

# ORGANIC CHEMISTRY

## Structure and Function

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FIFTH EDITION

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#### ABOUT THE COVER

Taxol, a brand name for the generic drug paclitaxel, emerged through years of setbacks and controversy to become, by the end of the twentieth century, the best-selling anticancer drug in the world, saving and improving the quality of countless thousands of lives. The front cover shows a model of the three-dimensional structure of the molecule, superimposed on a picture of the magnificent Pacific yew tree, from the bark of which the first samples of Taxol were isolated. During the last decade, the medicinal importance of this molecule enticed several research groups to tackle its total synthesis, applying new synthetic methodologies and strategies to assemble its complicated structure. First, in what turned out to be a veritable race, were the teams of K. C. Nicolaou at The Scripps Research Institute and the University of California, San Diego (who provided the idea for the cover picture), and R. A. Holton at Florida State University (in 1994). These syntheses were followed by those of S. J. Danishefsky (Sloan-Kettering Institute for Cancer Research and Columbia University), P. A. Wender (Stanford University), T. Mukaiyama (Science University of Tokyo), and I. Kuwajima (Tokyo Institute of Technology), each featuring its own unique approach. Synthetic strategies used to construct complex molecules are discussed in Chapter 8 and subsequently throughout the text. The biological and medicinal context of organic molecules is addressed in many Chemical Highlights, in the general text (for example p. 152 for Taxol), and in numerous problems.

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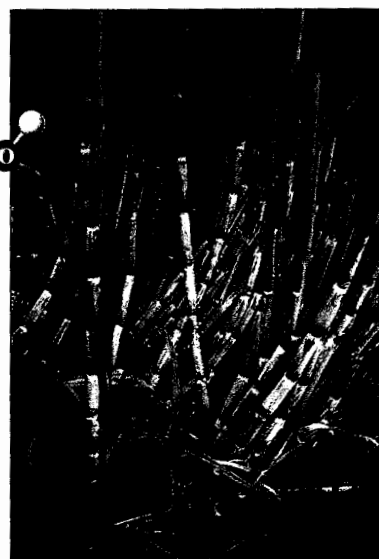
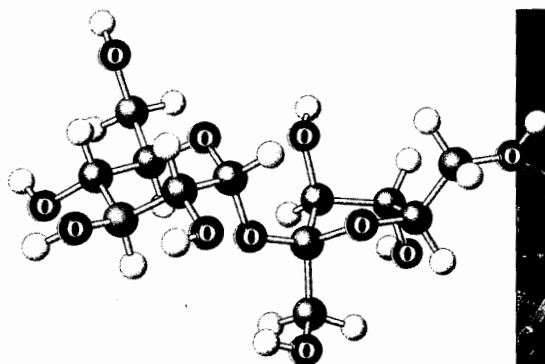
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# CARBOHYDRATES

## Polyfunctional Compounds in Nature

# 24



In everyday life, when we say the word "sugar" we usually refer to sucrose, the most widely occurring disaccharide in nature. Obtained from sugar beet and sugar cane (illustrated here), sucrose is prepared commercially in pure form in greater quantities than any other chemical substance.

**T**ake a piece of bread and place it in your mouth. After a few minutes it will begin to taste distinctly sweet, as if you had added sugar to it. Indeed, in a way, this is what happened. The acid and enzymes in your saliva have cleaved the starch in the bread into its component units: glucose molecules. You all know glucose as dextrose or grape sugar. The polymer, starch, and its monomer, glucose, are two examples of carbohydrates.

Carbohydrates are most familiar to us as major contributors to our daily diets, in the form of sugars, fibers, and starches, such as bread, rice, and potatoes. In this capacity, they function as chemical energy-storage systems, being metabolized to water, carbon dioxide, and heat or other energy. Members of this class of compounds give structure to plants, flowers, vegetables, and trees. They also serve as building units of fats (Sections 19-13 and 20-5) and nucleic acids (Section 26-9). All are considered to be **polyfunctional**, because they possess multiple functional groups. Glucose,  $C_6(H_2O)_6$ , and many related simple members of this compound class form the building blocks of the complex carbohydrates and have the empirical formulas  $C_n(H_2O)_n$ , essentially hydrated carbon.

1096

We shall first consider the structure and naming of the simplest carbohydrates—the sugars. We then turn our attention to their chemistry, which is governed by the presence of carbonyl and hydroxy functions along carbon chains of various lengths. We have already seen an example of the biosynthesis of carbohydrates (Chemical Highlight 18-1). Here we examine several methods for sugar synthesis and structural analysis. Finally, we describe a sampling of the many types of carbohydrates found in nature.

## 24-1 Names and Structures of Carbohydrates

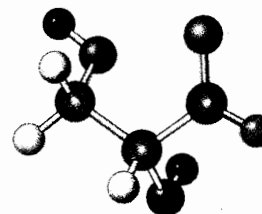
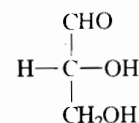
The simplest carbohydrates are the sugars, or **saccharides**. As chain length increases, the increasing number of stereocenters gives rise to a multitude of diastereomers. Fortunately for chemists, nature deals mainly with only one of the possible series of enantiomers. Sugars are polyhydroxycarbonyl compounds and many form stable cyclic hemiacetals, which affords additional structural and chemical variety.

### Sugars are classified as aldoses and ketoses

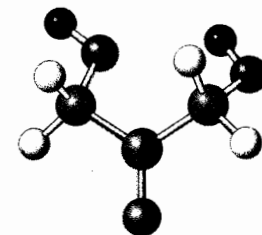
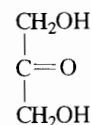
**Carbohydrate** is the general name for the monomeric (monosaccharides), dimeric (disaccharides), trimeric (trisaccharides), oligomeric (oligosaccharides), and polymeric (polysaccharides) forms of sugar (*saccharum*, Latin, sugar). A **monosaccharide**, or **simple sugar**, is an aldehyde or ketone containing at least two additional hydroxy groups. Thus, the two simplest members of this class of compounds are 2,3-dihydroxypropanal (glyceraldehyde) and 1,3-dihydroxyacetone. **Complex sugars** (Section 24-11) are those formed by the linkage of simple sugars through ether bridges.

Aldehydic sugars are classified as **aldoses**; those with a ketone function are called **ketoses**. On the basis of their chain length, we call sugars **trioses** (three carbons), **tetroses** (four carbons), **pentoses** (five carbons), **hexoses** (six carbons), and so on. Therefore, 2,3-dihydroxypropanal (glyceraldehyde) is an aldotriose, whereas 1,3-dihydroxyacetone is a ketotriose.

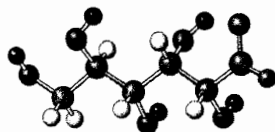
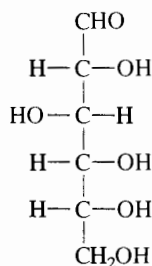
**Glucose**, also known as dextrose, blood sugar, or grape sugar (*glykys*, Greek, sweet), is a pentahydroxyhexanal and hence belongs to the class of aldohexoses. It occurs naturally in many fruits and plants and in concentrations ranging from 0.08 to 0.1% in human blood. A corresponding isomeric ketohexose is **fructose**, the sweetest natural sugar (some synthetic sugars are sweeter), which also is present in many fruits (*fructus*, Latin, fruit) and in honey. Another important natural sugar is the aldopentose **ribose**, a building block of the ribonucleic acids (Section 26-9).



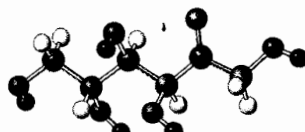
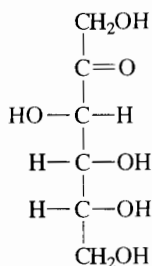
2,3-Dihydroxy propanal  
(Glyceraldehyde)  
(An aldotriose)



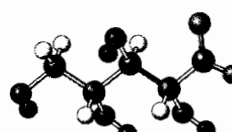
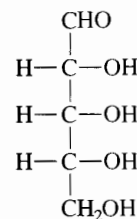
1,3-Dihydroxy acetone  
(A ketotriose)



Glucose  
(An aldohexose)



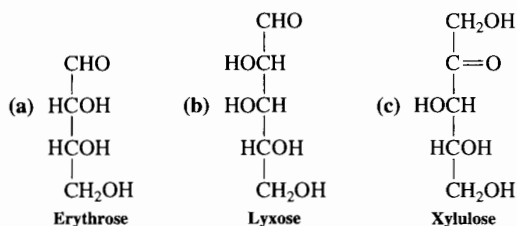
Fructose  
(A ketohexose)



Ribose  
(An aldopentose)

## EXERCISE 24-1

To which classes of sugars do the following monosaccharides belong?



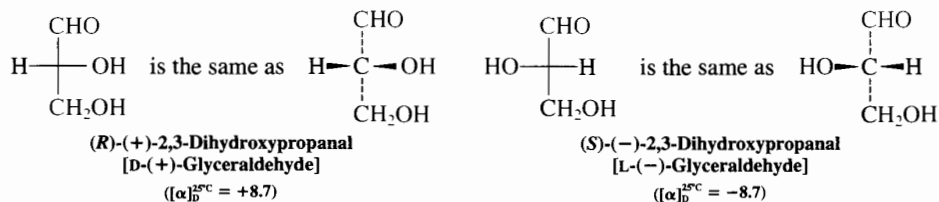
A **disaccharide** is derived from two monosaccharides by the formation of an ether (usually, acetal) bridge (Section 17-7). Hydrolysis regenerates the monosaccharides. Ether formation between a mono- and a disaccharide results in a trisaccharide, and repetition of this process eventually produces a natural polymer (polysaccharide). Polysaccharides constitute the framework of cellulose and starch (Section 24-12).

### Most sugars are chiral and optically active

With the exception of 1,3-dihydroxyacetone, all the sugars mentioned so far contain at least one stereocenter. The simplest chiral sugar is 2,3-dihydroxypropanal (glyceraldehyde), with one asymmetric carbon. Its dextrorotatory form is found to be *R* and the levorotatory enantiomer *S*, as shown in the Fischer projections of the molecule. Recall that, by convention, the horizontal lines in Fischer projections represent bonds to atoms *above the plane of the page* (Section 5-4).



### Fischer Projections of the Two Enantiomers of 2,3-Dihydroxypropanal (Glyceraldehyde)



Even though *R* and *S* nomenclature is perfectly satisfactory for naming sugars, an older system is still in general use. It was developed before the absolute configuration of sugars was established, and it relates all sugars to 2,3-dihydroxypropanal (glyceraldehyde). Instead of *R* and *S*, it uses the prefixes *D* for the (+) enantiomer of glyceraldehyde and *L* for the (-) enantiomer (Chemical Highlight 5-2). Those monosaccharides whose *highest-numbered stereocenter* (i.e., the one farthest from the aldehyde or keto group) has the same absolute configuration as that of D-(+)-2,3-dihydroxypropanal [D-(+)-glyceraldehyde] are then labeled *D*; those with the opposite configuration at that stereocenter are named *L*. Two diastereomers that differ *only at one stereocenter* are also called **epimers**.



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