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Unit 4: Macromolecules

Module Name: Carbohydrates: Polysaccharides-storage and structural

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Carbohydrates, one of the four major classes of biomolecules along with proteins, nucleic acids, and lipids. Carbohydrates are aldehyde or ketone compounds with multiple hydroxyl groups. They make up most of the organic matter on Earth because of their extensive roles in all forms of life.

Significance of carbohydrates:

1) Carbohydrates serve as energy stores, fuels, and metabolic intermediates.
2) Ribose and deoxyribose sugars form part of the structural framework of RNA and DNA.
3) Carbohydrate polymers (also called glycans) or Polysaccharides are structural elements in the cell walls of bacteria and plants and in the connective tissues of animal. In fact, cellulose, the main constituent of plant cell walls, is one of the most abundant organic compounds in the biosphere.
4) Carbohydrates are linked to many proteins and lipids, where they play key roles in mediating interactions among cells and interactions between cells and other elements in the cellular environment.

Polysaccharides

Polysaccharides, which are also known as glycans, consist of monosaccharides linked together by glycosidic bonds. They are classified as homopolysaccharides or heteropolysaccharides if they consist of one type or more than one type of monosaccharide. Although the monosaccharide sequences of heteropolysaccharides can vary, many are composed of only a few types of monosaccharides that alternate in a repetitive sequence. Polysaccharides, in contrast to proteins and nucleic acids, form branched as well as linear polymers. This is because glycosidic linkages can be made to any of the hydroxyl groups of a monosaccharide. Most polysaccharides are linear and those that branch do so in only a few well-defined ways. They serve a number of crucial biological functions in organisms such as cell wall support (structural polysaccharides), food (energy) storage (storage polysaccharides), and as the extra-cellular matrix surrounding connective tissue (mucopolysaccharides). Polysaccharides are also present in many proteins called glycoproteins (protein which contains oligosaccharide chains or glycans attached to amino acid side chain).

Storage Polymer

Starch and glycogen as storage homopolysaccharides

Their function is to store the energy. Glycogen and starch ingested in the diet are hydrolyzed by α -amylases -enzymes in saliva and intestinal juice that break α--1→4--glycosidic bonds between glucose units. So digestion of these homopolysaccharides occurs in the mouth and in the intestine. More than half the carbohydrate ingested by human beings is starch.

Starch: is a homopolysaccharide, a polymer of glucose with formulae $(C6H10O5)\ n$ that is constructed by α-D-glucose units bonded by α-glycosidic bonds. Starch serves as a major source of energy storage in plants – it is found chiefly in the seeds, fruits, tubers, roots, and stem pith of plants, notably in corn, potatoes, wheat, and rice, and varying widely in appearance according to source but commonly prepared as a white amorphous tasteless powder. The storage of glucose as starch greatly reduces the large intracellular osmotic pressure that would result from its storage in monomeric form, because osmotic pressure is proportional to the number of solute molecules in a given volume. Starch is a reducing sugar, although it has only one residue, called the reducing end that lacks a glycosidic bond. Starch is present in the chloroplasts of plant cells as insoluble granules composed of amylose and amylopectin. Amylose is composed of continuous, unbranched (linear) chains of thousands of D-glucose units joined by α (1→4)-glycoside bonds. Amylopectin consists mainly of α (1→4)-linked glucose residues but is a branched molecule with α (1→6) branch points every 24 to 30 glucose residues on average. Amylopectin molecules contain up to 106 glucose residues, making them some of the largest molecules in nature. Amylopectin is similar in fashion to glycogen except for its lower degree of branching.

Glycogen: The most common homopolymer in animal cells is glycogen also known as "animal starch", is the storage form of glucose and energy in animals and humans which is analogous to the starch in plants. Glycogen is a very large, branched polymer of glucose residues. Most of the glucose units in glycogen are linked by α -1,4-glycosidic bonds. The branches are formed by α-1,6-glycosidic bonds, present about once in 10 units. Glycogen is synthesized and stored mainly in the liver and the muscles. The primary structure of glycogen resembles that of amylopectin, but glycogen is more highly branched, with branch points occurring every 8 to 14 glucose residues. In the cell, glycogen is degraded for metabolic use by glycogen phosphorylase. Glycogen's highly branched structure, which has many nonreducing ends, permits the rapid mobilization of glucose in times of metabolic need. Glycogen and starch have as many non-reducing ends (glucose residue with free –OH on C4) as they have branches, but only one reducing end (glucose residue with free –OH on C1 (anomeric carbon).

Structural Polymer

Cellulose, the Major Structural Polymer of Plants

Cellulose, the other major polysaccharide of glucose found in plants, serves a structural rather than a nutritional role. This fibrous, tough, water-insoluble substance is found in plants as microfibrils that form the structurally strong framework in the cell walls. Cellulose is one of the most abundant organic compounds in the biosphere. Some 1015 kg of cellulose is synthesized and degraded on Earth each year. It is hydrolyzed (not in human) to disaccharide cellobiose (partial hydrolysis) and β-D-glucose (complete hydrolysis), so β- D-glucose is its monomeric unit. It is an unbranched, linear polymer of glucose residues joined by β-1, 4 linkages. The three-dimensional structures of starch, glycogen and cellulose differ each from other. The linkage by α-1, 4-glycosidic bonds in amylose fraction of starch and also in glycogen give them a very different structure than cellulose (linked by β-1, 4-glycosidic bonds). The α-1, 4-glycosidic linkage results in a hollow helical structure that is more suitable for energy storage. The β-1-4-glycosidic bonds allows cellulose to form linear chains that are stabilized by hydrogen-bonding with adjacent chains to form tensile fibers. The β configuration allows cellulose to form very long, straight chains. Stacks of these sheets are held together by hydrogen bonds and van der Waals interactions. This highly cohesive structure gives cellulose fibers exceptional strength and makes them water insoluble despite their hydrophilicity. In plant cell walls, the cellulose fibers are embedded in and cross-linked by a matrix containing other polysaccharides and lignin, a plastic-like phenolic polymer. The resulting composite material can withstand large stresses. Mammals lack cellulases and therefore cannot digest wood and vegetable fibers. The digestive tracts of herbivores and termites contain symbiotic microorganisms that secrete a series of cellulases enzymes.

Peptidoglycan in bacterial cell wall

Peptidoglycan or murein is a polymer consisting of sugars and amino acids that forms a mesh-like layer outside the plasma membrane of most bacteria, forming the cell wall. Bacteria are surrounded by a rigid cell wall. Peptidoglycan layer serves a structural role in the bacterial cell wall, giving the wall shape and structural strength, as well as counteracting the osmotic pressure of the cytoplasm. Murein is a heteropolysaccharide formed by disaccharide units. Every disaccharide unit contains N-acetylglucosamine and N-acetylmuramic acid. They are linked by β-1→4)-glycoside bond. In peptidoglycan the lactyl group of each N-acetylmuramic acid residue bonds to tetrapeptide side chain that contains amino acids. Crosslinking between these tetrapeptides gives peptidoglycan its strong structure and the 3D mesh-like layer. Occurrence of amino acids in murein structure causes resistance of bacterial cell wall to proteases. The peculiarities of peptidoglycan layer structure in cell wall defines the differences in Gram Staining of Gram (-) and Gram (+) bacteria. Peptidoglycan forms around 90% of the dry weight of Gram positive bacteria but only 10% of Gram-negative strains.