→ Carbohydrates:-

- Carbohydrates are important organic compounds and widely distributed in nature. They play vital role in our daily life.
  e.g. Glucose, sucrose, fructose, glucose, starch, cellulose etc.
- Carbohydrates may be regarded as hydrates of carbon and the general formula for most of carbohydrates is $C_n(H_2O)_n$.

This definition was not found to be correct because many sugars such as rhamnose ($C_6H_{12}O_5$) and fucose ($C_6H_{12}O_5$) not fitted in this definition. These sugars do not have the hydrogen and oxygen atom in 2:1 ratio as is found in water and hence cannot be called hydrates of carbon.

Many compounds of carbon, hydrogen and oxygen (e.g. HCHO, CH_3COOH) have the last two elements in the same ratio as in water, but they are not carbohydrates

- Modern definition:-

- Carbohydrates are regarded as polyhydroxy aldehydes or polyhydroxy ketones or substances that can be hydrolysed to either of them.
- It may noted that aldehydic or ketonic groups in carbohydrates do not occurs as free aldehyde or keto groups but usually exist in the form of hemiacetal or hemiketal groups, respectively.
- carbohydrates are produced in nature by green plants by a process called photosynthesis.

$$6CO_2 + 6H_2O \xrightarrow[\text{Chlorophyll}]{h\nu} C_6(H_2O)_6 + 6O_2$$

$$C_6(H_2O)_6 + 6O_2 \xrightarrow[\text{metabolism}]{\text{Animal}} 6CO_2 + 6H_2O + \text{Energy}$$

→ Classification and Nomenclature:→

- The names of most of the simple carbohydrates end in –ose; those with an aldehyde group are known as aldose, and those with a keto group, ketose.
- Carbohydrates are also called saccharides (Greek: sakcharon means sugar)
- Saccharides classified into three major groups–

1. Monosaccharides:-

- Monosaccharides are the simplest carbohydrates and include 3, 4, 5 and 6 carbon sugars.
- They cannot be hydrolysed further to smaller units.
- They are further classified according to number of carbon atoms and nature of carbonyl group present.

No. of carbon atoms	General term	Aldehyde	Ketone
3	Triose	Aldotriose	Ketotriose
4	Tetrose	Aldotetrose	Ketotetrose
5	Pentose	Aldopentose	Ketopentose
6	Hexose	Aldohexose	Ketohexose

2. Oligosaccharides :- (Greek : Oligoes = few)

- The hydrolysis of these carbohydrates give two or more monosaccharide units.
- They are subdivided into following sub groups-

(i) Disaccharides:-

- These are hydrolysed to give two molecules of monosaccharides.

e.g. sucrose

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

(ii) Trisaccharides:-

- These are hydrolysed to give three molecules of monosaccharides.

e.g. raffinose

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

3. Polysaccharides:-

- Polysaccharides are high-molecular weight carbohydrates having general formula $(C_6H_{10}O_5)_n$. where $n = 300-1000$
- Polysaccharides are tasteless and water insoluble substances while monosaccharides are sweet in taste and water soluble.

- Polysaccharides give many monosaccharide units on hydrolysis.

e.g. starch

$$\underset{\text{starch}}{(C_6H_{10}O_5)_n} \xrightarrow{n(H_2O)} \underset{\text{glucose}}{n\,C_6H_{12}O_6}$$

- Alternatively carbohydrates are classified into two categaries -

(a) Sugars and non-sugars:-

- All monosaccharides and oligosaccharides, such as glucose, fructose and cane sugar are crystalline, water soluble solids which are sweet in taste. These are called sugars.
- All polysaccharides such as starch, cellulose etc. are amorphous, water insoluble and tasteless. These are called non-sugars.

(b) Reducing or non-reducing sugars or carbohydrates:-

- The sugars or carbohydrates which reduce Fehling solution and Tollen's reagent are called reducing sugars or carbohydrates.

e.g. All monosaccharides and disaccharides (except sucrose)

- The sugars or carbohydrates which do not reduce Fehling solution and Toller's reagent are called non-reducing sugars or carbohydrates.

e.g. maltose and lactose.

→ Monosaccharides:-

- Monosaccharides are colourless, water-soluble compounds, sweet in taste and cannot be hydrolysed to smaller molecules.
- They occur either in the free or combined state and contain 3-8 carbon atoms.
- These are of two types-

(i) Aldose are monosaccharides which contain an aldehyde group $(-CHO)$.

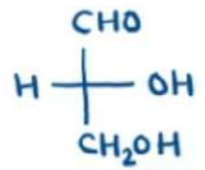
(ii) Ketose are monosaccharides which contain a keto group $(>C=O)$.

- They are further classified on the basis of number of carbon atoms and type of carbonyl group.

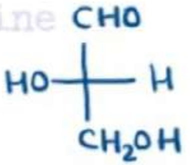
1. Aldotrise :-

- Aldo → Aldehyde group , triose → three carbon atoms

e.g. Glyceraldehyde - it has one chiral center and exists in two enantiomeric forms D- and L-



D- Glyceraldehyde

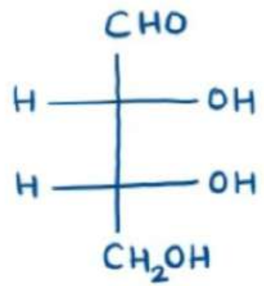


L - Glyceraldehyde

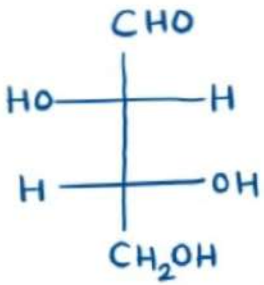
2. Aldotetrose:-

- Aldo → Aldehyde group , tetrose → four carbon atoms.

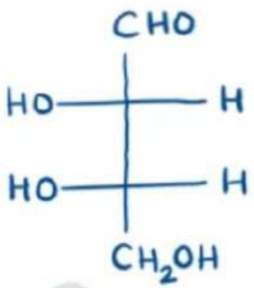
- Aldotetros have two dissimilar chiral carbon atom and hence four stereoisomeric ($2^2 = 4$) forms are possible.



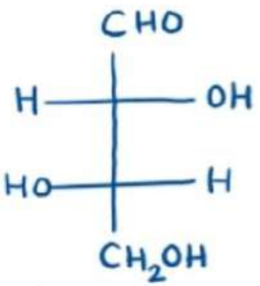
D- Erythrose



D- Threose



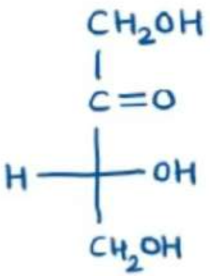
L-Erythrose



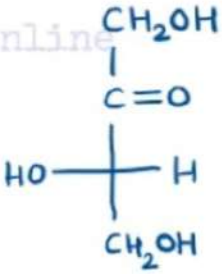
L - Threose

3. Ketotetrose:-

- Keto → Ketone group , tetrose → four carbon atoms.
- ketotetrose have only one chiral carbon atoms and hence only two stereoisomers are possible.



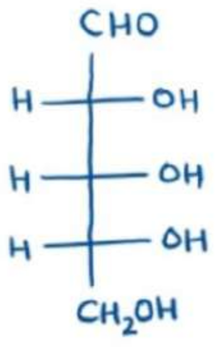
D- Erythrulose

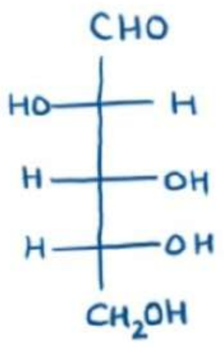


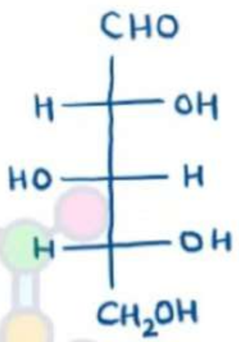
L - Erythrulose

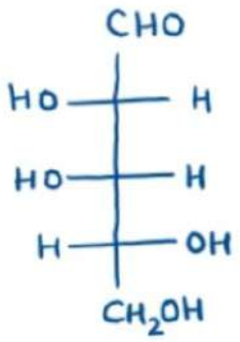
4. Aldopentoes:-

- Aldo→ Aldehyde group, pentose→ five carbon atoms.
- Aldopentose contains three chiral carbon atoms and exists in eight stereoisomer forms ($2^3 = 8$)


D - Ribose


D - Arabinose

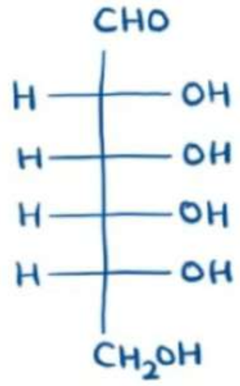

D- xylose

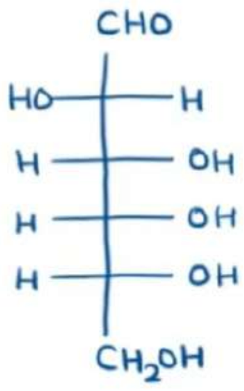

D - Lyxose

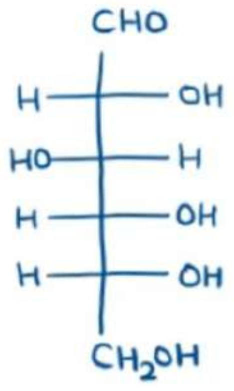
- The remaining four aldopentos are mirror-image of above mentioned sugars, belong to L- series.

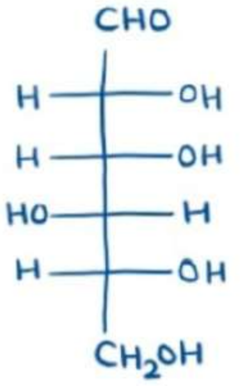
5. Aldohexoses:-

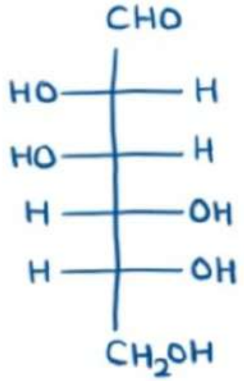
- Aldo → Aldehyde group, hexose → six Carbon atoms
- Aldohexoses contains four chiral carbon atoms and exists in sixteen stereoisomer forms. ($2^4 = 16$)

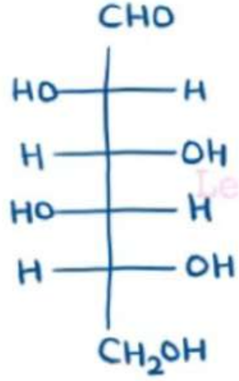

D-Allose

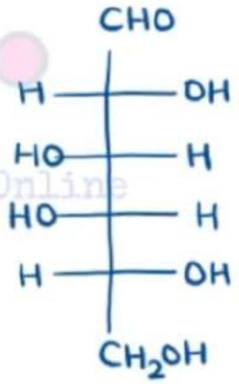

D-Altrose

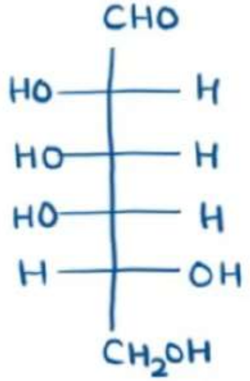

D-Glucose


D-Gulose


D-Mannose


D-Idose


D-Galactose


D-Talose

- The remaining eight aldohexoses are mirror images of the above mentioned sugars, belong to L-series.

→ Glucose:-

- D-(+) Glucose, Dextrose or Grape sugar.
- Glucose is the most abundant sugar. It occurs in honey (which is mixture of glucose and fructose) and sweet fruits such as grapes and mangoes.
- It is a constituent of sucrose and of many polysaccharides such as starch and cellulose
- It is also present in human blood (approx. 0.1%).

- Physical properties:-

- It is a colourless, crystalline solid and is sweet in taste.
- It melts at 419 K with decomposition.
- It is a dextrorotatory substance. The optical rotation of a fresh solution of glucose is +112° which gradually decrease to +52° on keeping the solution for sometimes. Because of its dextrorotatory properties, it is also called dextrose.

- Preparation of D-(+) glucose:-

(i) Laboratory method:-

$$\underset{\substack{\text{Sucrose}\\ \text{or}\\ \text{Can sugar}}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{Ethanolic medium}]{HCl} \underset{\text{D-(+)-Glucose}}{C_6H_{12}O_6} + \underset{\text{D-(-)-Fructose}}{C_6H_{12}O_6}$$

- Since glucose is less soluble in ethanol, it separates out on cooling the reaction mixture.

(ii) commercial method:-

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

- Starch is obtained from inexpensive sources such as maize, potatoes and rice.
- After hydrolysis, the reaction mixture is neutrilised with chalk ($CaCO_3$) and filtered.
- The filtrate is decolorised with animal charcoal and concentrated under reduced pressure when crystallises out.

- Chemical properties of D-(+) Glucose:-

- D-(+) Glucose is a monosaccharide which give the reactions of aldehydic and ketonic groups and may be represented as open chain pentahydroxy aldehyde as shown below-

$$CHO-CHOH-CHOH-CH-OH-CH-OH-CH_2OH$$

(A) Reactions of the aldehyde group:-

- Glucose shows the general reactions of aldehydes. However, it does not form addition compounds with sodium bisulphite and does not respond to Schiff's test.

ⓐ Reaction with hydrogen cyanide:-

$$\underset{\text{D-(+)-Glucose}}{CH_2OH(CHOH)_4CHO} + HCN \longrightarrow \underset{\text{Glucose cyanohydrin}}{CH_2OH(CHOH)_4CH\begin{matrix}CN\\OH\end{matrix}}$$

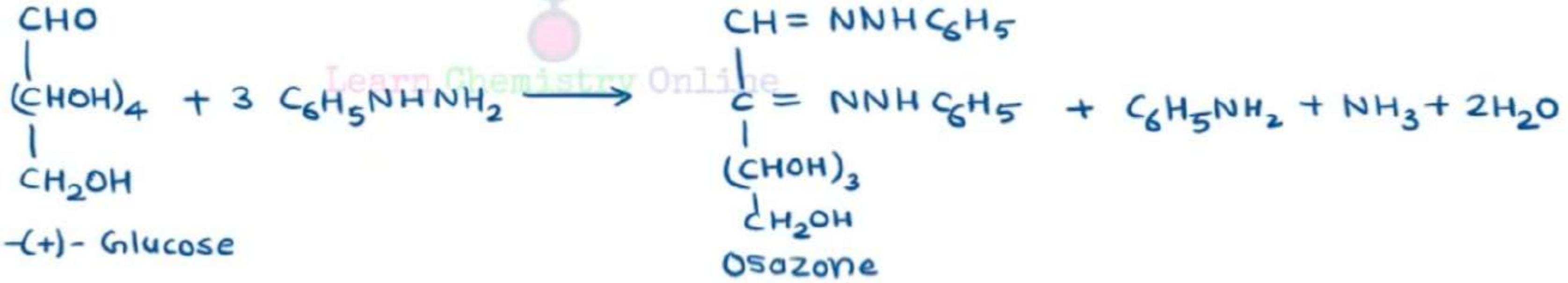
ⓑ Reaction with hydroxylamine:-

$$\underset{\text{D-(+)-Glucose}}{CH_2OH(CHOH)_4CHO} + NH_2OH \xrightarrow[-H_2O]{} \underset{\text{Glucose oxime}}{CH_2OH(CHOH)_4CH=N-OH}$$

ⓒ Reaction with phenylhydrazine:-

$$\underset{\text{D-(+)-Glucose}}{CH_2OH(CHOH)_4CHO} + NH_2NHC_6H_5 \xrightarrow[-H_2O]{} \underset{\text{Glucose phenylhydrazone}}{CH_2OH(CHOH)_4CH=NNHC_6H_5}$$

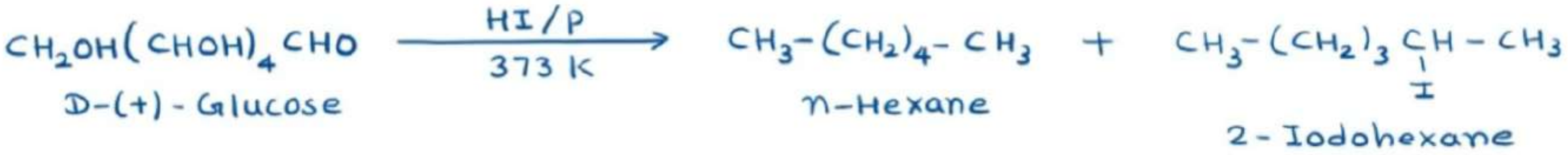
– Osazone formation:- If glucose is warmed with excess of phenylhydrazine, then the reaction goes further to give a crystalline product, known as osazone, which contains two phenylhydrazine residue per molecule.



$$\underset{\text{D-(+)-Glucose}}{\begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}} + 3\,C_6H_5NHNH_2 \longrightarrow \underset{\text{Osazone}}{\begin{array}{l} CH=NNHC_6H_5 \\ | \\ C=NNHC_6H_5 \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{array}} + C_6H_5NH_2 + NH_3 + 2H_2O$$

ⓓ Reduction:-

$$\underset{\text{D-(+)-Glucose}}{CH_2OH(CHOH)_4CHO} \xrightarrow[\text{Reduction}]{H_2/Cat \text{ or } Na\text{-}Hg/H_2O} \underset{\text{Sorbitol or glucitol}}{CH_2OH(CHOH)_4CH_2OH}$$



$$\underset{\text{D-(+)-Glucose}}{CH_2OH(CHOH)_4CHO} \xrightarrow[373\ K]{HI/P} \underset{\text{n-Hexane}}{CH_3-(CH_2)_4-CH_3} + \underset{\text{2-Iodohexane}}{CH_3-(CH_2)_3\underset{\mid \atop I}{C}H-CH_3}$$

ⓔ Oxidation:-

$$\underset{\text{D-(+)-Glucose}}{CH_2OH(CHOH)_4CHO} \xrightarrow[\text{Mild oxidising agent}]{Br_2/H_2O} \underset{\text{gluconic acid}}{CH_2OH(CHOH)_4COOH}$$

$$\underset{\text{D-(+)-Glucose}}{CH_2OH(CHOH)_4CHO} \xrightarrow[\text{strong oxidising agent}]{HNO_3} \underset{\text{Saccharic acid or glucaric acid}}{COOH(CHOH)_4COOH}$$

ⓕ Reducing nature:-

- The aldehydic group (–CHO) of glucose is easily oxidesed to –COOH group. due to this glucose acts as reducing agent and reduces following reagents and itself oxidised to gluconic acid

- Fehling reagent (alkaline $CuSO_4$ + Roschelle salt)
- Benedict's reagent (alkaline solution of cupric acetate containing citrate ions)
- Tollen's reagent (Ammonical solution of $AgNO_3$)

$$\underset{\text{D-(+)-Glucose}}{CH_2OH(CHOH)_4CHO} + \underset{\text{Tollen's reagent}}{2[Ag(NH_3)_2]^{\oplus}OH^{\ominus}} \longrightarrow \underset{\text{Ammo. gluconate}}{CH_2OH(CHOH)_4CO\overset{\ominus}{O}\overset{\oplus}{N}H_4} + \underset{\text{Silver mirror}}{2Ag\downarrow} + 3NH_3 + H_2O$$

$$\underset{\text{D-(+)-Glucose}}{CH_2OH(CHOH)_4CHO} + \underset{\text{Fehling or Benedict's reagent}}{2Cu^{+2} + 5OH^{\ominus} + Na^{\oplus}} \longrightarrow \underset{\text{Sodium gluconate}}{CH_2OH(CHOH)_4CO\overset{\ominus}{O}Na} + \underset{\text{Red ppt}}{Cu_2O\downarrow} + 3H_2O$$

Ⓑ Reactions of the hydroxyl group:-

ⓐ Acylation:-

$$\underset{\text{D-(+)-Glucose}}{CH_2OH(CHOH)_4CHO} \xrightarrow[\text{Acetic anhydride} \\ -5CH_3COOH]{5\ (CH_3CO)_2O} \underset{\text{Glucose penta acetate}}{CH_3COOCH_2(CHOOCCH_3)_4CHO}$$

ⓑ Reaction with methanol and HCl:-

$$\underset{\text{D-(+)-Glucose}}{CH_2OH(CHOH)_4CHO} + CH_3OH \xrightarrow[-H_2O]{\text{HCl gas}} \underset{\alpha\text{- and }\beta\text{- methyl glucoside}}{C_6H_{11}O_5(OCH_3)OH}$$

ⓒ Reaction with Calcium hydroxide:-

$$\underset{\text{D-(+)-Glucose}}{CH_2OH(CHOH)_4CHO} + Ca(OH)_2 \longrightarrow \underset{\text{Calcium gluconate}}{C_6H_{14}O_6OCaO} + H_2O$$

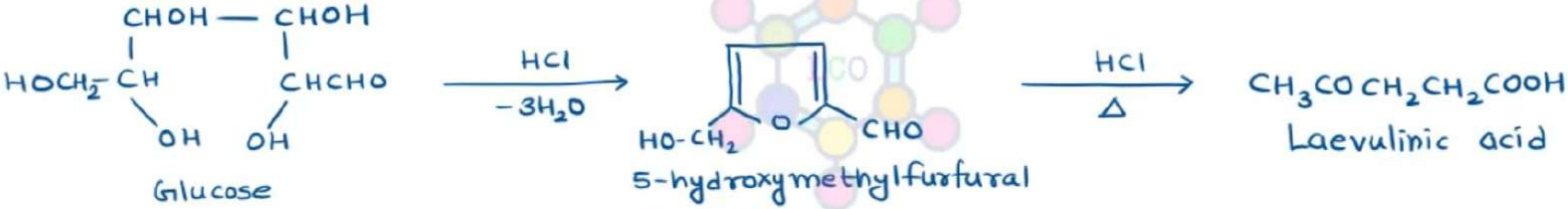
Ⓒ other reactions:-

ⓐ Fermentation:-

$$\underset{\text{D-(+)-Glucose}}{CH_2OH(CHOH)_4CHO} \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

ⓑ Action of acids:-

- Dilute acids have no effect. However, when heated with conc. HCl, glucose gives 5-hydroxymethylfurfural, which is further reacts with hot HCl to give laevulinic acid.

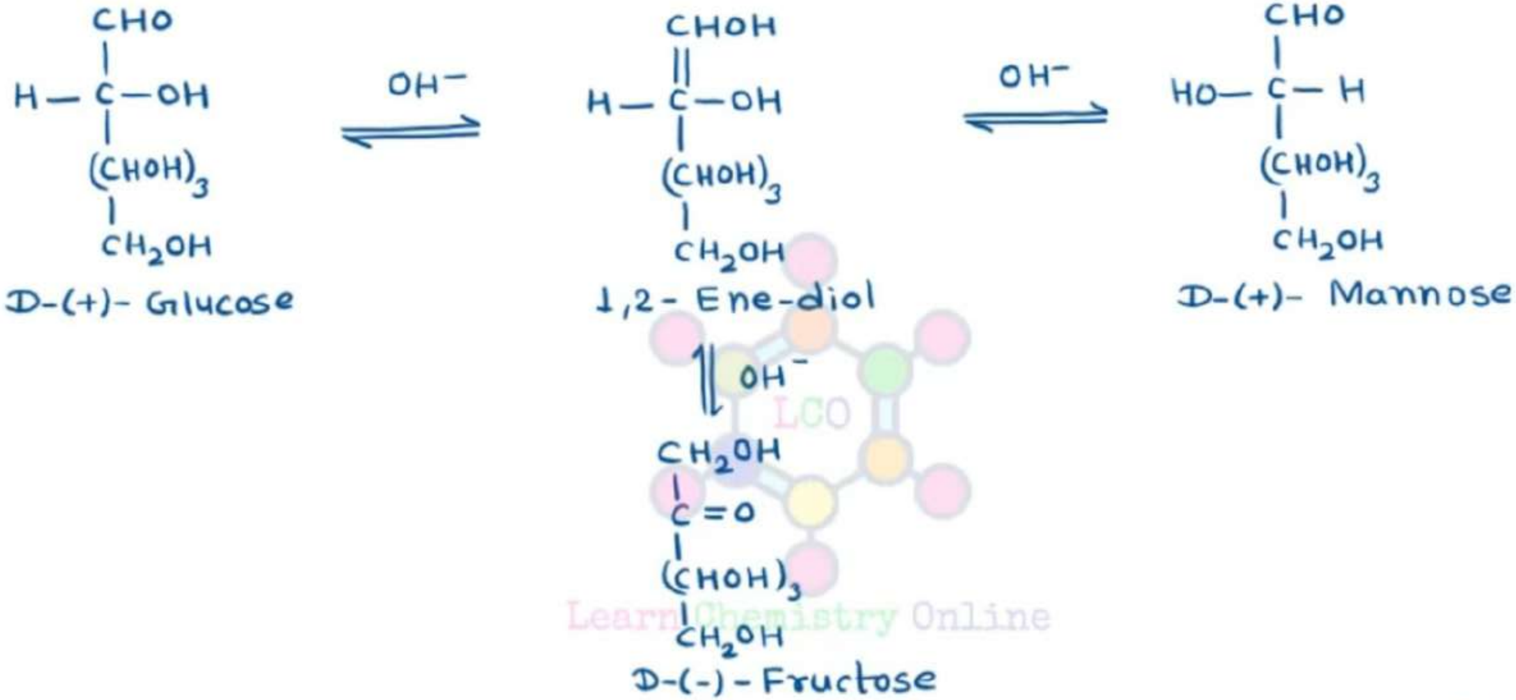


- 5-hydroxymethylfurfural reacts with α-naphthol give violet colour. which forms the basis of Molish test for carbohydrates.

Ⓒ Action of alkalies: Lobry de Bruyn-van Ekenstein rearragement:-

- Concentrated alkalies turn glucose in to Brown resins.
- Dilute alkalies give a mixture of (+)-glucose, (+)-mannose and (-)-fructose

- This reaction proceeds through 1,3-enolisation, in which chirality of C_2 carbon is destroyed due to formation of C=C bond.



- The same equilibrium mixture is obtained when (+)-mannose or (-)-fructose reacts with dilule alkali.

→ Uses of D-(+)-Glucose:-

- used as instant energy source for childrens and invalids.
- used as starting material in the manufacture of vitamin C.
- used in manufacture of confectionery, syrups, jams, candies, wine etc.
- Used in many pharmaceutical preparations.
- used as reducing agent in making silver mirrors.

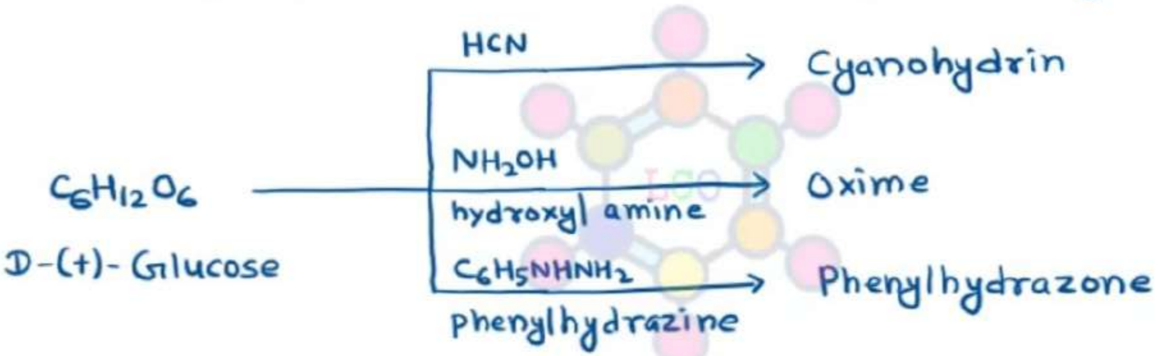
→ Structure of Glucose :-

1. Molecular formula:-

- The molecular formula of glucose is $C_6H_{12}O_6$ which is estabilised by elemental analysis and molecular weight determination.

2. Presence of aldehyde group:-

- The presence of carbonyl group is deteremined by following reactions-



- The presence of aldehyde group is confirmed by mild oxidation.

$$\underset{\text{Glucose}}{C_5H_{11}O_5(CHO)} \xrightarrow{Br_2/H_2O} \underset{\text{Gluconic acid}}{C_5H_{11}O_5(COOH)}$$

Gluconic acid is a monocarboxylic acid containing same number of carbon atoms as glucose. This shows that the carbonyl group is aldehyde.

3. Presence of five hydroxyl group:-

- The reaction of glucose with acetyl chloride or acetic anhydride gives a pentaacetate. This confirms the presence of five hydroxyl groups in glucose molecule.

$$\underset{\text{Glucose}}{C_6H_7O(OH)_5} \xrightarrow[-5\,CH_3COOH]{5(CH_3CO)_2O} \underset{\text{Glucose pentaacetate}}{C_6H_7O(OOCCH_3)_5}$$

- The presence of an aldehyde and five hydroxyl groups in glucose is further confirmed by the following reaction

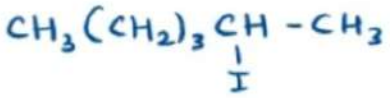
$$C_5H_6(OH)_5(CHO) \xrightarrow[Na\text{-}Hg/H_2O]{\text{Reduction}} \underset{\text{Sorbitol}}{C_6H_8(OH)_6} \xrightarrow[-6\,CH_3COOH]{6\,(CH_3CO)_2O} \underset{\text{Sorbitol hexaacetate}}{C_6H_8(OOCCH_3)_6}$$

4. Presence of primary -OH group:-

$$\underset{\text{Glucose}}{CH_2OH(CHOH)_4CHO} \xrightarrow[\text{oxidation}]{HNO_3} \underset{\text{Glucaric acid or saccharic acid.}}{HOOC(CHOH)_4COOH}$$

5. Presence of straight chain of carbon atoms.

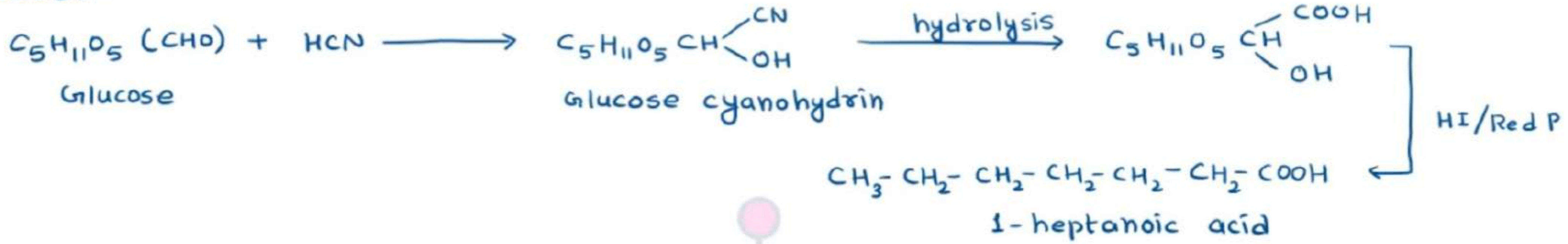
$$\underset{\text{Glucose}}{CH_2OH(CHOH)_4CHO} \xrightarrow[373\,K]{HI/P} \underset{n\text{-hexane}}{CH_3(CH_2)_4CH_3} + \underset{\text{2-Iodohexane}}{CH_3(CH_2)_3\underset{\displaystyle I}{\underset{|}{CH}}-CH_3}$$



$CH_3(CH_2)_3\underset{\displaystyle I}{\underset{|}{CH}}-CH_3$

2-Iodohexane

- The presence of straight chain of carbon atoms can be confirmed by the following reaction-



$$\underset{\text{Glucose}}{C_5H_{11}O_5(CHO)} + HCN \longrightarrow \underset{\text{Glucose cyanohydrin}}{C_5H_{11}O_5CH\begin{smallmatrix}CN\\OH\end{smallmatrix}} \xrightarrow{\text{hydrolysis}} C_5H_{11}O_5CH\begin{smallmatrix}COOH\\OH\end{smallmatrix} \xrightarrow{HI/\text{Red P}} \underset{\text{1-heptanoic acid}}{CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-COOH}$$

– Open chain structure of D-(+)-Glucose:-

- Based upon the above observations, it can be concluded that glucose contains-

(i) A straight chain of six carbon atoms.

(ii) One aldehyde group

(iii) A primary alcoholic group

(iv) Both aldehyde and primary alcoholic groups present at terminals.

(v) Each of the remaining four carbon atoms carries one hydrogen and a hydroxyl group.

- There for, the following open chain structure was proposed for glucose.

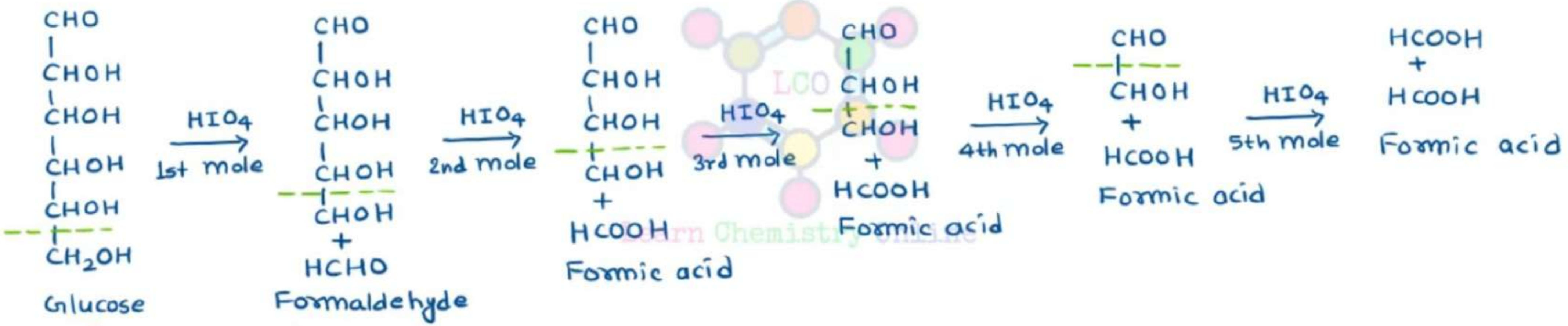
$$\overset{6}{C}H_2OH - \overset{5}{C}HOH - \overset{4}{C}HOH - \overset{3}{C}HOH - \overset{2}{C}HOH - \overset{1}{C}HO$$

→ Further confirmation:-

- The open chain structure of glucose is confirmed by the oxidative cleavage of glucose by HIO_4, Periodic acid (Malaprade reagent).
- Glucose consumes five moles of HIO_4 and gives 1 mole of formaldehyde and 5 moles of formic acid.

$$C_6H_{12}O_6 + 5HIO_4 \longrightarrow HCHO + 5HCOOH + 5HIO_2 \text{ (Iodous acid)}$$

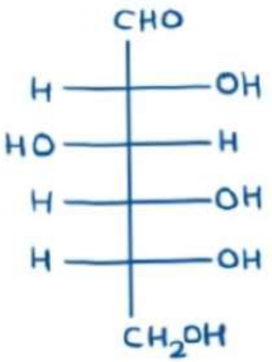
- This oxidative cleavage can be represented as follows-



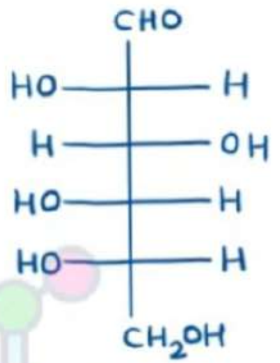
- Configuration of D-(+)-Glucose:-

- The open chain structure of glucose have 4 chiral carbons. Therefore possible number of stereoisomers are 16 ($2^4 = 16$).
- All 16 Stereoisomer are known in the form of 8 pairs of enatiomers (8 D + 8 L).

- The naturally occuring D-(+)-glucose is only one of 16 stereoisomers whose absolute configuration was assigned by Emil Fischer in 1891 (Nobel prize 1902). Its enatiomer is L-(-)-glucose.



D-(+)-Glucose



L-(-)-Glucose

D and L are non-superimposable and mirror image of each other

→ Limitations of open chain structure:-

- Although the open chain structure, explains the most of the reaction given by the D-(+)-glucose but some facts cannot be explained satisfactory by this structure.
- These facts are as under-

(i) Glucose does not form an addition compound with sodium bisulphite and does not respond to schiff's test, which are characteristic reactions of aldehyde.

(ii) Glucose reacts with NH_2OH to give an oxime but glucose pentaacetate does not. It means that the -CHO group is not present in glucose pentaacetate.

(iii) D-(+)- Glucose is exist in two isomeric forms -

α - Glucose	β - Glucose
- crystallise from aq. solution of glucose using cold ethanol at room temp.	- crystallise from aq. solution of glucose using hot pyridine at 371 K.
- m.p 419K	- m.p. 423 K
- specific rotation of aq. solution is +112° which gradually drop to +52° after some time.	- specific rotation of aq. solution is +19° which gradually rise to +52° after some time.

- In aqueous solution, each form slowly changes into an equilibrium mixture of both the forms. This prooves the change in specific rototation of both the forms.

$$\underset{[\alpha]_D = +112^\circ}{\alpha\text{-D-(+)-Glucose}} \rightleftharpoons \underset{[\alpha]_D = +52^\circ}{\text{equilibrium mixture}} \rightleftharpoons \underset{[\alpha]_D = +19^\circ}{\beta\text{-D-(+)-Glucose}}$$

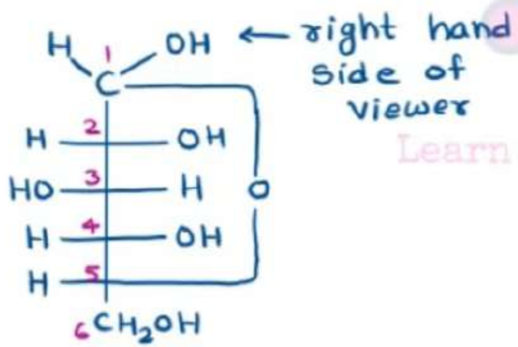
This phenomenon of change in specific rotation of an optically active compound, with time, to an equilibrium value is known as Mutarotation.

(iv) Glucose reacts with methanol in the presence of dry HCl to form mixture of methyl-α-D-glucoside and methyl-β-D-glucoside. Although either of the methyl glucoside contains only one extra methyl group, its behaviour similar to that of a full acetal.

(v) The UV spectrum of glucose does not show the presence of an aldehyde group.

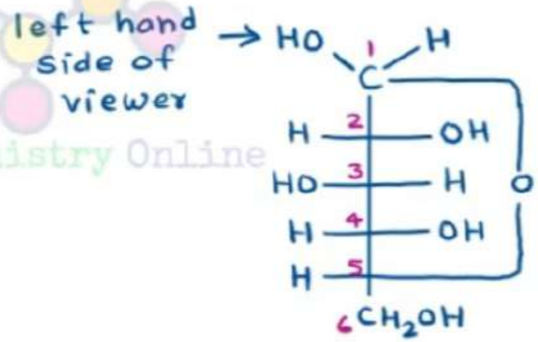
→ Cyclic structure of D-(+)-Glucose :-

- The open chain structure of glucose has certain limitations. Therefore a cyclic structure was proposed for glucose in which the aldehyde group is not free.
- The aldehyde group forms an internal hemiacetal with C_5-OH.
- Due to formation of cyclic hemiacetal, new chirality center generates at C_1. Thus two stereoisomers are differing in configuration at C_1 are possible.
- The isomer having -OH group on the right hand side of the viewer is called α-form whereas that having -OH group on the left hand side of the viewer is called β-form. Such a pair of diastereomers, which differe in configuration at C_1, are called anomers.



α-D-(+)-Glucose

$[\alpha]_D = +112°$



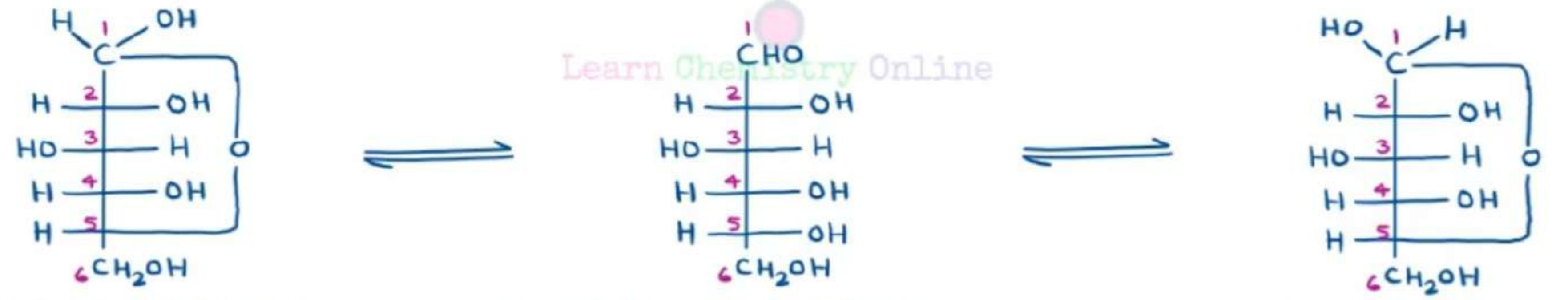
β-D-(+)-Glucose

$[\alpha]_D = +19°$

→ Evidence in favor of cyclic or ring structure:-

1. Explanation of mutarotation:-

- The phenomenon of mutarotation can be explained on the basis of cyclic structure of glucose.
- Each of the two α- and β- anomers of glucose hemiacetal, is readily hydrolysed by water into the open chain form of glucose having free aldehyde group.
- Therefore, in aq. solution either of the anomer is converted in to equilibrium mixture through open chain form. This equilibrium mixture containing both anomers (36 % α- + 64 % β-) and small amount of open chain form. The equilibrium mixture has a specific rotation of +52°.
- Hence the phenomenon of mutarotation is due to opening or closure of hemiacetal ring



α-D-(+)-Glucose $[\alpha]_D = +112°$

open chain D-(+)-Glucose $[\alpha]_D = +52°$

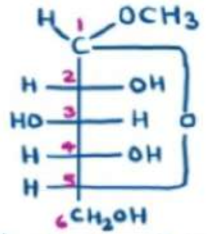
β-D-(+)-Glucose $[\alpha]_D = +19°$

2. Typical reactions of aldehyde :-

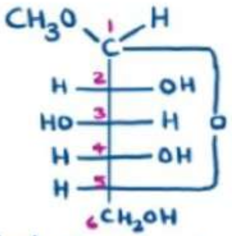
- The tpyical aldehydic reactions of D-(+)-glucose such as formation of cyanohydrin, oxime, osazone and reduction of Fehling and Tollen's reagents can be explained on the basis of small amount of open chain free aldehyde form present in the equilibrium mixture of the two anomers.
- When open chain form reacts with a particular reagent it gets consumed and initial equilibrium is disturbed. Therefore more open chain is produced to restore the equilibrium. This pushing the reaction forward.
- The concentration of the open chain form in the initial equilibrium mixture is too low (less than 0.5%) that it cannot initiate certain reversible aldehydic reactions such as bisulphite addition and Schiff's reaction. As a result glucose does not undergo these reactions.

3. Formation of Glucosides:-

- Both α- and β- glucose present in equilibrium mixture react differently with CH_3OH and dry HCl to give corresponding methyl-D- glucosides.



methyl-α-D-glucoside

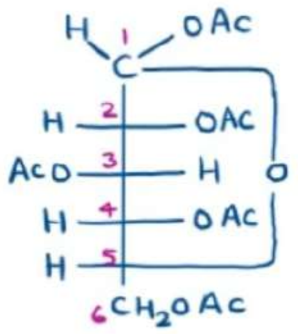


methyl-β-D-glucoside

- The glucosides behave as full acetals as they have been formed by the reaction of hemiacetal with one mole of methanol. Being acetals they are hydrolysed back to glucose and methanol only in acidic solution. As they are not hydrolysed by aq. solution they do not undergo mutarotation. Similarly they are not hydrolysed by alkali present in Fehling solution or Toller's reagent and hence they do not reduce these reagents.

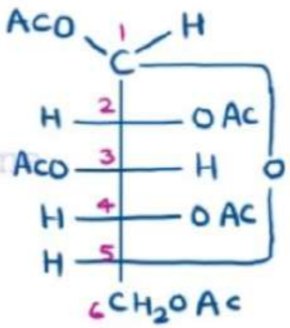
4. Formation of two pentacetate:-

- Like methyl glucosides, glucose pentaacetate also exist in two anomeric forms which do not have free -OH group. Due to this they are not hydrolysed in aqueous solution to give open chain aldehydic form and hence do not react with NH_2OH to form corresponding oximes.



α-D-(+)-Glucose pentaacetate

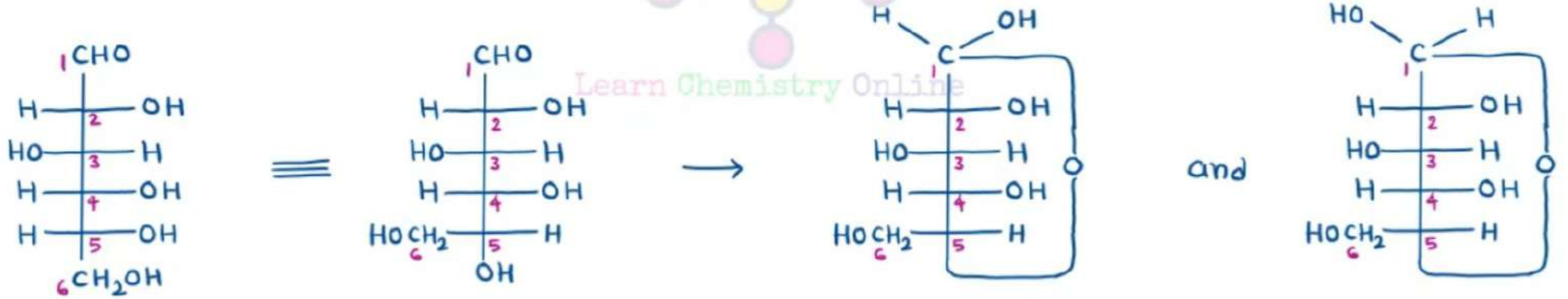
$\boxed{Ac = CH_3CO-}$



β-D-(+)-Glucose pentaacetate

→ Haworth projection formula of α- and β-D-Glucose :→

- Although cyclic structure of glucose, nicely explain the chemical reactions of D-(+)-glucose, but they are not true representation of molecules.
- The oxide link which joins C_1 and C_5 appears to extend from backside of the molecule to the front side.
- The actual molecule can be represented by rotating C_1 and C_5 bond (this does not change the configuration) to bring -OH group vertically, attached to C_5 and then linking C_1 and C_5 positions by oxide bridge which extends from back of C_1 to back of C_5.
- Base on these considerations, Haworth proposed hexagonal structure for α-D-glucose and β-D-glucose.



D-(+)-Glucose

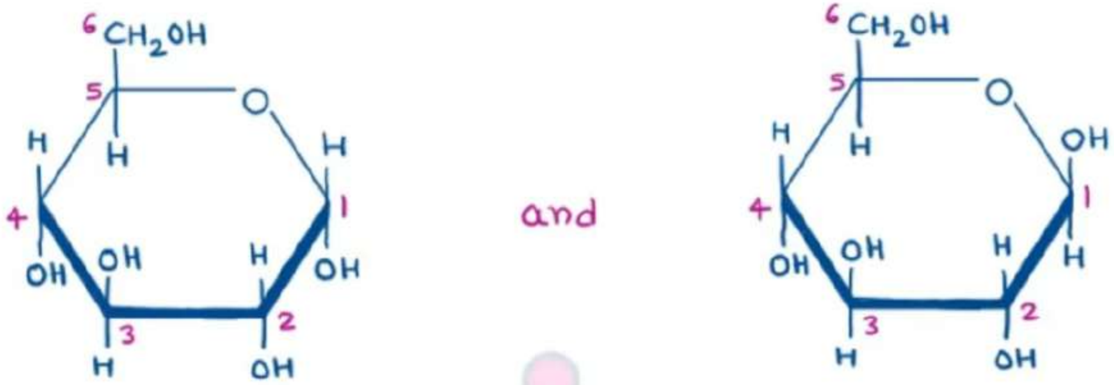
α-D-(+)-Glucose

β-D-(+)-Glucose

Two interchanges at C_5

Fisher projection of cyclic glucose

≡



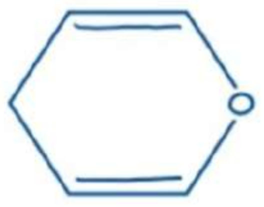
(I)
α- D-(+)- Glucose (Glucopyranose)

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

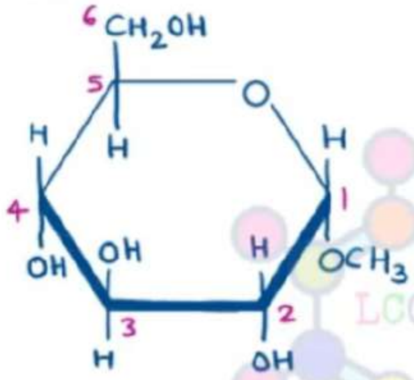
fig:- Haworth projection formula

- By convention the oxygen atom of the hexagon is placed on the right hand side and away from viewer.
- The $-CH_2OH$ group is written above the plane of the ring for sugars belonging to D-series, whereas for L- sugars it is written below the plane.
- All the -OH groups located on the right hand side of the planar diagram are placed down and those on left hand side are placed above the plane.
- The difference between the α- and β- forms is that the -OH at C_1 is written down in the α- form and up in β-form.

- In analogy with pyran (the six membered heterocyclic ring containing oxygen) the six membered ring written for (+) glucose and other aldohexoses is called pyranose ring and its glycosides are called pyranosides. Thus III represents methyl α-D-(+)-glucopyranoside and methyl β-D-(+)-glucopyranoside is IV.

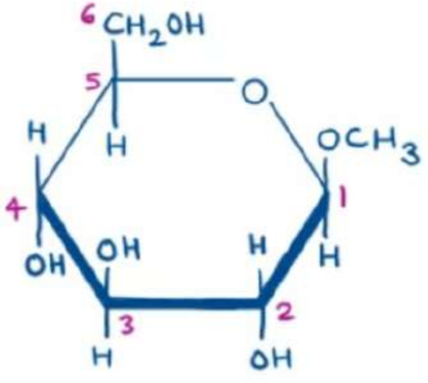


Pyran



(III)

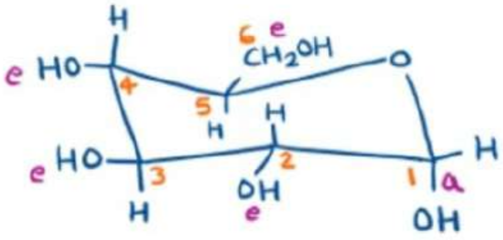
and



(IV)

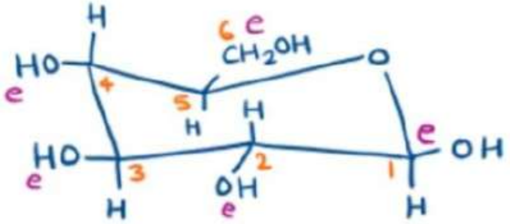
- Conformations of α- and β-D-(+)-Glucose:-

- Glucose is six membered ring and analogous with cyclohexane and hence shows the conformational structures.
- X-Ray analysis of crystalline α-D-glucose shows that it has chair form.



(V)

α-D-Glucose



(VI)

β-D-Glucose

e → equatorial
a → axial

→ D-(-)-Fructose:-

- Fructose is the most important ketohexose.
- It occurs widely in fruits and combined with glucose in sucrose.
- It may be prepared by hydrolysis of sucrose followed by fractional crystallisation.
- It is commercially obtained by acid-catalysed hydrolysis of inulin(a polysaccharide which occurs in dahlia tubers).

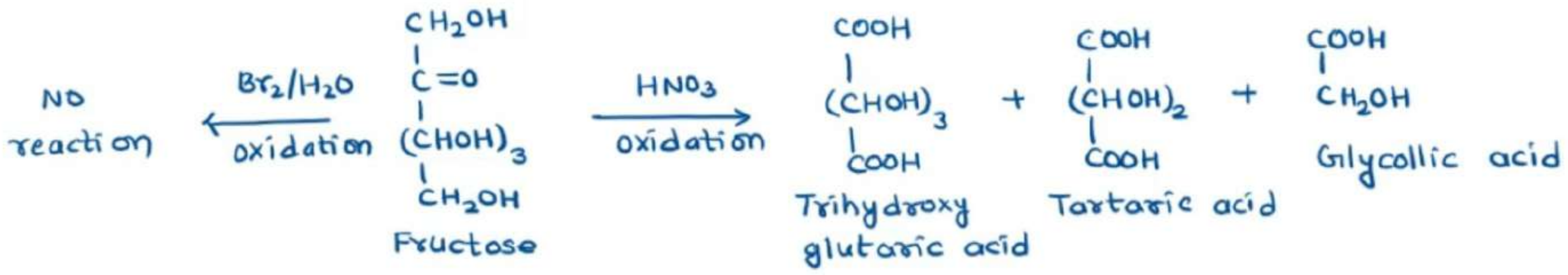
$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow{H^{\oplus}} \underset{\text{Fructose}}{nC_6H_{12}O_6}$$

→ Physical properties:-

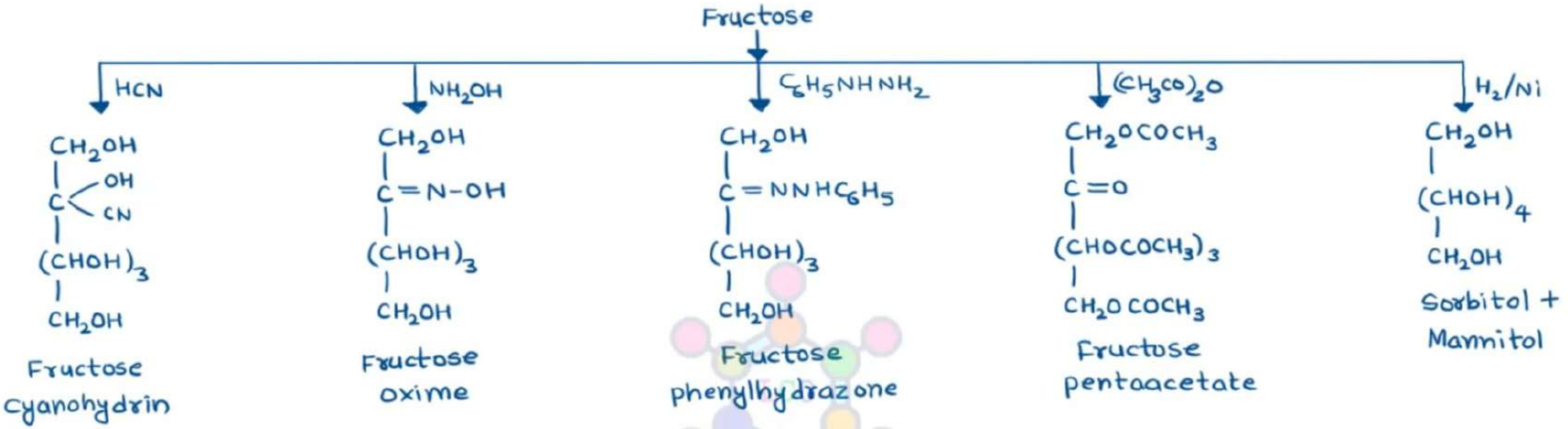
- Fructose is a colourless crystalline solid.
- m.p. → 375K
- sweet in taste.
- highly soluble in water and alcohol.
- It is laevorotatory and known as laevulose.

→ chemical reactions:-

- Fructose is a ketohexose, so it shows reactions of ketonic group.



$$\text{No reaction} \xleftarrow[\text{oxidation}]{Br_2/H_2O} \underset{\text{Fructose}}{\begin{matrix} CH_2OH \\ | \\ C{=}O \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{matrix}} \xrightarrow[\text{oxidation}]{HNO_3} \underset{\text{Trihydroxy glutaric acid}}{\begin{matrix} COOH \\ | \\ (CHOH)_3 \\ | \\ COOH \end{matrix}} + \underset{\text{Tartaric acid}}{\begin{matrix} COOH \\ | \\ (CHOH)_2 \\ | \\ COOH \end{matrix}} + \underset{\text{Glycollic acid}}{\begin{matrix} COOH \\ | \\ CH_2OH \end{matrix}}$$



→ Structure of fructose:-

- like glucose, a tentative structure for fructose may be established on the basis of following observing-

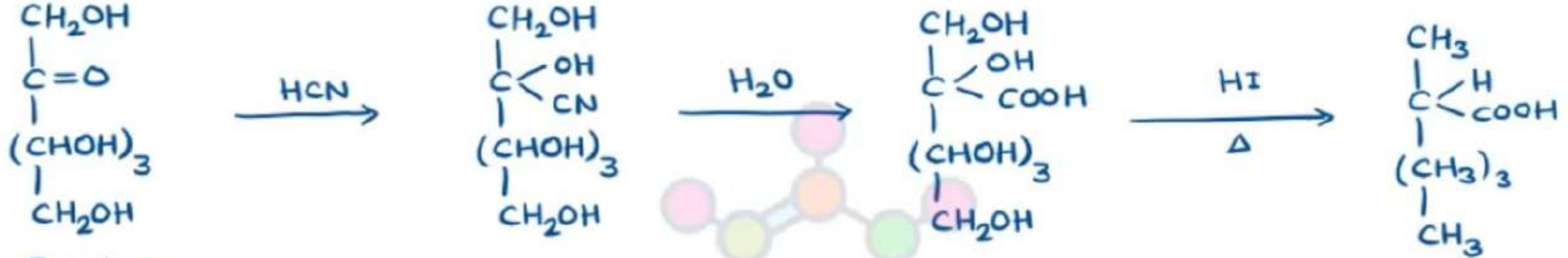
(i) The molecular formula of fructose is $C_6H_{12}O_6$. which is determined on the basis of elemental analysis and molecular weigh determination.

(ii) The presence of a carbonyl group in fructose is established by the formation of oxime, phenylhydrazone and cyanohydrin.

(iii) Reduction with conc. HI and red P at 373 K gives n-hexane and 2-iodohexane. This indicates that the six carbon atoms in fructose are arranged in a straight chain.

(iv) On oxidation with nitric acid, a mixture of trihydroxyglutaric acid, tartaric acid and glycolic acid is obatained. Since all these acids contain fewer carbon atom than fructose, the carbonyl group must be present as a keto group.

(v) That fructose is a 2-ketohexose is shown by the following sequence of reactions.



$$CH_2OH\text{-}CO\text{-}(CHOH)_3\text{-}CH_2OH \xrightarrow{HCN} CH_2OH\text{-}C(OH)(CN)\text{-}(CHOH)_3\text{-}CH_2OH \xrightarrow{H_2O} CH_2OH\text{-}C(OH)(COOH)\text{-}(CHOH)_3\text{-}CH_2OH \xrightarrow[\Delta]{HI} CH_3\text{-}C(H)(COOH)\text{-}(CH_3)_3\text{-}CH_3$$

Fructose

α-Methylcaproic acid

(vi) Unlike simple Ketones fructose reduces Fehling and Tollen's reagent.

(vii) Formation of a pentaacetate on treatment with acetic anhydride indicates the presence of five hydroxyl group.

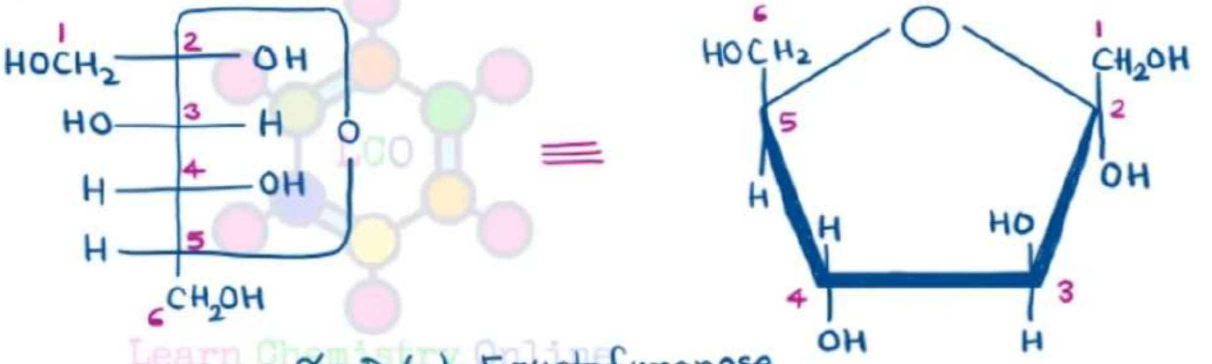
(viii) On warming with alkali it gives an equilibrium mixture of glucose, fructose and mannose.

— on the basis above reactions, a tentative structure for fructose may be written as follows-

$CH_2OH\ CO\ CHOH\ CHOH\ CHOH\ CH_2OH$

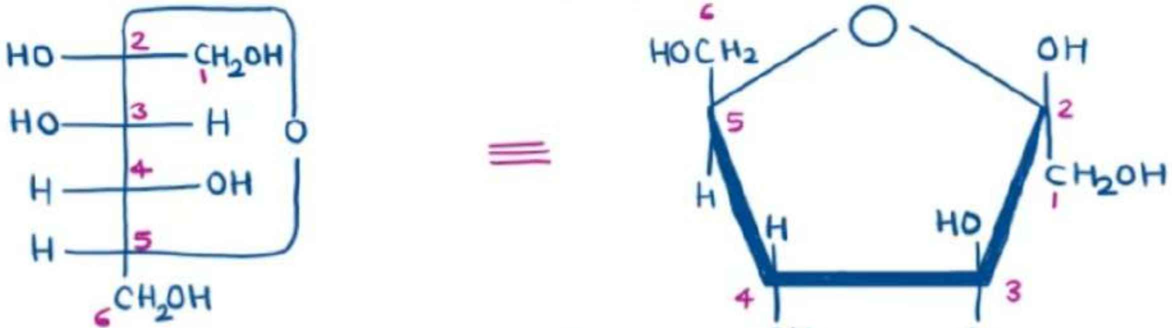
→ Haworth structure of α-and β-(D)-fructose:-

- Although in free state fructose has the six-membered cyclic or the pyranose structure but in the combined state such as in fructosides, disaccharides such as sucrose etc., fructose always has five membered cyclic ring structure or the furanose structure.
- The five membered ring of fructose is similar to furan (five membered heterocyclic compound containing oxygen), Therefor fructose is called furanose.
- The Fischer and Howarth projection formulas for α- and β-D fructuose are as below:-



α-D-(-)-Fructofuranose

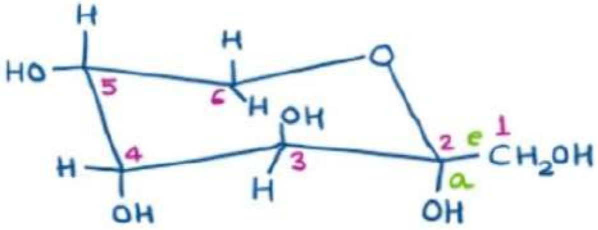
Furan



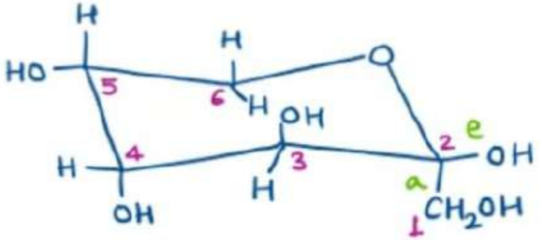
β-D-(-)-Fructofuranose

→ Conformations of α- and β-D-Fructose:-

- Like glucose, α- and β-D-fructopyranose also exists in the chair conformations-

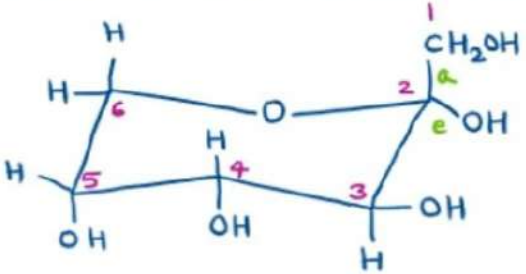


α-D-(-)-Fructopyranose (C1)

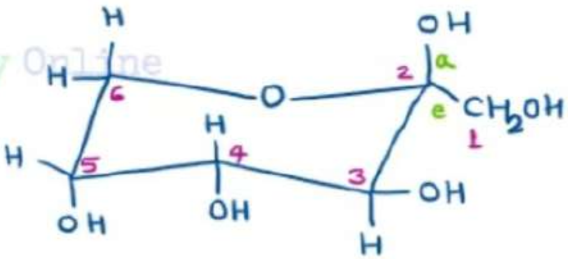


β-D-(-)-Fructopyranose (CL)

- when bulky CH_2OH alone or along with one or more -OH groups are present in the less stable axial position, ring flipping takes place to avoid 1,3-diaxial interactions.
- Hence, the monosaccharides prefer to exist in the reverse chair conformation called 1C rather than in the normal chair conformation called C1



α-D-(-)-Fructopyranose(1C)



β-D-(-)-Fructopyranose(1C)

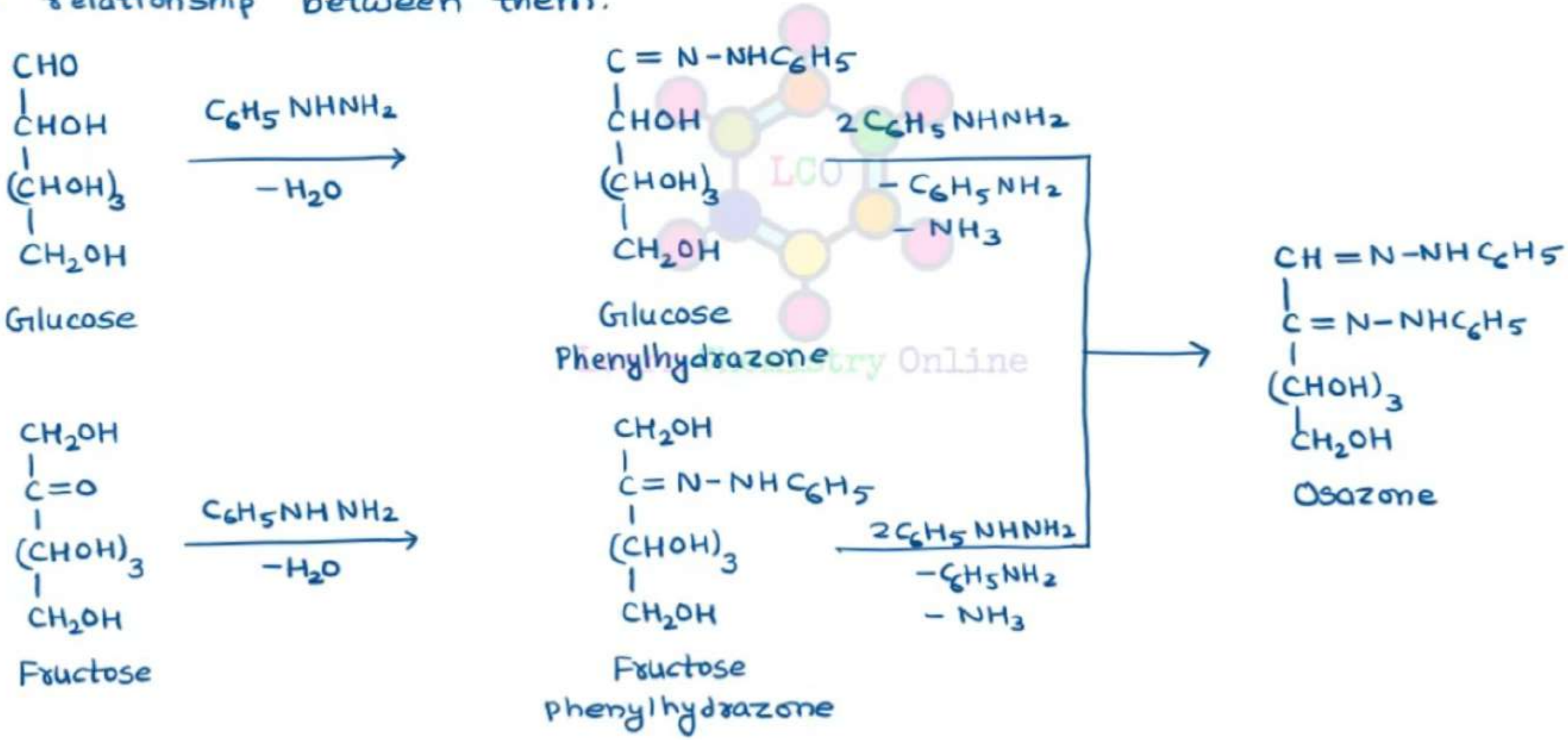
- 1C and C1 conformations of α-D-(-)-fructopyranose are almost equally stable because the instability due to axial-CH_2OH and axial C_5-OH in 1C is compensated by three axial -OH in C1.

- 1C conformation of β-D-(-)-fructopyranose is much more stable than C1 conformation because in C1 conformation, CH_2OH group, C_3-OH and C_5-OH are in axial orientation while in 1C conformation there are only two axial groups at C_2 and C_5.
- The PMR studies show that in aqueous solution, D-(-)-fructose exists as an equilibrium mixture of the following four conformations -

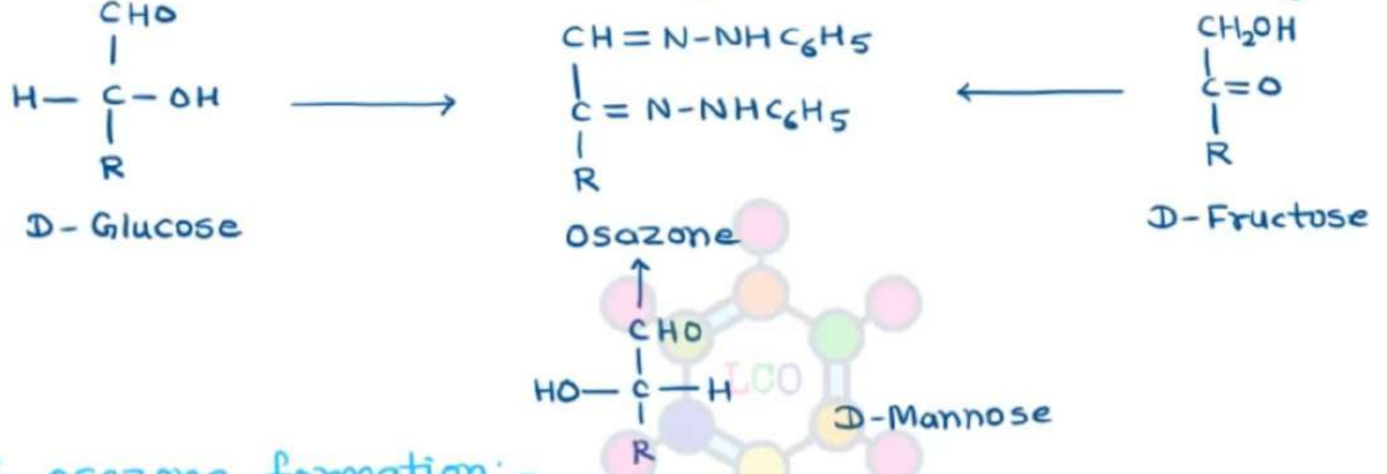
$$\begin{tikzcd}
\begin{array}{c}\alpha\text{-D-(-)-Fructopyranose}\\(9\%)\end{array} \arrow[r, shift left] \arrow[d, shift left] & \begin{array}{c}\beta\text{-D-(-)-Fructopyranose}\\(31\%)\end{array} \arrow[l, shift left] \arrow[d, shift left] \\
\begin{array}{c}\alpha\text{-D-(-)-Fructopyranose (1C)}\\(3\%)\end{array} \arrow[r, shift left] \arrow[u, shift left] & \begin{array}{c}\beta\text{-D-(-)-Fructopyranose (1C)}\\(57\%)\end{array} \arrow[l, shift left] \arrow[u, shift left]
\end{tikzcd}$$

→ Osazone formation : Action of Phenylhydrazine on Hexose :-

- Like other carbonyl compounds, glucose and fructose react with one molecule of phenylhydrazine to give corresponding phenylhydrazones.
- If excess amount of phenylhydrazine is used then a compound containing two phenylhydrazine residue is obtained which is known as osazone.
- Glucose and fructose form the same osazone and this fact help in estabishing the stereo-chemical relationship between them.



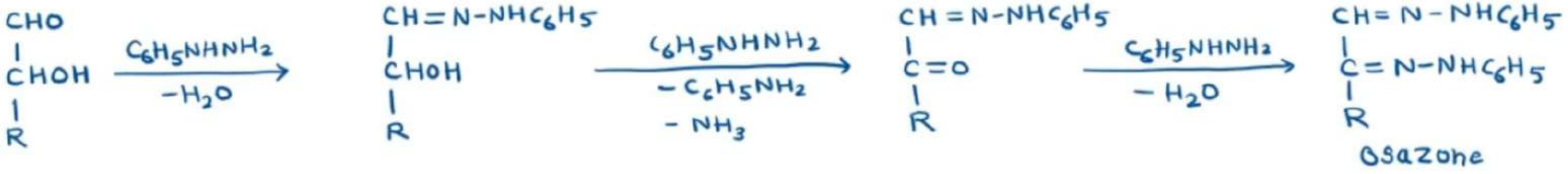
- The osazone formation involves the first two carbon atoms, Therefore D-mannose is also give same osazone.
- D-mannose differes from D-Glucose only in the stereochemistry around carbon-2.



→ Mechanism of osazone formation:-

(i) Fischer mechanism:-

- Emil Fischer suggested that the hydroxyl group adjacent to the carbonyl group in the initially formed phenylhydrazone is oxidised by excess phenylhydrazine (2nd molecule) to generate a second carbonyl group, which subsequently reacts with 3rd molecule of phenylhydrazine to give osazone.

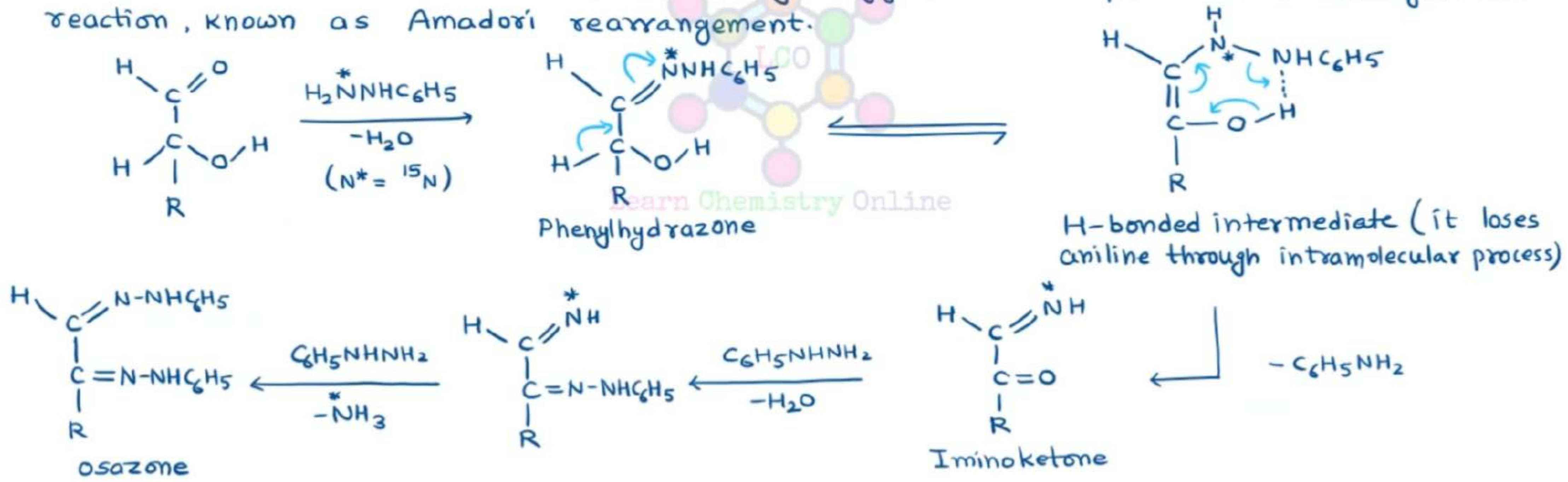


- Limitations of Fischer Mechanism:-

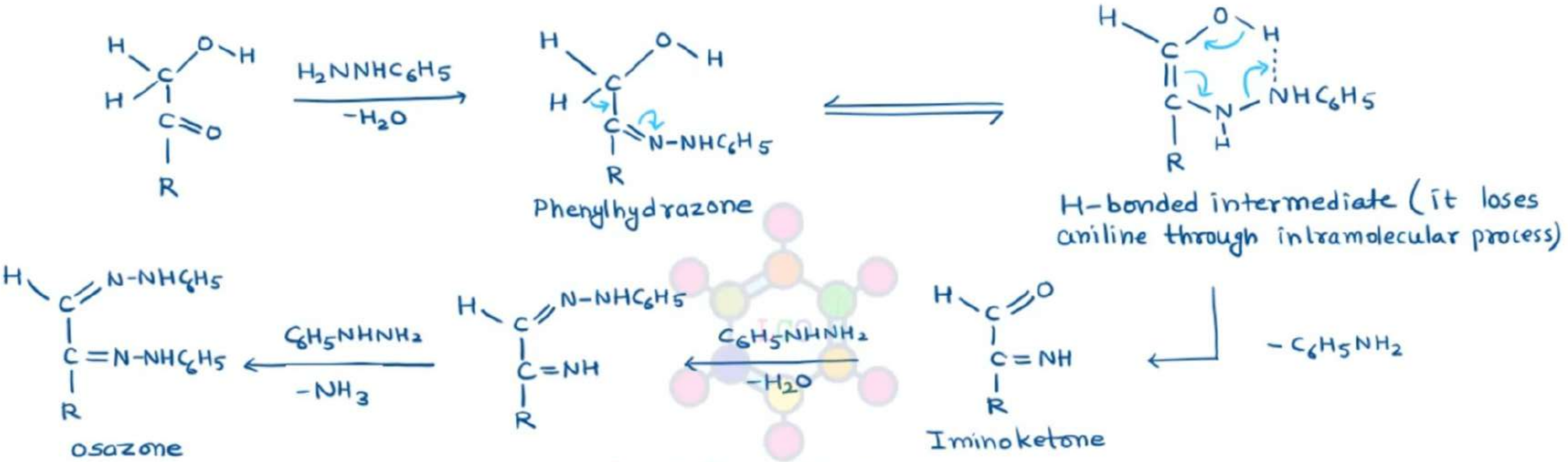
- It does not explain the oxidation of hydroxyl group by phenylhydrazine which in fact is a strong reducing agent.
- Only one hydroxyl group undergoes oxidation and the excess reagent does not oxidise the remaining hydroxyl group.
- This mechanism does not explain the formation of aniline and ammonia.

(ii) Weygand Mechanism:-

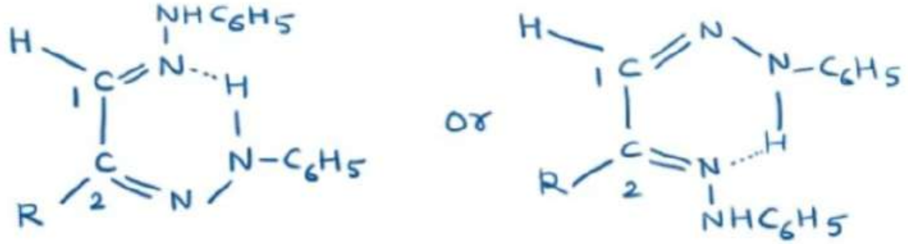
- An alternative mechanism was proposed by Weygand which predict a rearrangement reaction, known as Amadori rearrangement.



- The mechanism of osazone formation from fructose :-

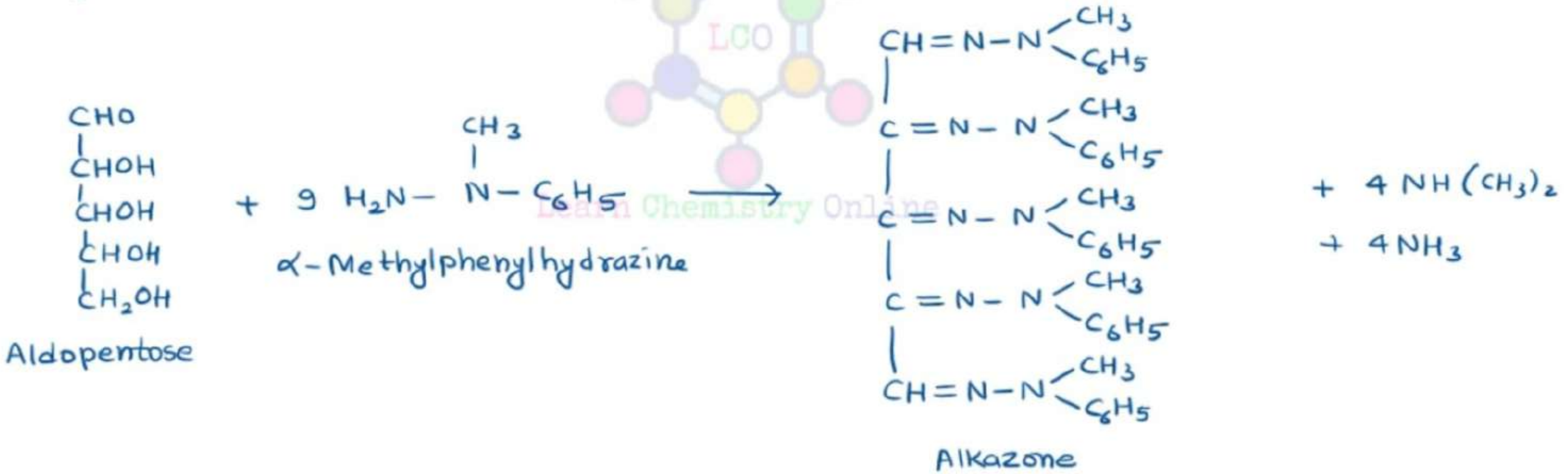


- However this mechanism does not explain why the reaction stop with the introduction of two residues of phenylhydrazine. In other words, why the osazone does not undergo a further intramolecular rearrangement involving the C_3 position.
- This problem is further explained on the basis of spectroscopic method.
- Spectroscopic method explains that further reaction of the osazone is prevented due to its stability by chelation.



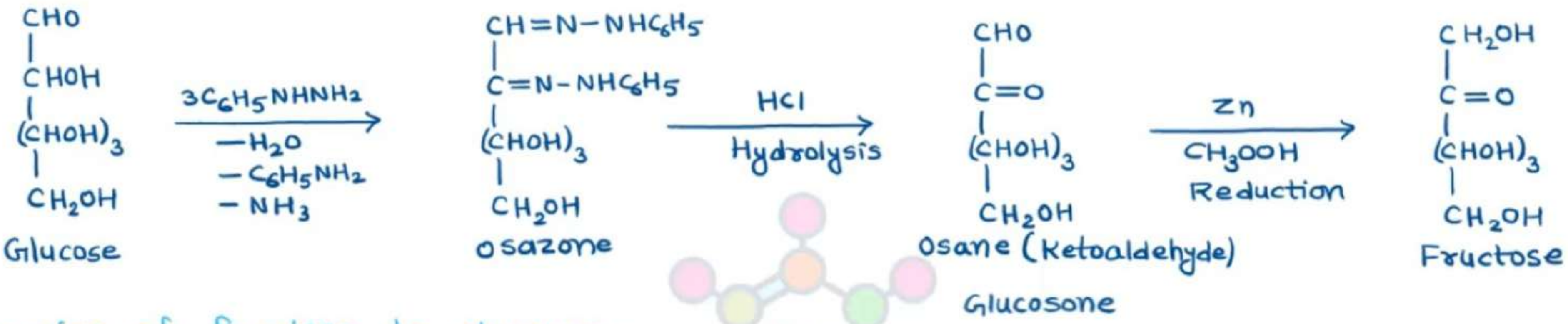
R → $CH_2OH(CHOH)_3-$

- This explanation is further supported by the observation that unsymmetrically disubstituted hydrazine (like α-methylphenylhydrazine) which cannot form chelate ring in osazone form, reacts further with aldose to giving alkazones in which osazone formatio proceed along the whole carbon chain of the sugar.

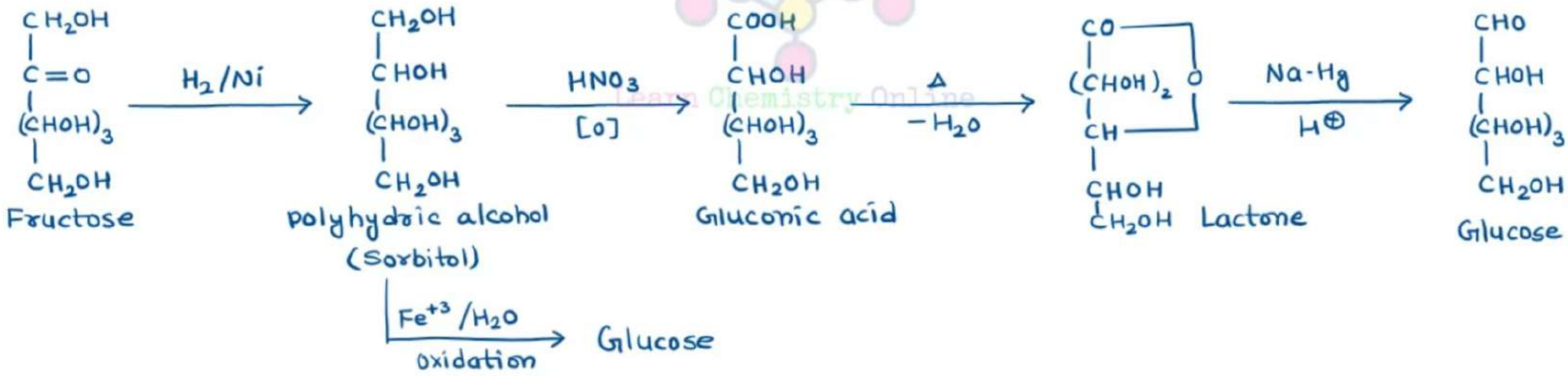


→ Interconversion of Glucose and Fructose:-

(i) Conversion of glucose to fructose:-



(ii) Conversion of fructose to glucose:-

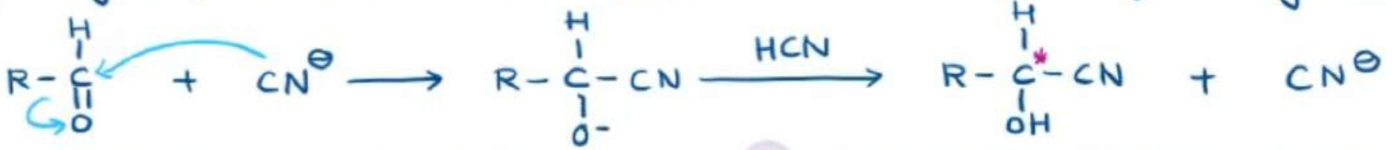


→ Chain lengthening and chain shortening in Aldose:-

(A) Chain lengthening in Aldose:- 1. Kiliani synthesis:-

– This synthesis consists of following four steps:-

(i) The aldehyde group of an aldose reacts with HCN to give cyanohydrin.



$$R-CHO + CN^{\ominus} \longrightarrow R-CH(O^{-})-CN \xrightarrow{HCN} R-\overset{*}{C}H(OH)-CN + CN^{\ominus}$$

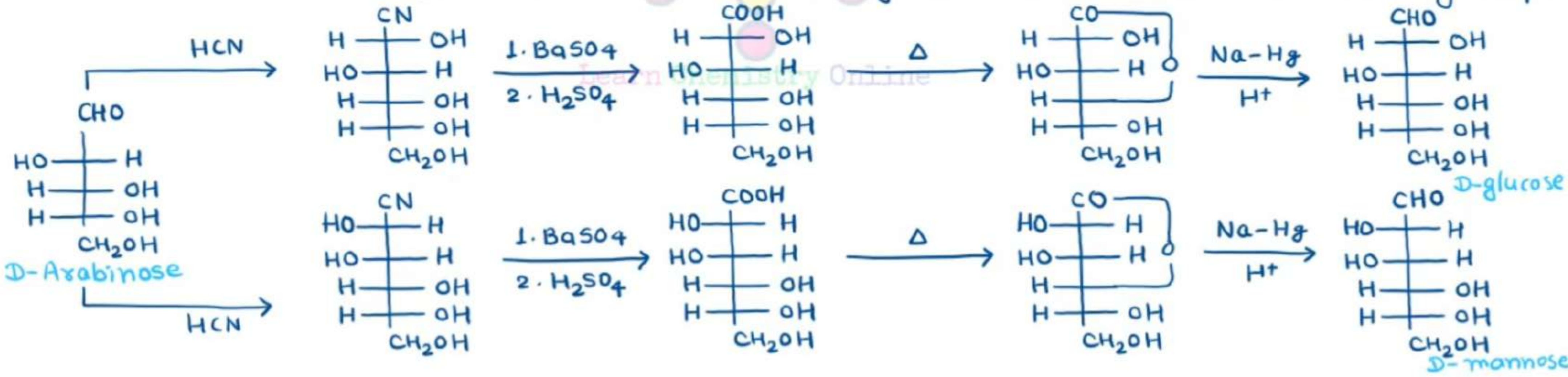
* New chirality center

– Since a new chirality center (C*) is generated in this process, a mixture of two stereo-isomeric cyanohydrins is obtained.

(ii) Hydrolysis of cyanohydrin gives corresponding carboxylic acids.

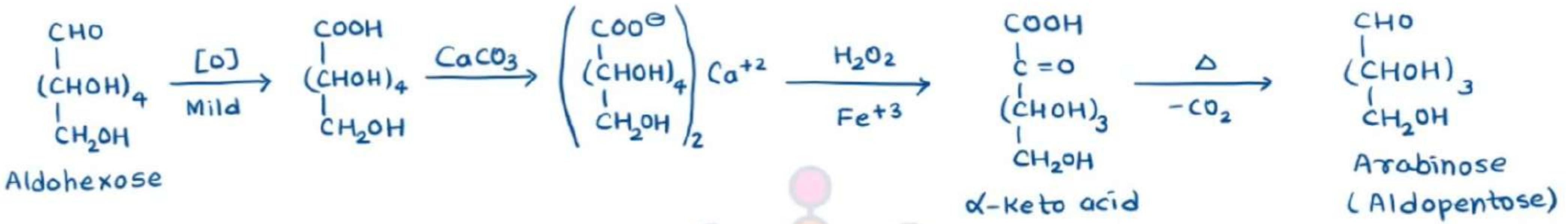
(iii) Carboxylic acids converts in to lactones on heating

(iv) Reduction of lactones gives an aldose containing one more carbon than starting comp.

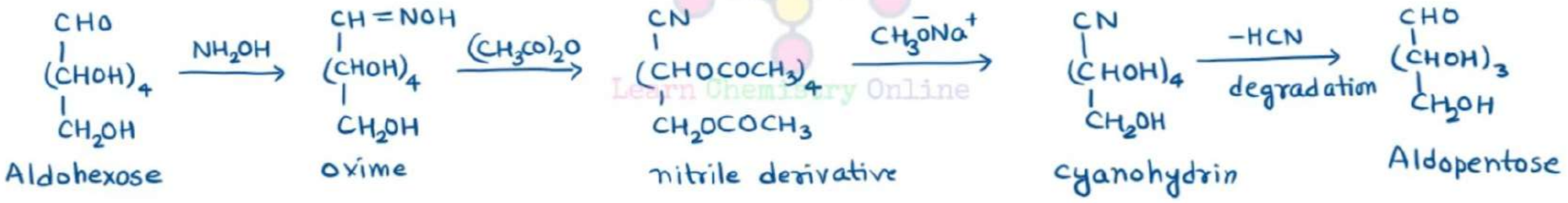


(B) Chain shortening in Aldose:-

1. Ruff degradation:-



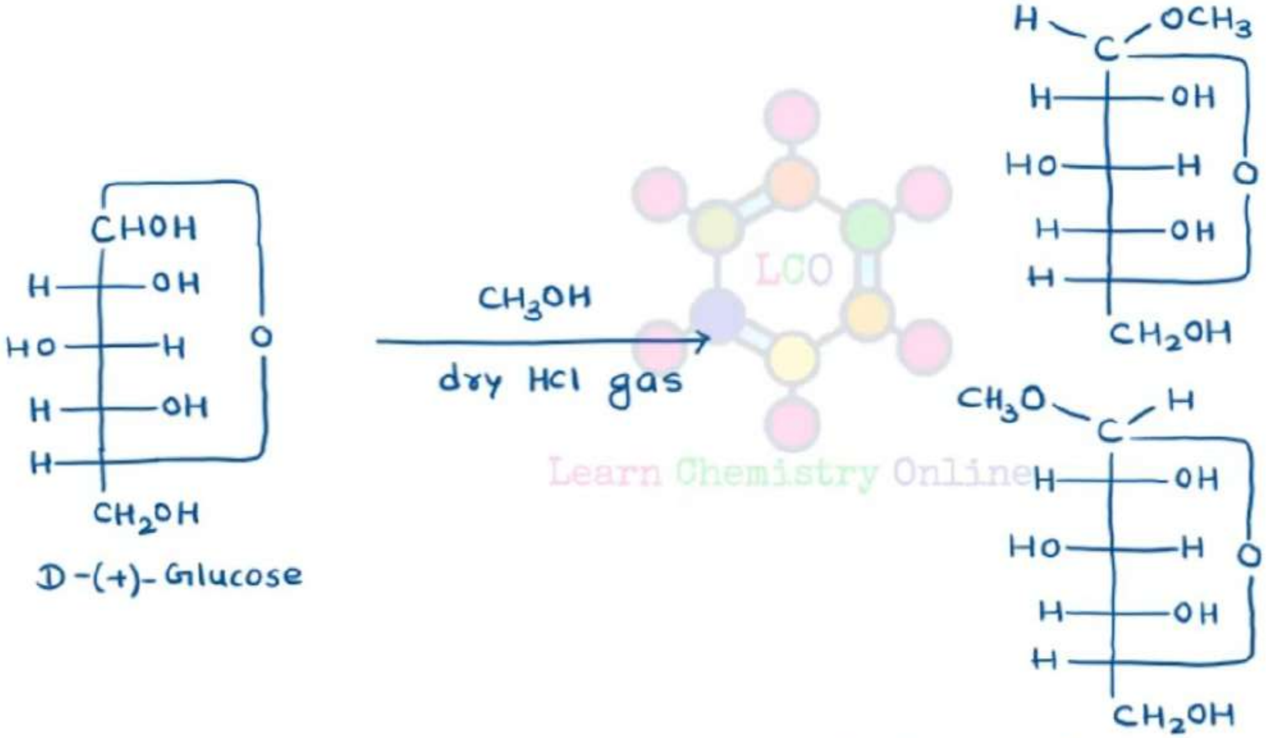
2. Zemplen modification of Wohl's method:-



→ Determination of ring size of monosaccharides:→

→ Ring size of D-(+)-glucose:-

- Howarth method (1926)
- D-(+)-Glucose, on treatment with CH_3OH and dry HCl gas under reflux, give a mixture of methyl-α-D-glucoside and methyl-β-D-glucoside.



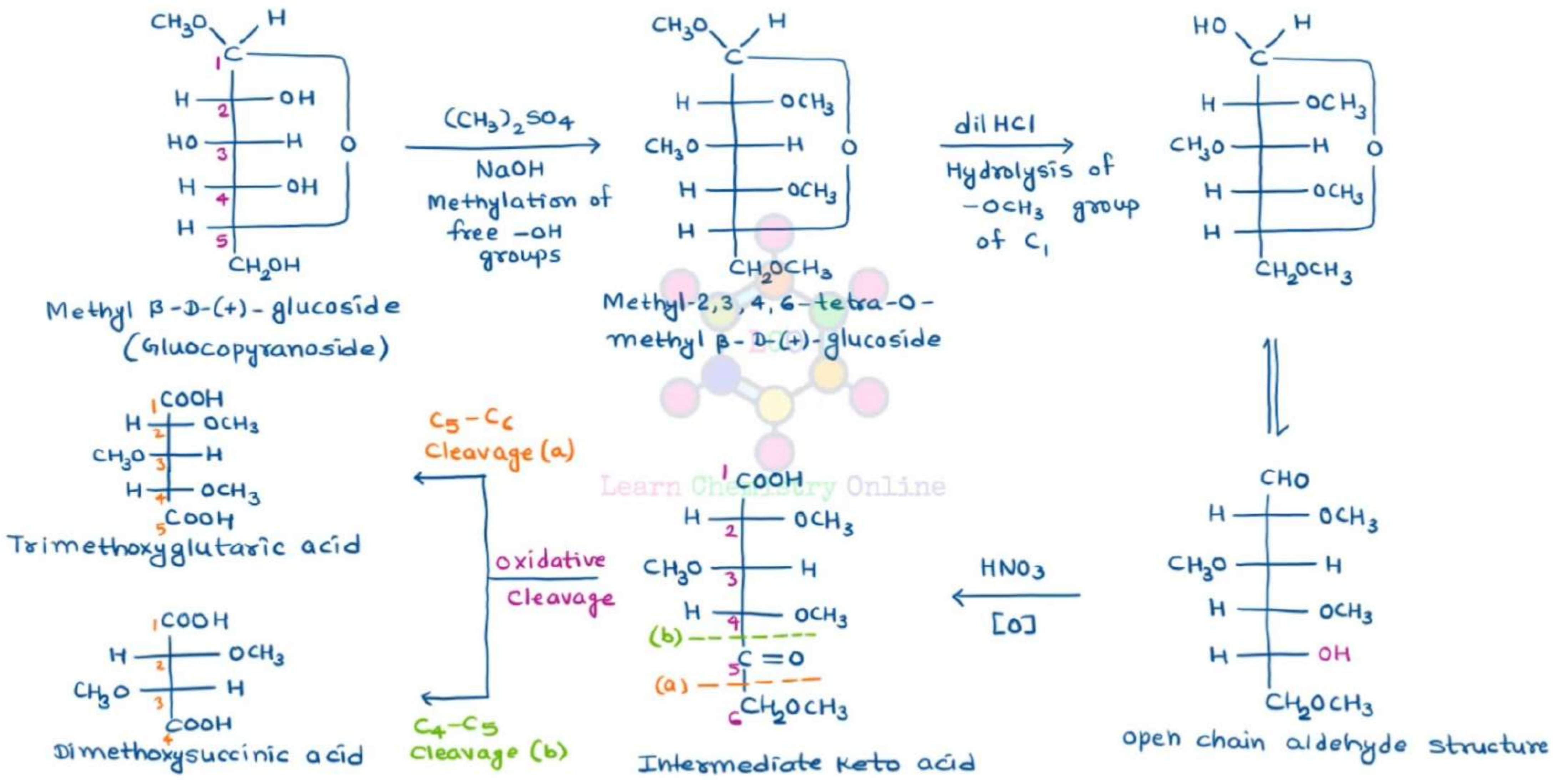
D-(+)-Glucose

Methyl-α-D-(+)-Glucoside

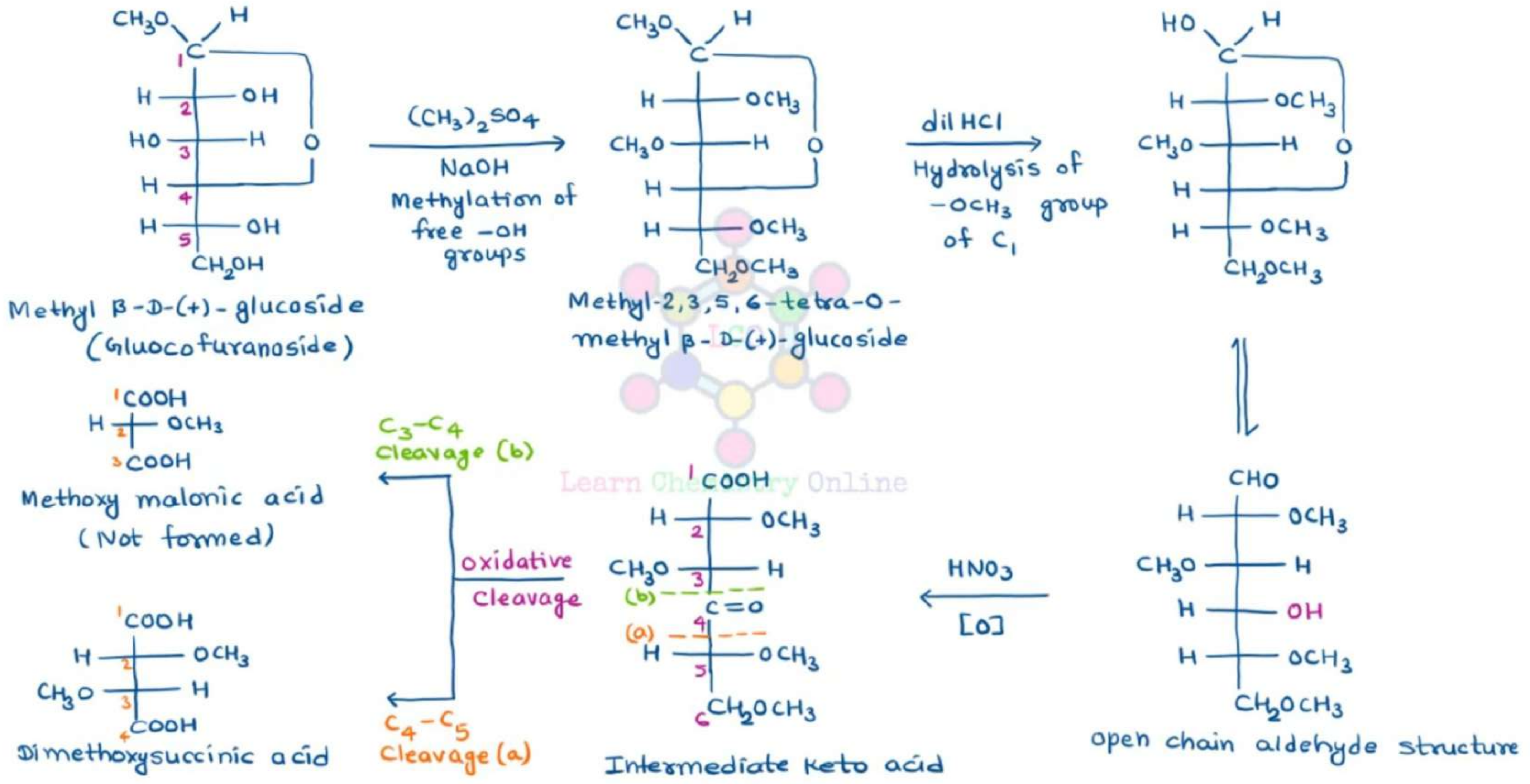
Methyl-β-D-(+)-Glucoside

- These two isomer separated and β-isomer is used for ring size determination

→ If glucose exist as six membered ring i.e. C_1 and C_5 carbon atoms involved in ring formation

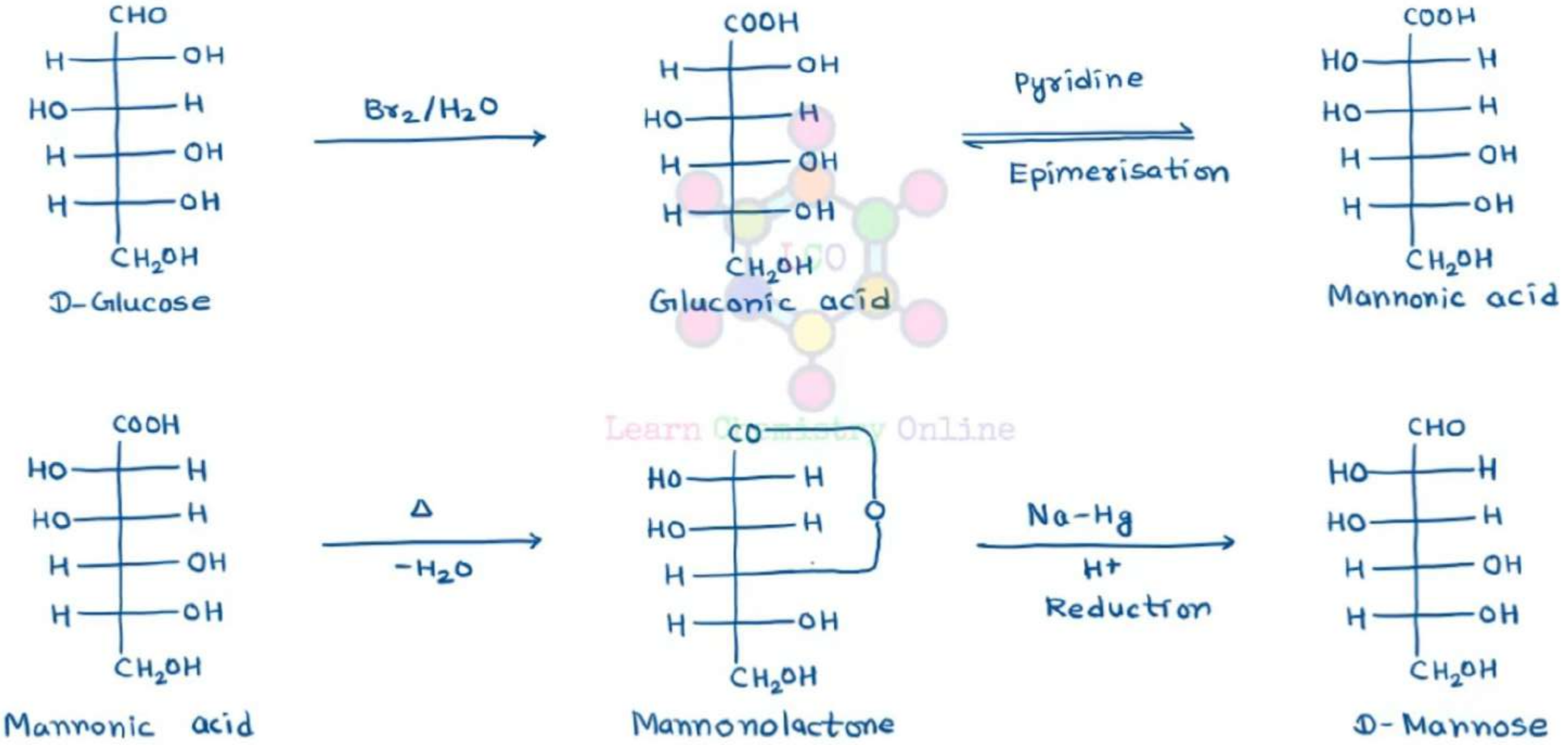


→ If glucose exist as five membered ring i.e. C_1 and C_4 carbon atoms involved in ring formation



→ Conversion of glucose into mannose : Epimerisation :-

- A pair of diastereomeric aldose whose configuration differes only about c-2 are called epimers.
  example :- D- glucose is an epimer of D-mannose.
- Interconversion of such diastereomers is called epimerisation.



→ Mutarotation :→

- D-(+)-glucose exists in two isomeric forms.

(i) α- glucose → specific rotation → +112°, m.p. → 419 K

(ii) β - glucose → specific rotation → +19°, m.p. → 423 K

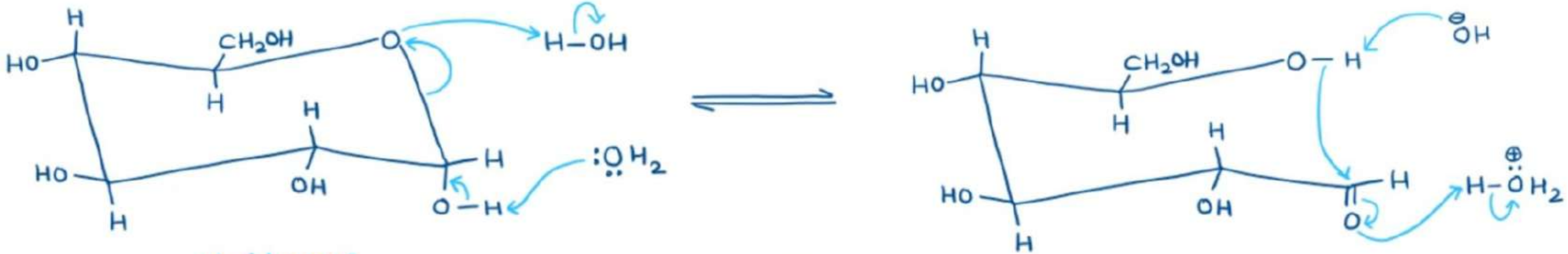
- Both crystalline forms α- and β- are quite stable. However, in aqueous solution, each form slowly changes in to a equilibrium mixture.
- This equilibrium mixture has a specific rotation of +52°.

$$\begin{array}{c} \alpha\text{-D-(+)-Glucose} \\ +112^\circ \\ \text{m.p. } 419\,K \end{array} \rightleftharpoons \begin{array}{c} \text{Equilibrium mixture} \\ +52^\circ \\ \end{array} \rightleftharpoons \begin{array}{c} \beta\text{-D-(+)-Glucose} \\ +19^\circ \\ \text{m.p. } 423\,K \end{array}$$

- This phenomenon of change in specific rotation of an optically active compound, with time, to an equilibrium mixture is known as mutarotation.
- The equilibrium mixture contain 36% of α-anomer and 64% of β-anomer.

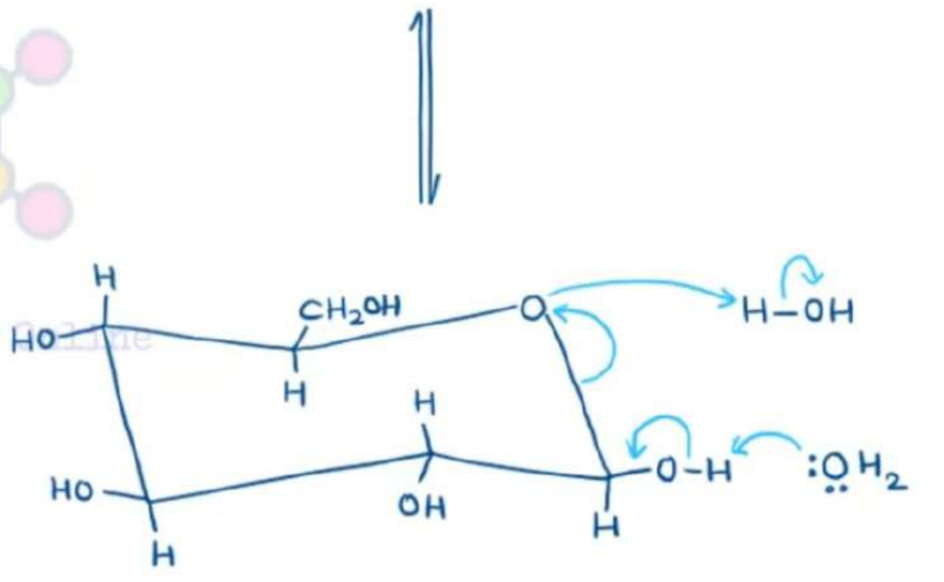
→ Mechanism of Mutarotation :→

- Mutarotation of (+)-glucose is completed througth both general acid and general base catalysis
- Since water has both acidic and basic properties, mutarotation proceeds most readily in aqueous solution.



α-Glucose

- Mutarotation can also be done in the presence of pyridine (weak base) and cresol (weak acid) mixture or in the presence of 2-hydroxypyridine.
- Since methyl α-D-glucoside and methyl β-D-glucoside are acetals, they are quite stable in aqueous solution and hence do not undergo mutarotation.



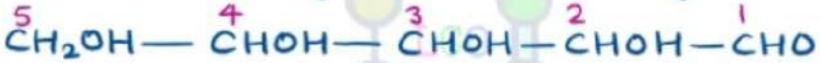
β-Glucose

→ Structure of Ribose and Deoxyribose :→

- Ribose and deoxyribose are well known aldopentose occuring as consitituents of nucleic acids.

- Structure of D-(-)-Ribose :-

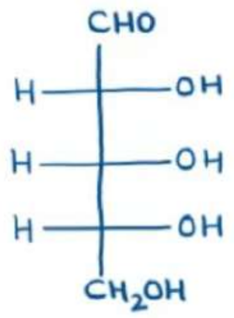
- It is an important constituent of ribonucleic acid (RNA).
- The molecular formula of D-(-)-ribose is $C_5H_{10}O_5$. which is determined on the basis of analytical data and molecular weight determination.
- It has straight chain of five carbon atoms.
- It shows the presence of an aldehydic group and four hydroxyl group (one primary and three secondary). Therefore, the following structure may be proposed.



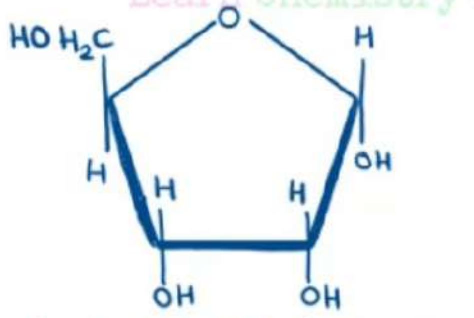
$$\overset{5}{C}H_2OH - \overset{4}{C}HOH - \overset{3}{C}HOH - \overset{2}{C}HOH - \overset{1}{C}HO$$

open chain structure

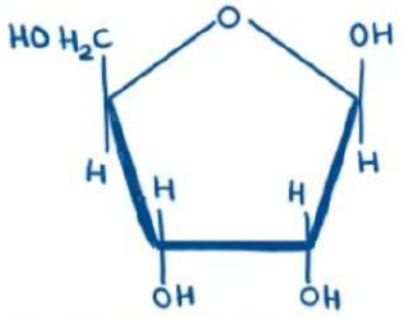
- Like glucose and fructose, ribose also has a cyclic structure -



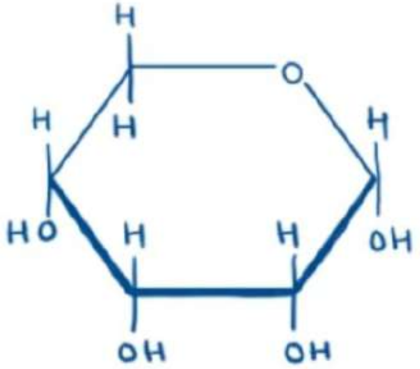
D-(-)- Ribose



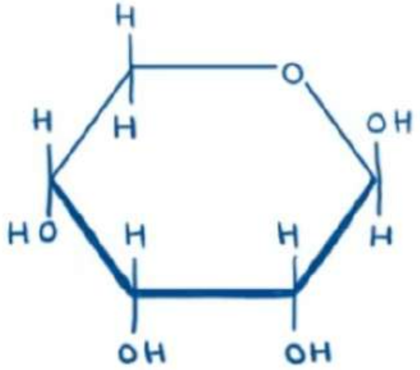
α- D-(-)- Ribofuranose



β - D-(-)- Ribofuranose



α-D-(-)-Ribopyranose



β-D-(-)-Ribopyranose

- In aqueous solution, D-(-)-ribose exists as an equilibrium mixture of all the four forms with a very small amount of open chain structure. This is confirmed by PMR studies of aqueous solution.

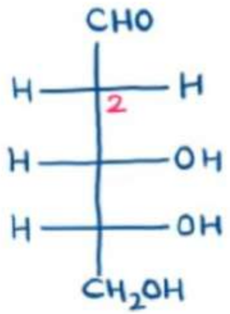
$$\alpha\text{-D-(-)-Ribofuranose (6\%)} \rightleftharpoons \text{open chain form (2\%)} \rightleftharpoons \alpha\text{-D-(-)-Ribopyranose (20\%)}$$

$$\beta\text{-D-(-)-Ribofuranose (18\%)} \rightleftharpoons \text{open chain form (2\%)} \rightleftharpoons \beta\text{-D-(-)-Ribopyranose (56\%)}$$

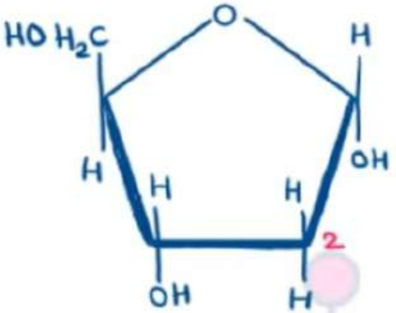
- Structure of 2-Deoxy-D-(-)-Ribose :-
- It is a fundamental constituent of deoxynucleic acid (DNA).
- It is an aldopentose in which the hydroxyl group at C-2 of ribose has been replaced by hydrogen due to which it is called deoxyribose.
- It contains an aldehyde group and three hydroxyl groups (one primary and two secondary).

$$\overset{5}{C}H_2OH - \overset{4}{C}HOH - \overset{3}{C}HOH - \overset{2}{C}H_2 - \overset{1}{C}HO$$ open chain structure (oxygen removed from C-2)

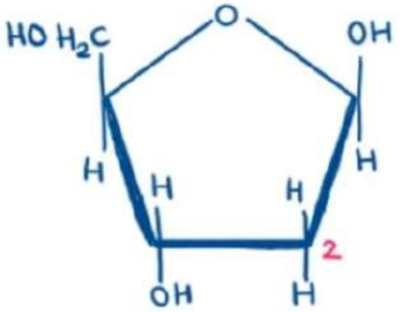
- The cyclic structures of Deoxyribose are as under:-



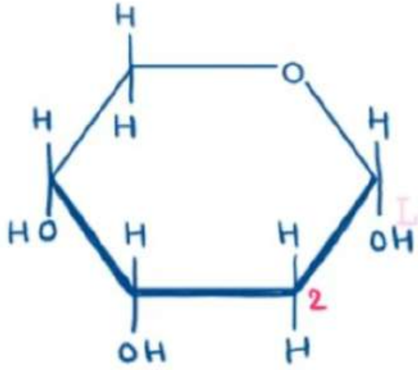
2-Deoxy-D-(-)-Ribose



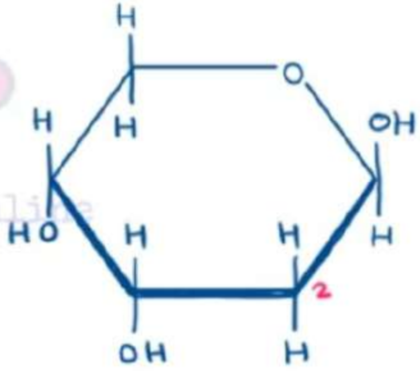
2-Deoxy-α-D-(-)-Ribofuranose



2-Deoxy-β-D-(-)-Ribofuranose



2-Deoxy-α-D-(-)-Ribopyranose



2-Deoxy-β-D-(-)-Ribopyranose

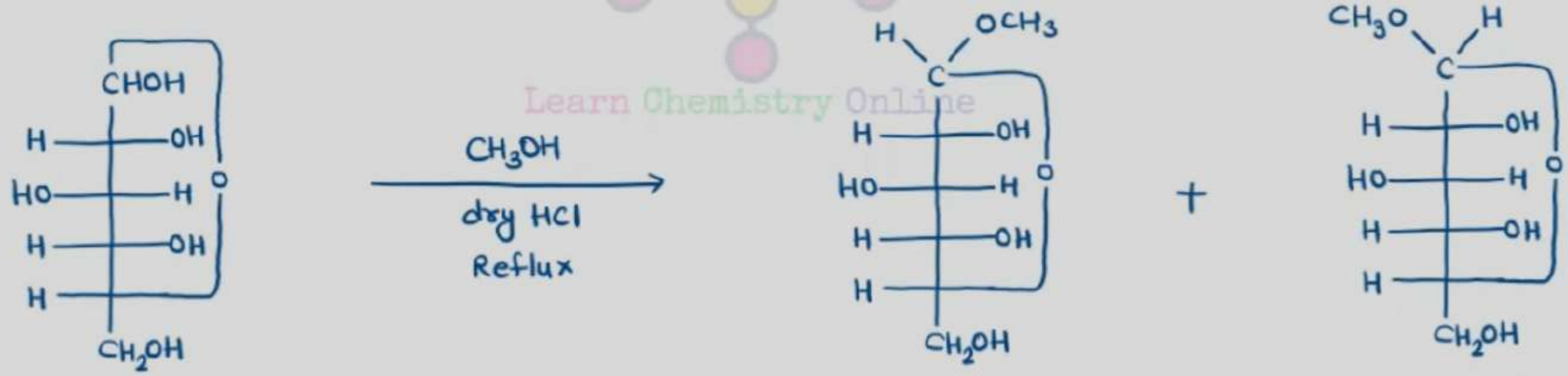
→ Formation of Glycosides, Ethers and Esters:-

① Glycosides:-

- When monosaccharides having cyclic hemiacetal/hemiketal structures such as glucose, fructos ribose etc. are treated with alcohols in presence of dry HCl gas, they are converted into cyclic acetals/ketals in which the anomeric hydroxyl group is replaced by an alkoxy group. Such cyclic acetals or ketals known as glycosides.

  Example:- Acetals and ketals fromed glucose are called glucosides.

- If D-(+)- glucose (α- or β- anomer) is refluxed with methyl alcohol in presence of dry HCl, an equilibrium mixture of anomeric glucosides is obtained in which the more stable β-glucoside predominates.



D-(+)- Glucose

Methyl-α-D-(+)-Glucoside

Methyl-β-D-(+)-Glucoside

- The bond between anomeric carbon and the OR part of alcohol is called glycosidic linkage. The glycosidic linkage present in α- and β- glucosides are called α- and β- glycosidic linkage.
- These glycosidic linkage can be distinguished by their specific reaction towards enzymes- α- glycoside linkage are hydrolysed by the maltase enzyme and β-glycoside linkage are hydrolysed by the enzyme emulsion.
- The anomeric carbon of the monosaccharides at which acetal formation occurs is called the glycosidic carbon and the hydroxyl group attached to it is called the glycosidic hydroxyl group.

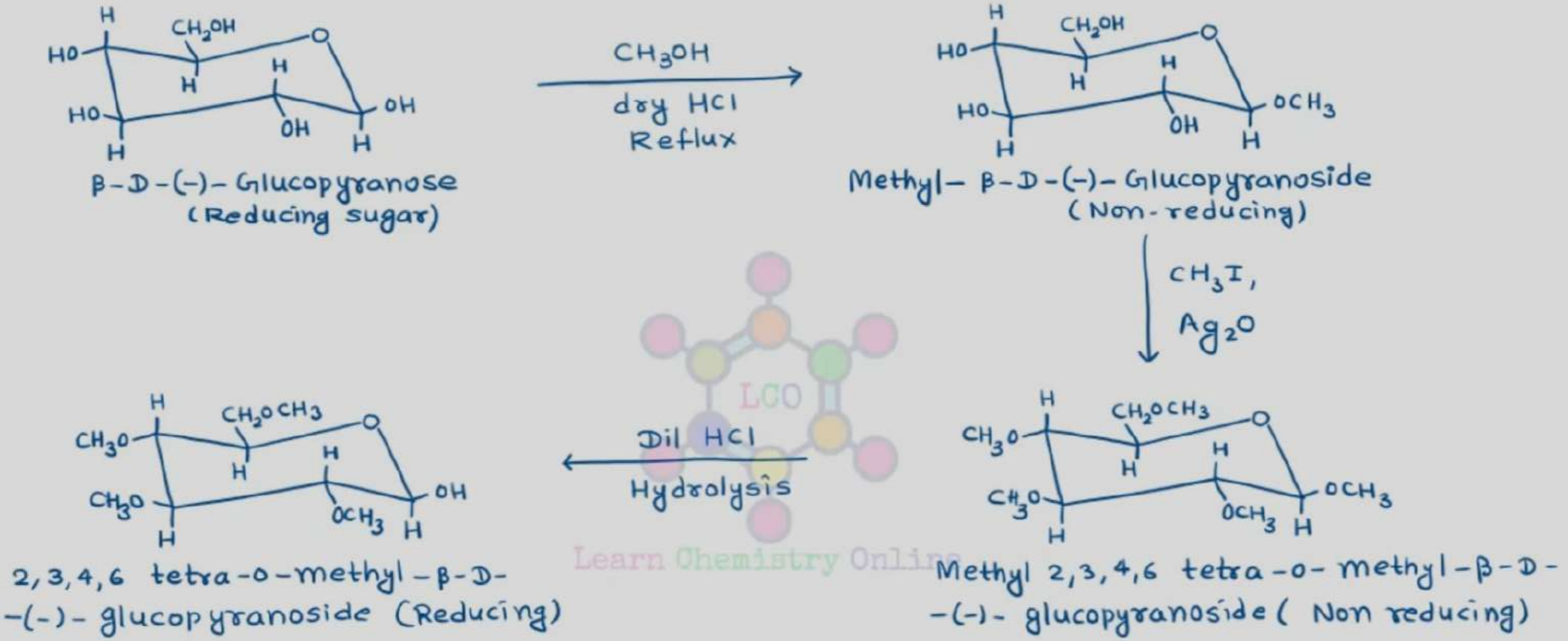
② Formation of Ethers:-

- Monosaccharides and other reducing carbohydrates cannot be directly converted into ethers by treatment with an alkyl halide in presence of a base (Williamson's ether synthesis). because carbohydrates undergo Lobry de Bruyn van Eikenstein rearrangement under these conditions.
- To avoid such complications, the anomeric hydroxyl group is first protected by forming its glycoside which is then converted into the corresponding ethers by the following methods-

① Purdie method.

② Haworth method

(i) Purdie method :-



β-D-(-)-Glucopyranose (Reducing sugar)

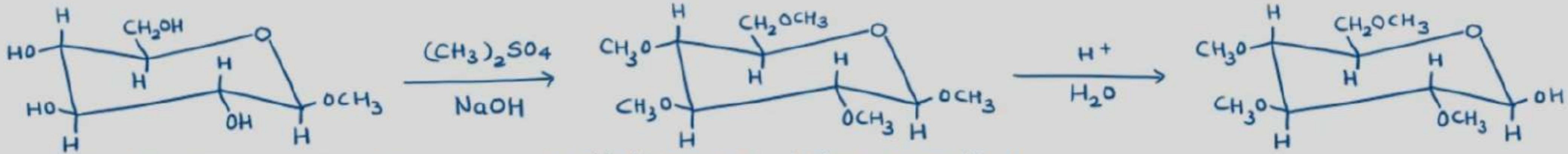
Methyl- β-D-(-)-Glucopyranoside (Non-reducing)

Methyl 2,3,4,6 tetra-o-methyl-β-D--(-)-glucopyranoside (Non reducing)

2,3,4,6 tetra-o-methyl-β-D--(-)-glucopyranoside (Reducing)

(ii) Haworth method :-

- In this method, the methyl D-glycoside is treated with excess of dimethyl sulphate in the presence of aq. NaOH.
- In Haworth and purdie method, all -OH groups converted into OCH$_3$, due to which the reaction is called permethylation.



Methyl β-D-(-)-Glucopyranoside

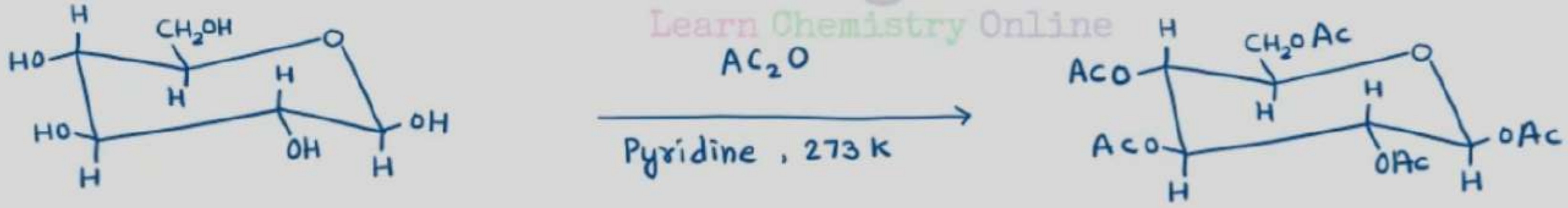
Methyl 2,3,4,6-tetra-O-methyl-β-D-(-)-glucopyranoside

2,3,4,6-Tetra-O-methyl-β-D-(-)-glucopyranoside

- The process of permethylation of glycosides followed by acidic hydrolysis of the glycoside linkage has been used in determination the ring size of monosaccharides.

③ Formation of Esters:-

- Monosaccharides can be easily converted into esters on treatment with an acid chloride or an anhydride in presence of pyridine.
- All hydroxyl groups, including the anomeric ones, are converted into ester groups.



β-D-Glucopyranose

Penta-O-acetyl-β-D-glucopyranoside

→ Disaccharides :-

- A molecule of disaccharide consist of two monosaccharide units and give two monosaccharide units on hydrolysis.
- A large number of such compounds have been found in nature.
- Disaccharides are crystalline, water soluble, sweet compounds.
- Commonly occuring natural disaccharides are Maltose, lactose and sucrose. The hydrolysis of these disaccharides give following monosaccharide units on hydrolysis.

$$\text{Maltose} \longrightarrow \text{Glucose} + \text{Glucose}$$

$$\text{Lactose} \longrightarrow \text{Glucose} + \text{Galactose}$$

$$\text{Sucrose} \longrightarrow \text{Glucose} + \text{Fructose}$$

- The two monosaccharide units may be linked througth the following groups -

① Anomeric -OH of one unit and -OH of other.

e.g. reducing disaccharides, maltose and lactose

② Anomeric -OH of both the units.

e.g. non-reducing disaccharides, sucrose.

- The two monosaccharide units may be linked througth the following glycosidic linkage -

① 1,4 - Glycosidic linkage:-

- C_1 (Anomeric) carbon of one unit and C_4 carbon of another unit.

② 1,6 - Glycosidic linkage:-

- C_1 (Anomeric) carbon of one unit and C_6 carbon of another unit.

③ 1,2- Glycosidic linkage:-

- C_1 (Anomeric) carbon of one unit and C_2 carbon of another unit.

④ 1,1 - Glycosidic linkage:-

- C_1 (Anomeric) carbon of one unit and C_1 (Anomeric) carbon of another unit.

→ The structure of a disaccharide is established in the following steps -

1. Hydrolysis and identification of component monosaccharide units.
2. Determination of ring size of each monosaccharide units.
3. Determination of position of linkage through two monosaccharide units attached.
4. Finally, anomeric configuration (α- or β-) of the linkage is estabilised through enzymatic hydrolysis.

→ (+)- Maltose:-

- Malt sugar, $C_{12}H_{22}O_{11}$
- (+)- Maltose occurs in germinating seeds, particularly cereals.

- Preparation:-

- It is obtained by partial hydrolysis of starch by action of diastase or dilute HCl.

$$\underset{\text{starch}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow[\substack{\text{diastase} \\ (\beta\text{-amylase})}]{\substack{\text{dilute HCl} \\ \text{or}}} \underset{\text{Maltose}}{C_{12}H_{22}O_{11}}$$

- Properties:-

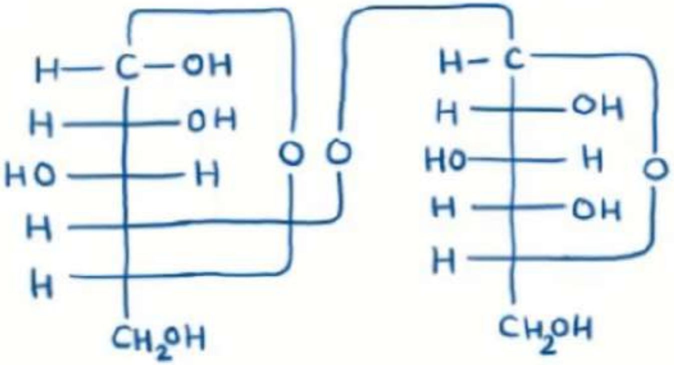
- It is a colourless crystalline solid and soluble in water.
- m.p. 438 K
- It is readily hydrolysed to glucose on heating with acid.

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Acid}} \underset{\text{Glucose}}{2\,C_6H_{12}O_6}$$

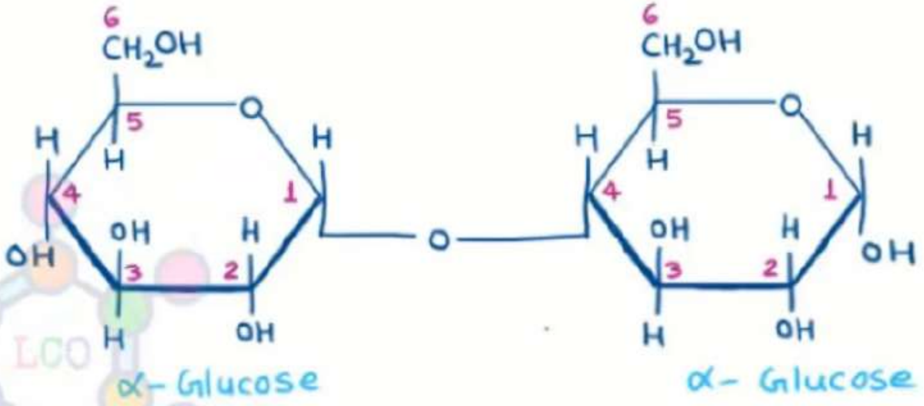
- It reduces Tollen's reagent and Fehling solution.
- It is dextrorotatory
- It forms osazone when react with excess amount of phenylhydrazine.
- It exists in anomeric α- and β- forms which undergo mutarotation in solution.

$$\underset{[\alpha]_D\ +168^\circ}{\alpha\text{-form}} \rightleftharpoons \underset{[\alpha]_D\ +136^\circ}{\text{Equilibrium}} \rightleftharpoons \underset{[\alpha]_D\ +112^\circ}{\beta\text{-form}}$$

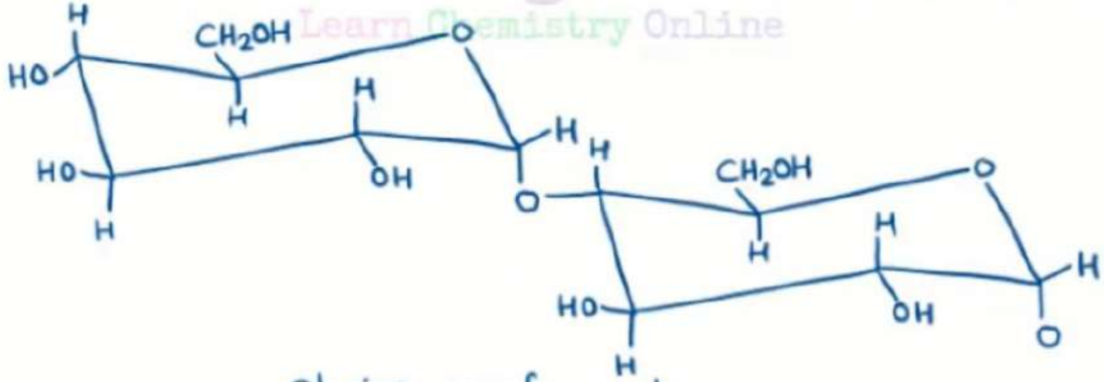
- It reacts with acetic anhydride and undergo acetylation reaction to form octaacetate.
- Oxidation with Br_2 water gives maltobionic acid, a monocarboxylic acid.
- Structure of Maltose :-
- Molecular formula → $C_{12}H_{22}O_{11}$



Fischer projection



Maltose (1,4-glycosidic linkage)
Haworth structure



Chair conformation

→ (+)-Lactose:-

- Milk sugar , $C_{12}H_{22}O_{11}$
- (+)- Lactose is found in the mammalian milk to the extent of 4-8%.
- cow milk contains 4-6% lactose whereas human milk contains 5-8% of this sugar.
- When milk turns sour, lactose converted into lactic acid by bacterial action (*Lactobacillus bulgarics*)
- Whey (watery part of milk produced when raw milk sours and coagulates) is a by product of cheese manufacture and gives lactose on evaporation.
- upon acid or enzymatic (lactase) hydrolysis, lactose gives D-(+)-glucose and D-(+)-galactose in equimolar amounts.

$$\underset{\text{Lactose}}{C_{12}H_{22}O_{11}} \xrightarrow[\text{Acid or lactase}]{H_2O} \underset{\text{D-(+)-glucose}}{C_6H_{12}O_6} + \underset{\text{D-(+)- galactose}}{C_6H_{12}O_6}$$

→ Properties:-

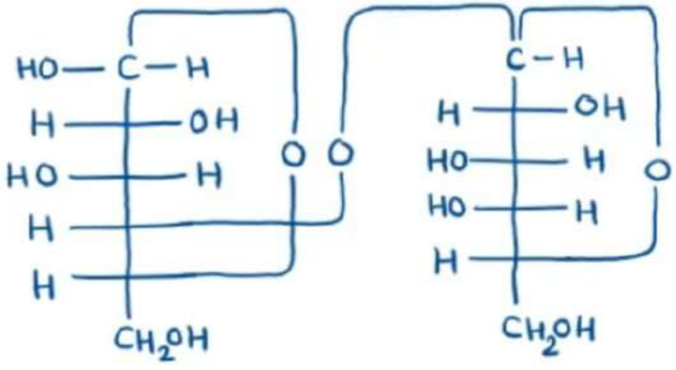
- Lactose is a colourless crystalline solid.
- Melts at 476.5K with decomposition.
- Lactose is water soluble and sweet in taste.
- specific gravity is 1.525.
- It reduces Tollen`s reagent and Fehling's solution.
- It is dextrorotatory
- It forms osazone when reacts with phenylhydrazine.

- It exists in two anomeric α- and β-forms and exhibits mutarotation.

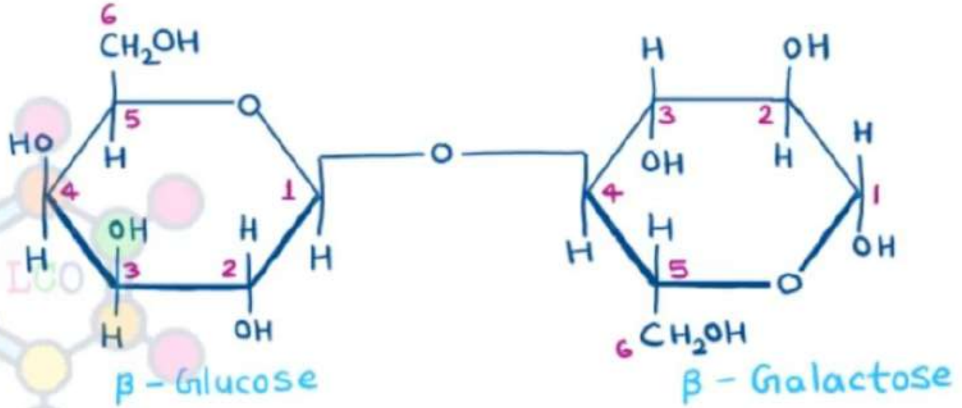
α-form	$\rightleftharpoons$	Equilibrium	$\rightleftharpoons$	β-form
m.p. 496K				m.p. 525 K
$[\alpha]_D$ +90°		$[\alpha]_D$ +55°		$[\alpha]_D$ + 35°

- Structure of Lactose :-

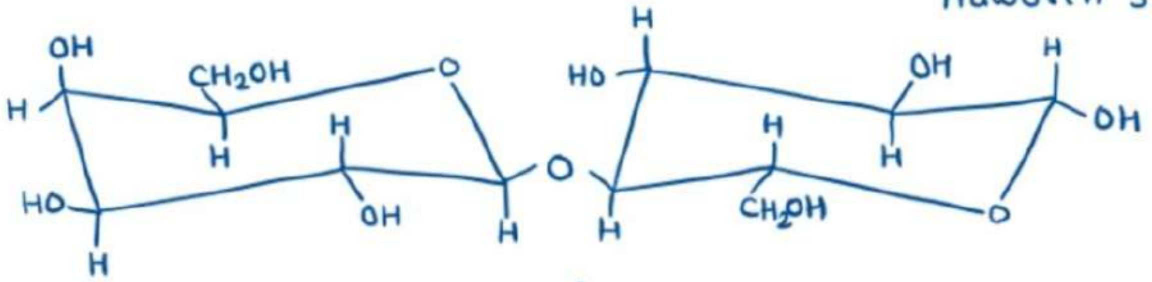
- Molecular formula → $C_{12}H_{22}O_{11}$



Fischer projection



Lactose (1,4 - glycosidic linkage)
Haworth structure

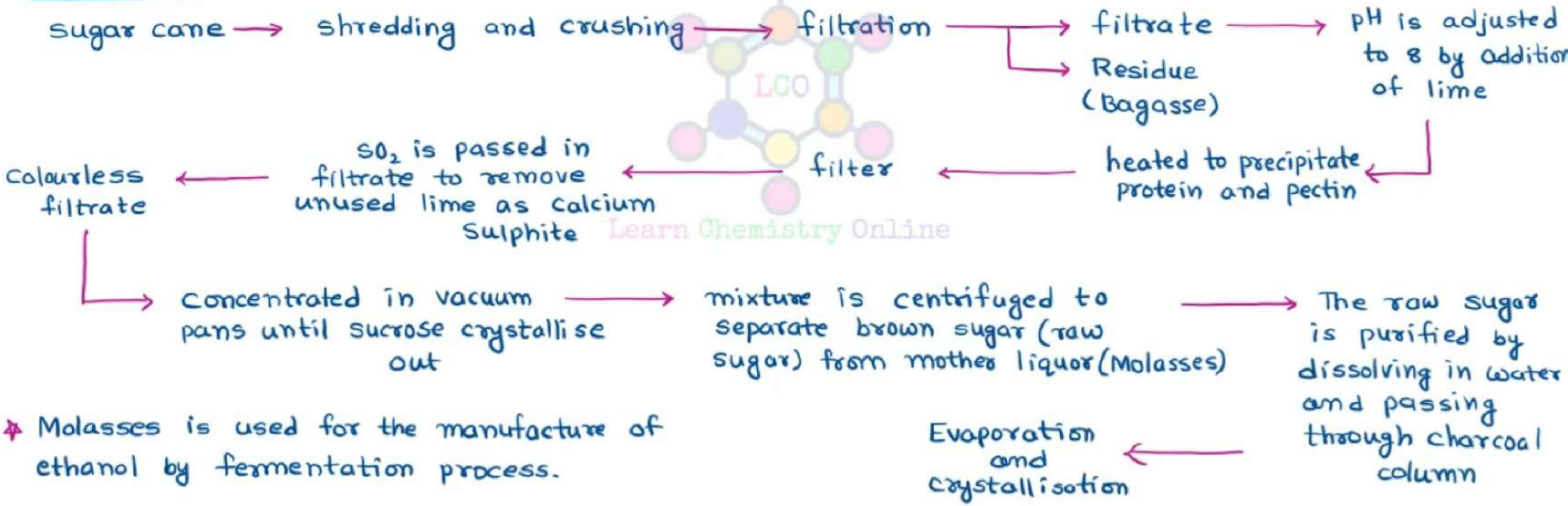


chair conformation

→ (+)- Sucrose:-

- (+)- sucrose is the most common sugar used by people every day to sweeten the food.
- It is manufactured from sugar cane or sugar beets.
- It is the one of the commercial organic chemical which is manufactured in large quantity in pure form.
- In India, the principal source of sucrose is sugar cane. The residue, known as bagasse, is used as fuel or in the manufacture of paper.

→ Preparation:-



✱ Molasses is used for the manufacture of ethanol by fermentation process.

→ Properties :-

- Sucrose is a colourless, crystalline solid.
- m.p. 453 k
- It is soluble in water but insoluble in alcohol and ether.
- It is dextrorotatory and has a specific rotation of +66.5°. It does not exhibit mutarotation.
- When heated above its melting point, it loses water and gives a brown mass known as caramel which is used for colouring confectionary and spirit. on heating still further, it gets charred and gives a smell of burnt sugar.
- Sucrose on hydrolysis with dilute acids or with invertage (an enzyme present in yeast) gives D-(+)-glucose and D-(-)-fructose in equal amounts.

$$\begin{array}{cccccc} C_{12}H_{22}O_{11} & + \; H_2O & \xrightarrow[\text{Invertase}]{\text{Acid or}} & C_6H_{12}O_6 & + & C_6H_{12}O_6 \\ \text{Sucrose} & & & (+)\text{-Glucose} & & (-)\text{-Fructose} \\ [\alpha]_D \; +66.5^\circ & & & [\alpha]_D \; +52.5^\circ & & [\alpha]_D \; -92.4^\circ \end{array}$$

- The above reaction involves an overall change in sign of rotation from + to −.
- The reasonable explanation for this change in sign of rotation can be that the $[\alpha]_D$ of sucrose is +66.5°, whereas the rotation of products, glucose and fructose are +52.5 and −92.4° respectively. The hydrolysed product, therefore, shows $[\alpha]_D = -39.9^\circ$ (i.e. $-92.4^\circ + 52.5 = -39.9^\circ$
- Since, the hydrolysis involves a change of rotation from +ve to −ve, it is called inversion of sugar and the hydrolysed products are called invert sugar.

- On boiling with nitric acid, sucrose is oxidised to oxalic acid.

$$C_{12}H_{22}O_{11} \xrightarrow[HNO_3]{\text{oxidation}} \begin{array}{c} COOH \\ | \\ COOH \end{array}$$

- Conc. H_2SO_4 chars sucrose with the evolution of CO_2 and SO_2

$$C_{12}H_{22}O_{11} \xrightarrow{\text{Conc. } H_2SO_4} 12C + 11H_2O$$

$$2H_2SO_4 + C \longrightarrow CO_2 + 2SO_2 + 2H_2O$$

- On reaction with acetic anhydride in presence of pyridine, sucrose undergoes acetylation and forms octaacetate.

$$C_{12}H_{22}O_{11} \xrightarrow{(CH_3CO)_2O} C_{28}H_{38}O_{19}$$

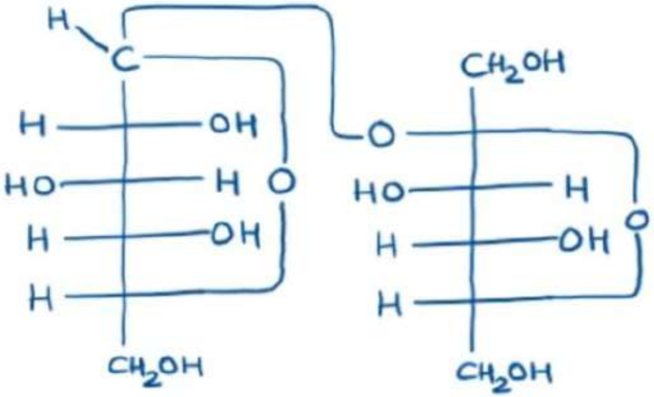
- Sucrose is a non-reducing sugar and does not form any cyanohydrin or oxime or osazone

→ Use of sucrose

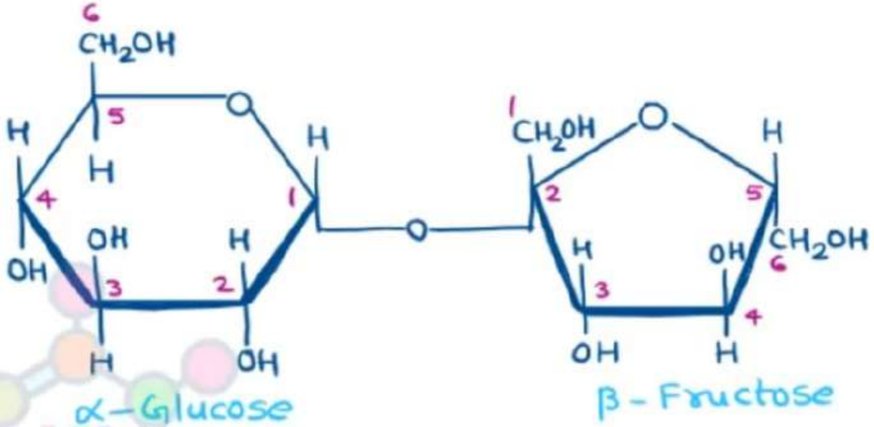
- It is used as a food and as a sweetening agent.
- It is preservative for fruit products such as jams.
- It is used in the laboratory preparation of oxalic acid.
- Its octaacetate is used for denaturing alcohol.

→ Structure of Sucrose:-

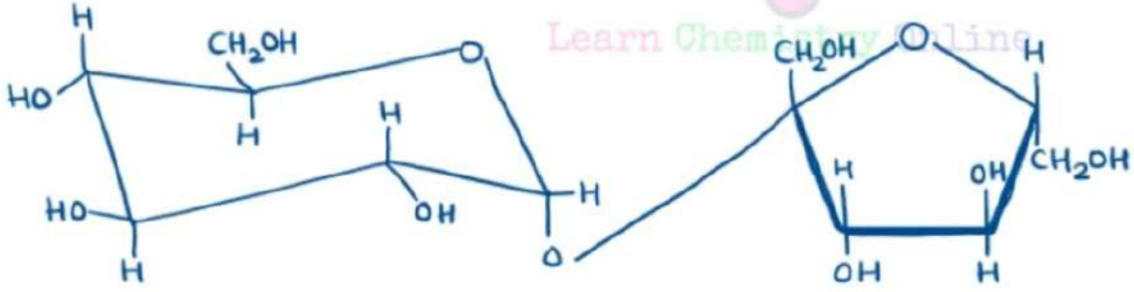
- Molecular formula:- $C_{12}H_{22}O_{11}$



Fisher projection



Haworth projection (1,2-glycosidic linkage)



Conformation.

→ Polysaccharides:-

- Polysaccharides consist of many monosaccharide units joined together through glycosidic linkage, which can be broken by acid or enzymatic hydrolysis.
- Polysaccharides are important organic compounds obtained from plants, which produce them from CO_2 and water by photosynthesis.
- They are colourless, tastless amorphous powders.
- They are insoluble in water, alcohol and ether.
- There may be hundreds or even thousands of monosaccharide units per molecule.

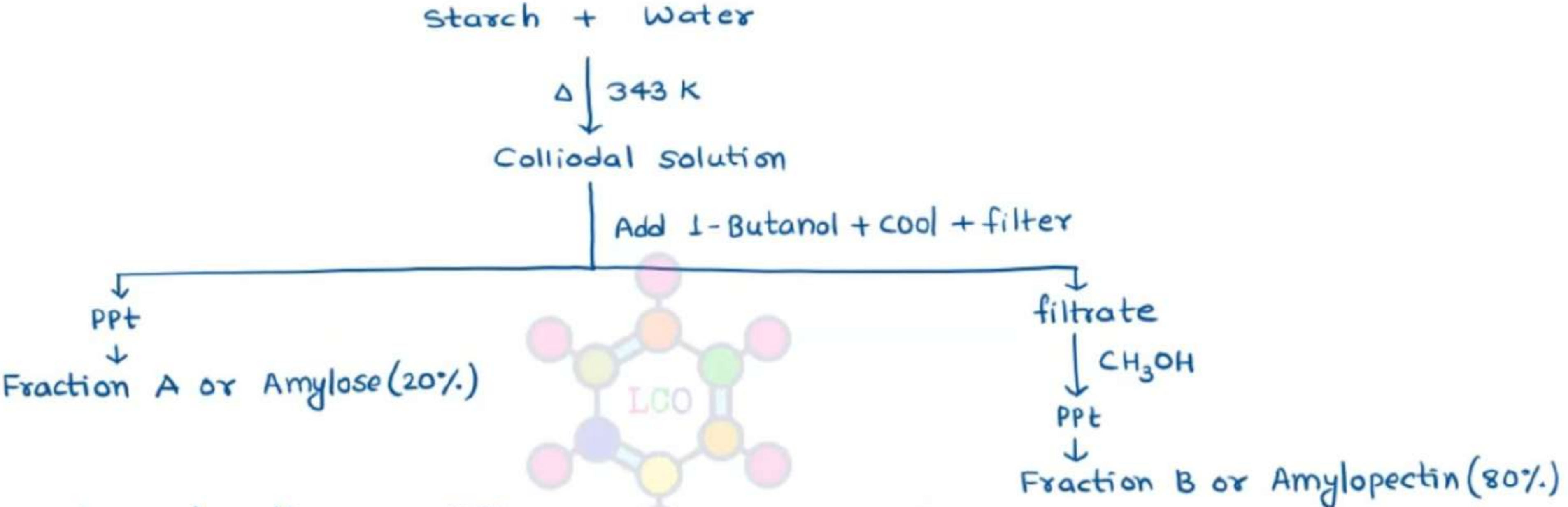
→ Starch:-

- Amylum, $(C_6H_{10}O_5)_n$
- Starch is one of the most important source of carbohydrates in the human diet.
- It found mainly in seeds, roots and tubers.
- Wheat, rice, potatoes and corns are most edible forms of starch.
- Starch is made up of D-(+)-glucose units.

→ Properties:-

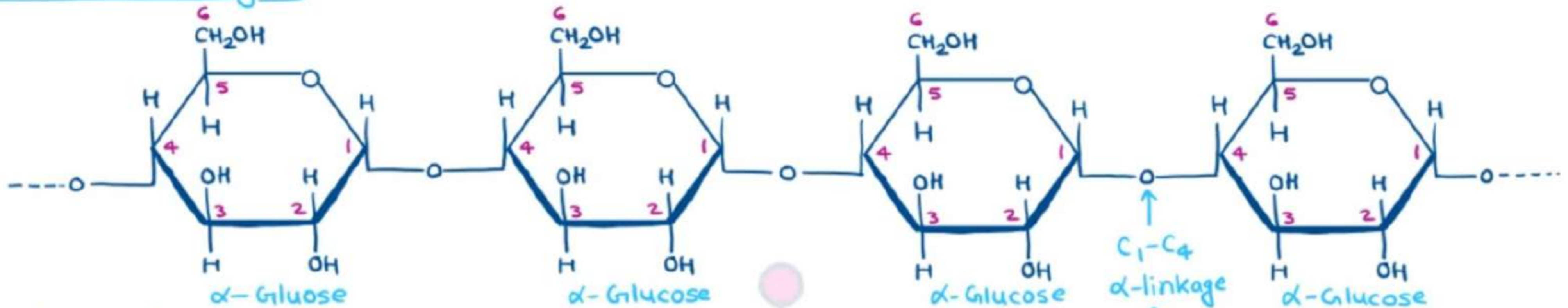
- Starch is insoluble in cold water but if water suspension is heated, the starch granules swell and burst to form a paste.
- Starch is a non-reducing polysaccharide. It does not reduce Tollen's reagent and Fehling solution. It also does not form osazone.

- Starch can be separated into two fractions A and B as described below -



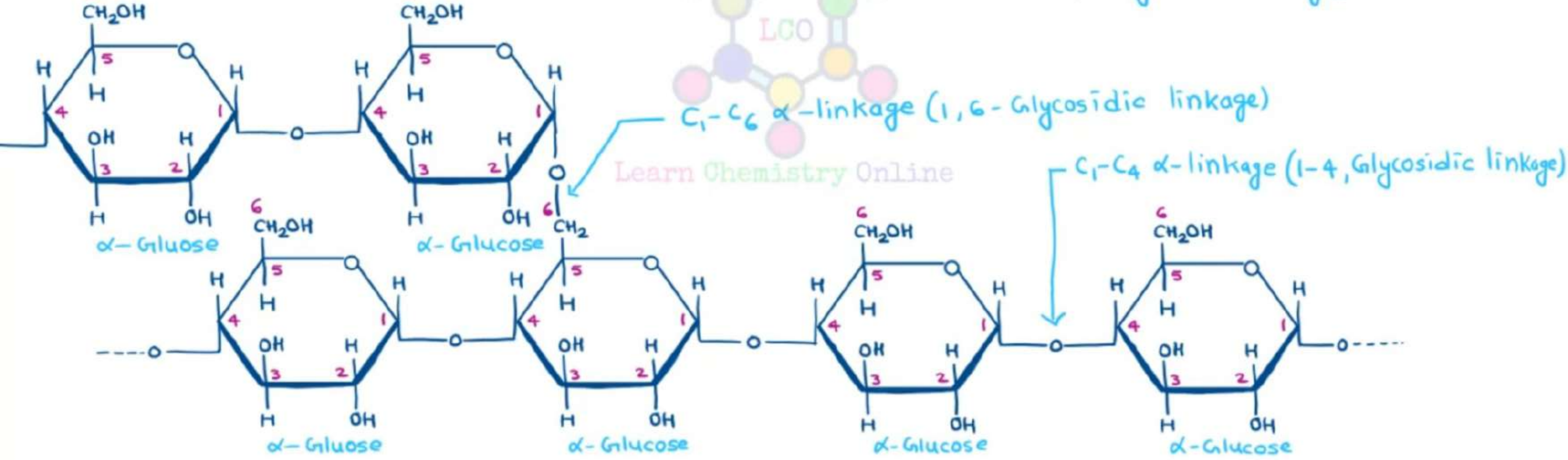
- Both amylose and amylopectin are different carbohydrates of high molecular weight with molecular formula $(C_6H_{10}O_5)_n$.
- Both gives D-glucose on complete hydrolysis.
- However, acid hydrolysis under controlled conditions or enzymatic hydrolysis give low mol. weight polysaccharide called dextrin, followed by (+) maltose and finally D-(+)-glucose.

→ Structure of Amylose :-



C_1-C_4 α-linkage
↑
(1,4-Glycosidic linkage)

→ Structure of Amylopectin :→



C_1-C_6 α-linkage (1,6-Glycosidic linkage)

C_1-C_4 α-linkage (1-4, Glycosidic linkage)

→ Uses of starch:-

- It is used in the preparation of candy and other sweets, glucose, dextrins and alcohol.
- Partial hydrolysis of corn starch give corn syrup, which is a mixture of carbohydrates of different chain length, maltose and glucose.
- It is an important constituent of many types of food.
- It is used as an indicator in idometric titrations.
- It is used for sizing and stiffening paper and textiles.

→ Cellulose :→

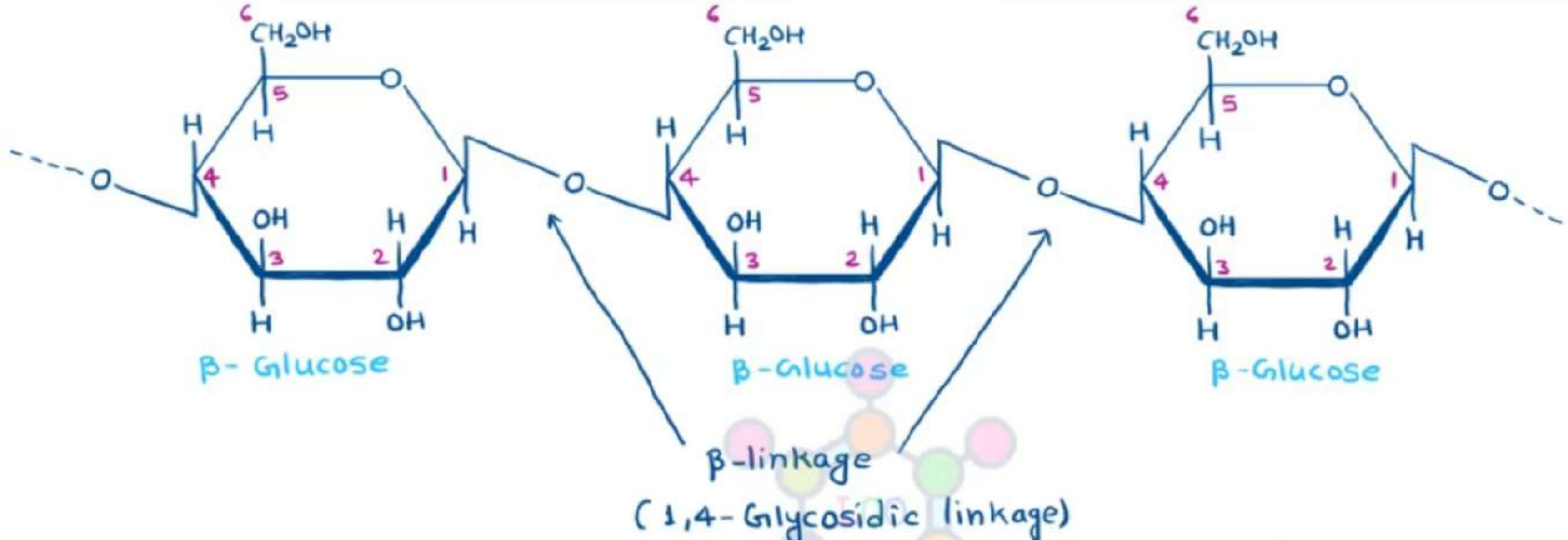
- Cellulose probably is the most abundant organic compound that exists on earth.
- It is the main structural material of cell wall of plants. It is resposible for their texture, rigidity, shape and durability.
- It is also the main component of cotton, wood and jute.
- Wood contains about 50% of cellulose and cotton contains about 90-95% of cellulose.

→ Properties :-

- It is colourless, tasteless, fibrous solid.
- It is insoluble in water but soluble in Schweitzer's reagent [ammonical solution of cupric hydroxide, used for manufacuring of artificial silk (rayon) from cotton.]
- Conc. NaOH reacts with cellulose to form gelatinous translucent mass which imparts a silky lusture to cotton. This process is called mercerization and the cotton thus treated is colled mercerized cotton.
- Like, starch, cellulose is also non-reducing compound, i.e. it does not reduce Tollen's reagent or Fehling solution. It also does not form an osazone and is not fermented by yeast.
- Unlike starch, it does not undergo hydrolysis easily. However on heating with dil. H_2SO_4 under pressure, it does undergo hydrolysis to give only D-glucose.

→ Structure of cellulose :-

- Molecular formula $(C_6H_{10}O_5)_n$
- Cellulose containing monosaccharide units of β-D-(+)-glucose



- Because of its linear structure, it can be easily converted into fibers.

→ Why is cellulose not digestible by human beings?

- The human tract break down starch to glucose, but is unable to hydrolyse cellulose. This is because of the fact that the human digestive system does not contain enzyme cellulase which can hydrolyse cellulose into D-(+)- glucose and hence, is unable to digest cellulose.

This enzyme is, however, present in digestive system of grazing animals such as cow, deer etc. that is why grazing animals can use cellulose of grasses and plants as food by converting them into D-(+)- glucose.

→ Uses of cellulose :-

1. Cellulose is mainly used as raw material for paper and textile industries.
2. Treatment of cellulose with different reagents gives different commercial products as described below-

(i) Cellulose nitrate :- Nitration of cellulose with conc. HNO_3 and conc. H_2SO_4 gives different polynitrates of cellulose depending upon the extent of nitration. For example-

(a) Gun cotton :- It is a cellulose trinitrate and is used for making smokeless powder and as a binder for solid pocket propellants.

(b) Pyroxylin :- It is less highly nitrated cellulose containing between two and three nitrate groups. A mixture of cellulose dinitrate and cellulose trinitrate per glucose molecule and is used for the manufacture of the following products :-

- Celluloid :- The plastic celluloid is obtained when pyroxylin is mixed with a plasticizer such as camphor and alcohol. It is used for manufacturing of photographic films, piano keys, spectacle frames etc.
- Colloidon :- It is a solution of pyroxylin in ether and alcohol and is used in manufacture of lacqures.

(ii) Rayon :- Rayons are the fibres made by chemical treatment of cellulose. For example- Acetate rayon and viscose rayon.

(iii) Methyl cellulose is used for fabric sizing and in the manufacture of cosmetic paste.

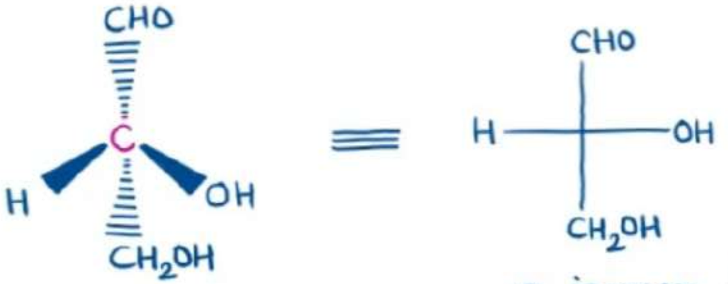
(iv) Ethyl cellulose is used for the manufacture of plastic coats and films.

(v) Cellophane:- When cellulose sheets are soften with glycerol, we get cellophane, which is used for protective films.

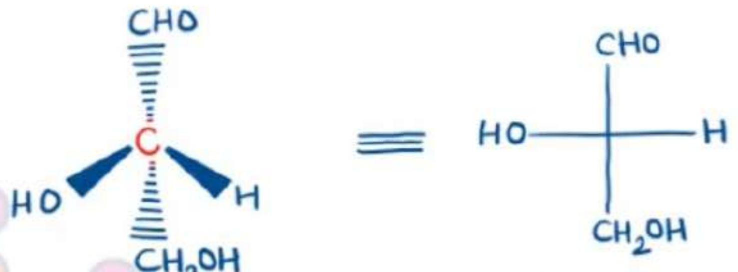
(vi) Cellulose gum:- Cellulose gum is sodium carboxymethyl cellulose. It is widely used as adhesive, detergent promotor and ceremic glaze binder.

→ Configuration of monosaccharides:-

- Glyceraldehyde was taken as an arbitrary standard for correlating the configurations of sugars.
- The two enantiomers of glyceraldehydes are called D and L.



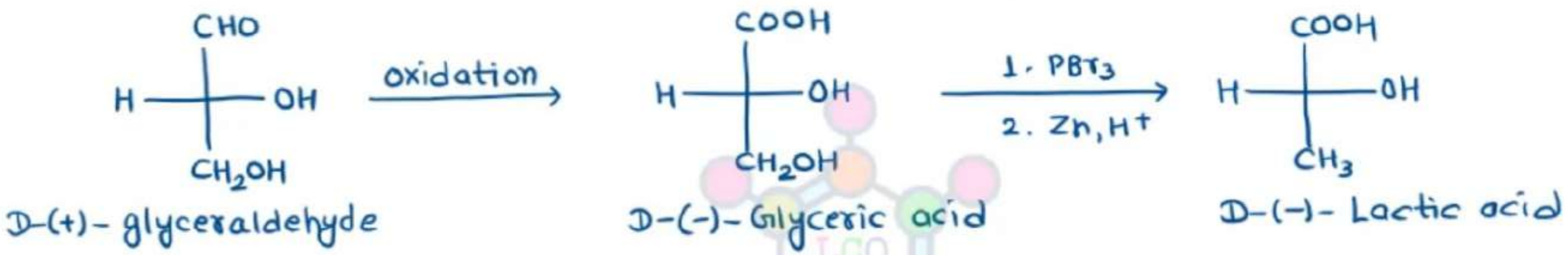
D-isomer

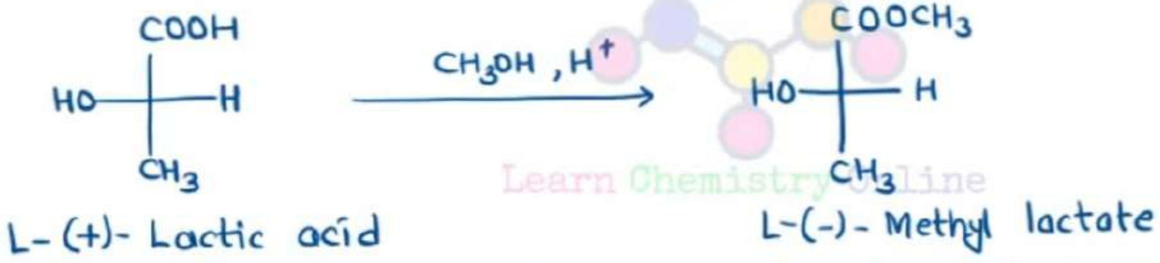


L-isomer

- one entiomer of glyceraldehyde which rotated the plane plane polarized light to the right was reffered as (+)- glyceraldehyde, while other enatiomer which rotated the plane polarized light to the left was reffered as (-)- glyceraldehyde.
- The chemist were arbitrary decided to assign the D- configuration to (+)- glyceraldehyde and the L-configuration to (-)- glyceraldehyde.
- D and L represent the configuration while (+) and (-) represent optical activity.
- D-(+)- glyceraldehyde was assigned a configuration in which Fischer projection contained -OH group on the right hand side of the viewer and H on the left side of the viewer. Similarly, L-(-)- glyceraldehyde was represented by showing H on the right side and -OH on the left side.

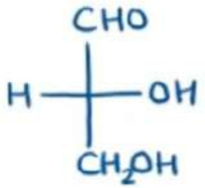
- The configuration of sugars containing chiral carbon is determined on the basis of glyceraldehyde. This is called relative configuration.
- The product obtained from D-isomer is belongs to D-series while the product obtained from L-isomer is belongs to L-series.
- There is no relationship of D and L with the sign of rotation i.e. + and –.



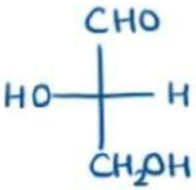


- The relative configuration assignements were found valid in 1951 on the basis of X-Ray crystallography.
- For determination of configuration of sugars, one of the glyceraldehyde of known configuration is taken and converted into tetrose using kiliani synthesis. Tetrose on oxidation converted into dicarboxylic acid and configuration of tetrose is determined by identification of di-carboxylic acids. Similarly the configuration of all sugars is determined by kiliani synthesis & oxidation.

① Aldotrioes:-



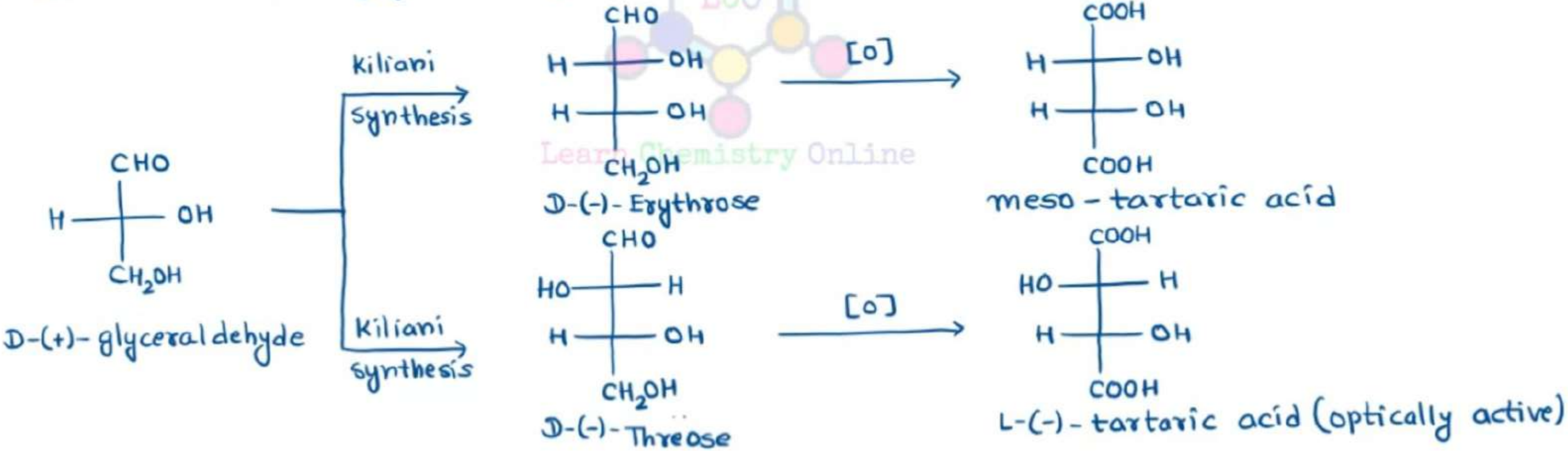
D- Glyceraldehyde



L - Glyceraldehyde

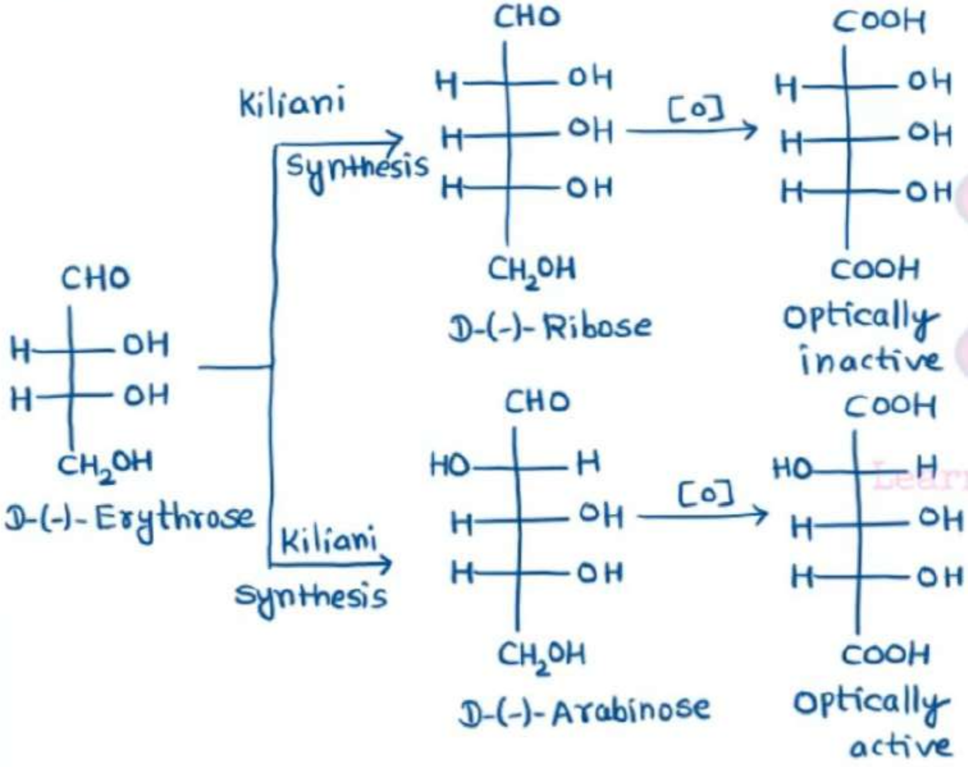
② Aldotetrose:- Because of the presence of two chiral carbon atoms, four optical isomers are possible (two pair of enentiomers), D- and L- threose and D- and L- erythrose.

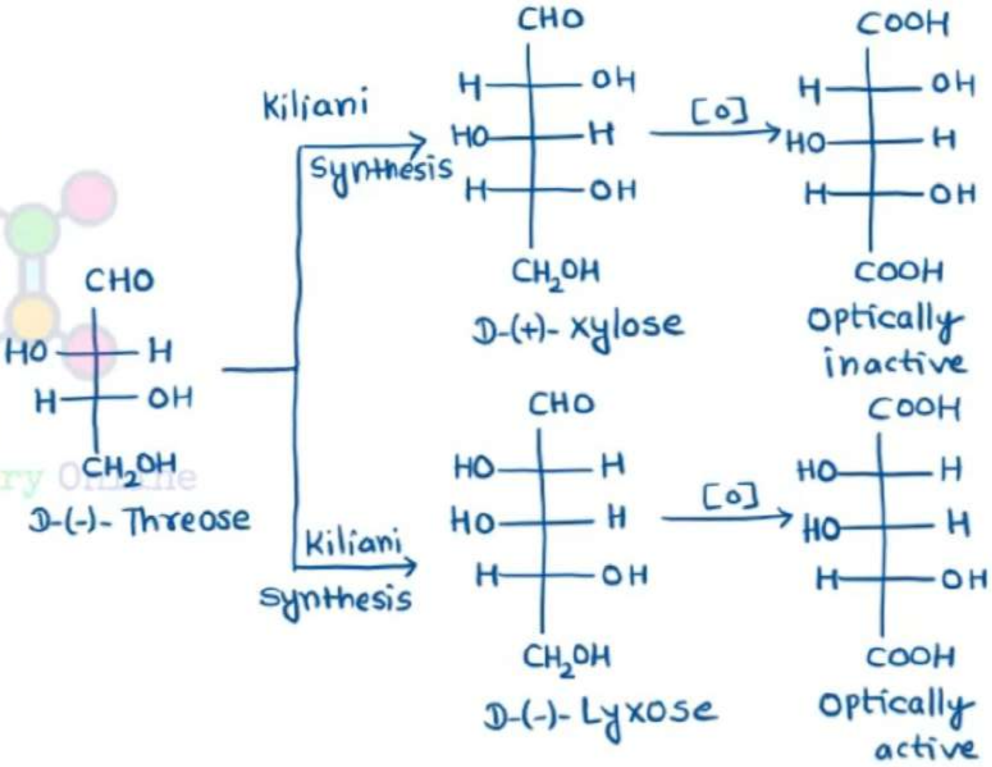
- The two D- tetrose can be obtained from kiliani synthesis of D-glceraldehyde while L-tetrose can be obtained from L- glyceraldehyde.



③ Aldopentose:→

- Because of presence of three chiral carbon atoms, eight optical isomers are possible (four pair of enatiomers), four belog to D-Series and four belong to L-series.
- Each pair differs only in configuration about C-2 can be identified upon oxidation, one giving optically active and optically inactive acid.

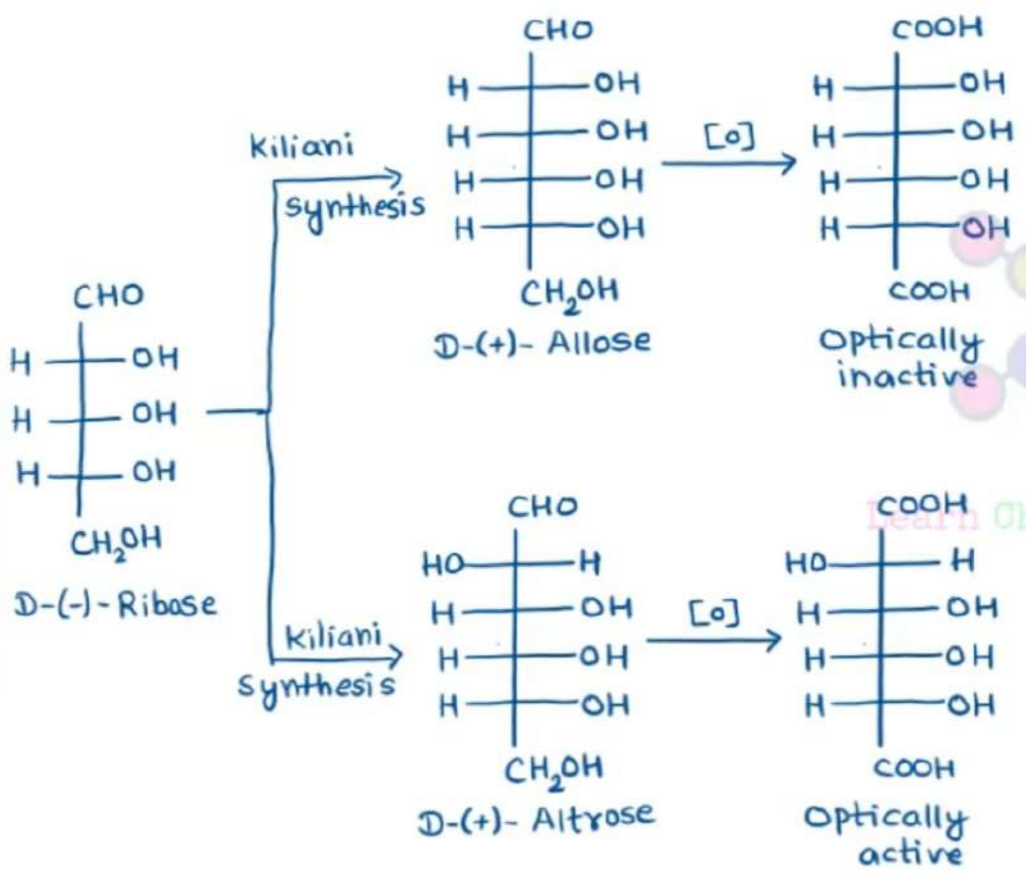


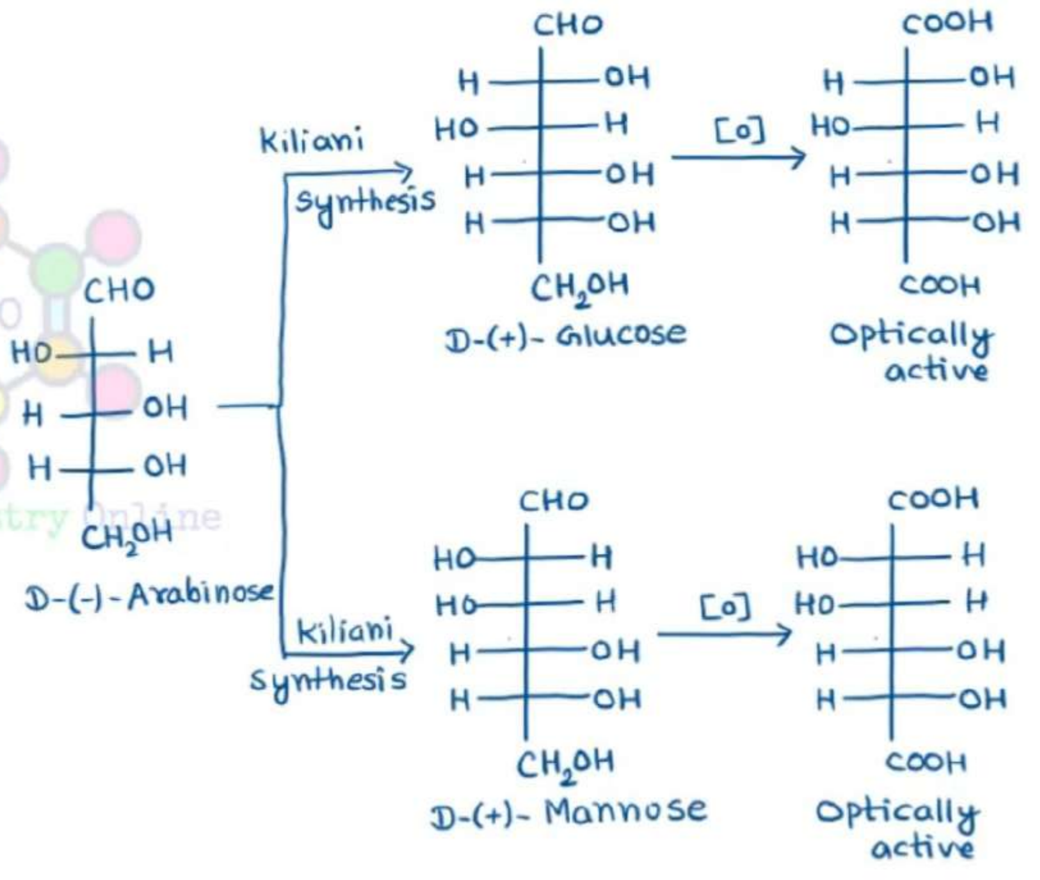


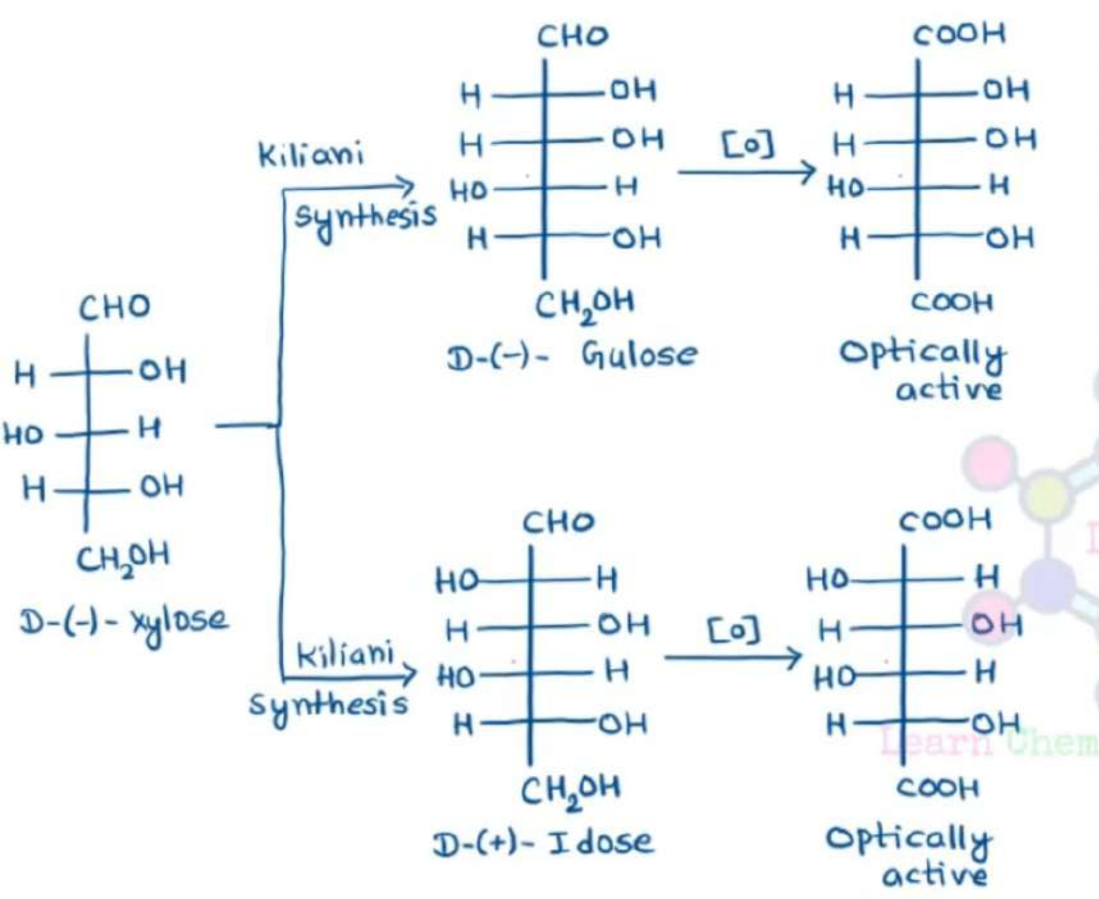
- Similary we can estabilised configuration of L-isomers

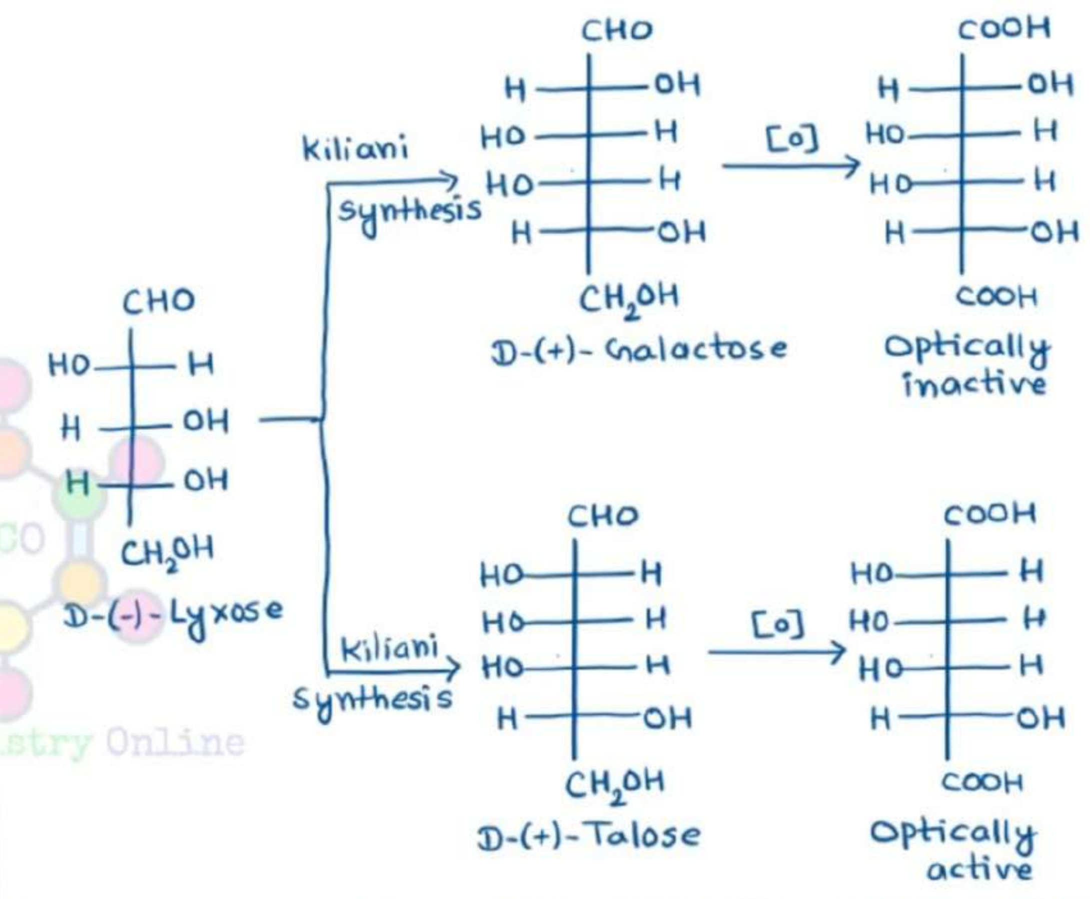
④ Aldohexose :-

- Because of the presence of four chiral carbons, sixteen optical isomers are possible (eight pairs of enantiomers), eight belong to D-series and eight belong to L-series.
- All aldohexose prepared from Kiliani synthesis of aldopentose.



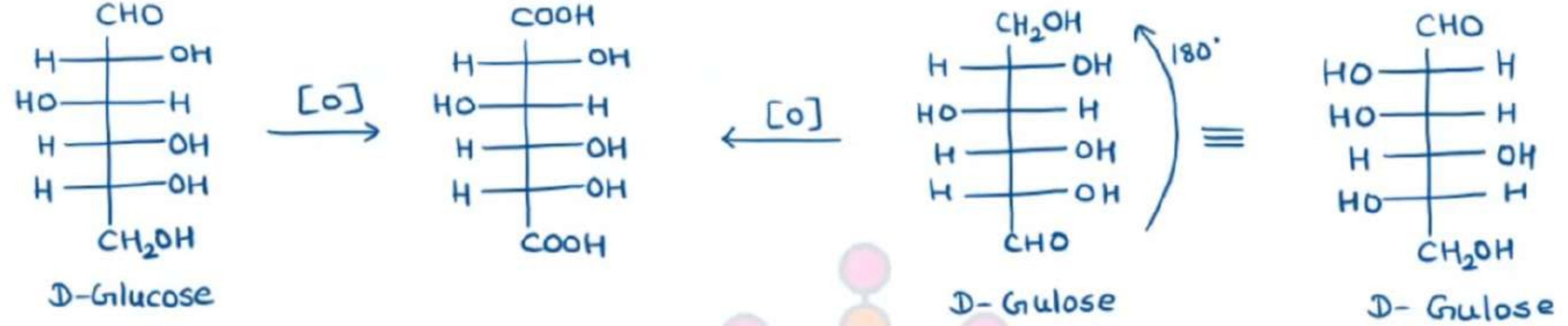




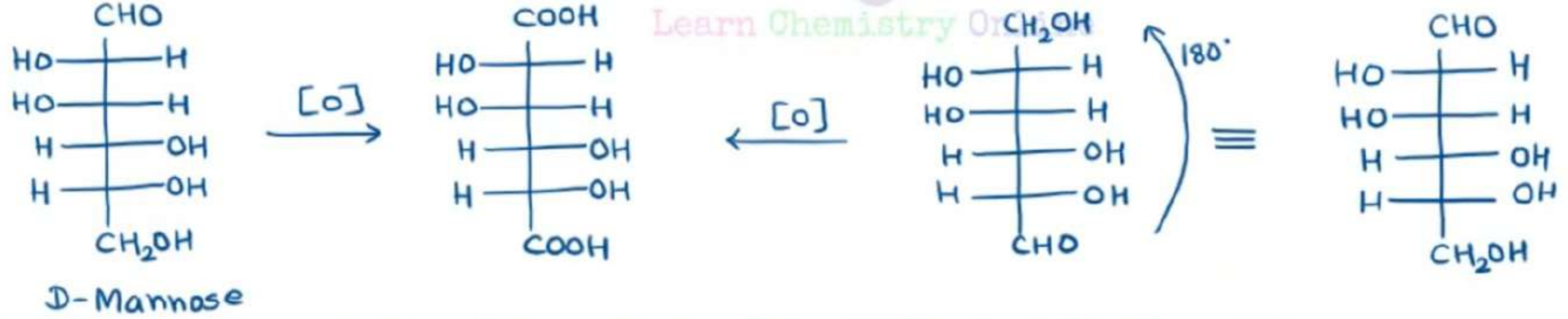


– since, oxidation of glucose and mannose, and of gulose and idose give optically active acids in each case, therefore these pairs cannot be differentiated by this procedure.

- Configuration of these sugars determined by Fisher by interchanging their ends.

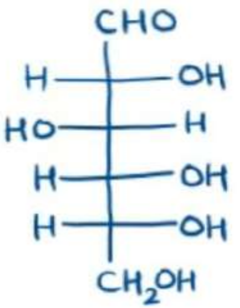


- Oxidation of D-Glucose gives a dicarboxylic acid which can be obtained from oxidation of D-Gulose
- Oxidation of D-Mannos gives a dicarboxylic acid which cannot be obtained from oxidation of any other aldohexose.

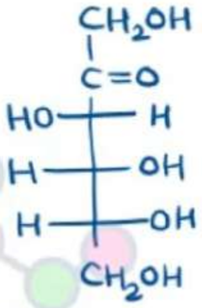


- D-(+)-Gulose is used to differentiate D-Glucose and D-Mannose.

- D-Fructose is a Ketohexose. Its configuration is estabilised by the fact that it gives the same osazone as obtained from D-glucose.
- Osazone formation involves only C-1 and C-2 and it can thus be concluded that the configuration at C-3, C-4 and C-5 of D-fructose is the same as in case of D-glucose



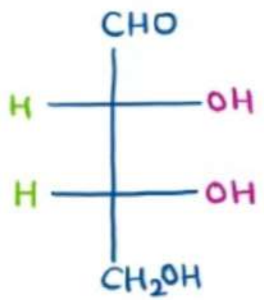
D- Glucose



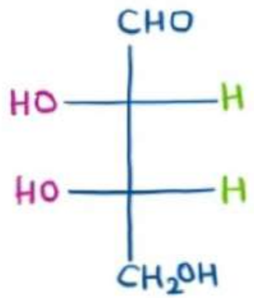
D-Fructose

→ ~~E~~rythro and Threo diastereomers:-

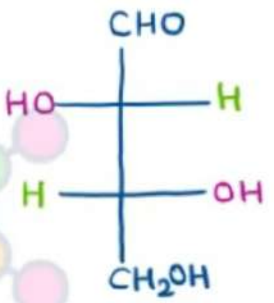
- Diasteromers are stereoisomers which have the same configuration at one chirality centre but different configuration at the other. In other words diastereomers are stereoisomers which are not mirror images of each other.
- Erythrose and Threose are four carbon containing sugars which have two dissimilar chiral carbon atoms.



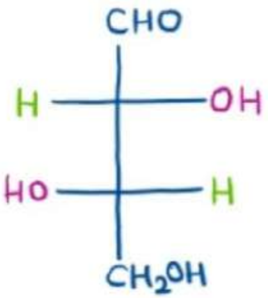
D-(−)-Erythrose
(I)



L-(+)-Erythrose
(II)



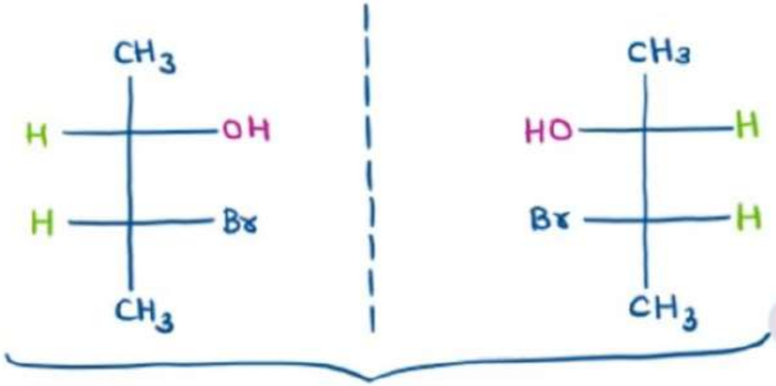
D-(−)-Threose
(III)



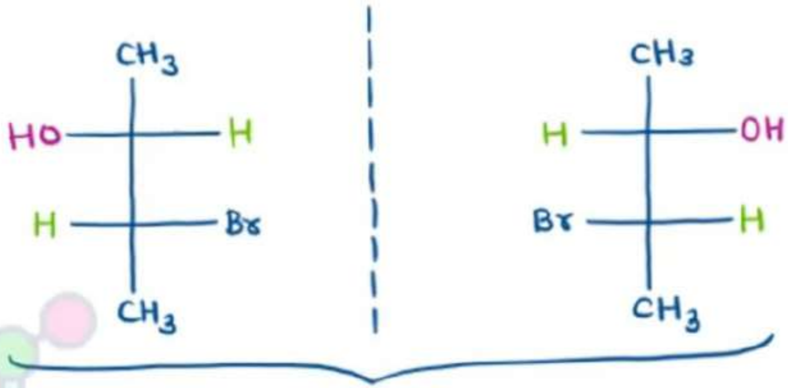
L-(+)-Threose
(IV)

- (I) and (II) , (III) and (IV) → Enatiomers
- (I) and (III), (I) and (IV), (II) and (III), (II) and (IV) → diasteromers.
- Diastereomers of compounds containing two dissimilar substitued chiral carbon atoms are distinguished from each other by using prefix erythro and threo.
- The erythro diasteromer is the one in which two like groups on the chiral atoms are on the same side in the Fischer projection formula as in erythrose.
- In contranst, threo diasteromer have two like groups on opposite side as in threose.

→ Example :-



Erythro- 3-bromo- 2-butanol



Threo - 3-bromo- 2-butanol