

Monographs on Biochemistry

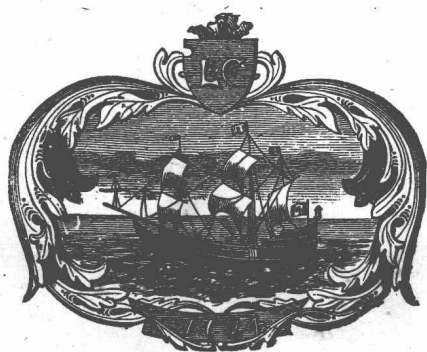
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THE  
SIMPLE CARBOHYDRATES  
AND  
THE GLUCOSIDES

BY  
E. FRANKLAND ARMSTRONG, D.Sc., Ph.D.

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AND  
THE GLUCOSIDES

BY  
E. FRANKLAND ARMSTRONG, D.Sc., Ph.D., F.I.C.  
FELLOW OF THE CITY AND GUILDS OF LONDON INSTITUTE



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## GENERAL PREFACE.

THE subject of Physiological Chemistry, or Biochemistry, is enlarging its borders to such an extent at the present time, that no single textbook upon the subject, without being cumbrous, can adequately deal with it as a whole, so as to give both a general and a detailed account of its present position. It is, moreover, difficult in the case of the larger textbooks to keep abreast of so rapidly growing a science by means of new editions, and such volumes are therefore issued when much of their contents has become obsolete.

For this reason an attempt is being made to place this branch of science in a more accessible position by issuing a series of monographs upon the various chapters of the subject, each independent of and yet dependent upon the others, so that from time to time, as new material and the demand therefor necessitate, a new edition of each monograph can be issued without re-issuing the whole series. In this way, both the expenses of publication and the expense to the purchaser will be diminished, and by a moderate outlay it will be possible to obtain a full account of any particular subject as nearly current as possible.

The editors of these monographs have kept two objects in view: firstly, that each author should be himself working at the subject with which he deals; and, secondly, that a *Bibliography*, as complete as possible, should be included, in order to avoid cross references, which are apt to be wrongly cited, and in order that each monograph may yield full and independent information of the work which has been done upon the subject.

It has been decided as a general scheme that the volumes first issued shall deal with the pure chemistry of physiological products and with certain general aspects of the subject. Subsequent monographs will be devoted to such questions as the chemistry of special tissues and particular aspects of metabolism. So the series, if continued, will proceed from Physiological Chemistry to what may be now more properly termed Chemical Physiology. This will depend upon the success which the first series achieves, and upon the divisions of the subject which may be of interest at the time.

R. H. A. P.  
F. G. H.

## PREFACE.

TWENTY-EIGHT years ago the late Sir John Burdon Sanderson described one of the aims of Physiology as the acquirement of an exact knowledge of the chemical and physical processes of animal life. The recent history of physiological progress shows that investigations confined to the study of physical and chemical processes have been the most fruitful source of physiological advance, and it is principally the exact chemical study of the substances found in animals and plants which has enabled the physiologist to make this advance.

The last decade has seen very material progress in our knowledge of the carbohydrates, more particularly with regard to their inner structure, biochemical properties, and the mechanism of their metabolism. In consequence, many problems of the greatest fascination for the biochemist have presented themselves for solution.

This monograph aims at giving a summary of the present position of the chemistry of the carbohydrates. The reader is assumed to be already acquainted with the subject so far as it is dealt with in the ordinary textbooks. The available information is, however, so widely scattered in the various scientific periodicals that it is impossible for any one approaching the subject to inform himself rapidly of what has been done. It is to meet such needs that this monograph is primarily intended.

A bibliography is appended, which contains references, classified under appropriate headings, to most of the recent works on the subject and to the more important of the older papers. It makes no claim to be exhaustive but serves to indicate how much is at present being done in this field.

E. F. A.



## PREFACE TO THE SECOND EDITION.

OUR interest in the carbohydrates has been again aroused by the return of Emil Fischer to the subject. He has announced his acceptance of the  $\gamma$ -oxide formula of glucose which was used in the First Edition of the Monograph to explain all the properties of this carbohydrate. In continuation of his work on the acyl derivatives of glucose he has been able to show the probable composition of the tannins: he seems to think that compounds of this type may be widely distributed in animals and plants and may account for some of the peculiar properties of carbohydrates known to biologists.

It has been found advisable to modify the arrangement of Chapter I. The treatment of the rarer carbohydrates has been extended and, wherever possible, their relation to enzymes has been demonstrated. The chapter on the glucosides has been considerably enlarged and a new chapter, dealing with the significance of the carbohydrates in plant physiology, has been added. The monograph should therefore appeal more generally to those interested in the subject from the botanical and agricultural sides. These problems are some of the most fascinating of those now under investigation, and their study must add to our conceptions of vital change.

It is a pleasant duty to express my thanks to Mr. F. W. Jackson, B.Sc., A.C.G.I., for his help in the revision of the proofs.

E. F. A.

## PREFACE TO THE THIRD EDITION.

SINCE the Second Edition of this Monograph was completed the chemistry of the carbohydrates has developed on two main lines, both of which now receive special recognition. The discovery of a third isomeric form of glucose differing from the pentaphane ring forms in structure—probably containing a three-membered (triphane) ring—opens up ways to much future work and in particular has served to elucidate that very vexed problem the structure of sucrose. The discovery of this new glucose derivative also affords an example of the temporary nature of the doctrines of chemical structure: if the arguments for the acceptance of what was known as the  $\gamma$ -oxide formula of glucose had been too rigidly construed there would have been no possibility of a third isomeride. Chemical formulæ are of service so long as they serve to express known facts and stimulate further investigation; they cease to be of value when used to give expression to observations with which they are not in harmony. We owe the recognition of the new form both to Emil Fischer and to J. C. Irvine, particularly to the latter and his students. The very patient and brilliant work of Irvine on the substituted methyl derivatives of the carbohydrates has done much to increase our knowledge of their structure.

The relationship of optical rotatory power to structure in the case of the carbohydrates has long been a source of speculation, but, because of the indifferent manner in which many of the carbohydrate derivatives had been characterised, nothing definite had been achieved until recently. Owing to the painstaking work of Hudson and his school in America, we are now in possession of many of the necessary data, and the

generalisations of this chemist have given a new and most promising aspect to this field.

Some of the rarer sugars have been made more available, thus stimulating inquiry; indeed, as the methods of investigation improve and more attention is paid to the composition of plant products, the occurrence of the scarcer sugars is found to be far more general than had been anticipated, and it may be prophesied that future researches in this direction will be very fruitful. In particular much progress has been made in establishing the structural formulæ of the disaccharides. References to new work have been introduced where appropriate.

Probably in no other branch of chemistry, at all events in that of the aliphatic compounds, is so great an opportunity afforded for the study in detail of the influence of structure on the properties of the molecule. Much has already been done in this direction but we are as yet only on the threshold of the inquiry.

During the past few years most chemists in the allied countries have had to follow more urgent national calls than those of the research laboratory. The British and American nations have, however, learnt to appreciate more fully the need of scientific research, and it is to be expected that in the near future the chemistry of the carbohydrates will be a subject that will attract the attention of workers.

It would have been very difficult for the writer to prepare this edition without the great assistance which he has so freely received from Dr. T. P. Hilditch.

E. F. A.

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## INTRODUCTION.

THE carbohydrates, together with the proteins, rank first in importance among organic compounds on account of the part they play, both in plants and animals, as structural elements and in the maintenance of the functional activity of the organism.

The interest attaching to the group may be said to centre around glucose, this carbohydrate being the first to arise in the plant and the unit group from which substances such as cane sugar, maltose, starch and cellulose are derived; it is also of primary importance in animal metabolism, as the main bulk of the carbohydrate in our food materials enters into circulation in the form of glucose.

Under natural conditions the higher carbohydrates are resolved into the simpler by the hydrolytic agency of enzymes, but these also exercise synthetic functions; the simpler carbohydrates are further resolved by processes which are undoubtedly akin to that of ordinary alcoholic fermentation. The carbohydrates are, therefore, of primary importance as furnishing material for the study of the processes of digestion and assimilation.

The carbohydrates are all remarkable on account of their optical characters; it is possible to correlate these with their structure. Of the large number of possible isomeric forms of the gluco-aldohexose,  $C_6H_{12}O_6$ , sixteen in all, of which glucose is one, only three are met with in nature, although fourteen have already been prepared by artificial means; this natural limitation of the number produced in the plant and utilised by it and by the animal is a fact of great significance and clear proof of the manifestation of a selective process at some period in the evolution of life. The elucidation of these peculiarities invests the inquiry into the nature and functions of the carbohydrates with particular interest and significance.

The simple carbohydrates are all of the empirical composition corresponding with the formula  $CH_2O$ , the most important being those containing five or six atoms of carbon. The members of the sugar group are usually distinguished by names having the suffix *ose*.

The simplest carbohydrate,  $CH_2O$ , formaldehyde or formal, is in all probability the first product of vital activity in the plant, the carbon



## 2 THE SIMPLE CARBOHYDRATES AND GLUCOSIDES

dioxide absorbed from the air being converted into this substance by the combined influence of sunlight and chlorophyll. The conversion of formaldehyde into glucose has been accomplished in the laboratory, but the transformation takes place in such a way that a variety of products is obtained which are optically inactive; there is reason to suppose that but the single substance dextro-glucose is formed in the plant and that this is almost immediately converted into starch; in other words, the vital process is in some way a directed change. The record of the synthetic production of glucose and of the discovery of methods of producing the isomeric hexoses, as well as of determining the structure of the several isomerides, is one of the most fascinating chapters in the history of modern organic chemistry.

A short outline of the ground covered by the complete carbohydrate group may be of value to some readers and will be given before the subject is developed in detail.

The numerical relation existing between the proportions of "carbon" and of "water" in a carbohydrate molecule,  $C_m(H_2O)_n$ , is the basis of general classification.

The simplest sugars are those in which  $m$  and  $n$  are equal and range in value from 2 upwards; these are known as *monosaccharides*, and include such carbohydrates as arabinose,  $C_5H_{10}O_5$ , and glucose,  $C_6H_{12}O_6$ .

The next, more complex, type of carbohydrate may be regarded, for the moment, as derived either from two molecules of a monosaccharide or from two different monosaccharides by elimination of a molecule of water, and will have the general formula  $C_{2m}(H_2O)_{2m-1}$ ; these are the *disaccharides*, of which cane sugar or sucrose is the most familiar.

Similarly, by elimination of two molecules of water from three of monosaccharide, or of three molecules of water from four of monosaccharide, we arrive at the empirical formulæ for the *tri-* or the *tetra-saccharides*, which are also found in nature.

Important exceptions to this numerical classification are the starches, gums, and celluloses of the general formula  $(C_6H_{10}O_5)_x$ ; these have, of course, little resemblance to the saccharide group beyond their empirical composition; they are of far greater molecular complexity than the sugars, and do not fall within the scope of this work.

The distinctive feature of saccharides other than the monosaccharides is their ready conversion into a mixture of the latter compounds by hydrolytic agency; in other reactions they show the same behaviour as the monosaccharides. The basis of all carbohydrates is

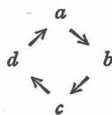
thus the class of monosaccharides, which are systematised according to the number of carbon atoms they contain.

In passing it may be said that the simplest member of the series,  $\text{CH}_2\text{O}$ , formaldehyde, is not a true carbohydrate, since it possesses neither the physical characteristics (a sweet syrup or solid material) nor the chemical (alcoholic) functions of the rest of the sugars.

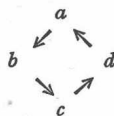
The compound,  $\text{CH}_2(\text{OH}) \cdot \text{CHO}$ , glycollic aldehyde, however, is a sweet-tasting crystalline substance readily soluble in water and possessing all the general properties of the carbohydrates. The next term of the series,  $\text{C}_3(\text{H}_2\text{O})_3$ , includes glycerose,  $\text{CH}_2(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot \text{CHO}$ , and dioxycetone,  $\text{CH}_2(\text{OH}) \cdot \text{CO} \cdot \text{CH}_2(\text{OH})$ , and here a further distinction appears, for glycerose is an aldehyde and dioxycetone a ketone. Moreover, a compound,  $\text{CH}_3 \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot \text{CHO}$ , has been prepared to which the name methylglycerose is given; this substance possesses the general properties of a sugar, and analogous compounds such as rhamnose,  $\text{CH}_2[\text{CH}(\text{OH})]_4 \cdot \text{CHO}$ , occur in nature.

The monosaccharides are therefore classified as dioses, trioses, etc., by the number of carbon atoms in the molecule, whilst each class may be subdivided according as it possesses an aldehydic, ketonic, or methyl radicle. So, whilst glucose is an aldohexose, and fructose a ketohexose, rhamnose is a methylaldopentose.

A carbon atom which has four different groups attached to it is known as asymmetric. These groups can obviously be written in order either clockwise :—



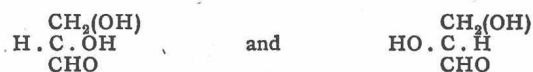
or counter clockwise :—



Two different forms of the substance are therefore possible, related as object to image, and they are termed stereoisomerides.

Nearly all the carbohydrates contain asymmetric carbon atoms and display optical activity, and the number of possible stereoisomerides is in many cases very large. Of the monosaccharides the diose, glycollic aldehyde, contains no asymmetric centres and only exists in one form, but in the triose, glyceric aldehyde, there are already possibilities of a dextro- and a lævo-rotatory form, with, of course, the corresponding racemic compound :—

#### 4 THE SIMPLE CARBOHYDRATES AND GLUCOSIDES

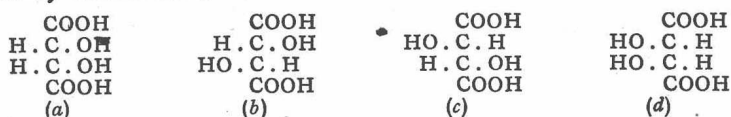


Similarly in the tetroses there are four possible active forms:—



In general, as van't Hoff has pointed out, the total number of active forms of sugars of the same structural formula containing  $n$  asymmetric carbon atoms is  $2^n$ .

On mild oxidation of the aldehydic group of the aldoses, optically active hydroxy-monocarboxylic acids corresponding to each active form are produced, but if by further oxidation the terminal primary alcoholic group is also converted to an acid, or if the original monosaccharide is reduced to a polyhydric alcohol, the number of possible forms of the respective dibasic acids or polyhydric alcohols is somewhat lessened. Thus, referring again to the tetroses, the dibasic acids formed by oxidation are:—



Of these, only (b) and (c) are optically active, and are, in fact, the *d* and *l* forms of tartaric acid, whilst (a) and (d) are identical and represent the “internally compensated” or *meso*-tartaric acid. So that there are only three stereoisomeric dibasic acids (and also tetrahydric alcohols) derived from the four tetroses, and of these only two are optically active.

Some of the possible stereoisomerides in the simpler aldomonosaccharides, with their related dibasic acids or polyhydric alcohols, are in number as follows:—

Aldoses.	Number of Asymmetric Atoms.	Number of Stereoisomerides.	Corresponding Stereoisomeric Alcohols or Dibasic Acids.		
			Total No.	Optically Active.	Meso-compounds.
Diose . . .	0	1	1	0	0
Trioses . .	1	2	1	0	0
Tetroses . .	2	4	3	2	1
Pentoses . .	3	8	4	2	2
Hexoses . .	4	16	10	8	2
Heptoses . .	5	32	16	12	4

Comparatively few of these sugars are found in nature, but tetroses, pentoses and all the hexoses except two are now known in active

forms corresponding to those predicted by stereochemical theory; those not occurring naturally have been produced synthetically, together with their reduction and oxidation products, by methods which will receive attention later in this monograph.

It would be impossible within the limits of a brief monograph to deal at length with the carbohydrates generally. In the following account, glucose will be taken as a typical sugar, and its properties and inter-relationships will be considered more particularly with reference to their biochemical importance. The disaccharides and glucosides will be dealt with in a similar manner. Those who desire fuller information should consult the comprehensive works compiled by Lippmann and by Maquenne.

In discussing the various problems associated with the carbohydrates, the writer will strive to indicate the alternative views which have been advanced. He will, however, endeavour to develop the subject as far as possible as a logical whole, rather than leave the reader undecided at every turn. Such a method of treatment is more likely to stimulate inquiry by giving a picture of the present attitude of workers towards the various problems which the carbohydrates present.