

# Carbohydrates

A **carbohydrate** is a biological molecule consisting of carbon (C), hydrogen (H) and oxygen (O) atoms, usually with a hydrogen–oxygen atom ratio of 2:1 with the empirical formula  $C_m(H_2O)_n$  (where  $m$  could be different from  $n$ ). Carbohydrates are technically hydrates of carbon structurally it is more accurate to view them as polyhydroxy aldehydes and ketones. The saccharides are divided into four chemical groups: monosaccharides, disaccharides, oligosaccharides, and polysaccharides. In general, the monosaccharides and disaccharides, which are smaller (lower molecular weight) carbohydrates, are commonly referred to as sugars.<sup>[6]</sup> The word *saccharide* comes from the Greek word (*sákkharon*), meaning "sugar". While the scientific nomenclature of carbohydrates is complex, the names of the monosaccharides and disaccharides very often end in the suffix -ose.

Carbohydrates perform numerous roles in living organisms. Polysaccharides serve for the storage of energy (e.g. starch and glycogen) and as structural components (e.g. cellulose in plants and chitin in arthropods). The 5-carbon monosaccharide ribose is an important component of coenzymes (e.g. ATP, FAD and NAD) and the backbone of the genetic molecule known as RNA. The related deoxyribose is a component of DNA. Saccharides and their derivatives include many other important biomolecules that play key roles in the immune system, fertilization, preventing pathogenesis, blood clotting, and development.

## Structure

Formerly the name "carbohydrate" was used in chemistry for any compound with the formula  $C_m(H_2O)_n$ . Following this definition, some chemists considered formaldehyde ( $CH_2O$ ) to be the simplest carbohydrate, while others claimed that title for glycolaldehyde.

Natural saccharides are generally built of simple carbohydrates called monosaccharides with general formula  $(CH_2O)_n$  where  $n$  is three or more. A typical monosaccharide has the structure  $H-(CHOH)_x(C=O)-(CHOH)_y-H$ , that is, an aldehyde or ketone with many hydroxyl groups added, usually one on each carbon atom that is not part of the aldehyde or ketone functional group. Examples of monosaccharides are glucose, fructose, and glyceraldehydes. However, some

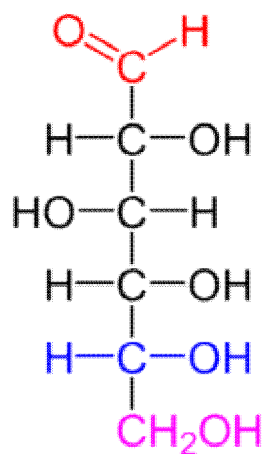
biological substances commonly called "monosaccharides" do not conform to this formula (e.g. uronic acids and deoxy-sugars such as fucose) and there are many chemicals that do conform to this formula but are not considered to be monosaccharides (e.g. formaldehyde  $\text{CH}_2\text{O}$  and inositol  $(\text{CH}_2\text{O})_6$ ).

The open-chain form of a monosaccharide often coexists with a closed ring form where the aldehyde/ketone carbonyl group carbon ( $\text{C}=\text{O}$ ) and hydroxyl group ( $-\text{OH}$ ) react forming a hemiacetal with a new  $\text{C}-\text{O}-\text{C}$  bridge.

Monosaccharides can be linked together into what are called polysaccharides (or oligosaccharides) in a large variety of ways. Many carbohydrates contain one or more modified monosaccharide units that have had one or more groups replaced or removed. For example, deoxyribose, a component of DNA, is a modified version of ribose; chitin is composed of repeating units of N-acetyl glucosamine, a nitrogen-containing form of glucose.

<b>Class</b>	<b>Subgroup</b>	<b>Components</b>
<b>Sugars (1–2)</b>	Monosaccharides	Glucose, galactose, fructose, xylose
	Disaccharides	Sucrose, lactose, maltose, trehalose
	Polyols	Sorbitol, mannitol
<b>Oligosaccharides (3–9)</b>	Malto-oligosaccharides	Maltodextrins
	Other oligosaccharides	Raffinose, stachyose, fructo-oligosaccharides
<b>Polysaccharides (&gt;9)</b>	Starch	Amylose, amylopectin, modified starches
	Non-starch polysaccharides	Cellulose, hemicellulose, pectins, hydrocolloids

## Monosaccharide



D-glucose is an aldohexose with the formula  $(\text{C}\cdot\text{H}_2\text{O})_6$ . The red atoms highlight the aldehyde group and the blue atoms highlight the asymmetric center furthest from the aldehyde; because this -OH is on the right of the Fischer projection, this is a D sugar.

Monosaccharides are the simplest carbohydrates in that they cannot be hydrolyzed to smaller carbohydrates. They are aldehydes or ketones with two or more hydroxyl groups. The general chemical formula of an unmodified monosaccharide is  $(\text{C}\cdot\text{H}_2\text{O})_n$ , literally a "carbon hydrate". Monosaccharides are important fuel molecules as well as building blocks for nucleic acids. The smallest monosaccharides, for which  $n=3$ , are dihydroxyacetone and D- and L-glyceraldehydes.

## Classification of monosaccharides

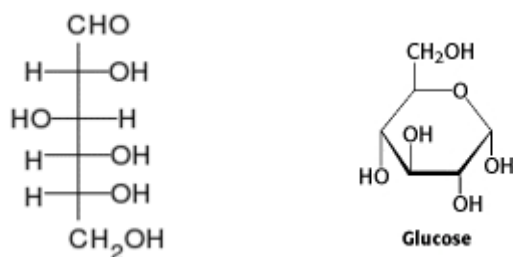


The  $\alpha$  and  $\beta$  anomers of glucose. Note the position of the hydroxyl group (red or green) on the anomeric carbon relative to the  $\text{CH}_2\text{OH}$  group bound to carbon 5: they either have identical absolute configurations (R,R or S,S) ( $\alpha$ ), or opposite absolute configurations (R,S or S,R) ( $\beta$ ).

Monosaccharides are classified according to three different characteristics: the placement of its carbonyl group, the number of carbon atoms it contains, and its chiral handedness. If the carbonyl group is an aldehyde, the monosaccharide is an aldose; if the carbonyl group is a ketone, the monosaccharide is a ketose. Monosaccharides with three carbon atoms are called trioses, those with four are called tetroses, five are called pentoses, six are hexoses, and so on. These two systems of classification are often combined. For example, glucose is an aldohexose (a six-carbon aldehyde), ribose is an aldopentose (a five-carbon aldehyde), and fructose is a ketohexose (a six-carbon ketone).

Each carbon atom bearing a hydroxyl group (-OH), with the exception of the first and last carbons, are asymmetric, making them stereo centers with two possible configurations each (R or S). Because of this asymmetry, a number of isomers may exist for any given monosaccharide formula. Using Le Bel-van't Hoff rule, the aldohexose D-glucose, for example, has the formula  $(C \cdot H_2O)_6$ , of which four of its six carbon atoms are stereogenic, making D-glucose one of  $2^4=16$  possible stereoisomers. In the case of glyceraldehydes, an aldotriose, there is one pair of possible stereoisomers, which are enantiomers and epimers. 1, 3-dihydroxyacetone, the ketose corresponding to the aldose glyceraldehydes, is a symmetric molecule with no stereo centers. The assignment of D or L is made according to the orientation of the asymmetric carbon furthest from the carbonyl group: in a standard Fischer projection if the hydroxyl group is on the right the molecule is a D sugar, otherwise it is an L sugar. The "D-" and "L-" prefixes should not be confused with "d-" or "l-", which indicate the direction that the sugar rotates plane polarized light. This usage of "d-" and "l-" is no longer followed in carbohydrate chemistry.<sup>[16]</sup>

### Ring-straight chain isomerism



Glucose can exist in both a straight-chain and ring form.

The aldehyde or ketone group of a straight-chain monosaccharide will react reversibly with a hydroxyl group on a different carbon atom to form a hemiacetal or hemiketal, forming a heterocyclic ring with an oxygen bridge between two carbon atoms. Rings with five and six atoms are called furanose and pyranose forms, respectively, and exist in equilibrium with the straight-chain form.

During the conversion from straight-chain form to the cyclic form, the carbon atom containing the carbonyl oxygen, called the anomeric carbon, becomes a stereogenic center with two possible configurations: The oxygen atom may take a position either above or below the plane of the ring. The resulting possible pair of stereoisomers is called anomers. In the  $\alpha$  anomer, the -OH substituent on the anomeric carbon rests on the opposite side (trans) of the ring from the CH<sub>2</sub>OH side branch. The alternative form, in which the CH<sub>2</sub>OH substituent and the anomeric hydroxyl are on the same side (cis) of the plane of the ring, is called the  $\beta$  anomer.

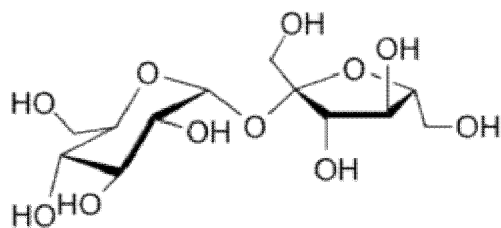
## Functions of monosaccharides

Monosaccharides are the major source of fuel for metabolism, being used both as an energy source (glucose being the most important in nature) and in biosynthesis. When monosaccharides are not immediately needed by many cells they are often converted to more space-efficient forms, often polysaccharides. In many animals, including humans, this storage form is glycogen, especially in liver and muscle cells. In plants, starch is used for the same purpose. The most abundant carbohydrate, cellulose, is a structural component of the cell wall of plants and many forms of algae. Ribose is a component of RNA. Deoxyribose is a component of DNA. Lyxose is a component of lyxoflavin found in the human heart.<sup>[18]</sup> Ribulose and xylulose occur in the pentose phosphate pathway. Galactose, a component of milk sugar lactose, is found in galactolipids in plant cell membranes and in glycoproteins in many tissues. Mannose occurs in human metabolism, especially in the glycosylation of certain proteins. Fructose, or fruit sugar, is found in many plants and in humans, it is metabolized in the liver, absorbed directly into the intestines during digestion, and found in semen. Trehalose, a major sugar of insects, is rapidly hydrolyzed into two glucose molecules to support continuous flight.

## Disaccharides

### Sucrose

Sucrose, also known as table sugar, is a common disaccharide. It is composed of two monosaccharides: D-glucose (left) and D-fructose (right).



Two joined monosaccharides are called a disaccharide and these are the simplest polysaccharides. Examples include sucrose and lactose. They are composed of two monosaccharide units bound together by a covalent bond known as a glycosidic linkage formed via a dehydration reaction, resulting in the loss of a hydrogen atom from one monosaccharide and a hydroxyl group from the other. The formula of unmodified disaccharides is  $C_{12}H_{22}O_{11}$ . Sucrose is the most abundant disaccharide, and the main form in which carbohydrates are transported in plants. It is composed of one D-glucose molecule and one D-fructose molecule. The systematic name for sucrose, *O*- $\alpha$ -D-glucopyranosyl-(1 $\rightarrow$ 2)-D-fructofuranoside, indicates four things:

- Its monosaccharides: glucose and fructose
- Their ring types: glucose is a pyranose and fructose is a furanose
- How they are linked together: the oxygen on carbon number 1 (C1) of  $\alpha$ -D-glucose is linked to the C2 of D-fructose.
- The *-oside* suffix indicates that the anomeric carbon of both monosaccharides participates in the glycosidic bond

## Lactose,

Lactose, a disaccharide composed of one D-galactose molecule and one D-glucose molecule, occurs naturally in mammalian milk. The systematic name for lactose is *O*- $\beta$ -D-galactopyranosyl-(1 $\rightarrow$ 4)-D-glucopyranose. Other notable disaccharides include maltose (two D-glucoses linked  $\alpha$ -1,4) and cellobiose (two D-glucoses linked  $\beta$ -1,4). Disaccharides can be classified into two types: reducing and non-reducing disaccharides. If the functional group is present in bonding with another sugar unit, it is called a reducing disaccharide or biose.

## Polysaccharide

**Polysaccharides** are polymeric carbohydrate molecules composed of long chains of monosaccharide units bound together by glycosidic linkages and on hydrolysis give the constituent monosaccharides or oligosaccharides. They range in structure from linear to highly branched. Examples include storage polysaccharides such as starch and glycogen, and structural polysaccharides such as cellulose and chitin.

Polysaccharides are often quite heterogeneous, containing slight modifications of the repeating unit. Depending on the structure, these macromolecules can have distinct properties from their monosaccharide building blocks. They may be amorphous or even insoluble in water.<sup>[1]</sup> When all the monosaccharides in a polysaccharide are the same type, the polysaccharide is called a *homopolysaccharide* or *homoglycan*, but when more than one type of monosaccharide is present they are called *heteropolysaccharides* or *heteroglycans*.

Natural saccharides are generally of simple carbohydrates called monosaccharides with general formula  $(\text{CH}_2\text{O})_n$  where  $n$  is three or more. Examples of monosaccharides are glucose, fructose, and glyceraldehyde.<sup>[4]</sup> Polysaccharides, meanwhile, have a general formula of  $\text{C}_x(\text{H}_2\text{O})_y$  where  $x$  is usually a large number between 200 and 2500. When the repeating units in the polymer backbone are six-carbon monosaccharides, as is often the case, the general formula simplifies to  $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ , where typically  $40 \leq n \leq 3000$ .

As a rule of thumb, polysaccharides contain more than ten monosaccharide units, whereas oligosaccharides contain three through ten monosaccharide units; but the precise cutoff varies

somewhat according to convention. Polysaccharides are an important class of biological polymers. Their function in living organisms is usually either structure- or storage-related. Starch (a polymer of glucose) is used as a storage polysaccharide in plants, being found in the form of both amylose and the branched amylopectin. In animals, the structurally similar glucose polymer is the more densely branched glycogen, sometimes called 'animal starch'. Glycogen's properties allow it to be metabolized more quickly, which suits the active lives of moving animals.

Cellulose and chitin are examples of structural polysaccharides. Cellulose is used in the cell walls of plants and other organisms, and is said to be the most abundant organic molecule on Earth. It has many uses such as a significant role in the paper and textile industries, and is used as a feedstock for the production of rayon (via the viscose process), cellulose acetate, celluloid, and nitrocellulose. Chitin has a similar structure, but has nitrogen-containing side branches, increasing its strength. It is found in arthropod exoskeletons and in the cell walls of some fungi. It also has multiple uses, including surgical threads. Polysaccharides also include callose or laminarin, chrysolaminarin, xylan, arabinoxylan, mannan, fucoidan and galactomannan.

## **Function**

Nutrition polysaccharides are common sources of energy. Many organisms can easily break down starches into glucose; however, most organisms cannot metabolize cellulose or other polysaccharides like chitin and arabinoxylans. These carbohydrate types can be metabolized by some bacteria and protists. Ruminants and termites, for example, use microorganisms to process cellulose. Even though these complex carbohydrates are not very digestible, they provide important dietary elements for humans. Called dietary fiber, these carbohydrates enhance digestion among other benefits. The main action of dietary fiber is to change the nature of the contents of the gastrointestinal tract, and to change how other nutrients and chemicals are absorbed. Soluble fiber binds to bile acids in the small intestine, making them less likely to enter the body; this in turn lowers cholesterol levels in the blood.<sup>[8]</sup> Soluble fiber also attenuates the absorption of sugar, reduces sugar response after eating, normalizes blood lipid levels and, once fermented in the colon, produces short-chain fatty acids as byproducts with wide-ranging physiological activities. Although insoluble fiber is associated with reduced diabetes risk, the mechanism by which this occurs is unknown



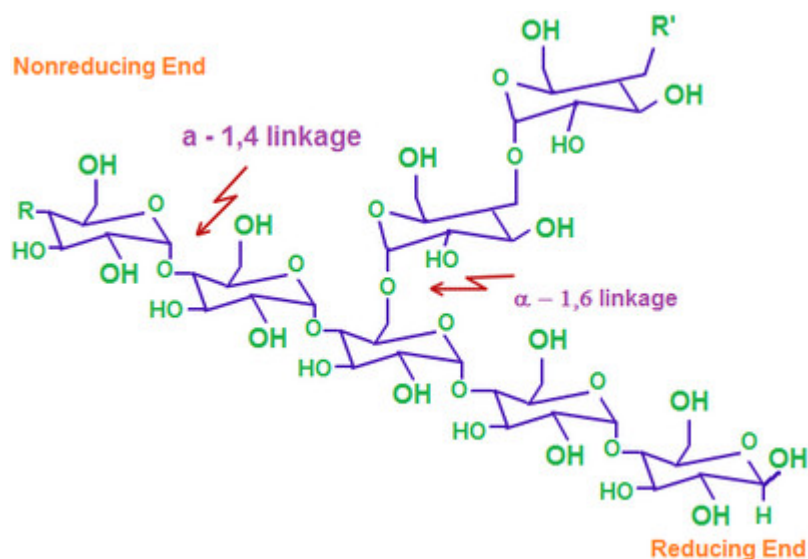
## Storage polysaccharides

### Starch

Starch is a glucose polymer in which glucopyranose units are bonded by *alpha*-linkages. It is made up of a mixture of amylose (15–20%) and amylopectin (80–85%). Amylose consists of a linear chain of several hundred glucose molecules and Amylopectin is a branched molecule made of several thousand glucose units (every chain of 24–30 glucose units is one unit of Amylopectin). Starches are insoluble in water. They can be digested which can break the *alpha*-linkages (glycosidic bonds). Both humans and animals have amylases, so they can digest starches. Potato, rice, wheat, and maize are major sources of starch in the human diet. The formations of starches are the ways that plants store glucose. .

### Glycogen

Glycogen serves as the secondary long-term energy storage in animal and fungal cells, with the primary energy stores being held in adipose tissue. Glycogen is made primarily by the liver and the muscles, but can also be made by glycogenesis within the brain and stomach.



Glycogen is the analogue of starch, a glucose polymer in plants, and is sometimes referred to as *animal starch*, having a similar structure to amylopectin but more extensively branched and

compact than starch. Glycogen is a polymer of  $\alpha(1\rightarrow4)$  glycosidic bonds linked, with  $\alpha(1\rightarrow6)$ -linked branches. Glycogen is found in the form of granules in the cytosol/cytoplasm in many cell types, and plays an important role in the glucose cycle. Glycogen forms an energy reserve that can be quickly mobilized to meet a sudden need for glucose, but one that is less compact and more immediately available as an energy reserve than triglycerides (lipids).

In the liver hepatocytes, glycogen can compose up to eight percent (100–120 g in an adult) of the fresh weight soon after a meal.<sup>[14]</sup> Only the glycogen stored in the liver can be made accessible to other organs. In the muscles, glycogen is found in a low concentration of one to two percent of the muscle mass. The amount of glycogen stored in the body—especially within the muscles, liver, and red blood cells varies with physical activity, basal metabolic rate, and eating habits such as intermittent fasting. Small amounts of glycogen are found in the kidneys, and even smaller amounts in certain glial cells in the brain and white blood cells. The uterus also stores glycogen during pregnancy, to nourish the embryo.<sup>[14]</sup>

Glycogen is composed of a branched chain of glucose residues. It is stored in liver and muscles.

- It is an energy reserve for animals.
- It is the chief form of carbohydrate stored in animal body.
- It is insoluble in water. It turns brown-red when mixed with iodine.
- It also yields glucose on hydrolysis.

## Structural polysaccharides

### Cellulose

The structural component of plants are formed primarily from cellulose. Wood is largely cellulose and lignin, while paper and cotton are nearly pure cellulose. Cellulose is a polymer made with repeated glucose units bonded together by *beta*-linkages. Humans and many animals lack an enzyme to break the *beta*-linkages, so they do not digest cellulose. Certain animals such as termites can digest cellulose, because bacteria possessing the enzyme are present in their gut.

Cellulose is insoluble in water. It does not change color when mixed with iodine. On hydrolysis, it yields glucose. It is the most abundant carbohydrate in nature.

### **Chitin**

Chitin is one of many naturally occurring polymers. It forms a structural component of many animals, such as exoskeletons. Over time it is bio-degradable in the natural environment. Its breakdown may be catalyzed by enzymes called chitinases, secreted by microorganisms such as bacteria and fungi, and produced by some plants. Some of these microorganisms have receptors to simple sugars from the decomposition of chitin. If chitin is detected, they then produce enzymes to digest it by cleaving the glycosidic bonds in order to convert it to simple sugars and ammonia.

### **Pectins**

Pectins are a family of complex polysaccharides that contain 1,4-linked  $\alpha$ -D-galactosyl uronic acid residues. They are present in most primary cell walls and in the non-woody parts of terrestrial plants.

of insulin in the blood plasma (e.g. after meals) cause the dephosphorylation of acetyl-CoA carboxylase, thus promoting the formation of malonyl-CoA from acetyl-CoA, and consequently the conversion of carbohydrates into fatty acids, while epinephrine and glucagon (released into the blood during starvation and exercise) cause the phosphorylation of this enzyme, inhibiting lipogenesis in favor of fatty acid oxidation via beta-oxidation.