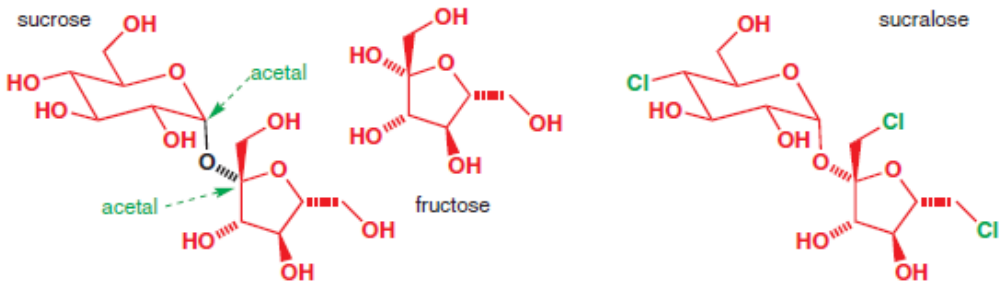
Sucrose

The most familiar disaccharide is sucrose (table sugar) obtained from sugar beets and sugar cane. Sugar cane was grown domestically as early as 600 B.C. in India. Words 'sucrose' and 'sugar' comes from Sanskrit word 'Sarkara'. Sucrose was encountered by the soldiers of Alexander the Great, who entered India in 325 B.C. In later centuries, the use of sucrose was spread by the Arabs and the Crusaders. Sugar cane was introduced into New World by Columbus, who brought some to Santo Domingo in 1493. In the 1700's it was discovered that certain beets also contain high levels of sucrose.

Sucrose consists of a D-glucose subunit and a D-fructose subunit linked by a glycosidic bond between C-1 of glucose (in the α-position) and C-2 of fructose (in the β-position). Unlike the disaccharides discussed earlier it is a non-reducing sugar and doesn't exhibit mutarotation because the glycosidic bond is between anomeric carbons of glucose and fructose i.e. it lacks a hemiacetal group and is not in equilibrium with aldehyde or keto group. It has a specific rotation of +66.5^o, on hydrolysis it yields equimolar mixture of glucose and fructose and has a specific rotation of -22.0^o. Due to this change in the sign of specific rotation, a 1:1 mixture of glucose and fructose is called invert sugar. The enzyme that catalysed the hydrolysis of sucrose is called invertase. Honeybees have this enzyme, the honey they produce is a mixture of sucrose, glucose, and fructose. Because fructose is sweeter than sucrose, invert sugar is sweeter than sucrose. A synthetic invert sugar called **Isomerose** is prepared by the enzymatic isomerisation of glucose in corn syrup. It has commercial use in the preparation of ice cream, soft drinks, and candy.



Sucralose

Sucralose is an artificial sweetner and a sugar substitute. It was first discovered in 1976 by chemists at Tate & Lyle in an interesting manner. Two researchers Leslie Hough and Shashikant Phadnis at Queen Elizabeth College (now part of King's College London) while researching novel uses of sucrose and its synthetic derivatives, Phadnis was told to "test" a chlorinated sugar compound. Phadnis thought Hough asked him to "taste" it, so he did. He found the compound to be exceptionally sweet and the company

got it patented. It is now used to sweeten soft drinks. It is also used in canned fruits wherein water and sucralose take the place of much higher calorie corn syrup-based additives (Source: Wikepedia). Sucralose is largely considered shelf-stable and safe for use at elevated temperatures (such as in baked goods).

It is produced by chlorination of sucrose, if three of its OH groups are replaced by chlorine atoms, a compound 'sucralose', 600 times as sweet is produced: less of it is needed to get the same sweet taste and the chlorines reduce the rate of metabolism so that much less fat is made, it does not promote dental cavities, is safe for consumption by diabetics and nondiabetics, and does not affect insulin levels. However, evidence of benefit is lacking for long-term weight loss with some data supporting weight gain and heart disease risks.

Glycosylated haemoglobin (HbA1c)

Glucose, a reducing sugar, can react with haemoglobin to form glycosylated haemoglobin. Changes in amount of glycosylated haemoglobin can be used to monitor the long term control of diabetes mellitus. As a person's blood sugar becomes higher, the level of glycosylated haemoglobin is increased in the red blood cells of persons. The glycosylated haemoglobin level is measured primarily to determine the three months average blood sugar level and can be used as a diagnostic test for glycemic control in people with diabetes.

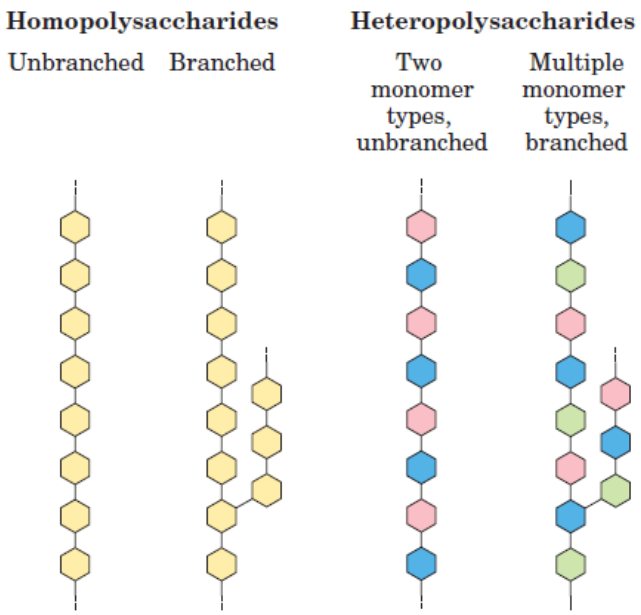
HbA1C Level

5.7 – 6.4 %: High risk

> 6.5 %: Diabetic

Polysaccharides

Most carbohydrates found in nature occur as polysaccharides, polymers of medium to high molecular weight. Polysaccharides, also called glycans, differ from each other in the identity of their recurring monosaccharide units, in the length of their chains, in the types of bonds linking the units, and in the degree of branching. Unlike proteins, polysaccharides generally do not have definite molecular weights. This difference is a consequence of the mechanisms of assembly of the two types of polymers. Unlike proteins synthesis on a template (messenger RNA) of defined sequence and length, by enzymes that follow the template exactly, for polysaccharide synthesis there is no template; rather, the program for polysaccharide synthesis is intrinsic to the enzymes that catalyze the polymerization of the monomeric units, and there is no specific stopping point in the synthetic process.

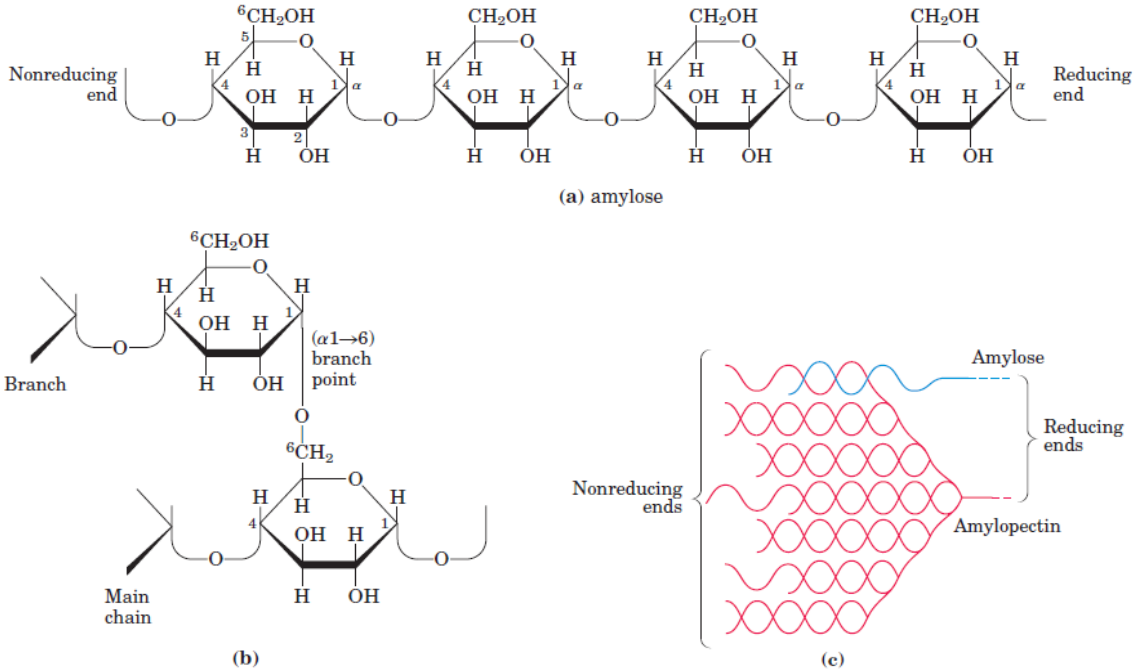


Homopolysaccharides

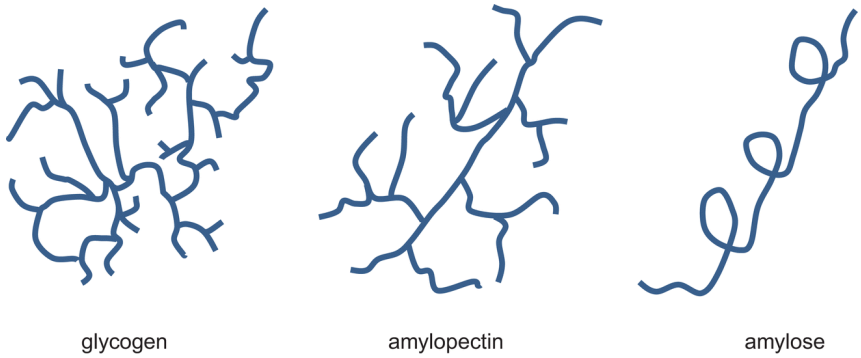
Homopolysaccharides contain only a single type of monomer; heteropolysaccharides contain two or more different kinds. Some homopolysaccharides serve as storage forms of monosaccharides that are used as fuels; starch and glycogen are homopolysaccharides of this type. The most important storage polysaccharides are starch in plant cells and glycogen in animal cells. Both polysaccharides occur intracellularly as large clusters or granules. Starch and glycogen molecules are heavily hydrated, because they have many exposed hydroxyl groups available to hydrogen-bond with water. Most plant cells have the ability to form starch, but it is especially abundant in tubers, such as potatoes, and in seeds. Other homopolysaccharides (cellulose and chitin, for example) serve as structural elements in plant cell walls and animal exoskeletons.

Starch

Starch contains two types of glucose polymer, amylase and amylopectin. The former consists of long, unbranched chains of D-glucose residues connected by (α-1-4) linkages. Such chains vary in molecular weight from a few thousand to more than a million. Amylopectin also has a high molecular weight (up to 100 million) but unlike amylose is highly branched. The glycosidic linkages joining successive glucose residues in amylopectin chains are (α-1-4); the branch points (occurring every 24 to 30 residues) are (α-1-6) linkages.



a. Amylose; b. Amylopectin



A comparison of branching.

Glycogen

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, but glycogen is more extensively branched (on average, every 8 to 12 residues) and more compact than starch. Glycogen is especially abundant in the liver, where it may constitute as much as 7% of the wet weight; it is also present in skeletal

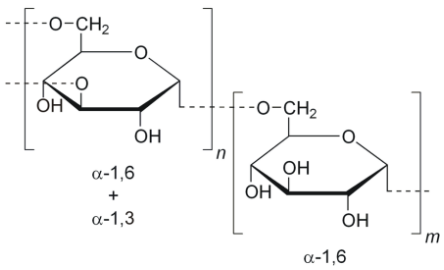
muscle. In hepatocytes glycogen is found in large granules, which are themselves clusters of smaller granules composed of single, highly branched glycogen molecules with an average molecular weight of several million. Such glycogen granules also contain, in tightly bound form, the enzymes responsible for the synthesis and degradation of glycogen. Because each branch in glycogen ends with a nonreducing sugar unit, a glycogen molecule has as many nonreducing ends as it has branches, but only one reducing end. When glycogen is used as an energy source, glucose units are removed one at a time from the nonreducing ends. Degradative enzymes that act only at nonreducing ends can work simultaneously on the many branches, speeding the conversion of the polymer to monosaccharides.

Why not store glucose in its monomeric form?

Glucose, due to its water solubility, present as monomers within the cell exert more osmotic pressure (hypertonic) than a single glycogen molecule (as Glycogen is insoluble), resulting in entry of water in the cells by endosmosis that might rupture the cell. Glycogen on the other hand is osmotically more stable.

Furthermore, with an intracellular glucose concentration of 0.4 M and an external concentration of about 5 mM (the concentration in the blood of a mammal), the free-energy change for glucose uptake into cells against this very high concentration gradient would be prohibitively large.

Dextran



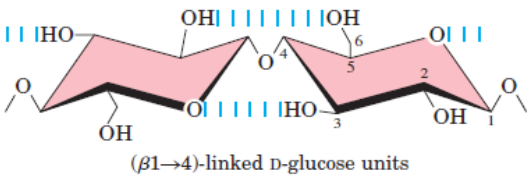
Dextrans are bacterial and yeast polysaccharides made up of (α-1-6)-linked poly-D-glucose; all have (α-1-3) branches, and some also have (α-1-2) or (α-1-4) branches. Dextran can be produced from sucrose by certain lactic acid bacteria present in mouth. About 10% of dental plaque is composed of dextran. Medicinally it is used as an antithrombotic (antiplatelet), to reduce blood viscosity, and as a volume expander in Hypovolemia (a codition in which the liquid portion of the blood (plasma) is too low). In laboratory, it is used in some size-exclusion chromatography matrices; an example is Sephadex. The dextrans in these products are chemically cross-linked to form insoluble materials of various porosities, admitting macromolecules of various sizes.

Cellulose

Cellulose, a fibrous, tough, water-insoluble substance, is found in the cell walls of plants, particularly in stalks, stems, trunks, and all the woody portions of the plant body. Cellulose constitutes much of the mass of wood, and cotton is almost pure cellulose. Like amylose and the main chains of amylopectin and glycogen, the cellulose molecule is a linear, unbranched homopolysaccharide, consisting of 10,000 to 15,000 D-glucose units.

But there is a very important difference: in cellulose the glucose residues have the β configuration whereas in amylose, amylopectin, and glycogen the glucose is in the α configuration. The glucose residues in cellulose are linked by (β-1-4) glycosidic bonds, in contrast to the (α-1-4) bonds of amylose, starch, and glycogen. This difference gives cellulose and amylose very different structures and physical properties. As a consequence of its α-linkages, amylase forms a helix that is extensively hydrogen bonded and, as a result, starch is soluble in water. β-linkages in cellulose cause the molecules to form intramolecular hydrogen bonds. Consequently, they are less extensively bonded to water and line up in linear arrays. The linear molecules form intermolecular hydrogen bonds and, as a result, cellulose is not soluble in water. The bundles of polymer chains causes cellulose to be an effective structural material.

Glycogen and starch ingested in the diet are hydrolyzed by α-amylases, enzymes in saliva and intestinal secretions that break (α-1-4) glycosidic bonds between glucose units. Most animals cannot use cellulose as a fuel source, because they lack an enzyme to hydrolyze the (β-1-4) linkages. However, bacteria that possess β-glucosidase inhabit the digestive tracts of grazing animals and secretes cellulase, which hydrolyzes the (β-1-4) linkages, thus they are capable of using cellulose as food only indirectly. So cows can eat grass and horses can eat hay to meet their nutritional requirements for glucose. Termites also harbour bacteria that readily digest cellulose (and therefore wood).

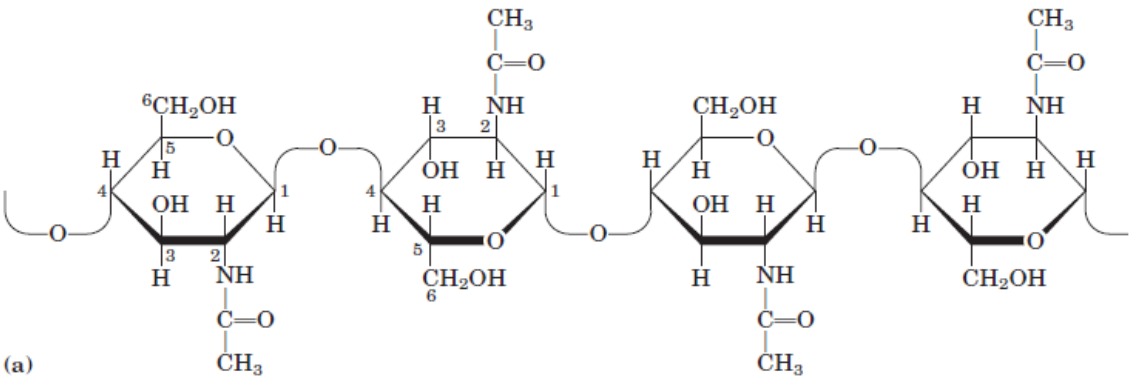


Structure of Cellulose

Chitin

Chitin is a linear homopolysaccharide composed of *N*-acetylglucosamine residues in β-linkage. The only chemical difference from cellulose is the replacement of the hydroxyl group at C-2 with an acetylated amino group. Chitin forms extended fibers similar to

those of cellulose, and like cellulose cannot be digested by vertebrates. Chitin is the principal component of the hard exoskeletons of nearly a million species of arthropods - insects, lobsters, and crabs, for example - and is probably the second most abundant polysaccharide, next to cellulose, in nature.



Structure of Chitin

Heteropolysaccharides

Heteropolysaccharides provide extracellular support for organisms of all kingdoms. For example, the rigid layer of the bacterial cell envelope (the peptidoglycan) is composed in part of a heteropolysaccharide built from two alternating monosaccharide units. In animal tissues, the extracellular space is occupied by several types of heteropolysaccharides, which form a matrix that holds individual cells together and provides protection, shape, and support to cells, tissues, and organs.

Bacterial and Algal Cell Walls

The rigid component of bacterial cell walls is a heteropolymer of alternating (β-1-4)-linked *N*-acetylglucosamine and *N*-acetylmuramic acid residues. The linear polymers lie side by side in the cell wall, cross-linked by short peptides, the exact structure of which depends on the bacterial species. The peptide cross-links weld the polysaccharide chains into a strong sheath that envelops the entire cell and prevents cellular swelling and lysis due to the osmotic entry of water.

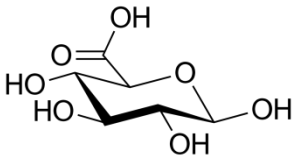
Agarose

Certain marine red algae, including some of the seaweeds, have cell walls that contain agar, a mixture of sulfated heteropolysaccharides made up of D-galactose and an L-galactose derivative ether-linked between C-3 and C-6. The two major components of agar are the unbranched polymer **agarose** (*M*r ~120,000) and a branched component, agaropectin. The remarkable gel-forming property of agarose makes it useful in the biochemistry laboratory. When a suspension of agarose in water is heated and cooled, the agarose forms a double helix: two molecules in parallel orientation twist together

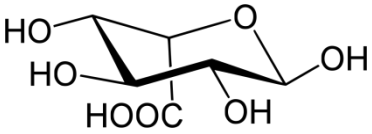
with a helix repeat of three residues; water molecules are trapped in the central cavity. These structures in turn associate with each other to form a gel - a three-dimensional matrix that traps large amounts of water. Agarose gels are used as inert supports for the electrophoretic separation of nucleic acids, an essential part of the DNA sequencing process. Agar is also used to form a surface for the growth of bacterial colonies. Another commercial use of agar is for the capsules in which some vitamins and drugs are packaged; the dried agar material dissolves readily in the stomach and is metabolically inert.

Glycosaminoglycans

The extracellular space in the tissues of multicellular animals is filled with a gel-like material, which holds the cells together and provides a porous pathway for the diffusion of nutrients and oxygen to individual cells. The extracellular matrix is composed of an interlocking meshwork of heteropolysaccharides and fibrous proteins such as collagen, elastin, fibronectin, and laminin. These heteropolysaccharides, the **glycosaminoglycans,** are a family of linear polymers composed of repeating disaccharide units One of the two monosaccharides is always either *N*-acetylglucosamine or *N*-acetylgalactosamine; the other is in most cases a uronic acid, usually D-glucuronic or L-iduronic acid. In some glycosaminoglycans, one or more of the hydroxyls of the amino sugar are esterified with sulfate. The combination of sulfate groups and the carboxylate groups of the uronic acid residues gives glycosaminoglycans a very high density of negative charge. To minimize the repulsive forces among neighboring charged groups, these molecules assume an extended conformation in solution. The specific patterns of sulfated and nonsulfated sugar residues in glycosaminoglycans provide for specific recognition by a variety of protein ligands that bind electrostatically to these molecules. Glycosaminoglycans are attached to extracellular proteins to form proteoglycans.



D-Glucuronic acid



L-Iduronic acid