Carbohydrates

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- The carbohydrates are a group of naturally occurring carbonyl compounds (aldehydes or ketones) that also contain several hydroxyl groups.
- It may also include their derivatives which produce such compounds on hydrolysis.
- They are the most abundant organic molecules in nature and also referred to as “saccharides”.
- The carbohydrates which are soluble in water and sweet in taste are called as “sugars”.

Structure

- Carbohydrates consist of carbon, hydrogen, and oxygen.
- The general empirical structure for carbohydrates is $(CH_2O)_n$.
- They are organic compounds organized in the form of aldehydes or ketones with multiple hydroxyl groups coming off the carbon chain.
- The building blocks of all carbohydrates are simple sugars called monosaccharides.
- A monosaccharide can be a polyhydroxy aldehyde (aldose) or a polyhydroxy ketone (ketose).
- The carbohydrates can be structurally represented in any of the three forms:

- Open chain structure.
- Hemi-acetal structure.
- Haworth structure.

- **Open chain structure** – It is the long straight-chain form of carbohydrates.

- **Hemi-acetal structure** – Here the 1st carbon of the glucose condenses with the -OH group of the 5th carbon to form a ring structure.

- **Haworth structure** – It is the presence of the pyranose ring structure.

Physical Properties of Carbohydrates

Stereoisomerism – Compound shaving the same structural formula but they differ in spatial configuration. Example: Glucose has two isomers with respect to the penultimate carbon atom. They are D-glucose and L-glucose.

Optical Activity – It is the rotation of plane-polarized light forming (+) glucose and (-) glucose.

Diastereo isomers – It the configurational changes with regard to C2, C3, or C4 in glucose. Example: Mannose, galactose.

Annomerism – It is the spatial configuration with respect to the first carbon atom in aldoses and second carbon atom in ketoses.

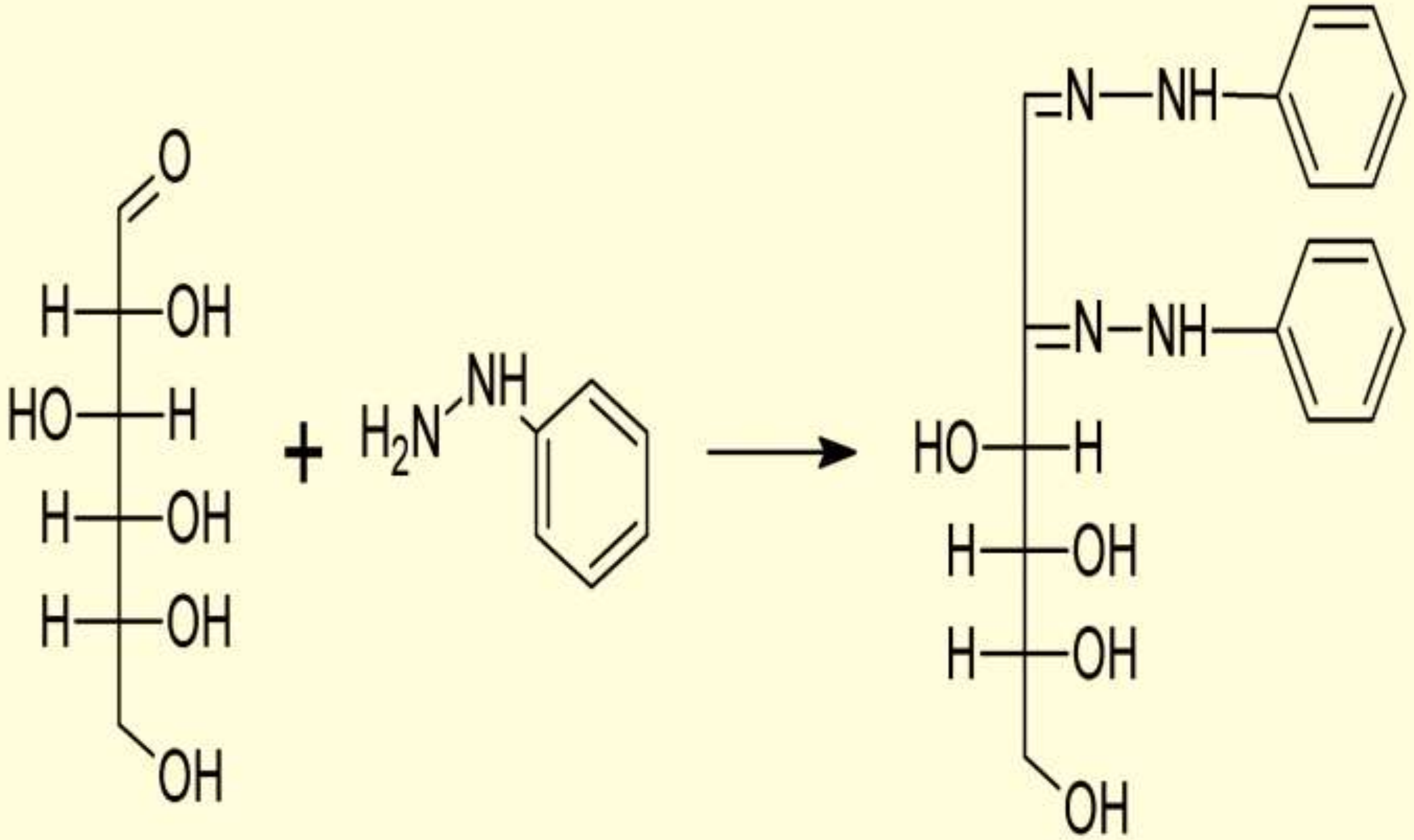
Chemical Properties of Carbohydrates

Osazone formation: Osazone are carbohydrate derivatives when sugars are reacted with an excess of phenylhydrazine. eg. Glucosazone

Benedict's test: Reducing sugars when heated in the presence of an alkali gets converted to powerful reducing species known as enediols. When Benedict's reagent solution and reducing sugars are heated together, the solution changes its color to orange-red/ brick red.

Oxidation: Monosaccharides are reducing sugars if their carbonyl groups oxidize to give carboxylic acids. In Benedict's test, D-glucose is oxidized to D-gluconic acid thus, glucose is considered a reducing sugar.

Reduction to alcohols: The C=O groups in open-chain forms of carbohydrates can be reduced to alcohols by sodium borohydride, NaBH4, or catalytic hydrogenation (H2, Ni, EtOH/H2O). The products are known as "alditols".



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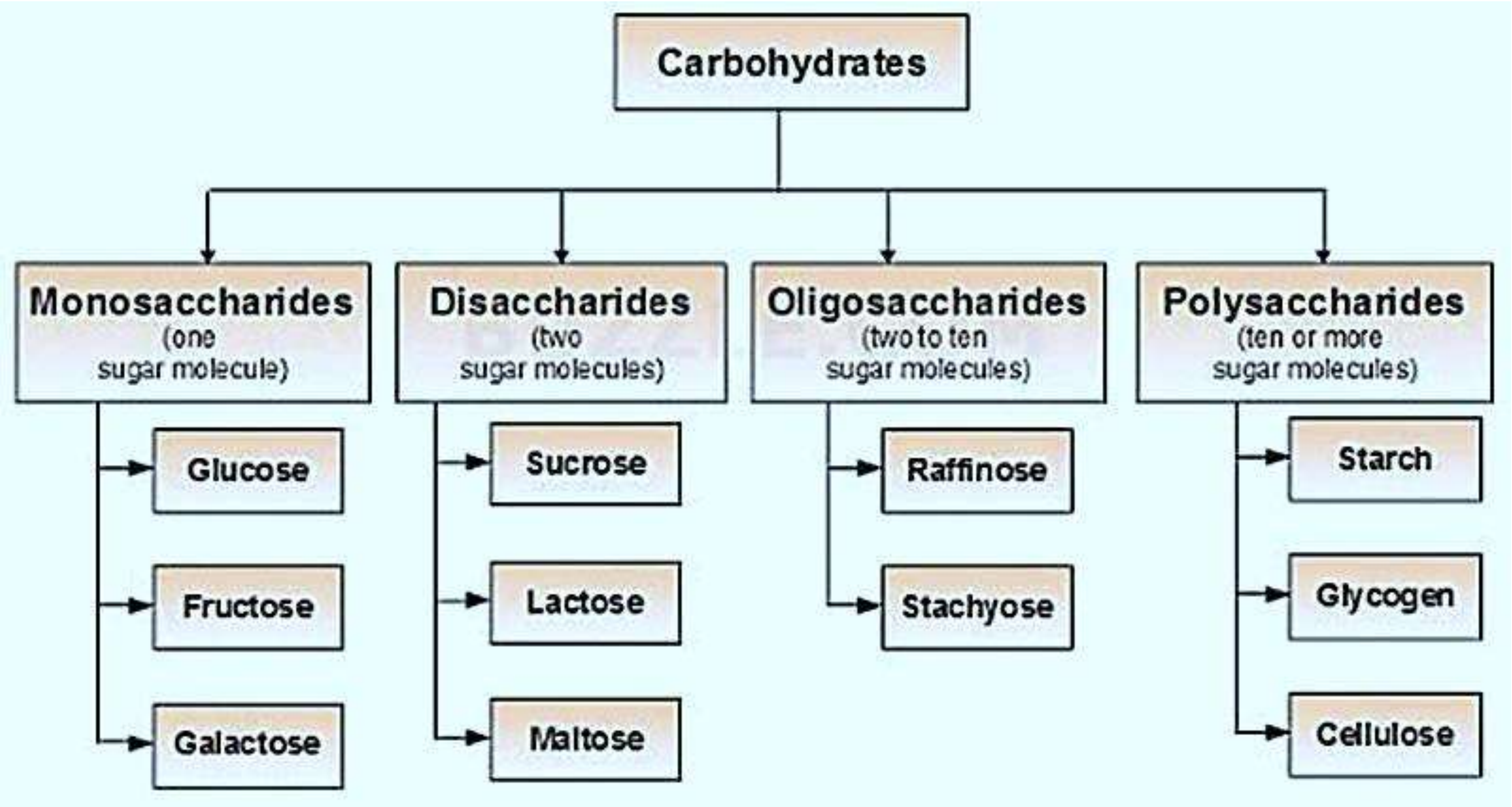
Osazone form when D-glucose reacts with phenylhydrazine to give glucosazone. The same product is obtained from fructose and mannose.

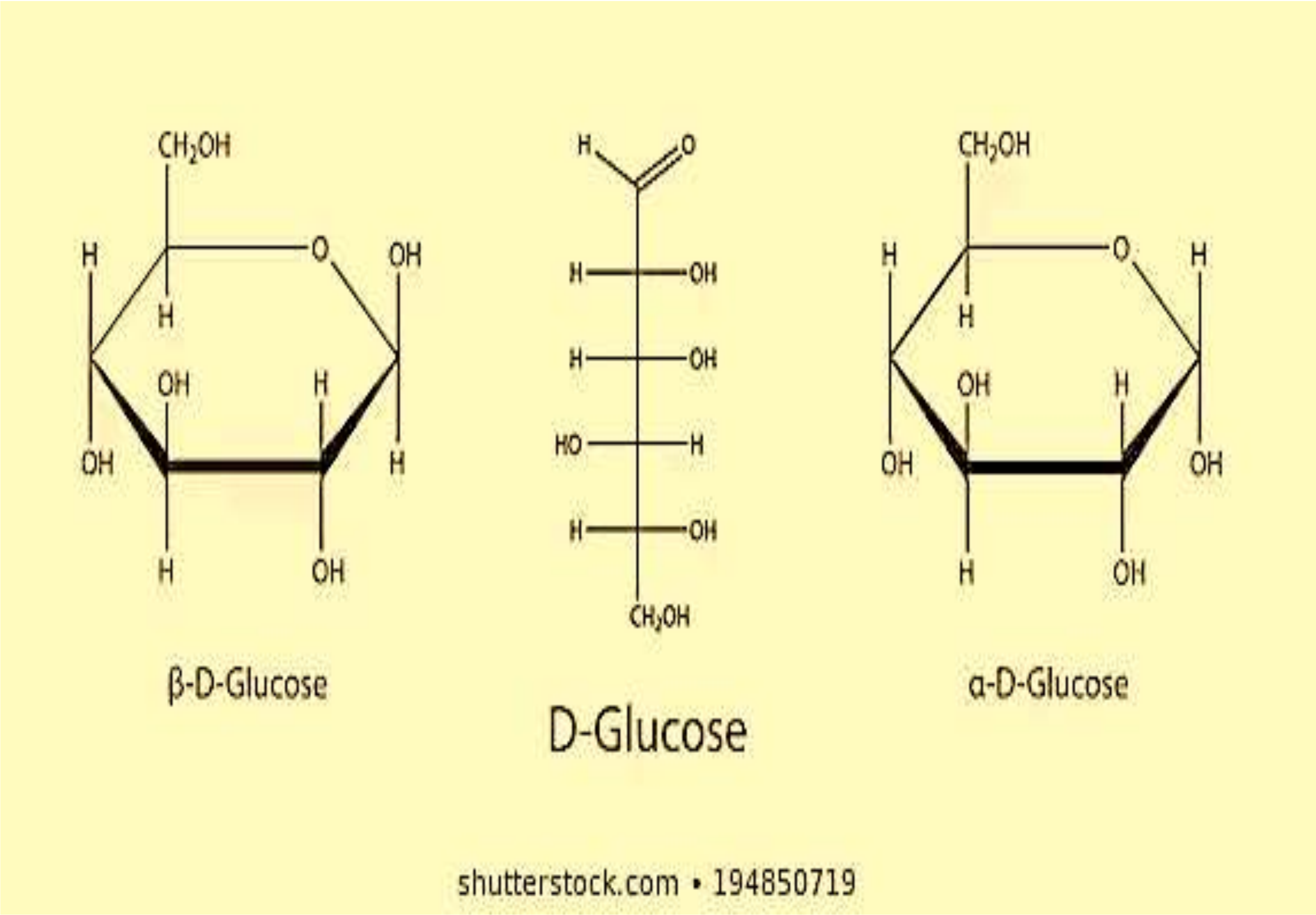

Carbohydrates
Monosaccharides (one sugar molecule)
Disaccharides (two sugar molecules)
Oligosaccharides (two to ten sugar molecules)
Polysaccharides (ten or more sugar molecules)
Glucose
Fructose
Galactose
Sucrose
Lactose
Maltose
Raffinose
Stachyose
Starch
Glycogen
Cellulose

- Monosaccharides, also called simple sugar, are the simplest form of sugar and the most basic units of carbohydrates.
- They cannot be further hydrolyzed to simpler chemical compounds. The general formula is $(CH_2O)_x$.
- They are usually colorless, water-soluble, and crystalline solids.
- The monosaccharide glucose plays a pivotal role in metabolism, where the chemical energy is extracted through glycolysis and the citric acid cycle to provide energy to living organisms. Some other monosaccharides can be converted in the living organism to glucose.

The oxygen will also bond to a hydrogen, creating a hydroxyl group. Because carbon can form 4 bonds, several of these carbon molecules can bond together.

One of the carbons in the chain will form a double bond with an oxygen, which is called a carbonyl group.

If this carbonyl occurs at the end of the chain, the monosaccharide is in the aldose family. If the carbonyl group is in the middle of the chain, the monosaccharide is in the ketose family.


β-D-Glucose
D-Glucose
α-D-Glucose
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- Glucose is one of the most common monosaccharides in nature, used by nearly every form of life.
- This simple monosaccharide is composed of 6 carbons.
- The first carbon is the carbonyl group. Because it is at the end of the molecule, glucose is in the aldose family.
- Typically, monosaccharides with more than 5 carbons exist as rings in solutions of water. The hydroxyl group on the fifth carbon will react with the first carbon.
- The hydroxyl group gives up its hydrogen atom when it forms a bond with the first carbon.
- The double bonded oxygen on the first carbon bonds with a new hydrogen when the second bond with the carbon is broken. This forms a fully connected and stable ring of carbons.

Properties

- Simplest group of carbohydrates and often called simple sugars since they cannot be further hydrolyzed.
- Colorless, crystalline solid which are soluble in water and insoluble in a non-polar solvent.
- These are compound which possesses a free aldehyde or ketone group.
- The general formula is Cn(H2O)nor CnH2nOn.
- They are classified according to the number of carbon atoms they contain and also on the basis of the functional group present.
- The monosaccharides thus with 3,4,5,6,7… carbons are called trioses, tetroses, pentoses, hexoses, heptoses, etc., and also as aldoses or ketoses depending upon whether they contain aldehyde or ketone group.
- Examples: Glucose, Fructose, Erythrulose, Ribulose.

Function

Monosaccharides are used to produce and store energy.

Most organisms create energy by breaking down the monosaccharide glucose, and harvesting the energy released from the bonds.

Other monosaccharides are used to form long fibers, which can be used as a form of cellular structure.

Plants create cellulose to serve this function, while some bacteria can produce a similar cell wall from slightly different polysaccharides.

Even animal cells surround themselves with a complex matrix of polysaccharides, all made from smaller monosaccharides.

Glucose

- Glucose is an important monosaccharide in that it provides both energy and structure to many organism.
- Glucose molecules can be broken down in glycolysis, providing energy and precursors for cellular respiration.
- If a cell does not need any more energy at the moment, glucose can be stored by combining it with other monosaccharides.
- Plants store these long chains as starch, which can be disassembled and used as energy later.
- Animals store chains of glucose in the polysaccharide glyocogen, which can store a lot of energy.

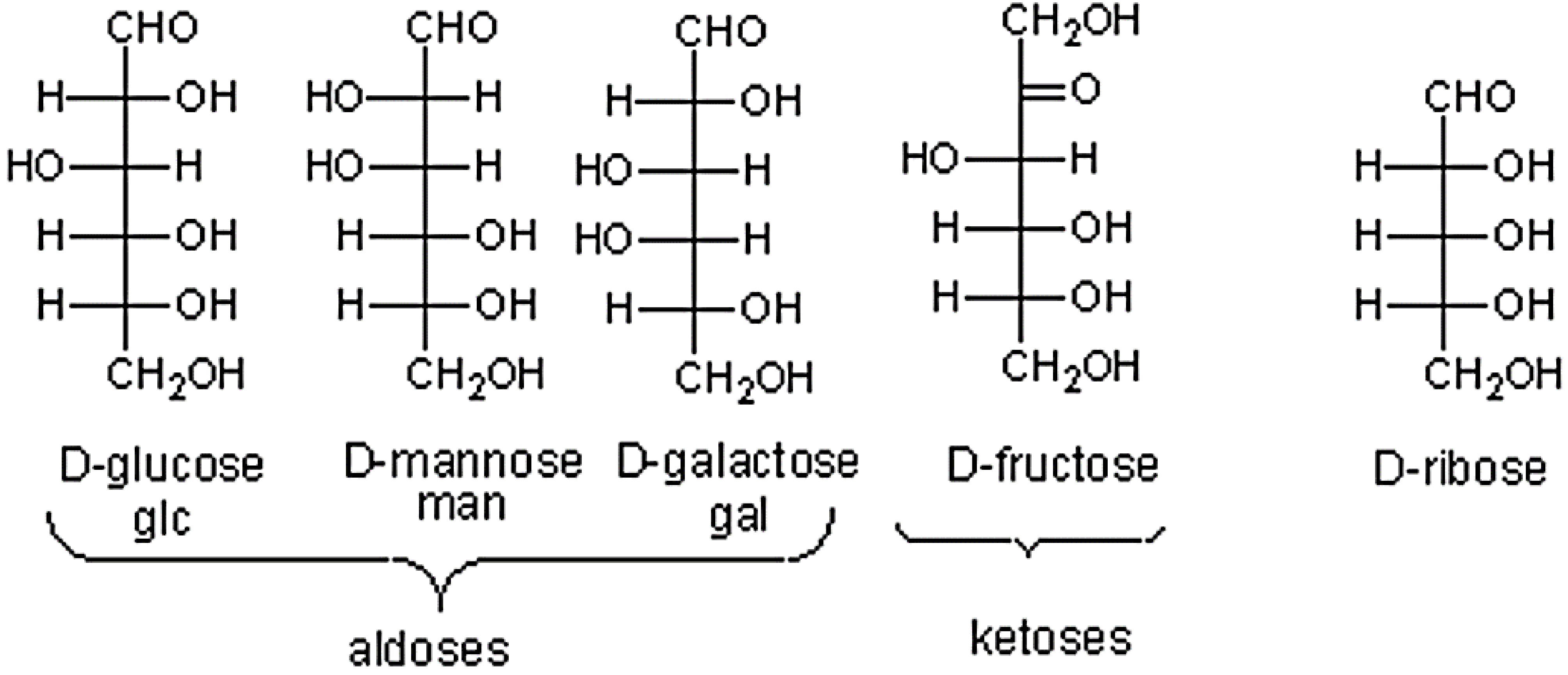
- Glucose can also be connected in long strings of monosaccharides to form polysaccharides that resemble fibers.
- Plants typically produce this as cellulose.
- Cellulose is one of the most abundant molecules on the planet, and if we could weigh all of it at once it would weigh millions of tons.
- Each plant uses cellulose to surround each cell, creating rigid cell walls that help the plants stand tall and remain turgid.
- Without the ability of monosaccharides to combine into these long chains, plants would be flat and squishy.

Fructose

- Although almost identical to glucose, fructose is a slightly different molecule.
- Notice that instead of the carbonyl group being at the end of the molecule, as in glucose, it is the second carbon down. This makes fructose a ketose, instead of an aldose. Like glucose, fructose still has 6 carbons, each with a hydroxyl group attached.
- Fructose, because it is a monosaccharide, can be combined with other monosaccharides to form oligosaccharides. A very common disaccharide made by plants is sucrose. Sucrose is one fructose molecule connected to a glucose molecule through a glycosidic bond.

Galactose

- Galactose is a monosaccharide produced in many organisms, especially mammals.
- Mammals use galactose in milk, to give energy to their offspring. Galactose is combined with glucose to form the disaccharide lactose. The bonds in lactose hold a lot of energy, and special enzymes are created by newborn mammals to break these bonds apart.
- Once being weaned of their mother’s milk, the enzymes that break lactose down into glucose and galactose monosaccharides are lost.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D-mannose
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CH2OH
D-galactose
gal
aldoses
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O
HO H
H OH
H OH
CH2OH
D-fructose
ketoses
CHO
H OH
H OH
H OH
CH2OH
D-ribose

- The sugar formed when two monosaccharides (simple sugars) are joined by glycosidic linkage. Glycosidic bonds are cleaved by enzymes known as glycosidases.
- Like monosaccharides, disaccharides are soluble in water. Three common examples are sucrose, lactose, and maltose.
- They have 12 carbon atoms, and their chemical formula is $C_{12}H_{22}O_{11}$.
- Disaccharides are formed through dehydration reactions in which a total of one water molecule is removed from the two monosaccharides.

Functions of Disaccharides

- Disaccharides are carbohydrates found in many foods and are often added as sweeteners. Sucrose, for example, is table sugar, and it is the most common disaccharide that humans eat.
- Plants store energy in the form of disaccharides like sucrose and it is also used for transporting nutrients in the phloem.
- Plants also use disaccharides to transport monosaccharides like glucose, fructose, and galactose between cells. Packaging monosaccharides into disaccharides makes the molecules less likely to break down during transport.

- When disaccharides are formed from monosaccharides, an -OH (hydroxyl) group is removed from one molecule and an H (hydrogen) is removed from the other.
- Glycosidic bonds are formed to join the molecules; these are covalent bonds between a carbohydrate molecule and another group (which does not necessarily need to be another carbohydrate).
- The H and -OH that were removed from the two monosaccharides join together to form a water molecule, H2O.
- the process of forming a disaccharide from two monosaccharides is called a dehydration reaction or condensation reaction.
- When disaccharides are broken down into their monosaccharide components via enzymes, a water molecule is added. This process is called hydrolysis.

Sucrose

- Sucrose, commonly known as table sugar in its refined form, is a disaccharide found in many plants.
- It is made up of the monosaccharides glucose and fructose. In the form of sugar, sucrose is a very important component of the human diet as a sweetener.
- William Miller, an English chemist, coined the word sucrose in the year 1857.
- Sugar was first extracted and purified from sugar cane in India as early as the 8th Century BCE. In fact, the word candy gets its name in part from the word khanda, which was a name for sugar crystals in Sanskrit. Today, around 175 metric tons of sugar are produced each year.

- Sucrose has a monoclinic crystal structure when subjected to high temperatures (over 186°C), this compound decomposes, yielding caramel. and is quite soluble in water.
- Chemical Formula of Sucrose is C12H22O11.
- White, crystalline solid.
- Sucrose can undergo a combustion reaction to yield carbon dioxide and water.
- When reacted with chloric acid, this compound yields hydrochloric acid, carbon dioxide, and water.

Uses

- Sucrose is one of the most important components of soft drinks and other beverages.
- This compound is used in many pharmaceutical products.
- It serves as a chemical intermediate for many emulsifying agents and detergents.
- It also serves as a food thickening agent and as a food stabilizer.
- The shelf lives of many food products, such as jams and jellies, are extended with the help of this compound.
- The use of sucrose in baking results in the brown colour of the baked products.
- This compound also serves as an antioxidant (a compound that inhibits oxidation).
- Sucrose is widely used as a food preservative.

Maltose

- known as maltobiose or malt sugar, is a disaccharide formed from two units of glucose joined with an α bond.
- Malt is formed when grains soften and grow in water, and it is a component of beer, starchy foods like cereal, pasta, and potatoes, and many sweetened processed foods.
- In plants, maltose is formed when starch is broken down for food. It is used by germinating seeds in order to grow.
- Maltose, malt sugar, $C_{12}H_{22}O_{11}.H_2O$, is prepared from starch by diastase.
- Hydrolysis by acids or maltase gives only d-glucose.

- It is White powder or crystals.
- Used for brewing as their composition is similar to wort. Also in doughs with strong fermenting yeasts as these are able to metabolize maltose quickly.
- Used as a carrying material for flavouring materials and volatile aromas. It is also used in infant foods.
- The medicinal use of maltose is based on its repair and protection of the liver, for which modern glucose is used.

Lactose

- Lactose, or milk sugar, is made up of galactose and glucose.
- These biomolecules have a significant role in daily life by providing three requirements, i.e., food (starch), shelter (cellulose) and cloth (cellulose).
- Lactose monohydrate is mainly present in milk and exists as a naturally occurring disaccharide. Lactose crystals contain water of crystallization, because of which molecular mass becomes 360.3 g/mol compared to 342.3 g/mol of anhydrous lactose. It is slightly soluble in ethanol but quite soluble in water, white and odorless crystalline powder.

- Today, the number of people who are lactose intolerant varies widely between populations, ranging from <10% in Northern Europe to 95% in parts of Africa and Asia.
- Its mild flavor and easy handling properties have led to its use as a carrier and stabiliser of aromas and pharmaceutical products.
- lactose use is in the pharmaceutical industry. Lactose is added to tablet and capsule drug products as an ingredient because of its physical and functional properties.

Polysaccharides

- long chains of monosaccharides linked by glycosidic bonds.
- Three important polysaccharides, starch, glycogen, and cellulose, are composed of glucose.
- Starch and glycogen serve as short-term energy stores in plants and animals, respectively.
- The glucose monomers are linked by α glycosidic bonds.
- A polysaccharide is also called a glycan.
- A polysaccharide can be a homopolysaccharide, in which all the monosaccharides are the same, or a heteropolysaccharide in which the monosaccharides vary.
- A molecule with a straight chain of monosaccharides is called a linear polysaccharide, while a chain that has arms and turns is known as a branched polysaccharide.

Properties

- They are not sweet in taste.
- Many are insoluble in water.
- They are hydrophobic in nature.
- They do not form crystals on desiccation.
- Can be extracted to form a white powder.
- They are high molecular weight carbohydrates.
- Inside the cells, they are compact and osmotically inactive.
- They consist of hydrogen, carbon, and oxygen. The hydrogen to oxygen ratio being 2:1.

Structure

- All polysaccharides are formed by the same basic process where monosaccharides are connected via glycosidic bonds.
- These glycosidic bonds consist of an oxygen molecule bridging two carbon rings.
- The bond is formed when a hydroxyl group is lost from the carbon of one molecule, while the hydrogen is lost by the hydroxyl group of another monosaccharide.
- Because two molecules of hydrogen and one of oxygen are expelled, the reaction is a dehydration reaction.
- The structure of the molecules being combined determines the structures and properties of the resulting polysaccharide.
- A polysaccharide used for energy storage will give easy access to the constituent monosaccharides whereas a polysaccharide used for support is usually a long chain of monosaccharides that form fibrous structures.

Homopolysaccharides

- Glycogen: It is made up of a large chain of molecules. It is found in animals and fungi.
- Cellulose: The cell wall of the plants is made up of cellulose. It comprises long chains of β-glycosides.
- Starch: It is formed by the condensation of amylose and amylopectin. It is found largely in plants, fruits, seeds, etc.
- Insulin: It is made up of a number of fructofuranose molecules linked together in chains. It is found in the tubers of dahlia, artichoke, etc.

Heteropolysaccharides

- Hyaluronic Acid: It is made up of D-glucuronic acid and N-acetyl-glucosamine. It is found in connective tissues and skin.
- Heparin: It is made up of D-glucuronic acid, L-iduronic acid, N-sulfo-D-glucosamine and is largely distributed in mast cells and blood.
- Chondroitin-4-sulfate: Its component sugars are D-glucuronic acid and N-acetyl-D-galactosamine-4-O-sulfate. It is present in the cartilages.
- Gamma globulin: N-acetyl-hexosamine, D-mannose, D-galactose are the component sugars of this polysaccharide. It is found in the blood.

Functions Of Polysaccharides

The polysaccharides serve as a structural organization in animals and plants. Other functions of polysaccharides include:

- They store energy in organisms.
- Due to the presence of multiple hydrogen bonds, the water cannot invade the molecules making them hydrophobic.
- They allow for changes in the concentration gradient which influences the uptake of nutrients and water by the cells.
- Many polysaccharides become covalently bonded with lipids and proteins to form glycolipids and glycoproteins. These glycolipids and glycoproteins are used to send messages or signals between and within the cells.
- They provide support to the cells. The cell wall of plants is made up of polysaccharide cellulose, which provides support to the cell wall of the plant. In insects and fungi, chitin plays an important role in providing support to the extracellular matrix around the cells.

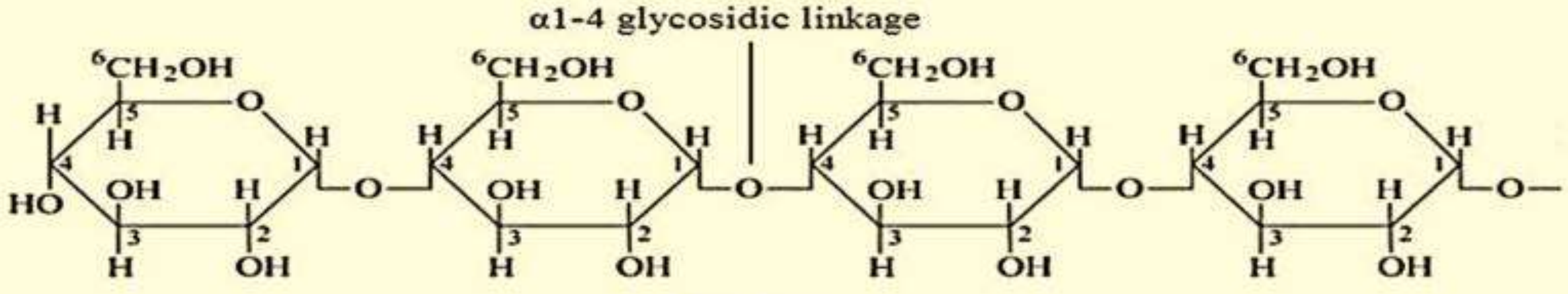
On the basis of functions

- **Storage polysaccharides-**They are those polysaccharides which serve as reserve food.At the time of need, storage polysaccharides are hydrolysed. Sugars thus released become available to the living cells for production of energy and biosynthetic activity. There are two main storage polysaccharides— starch and glycogen.
- **Structural polysaccharides-** They are polysaccharides that take part in forming the structural frame work of the cell walls in plants and skeleton of animals. Structural polysaccharides are of two main types: chitin and cellulose.

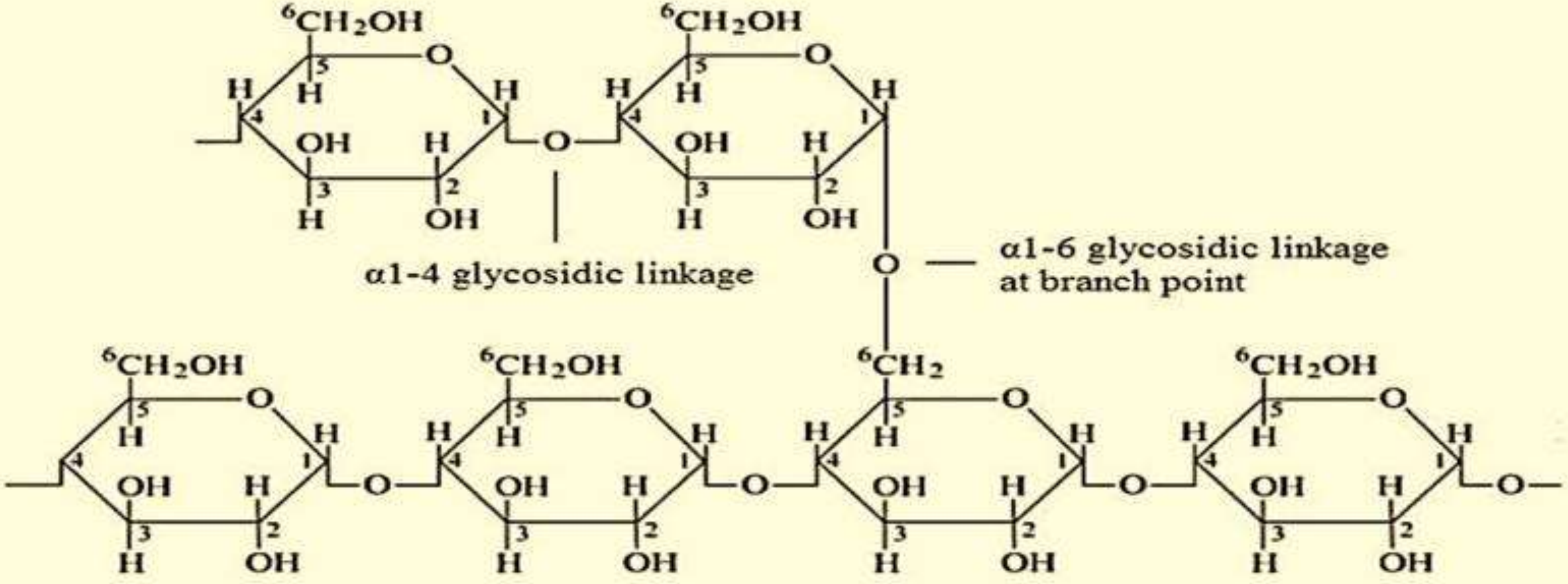
Starch

- A glucose polymer in which glucopyranose units are bonded by alpha-linkages.
- It is made up of a mixture of amylose (15–20%) and amylopectin (80–85%).
- Amylose consists of a linear chain of several hundred glucose molecules, and Amylopectin is a branched molecule made of several thousand glucose units (every chain of 24–30 glucose units is one unit of Amylopectin).
- Starches are insoluble in water. They can be digested by breaking the alpha-linkages (glycosidic bonds).
- Both humans and other animals have amylases, so they can digest starches. Potato, rice, wheat, and maize are major sources of starch in the human diet. The formations of starches are the ways that plants store glucose.
- Amylose is soluble in water and contains around 15-20% of starch.
- The starch content in Amylopectin is about 80-85% but this is not soluble in water.

- Bakery Products require starch for their elasticity, its examples would be cake and biscuit fillings.
- In industries, starch is used to increase the mechanical strength to resistance to friction and resist moisture penetration.
- Starch are used in detergents
- Confectionary energy for dextrose
- Brewing and alcoholic beverages are often derived from starch products.
- The production of dry sausages, salamis, brine cured hams etc require the use of starch products.



Amylose



Amylopectin

Glycogen

- It is the polysaccharide food reserve of animals, bacteria and fungi. Glycogen is popularly called animal starch.
- Glycogen is mainly stored inside liver (up to 0.1 kg) and muscles. but can also be made by glycogenesis within the brain and stomach
- Glycogen serves as the secondary long-term energy storage in animal and fungal cells, with the primary energy stores being held in adipose tissue.
- This is also called animal starch as its structure is somewhat similar to amylopectin and it has many branches.

- **It is an energy reserve for animals.**
- **It is the chief form of carbohydrate stored in animal body.**
- **It is insoluble in water. It turns brown-red when mixed with iodine.**
- **It also yields glucose on hydrolysis.**

Features

non-reducing end

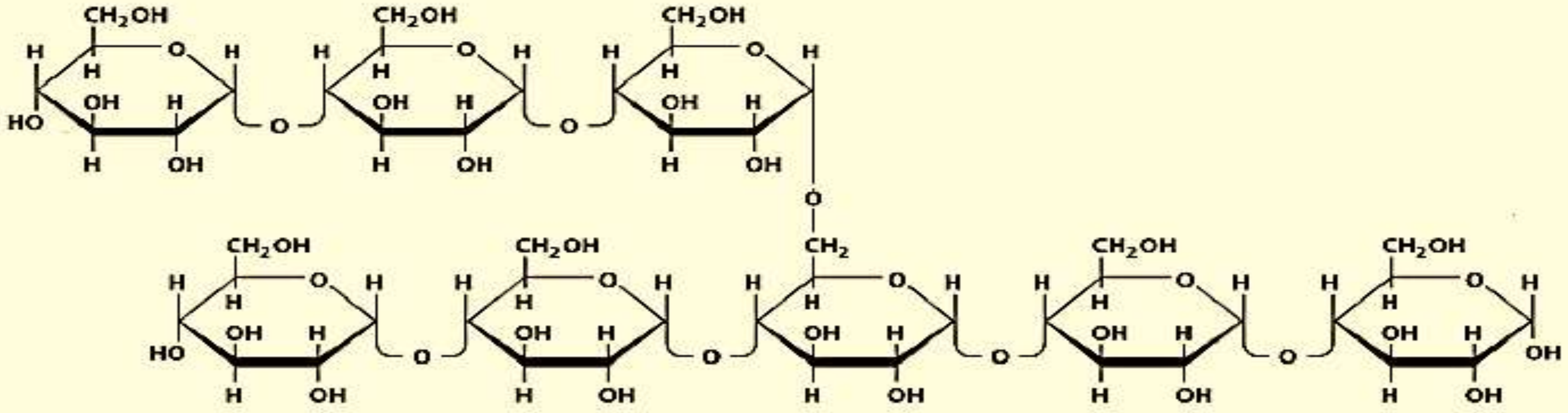
reducing end

alpha-1,4-linkage

alpha-1,6-linkage

atomic site of glycogen
phosphorylase catalysis

Glycogen Structure:



Chitin

- It is the second most abundant organic substance. Chitin is a complex carbohydrate of heteropolysaccharide type which is found as the structural component of fungal walls and exoskeleton of arthropods.
- In fungal walls, chitin is often known as fungus cellulose.
- Chitin is soft and leathery. Therefore, it provides both strength and elasticity. It becomes hard when impregnated with certain proteins and calcium carbonate.

- In chitin, basic unit is not glucose but a nitrogen containing glucose derivative known as N-acetyl glucosamine.
- Chitin has an un-branched configuration. Monomers are joined together by 1- 4 β-linkages. Adjacent residues lie at 180°. Molecules occur in parallel and are held together by hydrogen bonds.

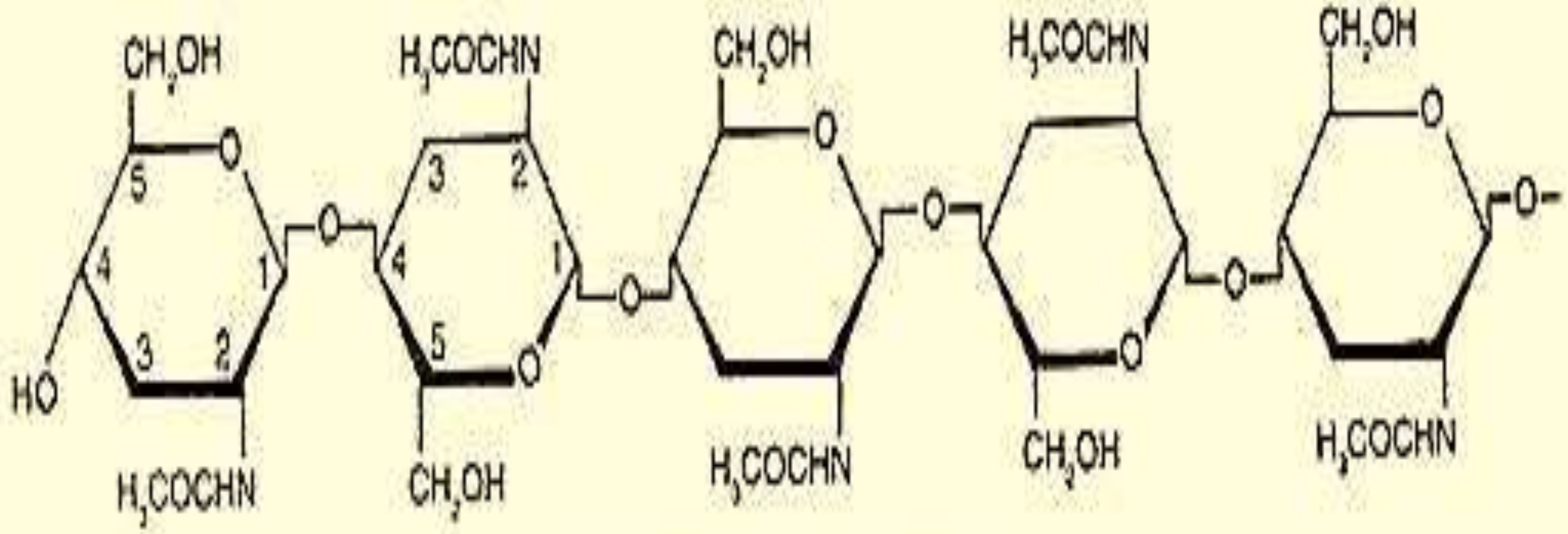


Fig. 9.9. Structure of Chitin.

Cellulose

- It is fibrous homopolysaccharide of high tensile strength which forms a structural element of cell wall in all plants, some fungi and protists. Tunicin of tunicates (=ascidians) is related to cellulose (also called animal cellulose).

- In absolute terms, cellulose is the most abundant organic substance of the biosphere forming 50% of carbon found in plants. Cotton fibres have about 90% of cellulose while wood contains 25-50% cellulose. The other materials of the cell wall include lignin, hemicellulose, pectins, wax, etc.

- Cellulose molecules have un-branched and linear chains unlike the branched and helical chains of starch and glycogen. A chain of cellulose molecule contains 6000 or more glucose residues.

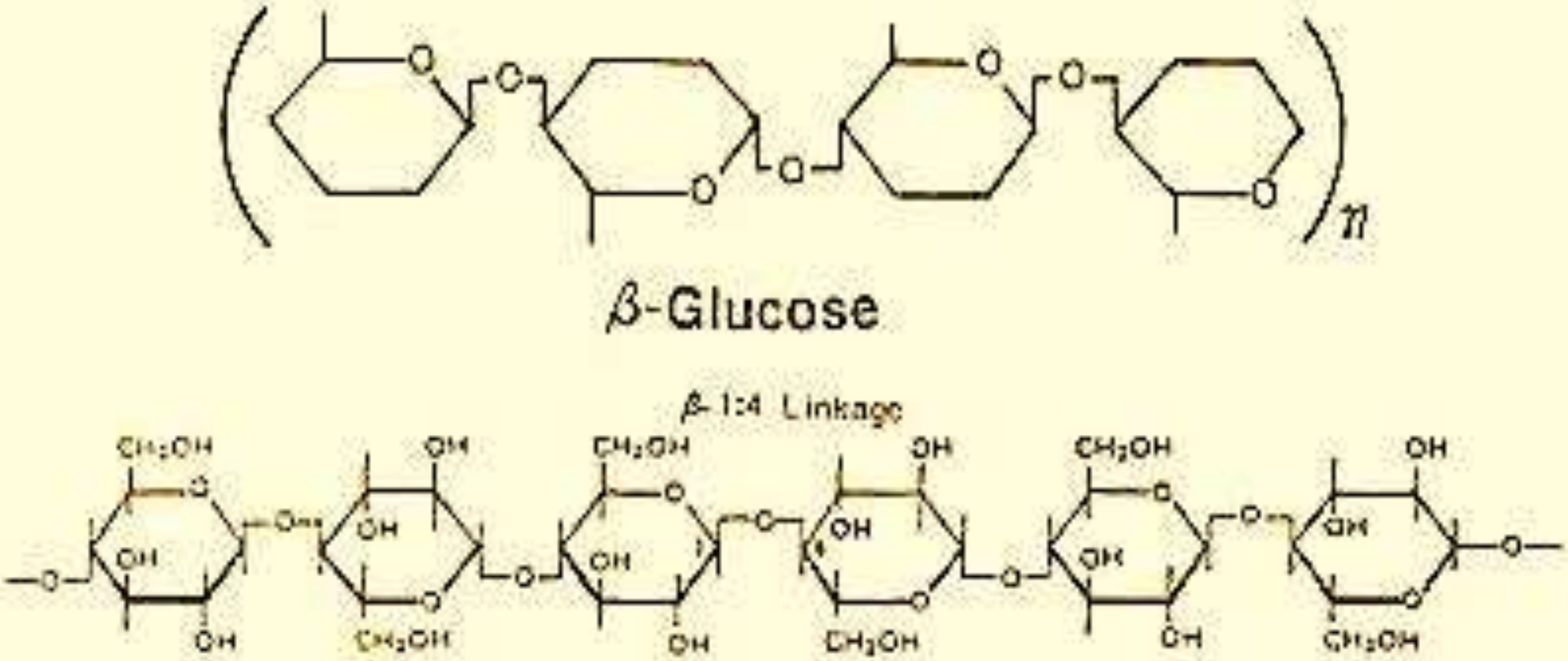


Fig. 9.10. Structure of cellulose.

- Cellulose constitutes the bulk of human food. However, due to being polymer of β-glucose, cellulose is not acted upon by amylases present in human digestive juices. In humans, cellulose has a roughage value which keeps the digestive tract in functional fitness.
- Cellulose is an important constituent of diet for ruminants like cows and buffaloes. The stomach of ruminants contain micro-organisms capable of digesting or breaking down cellulose. Termites and snails also possess micro-organisms in their gut for this purpose.
- Microbes are used in producing soluble sugars from cellulose. The sugars are then allowed to undergo fermentation for obtaining ethanol, butanol, acetone, methane, etc.
- Cellulose rich wood is employed in building furniture, tools, sports articles, paper etc.
- Depending upon the percentage of cellulose present in the fibres, the latter are used in textiles (e.g., Cotton, Linen), preparation of sacs (e.g., Jute) or ropes (e.g., Hemp, China Jute, Deccan Hemp).
- Rayon and cellophane are formed of cellulose xanthate.
- Cellulose acetate is obtained by treating wood pulp with acetic acid, acetic anhydride and a catalyst. Cellulose acetates are used in preparing fibres for double knits, tericot, wrinkle proof, and moth proof clothing. Cigarette filters are also prepared from these fibres. Other uses of cellulose acetates include preparation of plastics and shatter proof glass.
- Cellulose nitrate is used in propellent explosives.
- Carboxymethyl cellulose is used as emulsifier and smoothening reagent of ice creams, cosmetics and medicines.

Pectin

It is an acidic polysaccharide that occurs in the matrix of cell wall and middle lamella (as calcium pectate). Pectin is soluble in water and can undergo ↔ sol gel interchange. Pectin is formed of galacturonic acid, galactose, methylated galacturonic acid and arabinose. It is used in making Jelly and Jams.

Hemicellulose

It is a mixture of polysaccharides of xylans, mannans, galactans, arabino-galactans and glucomannans. Hemicellulose occurs in the cell wall where it forms a link between pectic compounds and cellulose micro fibrils.