: CARBOHYDRATES :

Hydrates of carbon. having gen. formula $(x(H_2O)_y$

Basically these are polyhydroxy aldehyde or polyhydroxy ketone.

- glucose: $C_6(H_2O)_6$. fructose: $C_6(H_2O)_6$
- Sucrose: $C_{12}H_{22}O_{11} \equiv C_{12}(H_2O)_{11}$

But in cyclic form it exists as hemiacetal or acetal

It is undergoing hydrolysis to form monosaccharide

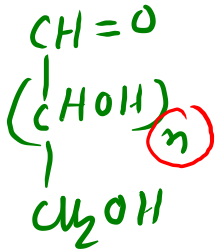
Classification

$CH=O$ $(CHOH)_n$ CH_2OH glucose	CH_2OH $C=O$ fructose $(CHOH)_3$ CH_2OH ~~ketose~~.

Polyhydroxy aldehyde / ketone

- Natural Polymer
  - Monosaccharide
    - It does not undergoes hydrolysis
      - Aldose (glucose)
      - ketose. (fructose)
  - Oligosaccharide
    - It is undergoing hydrolysis, it gives 2-10 unit of monosaccharide
    - Sucrose $\xrightarrow{H_3O^+}$ glucose + fructose
    - Maltose $\xrightarrow{H_3O^+}$ 2 unit of glucose
    - Lactose $\xrightarrow{H_2O}$ glucose + galactose
    - ⇒ Disaccharide (not polymer)
  - Polysaccharide
    - i) Starch
    - ii) Cellulose
    - iii) glycogen.

: **Aldose family:**



$n=1$, Aldotriose.
$n=2$ Aldotetrose
$n=3$ Aldopentose
$n=4$. Aldohexose.

Glucose; Galactose

⇓

open chain structure. (4)

Total no of stereoisomers $= 2^4 = 16$.

Polymer formula (Starch)

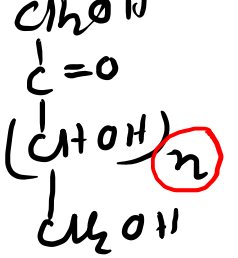
$$\left[\left(C_6H_{12}O_6\right) - H_2O\right]_n$$

$$\equiv \left(C_6H_{10}O_5\right)_n$$

$$\Rightarrow 2\left[C_6(H_2O)_6\right] - H_2O : \underset{\text{maltose}}{C_{12}H_{22}O_{11}}$$

sucrose.

Ketose family:



$n=0$; Ketotriose
$n=1$; Ketotetrose
$n=2$. Ketopentose
Ketohexose.

⇓

Fructose

(molecular formula)

i) Disaccharide of glucose Aldohexose

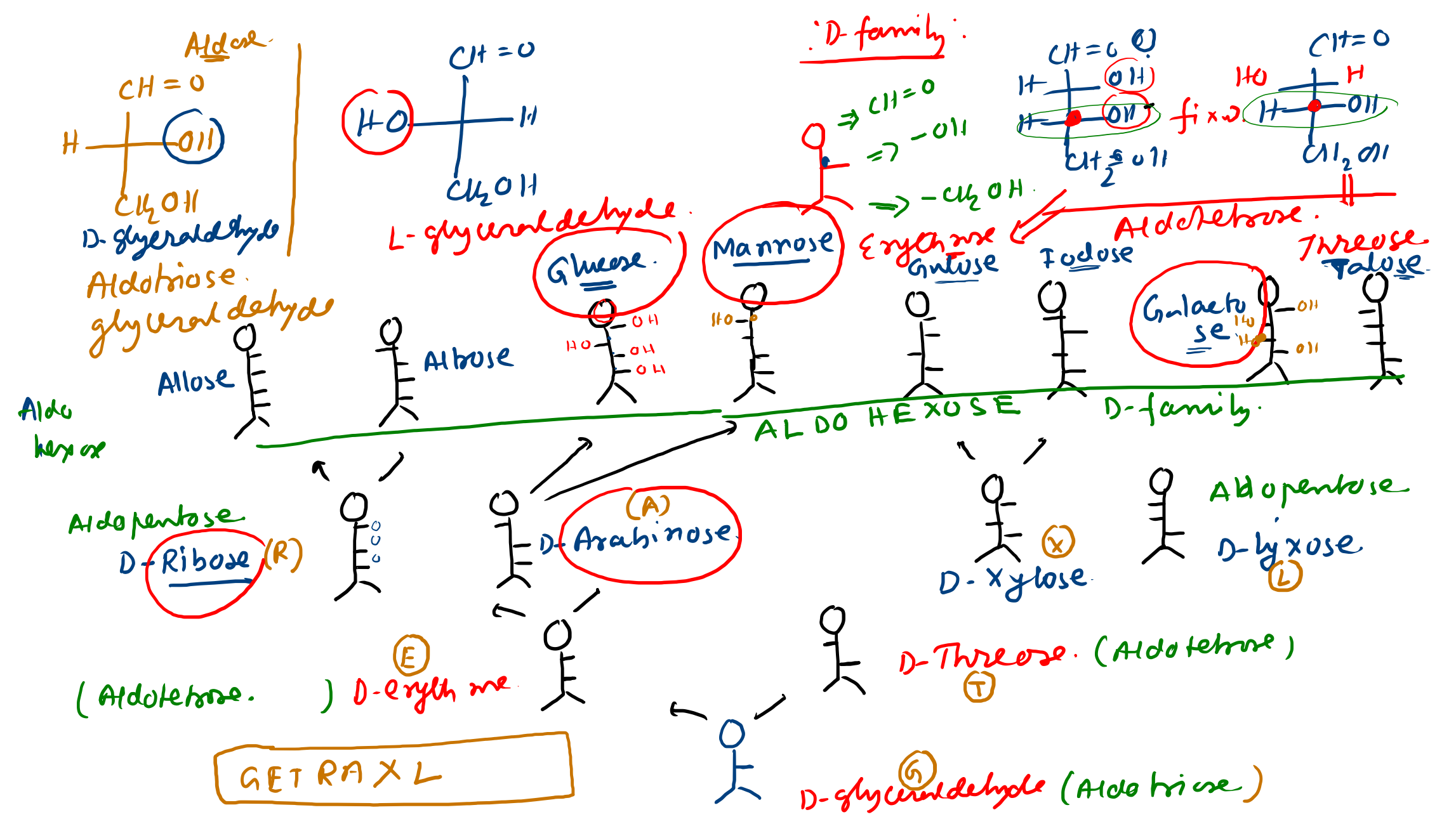
Total no of chiral carbon $= 3$.

Total no. of stereoisomer $= 2^3 = 8$.

ii) Tetrasaccharide of Aldohexose.

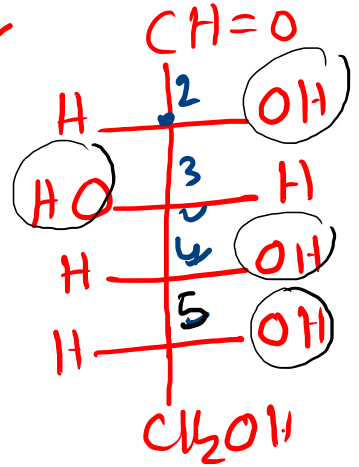
$$\left[C_6(H_2O)_6\right] \times 4 - 3 \times H_2O.$$

$$\left[C_{24}H_{42}O_{21}\right]$$


Aldose
CH=O
H
OH
CH2OH
D-glyceraldehyde
Aldotriose
glyceraldehyde
CH=O
HO
H
CH2OH
L-glyceraldehyde
D-family
⇒ CH=O
⇒ -OH
⇒ -CH2OH
Erythrose
fixed
Aldotetrose
Threose
Allose
Altrose
Glucose
Mannose
Gulose
Idose
Galactose
Talose
Aldo hexose
ALDO HEXOSE
D-family
Aldopentose
D-Ribose (R)
D-Arabinose (A)
D-Xylose (X)
Aldopentose
D-lyxose (L)
(Aldotetrose.)
D-erythrose (E)
D-Threose (T) (Aldotetrose)
D-glyceraldehyde (G) (Aldotriose)
GETRAXL

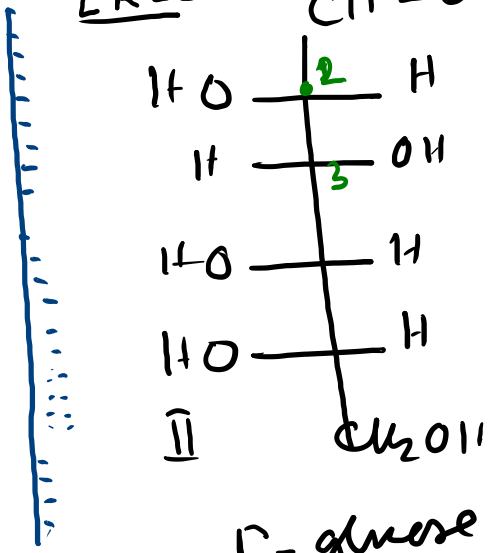
RLRR

Epimer.



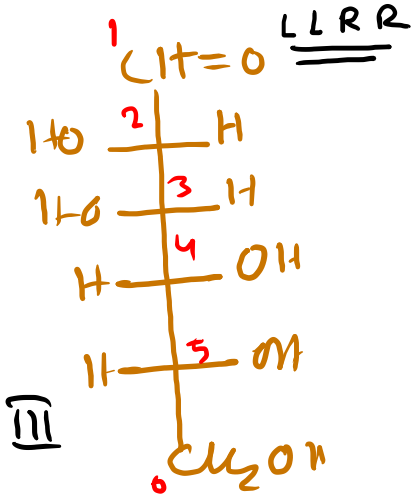
I

D-glucose.



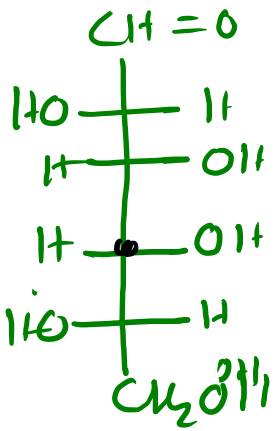
II

L-glucose.

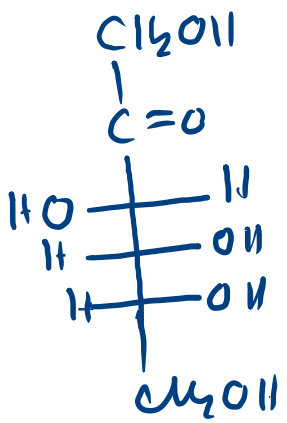


III

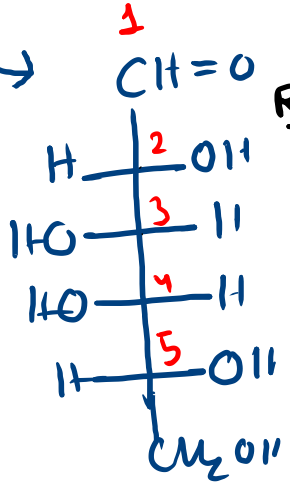
D-Mannose.



L-galactose

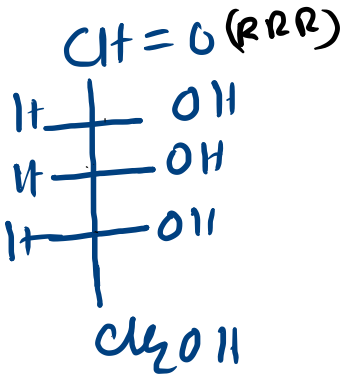


D-fructose.



RLLR

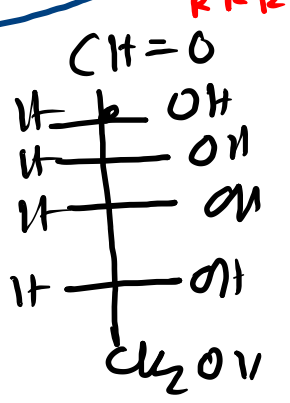
D-galactose.



D-Ribose.

(Aldopentose)

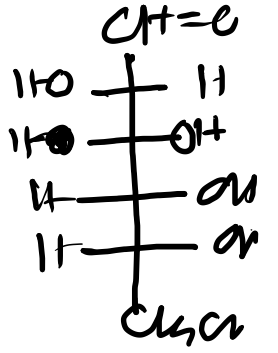
RRRR



D-Allose

(Aldohexose)

LRRR



D-Altrose

i) D-glucose & D-Mannose : C-2 epimers

ii) D-glucose & D-galactose : C-4 epimers.

iii) D-glucose & L-glucose : enantiomers

iv) D-glucose & D-fructose : functional Isomers.

D-Fructose ∝ [Last 3 chiral centre configuration same in D-fructose & D-glucose).

Ribose : Aldopentose (RRR)

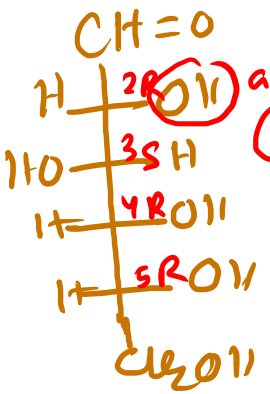
Allose : Aldohexose (RRRR)

Allose & Altose : C-2 epimer.

Glucose & Mannose : C-2 epimer

Gulose & Idose : C-2 epimer.

Galactose & Talose. C-2 epimer.



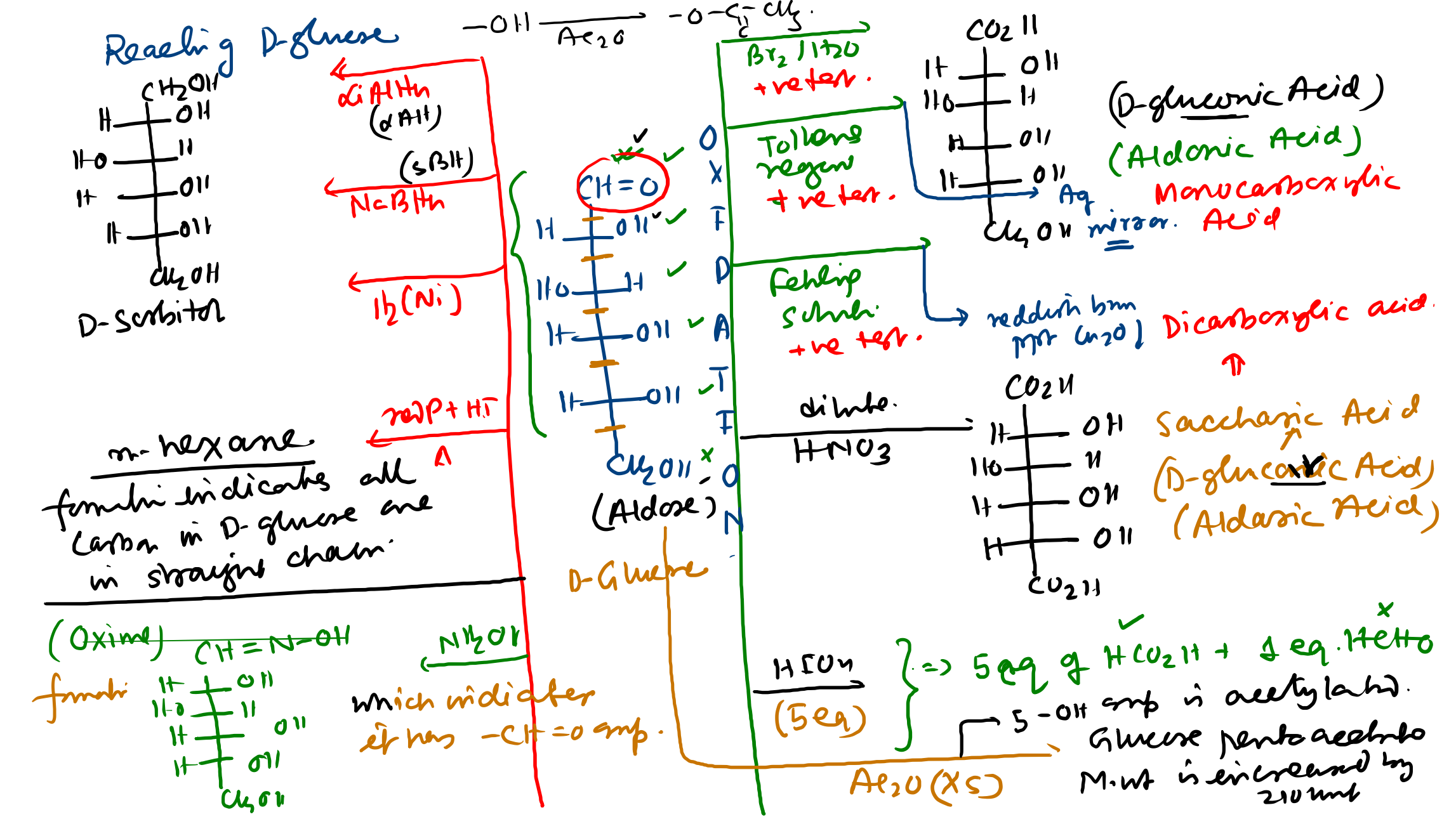
(2R, 3S, 4R, 5R) 2, 3, 4, 5, 6 pentahydroxy hexanal

C-4 epimer configuration.

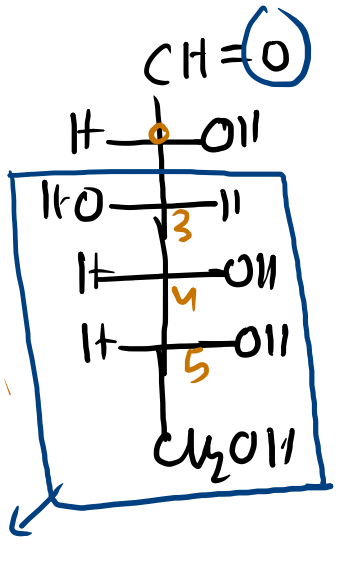
D-glucose

IUPAC Name: C-2 epimers configuration (2S, 3S, 4R, 5R)

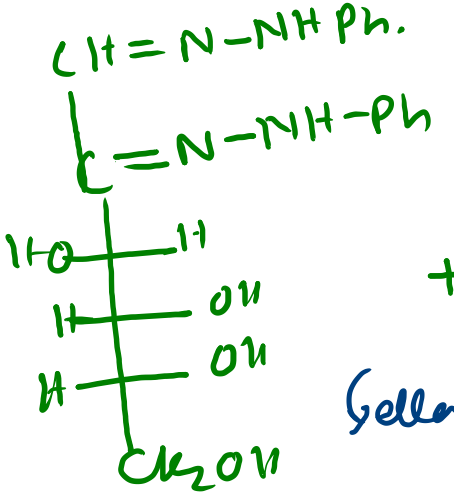
2R, 3S, 4S, 5R


Reacting D-glucose
$-OH \xrightarrow{Ac_2O} -O-C-CH_3$
Br_2/H_2O +ve test.
Tollens reagent +ve test.
Fehling Solution +ve test.
NaBH4
$H_2(Ni)$
red ppt Cu_2O
dilute HNO_3
HIO_4 (5eq)
Ac_2O (XS)
NH_2OH
D-Glucose
(Aldose)
D-sorbitol
(D-gluconic Acid)
(Aldonic Acid)
Monocarboxylic Acid
Dicarboxylic acid
Saccharic Acid
(D-glucaric Acid)
(Aldaric Acid)
5 eq of HCO_2H + 1 eq. HCHO
5-OH grp is acetylated.
Glucose pentaacetate
M.Wt is increased by 210 unit
n-hexane
formula indicates all Carbon in D-glucose are in straight chain.
(Oxime) CH=N-OH
formula
which indicates it has -CH=O grp.

Osazone formation: (This reaction can be used for glucose/carbohydrates)



$PhNH-NH_2$ (3 eq of Phenyl hydrazine)

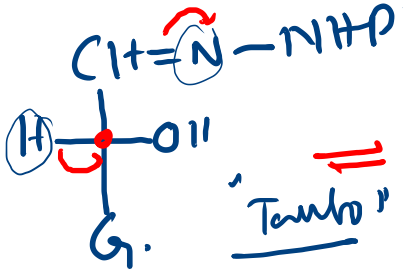


$16 \times 12 = 216$
$4 \times 14 = 56$
$4 \times 16 = 64$
$22 \times 1 = 22$
358.

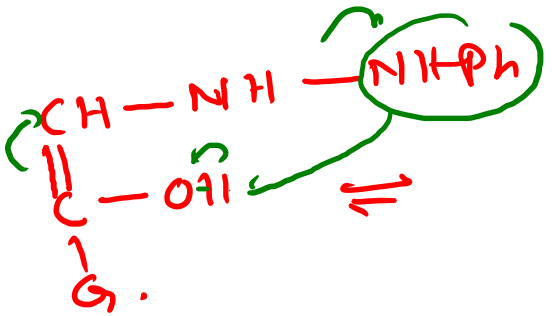
+ $PhNH_2$ + H_2O + NH_3

3 biproducts.

(Yellow color crystal)



Tautomer

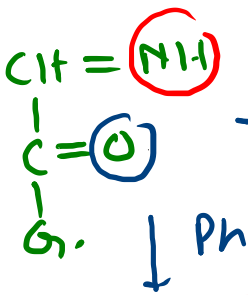


All C-2 epimers form same osazone.

Chiral centre of bottom 3 Carbon configuration same.

Glucose & fructose form same osazone.

G/F last 3 chiral centre configuration same



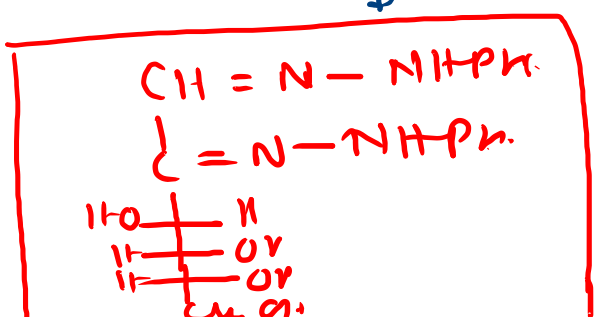
+ $PhNH_2$ ↑

$PhNH-NH_2$ (2eq)

M.wt = ??

$C_{18}N_4O_4H_{22}$

358

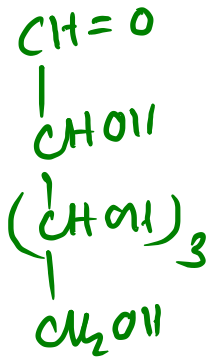


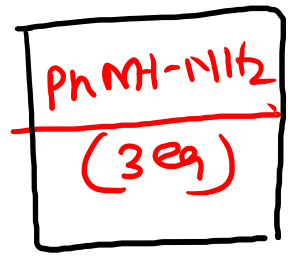
+ H_2O + NH_3

Osazone

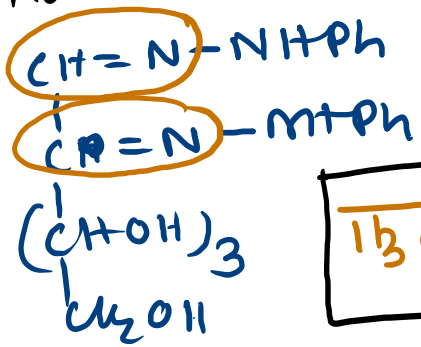

Step up:
Aldopentose.
KCN
H+
(Cyanohydrin)
Partial reduction
Lindlar Catalyst
Imine
H3O+
Aldohexose.
give + NH3↑ aldehyde
Fischer Kiliani Reaction
Step down
NH2OH
oxime
cyanide.
Δ
Esterification
NaBH4
conc H2SO4
=> cyclic ester is converted into aldehyde
Br2 + H2O
α-hydroxy acid
Aldohexose
dehydration
Ac2O
moist Ag2O
ether hydrolysis
+ HCN
Fe2+ H2O2
Aldopentose
Aldonic acid

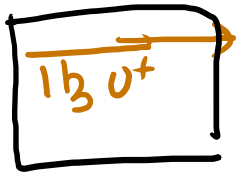
Aldopentose



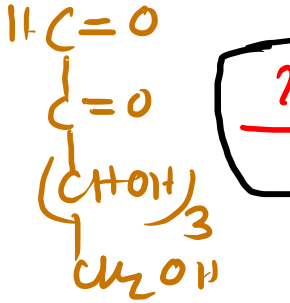


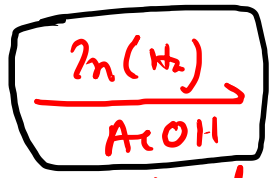
Aldohexose → ketohexose & vice versa.





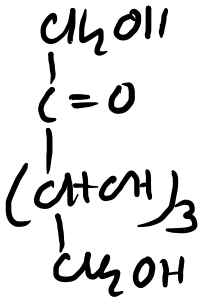
Osazone





Ozonolysis

reduce aldehyde not ketose.

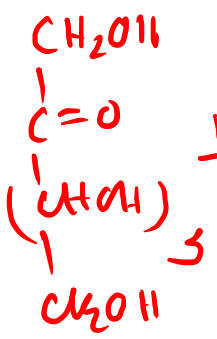


Ketohexose

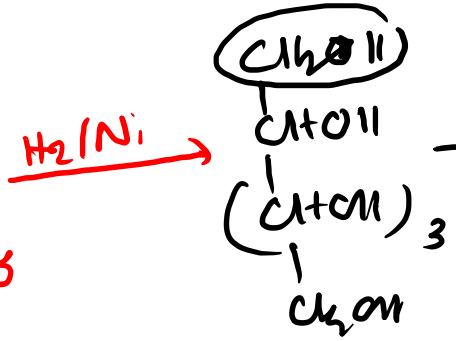
Aldohexose.

=> PhNH-NH2 ; H3O+ ; Zn(Hg) + AcOH.
(acetic Acid)

Ketohexose → Aldohexose

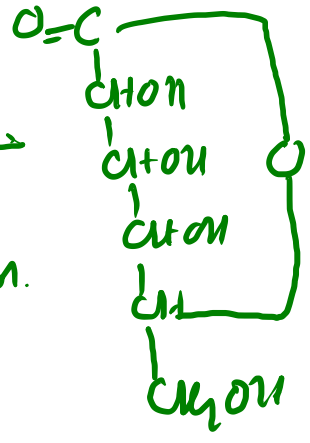


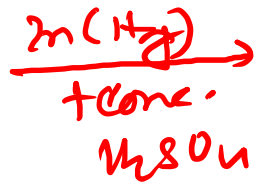
Ketohexose

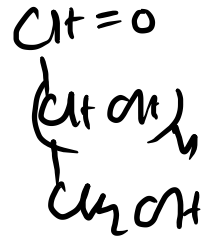


Acid

Alcohol.







Aldohexose