Chemistry and Functions of Carbohydrates

SYNOPSIS

- Introduction
- Definition of Carbohydrates
- Classification of Carbohydrates
- Study of Biomedically Important Carbohydrates:
- Monosaccharides
- Disaccharides
- Polysaccharides
- Mucoproteins and Glycoproteins.
- Biomedical Importance of Carbohydrates.

Introduction

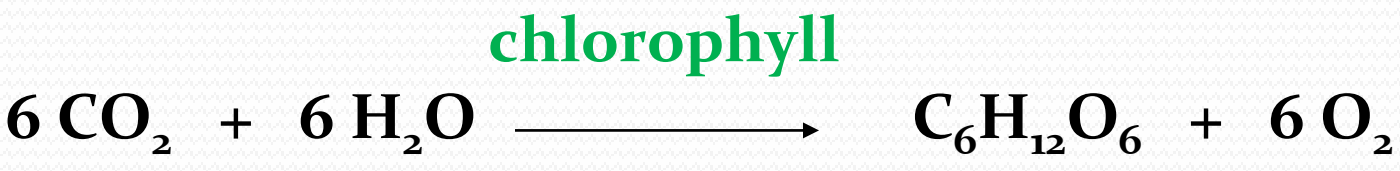
What are Carbohydrates?

- Carbohydrates are organic biomolecules abundantly present in the nature.
- Found in the cells of plants and animals.
- The term "**Carbohydrate**" was coined by "Karl Schmidt".

Carbohydrates Biosynthesis

- Carbohydrates are predominantly biosynthesized by plants through **photosynthesis**.
- Glucose is synthesized in plants from CO_2, H_2O, and solar energy from the sun.

Photosynthesis



- Animals and **Human beings cannot biosynthesize Carbohydrates** predominantly.

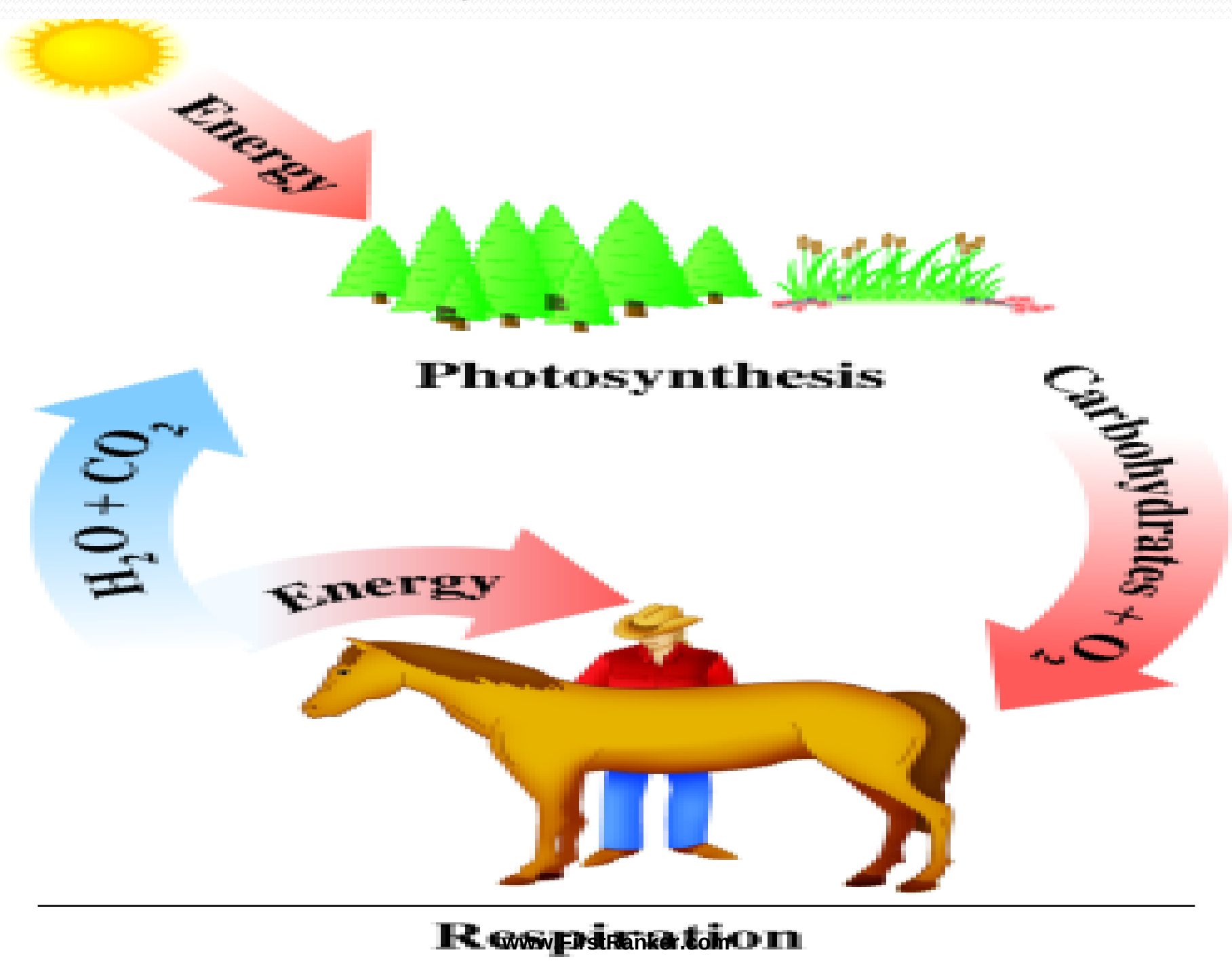
- To fulfill metabolic and structural role in human beings,
- **It is essential to ingest carbohydrates through food** substances of plant and animal origin.

- Thus Carbohydrates **are chief constituents** of **human food**.

- **R.D.A for Dietary Carbohydrates=**

400-600 gm/day.

- However in **a critical condition** when cells are deprived of Glucose
- Human body biosynthesizes Glucose using the **non carbohydrate precursors** present in body via **Gluconeogenesis**.



Functions of Carbohydrates

- Carbohydrates serve as **primary source of energy/Fuel of body (Metabolic role).**

- **Carbohydrate** (Glucose) is **oxidized** in living cells of human body to **produce CO_2, H_2O,** and **energy(ATP).**

- Carbohydrates provide **skeletal framework** to cells ,tissues, and organs of body.**(Structural role)**
- Carbohydrates are associated to **many other roles** with human beings.

DEFINITION OF CARBOHYDRATES

Old Definition of Carbohydrates

- Empirical formula/General formula for simple carbohydrates : $\mathbf{C_n(H_2O)_n}$
- Where ***n*** **= number of carbon atom** present in carbohydrate structure.
- **Old Definition-**

Carbohydrates are "**Hydrates of Carbon**"

- **Old definition is not valid since-**
- **Certain Carbohydrates** –

Rhamnose did not fit in the empirical formula of carbohydrates.

- **Certain non Carbohydrates** –

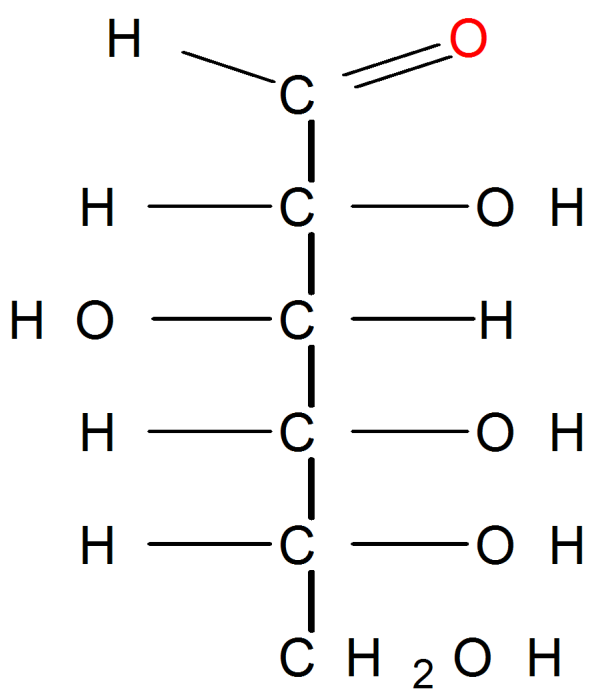
Lactate and Acetate fitted in the empirical formulae.

Observe the following chemical structures of simple Carbohydrates:

Glucose and Fructose

Aldose

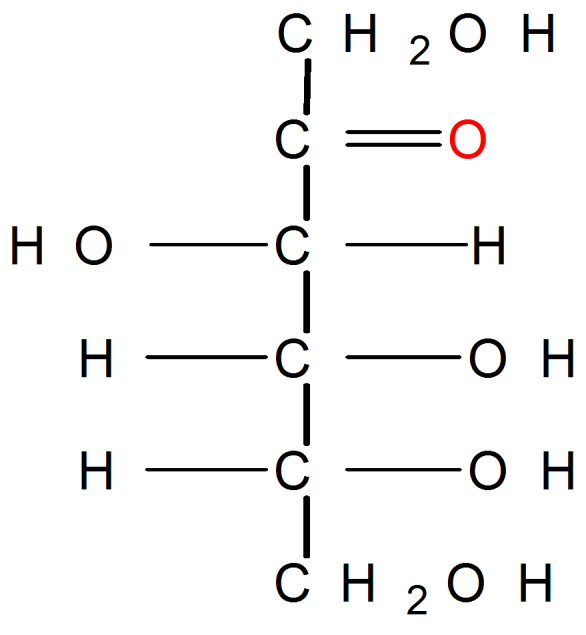
(e.g., Glucose) have an aldehyde group at one end.



D - g l u c o s e

Ketose

(e.g., Fructose) have a ketone group, usually at C2.



D - f r u c t o s e

- Simple Carbohydrates has **many Hydroxyl groups (Polyhydroxy).**
- Simple Carbohydrates has **carbonyl/ functional** groups as **Aldehyde or Ketone.**
- Simple Carbohydrates(Glucose/Fructose) repeatedly linked to form its **condensed complex** carbohydrates for ex **Starch, Inulin.**

- The hydroxyl groups may be free or substituted by any other groups.
- Simple Carbohydrates on chemical reactions produces **derivatives of Carbohydrates.**

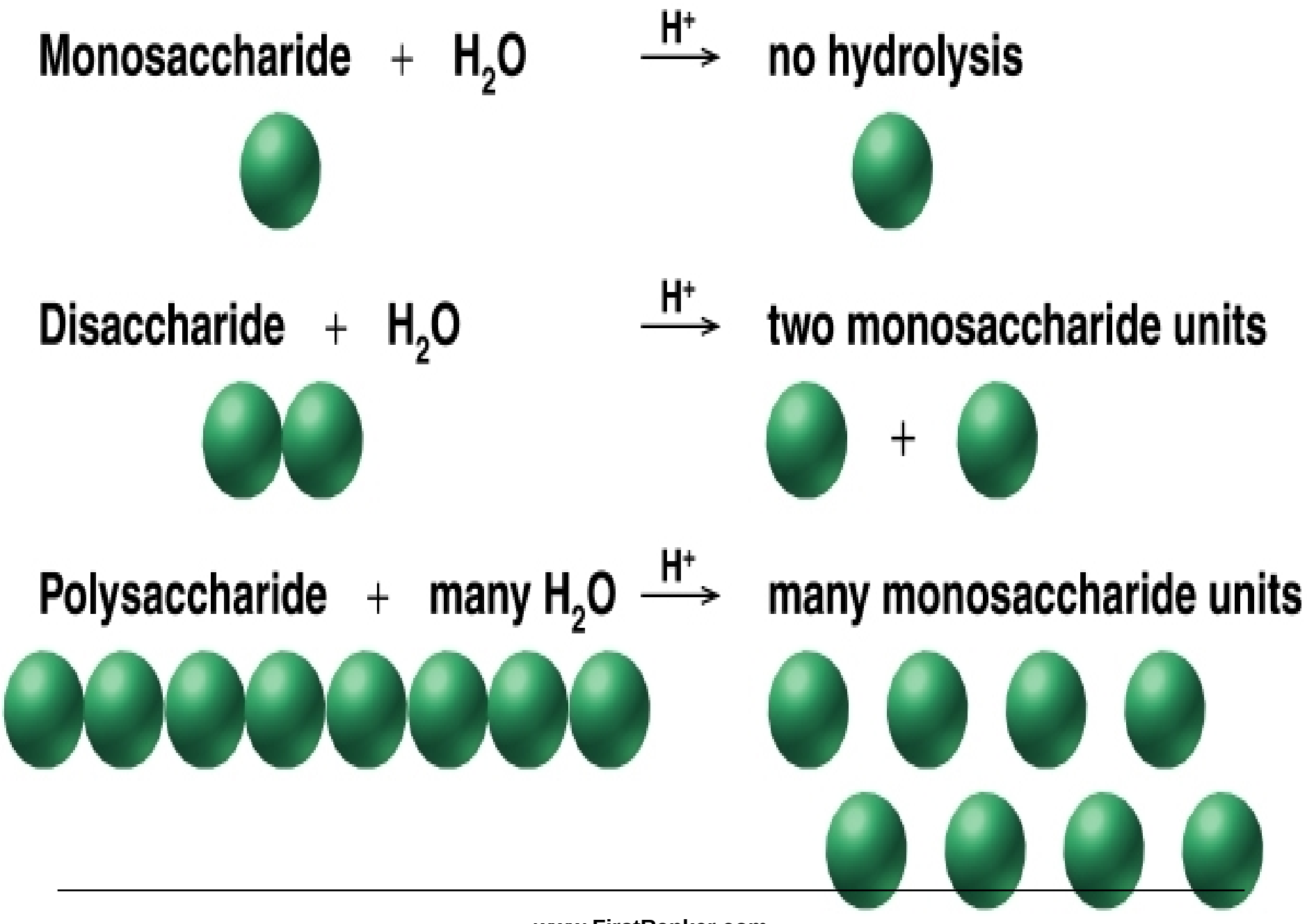
New Definition of Carbohydrates

Carbohydrates are organic biomolecules, abundantly present in the plant and animal bodies, chemically composed of **Polyhydroxy Aldehyde or Polyhydroxy Ketone**, their **condensed products or their derivatives.**

Classification Of Carbohydrates

- **Depending Upon Number of Saccharide Units**
  - **Four Main Classes of Carbohydrates**

- **Monosaccharides**
  (1 Saccharide Unit)
- **Disaccharides**
  (2 Saccharide Units)
- **Oligosaccharides**
  (3-10 Saccharide Units)
- **Polysaccharides**
  (More than 10 Saccharide Units)



Monosaccharides Sub Classification

- Monosaccharides are sub classified on the basis of:
  - Functional Group
  - Number of Carbon atoms.

Number of Carbon Atoms	Aldoses (Aldehyde-CHO)	Ketoses (Ketone -C=O)
3 Triose	Aldo Triose Glyceraldehyde	Keto Triose Di HydroxyAcetone
4 Tetrose	Aldo Tetrose Erythrose	Keto Tetrulose Erythrulose
5 Pentose	Aldo Pentose Ribose, Xylose, Arabinose	Keto Pentulose Ribulose, Xylulose
6 Hexose	Aldo Hexose Glucose, Galactose ,Mannose	Keto Hexose Fructose
7 Heptose	Aldo Heptose SedoHeptose	Keto Heptulose SedoHeptulose

Disaccharides

- Disaccharides has 2 Monosaccharide units linked by glycosidic bond.
- Disaccharides may be reducing or non reducing

Type Of Disaccharides

- **Reducing Disaccharides –**
  - **Lactose (Glu-Gal)**
  - **Maltose (Glu-Glu)**
- **Non reducing Disaccharides-**
  - **Sucrose(Glu-Fru)**

Oligosaccharides Sub Classification

- Oligosaccharides has 3-10 Monosaccharide units linked by glycosidic bonds.
- Oligosaccharides are sub classified on the basis of number of Saccharide units.

Number of Monosaccharide Units	**Type Of Oligosaccharides** (3-10 Monosaccharide Units)
3	**Trisaccharides** Maltotriose (Glu-Glu-Glu) Raffinose (Glu-Fru-Gal)
4	**Tetrasaccharides** Stachyose (Glu-Fru-2Gal)
5	**Pentasaccharides** Verbascose (Glu-Fru-3Gal)

Polysaccharide Sub Classification

- **Polysaccharides/ Glycans** contain **more than 10**, **same/ different Monosaccharide units** linked by **glycosidic linkages.**

Types of Polysaccharides

- **Homopolysaccharides/ Homoglycans-**
  Contains more than 10 same repeating units.
- **Heteropolysaccharides / Heteroglycans-**
  Contains more than 10, different repeating units.

POLYSACCHARIDES/ Glycans

(More than 10 Monosaccharide Units)

Homopolysaccharides/ Homoglycans

(> 10 Same Repeating Units)

Glucosans (Repeating Unit of Glucose/Polymer of Glucose)	Fructosans (Repeating Unit of Fructose/Polymer of Fructose)
Starch	
Glycogen	
Cellulose	Inulin
Dextrin	
Dextran	

Hetero Polysaccharides (More than 10 Different Repeating Units)

Animal Heteropolysacchrides

- **Mucopolysaccharides (MPS)**

OR

- **Glycosaminoglycans (GAGs)**

Types And Examples of Mucopolysaccharides

- **Acidic Non Sulfated MPS:**
  - Hyaluronic Acid
- **Acidic Sulfated MPS:**
  - Heparin
  - Heparan Sulfate
  - Chondritin Sulfate
  - Dermatan Sulfate
  - Keratan Sulfate
- **Neutral MPS:**
  - Blood Group Substances

Plant Heteropolysaccharides

- Agar
- Pectin
- Lignin
- Gum

What are Sugars?

- Sugars are chemically simple Carbohydrates Monosaccharides and Disaccharides.
- **Sugars** are Crystalline **Solid** substances.
- **Soluble** in water
- **Sweet** in taste
- Structure possess **asymmetric /chiral carbon atoms/stereogenic centers.**
- The carbonyl/ functional groups of Carbohydrates may be present as free or bound (involved in glycosidic bonds).

Types Of Sugars

- Reducing Sugars
- Non Reducing Sugars

Reducing Sugar

- Sugar structure **possessing free or potential(reactive)** aldehyde or ketone group is termed as **reducing sugar.**
- Reducing sugars **show reducing property** efficiently in alkaline medium and **reduces certain metallic ions** as- Cu^{++};Bi^{++};Fe^{+++}

- **Reducing Sugars** answer following **tests positive**
- Benedict's Test
- Fehling's test
- Nylander's Test
- Form Osazones.
- Reducing Shows Mutarotation (Change in Optical activity)

Examples Of Reducing Sugars

- All Monosaccharides are reducing sugars.
- Monosaccharides are strong reducing agents.
- Monosaccharides–
  - Ribose, Glucose, Galactose, Fructose.
- Disaccharides are weak reducing agents.
- Reducing Disaccharides-
  - Lactose, Maltose.

Non Reducing Sugars

- Sugar structure **not possessing free or potential aldehyde or ketone** group in its structure is termed as non reducing sugar.
- Non reducing sugar **does not show reducing property** and do not reduce metallic ions.

- **Non reducing sugars** give following **reducing tests negative.**
- Benedict's Test
- Fehling's test
- Nylander's Test
- Do not form Osazones
- Non Reducing sugars do not exhibit Mutarotation (Change in Optical activity)

Examples of Non reducing Sugars

- Non reducing Disaccharides.
  - **Sucrose** (Biomedically Important)
  - **Trehalose** (Glu-Glu linked with α (1-1) glycosidic bond)
- Polysaccharides/Complex Carbohydrates are Non reducing.

Sugar/Sugar Derivatives	Percent Sweetness
Glucose	75
Fructose (Sweetest Sugar)	175 (Highest)
Galactose	30
Sucrose	100
Lactose	20
Maltose	30
Xylitol	250

Non Carbohydrate Synthetic Sweetners	Percent Sweetness
Saccharin	45,000 times
Aspartame (Asp-Phe)	18,000 times
Thaumatin and Monellin	10,000 times
Cyclamate	1000 times

Biomedical Importance of Sugars

- Sugars are **sweetening agents** used in preparations of **fruit juices**, **sweet recipes** which gives delicious taste.

- Sugars have **dietary and calorific value**.
- Ingested sugars are digested ,absorbed and assimilated to **produce chemical form of energy –ATP**, which is further used for body activities.

Carbohydrates are Optically Active and Show Stereoisomerism

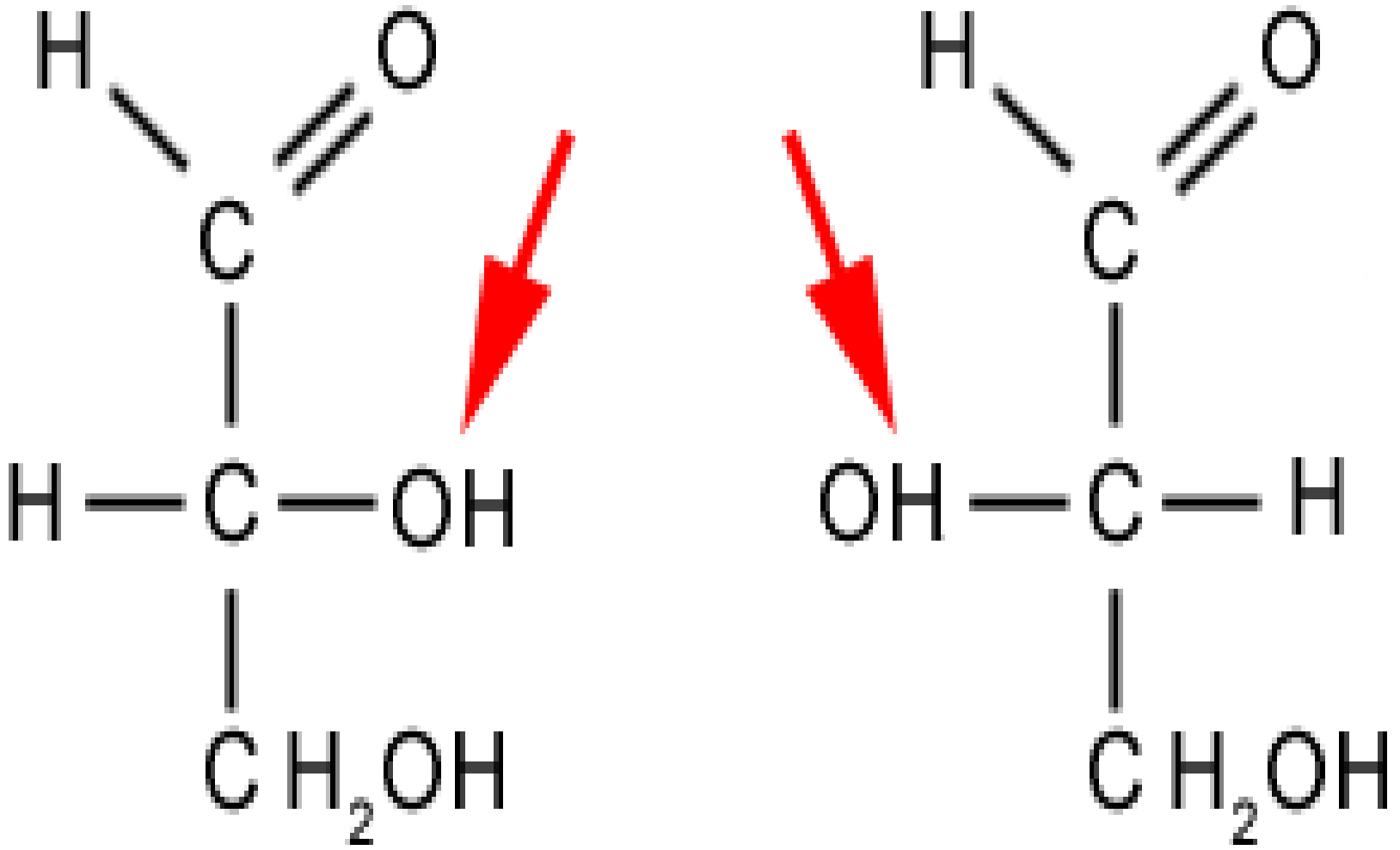
- All Carbohydrates except Di Hydroxy Acetone(DHA) possess asymmetric carbon atoms in their structure.
- Presence of Asymmetric carbon atoms confer two properties:
  - **Optical Activity**
  - **Stereoisomerism.**

Optical Activity

- Optically active solutions when placed in the tube of Polarimeter.
  - If moves the plane of polarized light toward right are **dextro rotatory (d/+).**
  - If moves the plane of polarized light toward left are **laevo rotatory (l/-).**

Stereoisomerism

- Stereoisomerism is due to presence of chiral carbon atoms/stereogenic centers.



D-Glyceraldehyde L-Glyceraldehyde

- **Stereoisomers** are type of isomers
- Which have **same chemical and molecular formula**,
- The **structure slightly differs** in **the spatial orientation of groups around the carbon atom.**

Biomedically Important Monosaccharides

- **Monosaccharides** (Simple Sugars)
- Monosaccharides are **simplest class** of Carbohydrates.
- They are composed of **one saccharide unit.**
- Monosaccharides **cannot** be further **hydrolyzed.**
- Monosaccharides are building blocks/monomeric units of higher forms of Carbohydrates.

Glyceraldehyde/Glycerose

Simplest Carbohydrate (Reference sugar)

- **Glyceraldehyde is a Monosaccharide**
- **Chemically** – **Aldo Triose**

$C_3H_6O_3$

- **Occurrence/Sources of Glyceraldehyde**

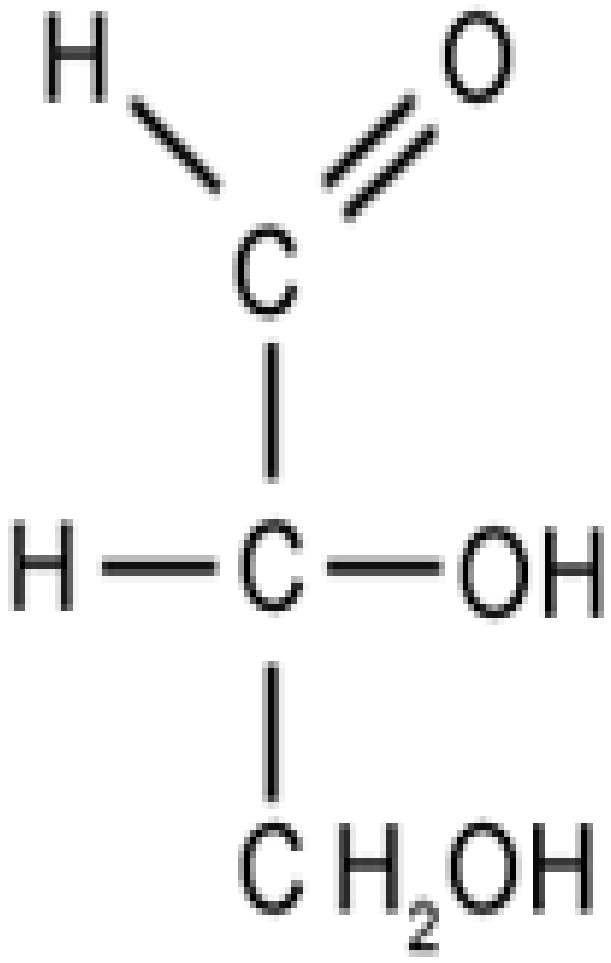
- In Cytoplasm of cells

Biomedical Importance's

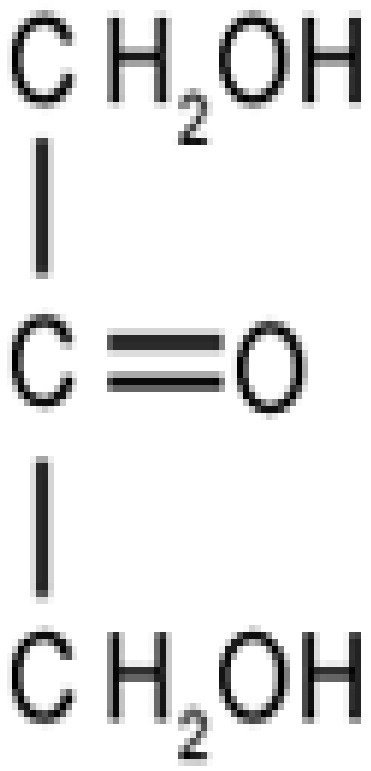
- Glyceraldehyde -3-Phosphate is an **intermediate of Glycolysis and HMP shunt.**
- Glyceraldehyde is **reduced to Glycerol** which is used during **Lipid and Glucose biosynthesis.**

DihydroxyAcetone

- **It is a Monosaccharide**
- **DHA is a Functional Isomer of Glyceraldehyde.**



D-Glyceraldehyde



Dihydroxyacetone

Chemistry Of DHA

- Dihydroxy Acetone is a Keto Triose.
- $C_3H_6O_3$
- DHA has no chiral atom in its structure.

Occurrence/Sources Of DHA

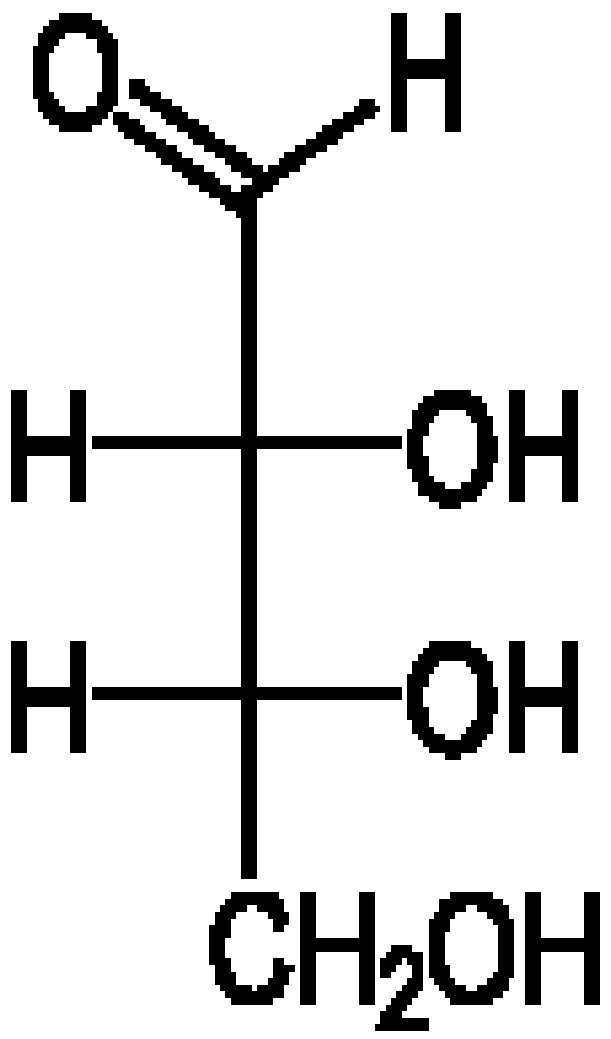
- In Cytoplasm of Cells

Biomedical Importance's Of DHA

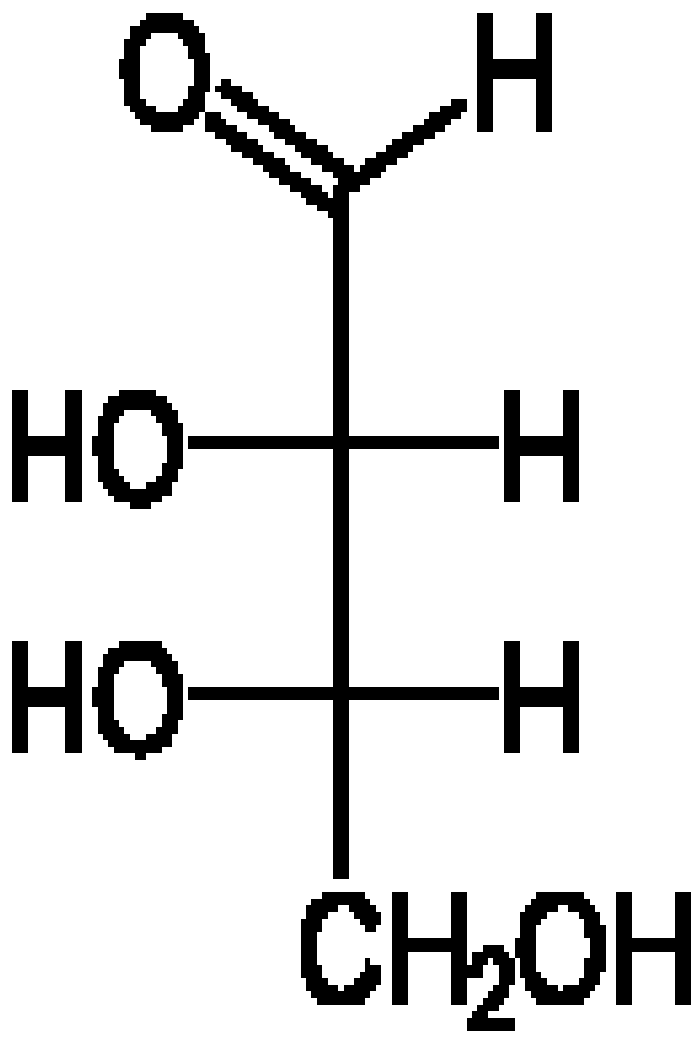
- Dihydroxy Acetone Phosphate(DHAP) is an **intermediate of Glycolysis.**
- DHAP is readily **interconvertable to Glyceraldehyde -3-PO4.**

Erythrose

- **Chemistry :**
- **Erythrose is a Monosaccharide**
- Erythrose is an Aldo Tetrose
- C4(H2O)4



D-Erythrose



L-Erythrose

- **Occurrence/Sources :**
- In Cytosol of cells
- **Biomedical Importances :**
- Erythrose -4-Phosphate is an intermediate of HMP shunt.

Ribose

- **Chemistry :**
- **Ribose is a Monosaccharide.**
- Ribose is an **Aldo Pentose**
- **$C_5(H_2O)_5$**

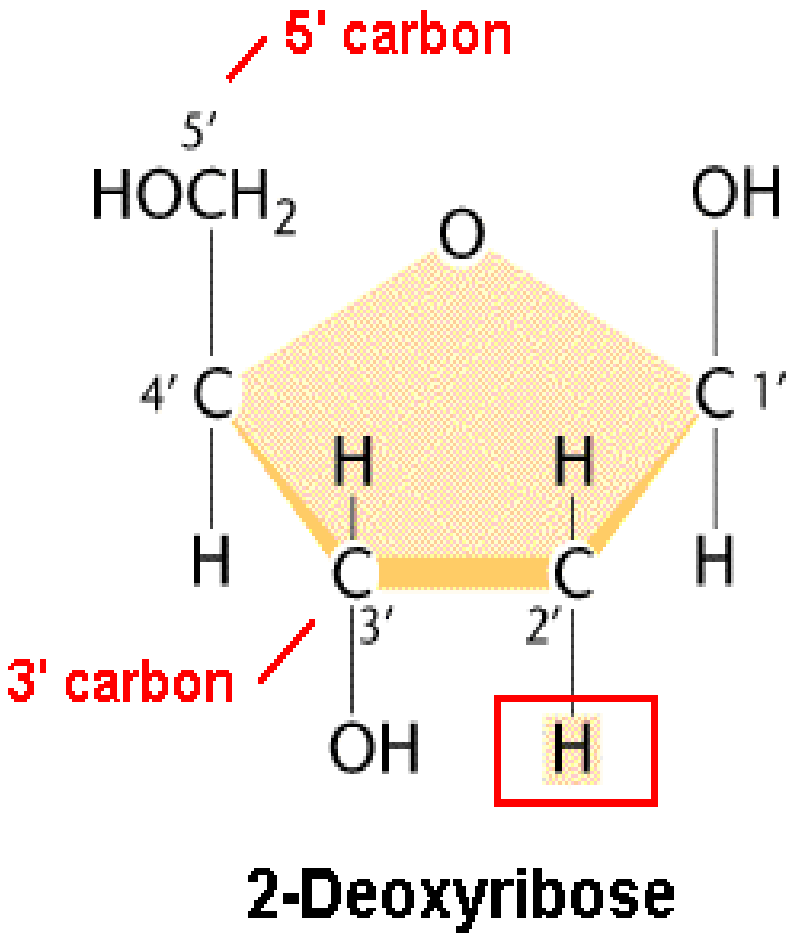
- **Occurrence/Sources :**
- In cells
- **Biomedical Importances of Ribose :**
- Ribose is an important component of **Ribonucleotides** which **forms RNA.**
- Ribose is component of certain **Nucleotide Coenzymes-**
- **ATP, NAD^+, $NADP^+$,FAD**

Deoxyribose

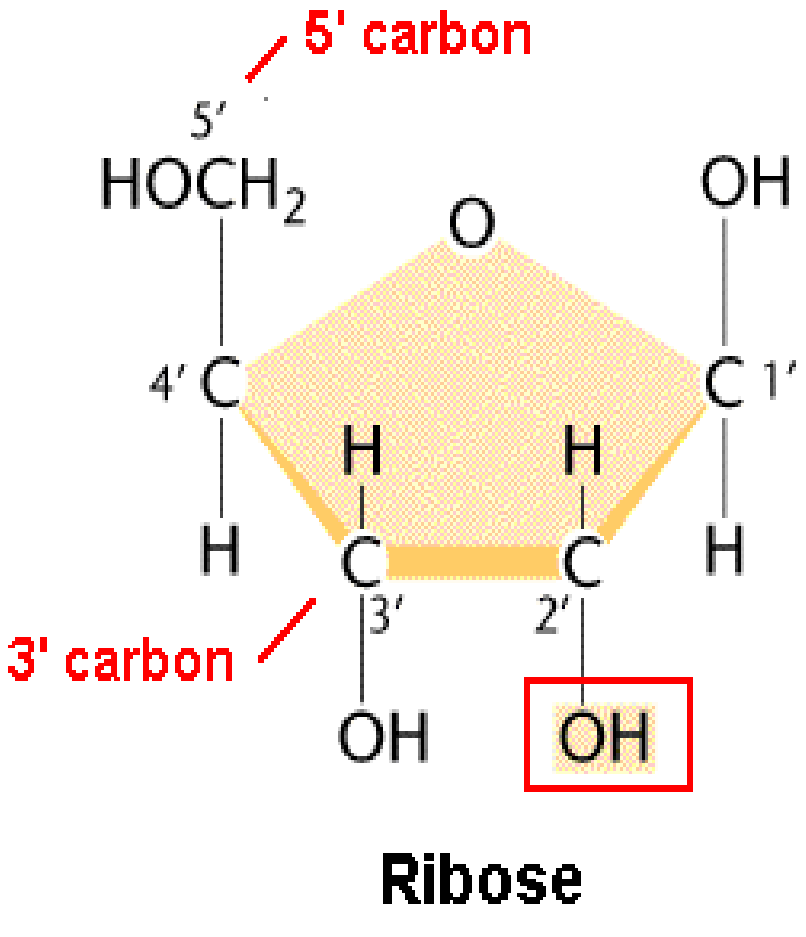
- **Deoxyribose is a Monosaccharide**
- Derived from Ribose/ **Derivative of Ribose**

- **Chemistry :**

- Deoxyribose is a **Aldo Pentose**
- Deoxyribose has one Oxygen atom less than Ribose at C2.
- Deoxyribose has **no –OH** group at **C2**
- Instead has –H at C2.



2-Deoxyribose



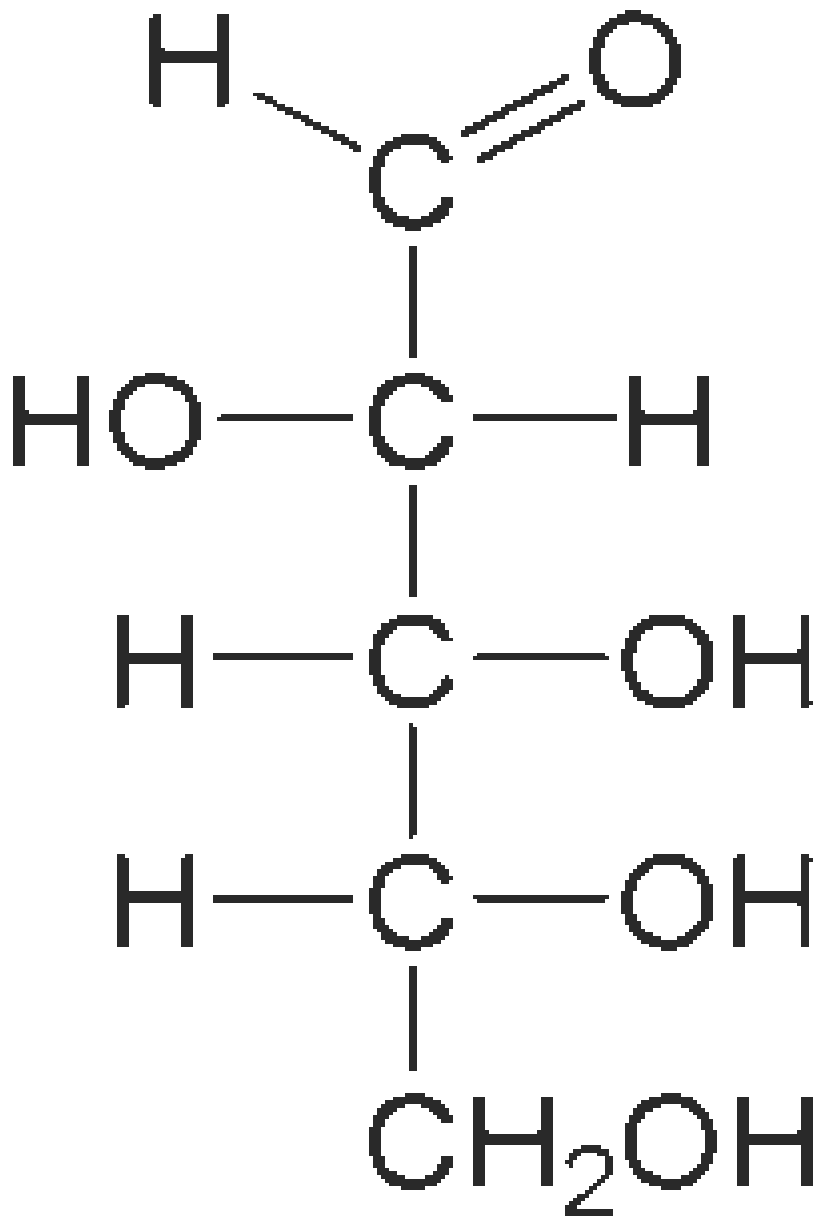
Ribose

(Klug & Cummings 1997)

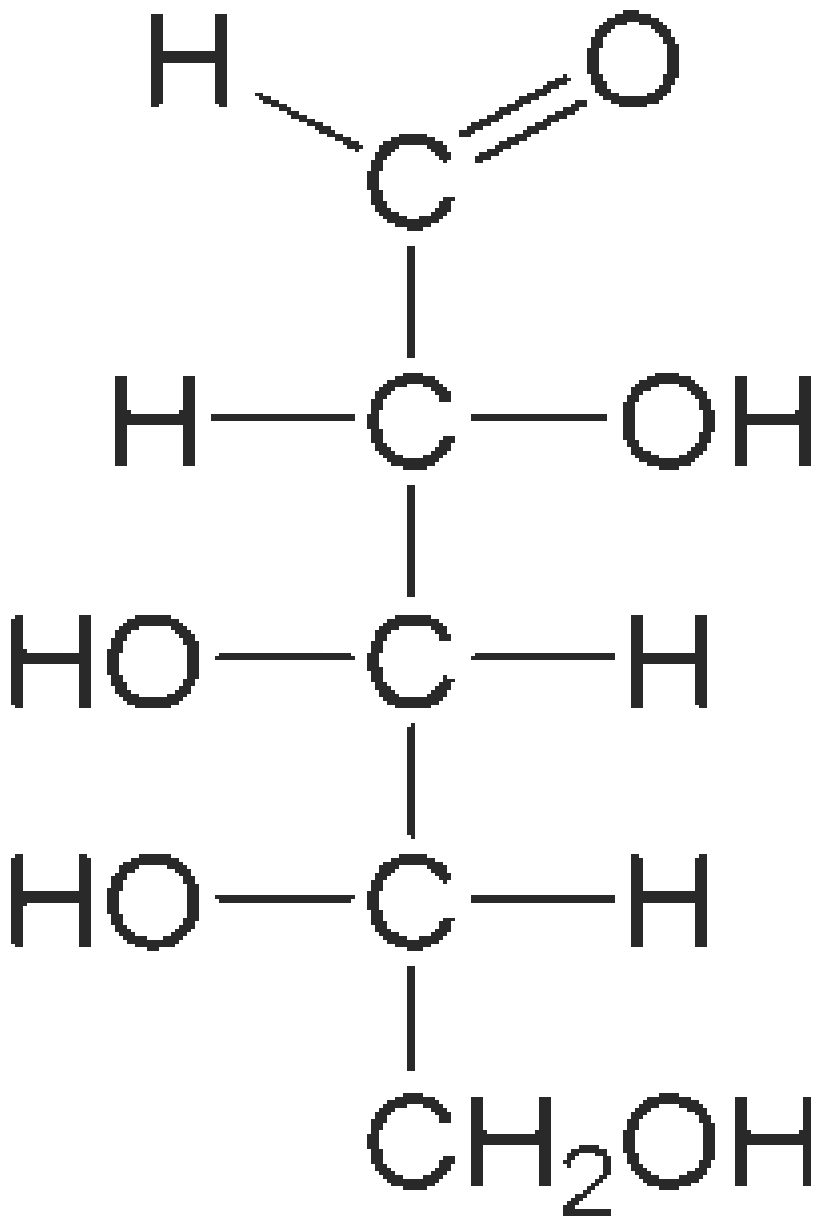
- **Occurrence/Sources :**
- In cells
- **Biomedical Importances Of Deoxyribose :**
- Deoxyribose is a component of Deoxyribonucleotides which forms DNA.

Arabinose

- **Arabinose** is a **Monosaccharide**
- **Chemistry :**
- Arabinose is a Aldo Pentose
- $C_5(H_2O)_5$



D-(-)-Arabinose



L-(+)-Arabinose

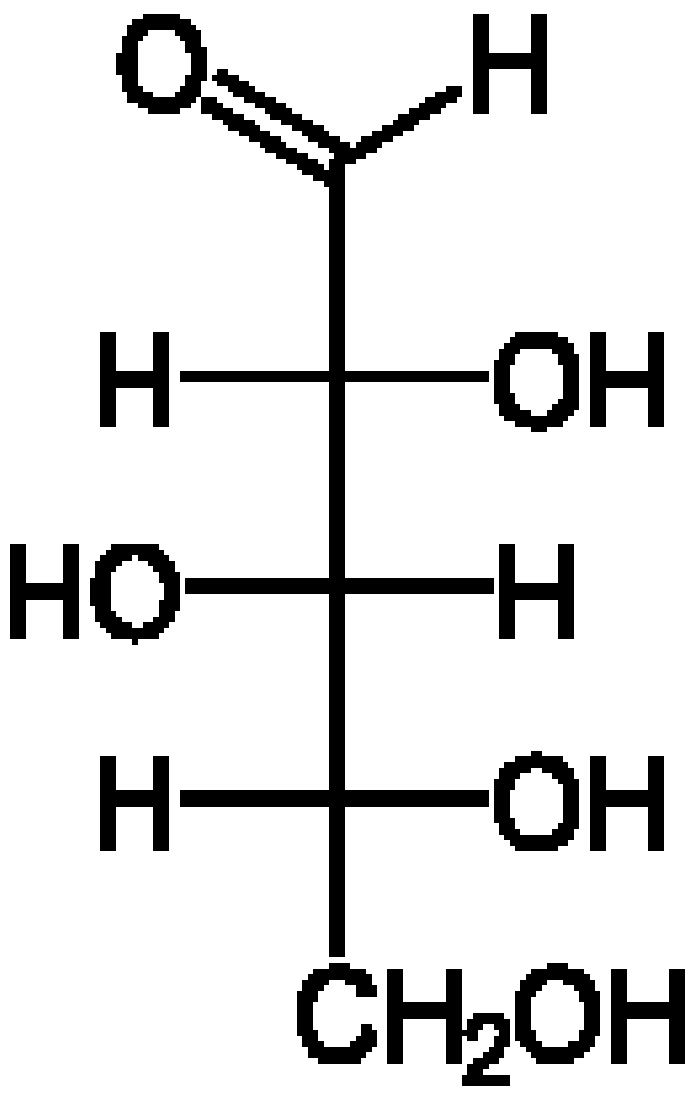
- **Occurrence/Sources:**
- Gum Arabic and Cherries.
- **Biomedical Importances**
- Arabinose is a component of Glycoproteins.

Xylose

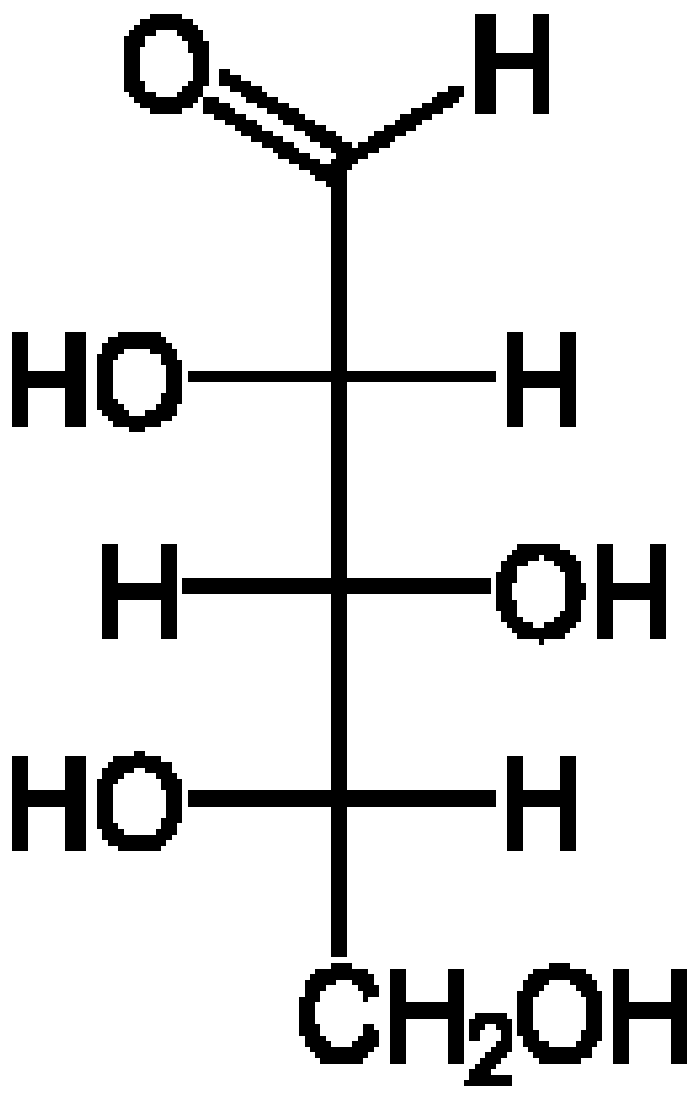
- **Xylose is a Monosaccharide**

- **Chemistry :**
- Xylose is an Aldo Pentose

- $C_5(H_2O)_5$



D-Xylose



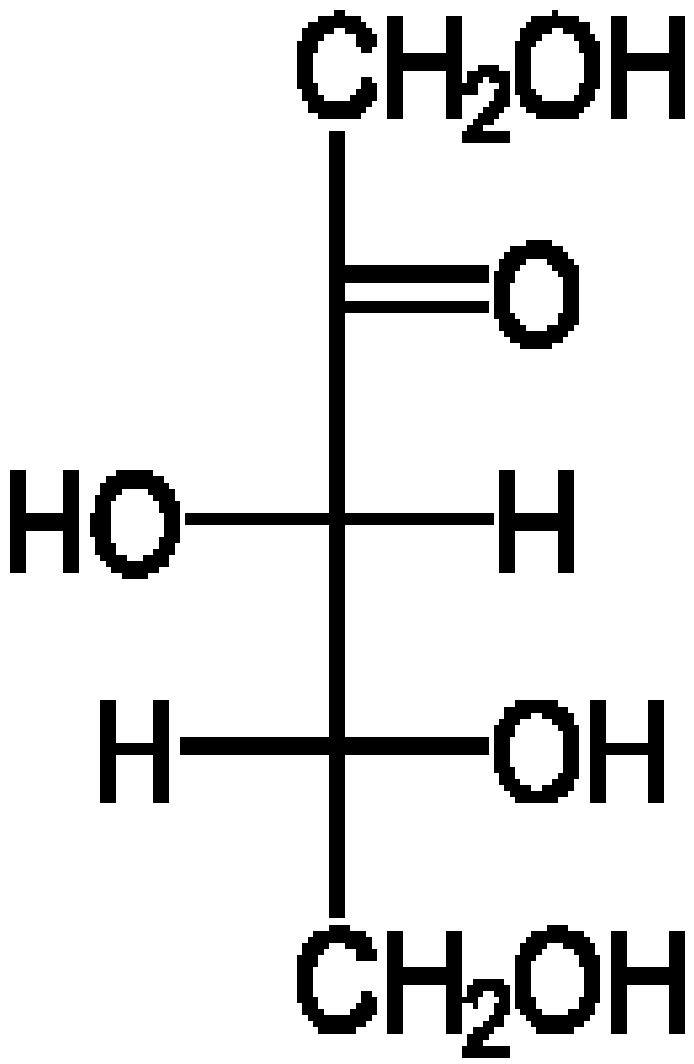
L-Xylose

- **Occurrence/ Sources :**
- Wood Gum
- **Biomedical Importances :**
- Xylose is a component of Glycoproteins and Proteoglycans

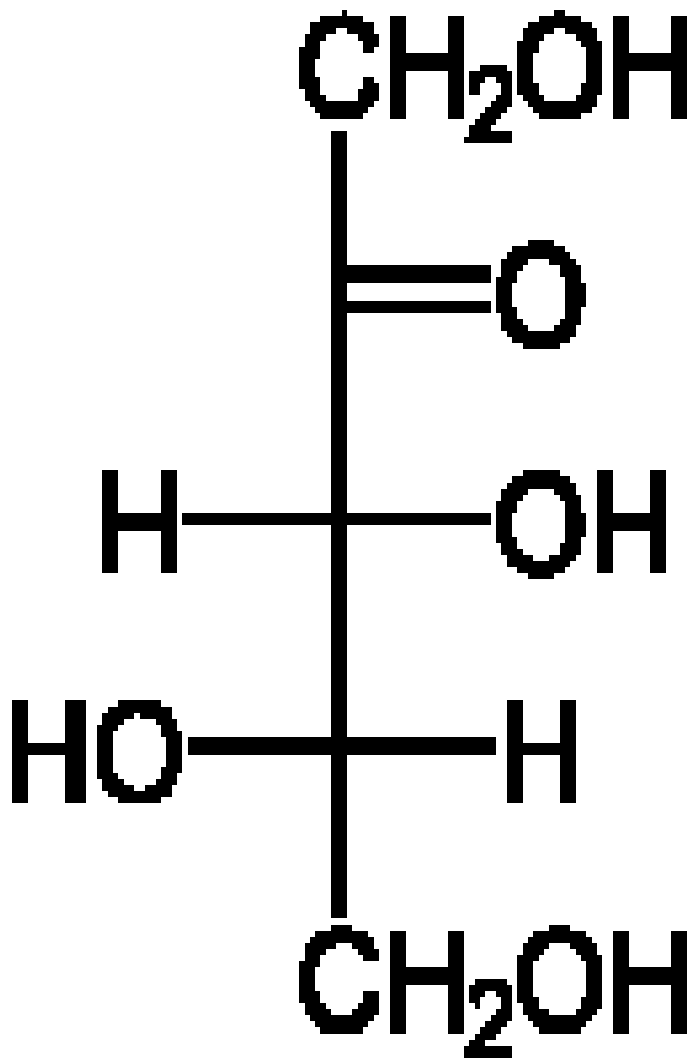
Xylulose

- **Xylulose is a Monosaccharide**
- **Chemistry :**
- Xylulose is a Keto Pentose

- $C_5(H_2O)_5$



D-Xylulose



L-Xylulose

- **Occurrence/ Sources :**
- In Cells
- **Biomedical Importances of Xylulose:**
- Xylulose -5-Phosphate is an intermediate of HMP Shunt.
- Xylitol reduced compound of Xylulose is used as sweetener (250% Sweetness).

Ribulose

- **Chemistry:**

- **Ribulose is a Monosaccharide**
- Ribulose is a Keto Pentose
- $C_5(H_2O)_5$

- **Occurrence/ Sources :**
- In Cytosol of cells.
- **Biomedical Importances of Ribulose:**
- Ribulose-5-Phosphate occurs as an intermediate of HMP Shunt.

Glucose

- Grape sugar
- Chief blood sugar
- Main sugar of body cells.
- Also termed as Dextrose

Chemistry of Glucose

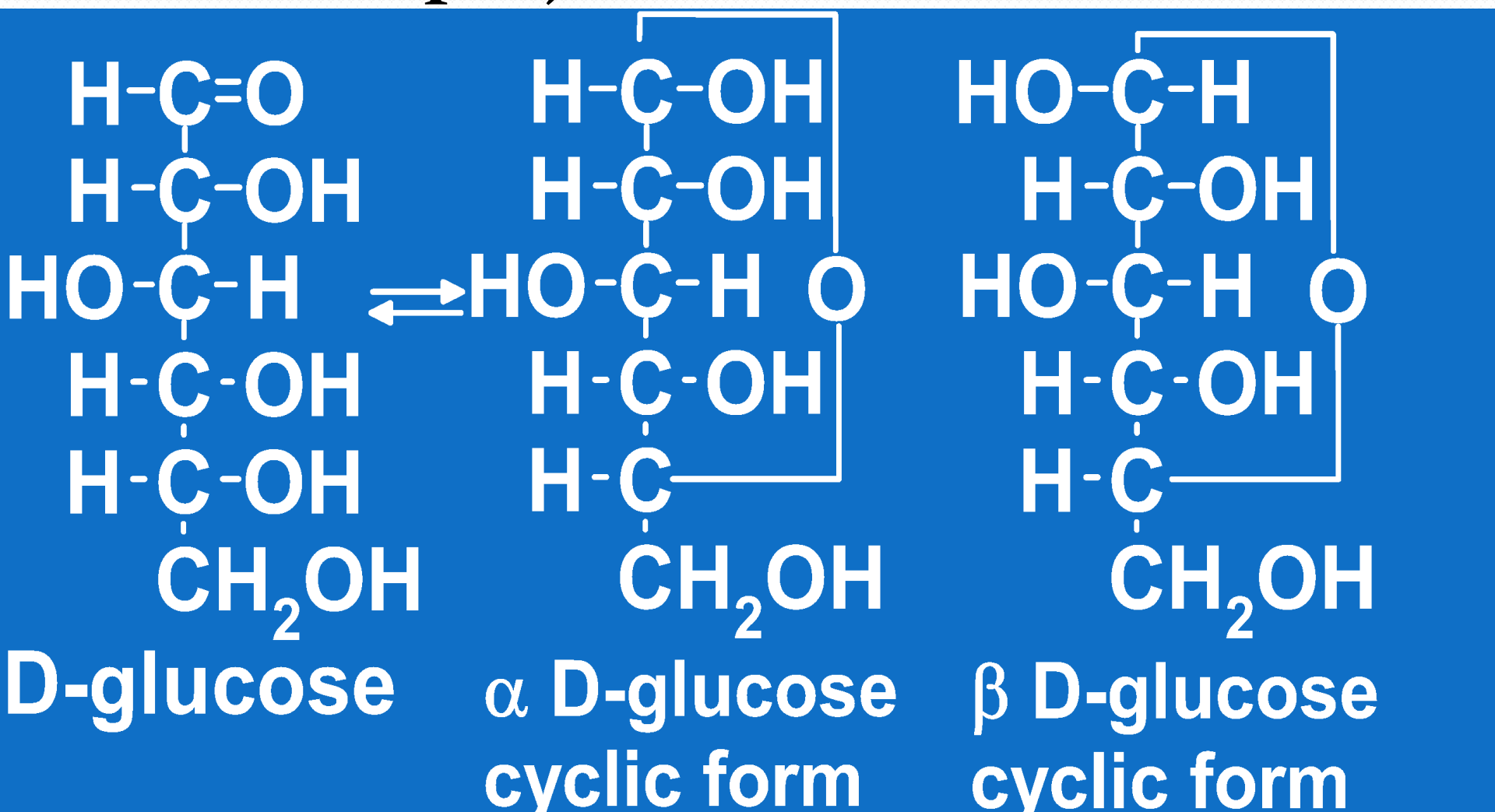
- Glucose Chemically – **Aldo Hexose.**
- Molecular Formula- $C_6H_{12}O_6$

- **C_1 is an Anomeric carbon** of Glucose.
- C1 has carbonyl/Functional group.

Structures Of Glucose

Cyclic forms for sugars

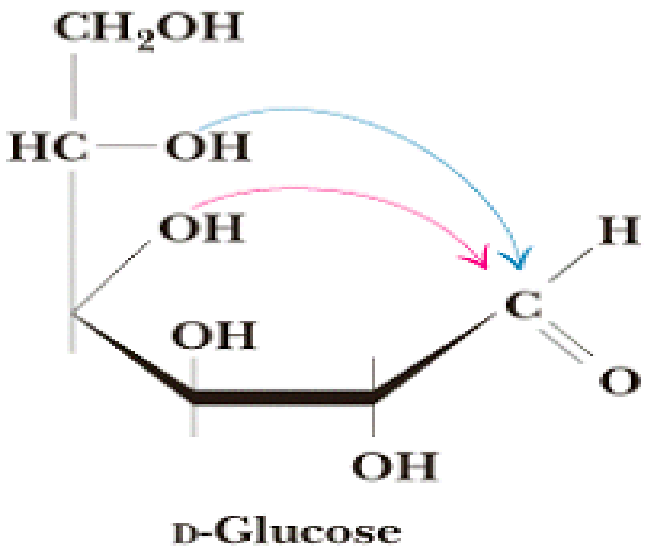
- **Fischer projections for α D Glucose**



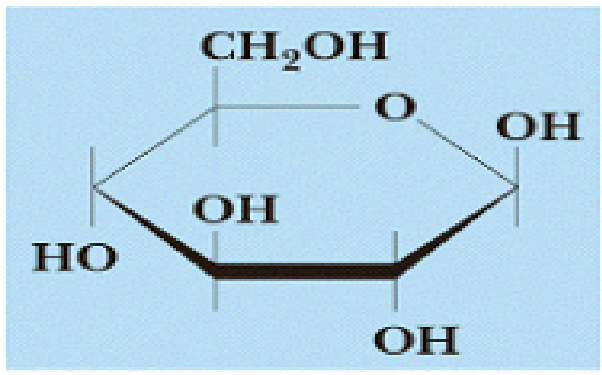
Fischer's and Haworth's Projection

- **Fischer's Projection**
- Cyclization of Glucose to hemiacetal is spontaneous to form stable ring structures.
- **Haworth's Projection**
- **Gluco Furanose** -5 membered ring with Oxygen atom in it.
- **Gluco Pyranose** -6 membered ring with Oxygen atom in it.

Monosaccharides can cyclize to form Pyranose / Furanose forms

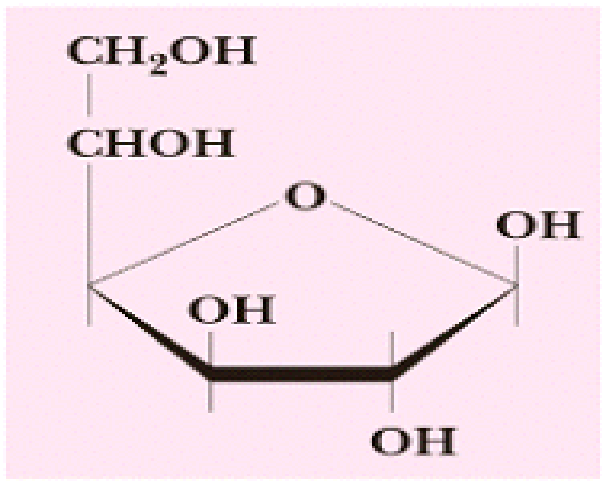


D-Glucose

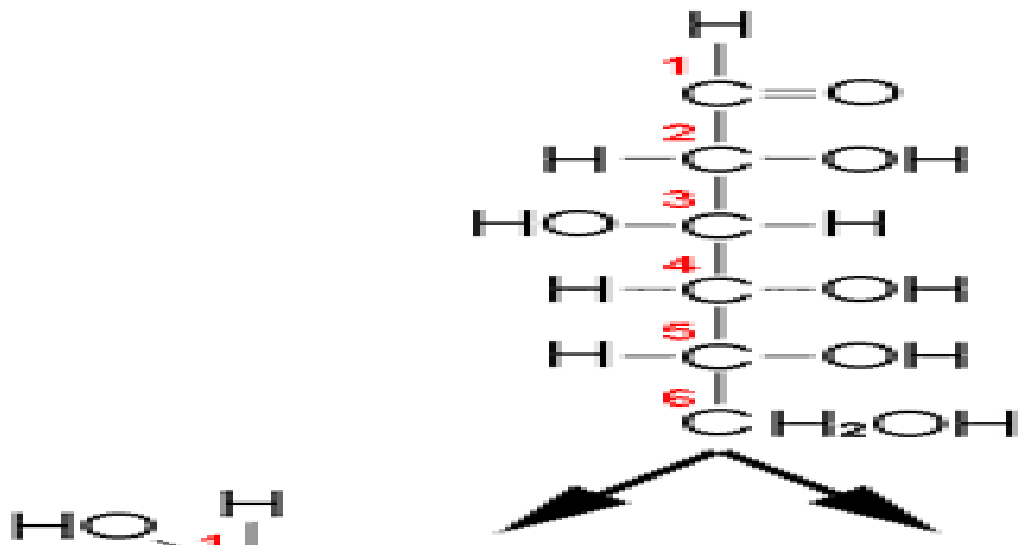


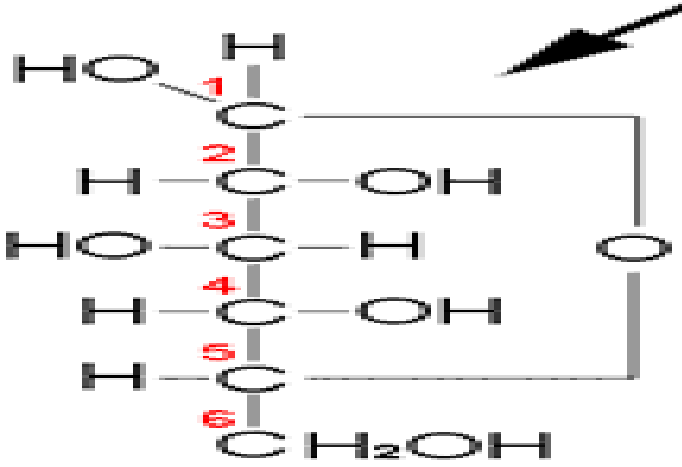
Pyranose form

β =64%
α = 36%

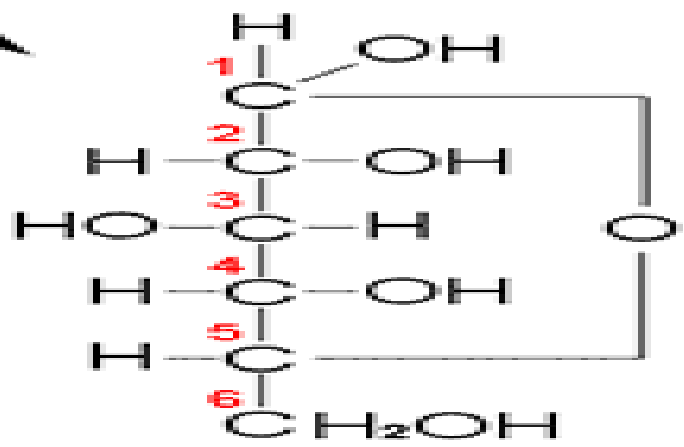


Furanose form

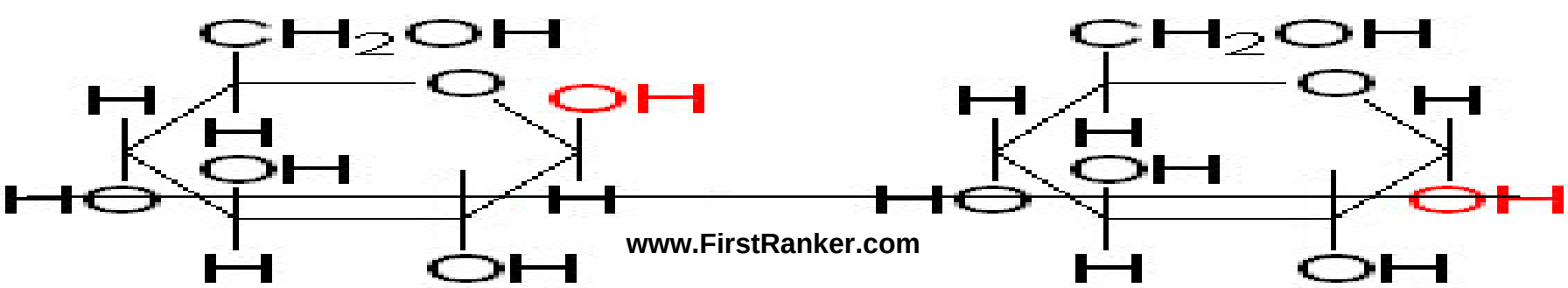




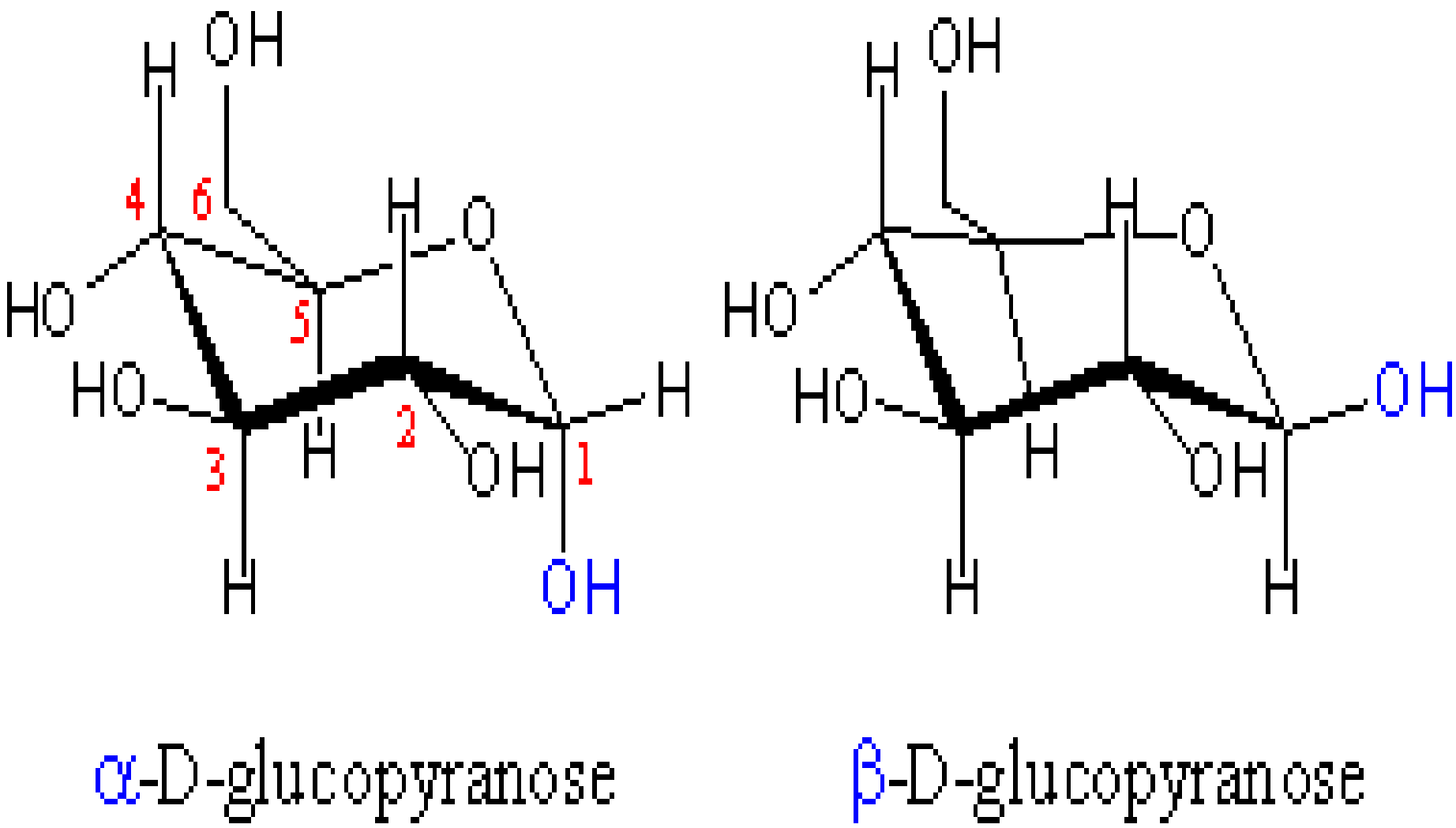
β-D-glucose



α-D-glucose



Chair Conformation Of Glucose



- Blood Glucose is more thermodynamically stable in

  β D Glucopyranose form.

Occurrence/Sources of Glucose

- Glucose is found in free or bound state in nature.
- Glucose is a **component** of Disaccharides and Polysaccharides.
- Glucose **found**-In fruits, human blood and body cells.

Physical properties of Glucose

- Glucose possess asymmetric/chiral carbon atoms in its structure, this confers 2 physical properties:
  - **Optical Activity**
  - **Stereoisomerism**

Optical Activity of Glucose

- Optical activity for an aqueous solution of **Glucose is dextrorotatory(+/d)**
- It rotates the plane of plain polarized light in Polarimeter towards right.
- **Hence Glucose** is also **termed as Dextrose.**

- **Specific rotation of Glucose optical activity:**
  - **Pure α-D Glucose** = specific rotation +112.2 º
  - **Pure β-D Glucose** = specific rotation +18.7 º

Isomers of Glucose

- **Cyclic structure** of Glucose **posses 5 asymmetric carbon atoms**.
- The number of isomers is 2^n, where n is the number of asymmetric centers.

- According to Vant Hoff rule 2^5
- Glucose posses 32 possible Isomers.

Functional / Structural Isomers of Glucose

- **Glucose** (Aldo Hexose) and **Fructose** (Keto Hexose) .
- These are Functional Isomers their structure differs only at functional groups.

Stereoisomer's Of Glucose

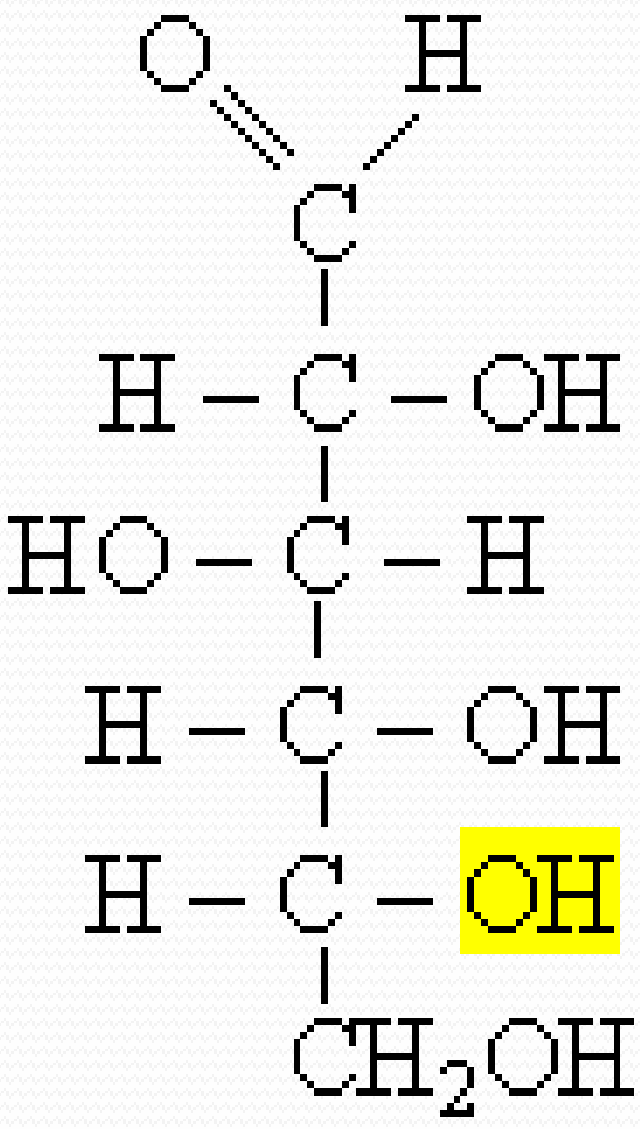
- Stereoisomers are type of isomers which have same molecular formula; structure differs only in the orientation of groups in space.

Glucose Stereoisomers

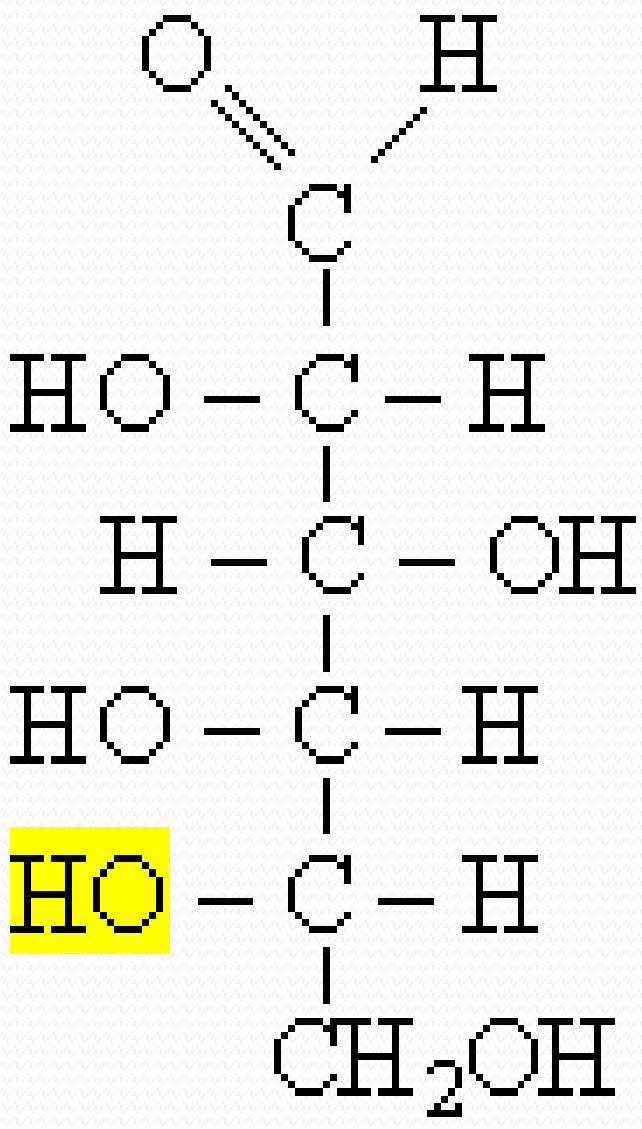
- **D and L Glucose**
- **Anomers**
- **Epimers**

D and L Glucose

- **Enantiomers/ Mirror images of each other/Left and Right Hand**
- **Non superimposible/Non overlapping.**



D-glucose



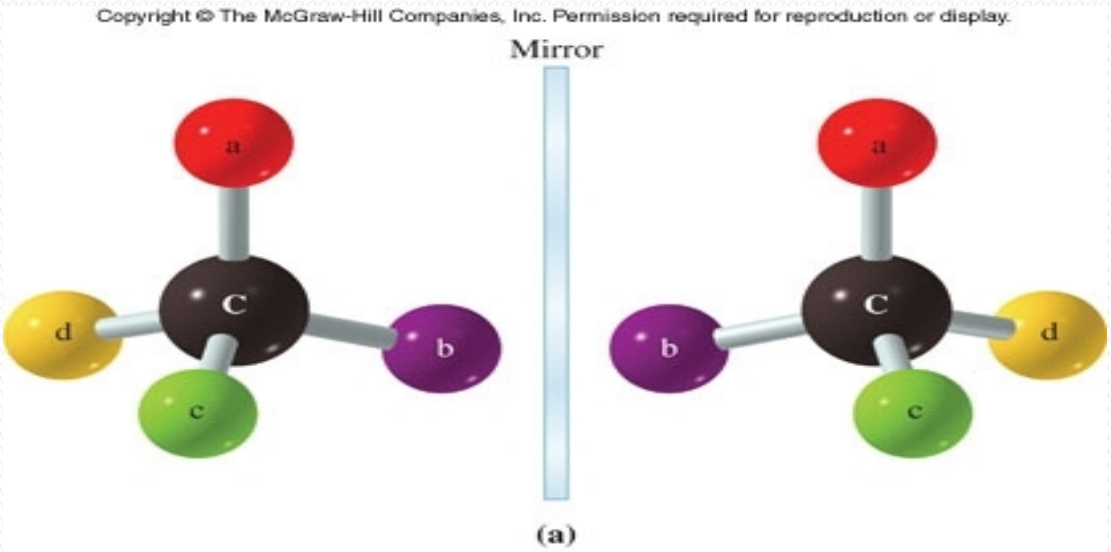
L-glucose

- **To identify D and L Glucose**

- Look at the penultimate carbon atom of Glucose (C5) /Farthest assymetric carbon atom from carbonyl carbon atom.

- In D Glucose -OH is at R.H.S.
- In L Glucose -OH is at L.H.S.

Enantiomers



Nonsuperimposable mirror images: enantiomers

- Physical and chemical properties of Enantiomers are same, except optical rotation.

- **Sugars** present in **human body** are of **'D' series.**

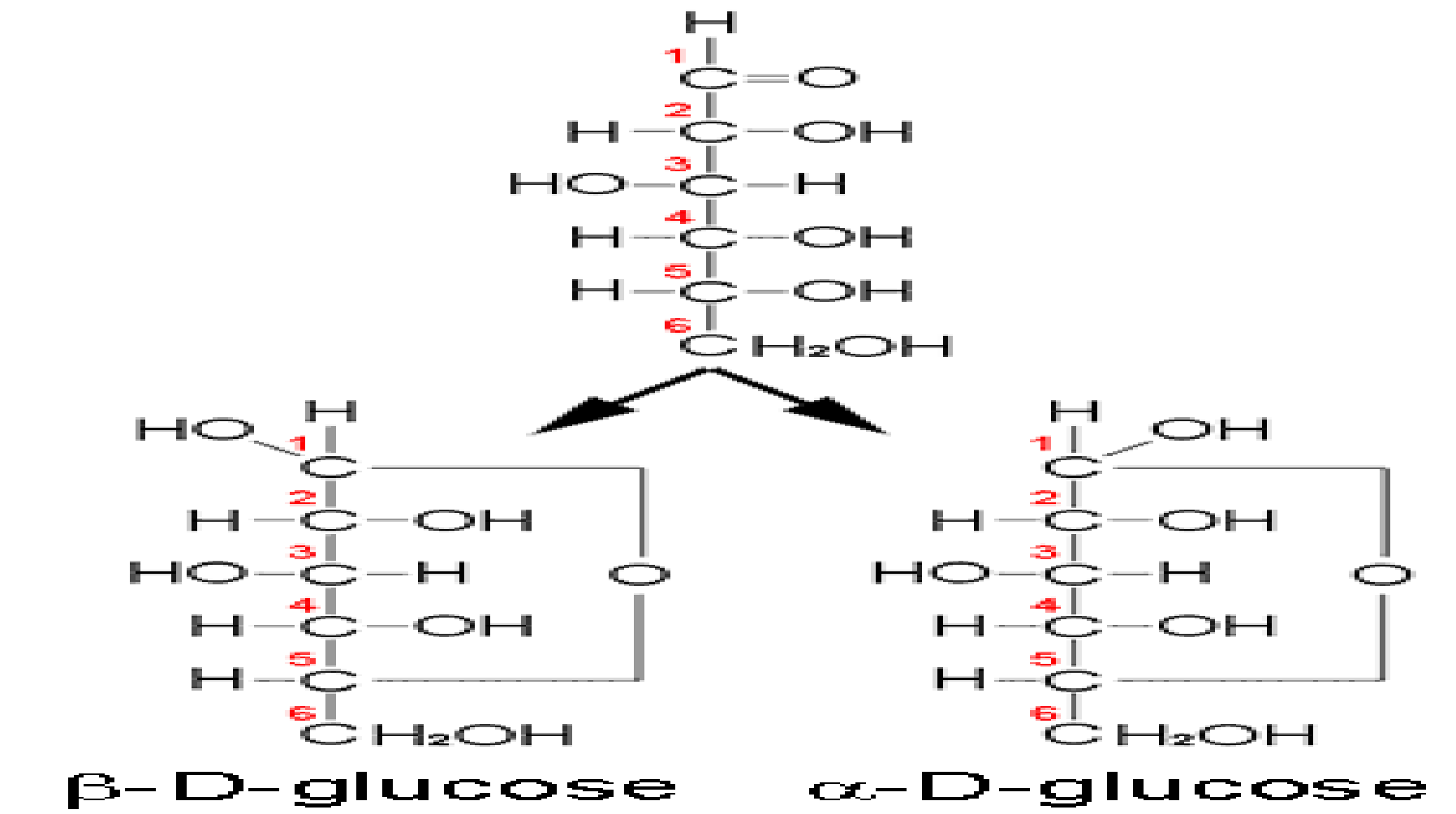
- Enzyme Racemase interconvert **'D'** and **'L'** isomers.

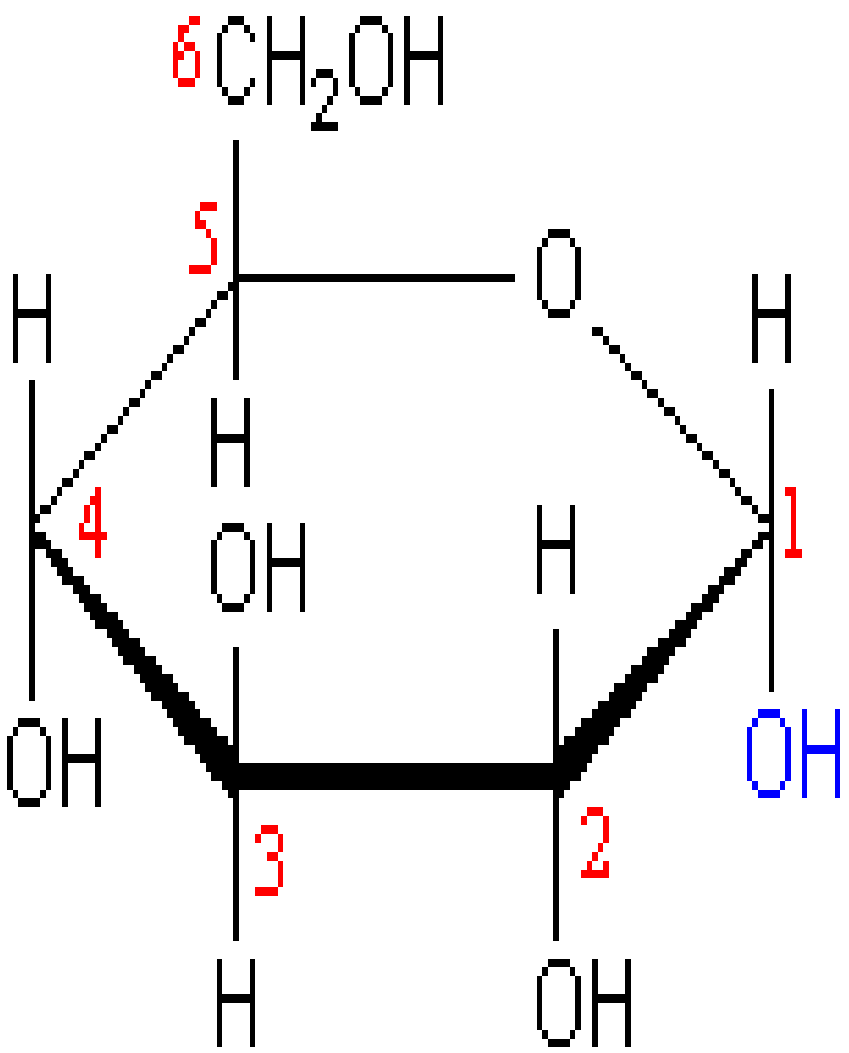
Anomers

- α-Glucose and β-Glucose.
- Anomers has group variations at C1 Anomeric carbon atom of Glucose .

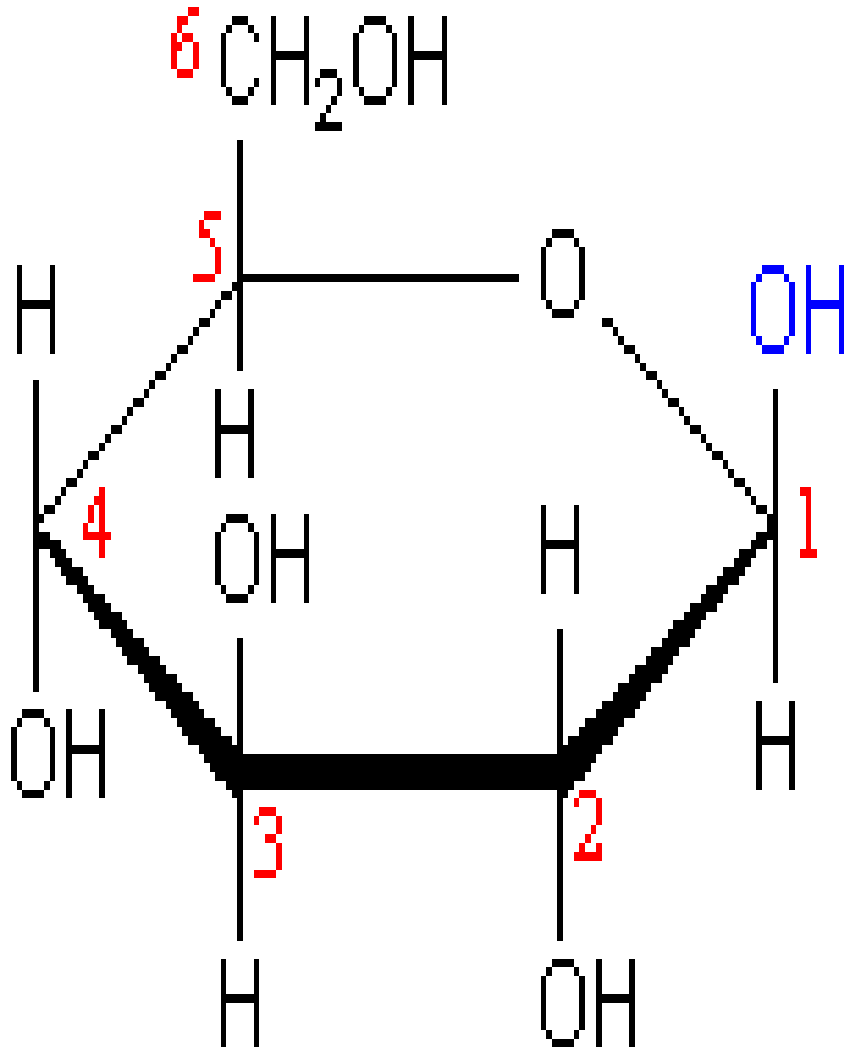
- In Fischer's projection at C1 α-Glucose has -OH group at R.H.S
- In Fischer's projection at C1 β-Glucose has –OH group at L.H.S.

- Glucose anomers of Haworth's projection shows as follows.
- **α-Glucose** has -OH group **below the plane.**
- β-Glucose has OH group **above the plane.**





α-D-glucose



β-D-glucose

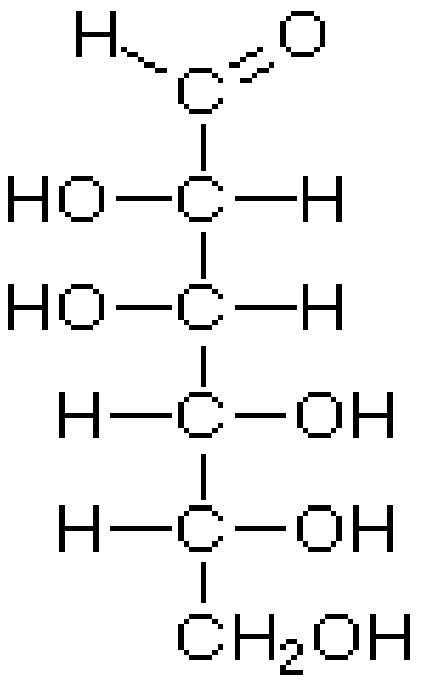
- In the body physiologically the most **thermodynamically stable form** of Glucose is **β D Glucopyranose** .

Anomerism

- Glucose anomers are not stable and tend to interconvert constantly by opening and reclosure of ring.
- Anomerism is interconversion of one form of anomer to another.
- Anomerism exhibit Mutarotaion.

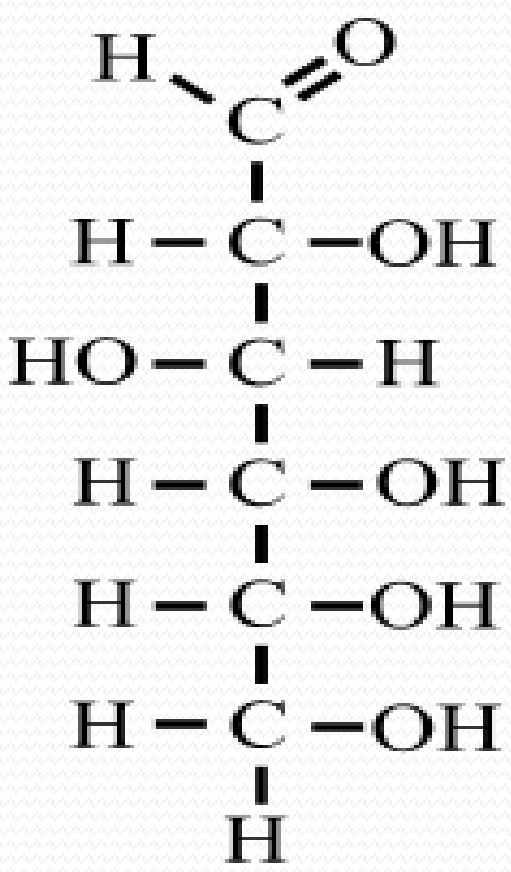
Epimers

- Epimers **are stereoisomers** which has variation in the orientation of groups at **C 2/ C3 / C4** of **Glucose**.
- **Epimers of Glucose**
  - Galactose (C4 Epimer)
  - Mannose (C2 Epimer)

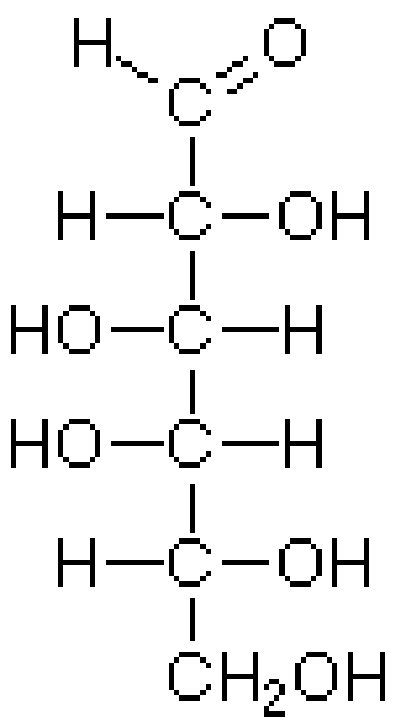


Mannose

(C2 Epimer)



glucose



Galactose

(C4 Epimer)

- When Mannose and Galactose structures are compared there is variation at two different carbon atoms (C2 and C4).
- **Mannose and Galactose** are not Epimers but they are "**Diastereoisomers**".

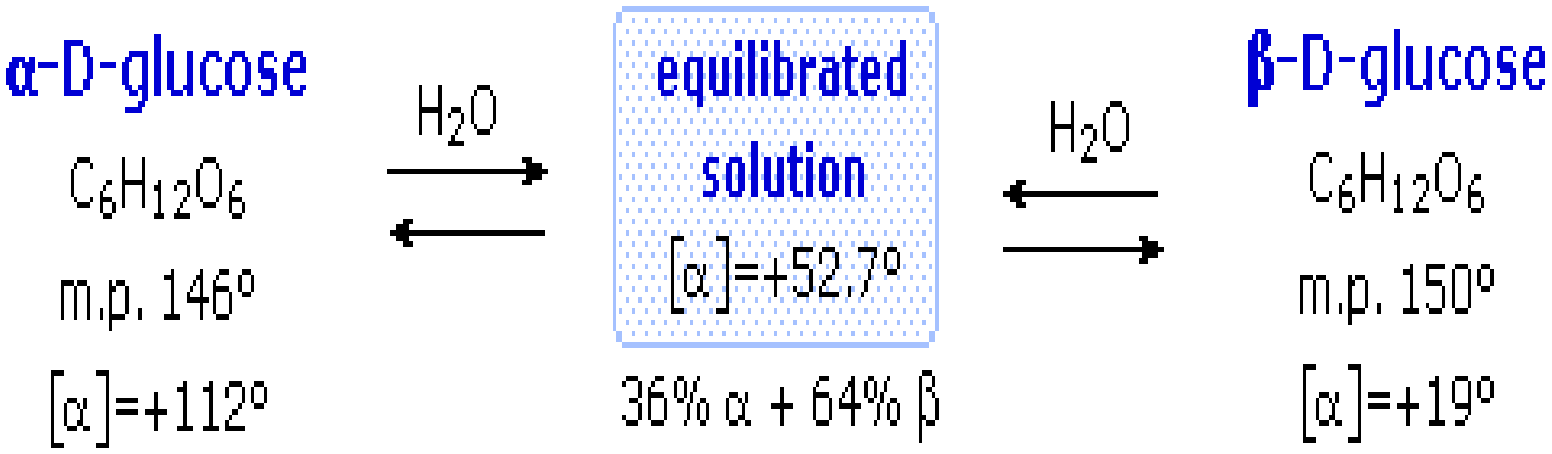
Mutarotation

- Mutarotation is change in specific rotation of an optically active substance.

- **Criteria for an optically active substance to exhibit Mutarotaion:**
- **Anomerism:**
- In aqueous solution the optically active substance should exist in two or more stereoisomeric forms by ready interconversions.

Glucose Exhibits Mutarotation

- Glucose in aqueous solution shows '**Anomerism**'.
- **Glucose** in aqueous solution readily **interconvert from α Glucose to β Glucose** and attain an equilibrium mixture to exhibit mutarotation.



- **Mutarotation** is a physico chemical property
- Shown by certain optically active substances ,who in aqueous solution **has capacity to interconvert from one stereoisomeric form to other and attain a constant equilibrium mixture**,
- This **changes an initial specific rotation to a constant specific rotation with the passage of time.**

Chemical Properties
OR
Chemical Reactions
OR
Derivatives Of Glucose

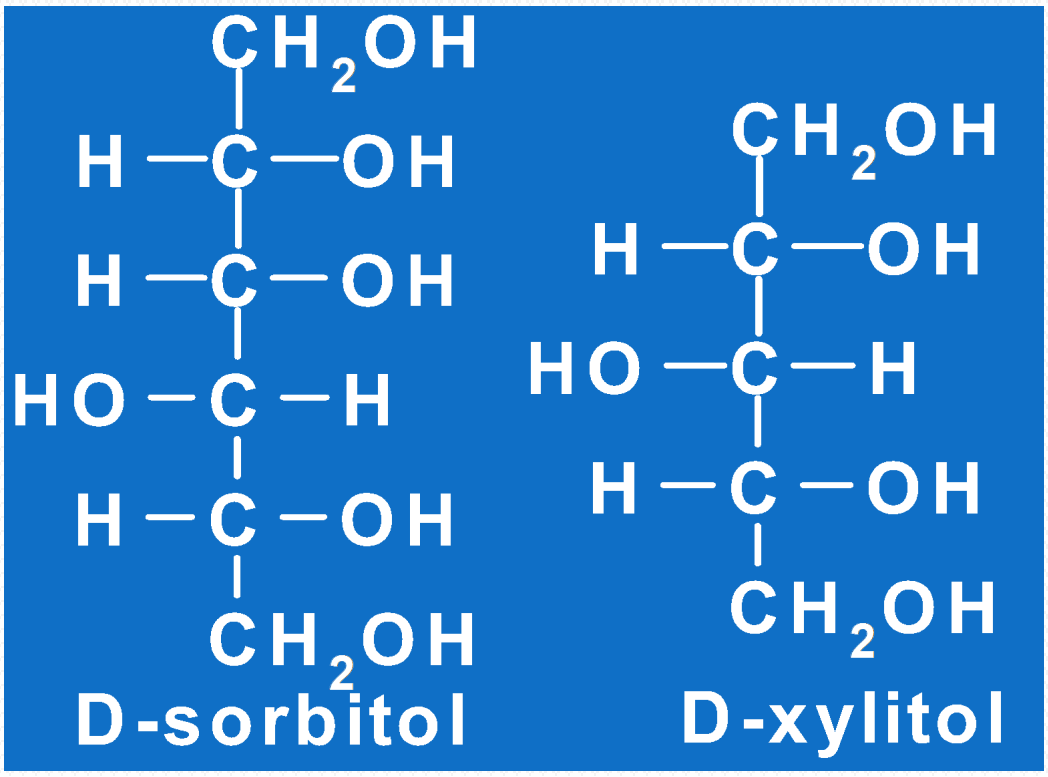
Reduction Reaction Of Sugars

Reduction Reaction

Glucose → Sorbitol

(Sugar) **(Sugar Alcohol)**

- During **reduction reaction** the **C1 carbonyl group (-CHO)** is reduced to **primary alcohol group (-CH2OH).**
- **Sorbitol is Polyol/Polyhydroxy Alcohol.**



- **Sugar Alcohols** taken in food are of **less calorific value.**
- They yield half energy in comparison to sugars.
- They are **poorly absorbed.**
- Sugar alcohols if ingested **reduces weight.**
- They are **prescribed** for **Diabetics.**

Abnormal levels of Sorbitol found in Diabetics, leads to Cataract

- **Excess** Blood Glucose in **Diabetics**, get reduced to **Sorbitol** which further deposits in the lens of eye and forms **Cataract**.

Oxidation Reaction Of Sugar

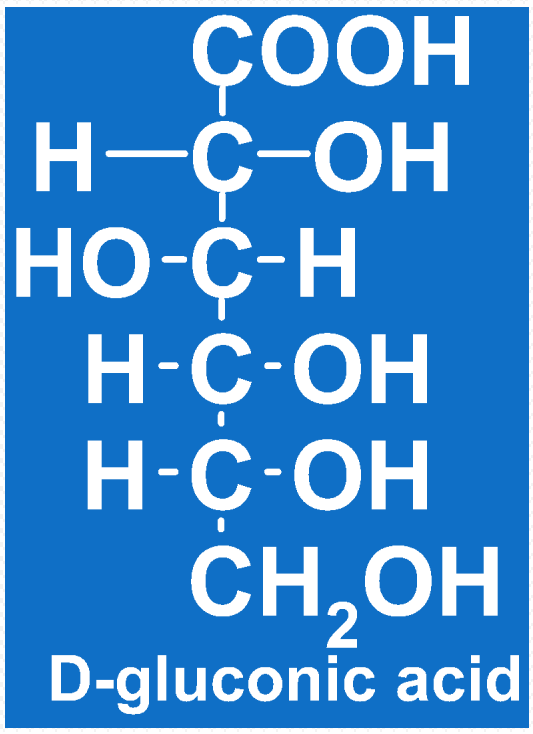
Glucose —*Oxidation Reaction*→

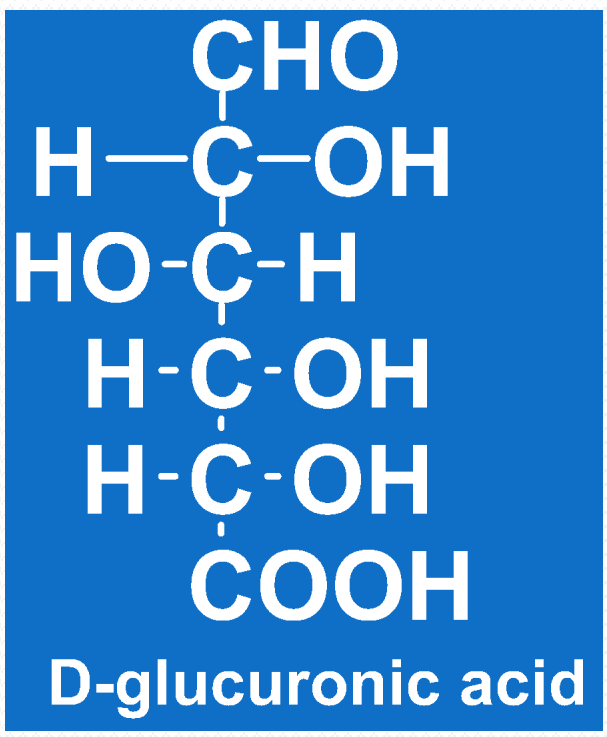
Gluconic Acid
(Aldonic Acid)
(-CHO to -COOH)

Glucuronic Acid
(Uronic Acid)
(-CH2OH to -COOH)

Glucosaccharic Acid
(Dibasic Aldaric Acid)
(-CHO &-CH2OH to –COOH)

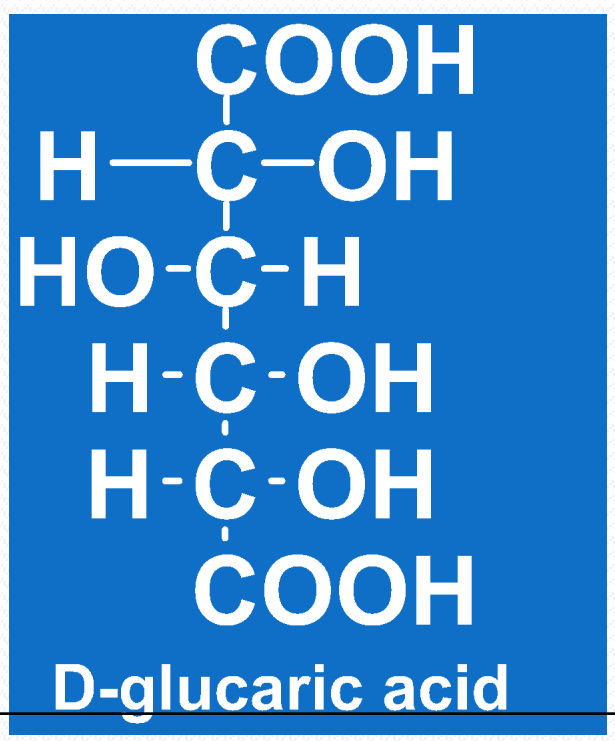
- Aldehyde oxid'n
- → aldonic acid



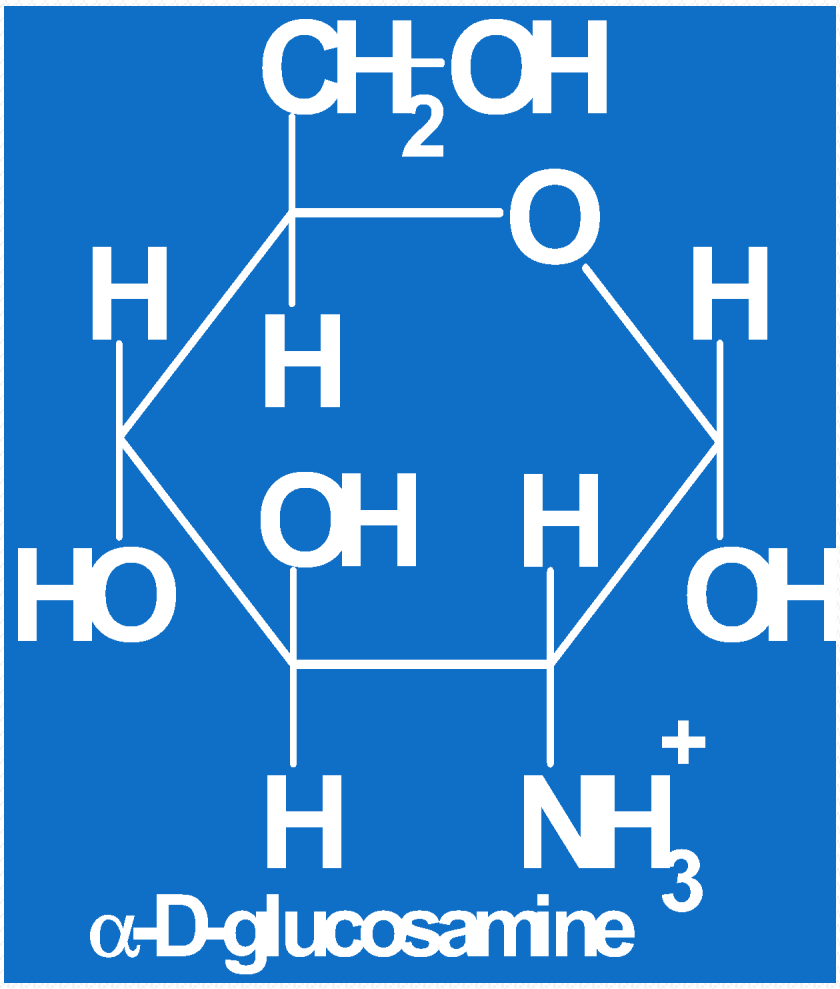


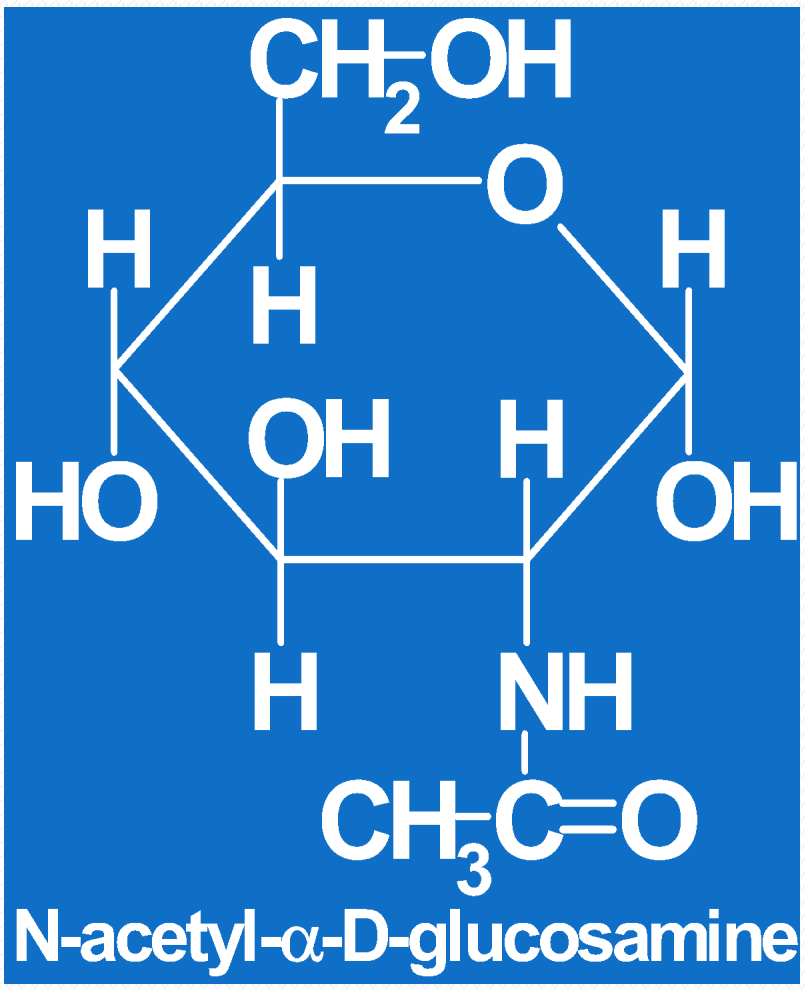
Terminal CH_2OH oxid'n→ Uronic acid

- Aldehyde + Terminal CH_2OH oxid'n →
- **Aldaric acid/Saccharic acid**



- **Uronic Acid** of Glucose Glucoronic acid is **component of Mucopolysaccharides.**
- Glucuronic acid serve as **conjugating agent** in detoxification reactions.





- N-Glucosamine
- N Acetyl Glucosamine
- N Acetyl Galactosamine
- Are Important constituents of **Mucopolysaccharides,** Glycoproteins and Glycolipids

Glucose —**Esteification**→ Glucose -6-Phosphate

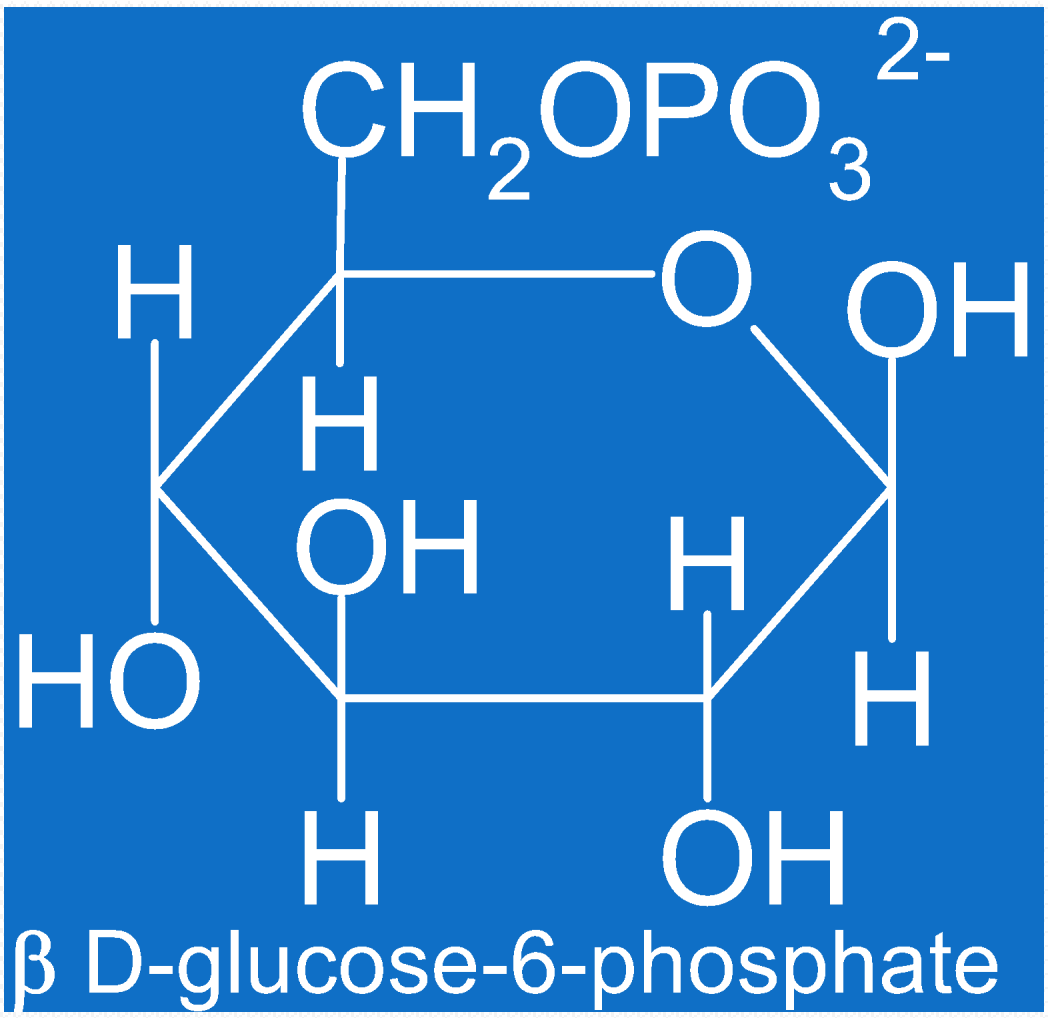
Phosphorylation Reaction

(Robinson Ester)

OR

Glucose-1-Phosphtae

(Cori Ester)



Reducing Property Of Glucose

- Reducing property of Glucose is **Enolization/ Tautomerization** reaction.
- Glucose show efficient **reducing property** in alkaline medium .

- Glucose in **alkaline medium** forms **Enediol**
- Enediol is a strong reducing agent which **reduces cupric ions to cuprous ions**.

- **Glucose give positive test results for following reducing tests:**
- Benedicts Test
- Barfoeds Test
- Fehlings Test
- Nylanders Test.

- **Benedicts Test**-Reduction of **Cupric ions in mild alkaline medium.**
- **Barfoeds Test**-Reduction of **Cupric ions in weak acidic medium.**
- **Fehlings Test**- Reduction of **Cupric ions in strong alkaline medium.**
- **Nylanders Test**-Reduction of **Bismuth ions in strong alkaline medium.**

Glycosides

- Glycosides are **derivatives of sugar.**
- Glycosides has Aglycone moiety linked to C1 (anomeric carbon atom) of sugar by an **acetal linkage**.

- **Aglycone moieties-**

(Non Sugar, Hydroxyl group containing compounds)

  - Methanol
  - Sterol
  - Phenol
  - Glycerol

- **Types of Glycosides-**

- **Glucoside**

(Contains Sugar as Glucose)

- **Galactoside**

(Contains sugar as Galactose)

Occurrence and Uses of Glycosides

- Glycosides are naturally occurring substances present in plants and animal bodies; which are extracted and used as drugs.

Glycosides
Examples and Therapeutic Use

S.No	Examples of Glycosides	Therapeutic Use
1	**Cardiac Glycosides** Digoxin /Digitonin **Ovabain**	In treatment of cardiac insufficiency.
2	**Phlorizin** (Glucose Transporter Inhibitor)	In treatment of Diabetes mellitus.
3	**Streptomycin**	Antibiotic used to treat bacterial infections.
4	**Glucovanillin**	Flavoring agent in Ice creams and Puddings.

Biomedical Importance of Glucose

- Glucose is a **reduced compound** and has bond energy in its structure.
- **Glucose** in body cells **Oxidized/Catabolized** to liberate chemical form of energy-**ATP**.
- 1 Glucose molecule on complete oxidation produces 32 ATPs.

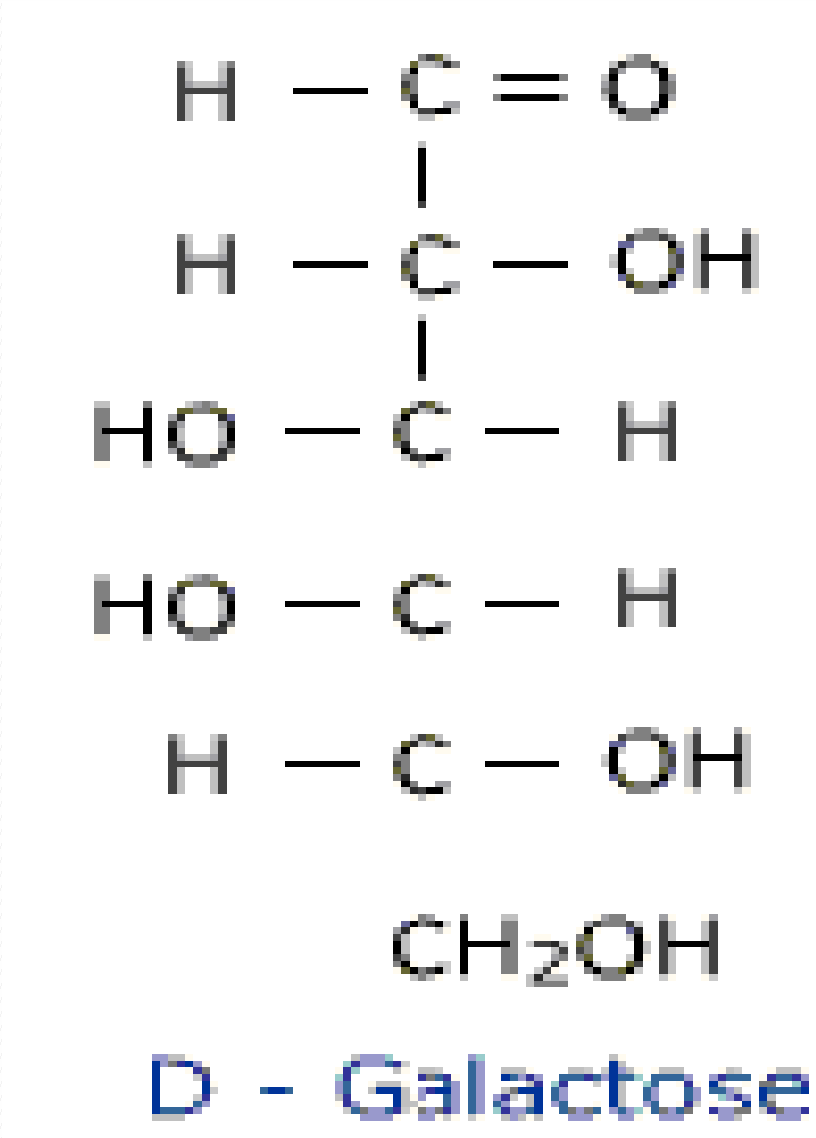
- Glucose serve as primary source of energy to all body cells.
- Glucose is an universal fuel of fetus.
- Brain, Erythrocytes ,lens cells, spinal cord, peripheral nerves are completely dependent on Glucose for its energy.

- After well fed condition the free and excess body Glucose is transformed to **Reservoir /Storage forms of Glucose**
  - **Starch (In Plants)**
  - **Glycogen** (In animals)
- Glucose still in excess is transformed to Fat (TAG) and stored as depot fat. (Unlimited).

- **Glucose is used for biosynthesis of:**
  - Glucuronic acid
  - Glucosamine
  - N-Acetyl Glucosamine
  - Galactose
  - Non essential amino acids
  - Glycosides

Galactose

- **Chemistry of Galactose**
- **Galactose is a Monosaccharide**
- Aldo Hexose
- C4 Epimer of Glucose



Occurrence/Sources

- **Galactose is never found free**

It is a component of :

- Milk Sugar Lactose
- Mucopolysaccharides
- Glycolipids and Glycoproteins.

- Galactose on reduction form Dulcitol.
- Galactose on strong oxidation forms **Mucic acid.** (Galactosaccharic acid).
- Galactose is abnormally elevated in blood and excreted in urine – **GALACTOSEMIA**.

Biomedical Importance

- Galactose has **dietary and calorific value.**
- Galactose is **transformed** to **Glucose in Liver and** metabolized.

- Galactose is used in biosynthesis of **Mucopolysaccharides, Glycoproteins, Glycolipids.**

- Galactose along with Glucose **forms Lactose in lactating mothers .**

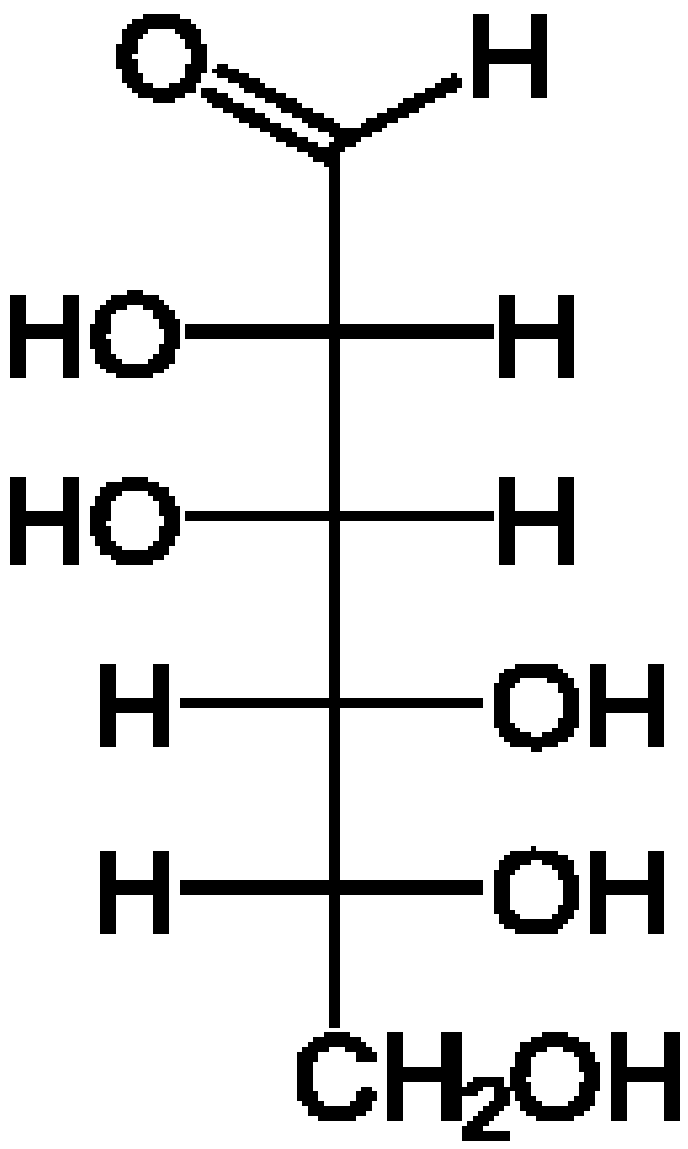
- Galactose is part of **nerve and brain biochemicals**, so milk is essential to infants.

Mannose

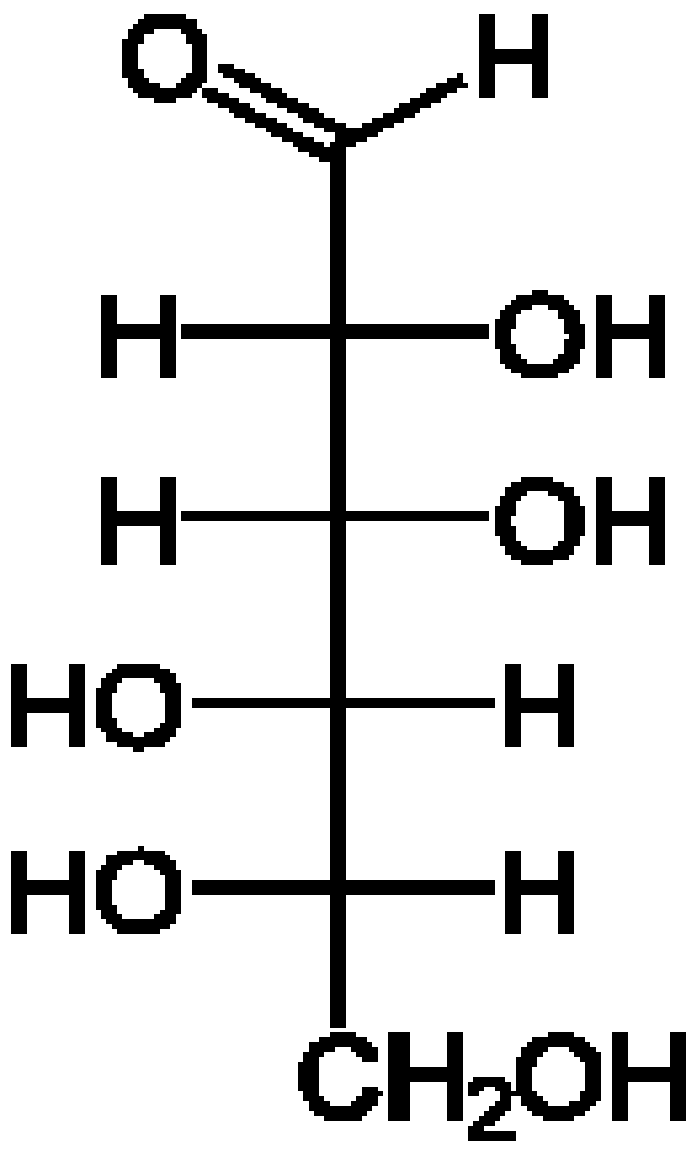
- **Mannose is a Monosaccharide**
- Chemically -Aldo Hexose
- C2 Epimer of Glucose

- **Occurrence/Sources of Mannose**

- In Plants
- Mannan (Polymer of Mannose)



D-Mannose



L-Mannose

Biomedical Importance Of Mannose

- **Mannose** component of **Glycoproteins.**

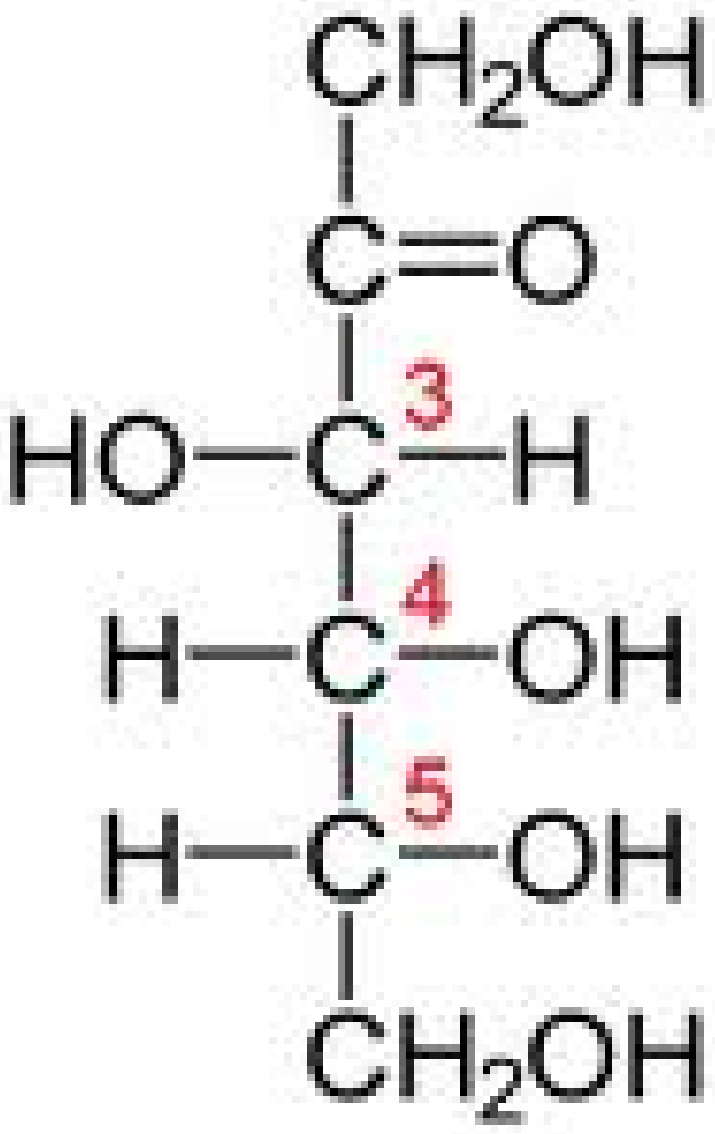
- **Mannitol** reduced compound of Mannose is used as **Diuretic** to treat **Acute Renal failure.**

Fructose

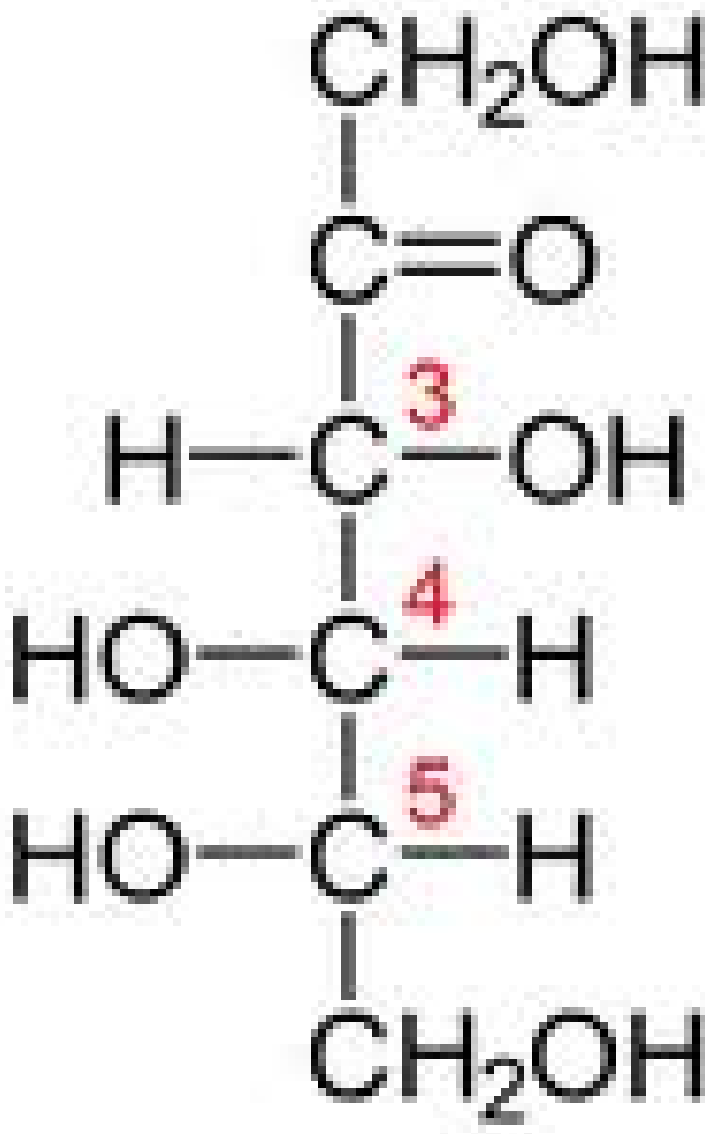
- **Fructose is a Monosaccharide**
- Fructose is Sweetest Sugar.
- Laevulose (Laevorotatory)

Chemistry Of Fructose

- Fructose is a Keto Hexose
- $C_6H_{12}O_6$
- C_2 is anomeric carbon of Fructose



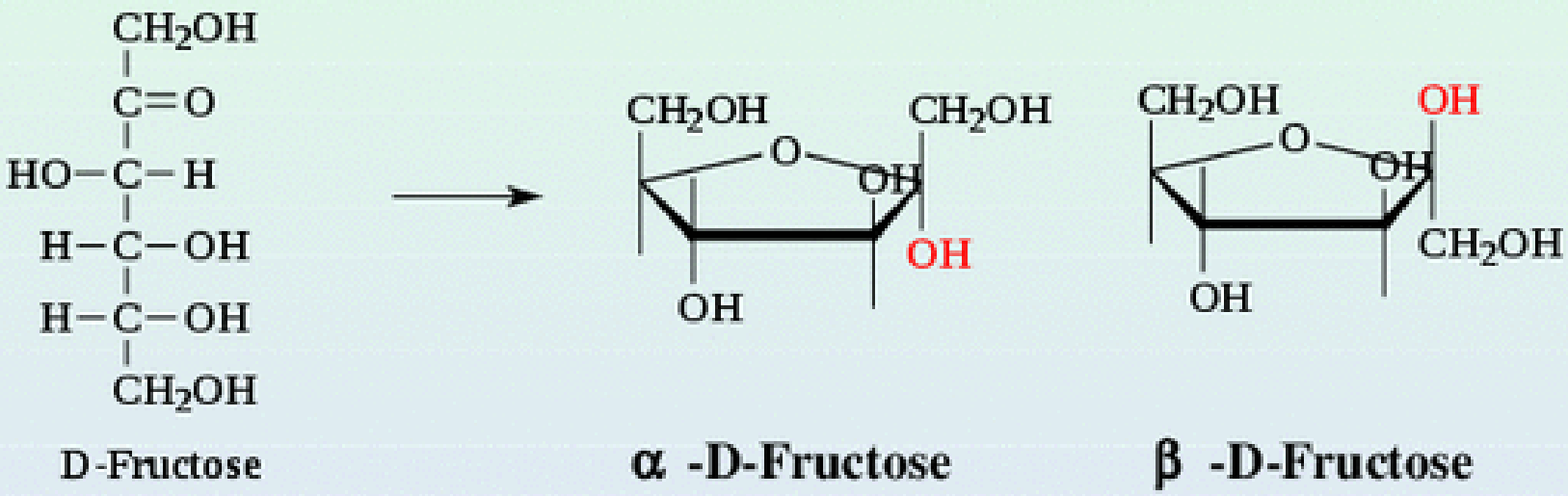
D-Fructose



L-Fructose

Cyclic Structure of Fructose

- As a ketohexose, fructose forms a 5-membered ring when the hydroxyl on C-5 reacts with the carbonly on C-2



D-Fructose α -D-Fructose β -D-Fructose

Occurrence/Sources Of Fructose

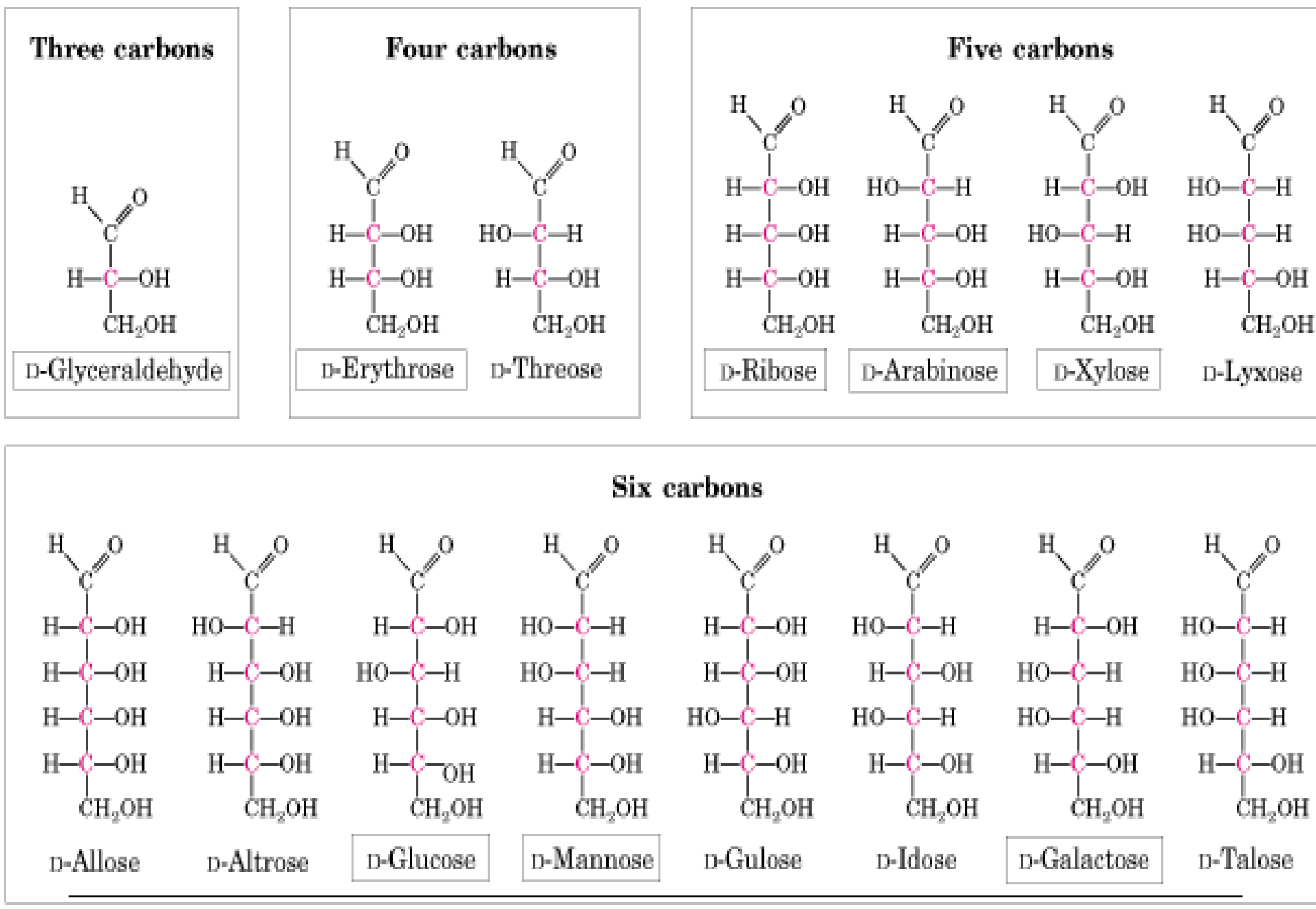
- In Fruits, Honey
- Body cells, Semen.
- Fructose is component of Sucrose.

- Fructose is more stable in **βD Fructofuranose** form.
- **Selivanoff 's test** is characteristic test for Fructose.

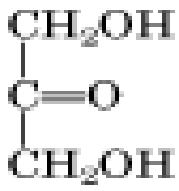
  (positive result-**Cherry red color**).
- Fructose on reduction forms **Sorbitol and Mannitol.**
- Fructose-6-PO_4 (Neubergs Ester)
- Fructose-1,6- Bis Phosphate (Harden Young Ester).
- Abnormal excretion of Fructose in urine is noted in persons suffering from **Essential Fructosuria.**

Biomedical Importance Of Fructose

- Fructose has **dietary and calorific value.**
- In Liver **Fructose is transformed** to **Glucose** and metabolized.
- Fructose **present in semen** serves as **nutrient for Sperms.**

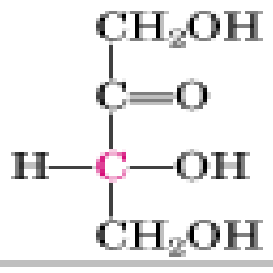


Three carbons



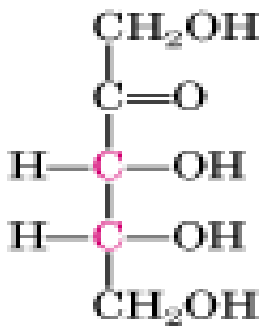
Dihydroxyacetone

Four carbons

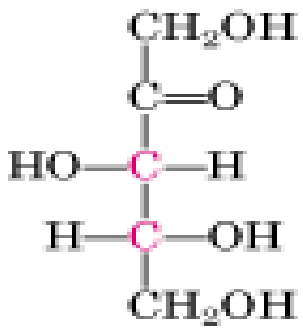


D-Erythrulose

Five carbons

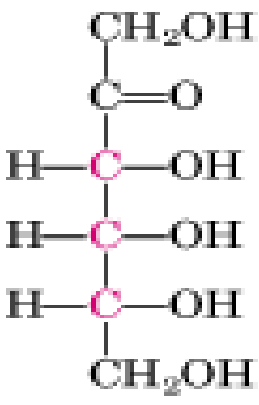


D-Ribulose

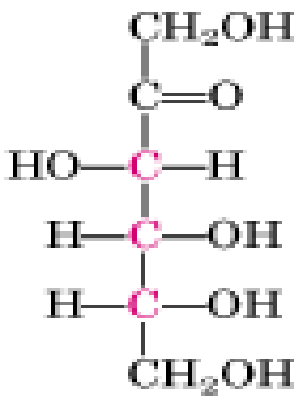


D-Xylulose

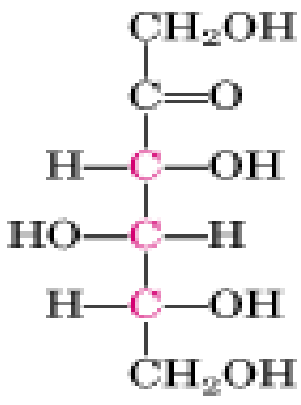
Six carbons



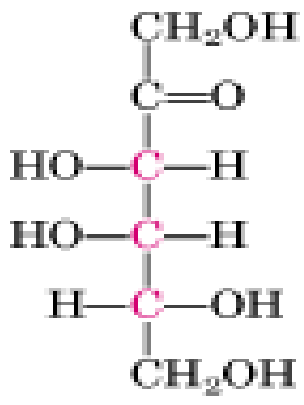
D-Psicose



D-Fructose



D-Sorbose



D-Tagatose

D-Ketoses

(b)

Biomedically Important Disaccharides

- Disaccharides are class of Carbohydrates, chemically **composed of two, same or different Monosaccharide units**, linked by glycosidic bond.

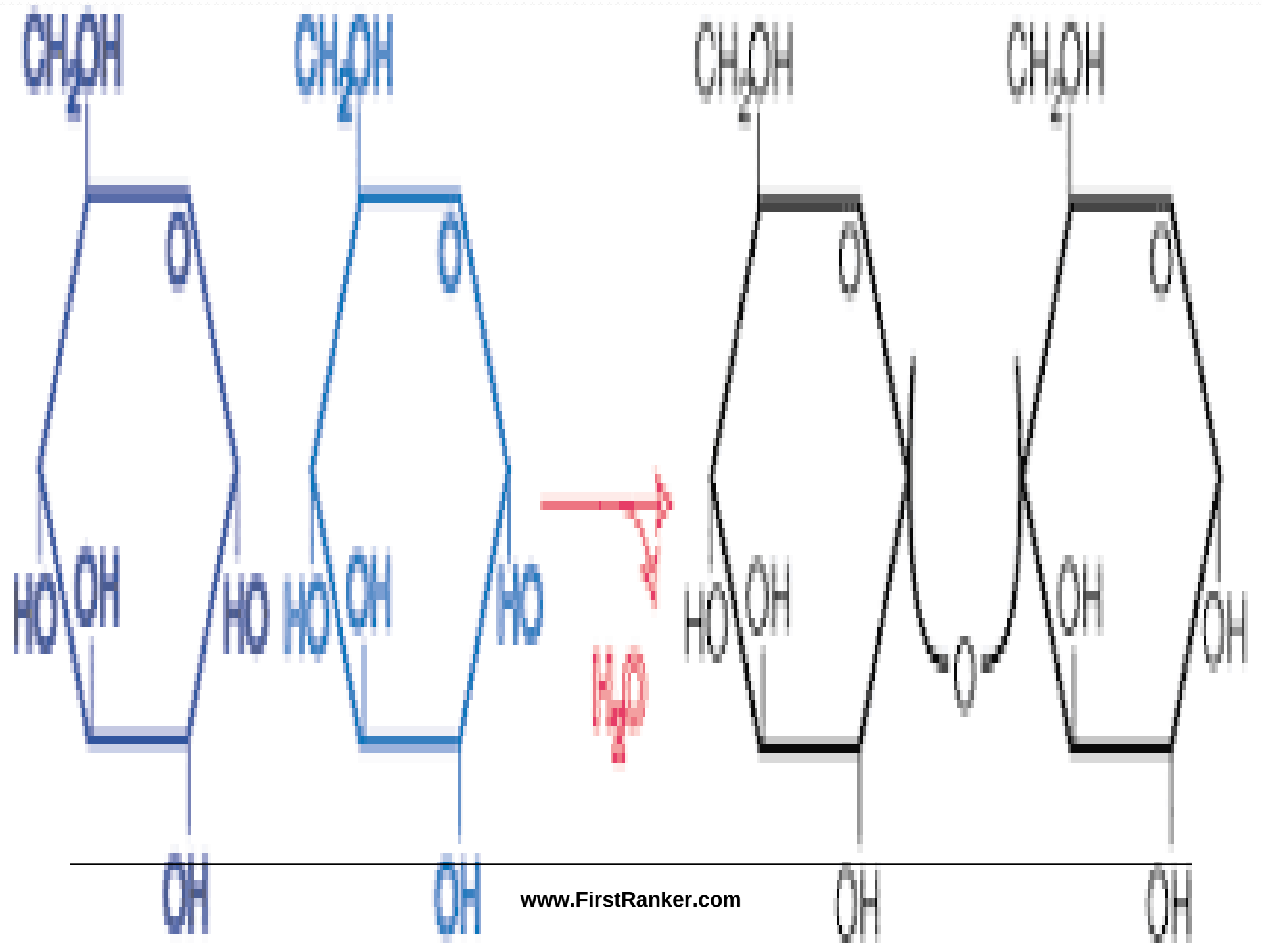
- **General Formula of Disaccharides $C_n(H_2O)_{n-1}$**

Glycosidic Bonds

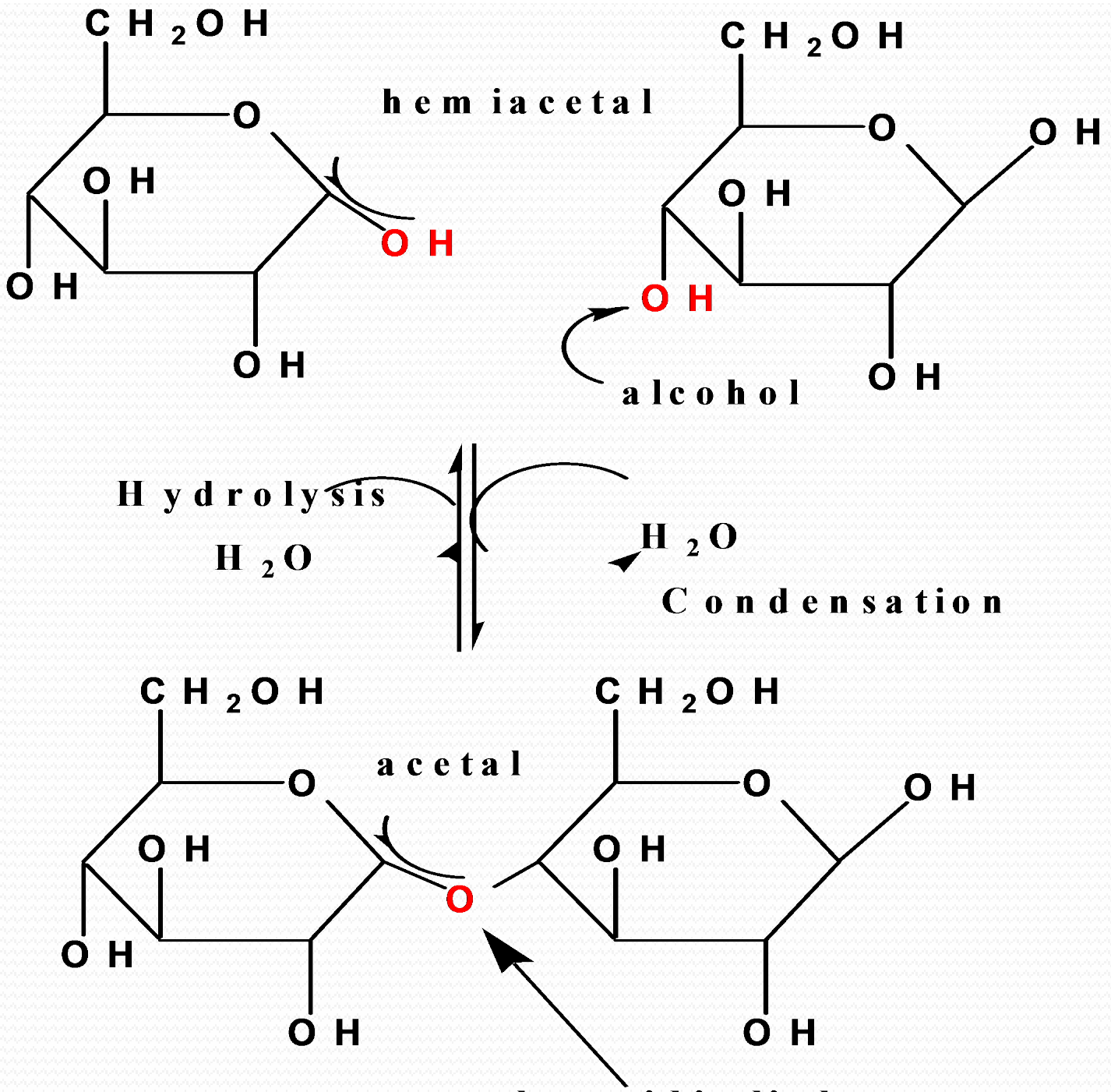
- Glycosidic bonds are **Acetal/ Ketal** bonds involving the anomeric carbon of Monosaccharides.

- The Aldehyde/Ketone groups participate in glycosidic bond,
- Its involvement looses reducing property since, they wont remain free.

- Glycosidic bonds are formed with the interaction of two hydroxyl groups of adjacent sugar residues(Monosaccharide) with an elimination of water molecule.



Glycosidic Linkage



- Glycosidic bonds are **covalent, strong bonds** ,linking one Monosaccharide to another.

- Glycosidic bonds are formed with α/β configuration.

- Different glycosidic bonds form a different molecule with different properties.

Types of Glycosidic bonds:

- α (1-4)
- α (1-6)
- α1-β2
- α(1-1)
- β (1-4)

- **Reducing end**- End with free anomeric carbon, not involved in formation of glycosidic bond.
- **Non reducing end**- End with no free anomeric carbon, since involved in formation of Glycosidic bond.

Types of Disaccharides

- **Reducing Disaccharides**
- **Lactose** (Milk Sugar)
- **Maltose**

(Malt Sugar, Product of Starch digestion))

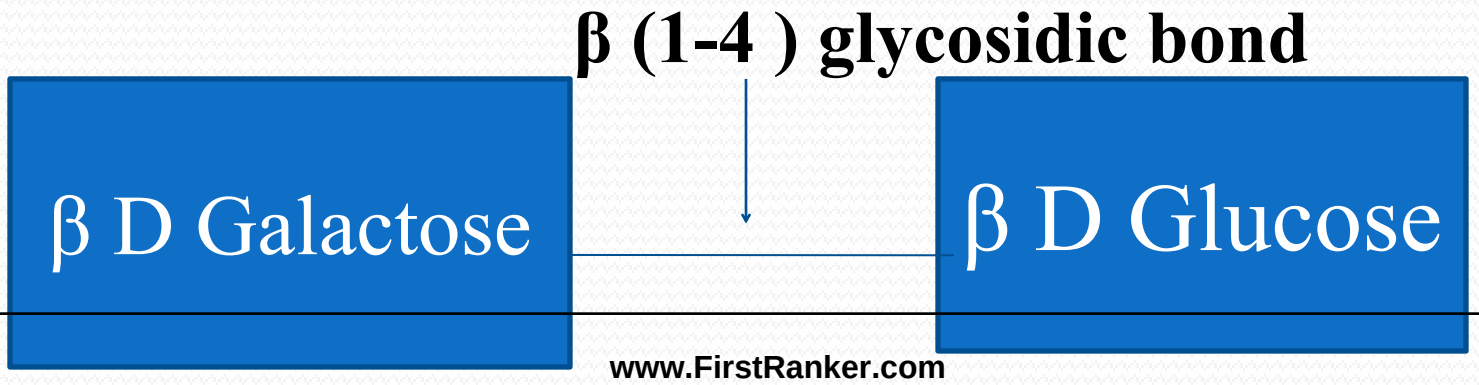
- **Isomaltose** (product of Starch digestion)
- **Lactulose** (Laxative)
- **Cellobiose** (Product of Cellulose)

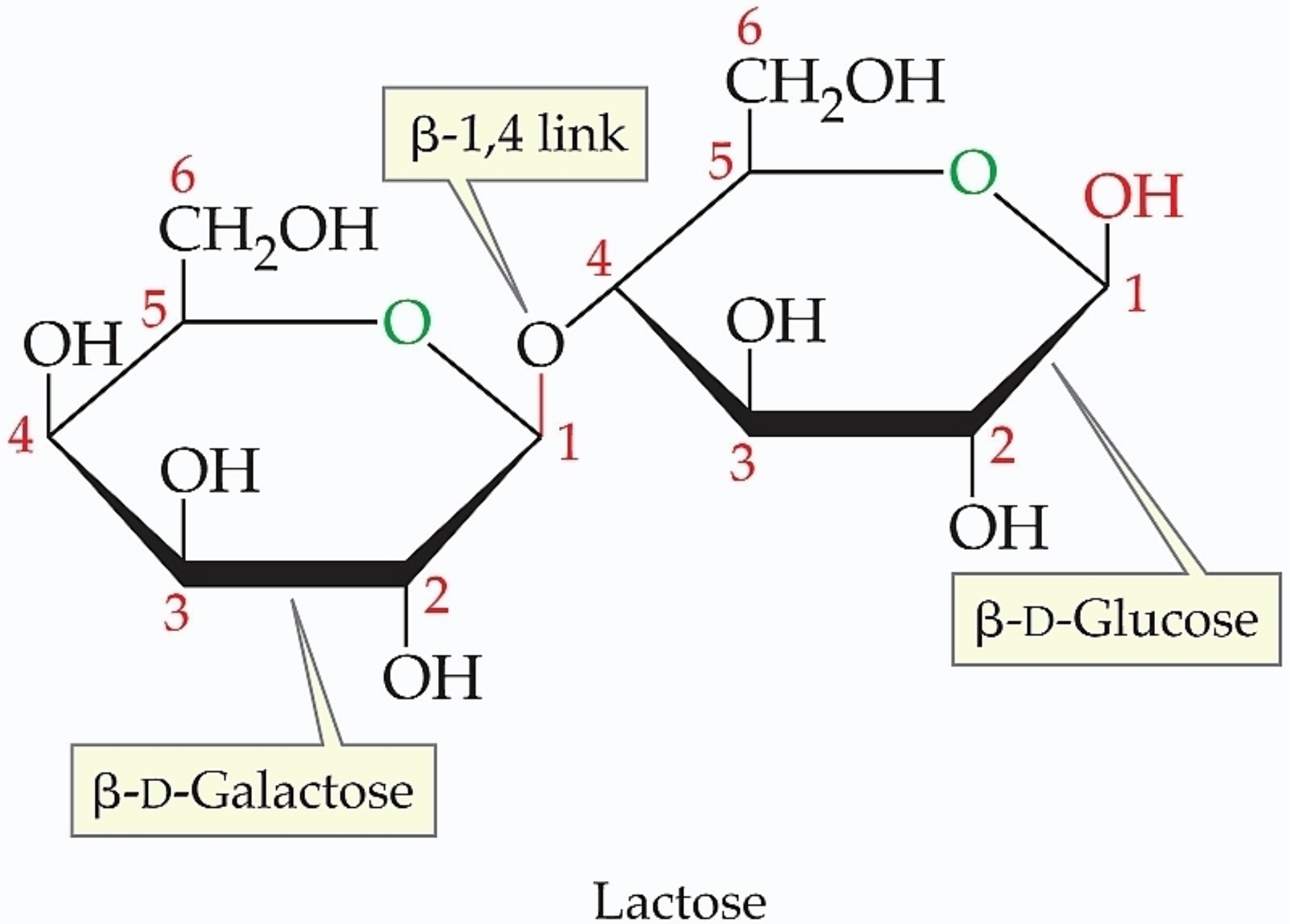
- **Non Reducing Disaccharides**
  - Sucrose (Cane Sugar)
  - Trehalose

Lactose (Milk Sugar)

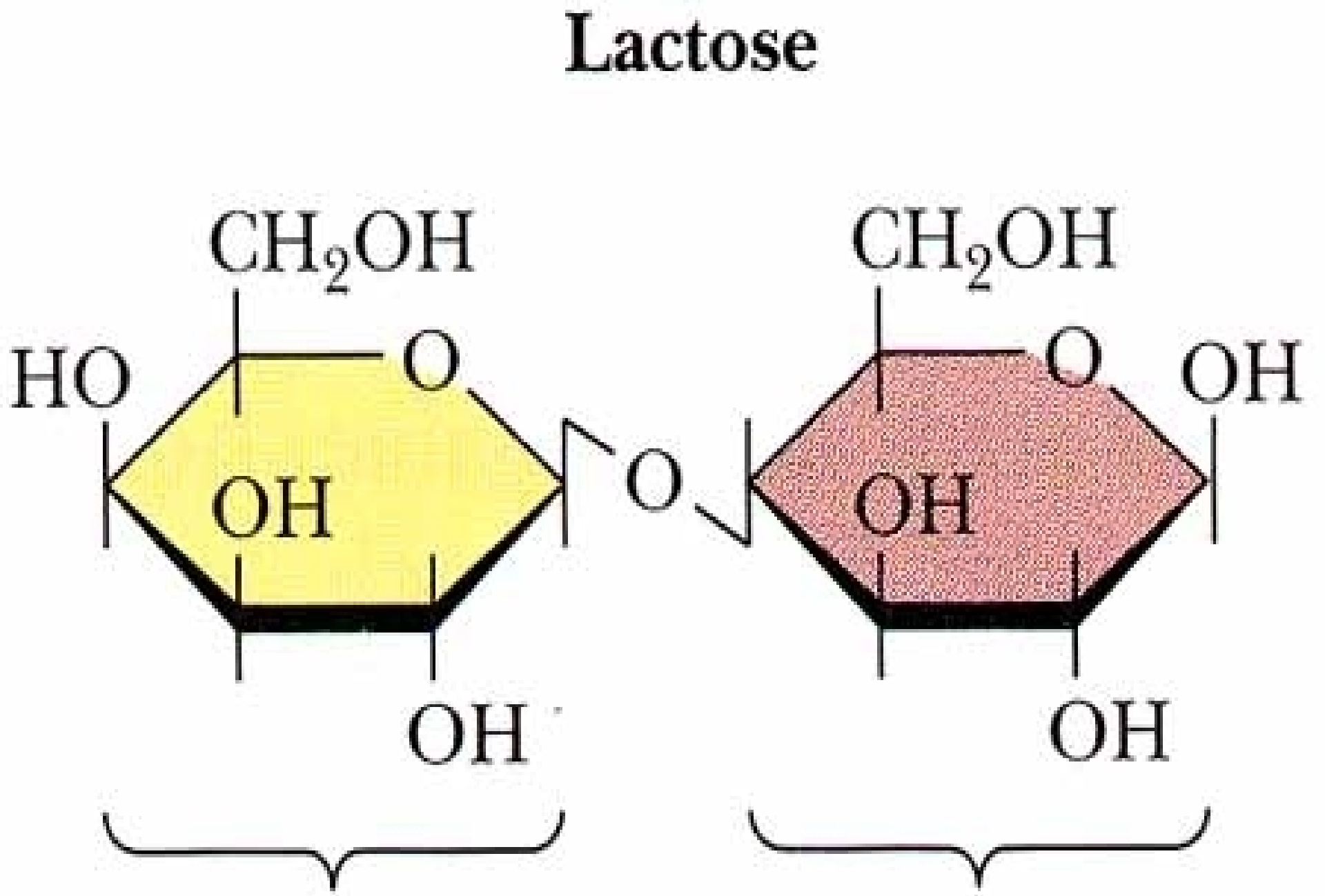
Components and Linkage of Lactose

- **Lactose is a Reducing Disaccharide**





Lactose



Source / Occurrence Of Lactose

- Milk and Milk products.
- Lactating Mothers body.

Biomedical Importance Of Lactose

- Lactose has dietary and calorific value.

- GIT **enzyme Lactase digests** Lactose by cleaving β (1-4) glycosidic bond and releases free Galactose and Glucose.

- **Lactase deficiency in GIT leads to suffer from Lactose Intolerance.**
- Certain bacteria can ferment lactose to lactic acid - souring of milk

(Lactobacillus).

- Lactose may occur in urine **during**

Maltose

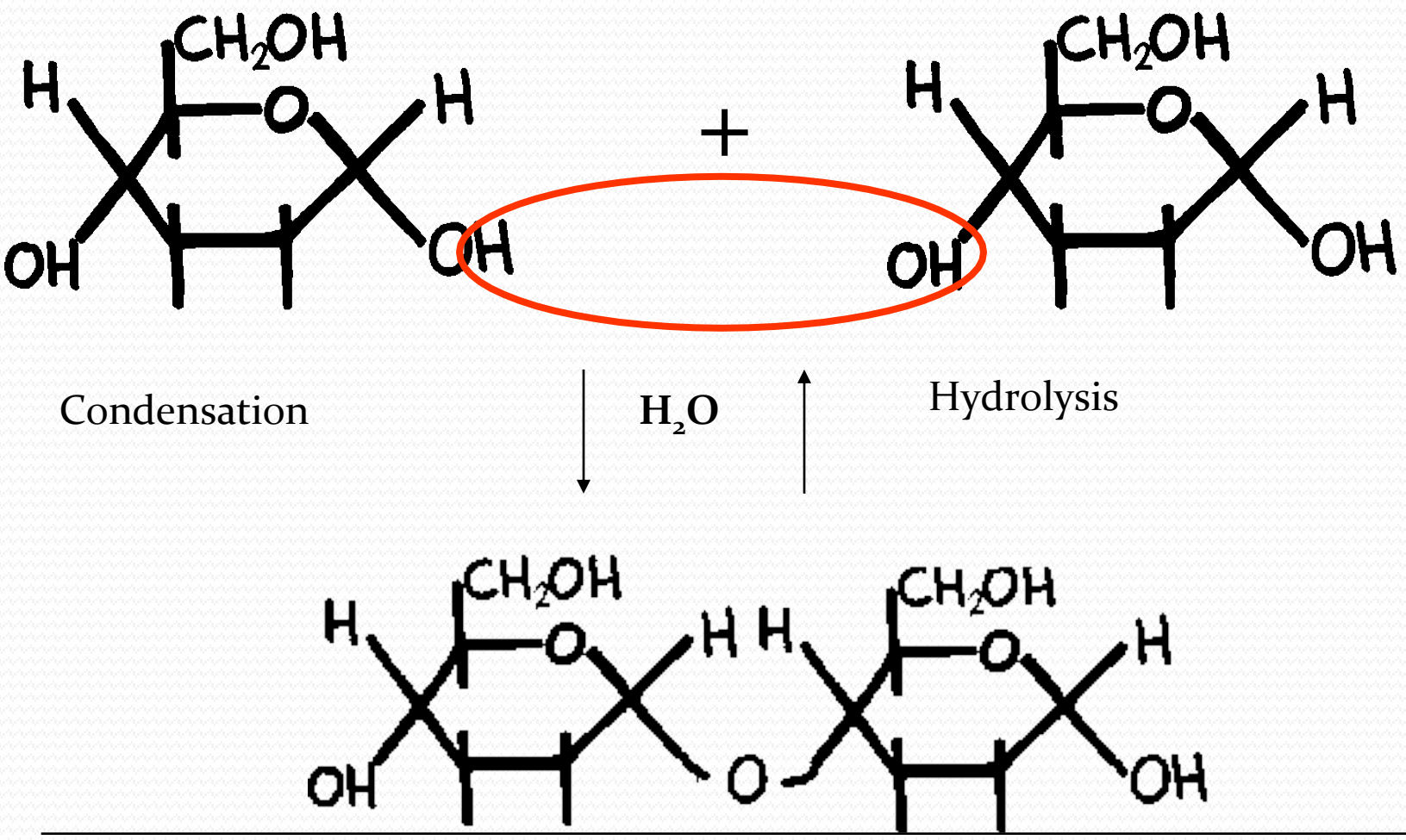
- Maltose is a reducing **Disaccharide**

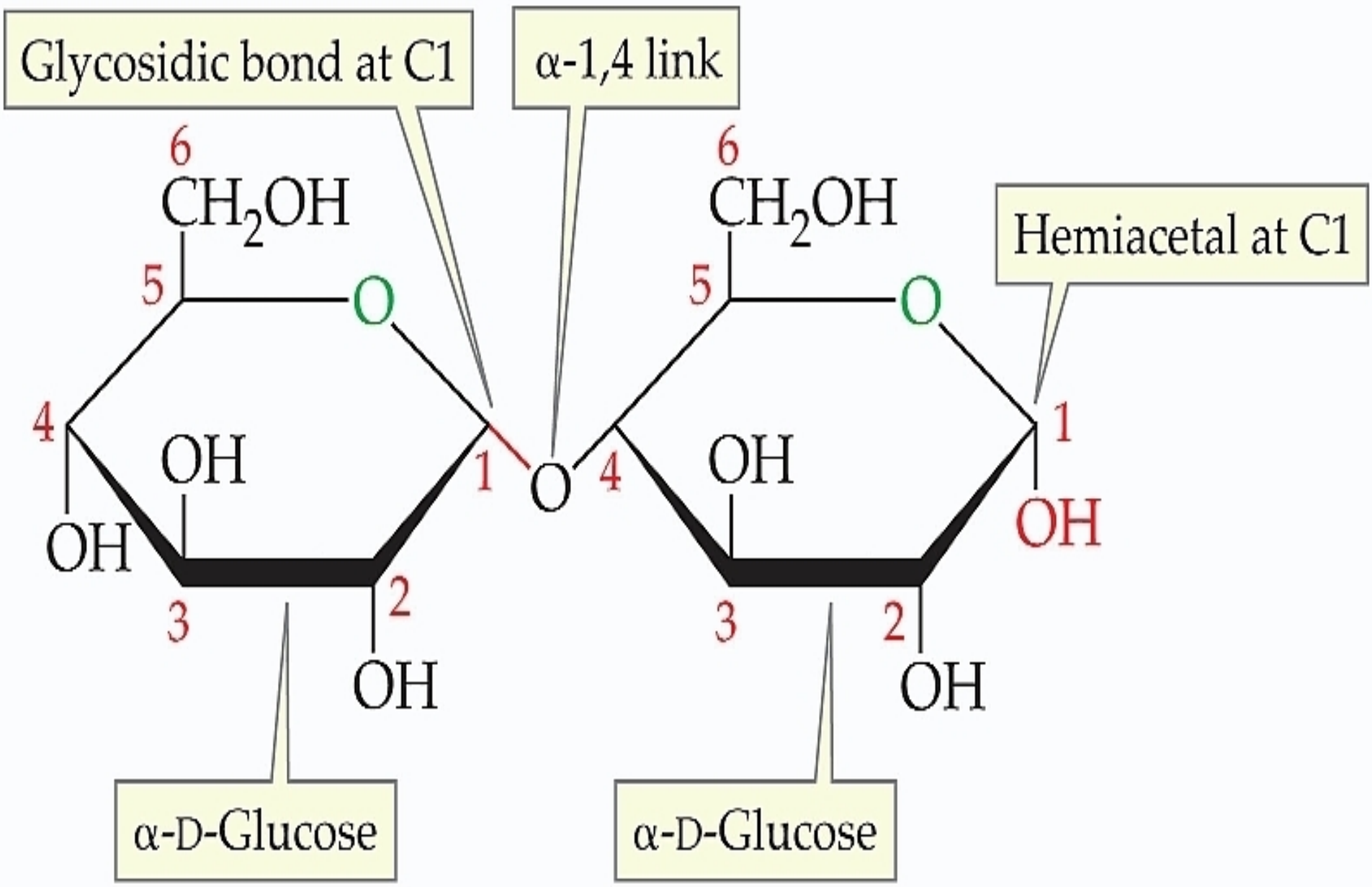
- Malt Sugar

Components and Linkage Of Maltose

- α D Glucose -α D Glucose
- α (1-4) glycosidic bond

Glucose to form Maltose





Maltose

Source / Occurrence Of Maltose

- Malt grain, Germinating seeds, Maltova.
- In human GIT, source of Maltose is through **Starch and Glycogen digestion** by α Amylase activity.

- Maltose is obtained in GIT as an end product of Starch and Glycogen digestion.

Biomedical Importance Of Maltose

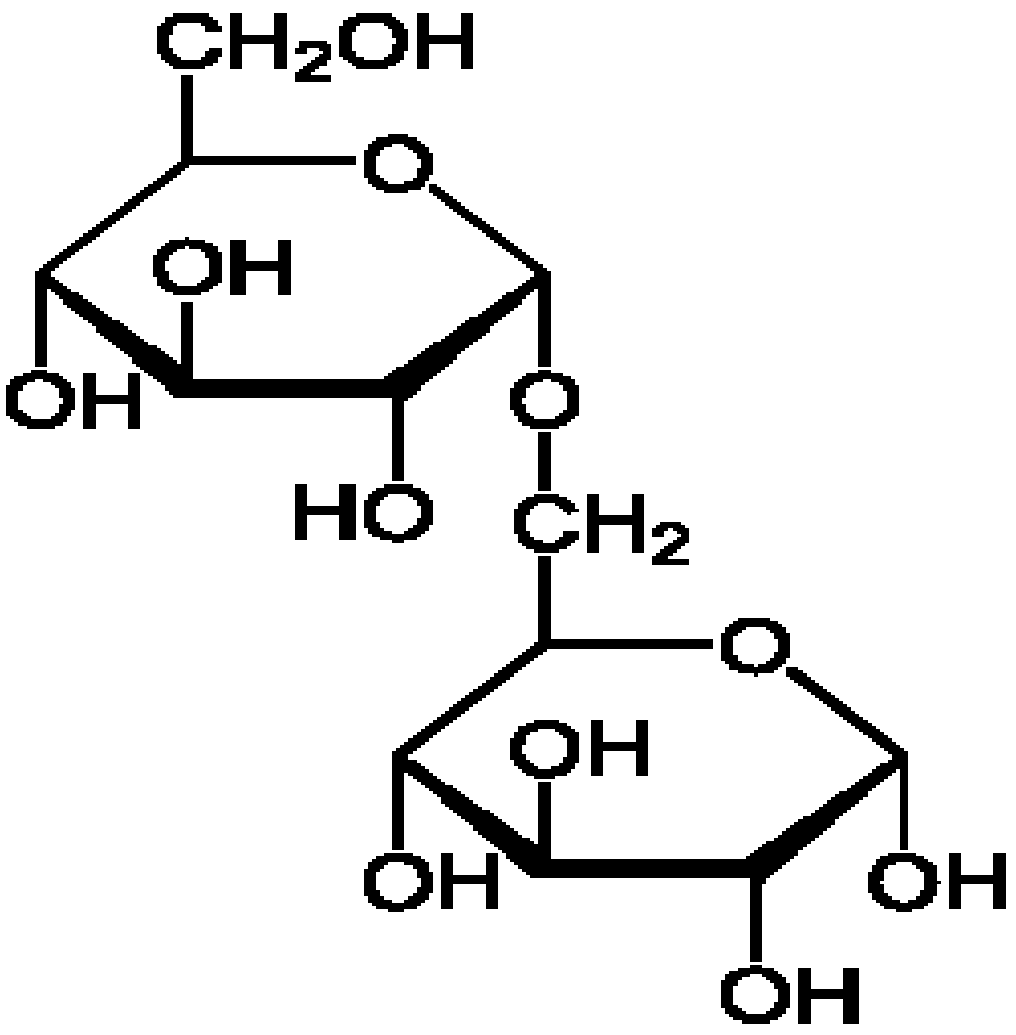
- Maltose has dietary and calorific value.
- GIT enzyme Maltase digests Maltose by cleaving α (1-4) glycosidic bond and releases two Glucose units.

Isomaltose

- Isomaltose is a reducing **Disaccharide.**
- **Isomaltose is a product of Starch and Glycogen digestion.**

Components and Linkage Of Isomaltose

- **α D Glucose -α D Glucose**
- **α (1-6) glycosidic bond**



Source /Occurrence Of Isomaltose

- In human GIT Isomaltose is obtained from **Starch and Glycogen digestion** by α-Amylase activity.

Biomedical Importance of Isomaltose

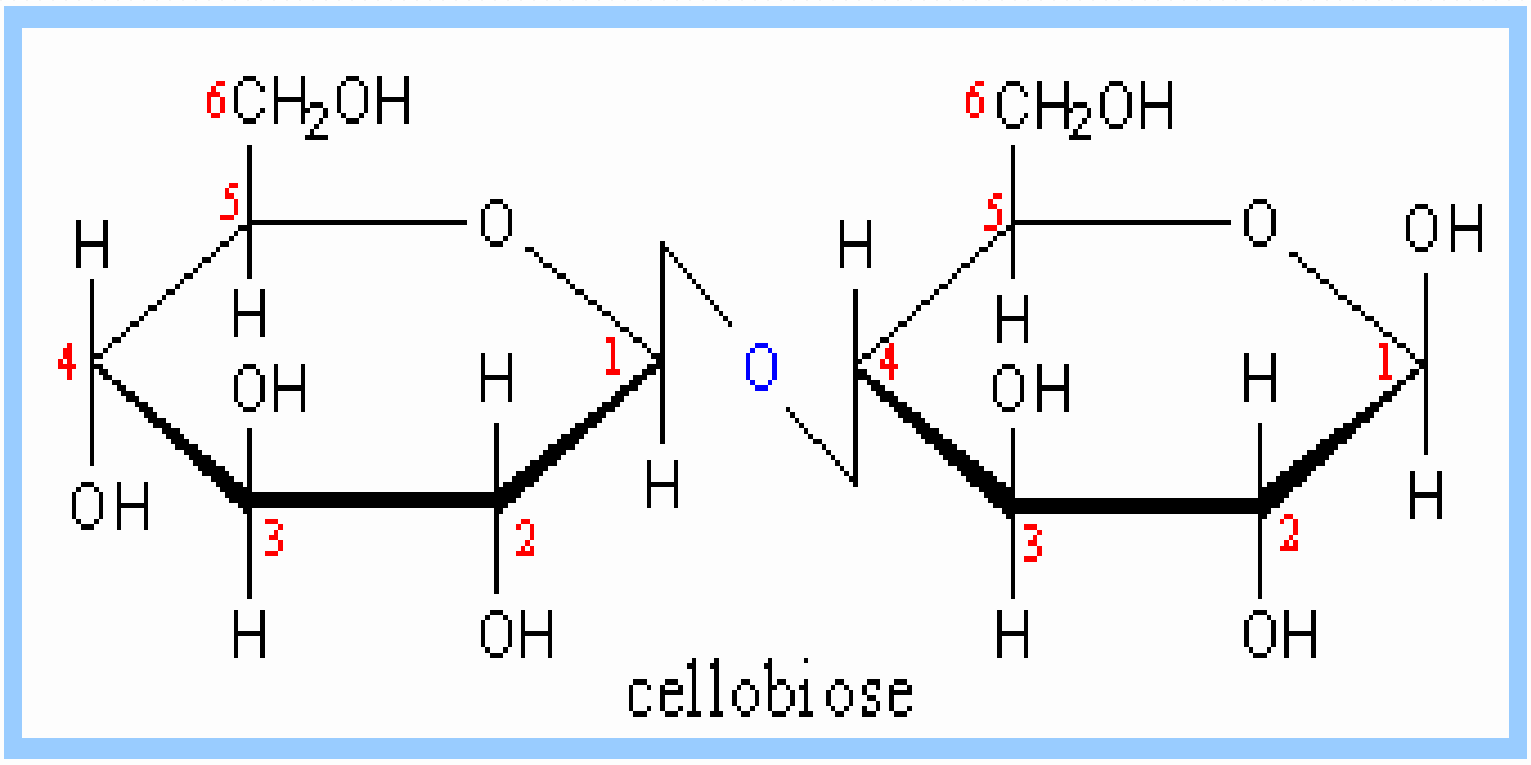
- Isomaltose has dietary and calorific value.
- Isomaltose is digested by GIT enzyme **Isomaltase** to release two Glucose units by cleaving **α (1-6) glycosidic** bond.

Cellobiose

- **Cellobiose is a reducing Disaccharide.**
- Disaccharide obtained from **Cellulose Digestion**.

Components and Linkage Of Cellobiose

- β D Glucose - β D Glucose
- β (1-4) glycosidic bond



Source / Occurrence of Cellobiose

- Cellobiose obtained from Cellulose digestion In GIT of ruminants (Cattle) .
- **Cellobiose** is **absent in human** GIT, since enzyme **Cellulase is absent** which do **not digest Cellulose**.

Biomedical Importance of Cellobiose

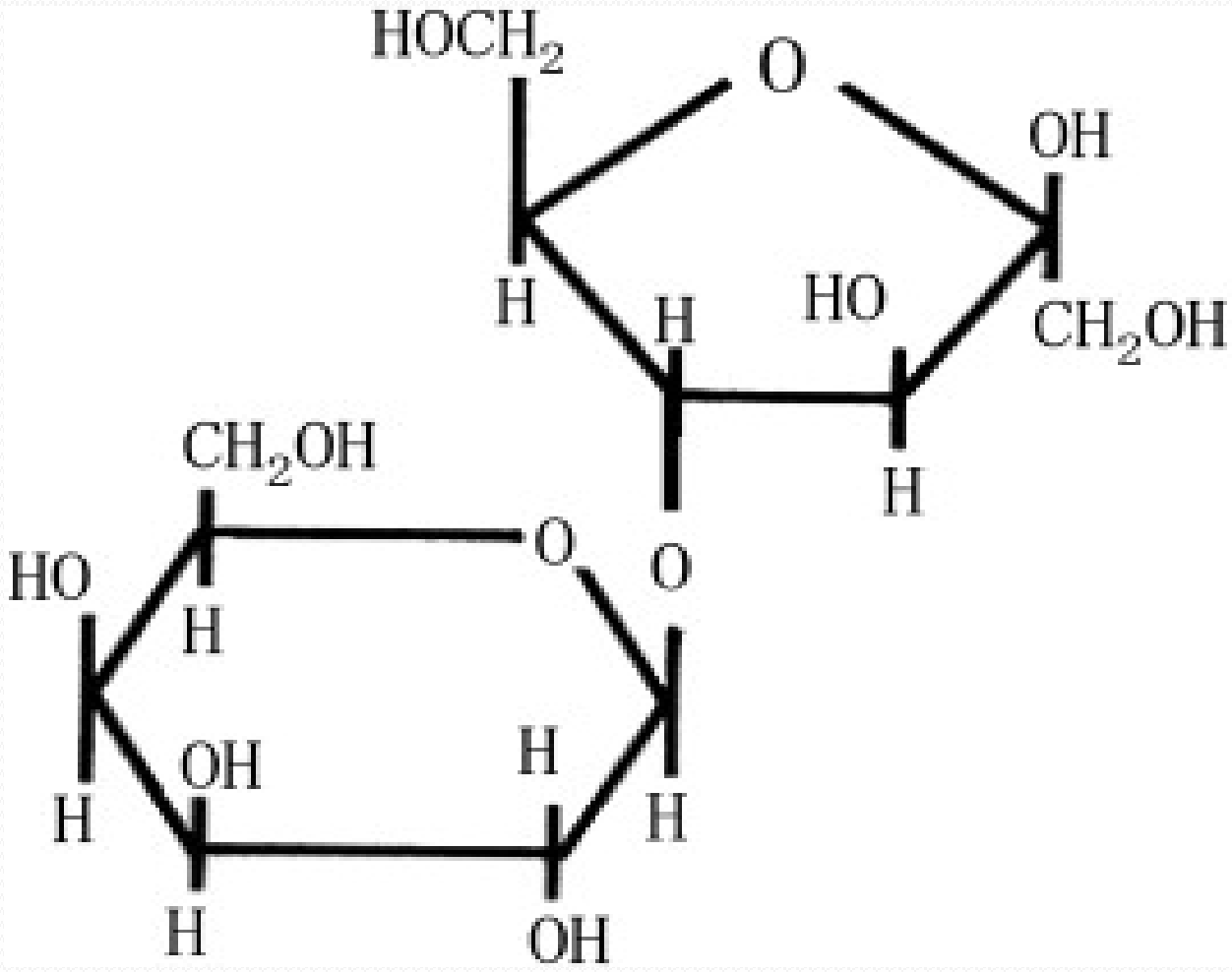
- Cellobiose is absent in human beings.
- Not of biomedical Importance.

Lactulose

- **Lactulose is a Reducing Disaccharide**

Type, Components and Linkage of Lactulose

- **β D Galactose -β D Fructose**
- **β (1-4) glycosidic bond**



Source / Occurrence Of Lactulose

- In Plants

- Lactulose:

Prepared by alkaline rearrangement of lactose

Biomedical Importance Of Lactulose

- Lactulose has therapeutic value; **act as** osmolar **laxative.**
- **Relieves Chronic Constipation.**

- Oral administration of Lactulose **relieves hyper Ammonaemia** in patients of Hepatic Encephalopathy.

Treatment of Systemic Encephalopathy By Lactulose.

- **Mechanism of action:**
- Lactulose is **not digestible**.
- Bacterial flora convert it to **Lactic and Acetic acids** that irritate the intestinal wall.
- Increases **acidity of intestine** ,this moves ammonia from blood to the intestine for neutralization.
- Relieves Hyperammonaemia.

Sucrose

- Sucrose is a **Non Reducing Disaccharide**
- Cane sugar/ Common Table Sugar /Beet sugar

Components and Linkage Of Sucrose

- **α D Glucose- β D Fructose**
- **α 1- β 2 glycosidic bond.**

α-Glucose

+

β-Fructose

Sucrose

α-Glucose

α,β-1,2-glycosidic bond

Sucrose

β-Fructose

Why Sucrose is Non reducing?

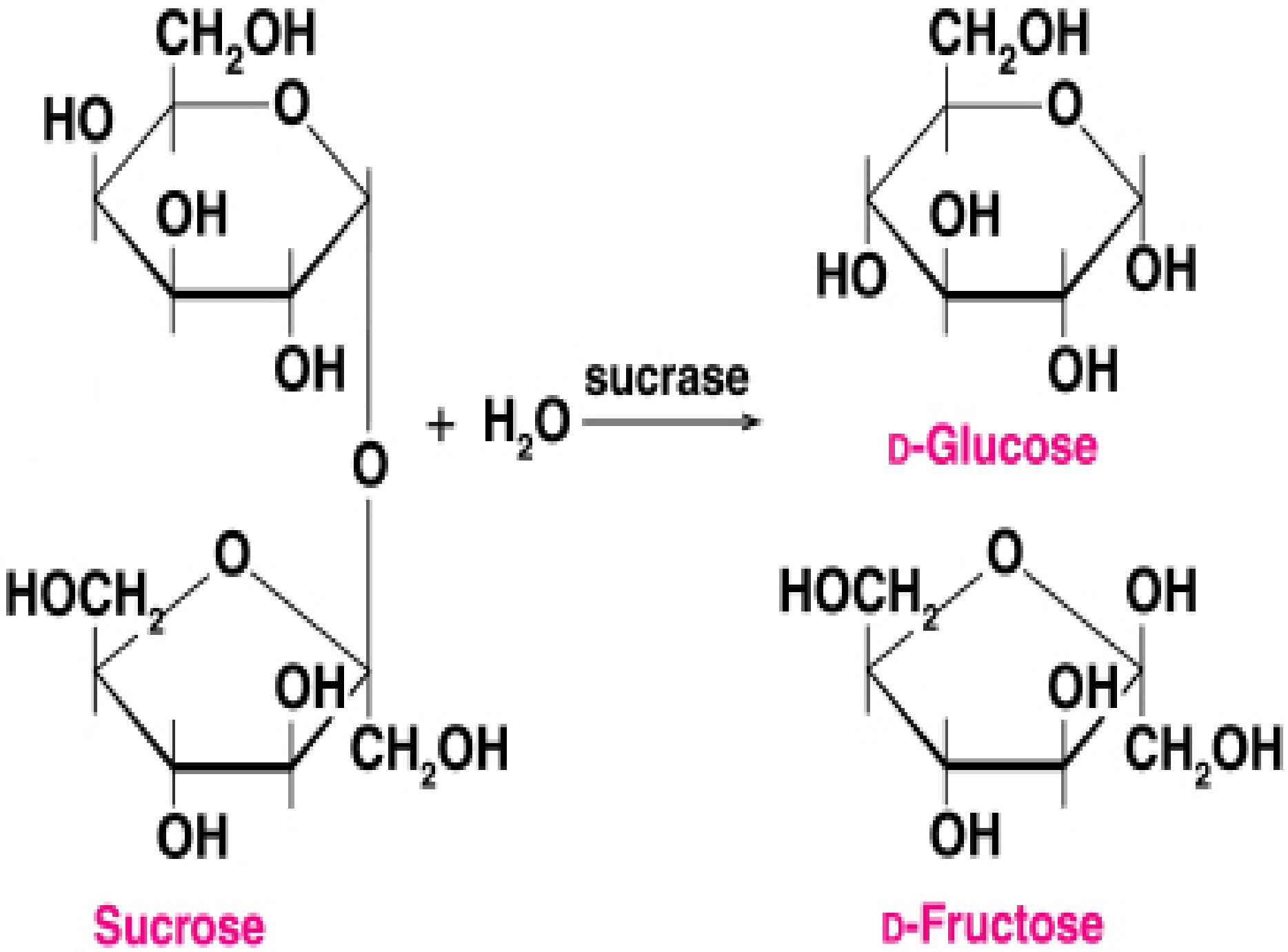
- Glucose (C1) and Fructose(C2) anomeric carbon atoms are involved in formation of Glycosidic bond.
- No **free anomeric carbon atoms**.
- Hence Non reducing.

- Sucrose has **no free aldehyde /ketone group hence non reducing**

- Sucrose is dextrorotatory (d/+) with specific rotation +66.5°.

Source /Occurrence Of Sucrose

- In Plants – Sugar cane, Beet root.
- Commercially prepared from sugar cane.



Invert Sugar

- Invert sugar is a **product of Sucrose hydrolysis.**
- Invert Sugar is a **product of Inversion Process.**

- Invert Sugar is a **hydrolytic mixture** of **free Glucose** and **Fructose** obtained from Sucrose hydrolysis.

Inversion process

- A **non reducing** and **dextrorotatory Sucrose**, on acid hydrolysis/by action of enzyme **Invertase** ,
- Produces a hydrolytic mixture of **free, Glucose**(+52.5°) and **Fructose**(-93°) which is reducing and **laevorotatory**(- 20.4°).

- Invert Sugar is **Reducing**.
- Invert sugar is **laevorotatory**.

  (since Fructose has high magnitude of optical rotation -93°)
- Invert Sugar is **sweeter** than Sucrose

  (since it contains free Fructose,a sweetest sugar)

Uses Of Invert Sugar

- **Sweetening agent** as it is more sweet than Sucrose.
- Used in adulteration of Honey.

Biomedical Importance Of Sucrose

- Sucrose has **dietary and calorific value.**
- Sucrase or **Invertase enzyme** of GIT cleaves α 1- β 2 Glycosidic bond of Sucrose and release free Glucose and Fructose – i.e. **Invert Sugar**.

Biomedically Important Oligosaccharides

- Oligosaccharides are composed of 3-10 Monosaccharide units linked by glycosidic bonds.
- Oligosaccharide may be **branched or unbranched chain.**

- Dietary Oligosaccharides are **not digested** by human hence has no calorific value.
- Oligosaccharides are **components of Glycoproteins.**

Biomedically Important Polysaccharides/Glycans

- **Polysaccharides** are complex class of Carbohydrates,
- Chemically composed of **more than ten,** same or different **Monosaccharide units or their derivatives**
- Repeatedly **linked** by **glycosidic linkages.**

- General Formula of Polysaccharides $(C_6H_{10}O_5)n$

- **Iodine test is a characteristic test for Polysaccharides**

- Iodine test is based on Physical property of adsorption.
- Iodine get adsorbed on complex structure of Polysaccharides to give characteristic color.

Homopolysaccharides

- Homopolysaccharides are type of Polysaccharides composed of **more than 10**, **same type** of Monosaccharide units repeatedly linked by glycosidic bonds.

Glucosan

- Type of Homopolysaccharide
- Repeating unit,of Glucosan is **Glucose**
- **Glucosan is a Polymer of Glucose.**

Examples Of Glucosans

- **Starch**
- **Glycogen**
- **Cellulose**
- **Dextrin**
- **Dextran**

Fructosan

- Type of Homopolysaccharide
- Repeating unit in Fructosan is **Fructose.**
- **Fructosan is a Polymer of Fructose.**

Example Of Fructosan

- **Inulin**

Starch

- Plant Homopolysaccharide

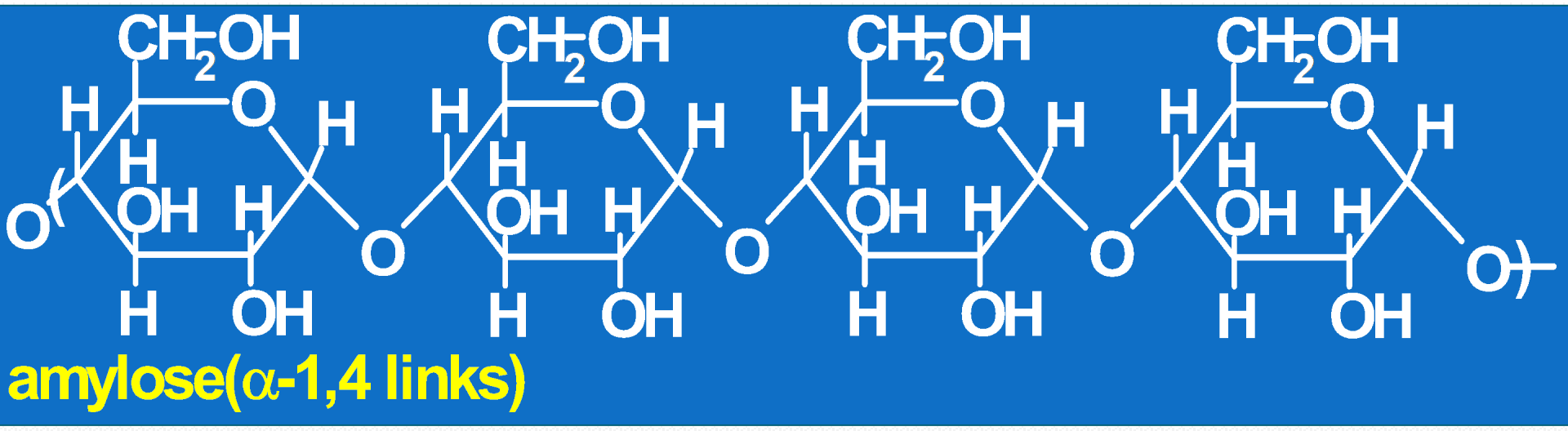
Chemistry Of Starch

- Starch is Glucosan
- **Repeating Unit -**

  α D Glucose (approx 7000)
- **Components of Starch-**
- Amylose and Amylopectin

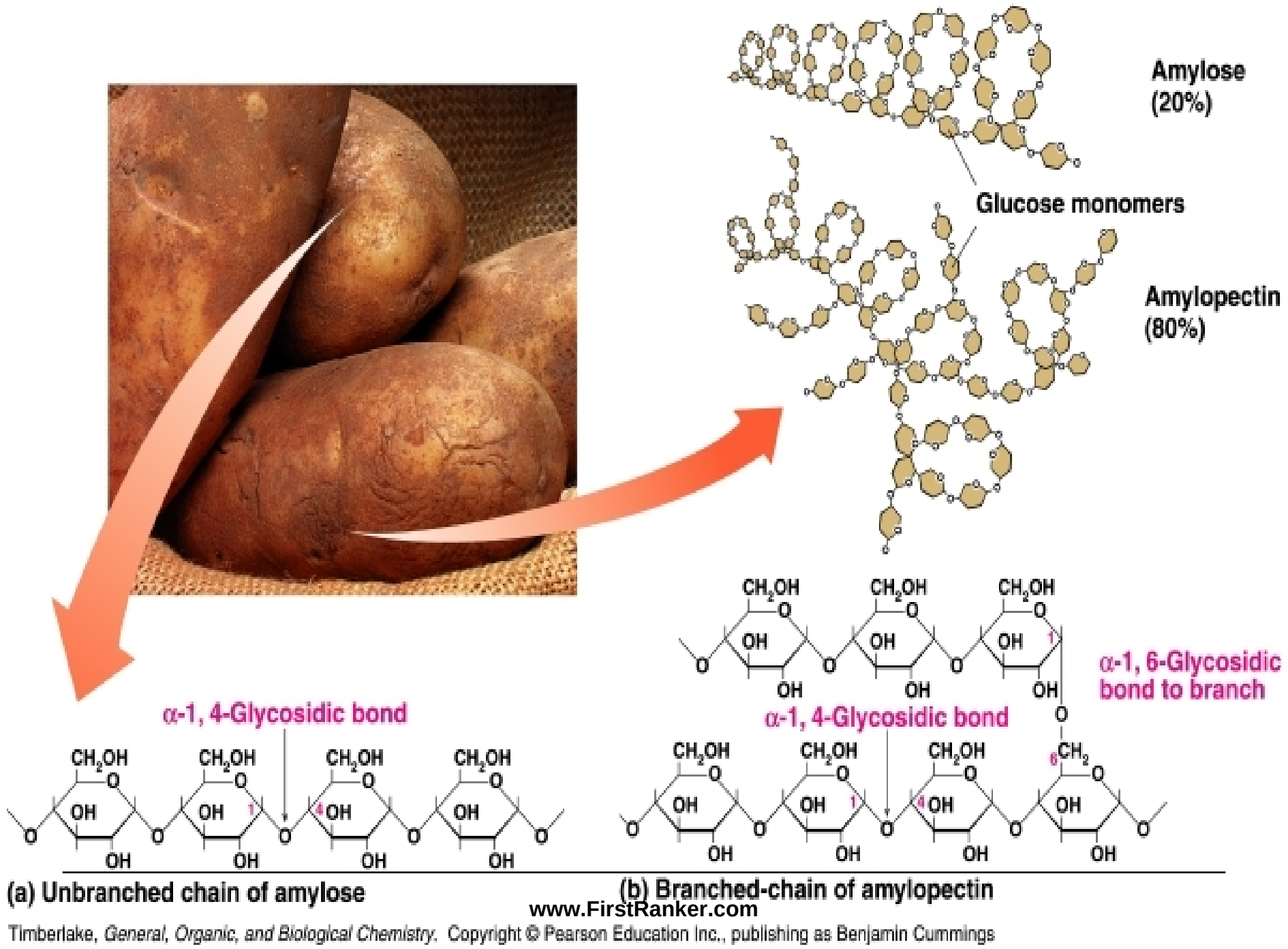
Amylose

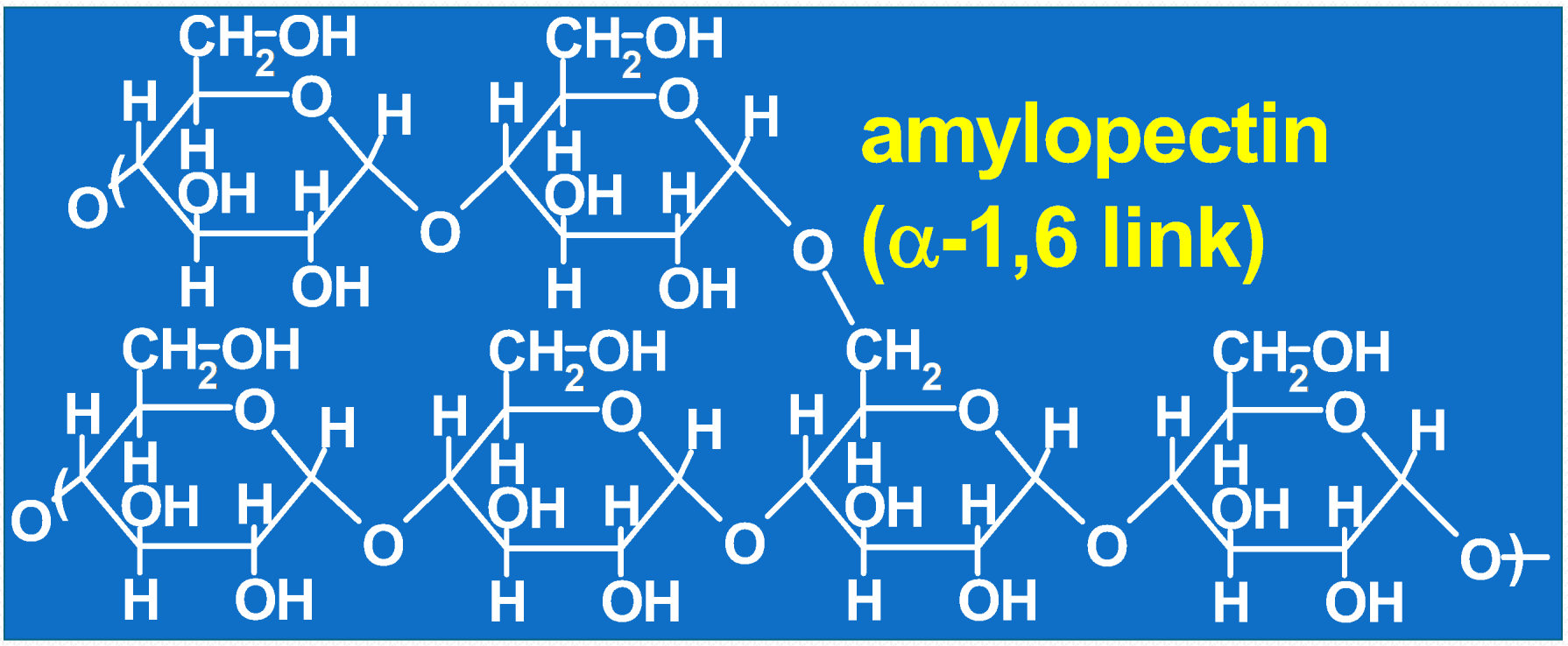
- Amylose is 15-20%
- Linear structure
- α D Glucose linked by α (1-4) glycosidic bond.



Amylopectin

- Amylopectin is 80-85 %
- Branched structure
- Branching point appears after every 25-30 Glucose units.
- It has α (1-6) glycosidic bond at branching point.
- α(1-4) glycosidic bonds in linear structure.





- Starch is white ,odourless, tasteless powder .
- Starch is **insoluble in cold** water, but get **solubilized on heating** and form gel /paste.
- Starch is **a non reducing** Carbohydrate.

Starch -Negative Benedicts Test.

- Starch on **Iodine reaction** gives **blue color.**

Source/Occurrence Of Starch

- Plants- Seeds, Tubers, Roots, Raw fruits.
- **Dietary Sources of Starch.**

- **Grains**- Rice ,Wheat, Jawar, Bajra
- Potatoes
- Beetroot.
- Sago (Tapioca)
- Vermicelli
- Suji.
- Raw Mangoes

Biomedical Importance Of Starch

- Starch is a **storage form** of **Glucose** and serves as reservoir of energy in **plants.**
- To humans Starch is a **predominant form** of dietary Carbohydrate ingested through foods which has **high dietary and calorific value.**

Digestion of Starch

- **In mouth-** by salivary **α Amylase**
- **In intestine -**by pancreatic **α Amylase**

- **α Amylase cleaves,** α (1-4) glycosidic bonds of Amylose and Amylopectin and releases **Maltose and Isomaltose.**

- **Maltose** and **Isomaltose** is then **digested by Maltase and Isomaltase** to release free Glucose units.

- Thus Starch on digestion gives **thousands of free Glucose units which have high calorific value.**

Glycogen

- Animal Homopolysaccharide
- Animal Starch

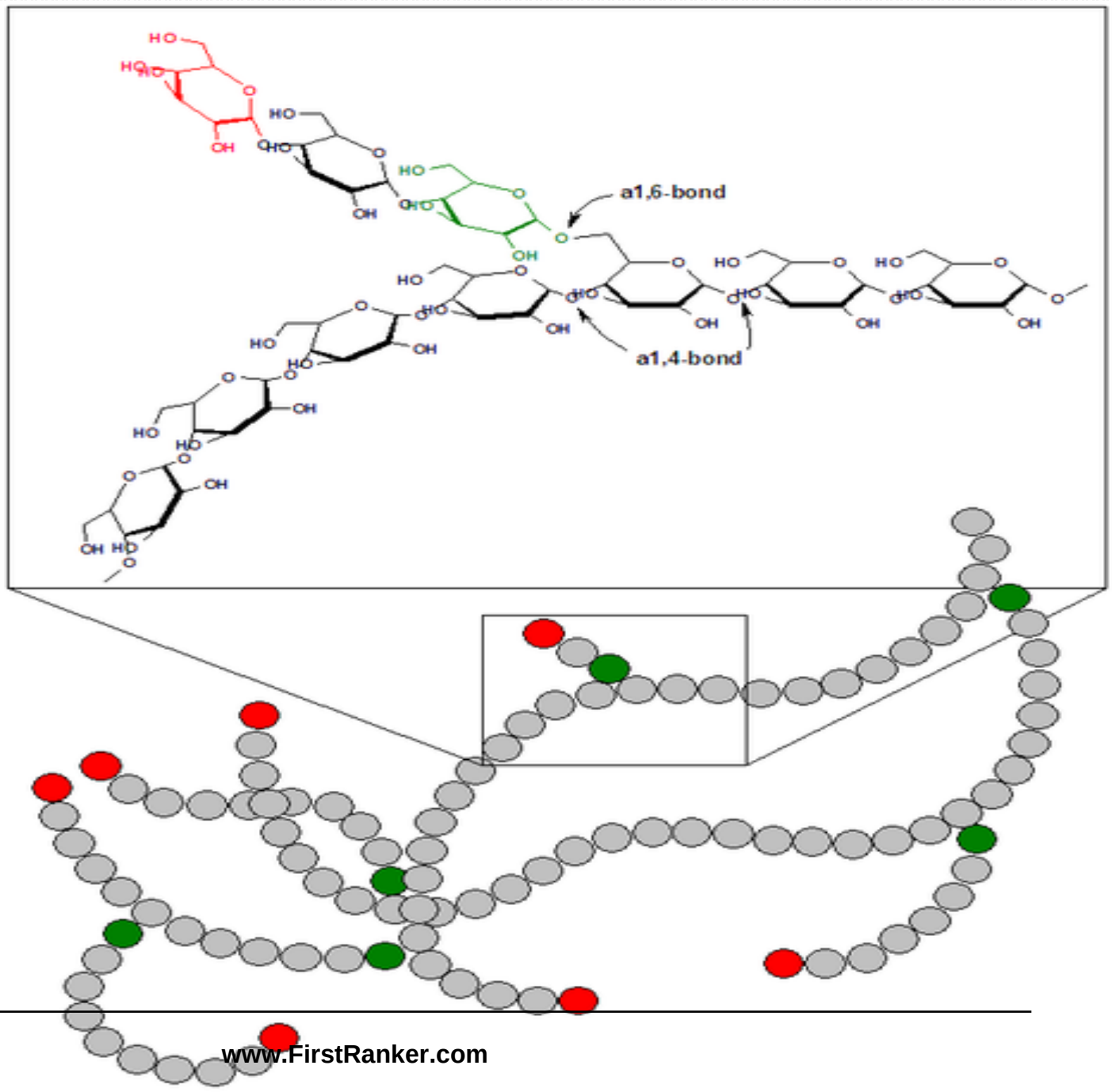
Chemistry Of Glycogen

- Glycogen is chemically Glucosan.

- **Repeating Unit –**
  α D Glucose (25-30 thousand Glucose units)

- **Glycogen** is like Amylopectin structure ,but it is **highly branched**
- **Branching points** appear after every **8-10 Glucose units**, linked by **α (1-6) glycosidic bond.**
- Linear structure has Glucose linked with **α (1-4) glycosidic bond.**

Glycogen



- Glycogen has **more** α(1→6) **branches**.

- The highly branched structure permits rapid glucose release from glycogen stores, in muscle during exercise.

Source/Occurrence Of Glycogen

- Glycogen is present in animal-
  - Liver (75 gm)
  - Muscle (125 gm).

- Non-Veg diet is a source of dietary Glycogen to human beings, which has high dietary and calorific value.

- After well fed condition, free and excess of Glucose is condensed to Glycogen via **Glycogenesis**.

- **Rate of Glycogen synthesis –**
  - **Liver- 6-8 %,**
  - **Muscle 1-2 %**

- Glycogen is broken down to Glucose via **Glycogenolysis** when body Glucose lowers in fasting and starvation condition.

Biomedical Importance Of Glycogen

- Glycogen is a **storage form of Glucose** in animal and human body after well fed conditions.

- It serves as reservoir of Glucose which can be used in emergency conditions
(Fasting /Between meals)

- Glucose stored in **polymeric/condensed** form **minimizes osmotic effects** and occupy **less space.**

- Glycogen produces **less osmotic pressure** and occupy **small space**.
- Glycogen is sparingly soluble in water.
- On **Iodine reaction Glycogen** gives **deep red color.**

- Dietary **Glycogen** in GIT is **digested** by **α- Amylase** to Maltose and Isomaltose and finally to thousands of Glucose Units.

- **Liver Glycogenolysis** in Human body **regulates Blood Glucose levels** in fasting condition.

- **Muscle Glycogenolysis** provides **energy** for **muscle activities** in fasting condition.

Cellulose

- Non digestible carbohydrate
- Cellulose serve as **dietary Fiber.**

Chemistry Of Cellulose

- **Cellulose is a Glucosan**
- **Repeating Unit -β D Glucose.**
  (approx 2,500- 14,000).

- Cellulose is a **linear ,unbranched** structure where **β D Glucose units** repeatedly linked by **β (1-4) glycosidic bonds**.

Source/Occurrence Of Cellulose

- Cellulose **is an abundant carbohydrate of nature** exclusively present in **Plants cell wall**.

- **Dietary rich sources of Cellulose**
- Whole Grains (outer covering)
- Green leafy vegetables
- Cabbage, Cucumber
- Legumes, Nuts, Beans
- Dates
- Fruits and Vegetable salads.

Biomedical Importance of Cellulose

- In **plants Cellulose** present in cell wall **provides structural and mechanical support.**

- Wood, cotton and paper are composed primarily of cellulose.

- In humans, **dietary Cellulose** is **not digested** and **absorbed.**
- Enzyme **Cellulase** is **absent** in **human GIT.**
- Cellulose has **no calorific value.**

- **Dietary Cellulose in humans serves as dietary fiber.**

Cellulose has Effect on Fecal Mass Formation

- Cellulose acts **as a roughage.**
- It holds water ,helps in **forming soft** and **bulky feces.**
- **Increases intra luminal pressure.**
- **Reduces transit time of feces to remain in gut.**
- **Eliminates daily, metabolic wastes and toxins** out of the body, through feces.
- **Defecation with greater ease and good frequency.**

- **Cellulose prevents constipation**, and **reduces risk of :**
  - colon cancer
  - varicose veins
  - diverticulosis of intestine
  - hemorrhoids

- Cellulose **reduces** the **absorption** of :
  - **Glucose**
  - **Cholesterol**
- Ameliorate the conditions of :
  - **Diabetes mellitus**
  - **Atherosclerosis** respectively.

- **Cellulose** being **non calorific** and possessing **high satiety value** helps in **managing obesity** in humans.

- For maintenance of good health ingest dietary fibers.

- RDA for dietary fiber to maintain good health:
  - **Adults= 20-25 gm/day.**
  - **Children's= 5-10 gm/day.**

- **Disadvantage** of dietary **Cellulose-**
- **It** decreases absorption of minerals.

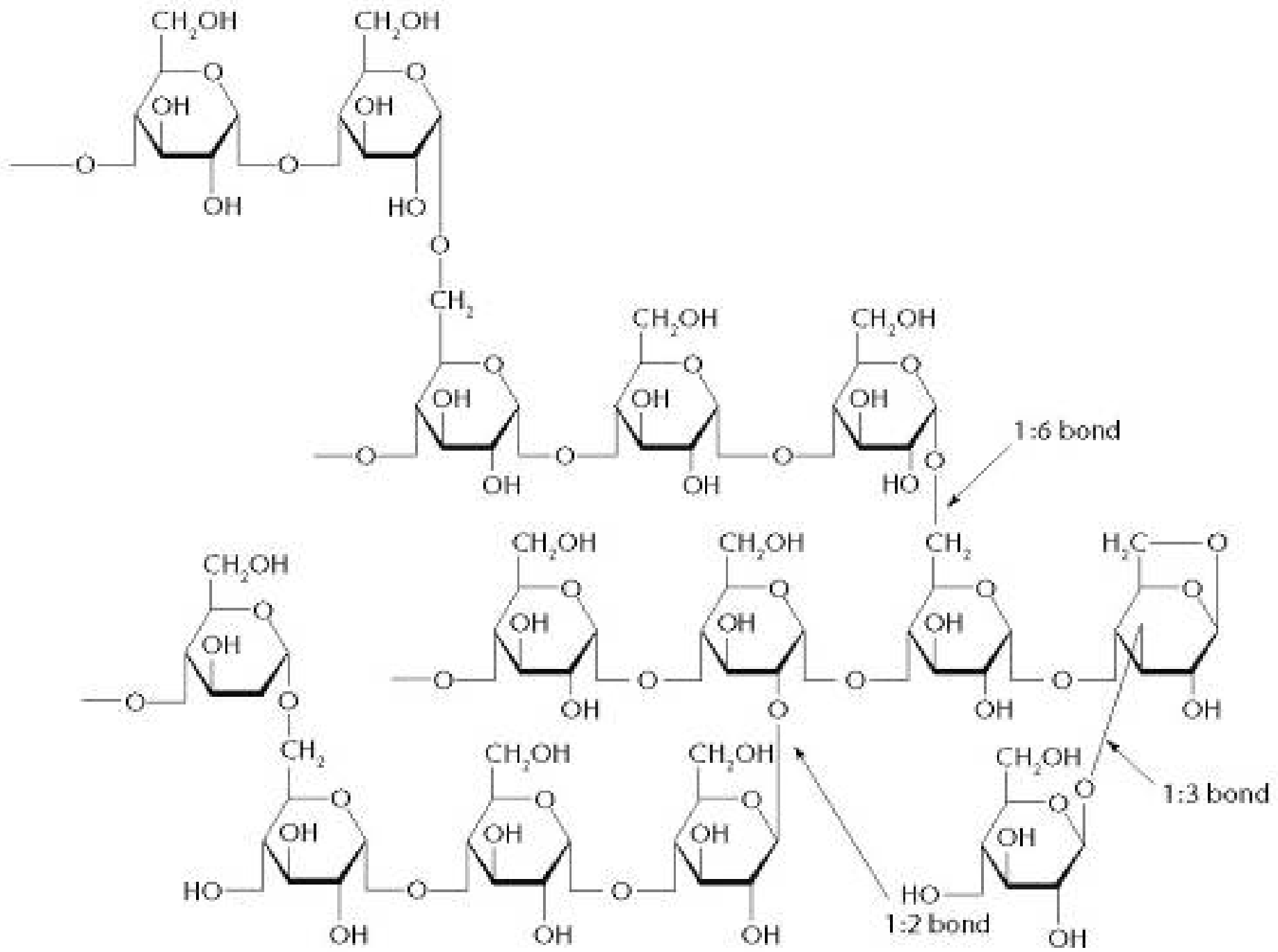
Dextrin

- Intermediate hydrolytic product of Starch digestion

Chemistry Of Dextrin

- **Dextrin is a Glucosan**
- **Repeating Unit** -α D Glucose.

- Dextrin is less complex than starch structure.
- Dextrin is broken Starch molecule.



Types Of Dextrin

- **Amylodextrin** -Violet to Iodine reaction
- **Erythrodextrin**- Red to Iodine reaction
- **Achrodextrin** -Colorless to Iodine reaction.

Source/Occurrence of Dextrin

- In human GIT **Dextrin** is obtained as an **intermediate hydrolytic product of Starch digestion** by the action of α-Amylase activity.

- Dextrin is Present in **commercially** prepared **infant foods**.

Biomedical Importance Of Dextrin

- Dextrin has **mucilage nature(sticky)** hence used as binding and **adhesive agent**.

- Dextrin is used as **infant food.**

Dextran

- Dextran is a Bacterial Homopolysaccharide

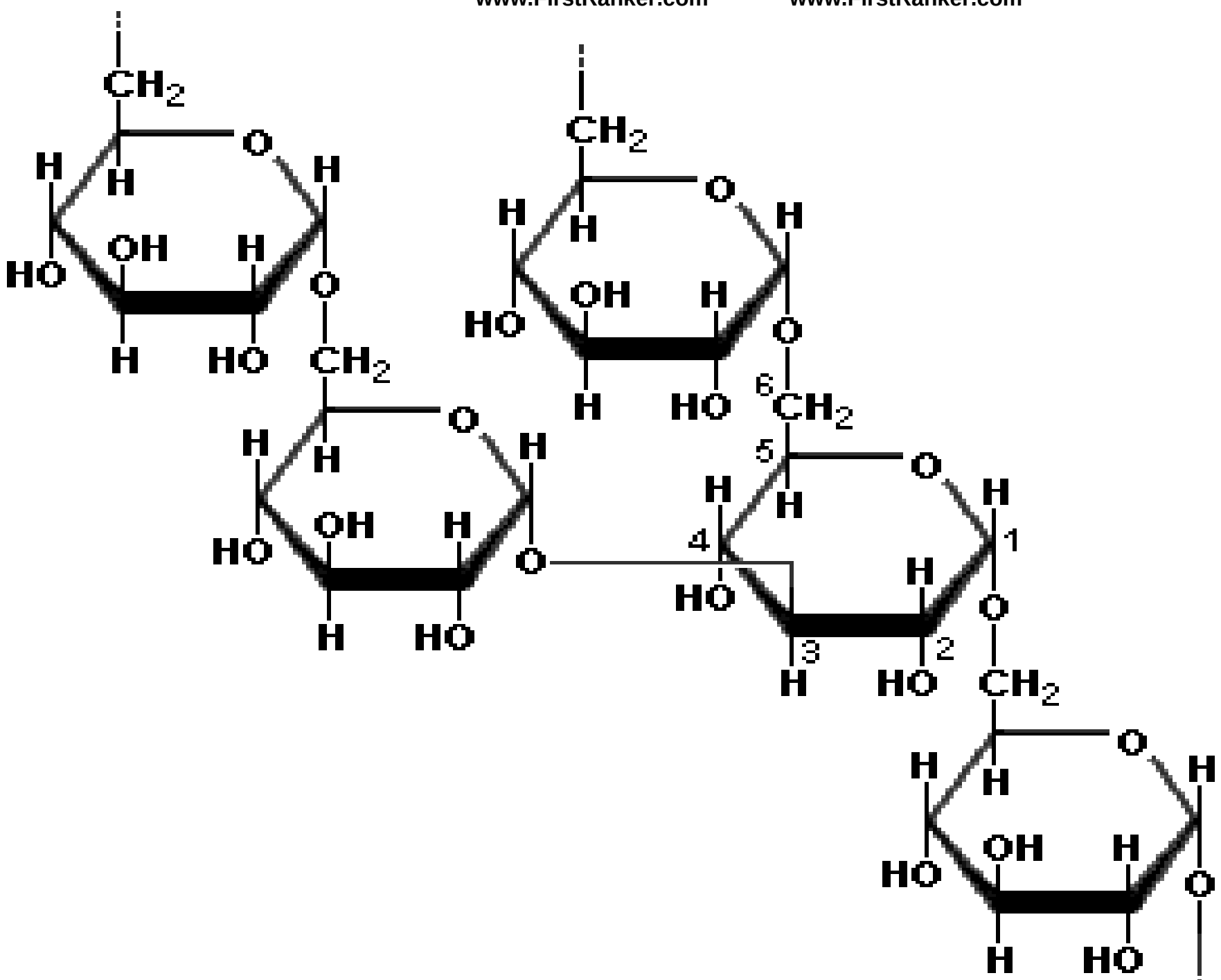
Chemistry Of Dextran

- **Dextran is a Glucosan**
- **Repeating Unit** –α D Glucose.

- Highly branched, complex, network like structure

  Glucose units linked **by**

  α(1-4) ,α(1-6) and α (1-3) glycosidic linkages.



Source/Occurrence Of Dextran

- Dextran is obtained from **Sucrose** solution incubated with bacteria **Leuconostoc mesenteroides**

Biomedical Importance Of Dextran

- Dextran solution is **high molecular weight**, **viscous** solution with **osmotic pressure** equivalent to **plasma Albumin.**

- Dextran **maintains blood volume** and **osmotic pressure.**

- **Dextran solution** is used as
- **Plasma substitute/plasma volume expander**
- Dextran infusion manages a **hemorrhagic case** and **prevent** from **hypovoluemic shock.**

Sephadex

- Sephadex is a **modified Dextran**.
- The dextran macromolecules are cross-linked to give a three-dimensional network of polysaccharide chains.
- Insoluble in water but absorb water and swell.
- **Uses:** In Chromatographic separation.

Fructosan

- Homopolysaccharide with repeating units as Fructose.

Inulin

- Diagnostic Carbohydrate
- **Diagnoses Kidney Function-** GFR of Kidney.

Chemistry Of Inulin

- **Inulin is a Fructosan**
- **Repeating Unit-**

  βD Fructose units (33-35 units)
- Repeatedly linked by

  β (1-2) glycosidic bonds.

Source/Occurrence Of Inulin

- Naturally present in Plants
  - **Roots and tubers of Dandelions**
  - **Onion and Garlic bulbs**
  - **Chicory Plant.**

Biomedical Importance Of Inulin

- Inulin is non digestible and non absorbable form in human GIT, hence have no calorific value.

- Inulin solution infused intravenously during **Inulin Clearance Test**, **checks Glomerular Filtration Rate** (GFR) of Kidney **(120-125 ml/min).**

Heteropolysaccharides

- Heteropolysaccharides are type of Polysaccharides composed of **more than 10 different**
- **Monosaccharide units or their derivatives** repeatedly linked by glycosidic bonds.

Animal Heteropolysaccharides

Mucopolysaccharides (MPS)

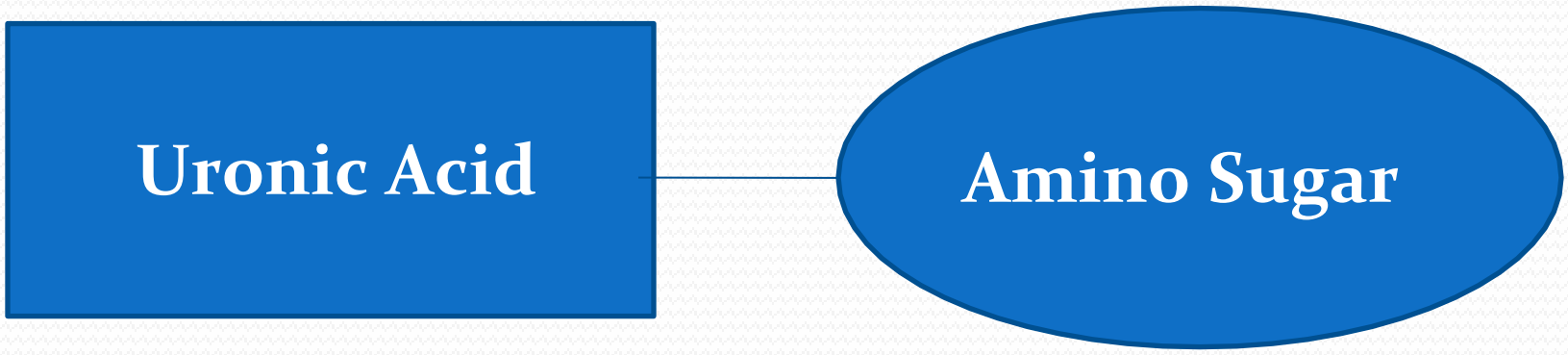
- **Human Heteropolysaccharides**
- **Animal Heteropolysaccharides**
- **Glycosaminoglycans (GAGs)**

- Mucopolysaccharides were first isolated from **Mucin** hence the name **Mucopolysaccharides.**

- Mucopolysaccharides chemically composed of more than 10 Monosaccharide units and its derivatives repeatedly linked by glycosidic bonds.

- Mucopolysaccharides are complex, long, linear, unbranched, polyanionic.

The Glycosaminoglycans has **Disaccharide repeating unit** linked by glycosidic bonds of



- **Uronic Acid –**
  Glucuronic acid /Iduronic acid
  (Iduronic acid is 5' Epimer of Glucuronic acid)

- **Amino Sugar-**
  Glucosamine / Galactosamine
  (Acetylated or Sulfated or Both)

- **Jeanloz** suggested the term **GAG's** as these biomolecules has **amino sugars as repeating units.**

Properties of GAG's

- GAG's are **polyanionic and acidic** due to presence of
  $-COO^-$ and SO_4^{--} -

- GAG's are **hydrophillic** and attract water and **helps in distributing water.**

- **MPS due to repulsion of charges:**
- It appear **slippery or sticky** in appearance/mucus like secretions
- It **expand to occupy large space.**

- MPS/GAG's imparts following **physical properties-**
  - **Turgor**
  - **High Viscosity**
  - **High Density**
  - **High Buoyancy.**

Body Mucopolysaccharides

- **Acidic Non Sulfated MPS:**
  - Hyaluronic Acid
- **Acidic Sulfated MPS:**
  - Heparin
  - Heparan Sulfate
  - Chondritin Sulfate
  - Dermatan Sulfate
  - Keratan Sulfate
- **Neutral MPS:**
  - Blood Group Substances

Hyaluronic Acid

- Acidic Non sulfated MPS
- **Repeating Disaccharide Unit**
  - **Glucuronic acid**
  - **NAcetylGlucosamine.**

Occurrence and Functions Of Hyaluronic acid

- Hyaluronic acid is present as **ground substance/cementing substance** in extra cellular spaces of connective tissue.

- Hyaluronic acid in **synovial fluid of joints** and **vitreous humor** of **eye** serve as lubricant and shock absorbant.

- Hyaluronic acid around ovum gives protection.

- Hyaluronic acid plays role in cell migration during morphogenesis.

- **Enzyme "Hyaluronidase "** hydrolyses Hyaluronic acid.
- **Hylauronidase** present in **head of sperm** , hydrolyzes the Hyaluronic acid present on ovum which **facilitates its penetration and fertilization.**
- **Snake venom** is **rich in Hyaluronidase**, thus snake bite hydrolyzes and liquifies the Hyaluronic acid present in extracellular spaces of cells **(TOXIN)**

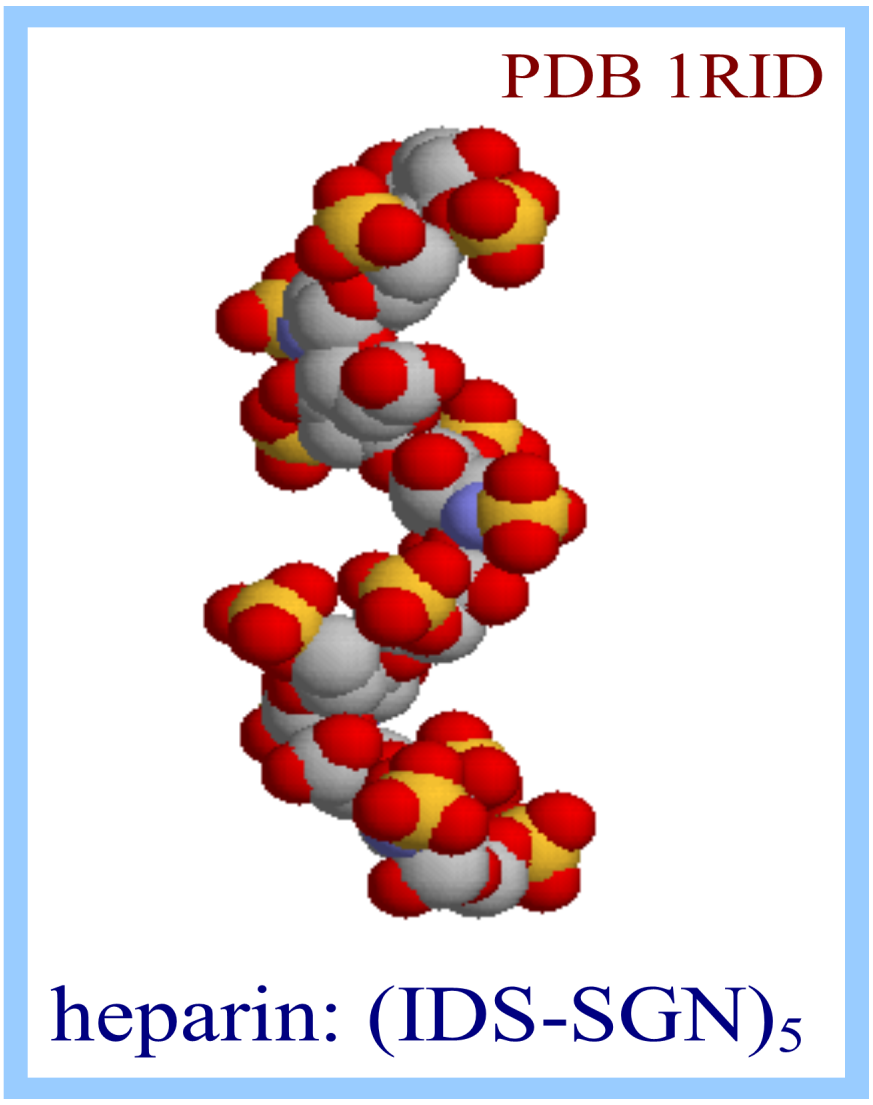
Heparin

- **Most Acidic Sulfated MPS.**

Disaccharide Repeating Unit:

- Glucuronate sulfate (minor)
- Iduronate sulfate (major)
- N-Glucosamine Sulfate.

- **Heparin**, a soluble glycosaminoglycan found in granules of mast cells and is **highly sulfated**.
- Heparin has an **extended helical conformation**.



Occurrence and Functions Of Heparin

- Heparin present in blood vessels, Liver, Lung, Spleen and Monocytes
- Heparin is a natural anticoagulant.
- Prevents intravascular blood coagulation by inactivating clotting factor IX and XI.

- When released into the blood, it **inhibits clot formation** by interacting with the protein antithrombin.

- Heparin is an indirect Thrombin inhibitor .
- Rapid inactivator of Thrombin.
- Thus antithrombotic agent.
- Prevents intravascular blood clotting.

- Heparin releases enzyme Lipoprotein Lipase from endothelial lining and serve as coenzyme for it.

- Lipoprotein Lipase is Lipid clearing Enzyme of blood.

Therapeutic Use of Heparin

- Heparin is infused to **prevent and treat** thrombous located in vein/artery in MI cases.
- Deep Vein Thrombosis.
- Pulmonary Embolism
- Strokes

- Heparin(LMW Heparin) injections are given to M.I patients
- To liquify blood ,prevent thrombosis and clear blood with lipids.

Heparan Sulfate

- Acidic Sulfated Mucopolysaccharide

- **Disaccharide repeating units**
- Glucuronate Sulfate (major)/ Iduronate Sulfate (minor)-N Acetyl Glucosamine

Occurrence and Functions Of Heparan Sulfate

- **Heparan Sulfate** present on extracellular **cell surfaces** or **plasma membranes** and serves as **receptors**
- **Participate in cell growth, cell adhesion, and cell -cell communication.**

- Heparan sulfate in basement membrane of kidney helps in determining **charge selectiveness of Glomerular filtration.**
- Heparan sulfate are also components of aorta, liver, fibroblasts, synaptic and vesicles.

Chondritin Sulfate

Acidic Sulfated Mucopolysaccharide

- **Disaccharide Repeating Unit**
- Glucuronate-
- N –Acetyl Galactosamine –Sulfated.

- **Chondritin Sulfate A-**4 sulfated.

- **Chondritin sulfate C-**6 sulfated.

Occurrence and Functions Of Chondritin Sulfate

- Chondritin Sulfate is present in connective tissues-bones, cartilage, tendons .
- It gives mechanical strength, compressibility and support to connective tissues.

- Chondritin sulfate present in **cornea** give over all **shape to eye**.

Dermatan Sulfate

- Acidic Sulfated Mucopolysaccharide.
- **Chondritin sulfate-B / β-Heparin**
- **Disaccharide Repeating Unit**
- L-Iduronate-
- N-AcetylGalactosamine-sulfated

Occurrence and Functions Of Dermatan Sulfate

- Dermatan sulfate especially present in skin, blood vessels and heart valves gives mechanical strength and structural support to these tissues.

- Dermatan sulfate **plays structural role in sclera of eye.**

Keratan Sulfate

- Acidic Sulfated Mucopolysaccharide

- **Keratan Sulfate** is a MPS **without Uronic acid** instead contains Galactose.

- **Disaccharide Repeating Unit**
- Galactose-N-Acetyl Glucosamine –sulfated

- Keratan sulfate present in cartilage, aorta walls, gives structural supports and mechanical strength.

- **Keratan sulfate** present in cornea and lens of eye has **role in lens transparency and shape of eye.**

Blood Group Substances

- Blood group substances are Neutral MPS

- **Components of Blood Group substances**

- Galactose, Fucose,
- N-Acetyl Glucosamine, N-Acetyl Galactosimne

- Blood group substances neutral MPS, present on cell surfaces of Erythrocytes serves as blood group antigens.

Applied aspects of Mucopolysaccharides/ GAGs

- On ageing or during pathogenesis the biosynthesis of certain specific Mucopolysaccharide /Glycosaminoglycan is either increased or decreased leading to disorders and manifestations.

- **Tumors cells-**
- **Increased Hyaluronic acid** (Increases cell migration)
- **Decreased Heparan Sulfate** (Decreases cell adhesion)
- **This Increases Metastasis**

- **Rheumatic Arthritis-**
- Rheumatic nodule shows increased Hyaluronic acid deposition.

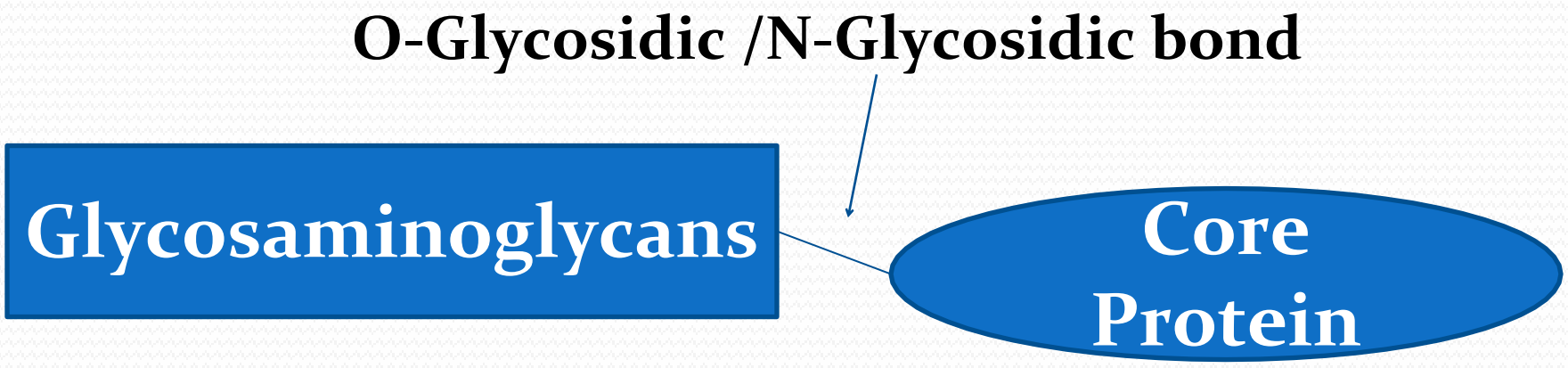
- **Atherosclerotic plaque-**
- Excess production of Dermatan Sulfate
- Decreased production of heparin.

- **Osteoarthritis-**
- Imbalance biosynthesis of Hyaluronic acid, Chondritin Sulfate and Keratan Sulfate

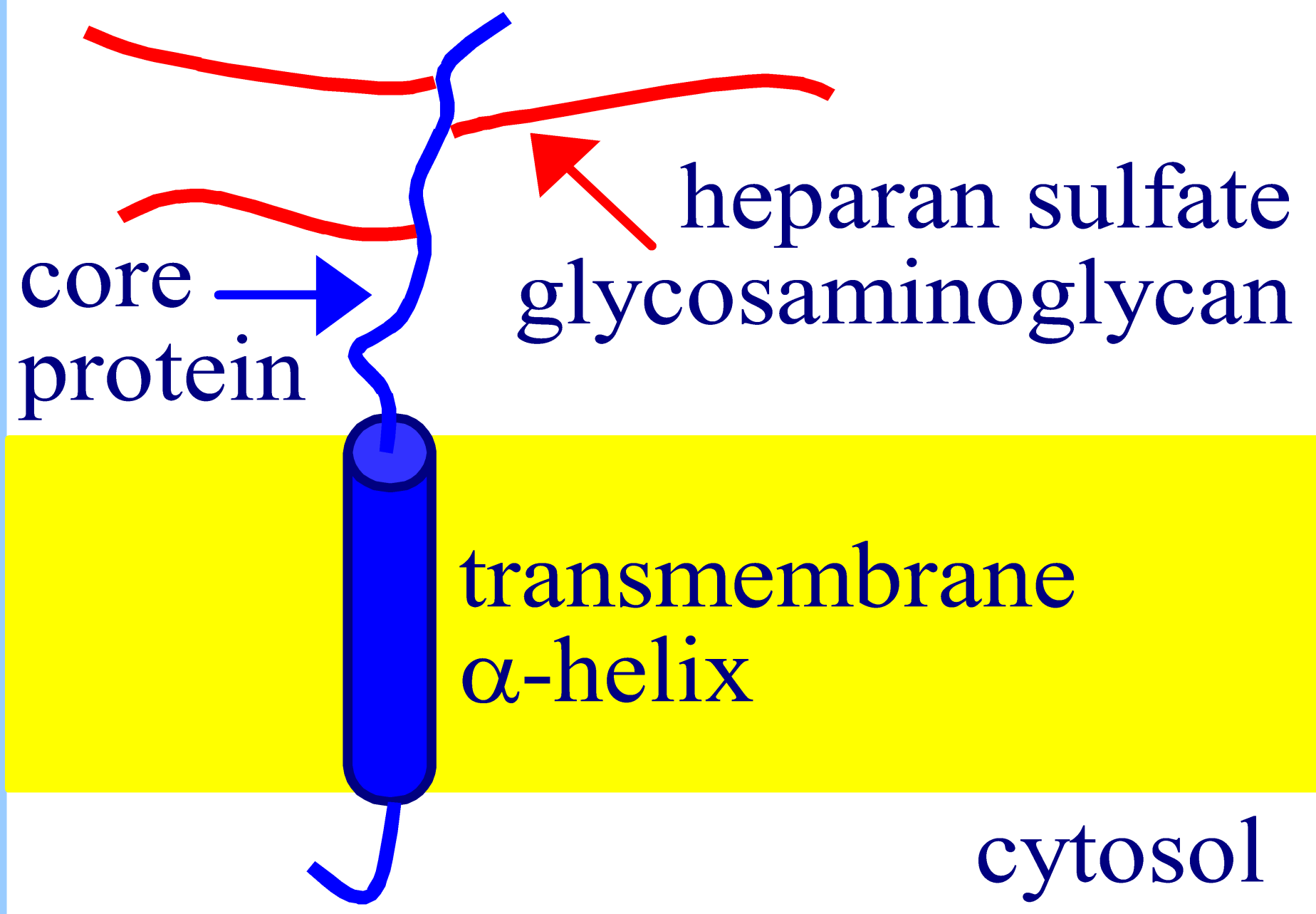
Mucoproteins Or Proteoglycans

- Mucoproteins/ Proteoglycans are conjugated Proteins.

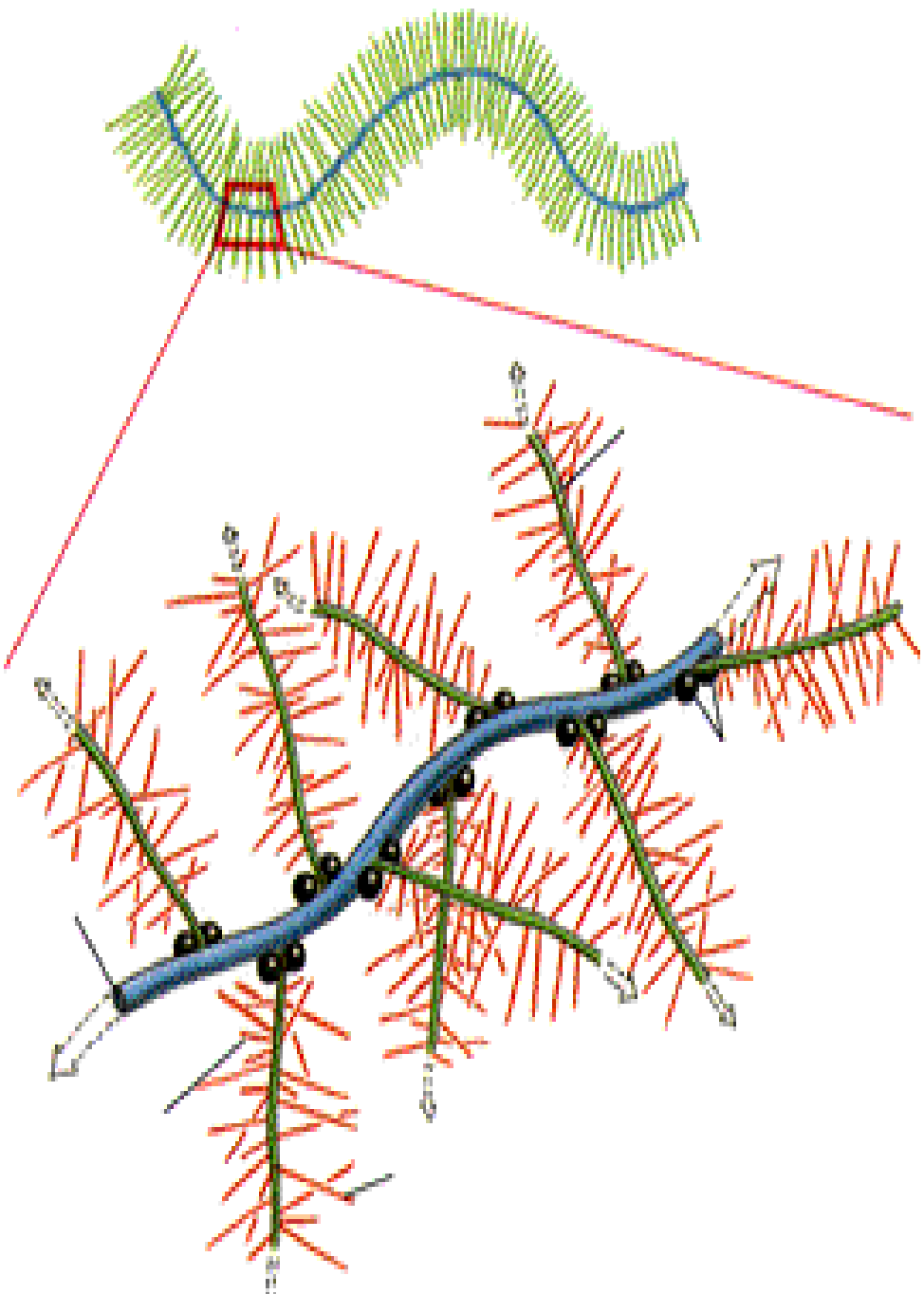
- **Mucopolysaccharides/ Glycosaminoglycans (Prosthetic group)** are never found free but always covalently linked to a **core protein** by N-Glycosidic/O-Glycosidic bond to formMucoproteins/Proteoglycan

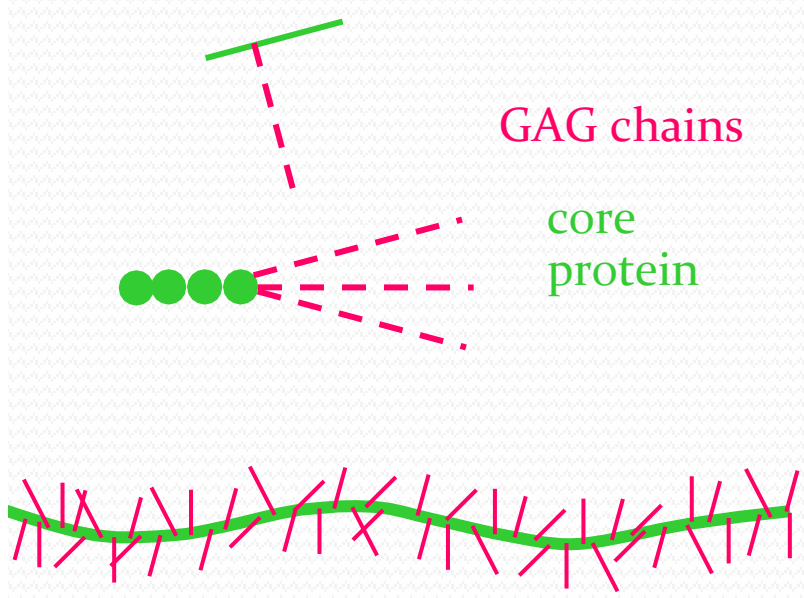


- **Mucoproteins have** Carbohydrate content **more than 10 %** and are viscous in nature.

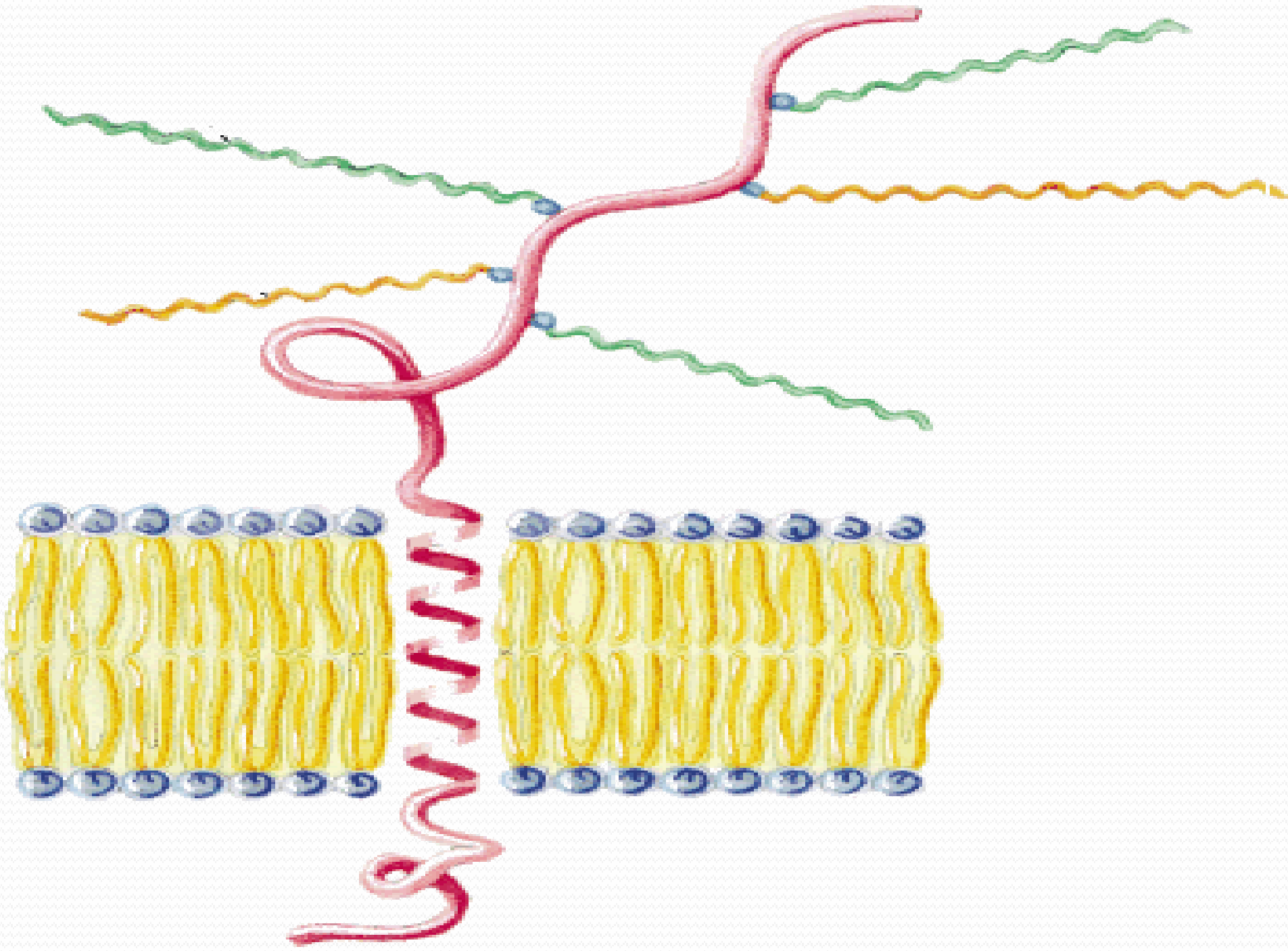


- **Mucoproteins/ Proteoglycans** are more complex, viscous, highly dense, molecular aggregates.





- Proteoglycans are composed of as many as 200 GAG chains covalently bonded to a core protein via Serine/ Threonine side chains.



- Molecular weight range: 10^5 – 10^7 Daltons.
- GAG chains linked:
- Hyaluronic acid
- Chondroitin sulfate
- Heparan sulfate
- Dermatan sulfate
- Keratan sulfate

Examples of Proteoglycans

- Aggrecan
  (Hyaluronate-Core Protein non covalently linked In Cartilage)
- Biglycan
- Beta Glycan
- Decorin
- Serglycin
- Syndecan
- Perlecan
- Versican

- Mucoproteins has properties like of Mucopolysaccharides.
- Mucoproteins widely distributed in **Extracellular Matrix of connective tissues** (Bone and Cartilage).
- Mucoproteins **provide structural framework** and **mechanical support** to those tissues which constitute them.

Mucopolysaccharidoses

- **Mucopolysaccharidoses** are group of inherited disorders related to defective Mucopolysaccharide metabolism.
- **Cause**:

  Impaired degradation of GAG's by defective **Lysosomal enzymes.**

- Half life period of GAG's is short.
- 3-10 days for most of the GAG's.
- 120 days for Keratan –SO_4.

- **Biochemical Alterations :**
- No catabolism of GAG's.
- Abnormal widespread intra Lysosomal deposition of GAG's in functional tissues affecting their functions.
- Excretion of MPS in Urine.

Mucopolysaccharidoses Type	Syndrome	Enzyme Defect (Lysosomal)	Accumulated GAG
I	**Hurler's Syndrome**	α- L Iduronidase	DS, HS
II	**Hunters' Syndrome**	Iduronate Sulphatase	DS , HS
III	**Sanfilippo's Syndrome**	Heparan Sulphatase	HS
IV	**Morquio's Syndrome**	Galactosamine Sulphatase.	KS, CS
V	**Scheie's Syndrome**	L- Iduronidase	DS
VI	**Maroteaux Lamy Syndrome**	N-AcetylGalactosamine -4-sulphatase.	DS
VII	**SLY's**	β- Glucuronidase.	DS, HS
IX	**Naowicz Syndrome**	Hyaluronidase	HA

- **All** Mucopolysaccharidoses are of **autosomal recessive inheritance.**

- **Hunter's Syndrome** is of **X linked inheritance.**

- **Consequences /Clinical Manifestations:**

- Lysosomal vesicles become swollen with incomplete degraded GAG's in it.
- Coarse facial features.
- Thick skin, skeletal damage.
- Corneal Opacity, Hearing loss.
- Mental Retardation.
- Hepatosplenomegaly.
- Cardio pulmonary defects.
- Growth deficiency and skeletal dysplasia.

- **Diagnosis:**

- Measuring concentration of **Lysosomal Hydrolases.**

- Detection of **GAG in Urine**.

Plant Heteropolysaccharides

Agar-Agar

- Agar is obtained from red algae.(Sea weed)
- Agar is formed of two main components, Agarose and Agaropectin.
- Agarose is a neutral galactose polymer, free from sulfate.
- Agaropectin is formed of galactose and galacturonic acid units partially esterified with sulfuric acid.

Uses of Agar

- Preparation of **bacteriological culture media.**
- **Emulsifier**, thickener for **ice creams,puddings.**
- **Laxative**-for treatment of ulcers and chronic constipation.

Pectin

- Obtained from **apple pomace** and inner portion of **citrus rind**.
- Form viscous solutions in water.
- Composed of **Arabinose, Galactose** and **Galactouronic acid.**
- Average molecular weight 100,000-250,000.

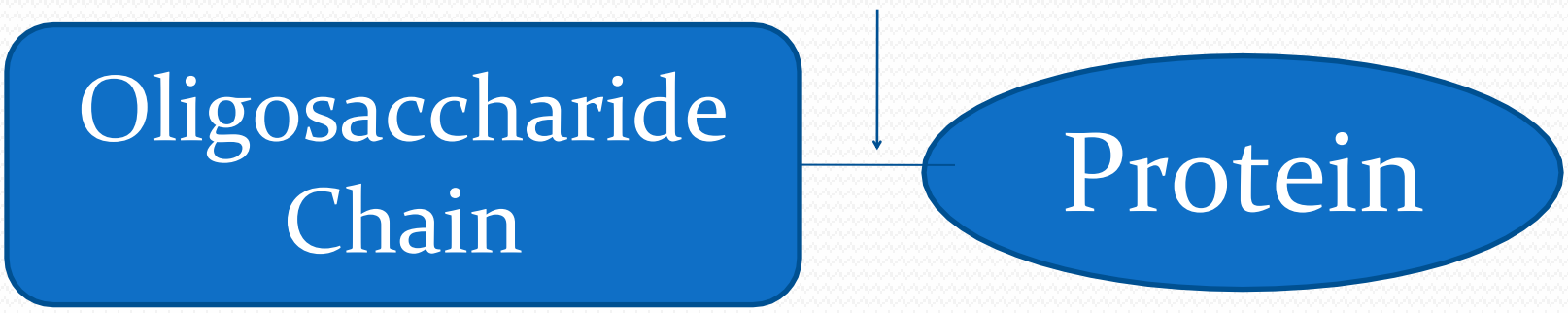
Uses Of Pectin

- Pectin is **topically applied** as a paste in cases of **burns and ulcers.**
- It acts as a **detoxifying agent** by conjugation with toxins.
- It is of great importance in **treatment of diarrhea and dysentery.**
- It is used as a **gel and emulsion** stabilizer and in **manufacture of jellies and jams.**

Glycoproteins

- Glycoproteins are **conjugated proteins**
- Where the prosthetic group, branched or unbranched chain of Oligosaccharide
- Is linked to a protein backbone with **O-Glycosidic** or **N-Glycosidic linkage**.

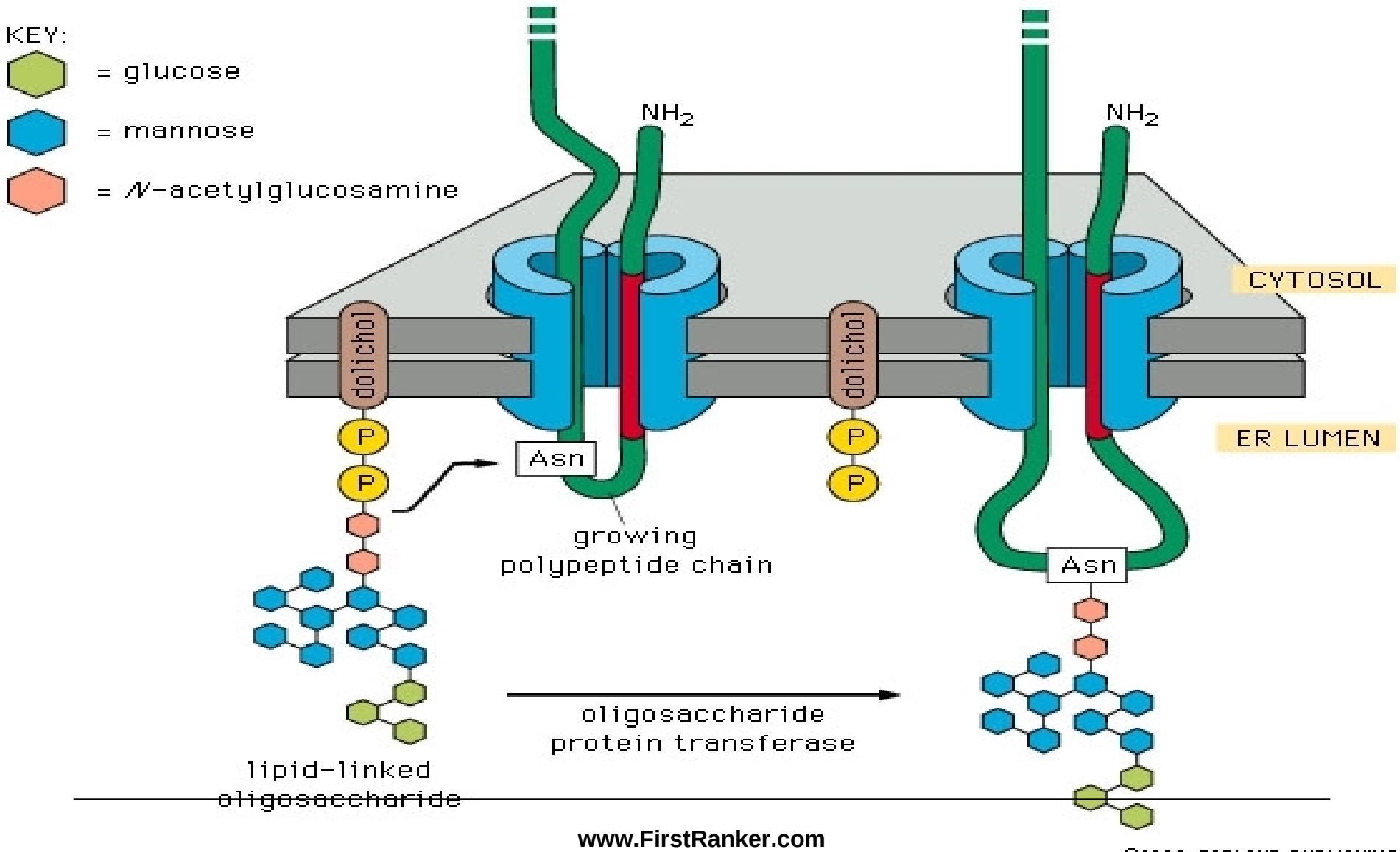
O-Glycosidic/N-Glycosidic bonds



- Carbohydrate content of Glycoprotein is less than 10%.

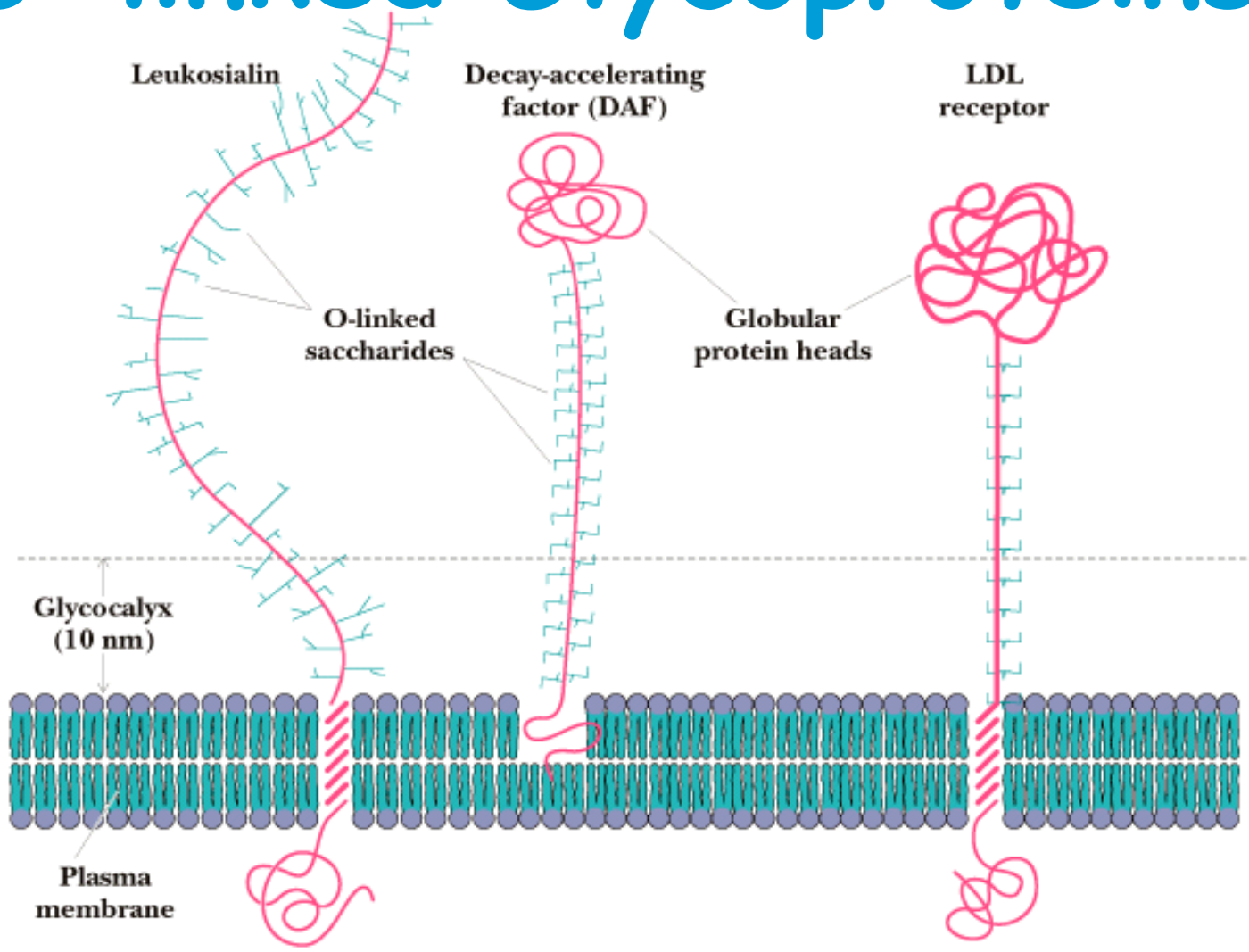
- N-linked saccharides are attached via the **amide nitrogens of Asparagine residues .**
- O-linked saccharides are attached to **hydroxyl groups of Serine, Threonine or hydroxy Lysine .**

N-linked Glycoproteins



O-linked Glycoproteins

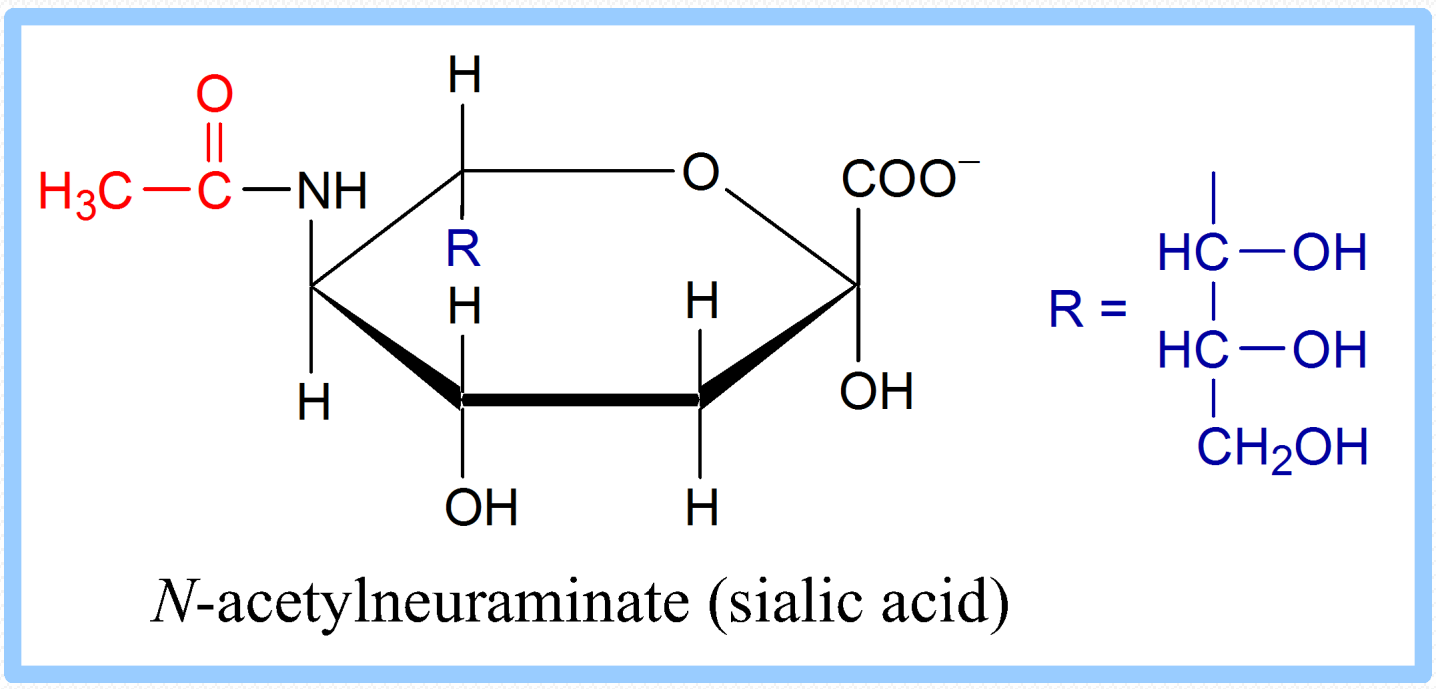
Garrett & Grisham: Biochemistry, 2/e
Figure 9.27



- Oligosaccharides have
- different sequences of monosaccharide units
- different sequences of glycosidic linkages.
- different kinds of branching.

- This imparts a very high degree of diversity for Oligosaccharides and their structure-function relationships

- **Varied glycosidic linkages** in Oligosaccharide chain of Glycoproteins create **enormous variability** required for identifying different cells.
- This variation is the basis for the mechanism of **cell-cell recognition.**



N-acetylneuraminate (sialic acid)

N-acetylneuraminate (N-acetylneuraminic acid, also called sialic acid) is often found as a terminal residue of oligosaccharide chains of glycoproteins.

Sialic acid imparts negative charge to glycoproteins, because its carboxyl group tends to ~~dissociate a proton at physiological pH, as shown~~ here.

- **Significance of Oligosaccharide chains in Glycoproteins :**
- **Stabilizes** the Proteins against denaturation.
- Protect Proteins from **Proteolytic degradation.**
- Enhances the solubility.
- Serve as a recognition signals to facilitate **cell-cell interaction.**

Glycoproteins of human body:

- All **plasma proteins** are Glycoproteins.
- Structural **protein Collagen** of bone is glycoprotein.
- **Enzymes**- Ribonuclease-B, Alkaline Phosphatase.

- Hormonal receptors on cell membranes.
- **Glycophorin** is a major integral membrane Glycoprotein of RBC's.
- Lubricant **Mucin.**
- Proteins-**Transferrin** and Ceruloplasmin are Glycoproteins.

- Glycoproteins and Glycolipids are Glycocalyx of cell membranes.
- Clotting factor-**Prothrombin**.
- Hormones-**Thyroglobulin**, Erythropoietin, TSH, HCG.
- **Immunoglobulin**- IgG, IgA, IgD, IgE, IgM.

Biomedical Importance's of Carbohydrates.

- **Energy Aspects of Carbohydrates/Carbohydrates have dietary and calorific value**

Carbohydrates serve as primary source of energy, with calorific value 4Cal/gm.

Carbohydrates of Dietary and Calorific value

- Starch **(Predominant-Grains, Potatoes, Vegetables)**
- Glycogen (Non Veg diet)
- Sucrose (Common table Sugar)
- Lactose (Milk and Milk Products)
- Maltose (Starch digestion, Malt)
- Glucose (Glucon-D, Fruits)
- Fructose (Fruits, Honey)

- **Reserve Store Capacity Of Carbohydrates:**

  Dietary Carbohydrate (Glucose) when free and excess in the body get transformed to reserve store forms Glycogen and Triacylglycerol (Fat), which are utilized during emergency conditions.

- **Non digestible Carbohydrate- Cellulose serves as dietary fiber :**
- Cellulose act as roughage and prevents from constipation.
- Cellulose has no calorific value hence help in management of obesity.

Carbohydrates as Dietary Fiber

- **Cellulose**
- **Pectin**
- **Lignin**
- **Agar**
- **Gum**
- **Hemicellulose**

- **Carbohydrates are components of**
- Mucoproteins
- Glycoproteins
- Glycolipids
- Blood Group Substances

- **Structural and other functional roles of Carbohydrates :**
- **Mucoproteins** present in connective tissues provide **structural and mechanical support.**
- **Hyaluronic acid** in synovial fluid of **joints** and vitreous humor of **eye** serve as **lubricant and shock absorbent.**

- Heparin serves as natural anticoagulant and prevents intravascular coagulation.

- **Heparan sulfate** present on cell surfaces act as recognition elements on cell membrane ,**cell receptors** and helps in **cell growth, cell adhesion, and cell-cell communication.**

- Pentose sugars **Ribose** and **Deoxyribose** are **components** of Nucleotides which build Nucleic acids – **RNA** and **DNA** and other **nucleotide coenzymes.**

Diagnostic Value of Carbohydrate:

- Fructosan **Inulin**, is used to carry out:
- **Inulin Clearance Test**, which checks, Glomerular Filtration Rate of kidney.

Therapeutic Value of Carbohydrates:

- **Cardiac Glycosides Digoxin**- used to treat cardiac insufficiency.
- **Glycosides Ovabain and Phlorizin** - used in treatment of Diabetes mellitus.
- **Glycosides Streptomycin ,Erythromycin** used to treat bacterial infections.
- **Mannitol**- Serve as osmotic diuretic used in treatment of Acute Renal Failure.
- **Lactulose** -Relives Hyperammonaemia in patients of Hepato Encephalopathy.
- **Dextran**- Used as plasma substitute in hemorrhagic cases to prevent hypovoluemic shock.
- **Hyaluronan**- Used to treat osteoarthritis.

Sr.No	Reducing Sugars	Non Reducing Sugars
1.	Reducing sugars **possess free or potential aldehyde** or **ketone group** in it's structure	Non reducing sugars **does not possess free or potential aldehyde or ketone group** in it's structure
2.	Reducing sugars **show reducing property** .It form an Enediol in alkaline medium which then **reduces certain metallic ions of copper, bismuth**	Non Reducing Sugars **does not show reducing property.**
3.	Reducing Sugars answers following tests **positively- Benedicts, Fehlings, Nylanders, Osazone Tests**	Non Reducing Sugars answers following tests **negatively- Benedicts, Fehlings, Nylanders, Osazone Tests**
4.	Reducing sugars **exhibit Mutarotation**	Non Reducing sugars **does not show Mutarotation**
5.	Examples of Reducing Sugars - All Monosaccharide's are Reducing Sugars- ex Ribose, Glucose, Fructose etc Reducing Disaccharides-Lactose, Maltose	Examples of Non Reducing Sugars or Non reducing Disaccharide- Sucrose, Trehalose.

Sr. No	Amylose	Amylopectin
1.	Starch granule contains 15-20% of Amylose.	Starch granule has 80-85% of Amylopectin.
2.	Amylose is soluble and present in inner core of starch granule.	Amylopectin is insoluble part present at periphery of starch granule.
3.	Amylose is a linear, unbranched structure composed of 200-1000 α D Glucose units repeatedly linked by α (1-4) glycosidic bonds	Amylopectin is a branched structure, composed of more than 1000 α D Glucose units linked by α (1-4) glycosidic bond in linear and α (1-6) glycosidic bond at branching point, which appears after every 25-30 Glucose residues.
4.	Molecular weight of Amylose is 400000	Molecular weight of Amylopectin is 1 million .
5.	Amylose gives blue color with Iodine test.	Amylopectin gives reddish violet color with Iodine test.

Sr. No	Starch	Glycogen
1.	Starch is Plant Homopolysaccharide.	Glycogen is animal Homopolysaccharide
2.	Starch is composed of **Amylose** (Linear)&**Amylopectin** (Branched)	Glycogen is highly branched structure with branching points appearing after every 8-10 Glucose residues.
3.	Starch is composed of 4000-7000 Glucose units.	Glycogen is composed of 6000-30,000 Glucose units.
4.	Starch is a storage form of Glucose and reserve food material in plants.	Glycogen is storage form of Glucose and reserve form of energy in animals and human beings.
5.	Starch is stored in roots, tubers, seeds, raw fruits of plants.	Glycogen is stored in Liver and Muscles of animal and human body.
6.	Starch serves as predominant dietary Carbohydrate form in Veg and Nonveg eaters.	Glycogen is dietary form of Carbohydrate only in Non-Veg eaters**.**
7.	Starch with Iodine test gives deep Blue color.	Glycogen with Iodine test gives deep red color.

Sr.No	Starch	Cellulose
1.	Starch is a Glucosan composed of α DGlucose units, repeatedly linked by α (1-4) glycosidic bonds in linear and α (1-6) glycosidic bonds at branching point.	Cellulose is a Glucosan composed of β DGlucose units ,repeatedly linked by β (1-4) glycosidic bonds.
2.	Starch present in plants serve as storage form of Glucose and reserve food material.	Cellulose present in plant cell wall provides structural frame work to plants.
3.	Dietary Starch is digested in human GIT by enzyme α Amylase.	Dietary Cellulose is not digested in human GIT due to absence of enzyme Cellulase.
4.	Starch has dietary and calorific value.	Cellulose has no calorific value but serve as dietary fiber.

Sr.No	Dextrin	Dextran
1.	Dextrin is plant Homopolysaccharide	Dextran is bacterial Homopolysaccharide.
2.	Dextrin is an intermediary hydrolytic product of Starch digestion.	Dextran is a Glucosan obtained from Sucrose solution incubated with Leuconostoc mesenteroides.
3.	Structure of Dextrin contains α (1-4) & α (1-6) glycosidic bonds.	Structure of Dextran contains α (1-3), α (1-4) & α(1-6) glycosidic bonds.
4.	Dextrin solution is used in commercially prepared infant feedings and mucilage for pasting stamps.	Dextran solution is used as plasma volume expander in relieving hypovoluemic shock in cases of hemorrhage.

QUESTIONS

- Q.1.Define carbohydrates.

  Enumerate the biomedically important Carbohydrates.
- Q.2.Classify and sub classify Carbohydrates with terms and suitable examples.
- Q.3. Simple Sugars /Monosaccharides

- Q.4. Define stereoisomerism. Enumerate the stereoisomers of Glucose.
- Q.5. D & L Glucose
- Q.6. Anomers
- Q.7. Epimers

- Q.8. What is optical activity? Give its type.
- Q.9. Mutarotaion
- Q.10. Chemical Reactions of Glucose /Reactions of Monosaccharides.
- Q.11. Write 8 derivatives of Monosaccharides and their importance.
- Q.12. Glycosides and its importance.
- Q.13. Osazones Reaction. Draw the structures of Glucosazone, Fructosazone, Lactosazone & Maltosazone.
- Q.14. Explain why Glucosazone & Fructosazone show same shape.

- Q.15. Disaccharides (Definition, Types, Components, Glycosidic bonds, Sources ,Biomedical Importances).
- Q.16. Invert sugar,
- Q.17. Lobry- de- Bruyn- Von Ekenstein transformation

- Q.18. Haworth and Fischer's projection of Glucose.
- Q.19. Why sucrose is a non-reducing sugar?
- Q.20. Homoglycans / Homopolysaccharides
- Q.21. Glycosaminoglycans /Acid Mucopolysaccharides (structure & function)/Animal Heteropolysaccharides
- Q.22. Inulin and its importance.

- Q.23. Differences between Dextrin and Dextran.
- Q.24. Cellulose & its importance.
- Q.25. Distinguish between reducing & non-reducing sugars.

- Q.26. Write the components and glycosidic linkages involved in following carbohydrates.
  - Sucrose
  - Maltose
  - Lactose
  - Glycogen
  - Cellulose
  - Amylose
  - Amylopectin

- Q.27. Mucoproteins.
- Q.29. Biomedical Importance of carbohydrates.
- Q.30. Mucic acid test.
- Q.31. Test's to check the present of reducing sugars.
- Q.32. Glycosidic bonds.

- Q.33. Glycoproteins of human body.
- Q.34. Differentiate between Starch and Cellulose.
- Q.35 Differentiate between Starch and Glycogen.
- Q.36 Mucopolysaccharidoses.
- Q.37 Diagnostic and therapeutic uses of Carbohydrates.

THANK YOU