MSc. Botany

Semester IV

Paper VI

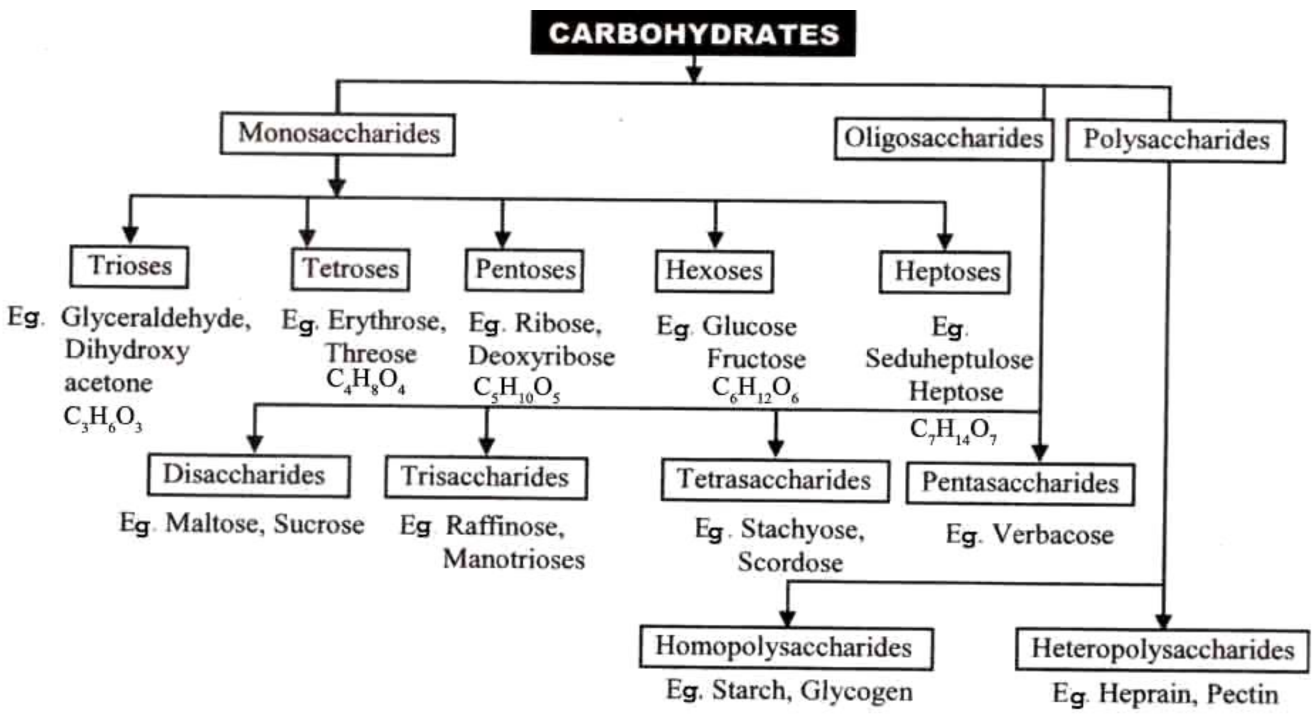
CARBOHYDRATES

Carbohydrates are probably the most abundant and widespread organic substances in nature, and they are essential constituents of all living things. Carbohydrates are formed by green plants from carbon dioxide and water during the process of photosynthesis.

A **carbohydrate** is a biomolecule consisting of carbon (C), hydrogen (H) and oxygen (O) atoms, usually with a hydrogen–oxygen atom ratio of 2:1. The carbohydrates were known as hydrates of carbon but structurally they are polhydroxy derivatives of aldehydes and ketones and are thus referred to as aldoses and ketoses. The aldehyde group occurs at position 1 of an aldose, and the keto group can occur at a further position (e.g., 2) in a ketose. The generic nomenclature ending for the monosaccharides is *–ose* for aldose sugars and –ulose for ketose sugars. In addition, because the monosaccharides contain a chemically reactive group that is either an aldehyde group or a keto group, they are frequently referred to as aldohexoses or ketohexoses. Thus glucose is an aldohexose—i.e., it contains six carbon atoms, and the chemically reactive group is an aldehyde group and fructose is a ketohexose with ketone as the functional reactive group

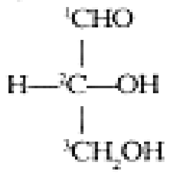
Carbohydrates perform numerous roles in living organisms. Carbohydrates serve as energy sources (e.g. starchand glycogen) and as essential structural components in organisms (e.g. cellulose in plants and chitin); in addition, part of the structure of nucleic acids, which contain genetic information, consists of carbohydrate. The 5-carbon monosaccharide ribose is an important component of coenzymes (e.g. ATP, FAD and NAD) and the backbone of the genetic molecule known as RNA. The related deoxyribose is a component of DNA. Saccharides and their derivatives include many other important biomolecules that play key roles in the immune system, fertilization, preventing pathogenesis, blood clotting, and development.

Cassification: carbohydrates are classified as three major groups- monosaccharides, oligosaccharides and polysaccharides. Sugars (mono- and oligosaccharides) are white, sweet, crystalline in shape, have sharp melting points and are soluble in cold water, while polysaccharides are white, tasteless, amorphous solids partially soluble in hot water.

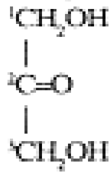


<u>Monosaccharide</u> or simple sugars, are found in grapes, other fruits, and honey. Although they can contain from three to seven carbon atoms, forming the triose (three carbon), tetrose (four), pentose (five); hexose (six) and heptose (seven) used for monosaccharides to form chainlike molecules, the most common representatives consist of *pentose* and *hexose*s. Three of the most important simple sugars—glucose (also known as dextrose, grape sugar, and corn sugar), fructose (fruit sugar), mannose and galactose—have the same molecular formula, ($C_6H_{12}O_6$), but, because their atoms have different structural arrangements, the sugars have different characteristics; i.e., they are isomers. Of these fructose is a functional isomer (ketose sugar) and the other three (aldose sugars) are <u>epimer</u>s with difference in the placement of a single OH group. The sugars are best represented by Emil Fischer's linear formula but sugars containing more than four carbon tend to cyclise to form a stable structure represented as Haworth's ring structure. The five carbon sugars formed a five member ring (furanose sugars) and six carbon sugars were more stable at a six member ring (pyranose sugar). Also due to mutarotation the sugars occur as α or β forms. The structures of important sugars are as follows:

(*i*) D-Glyceraldehyde

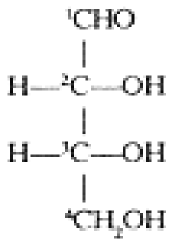


(*ii*) Dihydroxyacetone



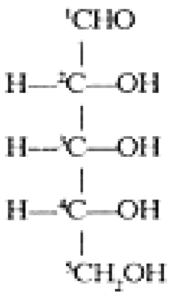
(TETROSES)

(*iii*) D-Erythrose

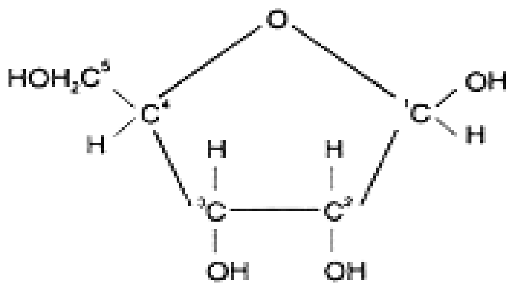


(PENTOSES)

(*iv*) Ribose

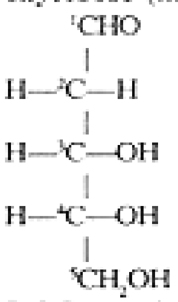


D-Ribose

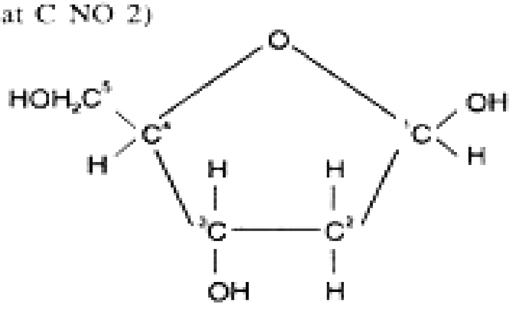


β - D-Ribose

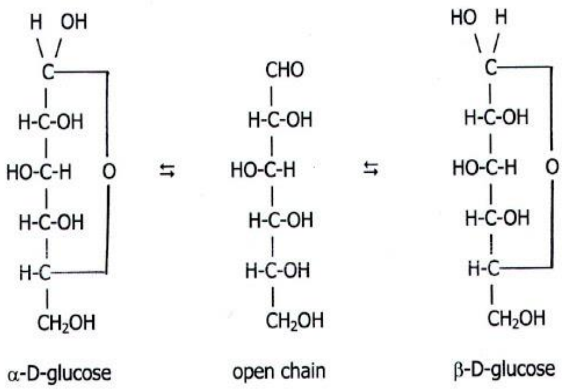
(*v*) Deoxyribose (instead of—OH there is H at C NO 2)

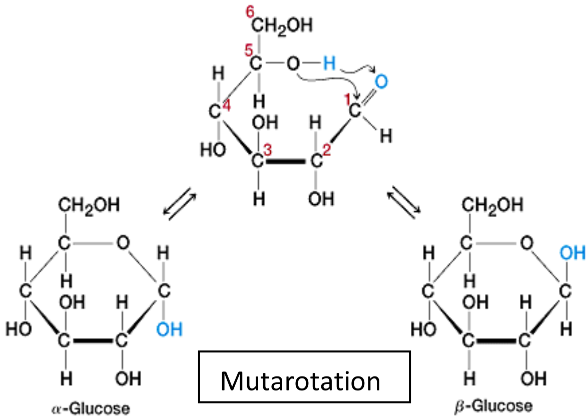


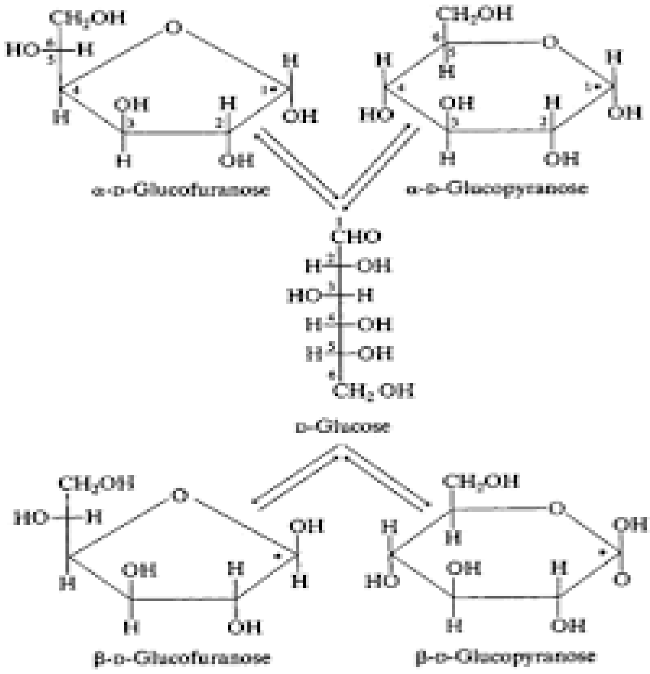
D-2-Deoxyribose



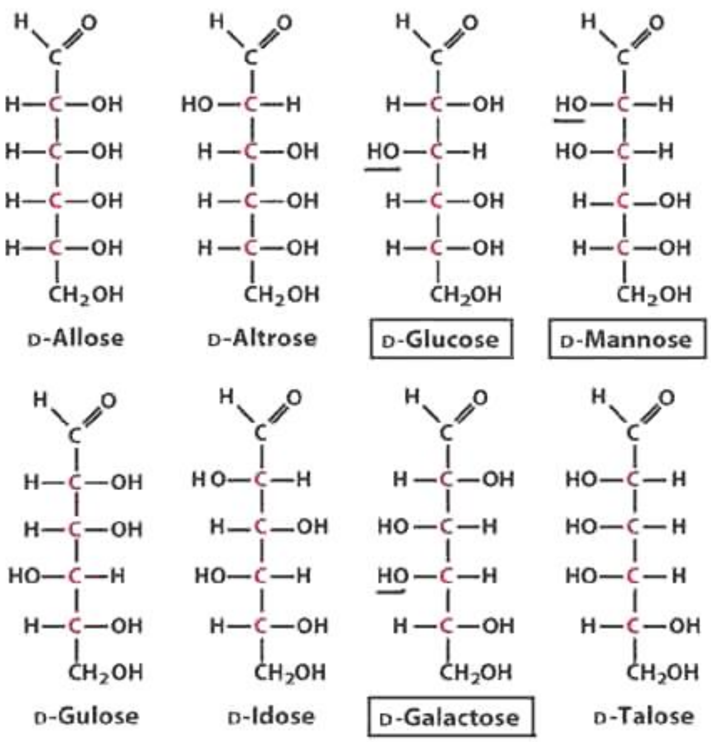
β - D-2-deoxyribose



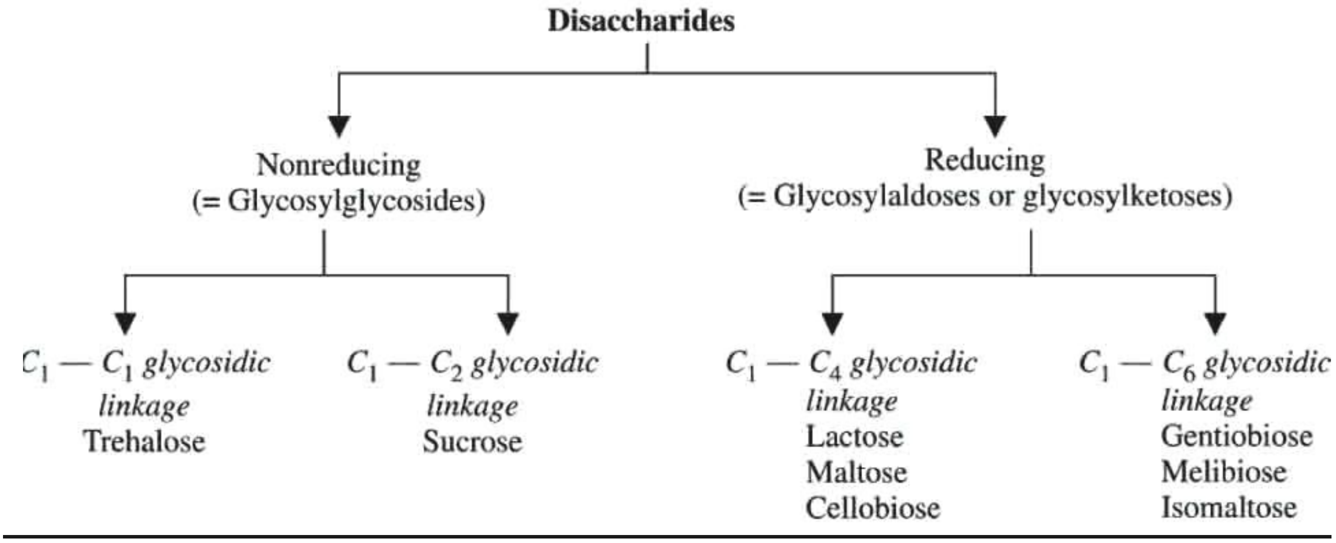


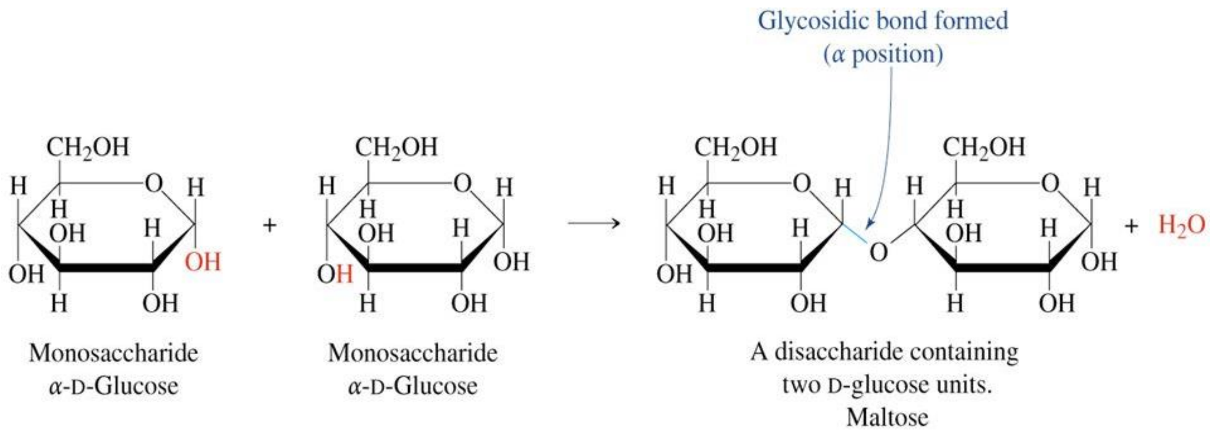


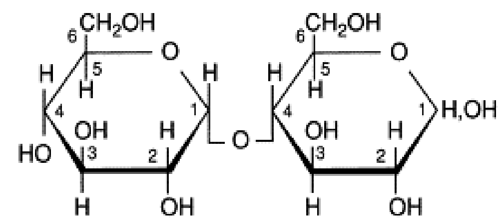
Six Carbon Aldoses



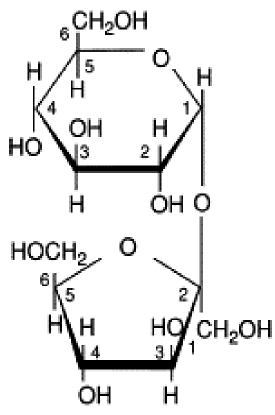
<u>Disaccharides:</u> is the sugar formed when two monosaccharides (simple sugars) are joined by glycosidic linkage with a loss of a water molecule. Like monosaccharides, **disaccharides** are soluble in water. Three common **examples** are sucrose, lactose, and maltose.



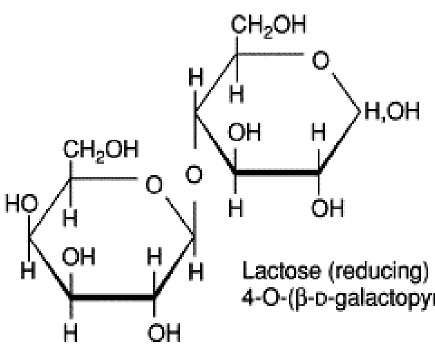




Maltose (reducing)
4-O-(α-D-glucopyransyl)-D-glucopyranose
or O-α-D-glucopyranosyl-(1→ 4)-α-D-glucopyranoside



Sucrose (non-reducing)
α-D-glucopyranosyl-β-D-fructofuranoside
or (β-D-fructopyranosyl)-α-D-glucopyranoside
or O-α-D-glucopyranosyl-(1→ 2)-β-D-fructopyranoside



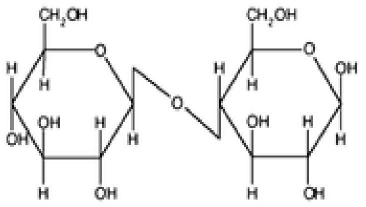
Lactose (reducing)
4-O-(β-D-galactopyranosyl)-D-glucopyranose

Maltose or malt sugar- it produced during hydrolysis of starch by amylase found in germinating cereals (barley) amylase splits starch into dextrin and maltose. One molecule is glucose is linked through hydroxyl groups on C-1 carbon atom by glycosidic bond to OH group only of 2nd molecule of glucose. The 2nd glucose molecule may be α and β form so the maltose may be α and β maltose.

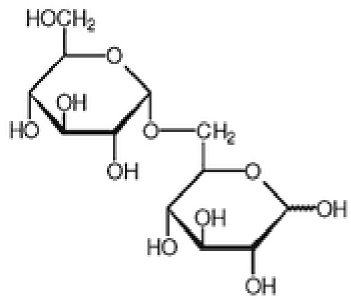
Iso-maltose has two glucose units similar to maltose except for α (1-6) linkage obtained during hydrolysis of certain polysaccharides.

Cellobiose – similar to maltose except that it has a β (1-4) glycosidic linkage. It is disaccharide formed during acid hydrolysis of cellulose or by enzyme cellulose.

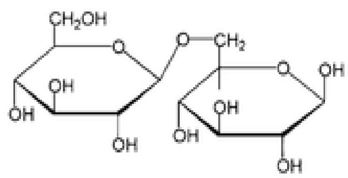
Trehalose has α-1,2 linkage between two glucose molecule. It is white, crystalline and non-reducing found in young mushroom and yeast. It acts as a cryoprotectant in response to cold stress.



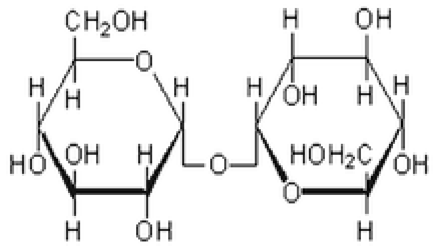
Cellobiose
β-D-glucopyranosyl-(1-4)-α-D-glucopyranose



Isomaltose
α-D-glucopyranosyl-(1-6)-β-D-glucopyranose



Gentobiose
β-D-glucopyranosyl-(1-6)-β-D-glucopyranose



Trehalose
α-D-glucopyranosyl-(1-1)-α-D-glucopyranose

<u>**Trisaccharide**</u> – Raffinose in sugar beet and cotton seed meal and fungi. Made up of α-galactopyranosyl-α, 1-6 glucopyranosyl-α,1-2 fructofuranoside. Gentionose found in rhizomes β- glucopyranosyl α, 1-6 glucopyranosyl -α, 1-2, fructofuranoside.

<u>**Tetrasaccharide**</u> **–** Stachyose found in *Stachys tuberifera* α, galactopyranosyl- α, galactopyranosyl- α,1-6 glucopyranosyl-α,1-2 fructofuranoside.

<u>Polysaccharide</u>

Most carbohydrate occur in nature as polysaccharide with high molecular weight is condensation polymers with monosaccharide’s joined by glyosidic linkage. All polysaccharides can be hydrolysed with acid or enzymes to yield monosaccharide and derivatives of monosaccharides. Simple homopolysaccharide glycans consists of same monsaccharides as repeating units and mixtures of monosaccharide derived products are heteropolysaccharide glycans. The degrees of polymerisation (DP) which is the number of monosaccharide units is in range of 80-100, up to 50,000 as in cellulose. Polysaccharides may be biological (1) storage forms e.g. Starch and glycogen or (2) structural form constituents of cell wall and connective tissue e.g. hyaluronic acid. Polysaccharides thus differ in nature of recurring monosaccharide unit, length of chain and degree of branching.

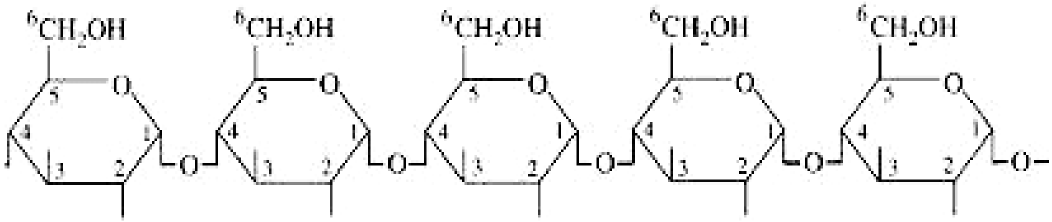
Homopolysaccharides

Starch is a storage homopolysaccharide in plants especially cereals, wheat, ice, maize, sorghum. In potato and cassava starch is in tubers occurring as intracellular large clusters Sago from sago palm (*Metroxylon rumphii*), arrowroot (Maranta), tapioca (*Manihot utilissima*). Starch is white amorphous, soft present as microscopic starch grains. It is water, alcohol and ether insoluble. On heating it breaks to dextrin which are large fragments.

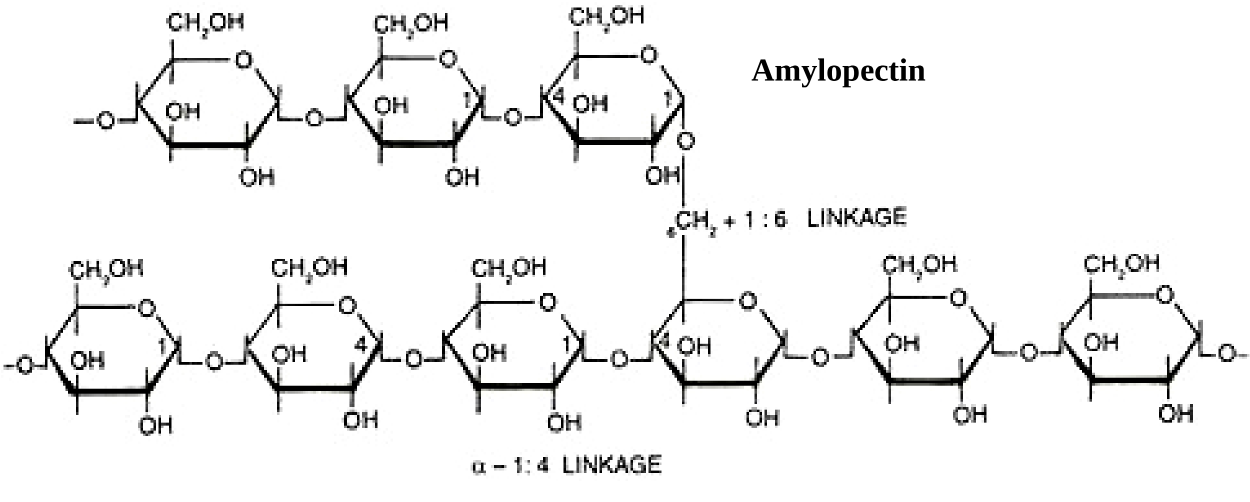
Starch has two components (1) straight chain long unbranched **Amylose**, which has about 1000-2000 D-glucose units linked in linear fashion by α(1-4) linkage. It has a non-reducing and reducing end, molecular wt. up to 150,000. It gives blue colour with iodine. In water glucose units occur in helical coil. α - amylase hydrolyses the linear amylose chain by attacking α (1-4) linkage randomly to yield glucose and maltose units. β amylase found in plants attack the non-reducing end to yield maltose units. All starch has lower content of amylose than amylopectin and overall the amylose content is generally in range 11-35% - maize (20-36%), potato (18-23%)and rice (8-37%). Amylopectin is more soluble form and is more abundant in early stages of starch synthesis.

Amylopectin: it is branched polysaccharide with short chain (about 30 units) of glucose units linked in α (1-4) linkage and joined by α (1-6) linkage (from which iso maltose can be obtained). It gives purple colour to iodine. Amylopectin can be hydrolyzed by α and β amylase at α (1-4) glyosidic bonds but near the branching point α (1-6) bond is hydrolysed by debranching enzymes α (1-6) glucosidase. Thus α amylase and β (1-6) glycosidase hydrolyses the amylopectin to glucose and maltose.

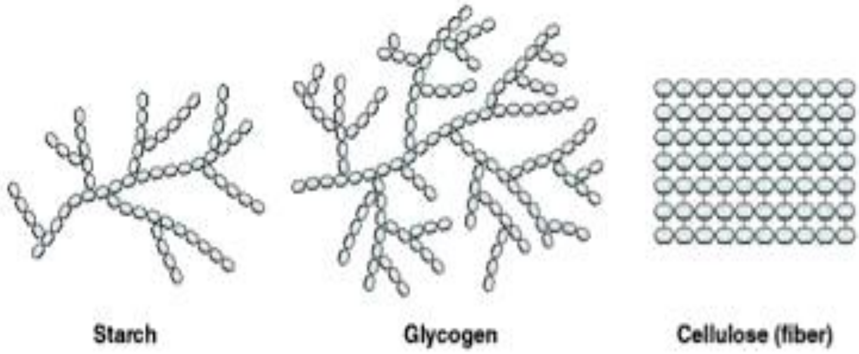
Amylose	Amylopectin
1. Simple and more soluble in water	Less soluble
2. Readily dispersed in water but does not form gel or paste.	Form gel paste, colloidal solution
3. Blue colour with iodine	Red colour.



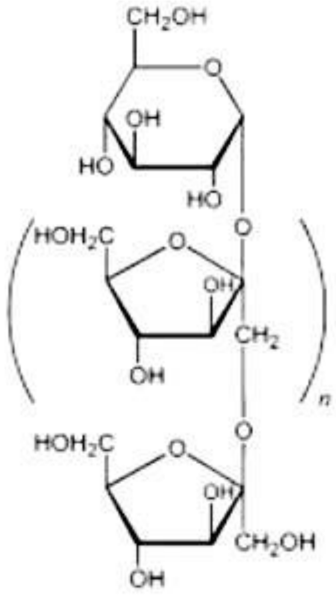
Structure of amylose (= A-fraction)



Glycogen- storage homopolysaccharide of animals similar to amylopectin except that is more highly branched with branch points at every 8 to 10 glucose unit and non-reducing sugar and give red colour with iodine. It is hydrolysed with by α and β amylase to form glucose and maltose. In animalglycogen phosphorylase gives glu 1-PO_4 rather than free glycogen.



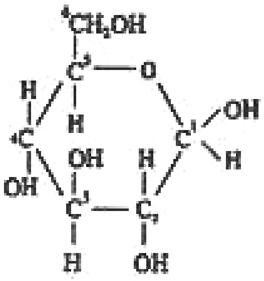
Fructans are a polymer of fructose found as reserve polysaccharide in Gramineae and Compositae. **Inulin** - storage form in tuber of Compositae artichokes. It consists of β-D-fructose units bound by β (2-1) linkage. It yields fructose on hydrolysis hence known as *fructans*. It has M.wt. of 5000, 30-35 monosaccharide residues linked in straight chain. It is white powder insoluble in cold water, non-reducing sugar, no colour to I_2. It dissolves in warm water forming a colloidal solution. The fructans found in leaves, stem, root of Gramineae show β, (2-6) linkage and are main source of water-soluble carbohydrate for fermentation.



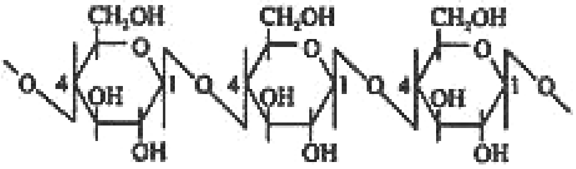
Inulin

Structural polysaccharides

Cellulose – most natural polysaccharides β (1-4) gluco-polysaccharide occurs in cell wall of plants where it contributes to the shape, support and physical structures. It occurs in nearly pure form in cotton flax (90%). Woods of plants are an insoluble organised structure composed of cellulose (60%) and lignin. It is linear unbranched homopolymer of D-glucose units linked by β (1-4) glycosidic bonds. It forms a structure ofparallel chains that are crossed linked by hydrogen bonding so that glucose units have an extended configuration and lie side by side forming insoluble fibrils. The β (1-4) linkage is highly resistant to acid hydrolysis and yields reducing disaccharide cellobiose units and very strong acid is required to produce D-glucose. It is not digested by higher animals. It is hydrolysed in ruminants a β-glucosidase. It is fibrous tough white insoluble in water and soluble in ammonium solution. No colour with I_2. No nutritive value. Cellulose is base of insulating tiles, packing and building material, paper is wood cooked in lime water and SO_2 (to remove lignin). Wood has 65% cellulose, 30% lignin, and 2% dextran. Cellulose nitrate forms explosive, celluloid films. **Hemicellulose** have D-xylose, D-mannose and galactose linked by β (1-4) or β (1-3) glycosidic bonds.



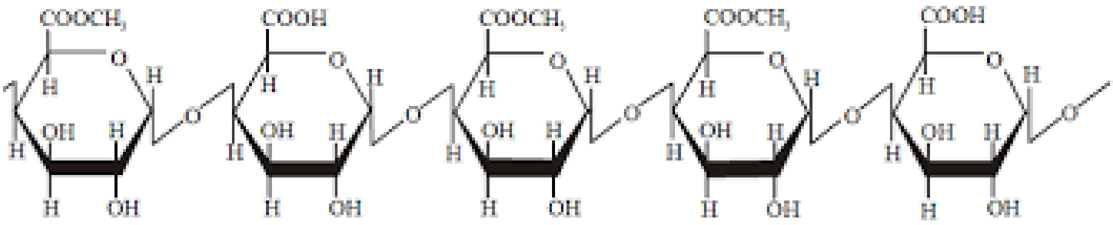
β-D-glucose



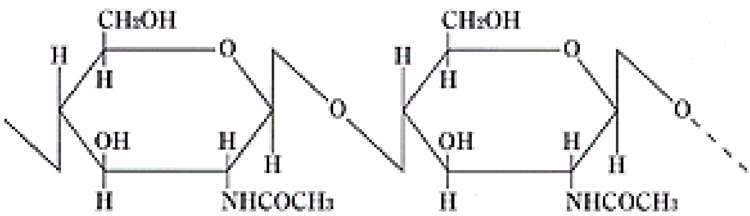
Part of cellulose chain..

B-glucans shows β, (1-3) linked D glucose units. It is formed in d response to wounding and also during pollen tube growth showing plugging. Other β glucans form major components of matrix material of cereals endosperm's cell-wall. These are linear molecules with 30 % β (1-3) and 70% β (1-4) glucoside linkage randomly dispersed in cell wall and bound to peptide sequences.

Pectin contains galacturonic acid as repeating units. Pectic acid is homopolymer of methyl ester of D-galacturonic acid, found in fruits.



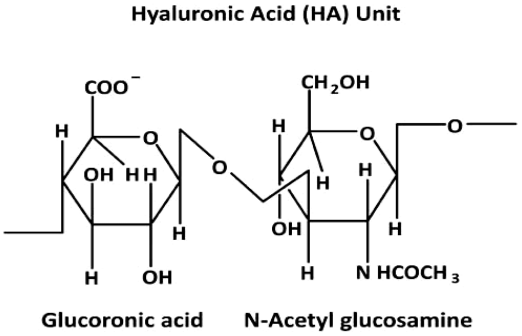
Chitin is a homopolymer of N-acetyl D-glucosamine linked by β (1-4) in structural polysaccharides of shells, non-reducing. On hydrolysis it gives glucosamine and acetic acid. Chitinase in bacteria decompose chitin.

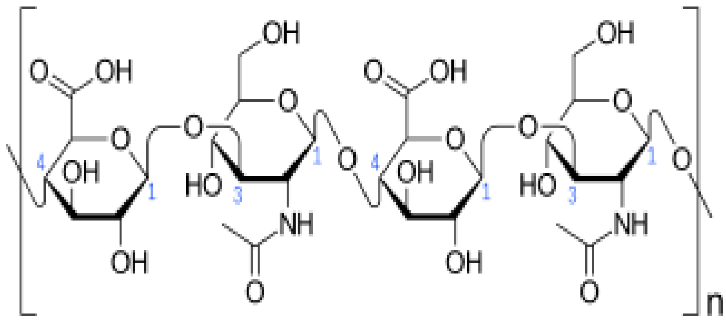


<u>Heteropolysaccharide</u> consists of different repeating units and are generally found in cell walls. The are mucopolysaccharide, glycolipid and glycoprotein.

Glycosaminoglycans are negatively charges and highly viscous molecules and are, therefore, also called **mucopolysaccharides.** ***Mucopolysaccharide*** acts as structural support for connective tissue and there are gelatinous substances mol.wt. is $5x10^{6}$. They act as lubricants, consist of long unbranched open chain They form gel like material in the extra cellular space and form a pathway for differentiation of oxygen and nutrients. The most important glycosaminoglycans are chondroitin sulphate, keratan sulphate,

Hyaluronic acid- is disaccharide units linked by β (1-3) bond and two repeating units are linked by β (1-4) linkage The repeating units are D-glucuronic acid and N-acetylglucosamine. Hyaluronic acid (hyaluronan) is water soluble. it forms viscous solution in vitreous humor of vertebrate eye, umbilical cord.



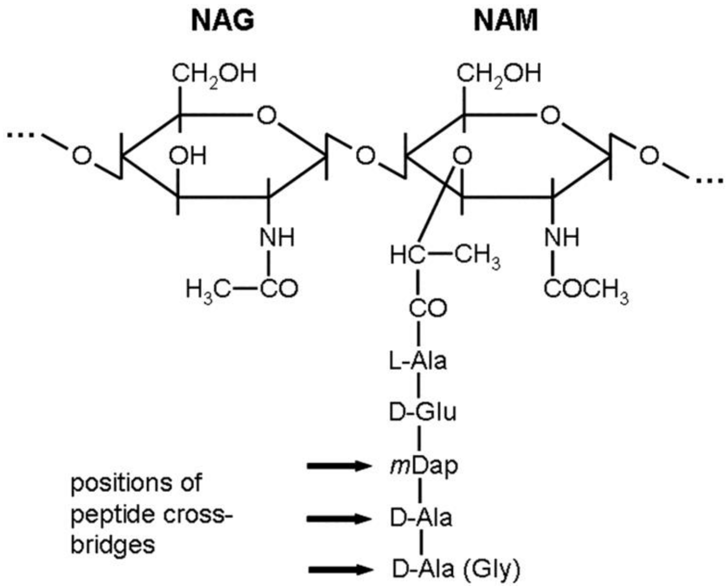


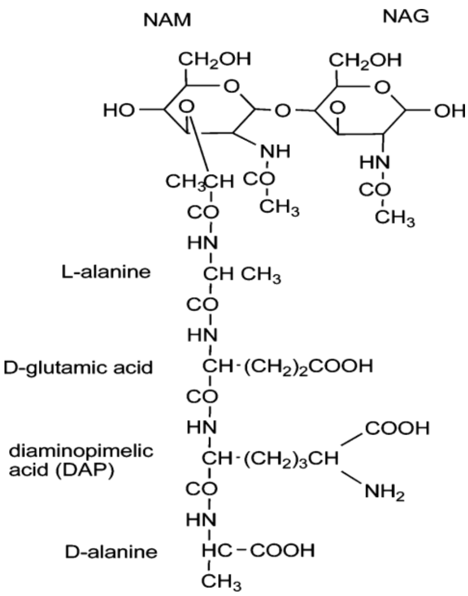
Chondroitin is similar to hyaluronic acid except sugar is N-acetyl D-galactosamine, found in cell coat.

Agar-Agar has D and L galactose repeating units bound by β,1-3 bonds with a sulphuric group attached at 6th carbon. It solidifies at room temperature, soluble in hot water, used as culture medium, preparation od medicines, cosmetic etc.

Complex polysaccharide like glycolipid and glycoprotein.

Peptidoglycan bacterial cell wall has heteropolysaccharide linked to amino acid short chain. Heteropolysaccharide of N-acetyl-D-glucosamine (NAG) and N-acetylmuramic acid (NAM) to which a tetrapeptide side chain is attached. Amino acid is alanine, glutamine, lysine and alanine. lysozyme kill bacteria by hydrolysing the β (1-4) glycosidic bond. Penicillin acts by preventing cross links at peptidoglycan between two units.





Glycoprotein have one or more oligosaccharides of varying complexity joined covalently to a protein. They are found on the outer face of plasma membrane, in the extracellular matrix, and in the blood. Inside cells they are found in specific organelles such as Golgi complexes, secretory granules, and lysosomes. Mostly amide group of asparagines is linked by glycosyl bond to trisaccharide of mannose and 2 molecules of N-acetyl glucosamine. Mannose forms the branch end where 3 or more mannose are linked in α (1-3) or α (1-6) linkage. Oligosaccharide linkage in glycoprotein having a glycosidic bond to threonoine hydroxyl groups of Ser or Thr residue (O-linked) or through an N- glycosyl link to the amide nitrogen of an Asn residue (N-linked) e.g. Receptor protein transport, growth control, regulation of protein structure andactivity. In fishes of arctic zone antifreeze protein present. Glycoprotein is a D-galactosyl-N-acetyl-D-galactosamine to which is linked tripeptide Alan-Alan-Threonine.

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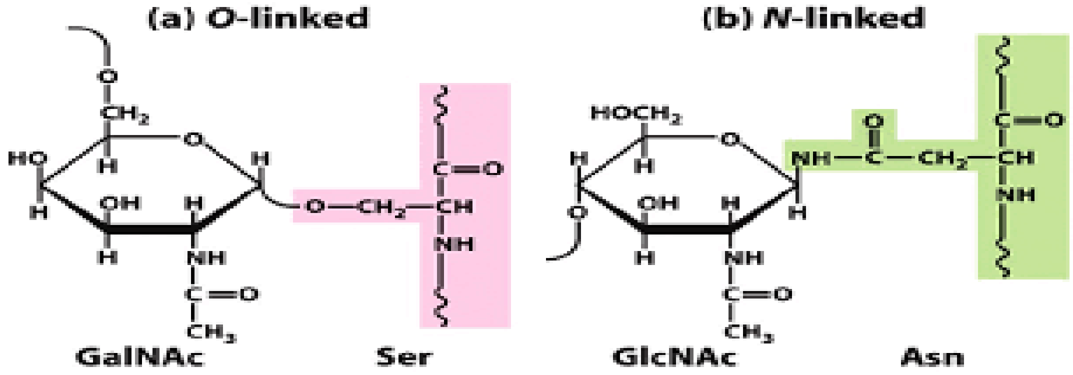
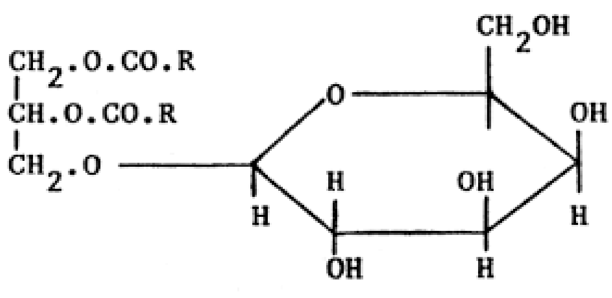
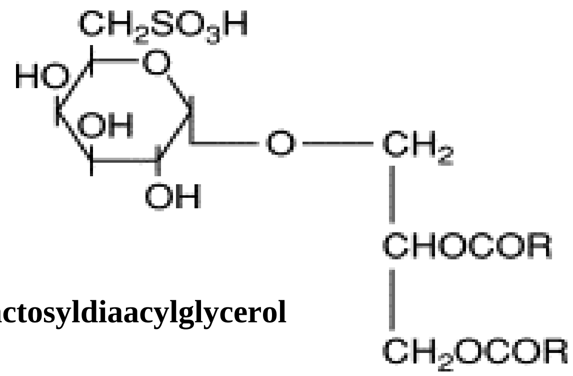


Proteoglycans are macromolecule of cell surface or extracellular matrix in which one or more glycosaminoglycans chains are joints covalently to a membrane protein or a secreted protein.The glycosaminoglycans moiety commonly forms the greater fraction (by mass) of the proteoglycan molecule, dominate the structure, and is often the main site of biological activity. Proteoglycans are major component of connective tissue such as cartilage, in which their many noncovalent interactions with other proteoglycans, protein, and glycosaminoglycans provide strength and resilience.

Glycolipids are membrane lipids in which the hydrophilic head groups are oligosaccharides, which, as in glycoprotein, act as specific sites for recognition by carbohydrate-binding protein. Galactolipids are major glycolipids with mono- or di- galactosyl diacylglycerol derivatives found in plasma membrane and chloroplast membrane.



Galactolipid



Galactosyldiaacylglycerol

Structure and roles of some polysaccharide

Polymer	**Type**	**Repeating Units**	**Size**	**Roles/Significances**
Starch Amylose Amylopectin	Homo- Homo-	(α1→4)Glc,linear (α1→4)Glc,with (α1→ 6)Glc branches every 24-30 residues	50-5,000 Up to 10^6	Energy storages: in plants
Glycogen	Homo-	(α1→4)Glc, with (α1→ 6)Glc branchesevery 8 -12 residues	Up to 50,000	Energy storage: in bacteria and animal cells
Cellulose	Homo-	(β1→4)Glc	Up to 15,000	Structural: in plants, gives rigidity and strength to cell walls.
Chitin	Homo-	(β1→ 4)GlcNAc	Very large	Structural: in insects, spiders, crustaceans, gives rigidity and strength to exoskeletons
Peptidoglycan	Hetero- Peptide attached	Mur2Ac(β1→ 4) GlcNAc(β1	Very large	Structural: in bacteria, gives rigidity and strength to cell envelope.
Hyaluronan (a glycosaminoglycan)	Hetero- acidic	GlcA(β1→ 3) GlcNAc(β1	Up to 100,000	Structural: in vertebrates, extracellular matrix of skin and connective tissue, viscosity and lubrication in joints.