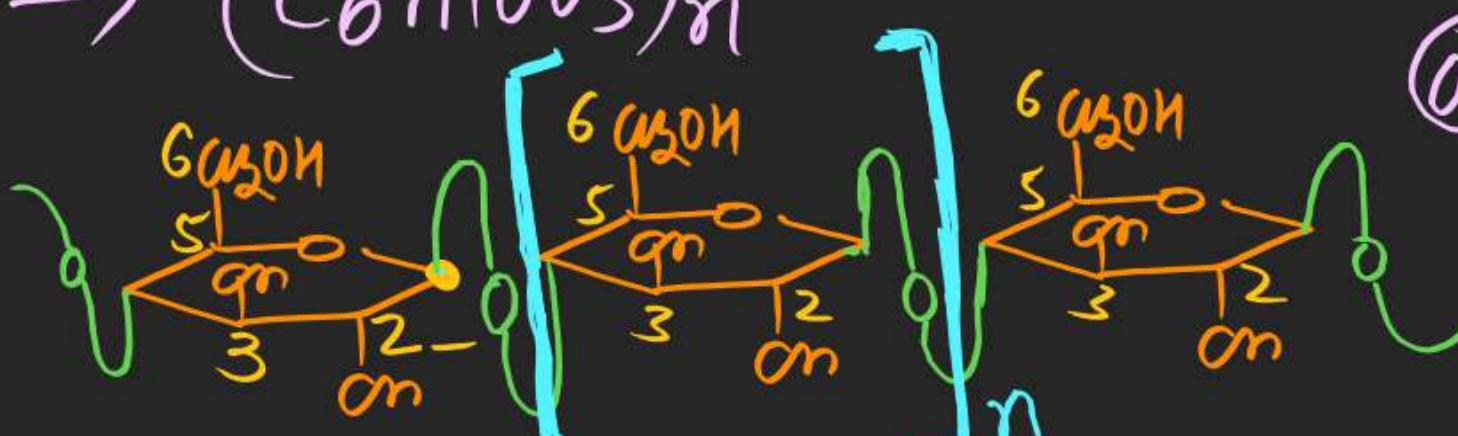
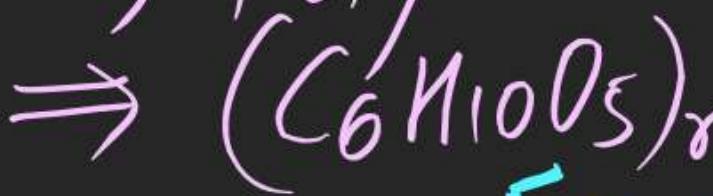


Polysaccharide:

(1) Cellulose:

⇒ Polymer of β -D-Glucopyranose



⇒ β -1,4-Glycosidic linkage

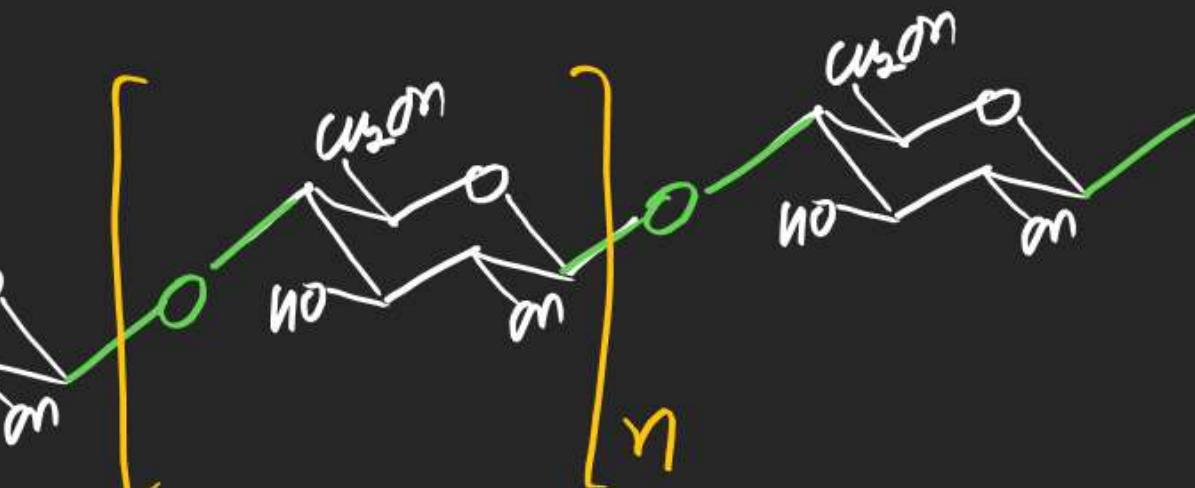
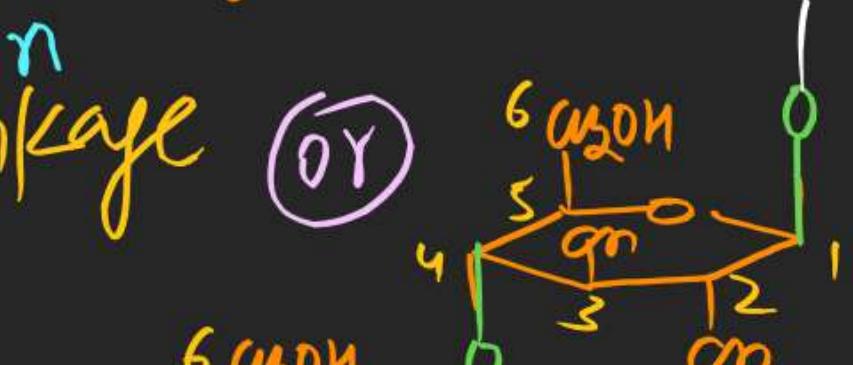
⇒ Non Reducing

⇒ No mutarotation

⇒ No Osazone formation

⇒ Insoluble in H_2O

⇒ Form β -Triakis(furan-2-yl) compound



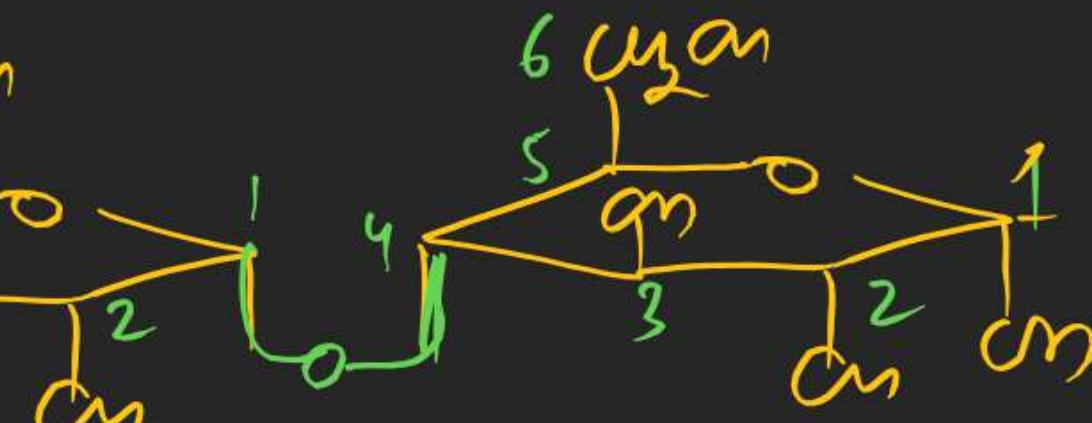
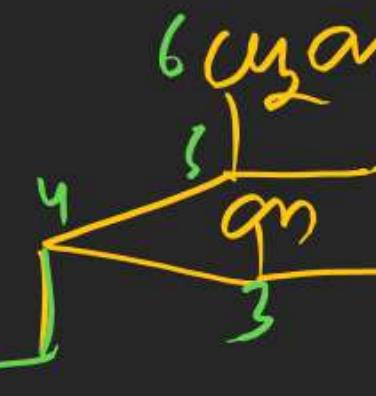
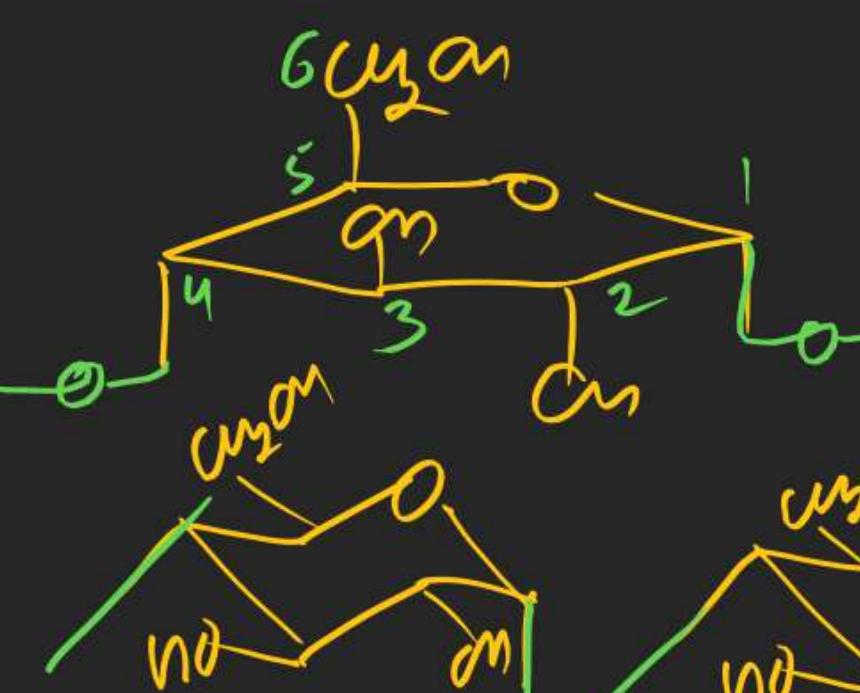
(2) Starch: \Rightarrow Polymer $\Rightarrow (C_6H_{10}O_5)_n$

Amylose is a Polymer of α -D-Glucopyranose
(10-20%) (water soluble)

Amylopectin is a Polymer of α -D-Glucopyranose
(80-90%) (water insoluble)

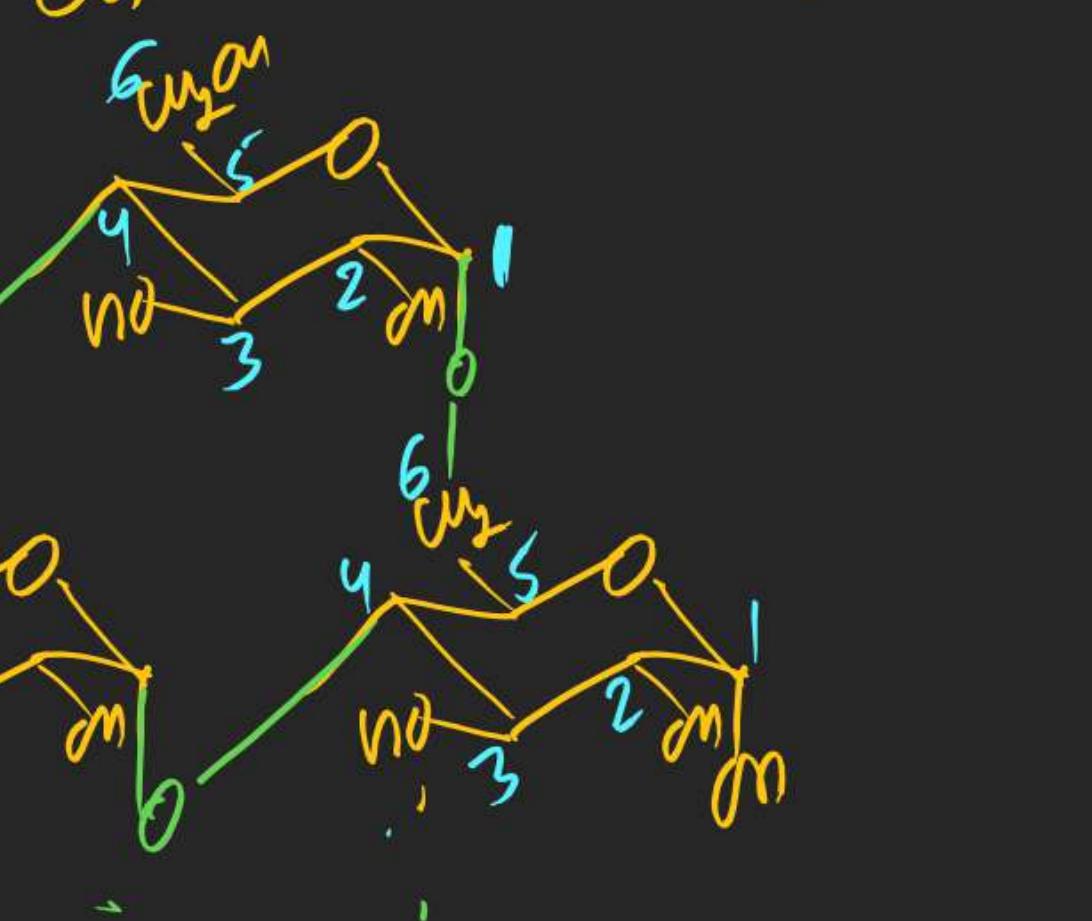
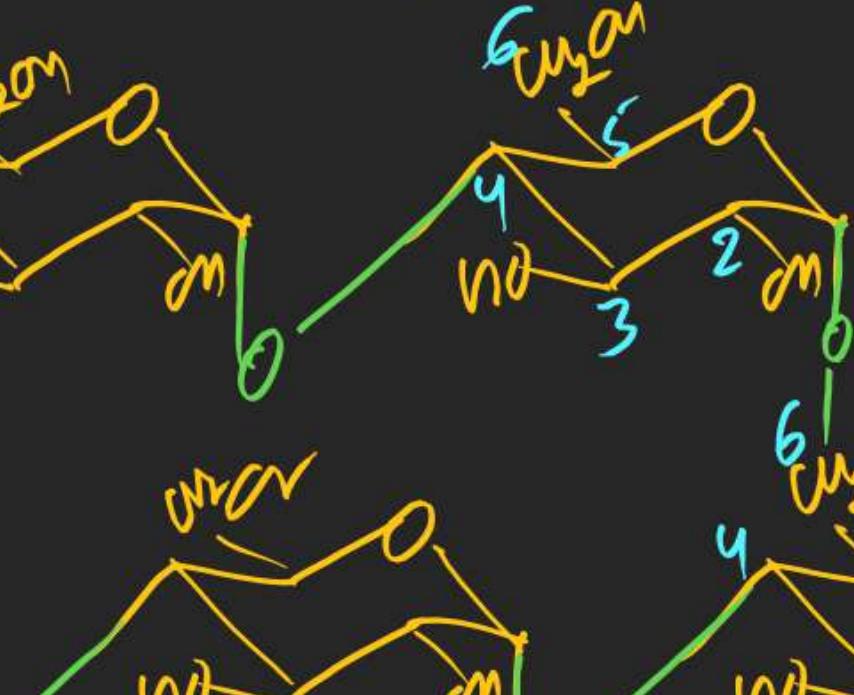
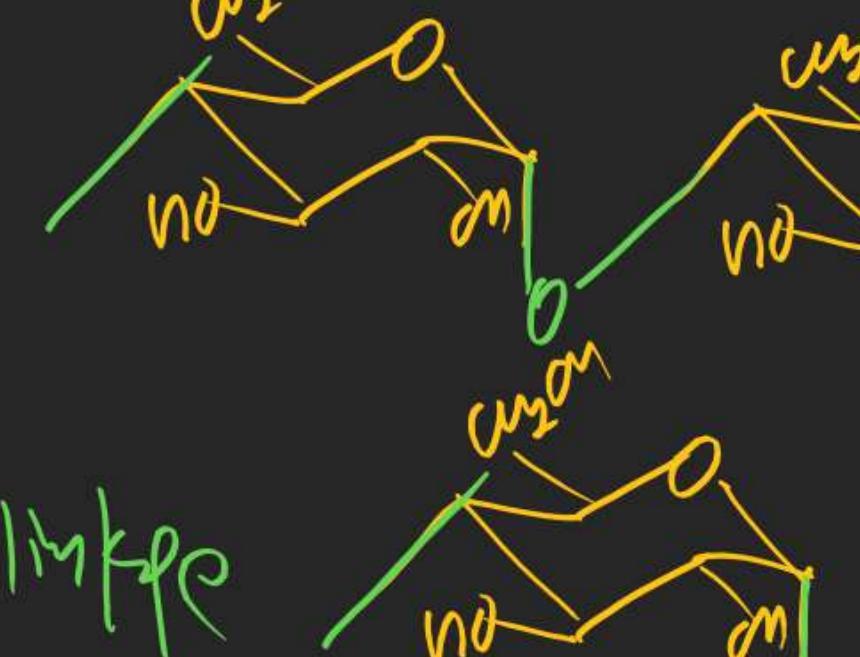
Amylose

α -1,4-Glycosidic
linkage

Amylopectin

α -1,4-Glycosidic linkage

1,6-Glycosidic linkage



- ⇒ Non Reducing
- ⇒ NO mutarotation
- ⇒ NO Osazone formation.
- ⇒ sparingly soluble in H₂O
- ⇒ Starch gives Blue colour with I₂-SO₄^M

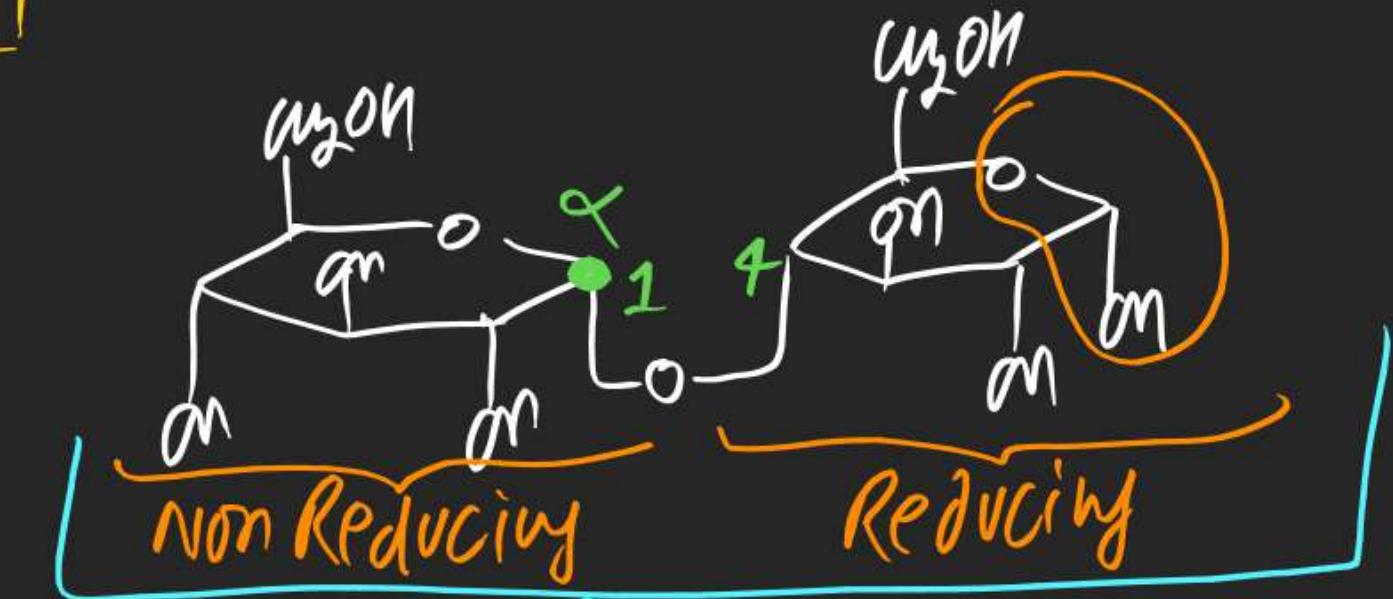
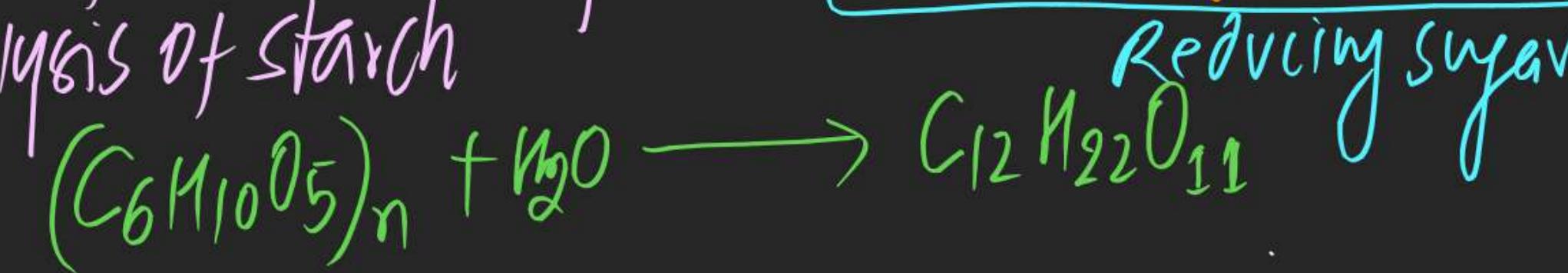
Disaccharides

(i) Maltose



⇒ Disachride of D-Glucopyranose

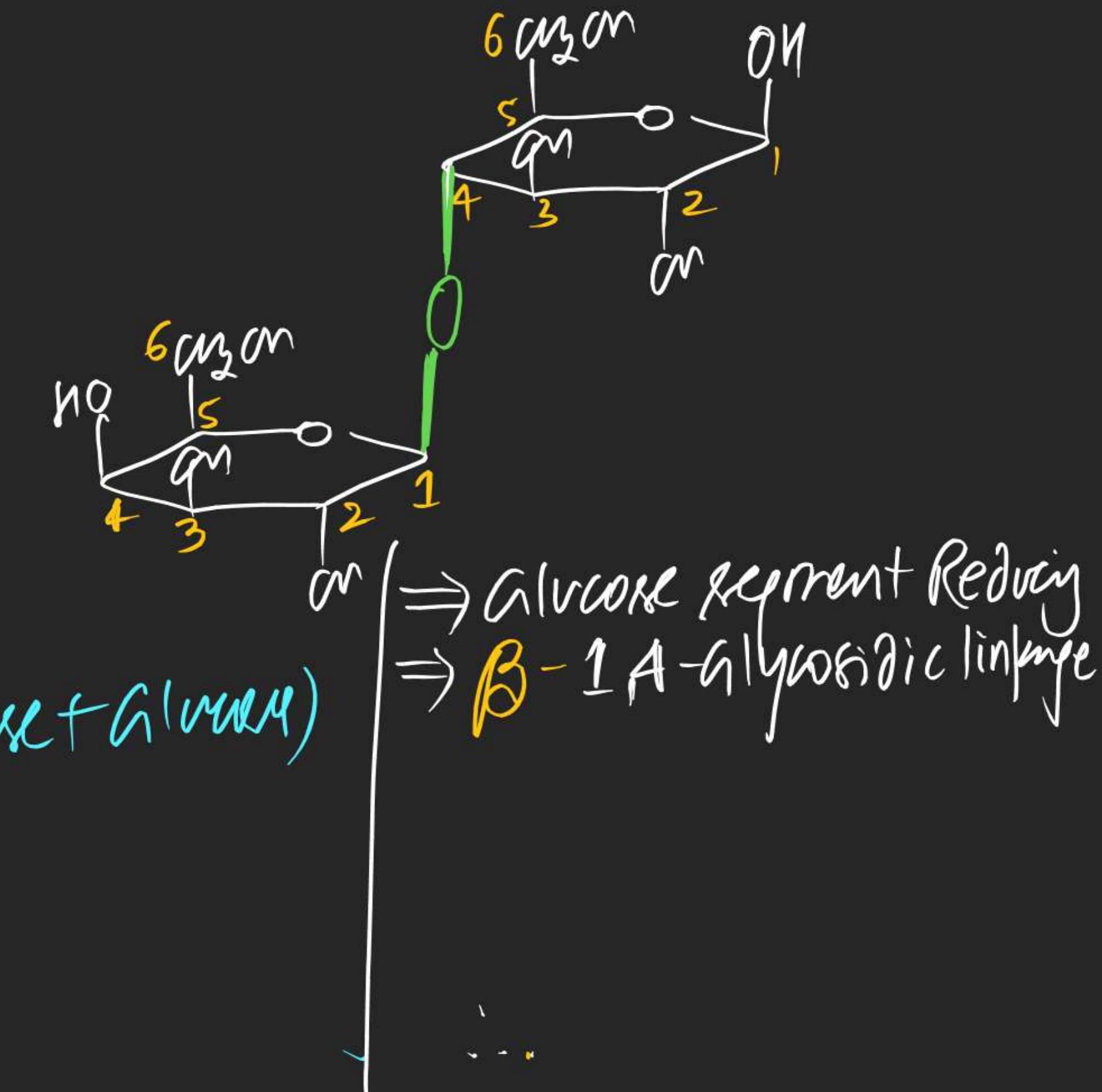
⇒ partial hydrolysis of starch



- ⇒ Reducing Sugar
- ⇒ Malt Sugar
- ⇒ Can show mutarotation
- ⇒ Can form osazone
- ⇒ $\alpha, 1, 4$ -Glycosidic linkage

(#) Lactose

- ⇒ MF $C_{12}H_{22}O_{11}$
- ⇒ Milk sugar
- ⇒ Disaccharides of (β -D-Galactose + Glucose)
- ⇒ Reducing Sugar
- ⇒ Can show mutarotation
- ⇒ Can form osazone



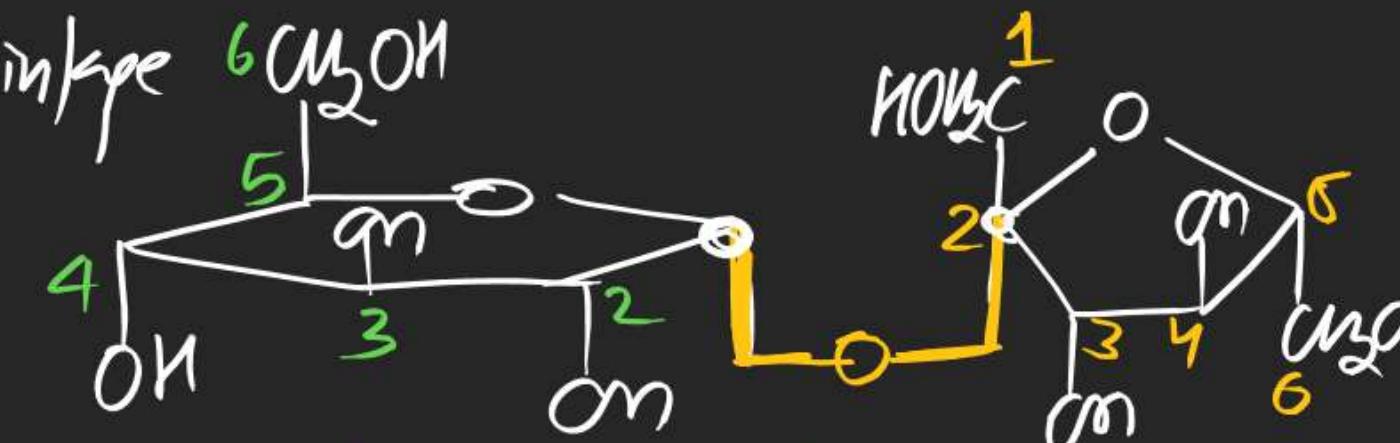
(#) Sucrose :- MMJW

⇒ MF $C_{12}H_{22}O_{11}(+)$
 ⇒ Disaccharide of α -D-Glucopyranose & β -D-(-)-Fructofuranose

⇒ α, β -1,2-Glycosidic linkage

⇒ Non Reducing Sugar

⇒ Cane Sugar



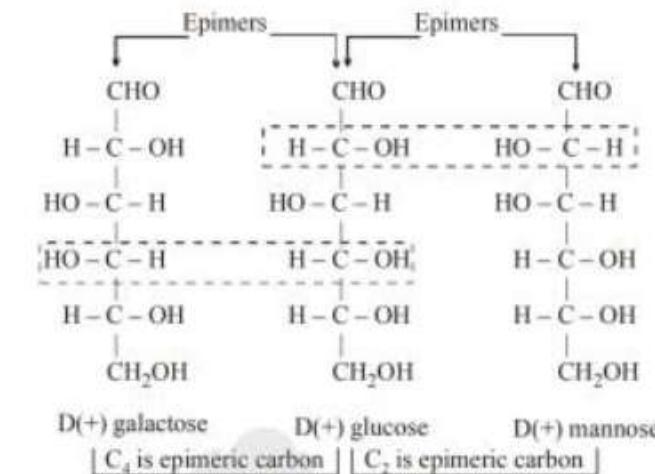
⇒ No Osazone formation (α -D-Glucopyranose) (β -D-Fructofuranose)

⇒ No mutarotation

$$\alpha_{D68} = +66.7^\circ$$

⇒ Sucrose + $H_2O \rightarrow$ [Glucose + Fructose] \Rightarrow Invert Sugar

$$\alpha_{D68} = 52.7^\circ \times \frac{1}{2} + (-92.7^\circ) \times \frac{1}{2} = -20^\circ$$

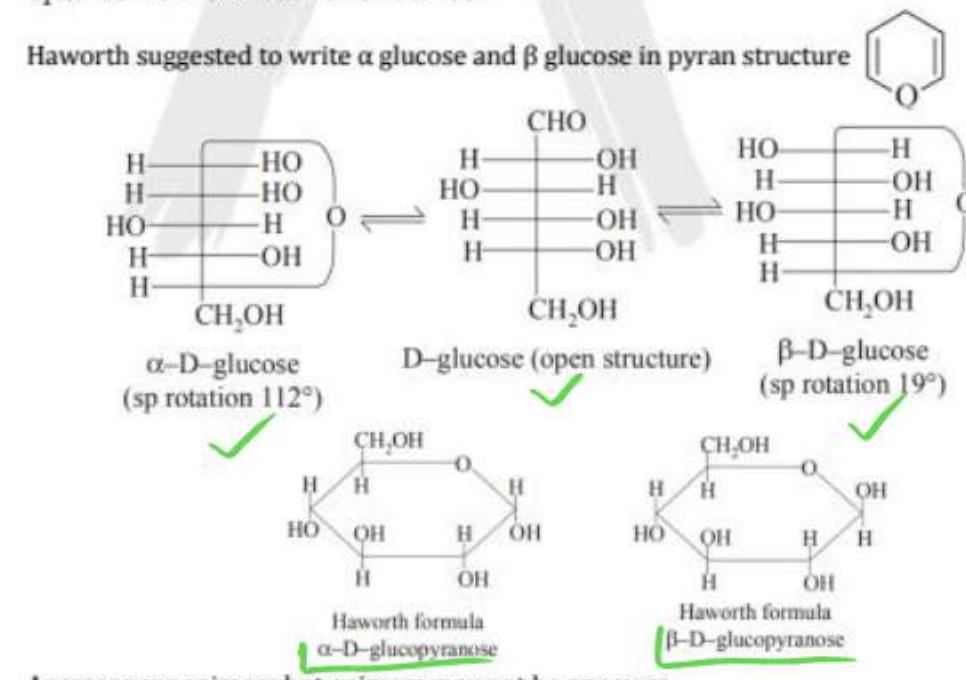


Another example with C₂ epimeric carbon is



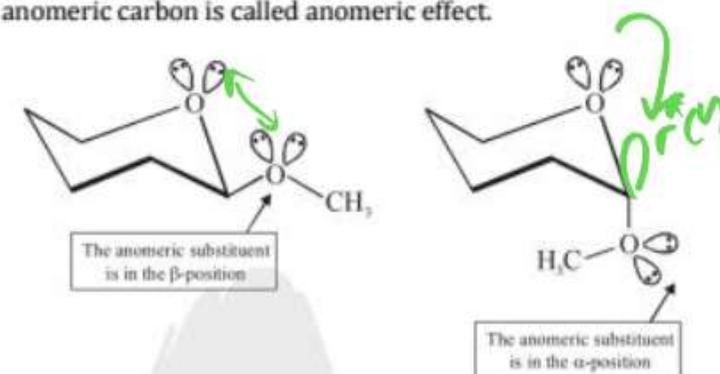
Anomers: Anomers are the stereoisomers which differs at a single chiral centre out of many & are ring chain tautomer of the same open chain compound.

The two sugars that differs in configuration only on the carbon that was the carbonyl carbon in the open chain form is called as anomers α glucose and β glucose are known as anomers their equilibrium mixture contains 36%α-D-glucose , 63.8%β-D-glucose and 0.2% open chain form.
C₁ Carbon is known as anomeric carbon.



Anomeric effect :

β -D-glucose is more stable than α -D glucose because there is more room for a substituent in the equatorial position. However when glucose reacts with an alcohol to form a glucoside, the major product is the α -glucoside. The preference for the axial position by certain substituents bonded to the anomeric carbon is called anomeric effect.



What is responsible for the anomeric effect? One clue is that all the substituents that prefer the axial position have lone pair electrons on the atom bonded to the ring. The lone pair electrons of the anomeric substituent have repulsive interaction with the lone pair electron of the ring oxygen if the anomeric substituent is the β -position, but not if it is the α -position.

Apparently attractive interaction of the hydrogen of the anomeric OH group of D-glucose with the lone pair electron of the ring oxygen decreases the importance of the anomeric effect making β -D glucose more stable than α -D glucose. However, when the hydrogen is replaced by an alkyl group, the anomeric effect decreases the stability of the β -position so, α -glycosides are more stable than β -glycosides.

Cyclic structures of monosaccharides

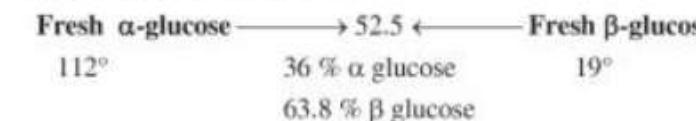
Many five membered and six membered monosaccharides occur in cyclic form. Cyclic structures of monosaccharides are established by many experiments. The cyclic structure is due to intramolecular hemiacetal formation between aldo / keto group and OH of any one carbon. The rings formed are generally six membered (pyranose) or five membered (furanose). Each cyclization results in creation of a new asymmetric centre apart from the existing ones. The isomers resulting from cyclizations are called anomers. Example, when D-glucose (open structure) cyclise, it gives α -D-glucose and β -D-glucose.

Haworth projection :-

Many of monosaccharides form cyclic structures. The actual structure is almost planar and be represented by Haworth projection, which is a way of depicting three-dimensional cyclic structure.

Rule -1 :- In a Haworth projection draw a fisher projection in which ring oxygen is in a down position.

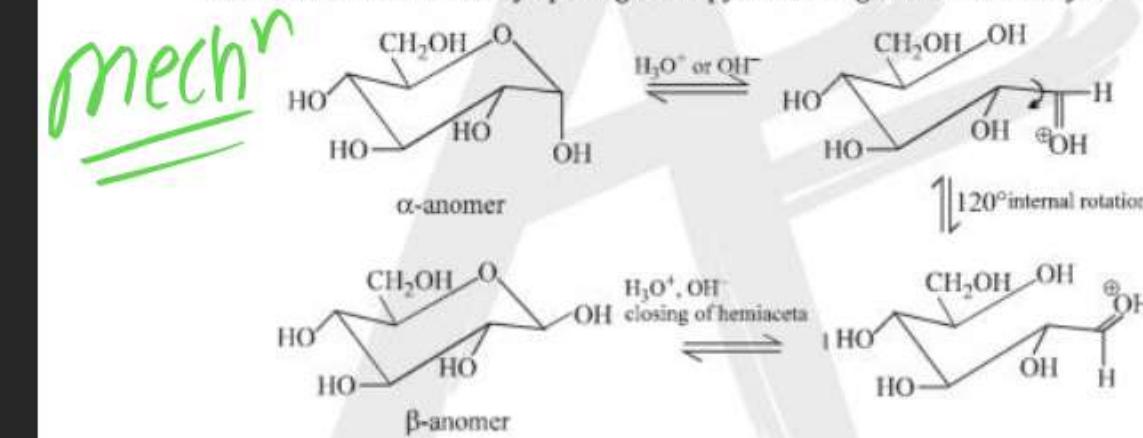
Rule -2 :- Imagine that carbon chain of fisher projection is folded around a barrel or drum, which provide a ring lies in a plane \perp to the page.

Specific rotation of α glucose +112°Equilibrium mixture $[\alpha]_D = 52.5 \text{ degree mL}^{-1}\text{dm}^{-1}$ 

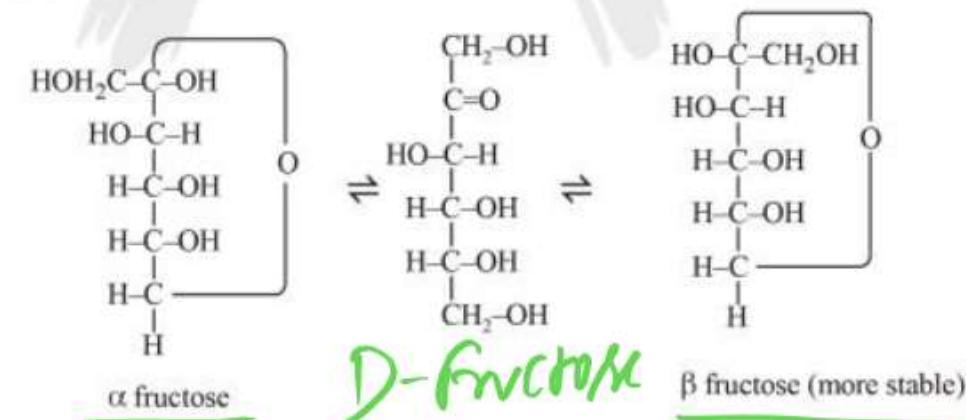
When pure α - D glucose is dissolved in water its specific rotation is found to be +112° with time, however the specific rotation of the solution decreases ultimately reaches stable value of +52.5°. When β D-glucose is dissolved in water, it has a specific rotation of 19°. The specific rotation of this solution increases with time also to +52.5°.

It is caused by the conversion of α and β glucopyranose anomers into an equilibrium mixture of both. Mutarotation is catalyzed by both acid and base, but also occurs in even in pure water. Mutarotation is characteristic of the cyclic hemiacetal form of glucose.

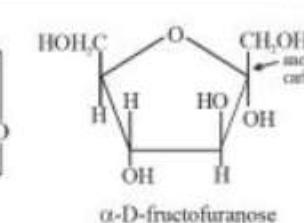
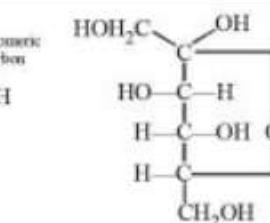
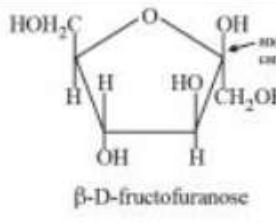
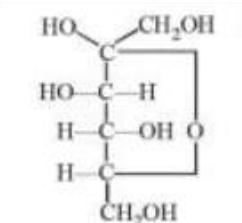
Mutarotation occurs first by opening of the pyranose ring to the free aldehyde form.



Structure of fructose



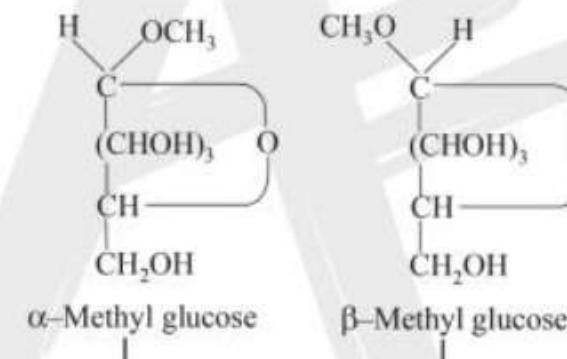
D-fructose



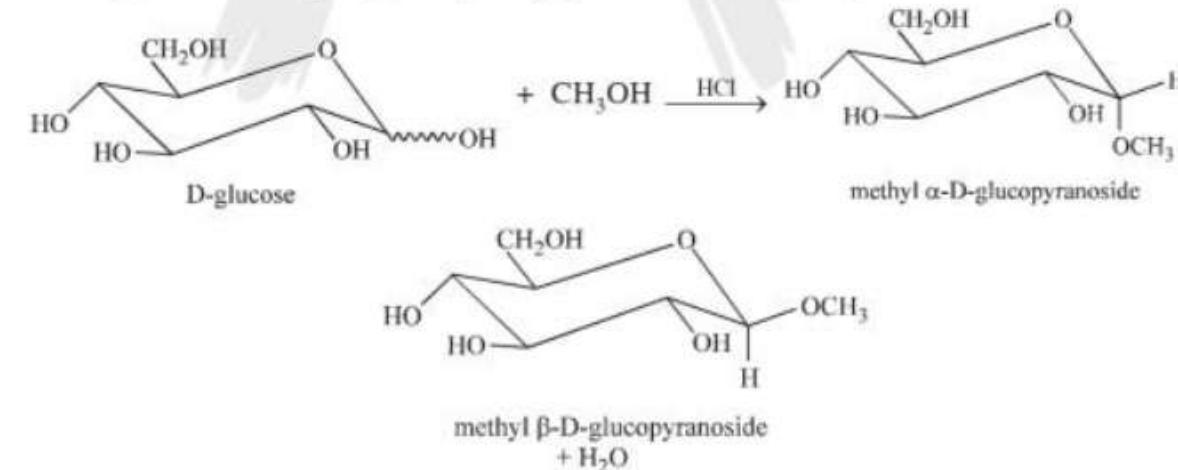
- All monosaccharides are reducing sugars and they show mutarotation.
- Starch, cellulose are Polymers of Glucose
- Lactose and sucrose are disaccharides
- Sucrose is a non reducing sugar, gives negative test for Benedict and tollen's reagent, they do not form osazone and do not show mutarotation.
- Acetals of carbohydrates are called as GLYCOSIDE

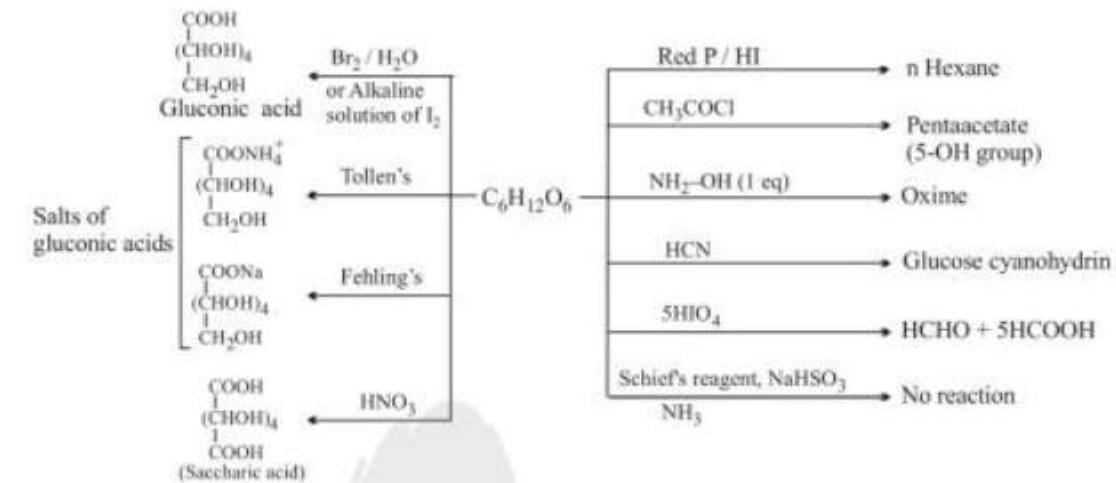
Formation of Glycosides

Glucose reacts with methyl alcohol in presence of dry HCl to form α and β -methyl glycoside of glucose. The reaction takes place only on OH of hemi-acetylic carbon. Other hydroxyl groups are unreactive.

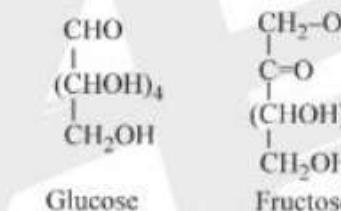
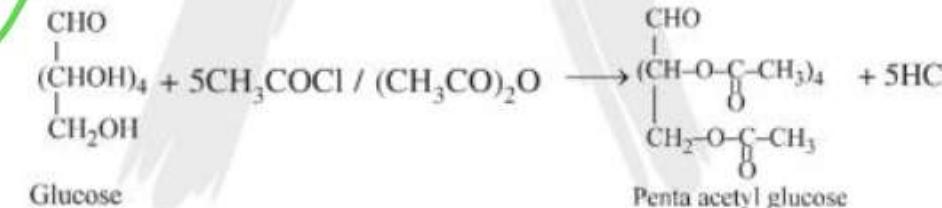


To methylate all the OH groups, methylating agent used is dimethyl sulphate.



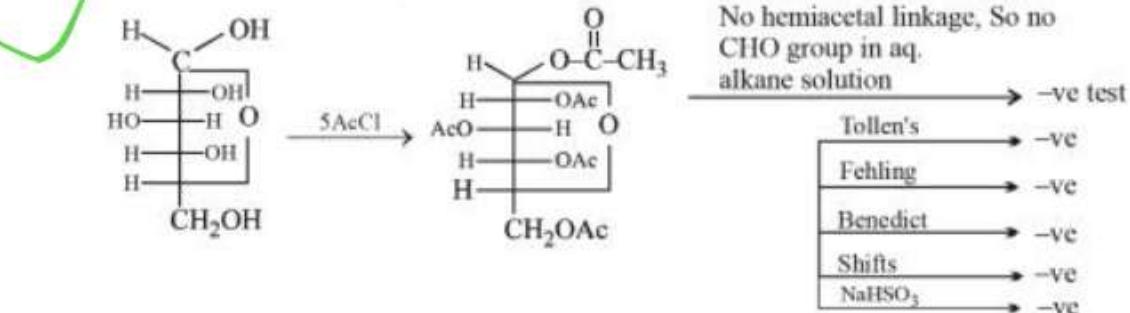
REACTIONS OF GLUCOSE

These reactions indicate that glucose has 6-C straight chain with one - CHO group & 5-OH group.

General reactions of monosaccharides1. Acetylation :

This reaction suggests presence of 5(OH) group.

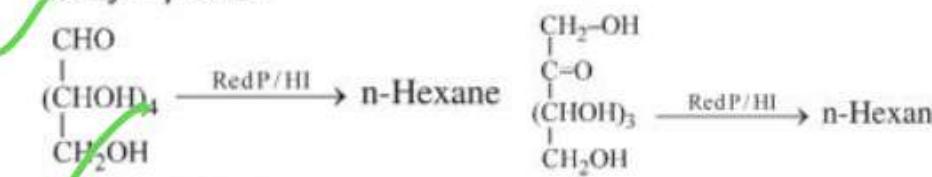
Q. The penta acetate of glucose give -ve test with Tollen's reagent & Fehling solution, explain?



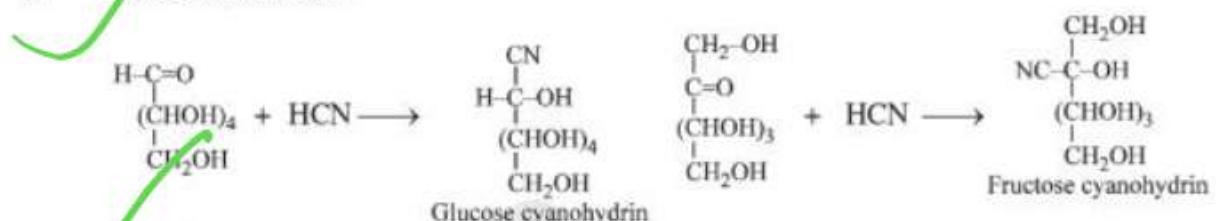
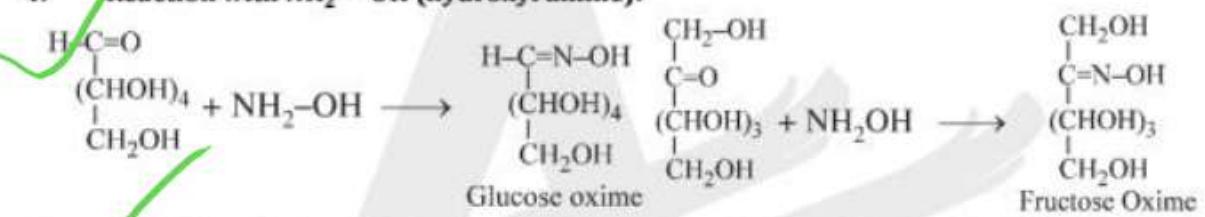
(Organic Chemistry)

BIOMOLECULES

2. Red by HI / Red P :

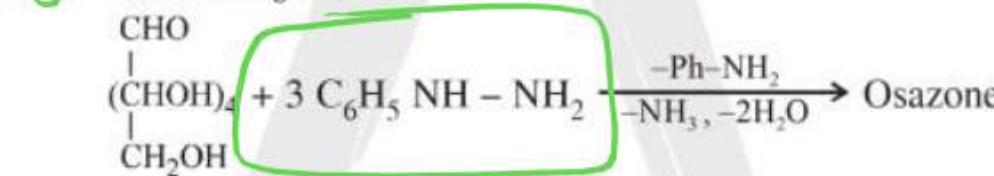


3. Reaction with HCN:

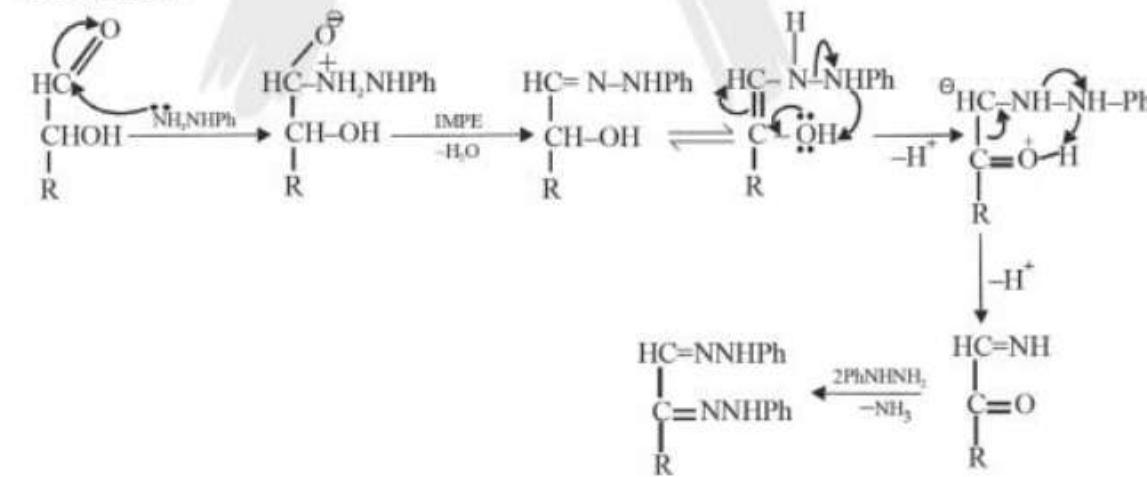
4. Reaction with NH₂ - OH (hydroxyl amine):

5. Reaction with phenyl hydrazine: Both glucose and fructose give "osazone". Reaction with glucose :

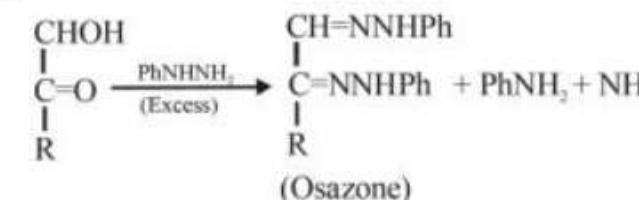
Reaction with glucose :



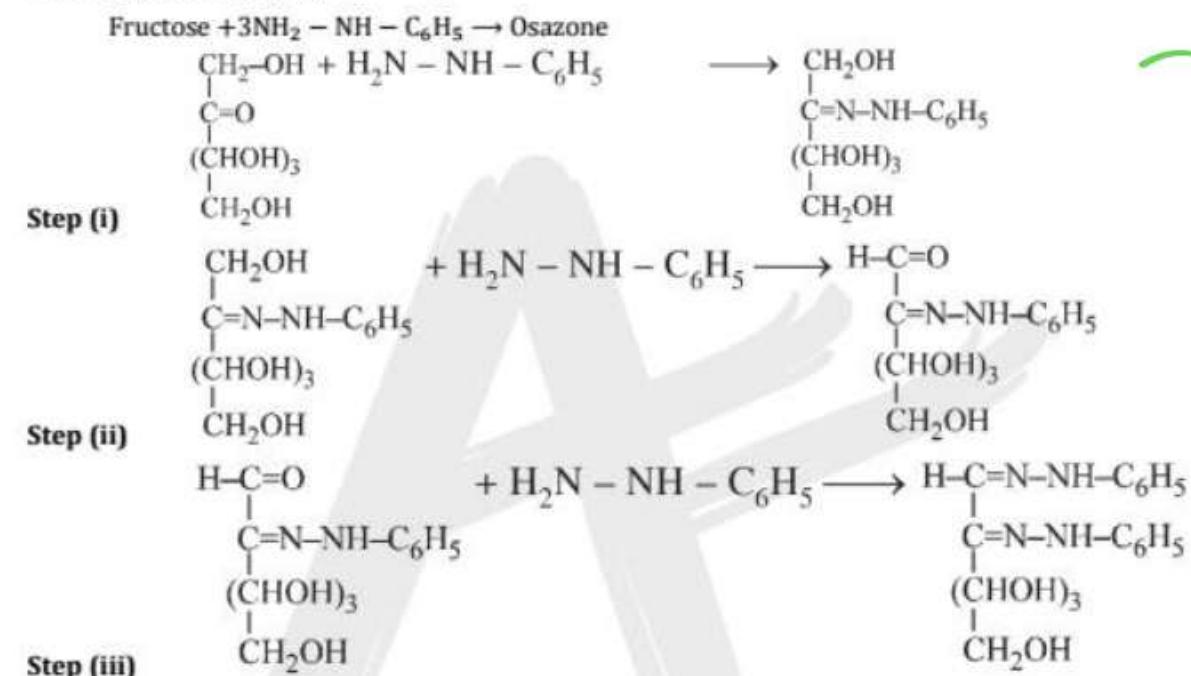
Mechanism :



Propose Mechanism for :



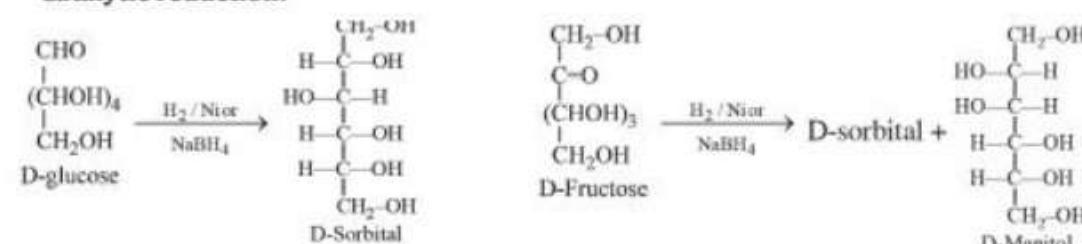
Reaction with fructose :



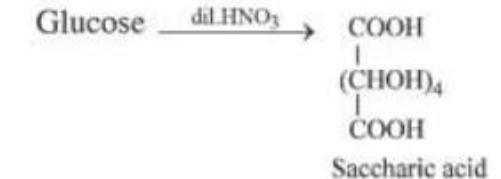
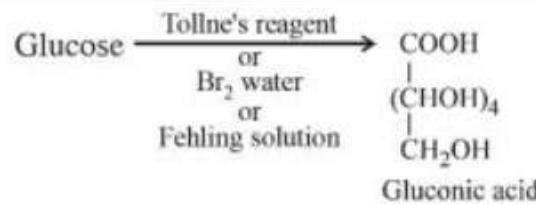
Glucose, Mannose & Fructose give same osazone because structure of last four carbons in these carbohydrates is same.

Only C-1 and C-2 in glucose and fructose are involved in osazone formation addition reaction do not run through out the chain. The failure to undergo further reaction has been explained by stabilization of the osazone by chelation.

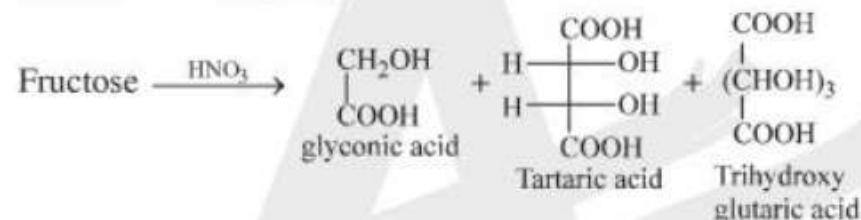
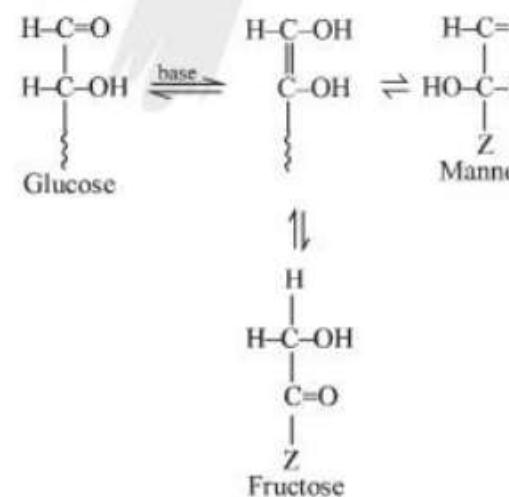
6. Catalytic reduction:



7. Oxidation:

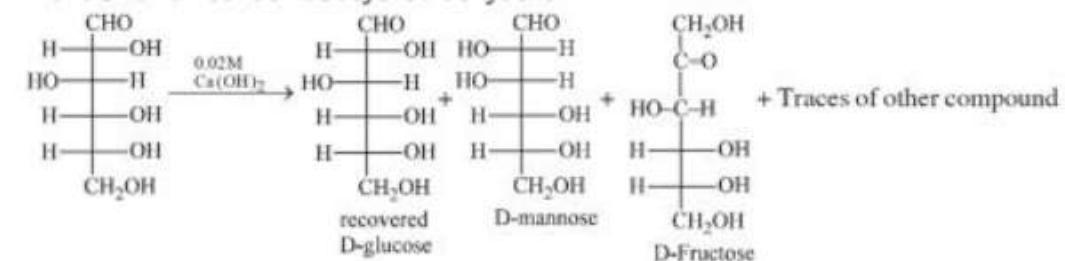
**Oxidation of fructose :**

Fructose also reduces tollen's & fehling reagent because in basic medium fructose isomerises to glucose.

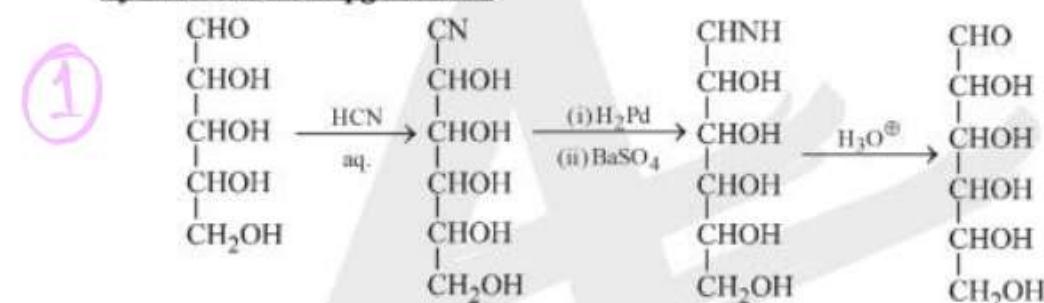
**8. Reaction with enzyme:****9. Reaction with dil NaOH / Ca(OH)₂****Mechanism :**

Base-catalyzed isomerisation of aldoses and Ketoses:

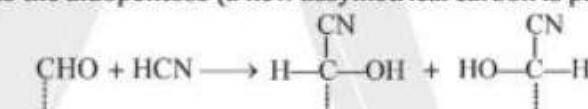
Although glucose in solution exists mostly in its cyclic hemiacetal forms it is also in equilibrium with a small amount of its acyclic aldehyde form.



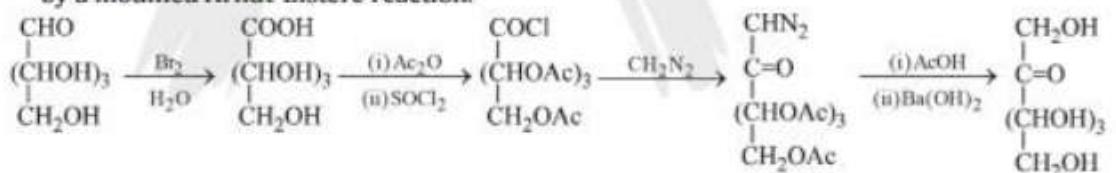
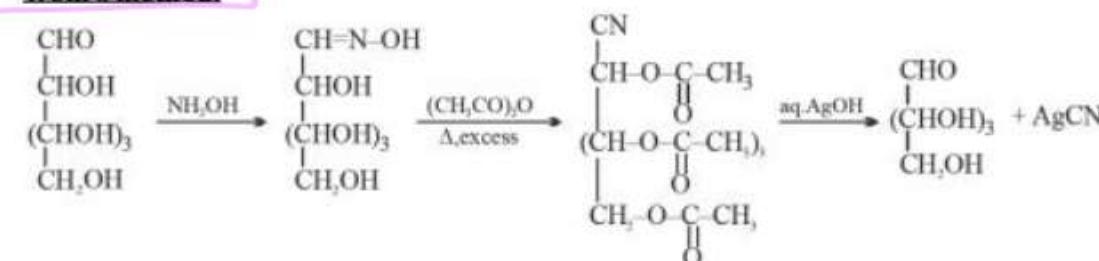
Method of ascending the sugar series: An aldose may be converted into its next higher aldose eg. an aldopentose into an aldohexose.

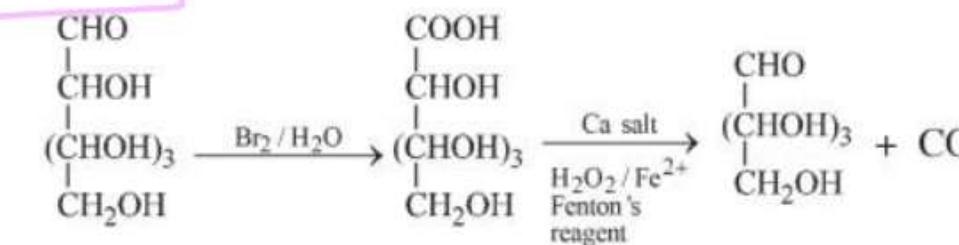
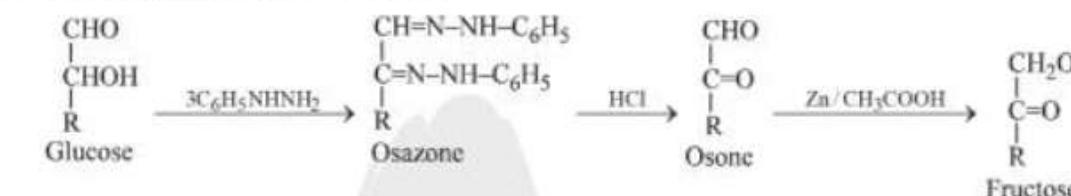
By Kiliani Fischer upgradation:

Theoretically two lactones are possible, since two cyanohydrin may be formed when hydrogen cyanide adds on to the aldopentose (a new assymetrical carbon is produced)

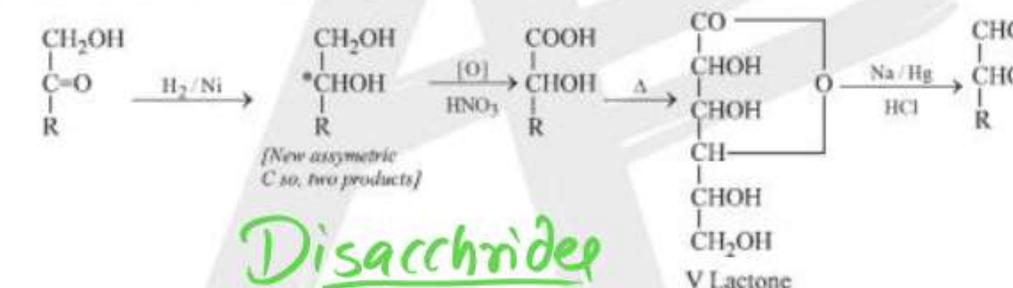


Wolfrom reaction: Wolfrom have stepped up an aldose to a ketose with one more carbon atom by a modified Arndt-Eistere reaction.

**Method of descending the sugar series:****Wohl's method:**

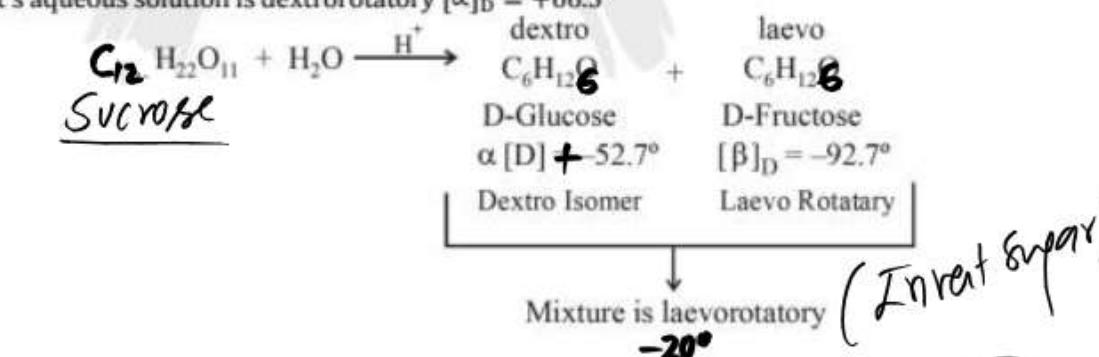
Ruff's method:Conversion of an aldose into a ketose :

An aldehyde group is reduced more readily than a ketonic group.

Conversion of a Ketose into an aldose :Disaccharides

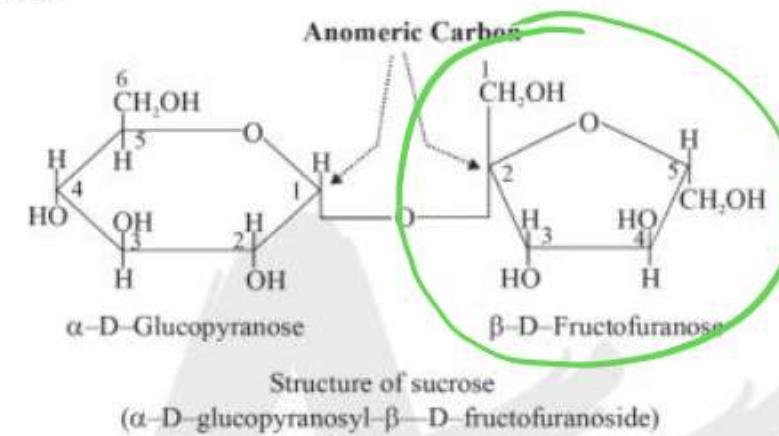
1 Sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$): → A dimer of α -D-Glucose & β -D-Fructose. It is white, crystalline & sweet substance soluble in water obtained from the sugar cane. When heated above its melting point. It forms a brown substance known as caramel.

It's aqueous solution is dextrorotatory $[\alpha]_D = +66.5^\circ$

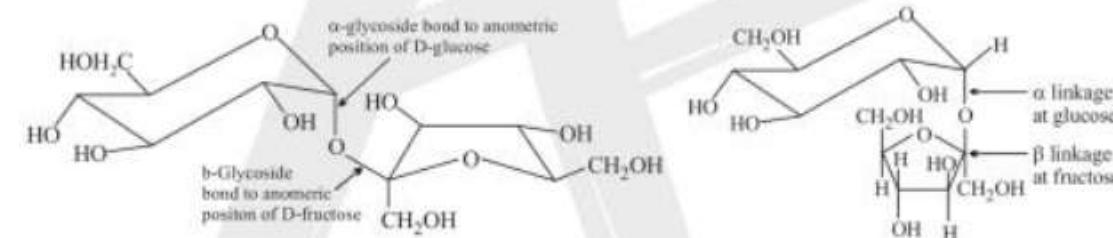


Thus hydrolysis of sucrose brings about a change in the sign of rotation, from dextro (+) to laevo (-) & such a change is known as inversion of sugar and the mixture obtained on acidic hydrolysis is known as invert sugar.

- The inversion of cane-sugar may also be done by the enzyme invertase which is found in yeast.
 - Sucrose is non-reducing sugar because it has stable acetal linkage & in aq. solution it does not give free carbonyl group and so it does not reduce Tollen's & Fehling's solution.
 - This indicates that neither the aldehyde group of glucose nor the ketonic group of fructose is free in sucrose.

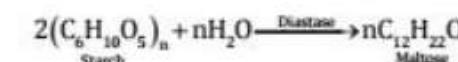


Do not show mutarotation



2. Maltose

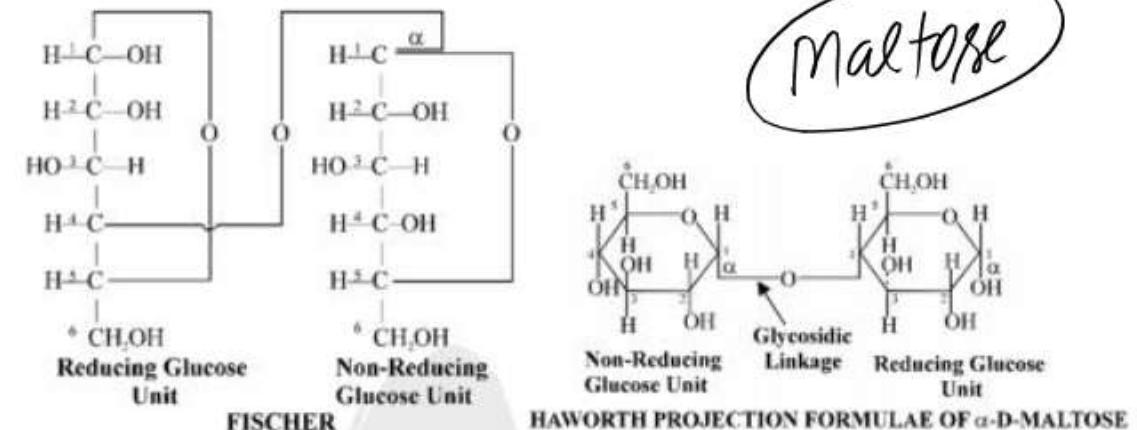
- It is dimer of α -D-Glucose
It is obtained by partial hydrolysis of starch by the enzyme diastase present in malt i.e., sprouted barely seeds.



- Hydrolysis of one mole of maltose yields two moles of D-glucose.
 - Maltose is a reducing sugar since it forms an osazone, undergoes mutarotation and also reduces Tollen's reagents and Fehling's solutions. Methylation studies have revealed that
 - (i) Both glucose units are present in the pyranose form.
 - (ii) C₆ of one glucose unit is linked to C₁ of the other

Further since maltose is hydrolysed by the enzyme maltase which specifically hydrolyses α -glycosidic linkage, therefore, the non-reducing glucose unit in maltose must be present in the

α -form. In other words, C₁ – α of non-reducing glucose unit is attached to C₄ of the reducing glucose unit as shown in the figure on next page.



3. Lactose (Milk sugar) C₁₂H₂₂O₁₁

Lactose occurs in milk and that is why it is called milk sugar.

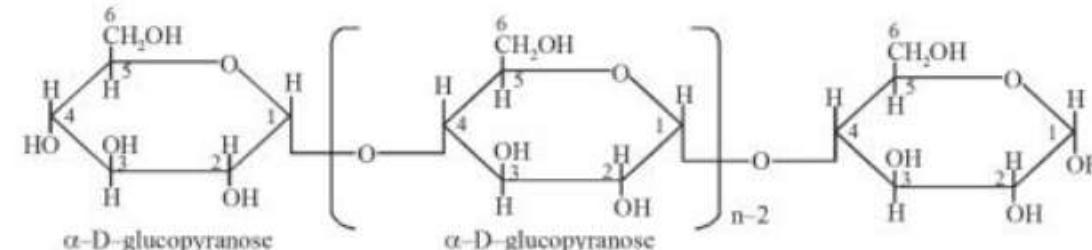
Lactose on hydrolysis with dilute acid or by enzyme lactase, yields an equimolar mixture of D-glucose and D-galactose. It is a reducing sugar it forms an osazone, undergoes mutarotation and also reduces Tollen's or Fehling's solution. Methylation studies have revealed that

- (i) both glucose and galactose are present in the pyranose form.
- (ii) glucose is the reducing half while β -galactose is the non-reducing half.
- (iii) C₁ of galactose unit is connected to C₄ of glucose unit.

4. Starch Amylum (C₆H₁₀O₅)_n

Occurrence : The value of n (100 – 3000) generally however it may varies from source to source. It is the chief food reserve material or storage polysaccharide of plants and is found mainly in seeds, roots tubers wheat, maize, rice, potatoes, barley, bananas and sorghum are the main sources of starch. Starch occurs in the form of granules, which vary in shape and size depending upon their plant source.

Occurs in all green plants. Starch consists of two fractions, one being known as (amylose), which gives blue colour with iodine. This blue colour is believed to be due to the formation of an inclusion complex. An aqueous solution of α - amylose slowly forms a precipitate, since α -amylose has a strong tendency to 'revert' to the insoluble state in solution. Amylopectin is insoluble in water and is stable towards both hydrolysis to maltose by the enzyme diastase and to D(+)-glucose by dilute acids (amylopectin gives about 50 percent of maltose).

Structure of Starch (α -D-glucoamylose)

α -amylose consists of an unbranched chain, with a molecular weight varying between 10,000($n \approx 60$) and 10,00,000($n \approx 6,000$). The value of n depends on the source and treatment of α -amylose.

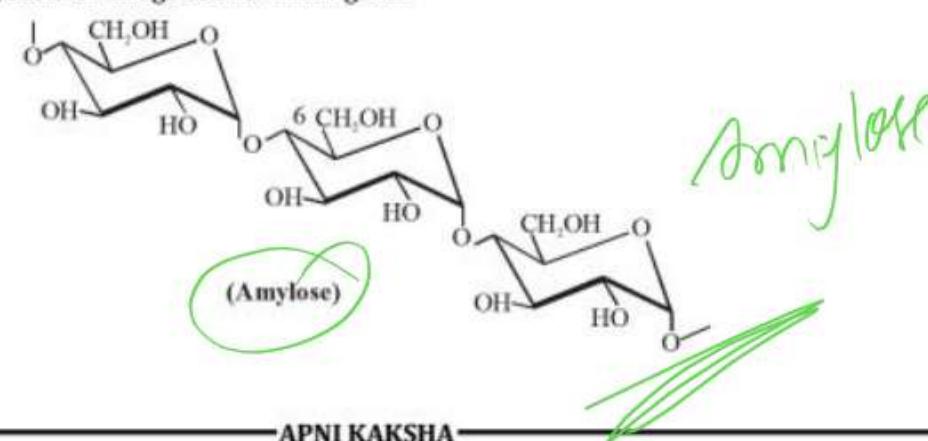
Properties : (i) Starch is a white amorphous powder sparingly soluble in water. Its aqueous solution gives a blue colour with iodine solution due to the formation of an inclusion complex. The blue pears on cooling. (ii) On hydrolysis with dilute mineral acids or enzymes, starch breaks down first to smaller molecules ($n > n'$), then to maltose and finally to D-glucose.

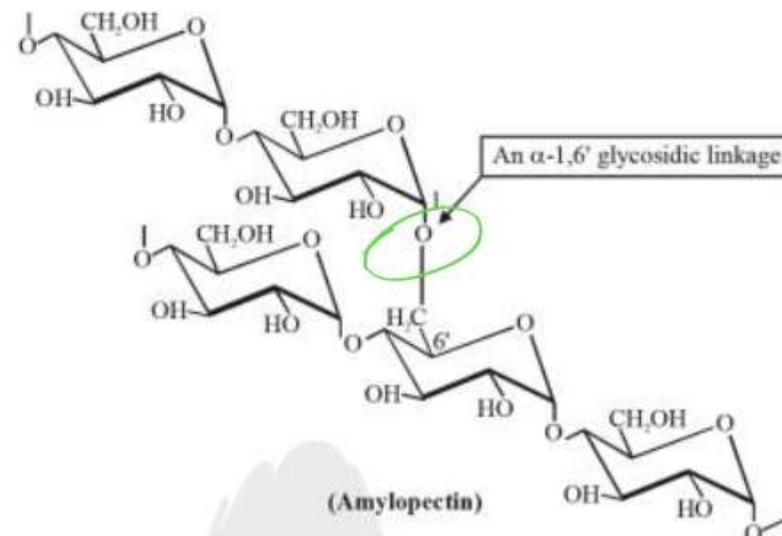


(iii) Starch is a non-reducing saccharide. It neither reduces Tollen's reagent or Fehling's solution nor forms an osazone. This suggests that all hemiacetal OH groups of glucose units at C_1 are not free but are involved in glycosidic linkages.

Composition : Starch is not a single compound but is a mixture of two components-a water soluble component called amylose (10-20%) and a water insoluble component called amylopectin (80-90%). Both amylose and amylopectin are polymers of α -D-glucose.

Structure of amylose : Amylose is water soluble and gives blue colour with iodine solution. It may have 100-3000 glucose units, i.e., its molecular mass can vary from 10,000 to 500,000. It is a linear polymer of α -D-glucose in which C_1 of one glucose unit is attached to C_4 of the other through α glycosidic linkage as shown in figure.



**Pectins**

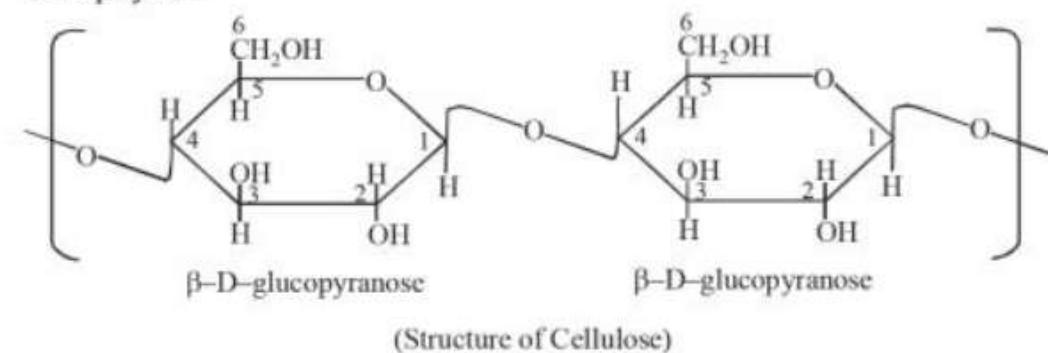
Pectins are found in plant and fruit juices. Their characteristic property is the ability of their solutions to gelate, i.e. form jellies. They have a high molecular weight and are polygalacturonic acid (linked 1,4) with the carboxyl groups partially esterified with methanol.

Glycogen ($C_6H_{10}O_5)_n$:

Glycogen is found in nearly all animal cells, occurring mainly in liver. It is the reserve carbohydrate of animals and so is often known as 'animal starch'. It has also been isolated from plant sources. Glycogen is a white powder, soluble in water, the solution giving a purplish-red colour with iodine. On hydrolysis with dilute acid, glycogen gives D(+)-glucose. The molecular weight of glycogen has been given as 10,00,000 to 50,00,000 and glycogen contains highly branched chains. Glycogen has a structure similar to amylopectin, except that it has more cross-linking.

5. Cellulose:

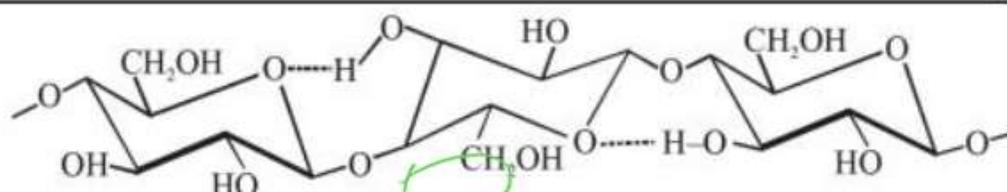
Cellulose is colourless, solid which is insoluble in water & organic solvents. But it is soluble in ammonical cupric hydroxide (Schweizer's reagent) or in conc. HCl cellulose is a regular polymer of d-glucopyranose residues connected by β - 1,4 glycosidic linkages. It is straight chain polymer.



✓
AK

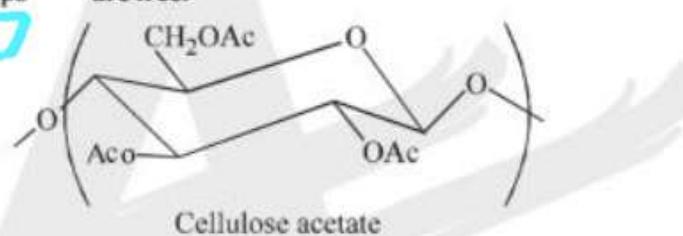
(Organic Chemistry)

BIOMOLECULES



Some points about cellulose :

1. General empirical formula ($C_{6}H_{10}O_5$)
2. Cellulose $+ H_2O \xrightarrow{H^+}$ 96% of crystalline D-glucose
3. No. of monomer units in cellulose are 1000 – 1500 in one molecule.
4. Cellulose doesn't show mutarotation (like starch)
5. It is non reducing sugar because there is no hemiacetal linkage.
6. Acetylation, nitration & methylation of cellulose give trisubstituted cellulose which suggest that only three - OH groups are free.

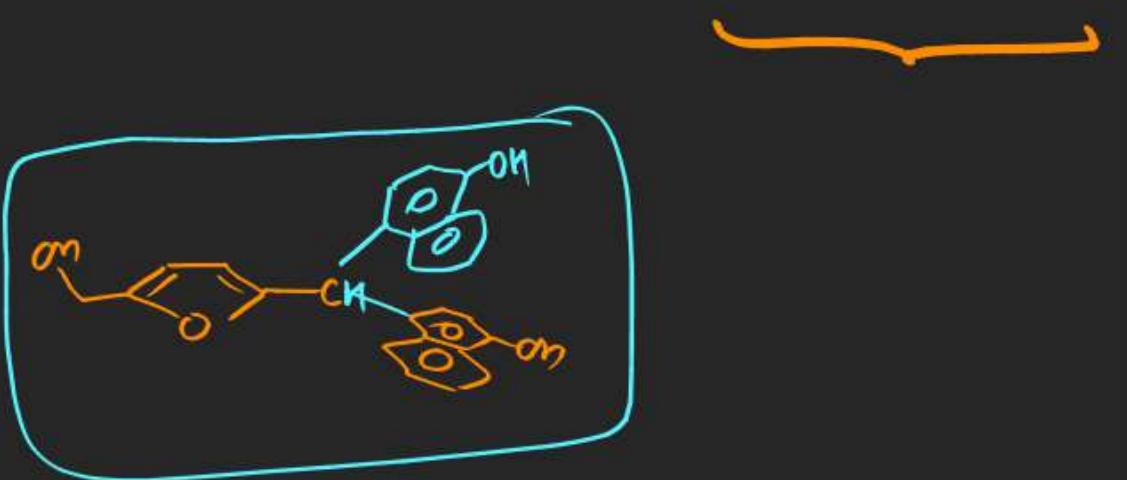


Tests for carbohydrates:

- (i) When heated in a dry test tube, it melts, turns brown and finally black, giving a characteristic smell of burning sugar.
- (ii) When warmed with a little concentrated H_2SO_4 , it leaves a charred residue of carbon.
- (iii) Molisch's Test (named after Austrian botanist Hans Molisch) is a sensitive chemical test for the presence of carbohydrates, based on the dehydration of the carbohydrate by sulfuric acid to produce an aldehyde, which condenses with two molecules of phenol (usually α -naphthol, though other phenols (e.g. resorcinol, thymol) also give colored products) resulting in a red- or purple-colored compound. The test solution is combined with a small amount of Molisch's reagent (α -naphthol dissolved in ethanol) in a test tube. After mixing, a small amount of concentrated sulfuric acid is slowly added down the sides of the sloping test-tube, without mixing, to form a bottom layer. A positive reaction is indicated by appearance of a purple ring at the interface between the acid and test layers.

All carbohydrates - monosaccharides, disaccharides, and polysaccharides — should give a positive reaction, and nucleic acids and glycoproteins also give a positive reaction, as all these

Sample →



Nucleic Acid (RNA)

Ribose

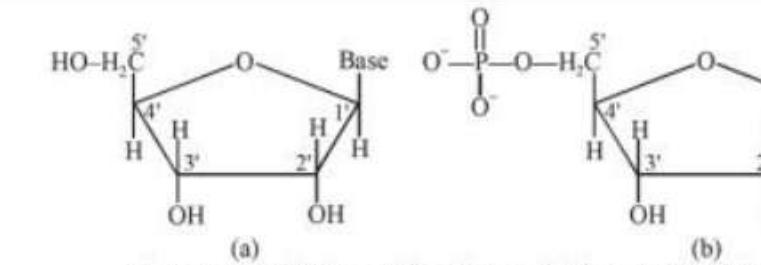
phospho ester Sugar Base

Nucleo Side on an $O=P-O-CH_3$ group

Nucleo Side on an $O=P-O-CH_3$ group

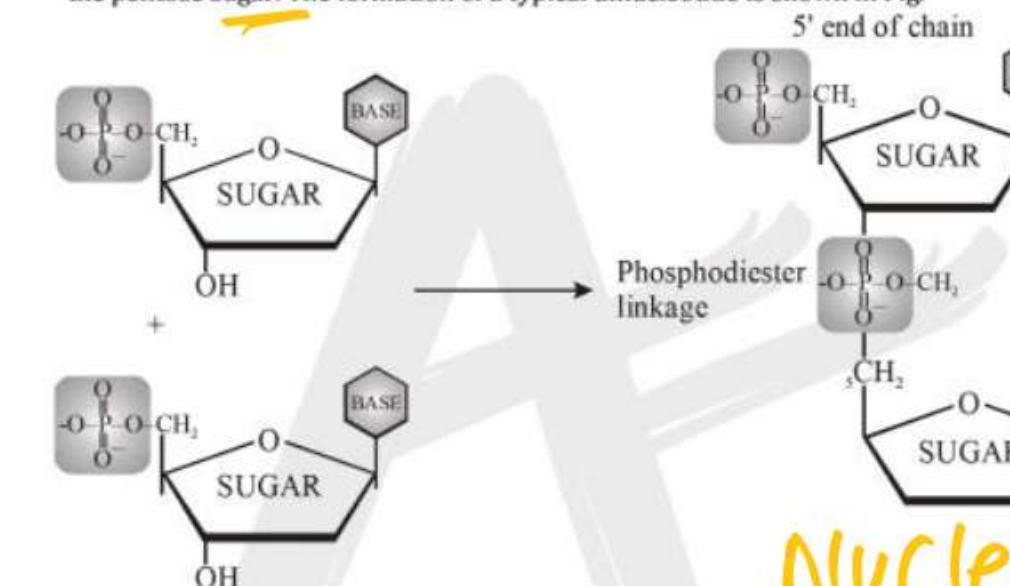
Nucleotide

Polymer Nucleic Acid



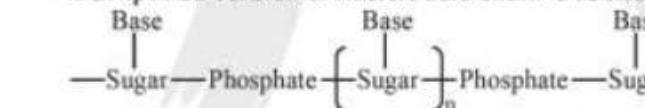
Structure of (a) a nucleoside and (b) a nucleo-

Nucleotides are joined together by phosphodiester linkage between 5' and 3' carbon atoms of the pentose sugar. The formation of a typical dinucleotide is shown in Fig.



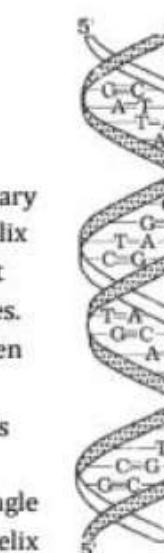
Formation of dinucleotides

A simplified version of nucleic acid chain is as shown below:



Information regarding the sequence of nucleotides in the chain of a nucleic acid is called its primary structure. Nucleic acids have a secondary structure also. James Watson and Francis Crick gave a double helix structure for DNA (Fig. 14.7). Two nucleic acid chains are wound about each other and held together by hydrogen bonds between pairs of bases. The two strands are complementary to each other because the hydrogen bonds are formed between specific pairs of bases. Adenine forms hydrogen bonds with thymine whereas cytosine forms hydrogen bonds with guanine.

In secondary structure of RNA, helices are present which are only single stranded. Sometimes they fold back on themselves to form a double helix.



(DNA)
De-oxyribonucleic acid

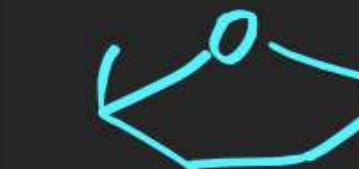
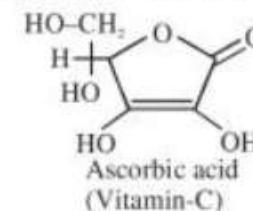


Table : Some important Vitamins, their Sources and their Deficiency Diseases

S. NO.	Name of Vitamins	Sources	Deficiency diseases
1.	Vitamin A	Fish liver oil, carrots, butter and milk	Xerophthalmia (hardening of cornea of eye) Night blindness
2.	Vitamin B ₁ (Thiamine)	Yeast, milk, green vegetables and cereals	Beriberi (loss of appetite, retarded growth)
3.	Vitamin B ₂ (Riboflavin)	Milk, egg white, liver, kidney	Cheilosis (fissuring at corners of mouth and lips), digestive disorders and burning sensation of the skin.
4.	Vitamin B ₃ (Pyridoxine)	Yeast, milk, egg yolk, cereals and grams	Convulsions
5.	Vitamin B ₁₂	Meat, fish, egg and curd	Pernicious anaemia (RBC deficient in haemoglobin)
6.	Vitamin B ₅ (Ascorbic acid)	Citrus fruits, amal and green leafy vegetables	Scurvy (bleeding gums)
7.	Vitamin D	Exposure to sunlight, fish and egg yolk	Rickets (bone deformities in children) and osteomalacia (soft bones and joint pain in adults)
8.	Vitamin E	Vegatable oils like wheat germ oil, etc.	Increased fragility of RBCs and muscular weakness
9.	Vitamin K	Green leafy vegetables	Increased blood clotting time

NOTE : Vitamin-D , E , K , A are fat soluble vitamins. Vitamin-B, C are water soluble vitamins.



NICERT

Polymer & POC

skm-nucleus^geduvacademy

(5070) mem

hw

Biomolecule sheet

OX-1

Aromatic sheet

OX-1