Chapter:

# Biochemistry

## Carbohydrates

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Chemistry with MJS

Chemistry Preparation by MJS

# Introduction To Biochemistry

1- Study of Biochemical process in living organisms. is called Biochemistry.

2- Study of Biomolecules called Biochemistry.

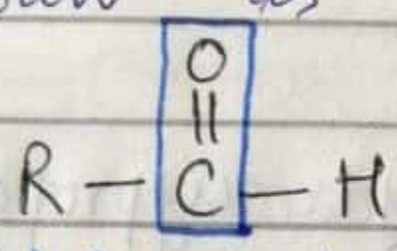
**Biomolecules:-**

The molecules which are the part of living organisms.

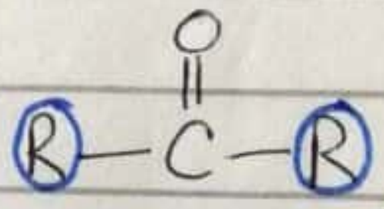
e.g:- Lipids, protiens, carbohydrates and nucleic acid.

**Carbohydrates:-**

Polyhydroxy compounds of Aldehydes and ketons are known as carbohydrates.

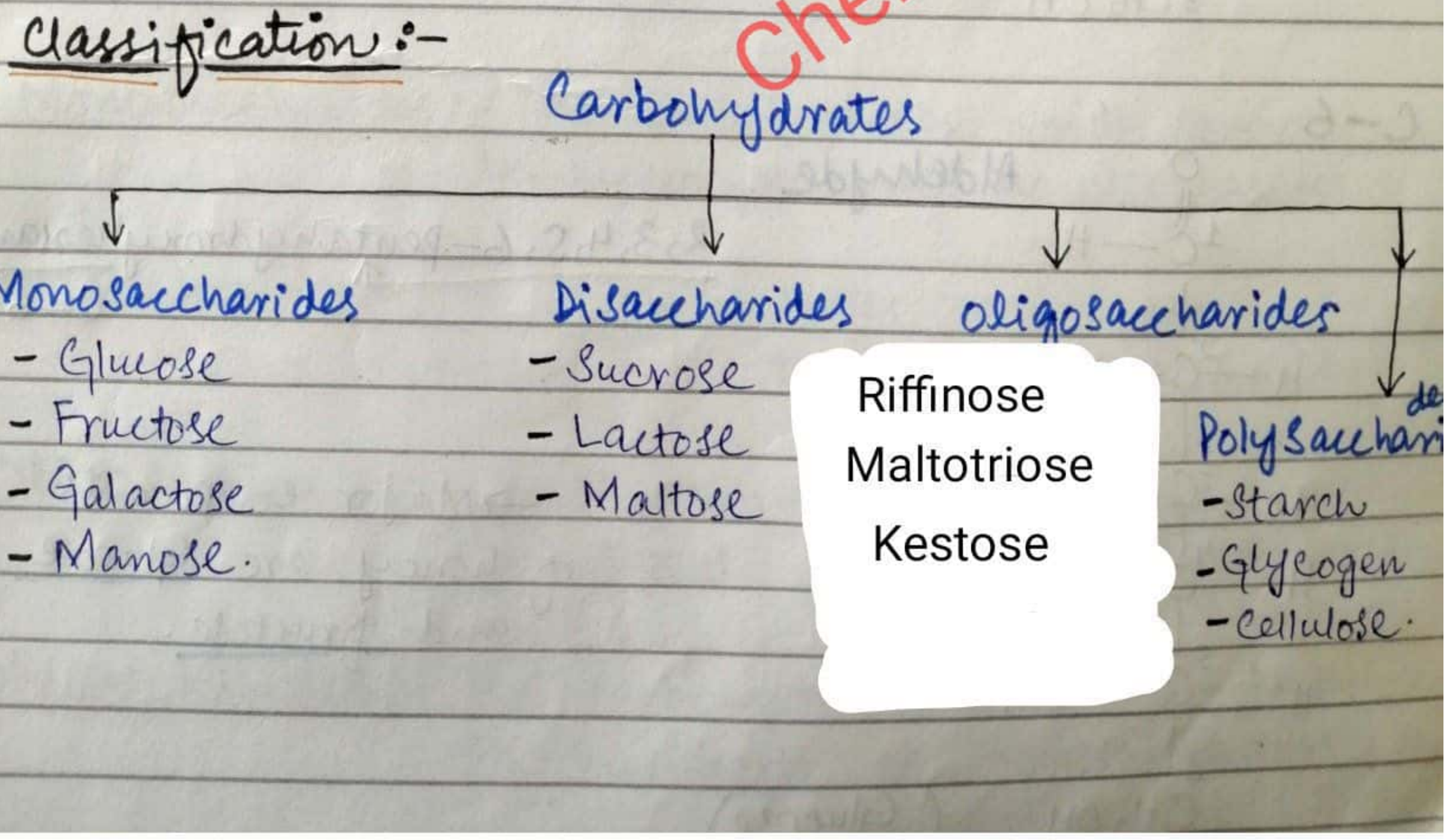


(Aldehydes)



(Ketones)

**Classification:-**

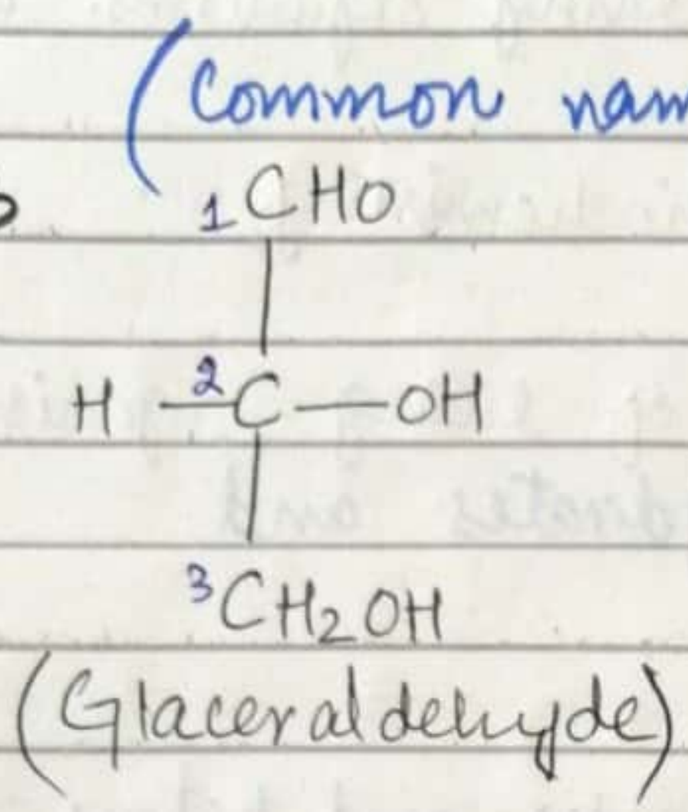


## Nomenclature :-

{ Aldehyde = -al
Ketone = -none }

C-3

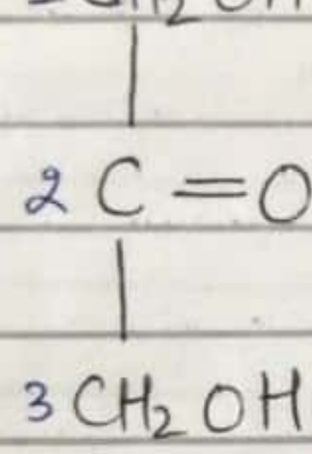
(Common name:-)




(Glaceraldehyde)

(IUPAC name:-)

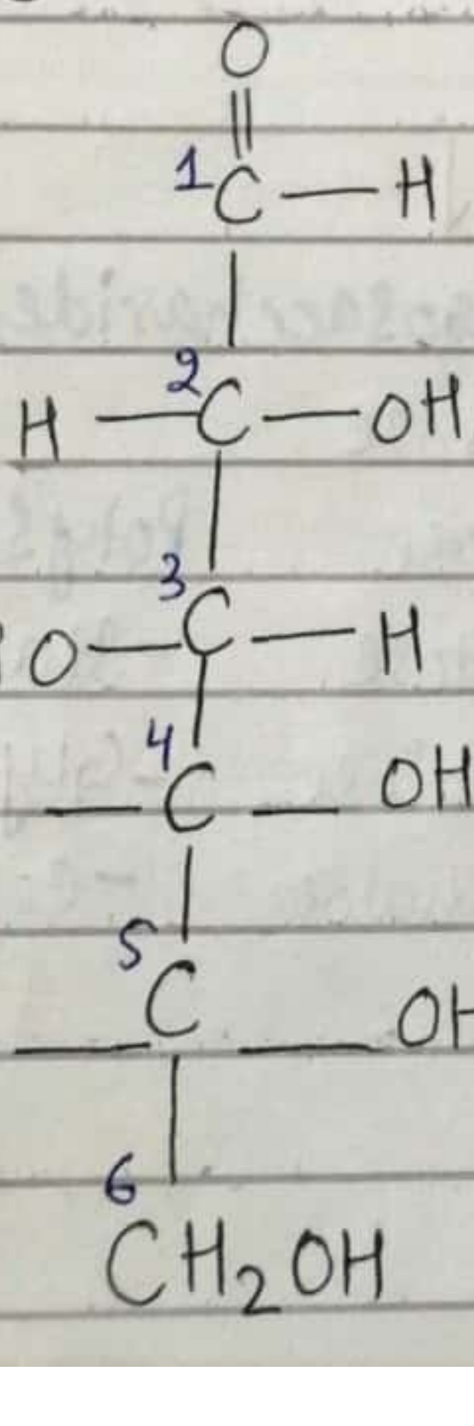
2,3-dihydroxypropanaldehy
or
2,3-dihydroxypropnal




1,3-dihydroxypropanone.



C-6



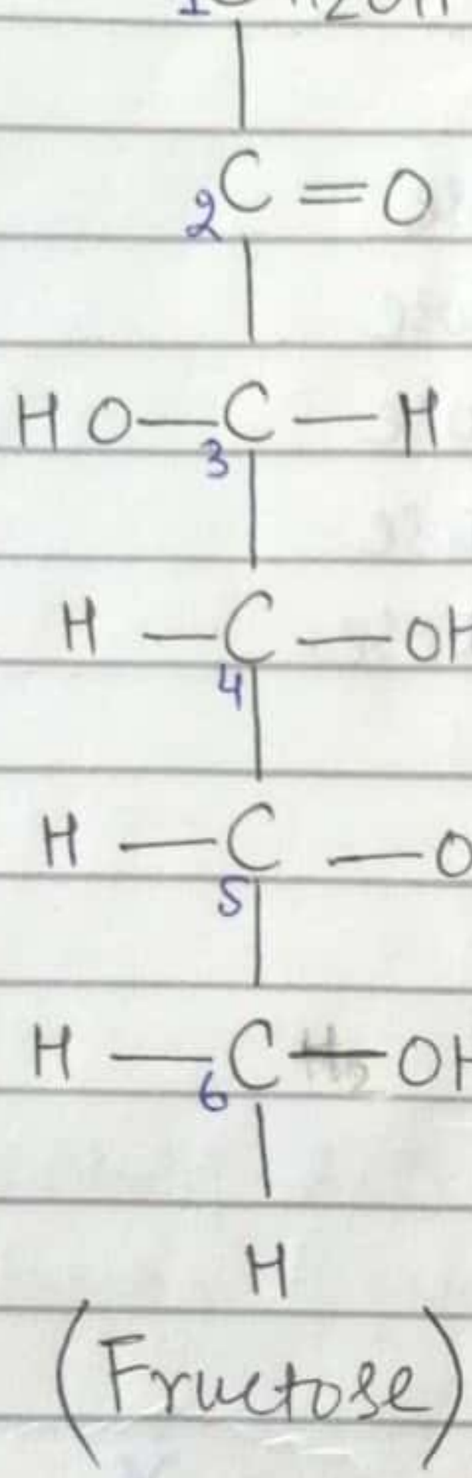

(Glucose)

Aldehyde

2,3,4,5,6-pentahydroxyhexanal

C-6

→ Major components of honey are Glucose and fructose.




1,3,4,5,6-pentahydroxyhexane-2-one



**Monosaccharides:-** The carbohydrates which cannot be hydrolysed are monosaccharides.

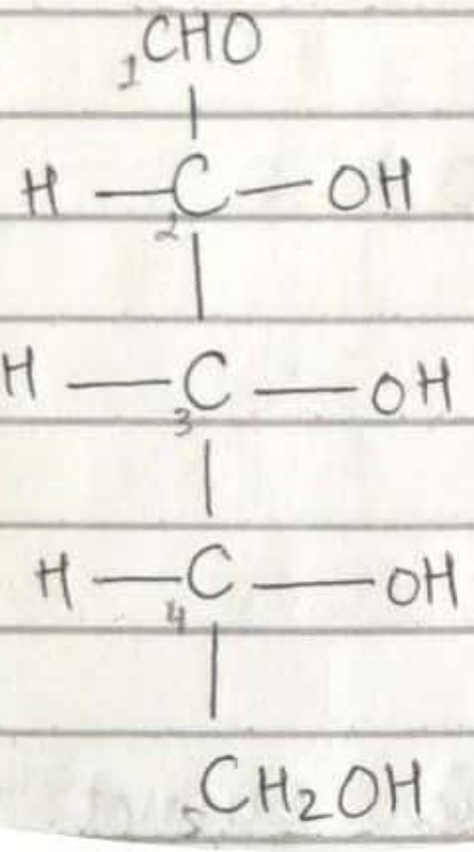
**Disaccharides:-** The carbohydrates which can hydrolysed to two monosaccharides.

**Oligosaccharides:-** The carbohydrates which can hydrolysed to 3—10 monosaccharides.

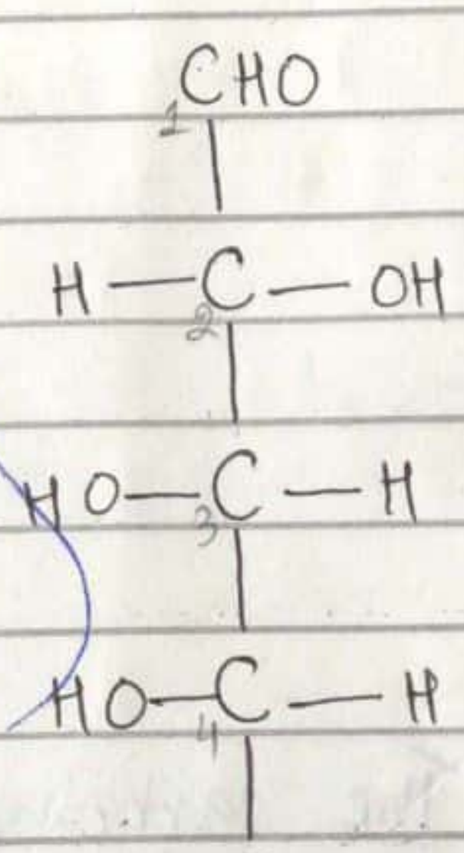
**Polysaccharides:-** The carbohydrates which can hydrolysed to hundreds of monosaccharides.

(Monosaccharides) have two groups Aldoses and Ketoses.

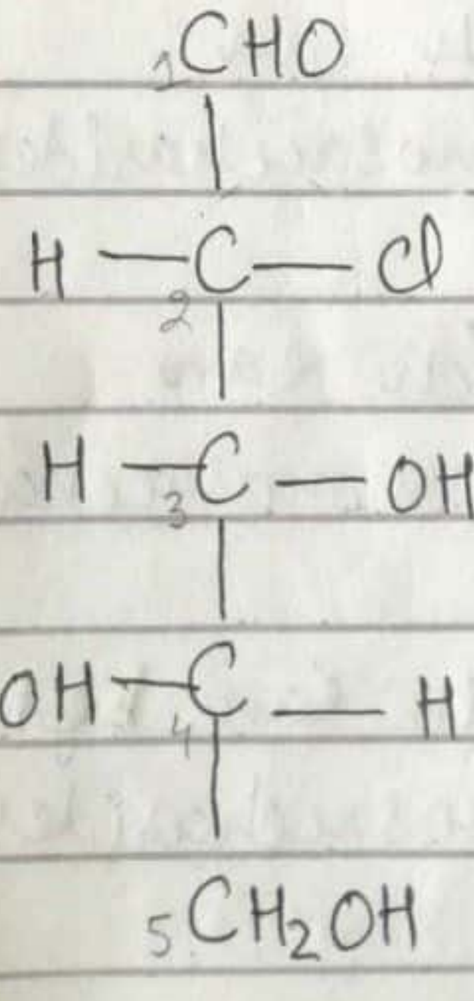
| | | | |
|---|---|---|---|
| C-4 | Aldotetrose | C-4 | Ketotetrose |
| C-5 | Aldopentose | C-5 | ketopentose |
| C-6 | Aldohexose | C-6 | ketohexose |
| C-7 | Aldoheptose | C-7 | ketoheptose |
| C-8 | Aldooctose | C-8 | ketooctose |

① 

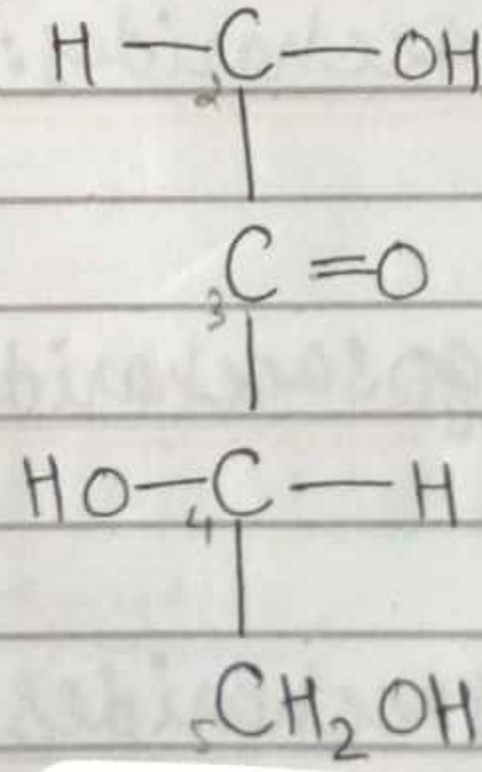
2,3,4,5-tetrahydroxy-pentanal

② 

2,3,4,5,6-penta hydroxy hexanal

③ 

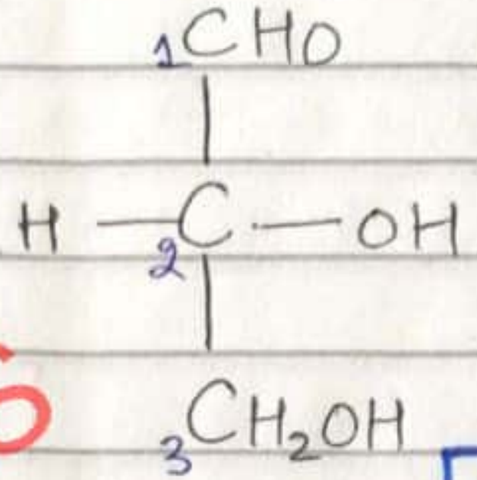
2-chloro 3,4,5 trihydroxy pental.

④ 

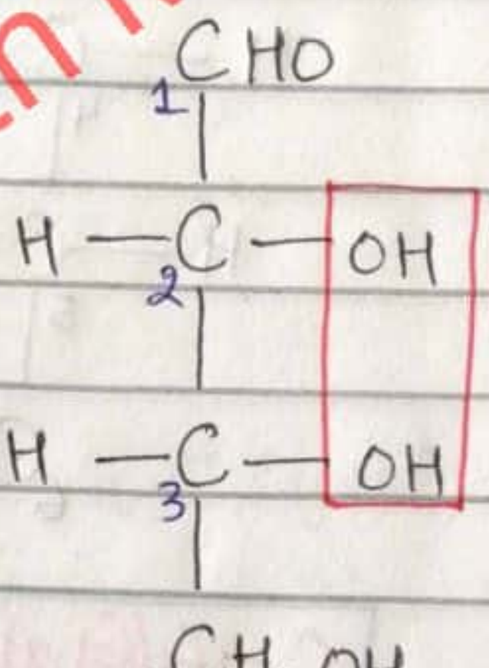
1,2,4,5-tetrahydroxy-pent-3-one

# Monosaccharides :-

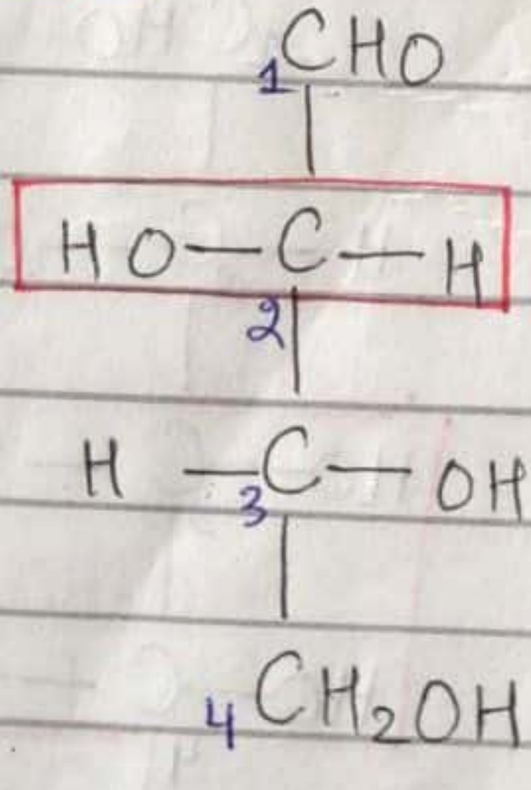
Aldoses :- 3-C (Galaceraldehyde)



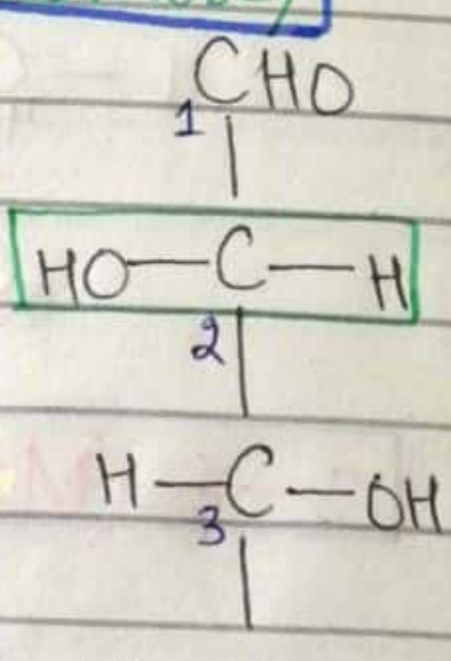
4-C (Erythrose)



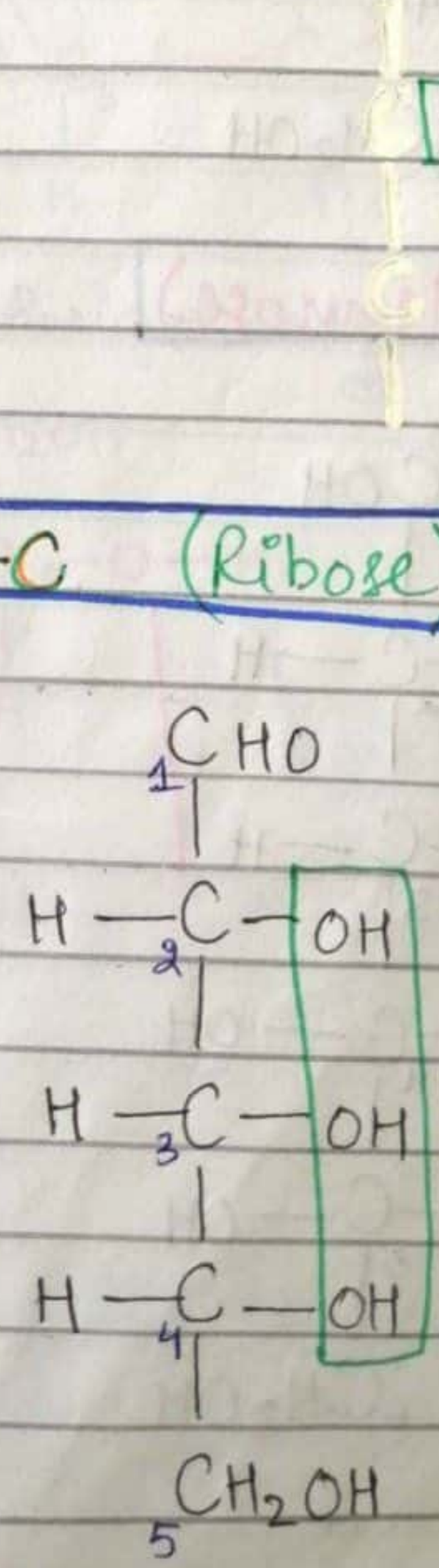
4-C (Threose)



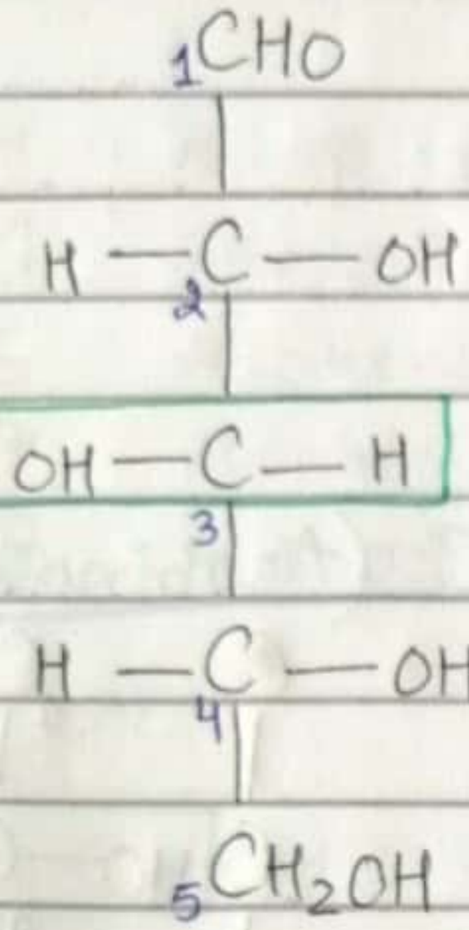
5-C (Arabinose)



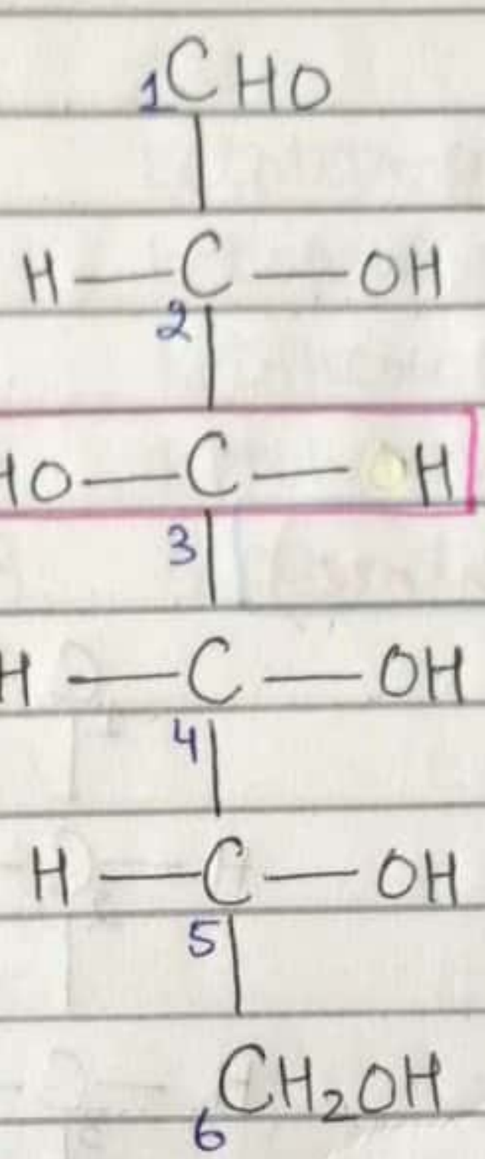
5-C (Ribose)



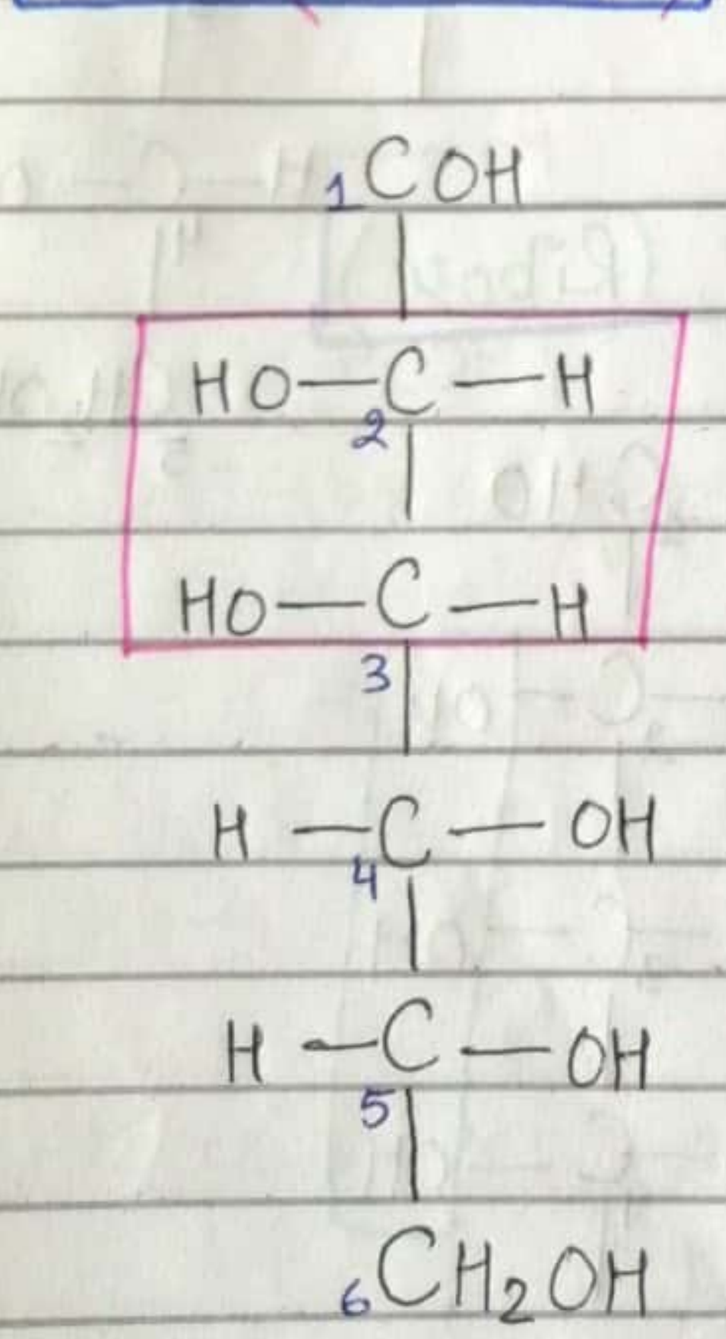
5-C (Xylose)



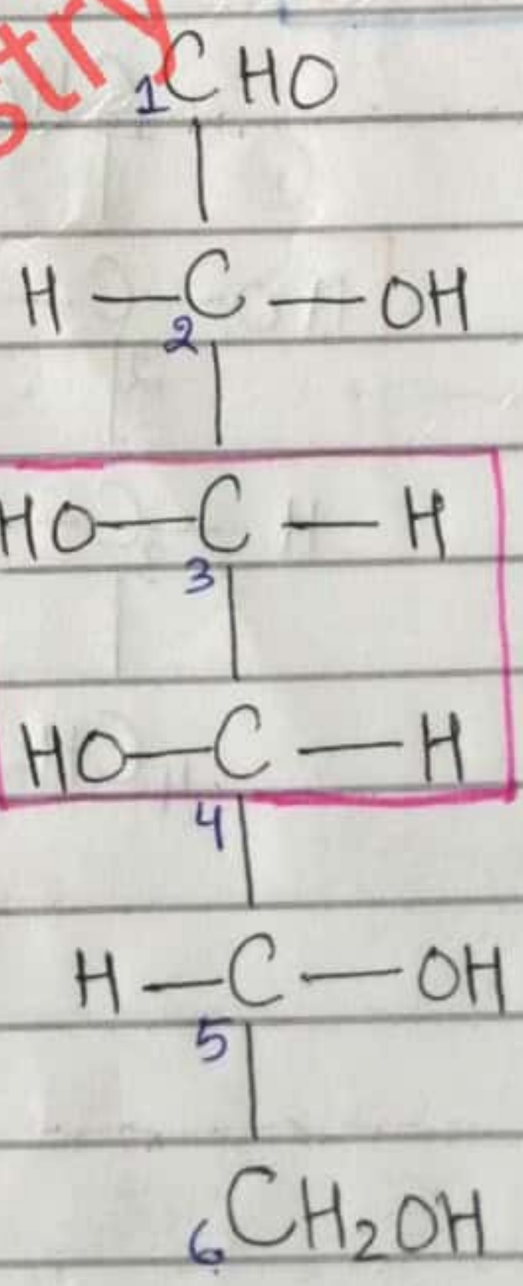
C-6 (Glucose)



C-6 (Mannose)



C-6 (Galactose)



# Importance of Monosaccharides

## Pentoses:

* **Ribose:**
  - Found in Nucleic Acids, RNA & DNA.
  - Found in ATP,
  - It is a part of coenzymes & Flavoproteins.
* **Arabinose & xylose:**
  - constituents of Glycoproteins in plants & animals.
* **Lyxose:**
  - constituent of a Lyxoflavin, isolated from human hearts muscles.
* **xylulose:**
  - intermediate in Uranic acid path-way (Minor pathway of Glucose-oxidation).

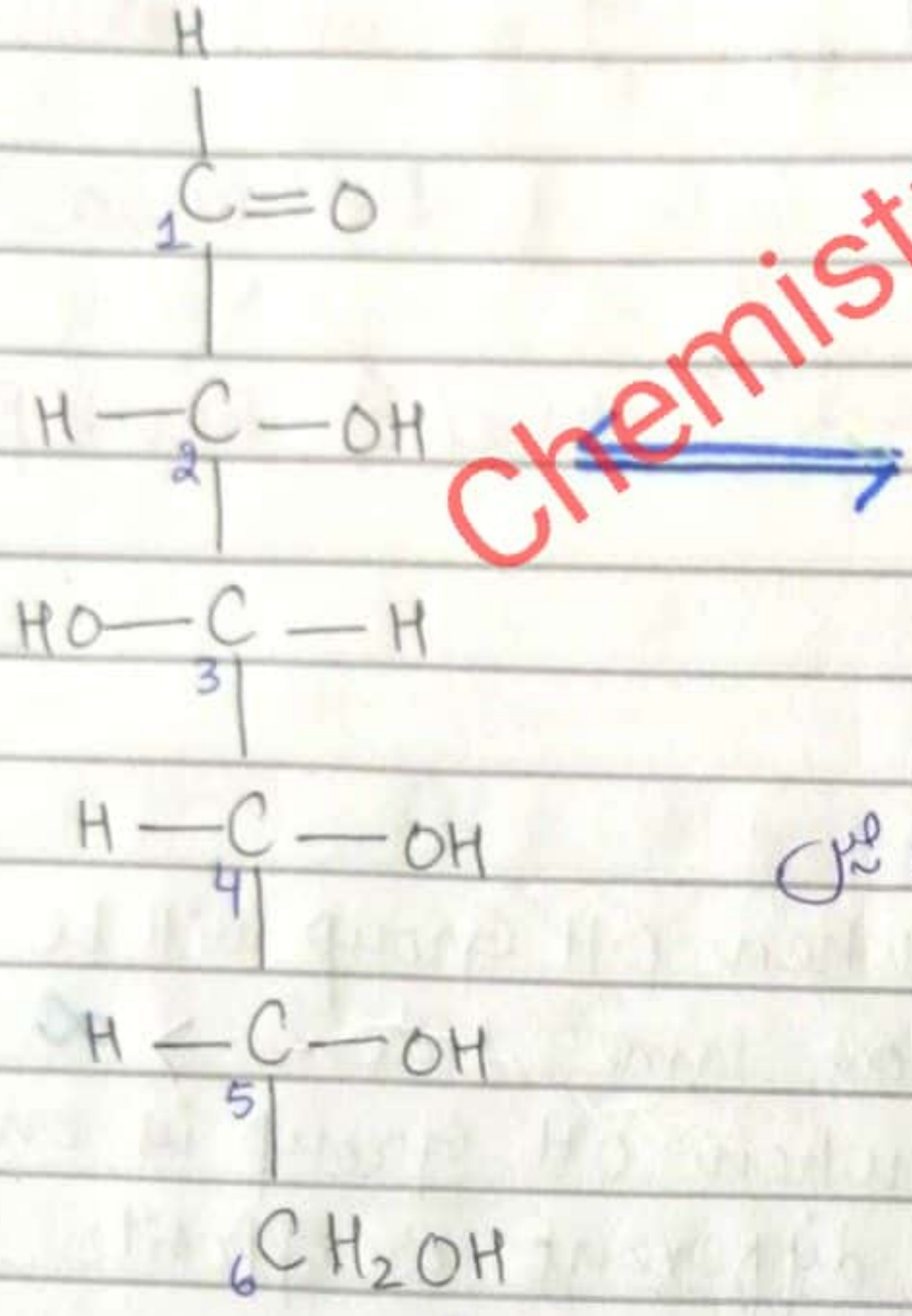
## Hexoses:

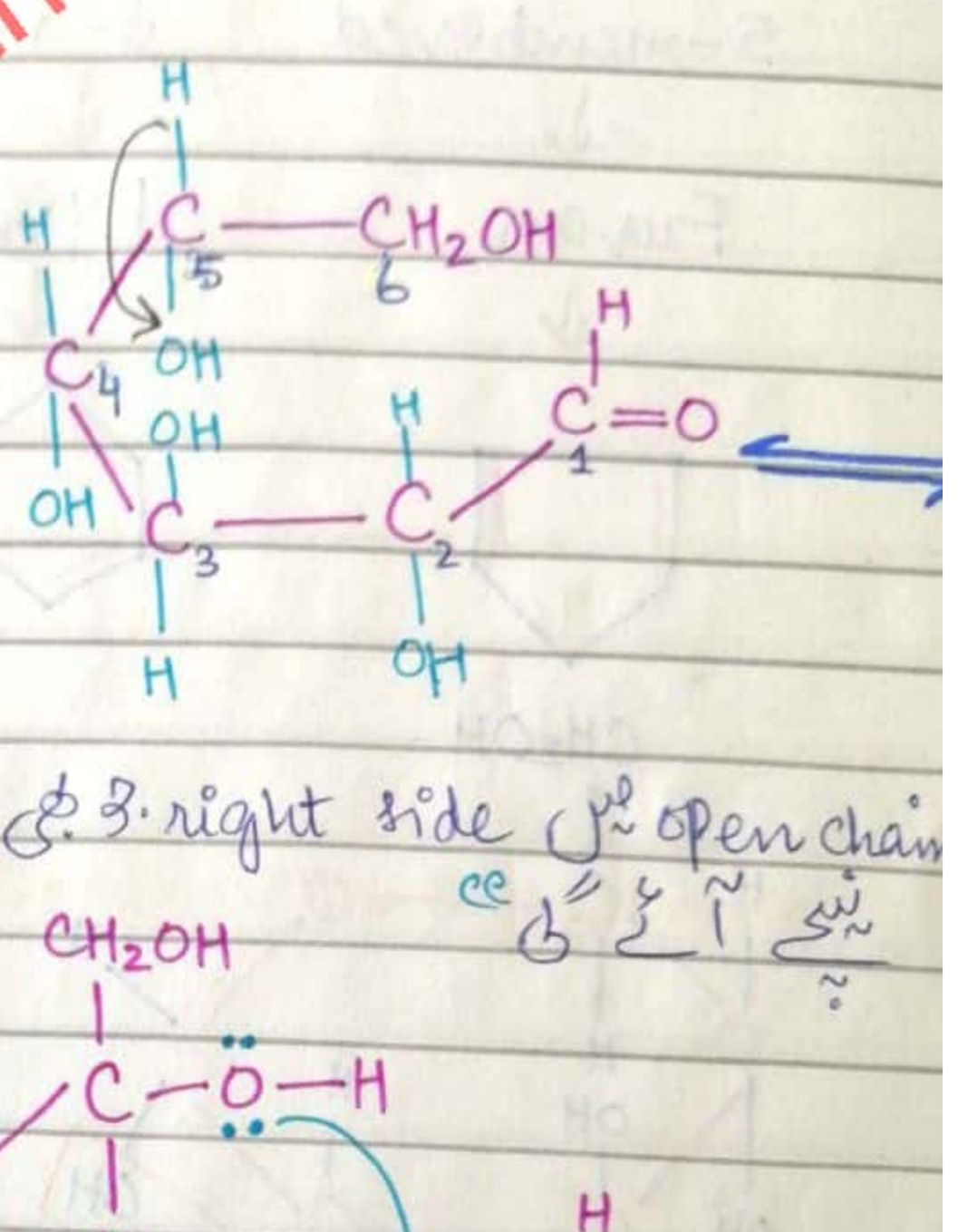
* **Glucose:** → most important sugar
  - Major source of energy
  - Dietary carbohydrate
  - In Liver & other tissues, it is converted into glycogen, glactose, Ribose & Fructose.
* **Fructose:** → called Fruit Sugar
  - can be converted into glucose in Liver.
  - Major carbohydrate in Honey.
  - Main sugar of semen.
* **Galactose:**
  - synthesized in mammary glands to make the Lactose of Milk (Milk Sugar)
* **Mannose:** constituent of Glycoproteins.

# Cyclic Structure of Sugars

→ In open chain structure Glucose is not much stable. But in cyclic structure Glucose is stable.

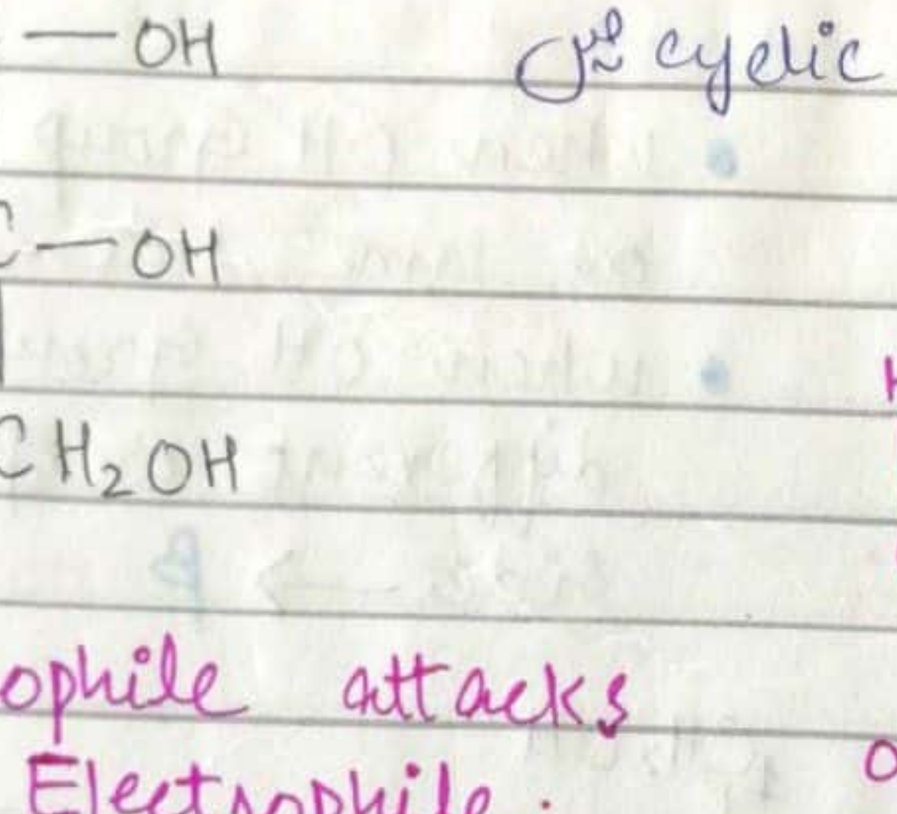
(Glucose)




⇒ Nucleophile attacks on Electrophile.

✓

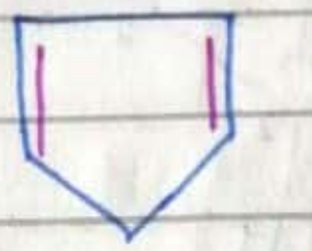


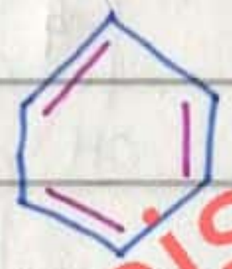

(Cyclic structure of Glucose)

# Cyclic Structure

Furanose → 5-membered → Furan

pyranose → 6-membered → PYran





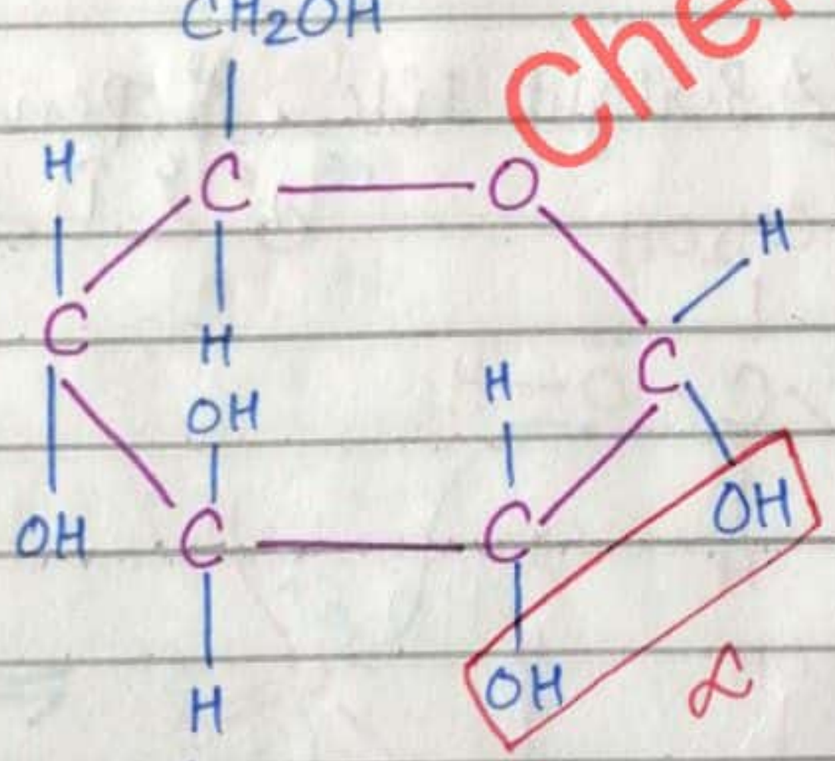
→ D-Glucose form in nature.

→ L-Glucose don't form in nature.

D-Glucose

Alpha(α) Beta(β)

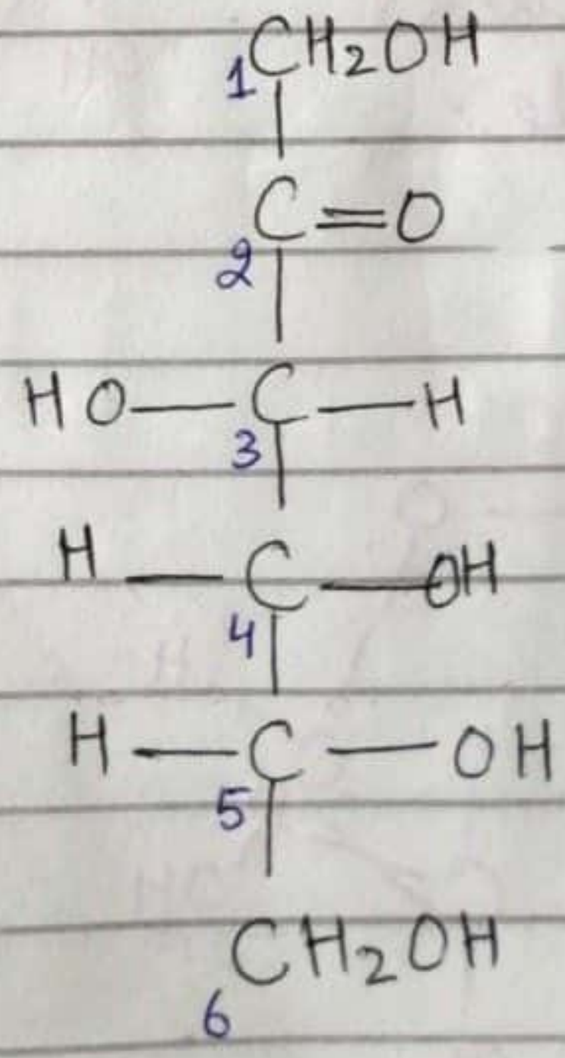




(Fructose)

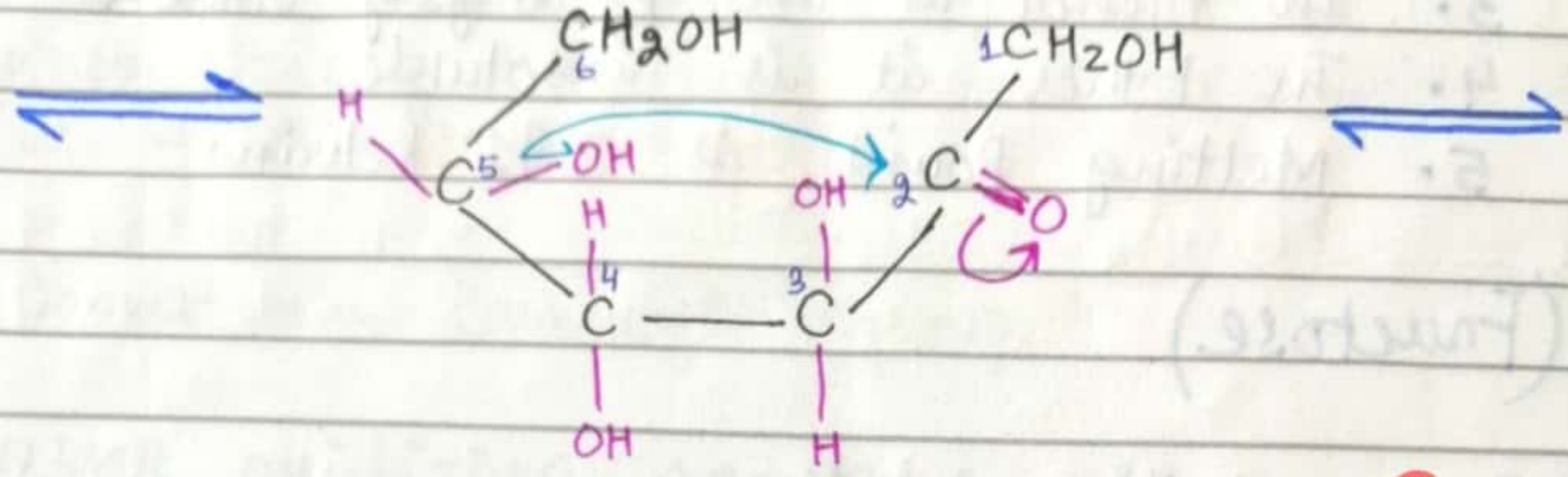
- when OH Group will be on same side → α
- when OH Group is on different or opposite side → β

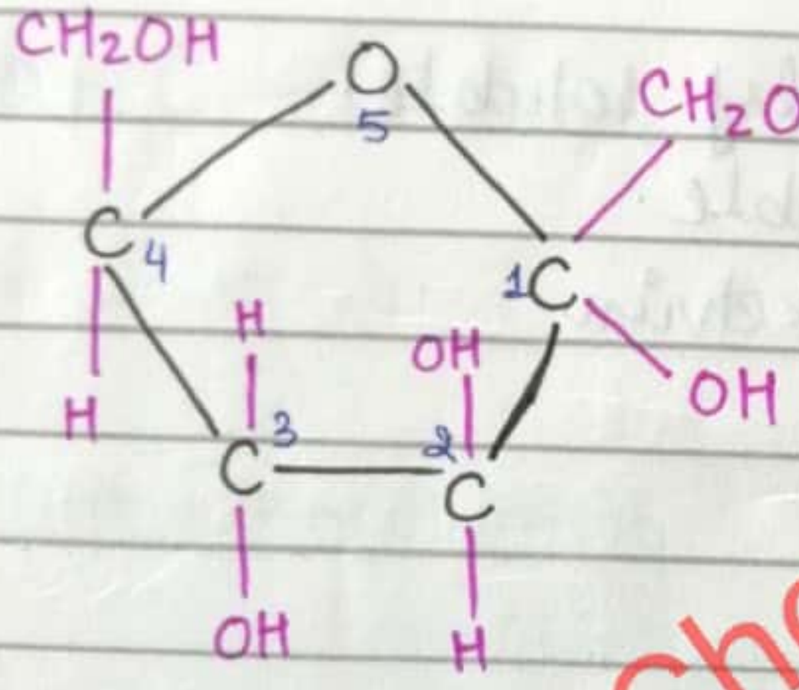
Open chain structure →



→ In Glucose ring is 1–5 carbon and 6–membered.

→ In Fructose ring is 2–5 carbon and 5–membered.




(α – Fructofuranose)



∴ Glucose is also called Blood sugar → 0.1%

**Origin** :- Occurance of Glucose → Honey, ripe grapes, Blood, urine → 8–10%

Occurance of Fructose → Fruit, Honey.

∴ Fructose is also called Fruit sugar.

# Isomerism in Monosaccharides

## * Optical Activity & optical isomerism

Any substance containing one or two Asymmetric carbons shows optical Activity OR optical isomerism.

**Dextrorotatory**

d-form (+)

e.g ↳ Glucose (naturally occuring)

↓

called dextrose

* glucose specific Rotation (+52.5°)

* Glucose shows 16 → optical isomers ($2^4 = 16$)

**Levo Rotatory**

l-form (−)

e.g ↳ Fructose (Naturally occuring)

(Levo Rotatory)

↓

called Levulose

* Fructose specific Rotation (−91°)

* Fructose shows 8 → optical isomers

$2^3 = 8$

**Enantiomers:**

pair of stereoisomers which are mirror image of each other.

e.g Glucose occurs in D & L Forms.

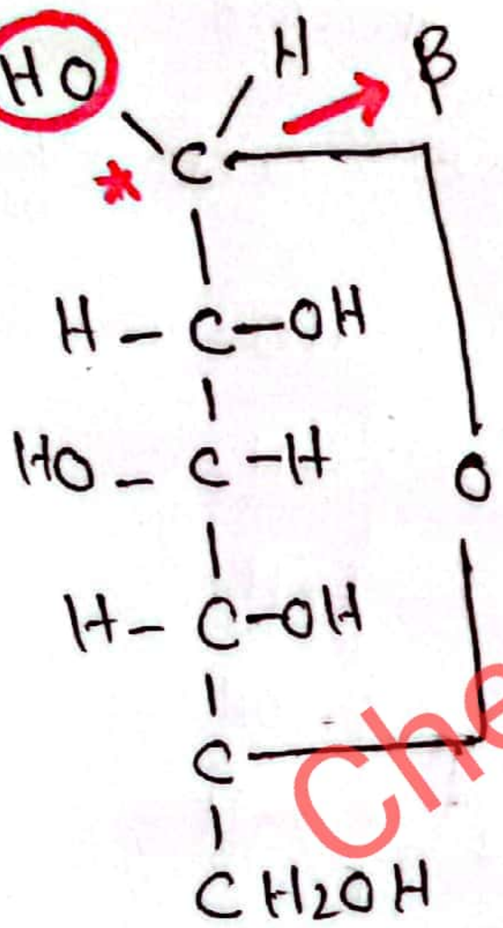
Both Forms are enantiomers.

## * Anomers:

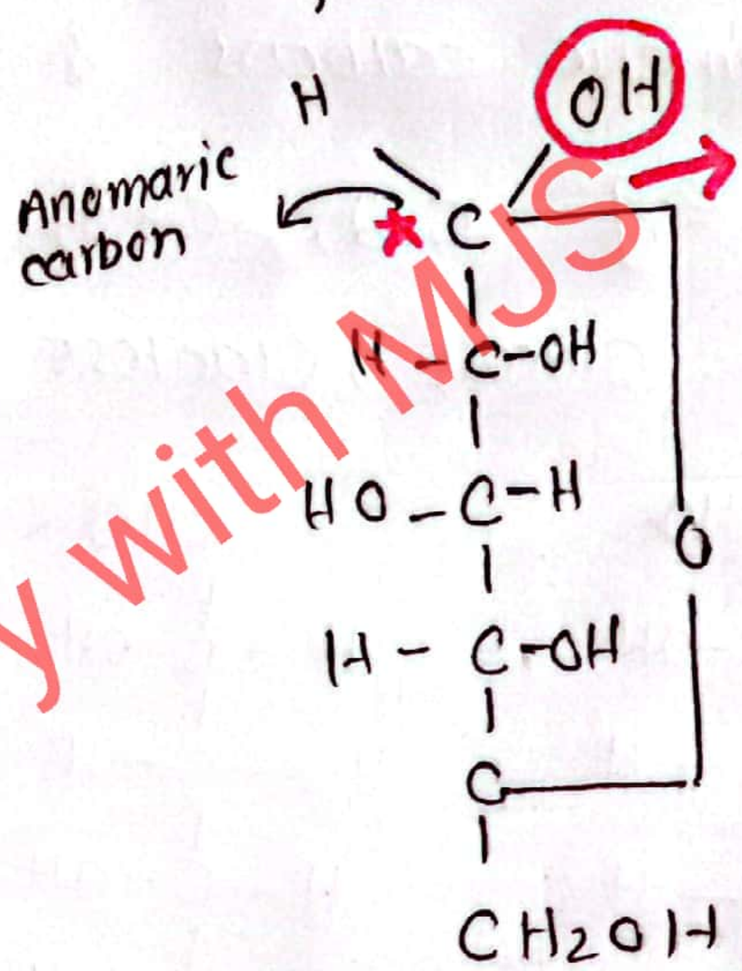
Asymmetric carbon atom obtained From active carbonyl Sugar group called Anomeric carbon

e.g C-1 in ALDOSES & C-2 in KETOSES

Abmers → 9someis obtained From the change of position OF -OH group attached to the anomeric carbon e.g ∝ & β glucose are 2- Anomers; Similarly ∝ & β-Fructose called Anomers.




β-D(+)-Glucopyranose




(∝-D-Glucopyranose)



* Mutarotation:

- Gradual change OF specific Rotation of any optically active substance having Free -CHO OR -C=O group called Mutarotation.

Example:

- ∝-Glucose Freshly dissolved in $H_2O$ → sp. Rotation = +112°
- β-Glucose " " in $H_2O$ → sp. ROT = +19°
- When Both Anomers are Left For sometimes

↓

∝-β sugars slowly change into an Equilibrium mixture HAS specific Rotation +52.5° (Dextro Rotaton)

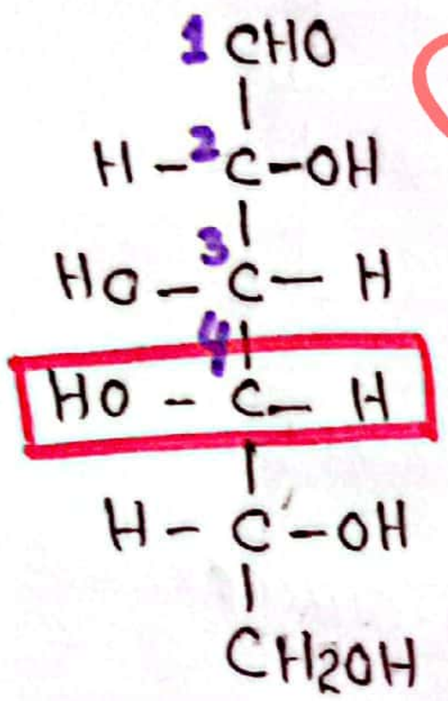
* GLUCOSE SHOWS Muta Rotation.

## Epimers:

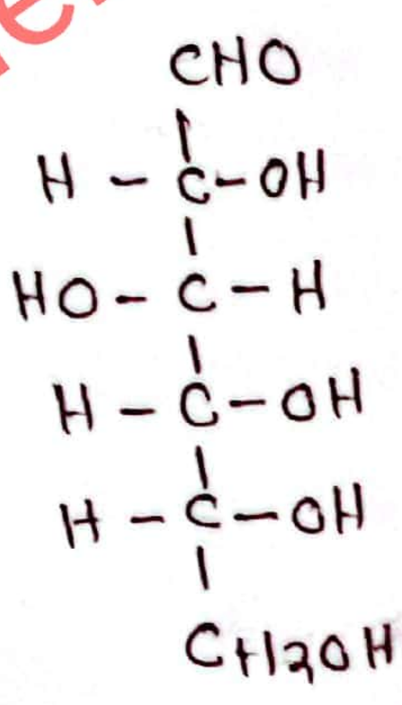
Asymmetric carbon Atoms other than Anomeric having different configuration at one stereogenic centre called epimeric carbons & isomers called Epimers.

e.g C-2, C-3, C-4 OF glucose.

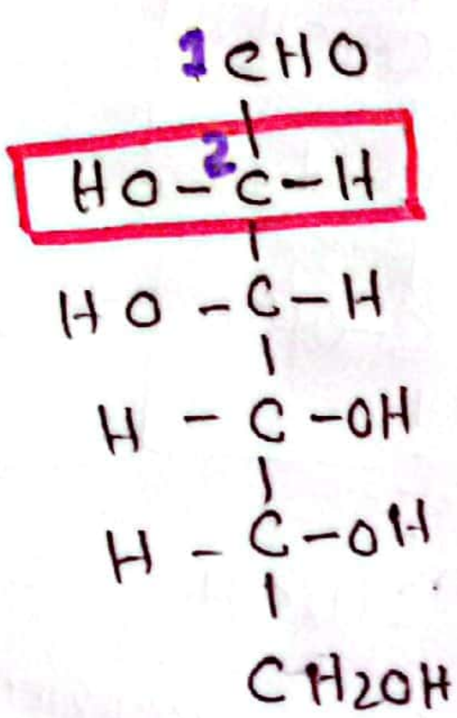
Glucose, Glactose & Mannose are epimers.



Glactose



Glucose



(Mannose)

* Glactose → Epimer OF C-4
* Mannose → Epimer of C-2

| Reducing Sugars | NON-Reducing Sugars |
|---|---|
| * Free Aldehyde or Keto group | * Not Free |
| * exhibit Muta-Rotation | * Do not exhibit |
| * Form osazone with phenyl Hydrazine | * Do not form osazones |
| * Form oximes with Hydroxalamine | * Do not Form oximes |
| **Examples;** Lactose, glucose, Fructose, cellobiase, Maltose | **Examples;** Sucrose, insuline, Glycogen etc. |

## Properties :- (Glucose)

1. Colourless crystalline solids.
2. Soluble in water
3. In Alchol it is sparingly soluble.
4. In Ether it is insoluble.
5. Melting point is 391 kelvin.

## (Fructose)

1. White crystalline solids.
2. Soluble in water
3. In Alcohol it is sparingly soluble.
4. In Ether it is insoluble.
5. Melting point is 375 kelvin.



## Chemical properties :-

### Oxidation Reactions

**Mild oxidizing Agent**

- → Br/H2O
- → Tollens Reagent
- → Fehling Reagent

**Strong oxidizing Agent**

- → Nitric Acid ($HNO_3$)

Amp 2

## Strong oxidizing agent:-

$HOCH_2-(CHOH)_4-CHO + HNO_3 \longrightarrow$ Glocaric Acid

Glucose

$HOOC-(CHOH)_4-COOH$

when strong oxidizing agent react with glucose it form Glocaric Acid.

- Convert in Carboxylic Group.

## Weak oxidizing agent:-

$HOH_2C-(CHOH)_4-CHO \xrightarrow[\text{Tolence reagent}]{Br_2/H_2O} \text{Gloconic Acid.}$

Fehling reagent

$HOH_2C-(CHOH)_4-COOH \rightarrow$ Gloconic Acid.

(oxidizing)

(oxidation)

Alkanes $\xrightarrow{(O)}$ Alcohol $\longrightarrow$ Aldehyde / Ketone

$\longrightarrow$ Carboxylic Acid.

- Strong reagent direct attack.

Reducing order:- (opposite).

# Chemical Properties :-

## Reduction Reactions :-

weak Agent ↖ (opposite)

$$HOH_2C-(CHOH)_4-CHO \xrightarrow[H_2O]{Na/Hg} HOH_2C-(CHOH)_5-OH$$

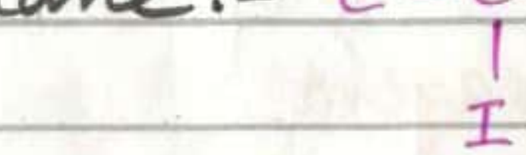
(Sorbitol)

Strong Agent ↖

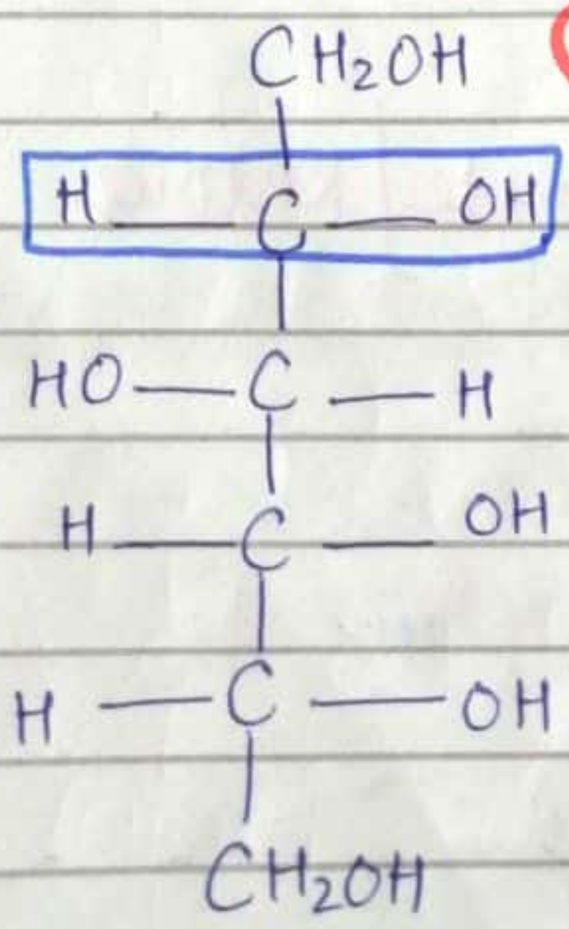
$$HOH_2C-(CHOH)_4-CHO \xrightarrow{HI/P} \text{n-hexane} + \text{2-aldohexane}$$

n-hexane :- $CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$

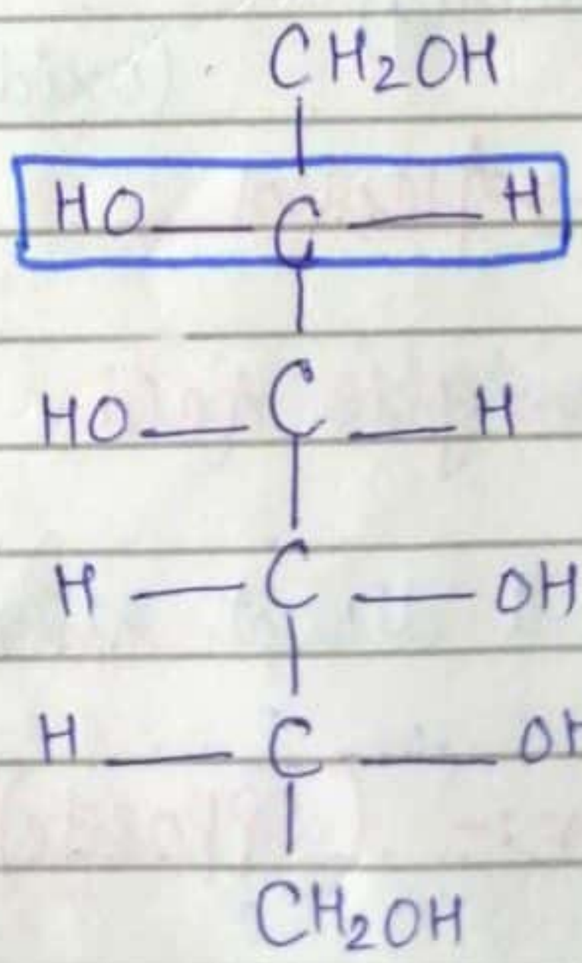
Aldohexane :-



$$\text{Fructose} \xrightarrow[H_2O]{Na/Hg} \text{Sorbitol} + \text{Mannitol}$$



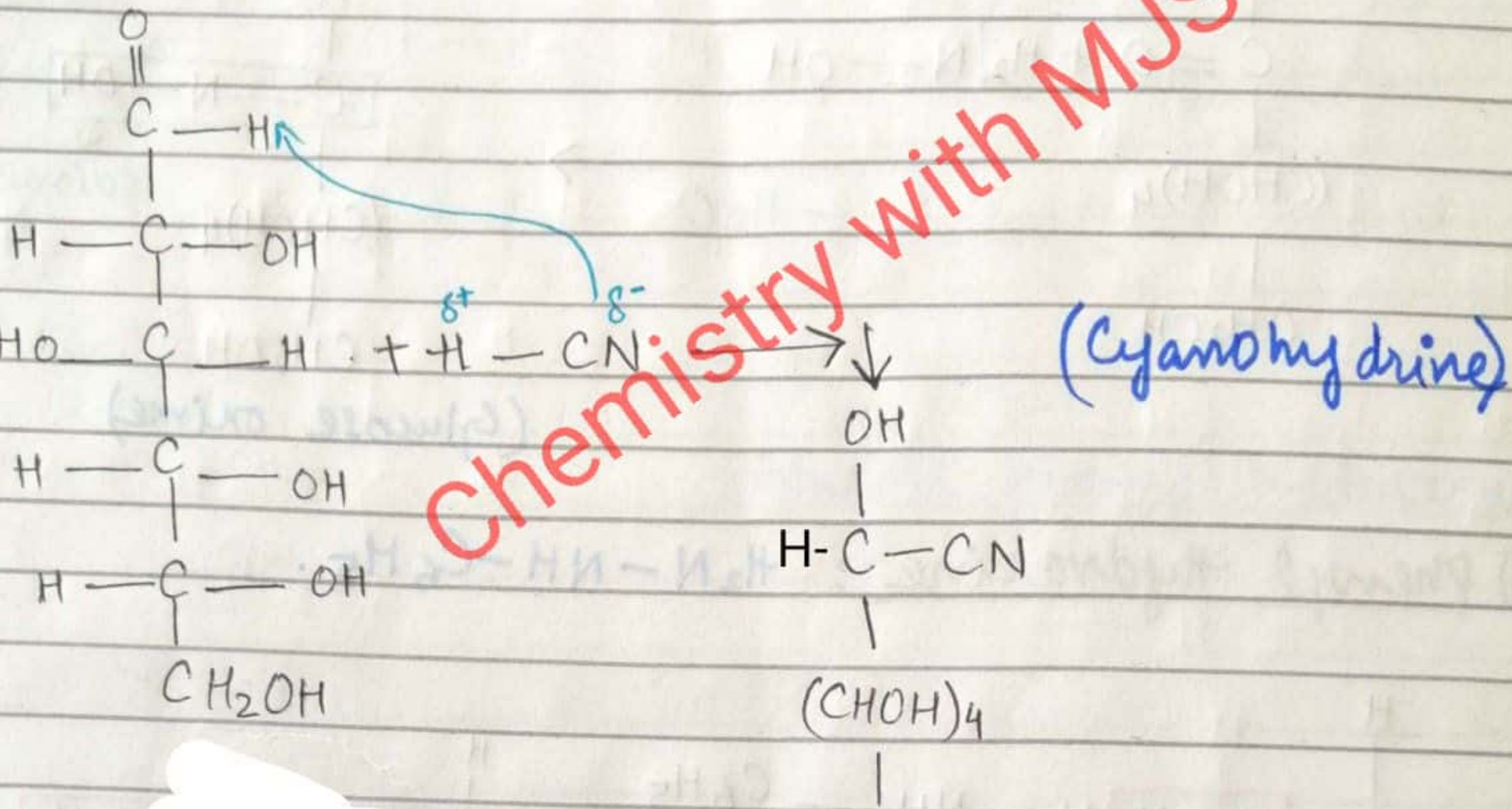
(Sorbitol)



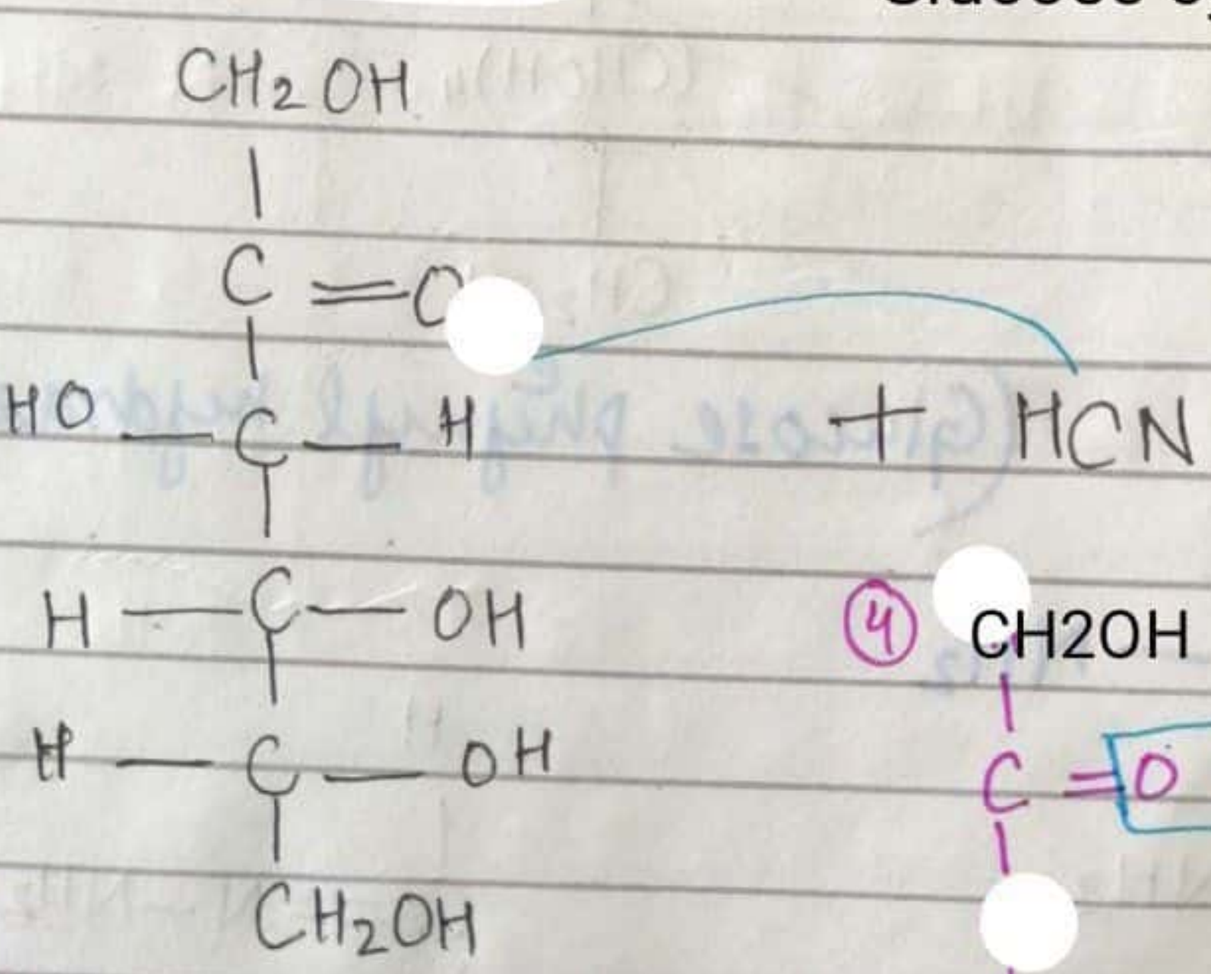
(Mannitol)

③ Reaction with Hydrogen cyanide: (HCN) →

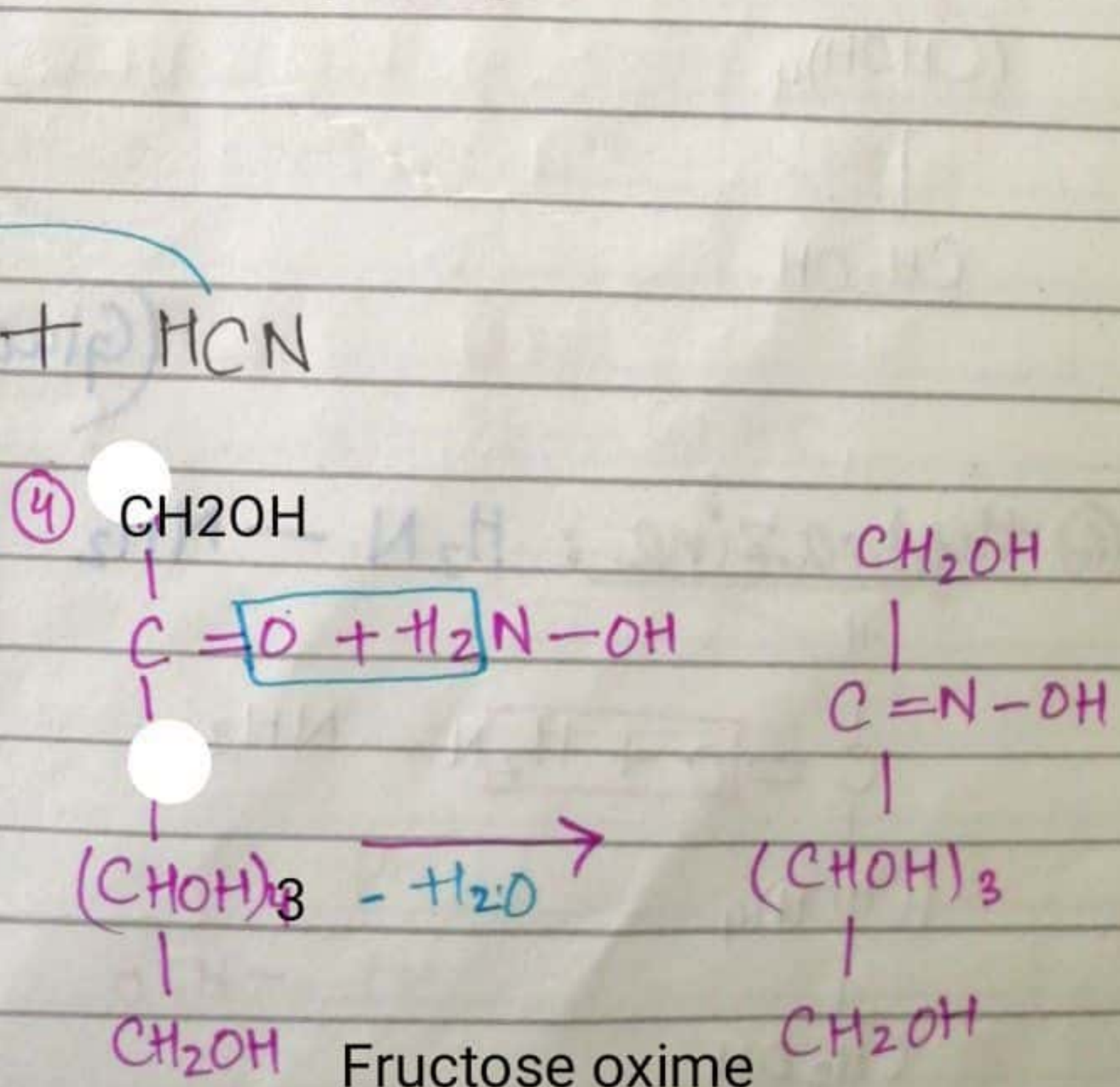
Nucleophilic Addition.




Glucose cyanohydrin

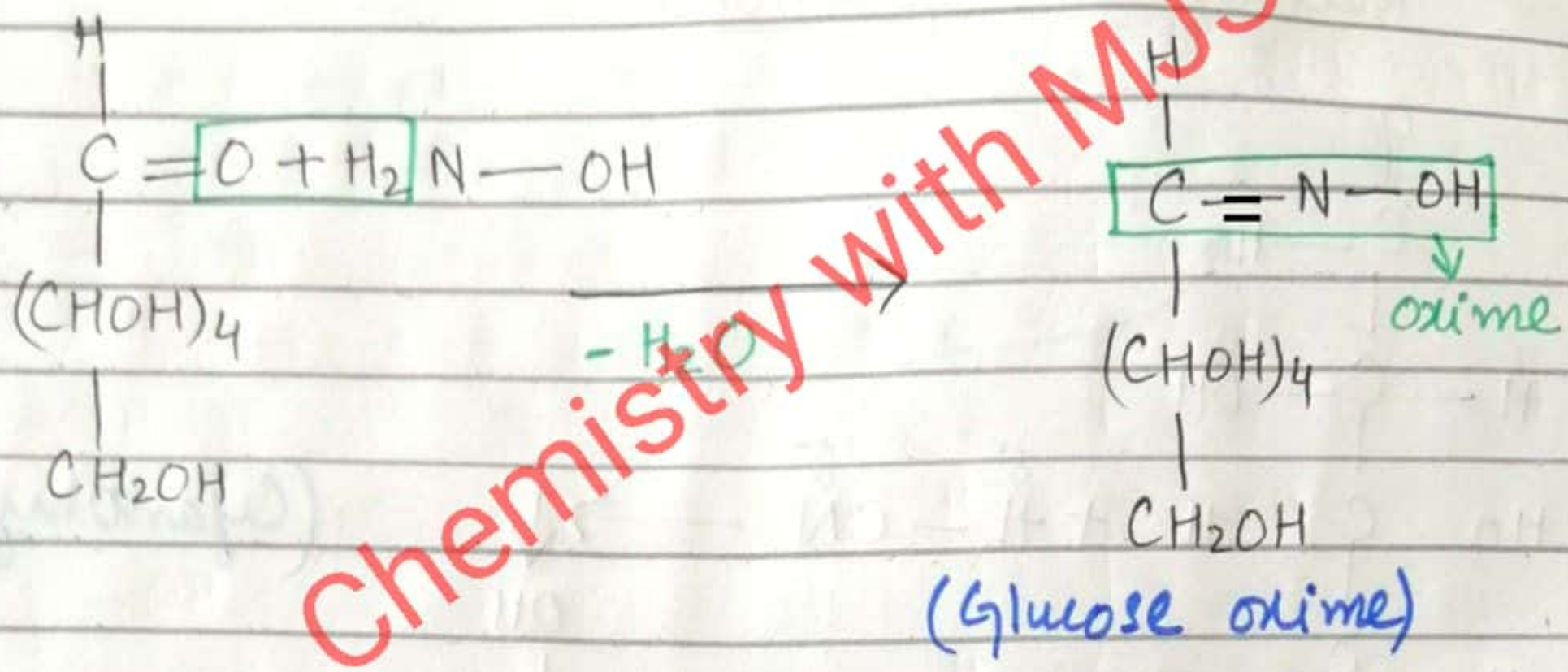



Fructose Cyanohydrin



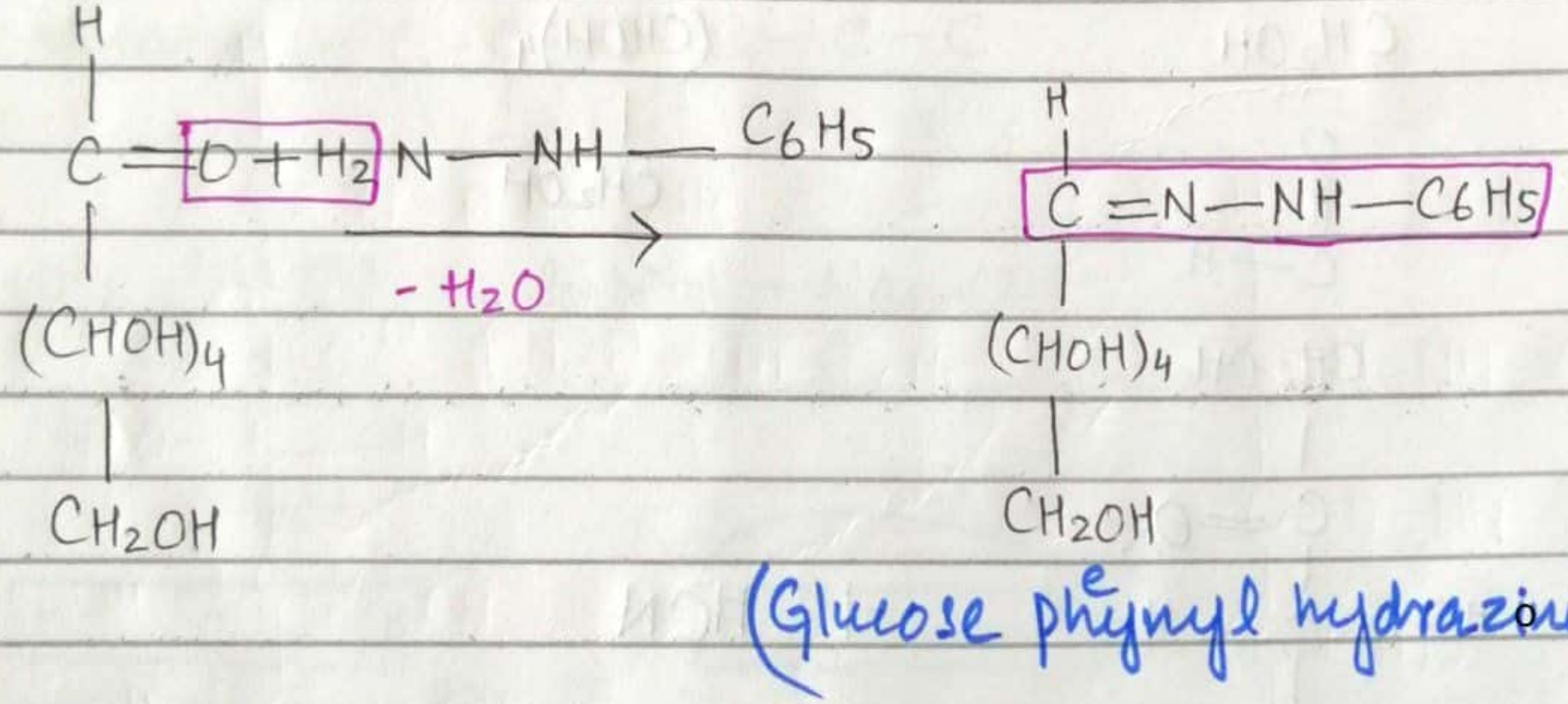

Fructose oxime

## ④ Hydroxyl Amine: $H_2N-OH$



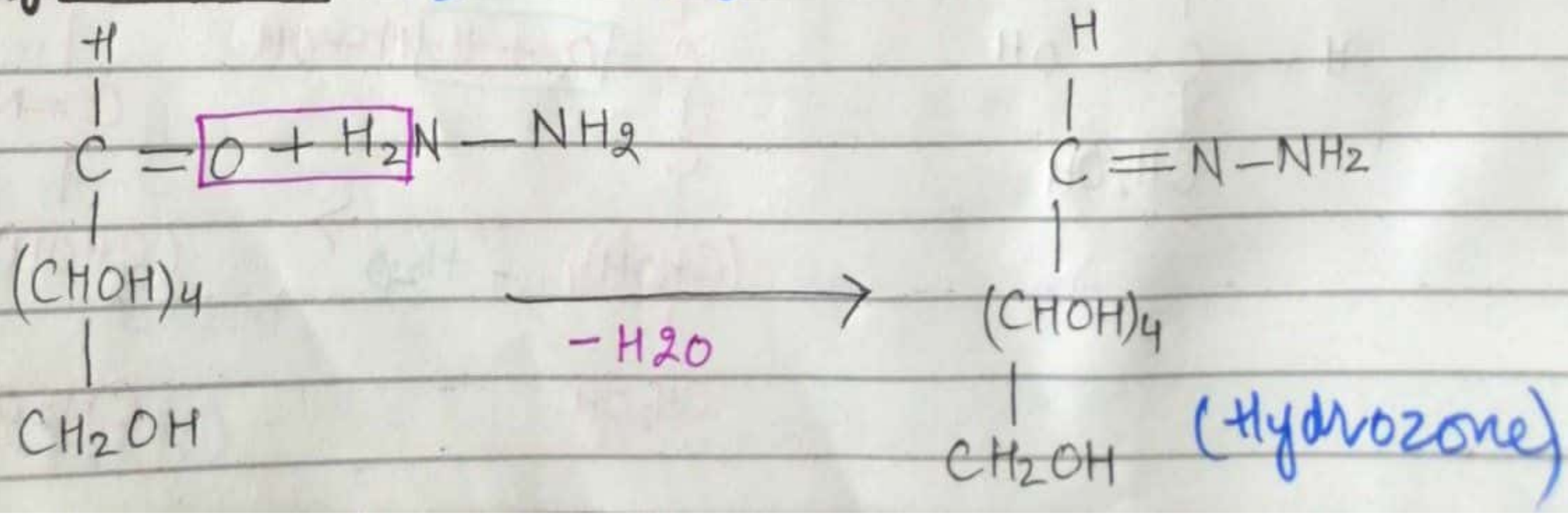

(Glucose oxime)

## ⑤ Phenyl Hydrazine: $H_2N-NH-C_6H_5$.




(Glucose phenyl hydrazine)

## ⑥ Hydrazine: $H_2N-NH_2$

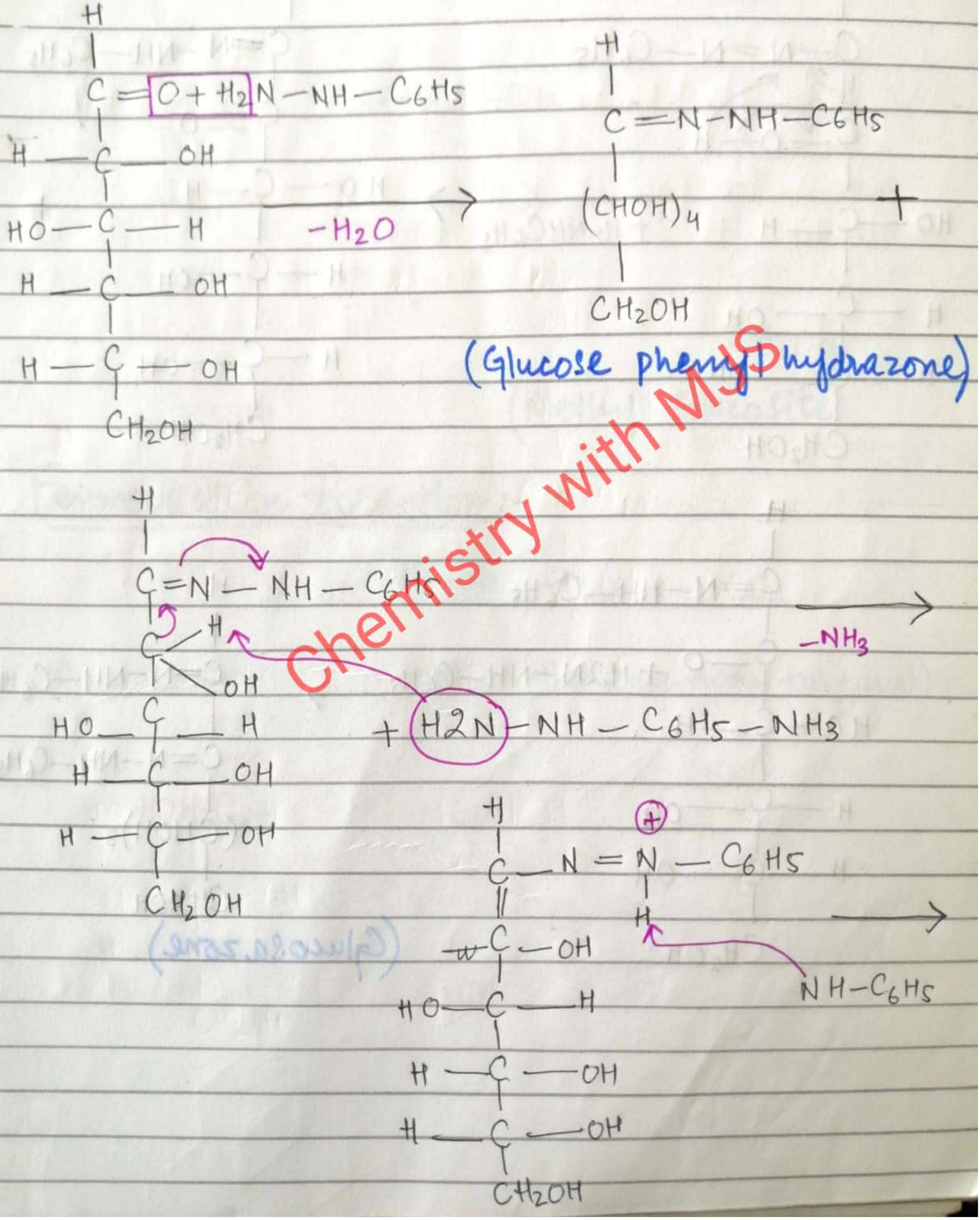


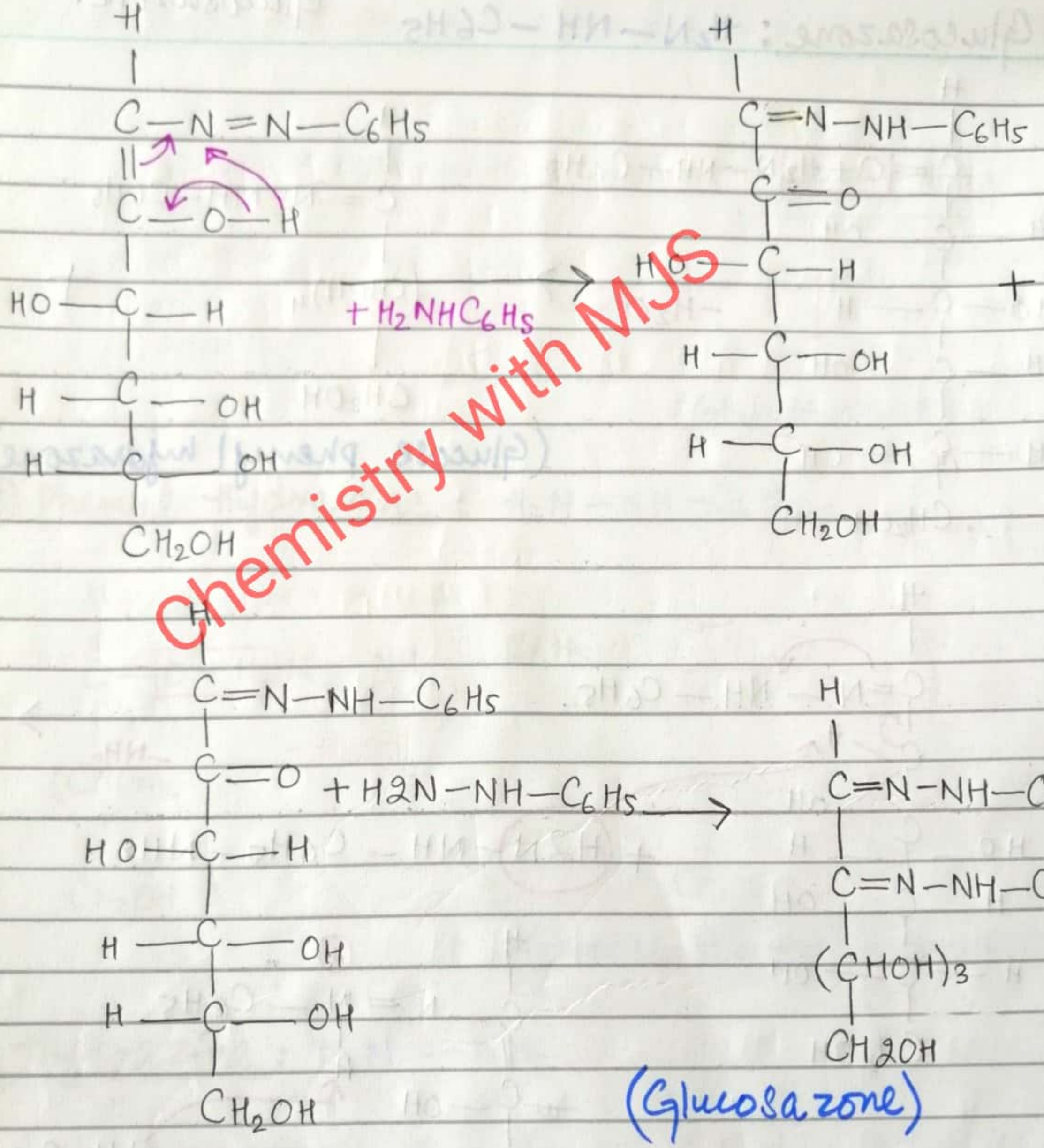

(Hydrozone)

3 molecules of

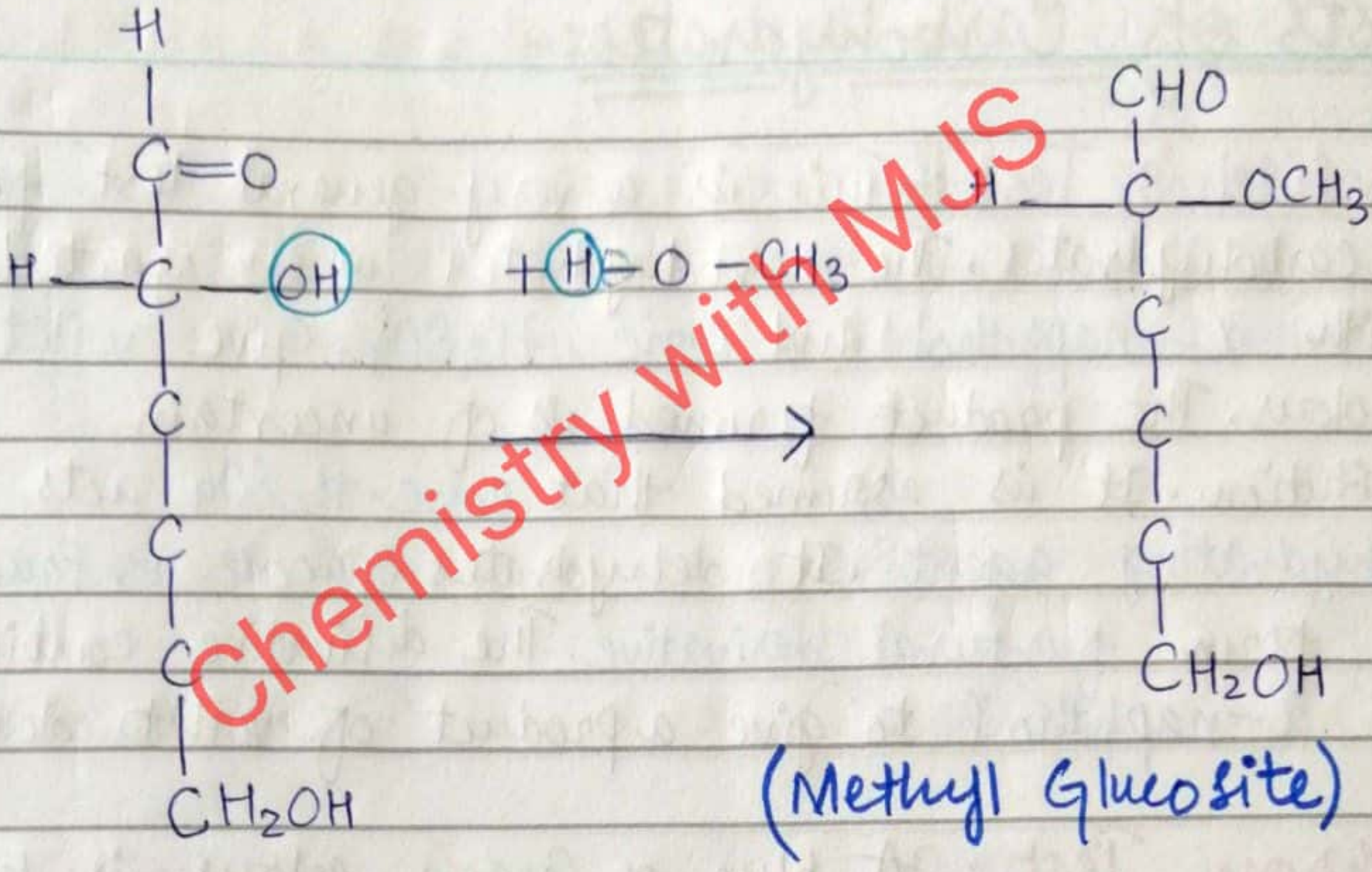
→ Glucose reacts with phenyl hydrazine to give Glucosazone.

⊕ **Glucosazone**: $H_2N-NH-C_6H_5$





# Reaction with Methyl Alcohol

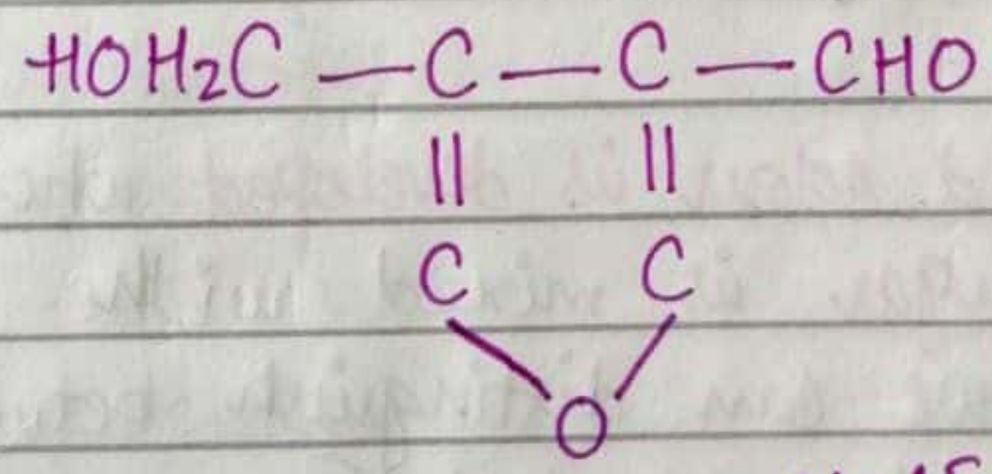





## Fermentation Reaction :-

Glucose $\xrightarrow{\text{Zymase}}$ Alcohol + $CO_2$

- Glucose $\xrightarrow[HCl]{\text{Acid}}$ HMF (Hydroxy methyfurfural)

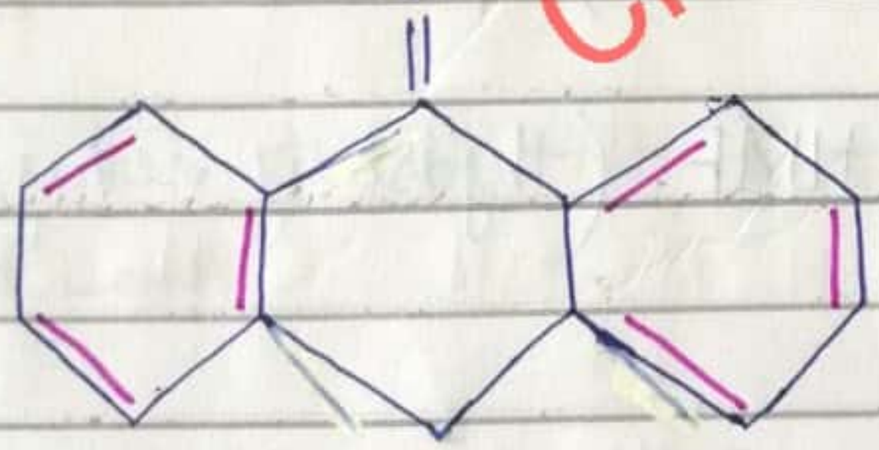



HMF

# Tests of Carbohydrates :-

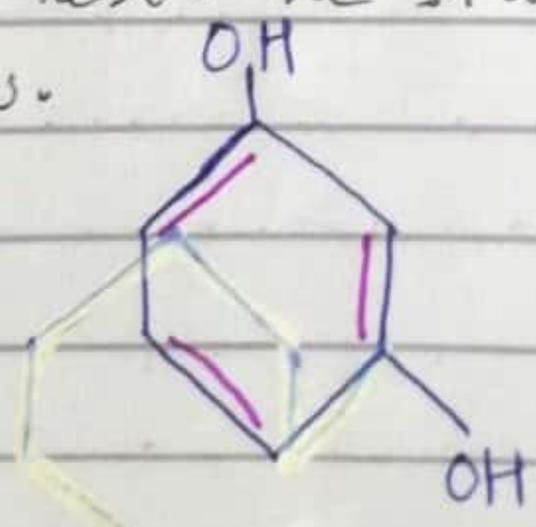
(a) **Molisch's Test** :- This is a very general test for carbohydrates. The carbohydrates when reacted with α-naphthol and conc. $H_2SO_4$, Give voilet colour. The product formed is of uncertain constitution. It is assumed that conc. $H_2SO_4$ acts as dehydrating agent. It dehydrates Glucose or Fructose to form furfural derivative. The derivative combines with α-naphthol to give a product of voilet colour.

(b) **Anthrone Test** :- A blue or Green colour is developed when anthrone is mixed with conc. $H_2SO_4$ and carbohydrate. The structure of anthrone is Given below.



(anthrone)

c) **Salivanoff Test** :- A red colour is developed when a Ketose sugar is mixed with resorcinol and HCl. We can distinguish between Glucose and Fructose by this test. The structure of resorcinol is given below.




(Resorcinol)

#05

**Disaccharides:-** Hydrolysis ⟶ 2 monosaccharides obtained.

- $H_2O$ soluble.
- For hydrolysis → specific enzymes are used.
- Disaccharidase enzyme.

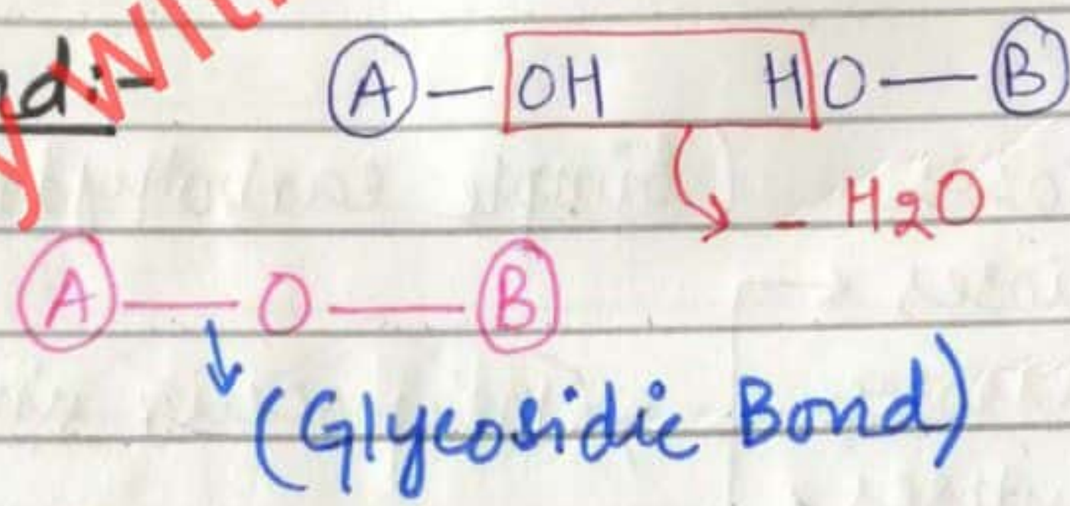
$(C_{12}H_{22}O_{11})$

→ Sucrose —Invertase→ D-Glucose + Fructose

→ Maltose —Maltose→ D-Glucose + Glucose

→ Lactose —Lactase→ D-Galactose + Glucose.

**Glycosidic Bond:-**



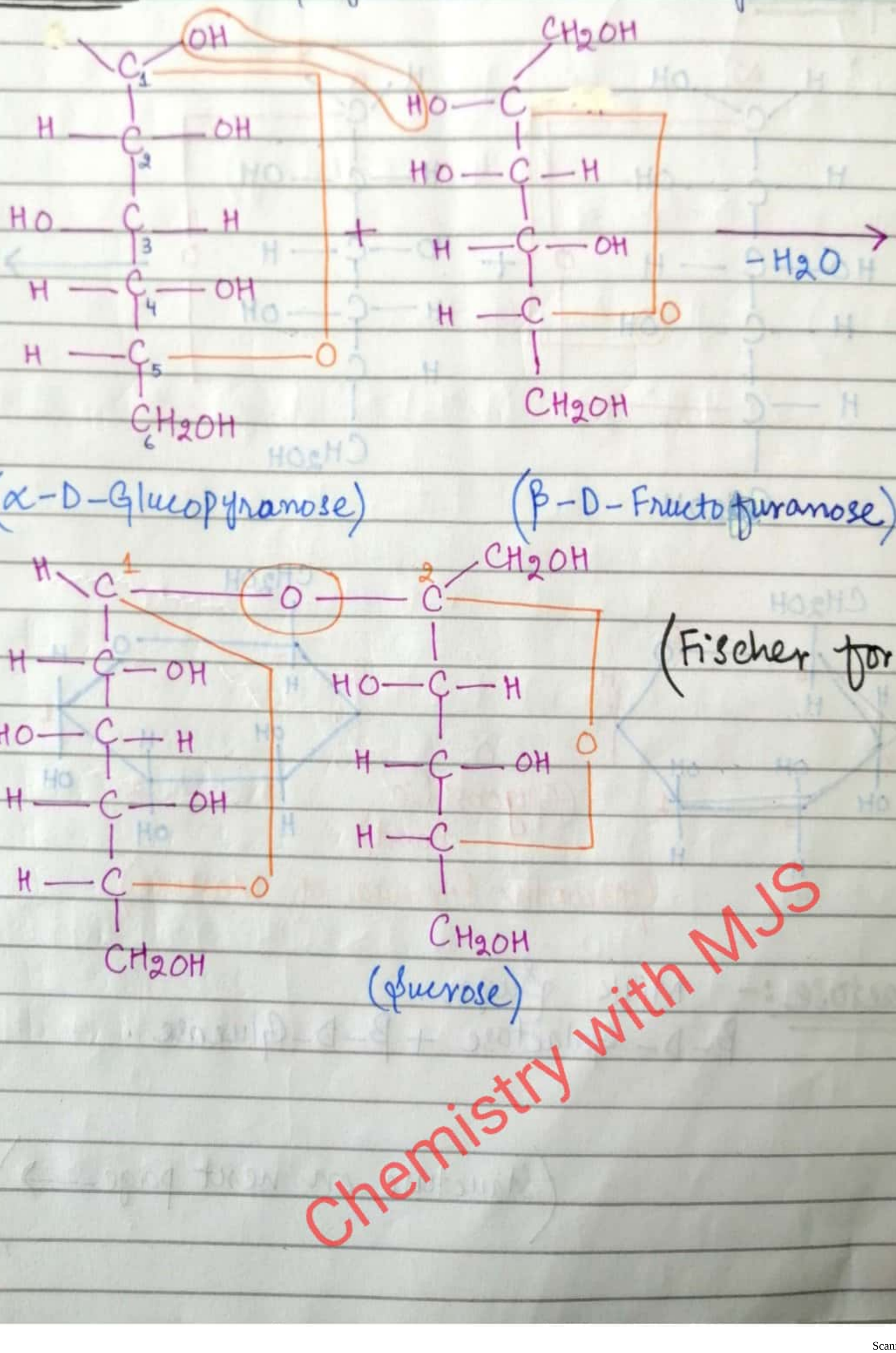



★ **Sucrose :-** α-D-Glucose + β-D-Fructose ⟶
1-2 linkage

★ **Maltose :-** α-D-Glucose + α-D-Glucose ⟶
1-4 linkage.

**Lactose :-** β-D-Glucose + β-D-Galactose
1-4 linkage

**Sucrose** :- Table sugar and colourless crystalline solid.



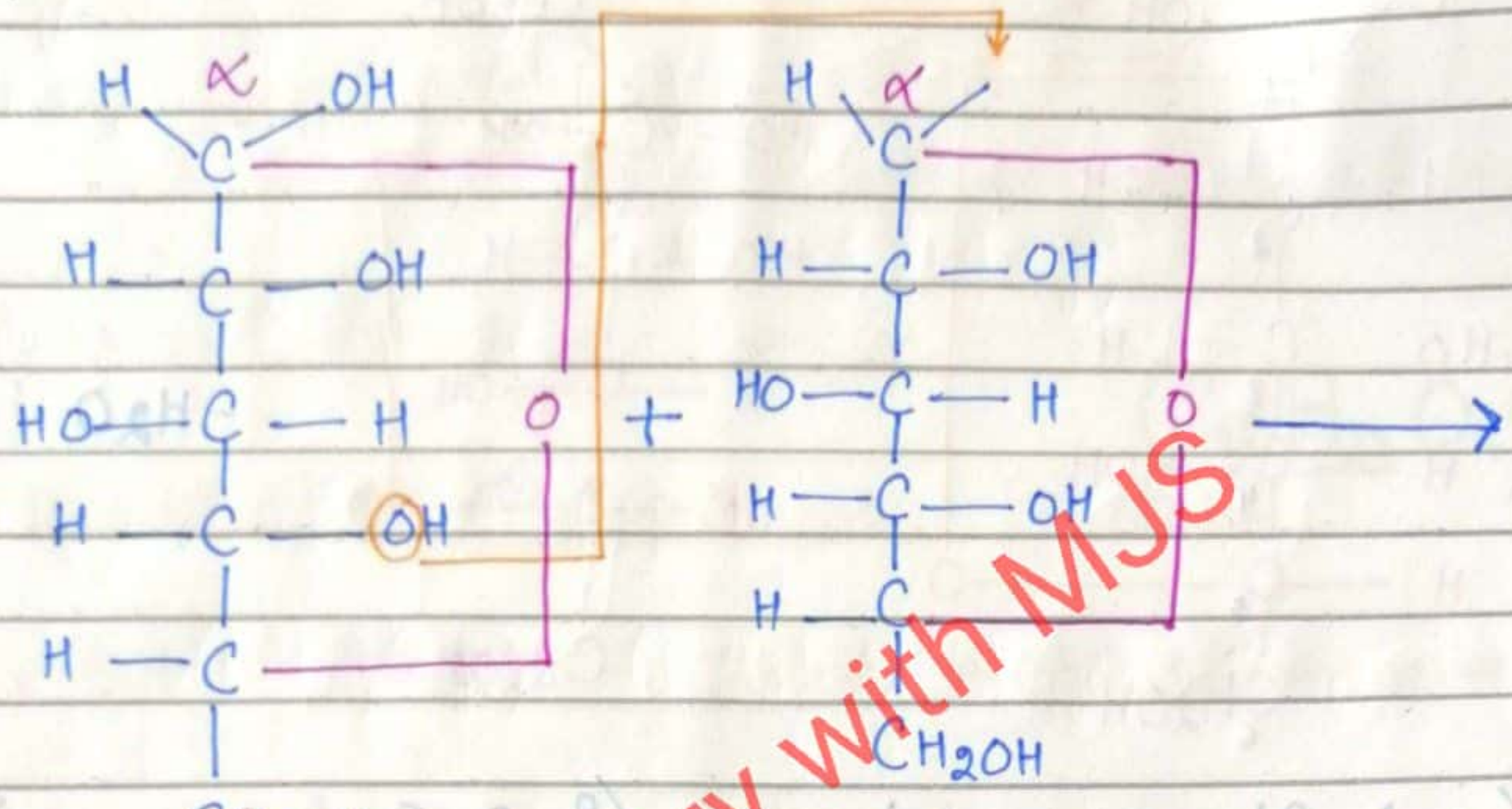

(α-D-Glucopyranose) (β-D-Fructofuranose)

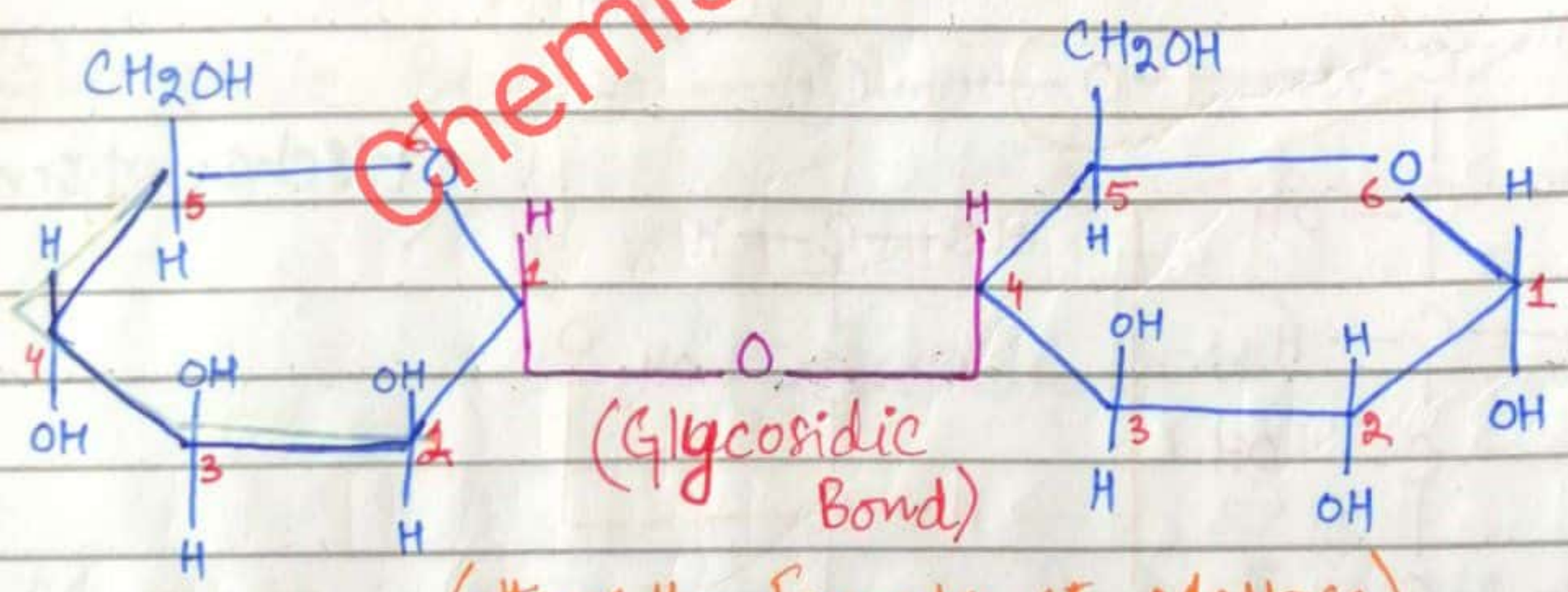
(Fischer formula)

(Sucrose)

## Maltose:- (1-4) → (α-D-Glucose + α-D-Glucose)

(Malt-Sugar)




(Haworth Formula of Maltose)

## Lactose:- Milk Sugar

β-D-Galactose + β-D-Glucose.

# Importance of Disaccharides

**Sucrose:** Known as "table sugar"

- Found in cane & Beet, pineapple & carrots
- NON-Reducing Sugar
- can not show mutarotation.
- cannot Form osazone.
- Sucrase enzyme hadrolyzes into glucose + Fructose.
  - ↳ invertase Enzyme →
    - ↓ Equal NO. of molecules
    - ↓ mixture
    - ↓ inverted Sugar
    - ↓ Levo Rotatory

* Sucrose → DextroRotatory
* inverted Sugar → Levo Rotatory

Glucose-Fructose (Sucrose) (Dextro) —invertase→ Glucose + Fructose

Glucose: Dextro (+52.5°); Fructose: Levo- -91°

Sugar of Honey Bee ← inverted Sugar (Levo Rotatory)

**Maltose:** → called "Malt Sugar"

- produced during digestion of starch by amylase.
- Reducing Sugar (can Reduce Benedict Reagent)
- shows Mutarotation
- Forms osazone.
- least common Disaccharide in nature.

**Lactose:** → called "Milk Sugar"

- Lactose is digested by intestinal Lactase into Glactose & Glucose.
- Naturally occurs exclusively in Milk
- Reducing Sugar
- shows Mutarotation
- Forms osazones.

# Polysaccharides

>10 units of monosaccharides

## Homopolysaccharides

- Same Repeated Sugar units
  - Starch
  - Glycogen
  - Cellulose
  - Dextrin
  - Insulin
  - Chitin

## Heteropolysaccharides

- Different Repeated Sugar units
  - Glycosaminoglycans (GAGs)
    - → Hyaluronic acid
    - → chondrotin sulfates
    - → Heparin
  - proteoglycans
  - Glycoproteins
  - Mucilages
    - → Agar
    - → pectins
    - → vegetable gums



## A) Homopolysaccharides:

**1. Starch:** → Also called Glucosan OR Glucan

Starch Granule is formed of two layers inner → Amylose & outer-Layer → Amylopectin

α-D-Glucose units

### Amylose

- 15-20% of Granule
- 1-4 α linkage of Glucose units
- Less branched / non-Branching structure
- Gives deep Blue color with iodine

### Amylopectin

- 80-85% composition
- 1-4 & 1-6 α. linkage OF two Branches.
- Branched structure
- Each chain contain approx. 25 units to or.
- Gives purple OR Red colour with iodine
- Forms Micellar / colloidal solution.

## 2- Glycogen: (called Animal starch)

- Highly Branched structure than Amylopectin
- 1-4 & 1-6 linkage (like Amylopectin)
- Each Branch contains of 12- 14 glucose units.
- Storage Form of carbohydrates in humans & Animals.
- Synthesized & stored in Liver, muscles & other tissues.
- containing 92% linkage 1→4 type & 8% 1→6 type.
- It gives Red colour with iodine.
- Tree like structure.

## 3- Cellulose:

↳ long chain of β-D-glucose units
↳ β- 1→4 linkage
↳ Non- Branching structure.
↳ chief constituent of plant
→ cotton 99% (cellulose)
→ NO colour with iodine
→ insoluble in $H_2O$
→ can not be digested by Human BIC OF Lack of Hydrolase enzyme (cellulase)
↓
β-glucosidase Enzyme

→ Ruminant Animals (cattle, deer, camels, Bacteria) containing β-glucosidase

## 4. Dextrin:

- Hydrolytic products of starch
- Formed of α-glucose units but simpler than starch.
- Including Amylodextrin, erythrodextrin & achrodextrin.

## 5. Insulin: (called Fructosan)

→ Formed by the repeating units OF Fructose linked together by β 1→2 linkage.

→ Found in Root of Artichokes plants.

→ soluble in warm wates.

→ insulin clearance is a diagnostic test For the investigation of glumerular Filteration Rate.

## 6- Chitin: (polysaccharide of invertebrates)

- polymer of N-acetylglucosamine units Joined by β, 1→4 linkage.
- Also present in the exoskeleton of insects & in mushrooms

# B) Heteropolysaccharides

## Glucosaminoglycans (GAGs):

consist OF two different Repeating units

Amino sugar + Acidic sugar

↓ (uronic acid)

N-Acetylglucosamine OR D-glucosamine

OR D-glucoronic acid

* Most of them forms the structural components of connective tissues, such as bone, elastin & collagen.

* Act as lubricants -

→ Hyaluronic acid (Glucoronic acid + N-Acetyl glucosamine)

→ Heparin:

- Iduronic acid with Sulfate on C-2
- \+
- Glucosamine with Sulfate on C-2 & C-6

→ Act as anti-coagulant

**Glycoproteins:** (Muco proteins)

↓

carbohydrate unit + protein

- composed of extracellular matrix
- components of Mucins
- components of cell membrane.

| Glycoproteins | proteoglycans |
|---|---|
| • Oligosaccharide units | • Glycosaminoglycans |
| • contains no uronic acid | • contains uronic acid. |
| • contains no sulfate | • contains Sulfate. |
| • Usually X Branched | • Linear, unbranched |
| • 2–15 units | • > 50 units |

Good Luck

MJS