

# Polysaccharides

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Polysaccharides are polymers containing from 20 (usually > 100) to as many as 60 000 monosaccharide units. Polysaccharides have a range of general structures (from linear to various branched structures) and shapes. They are structural components of cell walls of bacteria, fungi, algae and higher plants, are energy- and carbon-storage substances, and serve various other functions as extracellular materials of plants, animals and microorganisms. They are the most abundant (by mass) of all organic substances in living organisms, comprising about two-thirds of the dry weight of the total biomass. Some have commercial value as isolated substances.

## Introductory article

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## Nature, Occurrence and Classification

Polysaccharides are polymers whose monomer units are simple aldose (aldehyde) and/or ketose (ketone) sugars (monosaccharides). The number of monosaccharide units in polysaccharides varies from about 35 (although it is usually at least 100) to approximately 60 000. The monosaccharide units are in either five-membered (furanosyl) or six-membered (pyranosyl) ring forms, most often the latter. These units are joined together in a head-to-tail fashion by glycosidic linkages, a glycosidic linkage being one-half of an acetal structure, the other half being that which forms the pyranosyl or furanosyl ring. An example of a glycosidic linkage is given in **Figure 1**.

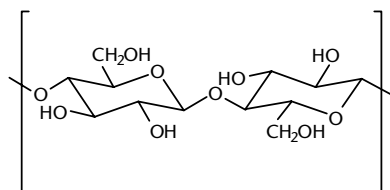
Polysaccharides may be linear or branched. There are a variety of branched structures, including structures with only a few, very long branches; linear structures with short branches regularly spaced, irregularly spaced, or in clusters; and branch-on-branch structures with branches clustered or positioned to produce bush-like structures with or without decoration with short branches. Representatives of the general kinds of branching found in polysaccharide molecules are shown in **Figure 2**. Each polysaccharide has one, and only one, reducing end, which is the end terminating in a hemiacetal (or carbonyl) group

(designated as  $\phi$  in **Figure 2**). Each branch generates an additional nonreducing end, which consists of a glycosyl unit that is attached to another through its anomeric hydroxyl group (see below) but has no glycosyl unit attached to it, making it a chain end with no carbonyl group. Therefore, a polysaccharide molecule may have many nonreducing ends. In terms of mass, linear polysaccharides are the most abundant, being structural components of higher plants and marine algae. However, there are many more branched polysaccharides than linear ones.

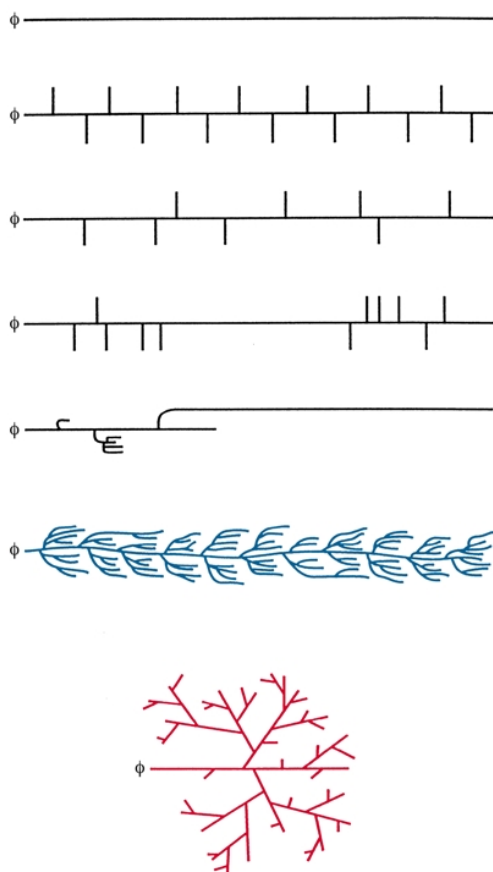
In addition to monosaccharide units, polysaccharides may contain ester, ether, and/or cyclic acetal moieties. Ester groups include acetate, glycolate, succinate, sulfate and phosphate groups on the polysaccharide's hydroxyl groups. Methyl and ethyl ether groups may be present. Pyruvic acid may be present as a cyclic acetal. In those polysaccharides containing amino sugars, the amino groups are usually not free but are present as amido groups, with the acid moiety being acetic, glycolic or sulfuric acid. In polysaccharides containing uronic acid units (sugar units with a carboxylic acid group in place of the hydroxymethyl group), the carboxylic acid functions may be present as methyl esters.

Glucose is the generic term for a monosaccharide (simple sugar). A glycosyl (saccharide) unit is the group formed by removing the OH group from the anomeric (originally the carbonyl) carbon atom of a pyranose or furanose ring form of the sugar. A glycosamine is a monosaccharide that contains an amino group in place of a hydroxyl group. In formal carbohydrate nomenclature, it is a deoxyamino sugar.

Glycan is the generic term for a polysaccharide. For example, a xylan is a polysaccharide made up primarily of D-xylopyranosyl units (it may contain minor amounts of other sugars); a  $\beta$ -glucan is constructed of  $\beta$ -D-glucopyranosyl units; an arabinoxylan has L-arabinose and D-xylose as its monomeric units; a glucuronoxylomannan consists of D-glucuronic acid, D-xylose, and D-mannose; and so on. If the polysaccharide has a backbone structure,



**Figure 1** Repeating unit structure of cellulose showing how the  $\beta$ -D-glucopyranosyl units are joined by (1 $\rightarrow$ 4) glycosidic linkages. The carbon atoms and hydrogen atoms bonded to the carbon atoms are omitted for clarity. The carbon atoms of each glycosyl unit are numbered, C1 being the anomeric carbon atom (that are on the extreme right of each unit in this structure), C2 being the carbon atom attached to C1, C3 being the next and so on to C6 in this case. The oxygen atoms attached to each carbon atom are numbered O1, O2, O3, etc.



**Figure 2** Portions of polysaccharide molecules showing the different kinds of branching.  $\phi$  indicates the reducing end.

it forms the latter part of the systematic name; for example, galactomannans have a main mannan chain to which are attached D-galactopyranosyl units; the same is true of arabinoxylans. Polysaccharides that were named before the systematic names were developed may not follow either of these rules; examples are cellulose, amylose, pectin, glycogen and alginic acid.

Polysaccharides may be attached to proteins, in which case they are known as protein-polysaccharides when they originate from plants, or proteoglycans when they originate from animals. Proteoglycans have different overall structures, but for the most part consist of a large number of polysaccharide (glycan) chains on one end of a polypeptide backbone to form a structure like a bottle brush, with the carbohydrate portion accounting for as much as 90% of the molecular weight of the proteoglycan. The polysaccharide chains contain amino sugars and are known as glycosaminoglycans. They are also acidic polysaccharides, containing uronic acid units and/or sulfate half-ester groups.

Lipopolysaccharides are cell wall components of Gram-negative bacteria (see Bacterial Exopolysaccharides below). Many bacteria also produce polysaccharides that are excreted outside the cell wall. They may be components of a capsule (capsular polysaccharides) or soluble in the extracellular medium. In either case, they are called exopolysaccharides.

A polymer called peptidoglycan is present in most, perhaps all, bacterial cell walls as the major structural component. Other carbohydrate polymers present in bacterial cell walls are teichoic acids (polymers of alditol phosphates) and teichuronic acids, which are linked to peptidoglycan.

Fungal, including yeast, cell walls may contain one or more of the polysaccharides chitin, cellulose, other  $\beta$ -glucans or mannans.

Because their synthesis does not involve a template molecule, polysaccharides are polydisperse; that is, molecules of a specific polysaccharide from a single source are present in a range of molecular weights. In addition, the degree of polydispersity, the average molecular weight, and the range of molecular weights in a polysaccharide preparation vary from source to source. Most polysaccharides are also polymolecular; that is, their fine structures vary from molecule to molecule. With the exception of cellulose and a few other plant polysaccharides, only bacterial polysaccharides have repeating-unit structures. Structures of other polysaccharides, and even of bacterial polysaccharides with regard to noncarbohydrate components, can vary between taxa and with growth conditions of the plant or microorganism and even between tissues of the same plant.

Polysaccharides are present in most living organisms. In fact, polysaccharides comprise about 70% of the dry weight of the total biomass. They serve a variety of functions, not all of which are known. They are most abundant in higher plants (1) as structural components of primary and secondary cell walls and in the middle lamella, (2) as reserve food materials in leaves, seeds, stems, roots, tubers, rhizomes and other tissues, (3) as exudates of unknown function, and (4) as extractable material of unknown function. They are cell wall constituents, non-cell wall constituents, and storage materials in algae. In microorganisms, they may be extracellular, in addition to being cellular constituents. The polysaccharide chitin is a structural component in the exoskeletons of crustaceans and insects.

There is no ideal system of polysaccharide classification. The best system should be that based on chemical structure. However, because of the polymolecularity, which limits descriptions to statistical structures in many cases, and because of the great variety of structures, classifying polysaccharides in this way has limitations. Combinations of the following categories are used:

- (1) Branching: (a) unbranched; (b) linear with short branches or side units (i) regularly spaced or (ii) irregularly spaced; (c) branches in clusters; (d) highly branched (branch-on-branch) structures
- (2) Different kinds of monomer units: (a) one (homoglycan); (b) two (diheteroglycan); (c) three (triheteroglycan); (d) four (tetraheteroglycan); (e) five (pentaheteroglycan)
- (3) Charge: (a) neutral; (b) anionic (acidic); (c) cationic

Specific sugars and linkage types may then be used within each of these general groups. There may also be variability in any noncarbohydrate constituents. Polysaccharides used industrially are most often classified by source. Examples of a very limited number of polysaccharides classified in these two ways are found in **Table 1** and **Table 4**.

## Determination of Structure

Because polysaccharides other than bacterial polysaccharides and a very few plant polysaccharides are chemically heterogeneous (i.e. their structures vary in proportions of monosaccharide constituents and/or in proportions of linkage types and in noncarbohydrate groups, if present, from molecule to molecule, as well as in molecular weight), a variety of chemical and instrumental methods are used together to determine structures, and a most probable statistical structure is deduced.

Polysaccharide preparation, whether in the laboratory for characterization or in commercial production, begins with extraction from the source in the case of a plant polysaccharide, or with isolation from a fermentation culture medium in the case of a bacterial polysaccharide. In laboratory preparations, extractions from a plant tissue are usually preceded by removal of interfering substances such as lipids and lignin. Extraction may be done with water in a few cases, but most often involves an alkaline solution. Both extraction and recovery from a fermentation medium are followed by purification and fractionation to separate the desired polysaccharide from noncarbohydrate materials, such as proteins, and from other polysaccharides. Purification most often involves precipitation, sometimes fractional precipitation. Precipitation is usually achieved by addition of a water-soluble alcohol such as ethanol (in the laboratory) or 2-propanol (industrially).

Structural analysis of a polysaccharide may be undertaken once it is obtained in an acceptable degree of purity. Polysaccharides have a great variety of structures, the only common feature being that each is composed, at least primarily, of monosaccharide units. Structural characterization involves determination of (1) monosaccharide composition; (2) linkage types; (3) ring size, i.e. pyranose or furanose; (4) anomeric configurations, i.e. configuration

at carbon atom 1 (C1) of an aldose or at carbon atom 2 (C2) of a ketose; (5) presence and location of substituent groups; and (6) degree of polymerization/molecular weight. Because there is such great variability in structures, there is some variability in methods used; however, some generalities can be described.

Determination of the monosaccharide composition begins with acid-catalysed hydrolysis. The monosaccharides released are then determined both qualitatively and quantitatively by high-performance liquid chromatography (HPLC) or by gas-liquid chromatography (GLC) after conversion to volatile, thermostable derivatives (often alditol acetates).

Linkages are determined by methylation analysis, which can reveal the linkage position, the ring size and the nature of the monosaccharide. In methylation analysis, all hydroxyl groups of the polysaccharide are converted into methyl ethers. Hydrolysis of the completely methylated polysaccharide then exposes the hydroxyl groups involved in glycosidic linkages as free (unmethylated) hydroxyl groups. The anomeric hydroxyl group of each unit will always be involved in a glycosidic bond, so only the other hydroxyl groups are significant. Each of the other hydroxyl groups involved in a glycosidic linkage before hydrolysis will be unmethylated, a characteristic that marks its location. Units that are nonreducing end-units are completely methylated, i.e. methyl ethers are formed at all hydroxyl groups of the pyranose or furanose ring form of the sugar unit. Thus, methylation analysis indicates the position of linkages to each monosaccharide unit, but not the sequence or any other structural information except which units are at nonreducing termini.

To obtain information about sequences, the polysaccharide is partially depolymerized using specific enzyme-catalysed and/or acid-catalysed hydrolysis to yield oligosaccharides, the structures of which are then determined.

## Higher Plant Cell Wall Polysaccharides

Differences in cell wall compositions occur within phyla, classes, families and genera of plants; with location within a given plant (because different cells have different functions and exist in different environments); and with stage of development. Nevertheless, some general features can be described.

Polysaccharides are the primary constituents of plant cell walls. Because cellulose is the principal component of the cell walls of higher plants, it is the most abundant organic compound on Earth. Cellulose is also present in brown, red and green algae and in certain fungi and slime moulds and is excreted extracellularly by certain bacteria. The amount of cellulose in a plant varies greatly from species to species. Wood, which is about half cellulose on a dry weight basis (db), has the highest percentage of

**Table 1** Classification of unmodified polysaccharides by structure, with examples**I. Linear molecules****A. Unbranched**

1. Neutral homoglycans
  - a. Cellulose
  - b. Laminarans<sup>a</sup>
  - c. Yeast glucans
  - d. Cereal  $\beta$ -glucans
  - e. Amyloses
  - f. Inulins
  - g. Yeast mannans
2. Neutral diheteroglycans
  - a. Konjac mannan
  - b. Agarose component of agar
3. Anionic/acidic homoglycans
  - a. Lambda-carrageenans
  - b. Pectins, pectic acids<sup>b</sup>
4. Anionic/acidic diheteroglycans
  - a. Algins/alginates
  - b. Kappa-carrageenans
  - c. Iota-carrageenans
5. Anionic/acidic triheteroglycan
  - a. Gellan gum
6. Cationic/basic homoglycan
  - a. Chitosan

**B. Linear with short branches/side units**

1. Branches irregularly spaced
  - a. Neutral homoglycans
    - i. Fungal (mushroom)  $\beta$ -glucans
  - b. Neutral diheteroglycans
    - i. Galactomannans (guar gum, locust bean gum, tara gum)
    - ii. Flour arabinoxylans
    - iii. Larch arabinogalactan
    - iv. Neutral tetraheteroglycans - Xyloglucans
2. Branches regularly spaced
  - a. Neutral homoglycan
    - i. Yeast mannan
  - b. Anionic/acidic triheteroglycan
    - i. Xanthan gum

**II. Nonlinear molecules****A. Branches in clusters, homoglycan**

1. Amylopectins

**B. Highly branched/branch-on-branch-on-branch structures, anionic/acidic**

1. Tetraheteroglycans
  - a. Gum karayas
  - b. Okra gum
2. Pentaheteroglycans
  - a. B-type hemicelluloses of cereal brans, etc. (arabinoxylans)

**Table 1 – continued**

- b. Gum arabic
- c. Psyllium seed gum

<sup>a</sup> Some laminarans contain D-mannitol units.

<sup>b</sup> Principal structure in commercial high- and low-methoxyl pectins. Pectins are actually complex, heterogeneous polysaccharides containing some percentage of  $\alpha$ -L-rhamnopyranosyl units in the main chain and perhaps arabinogalactan side-chains.

cellulose, except for the fibrous seed hairs of cotton, which are  $\sim 90\%$  cellulose. In wood, the majority of the cellulose is found in thickened, secondary cell walls. Even certain animals (tunicates and protozoans) synthesize cellulose. Thus cellulose is synthesized by both plants and animals, though almost exclusively by plants, and by both prokaryotes and eukaryotes, but primarily by eukaryotes. Cellulose differs from most other polysaccharides in being a homoglycan with a single type of linkage and in occurring naturally as a paracrystalline, but largely crystalline, polymer. It also has a higher average molecular weight than most other polysaccharides. In its native state, cellulose usually exists in the form of strong fibres. Chemically, all celluloses are the same; they all are polymers of  $\beta$ -D-glucopyranosyl units linked (1 $\rightarrow$ 4), but these (1,4)- $\beta$ -glucans differ in physical organization into fibrillar structures from source to source.

In both primary and secondary cell walls, cellulose is mixed with hemicellulose(s) (Table 2) and lignin. The term hemicellulose indicates a polysaccharide closely associated with cellulose, not structurally but physically, in cell walls. Hemicelluloses may be largely homoglycans (e.g. D-xylan), but are usually heteroglycans. Their structures vary from linear to highly branched and bush-like. The hemicellulose content of woods varies from  $\sim 17\%$  to  $\sim 23\%$  (db).

Pectic substances, another family of polysaccharides, are located in middle lamellae and primary cell walls. Pectic substances comprise 1–4% of woody tissue. Xyloglucans are also cell wall components of many higher plant cells.

The polysaccharides found in cell walls are specific to specific cell types. Most flowering plants have type I cell walls. These walls have a cellulose–xyloglucan interlocking framework ( $\sim 50\%$  of the wall mass) embedded in a matrix of pectic polysaccharides ( $\sim 30\%$ , rhamnogalacturonan I plus lesser amounts of galacturonans/partially methyl esterified poly(D-galacturonic acids)). Grasses have type II cell walls. The characteristic components of these walls are cellulose, glucuronoarabinoxylans, galacturonans, and mixed-linkage  $\beta$ -glucans/(1,3:1,4- $\beta$ -glucans).

Structural polysaccharides of algae vary greatly between phyla. Included as cell wall components of algae are cellulose, alginates, sulfated galactans (carrageenans, agars, etc.), lichenan (a 1,3:1,4- $\beta$ -glucan), xylans, mannans and pectic substances.

*continued*

**Table 2** Cell wall polysaccharides<sup>a</sup>***Higher land plants***

Cellulose  
Hemicelluloses  
  Arabinoxylans  
  Galactoglucomannans  
   $\beta$ -Glucans  
  Glucomannans  
  Mannans  
  Xylans  
  Xyloglucans  
Pectic polysaccharides  
  Arabinans  
  Arabinogalactans  
  Galactans  
  Galacturonans  
  Rhamnogalacturonans

***Marine algae***

Algins  
Cellulose  
L-Fucans  
Galactans  
  Agars  
  Carrageenans  
  Furcellarans  
 $\beta$ -Glucans  
Mannans  
Xylans

***Fungi and yeasts***

Cellulose  
Chitin  
 $\beta$ -Glucans  
 $\alpha$ -Glucans  
Mannans

<sup>a</sup>Many of these polysaccharides may contain monosaccharide units other than those indicated in the name. For example, xylans often contain uronic acid units, and polysaccharides named L-fucans may contain, in addition to the principal sugar (L-fucose), D-galactose, D-glucuronic acid, D-mannose and D-xylose.

**Table 3** Energy storage polysaccharides***Higher land plants***

Fructans  
Galactans  
Galactomannans  
Glucomannans  
Starches  
Xyloglucans

***Marine algae***

Fructans  
 $\alpha$ -Glucans<sup>a</sup>  
 $\beta$ -Glucans  
Xylans

***Freshwater algae***

$\alpha$ -Glucans<sup>a</sup>  
 $\beta$ -Glucans

***Fungi and yeasts***

$\alpha$ -Glucans<sup>a</sup>  
 $\beta$ -Glucans

<sup>a</sup>Starch-like and glycogen-like polymers.

compactness; and its highly branched, bush-like structure makes a large number of glucosyl units simultaneously available to enzyme molecules that release them. Liver glycogen is used to maintain blood glucose levels. Muscle glycogen is used as a supply of energy, even under less than fully aerobic conditions. Glycogen pools are generally in dynamic states.

Starch is the principal carbohydrate energy storage substance of higher plants and, after cellulose, is the second most abundant carbohydrate end product of photosynthesis. As well as being a reserve substance for most higher plants, starch is an energy source for animals that feed on these plants. Starch is found in leaves, where it serves as a transient D-glucose storage material, and in seeds (especially those of cereal grains), fruits, roots, rhizomes, stems, tubers and trunks for long-term storage. Starches provide at least 70% of human caloric intake on a worldwide basis.

Starch is unique among carbohydrates in that it occurs in discrete particles called granules. Starch granules are relatively dense and insoluble. Most starch granules contain two polymers: an essentially linear polysaccharide called amylose and a highly branched polysaccharide called amylopectin. Each starch from each plant source and tissue is unique in terms of granule morphology, composition, polysaccharide structures and characteristic properties.

Other energy storage polysaccharides include inulin and other fructans in roots, tubers and stems; galactomannans in legume seeds; mannans in palm seeds; and starch-type and laminaran-type polysaccharides of green and brown algae, respectively. (Laminaran is a (1,3)- $\beta$ -glucan.)

## Energy Storage Polysaccharides

Acting as a reserve energy supply is one function of polysaccharides in living systems (**Table 3**). Glycogen, a polysaccharide that serves in this role, is ubiquitous in mammals, fish, molluscs, insects, other animals, bacteria, fungi and some plants, and exists in different forms and amounts in these organisms. Glycogen is present in most mammalian tissues; the liver contains the highest concentration; skeletal muscle contains the greatest amount. Glycogen is well constructed to be an energy storage molecule: it stores a large number of units of D-glucose with negligible increase in osmotic pressure because of its high molecular weight and/or in viscosity because of its

**Table 4** Classification of commercial polysaccharides by source**I. Plant polysaccharides<sup>a</sup>****A. Higher plants**

1. Cell wall constituents
  - a. Cellulose
  - b. Native and extracted/commercial pectins
2. Storage polysaccharides
  - a. Starches (amyloses and amylopectins)
  - b. Galactomannans (guar gum, locust bean/carob gum, tara gum)
  - c. Konjac mannan
  - d. Inulin
3. Other non-cell wall polysaccharides
  - a. Exudate gums
    - i. Gum arabics
    - ii. Gum tragacanth
    - iii. Gum ghattis
    - iv. Gum karayas
  - b. Extractives
    - i. Larch arabinogalactan
    - ii. Psyllium seed gum

**B. Algae**

1. Cell wall constituents
  - a. Agars
  - b. Alginates
  - c. Carrageenans
  - d. Furcellarans (Danish agars)
2. Non-cell wall constituent
  - a. Laminaran

**C. Microorganisms**

1. Extracellular
  - a. Xanthans
  - b. Gellan
  - c. Curdlan

**II. Animal****A. Crustacean**

1. Chitin<sup>b</sup>

**III. Derived from native polysaccharides****A. From cellulose**

1. Carboxymethylcelluloses
2. Cellulose acetates
3. Cellulose acetate butyrates
4. Cellulose acetate propionates
5. Ethylcelluloses
6. Hydroxyethylcelluloses
7. Hydroxypropylcelluloses
8. Hydroxypropylmethylcelluloses
9. Methylcelluloses
10. Microcrystalline celluloses

**B. From starch**

1. Starch acetates
2. Starch 1-octenylsuccinates
3. Starch phosphates

**Table 4—continued**

4. Starch succinates
5. Starch adipates
6. Hydroxyethylstarches
7. Hydroxypropylstarches
8. Dextrins
- C. From guar gum
  1. Carboxymethylguar gum
  2. Carboxymethylhydroxypropylguar gum
  3. Hydroxypropylguar gum
  4. 2-Hydroxy-3-(trimethylammonium chloride)-propylguar gum
- D. From native pectins
  1. Pectic acids (low-methoxyl pectins)
  2. Amidated pectins
- E. Propylene glycol alginates
- F. Chitosan

<sup>a</sup>Generally restricted to those polysaccharides isolated in at least a semipurified form. Does not include those that are present as constituents of other materials; for example does not include the arabinoxylans of flours or the  $\beta$ -glucans of brans.

<sup>b</sup>Not produced in the native form, but rather in the deacetylated form (chitosan, III.F).

## Chitin and Other Fungal Cell Wall Polysaccharides

Fungal cell walls often contain 80–90% (db) polysaccharide. Fungal cell walls have been categorized into eight types by polysaccharide composition: cellulose–glycogen, cellulose– $\beta$ -glucan, cellulose–chitin, chitosan–chitin, chitin– $\beta$ -glucan (the most common), mannose-containing polysaccharide– $\beta$ -glucan, mannan–chitin, galactosaminoglycan–chitin. The primary cell wall component of many species is chitin. Chitin is also a primary matrix constituent of mollusc shells and the exoskeletons of insects. Its structure is identical to that of cellulose, with the exception of having an acetamido ( $-\text{NH}-\text{CO}-\text{CH}_3$ ) group in place of the hydroxyl group at C2 of each monomer unit. Thus, chitin is (1 $\rightarrow$ 4)-linked poly(*N*-acetyl- $\beta$ -D-glucosamine) or more properly a poly(2-acetamido-2-deoxy- $\beta$ -D-glucopyranose). Like cellulose, chitin is highly crystalline and insoluble.

Yeast cell walls may contain a (1,3)- $\beta$ -glucan, a (1,6)- $\beta$ -glucan, various mannans or a galactan. Other cell wall components of certain fungi include rhamnomannans, glucomannans, galactomannans, xylomannans, glucuronoxylomannans, and other polysaccharides.

## Bacterial Exopolysaccharides

Carbohydrate-containing polymers are components of bacterial cell walls and capsules and are also secreted into the culture medium. Of the cell wall polysaccharides, the

*continued*

lipopolysaccharides of Gram-negative bacteria should be mentioned. These materials consist of three parts: a compound called lipid A, a core polysaccharide section, and O-specific side-chains, which are attached to the core polysaccharide. The O-specific chains also are polysaccharides and are immunogenic. Lipopolysaccharide structures are quite diverse and often contain sugar units that are rarely or never found in other polysaccharides. Gram-positive bacteria do not synthesize lipopolysaccharides of the type present in Gram-negative bacteria, but do make other types of cell wall polysaccharides. Some also produce capsules of polysaccharide. Intracellular polysaccharides are present in some bacteria.

As with eukaryotes, the great diversity of types of bacteria leads to a great diversity in polysaccharide structures, but the overwhelming majority of bacterial polysaccharides are heteroglycans that are polymers of oligosaccharide repeating units. These repeating units generally contain 3–8 glycosyl units. The polymers often also contain noncarbohydrate components.

Bacterial exopolysaccharides (extracellular polysaccharides) include those that are made from sucrose, viz. dextrans and fructans. Dextrans are branched  $\alpha$ -glucans containing (1 $\rightarrow$ 3), (1 $\rightarrow$ 6) and occasionally (1 $\rightarrow$ 2) linkages. Fructans contain  $\beta$ -D-fructofuranosyl units linked (2 $\rightarrow$ 6) or (2 $\rightarrow$ 1).

Several extracellular microbial polysaccharides are commercial products (see Polysaccharides as Gums and Thickeners below).

## Glycosaminoglycans

Glycosaminoglycans are found primarily in animal tissues, mostly in connective tissue, and often as part of a larger supermolecular structure known as a proteoglycan. As the name implies, they contain amino sugars. These polysaccharides usually contain alternating units of an amino sugar (2-amino-2-deoxy-D-glucose (D-glucosamine) or 2-amino-2-deoxy-D-galactose (D-galactosamine)) and a uronic acid (D-glucuronic acid or L-iduronic acid); they usually contain *N*-acetyl or *N*- or *O*-sulfate groups. An exception to this overall general structure is keratan sulfate, which has a D-galactopyranosyl unit in place of a uronic acid unit alternating with an amino sugar. The glycosaminoglycan heparin, unlike the others, originates in mast cells in many nonconnective tissues. Glycosaminoglycans that do have the usual structure and are present in connective tissue, either free or as part of a proteoglycan, are hyaluronic acid, chondroitin 4- and 6-sulfates, dermatan sulfate and heparan sulfate.

## Polysaccharides as Industrial Gums

Many polysaccharides are used as they are obtained from plants or microorganisms in various industrial applica-

tions, including in food products, and they may also be modified before use. Their common characteristic is their hydrophilic nature. Many are water soluble; those that are not, like cellulose, absorb water (hydrate). The water-soluble polysaccharides and modified polysaccharides used in industrial applications are known as gums. When used in food products, they (and also the protein gelatin) may be referred to as hydrocolloids. Gums/hydrocolloids are used primarily to thicken and/or gel aqueous solutions and otherwise to modify and/or control the rheological properties of aqueous systems, but they may also be used for a wide range of other attributes, including, but not limited to, their ability to function as adhesives, crystallization inhibitors, emulsion and suspension stabilizers, film formers and texturing agents. **Table 4** lists commercial, water-soluble polysaccharides and polysaccharide derivatives by source.

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