ISOMERISM (UQ)

Q1 Stereoisomers.

The number of possible stereoisomers depend on number of asymmetric carbon atoms (n)

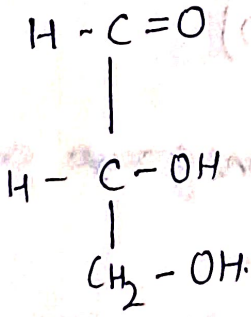
- asymetric carbon atom → four different groups are attatched to same carbon.

reference molecule is glyceraldehyde which has 1 asymetric carbon atom.

no. of stereoisomers = 2^n.

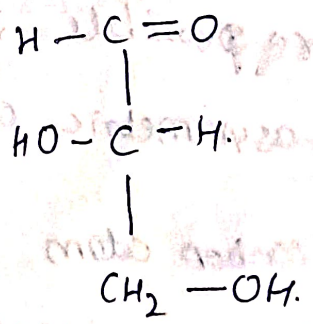
- all monosaccharides can be desived from glyceraldehyde by addition of C. atoms.
- penultimate C atom is reference carbon atom.
- two members of the pair are designated as D & L forms.
- In D form, the OH group on the asymetric carbon is on the right.
- In L form, the OH group is on left side.

D ≠ dextrorotatory d = dextro rotatory.



D - form.

D glyceraldehyde



L form.

L - glyceraldehyde.

D & L forms are stereoisomers

⇒ D-glucose & L glucose are enantiomers.

⇒ they are non-superimposable mirror image.

② Optical activity:

when a plane polarized is passed through a carbohydrate solution, the light will either shift to left or right.

the rotation is due to presence of assymetric carbon atom.

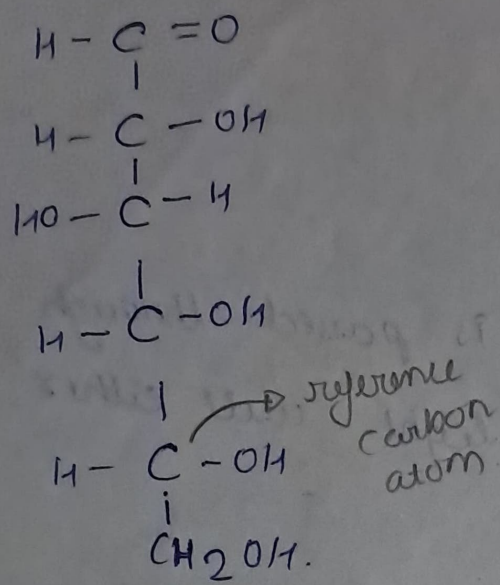
If it is rotated towards left → l - laevorotatory (-)
If right - right d - dextrorotatory (+).

→ D glucose → dextrorotatory

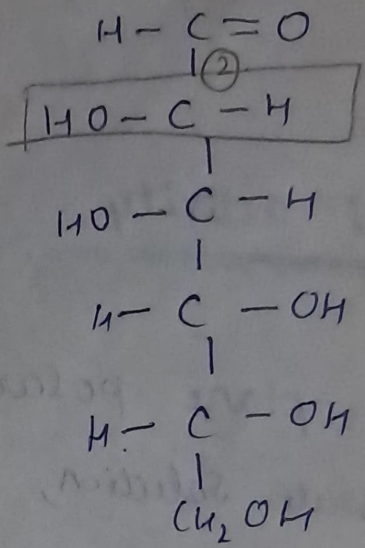
→ D fructose → laevorotatory.

Equimolar mixture of optical isomer has a net rotation - Racemic mixture (d l)

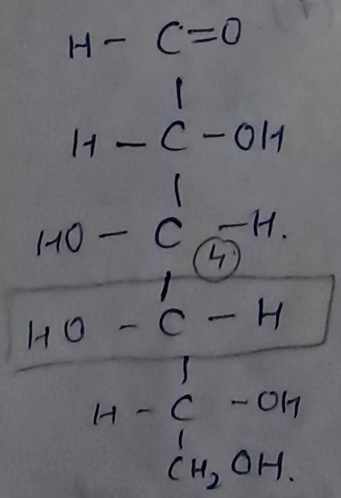
3 Epimerism.



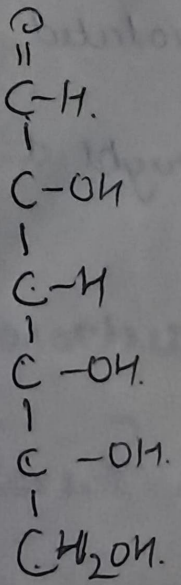
D-glucose.



D-Mannose.



D-galactose.

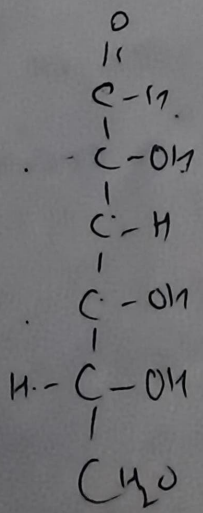


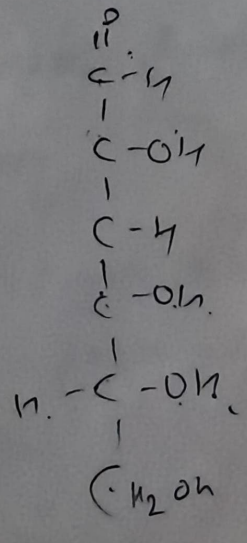
Epimerism

- Epimers are sugars which are differ with each other with respect to single carbon, other than reference carbon.
- galactose and mannose are epimers of glucose.
- they differ from glucose with respect of C-4 & C-2 respectively.

Examples.

- D glucose & D-galactose (epimeric at C_4)
- D glucose & D-mannose (epimeric at C_2)
- L-idose & D-glucose (epimeric at C_5)





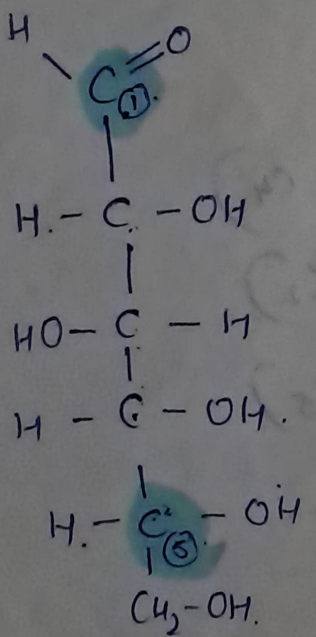
Cyclization.

* less than 1% of carbohydrates exist in open chain form.

*. predominantly found in ring form.

* involving reaction of C_5 OH group with C_1 aldehyde group.
or C-2 of keto group.

C_5 – OH.
C_1 – aldeh
C_2 – keto



Six membered ring str → pyranose.

* 5 membered ring str → furanose.

⇒ the carbonyl Carbon after cyclization becomes the anomeric carbon.

⇒ This creates α & β configuration.

α, β → anomers

D, L → enantiomers

⇒ β means that one -OH on the anomeric carbon lies on the same side of the ring as terminal $-CH_2OH$.

⇒ α means that the -OH on the anomeric carbon lies on the side of ring opp from term. CH_2OH.

Mutarotation. (8 marks / 4 Marks)

- Unlike the other stereoisomeric forms, α & β anomers spontaneously inter convert in solution.

Anomerism

- when D glucose is crystallised at room temperature and a fresh solution is prepared, its specific rotation of polarised light is +112°.

{ α form → +112°. eq mix +52.5°
β form → +19° }

{# glucose oxidase method. used to check glucose concentration.}

- after 12-18 hrs it changed to +52.5°.
- In initial crystalization is at 98°c and then solubised, the specific rotation is found to be +19°.
- which changes to +52.5° within a few hours.

Mutarotation.

- It is defined as "the change in the specific optical rotation representing interconversion of α and β forms of D-glucose to an equilibrium mixture with time".

α-D-glucose. → Eq. mixture ← β-D-glucose.

Specific rotation. → specific rotation ← specific rot

$(\alpha)_D = +112.2°$ → $(\alpha)_D = +52.5°$ ← $[\alpha]_D = +19°$.