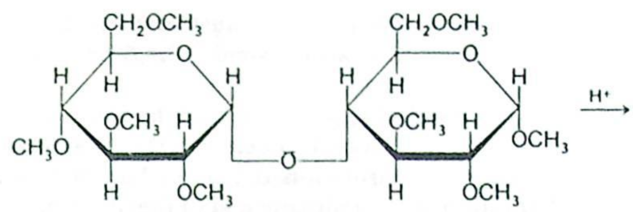
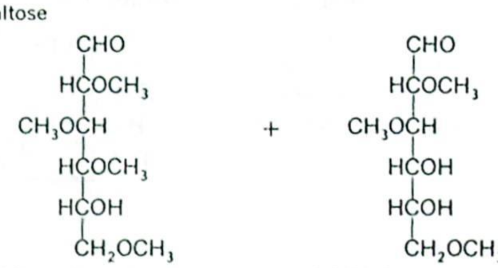


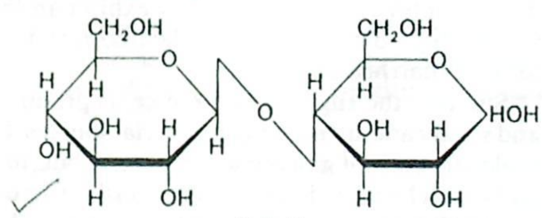
Octamethyl-D-maltose



2,3,4,6-Tetra-O-methyl-D-glucose 2,3,6-Tri-O-methyl-D-glucose

ysis. While the anomeric carbon of maltose is methylated on treatment of the disaccharide with dimethyl sulfate, this *O*-methyl glycosidic bond as well as the glycosidic bond between the two glucose units of the disaccharide is acid labile charide is acid labile and both are cleaved on hydrolysis with acid.

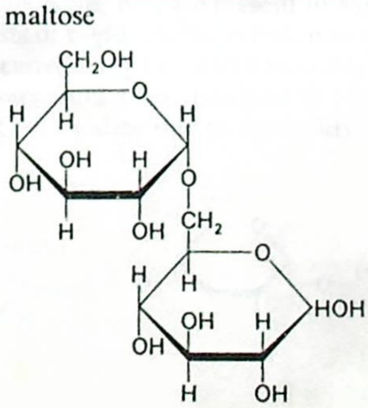
The disaccharide cellobiose is identical with maltose except that the former compound has a $\beta(1 \rightarrow 4)$ glycosidic linkage. Cellobiose is a disaccharide formed during the acid hydrolysis of



Cellobiose

cellulose. It is a reducing sugar and undergoes mutarotation. Treatment of cellobiose with dimethyl sulfate would also yield an octamethylated sugar, and acid hydrolysis would yield the same products that were obtained from octamethyl maltose.

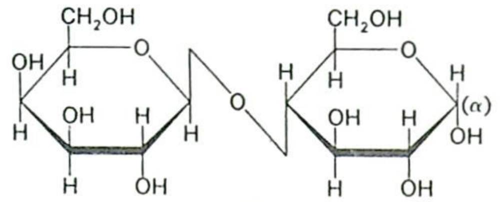
Isomaltose, another disaccharide obtained during the hydrolysis of certain polysaccharides, is similar to maltose



Isomaltose

except that it has an $\alpha(1 \rightarrow 6)$ linkage. Exhaustive methylation and acid hydrolysis of octamethyl isomaltose would yield 2,3,4,6-tetra-*O*-methyl-D-glucose and 2,3,4-tri-*O*-methyl-D-glucose.

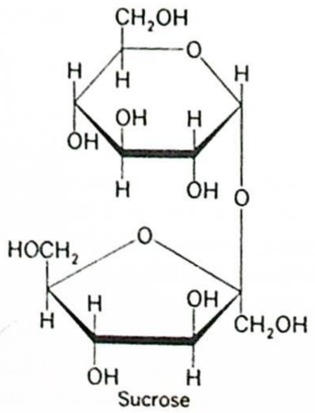
Lactose is a disaccharide found in milk; on hydrolysis, it yields one mole each of D-galactose and D-glucose. It possesses a $\beta(1 \rightarrow 4)$ linkage, is a reducing sugar, and can undergo mutarotation. α-Lactose has the following formula in which the configuration at the reducing end of the disaccharide is shown as α.



Lactose

Being the major carbohydrate in milk, lactose is extremely important in the nutrition of young mammals. Most of the world's human population relies on this sugar as a major form of energy during the first years of life. Lactose itself cannot be absorbed into the blood, but must first be hydrolyzed to its constituent monosaccharides by intestinal lactase. This enzyme is abundant in nursing infants but tends to disappear with age. Only Northern Europeans and a few other African peoples retain the enzyme in adulthood. Most other human groups have little intestinal lactase as adults and some, especially Mediterranean peoples and Orientals, may exhibit an intolerance to the sugar. In these people, high dietary intake of lactose results in intestinal disturbance in the form of diarrhea and pain.

Sucrose, the sugar of commerce, is produced by higher plants; sugar beets and sugar cane are major commercial sources. On hydrolysis, sucrose yields one molecule each of glucose and fructose, but, in contrast to all the other mono- and disaccharides described previously, sucrose is not a reducing sugar. This means that the reducing groups in both of the monosaccharide components must be involved in the glycosidic linkage between the two sugars. That is, the C-1 and C-2 carbon atoms, respectively, of the glucose and fructose moieties must be covalently linked in a glycoside bond. Permethylation studies of sucrose has shown that it must have the following structure with an α-configuration on the glucose subunit and a β-configuration on the fructose moiety.



Sucrose

Sucrose is a major product of plant photosynthesis (Section 11.2.2 and Chapter 15). Sucrose is also the form in which carbohydrate, produced in the leaves by photosynthesis, is transported into storage organs such as developing seeds, tubers, or roots. It has been suggested that sucrose has an advantage, both as a storage product and a transport form of carbohydrate, over glucose and the other common sugars since both of its anomeric carbon atoms are protected from oxidative attack.

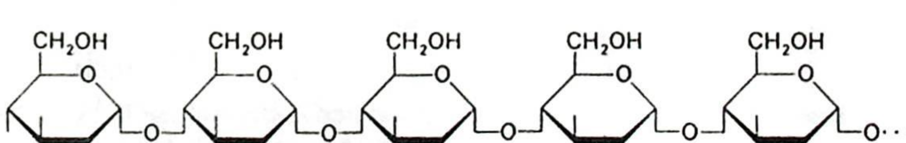
Sucrose, and maltose to a lesser extent, are important carbohydrate components of the human diet. However, they cannot be directly absorbed into the body and, like lactose, must first be hydrolyzed by specific enzymes, sucrase and maltase, found in the intestinal mucosa. Sucrose is used extensively as a sweetening agent in the food industry. It is readily available and is sweeter than the other common sugars maltose, lactose, and glucose. Only fructose is sweeter, and today enzymically produced mixtures of glucose and fructose, obtained from corn and other plant starches, are replacing sucrose as a commercial sweetener. Such mixtures are nutritionally equivalent to sucrose on a weight basis and significantly sweeter.

2.7 POLYSACCHARIDES

The polysaccharides found in nature either serve a structural function or play an important role as a stored form of energy. All polysaccharides can be hydrolyzed with acid or enzymes to yield monosaccharides and/or monosaccharide derivatives. Those polysaccharides that on hydrolysis yield only a single type of monosaccharide molecule are termed **homopolysaccharides. Heteropolysaccharides** on hydrolysis yield a mixture of constituent monosaccharides and derived products.

2.7.1 STORAGE POLYSACCHARIDES

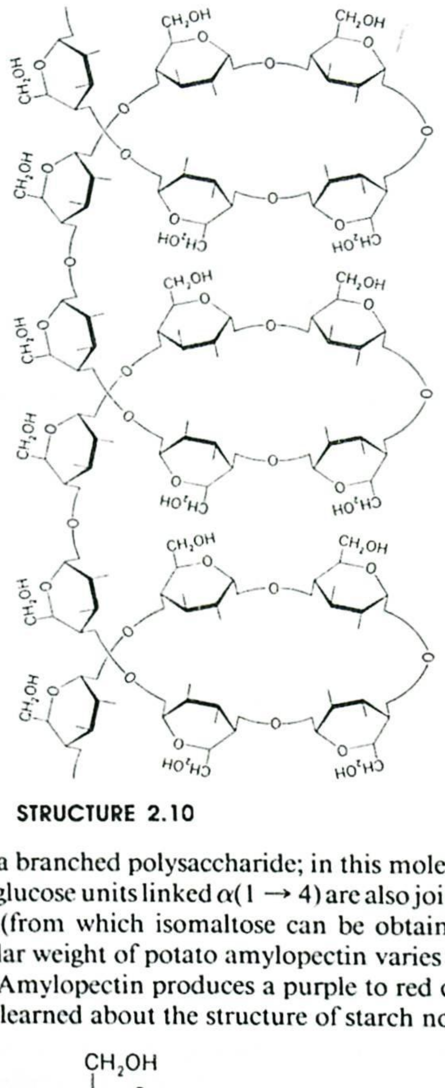
Starch is a storage homopolysaccharide produced by plants (see Section 10.6.5). Whereas all green plants produce starch as an end product of photosynthesis, the cereal crops (wheat, rice, maize, and sorghum) are noted for the high starch content of their seeds. Indeed, these cereals together with a few other crops like potato and cassava, where the starch is stored in an underground tuber, provide the majority of the calories for nearly all of mankind. Starch consists of two components, amylose and amylopectin, that are present in varying amounts. The amylose component consists of D-glucose units linked in a linear fashion by $\alpha(1 \rightarrow 4)$ linkages; it has a nonreducing end and a reducing end (Structure 2.9). Its molecular weight can vary from a few thousand to 150,000. Amylose gives a characteristic blue color with iodine due to the ability of the halide to



Amylose

STRUCTURE 2.9

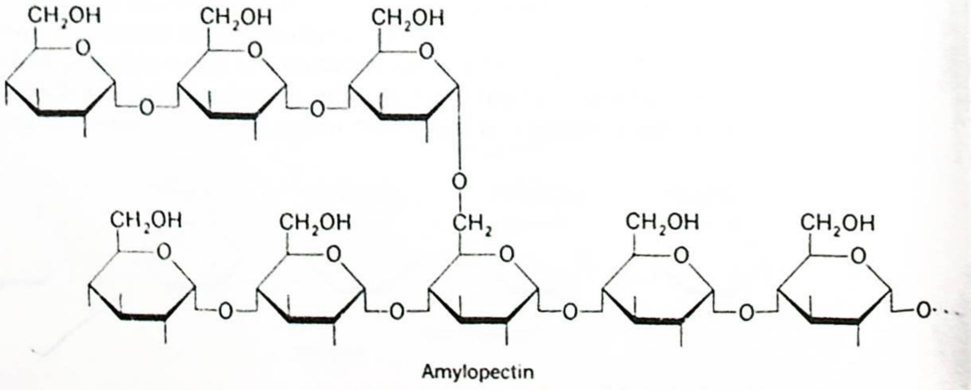
occupy a position in the interior of a helical coil of glucose units that is formed when amylose is suspended in water (Structure 2.10).



STRUCTURE 2.10

Amylopectin is a branched polysaccharide; in this molecule, shorter chains (about 30 units) of glucose units linked $\alpha(1 \rightarrow 4)$ are also joined to each other by $\alpha(1 \rightarrow 6)$ linkings (from which isomaltose can be obtained). (See Structure 2.11.) The molecular weight of potato amylopectin varies greatly and may be 500,000 or larger. Amylopectin produces a purple to red color with iodine.

Much has been learned about the structure of starch not only from studies



STRUCTURE 2.11

with exhaustive methylating and oxidizing agents, but also by the action of enzymes on the polysaccharide. One enzyme, α-amylase, found in the digestive tract of animals (in saliva and the pancreatic juice), hydrolyzes the linear amylose chain by attacking α(1 → 4) linkages at random throughout the chain to produce a mixture of maltose and glucose. β-Amylase, an enzyme found in plants, attacks the nonreducing end of amylose to yield successive units of maltose. (The prefixes α and β used with the amylases do not refer to glycosidic linkage, but simply designate these two enzymes.)

Amylopectin can also be attacked by α- and β-amylase, but the α(1 → 4) glycosidic bonds near the branching point in amylopectin and the α(1 → 6) bond itself are not hydrolyzed by these enzymes. A separate "debranching" enzyme, an α(1 → 6) glucosidase, can hydrolyze the bond at the branch point. Therefore, the combined action of α-amylase and the α(1 → 6) glucosidase will hydrolyze amylopectin ultimately to a mixture of glucose and maltose.

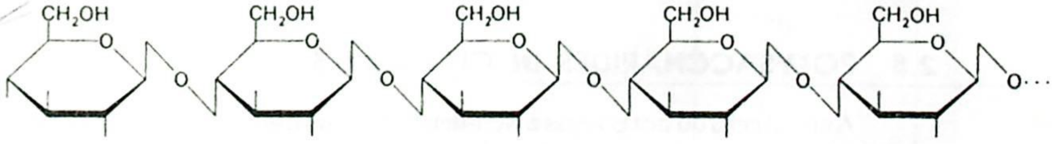
The storage polysaccharide of animal tissues is glycogen; it is similar in structure to amylopectin in that it is a branched homopolysaccharide composed of glucose units. It is more highly branched than amylopectin, however, having branch points about every 8 to 10 glucose units. Like amylopectin, glycogen is hydrolyzed by α- and β-amylases to form glucose, maltose, and a limit dextrin.

A final example of a nutrient polysaccharide will suffice. This is inulin, a storage carbohydrate found in the bulbs of many plants (e.g., dahlias and Jerusalem artichokes). Inulin consists chiefly of fructofuranose units joined together by β(2 → 1) glycosidic linkages.

2.7.2 STRUCTURAL POLYSACCHARIDES

The most abundant carbon compound in the world is the structural polysaccharide cellulose. Cellulose is found in the cell walls of plants where it contributes in a major way to the physical structure of the organism (see Section 8.1.2). Lacking a skeleton of bone onto which organs and specialized tissues may be organized, the higher plant relies on its cell walls to bear its own weight whether it is a sunflower or a sequoia. The wood of trees is an insoluble, organized structure composed of cellulose and another polymer called **lignin** derived from the amino acid phenylalanine.

Cellulose is a linear homopolymer of D-glucose units linked by β(1 → 4) glycosidic bonds (Structure 2.12). The seemingly small difference in structure



STRUCTURE 2.12

from amylose, however, confers very different and important properties on cellulose. Instead of forming a coiled helix, cellulose forms a structure of parallel chains that are cross-linked by hydrogen bonding.

In contrast to starch, the β(1 → 4) linkages of cellulose are highly resistant to acid hydrolysis; strong mineral acid is required to produce D-glucose; partial hydrolysis yields the reducing disaccharide, cellobiose. The β(1 → 4) linkages