

Paper III (c) Bsc.II -Hons

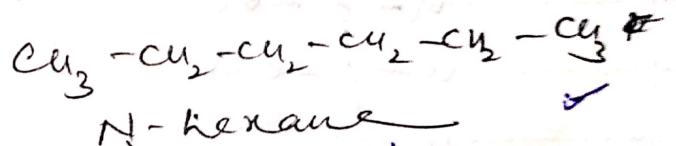
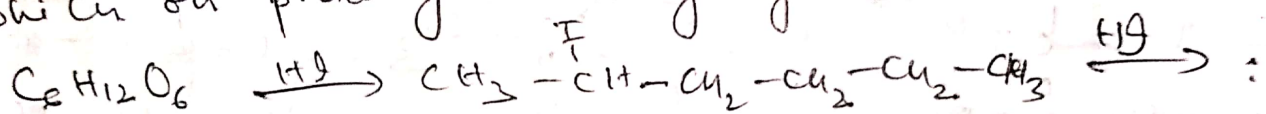
Constitution and Ring Structure of Glucose

by. Dr. Sarwat Tauheed
Deptt. Of chemistry

Constitution

① Structure of glucose follows from the following :-
elemental analysis, ~~100%~~ % age composition and
molecular wt. determination its mol. formula was
found to be $C_6H_{12}O_6$

② Glucose on reduction with HI gives 2-iodo hexane
which on prolong heating gives n-hexane.



This rxn indicates that glucose is a straight chain
Compound.

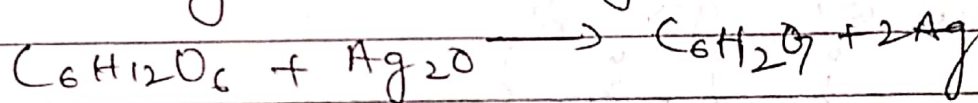
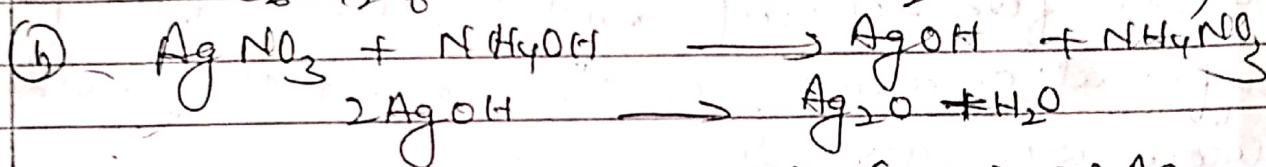
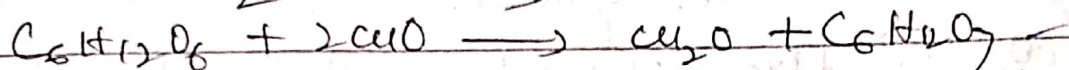
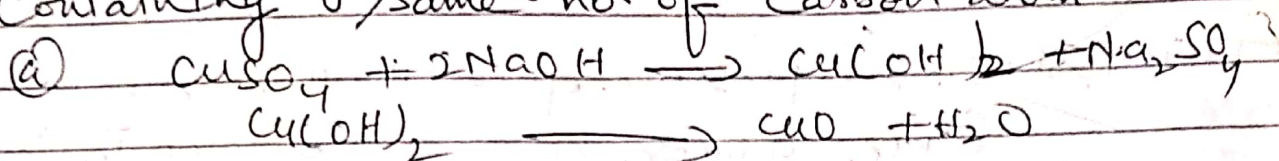
(3) Glucose dissolved in water giving neutral solution
 This suggests that it ~~does~~ does not contain -COOH group

(4) Glucose forms monoamine with hydroxyl amine

$$C_6H_{12}O_6 + H_2N-OH \rightarrow C_6H_{12}O_5 \cdot NH-OH + H_2O$$
 This indicates the presence of Carbonyl group

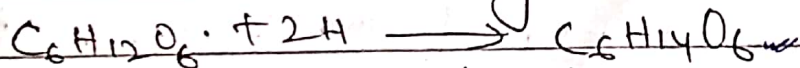
(5) Glucose reduces (a) Fehling solution

(a) Tollens' reagent giving red ppt. of Cu_2O and silver mirror being itself oxidised to gluconic acid containing same no. of Carbon atom.



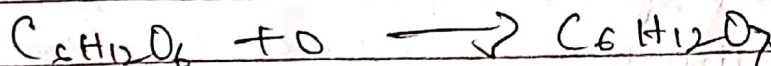
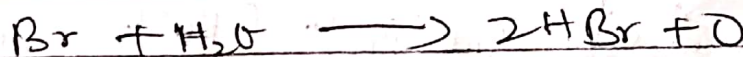
This indicates that Carbonyl group is in aldehyde form.

(6) Glucose on reduction give Sorbitol.



This also confirms the presence of aldehyde group.

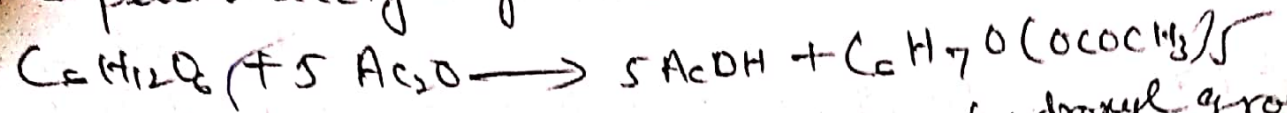
(7) Glucose is oxidised by Br_2 water to give gluconic acid, containing same no. of C-atom glucose has.



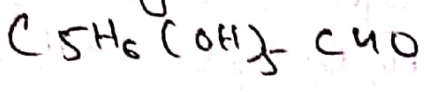
This also indicate the presence of (CHO) group

(8) Glucose reacts with five molecules of acetic anhydride

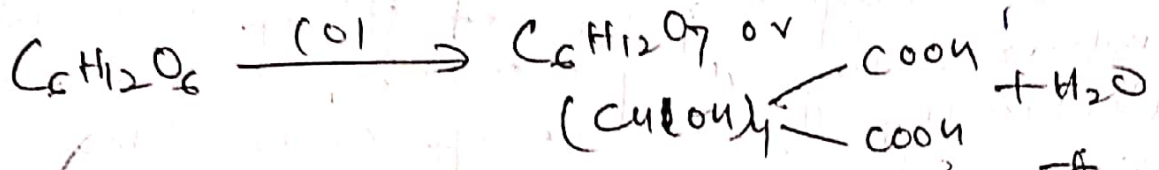
To give penta acetyl glucose.



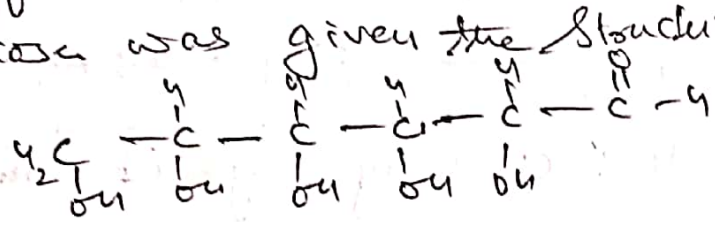
This indicates the presence of five hydroxyl groups in glucose - therefore glucose may be written as



(i) Glucose on oxidation with Nitric acid gives gluconic acid.

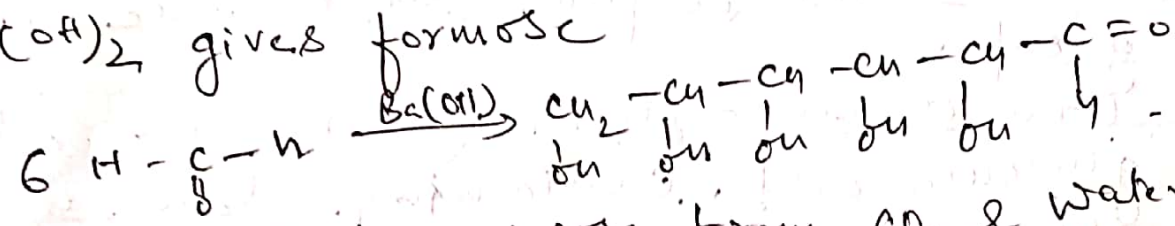


This shows the presence of $-CH_2OH$ at one terminal. Since glucose is a stable molecule, therefore all the five $-OH$ group must be linked with five different C -atoms. on the basis of above evidences glucose was given the structure

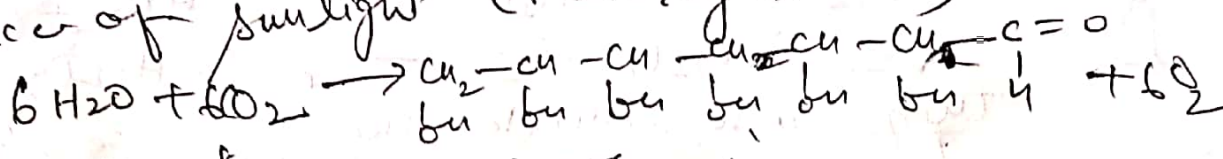


This structure is confirmed by synthesis -

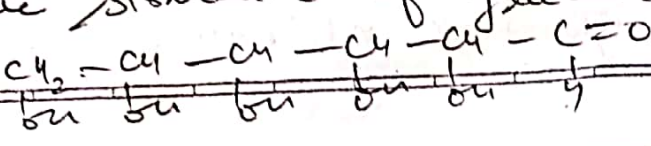
(i) Six member of formaldehyde in presence of $Ca(OH)_2$ gives formose



(ii) Plant synthesises glucose from CO_2 & water in presence of sunlight (Photosynthesis.)



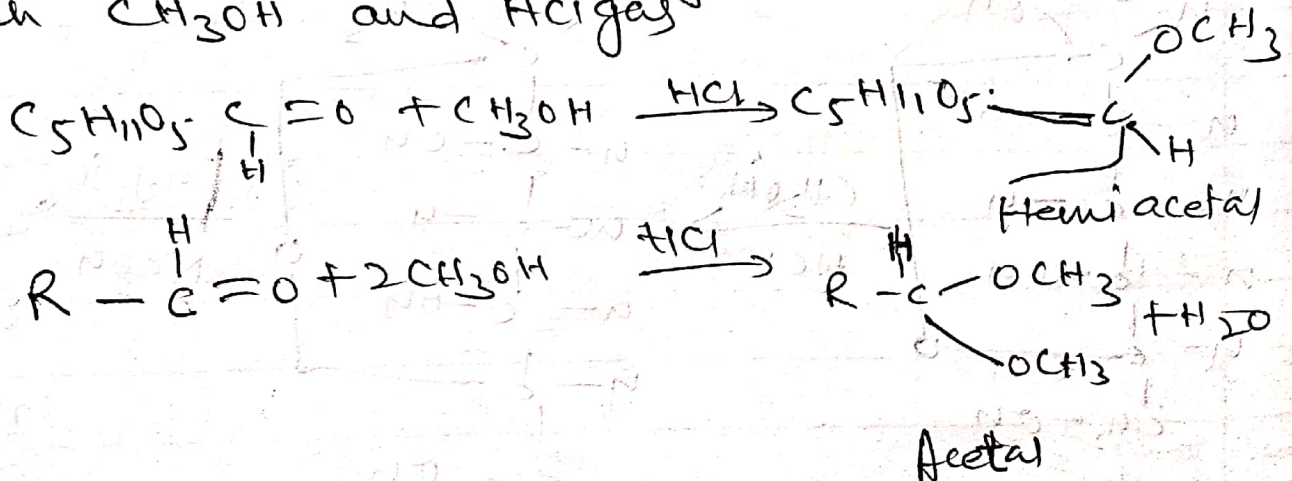
Hence the structure of glucose is

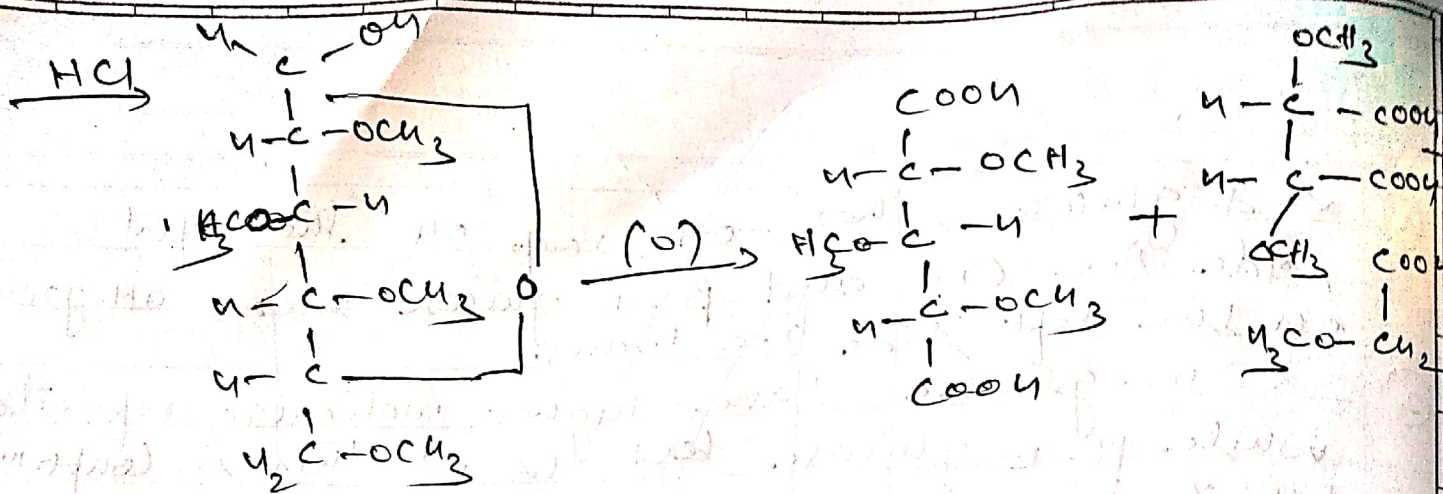


Ring Structure of glucose → Straight Chain

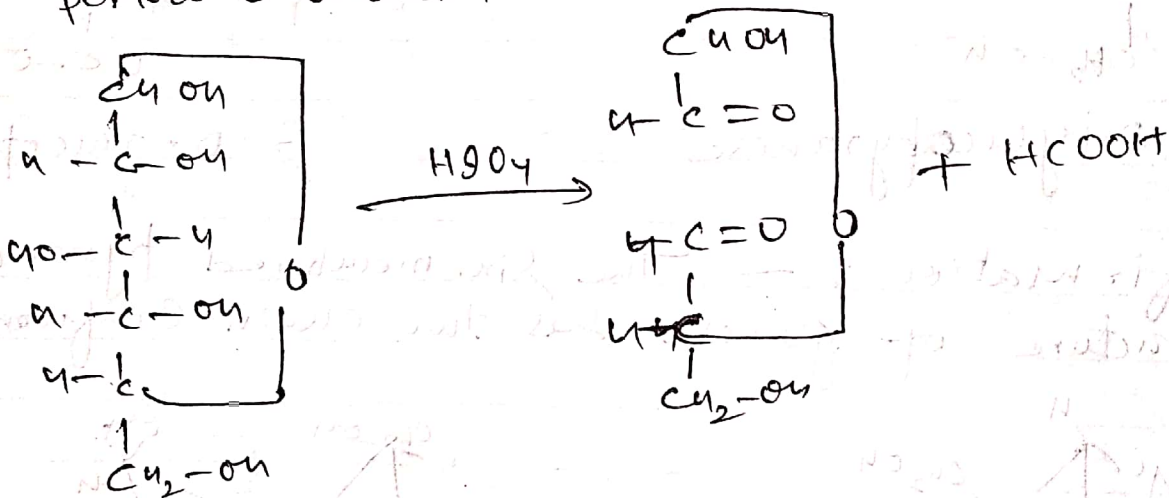
Structure of glucose does not explain the following things.

- ① It readily oxidised by Br₂ water to gluconic acid
- ② It does not restore the colour of Schiff's reagent
- ③ It does not form sodium bisulphite derivative with NaHSO₃
- ④ It does not form compound with ammoniac
- ⑤ It shows mutarotation, i.e. glucose crystal obtained from alcohol, the specific rotation drops from 111° to 52° as well as glucose crystal obtained from pyridine, specific rotation increases from 19° to 52°. The presence of two type of glucose cannot be explained by open chain structures. The mutarotation of sugar is only due to isomerisation of one cyclic form into another by opening the oxide
- ⑥ It forms two types of glucoside (hemiacetal) while, a normal aldehyde forms acetal with CH₃OH and HCl gas





② δ -oxide ring is further supported by periodic acid (HIO_4) oxidation, in which two moles of HIO_4 is consumed forming di aldehyde with the liberation of a molecule of formic acid and during periodic oxidation.

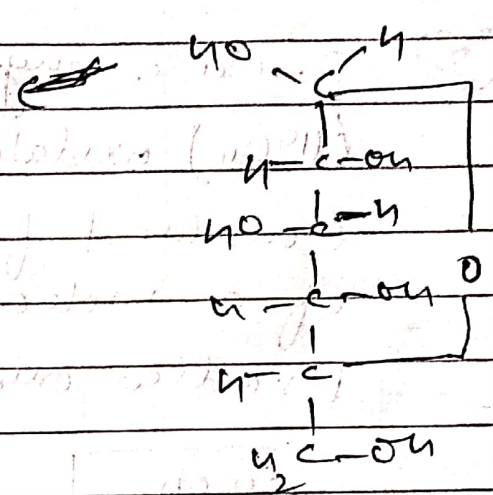
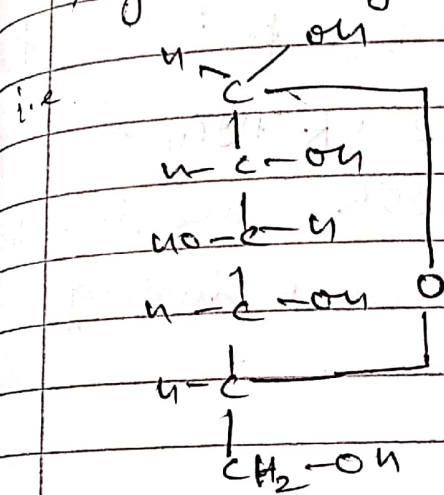


δ -oxide ring is further supported by x-ray analysis of glucose crystal.

③ Configuration of $\text{C}_1 \rightarrow$ Now we are to ascertain the configuration of newly emerged asymmetric C -atom. In 1909 configuration of C_1 was proposed as

① α -D-glucose has -OH group on the right side i.e. cis and β -D-glucose has -OH group on the left side i.e. trans.

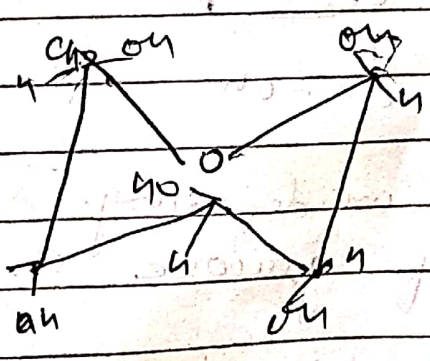
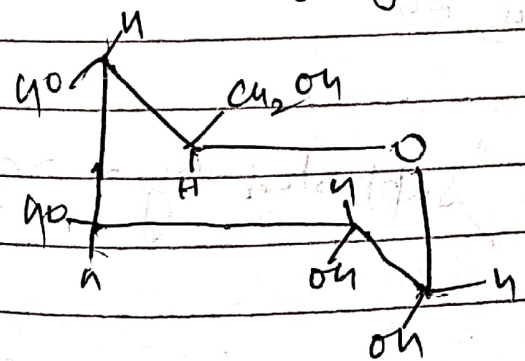
② α -D-glucose have higher molecular refractive index while β -D-glucose ~~has~~ less. This is confirmed by X-ray analysis.



α -D-glucopyranose

β -D-glucopyranose

Confirmation: — The six membered pyranose structure of glucose has two chair conformation

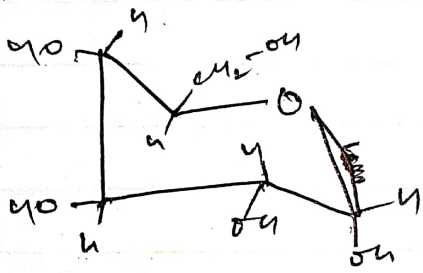


Chair form

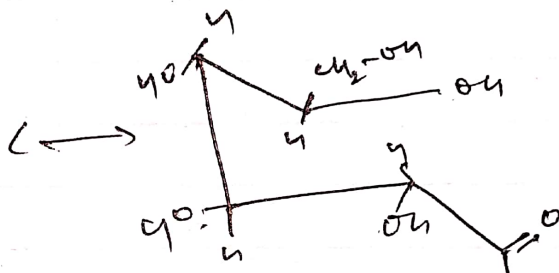
The chair conformation is supported by X-ray and N.M.R. (Nuclear magnetic resonance)

Teacher's Signature: _____

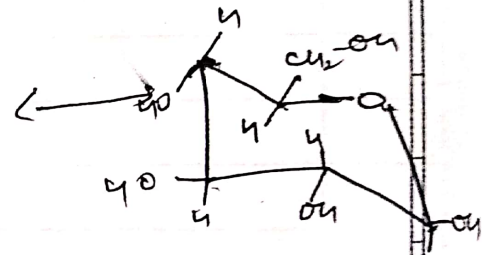
and mass spectroscopy. Either of the isomer readily hydrolysed by water and converted into another by opening the ring. Strom



α -D-glucopyranose



straight chain
formula
aldehyde



β -D-glucopyranose