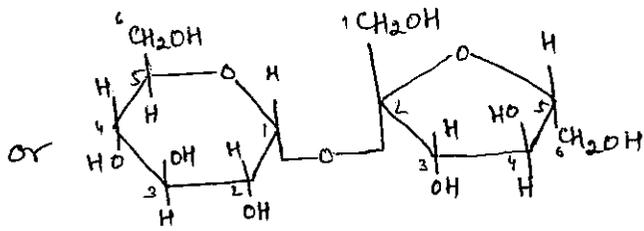
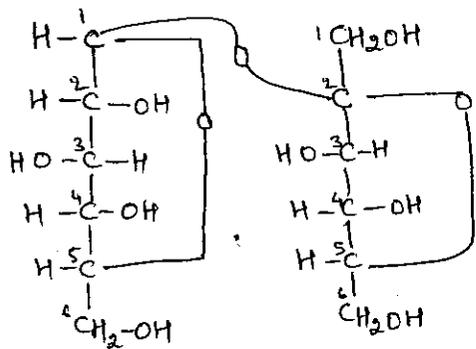
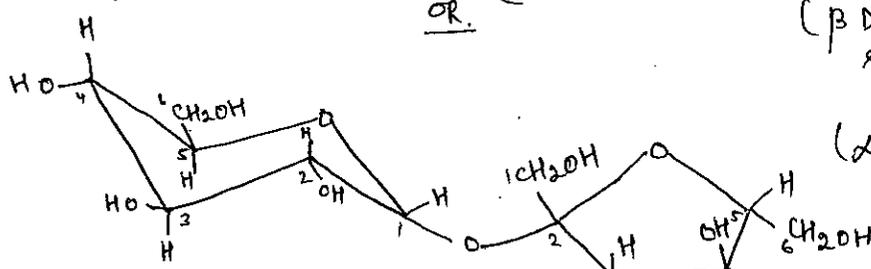


(+) SUCROSE



OR. (no anomers): non-mutarotating  
( $\beta$ -D-fructofuranosyl  $\alpha$ -D-glucopyranosyl)



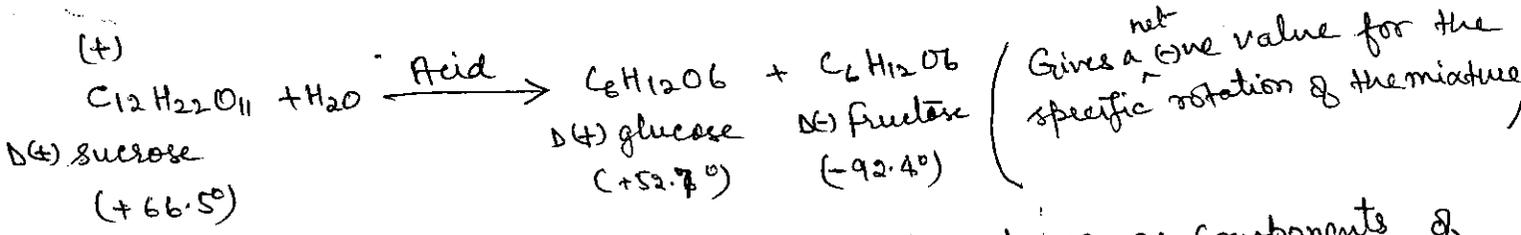
OR  
( $\alpha$ -D-glucopyranosyl  $\beta$ -D-fructofuranoside)

(non-reducing sugar)

⇒ It is very soluble in water but particularly insoluble in the common organic solvents.

⇒ On hydrolysis by dilute acids or enzyme invertase it yields equimolar mixture of D(+) glucose and D(-) fructose

⇒ Both D(+) glucose and (+) sucrose are dextro-rotary but fructose is so strongly laevorotatory that the hydrolysis mixture is laevorotatory i.e. on inversion of rotation has occurred and hydrolysate consisting of D glucose and D fructose is termed 'invert sugar' (honey is mostly invert sugar).



⇒ Because of their opposite rotations and their importance as components of (+) sucrose, D(+) glucose and D(-) fructose are commonly called dehiose and levulose.

⇒ Sucrose exists in two crystalline forms, a stable form, sucrose A, m.p. = 184-185 and the unstable form sucrose B, m.p. 169-170°C.

6.  
 ⇒ It is oxidised by concentrated  $\text{HNO}_3$  to oxalic acid.  
 A) Sucrose  $\xrightarrow{\text{conc HNO}_3}$   $\begin{matrix} \text{COOH} \\ | \\ \text{COOH} \end{matrix}$  + other products.

⇒ It is charred by concentrated  $\text{H}_2\text{SO}_4$  in the cold, evolving  $\text{CO}_2$  +  $\text{SO}_2$  gas.

⇒ It forms no osazone or oxime or cyanohydrin, It

⇒ It does not reduce Fehling solution and Tollen's reagent

⇒ It can be acetylated using acetic anhydride  $(\text{CH}_3\text{CO})_2\text{O}$  and sodium acetate (fund) to form sucrose octa-acetate.

⇒ It forms an octa-O-methylsucrose<sup>(Haworth method)</sup> when treated with dimethyl sulphate  $(\text{CH}_3)_2\text{SO}_4$  in the presence of alkali (NaOH) and this on hydrolysis with dil HCl, gives 2,3,4,6 tetra-O-methyl-D-glucose and 1,3,4,6 tetra-O-methyl-D-fructose.

Constitution of Sucrose:-

(1) The molecular formula of sucrose is  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ .

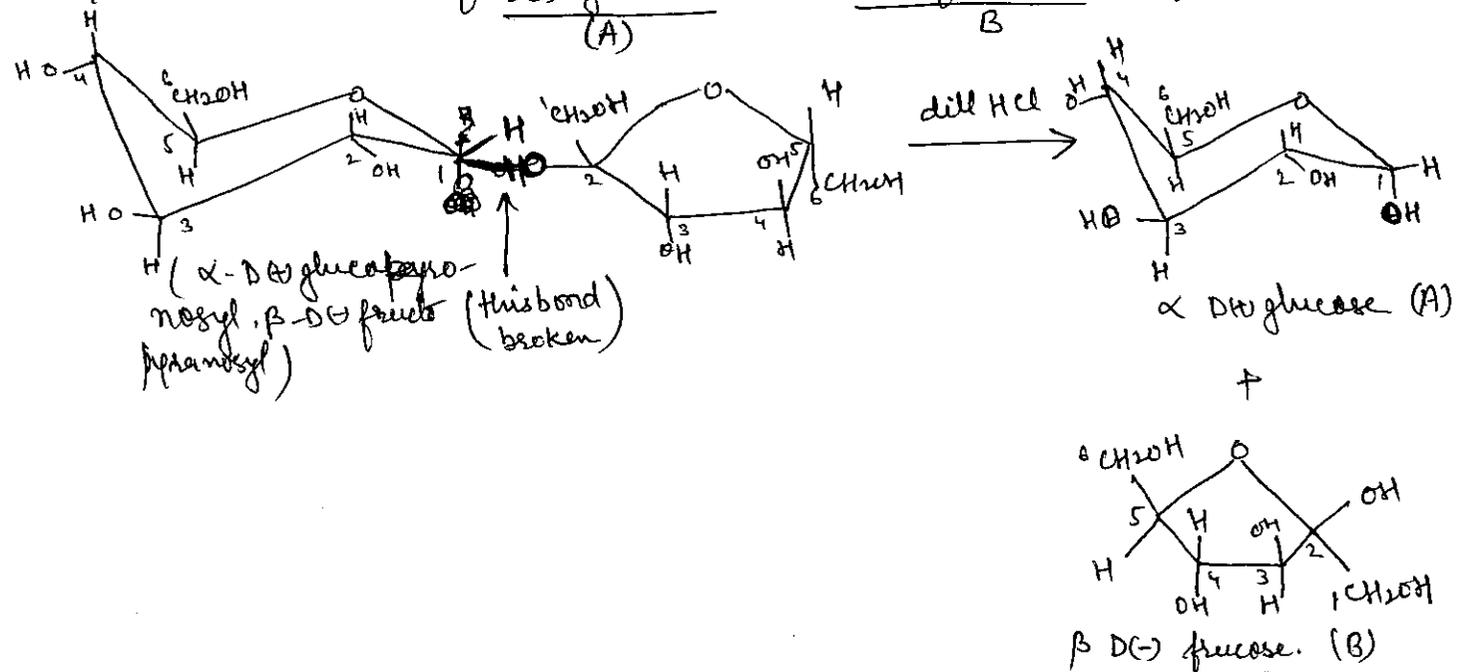
(2) It does not reduce Fehling solution, Tollen's reagent and Benedict solution, thus it does not contain free  $-\text{CHO}$  or  $>\text{C}=\text{O}$  group.

(3) It forms no osazone; it also shows that it has no  $-\text{CHO}$  or  $>\text{C}=\text{O}$  group in sucrose.

(4) It does not exhibit mutarotation.

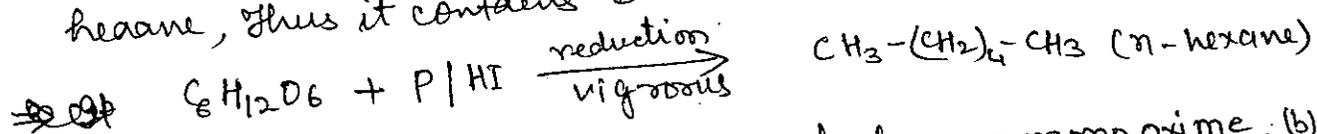
(5) It does not form methyl glucoside ( $\text{CH}_3\text{OH}$  in presence of HCl), means there is no free  $-\text{OH}$  on C1 atom.

(6) When sucrose hydrolysed by dil. HCl or by enzyme invertase to an equimolar mixture of D(+) glucose and D(-) fructose are formed.

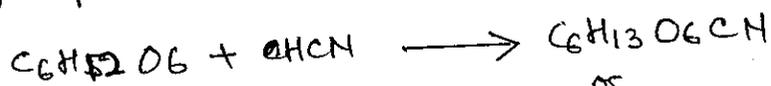


## Determination of Structure of (A) (i.e. $\alpha$ -D(+)-glucose)

- ⇒ The elemental analysis and molecular weight determination of compound (A) shows that the molecular formula of ~~glucose~~  $C_6H_{12}O_6$ .
- ⇒ Compound (A) rotates plane of polarised light in clock wise direction, thus it is dextro-rotatory in nature.  $[\alpha]_D = +112^\circ$  (specific rotation). Thus it is dextro-rotatory in form and  $\alpha$  form.
- ⇒ Vigorous reduction with phosphorus and hydroiodic acid yields n-hexane, thus it contains 6 carbon chain and straight chain.

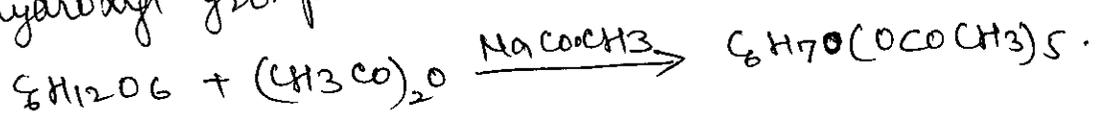


- ⇒ It reacts with (a) hydroxyl amine to form a monooxime, (b) with HCN to form a cyanohydrin, thereby indicating the presence of one carbonyl group.  $C_5H_{11}O_5(C=O)$



- ⇒ Gentle oxidation of glucose with  $\text{Br}_2/\text{water}$  or sodium hypobromite affords a monobasic acid, gluconic acid,  $C_5H_{11}O_5(\text{COOH})$ , containing the same number of carbon atoms as glucose, so the carbonyl group must be aldehydic. Thus the formula can be written as  $C_5H_{11}O_5(\text{CHO})$ .
- ⇒ Further, this compound reduces Fehling solution & Tollen's reagent which also suggests carbonyl group is aldehydic. Now since aldehydic group is monovalent, it must be present on the end of chain.

- ⇒ On acetylation with acetic anhydride and sodium acetate glucose (Compound A) gives pentaacetate indicating the presence of five hydroxyl group, since compound A is stable compound the five hydroxyl groups must be attached to different carbon atoms.



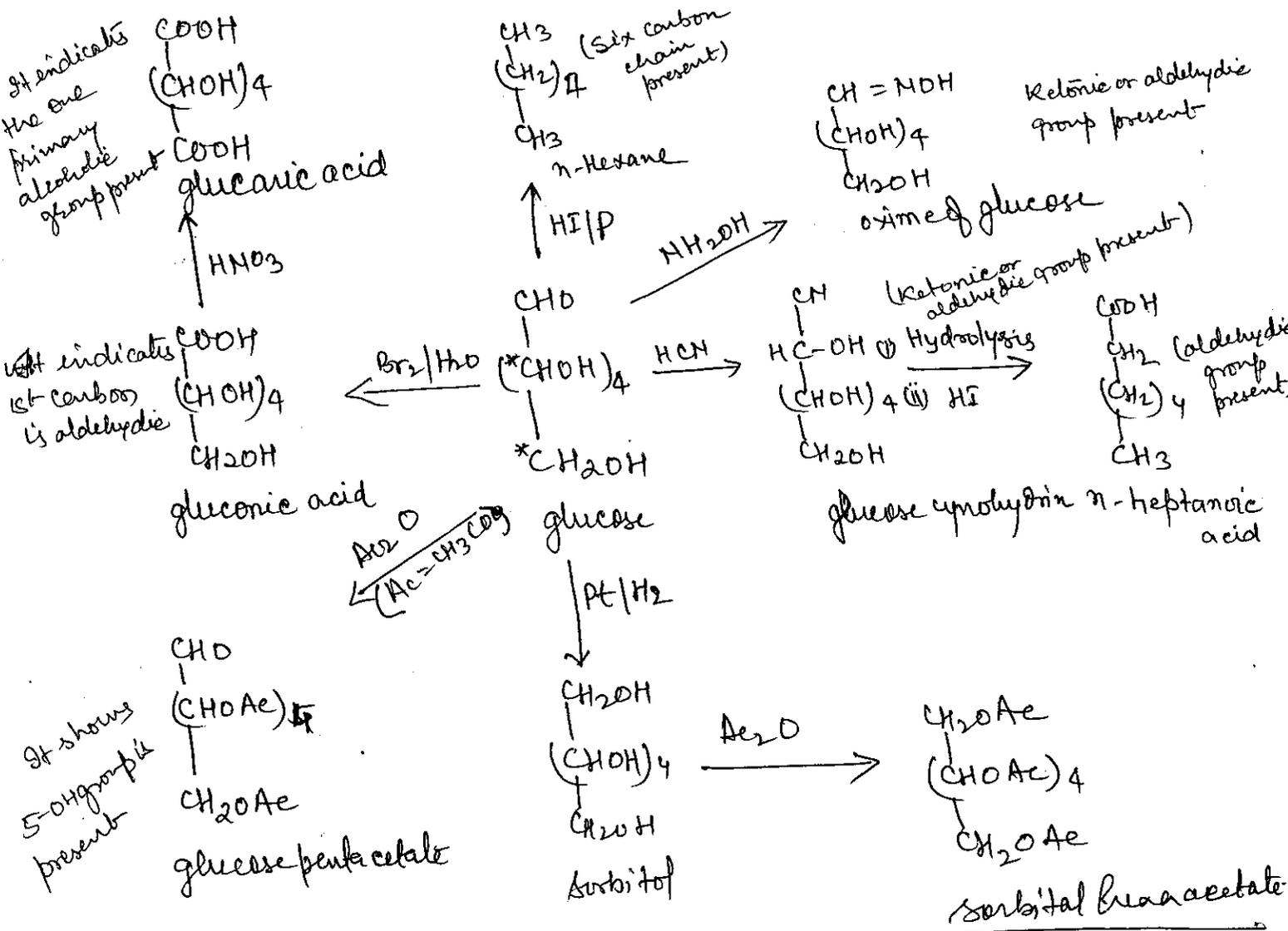
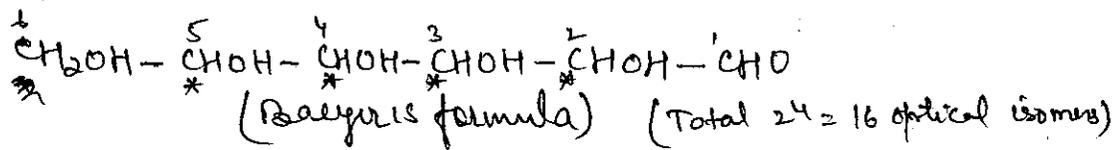
The glucose can now be formulated  $C_5H_6(\text{OH})_5(\text{CHO})$

8.

⇒ This was confirmed by catalytic reduction (Pt/H<sub>2</sub>) of compound (A) to a heptahydric alcohol i.e. glucitol or sorbitol (C<sub>6</sub>H<sub>14</sub>O<sub>6</sub>) and formation of heptaacetate by treatment of sorbitol with acetic anhydride.

⇒ oxidation of gluconic acid (obtained by oxidation of Br<sub>2</sub> water with glucose) with HNO<sub>3</sub> affords a dicarboxylic acid, glucaric acid or saccharic acid (C<sub>6</sub>H<sub>10</sub>O<sub>8</sub>), containing the same no. of carbon atoms as glucose or gluconic acid. Thus second carboxylic group must have arisen from primary alcoholic group. Hence the formula of glucose becomes C<sub>6</sub>H<sub>4</sub>(OH)<sub>4</sub>(CH<sub>2</sub>OH)(CHO)

Thus structure of compound (A)

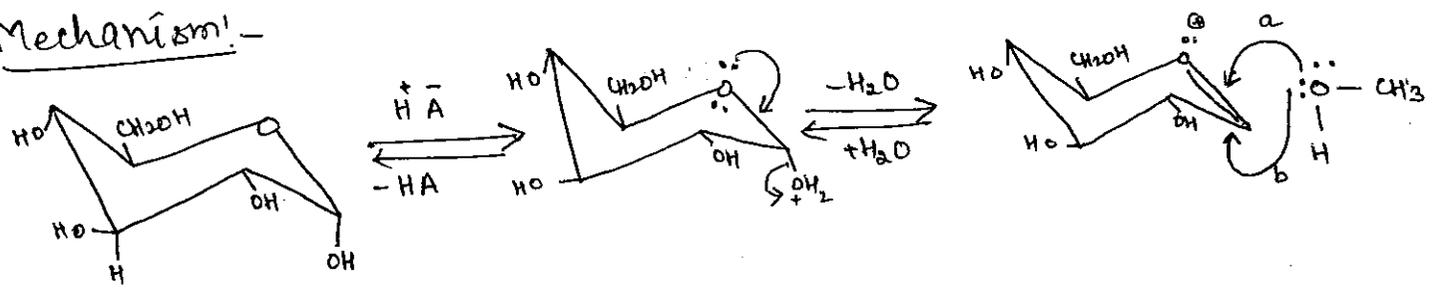


Chemical structure of D(+)-Glucose:- The open chain structure II can explain most of the reactions of glucose, however, it suffers from the following limitations:

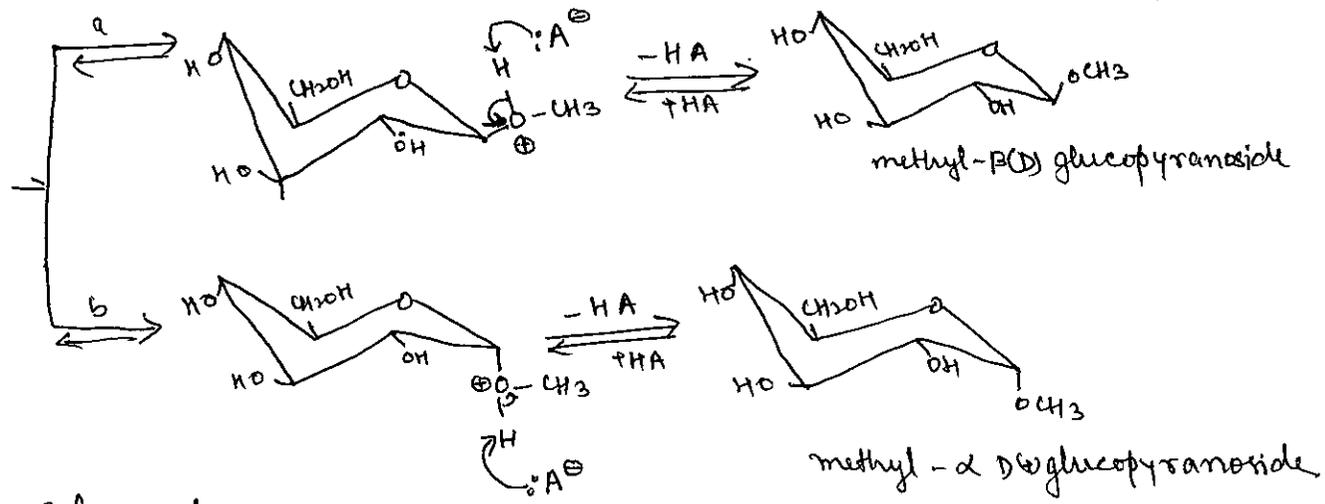
⇒ It does not give a Schiff's test and it does not form a bisulphite adduct, thus there is no free aldehydic group (because Schiff's reagent, a weak reagent for testing of aldehydic group), But on the other hand, it gives certain reactions of the carbonyl group viz. formation of cyanohydrin, oxime, phenylhydrazone etc, the reason being the strong carbonyl reagents like HCN, NH<sub>2</sub>OH, C<sub>6</sub>H<sub>5</sub>NHNH<sub>2</sub> etc. are able to open the ring to form a free aldehydic group, which react with these reagents.

⇒ treatment of D(+)-glucose with methyl alcohol and anhydrous HCl (gaseous HCl), a reaction takes place that results in the formation of anomeric methyl acetal. (Carbohydrate acetals, generally, are called glycosides and acetals of glucose is called a glucoside)

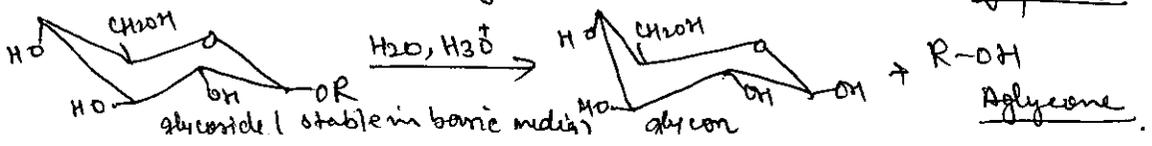
Mechanism:-



< D(+)-glucopyranose

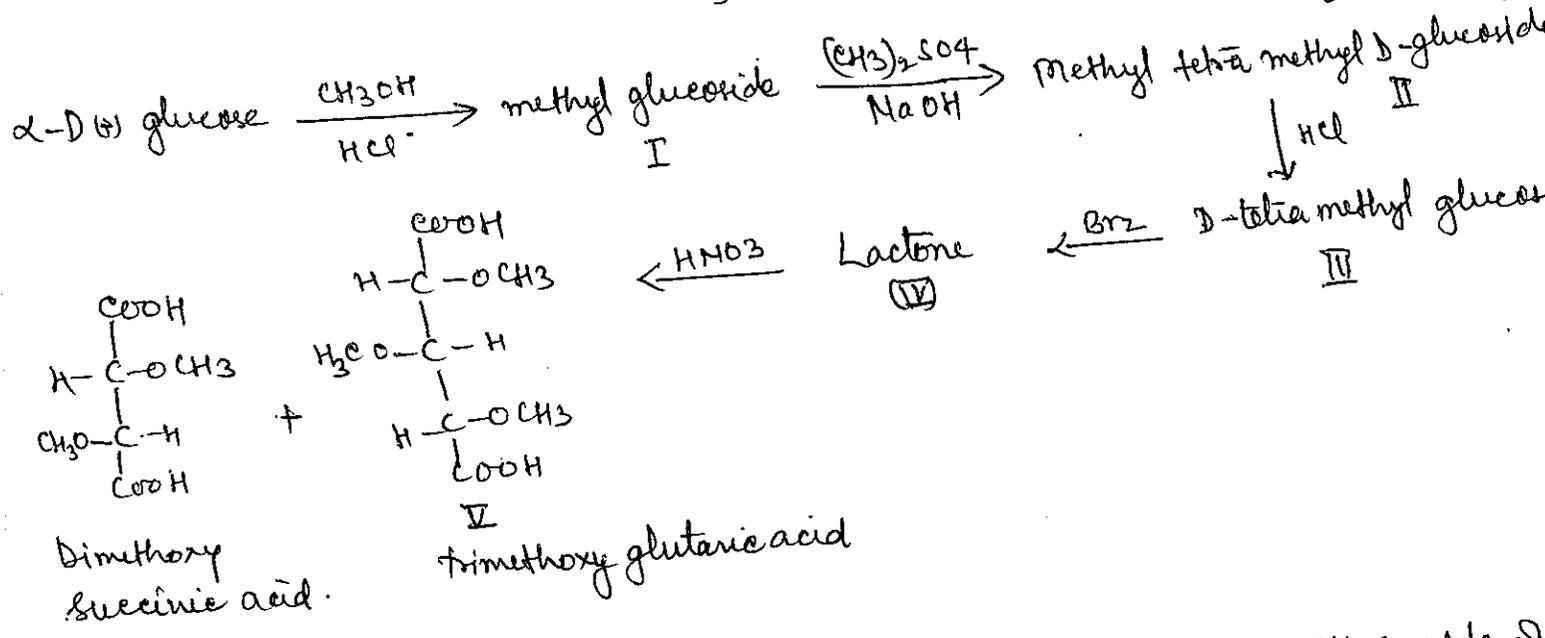
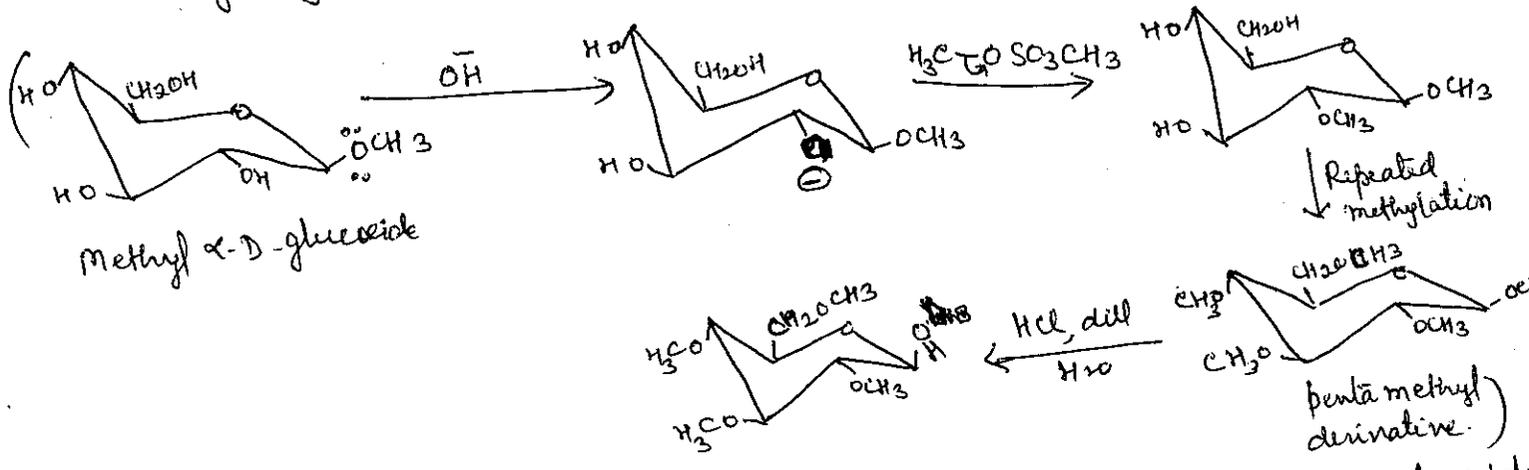


⇒ Glycosides are stable in basic solutions because they are acetals. In acidic solutions, however, glycosides undergo hydrolysis to produce a glucose and alcohol. The alcohol obtained by hydrolysis of glycosides is known as an aglycone.



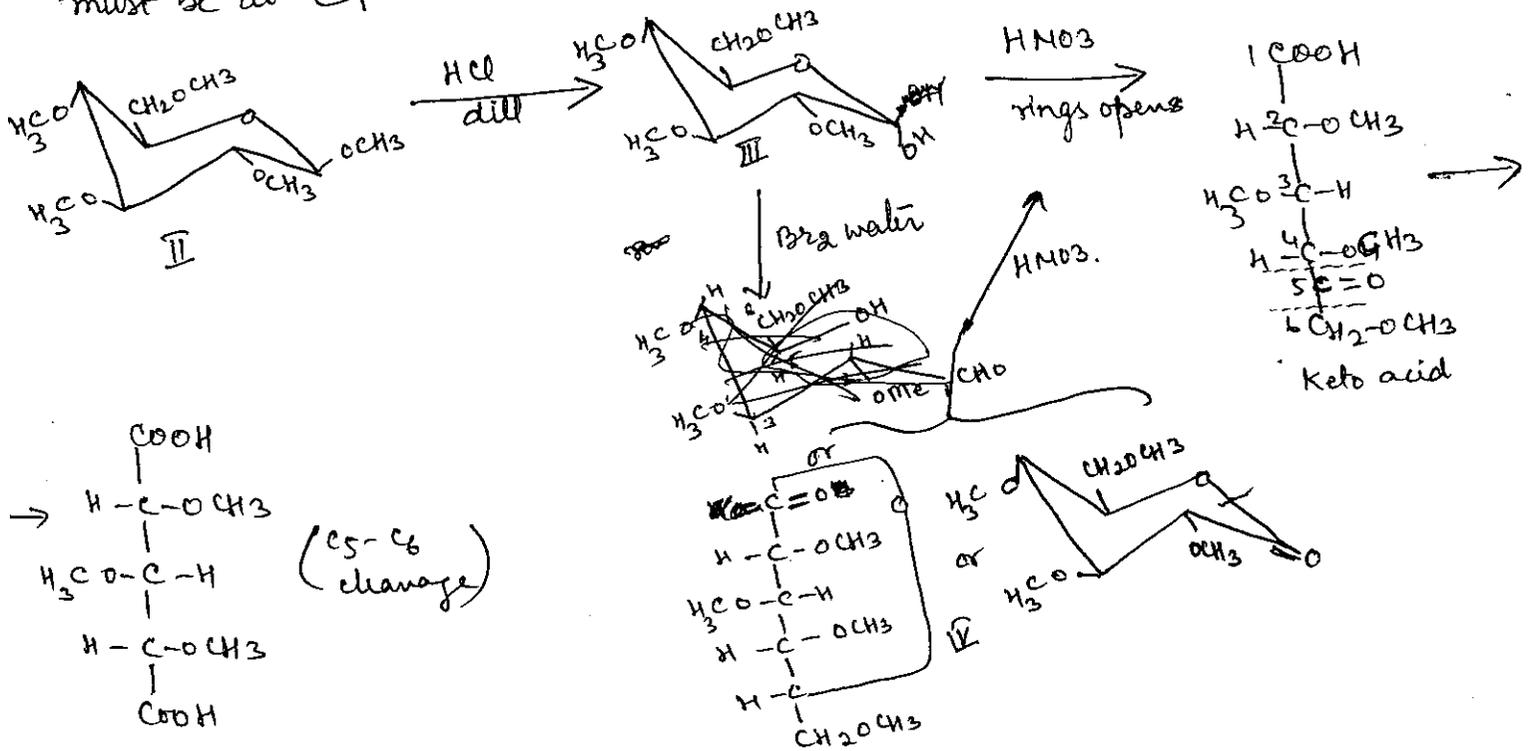
- ⇒ The structure (A) has assumed the formation of a 6 membered oxygen heterocycle 'pyran' (hence, the designation pyranose<sup>2</sup>)
- ⇒ The ring closure at C2 and C3 can be ruled out as the resulting 3 and 4 membered rings would be relatively less stable but cyclisation at C4 giving 5 membered ring, because 5 membered ring and 6 membered ring has almost the same order of stability
- ⇒ Let us discuss 6-membered ring, rather than 5-membered ring which is actually involved in the cyclic structure of glucose

⇒ Methyl α-D glucoside, on treatment with methyl sulphate in the presence of alkali followed by hydrolysis by dilute HCl gives α-2,3,4,6-tetra-O-methyl D glucose.

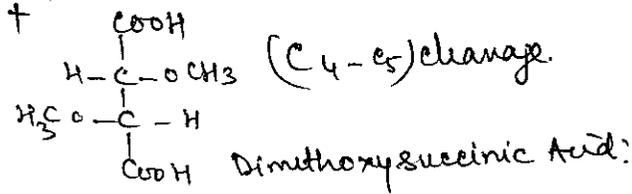


⇒ These degradation products can arise only by cleavage on either side of C-5. The keto group of the intermediate keto acid must be situated at C5

As the free -OH group in tetra-O-methyl-D-glucose would, obviously, be at C-5, hence the points of linkage of the acetal ring in methyl α-D-glucoside must be at C<sub>1</sub> and C<sub>5</sub>.

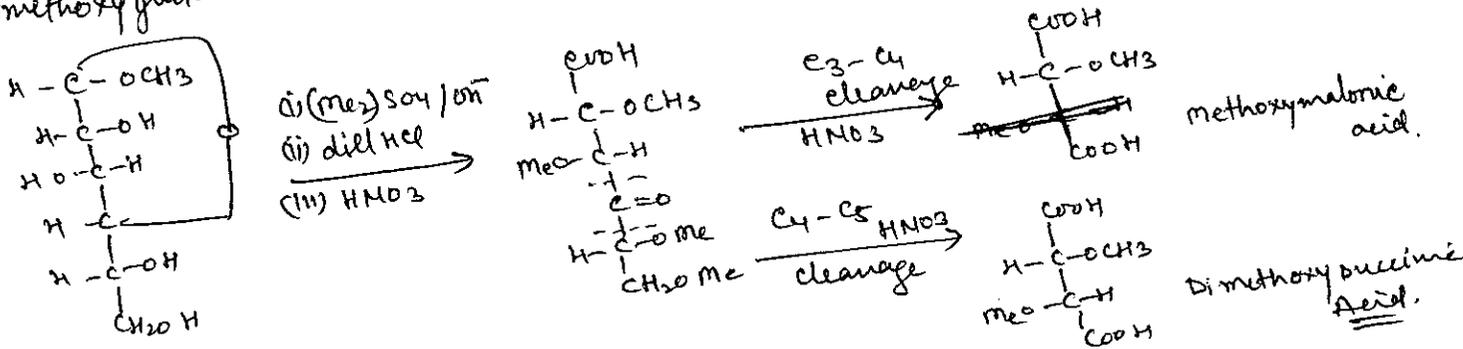


trimethoxyglutaric acid



⇒ Treatment with dil HCl removes the only reactive acetal methoxy group at C<sub>1</sub> whereas ordinary ether linkages at the other four carbon atoms remains intact under these mild conditions.

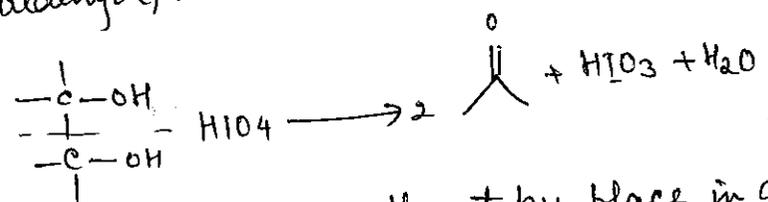
⇒ If C<sub>4</sub> were involved in the formation of the acetal ring of methyl D-glucoside trimethoxyglutaric acid could not have been arisen.



⇒ Thus glycoside linkage must be at C<sub>1</sub>-C<sub>5</sub> position.

Periodic Method for cyclic structure of  $\alpha$ -D-glucose:-

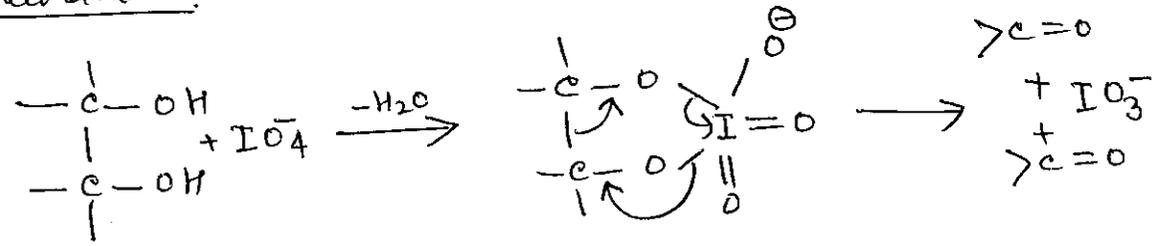
⇒ Compounds that have hydroxyl groups on adjacent carbon atom undergo oxidative cleavage when they are treated with aqueous periodic acid ( $HIO_4$ ). The reaction breaks carbon-carbon bond and produces carbonyl compounds (aldehyde, ketones and acids)



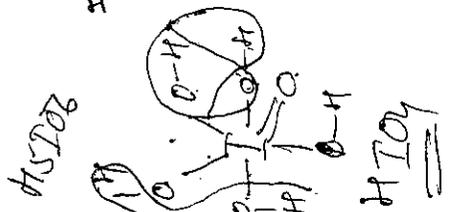
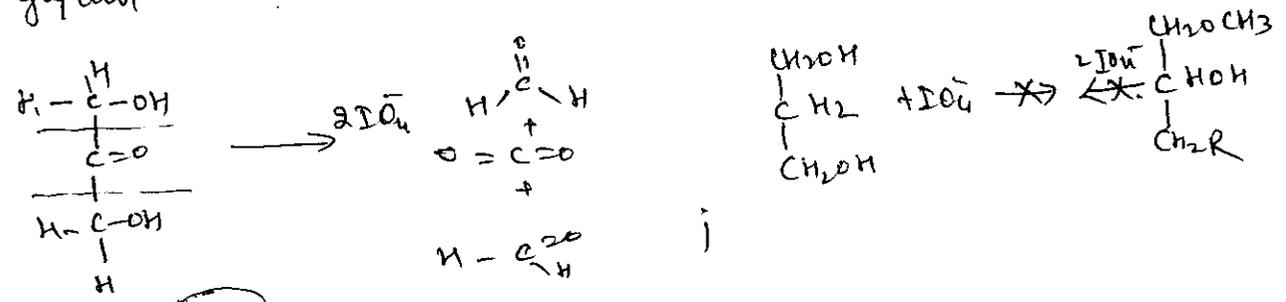
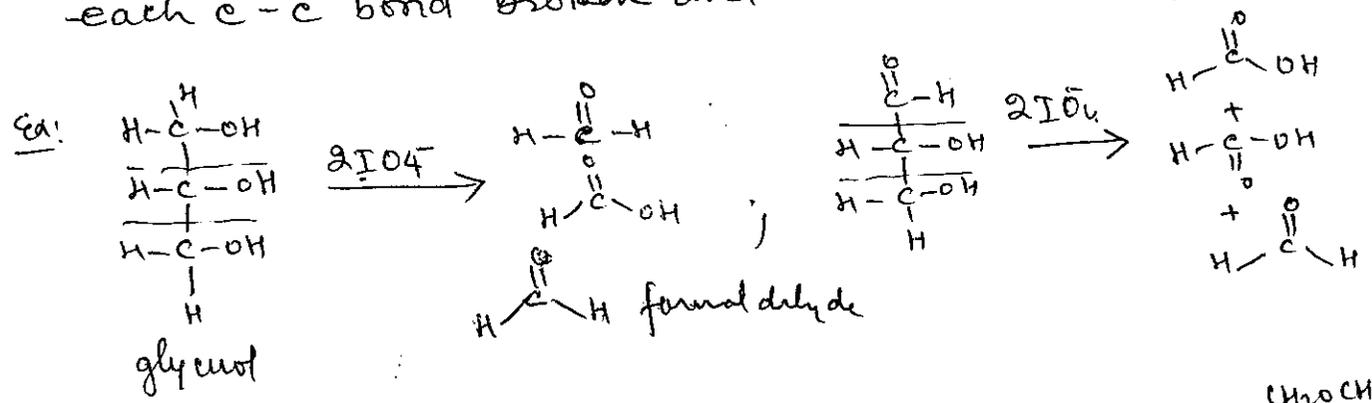
⇒ Since reaction usually takes place in quantitative yield, this molar equivalent of periodic acid that is consumed in the reaction can give no. of carbonyl products.\*

\* The reagent lead tetraacetate  $Pb(OAc)_4$ , brings about cleavage reaction similar to those of periodic acids. But Lead tetraacetate works in organic solvent and periodic acids work in aqueous  $SO_2$ .

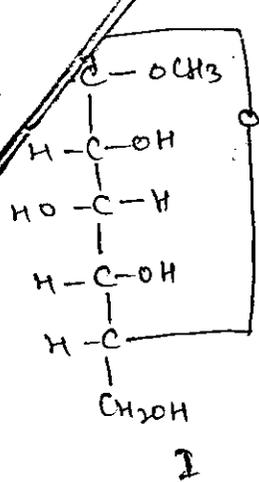
Mechanism:



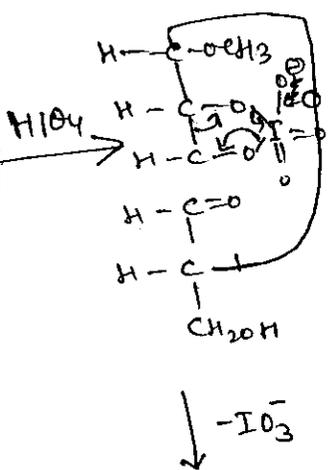
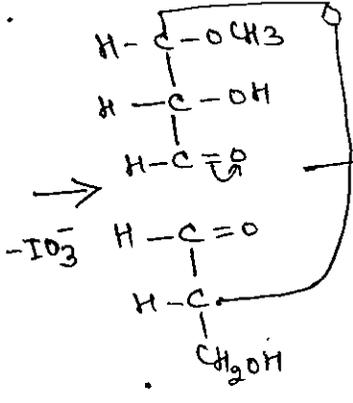
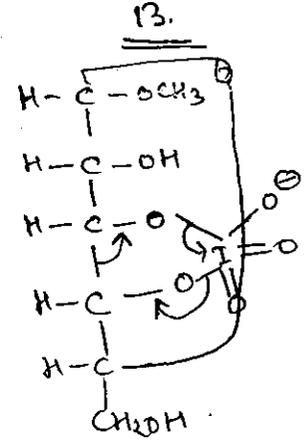
each c-c bond broken and a c-o bond is formed.



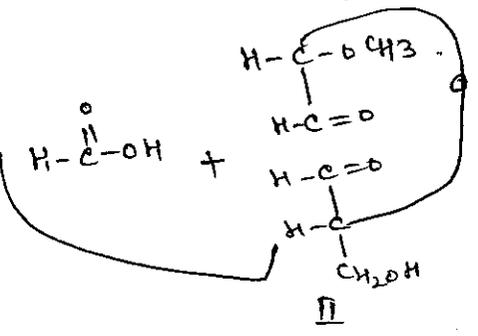
$HIO_4^-$   
Periodic Acid



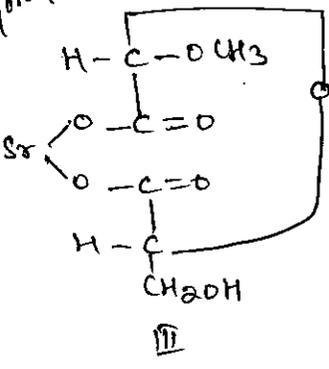
$\xrightarrow{\text{HIO}_4}$



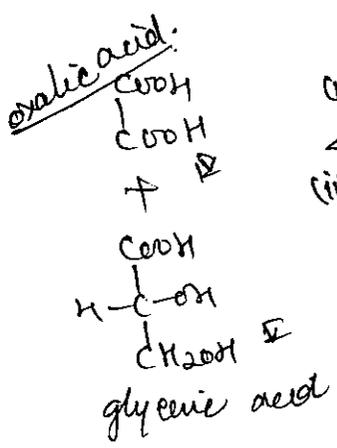
$\downarrow -\text{IO}_3^-$



$\xleftarrow[\text{SrCO}_3]{\text{Br}_2/\text{H}_2\text{O}}$

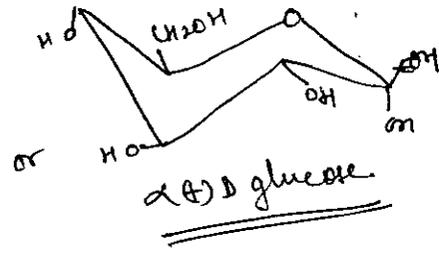
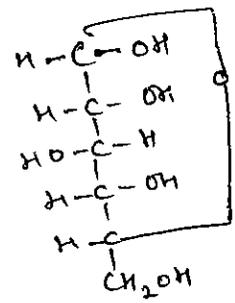


$\xrightarrow{\text{for hydrolysis}}$   
 (i)  $\text{H}_2\text{SO}_4$   
 (ii)  $\text{Br}_2/\text{H}_2\text{O}$

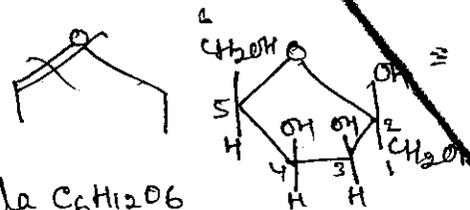


$\Rightarrow$  Isolation of II, III, IV & V indicated that ring in I is C<sub>4</sub>-C<sub>5</sub>. It is also supports that only one carbon eliminated as formic acid. and 2 molecules of periodic acid is consumed.

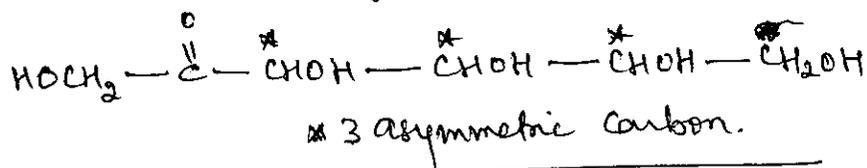
Thus cyclic structure of  $\alpha$ -D-glucose is



## Constitution of $\beta$ -D-G fructofuranoside (B)

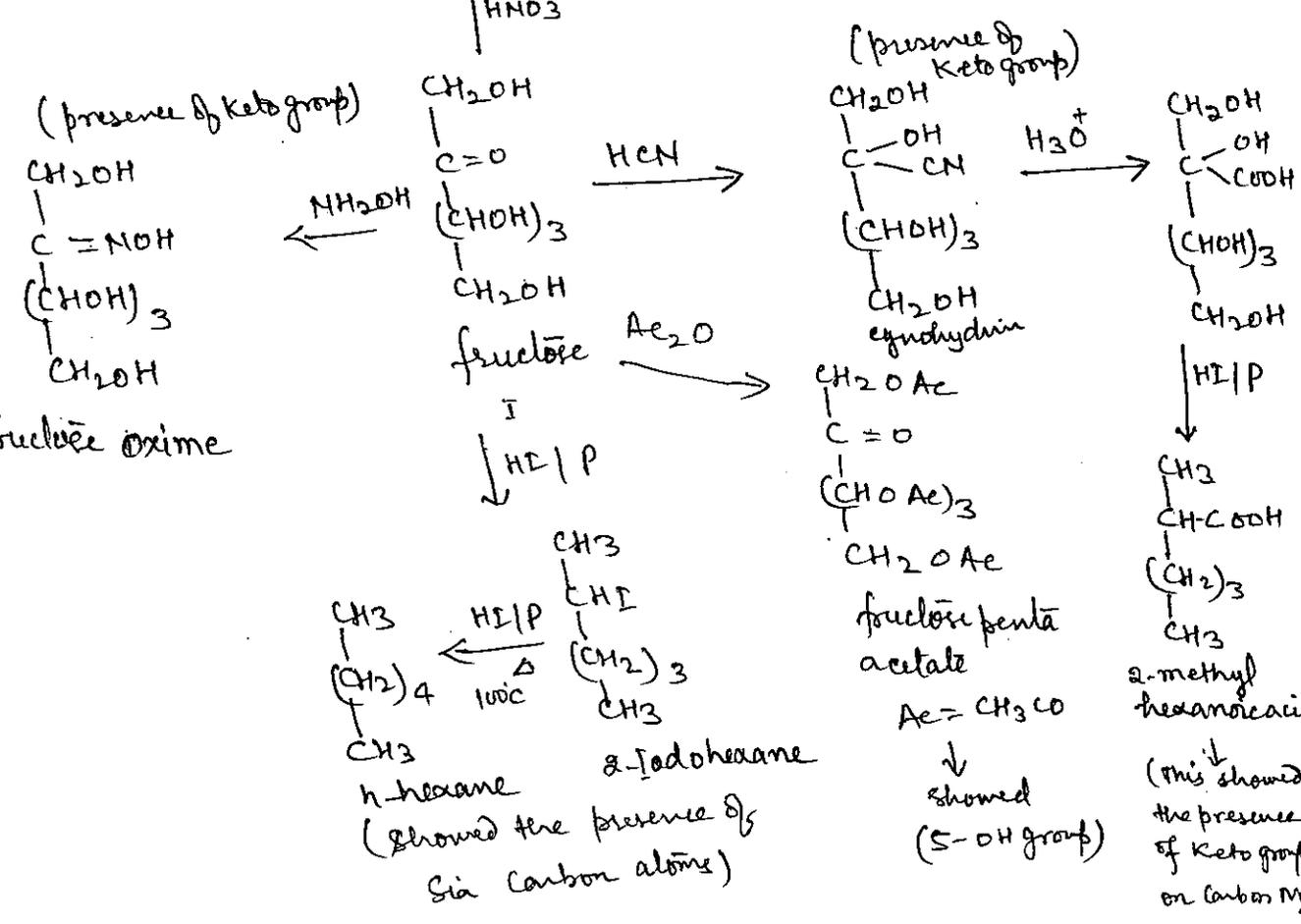
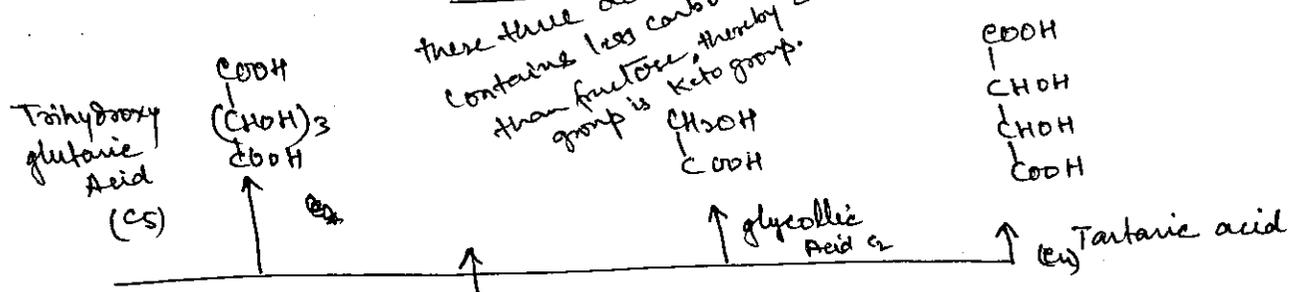


- ⇒ Compound (B) showed the molecular formula  $C_6H_{12}O_6$
- ⇒ It rotates plane of polarized light in anticlockwise direction with specific rotation  $92.4^\circ = [\alpha]_D^{20}$
- open chain structure :-
- ⇒ It forms cyanohydrin and an oxime, thereby showing the presence of a carbonyl group.
- ⇒ On oxidation with  $HNO_3$ , it yields a mixture of acids, mainly trihydroxyglutaric acid, tartaric and glycollic acid. Each of these acids contains a fewer number of carbon atoms than fructose thereby suggesting that the carbonyl group in fructose is a keto group and not an aldehyde group.
- ⇒ It forms a pentaacetate, thereby indicating the presence of 5-OH group
- ⇒ It does not lose water easily, thereby suggesting that the five-OH groups in the six-carbon fructose are present on different carbon atoms.
- ⇒ On reduction with Hydroiodic acid and red phosphorus at  $100^\circ C$ , it yields n-heptane and 2-iodoheptane. Obviously, the six carbon atoms in fructose form a straight chain.
- ⇒ Hydrolysis of the cyanohydrin of fructose yields a polyhydroxy acids which, on reduction with HI/P gives rise to 2-methylheptanoic acid. This shows that keto group in fructose is present on the second carbon of the straight chain carbon atoms in fructose.
- ⇒ on the basis of the foregoing experimental facts, the following open-chain structure I for fructose was proposed.



25.

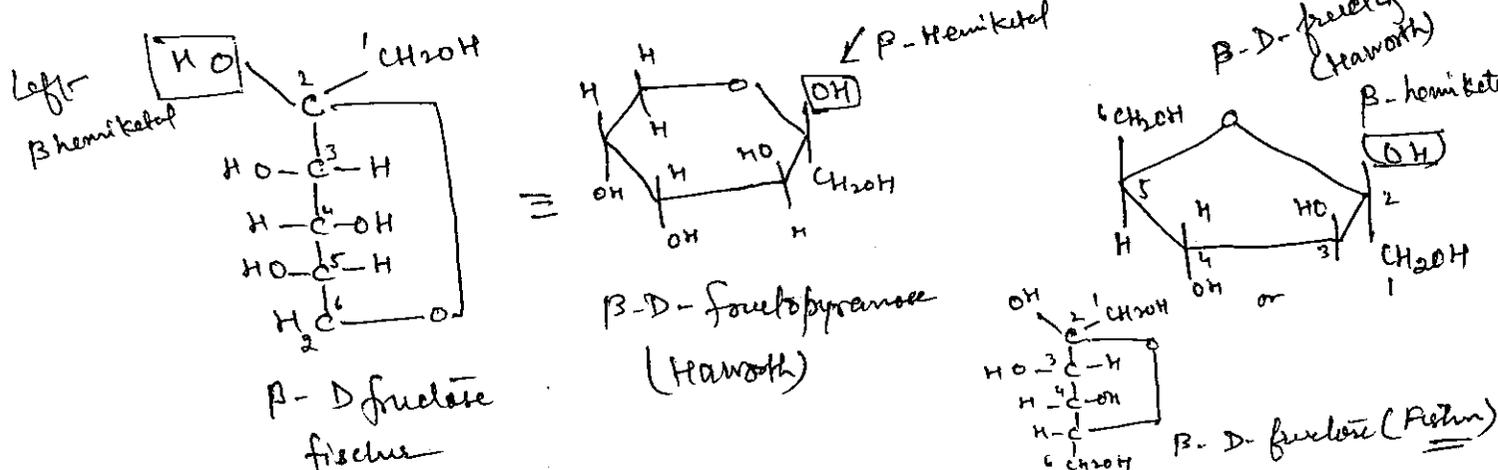
These three acids contain less carbon than fructose, thereby carbonyl group is Keto group.



$\Rightarrow$  In fructose, there is 3 asymmetric carbon, it may exist in eight ( $2^3=8$ ) optical isomers.

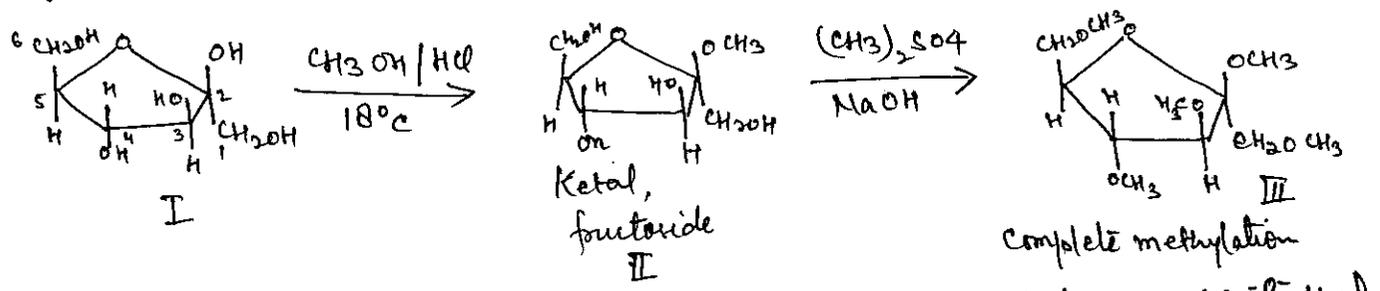
Ring Structure of Fructose :- The actual size of the ring of fructose is determined by the methylation method.

$\Rightarrow$  When fructose is component of a saccharide as in sucrose, it usually occurs in its furanose form (5-membered-hemiketal).



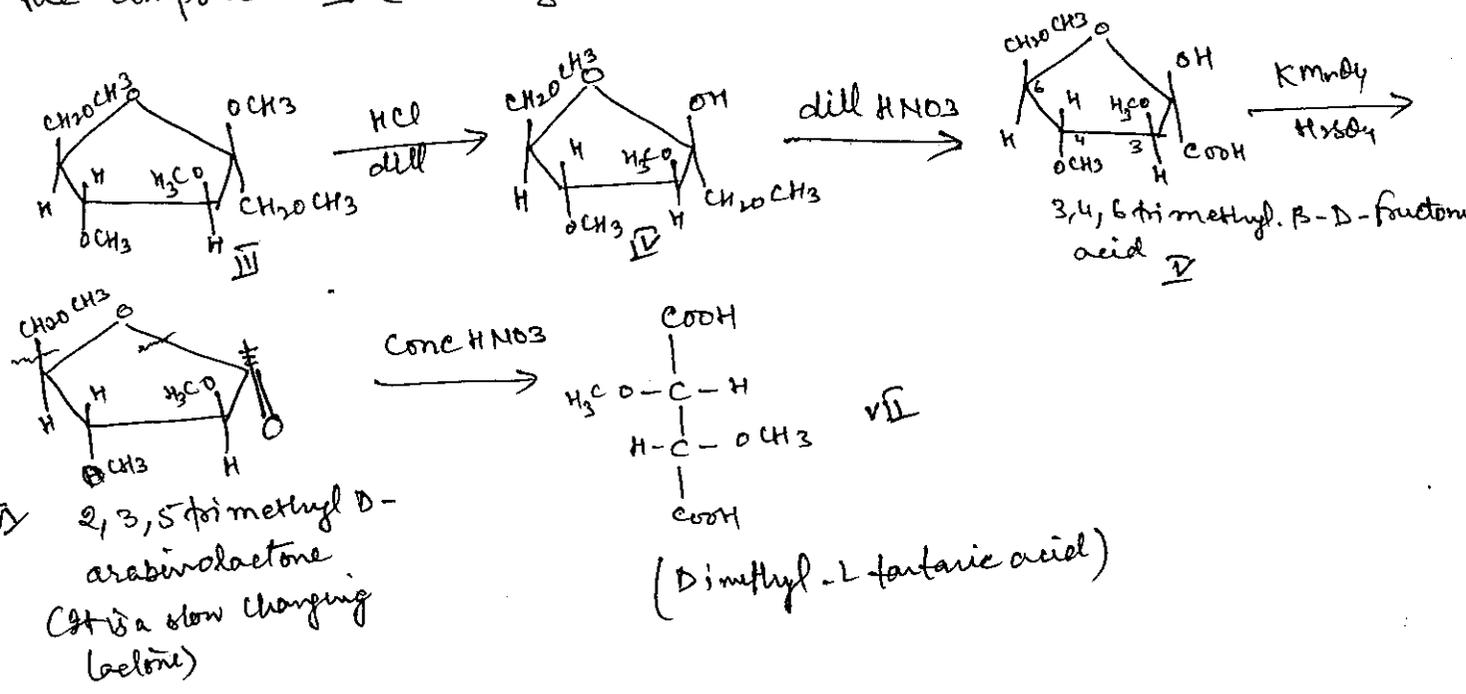
- ⇒ When fructose in pyranose form then its linkage is C<sub>2</sub> ≠ C<sub>5</sub>.
- ⇒ When fructose in furanose form, linkage involves between C<sub>2</sub> & C<sub>5</sub>.

⇒ When methyl alcohol is passed with anhydrous HCl at room temperature its carbon no 2 is methylated (But in case of pyranose structure for methylation refluxation required).



⇒ fructoside (methyl fructoside) is completely methylated in the presence of (CH<sub>3</sub>)<sub>2</sub>SO<sub>4</sub>/NaOH giving the methyl-1,3,4,6 tetra-O-methylfructofuranoside.

⇒ When compound III hydrolyzed with dil HCl it gives compound IV, which on oxidation with acidic KMnO<sub>4</sub> gives compound V, compound V on oxidation with conc HNO<sub>3</sub> gives the compound VII (Dimethyl-L tartaric acid) of well known structure.



⇒ 2,3,5-trimethyl D-arabinofuranose (CH is a slow changing lactone)

(Dimethyl-L tartaric acid)

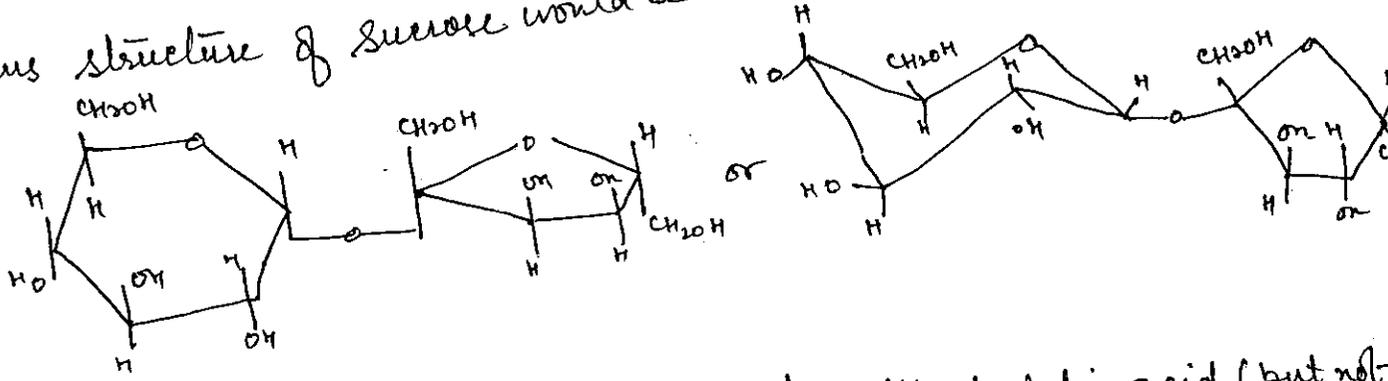
⇒ Thus structure of fructose must be I; and it is in the form of β-D-fructofuranoside in (sucrose).

17.

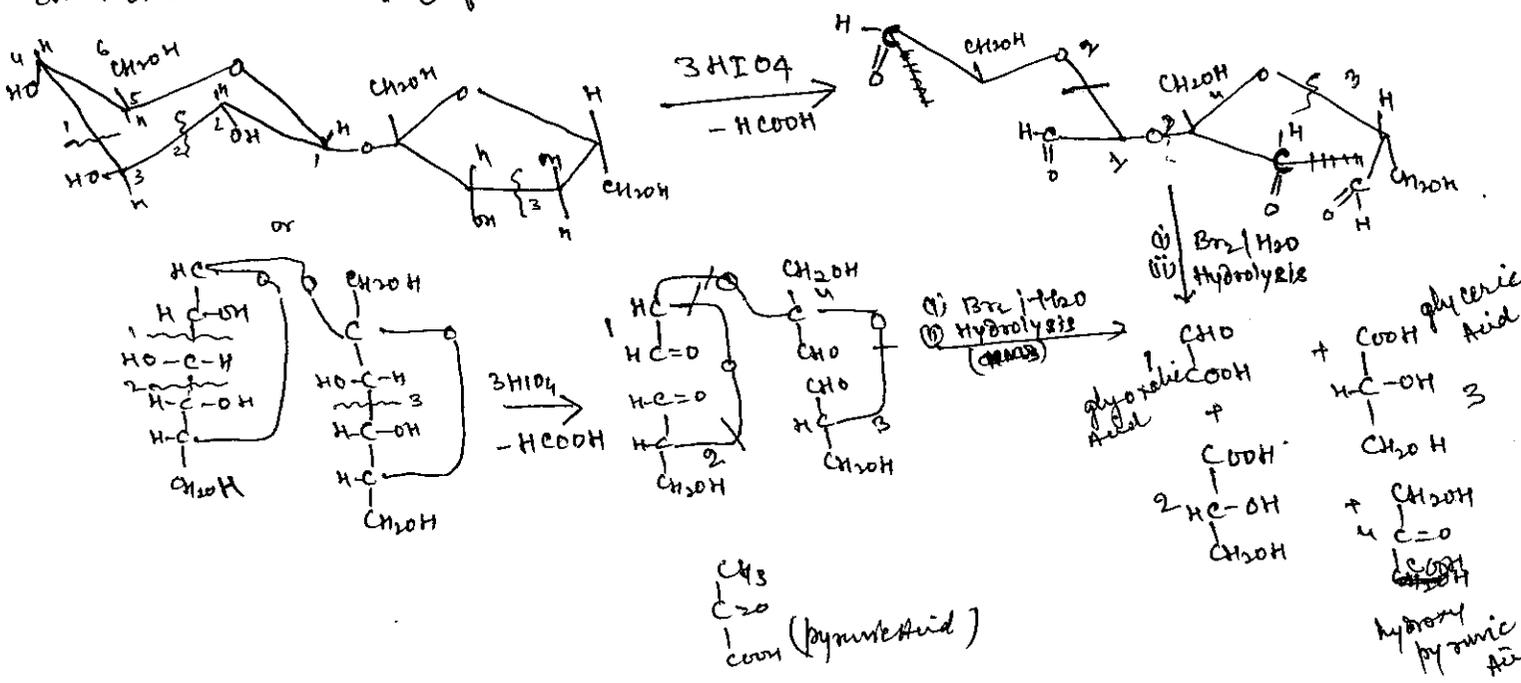
ring of  $\alpha$ -D(+) glucose and  $\beta$ (-)-fructose which are in the form of  $\alpha$ -D(+) glucopyranoside and  $\beta$ (-)-fructofuranoside:

- ⇒ Since glucose and fructose both are reducing sugars and while sucrose is not reducing sugar, thus they must be linked via their respective reducing groups.
- ⇒ The stereochemical nature of glycosidic link may be any one of the four possibilities  $\alpha_1-\alpha_2$ ,  $\alpha_1-\beta_2$ ,  $\beta_1-\alpha_2$ ,  $\beta_1-\beta_2$ . but evidence indicates that it is  $\alpha$ -glucose linked to  $\beta$  fructose. Maltase hydrolyses sucrose; therefore an  $\alpha$ -link is present.
- ⇒ Mutarotation showed that  $\alpha$  glucose liberated first (downward direction)
- ⇒ Mutarotation of fructose is too rapid. An enzyme which hydrolyses methyl- $\beta$ -D-fructofuranoside and it has been also found that it also hydrolyses sucrose, this suggests that fructose present in sucrose in the  $\beta$  form.

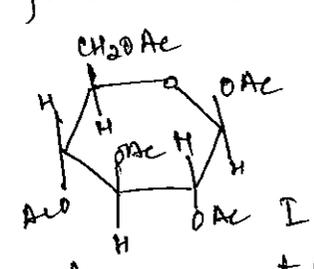
Thus structure of Sucrose would be



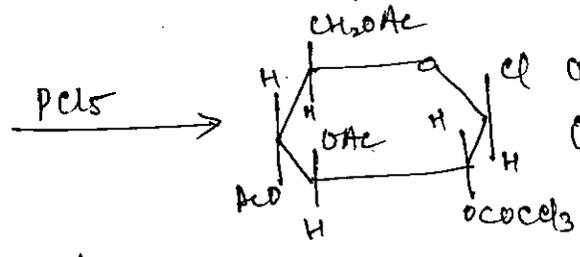
This structure can be confirmed by its oxidation with periodic acid (but not the nature of glycosidic linkage). Three molecules of periodic acid are consumed and one molecule of formic acid is produced.



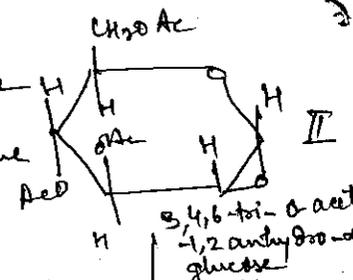
further its structure can be confirmed by its synthesis:



Acetyl tetra-O-acetyl-beta-D-glucose

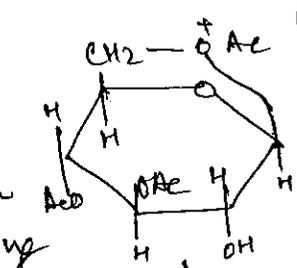


(i) NH3 in ether  
(ii) NH3 in benzene

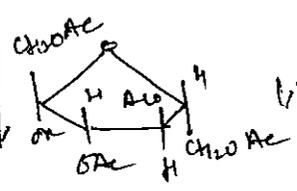


3,4,6-tri-O-acetyl-beta-D-glucopyranoside  
MeOH

II neighbour group participation opens the oxide ring

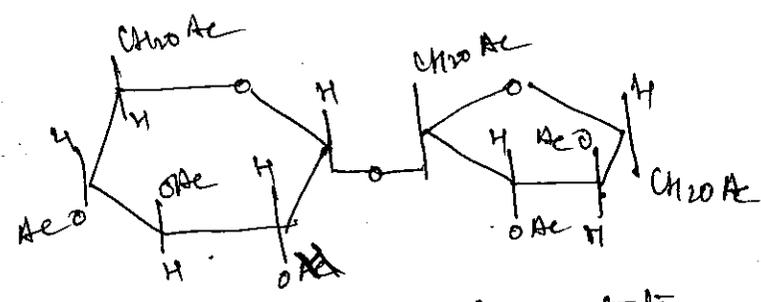


heated 100°C for 10 hrs.

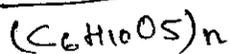


The CH2OAc at position 6 in the glucopyranose molecule enters into neighbour group participation in the cyclic intermediate, which hinders the attack of fructose unit from other side.

1,3,4,6-tetra-O-acetyl-beta-D-fructofuranose



Sucroheptaacetate



⇒ It is the chief structural material to which the plants owe their form and rigidity. Wood and natural fibres from cotton, flax, hemp and jute are also important sources of cellulose.

⇒ Cellulose is a colourless fibrous substance.

⇒ It is water insoluble, but dissolves in a solution of cupric hydroxide in ammonia water. Organic solvents can't dissolve it too.

⇒ Artificial silk is also made by making the derivative of cellulose.

⇒ Hemicellulose (lower molecular weight of cellulose) polysaccharides occurs with cellulose in plant cell walls. (Its unit is D-xyllose)

⇒ Three important cellulose forms are  $\alpha$ ,  $\beta$  and  $\gamma$ .

⇒  $\alpha$ -cellulose is very less degraded and is insoluble in 17.5% aq. NaOH

⇒  $\beta$ -cellulose is soluble in 17.5% aq. NaOH, but insoluble in dil. acid.

⇒  $\gamma$ -cellulose is insoluble in aq. NaOH & dil. acid.

⇒ It form slurry with lower alcohols.  $[Cellulose]$   
 $\downarrow$   $C_2H_5OH, C_3H_7OH$

⇒ When cotton fibres (cellulose) under tension are treated with 20% aq. NaOH solution and the fibres are washed free of alkali, the fibres swell and become more smoothed, this type of cotton is known as mercerized cotton.

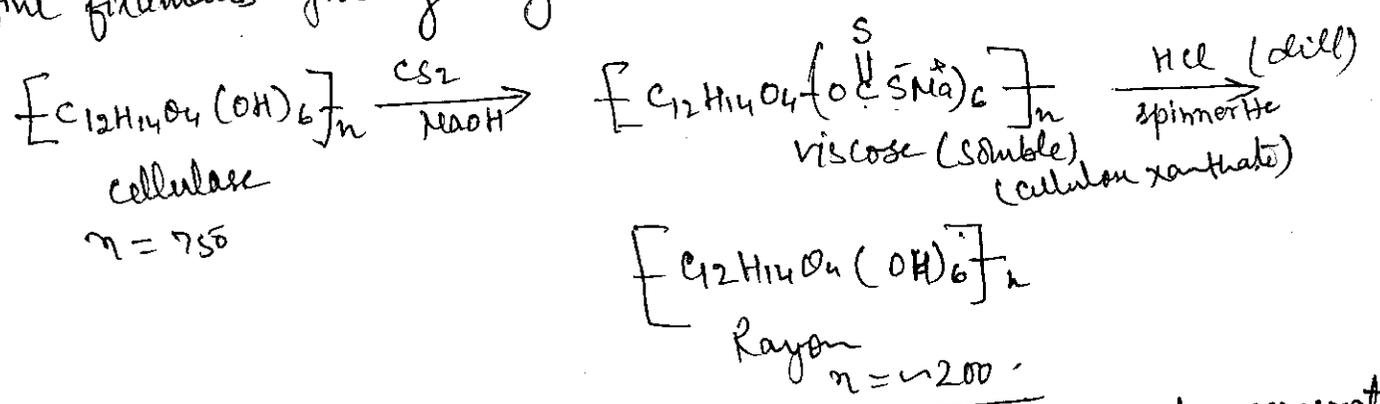
⇒ Cellulose nitrates are obtained after nitration of cellulose with a nitrating mixture (water,  $HNO_3$  &  $H_2SO_4$ ). The degree of esterification (nitration) is adjusted by the concentration of nitrating mixture. Almost three OH group of cellulose are nitrated, thus to nitrate (gun cotton). It is used in explosive, when it is plasticized with nitroglycerin gives cordite which is used as military explosive.

⇒ Cellulose also react with glacial acetic acid and acetic anhydride mixture and form triacetate derivative of cellulose. (acetate rayon)

⇒ Cellulose also forms esters & ethers (eg. CMC).

⇒ Cellulose xanthate: It is obtained with a mixture of aq. NaOH +  $CS_2$  with cellulose. The viscous solution is obtained, is called viscose, which is then forced through

a spinnerette into an acid solution to regenerate cellulose in the form of fine filaments yielding rayon thread.



⇒ Extrusion of viscose through a narrow slit and subsequent-regeneration gives thin sheets known as Cellophane.

Constitution of cellulose:-

⇒ The elementary analysis indicates that cellulose has empirical molecular formula  $(C_6H_{10}O_5)_n$

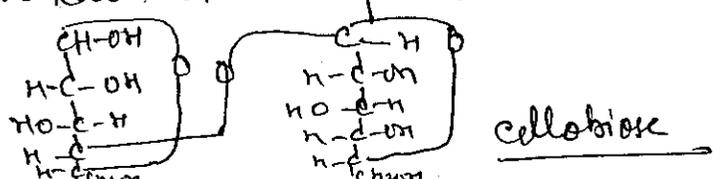
⇒ On acidic hydrolysis cellulose gives quantitative yield of D glucose suggests that it has D glucose unit.

⇒ Methylation, acetylation and nitration of cellulose produces a trisubstituted product thus each glucose unit is present thus have three free OH groups in uncombined state.

⇒ Hydrolysis of fully methylated cellulose gives 2,3,6-tri methyl-D-glucose (0.6%) and 2,3,4,6 tetra-O-methyl-D-glucose (0.6%) without any Di methyl glucose. This hydrolysis led to following results

⇒ (1) The formation of 2,3,6 tri-methyl-O-D glucose indicates that in cellulose free hydroxyl groups are present at C<sub>2</sub>, C<sub>3</sub> & C<sub>6</sub>, and position no C<sub>4</sub> & C<sub>5</sub> are occupied.

⇒ When cellulose is subjected to acetylation (simultaneous acetylation and hydrolysis) <sup>carried out by mixture of acetic anhydride & H<sub>2</sub>SO<sub>4</sub> (conc.)</sup>, cellulose form cellobiose octa-acetate, which suggests that glucose unit is present as a pyranose form i.e. C<sub>5</sub> is involved in ring formation and thus glucose unit are linked with each other by C<sub>1</sub>-C<sub>4</sub>. (Cellobiose is disaccharide)

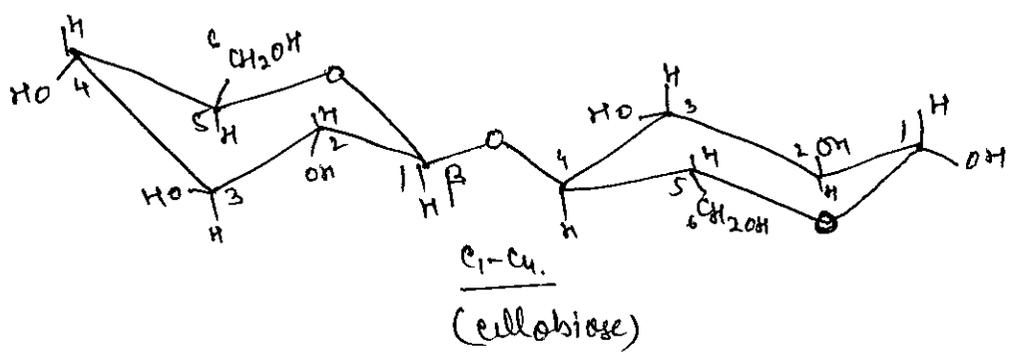


Formation of cellobiose does not indicate the linkage of unit i.e. it is either  $\alpha$  or  $\beta$ .

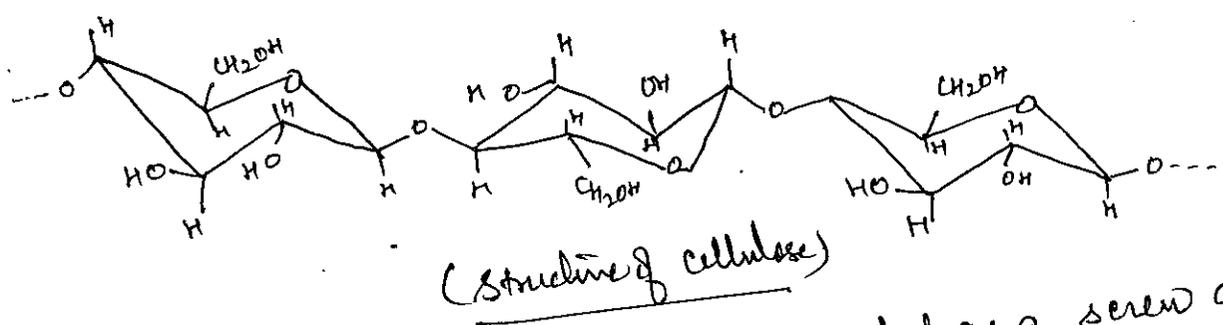
By gentle acidic hydrolysis of cellulose produces cellobiose, tetraose - pentaose and hexaose and lipase, suggests that have  $\beta$  link between C-1-C-4. (from the calculation of the optical rotations)

cellobiose is hydrolysed by emulsin (enzyme) not by maltase, showing thereby that D glucose units are joined by a  $\beta$ -linkage. (diastereomer amylose)

Formation of no di-substituted-methyl glucose suggests that cellulose has linear structure not a branched chain.



We therefore, conclude that  $\beta$  cellobiose is the structural unit of the cellulose polymer.



Cellulose molecule is not planar, but has a screw axis, each glucose unit being at right angles to the previous one. Although free rotation between C-O-C might appear at first sight. The long chains are held together by hydrogen bonding and thus cellulose is a brickwork three dimensional structure and that makes it water insoluble.