CARBOHYDRATES

Polysaccharides

Polysaccharides which are also known as glycans, consists 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, in principle, be even more varied than those of proteins, many are composed of only a few types of monosaccharides that alternate in a repetitive sequence.

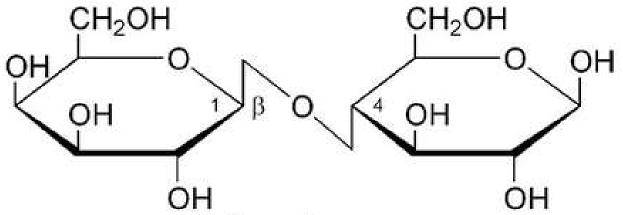
Polysaccharides, in contrast to proteins and nucleic acids, form branched as well as linear polymers. This is because glycosidic linkages can be made to any of the hydroxyl groups of a monosaccharide. Fortunately for structural biochemists, most polysaccharides are linear and those that branch do so in only a few well defined ways.

A complete description of an oligosaccharide or a polysaccharide includes the identities, anomeric forms, and linkages of all its components monosaccharide units. Some of this information can be gathered through the use of specific exoglycosidases and endoglycosidases, enzymes that hydrolyze monosaccharide units in much the same way that exopeptidases and endopeptidases cleave amino acid residue from polypeptides.

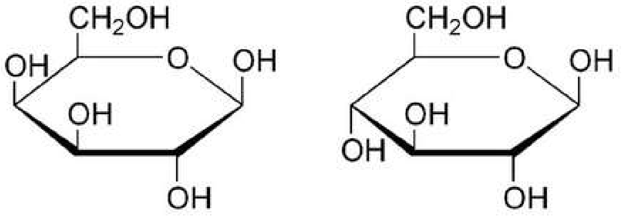
Disaccharides

The simplest polysaccharides are the disaccharides. Lactose, for example occurs naturally only in milk, where its concentration ranges from 0 to 7%

depending on the species. The most abundant disaccharide is sucrose. The major form in which carbohydrates are transported in plants. Sucrose is familiar to us as common table sugar. Other common disaccharides occur as the hydrolysis products of larger polysaccharides. Only a few tri- and higher oligosaccharides occur in nature, all of them are in plants.



Lactose



D-galactose **D-glucose**

Fig: Structure of Lactose and its two monosaccharides

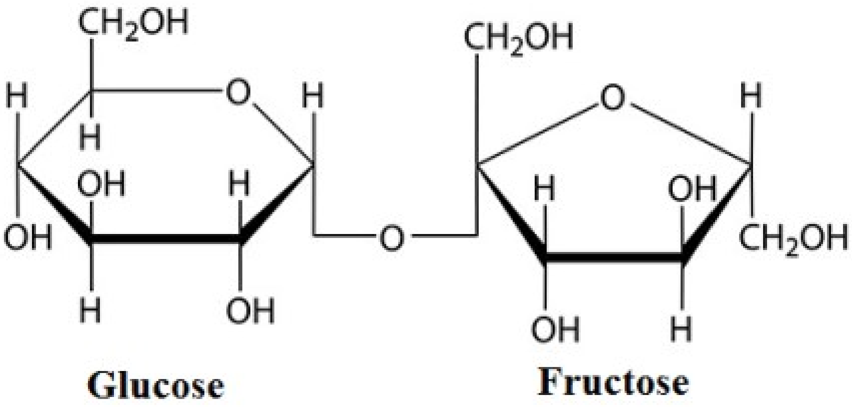
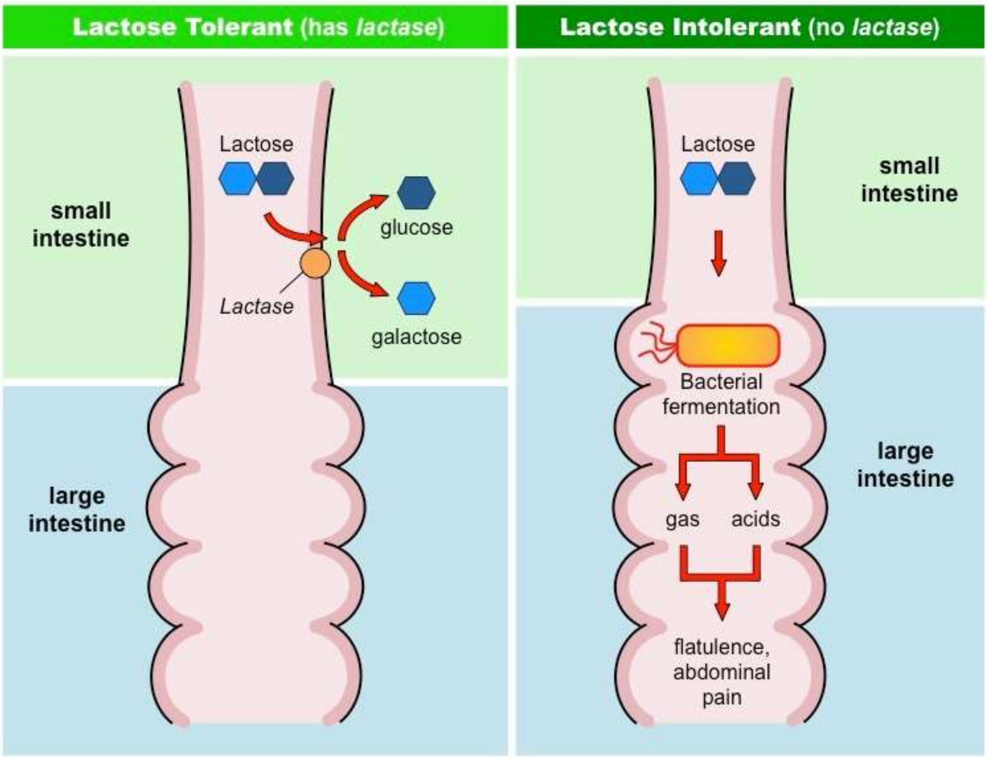


Fig: Structure of Sucrose

Lactose intolerance

In infants, lactose (also known as milk sugar) is hydrolyzed by the intestinal enzyme beta-galactosidase or lactase to its component monosaccharides for absorption into the blood stream. The galactose is enzymatically converted to glucose, which is the primary metabolic fuel of many tissues.

Since mammals are unlikely to encounter lactose after they have been weaned, most adult mammals have low levels of beta galactosidase. Consequently, much of the lactose they might ingest moves through their digestive tract to the colon, where bacterial fermentation generates large quantities of carbon dioxide, hydrogen and irritating organic acid. These products cause the embarrassing and often painful digestive upset known as lactose intolerance. Lactose intolerance which was once considered a metabolic disturbance, is actually the norm in adult humans, particularly those of African and Asian descent. Interestingly however, beta-galactosidase levels decrease only mildly with age in descendants of populations that have historically relied on dairy products for nutrition throughout life. Modern food technology has come to the aid of milk lovers who develop lactose intolerance : milk in which the lactose has been hydrolyzed enzymatically is widely available.



Structural polysaccharides: cellulose and chitin

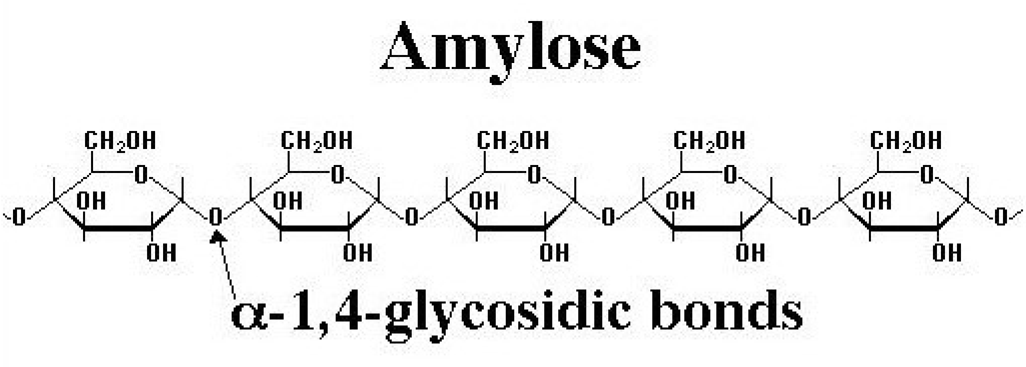
Plants have rigid cell walls that can withstand osmotic pressure differences between the extracellular and intracellular spaces of up to 20 atm. In large plants such as trees, the cell walls also have a load bearing function. Cellulose, the primary structural component of plant cell walls accounts for over half of the carbon in the biosphere: approximately 10^{15} kg of cellulose is estimated to be synthesized and degraded annually. Cellulose is a linear polymer of up to 15000 D-glucose residues linked by β (1-4) glycosidic bonds.

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 because the matrix evenly distributes the stresses among the cellulose reinforcing elements. Although vertebrate themselves do not possess an enzyme capable of hydrolyzing the beta (1-4) linkages of cellulose, the digestive tract of herbivores contain symbiotic microorganisms that secrete a series of enzymes collectively known as cellulases, that do so. The same is true of termites. Nevertheless, the degradation of cellulose is a slow process because it is tightly packed and hydrogen- bonded glycan chains are not easily accessible to cellulase and do not separate readily even after many of their glycosidic bonds have been hydrolyzed. Thus, cows must chew their cud and the decay of dead trees by fungi and other organisms generally takes many years.

Chitin is the principal structural component of the exoskeletons of invertebrates such as Crustaceans, insects and spiders and is also present in the cell walls of most fungi and many algae. It is therefore almost as abundant as cellulose. Chitin is a homopolymer of β (1-4) linked N- acetylglucosamine residues. It differs chemically from cellulose only in that each C2 OH group is replaced by an acetamide function. X-Ray analysis indicates that chitin and cellulose has similar structures.

Storage polysaccharides: starch and glycogen

Starch is a mixture of glycans that plants are synthesized as their principal food reserve. It is deposited in the chloroplast of plant cells as insoluble granules composed of α amylose and amylopectin. α amylose is a linear polymer of several thousand of glucose reduced linked by α(1-4)bonds.



Glycogen, the storage polysaccharide of animals, is present in all cells but is most prevalent in skeletal muscles and in liver, where it occurs as cytoplasmic granules. The primary structure of glycogen resembles that of amylopectin, but glycogen is more highly branched, with branch points occurring every 8 to 12 glucose residues. In the cell, glycogen is degraded for metabolic use by glycogen phosphorylase which cleave's glycogen's α (1-4) bonds sequentially inwards from its non reducing end. Glycogen's highly branched structure, which has many non reducing ends permits the rapid mobilization of glucose in times of metabolic need. The α(1-6) branches of glycogen are cleaved by glycogen debranching enzyme.

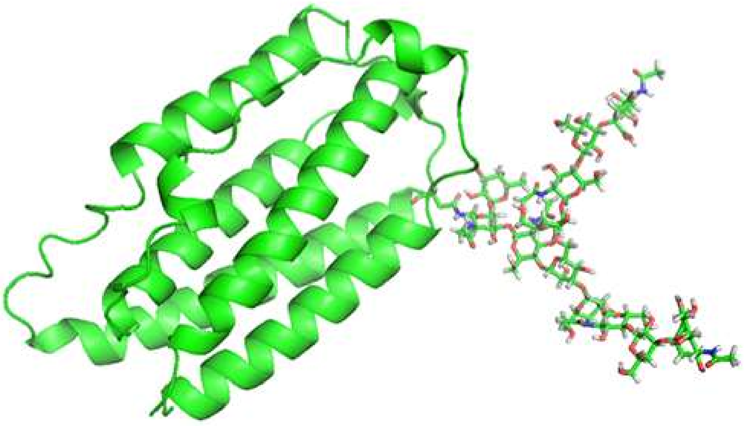
Glycosaminoglycans

The extracellular spaces particularly those of connective tissues such as cartilage, tendon, skin and blood vessel walls contain collagen and other protein embedded in a gel- like matrix that is composed largely of glycosaminoglycans. The unbranched polysaccharides consists of alternating uronic acid and hexosamine residues. Solutions of glycosaminoglycans have a slimy, mucus like constituency that results from their high viscosity and elasticity. Hyaluronic acid is an important glycosaminoglycan component of connective tissue, synovial fluid (the fluid that lubricates joints) and the vitreous humor of the eye. Hyaluronic acid molecules are composed of 250 - 25000 β(1-4)linked disaccharide units that consists of D-glucuronic acid and N-acetyl-D-glucosamine linked by a β(1-3) bond. The disaccharide units of hyaluronic acid are extended forming a rigid molecule whose numerous repelling anionic groups cations and water molecules. In solution hyaluronate occupies a volume near about 1000 times that in its dry state. Other examples of glucosaminoglycans are keratan sulfate and heparin.

Glycoproteins

Many proteins are actually glycoproteins with carbohydrates containing varying forms less than 1% to more than 90% by weight. Glycoproteins occur in all forms of life and have functions that span the entire spectrum of protein activities, including those of enzymes, transport proteins, receptor, hormones and structural proteins. The polypeptide chains of glycoproteins, like those of all proteins, are synthesized under genetic control. Their carbohydrates chains in contrast, are enzymatically generated and covalently linked to the polypeptide without the rigid guidance of nucleic acid templates. For this reason glycoproteins tend to have variable carbohydrate composition, a phenomenon known as micro heterogeneity.

GLYCOPROTEIN



The proteins and glycosaminoglycans in the extracellular matrix aggregates covalently and non covalently to form a diverse group of macromolecules which has known as the proteoglycans. Glycoproteins are also found in the cell wall of bacteria.

Reference:

Voet,D.Voet,J,D.Pratt,C.W. Fundamentals of Biochemistry.1998.Von Hoffmann Press.