CARBOHYDRATES

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Carbohydrates

- Carbohydrates are the most abundant biomolecules on Earth.
- Carbohydrates are formed in photosynthesis from CO_2 and H_2O.
- Carbohydrates (sugar and starch) are a dietary staple.
- Cells obtain energy by oxidation of carbohydrates.

Carbohydrates

Carbohydrates are **polyhydroxy aldehydes or ketones**.

Carbohydrates have the empirical formula **$(CH_2O)_n$**; some also contain nitrogen, phosphorus, or sulfur.

Carbohydrates

There are three major size classes of carbohydrates:

- **Monosaccharides**
- **Oligosaccharides, and**
- **Polysaccharides**

(the word “saccharide” is derived from the Greek sakcharon, meaning “sugar”).

Monosaccharides

Monosaccharides, or simple sugars, consist of a single polyhydroxy aldehyde or ketone unit.

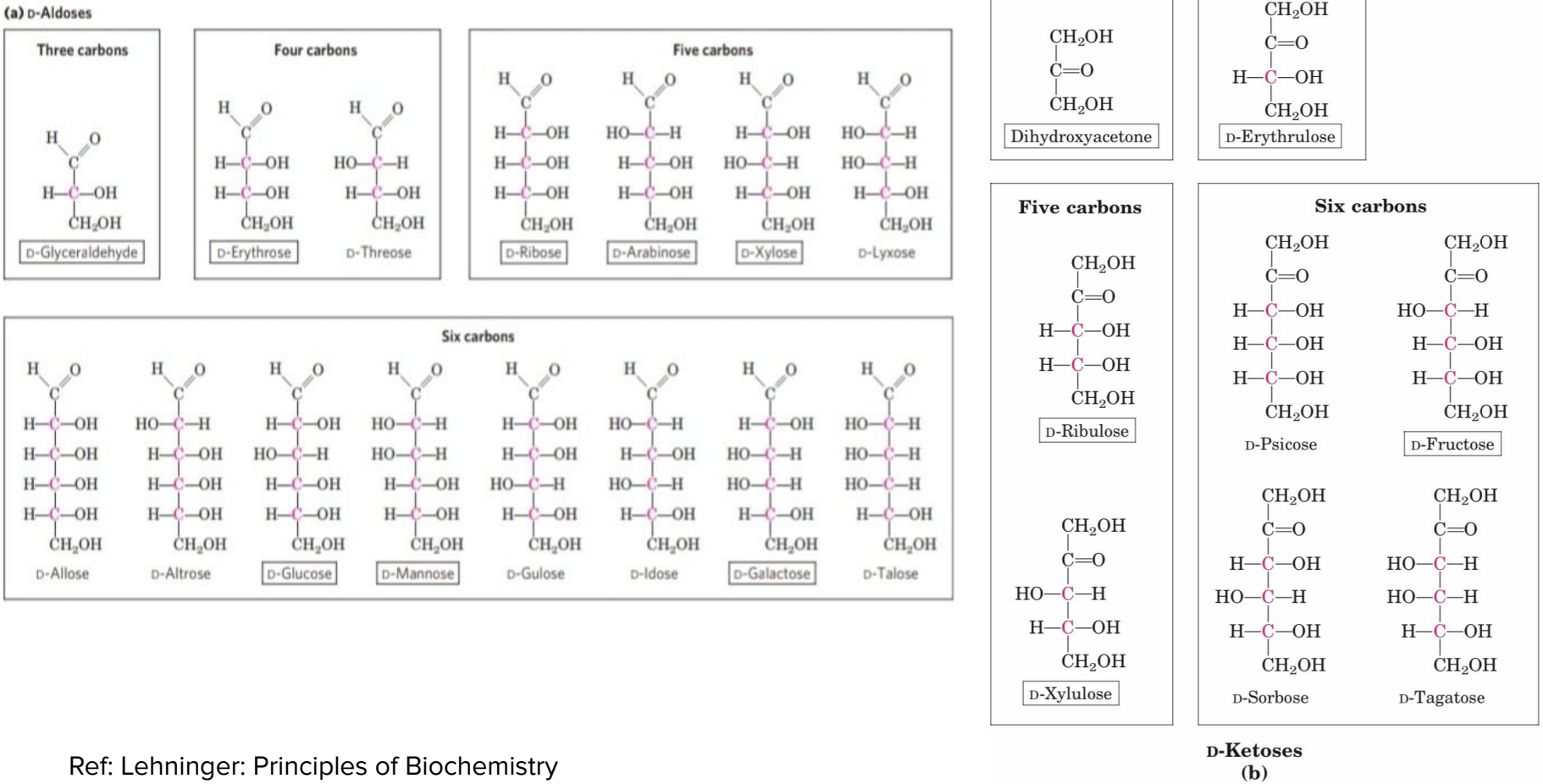
The most abundant monosaccharide in nature is the six-carbon sugar D-glucose (also known as dextrose).

Monosaccharides- Properties:

- Monosaccharides are colorless, crystalline solids.
- freely soluble in water but insoluble in nonpolar solvents.
- Most have a sweet taste.
- Monosaccharide molecules are unbranched carbon chains in which all the carbon atoms are linked by single bonds.

Monosaccharides

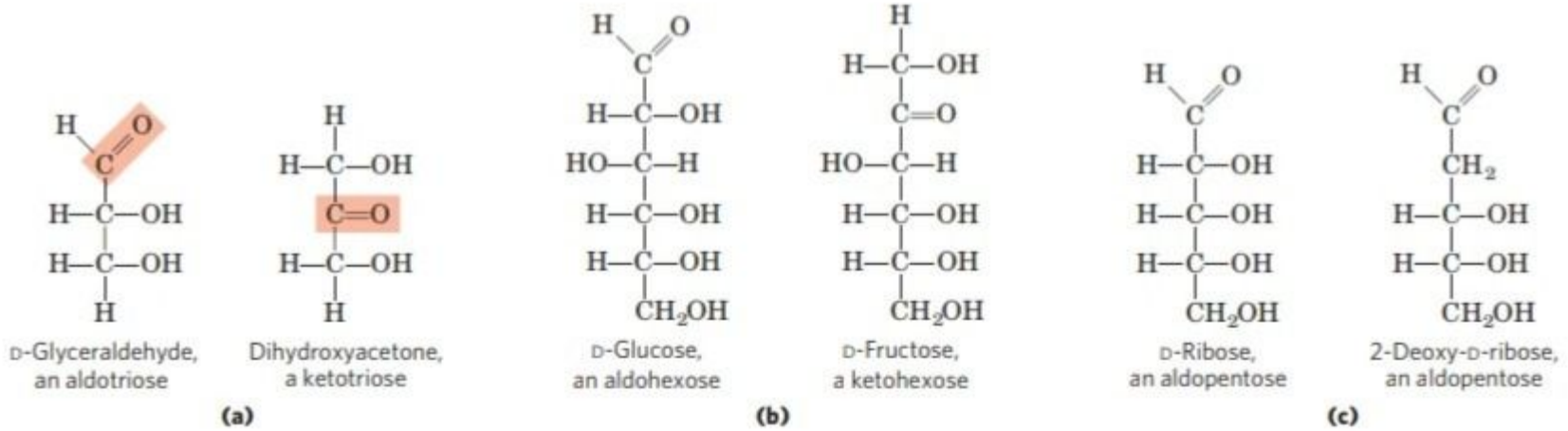
- In the open-chain form, one of the carbon atoms is double-bonded to an oxygen atom to form a carbonyl group; each of the other carbon atoms has a hydroxyl group.
- If the carbonyl group is at an end of the carbon chain (in the form of an aldehyde group) the monosaccharide is an aldose.
- If the carbonyl group is at any other position (in a ketone group) the monosaccharide is a ketose.



Ref: Lehninger: Principles of Biochemistry

Monosaccharides

- Trioses (3 C) : glyceraldehyde (aldotriose) and dihydroxyacetone (ketotriose).
- Four, five, six, and seven carbon atoms in their backbones are called, respectively, tetroses, pentoses, hexoses, and heptoses.
- Hexoses (6C): D-glucose (aldohexose) and D-fructose (ketohexose)
- Pentoses (5C): D-ribose and 2-deoxy-D-ribose (aldopentoses) -components of nucleotides and nucleic acids.



Two different optical isomers of Glyceraldehyde

Aldohexoses, with four chiral centers, have $2^4 = 16$ stereoisomers.

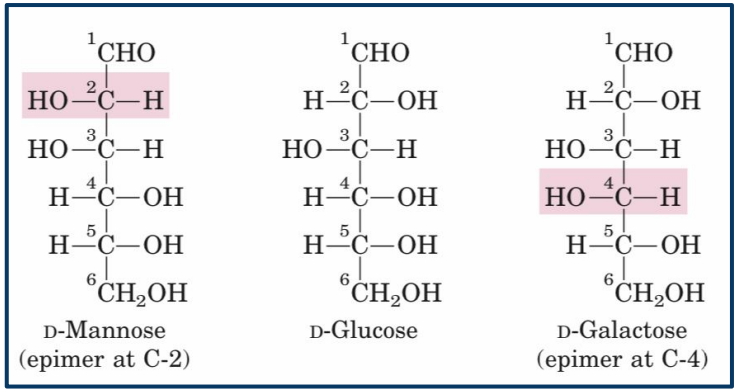
Chiral center most distant from the carbonyl carbon is taken as reference carbon.

Most of the hexoses of living organisms are D isomers.

Ref: Lehninger: Principles of Biochemistry

Monosaccharides

- Two sugars that differ only in the configuration around one carbon atom are called epimers.
- D-glucose and D-mannose differ only in the stereochemistry at C-2, are epimers, as are D-glucose and D-galactose (differ at C-4)



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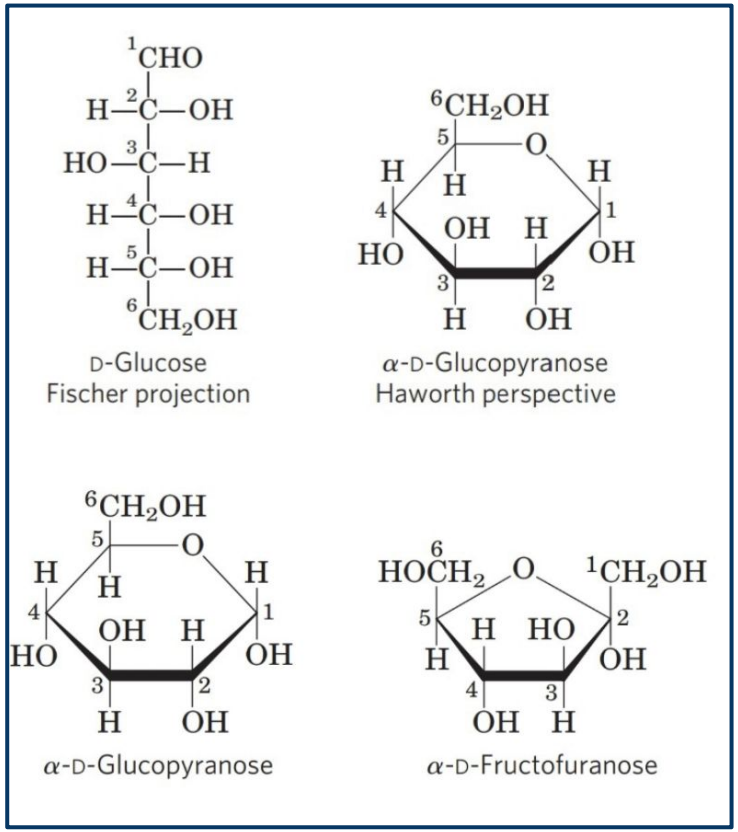
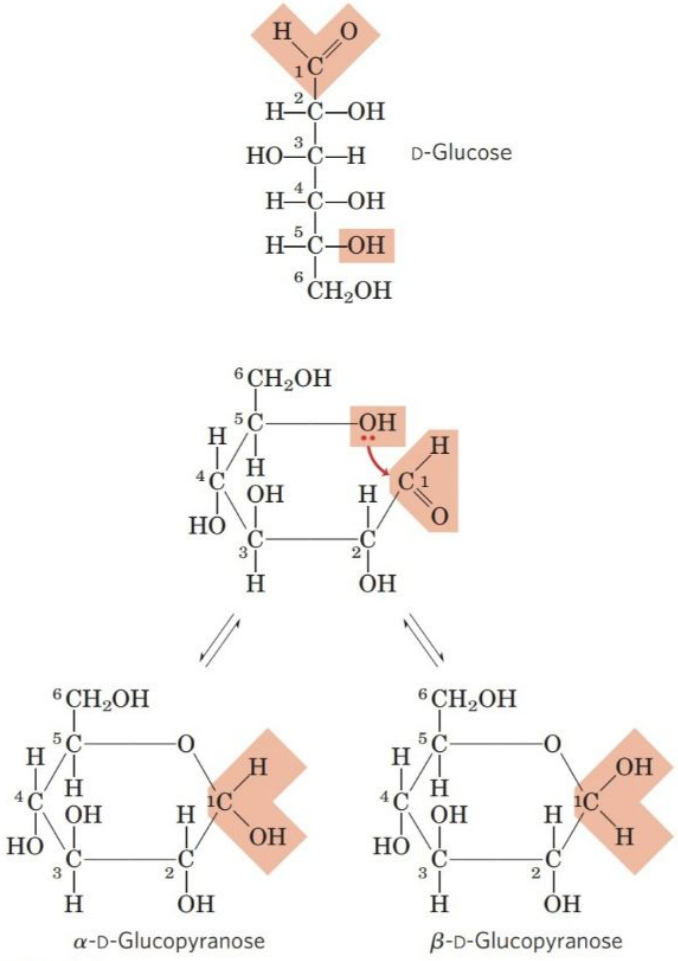
Monosaccharides – Pyranose and Furanose

- in aqueous solution, aldotetroses and all monosaccharides with five or more carbon atoms occur predominantly as cyclic (ring) structures
- Carbonyl group forms a covalent bond with the oxygen of a hydroxyl group along the chain.
- six-membered ring compounds - pyranoses
- five membered rings- furanoses.



Monosaccharides – Pyranose and Furanose

- Ring structures are called hemiacetals or hemiketals formed as a result of general reaction between alcohols and aldehydes or ketones
- These ring structures contain an additional asymmetric carbon atom and thus can exist in two stereoisomeric forms designated α and β.



- Isomeric forms of monosaccharides that differ only in their configuration about the hemiacetal or hemiketal carbon atom are called **anomers**.
- The hemiacetal (or carbonyl) carbon atom is called the anomeric carbon.
- The α and β anomers of D-glucose interconvert in aqueous solution by a process called **mutarotation**.

Ref: Lehninger: Principles of Biochemistry

Monosaccharides – Reducing agents

- Monosaccharides are Reducing Agents
- Monosaccharides can be oxidized by relatively mild oxidizing agents such as ferric (Fe3) or cupric (Cu2) ion.
- The carbonyl carbon is oxidized to a carboxyl group.
- Glucose and other sugars capable of reducing ferric or cupric ion are called reducing sugars.
- This property is the basis of Fehling's reaction, a qualitative test for the presence of reducing sugar.

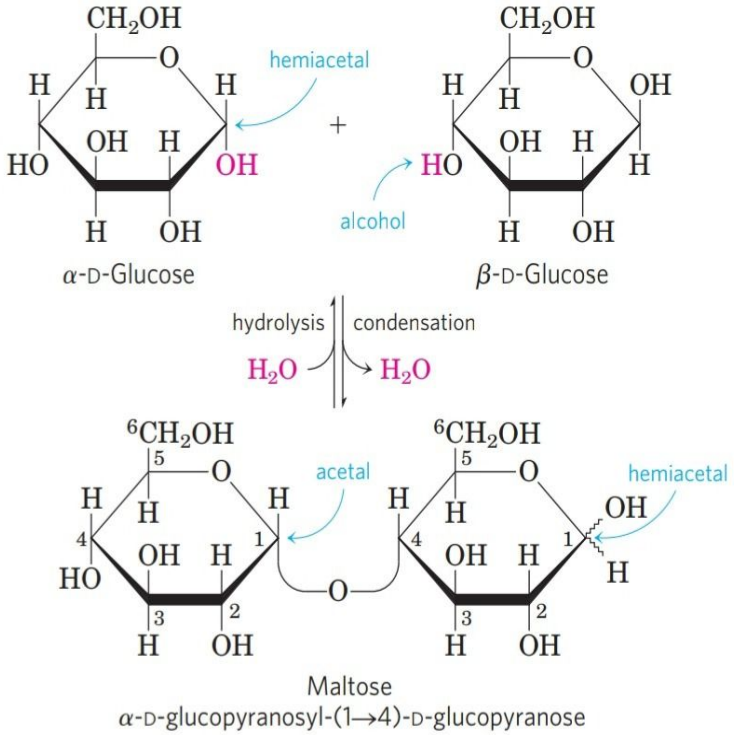
Disaccharides

- Disaccharides (such as maltose, lactose, and sucrose) consist of two monosaccharides joined covalently by an O-glycosidic bond, which is formed when a hydroxyl group of one sugar reacts with the anomeric carbon of the other.
- Glycosidic bonds are readily hydrolyzed by acid.

Disaccharides

- The oxidation of a sugar's anomeric carbon by cupric or ferric ion (the reaction that defines a reducing sugar) occurs only with the linear form, which exists in equilibrium with the cyclic form(s).
- When the anomeric carbon is involved in a glycosidic bond, that sugar residue cannot take the linear form and therefore becomes a nonreducing sugar.
- In describing disaccharides or polysaccharides, the end of a chain with a free anomeric carbon (one not involved in a glycosidic bond) is commonly called the reducing end.

Disaccharide- Maltose



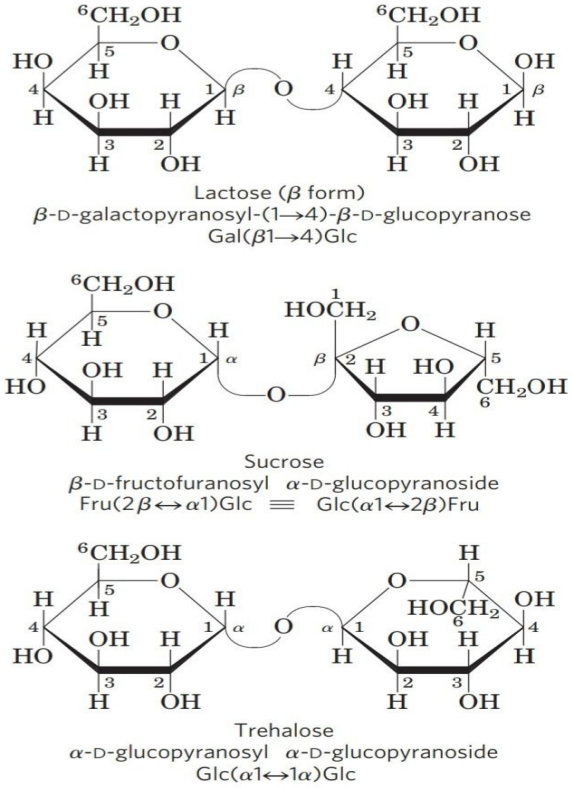
- The disaccharide maltose contains two D-glucose residues joined by a glycosidic linkage between C-1 (the anomeric carbon) of one glucose residue and C-4 of the other.
- Because the disaccharide retains a free anomeric carbon (C-1 of the glucose residue on the right), maltose is a reducing sugar.

Ref: Lehninger: Principles of Biochemistry

Disaccharide- Lactose & Sucrose

- The disaccharide lactose which yields D-galactose and D-glucose on hydrolysis, occurs naturally only in milk.
- The anomeric carbon of the glucose residue is available for oxidation, and thus lactose is a reducing disaccharide.
- Sucrose (table sugar) is a disaccharide of glucose and fructose. It is formed by plants but not by animals.
- Sucrose contains no free anomeric carbon atom; therefore it is a non-reducing sugar.

Disaccharides



- Sucrose is a major intermediate product of photosynthesis; in many plants it is the principal form in which sugar is transported from the leaves to other parts of the plant body.
- Trehalose, a disaccharide of D-glucose and is a nonreducing sugar (it is a major constituent of the hemolymph of insects, serving as an energy-storage compound.

Ref: Lehninger: Principles of Biochemistry

Important disaccharides

- **Maltose** (D glucose + D glucose), joined by an α-1,4-glycosidic linkage, reducing sugar, found in sprouting grains.

- **Lactose** (D galactose + D glucose), joined by β-1,4-glycosidic linkage,reducing sugar, found in milk.

- **Sucrose** (D glucose + D fructose), joined by α-1, β-2-glycosidic linkage, non-reducing sugar, known as cane sugar, found in sugarcane and sugar beets.

Oligosaccharides

Oligosaccharides consist of short chains of monosaccharide units, or residues, joined by characteristic linkages called glycosidic bonds.

In cells, most oligosaccharides consisting of three or more units do not occur as free entities but are joined to non-sugar molecules (lipids or proteins) in glycoconjugates.

Polysaccharides (Glycans)

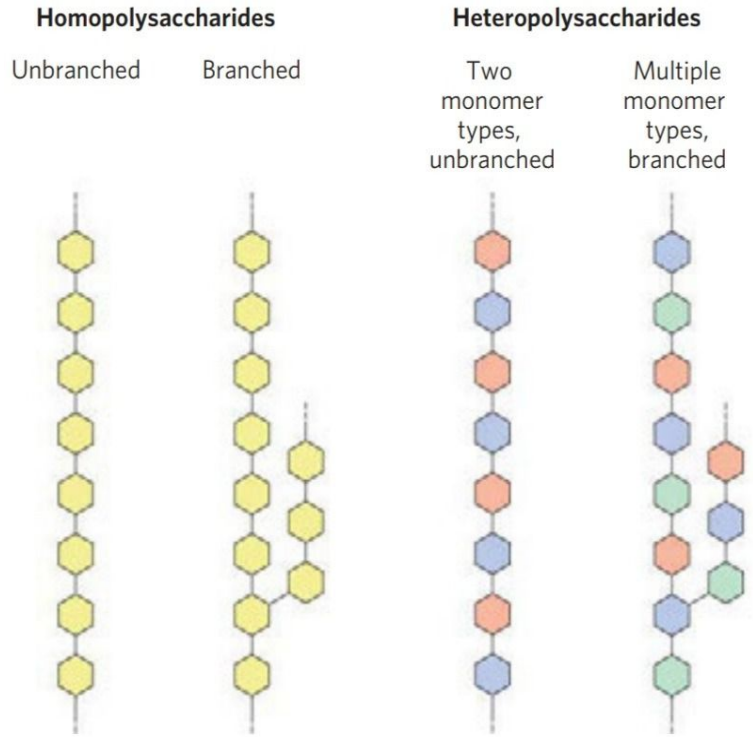
The polysaccharides are sugar polymers containing more than 20 monosaccharide units, and some have hundreds or thousands of units.

Polysaccharides (glycans) serve as stored fuel (starch & glycogen) and as structural components of cell walls (cellulose) and extracellular matrix .

Polysaccharides (Glycans)

Homopolysaccharides contain only a single type of monomer.
eg. Starch, Glycogen, Cellulose, Chitin. Dextrans

Heteropolysaccharides contain two or more different kinds of monomers.
eg. Agar, Peptidoglycan, Glycosaminoglycans



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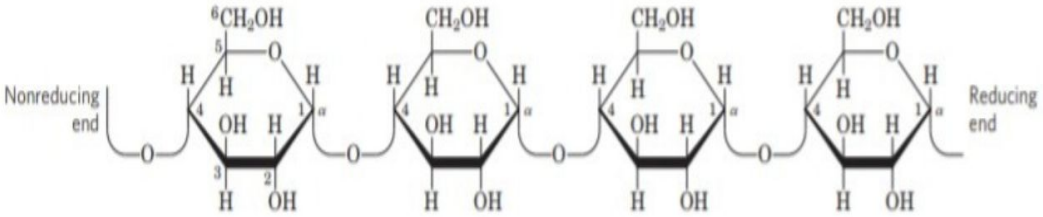
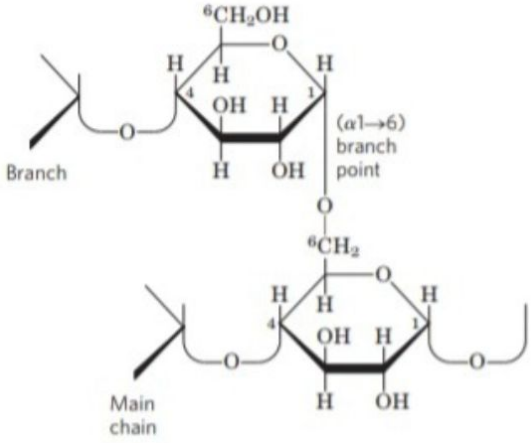
Polysaccharides-

Starch contains two types of **glucose polymer**- amylose and amylopectin





Amylose consists of long, unbranched chains of α D-glucose residues connected by α (1- 4) linkages.

Amylopectin is a highly branched polymer of α glucose. the branch points are α (1- 6) linkages.

Polysaccharides

- Cellulose is found in the cell walls of plants, cotton is almost pure cellulose.
- Cellulose molecule is a linear, unbranched homopolysaccharide, consisting of D-glucose units linked by β (1- 4) glycosidic bonds [α (1- 4) bonds of amylose, starch, and glycogen].
- Most animals cannot use cellulose as a fuel source, because they lack an enzyme to hydrolyze the β (1- 4) linkages.

(Glycogen and starch ingested in the diet are hydrolyzed by α-amylases, that break α (1- 4) glycosidic bonds between glucose units.)

Polysaccharides

- Glycogen is the main storage polysaccharide of animal cells.
- Like amylopectin, glycogen is a polymer of α (1- 4)-linked subunits of glucose, with α (1- 6)-linked branches.

- Dextrans are bacterial and yeast polysaccharides

- Chitin is a linear homopolysaccharide composed of N-acetylglucosamine residues, present in exoskeletons of arthropods.
- It is the second most abundant polysaccharide, next to cellulose, in nature.

Polysaccharides

- Glycoproteins are found on the outer face of the plasma membrane, in the extracellular matrix, and in the blood.
- Glycolipids are membrane lipids in which the hydrophilic head groups are oligosaccharides.

Recommended books