

# **Examples of Polysaccharides**

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### Polysaccharides

Most carbohydrates found in nature occur as polysaccharides, polymers of medium

to high molecular weight.

Polysaccharides do NOT have a defined molecular weight (WHY?)

Polysaccharides, also called glycans, differ from each other in:

- the identity of their recurring monosaccharide units,
- the length of their chains,
- the orientation of bonds linking the units, and
- the degree of branching.

#### We can classify them into:

- Homopolysaccharides contain only a single type of monomer;
- Heteropolysaccharides contain two or more different kinds.
- Unlike proteins, there is NO template (gene) used to make polysaccharides.



Homo- and heteropolysaccharides.

Polysaccharides may be composed of one, two, or several different monosaccharides, in straight or branched chains of varying length.

#### Homopolysaccharides

*Some homopolysaccharides* serve as storage forms of monosaccharides that are used as fuels;

Starch and glycogen are homopolysaccharides of this type.

*Other* homopolysaccharides (like cellulose and chitin) serve as structural elements in plant cell walls and animal exoskeletons, respectively.

#### *Heteropolysaccharides*

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

### Homopolysaccharides

The most important storage polysaccharides are starch in plant cells and glycogen in animal cells.

Both polysaccharides occur intracellularly as large clusters or granules. Starch and glycogen molecules are heavily hydrated, because they have

many exposed hydroxyl groups available to hydrogen-bond with water.

Most plant cells have the ability to form starch, but it is especially abundant in tubers, such as potatoes, and in seeds.

### Starch

- **Glucose** is not stored in plant cell because of its high solubility.
- Alternatively, it is polymerized in the form of starch granules that have different forms depending on the plant source.
- Starch: contains two types of glucose polymers (homopolysaccharide), amylose and amylopectin.
  - *Amylose* consists of long, unbranched chains of D-glucose residues connected by (α1→4) linkages. Such chains vary in molecular weight from a few thousands to more than a million. It takes a helical shape with about 6 glucose residues per turn.
  - *Amylopectin* also has a high molecular weight (up to 100 million Dalton) but unlike amylose is highly branched.
- The glycosidic linkages joining successive glucose residues in amylopectin chains are  $(\alpha 1 \rightarrow 4)$ ; the branch points (occurring every 24 to 30 residues) are  $(\alpha 1 \rightarrow 6)$  linkages.



#### Amylose and amylopectin, the polysaccharides of starch.

(a) A short segment of *amylose*, a linear polymer of D-glucose residues in  $(\alpha 1 \rightarrow 4)$  linkage. A single chain can contain several thousand glucose residues. *Amylopectin* has stretches of similarly linked residues between branch points.

(b) An  $(\alpha 1 \rightarrow 6)$  branch point of amylopectin.

(c) A cluster of amylose and amylopectin like that believed to occur in starch granules. Strands of amylopectin (red) form **double-helical structures** with each other or with amylose strands (blue).

### Starch (cont.)

- Starch is non-reducing polysaccharide.
- *Notice*, amylopectin has one reducing end and many non-reducing ends.
- Although starch has free terminal hemiacetal bond, it is non reducing because this terminus represents very small proportion in comparison to the number of internal acetal bonds of the whole molecule.
- Although starch has too many hydroxyl groups, it is not soluble in water because of its high molecular weight.
- Small quantity of starch can be dissolved with gentle heating.
- Starch is detected by the addition of iodine solution which upon binding with starch turns from yellow to dark blue, as iodine enters the helix of amylose and absorb all colors and reflect the blue. This color disappears by heating because the helix extends and the iodine liberates.



- Glycogen is the main storage polysaccharide of animal (up to 120,000 glucose residues).
- It is similar to amylopectin, a homopolymer of  $(\alpha 1 \rightarrow 4)$ -linked subunits of glucose, with  $(\alpha 1 \rightarrow 6)$ -linked branches, but glycogen is more extensively branched (on average, every 8 to 12 residues) and more compact than starch.
- Glycogen is especially abundant in the liver, where it may constitute as much as 7% of the wet weight; it is also present in skeletal muscle (1% of muscle weight). The total amount of muscle glycogen is 3-4 times the quantity in the liver.
- In hepatocytes glycogen is found in large granules of several million Daltons (Mwt), which are themselves clusters of smaller granules composed of single, highly branched glycogen molecules with an average molecular weight of several million.

Such glycogen granules also contain, in tightly bound form, the enzymes responsible for the synthesis and degradation of glycogen.

What is the difference between glycogen and glycogenin? Make a search.....



Glycogen is similar to plant amylopectin have one reducing end many non-reducing end.Glycogen represents the mail store of carbohydrate in mammals when person fed carbohydrate rich food.

This store is used only when the concentration of blood glucose fall below 70 mg%. Then glycogen starts to degrade to glucose to compensate the decrease of blood glucose.

The liver glycogen can be consumed after 12-18 hour of fasting but the muscular lasts longer.

Glycogen gives red color in the iodine test.



# Dextrans

- Dextrans are bacterial and yeast homopolysaccharides made up of  $(\alpha \ 1 \rightarrow 6)$ -linked poly-D-glucose; all have  $(\alpha \ 1 \rightarrow 3)$  branches, and some also have  $(\alpha \ 1 \rightarrow 2)$  or  $(\alpha \ 1 \rightarrow 4)$  branches.
- Dental plaque, formed by bacteria growing on the surface of teeth, is rich in dextrans.
- Synthetic dextrans are used in several commercial products (for example, Sephadex) that serve in the fractionation of proteins by size-exclusion (gel filtration) chromatography.
   The dextrans in these products are chemically cross-linked to form insoluble materials of various porosities, to separate the macromolecules depending on their molecular sizes.





**Cellulose**, a fibrous, tough, water-insoluble substance, is found in the cell walls of plants, and in all woody portions of the plant.

Cotton is almost pure cellulose.

The cellulose molecule is a linear, **unbranched** homo-polysaccharide, consisting of 10,000 to 15,000 D-glucose units. Cellulose chains bring together by hydrogen bonds.

The glucose residues are linked by  $\beta$ - (1 $\rightarrow$ 4) glycosidic bonds.



*The glucose residues in* cellulose are linked by  $(\beta 1 \rightarrow 4)$  glycosidic bonds, in contrast to the  $(\alpha 1 \rightarrow 4)$  bonds of amylose, starch, and glycogen.

- This difference gives cellulose and amylose very different structures and physical properties. Glycogen and starch ingested in the diet are hydrolyzed by  $\alpha$  -amylases, enzymes in saliva and intestinal secretions that break  $\alpha 1 \rightarrow 4$  (but not  $\beta 1 \rightarrow 4$ ) glycosidic bonds between glucose units.
- Most animals cannot use cellulose as an energy source, because they lack the enzyme that hydrolyze the  $(\beta 1 \rightarrow 4)$  linkages.
- Termites readily digest cellulose (and therefore wood), because their intestine harbors a symbiotic microorganism, *Trichonympha*, that secretes enzyme called cellulase, which hydrolyzes the  $(\beta 1 \rightarrow 4)$  linkages.

Ruminants have microbes in stomach.

Wood-rot fungi and bacteria also produce cellulase.





**Chitin** is a linear homopolysaccharide composed of *N*-acetylglucosamine residues in  $\beta \rightarrow 4$  linkage.

The only chemical difference from cellulose is the replacement of the hydroxyl group at C-2 with an acetylated amino group.

Chitin forms extended fibers similar to those of cellulose, and like cellulose cannot be digested by vertebrates.

Chitin is the principal component of the hard exoskeletons of million species of arthropods—insects, lobsters, and crabs, for example— and is probably the second most abundant polysaccharide, next to cellulose, in nature.





FIGURE 7-18 Chitin. (a) A short segment of chitin, a homopolymer of N-acetyl-D-glucosamine units in  $(\beta 1 \rightarrow 4)$  linkage. (b) A spotted June beetle (*Pellidnota punetatia*), showing its surface armor (exoskeleton) of chitin.





Chitin. (a) A short segment of chitin, a homopolymer of N-acetyl-D-glucosamine units in  $(\beta 1 \rightarrow 4)$  linkage.

Compare and contrast between cellulose and chitin?

(b)

## Quiz

#### 1-All of the following are polysaccharides except

A- cellulose.

B-lactose

C-glycogen D-amylopectin

#### 2-Cellulose, $\beta(1 > 4)$ -linked glucose polysaccharide, differs from starch in that starch is .....

A- $\beta$ (1->6)-linked mannose polysaccharide C- $\alpha$ (1->4)-linked glucose polysaccharide.

B- $\alpha$ (1->6)-linked glucose polysaccharide. D- β(1->6)-linked glucose polysaccharide.

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# Quiz

#### • Q: Physical Properties of Cellulose and Glycogen.

The almost pure cellulose obtained from the seed threads of *Gossypium* (cotton) is tough, fibrous, and completely insoluble in water.

In contrast, glycogen obtained from muscle or liver disperses readily in hot water to make a turbid solution. Although they have markedly different physical properties, both substances are composed of (1->4)-linked D-glucose polymers of comparable molecular weight.

What structural features of these two polysaccharides underlie their different physical properties?

*Explain the biological advantages of their respective properties.* 

# Quiz

- Q:Cellulose could provide a widely available and cheap form of glucose, but humans cannot digest it. *Why not*?
- If you were offered a procedure that allowed you to acquire this ability, would you accept? Why or why not?
- Ans: Humans cannot break down cellulose to its monosaccharides because they lack cellulases, a family of enzymes, produced chiefly by fungi, bacteria, and protozoans, that catalyze the hydrolysis of cellulose to glucose.
- In ruminant animals (such as cows and sheep), the rumen (one of four stomach compartments) acts as an anaerobic fermenter in which bacteria and protozoa degrade cellulose, making its glucose available as a nutrient to the animal.
- If cellulase were present in the human digestive tract, we could use foods rich in cellulose as nutrients. This would greatly increase the forms of biomass that could be used for human nutrition. This change might require some changes in the teeth that would allow cellulosic materials to be ground into small pieces to serve as cellulase substrates.

### Structural Heteropolysaccharides Bacterial Cell Walls

- The bacterial cell walls is a heteropolymer of alternating  $(\beta \rightarrow 4)$ linked *N*-acetylglucosamine and *N*-acetylmuramic acid residues.
- The linear polymers lie side by side in the cell wall, cross-linked by short peptides.
- The peptide cross-links weld the polysaccharide chains into a strong sheath that envelops the entire cell and prevents cellular swelling and lysis due to the osmotic entry of water.
- The enzyme lysozyme kills bacteria by hydrolyzing the
  (β 1→4) glycosidic bond between *N*-acetylglucosamine and *N*-acetylmuramic acid.
- Lysozyme is notably present in tears, presumably as a defense against bacterial infections of the eye.
- It is also produced by certain bacterial viruses to ensure their release from the host bacterial cell.
- Penicillin and related antibiotics kill bacteria by preventing synthesis of the cross-links, leaving the cell wall too weak to resist osmotic lysis.



Not to be **confused** with n-acetyl neuraminic acid

### **Structural Heteropolysaccharides Algal Cell Walls**

Certain marine red algae have **agar** in its cell walls. Agar is composed of two major polysaccharides:

- Agarose, is unbranched linear polymer ( $Mr \sim 120,000$ ) made up of repeating units of agarobiose (a disaccharide made up of D-galactose and 3,6-anhydro-L-galactopyranose bound by  $\beta 1 \rightarrow 4$  glycosidic bond in which an ether ring connects C-3 and C-6). These units are joined by ( $1 \rightarrow 3$ ) glycosidic links to form a polymer 600 to 700 residues long.



3)D-Gal( $\beta$ 1 $\rightarrow$ 4)3,6-anhydro-L-Gal2S( $\alpha$ 1 repeats

- Agaropectin, is branched chain sulphated polysaccharide composed of alternating units of D-galactose and an L-galactose .

#### • Agar and agarose have many applications:

- Agar is also used to form a surface for the growth of bacterial colonies.
- Agar is used for the capsules in which some vitamins and drugs are packaged; the dried agar material dissolves readily in the stomach and is metabolically inert.
- Agarose has a remarkable gel-forming property when a suspension of agarose in water is heated and cooled. This gel has a three-dimensional structure that traps large amounts of water and it is used in the laboratory for the electrophoretic separation of nucleic acids.



•Agar ---- capsules

•Agarose ----- laboratory for the electrophoretic separation of nucleic acids.

True or false Agar is a sulfated <u>glycosaminoglycan</u> composed of a chain of alternating sugars (F) It is not <u>glycosaminoglycan</u>



### **Conflicting terms**

- **Glycosaminoglycans** (mucopolysaccharides) are linear *polysaccharides* of repeating disaccharides containing amino sugar, either glucosamine or galactosamine
- Polysaccharides containing aminosugars
- **Peptidoglycans are** *polysaccharides* consisting of sugars and few amino acids.
- Polysaccharides + few amino acids
- Proteoglycans are *proteins* that are heavily glycosylated (95% carbohydrates of the biomolecule by weight). It consists of core protein covalently bound to glycoseaminoglycans.
- Protein + polysaccharide in the form of glycoseaminoglycans.
- **Glycoproteins** are *proteins* that contain covalently bound oligosaccharide chains (1-30% carbohydrates).
- Protein + few sugars