Carbohydrates

Def: polyhydroxy aldehydes / ketones (or) compounds which produce them on hydrolysis.

* Basic elements: C, H, O

General formula: $(CH_2O)_n$ → not satisified by all carbohydrates.

Classification:-

* 1) Based on no. of carbon atoms:

1) Trioses. eg: Glycerose, dihydroxy acetone
2) Tetraoses eg: Erythrose, Erythrulose
3) pentoses eg:- Ribose, Ribulose
4) Hexoses eg: Glucose, Fructose

2) Based on the functional group in the terminal chain.

1. Aldoses: The functional group is an aldehyde.

eg:- Glycerose, erythrose, Ribose, glucose.

2. Ketoses:- The functional group is ketone.

eg: dihydroxy acetone, erythrulose, Ribulose, fructose.

3) Based on the No. of sugar units:

1) Monosaccharides: General formula ~~en~~ $C_nH_{2n}O_n$

→ single sugar unit eg:- Glucose, fructose, erythrose.

2) oligosaccharides:- Few sugar units (2-10) monosaccharides units and these on hydrolysis gives monosaccharides.

- disaccharides
- tri saccharides
- tetrasaccharides

General formula $C_nH_{2n-2}O_{n-1}$

3) poly-saccharides:

* Several sugar units (20-100) and on hydrolysis gives monosaccharides.

Eg: of disaccharides

1. Sucrose (Glucose + fructose)
2. Lactose (Glucose + galactose)
3. Maltose (Glucose + glucose)

Eg: starch, cellulose, glycogen

* Molecular weight up to 1,00,000

4. According to reducing activity of sugar unit carbohydrates are classified into 2 types:

1) Reducing sugars :- which can donate e^- pair / which possess free aldehyde / keto groups.

Eg: Glucose, fructose, lactose, Maltose.

2) Non - Reducing sugars :- It doesn't have an available reducing group to react & donate e^-s

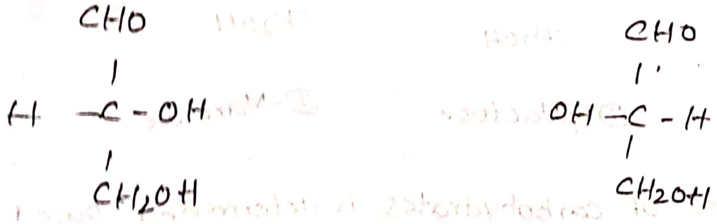
Eg:- Sucrose

Fischer structure → of different carbohydrates

Aldoses:-

1) Glyceraldehyde: (Glycerose)

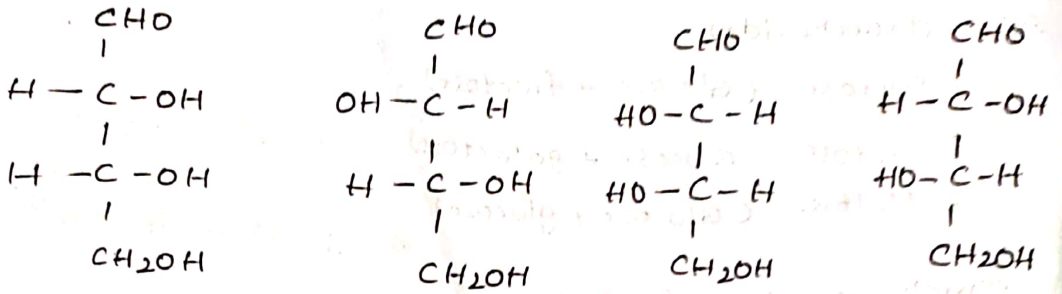
$2^n = 2^1 = 2$



D-Glyceraldehyde L-glyceraldehyde

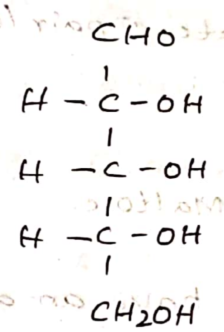
2) Tetraoses :- Eg:- erythrose

$2^n = 2^2 = 4$

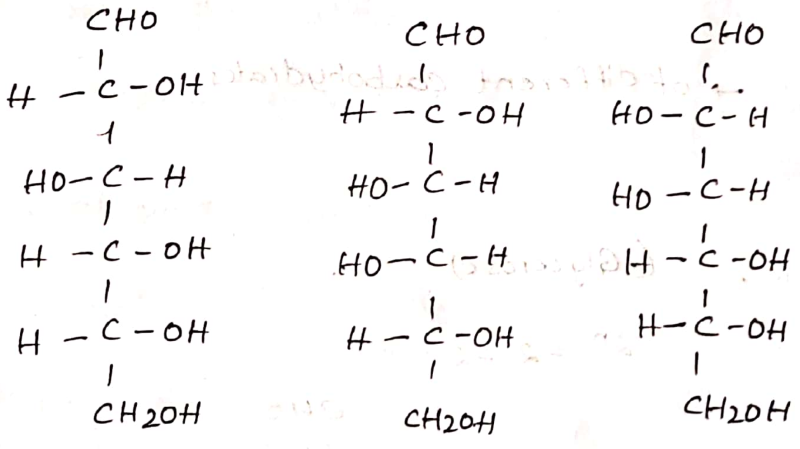


D-erythrose D-Threose L-erythrose L-Threose

B) pentoses :- Eg: Ribose



4) Hexoses :- Eg:- Glucose



D-glucose D-galactose D-Mannose

* configuration of carbohydrates is determined based on the arrangement of -H & -OH groups on the last carbon atom. If arrangement is similar to D-glycerose, the

Ketoses :

1) Trioses eg:- Dihydroxy acetone (no chiral carbon, so doesn't exhibit isomerism)

```
CH2-OH
 |
 C=O
 |
CH2-OH
```

2) Tetroses :- Eg: erythrulose → For ketoses, erythrulose is taken as std. for determining the configuration

$2^1 = 2^1 = 2$ isomers

```
   CH2-OH               CH2-OH
    |                    |
    C=O                  C=O
    |                    |
H - C*-OH           HO - C - H
    |                    |
   CH2OH                CH2OH

D-erythrulose       L-erythrulose
```

3) pentoses :- Ribulose

```
    CH2OH              CH2OH
     |                  |
     C=O                C=O
     |                  |
H  - C-OH          HO - C-H
     |                  |
H  - C-OH          HO - C - H
     |                  |
    CH2OH          HO - C - H
                        |
                       CH2OH
D-Ribulose         L- Ribulose
```

4) Hexoses Eg:- fructose

```
     CH2OH              CH2OH
      |                  |
      C=O                C=O
      |                  |
HO -  C-H           H -  C -OH
      |                  |
H  -  C -OH        OH -  C -H
      |                  |
H  -  C -OH        OH -  C -H
      |                  |
     CH2OH              CH2OH

D-fructose          L-fructose
```

Epimers :- Isomers which differ from one another only in the configuration around one carbon are called as epimers.

Eg: Glucose & galactose } epimers
Glucose & Mannose } epimers

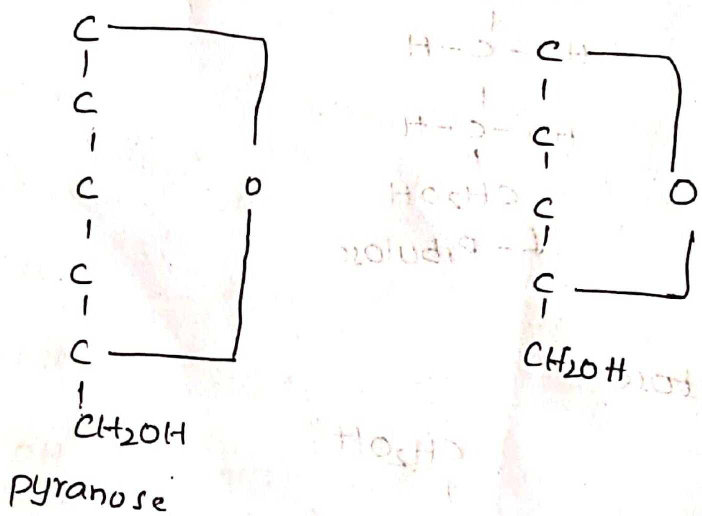
Haworth's structures :- Ring / cyclic strcutres :-

* Explained by Haworth in 1929.

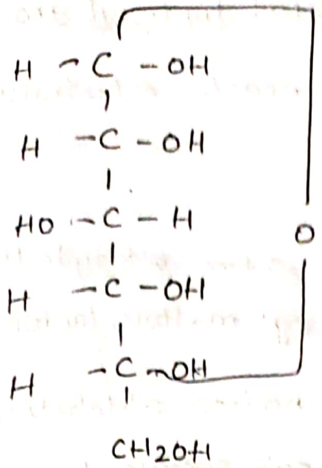
* In aqueous solution, aldotetroses & all monosaccharides c̄ 5 (or) more carbons exists as cyclic structures

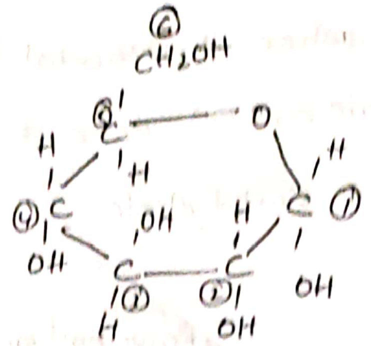
* If ring is formed b/w first & fifth carbons, they are called as pyranose.

* If ring is formed b/w second & fourth carbons, they are called as furanose.



Haworth's structure of glucose :-



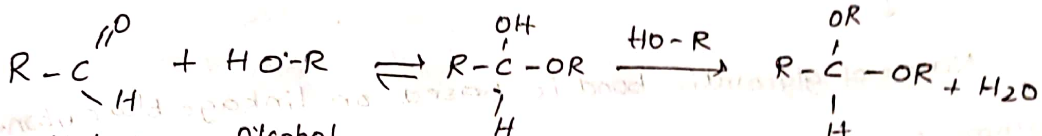


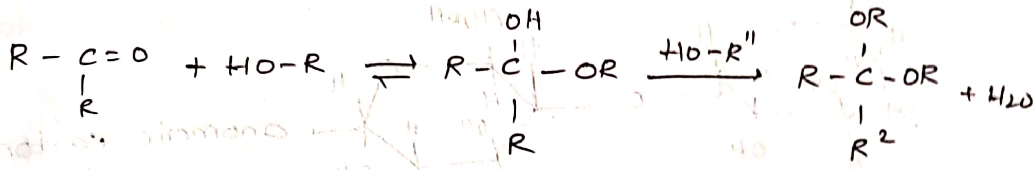
α-D glucopyranose.

($C_6H_{12}O_6$)

D-glucopyranose

* ring structures are formed due to reactions b/w aldehyde / ketone and alcohols to form derivatives called as hemiacetals / hemiketals





Anomers :- Isomeric forms of monosaccharides, that differ only in configuration about hemiacetal / hemiketal carbon atom.

* Hemiacetal / carbonyl carbon atom is called anomeric carbons.

Oligosaccharides :- contain few sugar units.

Disaccharides :-

* Among oligosaccharides, disaccharides are most common
* Disaccharides consists of 2 monosaccharides units.

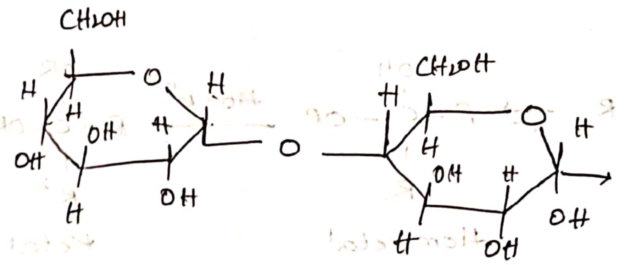
(similar or dissimilar) held together by glycosidic bond formed when hemiacetal / hemiketal hydroxyl group (of anomeric carbon) of carbohydrate reacts c̄ hydroxyl / group of another carbohydrates

Disaccharides → Reducing disaccharides → c̄ free aldehyde / keto group
Eg: maltose, lactose

Disaccharides → Non-Reducing " (glycosides) → no free aldehyde / keto group
Eg:- sucrose, halose

Maltose:

* doesn't occur in body.
* sources - germinating cereals.
* consists of 2 α D - glucose units based held together by α (1→4) glycosidic bond
↓
Name of glycosidic bond is based on linkage b/w carbon atoms & nature of anomeric carbon. (α or β)



(Maltose)
(α-D glucosyl (1→4) α-D glucose)

↓
is free, So it is oxidized
↓
So it is a reducing disaccharide

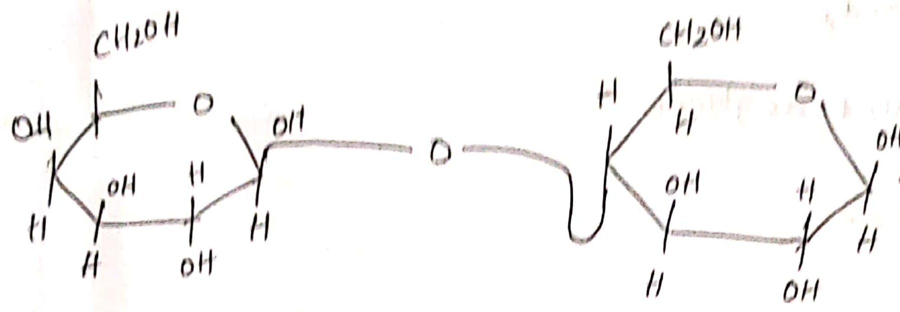
Maltose $\xrightarrow[\text{enzyme maltase}]{\text{c̄ dil acid}}$ 2 - D glucose

→ In disaccharides & polysaccharides, if anomeric carbon is free (i.e, not involved in glycosidic bond is called as reducing end.

→ glycosidic bond undergoes hydrolysis by acids readily & gives monosaccharides.

Lactose (milk sugar) * Naturally found in milk.

* β-D galactose & β-D glucose



→ anomeric carbon ↓ undergoes oxidation ↓ so reducing of sugar

β-D galactose β-D glucose

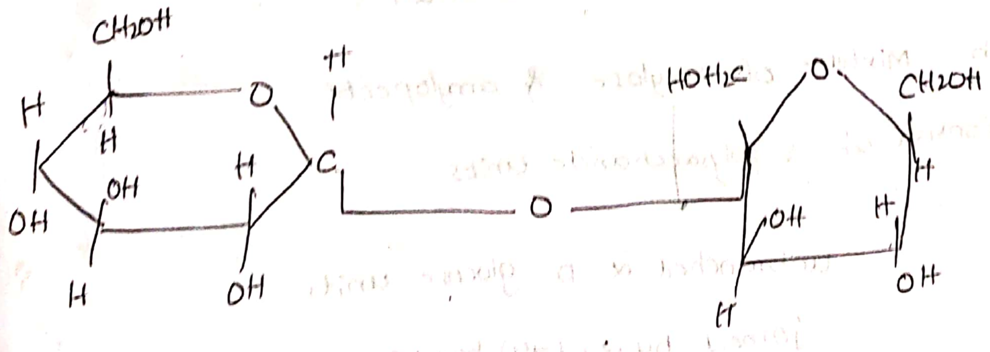
β-D galacto pyranosyl – (1→4) β-D glucopyranose.

Gal (β (1→4) gly

Lactose $\xrightarrow{\bar{c}\ \text{Lactase / dil. acid}}$ β-D galactose + β-D glucose

Sucrose :-

* combination of α-D glucose & α-D fructose.



* Intermediate product of photosynthesis & principal form of sugar in plants which is transported from leaves to other parts.

* It is a non-reducing diasaccharide, because the two

* It is more sweeter than all other carbohydrates so, used as sweetening agent.

III. polysaccharides:-

* Most Carbohydrates found in nature occur as Polysaccharides.

* also called as glycans

* 2 types:-

1) Homo polysaccharides :- only a single type on monomer which on hydrolysis gives only a single type of monosaccharide

eg: starch, glycogen.
Cellulose, chitin, Inulin

Glucosans → polymers of glucose Eg :- starch, glycogen, cellulose, Chitin

fructosans → polymers of fructose eg: Inulin

Starch - storage Material in plants.

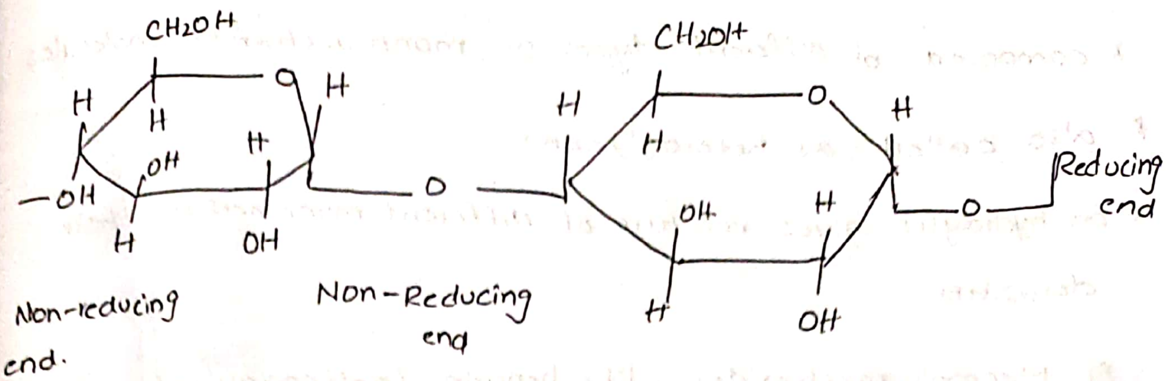
Glycogen - storage material in animals.

Starch - Mixture of amylose & amylopectin.
↓ consists of 2 polysaccharide units.

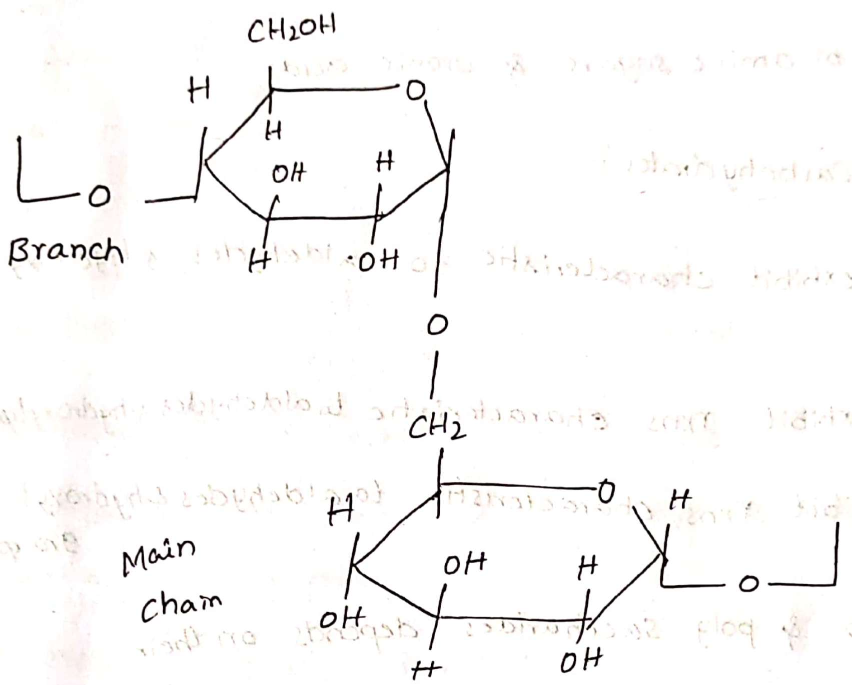
unbranched α-D glucose units joined by α(1→4) bonds)

Amylopectin → branched α-D glucose units joined by α(1→6) bonds

Amylose → H_2O structure



Amylopectin → H_2O insoluble



Glycogen → mol. wt − 1×10^8

glycogen is extensively branched

(1→4 bonds & 1→6 bonds)

* abundant in lives

Inulin :-

* polymer of fructose

Use: for assessing kidney function by measuring glomerular filtration rate

Cellulose - cell wall of plants

Chitin - In exoskeleton of invertebrates Eg: Insects

② Heteropolysaccharides :-

* composed of different types of monosaccharide molecules
* also called as heteroglycans.
* on hydrolysis gives mixture of different monomers (or) their derivaties

Eg: Mucopolysaccharides - like heparin (anticoagulant

- Mucopolysaccharides - also called as glycoaminoglycans
  ↳ mixture of amino sugars & uronic acids.

Reactions of Carbohydrates :-

* Aldohexoses exhibit characteristic to aldehydes & hydroxyl group.

ketohexoses exhibit rxns characteristic to aldehydes & hydroxyl group

ketones exhibit rxns characteristic to aldehydes & hydroxyl group.

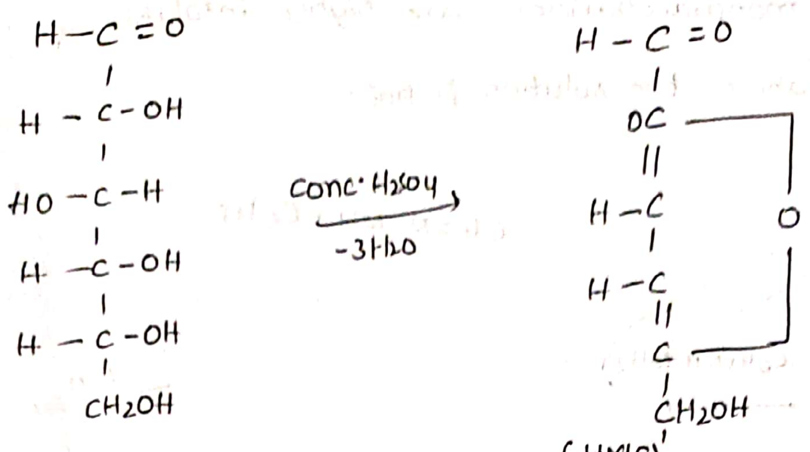
* rxns of oligo & poly saccharides depends on their constituent mono-saccharides.

Rxns of Monosaccharides :-

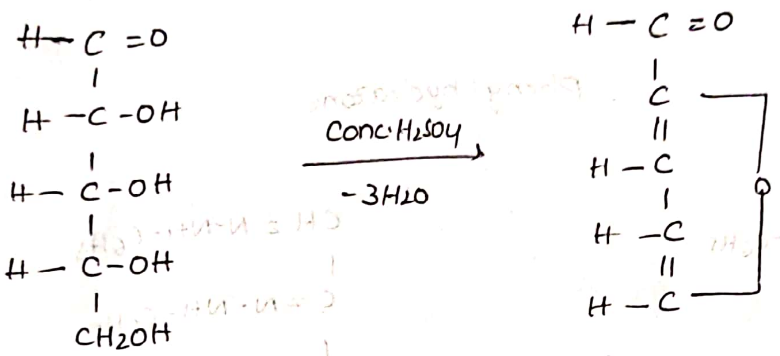
1) Dehydration :-

* Monosaccharides when treated with conc. H_2SO_4 undergo dehydration with elimination of 3 H_2O molecules

* Hexoses $\xrightarrow[-3H_2O]{conc.\ H_2SO_4}$ Hydroxy methyl furfural.



D-glucose → (HMF)



D-Ribose → furfural

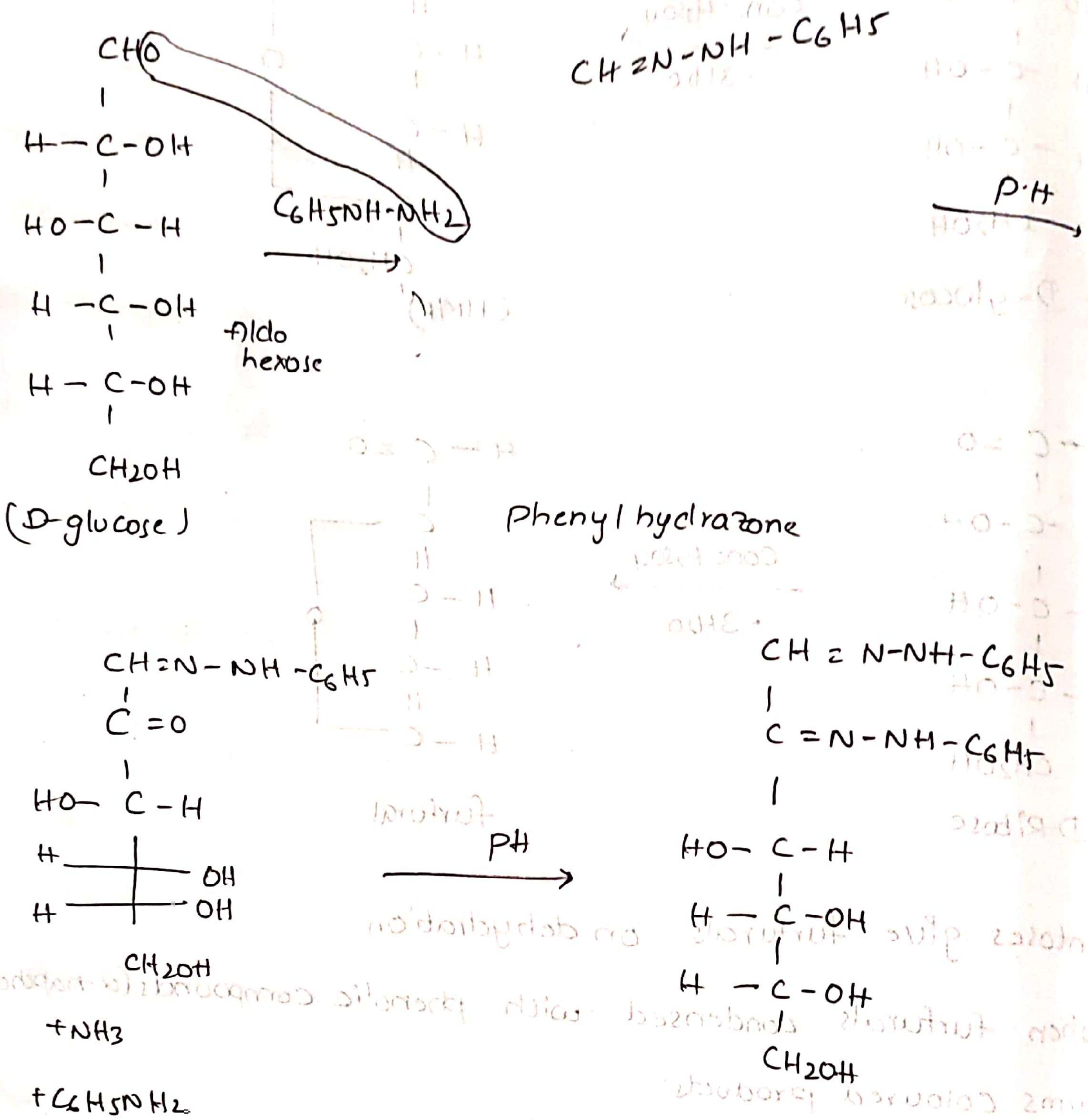
pentoses give furfurals on dehydration

* when furfurals condensed with phenolic compounds (α-napthol) forms coloured products.
* nothing but molisch test
* oligo & polysaccharides —first hydrolysed (acid)→ to monosaccharides & then dehydration.
* All carbohydrates gives this test.

2) osazone formation test :- (phenyl hydrazine test)

* when monosaccharides is treated with phenyl hydrazine gives phenyl hydrazones which on treatment with phenyl hydrazine gives osazone
* the osazone crystals of reducing sugars differ in
    1) crystal structure
    2) precipitation time
    3) melting point

* Osazones of monosaccharides are highly insoluble & crystallises while the solution is hot.



glucose, fructose & mannose give same needle shaped crystals.

Reducing disaccharides gives osazones,

1) Maltose - sunflower shape 

2) Lactose - Cotton ball shape 

3) Reduction :

When treated with reducing agents like NaHg, carbonyl group (aldehyde /keto) of monosaccharide reduces to alcohol.

$$\text{Glucose} \xrightarrow{[H]} \text{Sorbitol}$$

$$\text{Mannose} \longrightarrow \text{Mannitol}$$

$$\text{Ribose} \longrightarrow \text{Ribitol.}$$

4) Reducing properties :- (oxidation)

* By this, reducing sugars can be differentiated from non-reducing sugars.

* Reducing property is determined by using

1) Fehling's test → used to determine the presence of reducing sugar.

2) Barfoed's test → used to determine the presence of reducing monosaccharides

3) Benedict test :- used to determine the presence of sugar.

* Reduction in efficient in alkaline medium than in acid medium.