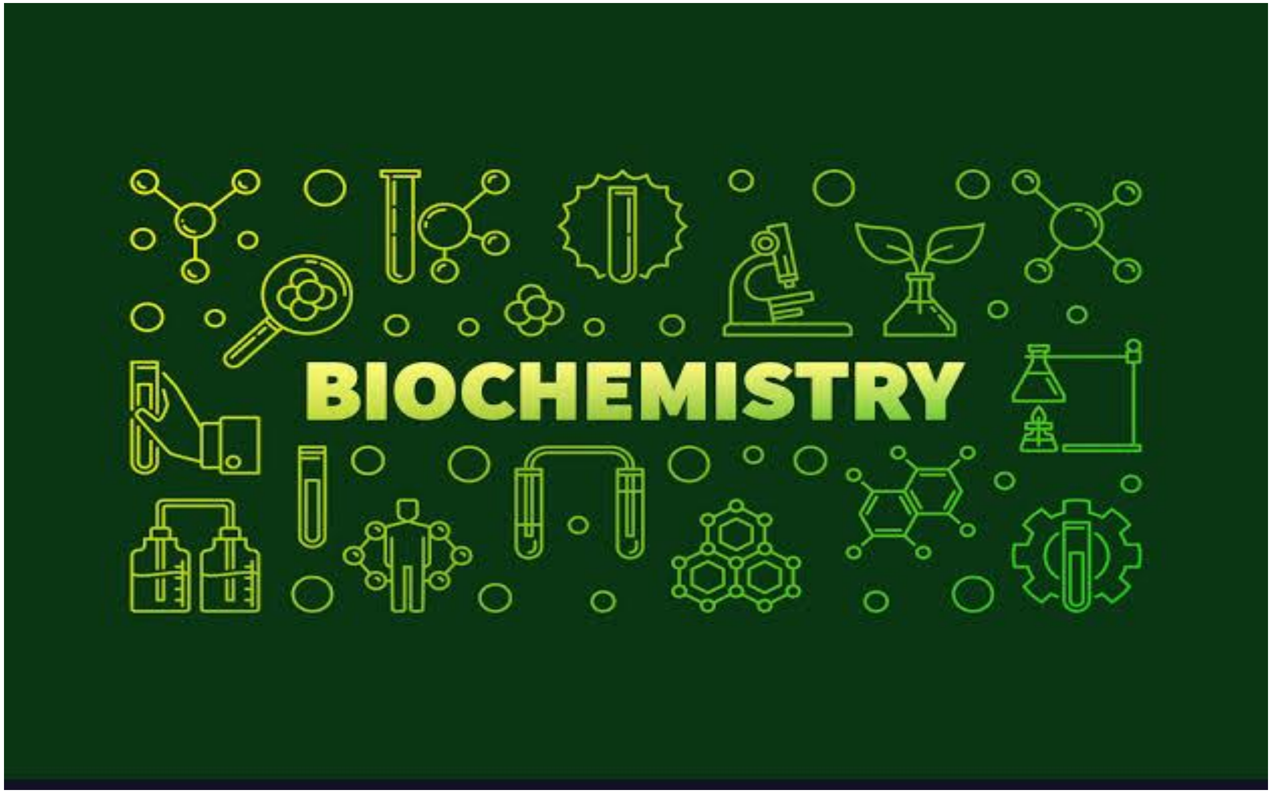


Chemistry of Carbohydrates

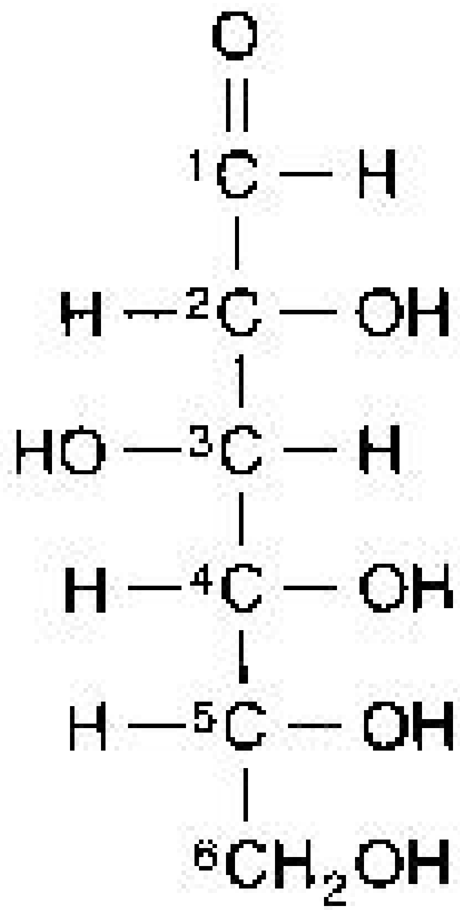
BC 3.1

- SLO 3.1.7 Student should be able to explain briefly <u>structure of Glucose</u>

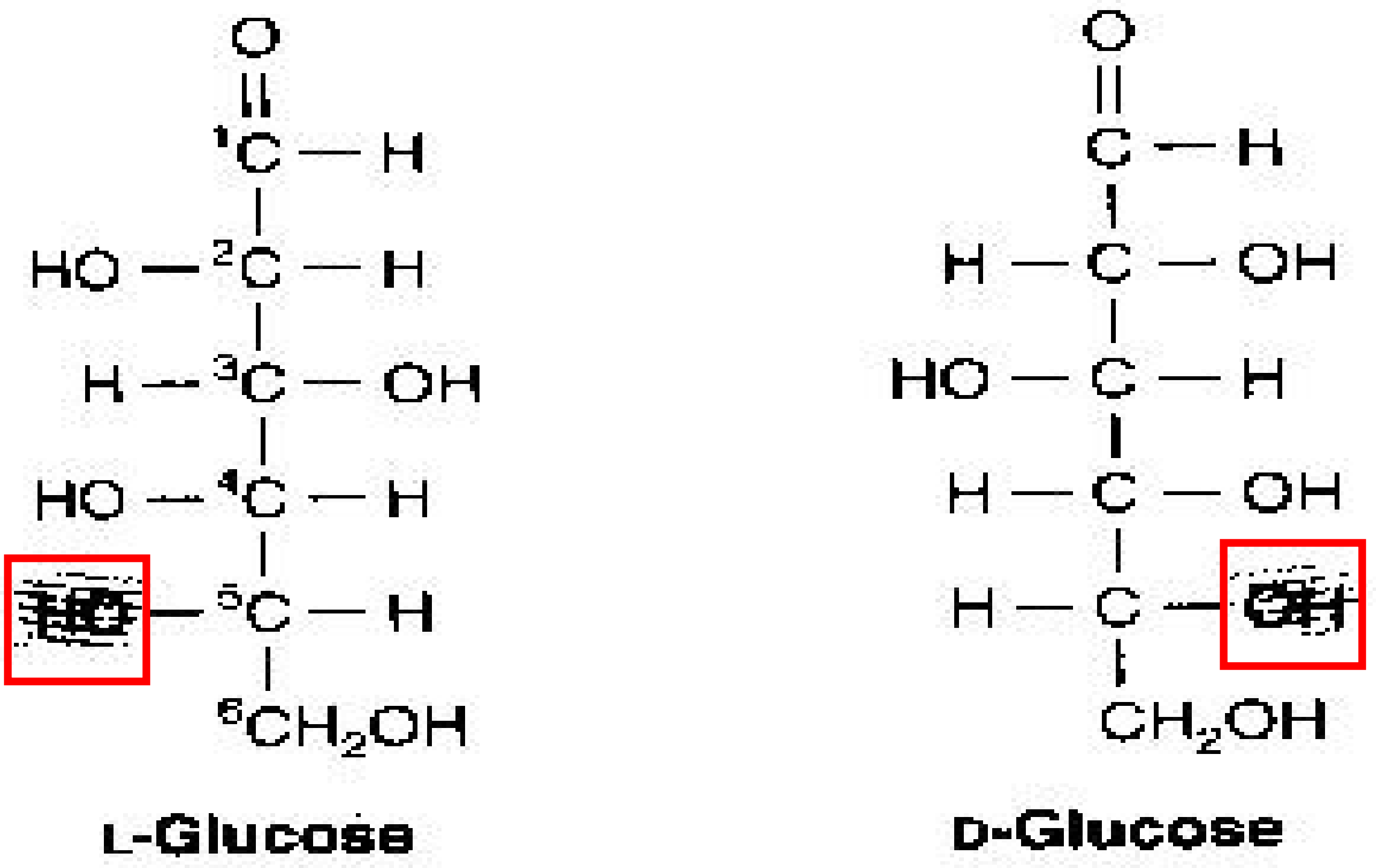
3.1.8 Disacharides & Polysacharides of biological significance

Structure of Glucose

Emil Fisher worked out the structural configurations of monosaccharides with reference to Glucose.



D and L forms of Glucose is represented by Fisher projection Formulas.

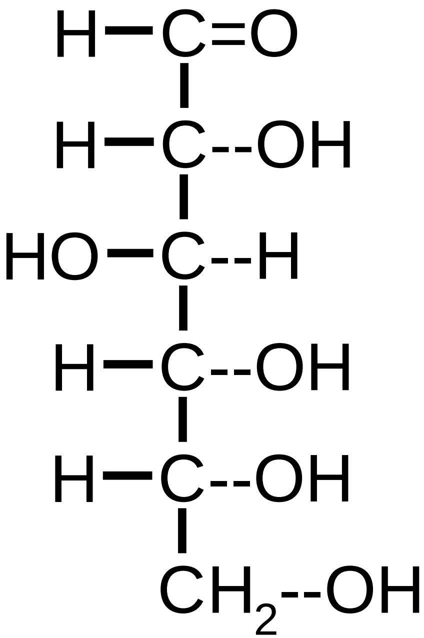


Ring Structure:

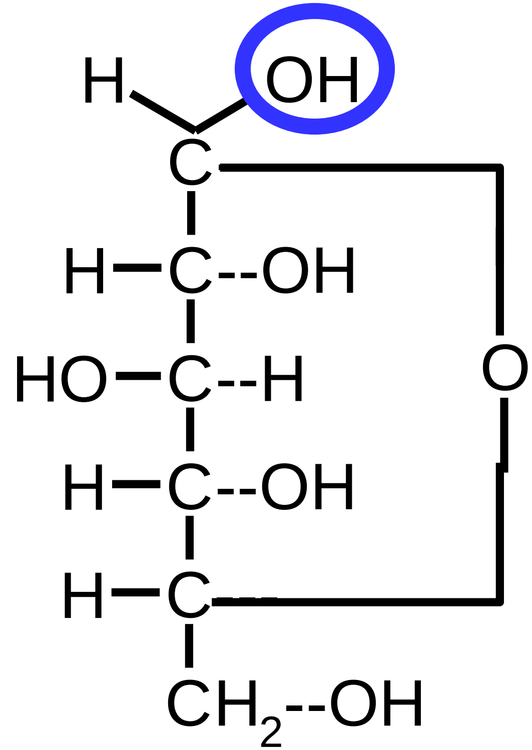
- Phenomenon of **mutarotation** can be explained only by **ring structure.**
- Experimental evidence show that 99.9 % of sugar molecule exist in ring forms and only 0.1% as straight chain in solution.
- Ring structure provide one more asymmetric center and hence exist as 2 more isomeric forms **– α and β isomers**.

In case of Glucose,

- Ring structure formed due to hemi acetal formation.
- Hemi acetal formation between carbonyl Carbon and with OH gp attached to 4th or 5th Carbon.

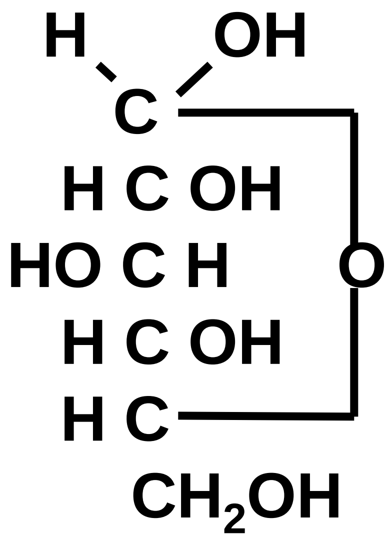


D-glucose, open chain projection formula

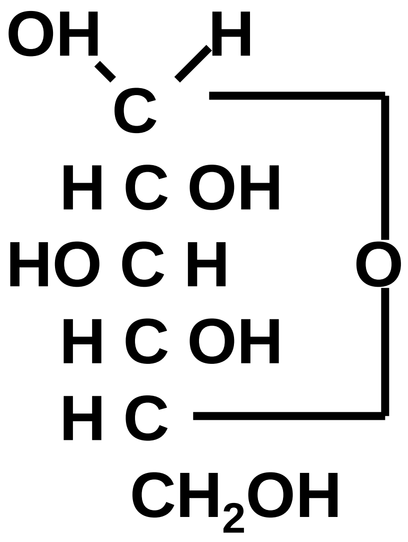


a-D-glucose, closed ring structure, Fischer formula

Fisher Projection formulas – 6 membered ring

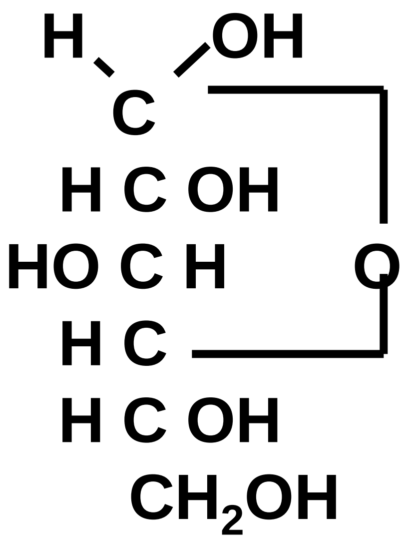


α D Glucopyranose

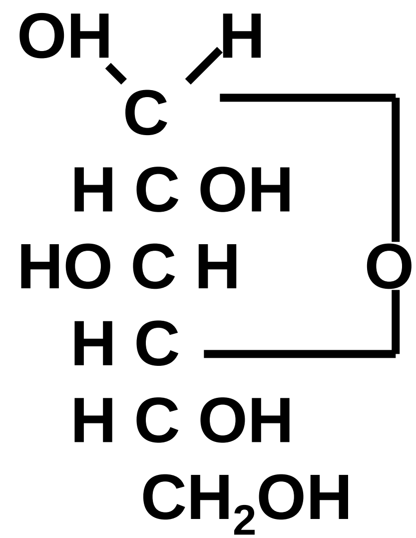


β D Glucopyranose

Fisher Projection formulas – 5 membered ring



α D Glucofuranose

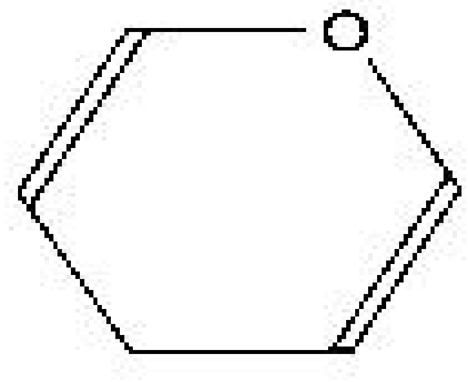


β D Glucofuranose

Haworth's Projection Formulas-
Sir Walter Haworth -1925

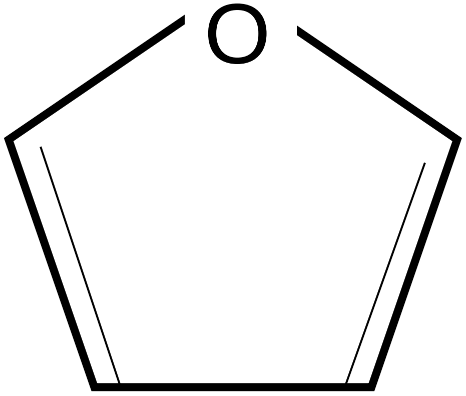
According to Haworth,

- 6 membered rings are designated as **<u>Pyranose forms.</u>**



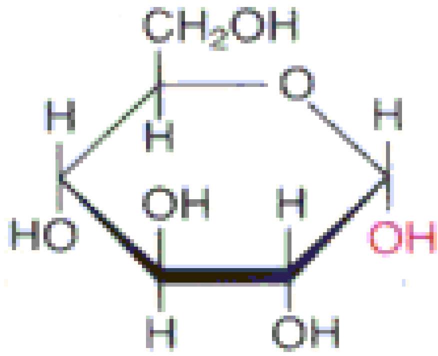
Pyran

- 5 membered rings - **<u>Furanose forms</u>**

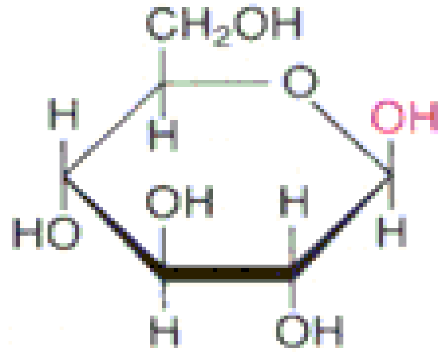


Furan

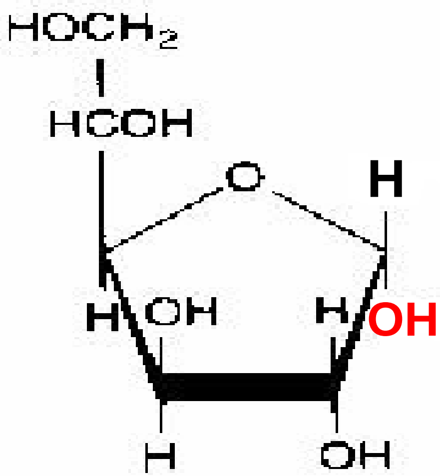
- Each of these can exist as Alpha and Beta forms



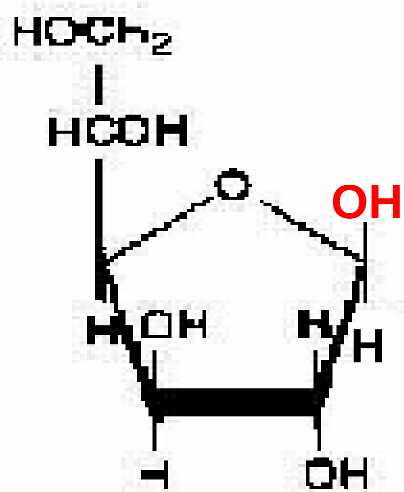
α-D-Glucopyranose



β-D-Glucopyranose

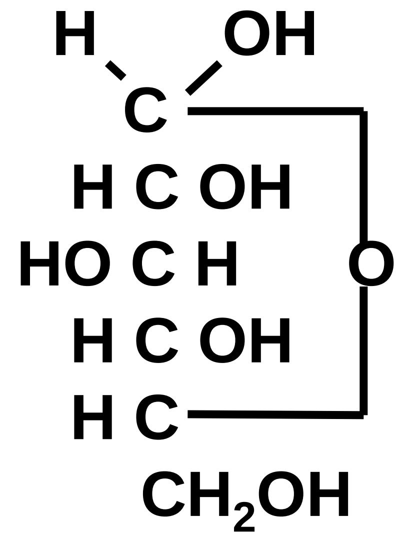


α-D-Glucofuranose

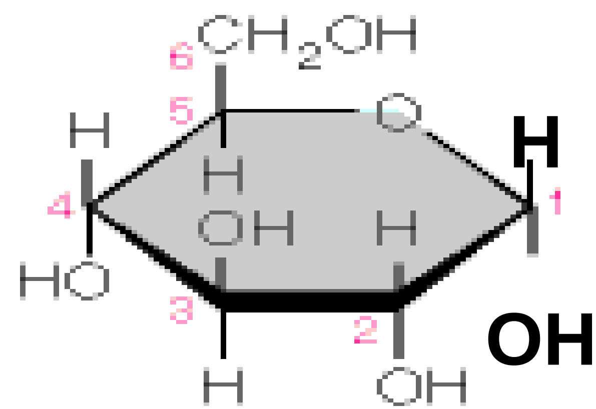


β-D-Glucofuranose

Assumptions



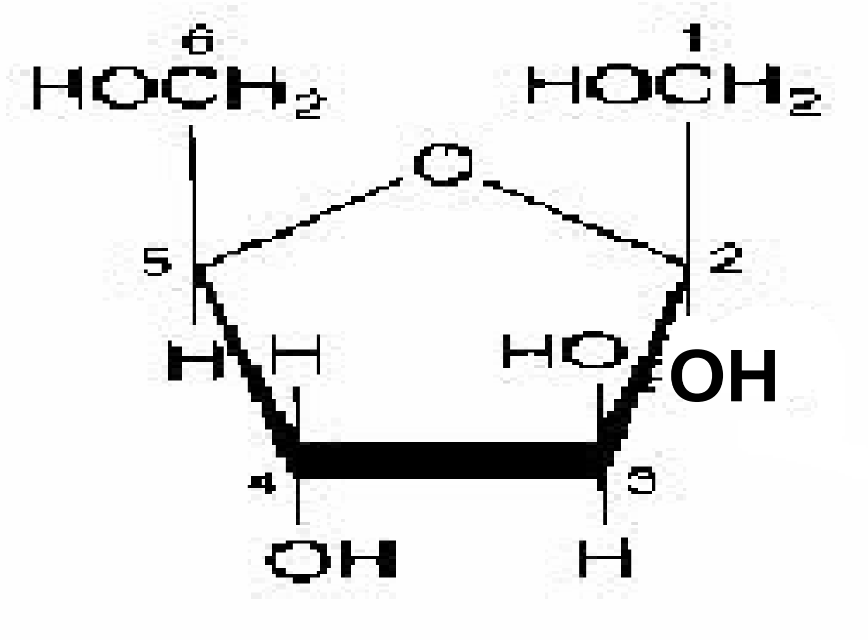
- Numbering of C atoms starts from right side and <u>in clock wise direction.</u>



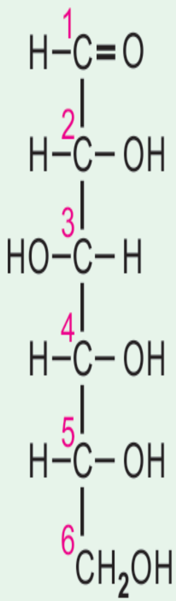
α--D-Glucopyranose

In case of Ketosugars of five or more Carbon atom the alcoholic OH gp on the 5th Carbon atom reacts with the carbonyl group at C2 and yield 5 membered **<u>hemi-ketal ring.</u>**

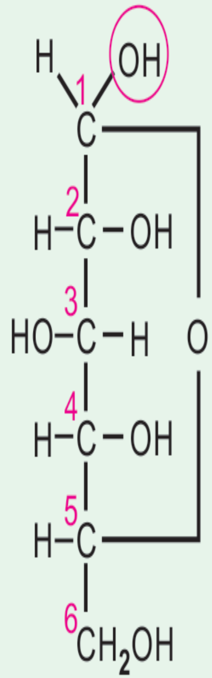
Eg. Fructose,



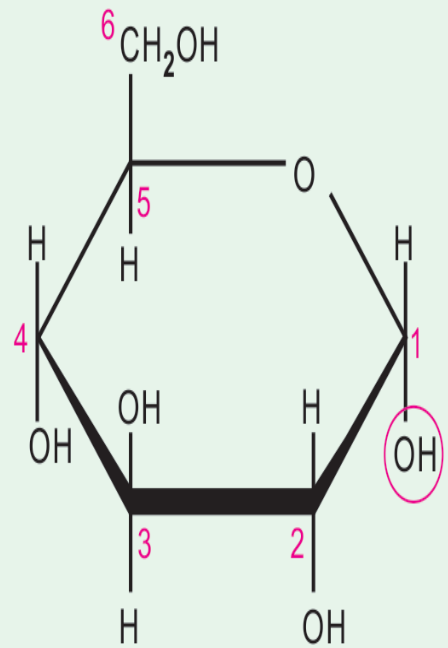
α-D-Fructofuranose



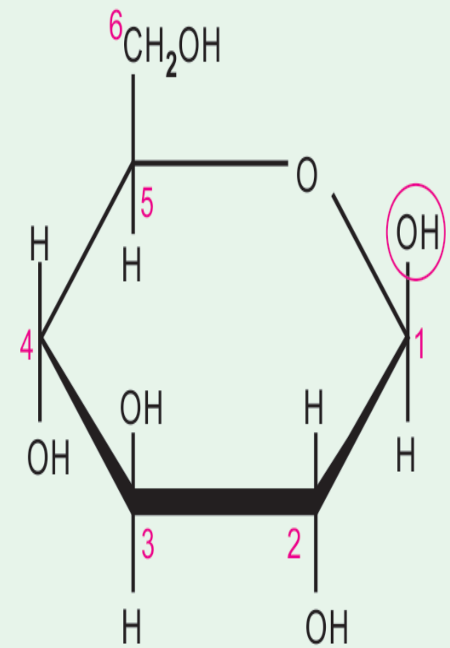
D-Glucose, Open chain projection formula



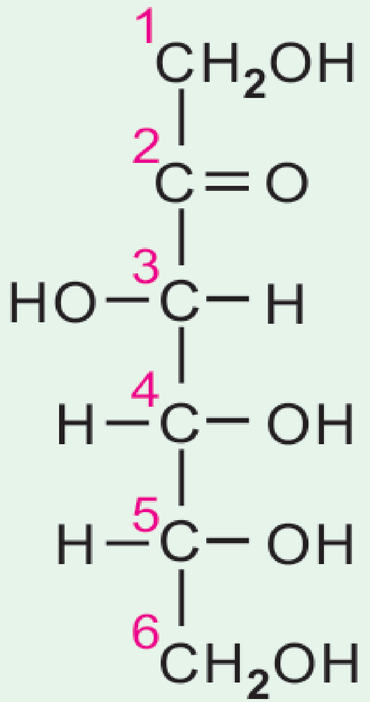
α-D-Glucose, Closed ring structure, Fischer formula



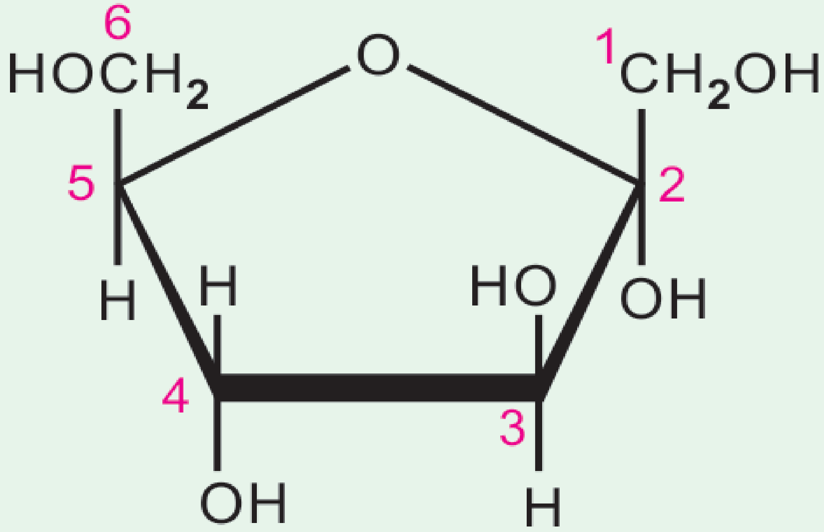
α-D-Glucopyranose, Haworth formula



β-D-Glucopyranose, Haworth formula



D-Fructose, Open chain projection formula

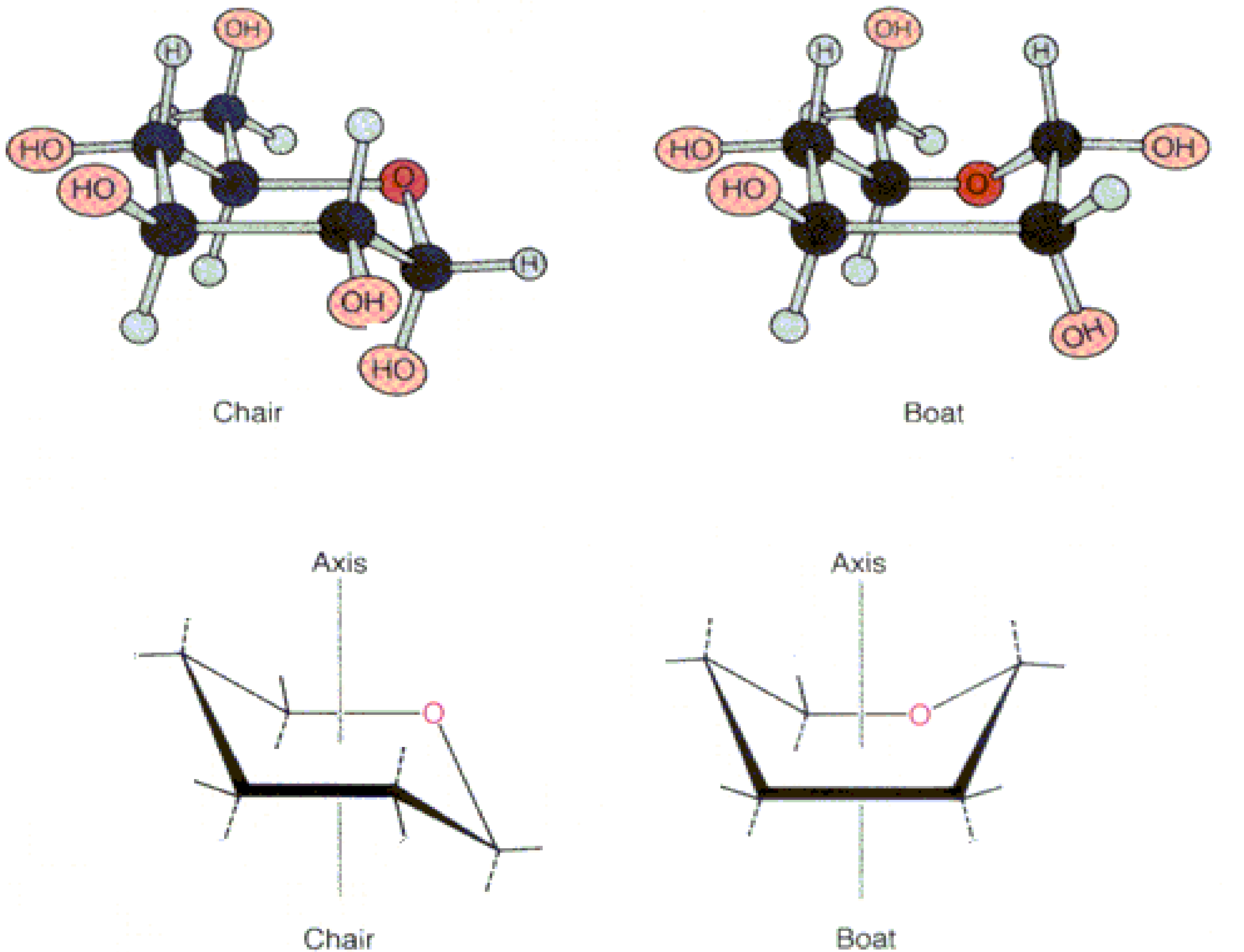


α-D-Fructofuranose, Haworth formula

- Haworth convention is useful for many purposes but even it does not represent the true conformation of the molecule.
- It is assumed that the Pyranose ring exists in 2 conformations.

Chair form and Boat form

Alpha D Glucose



Chair configuration is more stable

Disaccharides

Definition : Sugars which are composed of 2 monosaccharide residues or which yield 2 molecules of monosaccharides on hydrolysis.

- The sugar units are linked by glycosidic or acetal bonds.
- General Formula is $C_{12}H_{22}O_{11}$

Features of different disaccharides

- Can be reducing or non reducing depending on the presence of free functional group.

- Reducing sugars can exist as
  alpha /beta anomers.

Nomenclature of Disaccharides

Examples

- Alpha Maltose :

α D Glucopyranosyl α 1→4 α D Glucopyranoside

- Alpha Lactose:

β D Galactopyranosyl β 1→4 αD Glucopyranoside

- Sucrose

α D Glucopyranosyl β 1→2 β D Fructofuranoside

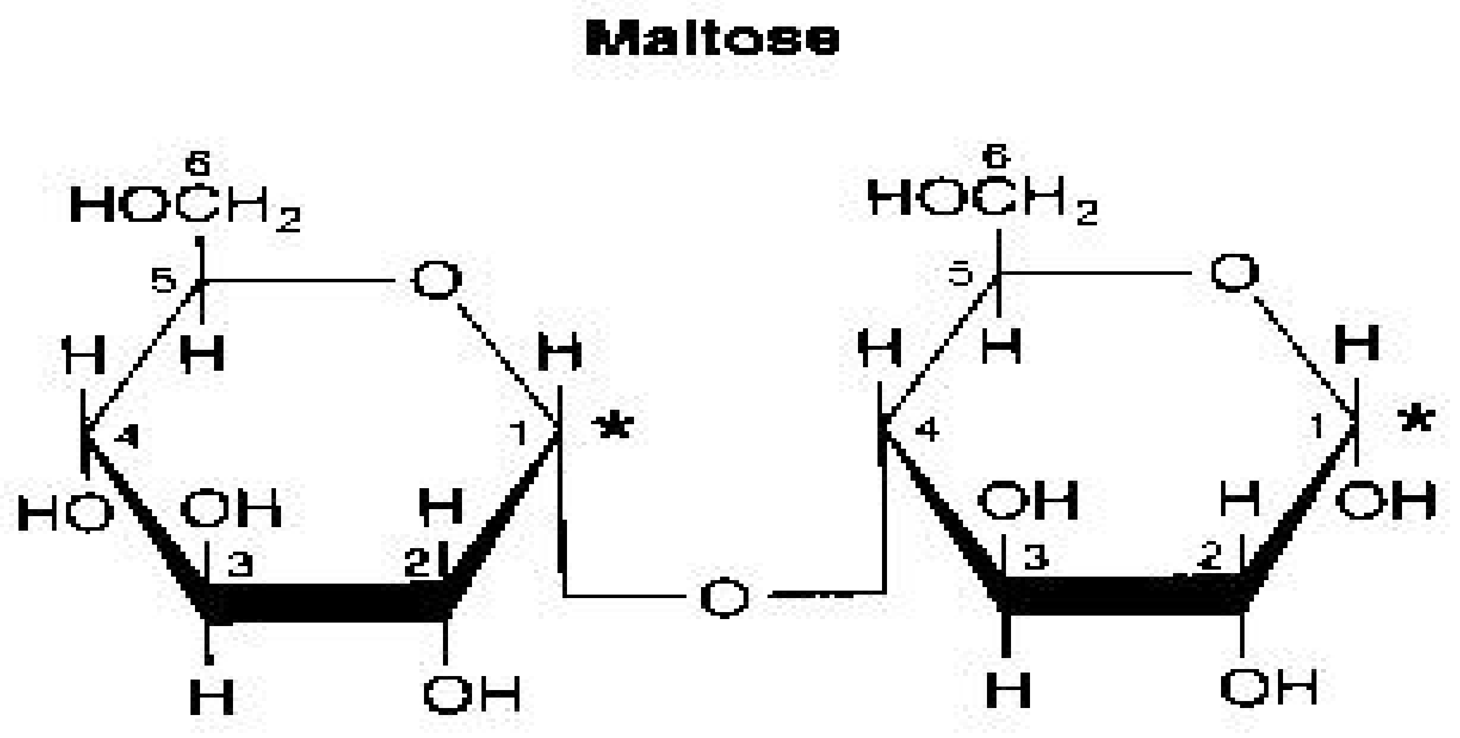
- Isomaltose

α D Glucopyranosyl α 1→6 α D Glucopyranoside

Biologically Important Disaccharides

Maltose

α D Glucopyranosyl **α 1→4** β D Glucopyranose



α-D-Glucopyranosyl-(1 → 4)-α-D-glucopyranose

Biologically Important Disaccharides

Maltose

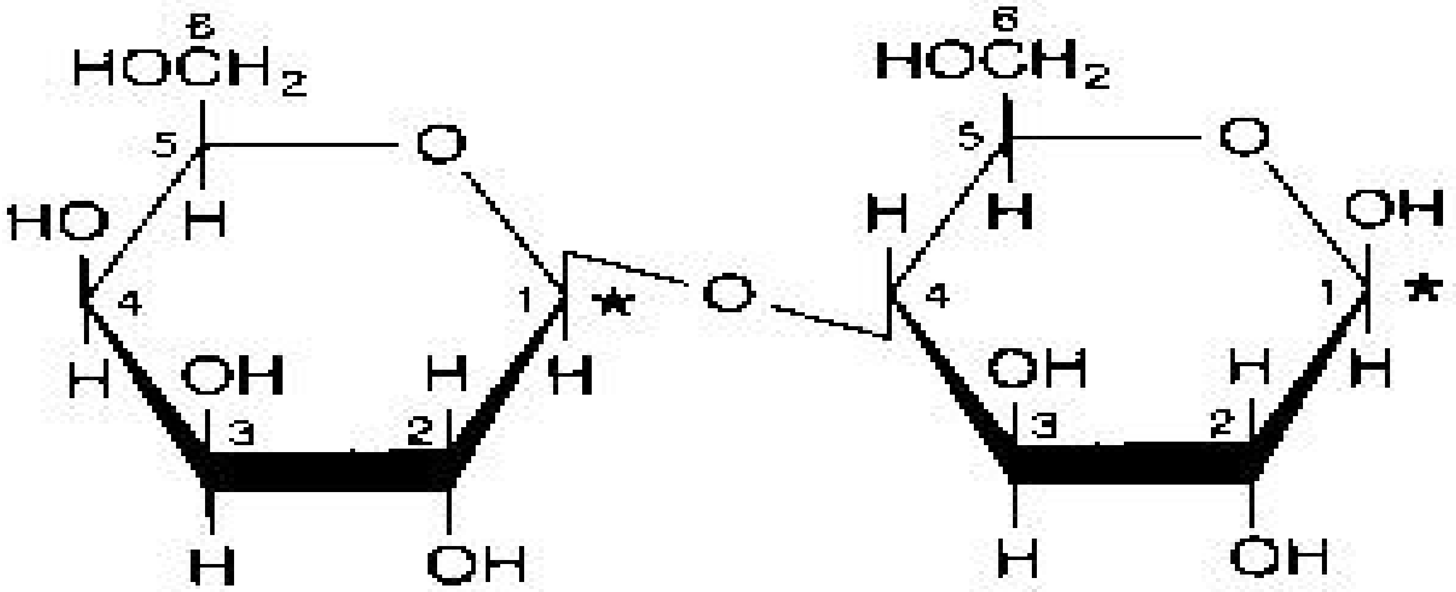
- Malt sugar
- Formed in intestine during digestion of starch and Glycogen
- Reducing sugar
- Alpha and Beta anomers
- Mutarotating

Biologically Important Disaccharides

Lactose:

β D Galactopyranosyl **β 1→4** β D Glucopyranoside

Lactose



β-D-Galactopyranosyl-(1 → 4)-β-D-glucopyranose

Biologically Important Disaccharides

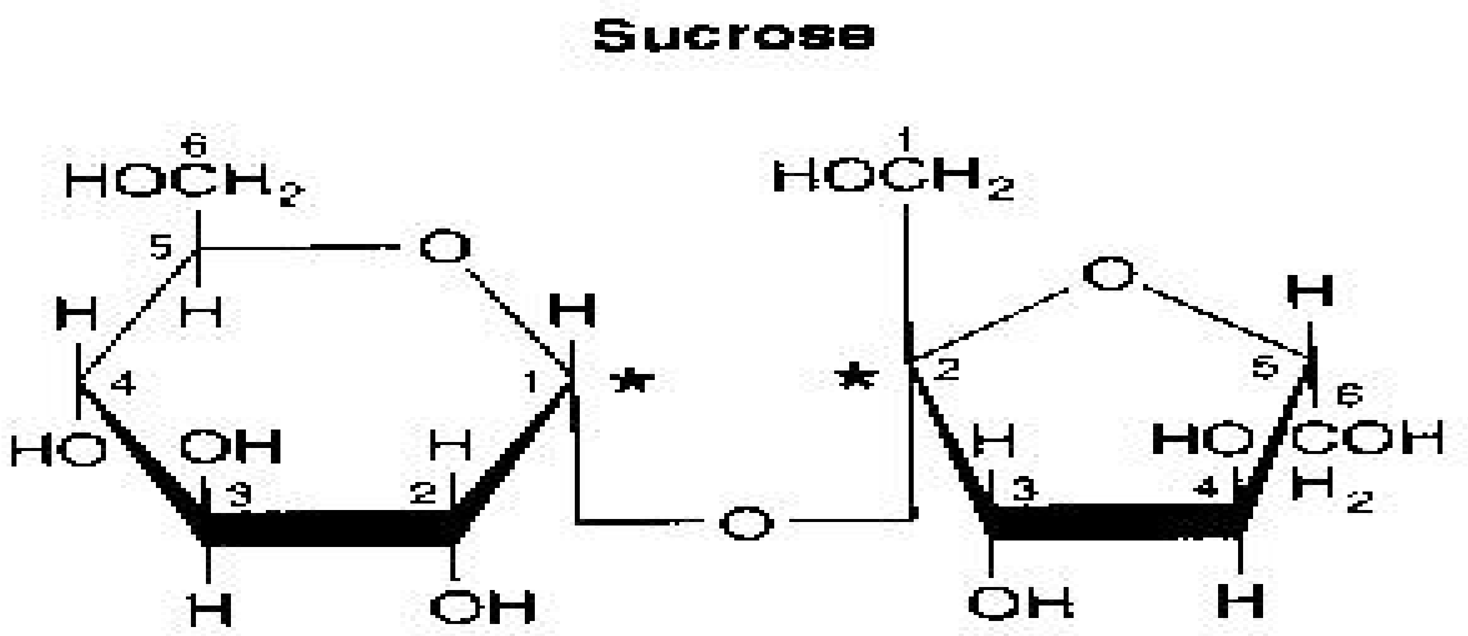
Lactose

- Milk sugar
- Digested by enzyme Lactase
- Reducing
- Can exist as alpha and beta anomers
- Mutarotating

Biologically Important Disaccharides

Sucrose

α D Glucopyranosyl **β 1→2** β D Fructofuranoside



α-D-Glucopyranosyl-(1 → 2)-β-D-fructofuranoside

Sucrose- Properties

- Non reducing
- No mutarotation
- Will not form osazone
- Dextrorotatory $+ 66.5^0$
- Hydrolysed by enzyme <u>Sucrase</u>

Sucrose $\rightarrow$ D Glucose + D Fructose

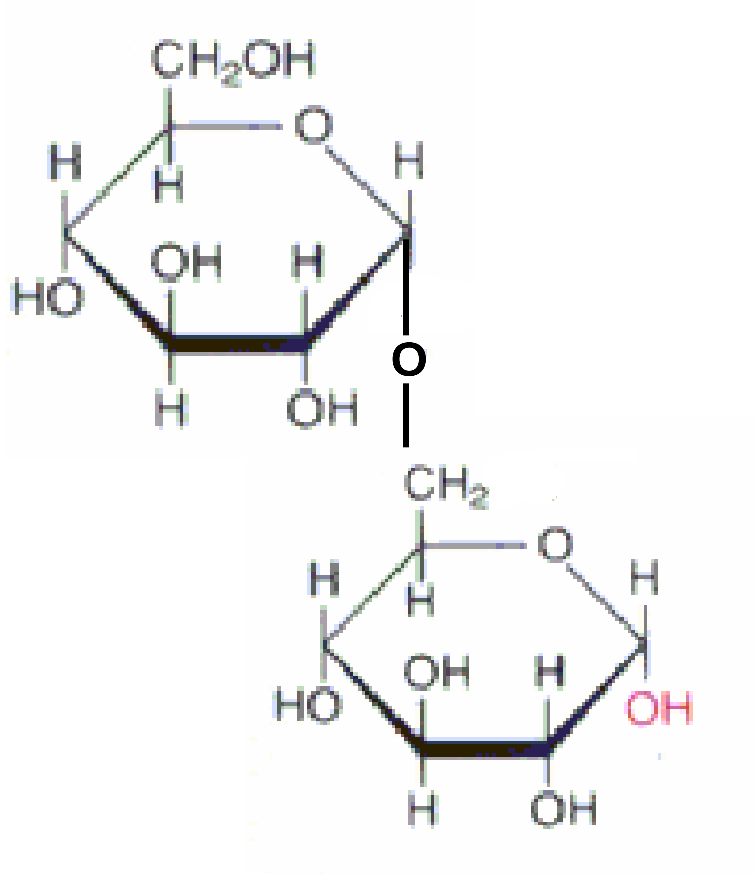
$+ 66.5^0$ $+ 52.5^0$ -92^0

Sucrose- Properties

- On hydrolysis the hydrolysate is laevorotatory due to the predominant laevo rotation of D Fructose
- This property of change in optical rotation of Sucrose on hydrolysis is called **Inversion.**
- Enzyme called **Invertase**
- The hydrolysate called **Invert sugar**
- **Honey contains large amount of Invert sugar**.

Biologically Important Disaccharides

Isomaltose:



α D Glucopyranosyl 1→6 α D Glucopyranoside

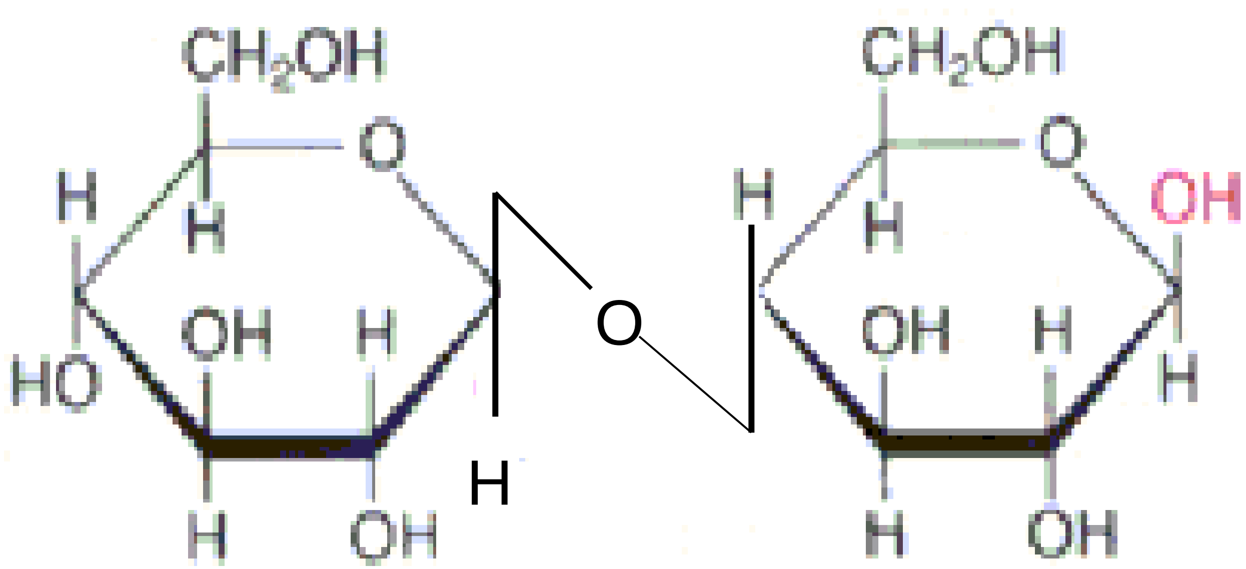
Biologically Important Disaccharides

Isomaltose:

- During hydrolysis of starch and Glycogen at the branch points
- Reducing sugar

Biologically Important Disaccharides

Cellobiose



βD Glucopyranosyl **β1→4** βD Glucopyranoside

Biologically Important Disaccharides

Cellobiose:

- During hydrolysis of cellulose
- Reducing sugar

Biologically Important Disaccharides

Trehalose:

α D Glucopyranosyl **1→1** α D Glucopyranoside

- Non reducing
- Insect haemolymph, Fungi and yeast
- Abundant in mushrooms

Oligosaccharides

- Sugars containing 3-10 sugar units
- Constituent of Glycoproteins, Glycolipids
- Determines the life span of proteins in circulation
- Involved in cell to cell recognition
- Antigenic specificity of blood group substance is due to oligosaccharide units.

On hydrolysis yield 3- 10 sugar units

- Rhamnose, Raffinose
- Carbohydrate moiety of Glycoproteins,Glycolipids & Proteoglycans

Polysaccharides

- Polysaccharides are polymers of monosaccharide units. (>10)

- Macromolecules of colloidal dimensions.

- Hydrolysed by mineral acids/ enzymes to monomeric units.

- Resistant to alkaline hydrolysis.

Polysaccharides

- Homopolysaccharides : If the monomeric units of a polysaccharide are all the same.

  Examples- Starch, Glycogen, Dextrins, Cellulose

- Heteropolysaccharides: If contains different sugar units.

  Glycosamino glycans

Polysaccharides

- In some, the monomeric units are **modified monosaccharides** –amino sugars, N- acetylated amino sugars etc.

- Polysaccharides differ in the composition of the monomeric unit, the linkages between them.

Biologically important Polysaccharides

Starch:

- Important plant source of Carbohydrate

- Found in cereals, legumes, roots and tubers.

Biologically important Polysaccharides

Starch:

- 2 types of polymeric chains-

  Amylose – 15-20%

  Amylopectin - 80-85%

Biologically important Polysaccharides

Starch:

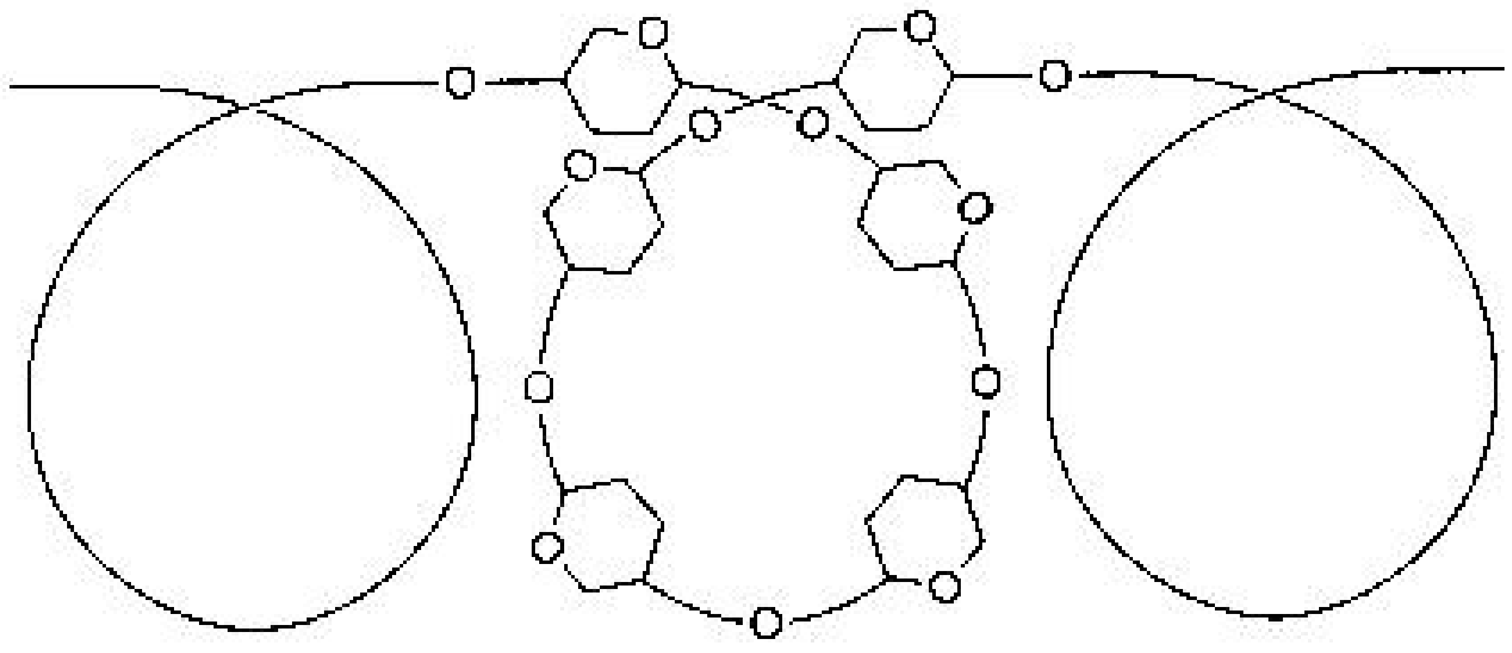
Amylose:

- Straight Chain
- Glc units linked together by 1→4 alpha glycosidic bonds
- M.Wt – 4000-40000
- Soluble in water
- Gives blue colour with Iodine.

Biologically important Polysaccharides

Starch:

Amylose



Biologically important Polysaccharides

Starch:

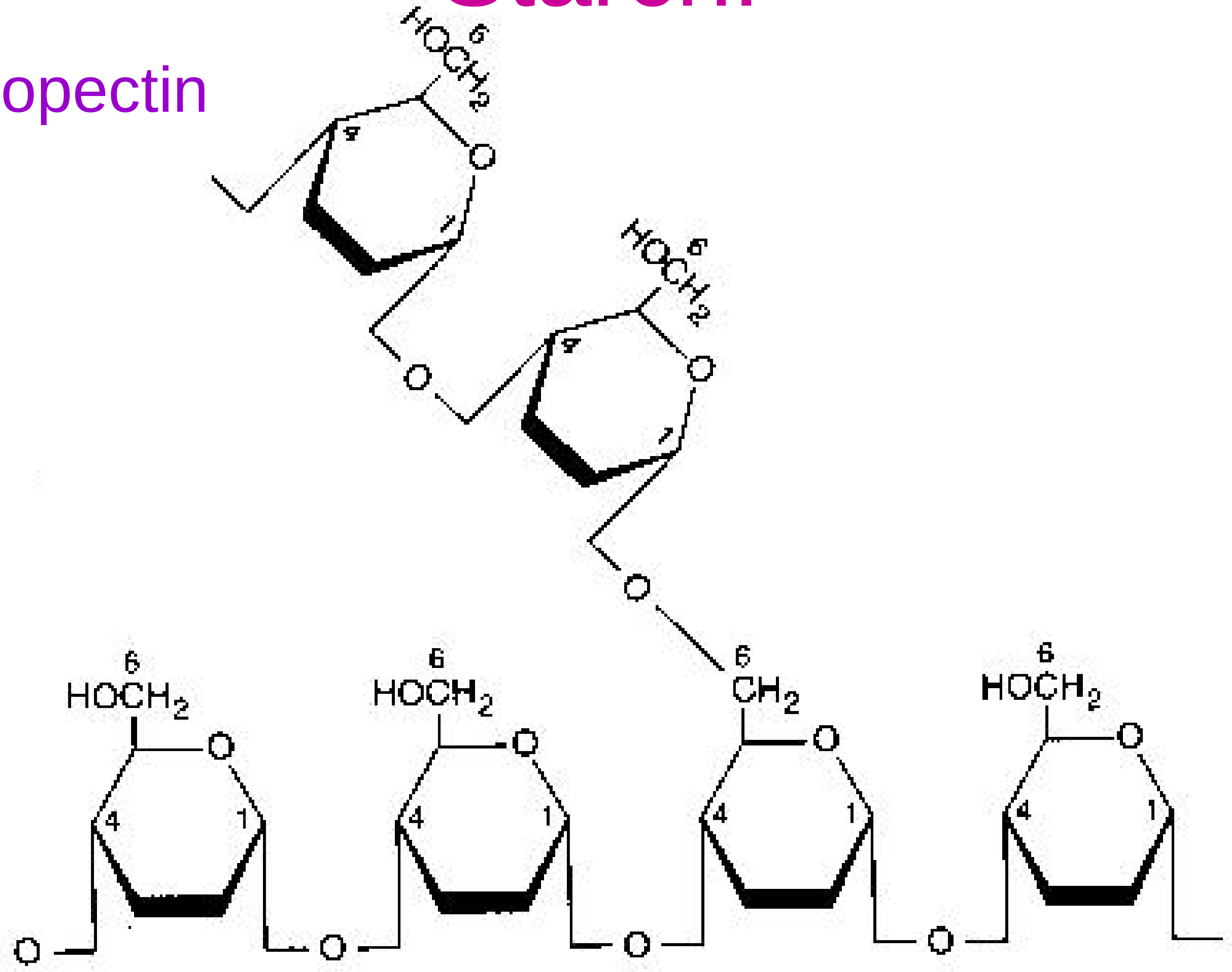
Amylopectin

- Branched structure, branching between 25-30 Glc units
- Alpha 1→4 Glycosidic bonds, branch points Alpha1→6 Glycosidic bonds.
- Insoluble in water
- Violet colour with Iodine

Biologically important Polysaccharides

Starch:

Amylopectin



Biologically important Polysaccharides

Starch:

Reaction with Iodine:

- Both amylose and amylopectin gives characteristic colour with Iodine

  Amylose- Deep Blue

  Amylopectin –Reddish Violet

- Disappears on heating, reappears on cooling

Biologically important Polysaccharides

Starch:

Hydrolysis of Starch

- Starch can be hydrolyzed by mineral acids or specific enzymes – **Amylases.**
- Gives a series of polysaccharides of decreasing M. Wt and size.

Biologically important Polysaccharides

Enzymatic Hydrolysis of starch

Amylases:

- Enzymes concerned with hydrolysis of starch and Glycogen
- 2 different types of Amylases

  Alpha amylase

  Beta amylase

- Both act on α 1→4 Glycosidic bonds.
- α 1→6 Glycosidic points are hydrolysed by α 1→6 Glycosidase enzyme.

Biologically important Polysaccharides

Dextrins

Products of partial hydrolysis of starch

Products	Colour with Iodine
Starch	Blue
Solble starch	Blue
Amylodextrin	Purple
Erythrodextrin	Red
Achrodextrin	Colourless
Maltose	Colourless
Glucose	Colourless

Biologically important Polysaccharides
Dextrins

- Consists of large molecules of various sizes and m.wt. depending on the degree of hydrolysis.
- Occur on leaves of plants and honey
- Used in <u>preparations of emulsions</u> and dry bandages.

Biologically important Polysaccharides
Dextrans

- <u>**Highly branched polymer of Glc.**</u>
- Linked by 1→6, 1→4,1→3 glycosidic linkages.
- Synthesized by bacteria.
- Used as a molecular sieve in <u>column chromatography.</u>
- Used in medicine as <u>a plasma volume expander in Hypovolemic shock.</u>

Biologically important Polysaccharides

Glycogen:

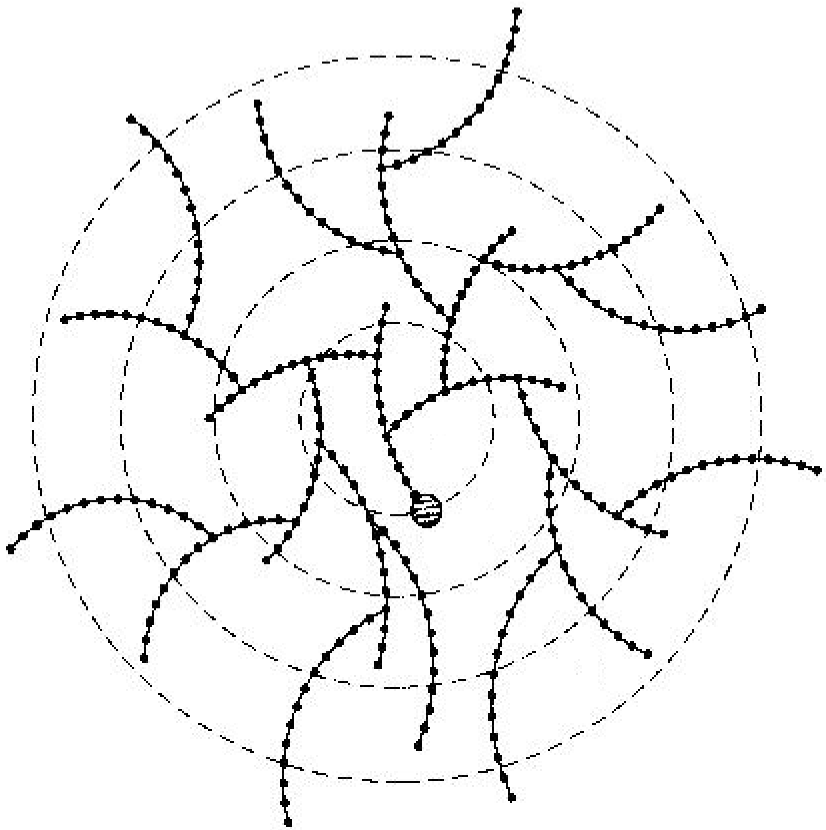
- Storage form of CHO in animals.
- Mainly found in Liver and Sk. Muscles.

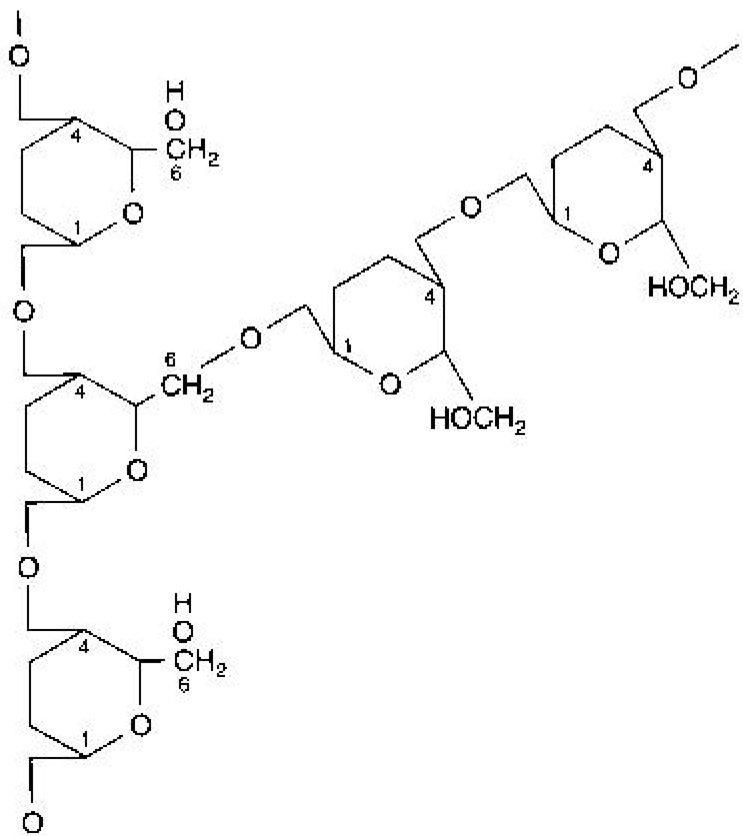
Structure:

- Highly branched, branching occur every 11-18 residues.
- Glc units are linked together by α 1→4 , and by α 1→6 at branched points.
- M.Wt varies from 4-5 million kd.

Biologically important Polysaccharides

Glycogen





Biologically important Polysaccharides
Glycogen:

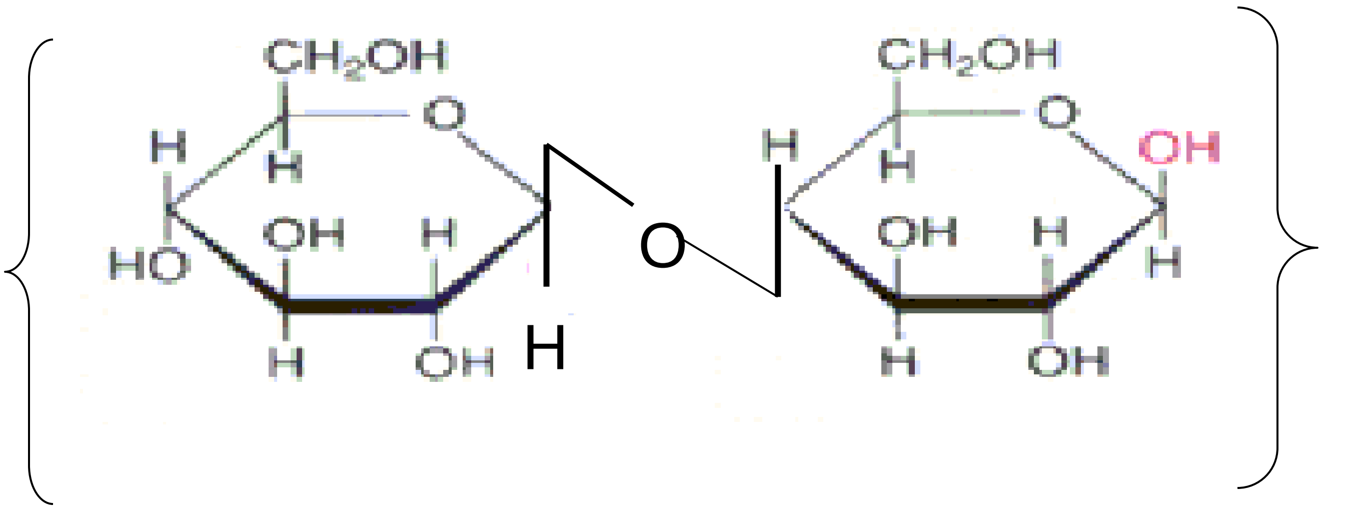
- Soluble in water to form an opalescent solution.
- Gives a deep red colour with Iodine
- Synthesized in the body by Glycogenesis and degraded by Glycogenolysis.
- Hydrolyzed by Pancreatic and salivary Amylases.

Biologically important Polysaccharides
Cellulose

- Chief constituent of the fibrous part of plants.
- Form structural frame work of plants.
- High M.Wt polymer of Glc.
- Glc units are linked together by **β 1→4 Glycosidic bonds.**
- Unbranched Polymer

Biologically important Polysaccharides
Cellulose

Repeating disacharide unit in cellulose is **cellobiose**.



Biologically important Polysaccharides
Cellulose

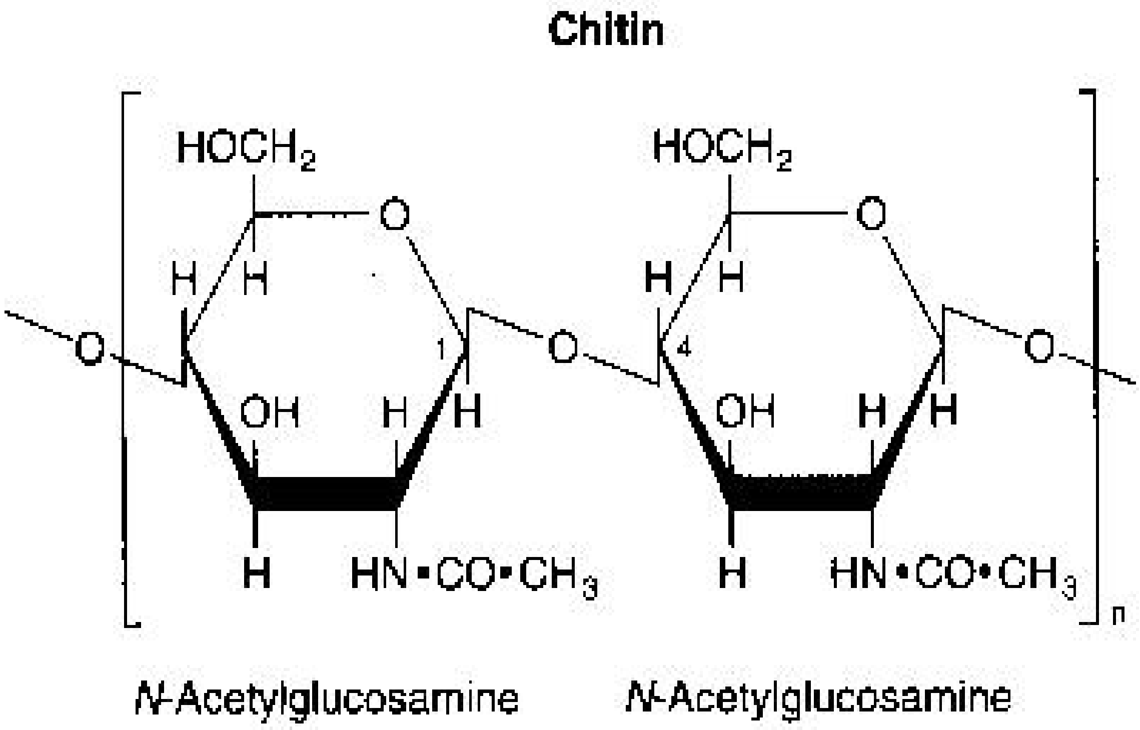
- Hydrolyzed by strong mineral acids.
- On hydrolysis yield β D Glucose.
- Bacteria possess enzymes capable of hydrolyzing Cellulose.
- Human digestive tract does not possess enzymes to hydrolyze the β 1→4 glycosidic linkage. Hence cannot digest cellulose. And cellulose forms the roughage.

Biologically important Polysaccharides
Inulin

- Polymer of β D Fructose.
- Linkage β 1$\rightarrow$2 glycosidic linkage.
- M. Wt 3000 to 5000.
- Occurs in tubers of Dhalia, onions, garlic.
- Used to **assess GFR** – Inulin clearance test.

Biologically important Polysaccharides
Chitin

- Present in <u>exoskeleton of insects</u>
- Composed of Gln NAc
- Linked by β 1→4 linkage




Thank You