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For: M.Sc. Semester II
Paper: CC VIII (CBCS)
Unit: IV ; Topic – Carbohydrate (IInd lecture)

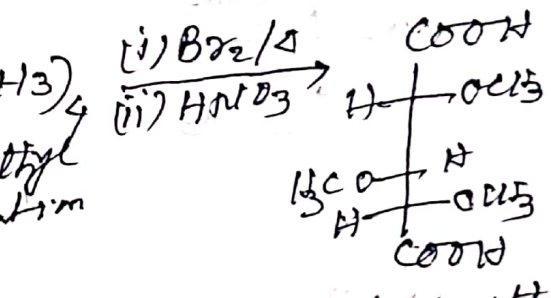
Some Important Informations about Carbohydrates

1. Determination of the ring size of the hexoses

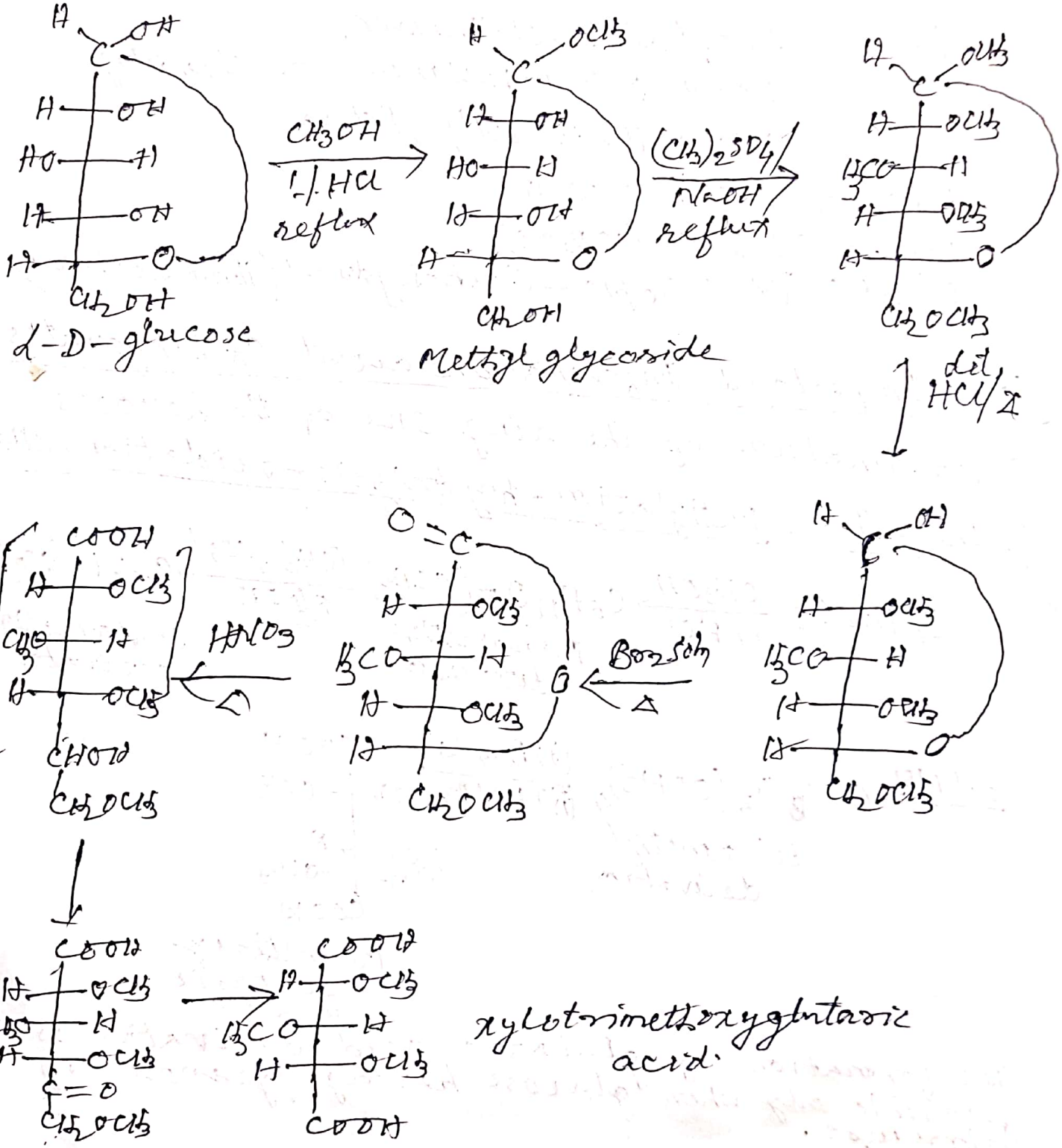
Method I → Methylation – hydrolysis – oxidation method

$C_6H_{12}O_6 \xrightarrow[1\%\ HCl]{CH_3OH} C_6H_{11}O_5(OCH_3)$ (Monomethyl derivative) $\xrightarrow[NaOH]{(CH_3)_2SO_4} C_6H_7O(OCH_3)_5$ (Pentamethyl derivative)

$\xrightarrow{dil\ HCl} C_6H_8O_2(OCH_3)_4$ (tetramethyl derivatim) $\xrightarrow[(ii)\ HNO_3]{(i)\ Br_2/\Delta}$ trimethoxy glutaric acid.



The formation of glutaric acid derivative is possible only when glucose having pyranose ring structure.

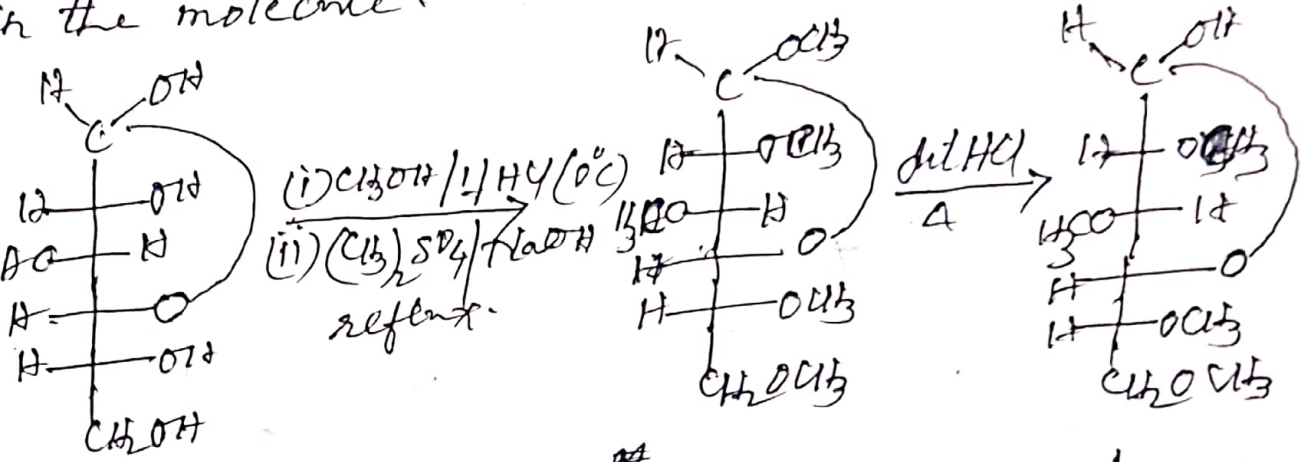


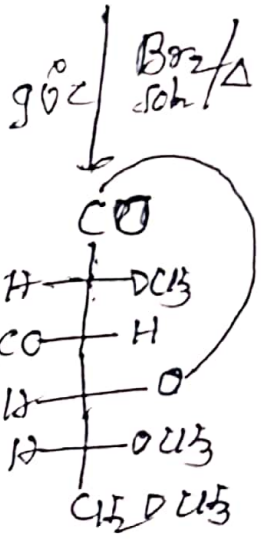
α-D-glucose

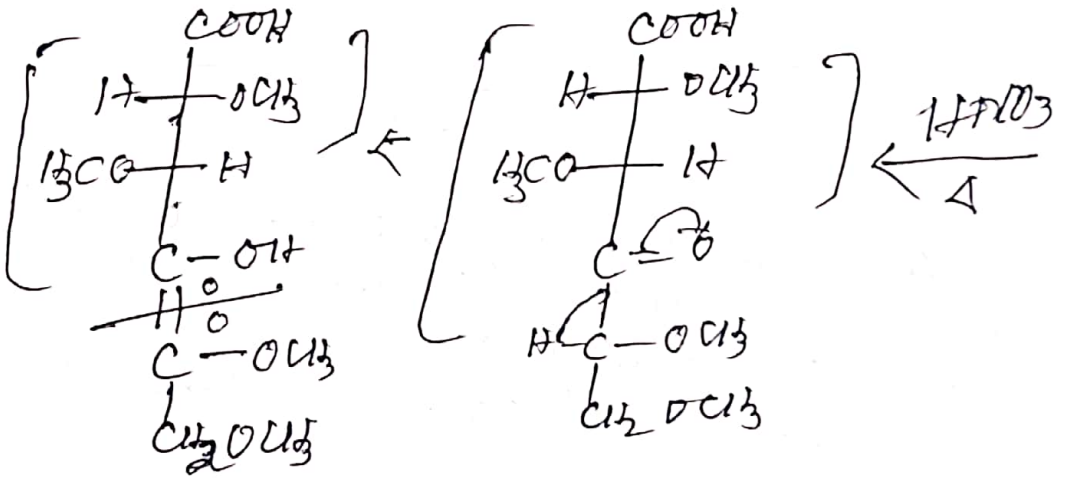
Methyl glycoside

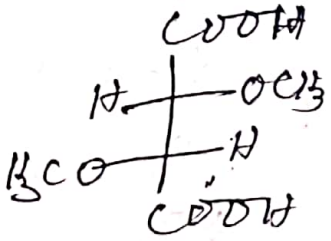
xylotrimethoxyglutaric acid.

The formation of tartaric acid derivative will indicate the presence of the furanose ring in the molecule.







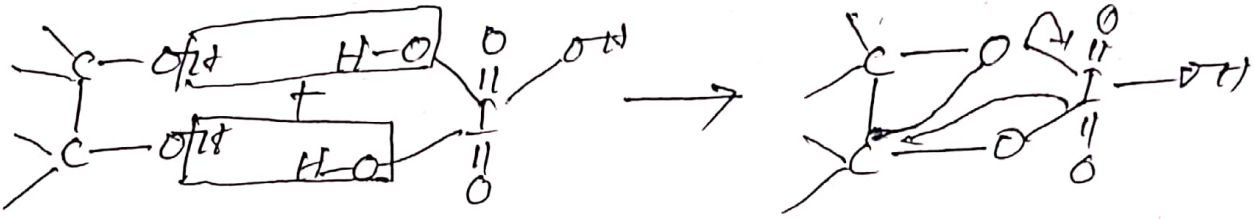


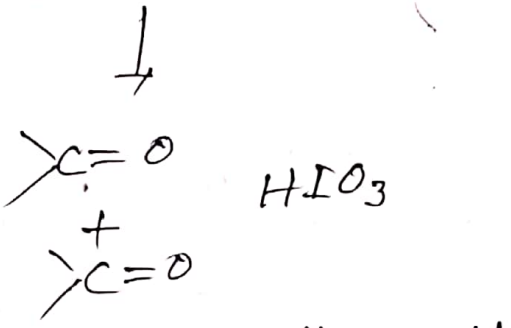
Now the question arises that ~~the~~ which ring is actually present with the glucose. It was found that methyl glycoside prepared at reflux temperature actually gives glutaric acid derivative and the methyl glycoside obtained at 0°C, gives tartaric acid derivative. Hence this experimental evidence is not sufficient to predict actual ring size.

Method II : Periodic Acid Degradation Method.

Periodic acid is mainly used for the degradation and the oxidation of the compounds having vicinal diol, α-hydroxy carbonyl compounds etc.

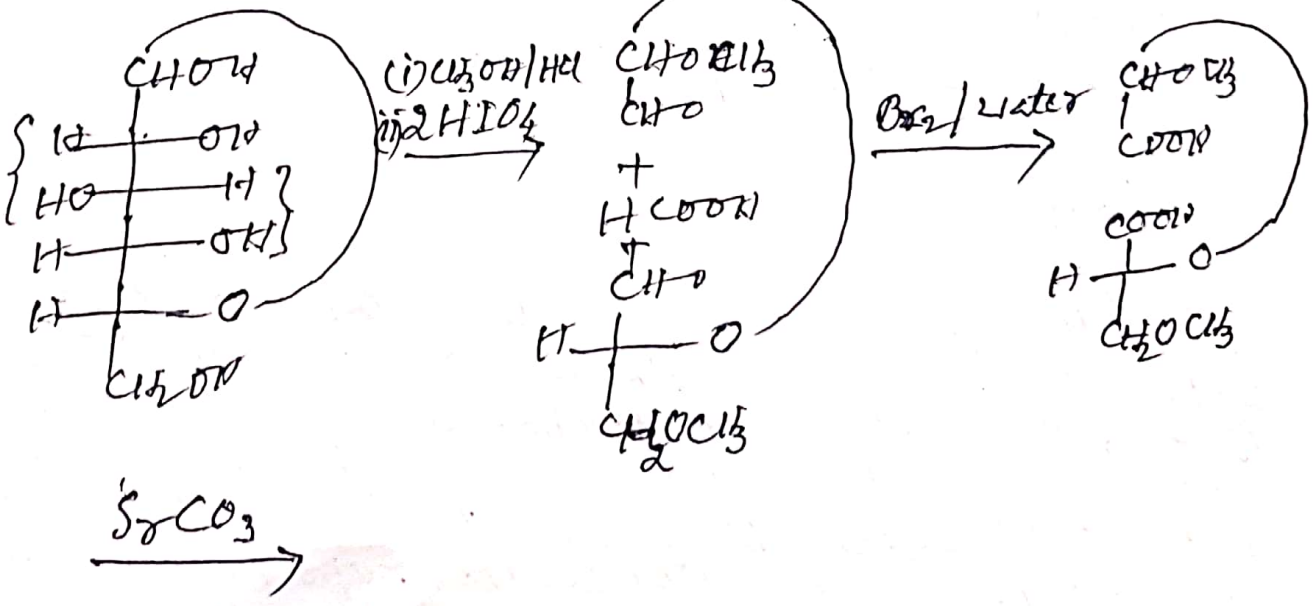
$$HIO_4 + H_2O \rightleftharpoons H_3IO_5$$

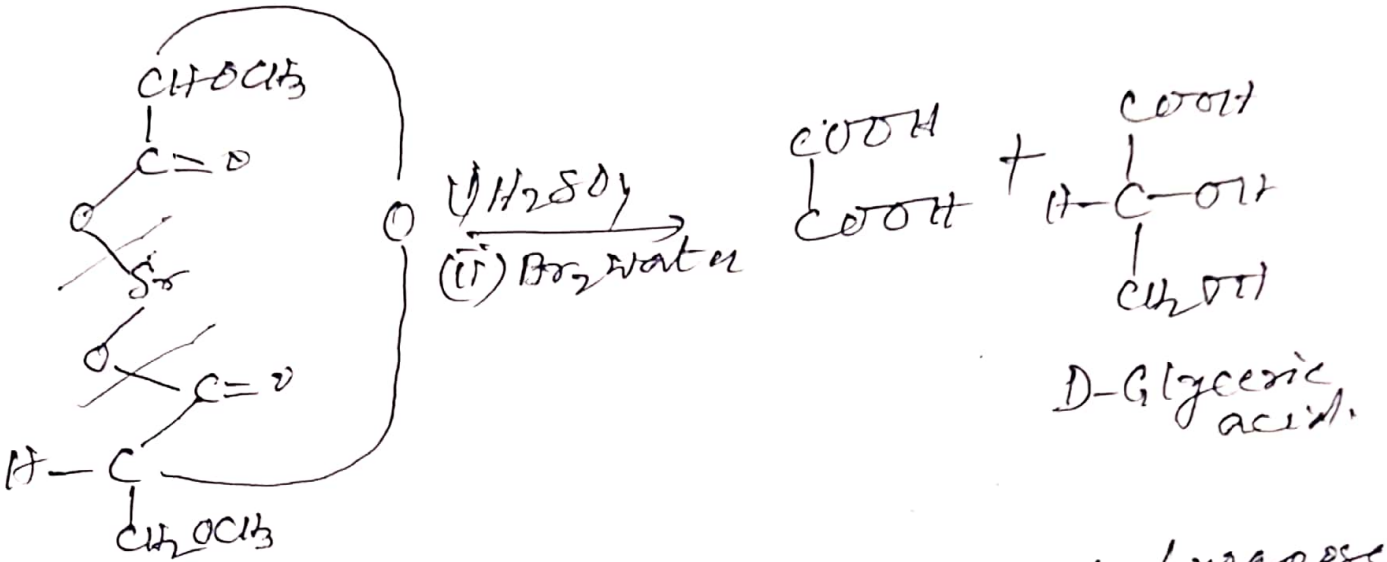




$>C=O$ + $>C=O$ $\quad HIO_3$

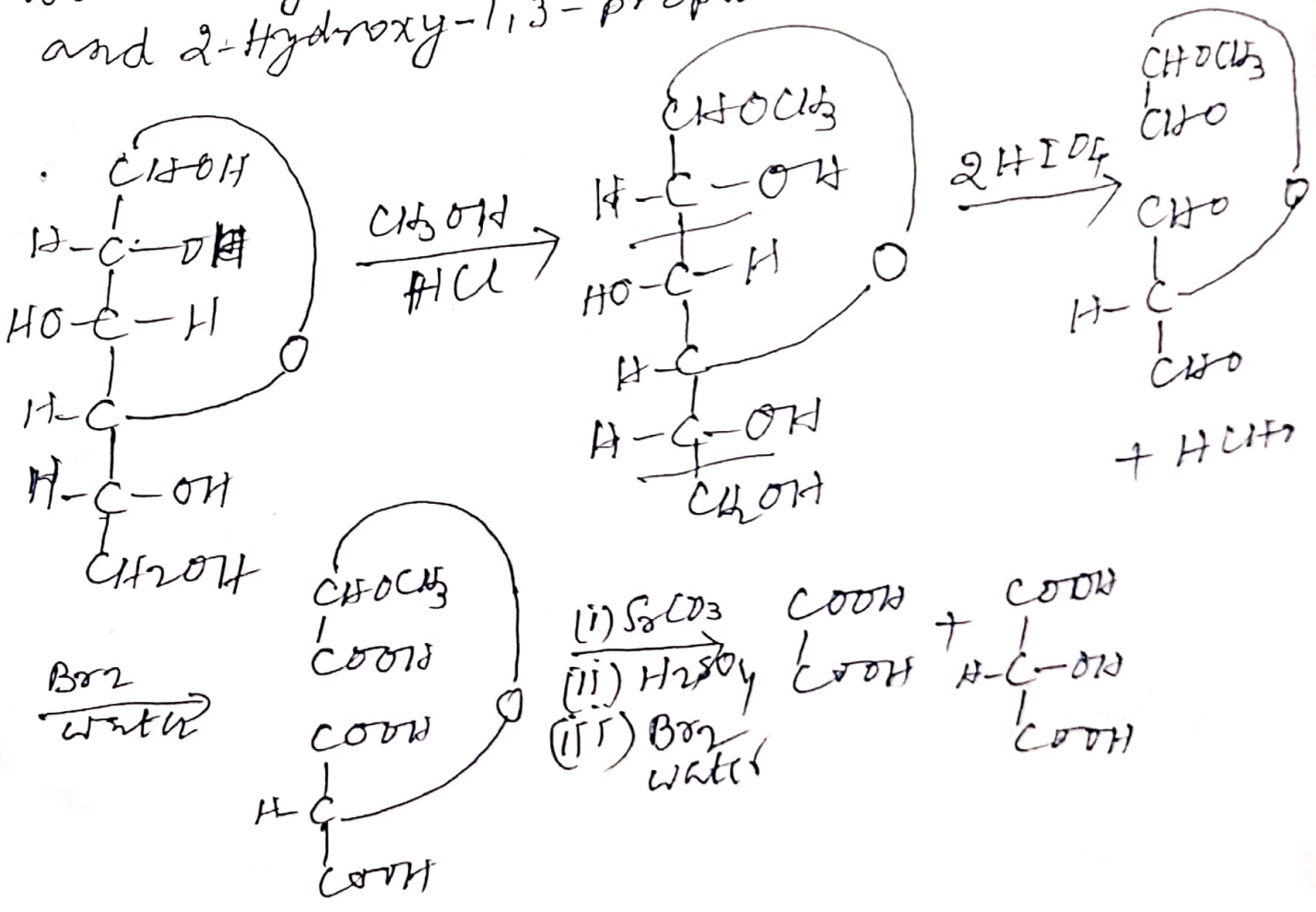
In order to determine the ring size, the methyl glycosides of hexose is allowed to react with HIO_4 and it was found that only two moles of the reagent was consumed with the release of 1 mole of HCOOH





This indicates the presence of pyranose ring in the aldohexoses.

But if the furanose ring is expected, the methyl glycoside of glucose would generate 1 mole HCHO, oxalic acid and 2-Hydroxy-1,3-propanedioic acid.



Mutarotation: The change in the optical rotation in a sugar when it is added in water.

It is the characteristic of a reducing sugar. Here the optical rotation slowly changes to another constant value.

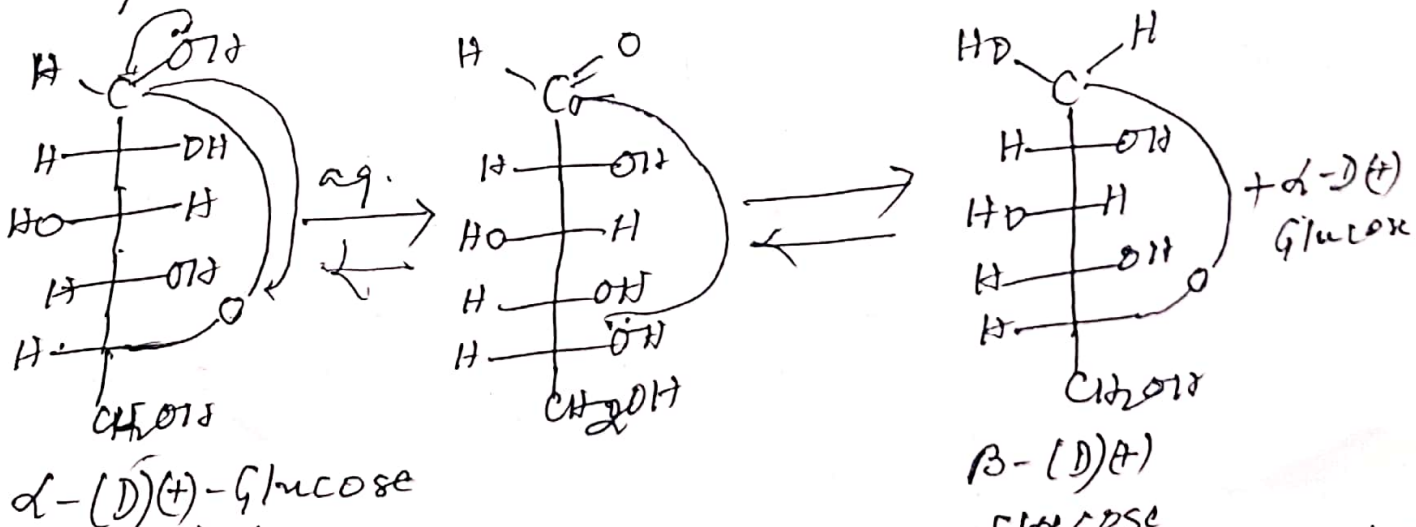
$$\alpha\text{-D(+) Glucose} \underset{}{\overset{aq.}{\rightleftharpoons}} \text{Glucose solution}$$

$$[\alpha]_D = +112^\circ \qquad [\alpha]_D = +52.5^\circ$$

$$\beta\text{-D(+)-Glucose} \overset{aq.}{\rightleftharpoons} \text{Glucose solution}$$

$$[\alpha]_D = +19.5^\circ \qquad [\alpha]_D = +52.5^\circ$$

It is believed that when any form of glucose is added in water, the ring opening starts and glucose may acquire another form. An equilibrium is slowly establish to acquire maximum stability in the solution.



α-(D)(+)-Glucose solid

β-(D)(+) Glucose

As the optical rotation is concentration dependent, the change in optical rotation starts with the dissolution and at equilibrium it

became constant.

The muta-rotation is not observed in the methyl glycoside of the reducing sugars.

Hence, the opening of the ring in a monosaccharide is due to the presence of the -OH group on the anomeric carbon. The carbonyl groups in the solution can only give the positive Tollen's test, phenylhydrazine test etc.