Structure of D(+) glucose :

Glucose is found to have a poly hydroxy hexanal structure, from the following experimental facts :

i) Molecular wt. & elimental ~~of chemical~~ composition of glucose conferms that it has the molecular formula $C_6H_{12}O_6$.

ii) Glucose forms mono oxime with NH_2OH and ~~HCN and~~ cyanohydrin with HCN. This rxns reveal that glucose contains aldehyde or ketone group.

iii) Mild oxidising agent like Br_2 water oxidises glucose to an acid with same number of C atom. This test is characteristics of -CHO group which is easily oxidized by Br_2/H_2O, not ketone.

iv) Glucose response +ve Tollen's reagent test. It is a characteristics test of -CHO gr. or α-hydroxy carboxyl group.

v) Glucose gives pentaacetate with acetic anhydride/py. So, glucose contains 5 -OH group.

vi) Glucose is a stable molecule and does not eliminated H_2O on mild heating. This proves that 5-OH grs. are on different C atom.

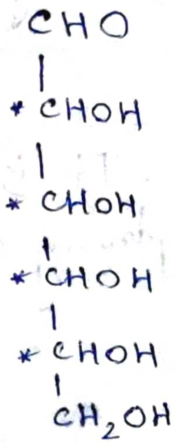
vii) Reduction of glucose with Na/EtOH yields hexahydric alcohol i.e. sorbitol, which produces normal hexane when it is reduced by red P/HI. So, glucose is a straight chain compound.

viii) Killiani rxn :

$$C_6H_{12}O_6 \xrightarrow{HCN} C_6H_{13}O_6CN \xrightarrow{H_3O^+} C_6H_{13}O_6COOH \xrightarrow{\text{red } P/HI} \text{heptanoic acid}$$

The sequence of rxn proves that glucose has -CHO gr. at it's terminal position.

Glucose is a straight chain, poly hydroxy aldehyde which contains 5 -OH group at different C. And this aldohexose contains 4 - chiral centres. i.e. we have total $2^4 = 16$ stereo isomers.



$$\begin{array}{l} CHO \\ | \\ {}^*CHOH \\ | \\ {}^*CHOH \\ | \\ {}^*CHOH \\ | \\ {}^*CHOH \\ | \\ CH_2OH \end{array}$$

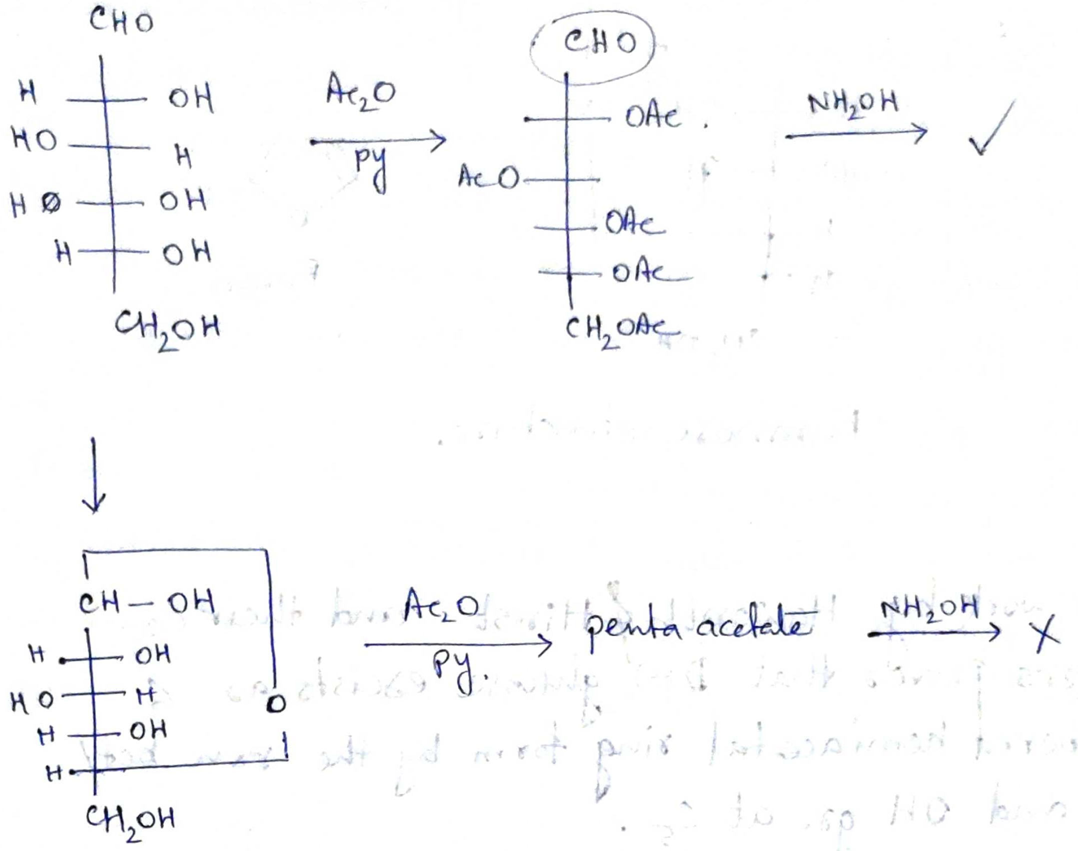
5 member ring → K.C.P
6 " " → T.C.P

▨ Cyclic hemi acetal structure of glucose :-

Although the open chain aldohexose structure of glucose can explain many of it's rxns, the following observations remain unanswered.

i) D (+) glucose exist in two different isomeric form known as α & β - D -(+) glucose.

ii) Pentaacetate does not react with NH_2OH.



5-OH

iii) Spontenious change in sp. rotation of glucose either α or β when they are dissolved in H_2O (mutarotation).

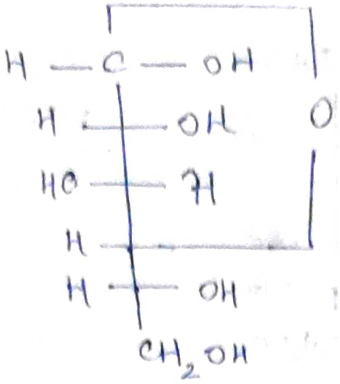
iv) 1 mole of ROH is necessary for acetal formation. So, glucose exist in hemiacetal form.

v) Many common properties of -CHO are absent. No $NaHSO_3$ addition occur (carbonyl test).

vi) X-ray analysis definitely proves the existance of ring structure of glucose.

Considering all these facts, Tollen's proposed a 5 membered oxide ring structure of glucose. The oxide ring struc. is infact a cyclic hemi acetal form by the intramolecular rxn between -OH (C_4) and -CHO group. There fore 2 forms of D (+) glucose can exist which differ only in the configuration at newly formed acemetric centre.

Tollen's:



Furanose structure.

Furan.

- Latter work by Haworth & Hirst and their co-workers proves that D(+) glucose excists as 6 membered hemiacetal ring form by the rxn bet/ CHO and OH gr. at C_5.

Q:) Under certain condition, glucose may exist in furanose ring structure. How far this statement is correct?

→ It has been established that under certain rxn conditions, D(+) glucose furnishes (দেয়). D-glucosides having two distinctly different ring structure. One is 5 membered ring and another is six membered ring.

Under low temp. and short rxn times, D-glucose furnishes primarily the 5 membered ring -D-gluco-furanosides on dissolving the substance in MeOH in presence of HCl. On the other hand D-glucose on prolonged heating with MeOH in presence of HCl gives mainly the 6 membered ring methyl-D-glucopyranoside.

5 membered ring are formed faster than 6 membered ring. The methyl-D-glucofuranosides

as formed fast at low temp. are the K.C.P. while the methyl-D-glucopyranosides formed at relatively higher temp. and over longer period of times are the T.C.P. However under rxn conditions, the 5 membered rings can reopen so as to develop equilibrium among all possible forms - at relatively higher temp. and longer period of time and equ^m is established where methyl-D-glucopyranosides are appeared as predominant pdts with the α-isomer (having the -OMe gr. at axial position) being the thermodynamically most stable.