

Starch and Cellulose— Polymers of Sugars

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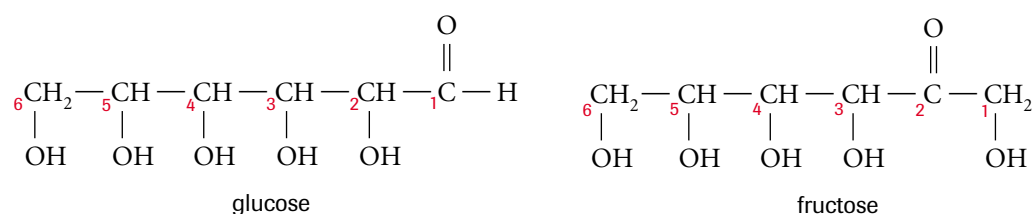
Starch and cellulose are natural polymers, belonging in a group of compounds called carbohydrates. Carbohydrates include sugars (which are monosaccharides or disaccharides) as well as starches and cellulose (which are polysaccharides composed of sugar monomers). Carbohydrates are very important components in our food, being a major source of energy for many of us. Plants are the source of most of the carbohydrates we eat: sugar from sugar cane or beets; starch from potatoes or wheat; and cellulose in bran and vegetables. The differences among these forms of carbohydrates are those of molecular size and shape, sugars being the smallest units and starches and cellulose being polymers of the simple sugar, glucose.

Monosaccharide Sugars

All **carbohydrates** have the empirical formula $C_x(H_2O)_y$, hence their name, which is derived from “hydrated carbon.” Like other compounds of carbon, hydrogen, and oxygen, carbohydrates undergo complete combustion to produce carbon dioxide and water.

Glucose, the sugar formed in the process of photosynthesis, has the formula $C_6H_{12}O_6$, or $C_6(H_2O)_6$; however, the molecules are not actually in the form of carbon and water. The atoms in simple sugar molecules are arranged as a carbon backbone, often six carbons long, with functional groups attached to each carbon atom. In some simple sugars, the first carbon atom is a part of a carbonyl group ($C=O$), forming an aldehyde. In other sugars, it is the second carbon atom that is a part of a $C=O$ group, forming a ketone. The other carbon atoms in the molecule each hold a hydroxyl group.

Two simple sugars, glucose and fructose, are shown below. Glucose is the sugar molecule most widely produced by plants, and is the monomer that makes up all the larger carbohydrates. Glucose belongs to the group of sugars called **aldoses**, due to its aldehyde group. Fructose, with its ketone group, is a **ketose**. It is the sugar found widely in fruits, so is sometimes called fruit sugar, and is a **key** sugar in honey. Both glucose and fructose are single units of sugar and are called **monosaccharides**.



The presence of both $-OH$ groups and $C=O$ groups on a flexible backbone also provides opportunity for these groups on the same molecule to react with each other. When a bond is formed in this way, like a snake grabbing its own tail, a ring structure is formed. Essentially, the $C=O$ group reacts with the $-OH$ group to form an oxygen link, resulting in either a five-membered ring or a six-membered ring. When aqueous solutions of glucose are analyzed, it is found that more than 99.9% of glucose molecules are in ring form.

When these rings are formed, a very important structural “decision” is made. In the open-ended linear sugar molecule, the single covalent bonds in the carbon backbone allow for free rotation of any attached atoms or groups. Once a ring structure is formed, there is no longer free rotation about the ring. The ring itself is not planar, but is in a “chair” conformation (**Figure 1**). Functional groups may be fixed in a position “above the ring”

DID YOU KNOW?

A Sweet Tooth

If you have a sweet tooth, you may be happy to know that sugar does not rot your teeth: It is acid that leads to painful cavities. However, sugar does turn into acid in your mouth. Bacteria adhere to your teeth as plaque, and feed on the sugars you eat. One of the products formed is lactic acid, which lowers pH and causes the protective tooth enamel to dissolve, leaving teeth vulnerable to decay. Your mouth balances this change in pH by its slightly alkaline saliva, which uses buffers such as the carboxyl and amino groups of proteins.

carbohydrate a compound of carbon, hydrogen, and oxygen, with a general formula $C_x(H_2O)_y$

aldose a sugar molecule with an aldehyde functional group at C 1

ketose a sugar molecule with a ketone functional group, usually at C 2

monosaccharide a carbohydrate consisting of a single sugar unit

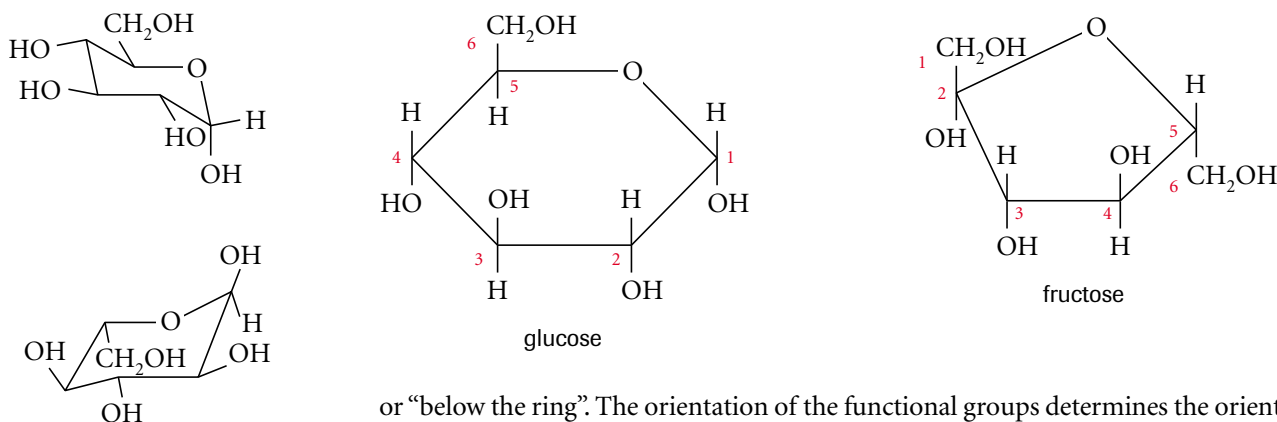


Figure 1

The “chair” conformation of the glucose molecule: functional groups are “fixed” above or below the ring.

disaccharide a carbohydrate consisting of two monosaccharides

DID YOU KNOW?

Lactose Intolerance

Nearly all babies thrive on milk, but many grow up to become lactose intolerant. These children and adults have stopped producing the enzyme lactase, which breaks down the milk sugar lactose. Undigested lactose accumulates in the small intestine and, by osmosis, causes an influx of fluid with accompanying consequences, such as diarrhea. The occurrence of lactose intolerance in human populations varies greatly. It appears that the ability to continue production of lactase beyond infancy has developed in some human populations since dairy farming began, about 10 000 years ago.

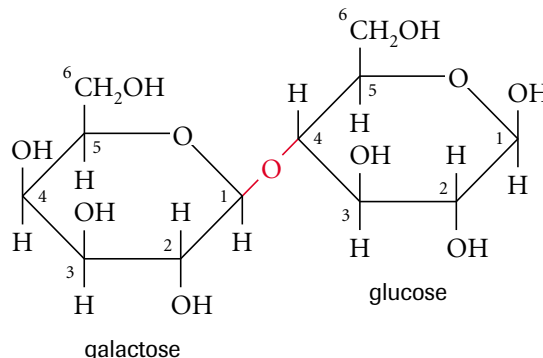
Table 1 Physical Properties of Common Sugars

Sugar	Melting point (°C)	Solubility
glucose	150	extremely soluble (91 g/100 mL at 25°C)
fructose	103–105	very soluble
sucrose	185–186	very soluble
maltose	102	soluble

or “below the ring”. The orientation of the functional groups determines the orientation of any further bonds the molecule forms with other molecules. As we will see later, this orientation affects the shape, and hence the properties, of the polymers of these sugars.

Disaccharide Sugars

When a glucose molecule is joined to a fructose molecule, the dimer formed is a **disaccharide** called sucrose, the common sugar we use in our coffee or on our cereal. All disaccharides, as their name implies, are made of two simple sugar molecules. Lactose, the sugar found in milk, is not as sweet as sucrose. It is also a disaccharide: a dimer of glucose and galactose (which is another isomer of glucose).



When disaccharides are ingested, specific enzymes are required to break the bonds between the monomers. This is a hydrolysis reaction in which the disaccharide is broken down to its component monosaccharides. For example, the enzyme lactase is required in the hydrolysis of lactose, to separate the glucose from the galactose before further digestion can occur. People who lack this enzyme cannot break down this sugar, and are thus “lactose intolerant.”

While many low-molecular-mass organic compounds are gases or volatile liquids at room temperature, sugars are solids with relatively high melting points. You may have heated table sugar in a pan on a stove, to melt it into a thick, sticky liquid, perfect for gluing gingerbread houses or for making peanut brittle. Or you may have melted marshmallows over a campfire. Sugars are also readily soluble in water, as the number of sweet drinks in our refrigerators attests. These two properties—high melting point and solubility in water—are accounted for by the abundance of –OH groups in sugar molecules, allowing for hydrogen bonding both with other sugar molecules and with water molecules (**Table 1**).

Starch for Energy; Cellulose for Support

Starchy foods such as rice, wheat, corn, and potatoes provide us with readily available energy. They are also the main method of energy storage for the plants that produce them, as seeds

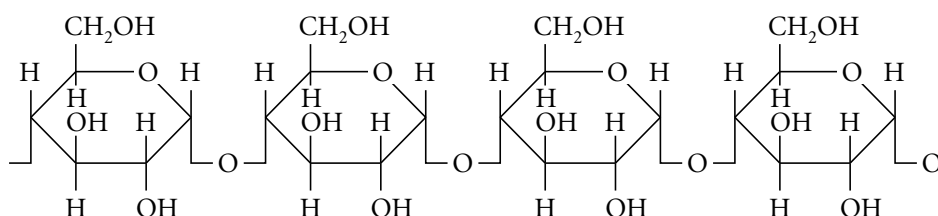
or tubers. **Starches** are polymers of glucose, in either branched or unbranched chains; they are thus **polysaccharides**. Animals also produce a starch-like substance, called **glycogen**, that performs an energy storage function. Glycogen is stored in the muscles as a ready source of energy, and also in the liver, where it helps to regulate the blood glucose level.

We have, in our digestive tracts, very specific enzymes: one that breaks down starch and another that breaks down glycogen. However, the human digestive system does not have an enzyme to break down the other polymer of glucose: **cellulose**. Cellulose is a straight-chain, rigid polysaccharide with glucose–glucose linkages different from those in starch or glycogen. It provides structure and support for plants, some of which tower tens of metres in height. Wood is mainly cellulose; cotton fibres and hemp fibres are also cellulose. Indeed, it is because cellulose is indigestible that whole grains, fruits, and vegetables are good sources of dietary fibre. Herbivores such as cattle, rabbits, termites, and giraffes rely on some friendly help to do their digesting: They have specially developed stomachs and intestines that house enzyme-producing bacteria or protozoa to aid in the breakdown of cellulose.

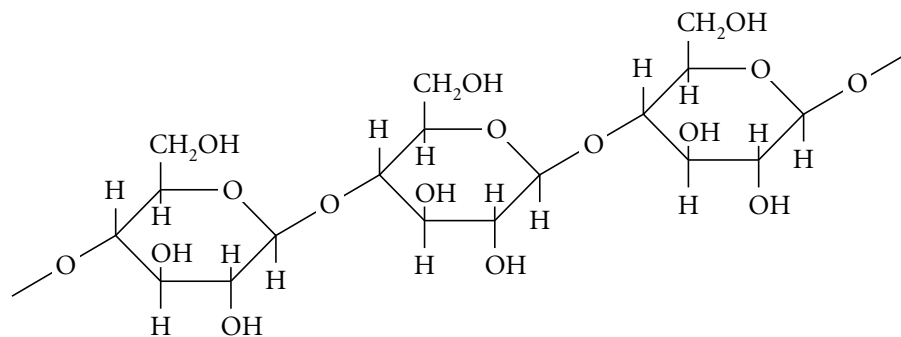
It is the different glucose–glucose linkages that make cellulose different from starch or glycogen. Recall that, when glucose forms a ring structure, the functional groups attached to the ring are fixed in a certain orientation above or below the ring (**Figure 1**). Our enzymes are specific to the orientation of the functional groups, and cannot break the glucose–glucose linkages found in cellulose.

In starch and glycogen, glucose monomers are added at angles that lead to a helical structure, which is maintained by hydrogen bonds between–OH groups on the same polymer chain (**Figure 2(a)**). The single chains are sufficiently small to be soluble in water. Thus, starch and glycogen molecules are both mobile and soluble—important properties in their role as readily available energy storage for the organism.

In cellulose, glucose monomers are added to produce linear polymer chains that can align side by side, favouring interchain hydrogen bonding (**Figure 2(b)**). These interchain links produce a rigid structure of layered sheets of cellulose. This bulky and inflexible structure not only imparts exceptional strength to cellulose, it also renders it insoluble in water. It is, of course, essential for plants that their main building material does not readily dissolve in water.



(a) starch



(b) cellulose

DID YOU KNOW?

The Centre of the Chocolate

Sucrose, a disaccharide, is slightly sweeter than glucose but only half as sweet as fructose. The enzyme sucrase, also called invertase, can break sucrose down into glucose and fructose: a mixture that is sweeter and more soluble than the original sucrose. The centres of some chocolates are made by shaping a solid centre of sucrose and invertase, and coating it with chocolate. Before long, the enzyme transforms the sucrose centre into the sweet syrupy mixture of glucose and fructose.



polysaccharide a polymer composed of monosaccharide monomers

starch a polysaccharide of glucose; produced by plants for energy storage

glycogen a polysaccharide of glucose; produced by animals for energy storage

cellulose a polysaccharide of glucose; produced by plants as a structural material

Figure 2

The difference in linkages between glucose monomers gives very different three-dimensional structures.

- (a) In starch the polymer takes on a tightly coiled helical structure
 (b) In cellulose, the linked monomers can rotate, allowing formation of straight fibres.

DID YOU KNOW?

Prehistoric Polymer

Contrary to popular belief, amber is not a fossil but is a natural polymer formed by the crosslinking of the resin molecules produced by some plants; hence its hard, plastic-like properties. Small insects, lizards, and even frogs have been trapped in the sticky resin (a viscous liquid, generally composed of mixtures of organic acids and esters) that gradually penetrates their bodies and replaces the water in their tissues.



Practice

Understanding Concepts

1. Identify the functional groups present in a molecule of glucose and in a molecule of fructose.
2. Describe several functions of polysaccharides and how these functions are served by their molecular structures,
 - (a) in animals
 - (b) in plants.
3. Compare the following pairs of compounds, referring to their structure and properties:
 - (a) sugars and starch
 - (b) starch and cellulose
4. (a) Draw a structural diagram of the most common configuration of a glucose molecule.
(b) Why does glucose exist in two different forms?
5. Explain in terms of molecular structure why sugars have a relatively high melting point compared with hydrocarbons of comparable size.
6. Discuss why starch molecules are helical and cellulose molecules are linear, given that they are both polymers of glucose. Draw a simple sketch to illustrate your answer.

Section 2.5 Questions

Understanding Concepts

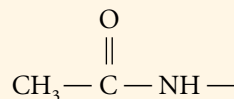
1. Give an example of each of the following:
 - (a) aldose
 - (b) ketose
 - (c) monosaccharide
 - (d) disaccharide
2. Are polysaccharides addition polymers or condensation polymers? Explain.
3. Write a chemical equation, using condensed formulas, to show
 - (a) the hydrolysis of sucrose;
 - (b) the complete combustion of sucrose.
4. Some sugars are referred to as “reducing sugars,” indicating that they will undergo oxidation under suitable conditions. Give an example of a sugar containing an aldehyde functional group and an example of a sugar with a ketone functional group. Which of these two sugars is a reducing sugar?
5. Many organic compounds that we use in the home are gases or volatile liquids, e.g., propane for cooking, rubbing alcohol, and paint remover. However, table sugar is a solid organic compound that is stable enough to store for long periods of time. Identify the functional group(s) in each of the compounds named above, and give reasons for the differences in their physical state and properties.
6. When a starchy food such as boiled potato is chewed in the mouth for a long time, the potato begins to taste sweet, even though no sugar is added.
 - (a) Explain why potatoes taste sweet to us after chewing.
 - (b) Would grass, which is mostly cellulose, taste sweet after chewing?
7. Starch and cellulose have the same caloric value when burned, but very different food values when eaten by humans. Explain.
8. Explain why the sugars in a maple tree dissolve in the sap but the wood in the tree trunk doesn't.

Applying Inquiry Skills

9. From what you have learned about the reactions of aldehydes and ketones, design a test to distinguish an aldose sugar such as glucose from a ketose sugar such as fructose. Include your Experimental Design, a list of the Materials you will need, and a Prediction of the observations you would expect to make for each sugar.

Making Connections

10. Many consumer products are available in natural or synthetic materials: paper or plastic shopping bags, wood or plastic lawn furniture, cotton or polyester clothing. Choose one consumer product and discuss the advantages and disadvantages of the natural and synthetic alternatives, with particular reference to structure and properties of the material used as it relates to the function of the product.
11. Chitin is the main component of the exoskeleton of insects, crabs, lobsters, and other arthropods. It is structurally similar to cellulose, with the sole difference of the substitution of one of the hydroxyl groups on the glucose ring with an acetylated amino group:



- (a) Predict the effect of the acetylated amino group on the attractive forces in the chitin molecule.
- (b) Predict the physical properties of chitin.
- (c) Discuss the suitability of chitin as a protective covering for insects, crabs, and lobsters.