THE BIOCHEMISTRY OF PLANTS

A COMPREHENSIVE TREATISE

Volume 3

Carbohydrates: Structure and Function

Jack Preiss, editor

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Carbohydrates: Structure and Function

Jack Preiss, editor

Department of Biochemistry and Biophysics
University of California
Davis, California

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List of Contributors

Numbers in parentheses indicate the pages on which the authors' contributions begin.

Takashi Akazawa (199), Research Institute for Biochemical Regulation, School of Agriculture, Nagoya University, Chikusa, Nagoya 464, Japan

T. ap Rees (1), University of Cambridge Botany School, Cambridge CB2 3EA, England

Gerald O. Aspinall (473), Department of Chemistry, York University, Toronto, Ontario M3J 1P3, Canada

Gad Avigad (101), Department of Biochemistry, CMDNJ-Rutgers Medical School, Piscataway, New Jersey 08854

W. Banks (321), Hannah Research Institute, Ayr KA6 5HL, Scotland

David A. Brant (425), Department of Chemistry, University of California, Irvine, California 92717

J. Ross Colvin (543), Division of Biological Sciences, National Research Council, Ottawa K1A OR6, Canada

Alan D. Elbein (571, 589), Department of Biochemistry, University of Texas Health Science Center, San Antonio, Texas

Mary C. Ericson (589), Department of Biochemistry, University of California, Davis, California 95618

David Sidney Feingold (101), Department of Microbiology, School of Medicine, University of Pittsburgh, Pittsburgh, Pennsylvania 15261

Robert T. Giaquinta (271), E. I. Du Pont de Nemours and Company, Central Research and Development Department, Experimental Station, Wilmington, Delaware 19898

Hans Grisebach (171), Institut für Biologie II der Universität Freiburg, D-7800 Freiburg i. Br., Germany

Herbert Hopf (221), Botanisches Institut der Universität München, München, Federal Republic of Germany
Otto Kandler (221), Botanisches Institut der Universität, München, München, Federal Republic of Germany
Derek T. A. Lamport (501), MSU/D.O.E. Plant Research Laboratory, Michigan State University, East Lansing, Michigan 48824
Carolyn Levi* (371), Plant Growth Laboratory, University of California, Davis, California 95616
Frank A. Loewus (43, 77), Department of Agricultural Chemistry, Washington State University, Pullman, Washington 99164
Mary W. Loewus (43), Department of Agricultural Chemistry, Washington State University, Pullman, Washington 99164
D. D. Muir (321), Applied Studies Department, Hannah Research Institute, Ayr KA6 5HL, Scotland
Kazuo Okamoto (199), Research Institute for Biochemical Regulation, School of Agriculture, Nagoya University, Chikusa, Nagoya 464 Japan
Jack Preiss (371), Department of Biochemistry and Biophysics, University of California, Davis, California 95616

* Present address: Department of Brewing and Biological Sciences, Heriot-Watt University, Edinburgh EH1 1HX, Scotland.

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General Preface

In 1950, James Bonner wrote the following prophetic comments in the Preface of the first edition of his "Plant Biochemistry" published by Academic Press:

> There is much work to be done in plant biochemistry. Our understanding of many basic metabolic pathways in the higher plant is lamentably fragmentary. While the emphasis in this book is on the higher plant, it will frequently be necessary to call attention to conclusions drawn from work with microorganisms or with higher animals. Numerous problems of plant biochemistry could undoubtedly be illuminated by the closer application of the information and the techniques which have been developed by those working with other organisms . . .
>
> Certain important aspects of biochemistry have been entirely omitted from the present volume simply because of the lack of pertinent information from the domain of higher plants.

The volume had 30 chapters and a total of 490 pages. Many of the biochemical examples cited in the text were derived from studies on bacterial, fungal, and animal systems. Despite these shortcomings, the book had a profound effect on a number of young biochemists since it challenged them to enter the field of plant biochemistry and to correct "the lack of pertinent information from the domain of higher plants."

Since 1950, an explosive expansion of knowledge in biochemistry has occurred. Unfortunately, the study of plants has had a mixed reception in the biochemical community. With the exception of photosynthesis, biochemists have avoided tackling for one reason or another the incredibly interesting problems associated with plant tissues. Leading biochemical journals have frequently rejected sound manuscripts for the trivial reason that the reaction had been well described in *E. coli* and liver tissue and thus was of little interest to again describe its presence in germinating pea seeds! Federal granting agencies, the National Science Foundation excepted, have

also been reluctant to fund applications when it was indicated that the principal experimental tissue would be of plant origin despite the fact that the most prevalent illness in the world is starvation.

The second edition of "Plant Biochemistry" had a new format in 1965 when J. Bonner and J. Varner edited a multiauthored volume of 979 pages; in 1976, the third edition containing 908 pages made its appearance. A few textbooks of limited size in plant biochemistry have been published. In addition, two continuing series resulting from the annual meetings and symposia of phytochemical organizations in Europe and in North America provided the biological community with highly specialized articles on many topics of plant biochemistry. Plant biochemistry was obviously growing.

Although these publications serve a useful purpose, no multivolume series in plant biochemistry has been available to the biochemist trained and working in different fields who seeks an authoritative overview of major topics of plant biochemistry. It therefore seemed to us that the time was ripe to develop such a series. With encouragement and cooperation of Academic Press, we invited six colleagues to join us in organizing an eight volume series to be known as "The Biochemistry of Plants: A Comprehensive Treatise." Within a few months, we were able to invite over 160 authors to write authoritative chapters for these eight volumes.

Our hope is that this Treatise not only will serve as a source of current information to researchers working in plant biochemistry, but equally important will provide a mechanism for the molecular biologist who works with *E. coli* or the neurobiochemist to become better informed about the interesting and often unique problems which the plant cell provides. It is hoped, too, the senior graduate student will be inspired by one or more comments in chapters of this Treatise and will orient his future career to some aspect of this science.

Despite the fact that many subjects have been covered in this Treatise, we make no claim to have been complete in our coverage nor to have treated all subjects in equal depth. Notable is the absence of volumes on phytohormones and on mineral nutrition. These areas, which are more closely associated with the discipline of plant physiology, are treated in multivolume series in the physiology literature and/or have been the subject of specialized treatises. Other topics (e.g., alkaloids, nitrogen fixation, flavonoids, plant pigments) have been assigned single chapters even though entire volumes, sometimes appearing on an annual basis, are available.

Finally, we wish to thank all our colleagues for their enthusiastic cooperation in bringing these eight volumes so rapidly into fruition. We are grateful to Academic Press for their gentle persuasive pressures and we are indebted to Ms. Barbara Clover and Ms. Billie Gabriel for their talented assistance in this project.

P. K. Stumpf
E. E. Conn

Preface to Volume 3

The vast expansion of information in the area of plant carbohydrates in the past decade makes it an opportune time to integrate and relate their many facets of chemistry, biochemistry, and physiology. This is the objective of this volume.

The volume is organized in three sections. The first deals with topics concerning the monosaccharides and their derivatives found in plants. Thus, the integration and control of the well-known and the vital pathways concerned with hexose phosphate metabolism, glycolysis, gluconeogenesis, and the pentose phosphate pathways are discussed first. The metabolism of monosaccharide derivatives, *myo*-inositol and L-ascorbic acid, important plant components, are treated in Chapters 2 and 3, respectively, while Chapter 4 deals with formation of sugar nucleotides and their various transformations to the many novel sugar derivatives normally found in plant cell walls and complex carbohydrates. Since the original discovery of Luis Leloir and his colleagues of UDP-glucose in yeast in 1950, more than 35 sugar nucleotides have been found in plant sources, and much information about their biosynthesis has accrued. Chapter 5 describes biosynthesis and occurrence of the branched-chain sugars, apiose and hamamelose, that are unique to plants and concludes the discussion of plant monosaccharides.

The second section of the volume, Chapters 6, 7, and 8, deal with the occurrence, biosynthesis, and transport of disaccharides and oligosaccharides. While significant information is currently known about sucrose and various plant oligosaccharides there is still much to learn about their precise function in plants and about the detailed biochemical mechanism of active transport of these sugars to the various parts of the plant. It is hoped these chapters, presenting the state of the art, will stimulate further interest in these vital areas.

The third and final section of the volume is concerned with the occurrence, structure, and biosynthesis of simple and complex polysaccharides and glycoconjugates associated with cell walls and membranes. Ever since the initial discovery of starch in leaf by Sachs at the end of the nineteenth century, the chemistry, structure, and function of this polymer has been of great interest to chemists, biochemists, and plant physiologists. Chapters 9 and 10 deal with the literature describing the current notions and theories concerning structure and regulation of biosynthesis and degradation and their relation to plant development.

Recently there has been a great increase of interest in the three-dimensional shape of polysaccharides and their behavior in solution due to their secondary, tertiary, and quarternary structures. Undoubtedly structure and shape of polysaccharides in solution play a role in determining biological function. This topic is amply covered in Chapter 11. The 1970s have seen significant advances in information in the area of chemistry, synthesis, and function of cell wall components. Thus, three chapters (12, 13, and 16) are devoted to these topics. No volume on plant carbohydrates would be complete without discussion of the most abundant product of plants, cellulose. This occurs in Chapter 14. Finally a class of compounds, glycolipids, whose roles in nature have been amplified by recent information, is discussed in Chapter 15.

It should also be pointed out that chapters on carbohydrates related to the subjects covered in this volume are also found elsewhere in other volumes in the treatise. Volume 1 contains a chapter on the primary cell wall while in Volume 2, carbohydrate metabolic pathways are discussed in relation to plant respiration, regulation, and photorespiration. Volume 4 also contains the subject glycolipids. In Volume 6, the subject of lectins, proteins that exhibit sugar-binding properties, is discussed, and in Volume 7, cyanogenic glucosides, glucosinolates and glycosidases are discussed. Finally, in Volume 8, one will find the topics, photosynthetic carbon reduction cycle and the C_4 pathway.

I am very grateful for the contributions made by each of the authors. They certainly made my job easier by their cooperation and by providing authoritative and fascinating reviews, and the success of this volume is due to their efforts.

Jack Preiss

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I. INTRODUCTION

In higher plants hexose phosphates are formed in photosynthesis and gluconeogenesis, and also from the breakdown of storage carbohydrates; they are consumed by glycolysis and the oxidative pentose phosphate pathway, and also in the synthesis of oligo- and polysaccharides. Thus hexose phosphates play a dominant role in carbohydrate metabolism, and,

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consequently, in the economy of the plant as a whole. The reductive and oxidative pentose phosphate pathways, glycolysis, and gluconeogenesis share other intermediates in addition to hexose phosphates, and have sufficient in common for them to be discussed as a whole. The aim of this chapter is to give a general and integrated view of our present understanding of the functioning and relationship of these four pathways in higher plants. The role of hexose phosphates as products or precursors of oligo- and polysaccharides will not be treated in detail because these topics fall outside the essential unity of the four chosen pathways, and because they are dealt with elsewhere in this volume. As my topic is wide, detailed treatment of every issue is not practicable and the reader is referred to more specific articles, where satisfactory ones exist. I shall concentrate on establishing the sequence of each pathway and its role in metabolism, on the organization of the pathways, and on the principal features of their control.

II. EXPERIMENTAL APPROACH

The theoretical and practical aspects of the study of the sequence, organization, and location of the reactions of hexose phosphate metabolism in plants are well established. Most of the pitfalls are recognized even if they are not always avoided. In contrast, plant biochemists have been slow to appreciate the experimental approach to the study of the control of metabolism that has been developed from and used so successfully in the study of the regulation of mammalian metabolism. The features of this experimental approach have been set out admirably by Newsholme and Start (1973) and I shall attempt to apply this method to the study of the control of hexose phosphate metabolism in plants.

The key to this approach is the concept that most of the control of a metabolic pathway is vested in a minority of steps, the regulatory reactions. These have been defined as nonequilibrium reactions which are catalyzed by enzymes which are controlled by factors other than substrate concentration. The extent to which two or three reactions dominate control of a sequence is unlikely to be complete and will probably be found to vary with the sequence. Every reaction in the sequence must make some contribution to control as change in flux through the sequence will involve an alteration in the activity of each enzyme. In a detailed theoretical treatment of this question Kacser and Burns (1973) showed that it is possible that no one enzyme in a sequence is of particular importance in control, and argued that the concept of regulatory reactions is not necessarily applicable. This possibility is conceivable but it is important to remember that it has yet to be demonstrated in respect of any major pathway of metabolism. In studies of the control of hexose phosphate metabolism the evidence strongly indicates

that most of the control is exercised by selected regulatory enzymes. Such enzymes are regarded as those which respond to the original metabolic signal and which initiate changes in the activities of the remaining enzymes of the pathways.

Regulatory enzymes catalyze what are referred to as nonequilibrium reactions. No reaction through which there is a net flux can be at equilibrium, but many enzymes are so fast that their reactions *in vivo* do not show much deviation from equilibrium. Such equilibrium reactions may play important roles in regulation by changing the concentrations of metabolites and by transmitting the state of one pathway to another. However their nearness to equilibrium does not permit them to regulate flux directly (Heinrich *et al.*, 1977).

The above experimental approach to the study of control involves the following four stages.

1. Recognition of regulatory reactions. First the nonequilibrium reactions must be identified. An indication of these is given by comparison of the maximum catalytic activities of all the enzymes of the pathway. The latter term refers to the maximum activity of an enzyme from a given sample of tissue which can be achieved under optimum conditions *in vitro*. Reactions are displaced from equilibrium *in vivo* because the enzymes catalyzing them are not sufficiently active to achieve equilibration between substrates and products. This low activity is often reflected in a low maximum catalytic activity. This approach is not conclusive because low activity *in vivo* could be due to inhibition of the enzyme rather than to low maximum catalytic activity. A better method is comparison of the apparent equilibrium constants of the enzymes with the ratios of products to substrates present *in vivo*. The latter are called mass-action ratios. Substantial discrepancy between the apparent equilibrium constant and the mass-action ratio is clear evidence that a reaction is displaced from equilibrium *in vivo*. The decision as to what is substantial in the above context is sometimes difficult to make but Rolleston (1972) has made a good case for regarding as nonequilibrium any reaction in which the difference between the equilibrium constant and the mass-action ratio is 20-fold or more. The fact that a reaction is far from equilibrium permits it to control flux but does not prove that it does (Newsholme and Start, 1973; Heinrich *et al.*, 1977). Proof that a non-equilibrium reaction is regulatory may be obtained by demonstrating that the amount of substrate present *in vivo* changes in the opposite direction to flux through the pathway when the latter is varied. Both Rolleston (1972), and Newsholme and Start (1973) have emphasized the fact that only changes in substrate, and not those in product, are diagnostic in pathways, such as those of hexose phosphate metabolism, in which the enzymes and substrates are freely dissociable. There are considerable dangers in applying Chance's cross-over theorem to such pathways.

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