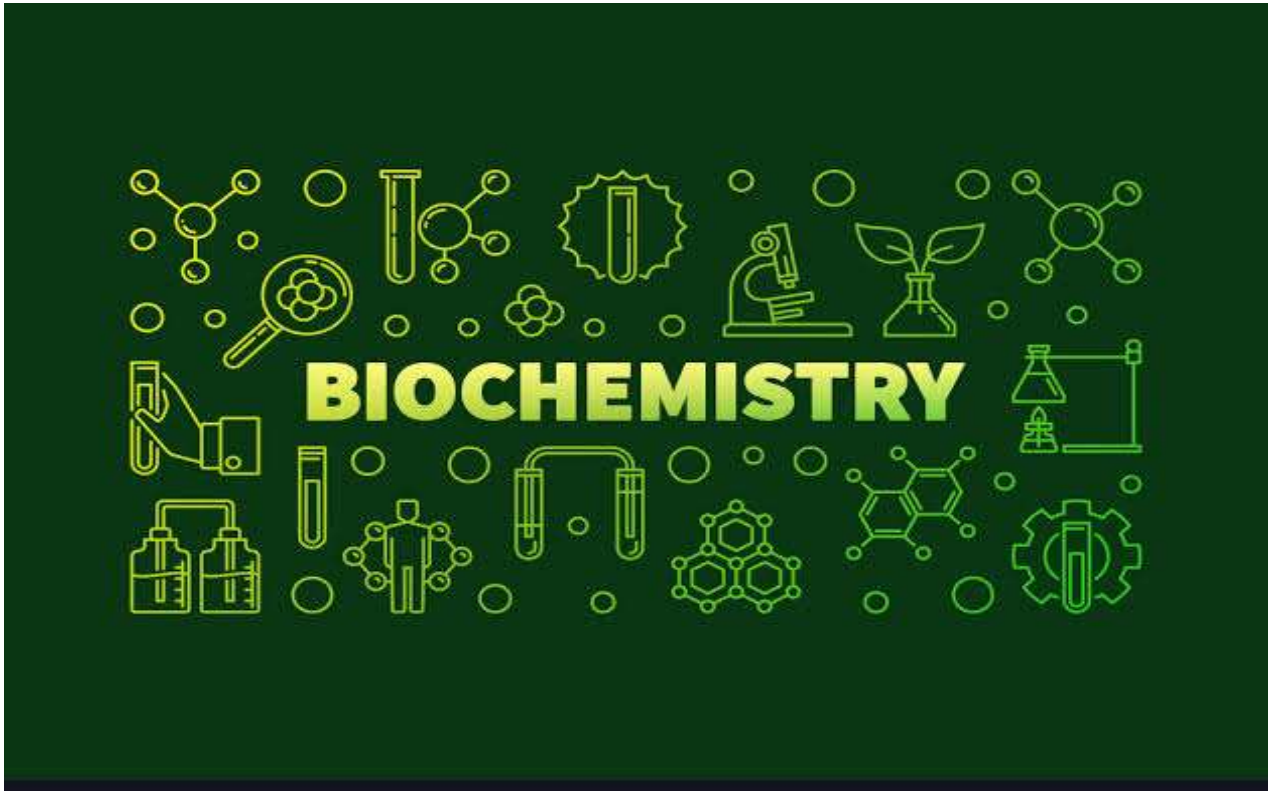


Chemistry of Carbohydrates

BC 3.1

SLO

Student should be able to

- BI 3.1.1 Describe Carbohydrate classification
- BI 3.1.2 Differentiate- Monosacharides,Disacharides,& Polysacharides
- BI 3.1.3 Describe the structural , Storage ,& energy production role of Carbohydrates
- <u>BI 3.1.4 Describe the reactions of monosacharides</u>

  a)Tautomerisation & enediol formation

- SLO Student should be able to explain

  3.1.4 various reactions of monosacharide with clinical applications

  3.1.5 Monosacharides of biological significance

  3.1.6 Derivatives of monosaccharides

Reactions of Monosacharides

A)Reducing property & Tautomerisation

B)Osazone formation

C)Oxidation

D)Reduction

E)Dehydration

F)Esterification

G) Action of Strong Alkali on Sugars

H)Action of Acids on Sugars

A)Reducing propertyTautomerization& enediol formation

- Shift of hydrogen from one carbon position to other carbon is the phenomenon called tautomerisation

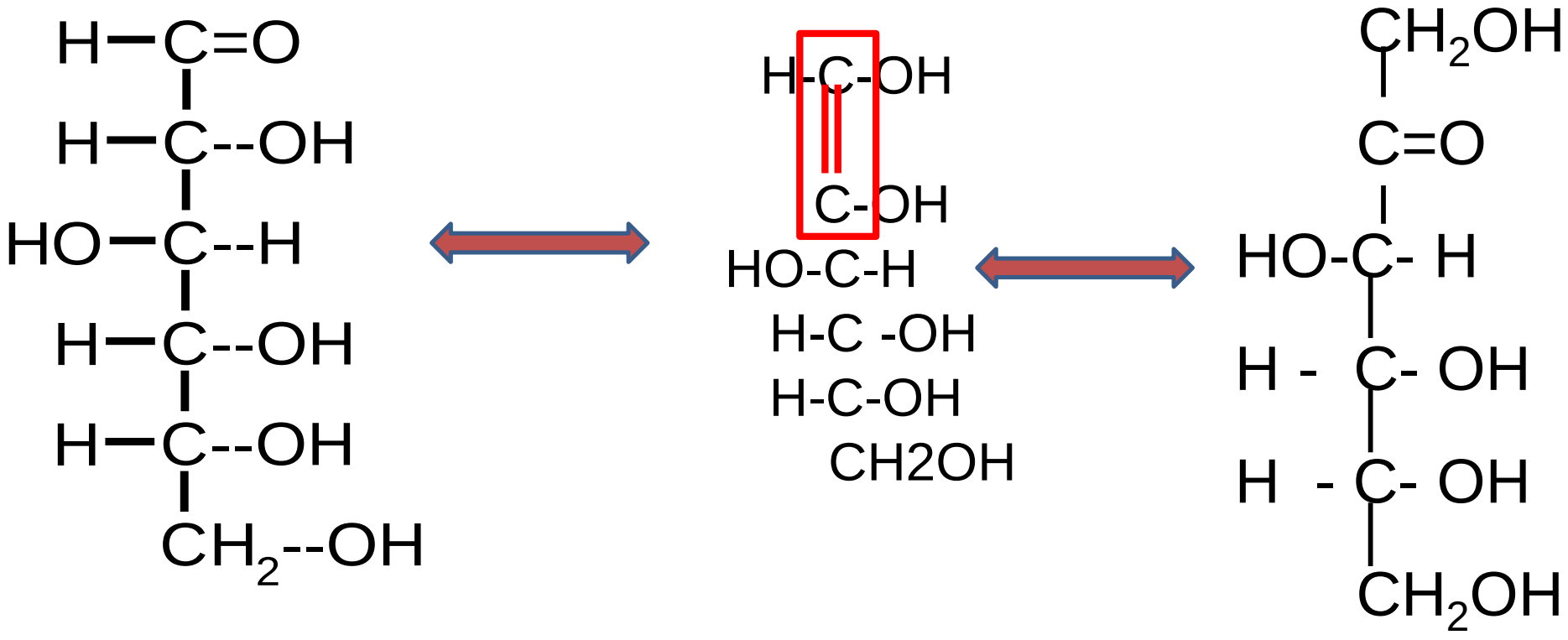
Enediol Formation

In mild alkaline solutions, carbohydrates containing a free sugar group (aldehyde or keto) will tautomerise to form *enediols*.

In mild **alkaline conditions**, glucose is converted into fructose and mannose.

The **interconversion of sugars through a common enediol form is called**

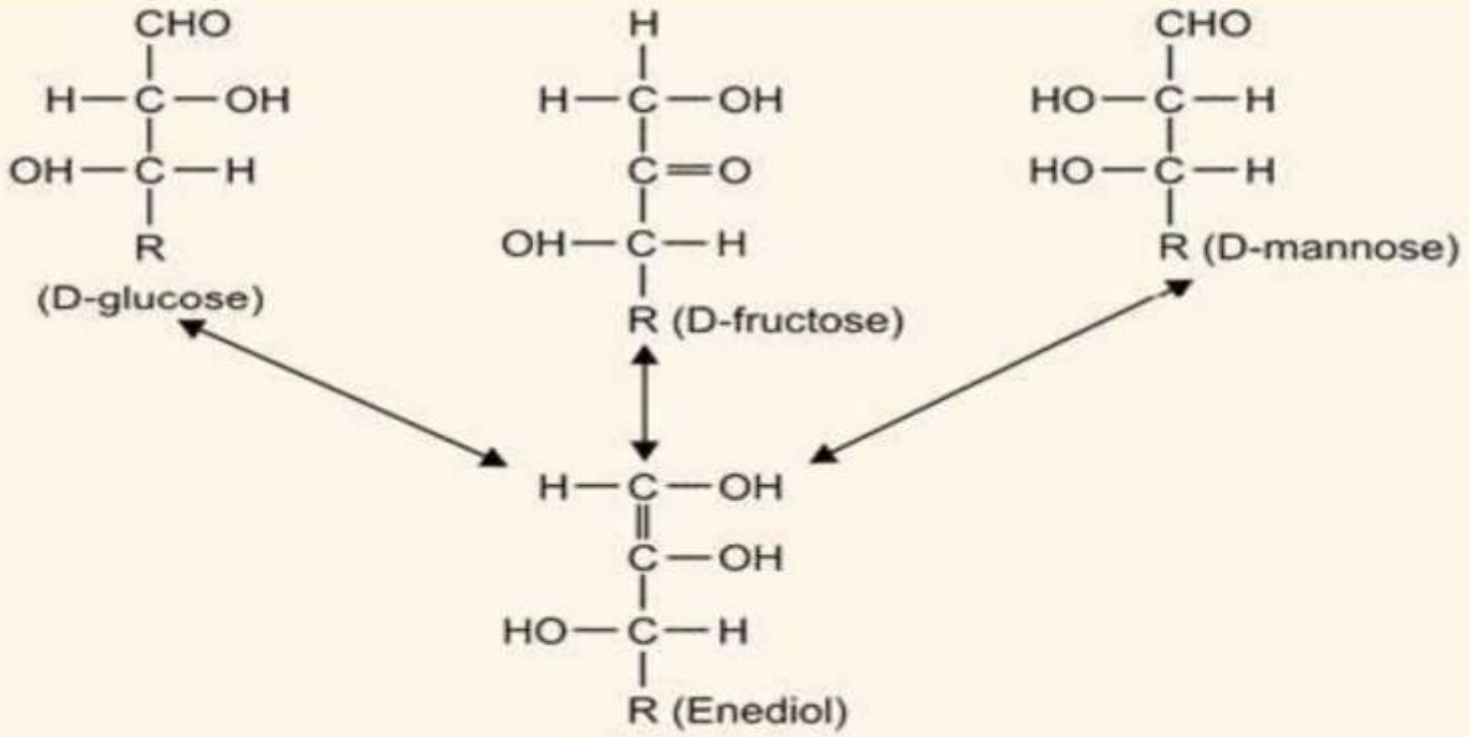
Lobry de Bruyn-Van Ekenstein transformation.



GLUCOSE **1,2-ENEDIOL FORMATION** **FRUCTOSE**

REACTION OF MONOSACCHARIDE

A. **Tautomerization or Enolization**



Benedict’s Reaction

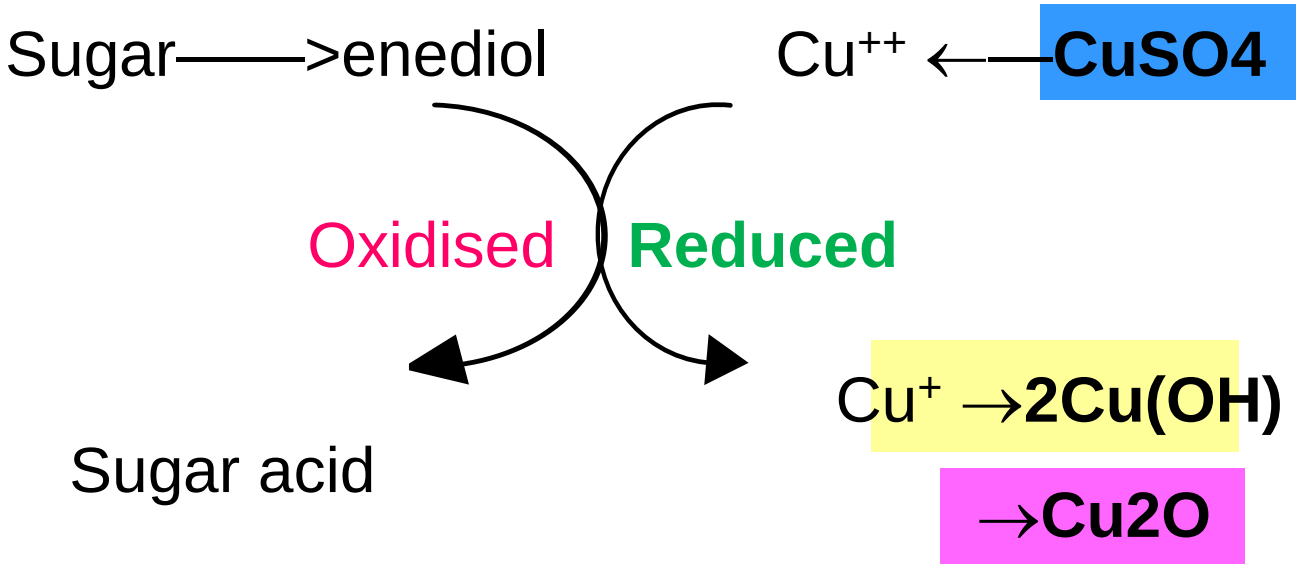
Benedict's test is a chemical test that identifies the presence of reducing sugars in a sample:

Very commonly employed to detect the presence of glucose in urine (glucosuria) and is a standard laboratory test employed in diabetes mellitus.

Benedict's reagent
Contains

Sodium carbonate,
copper sulphate &
Sodium citrate.

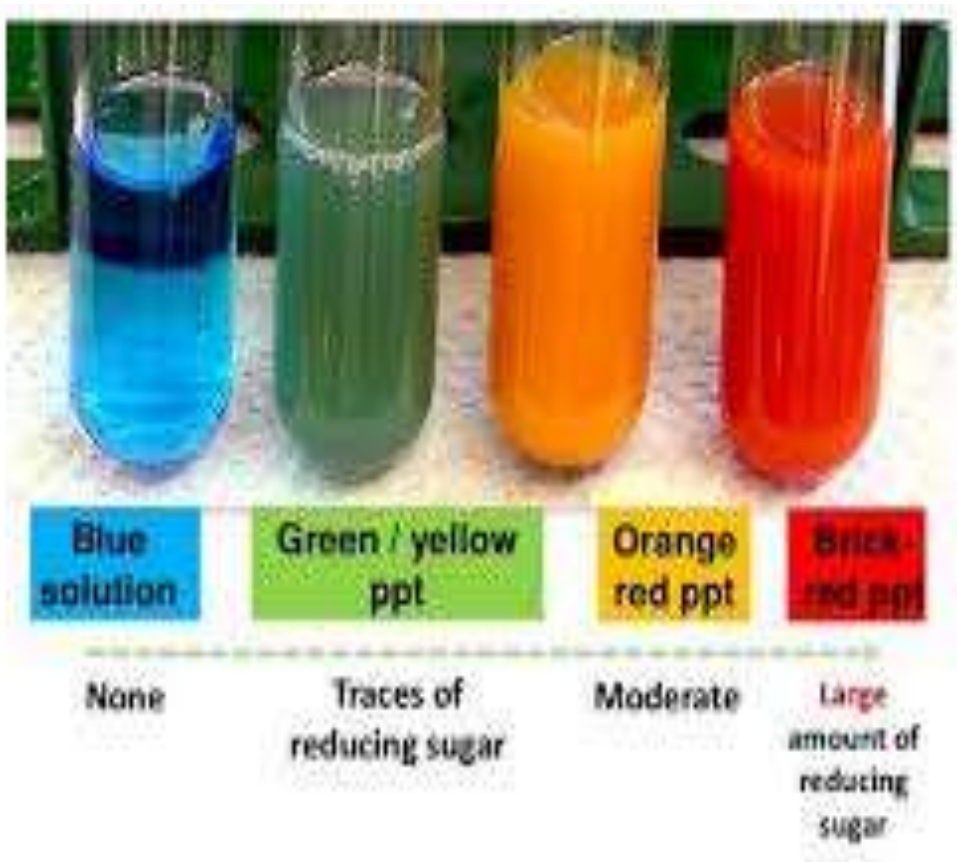
Benedict's Reaction



Glucose is a Reducing sugar

Semi-quantitative test

5 ml Benedicts reagents
+ 0.5 ml Urine
+ boil for 2 min



Clinical application of reducing property of Sugar

- In uncotrolled Diabetes mellitus when blood sugar exceeds 180mg/dl, glucose gets excreted in urine.

  This can be detected by Benedicts test

Principle: Reducing property of glucose

- In metabolic defects:

egs

1)Essential fructosuria, Fructose intolerance

2) Galactosuria in Galactosemia

These sugars can be detected in urine.

Reactions of Monosacharides

A)Reducing property & Tautomerisation

B)Osazone formation

C)Oxidation

D)Reduction

E)Dehydration

F)Esterification

G) Action of Strong Alkali on Sugars

H)Action of Acids on Sugars

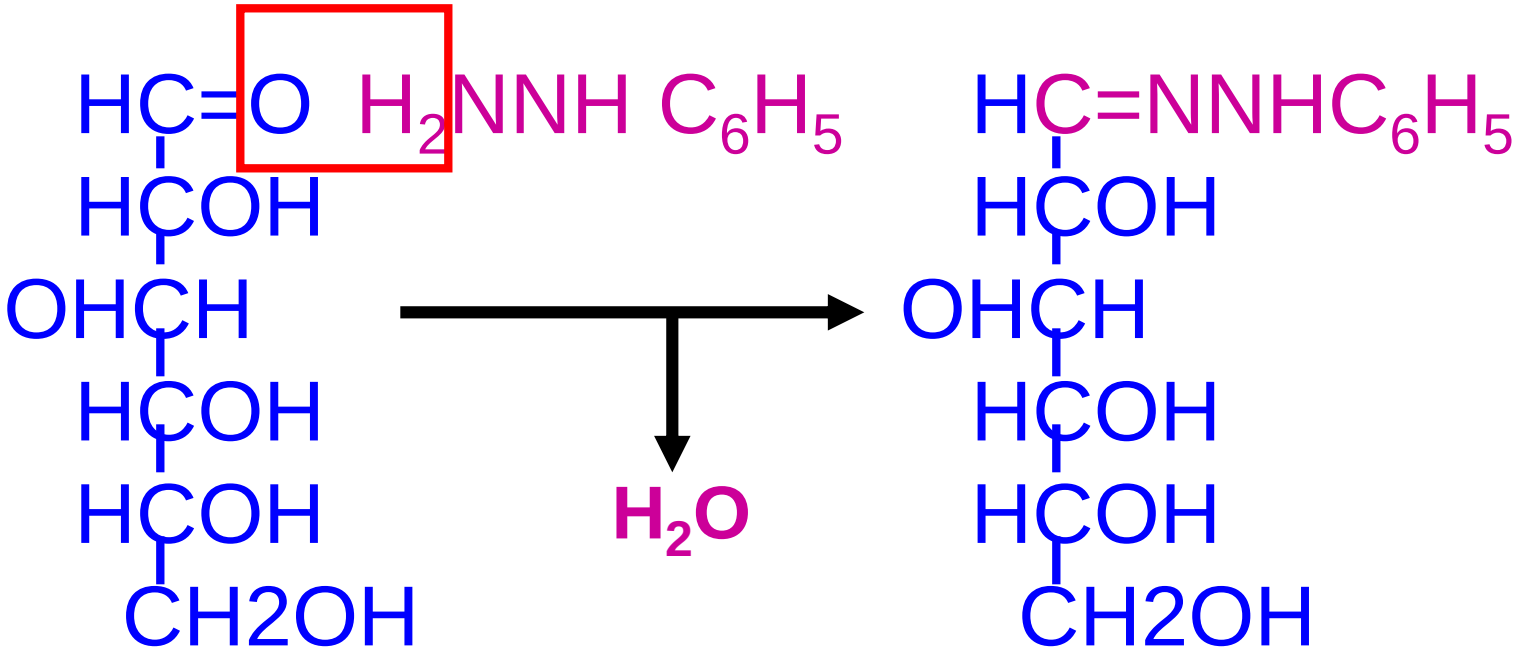
B)Osazone Formation

All reducing sugars will form osazones with excess of **phenylhydrazine** when kept at boiling temperature.

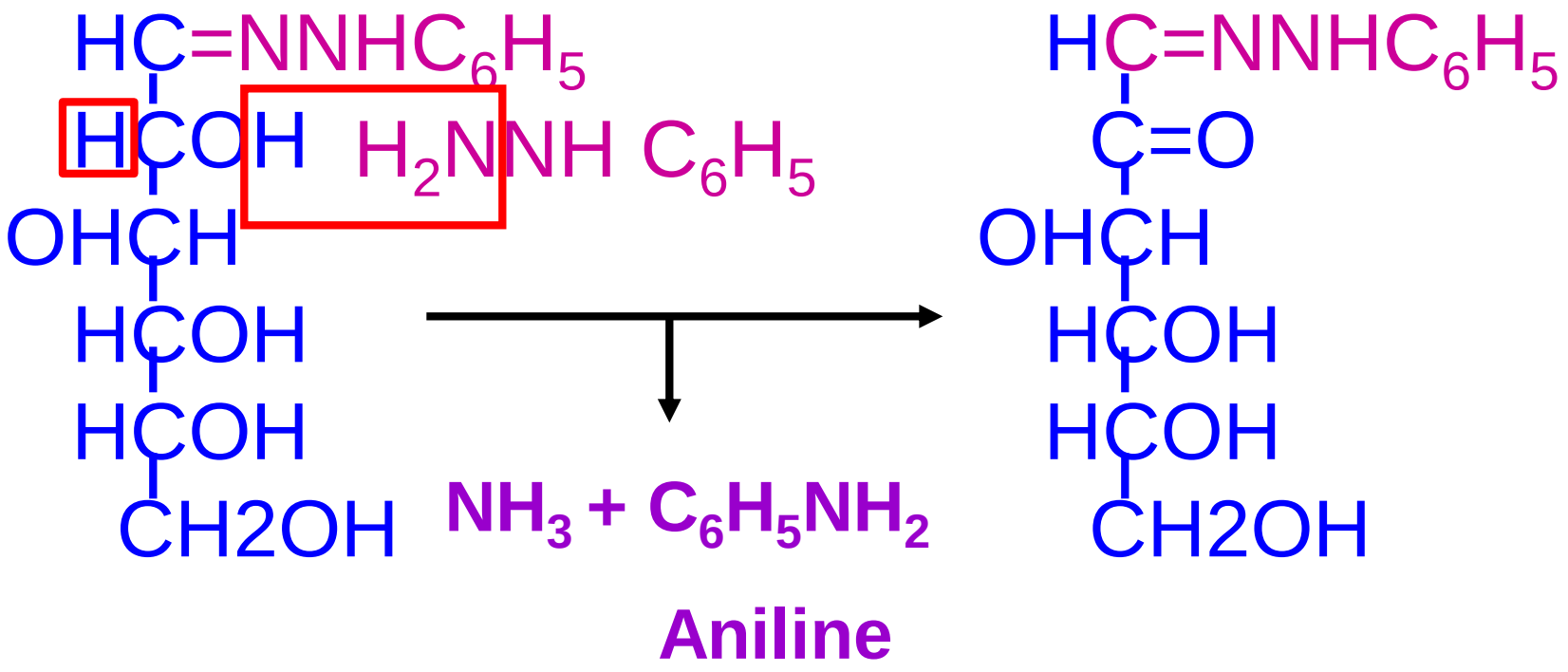
Osazones are insoluble.
Each sugar will have characteristic crystal form of osazones.

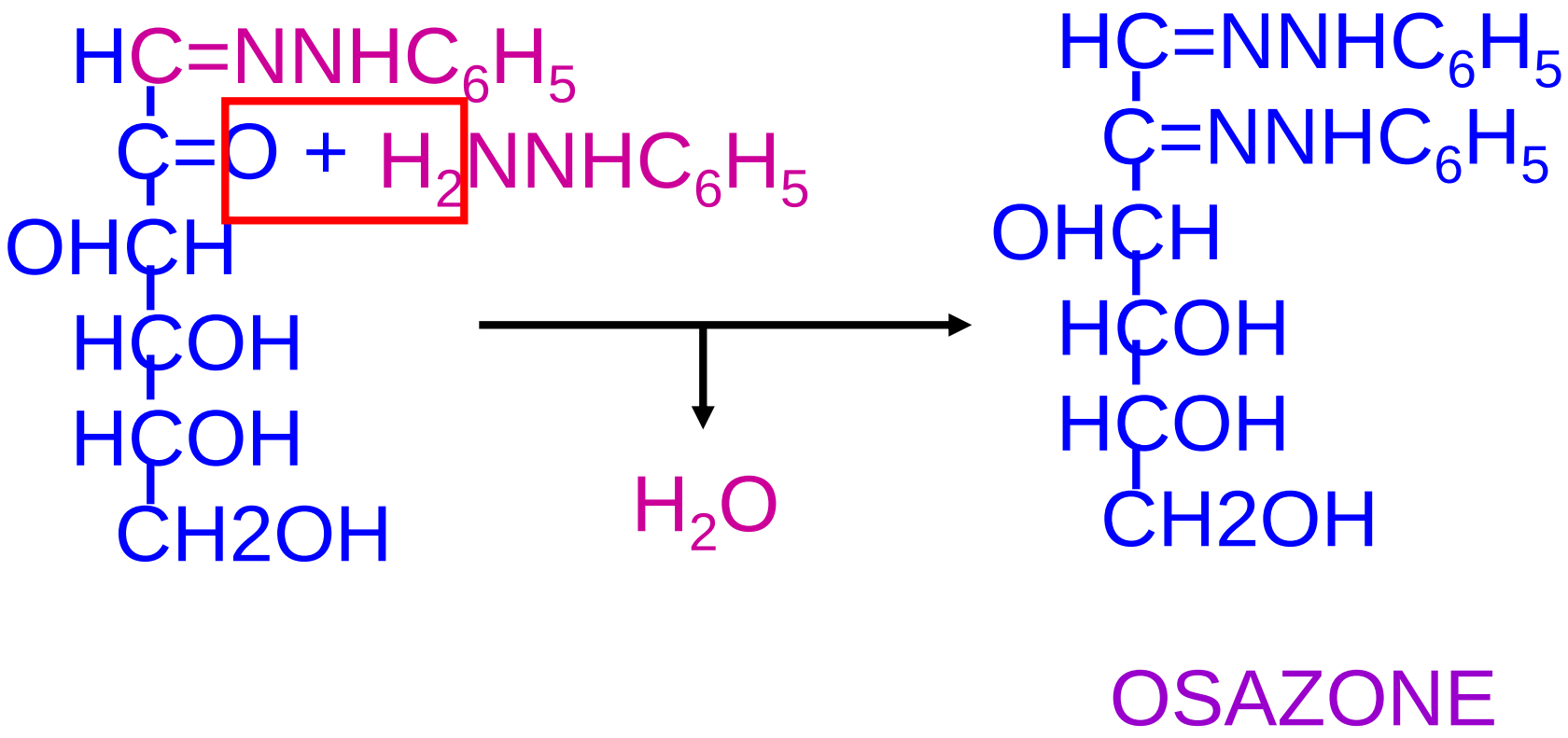
OSAZONE FORMATION

- Sugars react with 3 molecules of Phenyl hydrazine to give hydrazones and osazones



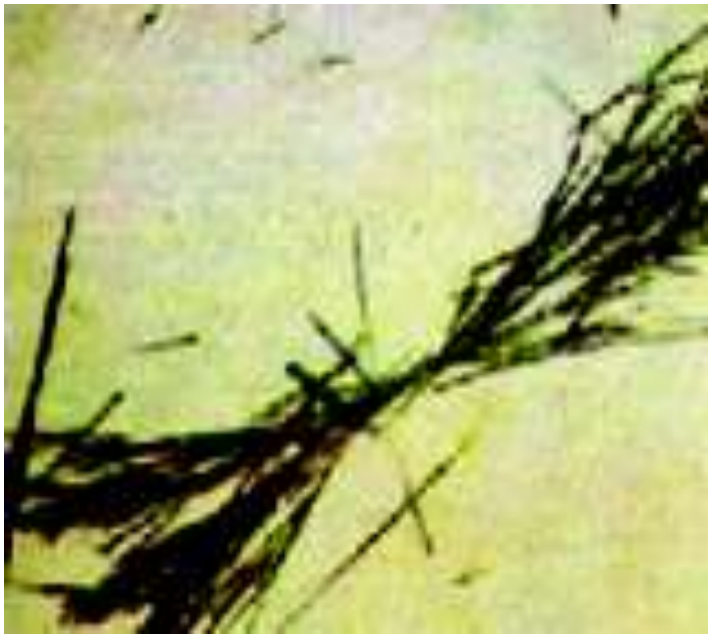
Phenyl Hydrazone


HC=NNHC6H5
HCOH
OHCH
HCOH
HCOH
CH2OH
H2NNH C6H5
NH3 + C6H5NH2
Aniline
HC=NNHC6H5
C=O
OHCH
HCOH
HCOH
CH2OH


HC=NNHC6H5
C=O + H2NNHC6H5
OHCH
HCOH
HCOH
CH2OH
H2O
HC=NNHC6H5
C=NNHC6H5
OHCH
HCOH
HCOH
CH2OH

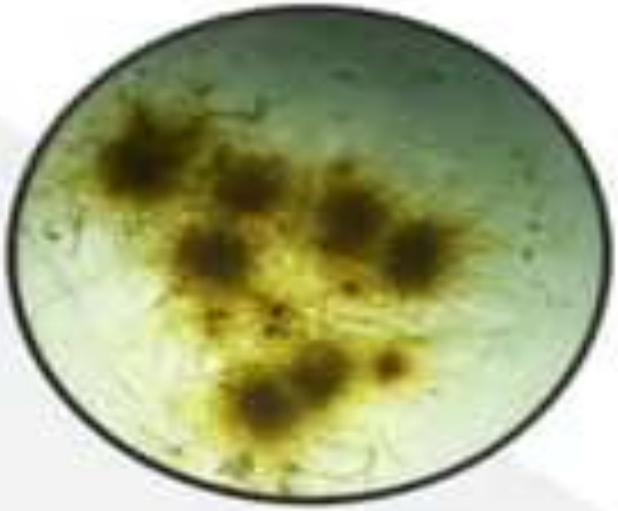
OSAZONE

- Glucose,Fructose & Mannose form needle shaped crystals arranged like a broom or sheaves of corn

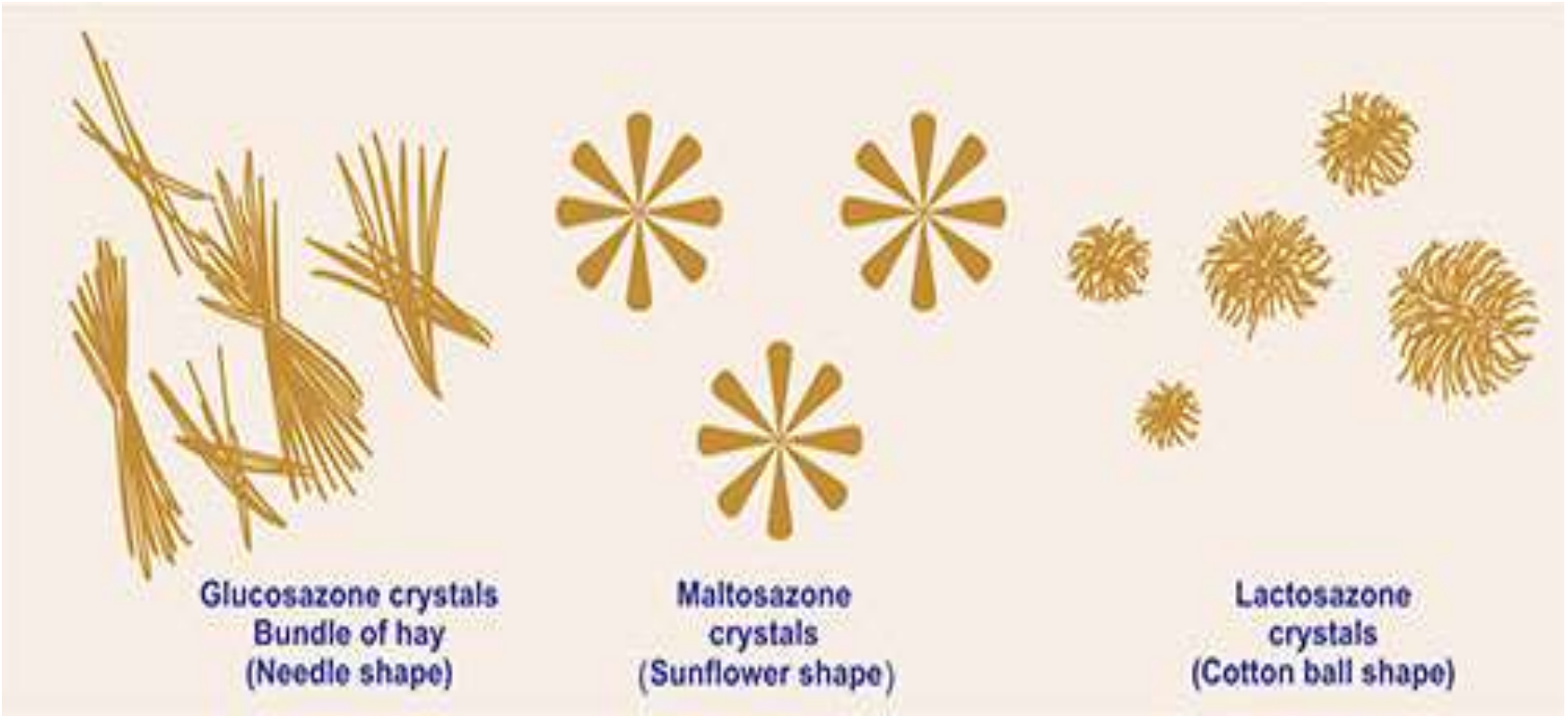


- Differences in glucose,fructose and mannose are dependent only on the **1st and 2nd carbons**,and when osazone is formed these differences are masked ⟶ So these 3 sugars produce the same type of crystals(needle shaped)

Lactosazone



Powderpuff or hedgehog shaped crystals


Glucosazone crystals
Bundle of hay
(Needle shape)
Maltosazone
crystals
(Sunflower shape)
Lactosazone
crystals
(Cotton ball shape)

Reactions of Monosacharides

A)Reducing property & Tautomerisation

B)Osazone formation

C)Oxidation

D)Reduction

E)Dehydration

F)Esterification

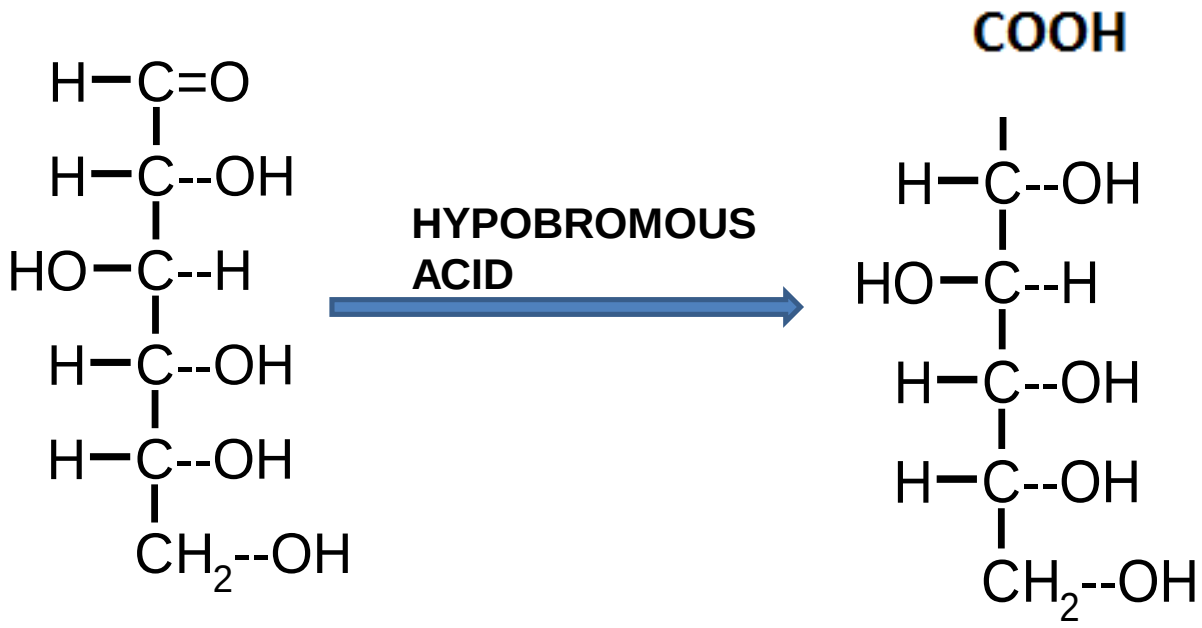
G) Action of Strong Alkali on Sugars

H)Action of Acids on Sugars

C) OXIDATION OF SUGARS

A. Under mild oxidation conditions,aldehyde group is oxidised to produce **aldonic acid**.

- Glucose → Gluconic acid
- Mannose → Mannonic acid
- Galactose → Galactonic acid



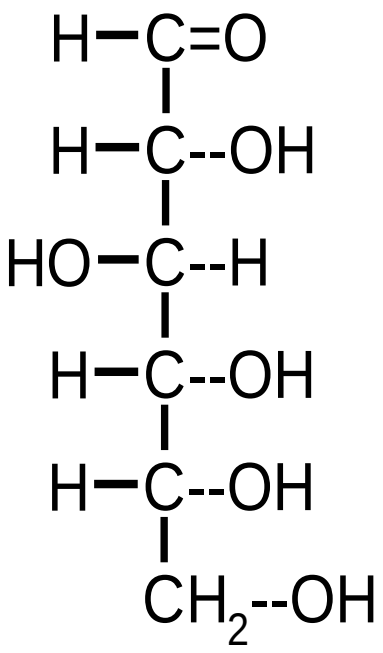
GLUCOSE **GLUCONIC ACID**

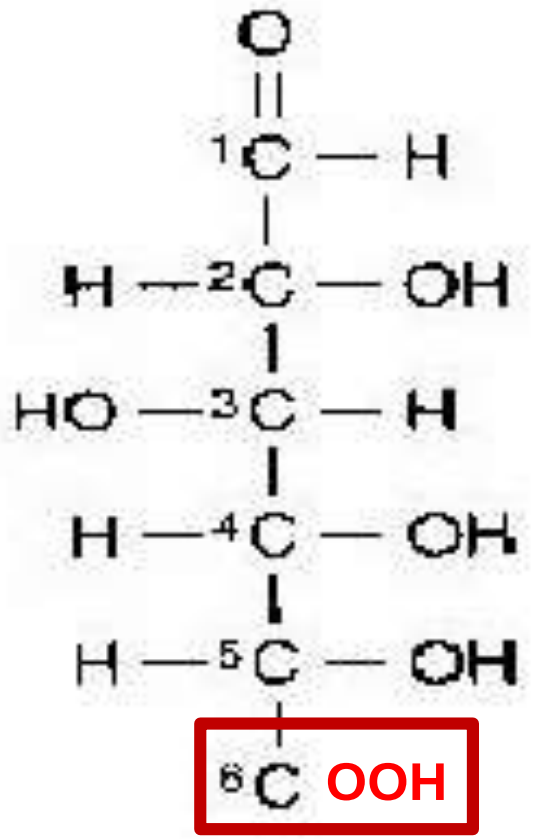
- If aldehyde gp is masked & subjected to mild oxidation terminal carboxyl gp is oxidised to **uronic acid**

Glucose to glucuronic acid

Mannose to mannuronic acid

Galactose to galacturonic acid





GLUCOSE **GLUCURONIC ACID**

Strong oxidation conditions

- By nitric acid

  Both aldehyde & terminal gp oxidised to produce **saccharic acid**

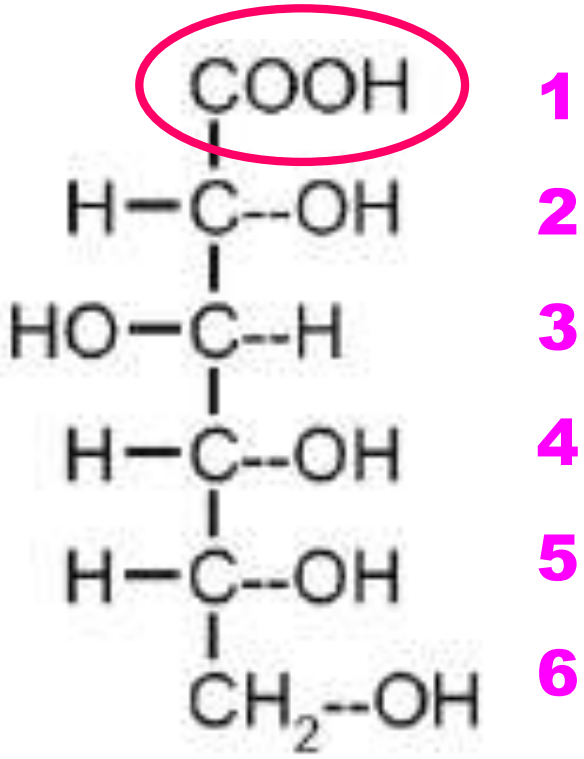
egs:

Glucose glucosaccharic acid

Mannose to mannaric acid

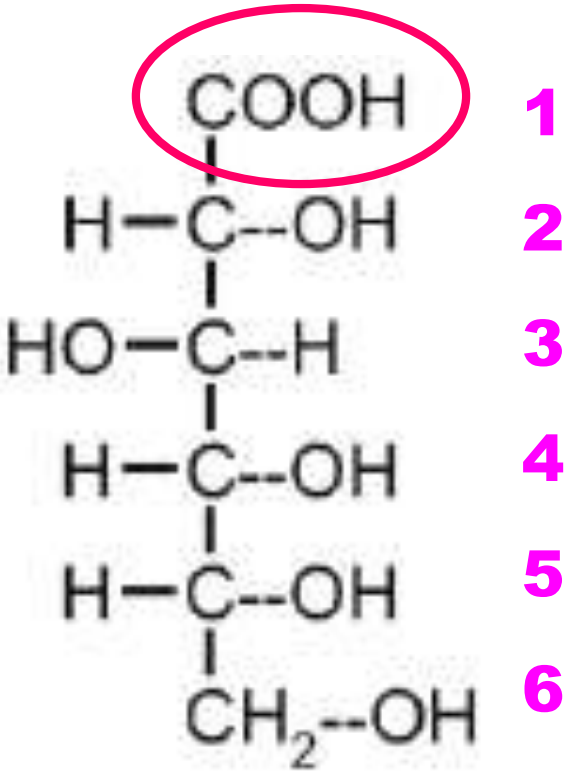
Galactose to mucic acid

Oxidation

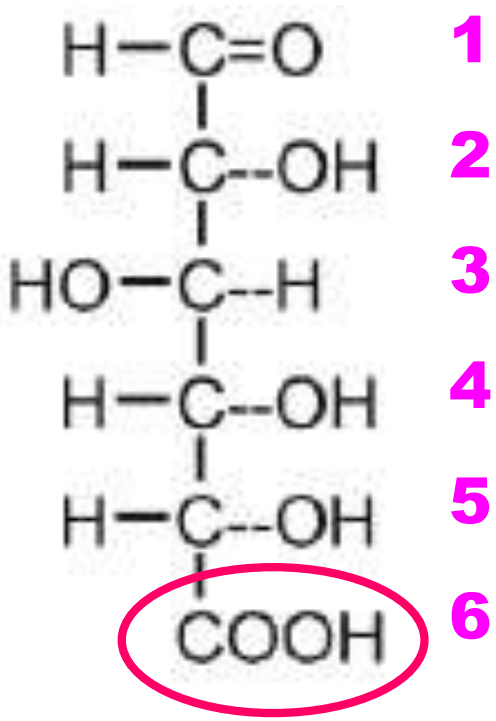


Gluconic acid

Oxidation

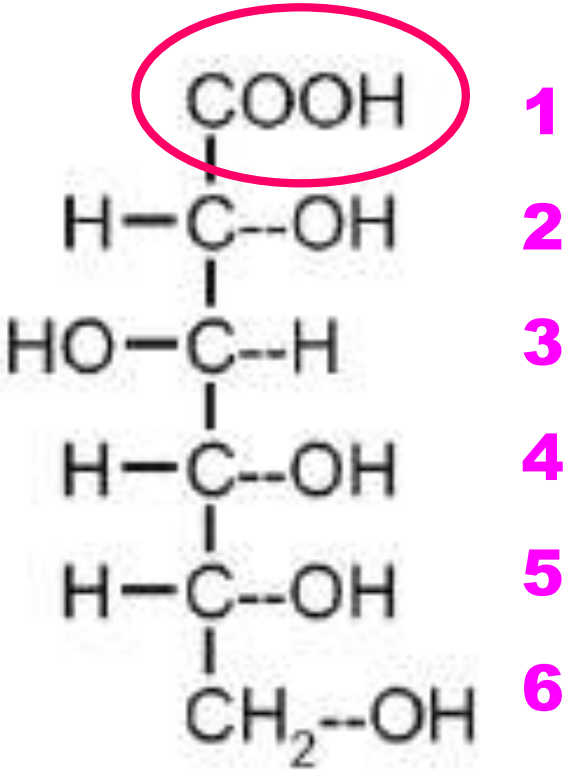


Gluconic acid

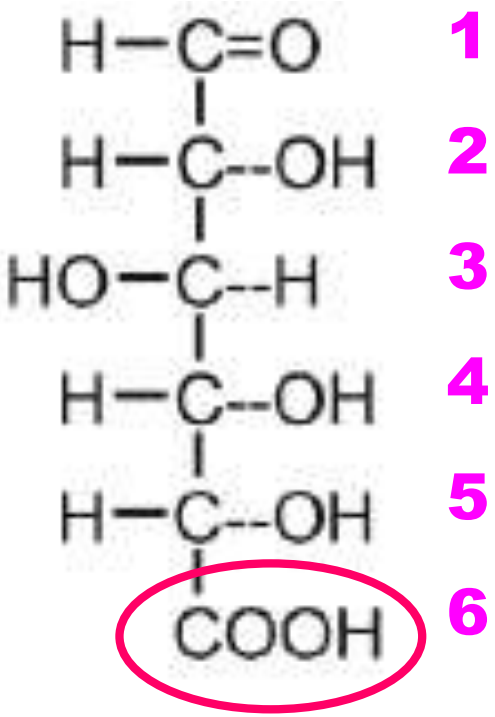


Glucuronic Acid Used for conjugation with insoluble molecules

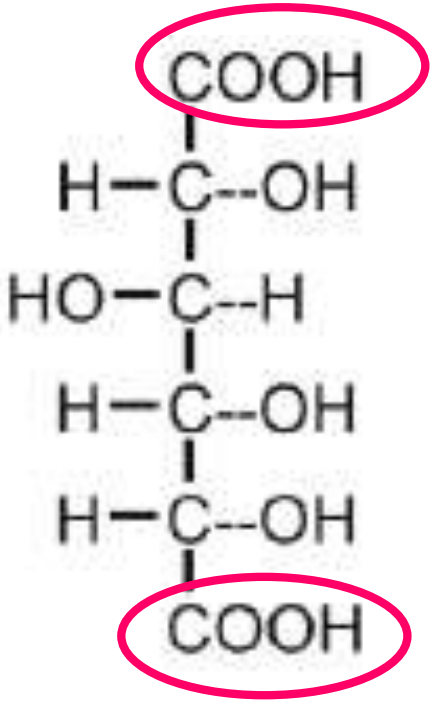
Oxidation



Gluconic acid



Glucuronic Acid



Gluco-saccharic acid

Clinical significance of Glucuronic acid

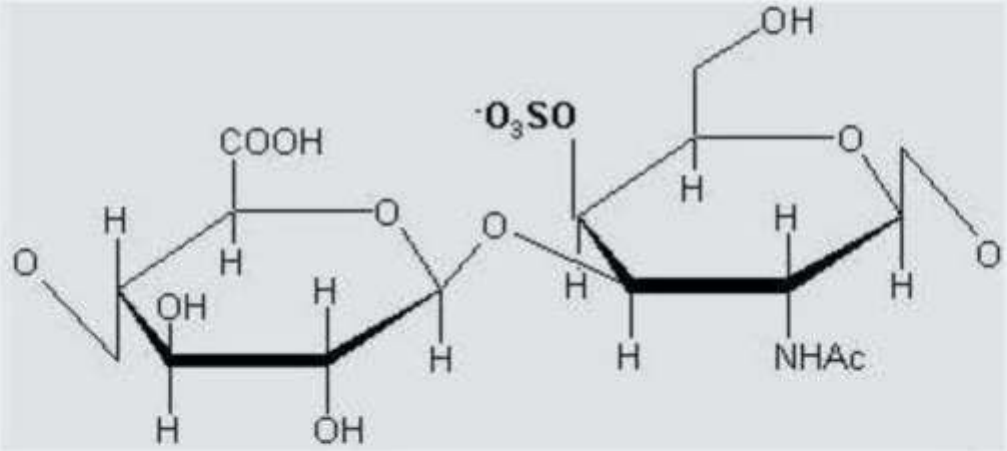
Glucuronic acid is a biologically important compound

1) Required for synthesis of **mucopolysacharides**

2) Required for **conjugation** of various xenobiotics &Toxic compounds in body.

CHONDROITIN SULFATE

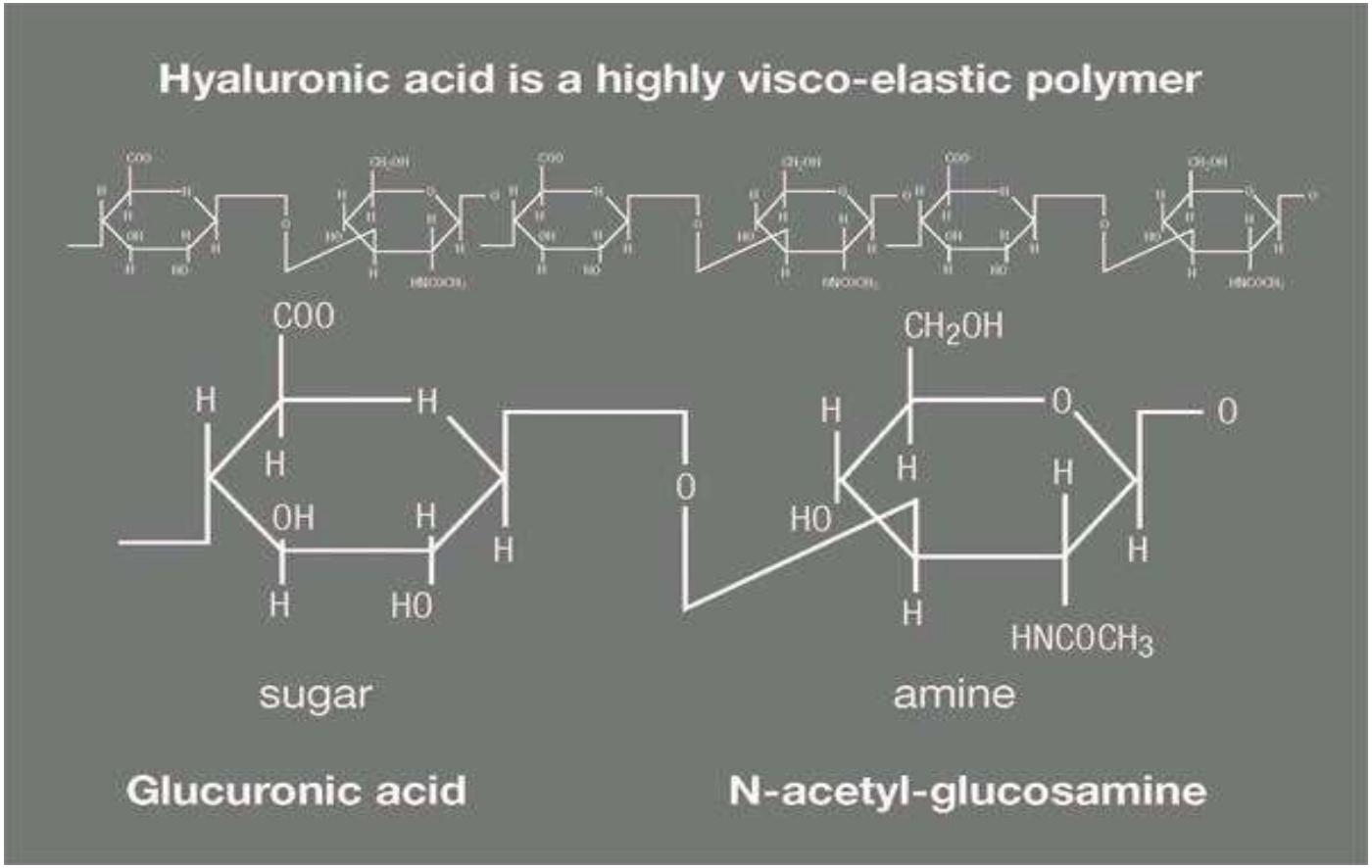
- Chondroitin word is derived from Greek word "chondros" means cartilage .
- Contains D-Glucoronic acid + Galactosamine.
- Most abundant GAG in body.



D-Glucuronic acid N-Acetylgalactosamine 4-sulfate

Fig- Chondroitin 4-sulfate

fppt.com


Hyaluronic acid is a highly visco-elastic polymer
COO
H
H
H
OH
H
H
H
HO
O
CH2OH
H
O
O
H
H
HO
H
H
HNCOCH3
sugar
amine
Glucuronic acid
N-acetyl-glucosamine

Reactions of Monosacharides

A)Reducing property & Tautomerisation

B)Osazone formation

C)Oxidation

D)Reduction

E)Dehydration

F)Esterification

G) Action of Strong Alkali on Sugars

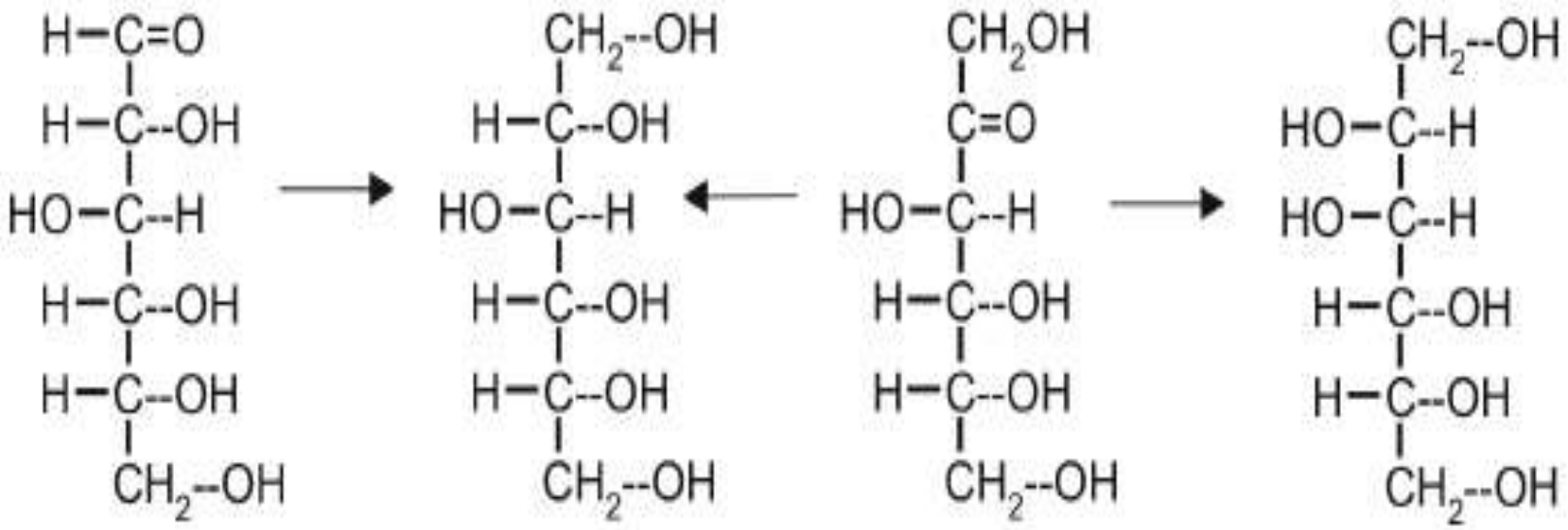
H)Action of Acids on Sugars

D)Reduction

When treated with reducing agents,sugars form alcohol

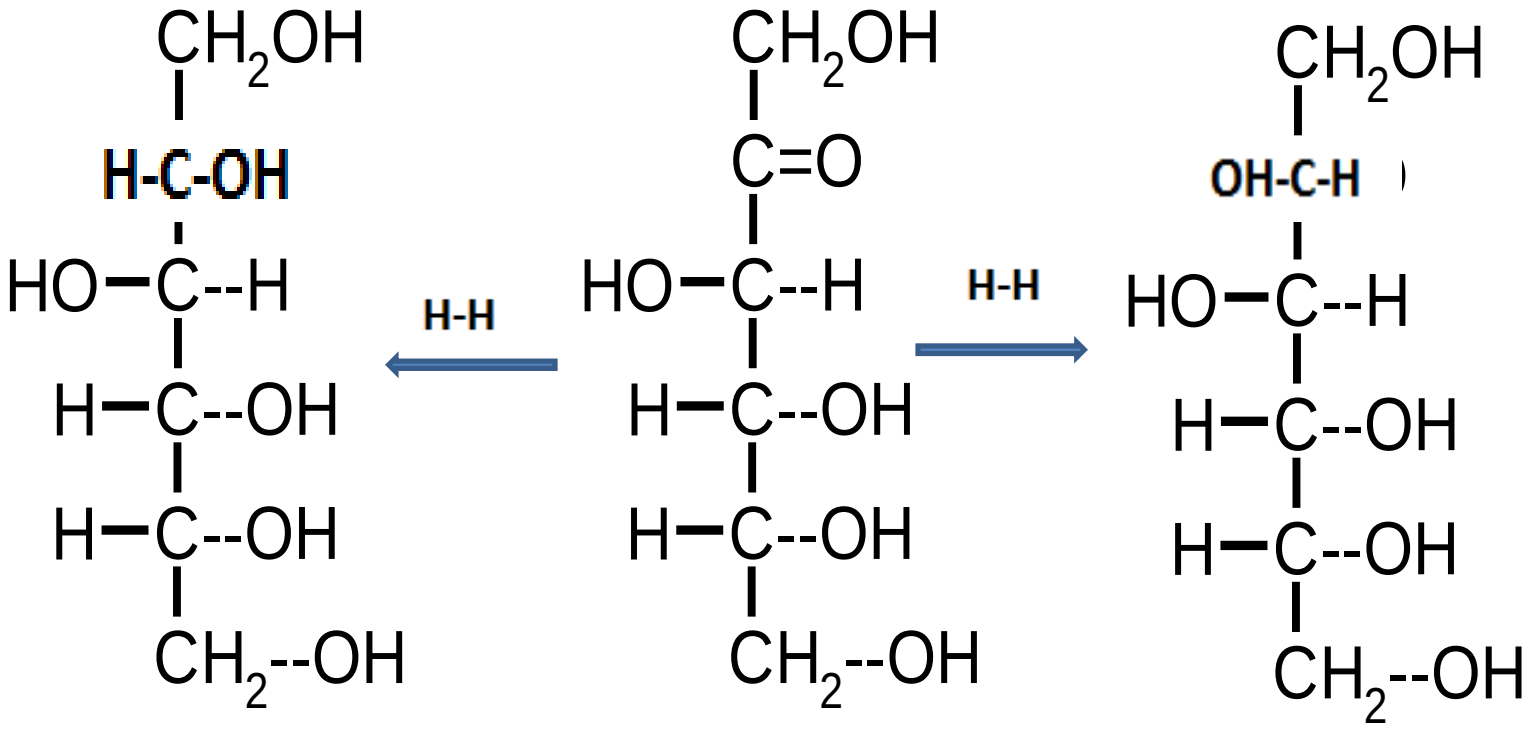
Glyceraldehyde→ **Glycerol**
Ribose→**Ribitol**
Glucose is reduced to **sorbitol ,**
Mannose to **mannitol**
Fructose to **sorbitol and mannitol.**
Galactose is reduced to **dulcitol**

Reduction



Glucose **Sorbitol** **Fructose** **Mannitol**

Ketoses gives 2 alcohols



D-SORBITOL D-FRUCTOSE D- MANNITOL

Clinical significance

1)Sorbitol, mannitol and dulcitol are used to **identify bacterial colonies.**

2)Mannitol is also used to **reduce intracranial tension by forced diuresis.**

3)The osmotic effect of sorbitol and dulcitol produces changes in tissues when they accumulate in abnormal amounts,

e.g. **cataract of lens.**

Reactions of Monosacharides

A)Reducing property & Tautomerisation

B)Osazone formation

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D)Reduction

E)Dehydration

F)Esterification

G) Action of Strong Alkali on Sugars

H)Action of Acids on Sugars

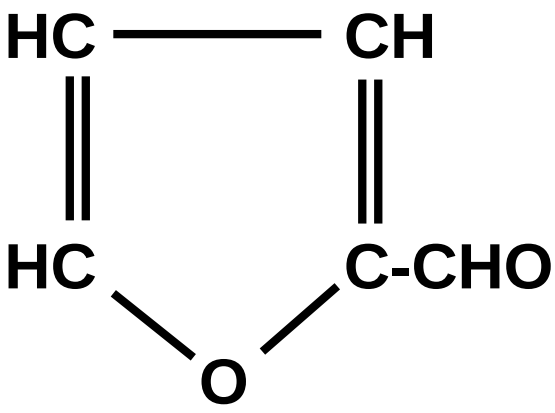
E) Dehydration & Furfural formation

- When treated with **con.H_2SO_4,** monosaccharides undergo dehydration with removal of 3 molecules of water

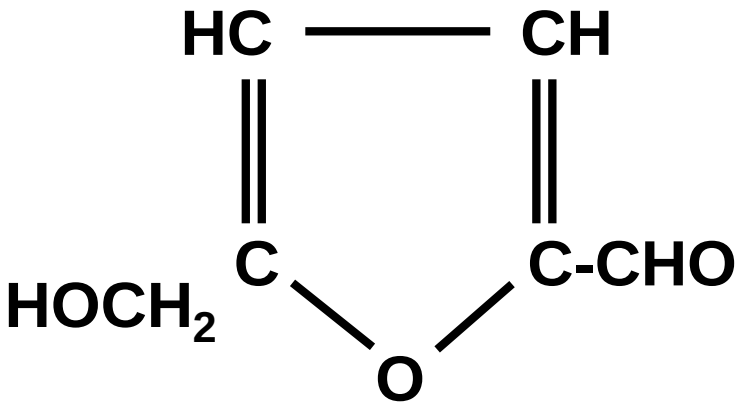
- **Hexoses- hydroxymethyl furfural**

- **Pentoses- furfural**

Action of Acids on Sugars



Furfural



Hydroxymethyl Furfural

- Furfural derivatives condense with phenolic compounds to give coloured products – **MOLISCH TEST**

- ***GENERAL TEST OF CARBOHYDRATES***

Reactions of Monosacharides

A)Reducing property & Tautomerisation

B)Osazone formation

C)Oxidation

D)Reduction

E)Dehydration

F)Esterification

G) Action of Strong Alkali on Sugars

H)Action of Acids on Sugars

F) FORMATION OF ESTERS

- Hydroxyl groups of sugars can be esterified to form etc phosphates, acetates , propionates, benzoates

- Sugar phosphates are of biological importance
- Glucose-6-phosphate and glucose-1-phosphate are important intermediaries of glucose metabolism

G) Action of Strong Alkali on Sugars

- When treated with strong alkali, sugars are enolised and the double bond will shift from 1:2 to 2:3, 3:4 or 4:5 to form the corresponding ene diols and gets fragmented.

- The fragmented molecules will polymerise to form a yellow resinous material called **Caramel.**

- **H)Action of Acids on Sugars**

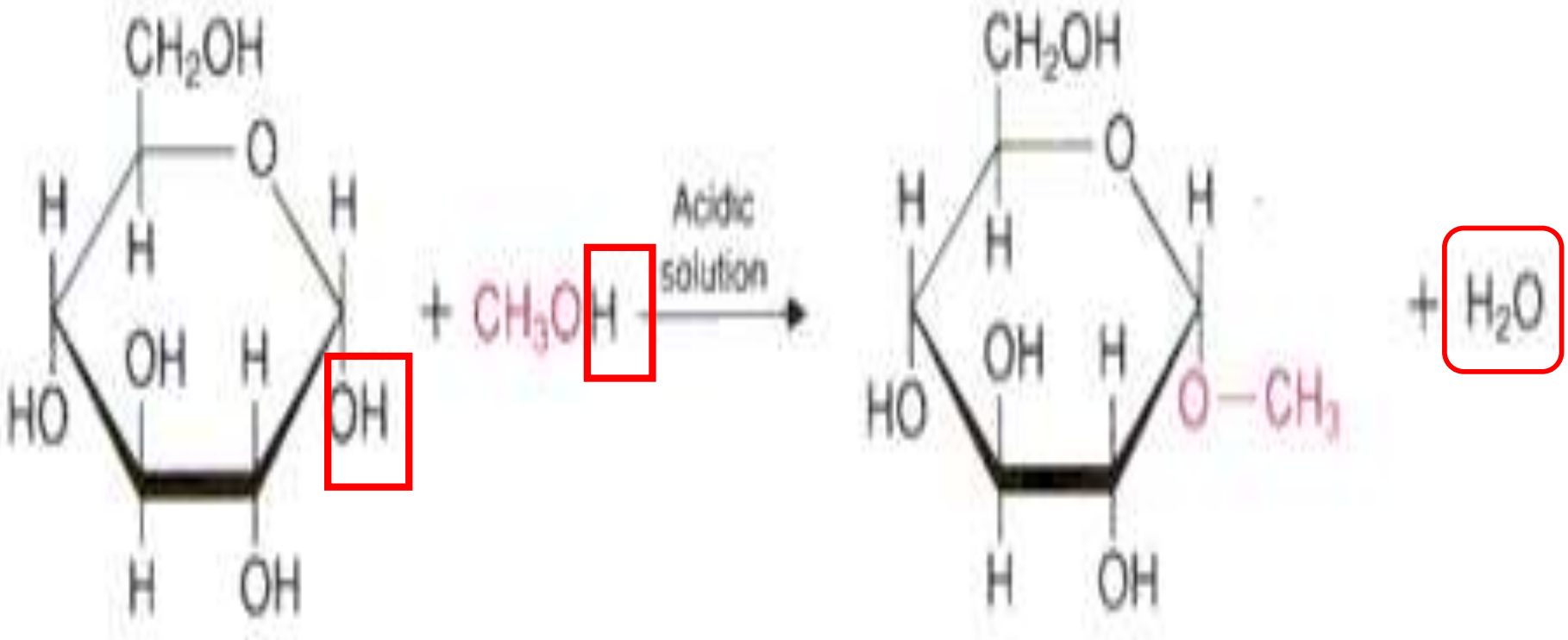
- Dilute acids –
  Aldoses in general are relatively stable.
  Ketoses degraded.

- Concentrated acids –

  Dehydrated to cyclical derivatives
  Pentoses: Furfural
  Hexoses : Hydroxy methyl furfural

GLYCOSIDES

- When the hemiacetal group of a monosaccharide(hydroxyl group of the anomeric carbon) is condensed with an alcohol or phenol group ,it is called a **glycoside.**



α-D-Glucopyranose

Methyl-α-D-glucopyranoside

- Non carbohydrate group is called Aglycone
- They do not reduce Benedicts reagent because the sugar group is masked
- On boiling with dilute acid, they are hydrolysed ⟶ sugar is free and can reduce

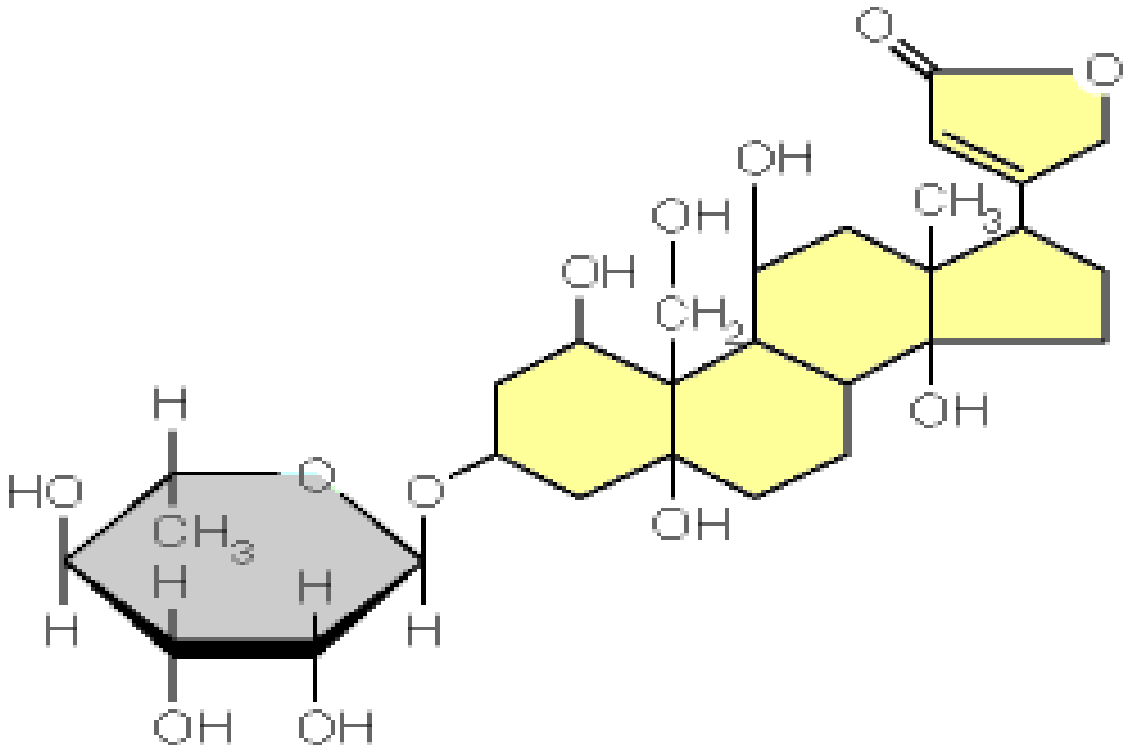
- 2 forms -------alpha and beta glycosides
- α glycosides are hydrolysed by maltase and β glycosides by emulsins
- Thus the 2 forms can be distinguished

Significance:

- Cardiac glycoside- Digitalis- action on heart. Aglycon part is steroid.

- Streptomycin- an antibiotic used in Tuberculosis is a glycoside

- Oubain is a glycoside which inhibits active transport of Glc.



Ouabain

Monosaccharides of Biological Significance

Trioses- Glyceraldehyde & Dihydroxyacetone

- Phosphorylated esters are intermediates in metabolism of Glucose.

- They are precursors of glycerol which is incorporated to lipids.

Monosaccharides of Biological significance

Tetroses

D Erythrose 4P occur as an intermediate of HMP shunt pathway - an alternate pathway of Glucose oxidation

Monosaccharides of Biological significance

PENTOSES

- Sugars containing **5** carbon atoms
- Eg: Ribose, Xylose, Arabinose (aldoses)
- Ribulose, Xylulose (ketoses)

- Ribose- constituent of RNA ,seen in ATP and NAD.
- Ribulose- intermediate of HMP shunt pathway

- Arabinose- found in cherries and glycoproteins
- Xylose – seen in proteoglycans
- Xylulose- intermediate of uronic acid pathway

Monosaccharides of Biological significance

Hexoses

D Glucose (Dextrose)

- Sugar of the body
- Major sugar in blood and body fluids.
- Immediate energy source
- Constituent sugar of Maltose, Lactose, Sucrose, Starch, Glycogen, Dextrins and Cellulose.

Monosaccharides of Biological significance

Hexoses:

D Fructose: Ketohexose

- Fruits and Seminal fluid
- Sweetest sugar
- Laevorotatory
- Exhibit mutarotation

α D Fru(-21^0) → D Fru(-92^0) ← βD Fru (-113.5^0)

Monosaccharides of Biological significance

Hexoses:

D Galactose (Gala= milk)

- Structural carbohydrate
- Glycoproteins
- Mucopolysaccharides
- Constituent of Lactose
- Most rapidly absorbed from intestinal tract.

Derivatives of Monosaccharide

1)PHOSPHOSUGARS

2)AMINO SUGARS & Aminosugar acids

3)URONIC ACIDS

4)SUGAR ALCOHOLS(POLYOLS)

5)DEOXY SUGARS

6)L ASCORBIC ACID

Derivatives of Monosaccharide

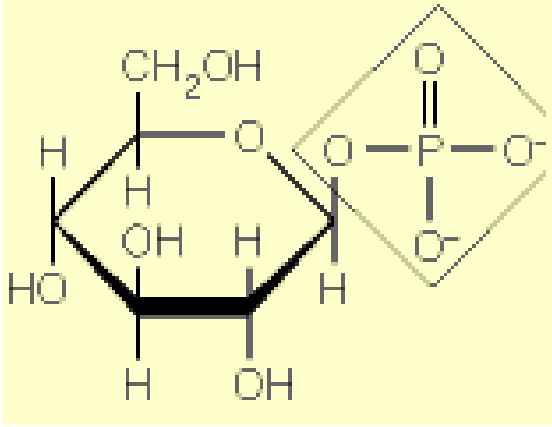
Monosaccharide can be chemically altered in several ways to provide new classes of compounds.

- Phosphosugars - made by esterifying a phosphate group to one of the hydroxyls.

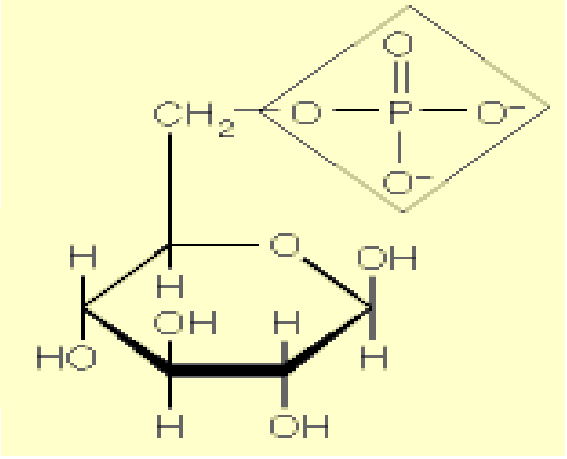
Examples:

G1P, G6P, F6P, F1,6P, Ribose 5 P etc.

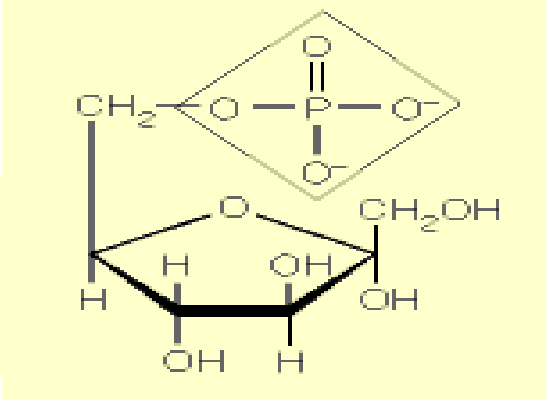
Glucose 1 Phosphate



Glucose 6 Phosphate



Fructose 6 Phosphate



Sugar Phosphates

- Phosphorylated sugars are **"activated compounds"** in metabolic reactions because of the free energy content released on hydrolysis.

AMINO SUGARS

- Amino groups may be substituted for hydroxyl of groups of sugars to form amino sugars
- Will not show reducing properties
- Will not produce osazones

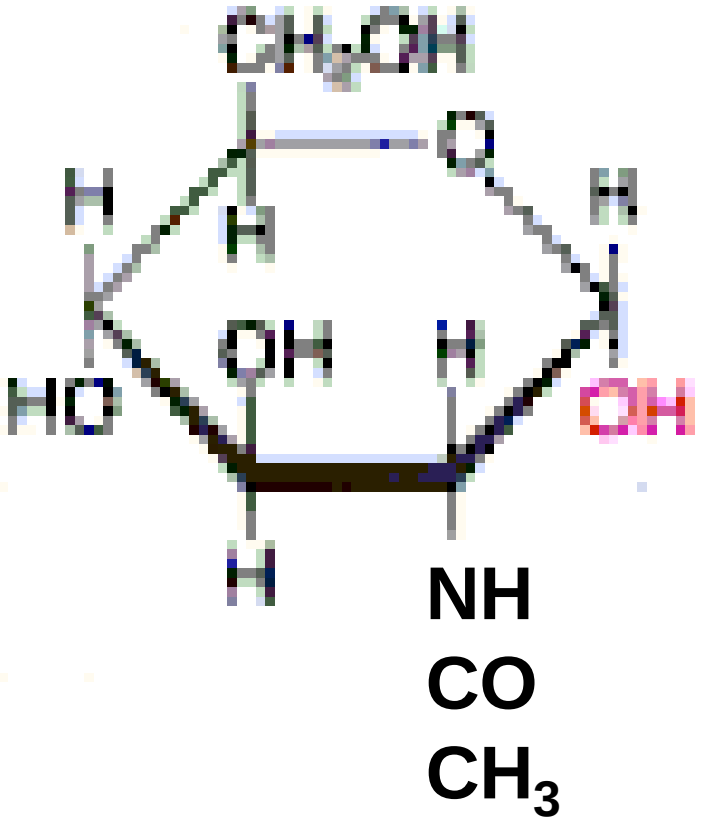
- Structural role- **Glycosaminoglycans(GAG)**.
- Can be modified by N acetylation.
- Several antibiotics Erythromycin, Carbomycin contain amino sugars.

- **Glucosamine** → hyaluronic acid,heparin and blood group substances
- **Galactosamine** → chondroitin of cartilage,bone and tendons
- **Mannosamine** → glycoproteins

- Amino group can be further acetylated to form N-acetyl glucosamine and N-acetyl galactosamine

- These are important constituents of glycoproteins,mucopolysaccharides and cell membrane antigens

N- acetyl D Glucosamine



Derivatives of Monosaccharide

Aminosugar acids:

Sialic acids

- Naturally occurring N acetyl derivatives
- Example-N acetyl Neuraminic acid – NANA
- 9 C
- Present in **Glycoproteins and Gangliosides**

Derivatives of Monosaccharide

Uronic Acids:

- C_6 is oxidized to acid

GlcUA - important role in detoxification

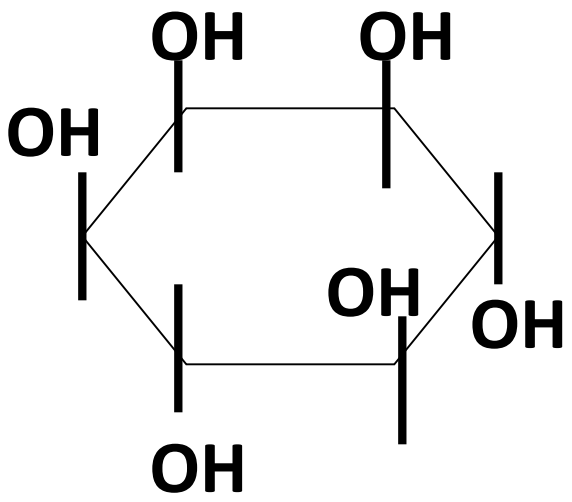
- Bilirubin, Steroids etc

- Constituent of glycosaminoglycans(GAG)

Derivatives of Monosaccharide

Sugar alcohols (Polyols)

- Inositol are derivatives of cyclohexane in which one of the H attached to each of the C is replaced by OH gp.



Myoinositol

Derivatives of Monosaccharide

- Inositol triphosphate acts as a second messenger.

Derivatives of Monosaccharide

DEOXY SUGARS

- Oxygen of the hydroxyl group may be removed to form deoxy sugars

- Will not show reducing properties
- Will not produce osazones

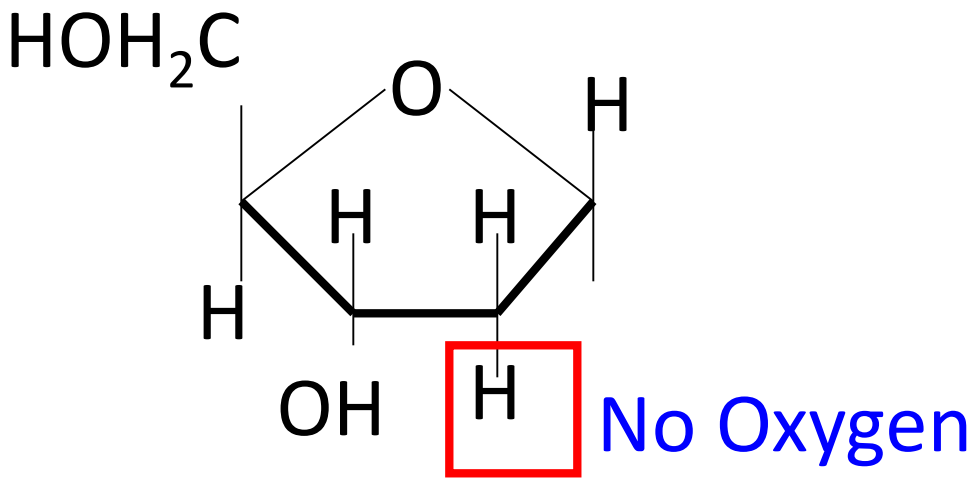
- **Eg: L-fucose,L-rhamnose**

- L-fucose-present in blood group antigens and many other glycoproteins

- Deoxyribose-important part of nucleic acid,seen in DNA

Derivatives of Monosaccharide

- Deoxy ribose (Constituent of DNA)



Derivatives of Monosaccharide

L Ascorbic Acid

- Vit C is a sugar acid
- Widely distributed in plants and animals
- Abundant in citrus fruits