

ORGANIC CHEMISTRY

Structure and Function

FIFTH EDITION

K. PETER C. VOLLHARDT
University of California at Berkeley

NEIL E. SCHORE
University of California at Davis

 W. H. FREEMAN AND COMPANY
New York

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.

Publishers: Susan Finnemore Brennan, Craig Bleyer
Senior Acquisitions Editor: Clancy Marshall
Senior Marketing Manager: Krista Bettino
Developmental Editor: David Chelton
Media Editor: Victoria Anderson
Associate Editor: Amy Thorne
Photo Editor: Cecilia Varas
Photo Researcher: Elyse Reider
Cover Designer: Cambraia Fernandes
Text Designer: Blake Logan
Project Editor: TechBooks
Illustrations: Network Graphics
Illustration Coordinator: Bill Page
Production Coordinator: Susan Wein
Composition: TechBooks
Printing and Binding: RR Donnelley

Library of Congress Cataloging-in-Publication Data

Vollhardt, K. Peter C.
Organic chemistry : structure and function.— 5th ed. / K. Peter C. Vollhardt, Neil E. Schore.
p. cm.
Includes index.
ISBN-13: 978-0-7167-9949-8
ISBN-10: 0-7167-9949-9
1. Chemistry, Organic—Textbooks. I. Schore, Neil Eric, 1948– II. Title.
QD251.3.V65 2007
547—dc22

2005025107

©2007

All rights reserved

Printed in the United States of America

Third printing

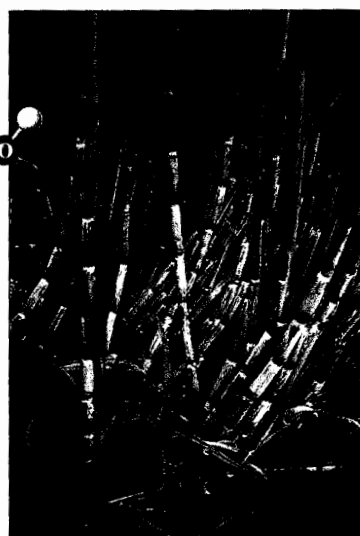
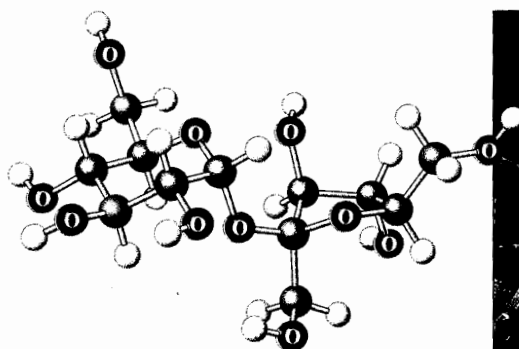
W. H. Freeman and Company
41 Madison Avenue
New York, NY 10010
Houndmills, Basingstoke RG21 6XS, England

www.whfreeman.com

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.

Take 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

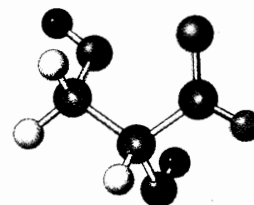
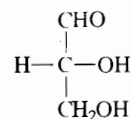
The simplest carbohydrates are the sugars, or **saccharides**. As chain length increases, the increasing number of stereocenters gives rise to a multitude of diastereomers. Fortunately for chemists, nature deals mainly with only one of the possible series of enantiomers. Sugars are polyhydroxycarbonyl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

Sugars are classified as aldoses and ketoses

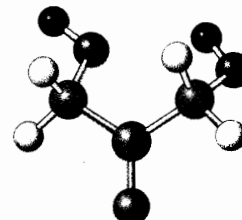
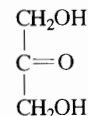
Carbohydrate is the general name for the monomeric (monosaccharides), dimeric (disaccharides), trimeric (trisaccharides), oligomeric (oligosaccharides), and polymeric (polysaccharides) forms of sugar (*saccharum*, Latin, sugar). A **monosaccharide**, or **simple sugar**, is an aldehyde or ketone containing 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.

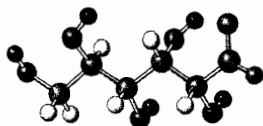
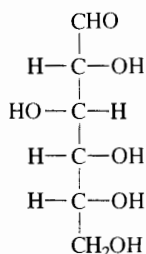
Glucose, also known as dextrose, blood sugar, or grape sugar (*glykys*, Greek, sweet), is a pentahydroxyhexanal and hence belongs to the class of aldohexoses. It occurs naturally in many fruits and plants and in concentrations ranging from 0.08 to 0.1% in human blood. A corresponding isomeric ketohexose 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).



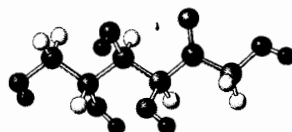
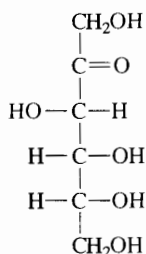
2,3-Dihydroxypropanal
(Glyceraldehyde)
(An aldotriose)



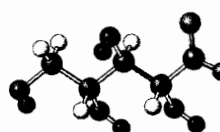
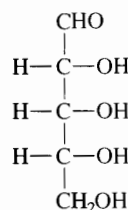
1,3-Dihydroxyacetone
(A ketotriose)



Glucose
(An aldohexose)



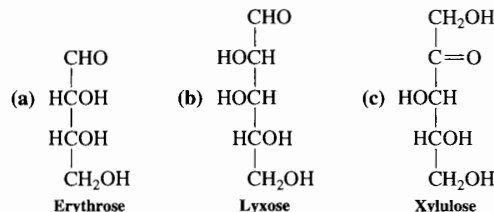
Fructose
(A ketohexose)



Ribose
(An aldopentose)

EXERCISE 24-1

To which classes of sugars do the following monosaccharides belong?



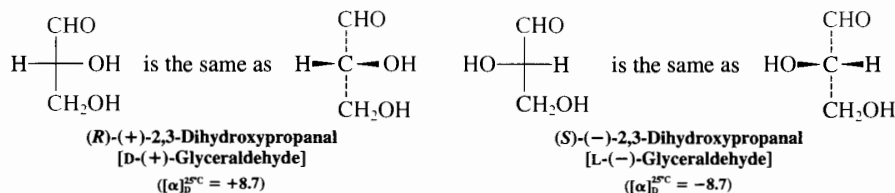
A **disaccharide** is derived from two monosaccharides by the formation of an ether (usually, acetal) bridge (Section 17-7). Hydrolysis regenerates the monosaccharides. Ether formation between a mono- and a disaccharide results in a trisaccharide, and repetition of this process eventually produces a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

Explore Litigation Insights

Docket Alarm provides insights to develop a more informed litigation strategy and the peace of mind of knowing you're on top of things.

Real-Time Litigation Alerts



Keep your litigation team up-to-date with **real-time alerts** and advanced team management tools built for the enterprise, all while greatly reducing PACER spend.

Our comprehensive service means we can handle Federal, State, and Administrative courts across the country.

Advanced Docket Research



With over 230 million records, Docket Alarm's cloud-native docket research platform finds what other services can't. Coverage includes Federal, State, plus PTAB, TTAB, ITC and NLRB decisions, all in one place.

Identify arguments that have been successful in the past with full text, pinpoint searching. Link to case law cited within any court document via Fastcase.

Analytics At Your Fingertips



Learn what happened the last time a particular judge, opposing counsel or company faced cases similar to yours.

Advanced out-of-the-box PTAB and TTAB analytics are always at your fingertips.

API

Docket Alarm offers a powerful API (application programming interface) to developers that want to integrate case filings into their apps.

LAW FIRMS

Build custom dashboards for your attorneys and clients with live data direct from the court.

Automate many repetitive legal tasks like conflict checks, document management, and marketing.

FINANCIAL INSTITUTIONS

Litigation and bankruptcy checks for companies and debtors.

E-DISCOVERY AND LEGAL VENDORS

Sync your system to PACER to automate legal marketing.