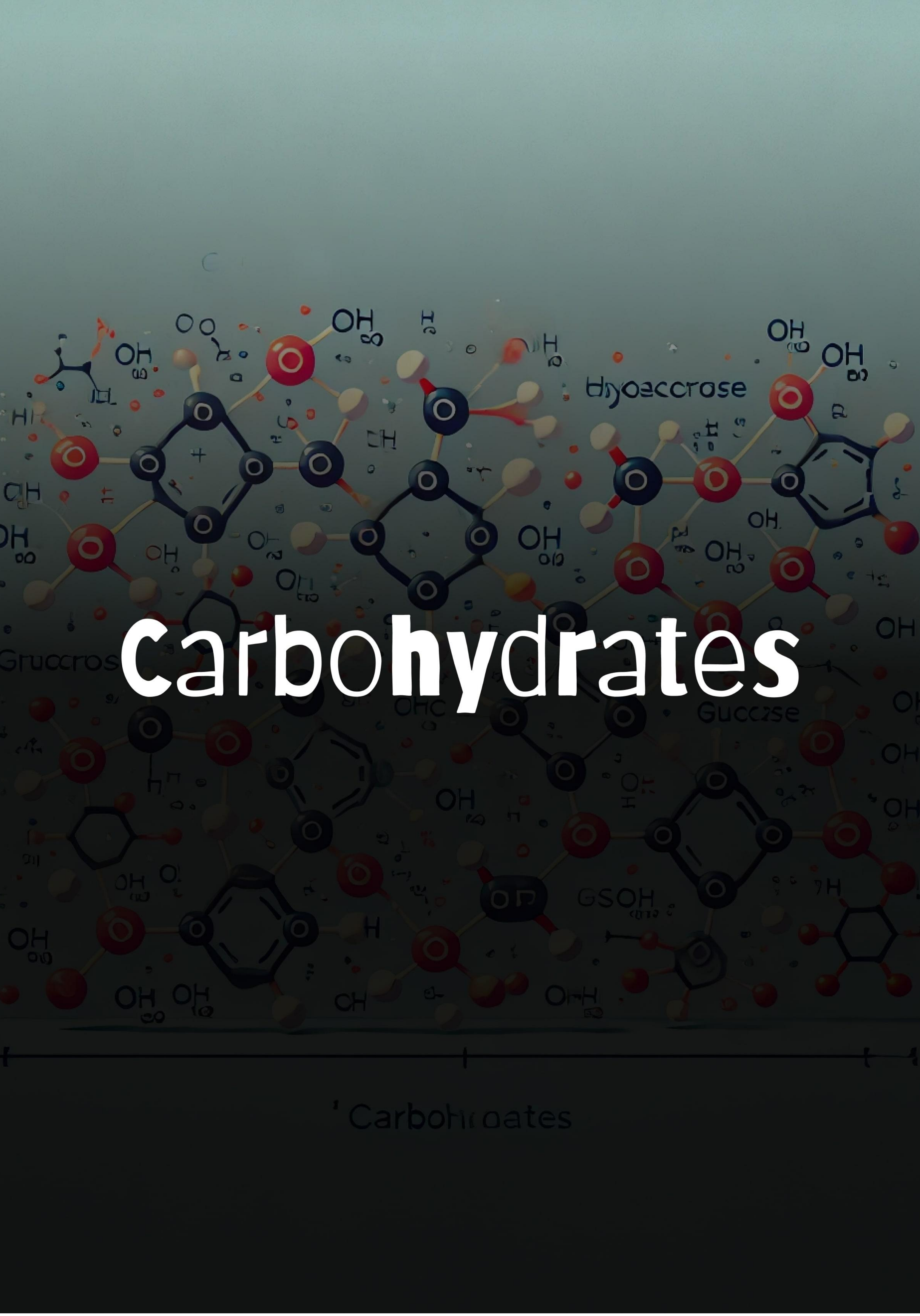


Carbohydrates

CARBOHYD-RATES

GENERAL FORMULA: $C_x(H_2O)$

e.g. $C_6H_{12}O_6 = C_6(H_2O)$

$C_{12}H_{22}O_{11} = C_{12}(H_2O)_{12}$

CLASSIFICATION

(i) Sugars

(ii) Polysaccharides

- Sugars are white crystalline products. All sugars are water soluble. Sugars are organic but still soluble in water due to the strong intermolecular hydrogen bonding between sugar molecules and water. Sugar does not melt due to this hydrogen bonding, hence they only decompose.

Carbohydrate don't melt....

Sugars are insoluble in organic solvents because these solvents are unable to break the strong hydrogen bonding between them.

Sugars are sweet in test...

- Polysaccharides are water insoluble. they donot melt. They do not dissolve in organic solvents due to high molecular mass.

- Sugars further are devided into –

(i) Monosaccharides

(ii) oligosaccharides

Tower molecular wt. polymer are called oligomers.
They stand in between monomers & polymers.
$-(CH_2-CH_2)_n-$ in these n varies from 2 to 20.

Monosaccharide, is a carbohydrate which does not undergo into further simpler carbohydrats on hydrolysis. e.g. Glucose

Oligosaccharide, are carbohydrates which upon hydrolysis will give many monosaccharides.

Monosaccharides are divided into :-

i. Aldoses ii. Ketoses

A carbohydrate which contains aldehyde functional group is called aldose.
e.g. Glucose

e.g. CHO → Glucose has aldose group.

Aldohexose	Aldopentose	Aldotetrose
CHO	CHO	CHO
$CH-OH$	$CH-OH$	$CH-OH$
$CH-OH$	$CH-OH$	$CH-OH$
$CH-OH$	$CH-OH$	CH_2-OH
$CH-OH$	CH_2-OH	
$CH-OH$		

A carbohydrate which contains keto functional group is called ketose.

e.g.

	Keto Hexose ← Fructose
CH_2-OH	CH_2-OH
$C=O$	$C=O$
CH_2-OH	$CH-OH$
CH_2-OH	$CH-OH$
CH_2-OH	$CH-OH$
CH_2-OH	CH_2-OH

Aldose are divided into -

i. Aldotetrose → Possesses four carbon

ii. Aldopentose → Possesses five carbon

iii. Aldohexose → Possesses six carbon

iv. Aldo heptose → Possesses seven carbon

Ketons are also divided into -

(i) ketatetrose (ii) ketopentose (iii) ketohexose (iv) ketoheptose

All compounds having general formula $C_x(H_2O)_y$ may not be carbohydrats but all carbohydrates will have $C_x(H_2O)_y$ as general formula.

E.g. Acetic acid - $CH_3-\overset{O}{\overset{\|}{C}}-OH \Rightarrow C_2H_4O_2 = C_2(H_2O)_2$ is not a carbohydrat

Oligosaccharides are further divided into -

(i) Disaccharides (ii) Trisaccharides (iii) Tetrasaccharides

Disaccharides are carbohydrates which give two monosaccharides on hydrolysis.

E.g. maltose, Lactose, sucrose & cellubiose.

Polysaccharides are divided into -

(i) Starch (ii) cellulose

Similarly, trisaccharides give three monosaccharides on hydrolysis.

Fructose is a monosaccharide.

ALDOHEXOSE

GENERAL FORMULA: $C_6H_{12}O_6 \longrightarrow C_6(H_2O)_6$

EVIDENCES

(i) Leibig's method (carbon oxygen hydrogen analysis)

All aldodexose seem to have formula $C_6(H_2O)_6$

(ii) Reaction with NH_2OH (hydroxy amine)

NH_2OH + aldohexose $\longrightarrow$ oximes

Hence, they contain carbonyl group.

(iii) Reaction with Br_2 water

$C_6H_{12}O_6 + Br_2$ water $\longrightarrow C_6H_{12}O_7$ (aldonic acid) → Gluconic acid

A carbohydrate gives same no. of carbon before & after reaction with Br_2 water Hence, it contains aldehydes.

(iv) Reaction with acetic anhydride

$C_6H_{12}O_6 + 5AC_2O \longrightarrow$ Forms a penta acetyl derivative $+ 5CH_3COOH$

$$R-OH + CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 \longrightarrow R-O-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3-\overset{O}{\overset{\|}{C}}-OH$$

Hence, All aldohexoses contain 5 hydroxy groups because 1 hydroxy group requires 1 mole of AC_2O and librate 1 mole of CH_3COOH.

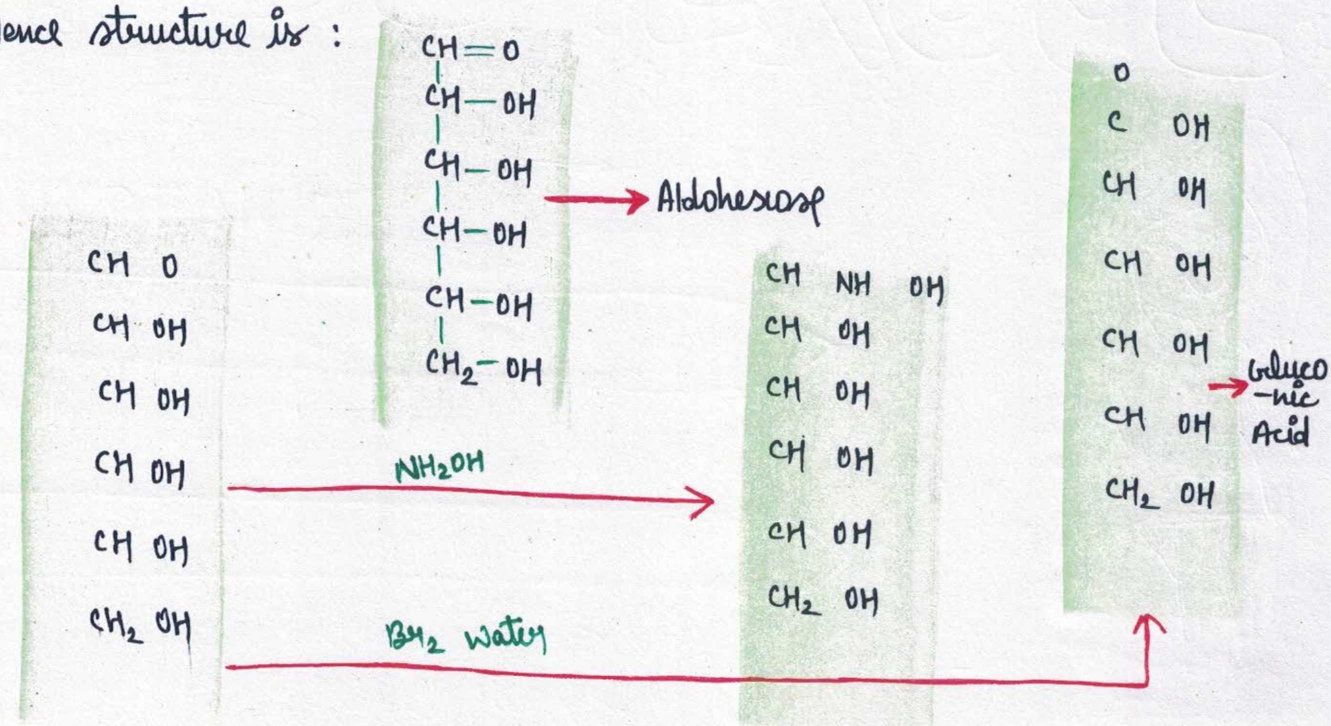
(v) Reaction with P HI

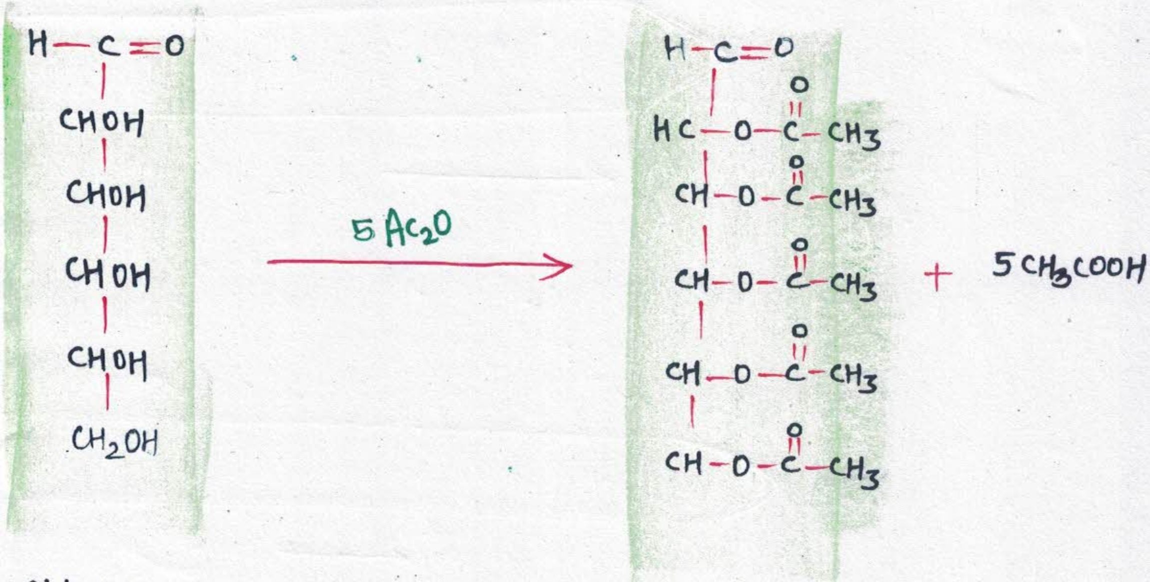
$C_6H_{12}O_6 + P + HI \longrightarrow$ n hexane

It indicates that it has a linear carbon skeleton. Hence, aldohexose is a linear carbon skeleton, not branched.

Hence, aldohexose has formula $C_6H_{12}O_6$, has linear structure, aldehyde group, 5 hydroxy groups & two hydroxy groups cannot be on same carbon.

Hence structure is :





Aldohexose has 4 chiral centres. Hence it has 2^4 16 stereoisomers. Hence it has 8 enantiomers.

It's types are—

It has 8 aldohexoses—

(i) Glucose → Dextro, Levo

(ii) Mannose → Dextro, Levo

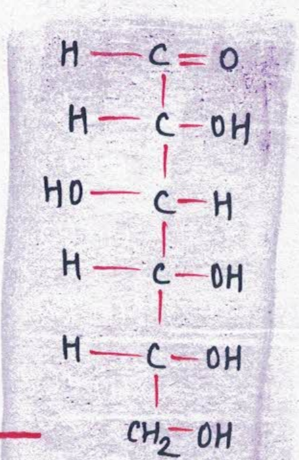
(iii) Galactose → Dextro, Levo

(iv) ......

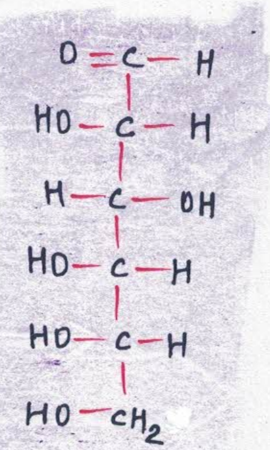
GLUCOSE

STRUCTURE

Structure of Glucose



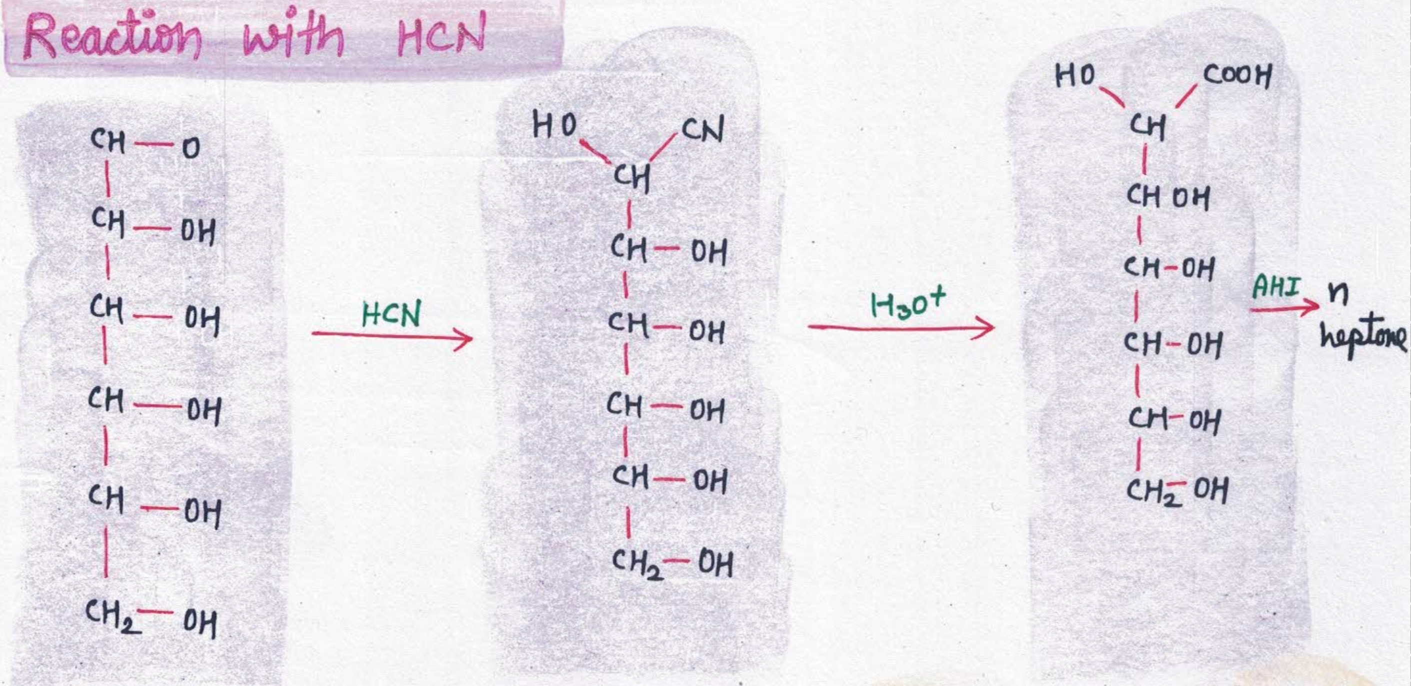
Dextro (+) Glucose
(D+) Glucose

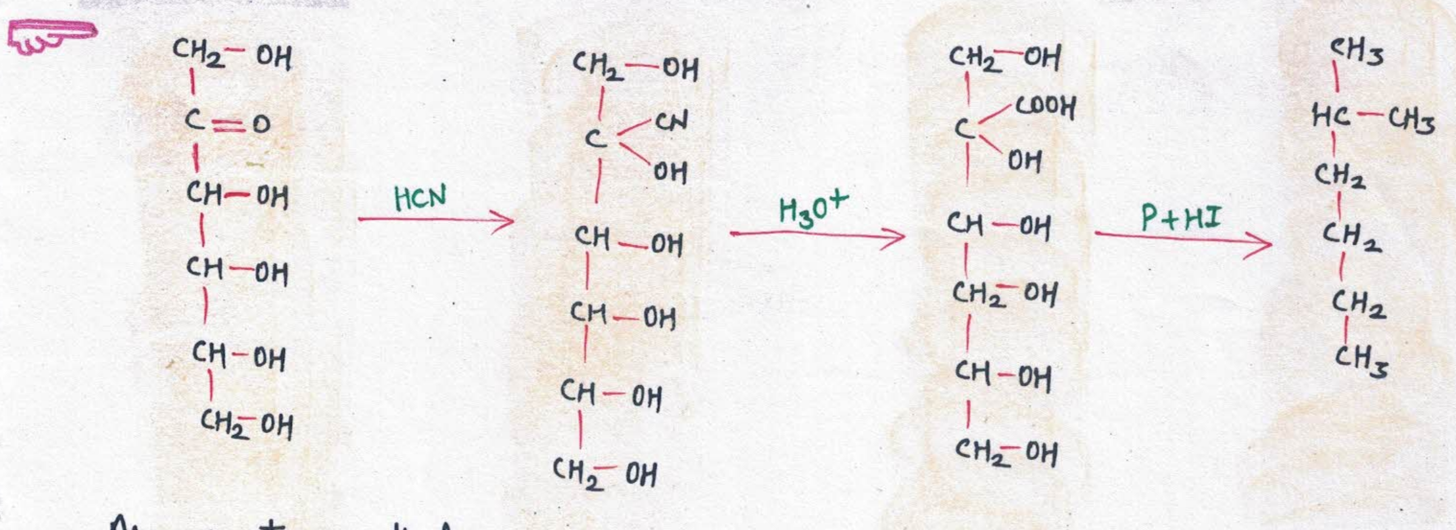


Levo Glucose
(L) glucose

Nature produces D+ glucose, body digests Dextro group not levo.

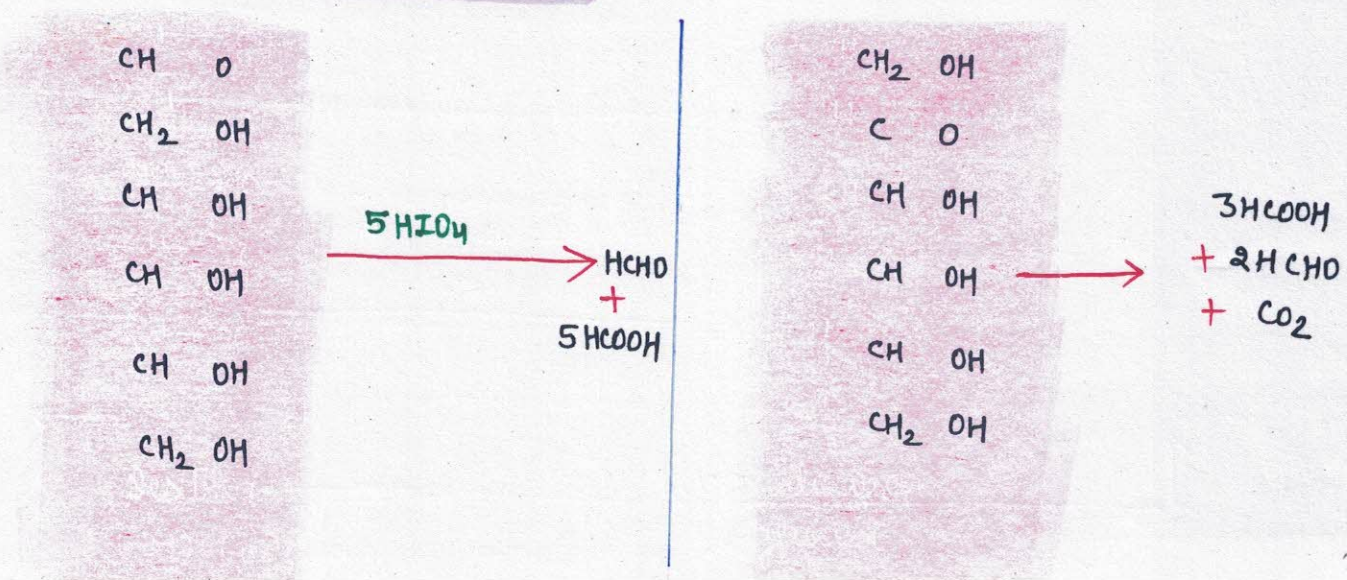
(i) Reaction with HCN



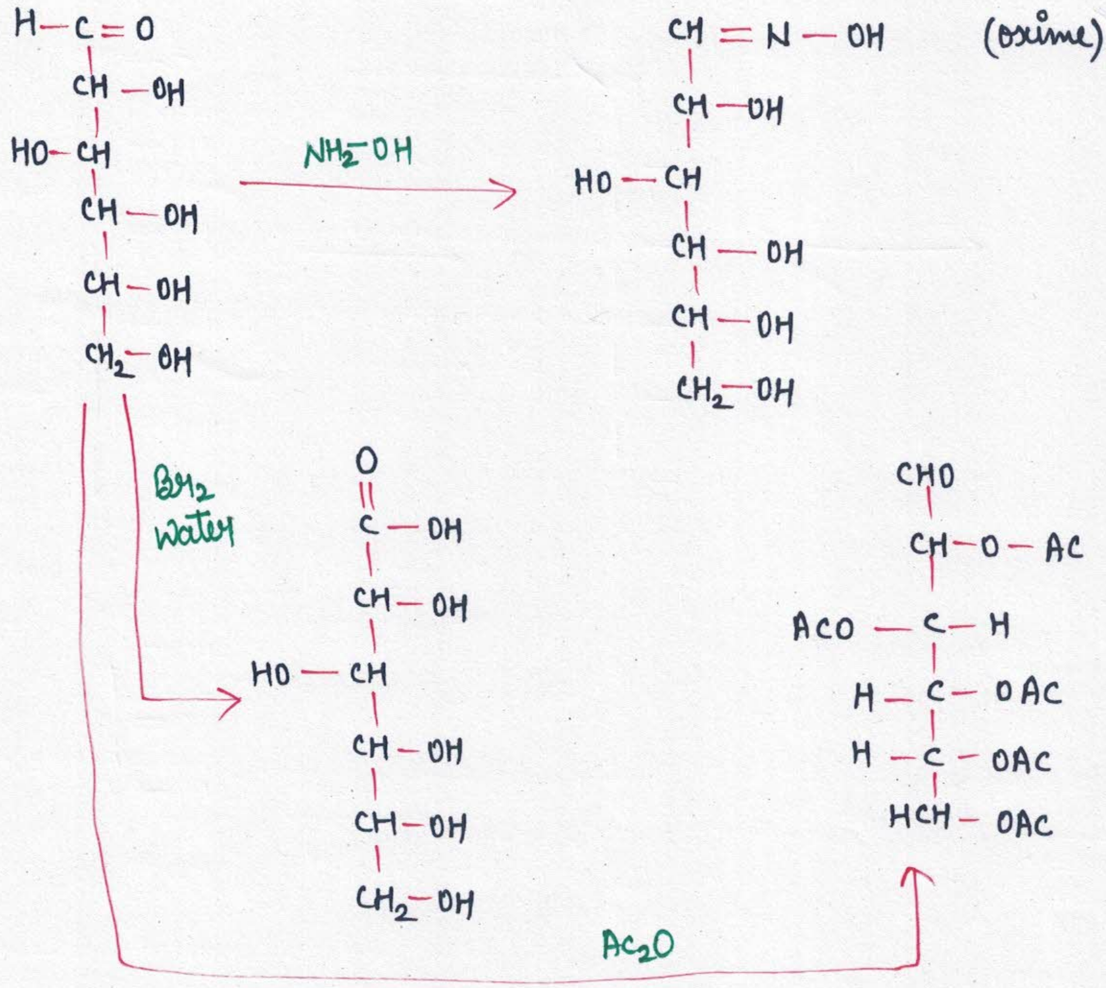


As we get 2 methyl hexane, hence all ketoses are 2 keto compds.

(ii) Reaction with HIO_4

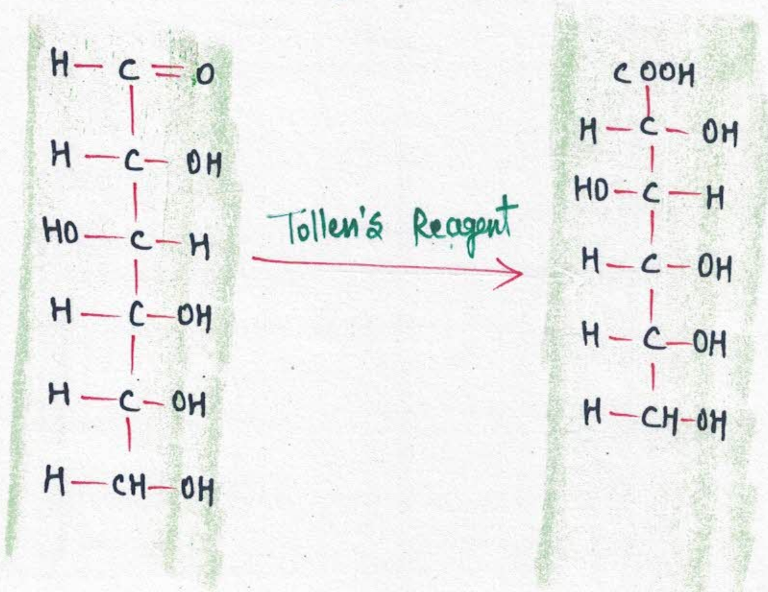


Hence ketoses give effervescene of CO_2 on reactive with HIO_4 but aldoses do not.

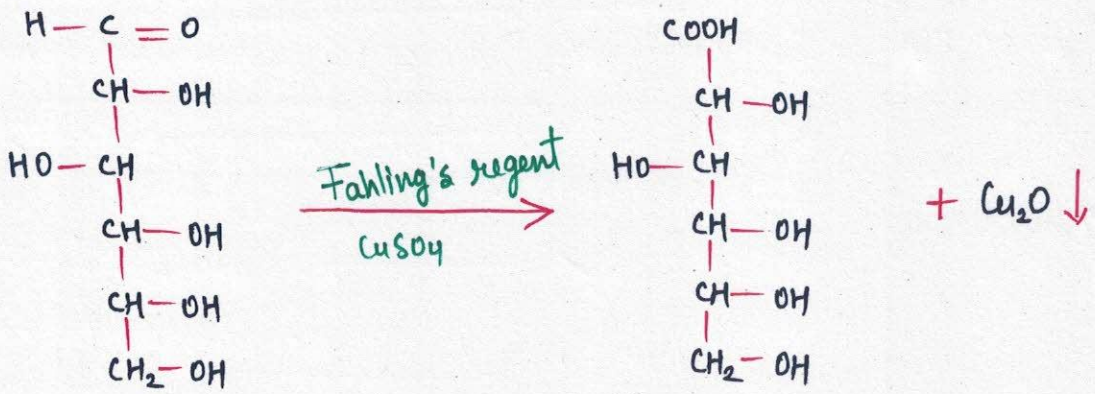


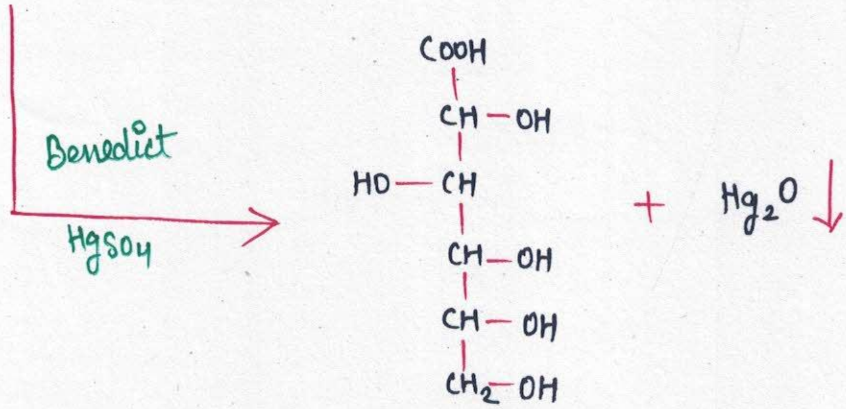
iii) Reaction with Tollen's Reagent

Aldehydes give Tollen's test.
Hence glucose will give tollen's test.



one mole of aldehyde requires 2 moles of $AgNO_3$.
So glucose requires 2 moles of $AgNO_3$.





A sugar which undergoes ⊕ fehling' test, tollen's test, benedict test is called "reducing sugar."

All aldoses are reducing sugar as they will give all ⊕ tests as they contains aldehyde groups.

KETOHEXOSE

General molecular formula found to be ($C_6H_{12}O_6$) (by C, H analyses).

(i) With NH_2-OH

It forms oximes.

(ii) By Br_2 water

No Reaction ⟶ Hence it has keto functional group.

(iii) With P+HI

$C_6H_{12}O_6 \xrightarrow{P+HI}$ n hexane + 2 iodo hexane (traces)

It may be two keto compound and has linear structure.

(iv) With Ac_2O

Forms a penta acetyl derivative & 5 CH_3COOH. Hence, it contains 5 hydroxy groups.

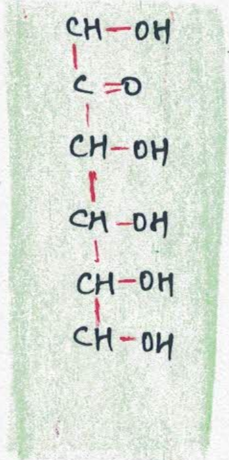
(v) With HCN

$$C_6H_{12}O_6 \xrightarrow[\text{2. } H_3O^+ \quad \text{3. } P+HI]{\text{1. } HCN} \text{2 methyl hexane}$$

It is 2 keto hexose.

No two hydroxy on same carbon.

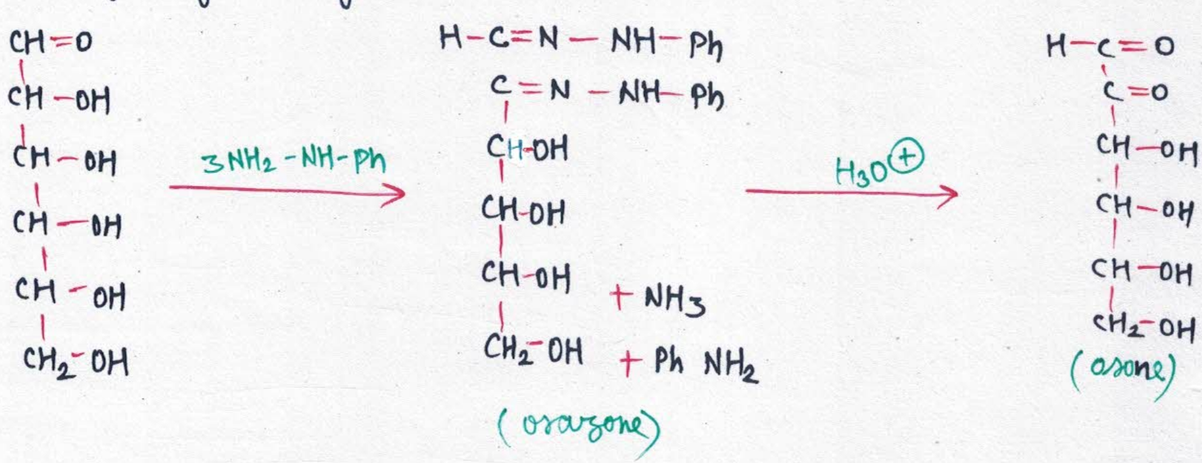
Hence, structure is :

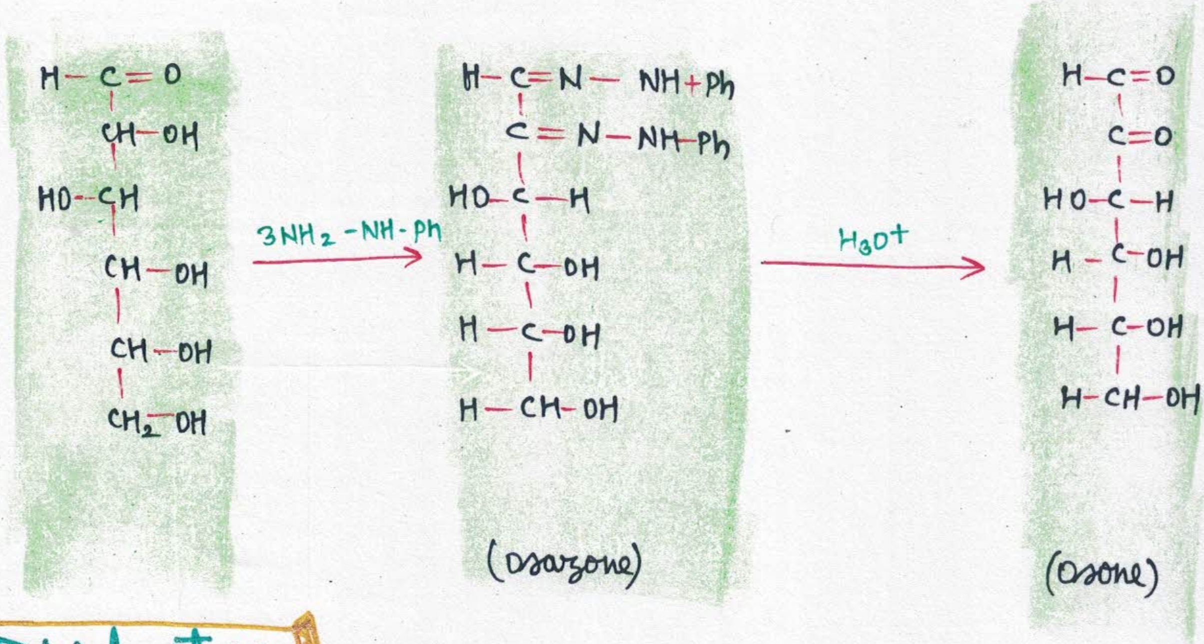


Reaction With NH_2NH-Ph

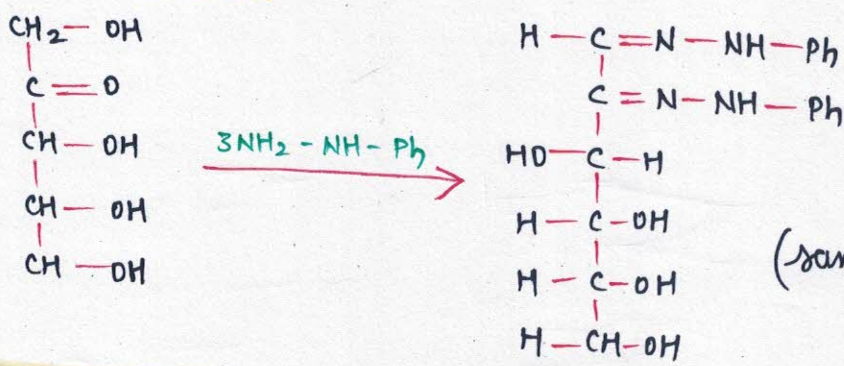
$$R-\overset{OH}{CH}-\overset{O}{\overset{\|}{C}}-H + \underbrace{3NH_2-NH-Ph}_{\text{Phenyl hydrazine}} \longrightarrow R-\underset{\|\ N-NH-Ph}{C}-CH=N-NH-Ph + Ph-NH_2 + NH_3$$

1 mole of hydroxy carbonyl reacts with 3 moles.





D(-) fructure

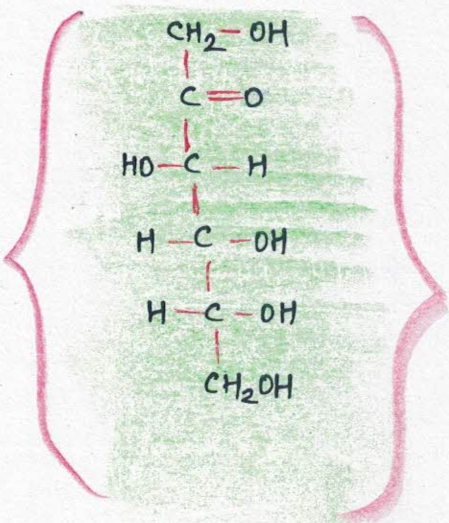


(same product as glucose)

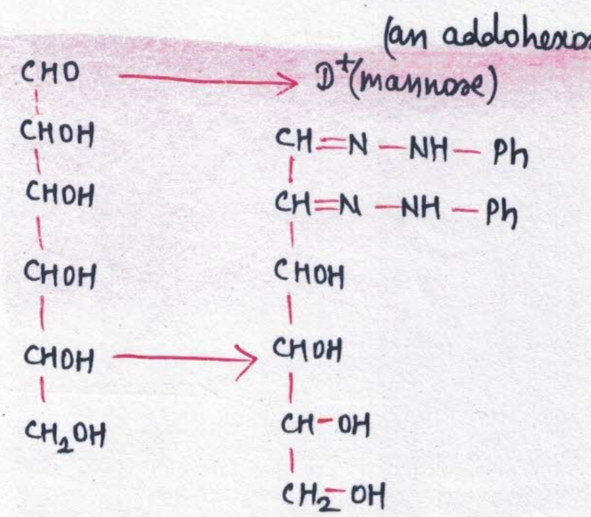
Hence, any two sugars forming same and identifie osazone must have same C_3, C_4 & C_5 configuration.

Hence, as fructose & glucose have same and identical osazone. they have same C_3, C_4, C_5 configuration.

So, structure of fructose:-

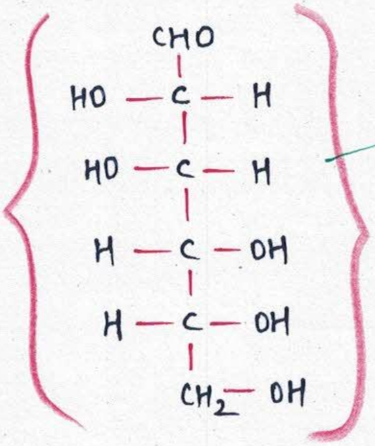


D(-) fructose



As it forms same product as glucose & fructose, it has identical C_3 C_4 & C_5 configuration. Mannose is different from glucose.

Its structure is —



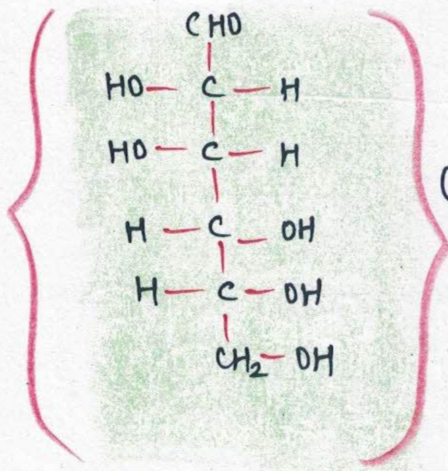
Mannose

Glucose and Mannose are distereoisomers as their mirror images do not coincide.

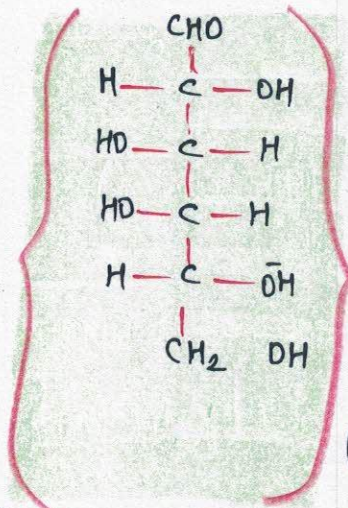
Of the so many stereocentres in a molecule, if the configuration is different at only one centre, they are called as Epimers.

All epimers are distereoisomers as they are not mirror images.

Two distereoisomers where configuration is differing at only one centre is known as epimers.



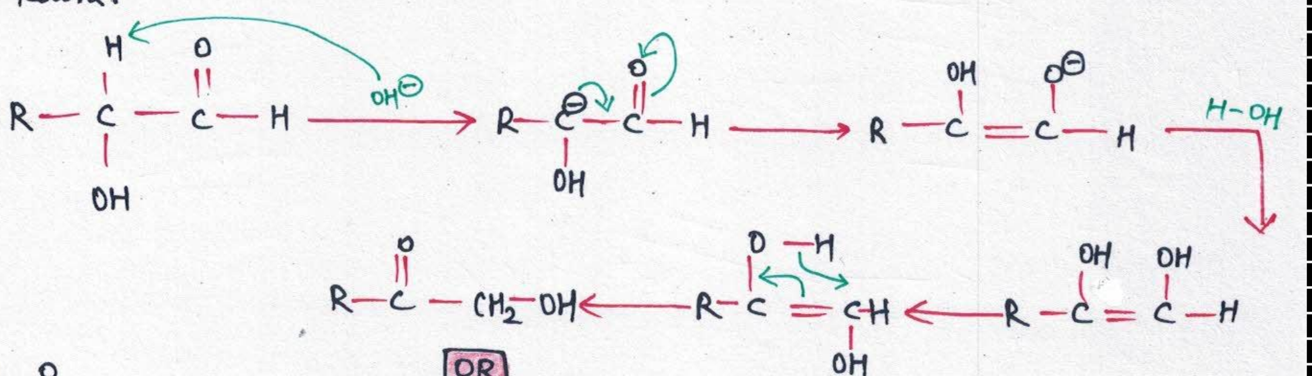
(D+) Mannose is C_2 epimers of Glucose



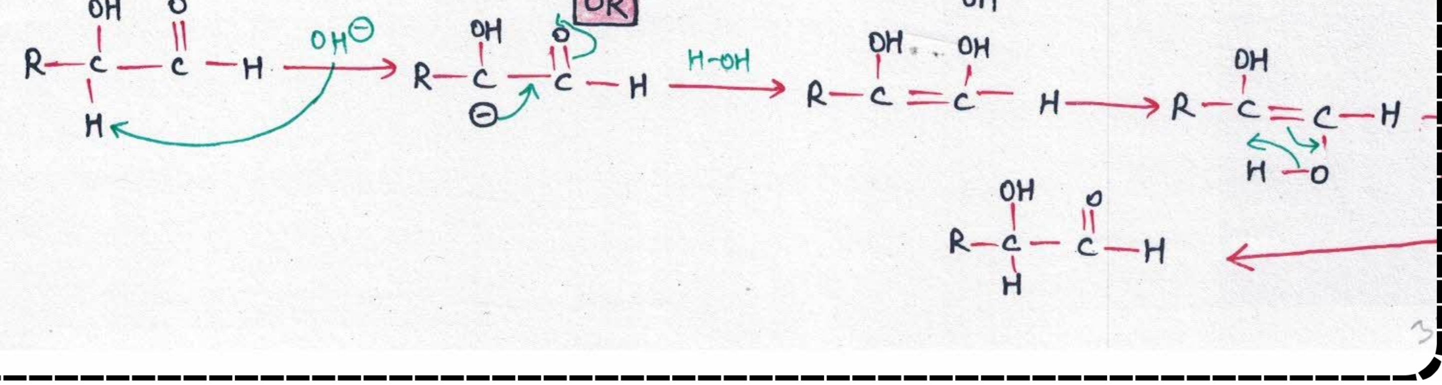
D^+ Galactose is a C_4 epimer of Glucose. But Galactose & mannose are not Epimers.

(D+)

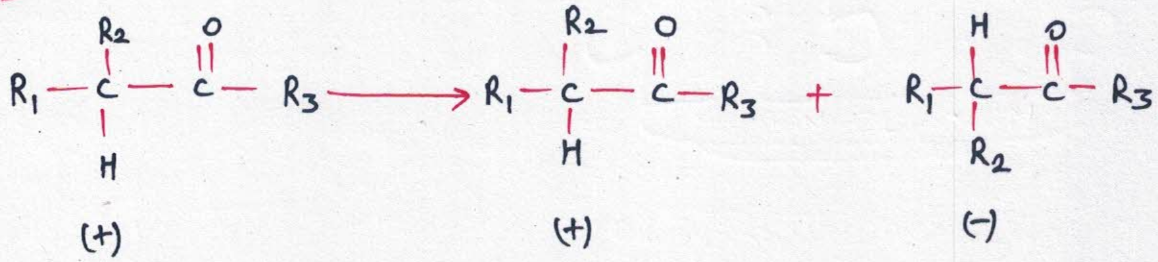
In basic conditions, α hydroxy aldehyde can tautomerise into α hydroxy ketone.

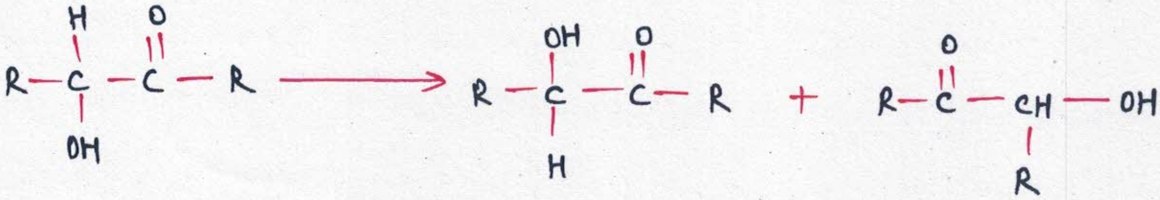


OR



CONCEPT





SCHIFF'S REAGENT

A Dye stuff (Pink) (Rosaniline) + SO_2 → becomes colourless product (schiff Reagent)

Schiff's reagent $\xrightarrow{R-CHO}$ original pink colour restored

Schiff's reagent $\xrightarrow{\text{ketone}}$ No Pink colour

GLUCOSE

GLUCOSE $\xrightarrow{NH_2OH}$ ✓
GLUCOSE $\xrightarrow{\text{Tollen's reagent}}$ ✓
GLUCOSE $\xrightarrow{\text{Bendict}}$ ✓
GLUCOSE $\xrightarrow{\text{Fahling's}}$ ✓

} Irreversible reactions

GLUCOSE $\xrightarrow{NaHSO_3}$ ✗
GLUCOSE $\xrightarrow{2,4,DNP}$ ✗
GLUCOSE $\xrightarrow{\text{schiff's reagent}}$ ✗

} Reversible reactions

because glucose exists as cyclic compound and is very stable as equilibrium moves towards more stable side

E.g. towards cyclic glucose which is more stable. Hence glucose does not react.

Glucose on crystallisation in both & concⁿ solution $\longrightarrow \beta\ (D^+)$ glucose

Glucose on crystallisation in cold & dilute solution gives $\longrightarrow \alpha\ (D^+)$ glucose

$\rightarrow$ Solubilities difference is the reason.

$\alpha\ (D^+)$ and $\beta\ (D^+)$ glucose are epimers as configuration differs at only one centre. $\alpha\ (D^+)$ has $+19°$ angle of rotation and $\beta\ (D^+)$ has $+111°$ angle of rotation. so, $\alpha (D^+)$ angle of rotation $\uparrow$ to 52.7 and $(\beta)(D^+) \downarrow$ to 52.7. Hence an equilibrium constant value of rotation is formed, i.e $52.7°$

Epimers which have a constant equilibrium value of angle of rotation are called anomers...

This phenomenon of changing angle of rotation of two stereoisomers to a constant equilibrium value is called "Muta Rotation".

All monosaccharides show muta rotation.

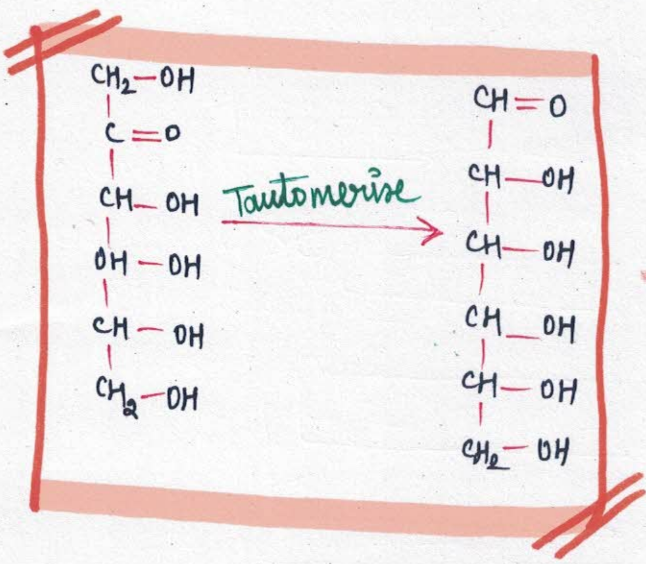
All epimers $\longrightarrow$ distereoisomers

All anomers $\longrightarrow$ epimers

Muta rotation is shown by anomers which are epimers which are distereoisomers.

Anomers are hemiacetals.

$$R-\overset{O}{\overset{\|}{C}}-CH_2-OH \longrightarrow R-\overset{OH}{\overset{|}{CH}}-CH=O$$



NOTE

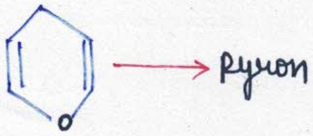
- Fructose will show all test (tollen's test, benedid) etc.
- All monosaccharides are reducing sugar.
- All reducing sugars show muta rotation.
- All reducing sugars show are anomers.
- All sugars which show muta rotation are reducing sugars.

All sugars which can exist as anomers are reducing sugars.

All hemeacetalic sugars exist as anomers, hence they are reducing sugars and will show muta rotation.

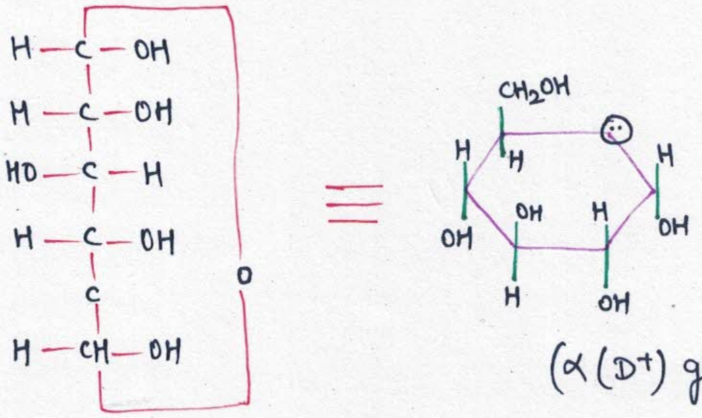
α and β(D+) glucose differ in the hydroxy group side. this is known as glycosidic hydroxy.

The carbon responsible for muta rotation is called anomeric carbonn.

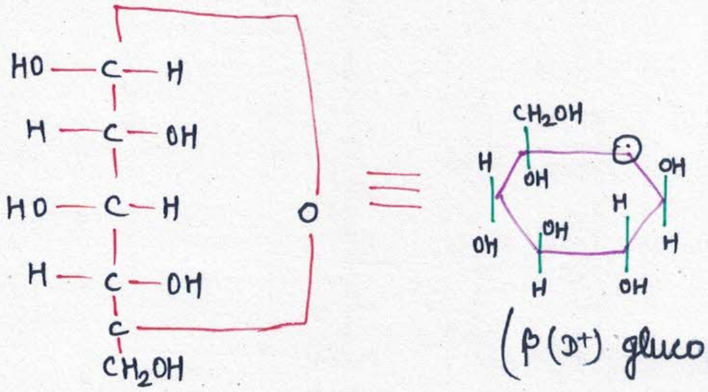


Glucose's cyclic structure too has a structure like this, hence this structure is "Pyranose structure".

Glucose structure can also be drawn in the form of ring called "Haworth structure".



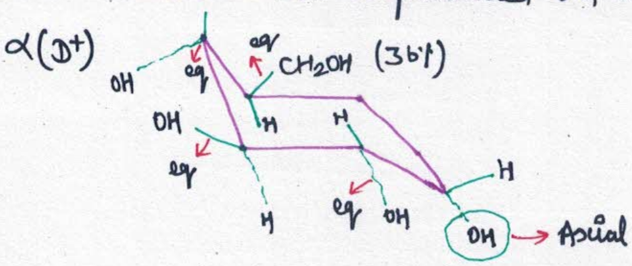
(α (D+) glucopyranose)



(β(D+) glucopyranose)

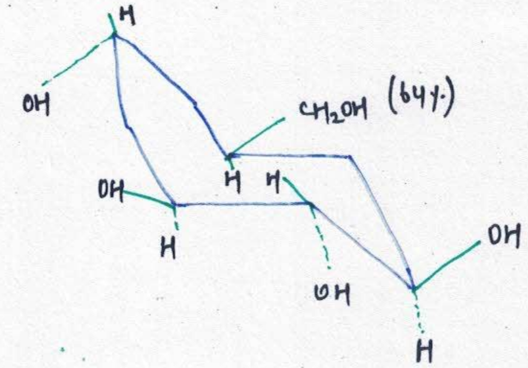
All substituents are equitorial

These structures can be represented in chair form.



one OH in axial & others in equitorial. Hence less stable.

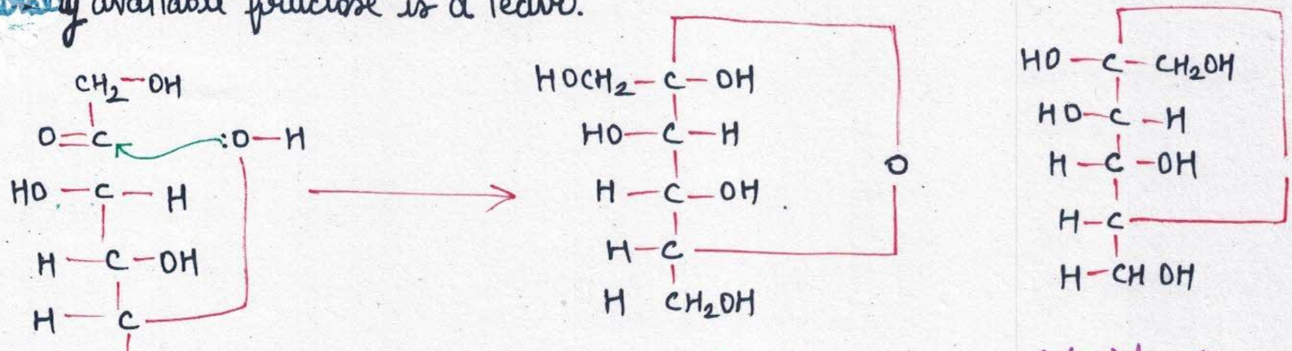
β (D⁺)



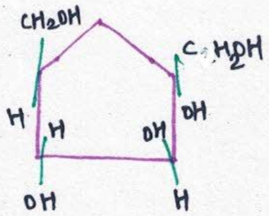
All OH in equitorial position. Hence most stable structure.

This is the reson why nature produces only β (D⁺) glucose because it is more stable.

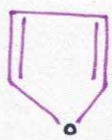
Naturally available fructose is a leavo.



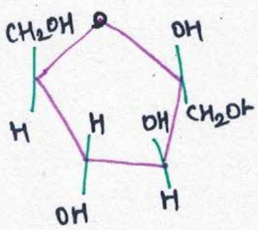
α (D⁻) fructose β (D⁻) fructose



[α (D⁻) fructofuranose] → as it resemble



furon structure



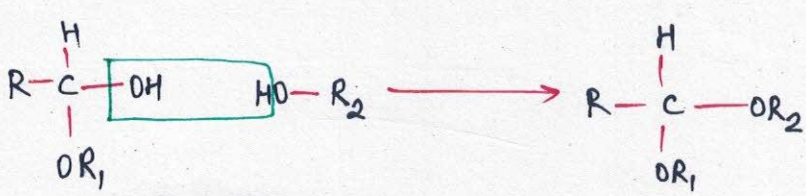
[β (D⁻) fructo furonose]

Both of these are called anomers.

MALTOSE

It is a disaccharide

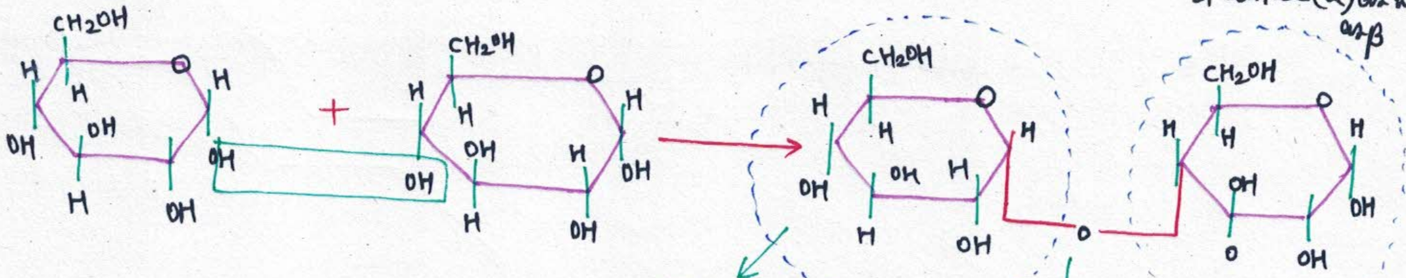
Maltose 2 (D⁺) Glucose



(Hemiacetal) (acetal)

C_1 hydroxy of anomer is always glycosidic.

It can be (α) as well as β



This has to be $\alpha(D^+)$ Glucose

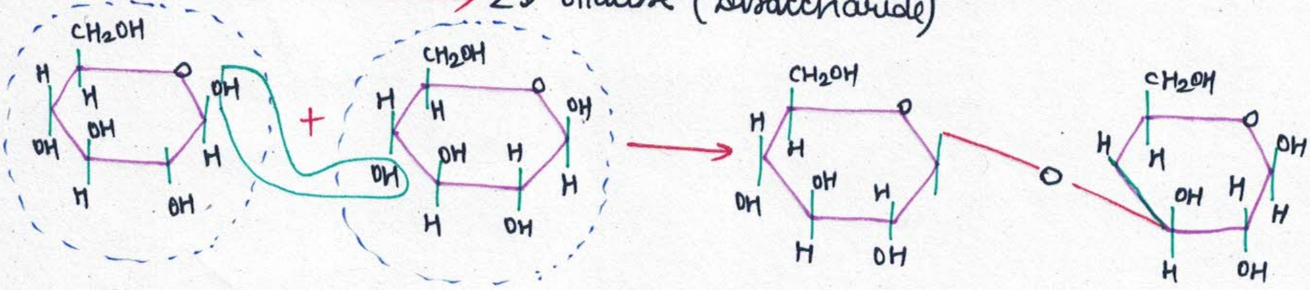
Glycosidic

(C_1+C_4) react

It has anomeric carbon hence shows muta rotation so it is reducing sugar.

CELLUBIOSE

cellubiose $\xrightarrow{\text{heat}}$ $2\,D^+$ Glucose (Disaccharide)



(any b α β β)

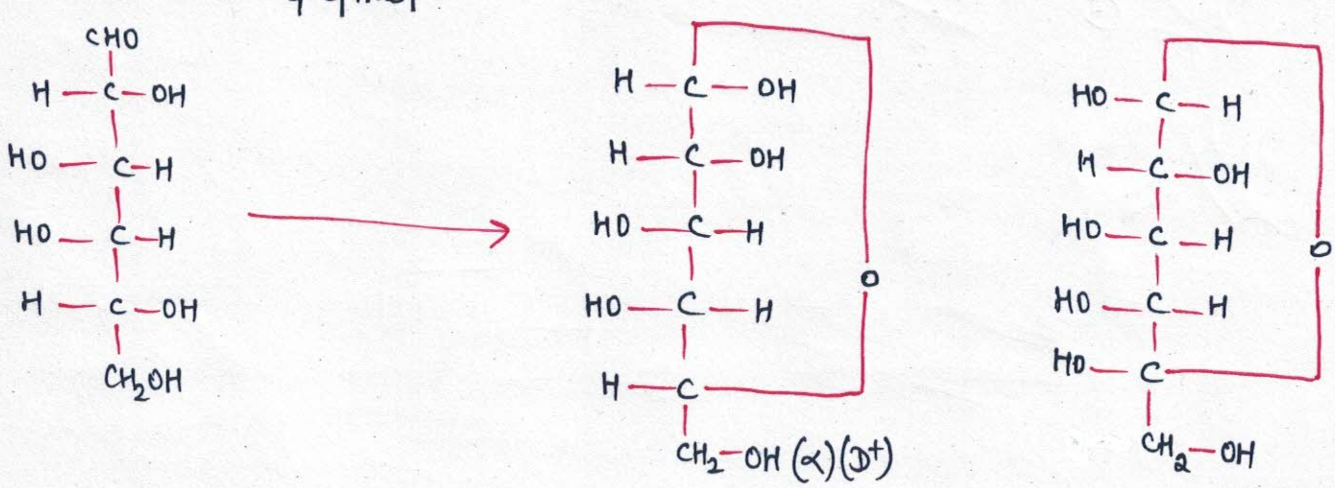
(C_1+C_4) react

As it has anomeric carbon, it shows muta rotation hence it is reducing sugar.

LACTOSE

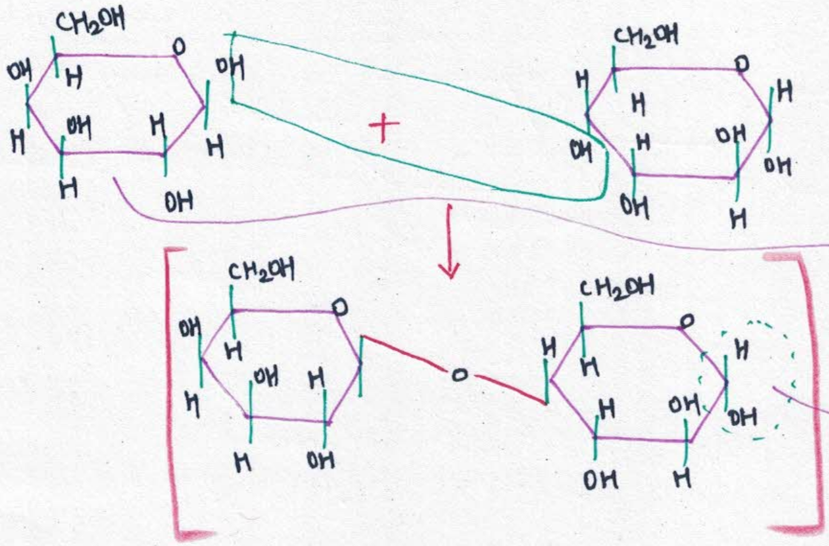
Lactose $\xrightarrow{H_2O^+}$ βD^+ Galactose + βD^+ Glucose

Galactose is a C_4 epimer



(α)(D+)

β(D+)



It has to be $\beta(D^+)$ galactose

can be any (α) or β

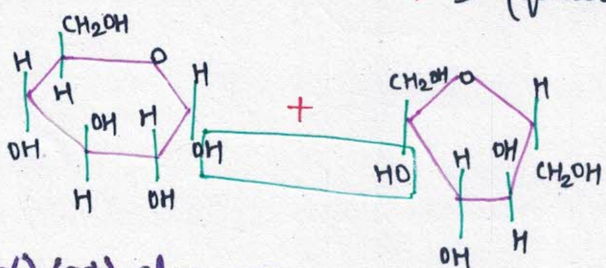
Reducing sugar ($C_1 + C_4$)
Anomeric

SUCROSE

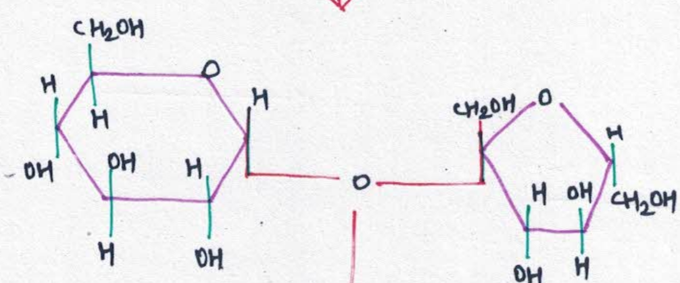
Sucrose $\xrightarrow{H_3O^+}$ D^- (fructose) + D^+ (Glucose)

(one is α, one is β)

Glucose   fructose



(α) (D^+) glucopyranose   (β) (D^-) fructofurnose



Both side glycosidic
Ring cannot be formed
Hence no muta rotation
Not a reducing sugar.

($C_1 + C_2$) react

Sucrose $\xrightarrow{H_3O^+}$ (D^+) glucose + D^- (fructose) = (−92.4)

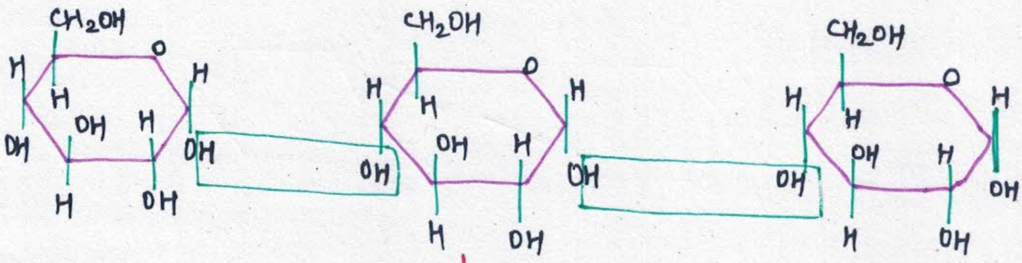
52.7°

Sucrose is levorotatory ~~sugar~~ dextro sugar → levo

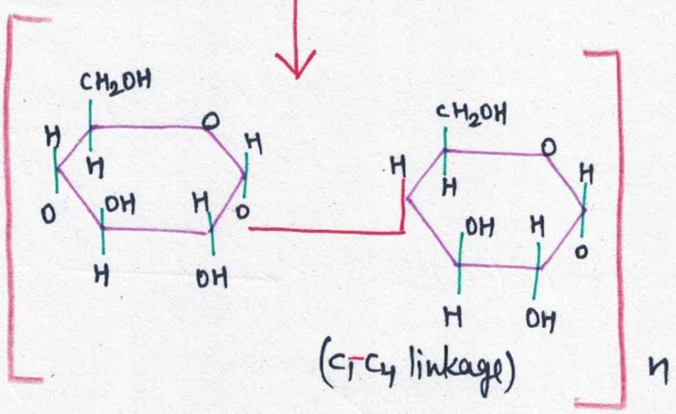
Resultant is $-(92.4 - 52.7)^\circ \rightarrow \ominus$

So sucrose is dextro but hydrolysed sucrose is leavo. Hence it is called invert sugar.
Most sweetest sugar is fructose.

STARCH



(Amylose)



(C_1–C_4 linkage)

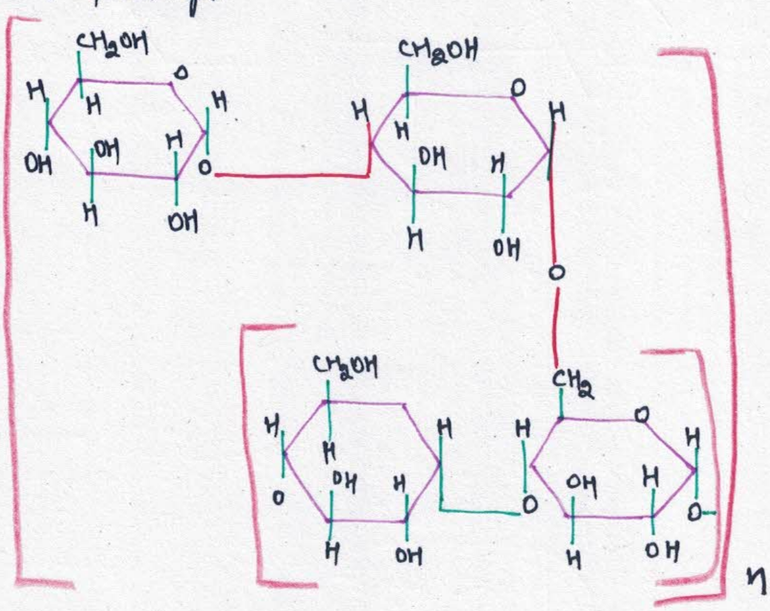
(n = 200–1000)

Starch consists of α (D$^+$) glucopyranose.
Starch consists of two parts –

(i) Amylose ⟶ 15% of starch (water soluble starch)

(ii) Amalopeptin ⟶ 85% of starch (water insoluble starch)

Amylose has low molecular mass and has a linear structure, hence it is more soluble.
It has C_1–C_4 linkage.

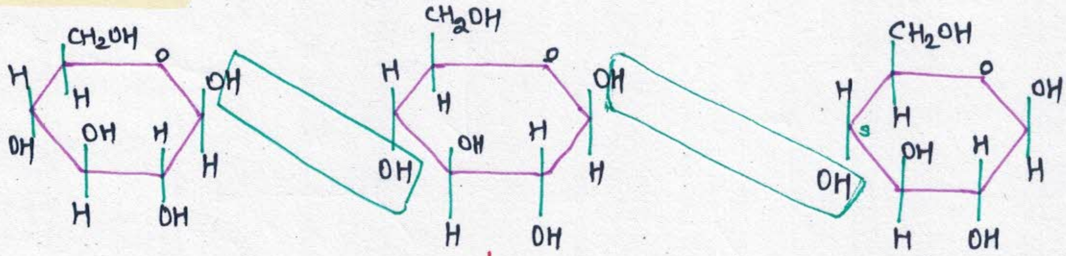


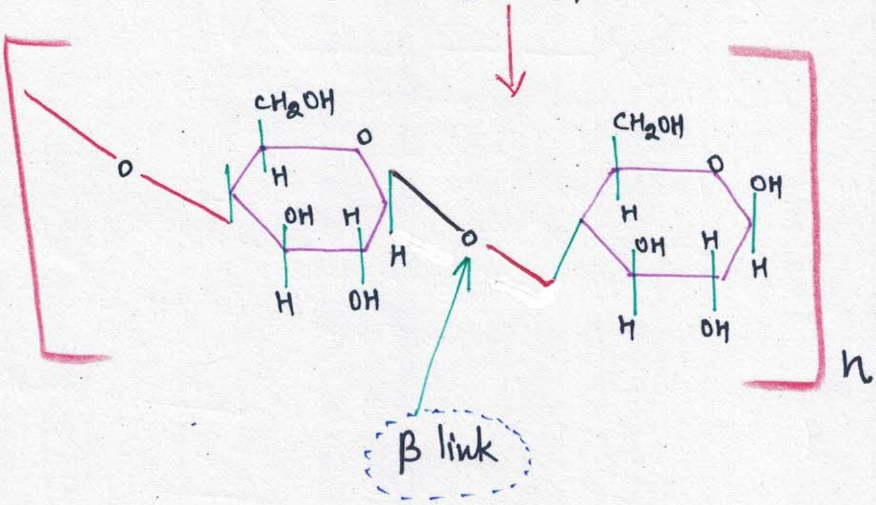
Amylopeptin
(C_1 + C_6 linkage)
High molecular mass. Hence insoluble in water.

GLUCOGEN

Glycogen is also a starch (amylopeptin) but has even higher branchings than amylopeptin. So it has more molecular mass and is insoluble.
Glycogen is stored in liver, As it as insoluble it does not dissolve in blood.
Glycogen also called animal starch.

CELLULOSE





Straight chain

It has β (D⁺) glucose structure.