Carbohydrates

5th Sem
Lecture – 2
Paper – CC12

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Establishment of the openchain structure of fructose:

Structure of fructose may be establish on the basis of following observations:-

(i) Elimental analysis and M.W determination of fructose show that it has molecular formula $C_6H_{12}O_6$.

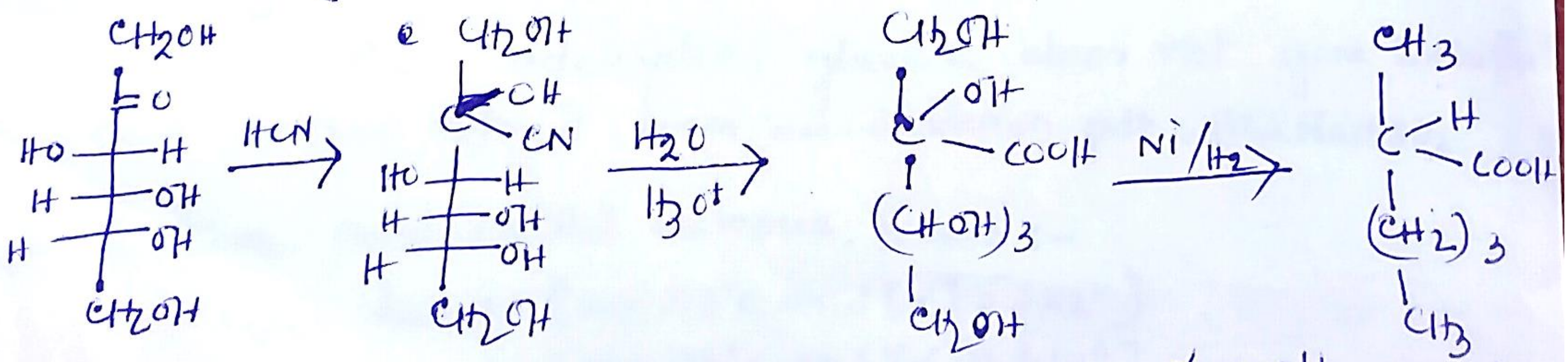
ii) Fructose on reduction with ~~HI~~ ~~or~~ [Na(Hg)/H_2O] gives sorbitol ~~with~~ which on reduction with HI and P_4 gives n-hexane. This indicates the presence of six carbon in a straight chain.

(iii) Fructose reacts with HCN, NH_2OH and $PhNHNH_2$, which indicates the presence of >C=O group.

(iv) Fructose does not react in Br_2/H_2O which indicate the absence of –CHO group.

(v) On oxidation with HNO_3, a mix^r of trihydroxy glutaric acid, tartaric acid and glycolic acid → all these acids contain fewer carbon atoms than fructose, the carbonyl group must be present as keto group.

(vi) That fructose is a 2-ketohexose is shown by the following reac^n sequence.



α-methyl caproic acid

(XII) The presence of five $-OH$ groups is also indicated by the formation of pentaacetate with Ac_2O.

– Base on above observation, the st. chain str. of fructose is as: $HO-CH_2-\overset{O}{\overset{\|}{C}}-(CHOH)_3-CH_2OH$

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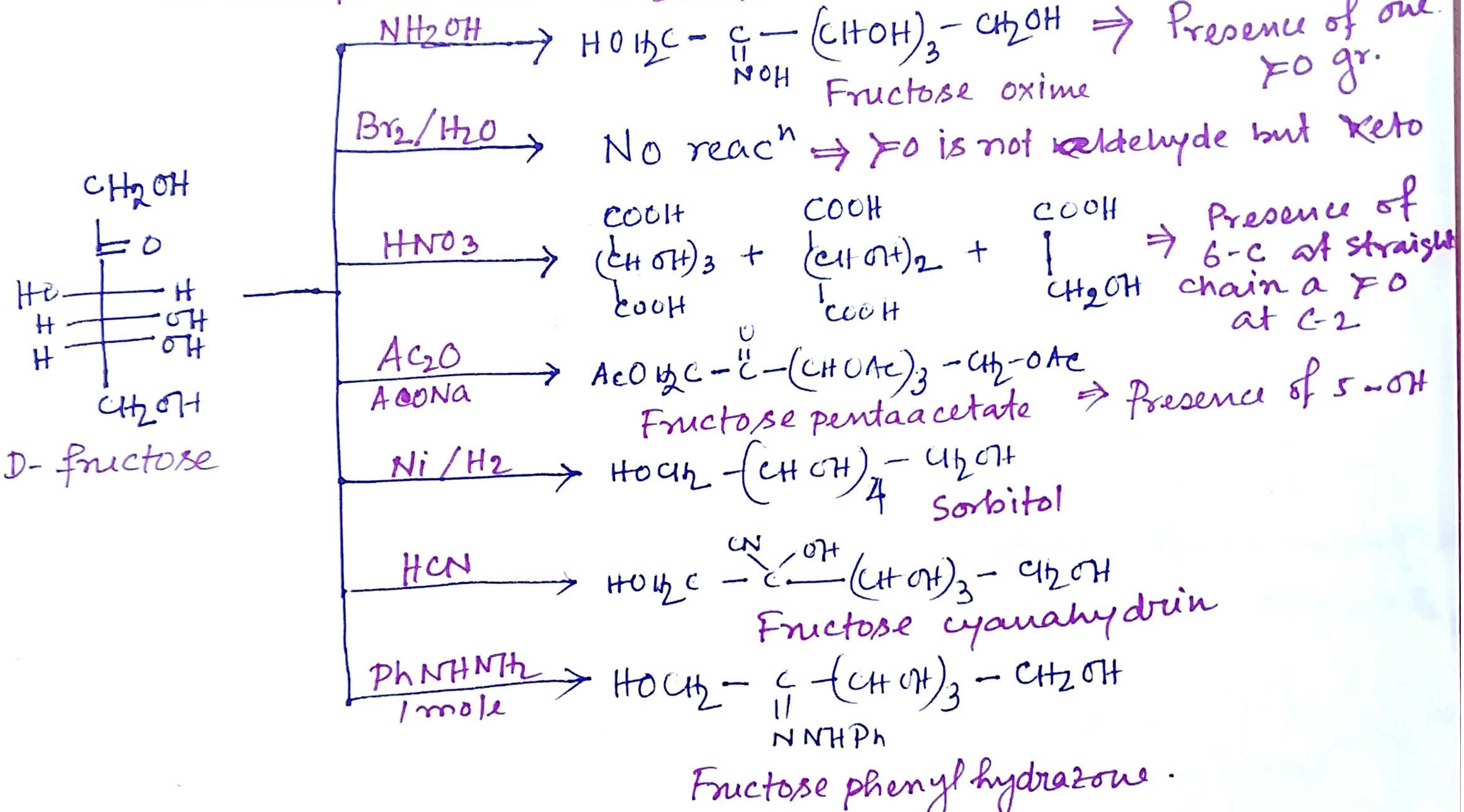
Some typical reac^n of fructose



Cyclic structure of D(+) glucose :-

Open chain structure of glucose fails to explain the following points, which is the basis of its cyclic structure:

(i) Unlike other aldehydes, glucose does not give Schiff's test neither does it form an addition pdt with $NaHSO_3$

(ii) Glucose exist in two isomeric forms :-

α-D-(+)-glucose (mp 146°c and $[\alpha] = +112°$)

β-D-(+) glucose (mp 150°c and $[\alpha] = +19°$)

(iii) Aldehyde, when treated with alcohols in the presence of HCl forms acetals by consuming two molecules of alcohols

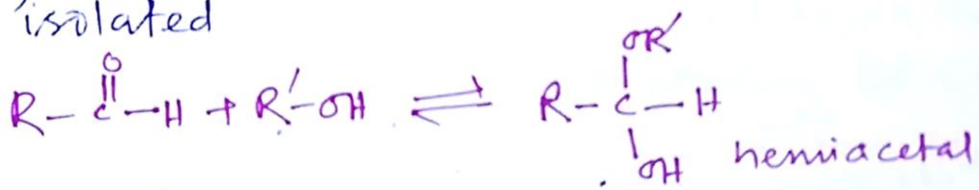
$$R-CHO + 2CH_3OH \xrightarrow{H^+} R-CH\begin{matrix} OCH_3 \\ OCH_3 \end{matrix}$$

Glose however, consumes only one molecule of alcohol in presence of dry HCl to form a mix^r of two crystalline isomeric acetals called methyl glucosides. This results cannot be explained by open chain str. of glucose.

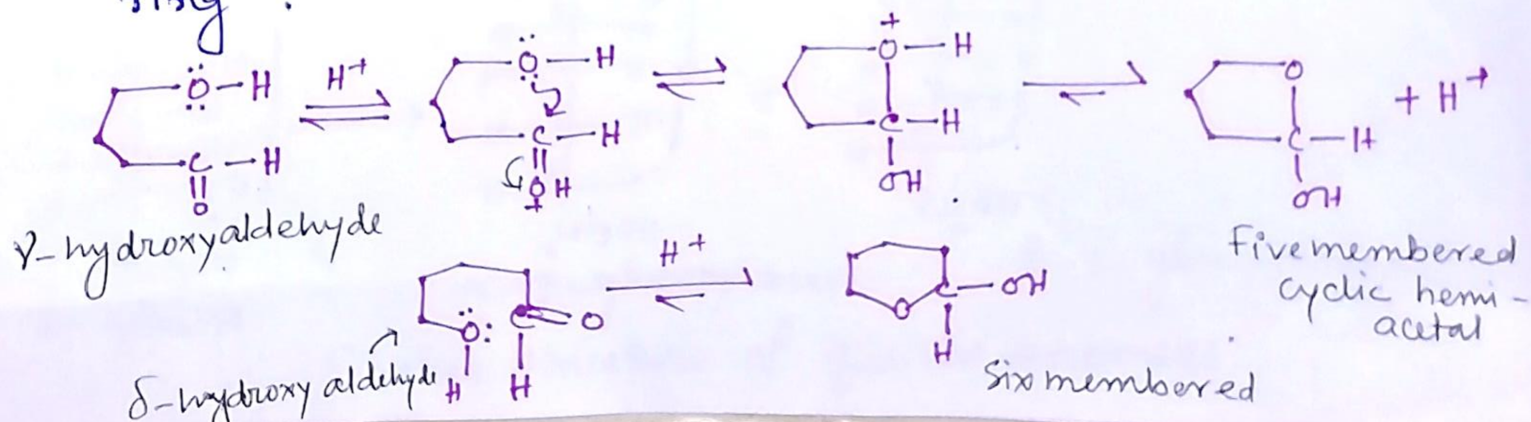
(iv) Mutarotation phenomenon cannot be explain by open chain str. of glucose.

cyclic str. of glucose & other aldohexose:

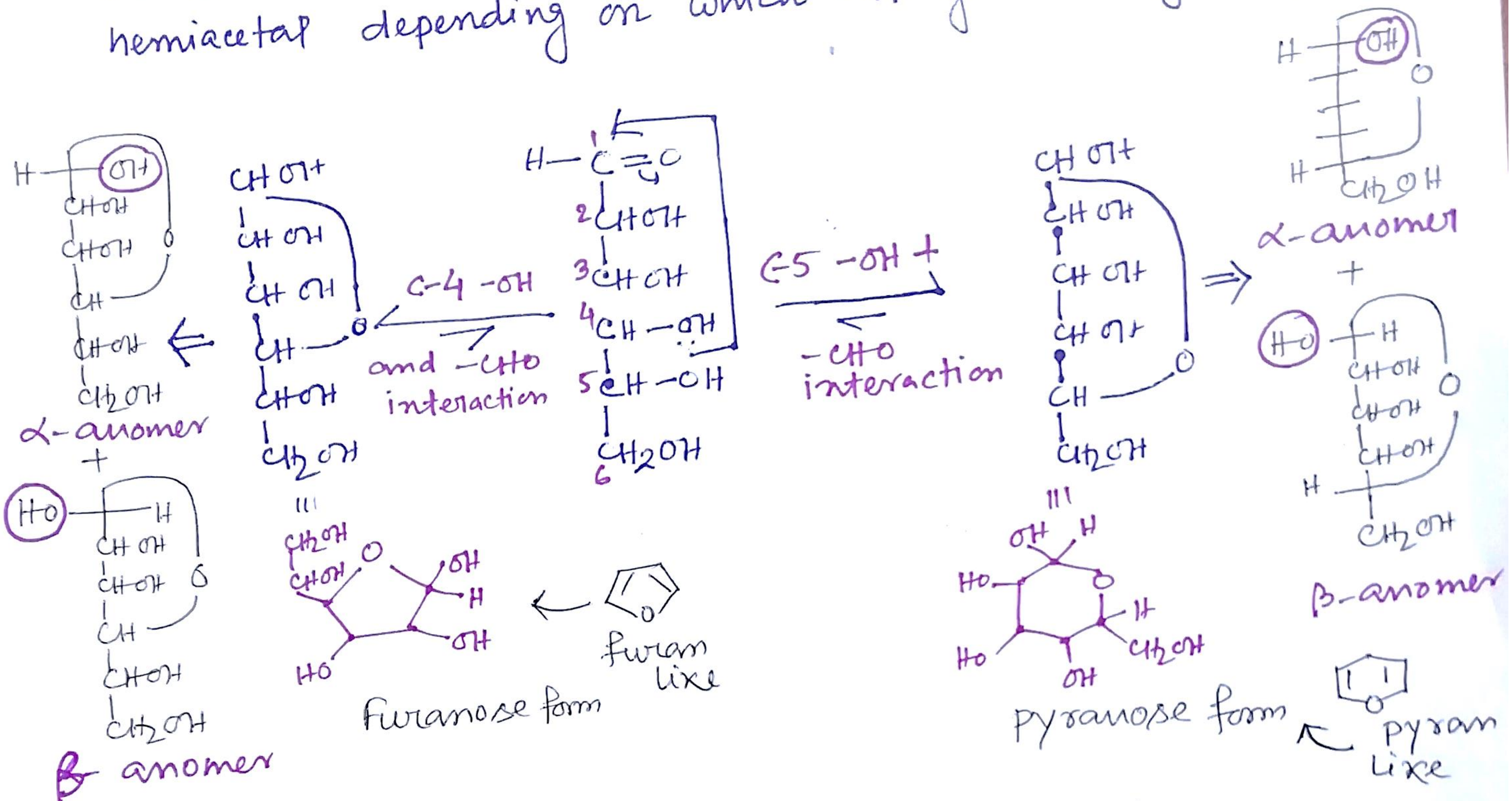
We know that an ~~CHO~~ aldehyde reacts with one molecule of an alcohol to form a hemiacetal which is not stable and decompose spontaneously to the aldhyde and alcohol. Therefore hemiacetals are rarely isolated



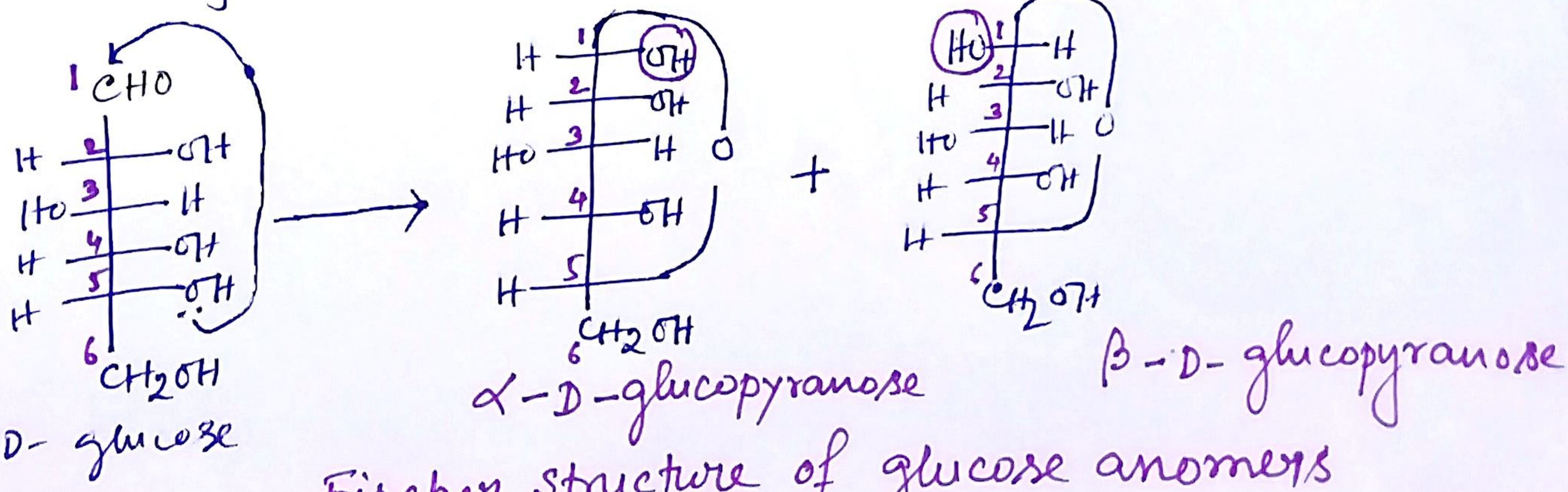
Now if –CHO and –OH groups are present in same molecule, a cyclic hemiacetal is formed which are stable if they results in five or six membered ring.



The same is true for sugars. Although sugars are often written by convention as acyclic carbonyl compd, they exist predominantly as cyclic hemiacetals. An aldohexose can exist as either a five-membered or six-membered cyclic hemiacetal depending on which -OH gr undergoes cyclisation.

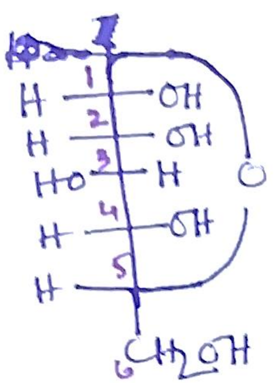


* The two faces of >C=O are diastereotopic and hence cyclisation leads to two diastereoisomers. In this case a new chiral centre is generated at C-1 and hence two isomers are formed differing in configuration at C-1. Such a pair of diastereoisomers which differ in configuration at C-1 are called anomers. The isomer having -OH at right is called α-anomer and -OH at the left is called β-anomer.

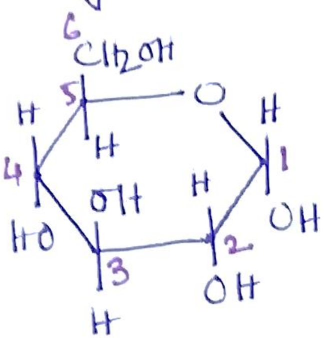


Fischer structure of glucose anomers

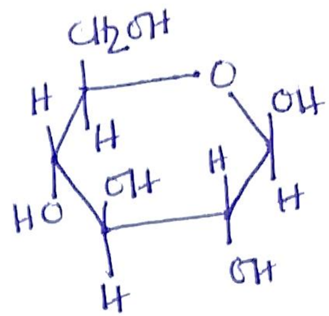
Haworth structure :- In Haworth str. drawn with the heterocyclic oxygen in the upper right corner, The groups on the left of F.P.F are up and those on the right are down in Haworth structure.



F.P.F

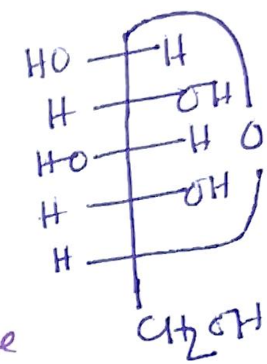


α-D-glucopyranose



β-D-glucopyranose

↳ Haworth str. ↲



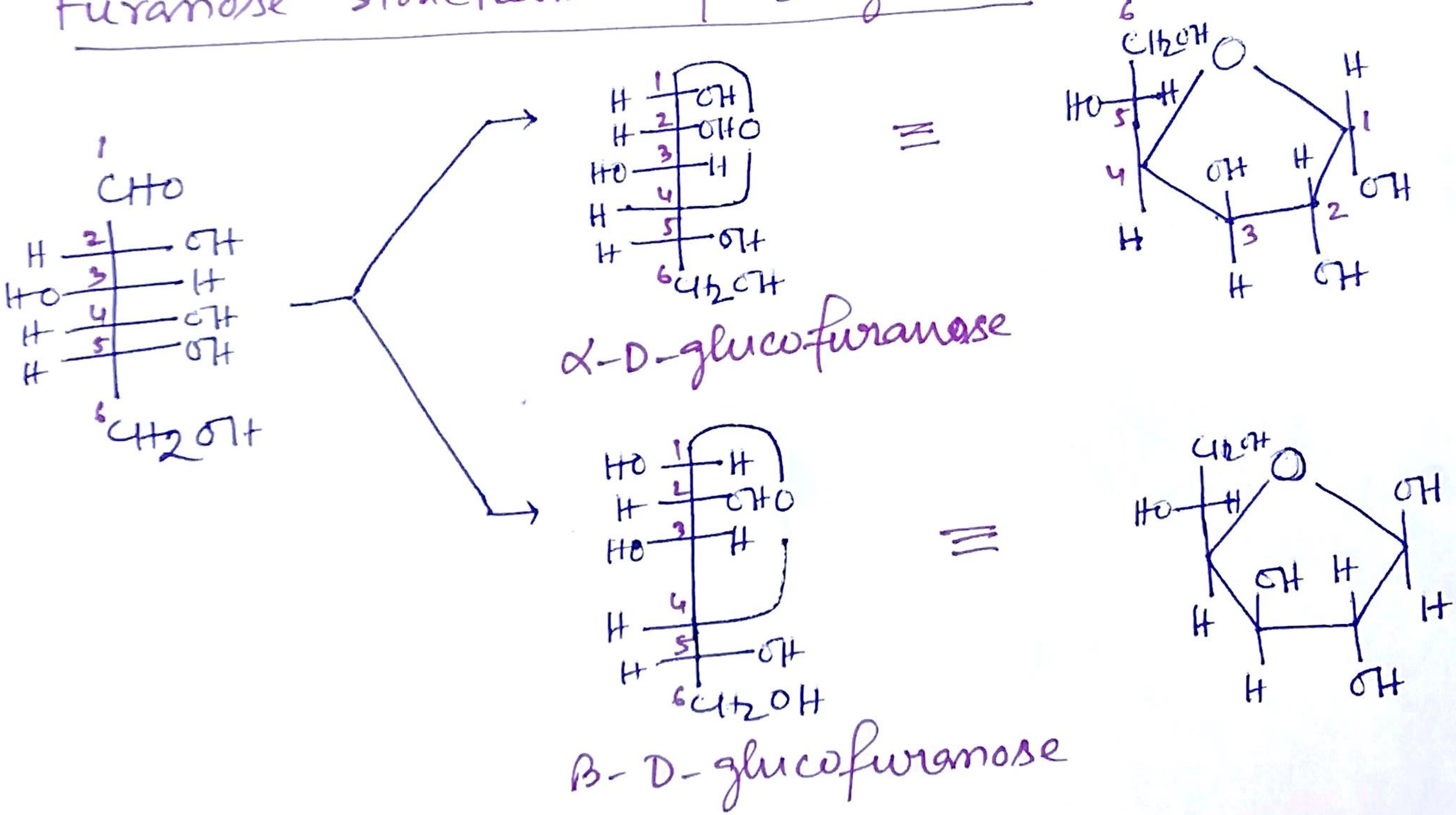
F.P.F

L → U

R → D

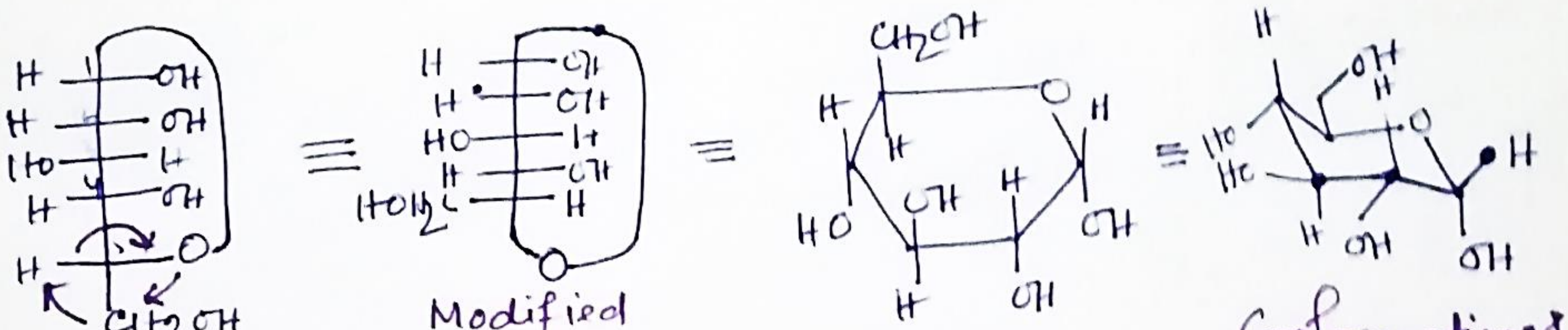
ডান → Down

Furanose structure of D-glucose



Conformational representation of cyclic structure of monosaccharides

The conventions used to draw Haworth structures can be extented to conformation diagram. In the chain conformation the ring oxygen atom is located at the upper right and groups to the left in F.P.F are drawn upward from the ring. Axial and equitorial positions will logically follow

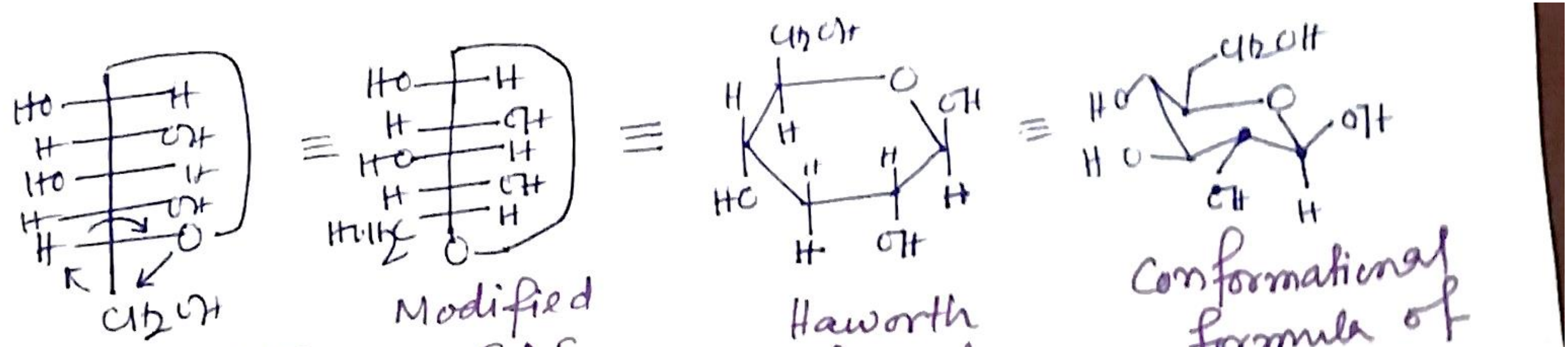


Common F.P.F of α-D-glucopyranose

Modified F.P.F

Haworth formula

Conformational formula of α-D-glucopyranose



Common F.P.F of β-D-glucopyranose

Modified F.P.F

Haworth formula

Conformational formula of β-D-glucopyranose

F.P.F → Conformation formula / chair conformation

Right groups → Downwards

Left side groups → Upward

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