CARBOHYDRATES

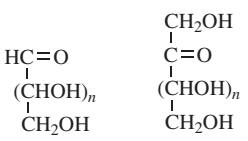
1. Introduction

Carbohydrates are found in all plant and animal cells. They are the most abundant of the organic compounds, so abundant that it is estimated that well over one-half of the organic carbon on earth exists in the form of carbohydrates. Most carbohydrates are produced and found in plants. Carbohydrate molecules make up about three-fourths of the dry weight of plants; most is found in cell walls as structural components. Carbohydrates also constitute important energy reserves in plants; one carbohydrate, starch, provides about three-fourths of the calories in the average human diet on a worldwide basis. But the nutritional aspects are only a part of the story of carbohydrates. They have many important commercial uses in such diverse areas as adhesive, agricultural chemicals, fermentation, food, pharmaceutical, textile and paper and related products, and in petroleum production. Because the basic carbohydrate molecule is functionalized at every carbon atom, and because carbohydrates seldom occur as simple sugars but rather combined with each other or other compounds, the variety of carbohydrates in nature is large, and the number of theoretical possibilities is almost limitless.

2. Classification

The basic carbohydrate molecule possesses an aldehyde or ketone group and a hydroxyl group on every carbon atom except the one of the carbonyl group. As a result, carbohydrates are defined as aldehyde or ketone derivatives of polyhydroxy alcohols and their reaction products. The formula for glucose and related sugars ($C_6H_{12}O_6$) contains hydrogen and oxygen atoms in the ratio in which they are found in water. The name carbohydrate (hydrate of carbon) is derived from the fact that the basic carbohydrate molecule has the formula $C_n(H_2O)_n$.

Monosaccharides, commonly referred to as the simple sugars, are carbohydrates that cannot be broken down by hydrolysis (1,2). They are classified both according to the kind of carbonyl group and according to the number of carbon atoms contained in the molecule. An aldose is a polyhydroxy aldehyde, ie, an aldehyde that has a hydroxyl group on every carbon atom except the carbonyl carbon atom. A ketose is a polyhydroxy ketone. Numical prefixes designating the number of carbon atoms are tri-, tetra-, penta-, hexa-, hepta-, etc. In systemic nomenclature, the suffix for the names of aldehyde sugars is -ose and for ketone sugars-ulose. The two classification systems can be joined in a single-word description. For example, a three-carbon aldose is an aldotriose and a six-carbon ketose is a ketohexose (or hexosulose). Common names are frequently used, creating exceptions to systematic nomenclature.



aldose ketose

Monosaccharides are most often joined together in chains. Oligosaccharides are carbohydrate chains that yield 2–10 monosaccharide molecules upon hydrolysis (2,3). Oligosaccharides are classified according to the number of monosaccharide units in them, eg, di-, tri-, tetra-, pentasaccharides, etc. Polysaccharides are carbohydrate chains that yield at least 35 monosaccharide molecules upon hydrolysis (4–10). Polysaccharides may be linear (unbranched) or branched. They may contain a single kind of monosaccharide unit (homopolysaccharides) or two or more different monosaccharide units (heteropolysaccharides). The generic term for polysaccharides is glycan; therefore, these two groups of polysaccharides are also termed homoglycans and heteroglycans.

Most carbohydrates exist in the form of polysaccharides. Polysaccharides give structure to the cell walls of land plants (cellulose), seaweeds, and some microorganisms and store energy (starch in plants, glycogen in animals). They are important in the human diet and in many commercial applications.

3. Representations

D-Glucose is an aldohexose. Four of the six carbon atoms (C-2, C-3, C-4, C-5) are chiral carbon atoms. To compare the arrangements of atoms in common, simple monosaccharides, structural formulas are written using the convention that all bonds connecting carbon atoms are vertical and project into the plane of the page away from the viewer and the bond to the hydrogen atom and the hydroxyl group on each chiral carbon atom projects out of the plane of the page towards the viewer. Horizontal bonds are often omitted. The acyclic structural formula of D-glucose shown is known as the open-chain, or Fischer, formula. If the hydroxyl group on the most distant chiral carbon atom from the top end (the penultimate carbon atom of the structures in Fig. 1; C-5 of D-glucose) is on the right when the carbon chain of an aldose or ketose is written using this convention, the sugar is said to have the D configuration; if that hydroxyl group is on the left, the sugar belongs to the family of L sugars. Most naturally occurring monosaccharides have the D configuration. An exception is arabinose, which most often occurs as L-arabinose [5328-37-0]. All possible structures of the three-, four-, five-, and six-carbon atom aldoses with the D configuration are given in Figure 1.

Because an aldohexose contains four chiral carbon atoms, there are $2^4 = 16$ different possible arrangements of the hydroxyl groups in space, ie, there are 16 different stereoisomers of an aldohexose. The structures of one-half of these, the eight D isomers, are shown in Figure 1. Only three of these 16 stereoisomers are commonly found in Nature: D-glucose [50-99-7], D-galactose [59-23-4], and D-mannose [3458-28-4].

4. Chemistry of Saccharides

Most carbohydrates have two kinds of reactive groups: the carbonyl group and primary and secondary hydroxyl groups.

4.1. Reactions of The Carbonyl Group. *Ring Forms.* Aldehydes and ketones react with compounds containing a hydroxyl group (alcohols) to form first hemiacetals and then acetals. Because aldose and ketose molecules have a carbonyl group and hydroxyl groups on the same carbon chain, they

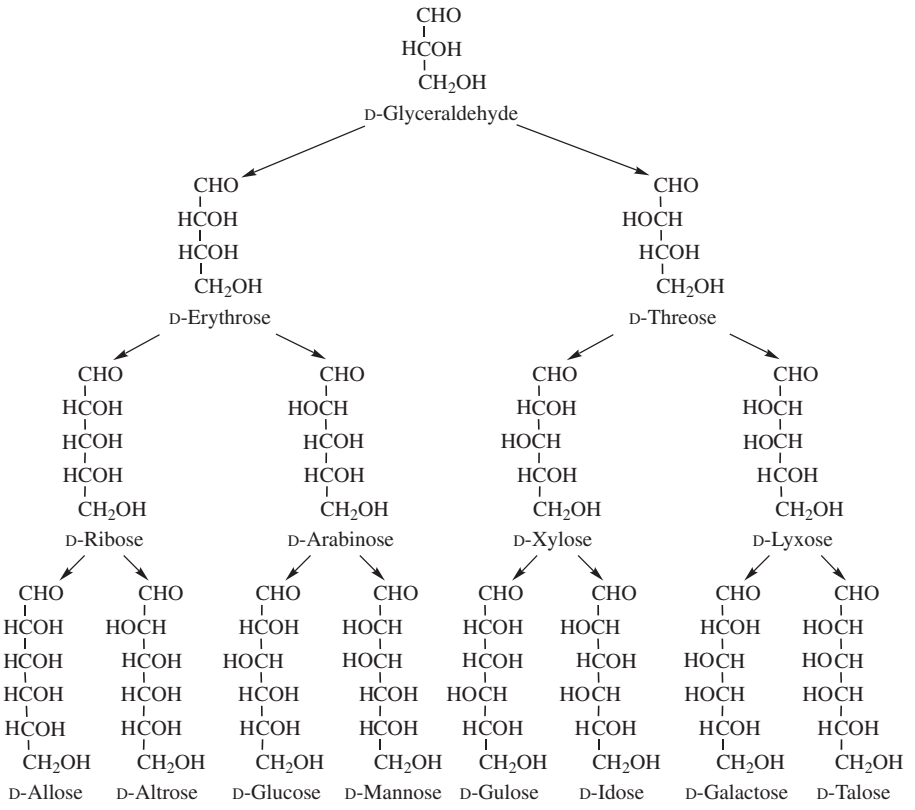


Fig. 1. The family of D-aldoses derive from D-glyceraldehyde by chain extension at the carbonyl carbon atom.

can form hemiacetal structures intramolecularly. Such an intramolecular reaction forms a ring. The most common rings are the six-membered pyranose ring, a cyclic structure composed of five carbon atoms and one oxygen atom, and the five-membered furanose ring, a cyclic structure composed of four carbon atoms and one oxygen atom (Fig. 2).

It is easy to picture the formation of a ring from an open-chain structure if it is remembered that the carbon chain is curving into the plane of the page. When this structure is laid on its side, it is naturally curved into almost the correct shape, with the ends almost touching. However, in order to close the ring, ie, to form the hemiacetal between the hydroxyl group on C-5 and the aldehyde group, C-5 must rotate to bring the hydroxyl group closer to the aldehyde group. The result of this rotation is that the $-CH_2OH$ group sticks up in this (the Haworth) representation of the pyranose ring of the D sugars and the $-CH_2OH$ group projects down in representations of the L sugars. Most, but not all, naturally occurring sugars are D sugars. For C-2, C-3, and C-4, the carbon atoms that are not involved in ring formation, the hydroxyl groups that are on the right in the Fischer projection project down in the Haworth ring form and the hydroxyl groups that are on the left in the Fischer projection stick up in the Haworth ring form.

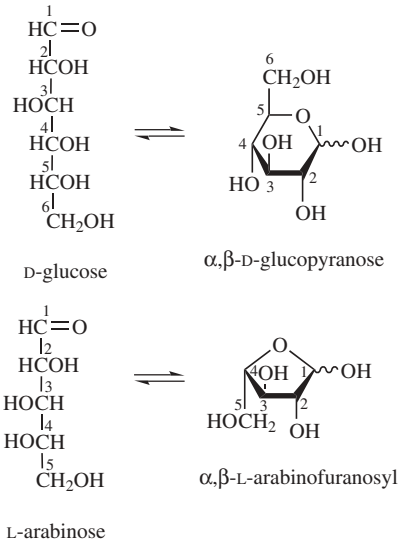
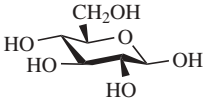


Fig. 2. Conversion from open-chain to ring forms of aldoses (aldehydo sugars). When ring closure occurs, a new chiral center is formed and two C-1 configurational isomers, called anomers, are formed.

When the pyranose (six-membered) ring is formed, a new chiral carbon atom is formed from C-1. Thus there can be two forms of the pyranose ring. D Sugars with the hydroxyl group at C-1 in the up position are said to be in the beta (β) configuration; D sugars with the hydroxyl group at C-1 projecting down are said to be in the alpha (α) configuration. α-D-Glucopyranose [492-62-6] and β-D-glucopyranose [492-61-5] are anomers of each other. In β-L-pyranoses, the hydroxyl group on C-1, termed the anomeric carbon atom, projects down in the Haworth representation. Thus, eg, β-D- and β-L-glucopyranose [39281-65-7] are complete mirror images of each other.

Most free pentoses, hexoses, and heptoses occur primarily in less-strained pyranose rings, but the furanose ring is also quite important. The furanose ring is formed in the same way as the pyranose ring and also occurs in α and β forms. This is demonstrated with L-arabinose, which is commonly found in polysaccharides in the form of α-L-arabinofuranosyl units (see Fig. 2).

Whereas furanose rings are almost, but not quite, flat, pyranose rings are not, thus Haworth representations do not show the actual molecular shape. Pyranose rings assume one of two chair forms designated the $^4C_1$ chair because C-4 is up and C-1 is down (with respect to the plane of O-5, C-2, C-3, and C-5) and the $^1C_4$ form. The $^4C_1$ chair is by far the most prevalent shape of the β-D-glucopyranose molecule because all the bulky groups (the hydroxyl groups at C-1, C-2, C-3, and C-4 and the hydroxymethyl group at C-5) are in equatorial positions which minimizes nonbonded (steric) interactions.



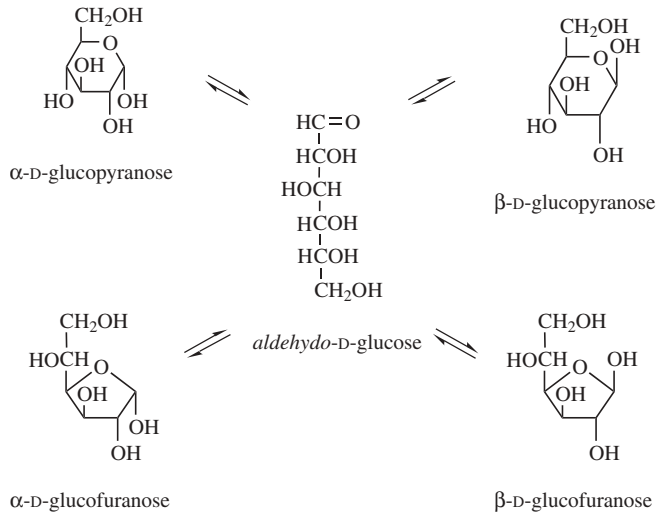


Fig. 3. Equilibrium mixture of D-glucose forms in solution. Pyranose ring forms predominate.

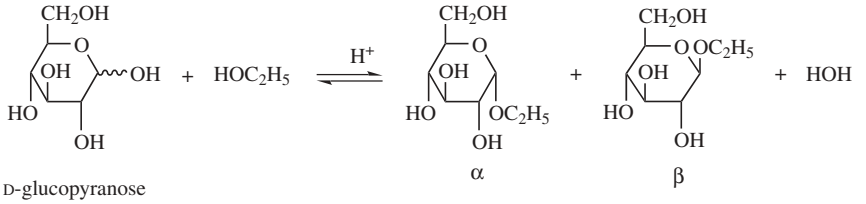
Solutions of aldoses and ketoses reach an equilibrium among various forms, as shown for D-glucose in Figure 3. The exact composition of an equilibrium mixture depends on the temperature and the specific sugar; for D-glucose the approximate composition of a solution at room temperature is <0.01% aldehydo form, 36.2% α-D-glucopyranose, 63.8% β-D-glucopyranose, and traces of the furanose ring forms. The process of conversion among forms is called mutarotation (1) because, when crystals of α-D-glucopyranose are dissolved in water, the initial specific optical rotation ($[\alpha]_D$ at 20°C) of +112° gradually decreases to the equilibrium value of +52.7°. Likewise, when crystals of β-D-glucopyranose are dissolved in water, the initial specific optical rotation of +18.7° gradually increases to the equilibrium value of +52.7°. Mutarotation is both acid and base catalyzed.

The structure of monosaccharides is often written in the acyclic form although only very minor amounts of it ever occur in that form. Because the interconversions are rapid, the carbonyl groups of sugars can and do react both as if they are free and as if they are in a hemiacetal ring form.

Glycosides, Oligosaccharides, and Polysaccharides. Few monosaccharides are found free in nature, and these few are usually present in only small amounts. Most monosaccharides occur in combinations, most often with either more of the same sugar or different sugars in the form of polymers (polysaccharides). Less frequently, except in the case of sucrose, they are joined together in oligosaccharide chains. Mono- and oligosaccharides may also be linked to nonsugar organic compounds. These combined forms of sugars are known as glycosides.

Pyranose and furanose ring forms of carbohydrate molecules are hemiacetals and can react with an alcohol to form glycosides, which are acetals of sugars. Hydrolysis of a glycoside in an acidic solution releases the monosaccharide and the alcohol (1). This forward and reverse process is shown for the reaction of

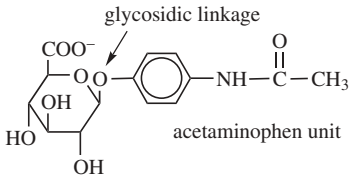
D-glucose with ethanol to form ethyl α-D-glucopyranoside [19467-01-7] and ethyl β-D-glucopyranoside [3198-49-0].



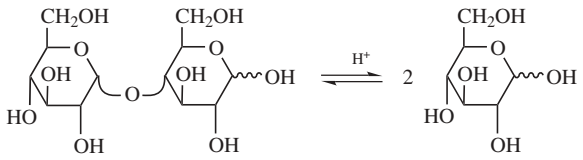
D-glucopyranose

Glycosides, particularly of phenolic compounds, are widely distributed in plant tissues (11,12). Glycosides of anthocyanidins, flavones, flavanols, flavanones, flavanonols, stilbenes and saponins, gallic acid derivatives, and condensed tannins are all common.

In the body, detoxification of drugs and poisonous compounds often involves converting the substance into a more water-soluble compound, which is then excreted in urine. The most common conversion reactions are hydroxylations, oxidations, reductions, and conjugations. Acetaminophen [103-90-2], an analgesic used as an aspirin substitute, contains a hydroxyl group which is combined with the monosaccharide D-glucuronic acid to form the water-soluble β-D-pyranoside. After deacetylation, aspirin [50-78-2] may be conjugated with either D-glucuronic acid or the amino acid glycine (uronic acids are monosaccharides in which the terminal primary alcohol group has been oxidized to a carboxylic acid group).



Frequently, the alcohol that forms a glycoside with a sugar is a hydroxyl group of another sugar. The formation of a glycoside between two sugar units joins them, forming a disaccharide, eg, two D-glucopyranosyl units may be linked to form the disaccharide maltose [69-79-4].



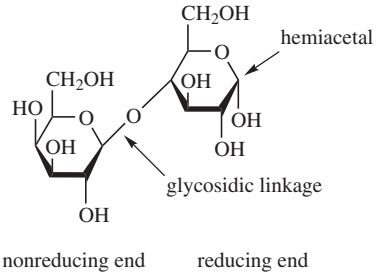
maltose D-glucose

In Nature, however, monosaccharide units are not joined together by such a simple acid-catalyzed condensation as that shown above, which is why the reaction is written as a hydrolytic reaction. For chemical synthesis of di- and higher

saccharides, activation of the anomeric carbon atom and blocking of hydroxyl groups not involved in the linkage are required and employed. An exception is found in the manufacture of polydextrose [68424-04-4], which is made by heating D-glucose under dehydrating conditions (vacuum) in the presence of sorbitol (D-glucitol), and citric acid (catalyst) to make a highly branched, low molecular weight polymer.

For the most part, low molecular weight carbohydrates of commerce are made by depolymerization of polysaccharides via enzyme- or acid-catalyzed hydrolysis. Only sucrose and, to a very much lesser extent, lactose (both disaccharides) are commercial low molecular weight carbohydrates not obtained in this way.

Oligo- and polysaccharides have reducing and nonreducing ends. A reducing sugar is a carbohydrate that contains an aldehyde or ketone group, either free or in a hemiacetal form, which in aqueous solution is always in equilibrium with the free form. The aldehyde group (and the ketone group, after isomerization to an aldehyde group under basic conditions) can be oxidized to a carboxyl group, ie, act as a reducing agent. The reducing end of an oligo- or polysaccharide is the one end not involved in a glycosidic linkage and can, therefore, react as an aldehyde or ketone. The sugar units constituting all other ends are attached through glycosidic (acetal) bonds and are, therefore, nonreducing ends. Reducing and nonreducing ends can be demonstrated with the structure of lactose [63-42-3] (β-D-galactopyranosyl-α-D-glucopyranose), the reducing disaccharide of milk.



Additional sugar units added to either end of disaccharides form higher oligosaccharides. For example, if one α-D-glucopyranosyl unit is added to the disaccharide maltose in a $(1 \rightarrow 4)$ linkage, the trisaccharide maltotriose [1109-28-0] is obtained. Another unit extends to the tetrasaccharide maltotetraose [34612-38-9] and yet another to the pentasaccharide maltopentaose [1668-09-3], etc (malto- is a prefix indicating a product originating from depolymerization of starch molecules). When many sugar units are joined together by glycosidic linkages (the acetal bonds connecting sugar units), the structure is that of a polysaccharide.

Polysaccharides are naturally occurring polymers of monosaccharide (sugar) units (4–10). In precise chemical nomenclature, polysaccharides are glycans and are described as being composed of glycosyl units. Polysaccharides, like oligosaccharides, have ends that can be distinguished from each other because the individual monomer units are joined in a specific head-to-tail fashion. Polysaccharides have one reducing end (free or potential aldehyde or ketone group, although ketoses are uncommon constituents of polysaccharides) and one or

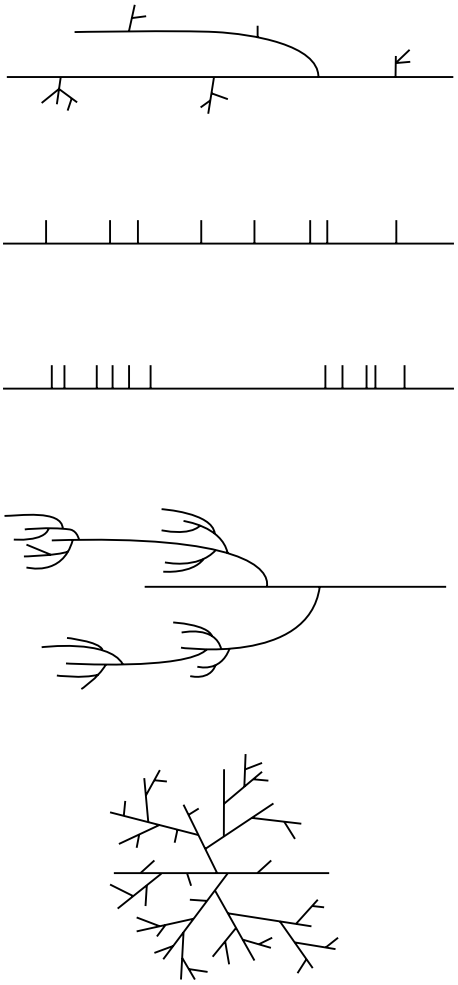


Fig. 4. Branching patterns in polysaccharides.

many nonreducing ends. Polysaccharide molecules can be linear or branched in any of several different ways (Fig. 4). They may be composed of a single type of glycosyl unit (a homoglycan) or from two to six different glycosyl units (a heteroglycan). They generally contain from hundreds to tens of thousands of glycosyl units; some may be larger. Of the heteroglycans, only the bacterial polysaccharides have regular repeating-unit structures, as opposed to plant and animal polysaccharides, because of a different pathway of biosynthesis.

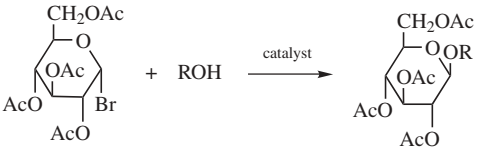
The polysaccharides of starch [9005-25-8] (13) are of great interest and importance. Because starch is the carbohydrate storage material of many plants and the principal component of the seeds of cereal grains (corn, wheat, rice, oat, barley, rye, sorghum, etc) and some edible roots and tubers (potato, cassava, taro, etc.), it is the principal source of carbohydrate in our diet. Starch is also widely used to make D-glucose (often called dextrose in commerce), syrups, and related products. It also has important nonfood applications.

Starch occurs in the form of granules composed of two polysaccharides. Both contain only α-D-glucopyranosyl units and are, therefore, glucans. Amylose [9005-82-7] is an essentially linear polysaccharide of (1 → 4)-linked α-D-glucopyranosyl units. Fine structure analysis has revealed that at least some, especially the larger molecules, are slightly branched. The basic structure of amylose, which is essentially an extension of the maltose structure shown previously, shows that there can be only one sugar unit in any polysaccharide that is not joined to another through a glycosidic bond involving its carbonyl group and only one reducing end. However, branching is possible in polysaccharides because of the multitude of OH groups (Fig. 4). The second polysaccharide in starch granules, amylopectin [9037-22-3], is a highly branched molecule.

Glycogen [9005-79-2], the principal carbohydrate food-reserve substance in animals, has a structure similar to that of amylopectin, ie, it is a branched polymer consisting of linear segments of (1→4)-linked α-D-glucopyranosyl units joined by the (1→6) glycosidic linkages that constitute the branch points. All cells of higher animals may contain some glycogen. Because it is in a dynamic state, glycogen is polymolecular with the range of molecular weights depending on the metabolic state of the tissue. The weight-average molecular weight of rabbit liver glycogen has been reported to be 2.7×10^8, with a range of 6×10^6 to 1.6×10^9. It contains 0.35% of covalently bound protein, a molecule that served as the primer upon which glycogenesis began. The average degree of polymerization (DP, the average number of monosaccharide units in a polysaccharide) of the chain segments depends on the source, but the majority of values are within the range DP 11–14. Glycogen is an amorphous polymer. It is highly soluble and exhibits a fairly ideal hydrodynamic behavior.

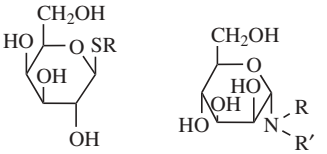
In commerce, hydrolysis of glycosidic bonds is far more important than is condensation of sugars with alcohols or other sugar units to form glycosidic bonds. Glycosidic bonds are formed in nature via biosynthetic reactions, and compounds containing them are isolated and used as starting materials for various transformations. Hydrolysis, whether catalyzed by acids or enzymes, follows the same general mechanism (1).

Synthetic Methods. Although mono- and oligosaccharides are most often made by depolymerization of polysaccharides, oligosaccharides and other compounds with glycosidic bonds can be made synthetically. The classic and still widely used reaction is the Koenigs-Knorr reaction; many modifications of it are known (14–17). The reaction in its simplest form is that given below. Modifications involve the nature of the promoter and blocking groups and have been developed to influence the anomeric configuration, ie, the stereochemistry, of the product.



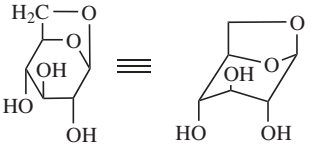
where Ac represents $CH_3-\overset{O}{\overset{\|}{C}}-$

The activated sugar used in this reaction is 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide [572-09-8], commonly called acetobromoglucose. A phenomenon known as the anomeric effect requires that this compound always has the α-D configuration, ie, that the halogen atom be in the axial position. Glycosyl chlorides and glycosyl fluorides are also used in the preparation of glycosides. The excocylic oxygen atom in the product can be replaced with a sulfur atom or an amino group (14,18).

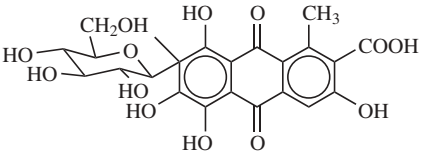


Nucleosides (15,19) and nucleotides are examples of the latter (glycosylamine) type.

The reaction to form an acetal can be an intramolecular reaction. The best known example is 1,6-anhydro-β-D-glucopyranose [498-07-7], commonly called levoglucosan.



C-Glycosyl compounds have a carbon atom in place of the exocyclic oxygen atom of the acetal group and, therefore, are branched cyclic ethers. An example is the naturally occurring anthraquinone dye, carminic acid [1260-17-9] (CI Natural Red 4).

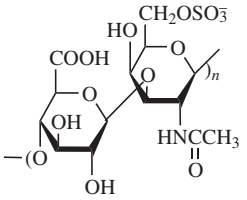


Glycoconjugates. Another class of carbohydrates is the glycoconjugates, which is composed of glycoproteins, proteoglycans, peptidoglycans, and glycolipids.

Glycoproteins. (4,20,21) are molecules containing saccharide chains, often but not always oligosaccharide chains, covalently attached to a polypeptide chain. The saccharide chains may be attached via a glycosidic linkage to a hydroxyl group of a seryl, threonyl, hydroxylysyl, or hydroxyprolyl unit or via a glycosylamine linkage to the amide group of an asparaginyl unit. The percentage of carbohydrate in glycoproteins, which includes the majority of all proteins, varies from <1 to $>80\%$. The surface of cells is covered with a complex mosaic of carbohydrates, called the glycocalyx, many of which are the saccharide units of

glycoproteins. Some of those on erythrocytes control blood group antigenicity (see BLOOD, COAGULANTS AND ANTICOAGULANTS).

Proteoglycans (20,21) are components of connective tissue. They have specific polysaccharide chains covalently attached to a polypeptide chain. The specific polysaccharides are glycosaminoglycans (4,20,21), commonly called mucopolysaccharides. As the name suggests, these polysaccharides contain amino sugars (2-amino-2-deoxysugars). All except keratan sulfate contain uronic acid units; all except hyaluronic acid contain sulfate half-ester groups. The polysaccharides found as components of proteoglycans are chondroitin 4-sulfate [24967-93-9], chondroitin 6-sulfate [25322-46-7], dermatan sulfate [24967-94-0], and keratan sulfate [9056-36-4]. The following structure is that of chondroitin 6-sulfate. In dermatan sulfate the −COOH group points down in the Haworth representation, ie, the uronic acid unit is an L-iduronic acid [2073-35-0] unit, and the sulfate group is at C-4.



There are other glycosaminoglycans. Hyaluronic acid [9004-61-9] occurs both free and in noncovalent association with proteoglycan molecules. Heparin [9005-49-6] and heparan sulfate [39403-40-2], also known as heparitin sulfate [9050-30-0], occur in mast cells and in the aorta, liver, and lungs.

Compounds with similar structures, ie, polysaccharide chains covalently attached to polypeptide chains, but where the polysaccharides are not glycosaminoglycans, are found commonly in plants and are known as protein-polysaccharides.

Peptidoglycans (4,10) are the primary components of bacterial cell walls. They consist of a heteropolysaccharide called murein cross-linked with short peptide chains.

Glycolipids (4,20) are primarily glycosphingolipids, molecules that have oligosaccharide groups attached to ceramide [104404-17-3]. They are present, at least in small amounts, in the membranes of most, if not all, animal tissues. They too, like cell-membrane glycoproteins, are recognition determinants.

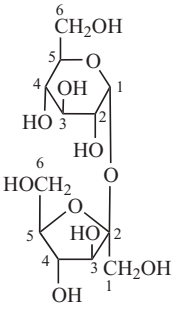
Lipopolysaccharides (10) are cell-wall components of gram-negative bacteria.

Teichoic acids (10) are bacterial polymers in which alditols (glycerol or ribitol) are joined through the primary hydroxyl groups via phosphate diester linkages.

Phosphonomannans (6) are bacterial polymers in which manno-oligosaccharides are joined by phosphate diester linkages. Phosphonogalactans are present in certain fungi.

Sucrose and Derivatives of Sucrose. By far the most abundant of the naturally occurring oligosaccharides is the disaccharide sucrose [57-50-1] (22), ordinary table sugar from sugar cane or sugar beets (see SUGAR). The two monosaccharide units in sucrose are α-D-glucopyranosyl and β-D-fructofuranosyl units.

In sucrose, the ketohexose, D-fructose [30237-26-4], exists as a five-membered furanose ring (β-D-fructofuranose [470-23-5]) formed by reaction between the carbonyl group at C-2 and the hydroxyl group on C-5. Sucrose is unique in that the two glycosyl units are linked head-to-head via an acetal bond rather than head-to-tail. Thus the molecule has no hemiacetal group and no reducing end, and is, therefore, classified as a nonreducing sugar.

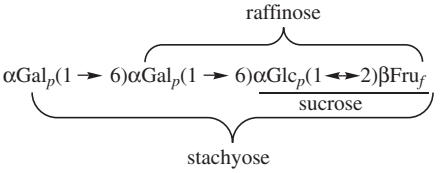


sucrose

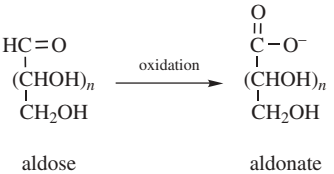
The trisaccharide raffinose [512-69-6] consists of a sucrose molecule with an α-D-galactopyranosyl unit linked $1 \rightarrow 6$ to its D-glucosyl unit. Raffinose is the second most abundant oligosaccharide and, like sucrose, may be ubiquitous in the plant kingdom. However, it is present in only minor amounts as compared to sucrose.

The tetrasaccharide stachyose [470-55-3], which contains an additional (1→6)-linked α-D-galactopyranosyl unit, is almost as widely distributed as raffinose, but is present in even lower concentrations. Although raffinose and stachyose occur in all parts of plants, they are concentrated in storage tissues, eg, in sugar beets and beans, and leaves for the most part.

Structures of raffinose and stachyose are given below using official shorthand designations. In this system, the D or L designation is not used if the sugars are D; if a glycosyl unit is from an L sugar, an L is placed before the three-letter abbreviation. Subscripts *p* and *f* refer to pyranosyl and furanosyl rings, respectively.

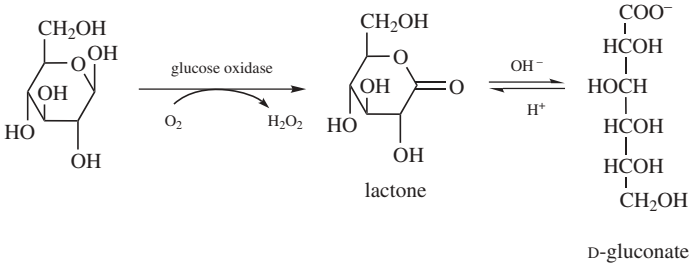


Oxidation to Sugar Acids and Lactones. When the aldehyde group of an aldose is oxidized, the resulting compound is an aldonic acid (salt form = aldonate) (14). Some aldonic acids are products of carbohydrate metabolism.

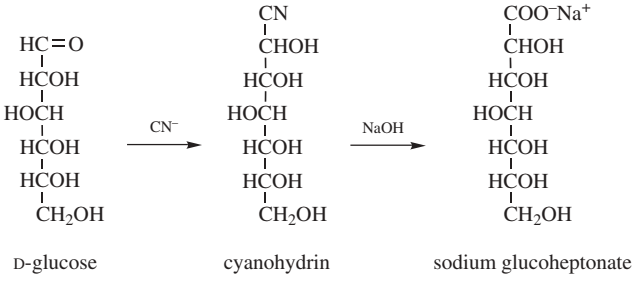


Oxidation of the aldehyde group of an aldose to form a carboxylic acid or carboxylate ion is often used analytically to determine the amount of reducing sugar. The Benedict and Fehling methods measure the amount of reducing sugar present in a fluid. In these reactions, the oxidant, Cu^{2+}, is reduced to Cu^{+}. The Cu^{+} ion precipitates as Cu_2O, which can be measured in a variety of ways. In the Tollens test, Ag^{+} is reduced to Ag^{0}.

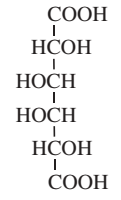
Monosaccharides in the pyranose or furanose ring forms can also be oxidized, forming an internal ester, a lactone, that can subsequently open to the acyclic form. The amount of D-glucose is often determined by this kind of oxidation catalyzed by the enzyme glucose oxidase [9001-37-0]. Glucose oxidase-catalyzed oxidation of D-glucose is also used in the commercial production of D-glucono-1,5-lactone (D-glucono-δ-lactone) [90-80-2], which is used for slow acidification, especially as a chemical leavening agent (see BAKERY PROCESSES, CHEMICAL LEAVENING AGENTS).



Preparation of another widely used aldonate, whose common name is sodium glucoheptonate [31138-65-5], and which is an epimeric mixture of heptonates, involves reaction of D-glucose with cyanide ion. The cyanohydrin is then hydrolyzed to the heptonic acid salt. Both sodium D-gluconate [527-07-1] and sodium D-glucoheptonate are used as components of washing compounds because of their ability to sequester divalent cations, in agriculture to carry trace minerals, and in concrete (largest use). Both can be, and are, produced from glucose syrups as well as from pure crystalline D-glucose.

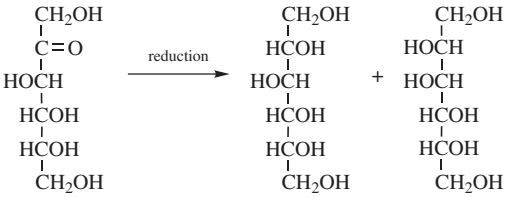


Oxidation of the carbon atoms at both ends of the carbon chain produces an aldaric acid. That made from D-galactose is galactaric acid [526-99-8], a meso compound commonly known as mucic acid.



galactaric acid

Reduction. Mono- and oligosaccharides can be reduced to polyols (polyhydroxy alcohols) termed alditols (1,14) (see SUGAR ALCOHOLS). Common examples of compounds in this class are D-glucitol (sorbitol) [50-70-4] made by reduction of D-glucose, and xylitol [87-99-0] made by reduction of D-xylose. Glycerol [56-87-5] is also an alditol. Reduction of D-fructose produces a mixture of D-glucitol and D-mannitol [69-65-8].



D-fructose D-glucitol D-mannitol

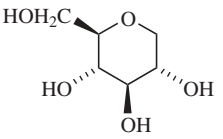
Sorbitol and mannitol are generally recognized as safe (GRAS) by the U.S. Food and Drug Administration. An important use of sorbitol is as a humectant. It can extend shelf life in confections and bakery products. Like other alditols, and unlike reducing sugars, it will not undergo Maillard browning and caramelization. Mannitol can be used as a dusting agent because of its low hygroscopicity. Most food applications of alditols are in dietetic products.

Alditols are sweet. Xylitol has essentially the same sweetness as sucrose; sorbitol is about one-half as sweet as sucrose. In chewing gum, polyols provide texture, sweetness, and mouthfeel and reduce the incidence of dental caries.

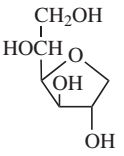
Reduction of oligomeric chains of monosaccharides results in the same oligosaccharide terminated at the reducing end with an alditol unit. Products made by hydrogenation of various corn syrups are viscous, hygroscopic, noncariogenic, and sweet, depending on the amounts of sorbitol and maltitol present. Their physical properties are generally similar to those of the syrup from which they are made, usually a high maltose syrup, but they exhibit a greatly decreased tendency to brown, a decreased tendency to crystallize, reduced fermentability, and slower conversion to D-glucose. The latter property makes these products of potential use as carbohydrate sources in diets for diabetics.

A series of sorbitol-based nonionic surfactants is used in foods as water-in-oil emulsifiers and defoamers. They are produced by reaction of fatty acids with sorbitol. During reaction, cyclic dehydration as well as esterification (primary hydroxyl group) occurs so that the hydrophilic portion is not only sorbitol but also its mono- and dianhydride. The product known as sorbitan monostearate [1338-41-6], for example, is a mixture of partial stearic and palmitic acid esters

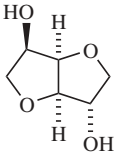
(sorbitan monopalmitate [26266-57-9]) of sorbitol, 1,5-anhydro-D-glucitol [154-58-8], 1,4-sorbitan [27299-12-3], and isosorbide [652-67-5]. Sorbitan esters, such as the foregoing and also sorbitan monolaurate [1338-39-2] and sorbitan monooleate [1338-43-8], can be further modified by reaction with ethylene oxide to produce ethoxylated sorbitan esters, also nonionic detergents approved for food use by the U.S. Food and Drug Administration.



1,5-anhydro-D-glucitol



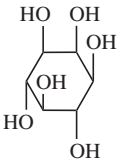
1,4-anhydro-D-glucitol
(1,4-sorbitan)



1,4:3,6-dianhydro-D-glucitol
(isosorbide)

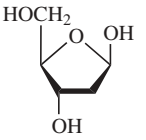
Isosorbide 5-nitrate and 2,5-dinitrate relax vascular smooth muscle and are prescribed as vasodilators for prevention of angina pectoris.

Cyclitols. Cyclitols are polyhydroxycycloalkanes and -alkenes (1,23). They are widely distributed in Nature, though never in large quantities. The most abundant of these carbocyclic compounds are the hexahydroxycyclohexanes, commonly called inositols, and their methyl ethers. The nomenclature of cyclitols is problematic; several systems have been proposed and used. *myo*-Inositol [87-89-8] is so common in plants that it is generally regarded as being ubiquitous. It is most often found as ester, ether, and/or glycoside derivatives. Phytic acid [83-86-3], the hexakisphosphate monoester of *myo*-inositol occurs in most, if not all, higher plants. It is present in relatively large amounts in cereal grains and may be recovered as phytin, its mixed calcium–magnesium salt.

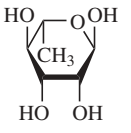


myo-inositol (a cyclitol)

4.2. Reactions of Hydroxyl Groups. *Reduction and Oxidation.* Hydroxyl groups can be both oxidized to carbonyl groups (2,14,17,18,24) and removed by reduction. Sugars that have the hydroxyl group missing from one or more of the carbon atoms are called deoxy sugars. The sugar known by the common name 2-deoxy-D-ribose (2-deoxy-D-*erythro*-pentose) [533-67-5], a component of DNA (deoxyribonucleic acid), is so designated because the hydroxyl group on C-2 of D-ribose is missing. A common component of polysaccharides is L-rhamnose (6-deoxy-L-mannose [3615-41-6]) as α-L-rhamnopyranosyl units.



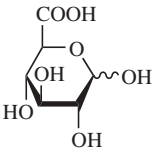
2-deoxy-β-D-ribofuranose



α-L-rhamnopyranose

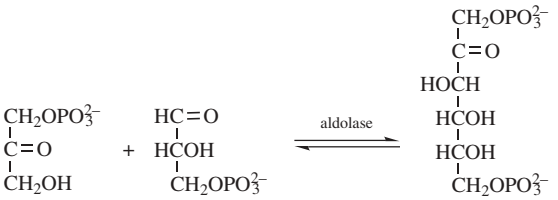
Oxidation of hydroxyl groups to carbonyl groups can form molecules with two aldehyde groups (dialdoses), two ketone groups (diuloses), or an aldehyde and a ketone group (osuloses). Keto acids are known as ulosonic acids.

Uronic acids are monosaccharides in which the terminal primary alcohol group is oxidized to a carboxylic acid functional group, eg, D-glucuronic acid [6556-12-3] (4,18).



D-glucuronic acid

Esterification. The hydroxyl groups of sugars can react with organic and inorganic acids just as other alcohols do. Both natural and synthetic carbohydrate esters are important in various applications (1,14,17,24). Phosphate monoesters of sugars are important in metabolic reactions. An example is the enzyme-catalyzed, reversible aldol addition of dihydroxyacetone phosphate [57-04-5] and D-glyceraldehyde 3-phosphate [591-57-1] to form D-fructose 1,6-bisphosphate [488-69-7].



Naturally occurring ester groups also occur on polysaccharides. They include phosphate, sulfate, acetate, glycolate, and succinate ester groups. Mono-, oligo-, and polysaccharides are often chemically acylated to give them desirable functional properties. Examples are the fatty acid esters of sorbitol and 1,4-sorbitan already mentioned, fatty acid esters of sucrose used as edible surfactants and biodegradable detergents, highly esterified cellulose acetate (acetate rayon), and starches with low degrees of phosphorylation (see CELLULOSE ESTERS).

Etherification. Carbohydrates are involved in ether formation, both intramolecularly and intermolecularly (1,14,17,24). The cyclic ether, 1,4-sorbitan, an 1,4-anhydroalditol, has already been mentioned. 3,6-Anhydro-α-D-galactopyranosyl units are principal monomer units of the carrageenans. Methyl, ethyl,

carboxymethyl, hydroxyethyl, and hydroxypropyl ethers of cellulose (qv) are all commercial materials. The principal starch ethers are the hydroxyethyl and hydroxypropylethers (see CELLULOSE ETHERS; STARCH).

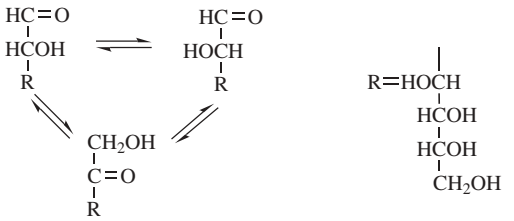
Acetalation. As polyhydroxy compounds, carbohydrates react with aldehydes and ketones to form cyclic acetals (1,14,17,24). Examples are the reaction of D-glucose with acetone in the presence of a protic or Lewis acid catalyst to form 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose [582-52-5] and its reaction with benzaldehyde to form 4,6-*O*-benzylidene-D-glucopyranose [25152-90-3]. The 4,6-*O*-(1-carboxyethylidine) group (related to pyruvic acid) occurs naturally in some polysaccharides, viz, xanthan.

Ester, ether, and cyclic acetal groups are used as blocking groups to allow regiospecific reactions to take place, ie, reaction at specific unblocked hydroxyl groups.

Replacement of Hydroxyl Groups. Replacement of a hydroxyl group with an amino group at any position produces an aminodeoxysugar (2,24). If a primary or secondary amino group is on the carbon atom delta from the carbonyl group, a six-membered ring containing −NH− or −NR− will form. Thiosugars are ones in which a thiol group has replaced a hydroxyl group (4,24). When the thiol group is on the carbon atom delta to the carbonyl group, a six-membered ring containing −S− will form. Replacement of one or more hydroxyl groups with halogen atoms forms deoxyhalogenosugars (1).

Isomerization. Both the carbonyl group and the adjacent hydroxyl group are involved in isomerization of monosaccharides. This reaction can be catalyzed by either a base or an enzyme. By this reaction, an aldose is converted into another aldose and a ketose, and a ketose is converted into two aldoses. It is for this reason that ketoses are reducing sugars. They cannot act as reducing agents because they cannot be oxidized to acids, but under alkaline conditions, they can be isomerized to aldoses that are reducing agents.

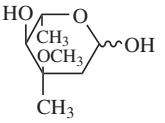
When this isomerization reaction is catalyzed by alkali, it is termed the Lobry de Bruyn-Alberda van Ekenstein reaction. By it, D-glucose, D-mannose, and D-fructose can be interconverted. The isomerizations involve a common intermediate, the 1,2-enediol.



isomerization

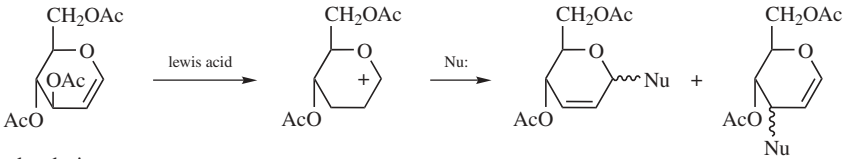
Enzymes are specific. For example, starch is depolymerized to D-glucose (dextrose) using a combination of enzymes, all categorized as amylases. The solution of glucose is then treated with glucose isomerase [9055-00-9] to give D-fructose in about 42% yield. No D-mannose is formed. Addition of isolated D-fructose to this solution gives the common 55% high fructose syrup (HFS) so widely used in soft drinks in the United States. HFS is about 1.5 times as sweet as sucrose.

4.3. Modifications of The Carbon Chain. Branched-chain sugars are found in nature. For example, cladinose (2,6-dideoxy-3-*C*-methyl-3-*O*-methyl-L-*ribo*-hexose [3758-45-0]) is a component of erythromycin.



cladinose

Unsaturated sugars are useful synthetic intermediates (14,15,18,25). The most commonly used are the so-called glycals (1,5- or 1,4-anhydroalditol-1-enes). In the presence of a Lewis acid catalyst, 3,4,6-tri-*O*-acetyl-1,5-anhydro-2-deoxy-D-*arabino*-hex-1-enitol [2873-29-2], commonly called D-glucal triacetate, adds nucleophiles in both kinetically controlled and thermodynamically controlled (soft bases predominately at C-3 and hard bases primarily at C-1) reactions (14,15,18,24,25).

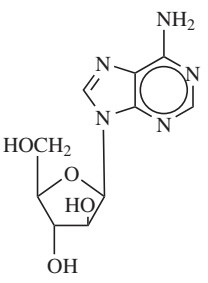


D-glucal triacetate

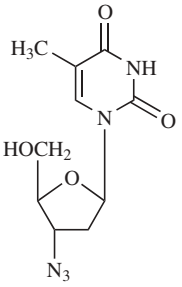
where Ac represents 

5. Uses

Carbohydrates have widespread utilization, both as low cost, high volume commodities and as low volume specialty chemicals. Significant uses in terms of volume are surveyed here. Not covered are the lower volume uses involving carbohydrates either in the native state or in modified form; these are mainly pharmaceutical applications involving antibiotics, antigens, and synthetic drugs (2,4,20,21,25,26). In the case of drugs, monosaccharides are important as chiral synthons (chirons) as well as being used more directly to make products such as the nucleoside analogues AraA [9-(β-D-arabinofuranosyl)-9*H*-purin-6-amine] [5536-17-4], an antineoplastic and antiviral compound known by a number of trade names, and AZT (3′-azido-3′-deoxythymidine [30516-87-1]), an antiviral compound also known by a variety of trade names (see ANTIVIRAL AGENTS).



AraA



AZT

Neither are the considerable uses of carbohydrates as carbon sources for various fermentations or the uses of unrefined carbohydrates, flours, eg, described here (see FERMENTATION).

5.1. Monosaccharides. D-Glucose is produced by complete depolymerization of starch with enzymes that catalyze the hydrolysis of both its $(1 \rightarrow 4)$ and $(1 \rightarrow 6)$ linkages. In commerce, crystalline α-D-glucopyranose is generally known as dextrose. Glucose is also isomerized to D-fructose to produce high-fructose syrup (HFS). Crystalline D-fructose also finds use in the food industry. The annual consumption, in the United States, of HFS is about 12,000,000 tons.

5.2. Oligosaccharides. Sucrose is widely used in the food industry to sweeten, control water activity, add body or bulk, provide crispness, give surface glaze or frost, form a glass, provide viscosity, and impart desirable texture. It is used in a wide variety of products from bread to medicinal syrups (22).

Lactose occurs in milk, mainly free, but to a small extent as a component of higher oligosaccharides. Cow and goat milks contain ∼4.5% lactose; human milk contains ∼7.0%. Lactose is obtained from whey, a by-product of cheese manufacture. It is used as an excipient in tablets to provide bulk and rapid disintegration. It is also used in some food products where it contributes body with only ∼40% the sweetness of sucrose and enhances colors and flavors.

Oligo- and higher saccharides are produced extensively by acid- and/or enzyme-catalyzed hydrolysis of starch, generally in the form of syrups of mixtures (13,27,28). These products are classified by their dextrose equivalency (DE), which is inversely proportional to their molecular size and is a measure of their reducing power, with the DE value of anhydrous D-glucose defined as 100.

Maltodextrins [9050-36-6] are mixtures of saccharides with average DE values of <20 (13,27,28). They are rather soluble, have a bland taste, and are widely used in foods. A dextrin is a product obtained by depolymerization of a polysaccharide; malto- is a prefix used with products derived from starch.

Syrup solids are also dry products, have a smaller average size, and are comparatively sweeter (13,27,28). Both maltodextrins and syrup solids are used to prevent caking; enhance dispersibility and solubility; provide body or bulk; impart desirable texture; bind, carry, and protect flavors; control extrusion expansion; provide viscosity; form films and coatings; provide an oxygen barrier; inhibit crystallization; control sweetness; improve sheen; improve organoleptic characteristics; slow meltdown; and improve freeze–thaw stability.

Specifically prepared low DE starch products in the maltodextrin class, especially those from tapioca and potato starches, mimic a fatty mouthfeel and are used as fat replacers and/or sparers (see FAT REPLACERS).

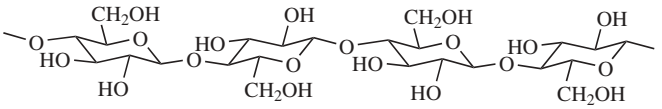
Another class of products are the cyclodextrins or cycloamyloses, a family of cyclic oligosaccharides containing α-D-glucopyranosyl units, most commonly seven (β-cyclodextrin [7585-39-9], cycloheptaamylose, cyclomaltoheptaose) (29,30). All members of this class of compounds are made by action of a specific enzyme, cyclodextrin glycosyltransferase [9030-09-5], on starch. In all, the glucosyl units are joined by (1→4) glycosidic linkages to form a ring, the cavity of which is especially useful for forming inclusion complexes with hydrophobic guest molecules. These stable complexes are useful in the food industry to provide stable flavors and fragrances in dry powder form, in the pharmaceutical industry, and in other applications where increased chemical and/or physical stability, solubility control, or controlled release is desired, eg, with agricultural chemicals (see INCLUSION COMPOUNDS).

More extensive depolymerization of starch yields syrups. Syrups are purified, concentrated, aqueous solutions of saccharides with an average DE value of >20. Enzymes are most often used to make syrups, although combinations of acid- and enzyme-catalyzed hydrolyses and complete acid conversion may be used. Syrups are grouped into subclasses. Some contain as little as 35% of maltooligosaccharides. The maltooligosaccharides are both linear and branched, the branched structures arising from amylopectin. Products with progressively higher concentrations of lower molecular weight products are progressively sweeter and less viscous. By using proper conditions, syrups with specific defined compositions, eg, high maltose syrups, are prepared. The annual consumption in the United States of crystalline dextrose and syrups from corn starch (other than high fructose syrups) is ∼ 5,000,000 tons.

5.3. Polysaccharides. It has been estimated that > 90% of the carbohydrate mass in nature is in the form of polysaccharides. In living organisms, carbohydrates play important roles. In terms of mass, the greatest amounts by far are structural components and food reserve materials, in that order and both in plants. However, carbohydrate molecules also serve as structural and energy storage substances in animals and serve a variety of other essential roles in both plants and animals.

Since polysaccharides are the most abundant of the carbohydrates, it is not surprising that they comprise the greatest part of industrial utilization. Most of the low molecular weight carbohydrates of commerce are produced by depolymerization of starch. Polysaccharide materials of commerce can be thought of as falling into three classes: cellulose, a water-insoluble material; starches, which are not water-soluble until cooked; and water-soluble gums.

Cellulose. Cellulose [9004-34-6] (qv) is the principal cell-wall component of higher plants and the most abundant polysaccharide. Approximately one-half the mass of perennial plants and one-third the mass of annual plants is cellulose. It is a high molecular weight, linear, insoluble polymer of repeating β-D-glucopyranosyl units joined by (1→4) glycosidic linkages. Because of their linearity and stereoregular nature, cellulose molecules associate in extended regions, forming polycrystalline, fibrous bundles (31,32).



cellulose

High quality cellulose can be obtained from wood through pulping (delignification) and subsequent purification. The measure of the quality of cellulose is its content of alpha-cellulose, that portion insoluble in 18% alkali, by far the largest fraction. Beta-cellulose is that portion that dissolves in 18% alkali, but precipitates when the solution is neutralized. Gamma-cellulose remains soluble after neutralization of the 18% alkali solution. The greatest amount of cellulose used is the purified, but not highly purified, wood pulp that is used in the manufacture of paper (qv), associated products, absorbants, rayons, and nonwovens. A number of derivatives of cellulose are also commercial entities. The water-soluble ones are covered later.

Every polysaccharide contains glycosyl units with unsubstituted hydroxyl groups available for esterification or etherification. Polysaccharide derivatives are described by their degree of substitution (DS), which is the average number of substituent groups per glycosyl unit. Because each monomeric unit of a cellulose molecule has free hydroxyl groups at C-2, C-3, and C-6, the maximum DS is 3.0 for cellulose and all polysaccharides composed exclusively of neutral hexosyl units, the majority of polysaccharides.

Several cellulose esters (qv) are prepared commercially. Cellulose xanthate [9032-37-5] is made by reaction of cellulose swollen in 8.5–12% sodium hydroxide solution (called alkali cellulose [9081-58-7]) with carbon disulfide and is soluble in the alkaline solution in which it is made. When such a solution, termed viscose, is introduced into an acid bath, the cellulose xanthate decomposes to regenerate cellulose as rayon fibers or cellophane sheets (see FIBERS, REGENERATED CELLULOSICS).

Cellulose acetate [9004-35-7], prepared by reaction of cellulose with acetic anhydride and acetic acid in the presence of sulfuric acid, is spun into acetate rayon fibers by dissolving it in acetone and spinning the solution into a column of warm air that evaporates the acetone. Cellulose acetate is also shaped into a variety of plastic products, and its solutions are used as coating dopes. Cellulose acetate butyrate [9004-36-8], made from cellulose, acetic anhydride, and butyric anhydride in the presence of sulfuric acid, is a shock-resistant plastic.

Cellulose nitrate (pyroxylin) [9004-70-0], made from cellulose and a mixture of nitric and sulfuric acids, is called gun cotton and is used in explosives. Nitrates of lower DS find application in some coatings and adhesives.

Ethylcellulose [9004-57-3] is a cellulose ether (qv). As prepared commercially, ie, of high DS, ethylcellulose is thermoplastic and has a low density. It forms films of good thermostability and excellent flexibility and toughness. Ethylcellulose is used in lacquers, inks, and adhesives and is combined with waxes and resins in the preparation of hot-melt plastics.

Treatment of cellulose with acids results in preferential hydrolysis in the more accessible amorphous regions and produces a product known as microcrystalline cellulose (MCC). MCC is used to prepare fat-free or reduced-fat food

products, to strengthen and stabilize food foams, as a pharmaceutical tableting aid, and as a noncaloric bulking agent for dietetic foods. It has GRAS status.

Hemicelluloses and Related Polysaccharides. Hemicelluloses [9034-32-6] are a large group of polysaccharides that are associated with cellulose in the primary and secondary cell walls of all higher plants, but otherwise have no relationship to cellulose (5). They are also present in some other plants.

Hemicelluloses (qv) are heteroglycans. They do not comprise a distinct class of chemical structures. Constituent monosaccharides are D-xylose, D-mannose, D-glucose, D-galactose, L-galactose [15572-79-9], L-arabinose, D-glucuronic acid, 4-*O*-methyl-D-glucuronic acid [4120-73-4], D-galacturonic acid [685-73-4], and to a lesser extent L-rhamnose, L-fucose, and various methyl ethers of neutral sugars, with a limit of perhaps six different glycosyl units per polysaccharide molecule. Both woody and nonwoody tissues contain 20–35% hemicelluloses. Some hemicelluloses are neutral polymers, but most are acidic. The most abundant have a xylan backbone, ie, a chain of (1→4)-linked β-D-xylopyranosyl units. The chain may be linear, but is often branched, usually containing short side chains and, therefore, being basically linear. The most common acidic hemicelluloses are *O*-acetylated (4-*O*-methyl-D-glucurono)xylans [9062-57-1] and L-arabino-(4-*O*-methyl-D-glucurono)xylans [69865-67-4, 9040-28-2, 98913-73-6], both often containing minor amounts of other sugar units as well. In the former, which are the preponderant hemicelluloses of woody angiosperms, the 4-*O*-methyl-α-D-glucopyranosyluronic acid units are most often joined to D-xylopyranosyl main chain units by (1→2) linkages. Some hemicelluloses contain unmethylated D-glucopyranosyluronic acid units, both the methylated and unmethylated forms in the same molecule being common. The number of uronic acid units varies considerably. Most hardwood xylans have approximately one uronic acid unit per 10 D-xylosyl units distribulted nonuniformly. Acetyl groups occur to the extent of 3–17%, with the greatest number being present in hardwood hemicelluloses.

The L-arabino-(4-*O*-methyl-D-glucurono)xylans are found in softwoods and annual plants. The L-arabinose is present primarily as α-L-arabinofuranosyl units, although β-L-arabinopyranosyl units may also be present. In either case, the arabinosyl units are often, but not always, present as single-unit branches, as are the uronic acid units.

Cell walls of woods contain other subgroups of hemicelluloses, in particular those composed primarily of D-mannopyranosyl or D-galactopyranosyl units. Glucomannans [11078-31-2] comprise 3–5% of the wood of angiosperms and 3–12% of the wood of gymnosperms. Galactoglucomannans [9040-29-3] are also common.

Arabinogalactans [9036-66-2] appear to be ubiquitous in plant materials. They form a family of branched polysaccharides with backbones made up predominately of (1 → 3)-linked β-D-galactopyranosyl units with varying amounts of (1 → 6)-linked β-D-galactopyranosyl units. The L-arabinose is present primarily as L-arabinofuranosyl units. Some are attached to the backbone as single units; others may be in short chains. Nonreducing ends may be terminated with β-L-arabinopyranosyl units. Other units that may be present in arabinogalactans are L-rhamnopyranosyl (up to 11%), D-mannopyranosyl (up to 16%), D-xylopyranosyl (up to 7%), D-glucopyranosyl (up to 4%), D-glucopyranosyluronic

acid and/or 4-*O*-methyl-D-glucopyranosyluronic acid (up to 28%), and D-galactopyranosyluronic acid and/or 4-*O*-methyl-D-galactopyranosyluronic acid (up to 26%) units. Not all arabinogalactans are acidic. Water-extractable arabinogalactans are abundant in the wood of larches. The fact that they are water-extractable indicates that they are not associated with lignin (qv) through chemical linkages or physical interactions and not involved in the construction of secondary cell walls. Therefore, larch arabinogalactans [37320-79-9] are probably not properly hemicelluloses.

Some hemicelluloses are partially extractable with water, but they are more completely extracted with alkaline solutions after removal of lipids and lignin. Delignified plant material is termed, holocellulose. Neutralization of the alkaline extract effects precipitation of the more linear and less acidic hemicelluloses, termed the hemicellulose A [63100-39-0] fraction. The more acidic and more branched material, termed hemicellulose B [63100-40-3], is precipitated with ethanol (70%) from the remaining neutral solution. Hemicellulose B types are usually water soluble after extraction.

Certain cereal grains, especially wheat and rye, contain hemicellulose-like arabinoxylans [9040-27-1], commonly called pentosans. Wheat flour pentosans are divided into two types: water-soluble and water-insoluble arabinoxylans, which respectively constitute ~1.1–1.6% and 0.4–0.7% of the total flour. These polysaccharides have functional roles in dough development and baking performance. The water-soluble wheat-flour arabinoxylans consist of a $(1 \rightarrow 4)$-linked chain of β-D-xylopyranosyl units substituted at O-2 and/or O-3 with single-unit α-L-arabinofuranosyl units. Preparations from each source consist of a family of molecules of various molecular weights and xylose/arabinose ratios.

Starches. Starch (qv) occurs in the form of granules, which must be cooked before they will release their water-soluble molecules. It is common to speak of solutions of polysaccharides, but in general, they do not form true solutions because of their molecular sizes and intermolecular interactions; rather they form molecular dispersions. The general rheological properties of polysaccharides like the starch polysaccharides are described below under the discussion of polysaccharides as water-soluble gums. Starch use is widespread and permeates the entire economy because it (corn starch in particular) is abundantly available, inexpensive, and occurs in the form of granules that can be easily handled and reacted.

All green plants package and store carbohydrate (D-glucose) in the form of starch granules. Starch granules are quasi-crystalline, dense, insoluble in cold water, and only partially hydrated. The sizes and shapes of granules are specific for the plant of origin. Granules can be easily isolated from suspensions by filtration or centrifugation, resuspended, reacted, and recovered (13,33).

Normal corn starch is composed of ~ 28% of the linear polysaccharide amylose and ~72% of the branched polysaccharide amylopectin. Amylose is a linear polysaccharide composed of $(1 \rightarrow 4)$-linked α-D-glucopyranosyl units. Its degree of polymerization (DP, the number of monosaccharide units it contains) is 200–22,000 (mol wt 32,000–3,600,000), depending on the source and method of preparation. Amylose can have several conformations. In the solid state, it probably exists most often as a left-handed, six-fold helix. In solution, it is a loosely wound and extended helix that behaves as a random coil.

Amylopectin has a branch-on-branch structure. Amylopectin molecules are composed of chains of α-D-glucopyranosyl units joined by $(1 \rightarrow 4)$ linkages; branches are formed by joining these chains with α-D-$(1 \rightarrow 6)$ linkages. The average chain length is 20–30, although branch points are not equally spaced. In the currently accepted model of an amylopectin molecule, the branches occur in clusters. The molecular weight of amylopectin has been measured as 5×10^7–2×10^8 (DP 3×10^5–2.5×10^6), depending on the source and method of preparation. Granules of the so-called waxy types of starch contain only amylopectin molecules. Potato starch amylopectin occurs as a natural phosphate ester (13).

Through genetic manipulation, corn cultivars with altered starch compositions have been developed. Various modified and derivatized starches are produced by treating a slurry of starch granules with chemicals or enzymes (13,33). After treatment, the products are again recovered, washed, and dried. Although these modifications and derivatizations are done to effect significant improvements in physical properties, the amount of chemical change required to effect functional property alteration is usually only very slight.

General Properties of Starches. Undamaged starch granules are not soluble in room temperature water. Heating a starch in water causes the granules to gelatinize. Gelatinization is the disruption of molecular order within starch granules, which occurs as they are heated in the presence of water. Loss of organized structure results in irreversible granule swelling and loss of crystallinity. Continued heating of starch granules in excess water effects pasting. Paste formation is a result of further granule swelling and leaching of soluble components, primarily amylose. If shear is applied at this stage, granules are disrupted. A starch paste is a viscous mass consisting of a continuous phase of dissolved starch polymer molecules and a discontinuous phase of granule framents and retrograded starch polymer molecules. Cooling of a hot paste usually produces a firm, viscoelastic gel.

The viscosity obtained by cooking a suspension of starch is determined by the starch type, derivatization and/or modification, solids concentration, pH, amount of agitation during heating, rate of heating, maximum temperature reached, time held at that temperature, agitation during holding, and the presence of other ingredients.

An aqueous dispersion of an unmodified starch containing amylose will gradually form a precipitate through association of linear segments. This process is called retrogradation or set-back.

The properties of starches are a reflection of the properties of their constituent amylose and amylopectin molecules. For example, high amylose starches are difficult to gelatinize because of the extra energy needed to disassociate and hydrate the aggregates of amylose; form firm, opaque gels; and can be used to make strong, tough films. Their solutions and gels will undergo retrogradation. Waxy maize starches, even when they are underivatized, gelatinize more easily and yield viscous, almost transparent solutions that will not form firm gels.

In general, derivatization (etherification or esterification, see below) increases solution and gel clarity, reduces the tendency to gel, improves water binding, increases freeze–thaw stability, reduces the gelatinization temperature, increases peak viscosity, and reduces the tendency to retrograde.

Combinations of substitutions are used to obtain desired properties for specific applications.

In general, all starches can be digested in the human small intestine, and the absorbed D-glucose is used for energy and a source of carbon. Cooked (pasted) starch is much, usually to a high degree, more digestible than is raw starch, and there are nondigestible (resistant) forms of starch.

Oxidized Starches. Alkaline hypochlorite treatment introduces carboxyl and carbonyl groups, effects some depolymerization, and produces whiter (bleached) products that produce softer, clearer gels (33). Ammonium persulfate is used in some paper mills with continuous thermal cookers to prepare *in situ* high solids, low-viscosity dispersions. Much of the hypochlorite-oxidized starch and all the ammonium persulfate-oxidized starch is used in the paper industry. The low solution viscosity at high solids and good binding and adhesive properties of oxidized starches make them especially effective as textile and paper sizes.

Dextrins. Dextrins [9004-53-9], like oxidized starches, are in the class of so-called converted starches (33). Dextrins are produced by dry heating starch with or without a catalyst (acidic or alkaline). Because there are a number of variables in the process, a wide range of dextrins with widely varying properties can be produced. All are characterized by higher solubility, lower viscosity, film-forming ability, and loss of the ability to gel. High-solids solutions of some of the more highly converted dextrins produce the tacky, quick-setting adhesives used in paper products.

Acid-Modified Starches. Acid-modified starches are prepared by treating a suspension of starch granules with dilute mineral acid. In this process, a small amount of glycosidic bond hydrolysis occurs, resulting in products that produce much less viscosity (33). A concurrent weakening of the granule structure occurs. The result is that there is less granule swelling and more granule disintegration when acid-modified starches are heated in water; and although they have reduced viscosity-imparting power, they form gels with improved clarity and increased strength. These acid-modified starches, also called thin-boiling and acid-thinned starches, are used in large quantities as textile warp sizes.

Starch Ethers. A large number of starch ethers has been prepared and patented; only a few are manufactured and used commercially (13,33). Commercially available starch ethers are the hydroxyalkyl ethers, hydroxyethylstarch [9005-27-0] and hydroxypropylstarch [9049-76-7], and cationic starches.

Essentially all starch derivatives are made by adding the required reagent (in the case of starch hydroxyalkyl ethers, ethylene oxide, or propylene oxide) to an agitated, alkaline (pH 7–12), aqueous starch suspension (35–45% solids) at a slightly elevated temperature. After the required reaction time, the derivatized granules are recovered, washed, and dried. The majority of starch derivatives have degrees of substitution of <0.1. Monofunctional starch derivatives are made to increase starch paste stability. Increased stability results from the introduction of substituent groups that interfere with intermolecular associations.

Hydroxyethylstarch is widely used with synthetic latexes in the surface sizing of paper and as a coating binder. For these uses, the hydroxyethylstarch is acid-thinned, oxidized, or dextrinized. Hydroxypropylstarch is used in foods to provide viscosity stability and to ensure water-holding during low-temperature storage.

Cationic starches are used as wet-end additives in the manufacture of paper (see later).

Starch Esters. As with the starch ethers, a large number of starch esters have been prepared and patented, but only a few are manufactured and used commercially. Both inorganic and organic acid esters can, and have been, made. The latter are prepared by the same general procedure used to make starch ethers.

Starch acetates [9045-28-7] are made by reaction of starch with acetic anhydride under alkaline conditions (13,33). Starch acetates are used in foods to provide paste clarity and viscosity stability at low temperatures. A waxy maize starch acetate is most commonly used. Waxy maize starch acetates for food use are often also cross-linked. Acetylated starches are also used in warp sizing of textiles.

Starch succinates [39316-70-6] are also used as thickening agents in foods. The 1-octenylsuccinate half-ester [52906-93-1], sold as its sodium salt [66829-29-6], has surface active (emulsifying) properties.

Starch sodium phosphate monoesters [11120-02-8] are prepared by heating mixtures of 10% moisture starch and sodium monohydrogen and dihydrogen phosphates or sodium tripolyphosphate (13,33). Starch phosphate monoesters are used primarily in foods as pudding starches and in oil-in-water emulsions.

Cross-linked Starches. The polymer chains in starch granules can be cross-linked with difunctional reagents that form diethers or diesters (13,33). The properties imparted to the starch by such cross-linking are unique and, therefore, these derivatives are considered separately. Diphosphate ester cross-links can be introduced by reaction of starch with phosphoryl chloride or sodium trimetaphosphate. Glycerol diethers of starch are made by reaction of starch with epichlorohydrin, although this reaction is no longer used in the United States to prepare modified food starch. A small amount of cross-linking, eg, 1 cross-link per 1000 D-glucopyranosyl units, greatly reduces both the rate and the degree of granule swelling and the sensitivity of starch slurries to processing conditions.

Cross-linking is employed when a stable, high viscosity starch paste is needed and particularly when the dispersion is to be subjected to high temperature, high shear, and/or low pH. Food starches, especially those made from waxy maize, potato, and tapioca starch, are usually both cross-linked and phosphorylated, acetylated, or hydroxypropylated to provide appropriate cooking, viscosity, and textural properties. Examples of their application are their use in canned foods that are to be retort-sterilized and in the preparation of spoonable salad dressings, where products stable to high shear at low pH are required. Starch products that do not gelatinize, even under autoclave conditions, can be made by introducing higher degreees of cross-linking. Starch products with properties of lightly cross-linked starches are made by dry heating under slightly alkaline conditions.

Cationic Starches. Commercial cationic starches are starch ethers that contain a tertiary amino or quaternary ammonium group, eg, the diethylaminoethyl ether of starch or the 2-hydroxy-3-(trimethylammonio)propyl ether of starch [9063-45-0], sold as its chloride salt [56780-58-6] (13,33).

Cationic starches are used in papermaking. When they are used as a wet-end additive, affinity between the cationic starch and cellulose fibers, which have a negative charge, results in almost complete and irreversible adsorption of the starch. Cationic starches are also used in surface sizing of paper and as coating binders. Amphoteric starches made by introducing anionic groups, such as phosphate monoester or sulfosuccinate ester groups or carboxyl groups produced by oxidation, to cationic starches perform better in some applications.

Pregelatinized Starches. Suspensions of starches and starch derivatives can be pasted/cooked and dried to yield a variety of products that can be dispersed in cold water to yield pastes comparable to those obtained by cooking granular starch products. These products are made for convenience of use.

Starch Graft Copolymers. Graft copolymers can be made by forming radicals on a chain of a starch or a modified starch, particularly hydroxyethylstarch, most commonly with cerium(III) ions, then introducing a monomer (13). Commercial products that have been made in this way are starch–graft–styrene–butadiene latex copolymer and starch–graft–polyacrylonitrile copolymer, which was subsequently treated with alkali to convert the nitrile groups to a mixture of carbamoyl and carboxylate groups.

Cold-Water Swelling Starches. Special physical treatment produces starch granules that will swell in water without heating. Molecular dispersions can be formed by application of shear to the swollen granules.

Water-Soluble Gums/Hydrocolloids. Gums (qv) are polymeric substances that, in an appropriate solvent or swelling agent, form highly viscous dispersions or gels at low dry-substance content. Commonly, the term industrial gums refers to water-soluble polysaccharides (glycans in official carbohydrate nomenclature) or polysaccharide derivatives used industrially (8,34). They are classified both by structure (Table 1) and by source (Table 2). Particularly in the food industry, the term hydrocolloid is often used interchangeably with gum.

The usefulness of such industrial gums is based on their physical properties, in particular their capacity to thicken and/or gel aqueous solutions and otherwise to control water. Because all gums modify or control the flow of aqueous solutions, dispersions, and suspensions, the choice of which gum to use for a particular application often depends on its secondary characteristics. These secondary characteristics are responsible for their utilization as adhesives, binders, bodying agents, bulking agents, crystallization inhibitors, clarifying agents, cloud agents, emulsifying agents, emulsification stabilizers, encapsulating agents, film formers, flocculating agents, foam stabilizers, gelling materials, mold release agents, protective colloids, suspending agents, suspension stabilizers, swelling agents, syneresis inhibitors, texturing agents, and whipping agents, in coatings, and for water absorption and binding.

Gums are tasteless, odorless, colorless, and nontoxic. None, except the starches and starch derivatives, are broken down by human digestive enzymes, but all are subject to microbiological attack. All can be depolymerized by acid- and enzyme-catalyzed hydrolysis of the glycosidic (acetal) linkages joining the monomeric (saccharide) units.

All native and modified polysaccharides have a range of molecular weights. The average composition and distribution of molecular weights in a gum sample can vary with the source, the conditions used for isolation or preparation, and

Table 1. **Classification of Selected, Native Polysaccharides by Structure**

	Examples
Classification by shape[a]	
linear	agarose, algins, amyloses, carrageenans, cellulose, chondroitins, chitins, colominic acid [poly(*N*-acetyl-neuraminic acid], curdlan, dermatan sulfate, furcellaran, gellan, glucomannans, heparin, hyaluronic acid, inulin, keratin sulfate, laminarans[b], mannans, nigeran, pectic acids/pectates, pullulan
branched	
short branches on an essentially linear backbone	arabinans[c], arabinogalactans, galactoglucomannans, galactomannans (guar gum, locust bean gum), konjac glucomannan, psyllium seed gum, rhamsan, scleroglucan, succinoglycan, welan, xanthan, xylans, xyloglucans
branch-on-branch structures	amylopectins, arabinoxylans, flaxseed polysaccharide (acidic), glycogens, gum arabics, gum ghatti, gum karaya, gum tragacanth (tragacanthin), okra gum, rhamnogalacturonans I and II
Classification by monomeric units[d]	
homoglycans	amylopectins, amyloses, arabinans, cellulose, chitins, colominic acid, curdlan, glycogens, laminaransb, mannans, nigeran, pullulan, scleroglucan
diheteroglycans	algins, arabinogalactans, carrageenans, chondroitins, furcellarans, galactomannans, glucomannans, hyaluronic acid, inulin, keratan sulfate, konjac mannan, pectic acids/pectates, succinoglucan, xylans
triheteroglycans	arabinoxylans, dermatan sulfates, galactoglucomannans, gellan, gum karaya, heparin, rhamsan, xanthan
tetraheteroglycans	flaxseed polysaccharide (acidic), gum arabics, okra gum, psyllium seed gum, welan, xyloglucans
pentaheteroglycans	gum ghatti, gum tragacanth (tragacanthin)
octaheteroglycan	rhamnogalacturonan I
nonaheteroglycan	rhamnogalacturonan II
Classification by charge	
neutral	agarose, amylopectins, amyloses, arabinans, arabinogalactans, cellulose, chitins, curdlan, galactoglucomannans, galactomannans, glucomannans, glycogens, inulin, laminarans, mannans, konjac mannan, nigeran, pullulan, scleroglucan, xyloglucans
anionic (acidic)[e]	algins, arabinoxylans, carrageenans, chondroitins, colominic acid, dermatan sulfates, flaxseed polysaccharide, furcellarans, gellan, gum arabics, gum ghatti, gum karaya, gum tragacanth (tragacanthin), heparin, hyaluronic acid, keratan sulfate, okra gum, pectic acids/pectates, pectins, rhamnogalacturonans I and II, psyllium seed gum, rhamsan, succinoglycan, welan, xanthan, xylans
cationic	chitosans (not native)

[a] Primary examples. For example, arabinoxylans occur in different architectures, compositions, and charges.

[b] Contains a few long-chain branches. Some chains are terminated at the reducing end with a second type of unit.

[c] The predominate structure.

[d] Considers only the basic monosaccharide units. A derivatized monosaccharide unit, such as a D-galactopyranosyl 6-sulfate unit, is not considered as a unit separate from a D-galactopyranosyl unit, for example.

[e] From the presence of uronic acid, sulfate half-ester, pyruvyl cyclic acetal, or succinate half-ester groups.

Table 2. **Classification of Commercial Polysaccharides by Source**

Class	Examples
algae (seaweeds)	agars, algins, carrageenans, furcellarans, laminarans
higher plants	
insoluble	cellulose
extract	pectins
seeds	corn starches, rice starches, wheat starches, guar gum, locust bean gum, psyllium seed gum
tubers and roots	potato starch, tapioca/cassava starch, konjac glucomannan
exudates	gum arabics, gum karaya, gum tragacanth
microorganisms (fermentation gums)	curdlan, dextrans, gellan, pullulan, scleroglucan, welan, xanthans
animal derived	chitins/chitosans (also a cell-wall constituent of some fungi)
from cellulose	carboxymethylcelluloses, cellulose acetates, cellulose acetate butyrates, cellulose nitrates, ethylcellulose, hydroxyalkylcelluloses, hydroxyalkylalkylcelluloses, methylcelluloses
from starches[a]	starch acetates, starch adipates, starch 1-octenylsuccinates, starch phosphates, starch succinates, carboxymethylstarches, hydroxyethylstarches, hydroxypropylstarches, cationic starches, oxidized starches, dextrins
from guar gum	carboxymethylguar gum, carboxymethyl(hydroxypropyl)-guar gum, hydroxyethylguar gum, hydroxypropylguar gum, cationic guar gum
synthetic	polydextrose

[a] It is common for a commercial modified starch to have undergone two or more different reactions or treatments.

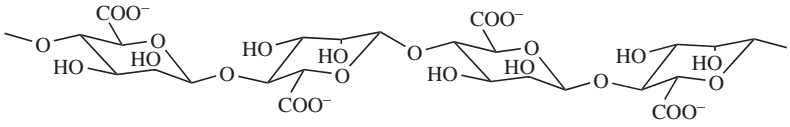
any subsequent treatment(s). In all except bacterial polysaccharides, the percentage of individual monomeric unit types varies from molecule to molecule and from sample to sample. Because both molecular size and structure determine physical properties, various functional types of a given gum are produced by controlling the source and isolation procedure (in the case of natural gums) or derivatization method (in the case of derived gums) and subsequent treatment(s).

In general, gums do not form true solutions. Rather, because of their molecular weights and intermolecular interactions, they form dispersions, where the particles may be dispersed molecules and/or aggregated clusters of molecules. The rheology or flow characteristics and gel properties of gum solutions is a function of particle solvation, particle size, particle shape, particle flexibility and ease of deformation, and the presence and magnitude of charges. In general, the rheology of gum solutions is pseudoplastic or thixotropic, ie, they exhibit shear thinning. Most gums are available in a range of viscosity grades.

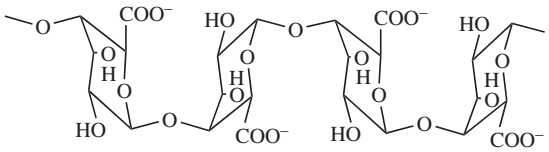
Polysaccharide gels in general are composed of 99.0–99.5% water and 0.5–1.0% gum. Important characteristics of gels are means of gelation (chemical gelation, thermogelation), reversibility, texture (brittle, elastic, plastic), rigidity (rigid or firm, soft or mushy), tendency for syneresis, and cutable or spreadable. Gels are composed of interconnected fringed micelles (junction zones).

Algins. Algins are salts (generally sodium [9005-38-3], ammonium [9005-34-9], or potassium [9005-36-1]) or esters (propylene glycol) of alginic acid.

Alginic acid [9005-32-7] is a generic term for polymers of D-mannuronic acid and L-guluronic acid. Alginic acid molecules contain at least three different types of polymer segments: poly(β-D-mannopyranosyluronic acid) segments, poly(α-L-gulopyranosyluronic acid) segments, and segments with alternating sugar units. The ratios of the constituent monomers and the chain segments vary with the source and determine the specific properties of the preparation. All linkages are $1 \rightarrow 4$, making alginates linear polymers. The shapes of the poly(D-mannopyranosyluronic acid) and the poly(L-gulopyranosyluronic acid) segments are quite different because the β-D-mannopyranosyluronic acid units are in the $^4C_1$ conformation and diequatorially linked, whereas the α-L-gulopyranosyluronic acid units are in the $^1C_4$ conformation and diaxially linked. The different conformations make the former segments flat and the latter buckled.



a poly(β-D-mannuronosyl) segment



a poly(α-L-guluronosyl) segment

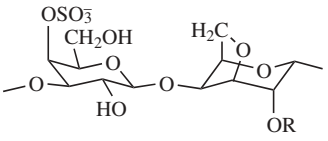
Algins are extracted from brown algae (Phaeophyceae). The primary U.S. source is the beds of giant kelp (*Macrocystis pyrifera*) that grow off the coast of southern California. The polymer is extracted by treating the seaweed with a sodium carbonate solution. It is recovered from the extract by precipitation as alginic acid or as the calcium salt [9005-35-0], which is then washed with acid to convert it into alginic acid. The alginic acid is then treated with a base to convert it into the desired salt, or partially neutralized alginic acid is treated with propylene oxide to make the propylene glycol ester [9005-37-2].

An important and useful property of alginates is their ability to form gels by reaction with calcium ions. Different types of gels are formed with alginates from different sources. Alginates with a higher percentage of polyguluronate segments form the more rigid, more brittle gels that tend to undergo syneresis. Alginates with the higher percentage of polymannuronate segments form the more elastic, more deformable gels with a lesser tendency to undergo syneresis.

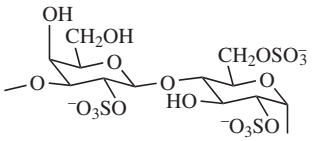
Carrageenans, Agars, and Furcellarans. Carrageenan is a generic term applied to polysaccharides extracted from a number of closely related species of red seaweeds. Agar [9002-18-0] and furcellaran [9000-21-9] are also red seaweed extracts and are members of the same larger family. All polysaccharides in this family are derivatives of linear galactans. All have alternating monosaccharide units and linkages. In all members of the family, one sugar unit is a β-D-galactopyranosyl unit with a glycosidic linkage to O-3. In all except agar,

the other unit is a 3,6-anhydro-α-D-galactopyranosyl unit with a glycosidic linkage to O-4. In agar, the other unit is a 3,6-anhydro-α-L-galactopyranosyl unit.

Commercial carrageenans are composed primarily of three types of polymers: kappa-, iota-, and lambda-carrageenan.



kappa-carrageenan, R = H
iota-carrageenan, R = SO_3^2



lambda-carrageenan

The molecular weights of the carrageenans, agars, and furcellaran average ~250,000. The half-ester sulfate contents are 0–3% in agarose [9012-36-6], more properly termed agaran, the linear component of agar, 12–16% in furcellaran, ~25% in kappa-carrageenan [1114-20-8], ~32% in iota-carrageenan [9062-07-1], and ~35% in lambda-carrageenan [9064-57-1]. Each polymer is heterogeneous. Each commercial gum is believed to be generated from native precursor polysaccharides during production.

Kappa- and iota-carrageenans exist as right-handed, threefold helices that form double helices reversibly. The double-helical segments of Kappa- and iota-carrageenans can then interact to form a three-dimensional gel network. The conformation of lambda-carrageenan, a nongelling gum, has been described as a zigzagging ribbon.

Carrageenans and agars are structural polysaccharides of the *Rhodophyceae* (red algae). Carrageenans are extracted primarily from *Chondrus* and *Gigartina* species. Furcellaran is obtained primarily from *Furcellaria* species. Agars are obtained primarily from *Gelidium* and *Gracilaria* species.

A useful property of the red seaweed extracts is their ability to form gels with water and milk. Kappa-carrageenan reacts with milk protein micelles, particularly Kappa-casein micelles. The thickening effect of Kappa-carrageenan in milk is 5–10 times greater than it is in water; at a concentration of 0.025% in milk, a weak thixotropic gel is formed.

Agars are the least soluble of this class of polysaccharides; they can be dispersed only at temperatures >100°C. When agar dispersions are cooled, strong, brittle, turbid gels form. Agar gels remelt when heated, synerese, and are unstable to freeze–thaw cycles. By far the greatest use of agar in the United States is in the preparation of microbiological culture media. Agar is also used in bakery icings. Agar and agarose are used in making gels for electrophoresis, in gel-filtration chromatography, and in several applications in biotechnology.

Guar and Locust Bean Gums. Guaran, the purified polysaccharide from guar gum [9000-30-0], is a galactomannan [11078-30-1]. It has a mannan backbone, a linear chain of (1 → 4)-linked β-D-mannopyranosyl units with, on the average, one of every 1.8 mannosyl units substituted with a (1 → 6)-linked α-D-galactopyranosyl unit. The mannan chain is rather evenly substituted with D-galactopyranosyl units, but still contains some unsubstituted or smooth regions. Its molecular weight is 220,000 ± 20,000 (DP1360 ± 125).

Like guaran, and the endosperm polysaccharides of other legumes, locust bean (carob) gum [9000-40-2] is also a galactomannan. Like guaran, it has a linear backbone of (1 → 4)-linked β-D-mannopyranosyl units. However, in locust bean gum, approximately only one of every 3.9 β-D-mannopyranosyl units, on the average, is substituted with an α-D-galactopyranosyl unit attached at O-6.

Commercial guar gum is not purified guaran but the ground endosperm of guar seeds. Guar gum forms very high viscosity, pseudoplastic solutions at low concentrations. Guar endosperm preparations can be derivatized with the same reagents and catalysts used to modify starch and cellulose. The following products are prepared by proprietary processes: hydroxypropyl- [39421-75-5], hydroxyethyl- [39465-11-7], sodium carboxymethyl- [51190-15-3], sodium carboxymethyl(hydroxypropyl)- [39454-79-0], and 2-hydroxy-3-(trimethylammonio) propyl - [67034-33-7] (made as its chloride salt [65497-29-2]) guar gums. Derivatives are made to control the rate of hydration, peak viscosity, ash content, insoluble material, heat stability, and compatibility with other materials.

Polymer chains of guar gum and its derivatives, in fact of all galactomannans, are readily cross-linked with borate and titanium ions. Gels formed in this way are rubbery in Nature.

Commercial locust bean gum is the ground endosperm of the seeds of the locust bean (carob) tree. The general properties of locust bean gum are similar to those of guar gum. Differences are its low cold-water solubility and its synergistic gelation with Kappa-carrageenan, furcellaran, and xanthan [11138-66-2].

Gum Arabic. Of the gums of ancient commerce, which were dried exudations collected by hand from various trees and shrubs, only gum arabic [9000-01-5], also called gum acacia and acacia gum, is still in significant use. Gum arabic preparations are mixtures of highly branched, branch-on-branch, acidic polysaccharides. The polysaccharides have a branched main chain of β-D-galactopyranosyl units. Attached to this backbone are side chains containing L-arabinofuranosyl, L-rhamnopyranosyl, D-galactopyranosyl, and D-glucopyranosyluronic acid units in varying amounts depending on the source. Generally accepted values for number average and weight average molecular weights are 250,000 and 580,000, respectively; these values correspond to DPs of 155 and 3600.

Gum arabic comes from various species of *Acacia*. The gum exudes through cracks, injuries, and incisions in the bark and is collected by hand as dried tears. Gum arabic is unique among gums because of its high solubility and the low viscosity and Newtonian flow of its solutions. While other gums form highly viscous solutions at 1–2% concentration, 20% solutions of gum arabic resemble a thin sugar syrup in body and flow properties.

Pectins. Pectic acids [9046-40-6] are galacturonans [poly(α-D-galactopyranosyluronic acids), galacturonoglycans] [9046-38-2, 84149-03-1, 25249-06-3] without, or with only a negligible content of, methyl ester groups. Pectic acids have various degrees of neutralization. Salts of pectic acids are pectates. Pectinic acids are galacturonans with various, but greater than negligible, contents of methyl ester groups. Pectinic acids may have varying degrees of neutralization. Salts of pectinic acids are pectinates. Pectins [9000-69-5, 16048-08-1, 58128-44-2] are mixtures of polysaccharides that originate from plants, contain pectinic acids as primary components, are water-soluble, and whose solutions will gel under

suitable conditions. The term pectin is often used in a generic sense to designate those water-soluble galacturonans of varying methyl ester content and degree of neutralization that are capable of forming gels. Commercial pectins are formed during extraction. They are essentially homogalacturonans, but do contain some L-rhamnopyranosyl units in the galacturonan chain.

Commercial pectins are subdivided according to their degree of esterification (DE), a designation of the percent of carboxyl groups esterified with methanol. Pectins with DE >50% are high-methoxyl pectins (HM pectins) [65546-99-8]; those with DE <50% are low-methoxyl pectins (LM pectins) [9049-34-7]. The degree of amidation (DA) indicates the percent of carboxyl groups in the amide form.

The key feature of all pectin molecules is a linear chain of (1→4)-linked α-D-galactopyranosyluronic acid units, making it an α-D-galacturonan [a poly (α-D-galactopyranosyluronic acid) or an α-D-galacturonoglycan] [9046-38-2, 84149-03-1, 25249-06-3]. In all natural pectins, some of the carboxyl groups are in the methyl ester form. Depending on the isolation conditions, the remaining free carboxylic acid groups may be partly or fully neutralized. The DE strongly influences the solubility, gel-forming ability, conditions required for gelation, gelling temperature, and gel properties of the preparation.

Inserted L-rhamnopyranosyl units may provide the necessary irregularities (kinks) in the structure required to limit the size of the junction zones and produce a gel. The presence of side chains composed of D-xylosyl units may also be a factor that limits the extent of chain association. Junction zones are formed between regular, unbranched pectin chains when the negative charges on the carboxylate groups are removed (addition of acid), hydration of the molecules is reduced (addition of a cosolute, usually sugar, to a solution of HM pectin), and/or pectinic acid polymer chains are bridged by multivalent, eg, calcium, cations.

Sodium and calcium pectates, pectic acid, and pectinic acid all occur in the solid state as right-handed helices. In solid pectinic acid, the polymer molecules pack so that the chains are parallel to each other; the pectates pack as corrugated sheets of antiparallel chains. Junction zones in pectinic acid (HM pectin plus sucrose) gels are believed to be formed by a columnar stacking of methyl ester groups to form cylindrical hydrophobic areas parallel to the helix axes. LM pectin [9049-34-7] gels only in the presence of divalent cations. Two models for the formation of junction zones in calcium pectate [12672-40-1, 40022-66-0] gels have been proposed. One suggests an aggregation of chains by a cross-linking of carboxylate groups with calcium ions to form a structure similar to that of the corrugated sheets of antiparallel helices (3–6 chains in an average junction zone) found in solid calcium pectate. The other is the "egg box" model used to describe the formation of calcium alginate [9005-35-0] gels.

Xanthan. Xanthan, known commercially as xanthan gum [11138-66-2], has a main chain of (1→4)-linked β-D-glucopyranosyl units; therefore, the chemical structure of the main chain is identical to the structure of cellulose [9004-34-6]. However, in xanthan, every other β-D-glucopyranosyl unit in the main chain is substituted on O-3 with a trisaccharide unit. The trisaccharide side chain consists of (reading from the terminal, nonreducing end in towards the main chain) a β-D-mannopyranosyl unit linked (1→4) to a β-D-glucopyranosyluronic acid unit

linked $(1 \rightarrow 2)$ to a 6-*O*-acetyl-α-D-mannopyranosyl unit. About one-half of the terminal β-D-mannopyranosyl units carry a pyruvic acid group as a 4,6-di-*O*-acetal. The molecular weight is probably on the order of 2×10^6, although much higher figures have been reported.

The unusual properties of xanthan undoubtedly result from its structural rigidity, which in turn is a consequence of its linear, cellulosic backbone that is stiffened and shielded by the trisaccharide side chains. The conformation of xanthan in solution is a matter of debate. It does appear that the conformation changes with conditions.

Xanthan is the extracellular (exocellular) polysaccharide produced by *Xanthomonas campestris*. As with other microbial polysaccharides, the characteristics (polymer structure, molecular weight, solution properties) of xanthan preparations are constant and reproducible when a particular strain of the organism is grown under specified conditions, as is done commercially. The characteristics vary, however, with variations in the strain of the organism, the sources of nitrogen and carbon, degree of medium oxygenation, temperature, pH, and concentrations of various mineral elements.

Xanthan solutions are extremely pseudoplastic and have high yield values. These properties make xanthan almost ideal for the stabilization of aqueous dispersions, suspensions, and emulsions. Whereas other polysaccharide solutions decrease in viscosity when they are heated, xanthan solutions containing a small amount of salt (0.1%) change little in viscosity over the temperature range 0–95°C. Although xanthan is anionic, pH has almost no effect on the viscosity of its solutions over the range pH 1–12. A synergistic viscosity increase results from the interaction of xanthan with galactomannans and with methylcellulose. A combination of xanthan and locust bean gum forms a thermally reversible gel when a hot solution of these two polysaccharides is cooled.

Cellulose Derivatives. Cellulose can be derivatized to make both water-soluble gums and hydrophobic polymers (8,31,32). Preparation of the hydrophobic cellulose esters (qv), cellulose acetates and cellulose nitrates, has already been mentioned. The water-soluble cellulose derivatives are cellulose ethers (qv).

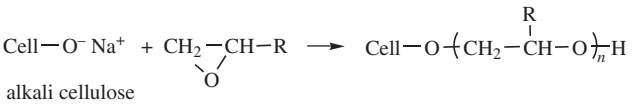
Carboxymethylcelluloses (CMC). Carboxymethylcellulose [9004-42-6] (CMC) is the carboxymethyl ether of cellulose. To prepare CMC, cellulose is steeped in sodium hydroxide solution, and the so-called alkali cellulose is treated under controlled conditions with sodium monochloroacetate to form the sodium salt of carboxymethylcellulose and sodium chloride. Therefore, the CMC of commerce is actually sodium carboxymethylcellulose [9004-32-4].

The physical properties (solution characteristics) of CMC, and all other linear polysaccharides, whether synthetic or natural, are determined by the average chain length or degree of polymerization (DP), the degree of substitution (DS), and the uniformity of substitution. The DS of different CMC types generally ranges from 0.4 to 0.8; some products may approach a DS of 1.5. The most widely used types have a DS of 0.7 or an average of 7 carboxymethyl groups per 10 β-D-glucopyranosyl units.

CMC hydrates rapidly and forms clear solutions. Viscosity building is the single most important property of CMC. Dilute solutions of CMC exhibit stable viscosity because each polymer chain is hydrated, extended, and independent. The sodium carboxylate groups are highly hydrated, and the cellulose molecule

itself is hydrated. The cellulose molecule is linear, and conversion of it into a polyanion (polycarboxylate) tends to keep it in an extended form by reason of Coulombic repulsion. This same Coulombic repulsion between the carboxylate anions prevents aggregation of the polymer chains. Solutions of CMC are either pseudoplastic or thixotropic, depending on the type.

Hydroxyethyl- and Hydroxypropylcelluloses. Hydroxyalkylcelluloses are cellulose ethers prepared by reaction of alkali cellulose with ethylene oxide, to prepare hydroxyethylcellulose (HEC) [9004-62-0], or propylene oxide, to prepare hydroxypropylcellulose (HPC) [9004-64-2].



These products are characterized in terms of moles of substitution (MS) rather than DS. MS is used because the reaction of an ethylene oxide or propylene oxide molecule with cellulose leads to the formation of a new hydroxyl group with which another alkylene oxide molecule can react to form an oligomeric side chain. Therefore, theoretically, there is no limit to the moles of substituent that can be added to each D-glucopyranosyl unit. MS denotes the average number of moles of alkylene oxide that has reacted per D-glucopyranosyl unit. Because starch is usually derivatized to a considerably lesser degree than is cellulose, formation of substituent poly(alkylene oxide) chains does not usually occur when starch is hydroxyalkylated and DS = MS.

In general, the MS controls the solubility of both HEC and HPC. For example, water-soluble grades of hydroxyethylcellulose have MS values of 1.6–3.0; those with MS 0.3–1.0 are soluble in aqueous alkali. Higher MS types of hydroxypropylcellulose become soluble in organic solvents, first polar, then nonpolar solvents.

Clear, water-soluble, oil-and grease-resistant films of moderate strength can be cast from hydroxyethylcellulose solutions. HEC is used in joint cements for wallboard, in high salt driling muds and to control the rheology and set time of oil-well cements, in latex paints, and as itself and in several modifications in other applications. Flexible, nontacky, heat-sealable packaging films and sheets can be produced from hydroxypropylcellulose by conventional extrusion techniques. Both gums can be used in the formulation of coatings. HPC can be used to form edible films and coatings.

Methylcelluloses and Hydroxyalkylmethylcelluloses. Methylcellulose [9004-67-5] contains methoxyl groups in place of some of the hydroxyl groups along the cellulose molecule. The primary hydroxyl group of cellulose is somewhat more reactive so, as with other cellulose derivatives, there is a somewhat higher degree of substitution at O-6. The next most acidic hydroxyl group is O-2. Hydroxyalkylmethylcelluloses contain, in addition to methoxyl groups, hydroxyalkoxyl groups in place of some of the hydroxyl groups. As with all other polysaccharide derivatives, the properties of methyl- and hydroxyalkylmethylcelluloses are a function of the type(s) of derivatization, the amount of each type of substituent group, the molecular weight distribution, and to some extent, the physical nature of the product, eg, fibrous vs powdered, granulation size, and surface treatment. Because these variables can be controlled to some degree, the members of this family, like other starch and cellulose derivatives, are a group of tailor-made products.

Methylcellulose is made by reaction of alkali cellulose with methyl chloride until the DS reaches 1.1–2.2. Hydroxypropylmethylcellulose [9004-65-3], the most common member of this family of products, is made by using propylene oxide in addition to methyl chloride in the reaction; MS values of the hydroxypropyl group in commercial products are 0.02–0.3. Both the true methylcelluloses and the hydroxypropylmethylcelluloses are often referred to simply as methylcelluloses. Use of 1,2-butylene oxide in the alkylation reaction mixture gives hydroxybutylmethylcellulose [9041-56-9, 37228-15-2] (MS 0.04–0.11). Hydroxyethylmethylcellulose [9032-42-2] is made with ethylene oxide in the reaction mixture.

Conversion of some of the hydroxyl groups of cellulose molecules into methyl ether groups increases the water solubility of the cellulose molecule and reduces its ability to aggregate, ie, reduces intermolecular interactions. Solubility is increased even more when hydroxyalkyl groups are added to methylcellulose. Solutions of all these products behave somewhat like those of guar and locust bean gums, ie, as linear polysaccharides with short side chains that give stable solutions of high viscosity. As substituent groups are added, the solubility of the products changes from insoluble to soluble in aqueous alkali, to soluble in water, to soluble in various polar organic solvents, such as water–alcohol solutions, alcohols, and alcohol–hydrocarbon solutions.

The most interesting property of these nonionic products is thermal gelation. Solutions of members of this family of gums that are soluble in cold water, like solutions of other polysaccharides, decrease in viscosity when heated. However, unlike most other gums, when a certain temperature is reached, depending on the specific product, the solution viscosity increases rapidly and the solution gels. Gelation can occur from $\sim 45^{\circ}$ to $\sim 90^{\circ}$C, depending on the product type. The thermal gelation is reversible.

Methylcelluloses reduce surface and interfacial tension. They form high strength films and sheets that are clear, water-soluble, oil- and grease-resistant, and have low oxygen and moisture vapor transmission rates (see BARRIER POLYMERS). They are used in a variety of applications ranging from shampoo and hair-conditioning compositions to construction applications, their largest volume use. Particularly important uses include formulation of tape joint compounds, gypsum spray plasters, and ceramic tile adhesives, grouts, and mortars.

5.4. Analysis. See references 35 and 36.

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