Lecture Series on Biochemistry (Part 3)

Discussion so far...

- What is cell?
- Cells of cellular organism.
  - Prokaryotic cell.
  - Eukaryotic cell.
  - Differences between prokaryotic and eukaryotic cell.
- Cytoplasmic matrix.
- Chemical composition of the cell.
  - Elements.
  - Ions.
  - Electrolytes and non-electrolytes.
- Inorganic compounds of the cytosol

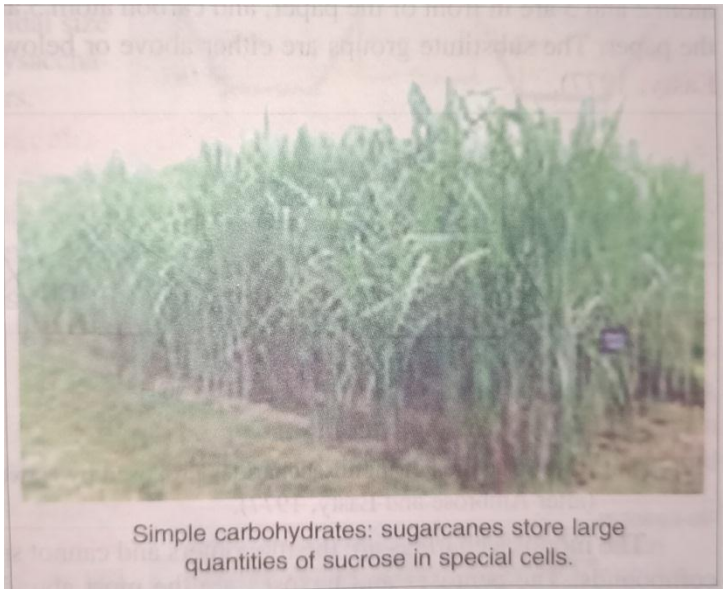
Organic compounds

- Carbohydrates
- Lipids
- Proteins
- Vitamins
- Hormones
- Nucleotides

Carbohydrates

- Carbohydrates (L. *carbo*=carbon, Gr. *hydro*=water) are the compounds of carbon, hydrogen and oxygen serving as the main source of energy of all living beings.
- Only green part of plants and certain microbes have the ability to synthesize carbohydrates from water and CO_2 in presence of sunlight and chlorophyll by the process of photosynthesis.

Simple sugars: Many animals consume sugar like this butterfly consuming nectar, a solution rich in glucose.



Simple carbohydrates: sugarcanes store large quantities of sucrose in special cells.

Chemically, carbohydrates are polyhydroxy aldehydes or ketones and they are classified as:

- Monosaccharides
- Oligosaccharides (Oligomers)
- Polysaccharides (Polymers)

Monosachharides

- Simple sugars with empirical formula $Cn(H_2O)n$.
- Classified and named according to the number of carbon atoms in their molecules.
  - Trioses: Contain 3 C atoms in their molecules. E.g. glyceraldehyde and dihyroxyacetone phosphate.
  - Tetroses: Contain 4 C atoms in their molecules. E.g. erythrulose and eruthrose.
  - Pentoses: Contain 5 C atoms in their molecules. E.g. ribose, deoxyribose, xylulose etc.
  - Hexoses: Contain 6 C atoms in their molecules. E.g. glucose, fructose, galactose etc.
  - Heptoses: Contain 7 C atoms in their molecules. E.g. sedoheptulose.

- Monosachharides usually exists as isomers. For e.g, 3 hexose sugars – glucose, fructose and galactose contain the same number of C, H and O atoms (i.e. $C_6H_{12}O_6$), but they are different sugars because of different arrangements of the atoms within the molecules.
- Most of the monosachharides are optically active, meaning that their asymmetric C cause the rotation of polarised light.
- Molecules that rotate the plane of polarisation to the right, as it faces the light source, are called dextrorotatory and are designated as d or (+), while the opposite case is called levorotation and is designated as l or (-) .

- The stereochemistry of monosaccharides is such that the ring formed is either 5 or 6 membered.
- In pentose sugars, a 5 membered furanose ring is formed.
- In hexose sugars, a 6 membered pyranose ring is formed.
- A good way of representing the structures was proposed by Haworth (1927).
- The furanose or pyranose ring is considered to be in the plane perpendicular to plane of the paper. Thus in gluco-pyranose, C atom 2 and 3 are in front of the paper, and C atom 5 and the ring O lie behind the plane of paper.

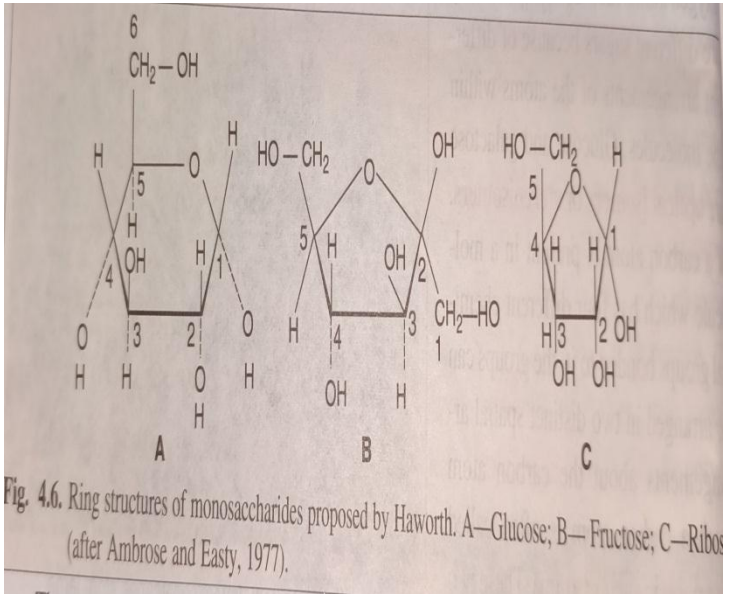


Fig. 4.6. Ring structures of monosaccharides proposed by Haworth. A—Glucose; B— Fructose; C—Ribos
(after Ambrose and Easty, 1977).

- Monosachharides are the monomers and cannot be further hydrolysed into simpler compounds.
- Pentoses and hexoses are the most abundantly occurring monosaccharides of the matrix.
- Pentose sugar ribose is an important constituent of RNA, NAD, NADP, ATP and coenzymeA.
- Pentose sugar ribulose is necessary for photosynthetic mechanism.
- Hexose sugar glucose is the primary source of energy for the cell. The other important hexoses of the matrix are fructose and galactose.

Oligosaccharides

- Consist of 10-20 monosaccharides (monomers) in their molecules.
- The monomers remain linked together with each other by glycosidic bonds.

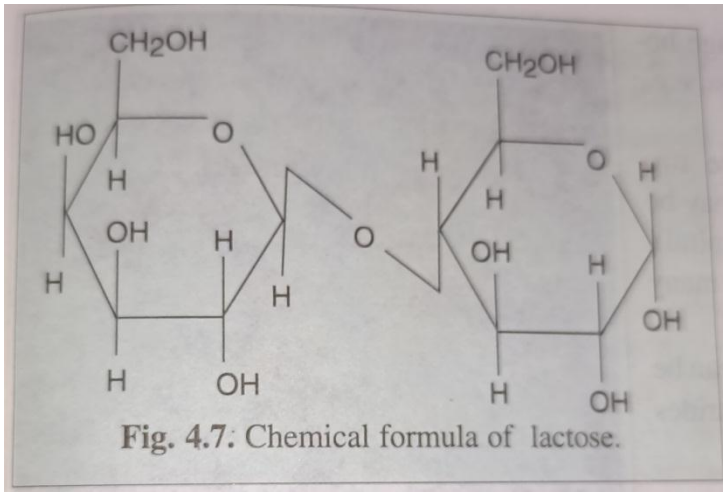


Fig. 4.7. Chemical formula of lactose.

Certain important oligosaccharides are:

- Disaccharides: Contain 2 monomers. E.g. sucrose, maltose, lactose etc.
- Trisaccharides: Contain 3 monomers. E.g. reffinose, mannotriose, rabinose, gentianose etc.
- Tetrasaccharides: Contain 4 monomers. E.g. Stachyose and scordose.
- Pentasaccharides: Contain 5 monomers. E.g. Verbacose

- Most abundant oligosaccharides of animal and plant cells are the disaccharides such as sucrose, maltose and lactose.
- Sucrose and maltose occur mainly in the matrix of plant cells, while lactose occurs exclusively in the matrix of animal cells.
- Molecules of sucrose are composed of D-glucose and D-fructose.
- Molecules of maltose are composed of two molecules of D-glucose.
- Molecules of lactose are composed of two monomers viz. D-glucose and D-galactose.

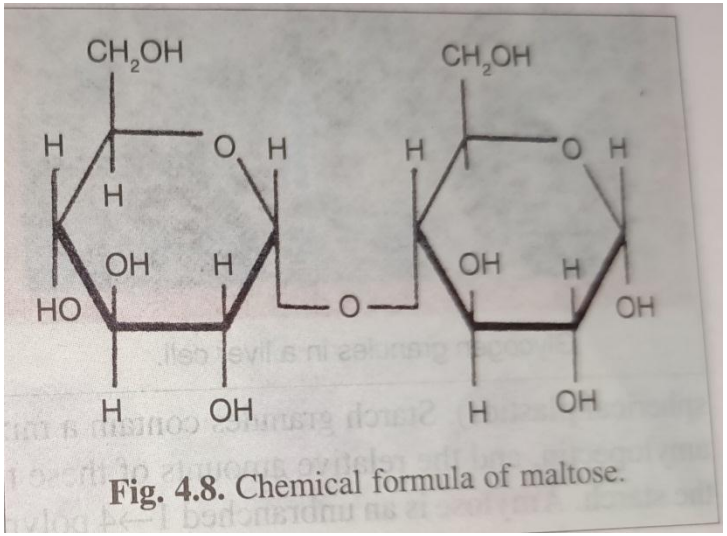


Fig. 4.8. Chemical formula of maltose.

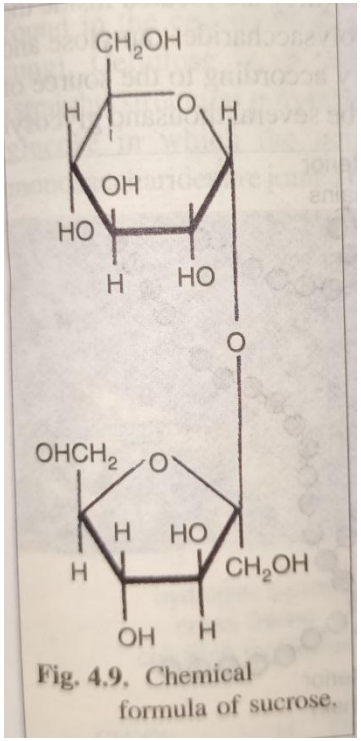


Fig. 4.9. Chemical formula of sucrose.

Polysaccharides

- Composed of ten to many thousand monosaccharides.
- Empirical formula is $(C_6H_{12}O_6)n$
- Molecules of polysaccharides are of colloidal size having high molecular weight.
- Can be hydrolysed into simple sugars.

Polysaccharides can be divided into 2 main functional groups:

- Structural polysaccharides and
- Nutrient polysaccharides

Structural polysaccharides

- Serve primarily as extracellular or intracellular supporting elements.
- Included in this group are cellulose (found in plant cell wall), chitin (in the exoskeleton of arthropods and cell wall of most fungi), hyaluronic acid, keratin sulphate and chondroitin sulphate (these 3 are found in cartilage and other connective tissue).

Nutrient polysaccharides

- Serves as reserves of monosaccharides and are in continous metabolic turnover.
- Included in this group are starch (plant cells and bacteria), glycogen (animal cells), inulin (plant ssuch as dandelions) and paramylum (an unbranched nutrient and storage homopolymer of glucose found in certain protozoa).
- Molecules of some polysaccharides are unbranched chains whose structure may be ribbon-like or helical (usually left-handed spiral)
- Some polysaccharides are however branched and assume a globular form.

On the chemical basis, polysaccharides can be divided into:

- Homopolysaccharides
- Heteropolysaccharides

Homopolysaccharides

- Contain similar kinds of monosaccharides in their molecules.
- Most important homopolysaccharides of the matrix are starch, glycogen, paramylum and cellulose.

Starch granules contain a mixture of 2 different poysaccharides, amylose and amylopectin, and the relative amount of these two polysaccharides vary according to the source of the starch. Amylose is an unbranched 1→4 polymer of glucose and may be several thousand glycosyl units long. The polysaccharide chain exists in the form of a left handed helix containing six glycosyl residues per turn.

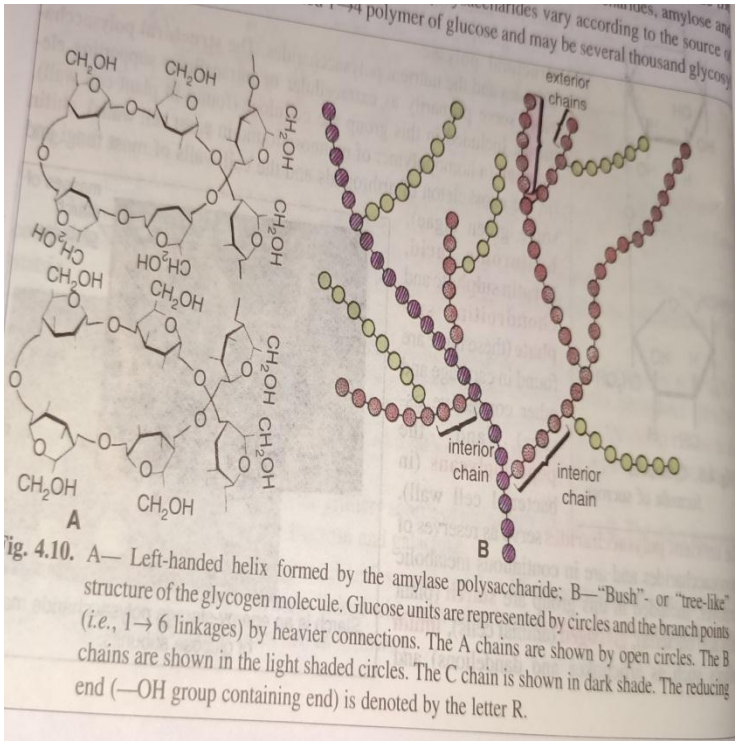


Fig. 4.10. A— Left-handed helix formed by the amylase polysaccharide; B—"Bush"- or "tree-like" structure of the glycogen molecule. Glucose units are represented by circles and the branch points (*i.e.*, 1→ 6 linkages) by heavier connections. The A chains are shown by open circles. The B chains are shown in the light shaded circles. The C chain is shown in dark shade. The reducing end (—OH group containing end) is denoted by the letter R.

Glycogen

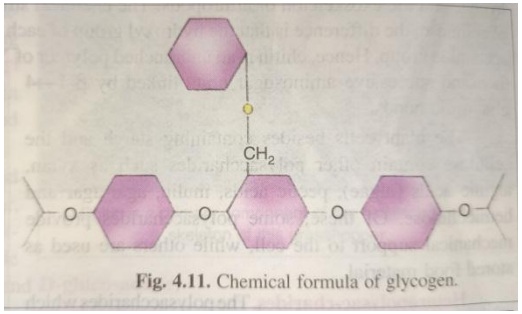


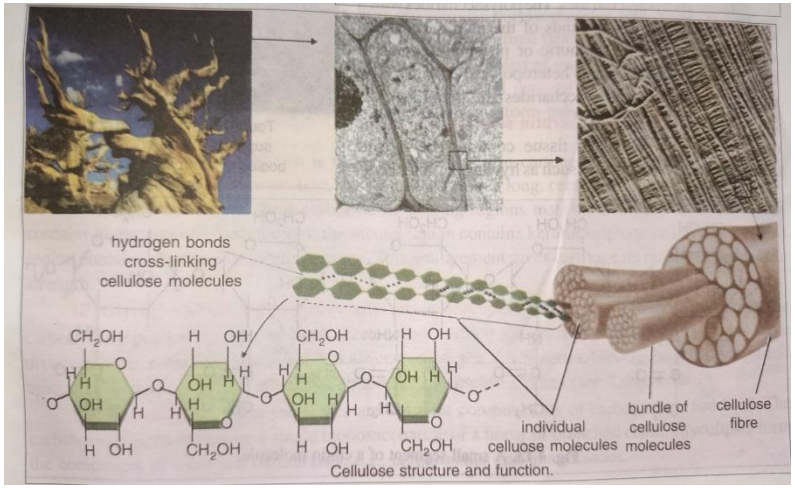
Fig. 4.11. Chemical formula of glycogen.

- It is a branched, nutrient, storage homopolysaccharide of all animal cells, certain protozoa and algae.
- Particularly abundant in liver cells and muscle cells of man man and other vertebrates.
- Glycogen molecules exists in a continous spectrum of sizes and, with the largest molecule containing many thousands glycosyl units.

- Each glycogen molecule consists of long, profusely branched (bush or tree like structure) chains of α-glucose molecules.
- Glycosidic bonds ae established between carbon 1 and 4 of glucose except at th ebranching points, which involve linkages between carbon 1 and 6.
- Glycogen molecule contains 3 types of chains-A, B and C.
- There is only one C chain which bears many B and A chains and ends in the free reducing group (i.e. carbon 1 of glucose at the end of C chain bears an OH group).
- The B chains are attached directly to C chain and bear one or more A chains.

Cellulose

- Major component of cell walls of plants and is also commonly found in the cell walls of algae and fungi.
- An unbranched structural polysaccharide of glucose in which the neighbouring monosaccharides are joined by β-1→4 glycosidic bonds .
- Chain lengths vary from several hundred to several thousand glycosyl units (e.g. in the algae Valonia, a single molecule of cellulose may contain more than 20,000 glycosyl units).



Cellulose structure and function.

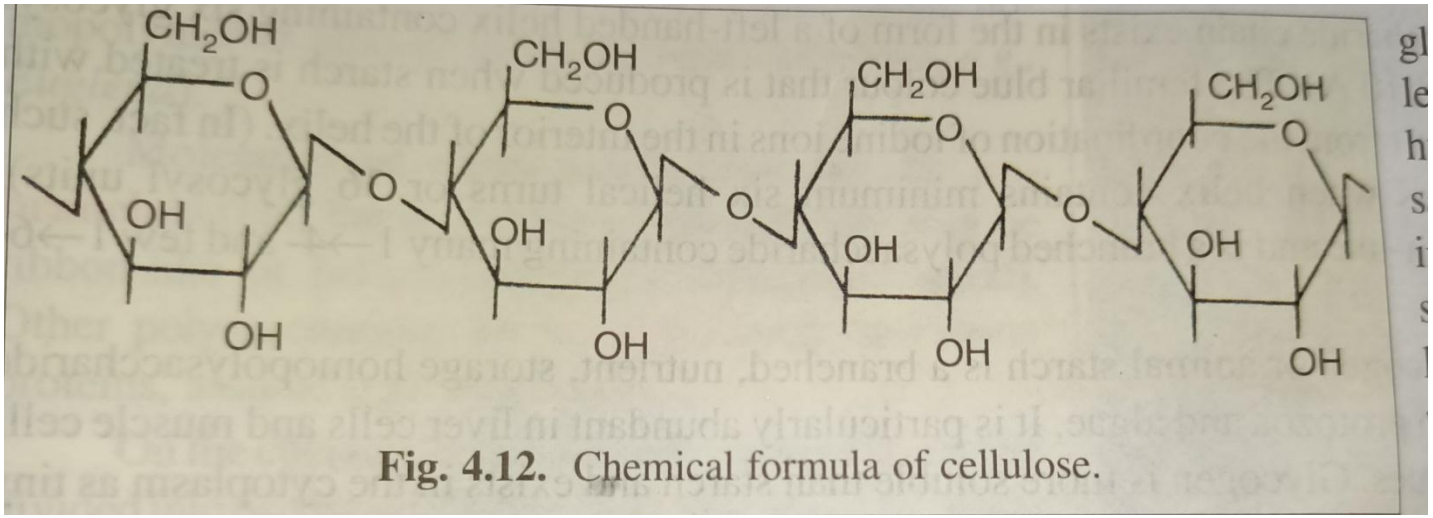


Fig. 4.12. Chemical formula of cellulose.

- In a cellulose molecule, successive pyranose rings are rotated 180^0 relative to one another so that the chain of sugars takes a flip-flop appearance.
- As such, the OH groups of sugar molecules stick outwards from the chain in all directions which can form hydrogen bonds with OH groups of neighbouring cellulose chains, thereby establishing a kind of 3D lattice.
- Thus, in plant cell walls, around 2000 cellulose molecules are organised into cross-linked, parallel microfibrils, whose long axis is that of the individual glucose chain.

Heteropolysaccharide

- Polysaccharides that are composed of different kinds of monosaccharides and amino-nitrogen or sulphuric or phosphoric acids in their molecules.
- Hyaluronic acid, keratin sulphate and chondroitin sulphate.
- Heparin.
- Proteoglycans, glycoproteins and glycolipids.

Hyaluronic acid, keratin sulphate and chondroitin sulphate

- Hyaluronic acid is an unbranched heteropolysaccharide containing repeating disaccharides of N-acetylglucosamine and glucuronic acid.
- Found in cartilage, synovial fluid of joints, vitreous humour of eyes and also in the capsules of bacteria.

- Keratin sulphate is also a repeating disaccharide forming an unbranched chain.
  - Each disaccharide unit of the polysaccharide consists of D-galactose and sulphated N-acetylglucosamine.
  - Found in cartilage and cornea.
- Chondroitin sulpahte is a repeating disaccharide consisting of alternating glucuronic acid and sulphated N-acetyl galactosamine residues.
  - Found in cartilage, bone, skin, notochord, aorta and umbilical cord.

Heparin

- It is a blood anticoagulant.
- Its molecule contains repeated disaccharide units, each having D-glucoronic acid and D-glucosamine.

Proteoglycans, glycoproteins and glycolipids

- Polysaccharides also occur in covalent combination with proteins and lipids, to form :
- Proteoglycans:
  - Molecules of proteoglycans consist of much longer portion of polysaccharide and a small portion of protein. Also called mucoproteins (De Robertis and De Robertis Jr., 1987)
  - They are amorphous and form gels which are able to hold large amounts of water.

- The cartilage proteoglycan is found extracellularly in cartilage and bone.
- In its molecule, strands of protein, called core protein, extend radially from a long central hyaluronic acid molecule.
- In each core protein strand, three carbohydrate bearing regions have been identified.
- The first region contains numerous oligosaccharides, the second region contains keratin sulphate chains and the third region contains chondroitin sulphate chains.
- This arrangement gives the cartilage its resilience and tensile strength.

- Glycoproteins (or glycosaminoglycans or mucopolysaccharides):
  - In these molecules, the carbohydrate portion consists of much shorter chains which are often branched.
  - Serve diverse roles in cells and tissues and include certain enzymes, hormones, blood groups, saliva, gastric mucin, serum, antibodies etc.

- Glycolipids:
  - These molecules are covalent combinations of carbohydrate and lipid.
  - The carbohydrate portion may be a single monosaccharide or a linear of branched chain.
  - Glycolipids form the component of most cell membranes. E.g. cerebrosides and gangliosides.