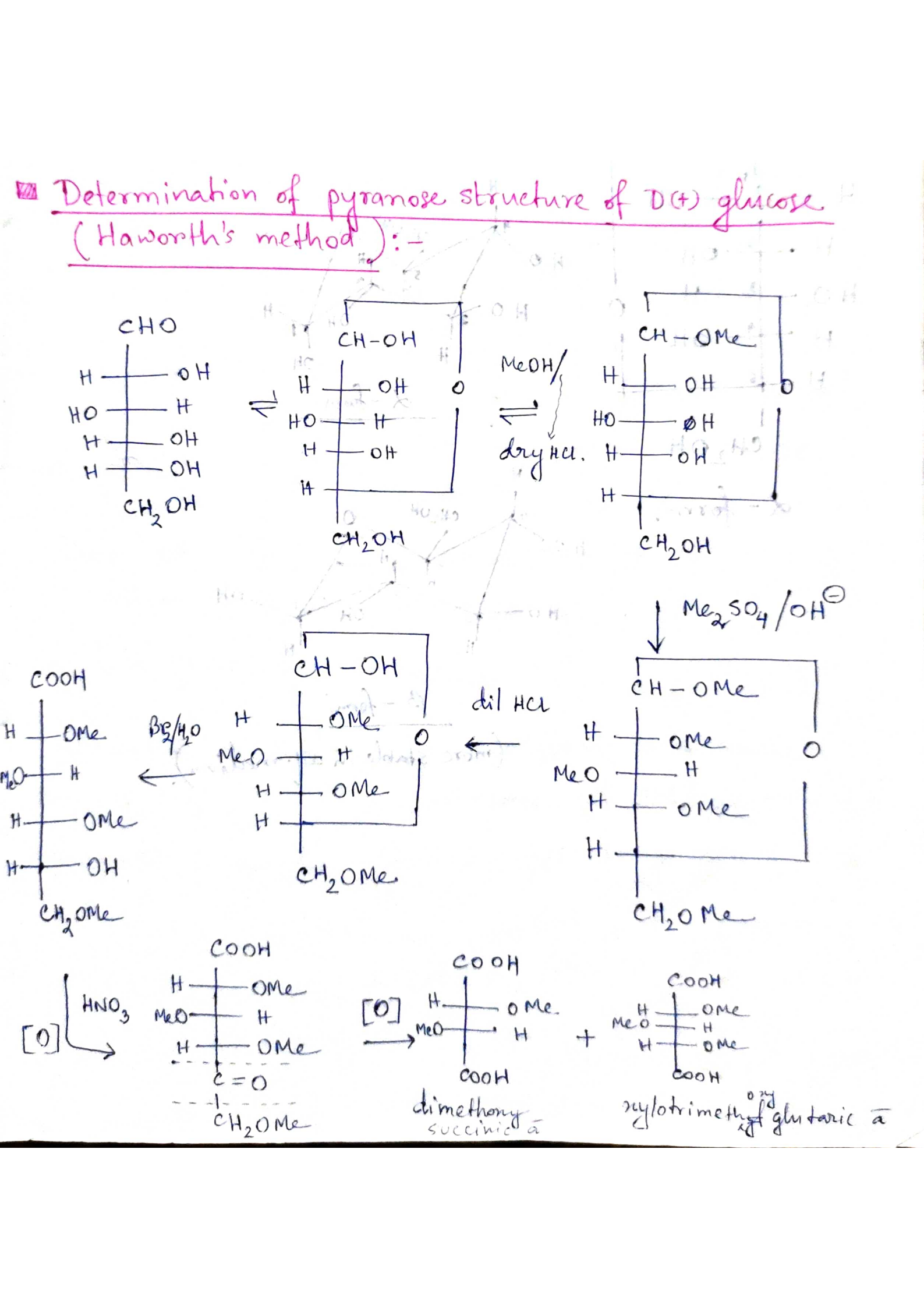
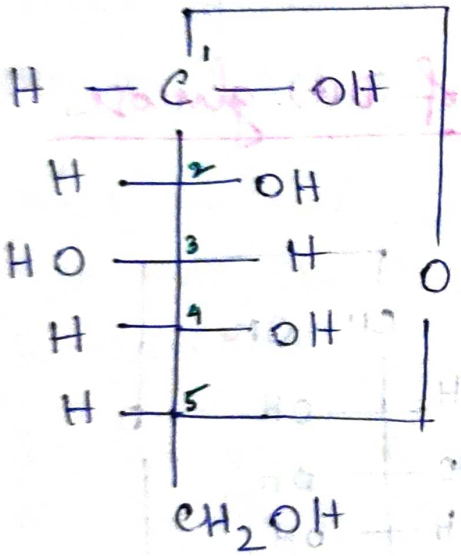
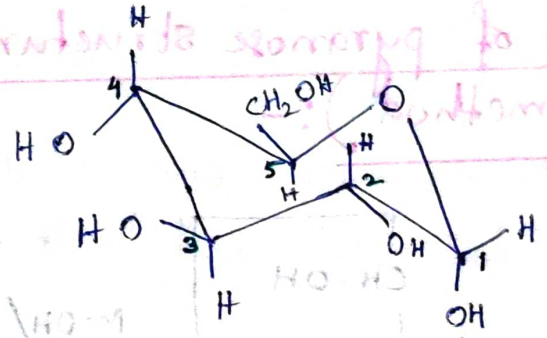
Determination of pyranose structure of D(+) glucose (Haworth's method):-



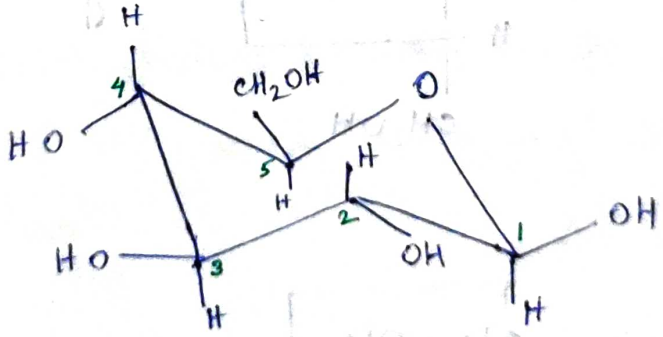
Formation of xylo-trimethoxy glutaric ā and dimetho-xy succini ā from the above degradation exp. are possible if we have a free $-CHOH$ gr. at C_5 position. This suggest that during hemiacetal ring formation OH gr. at C_5 aldohexose must participate and this centre has remain methylated during methylation with Me_2SO_4 and NaOH. So, it it confirmed that methyl -D-glucoside is 6 membered pyran ring.



α-form.



α-form

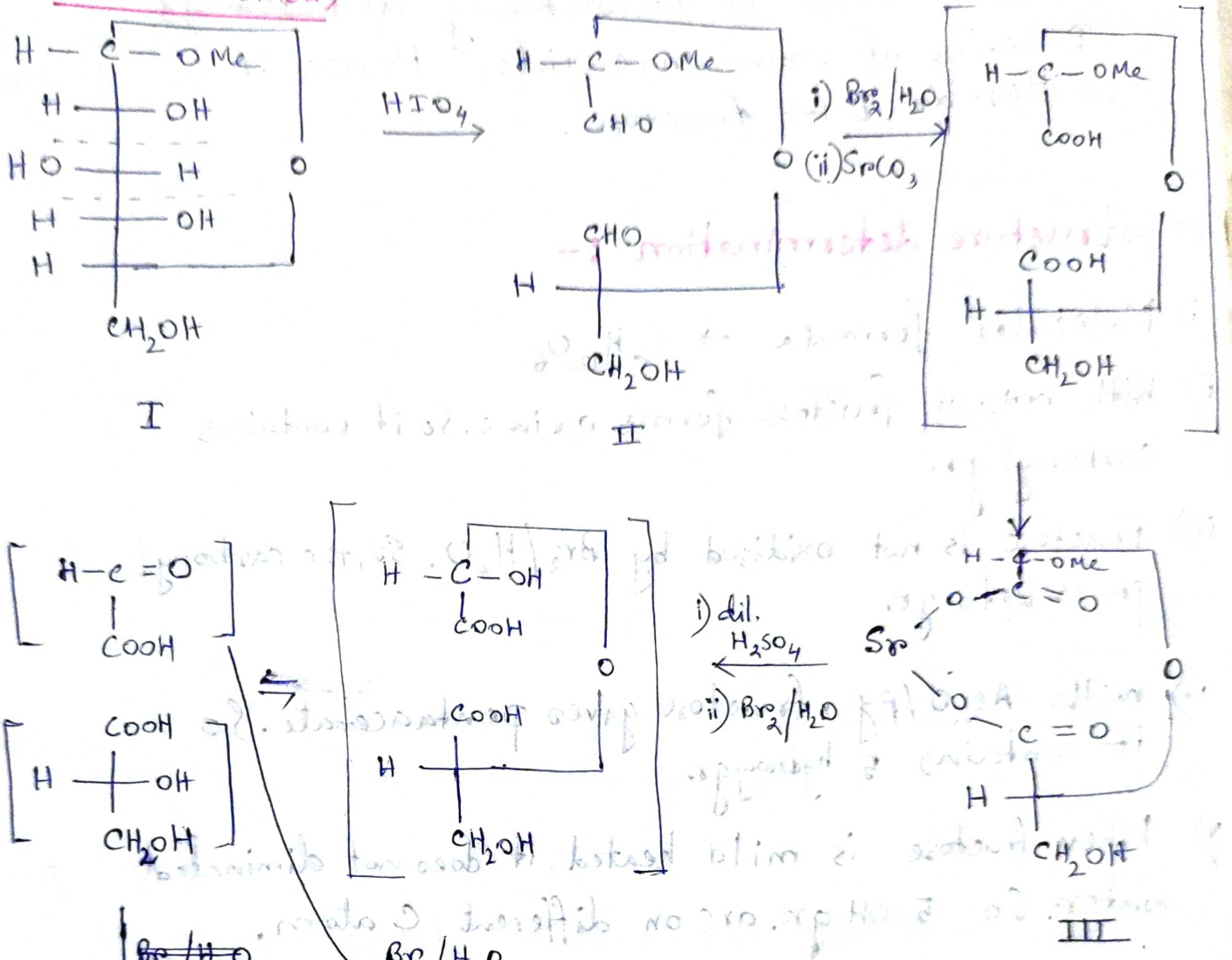


β-form

(more stable in aq. medium).

Determination of pyranose structure of D(+) glucose by HIO_4 - oxidation method :-

(Hudson method)



Isolation of 2,3,4 along with formic ā & oxalic ā confirm that the ring structure of methyl α-D (+) glucoside is a six membered oxide ring.

D (-) Fructose :-

Natural fructose is laevorotatory and belongs to D-series of monoschacaride. Hence it is written as D (-) fructose.

Structure determination :-

i) Molecular formula → $C_6H_{12}O_6$

ii) With NH_2OH, fructose forms oxime. So it contains carbonyl gr.

iii) Fructose is not oxidised by Br_2/H_2O. So, the carbonyl gr. is keto gr.

iv) With Ac_2O/Py, fructose gives pentaacetate. So it contains 5 hydroxy gr.

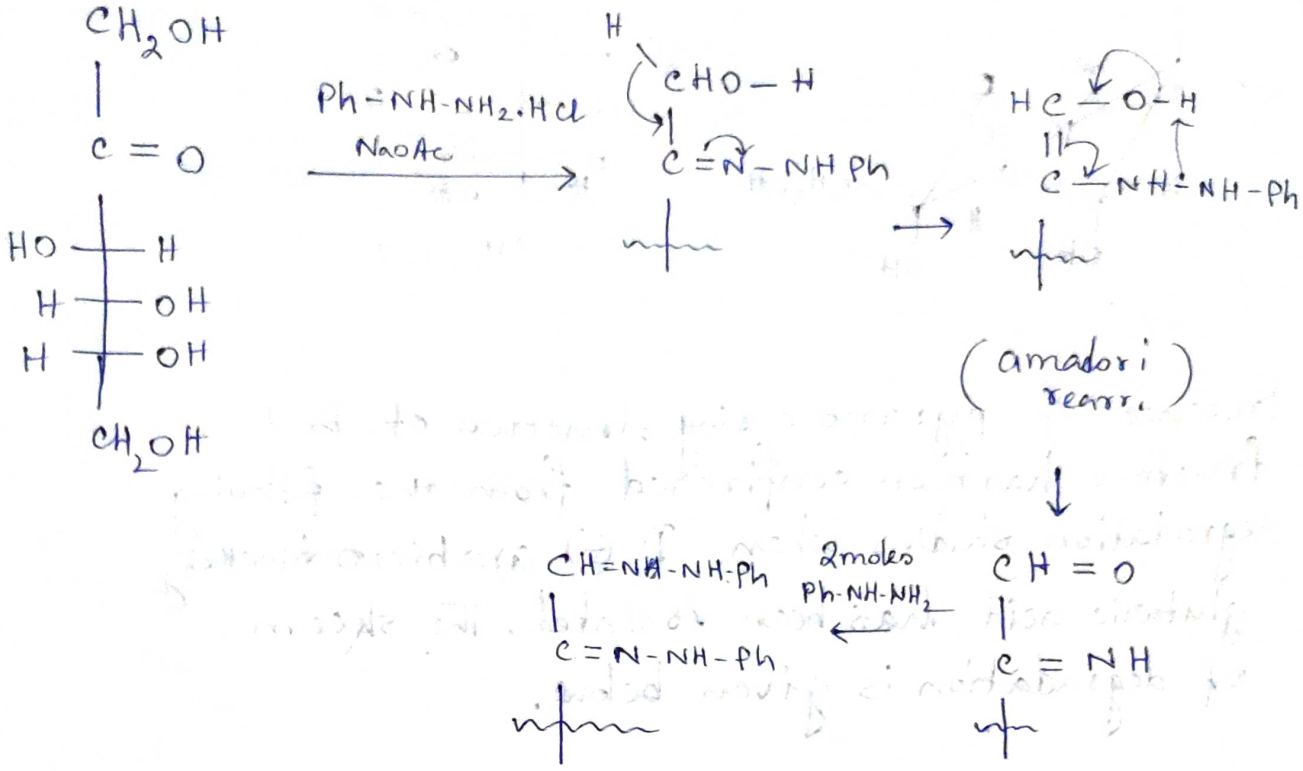
v) When fructose is mild heated, it does not diminated water. So 5 -OH grs. are on different C atom.

vi) Reduction of fructose by Na/ale. followed by further reduction with red P/HI results normal hexane. So, fructose is a straight chain compovnd.

$$\text{Fructose} \xrightarrow{HCN} (A) \xrightarrow{H_3O^+} (B) \xrightarrow{\text{red P/HI}} \text{2-methyl-hexanoic acid}$$

The above exp. confirms that fructose contains C=O gr. at C_2.

vii) Both glucose and fructose gives same osazone. Since, osazone formation involves only C_1 & C_2, one can say that the configuration of C_3, C_4, C_5 of both glucose and fructose is same.



Osazone.

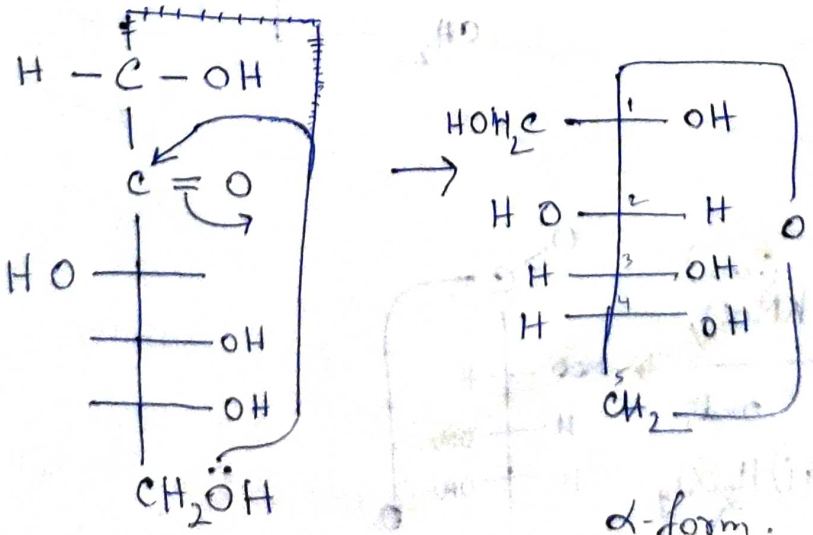
Ring structure of D(-) fructose :-

Evidence:

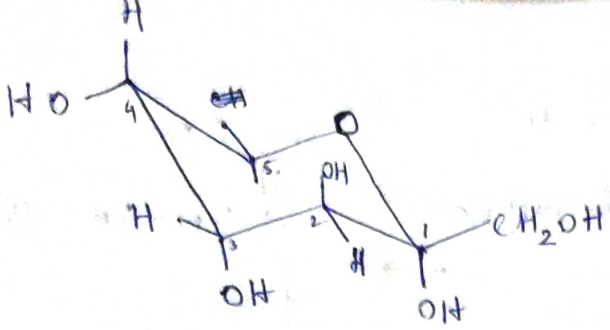
i) D(-) fructose exibits mutarotation like D(+) glucose.

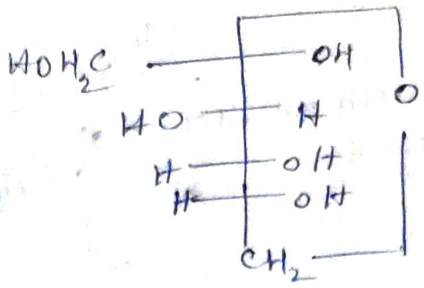
ii) In solution it exists α & β-form.

iii) D(-) fructose reacts with MeOH / dry HCl results methyl-D(-) fructoside, so ~~cyclic~~ hemiacetal form of D(-) fructoside is six membered ~~cycli~~ oxide ring.



α-form.





Presence of pyranose ring structure of D(-) fructose has been confirmed from the following degradation studies when D (-) arabino trimethoxy glutaric acid has been isolated. The skeem of degradation is given below.