble in benzene and ether. It is less soluble in water than glucose. It is the sweetest* of all sugars and its solution is laevorotatory. Like glucose, it also shows **mutarotation.**

Fructose is a pentahydroxy ketone and its open-chain and closed-chain structures can be represented as:

CH_2OH
|
$C = O$
|
$HO — C – H$
|
$H – C – OH$
|
$H – C – OH$
|
CH_2OH

D-Fructose

$[\alpha]_D = -92°$

or

CH_2OH
|
$C = O$
|
$(CHOH)_3$
|
CH_2OH

HOH_2C OH
\
C
|
$HO — C – H$
|
$H – C – OH$ O
|
$H – C – OH$
|
CH_2 ——

α- D- Fructose

$[\alpha]_D = -21°$

OH CH_2OH
\
C
|
$HO — C – H$
|
$H – C – OH$ O
|
$H – C – OH$
|
CH_2 ——

β- D- Fructose

$[\alpha]_D = -133°$
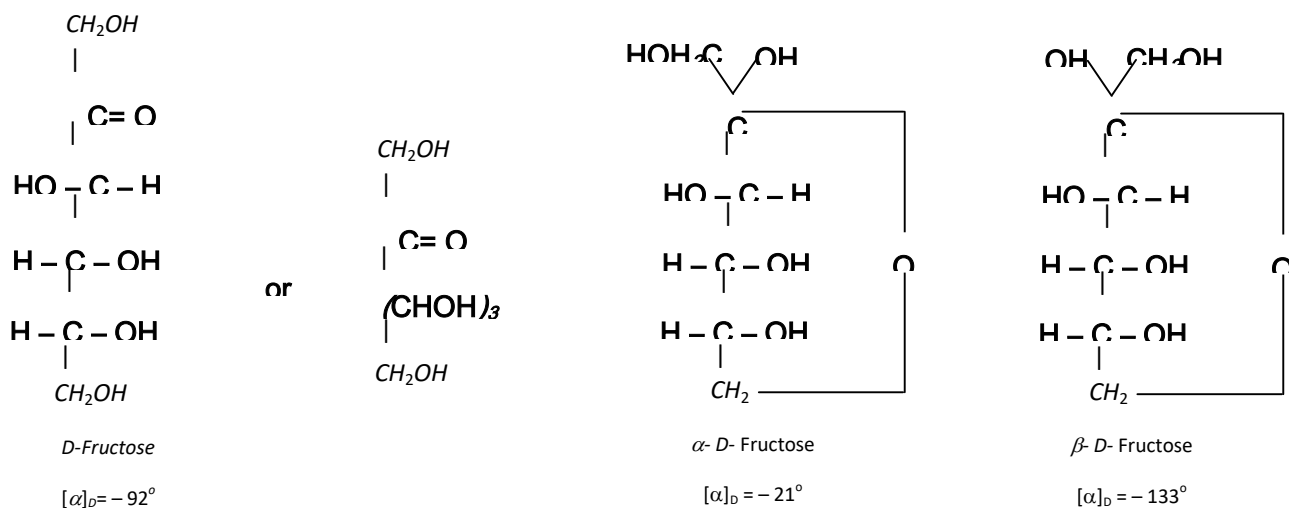
(5) Comparison between glucose and fructose

Property	Glucose	Fructose
Molecular formula	$C_6H_{12}O_6$	$C_6H_{12}O_6$
Nature	Polyhydroxy aldehyde.	Polyhydroxy ketone
Melting point	146°C	102°C
Optical activity of natural form	Dextrorotatory	Laevorotatory
With ethyl alcohol	Almost insoluble	More soluble
Oxidation (a) With bromine water (b) With nitric acid	Gluconic acid Saccharic acid (Glucaric acid)	No reaction Mixture of glycollic acid, tartaric acid and trihydroxyglutaric acid
Reduction	Sorbitol	Mixture of sorbitol and mannitol
Calcium hydroxide	Forms calcium glucosate, soluble in water	Forms calcium fructosate, insoluble in water
Molisch's reagent	Forms a violet ring	Forms a violet ring
Fehling's solution	Gives red precipitate	Gives red precipitate
Tollen's reagent	Forms silver mirror	Forms silver mirror

Phenyl hydrazine	Forms osazone	Forms osazone
Resorcinol + HCl (dil.) (Selivanoff's test)	No colouration	Gives red or brown colour or precipitate
Freshly prepared ammonium molybdate sol. + few drops of acetic acid (**Pinoff's test**).	Light blue colour	Bluish green colour on heating
Alcoholic α-naphthol + HCl (conc.) (**Furfural test**)	No colouration	A purple colour (violet) on boiling

Note: Fructose gives reactions similar to glucose. The difference in properties is due to the fact that it contains a ketonic group while glucose contains an aldehydic group.

(6) **Interconversions**

(i) **Chain Lengthening of Aldoses (Killiani-Fischer synthesis):** The conversion of an aldose to the next higher member involves the following steps:

(a) Formation of a cyanohydrin.

(b) Hydrolysis of – CN to – COOH forming aldonic acid.

(c) Conversion of aldonic acid into lactone by heating.

(d) The lactone is finally reduced with sodium amalgam or sodium borohydride to give the higher aldose.
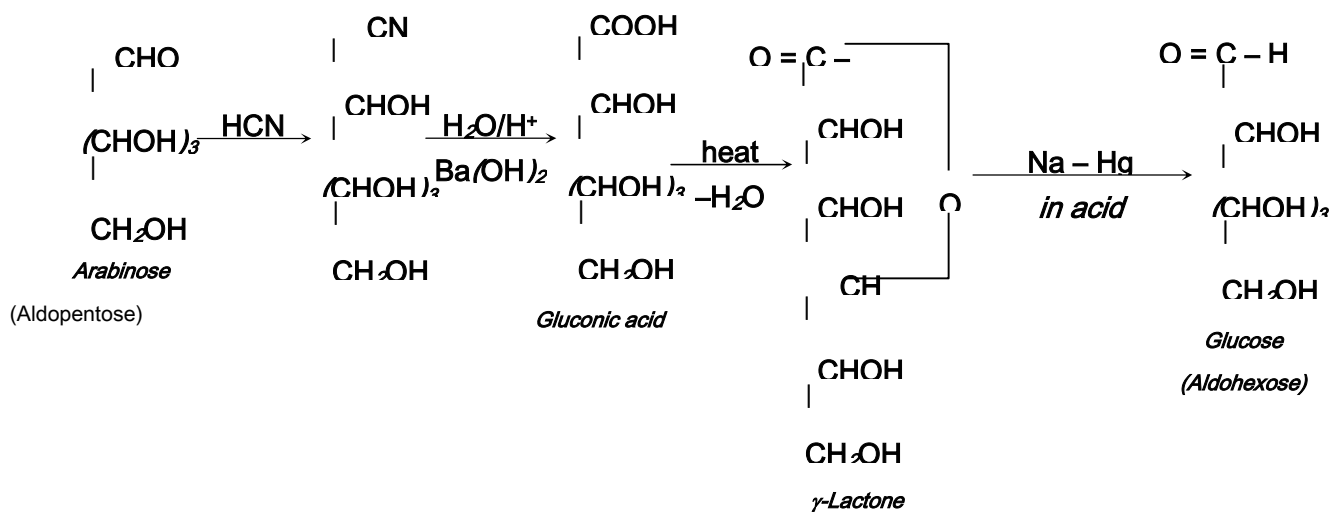
(ii) **Chain Shortening of Aldoses (Ruff Degradation)**

(a) An aldose can be converted to the next lower member by **Ruff Degradation.** It involves two steps:

• Oxidation of the aldose to aldonic acid by using bromine water.

• The aldonic acid is treated with $CaCO_3$ to give the calcium salt which is then oxidised by Fenton's reagent ($H_2O_2 +$ ferric sulphate) to form the next lower aldose.

```
    CHO                              COOH
    |                                |
    CHOH                             CHOH                         CHO
    |              Br₂               |            Ca- salt        |
   (CHOH)₃      ─────────→          (CHOH)₃     ─────────────→   (CHOH)₃
    |             H₂O                |           H₂O₂+Fe³⁺        |
    CH₂OH                            CH₂OH                        CH₂OH
   Aldohexose                      Aldonic acid
  (D-Glucose)                                                    Aldopentose
                                                                (D-Arabinose)
```
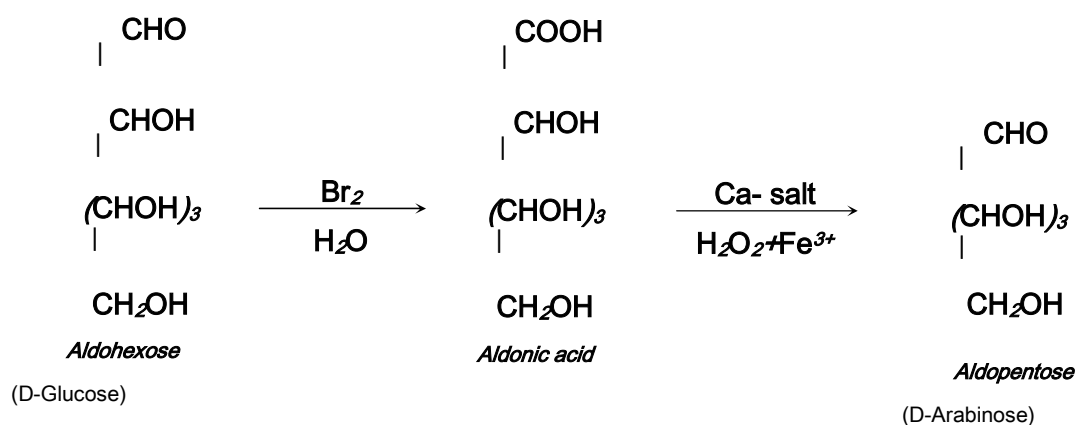
(b) By Wohl's method: It involves the following steps

• Formation of oxime with hydroxyl amine.

• Heating of oxime with acetic anhydride undergoes dehydration into cyano compound, whereas the hydroxyl groups get acetylated.

• The acetyl derivative is warmed with ammonical silver nitrate which removes the acetyl group by hydrolysis and eliminates a molecule of HCN.

```
  CH = O                CH = NOH            CN                   CN
    |                    |                  |                    |
    CHOH                 CHOH               CHO.COCH             CHO H              CHO
    |        H₂NOH       |      (CH₃CO)₂    |         AgOH       |       – HCN      |
   (CHOH)₃  ────────→   (CHOH)₃  ────────→ (CHO.COCH₃)₃ ──────→ (CHOH)₃  ───────→  (CHOH)₃
    |                    |                  |          warm      |                  |
    CH₂OH                CH₂OH              CH₂O.COCH₃           CH₂OH              CH₂OH
   Glucose                                                                       Aldopentose
  (Aldohexose)          CH₂OH              CH₂O.COCH₃           CH₂OH
                        Oxime
```
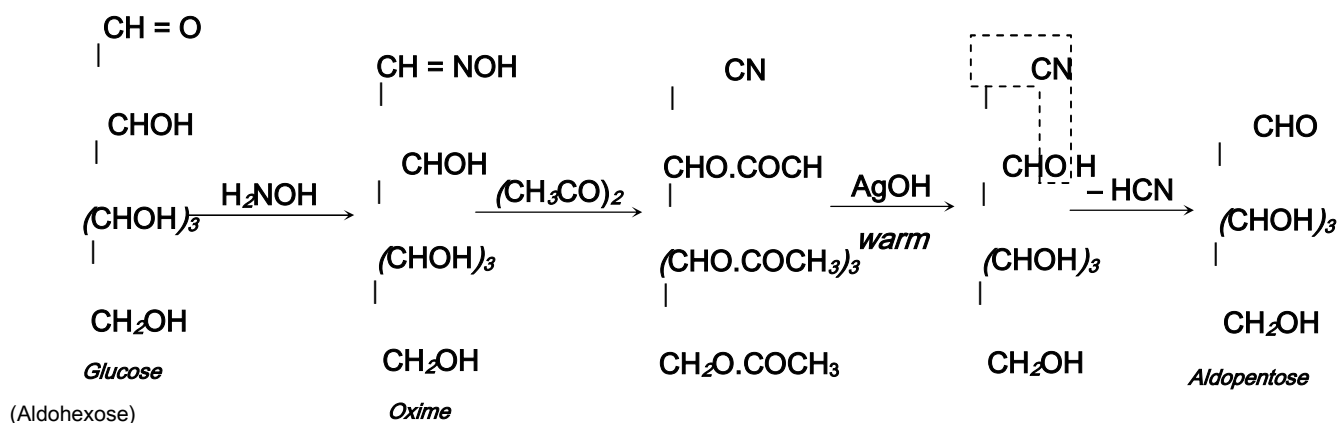
(iii) **Conversion of an Aldose to the isomeric Ketose:** Three steps are involved:

(a) Treatment of aldose with excess of phenyl hydrazine to form osazone.

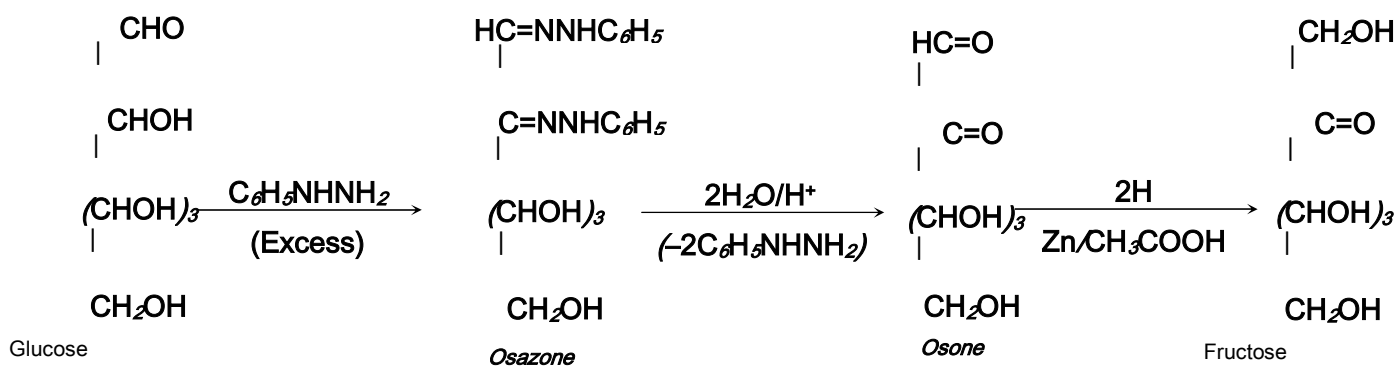(b) Hydrolysis of osazone with dil. HCl to form osone.

(c) Reduction of osone with zinc and acetic acid to form ketose.

$$
\begin{array}{c}
\text{CHO} \\
|\\
\text{CHOH} \\
|\\
(\text{CHOH})_3 \\
|\\
\text{CH}_2\text{OH}
\end{array}
\xrightarrow[\text{(Excess)}]{C_6H_5\text{NHNH}_2}
\begin{array}{c}
\text{HC=NNHC}_6H_5 \\
|\\
\text{C=NNHC}_6H_5 \\
|\\
(\text{CHOH})_3 \\
|\\
\text{CH}_2\text{OH}
\end{array}
\xrightarrow[(-2C_6H_5\text{NHNH}_2)]{2H_2O/H^+}
\begin{array}{c}
\text{HC=O} \\
|\\
\text{C=O} \\
|\\
(\text{CHOH})_3 \\
|\\
\text{CH}_2\text{OH}
\end{array}
\xrightarrow[\text{Zn/CH}_3\text{COOH}]{2H}
\begin{array}{c}
\text{CH}_2\text{OH} \\
|\\
\text{C=O} \\
|\\
(\text{CHOH})_3 \\
|\\
\text{CH}_2\text{OH}
\end{array}
$$

Glucose   *Osazone*   *Osone*   Fructose

(iv) **Conversion of a Ketose to the isomeric Aldose:** Two steps are involved,

(a) Reduction of a ketose with H_2 / Ni to form polyhydric alcohol.

(b) Oxidation with Fenton's reagent to form aldose.

$$
\begin{array}{c}
\text{CH}_2\text{OH} \\
|\\
\text{C=O} \\
|\\
(\text{CHOH})_3 \\
|\\
\text{CH}_2\text{OH}
\end{array}
\xrightarrow{H_2/Ni}
\begin{array}{c}
\text{CH}_2\text{OH} \\
|\\
\text{CHOH} \\
|\\
(\text{CHOH})_3 \\
|\\
\text{CH}_2\text{OH}
\end{array}
\xrightarrow[H_2O_2 + Fe^{3+}]{[O]}
\begin{array}{c}
\text{CHO} \\
|\\
\text{CHOH} \\
|\\
(\text{CHOH})_3 \\
|\\
\text{CH}_2\text{OH}
\end{array}
$$

Fructose   Glucose