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**THE CHEMICAL
CONSTITUTION
OF
NATURAL FATS**

**THIRD EDITION REVISED
AND ENLARGED**

Chapman & Hall

THE CHEMICAL CONSTITUTION OF NATURAL FATS

By
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THIRD EDITION
REVISED



LONDON
CHAPMAN & HALL LTD.
37 ESSEX STREET, W.C.2.

1956

PREFACE TO THE THIRD EDITION

THIS BOOK, which first appeared in 1940, was revised in its second edition, published in 1947, which included the results of subsequent investigations on fats up to about 1945. Since then, much has been added in several notable respects to our knowledge of natural fats and their components, and it has been necessary, in preparing a further edition, to make extensive alterations to the book as originally published in 1940. Its general plan, however, has been left unaltered.

Perhaps the most marked development has been the increased knowledge of the component glycerides present in a wide range of natural fats. Since 1940, methods of study of the glycerides in liquid fats have been more widely developed, so that it is now possible to present a fairly complete picture of glyceride structure over the whole range of natural fats. The Chapters (V, VI and VII) which deal with component glycerides have therefore been entirely rewritten; Chapter V is now devoted to a detailed general study of glyceride structure based upon the experimental procedures which have been evolved from the early studies of fifty years ago up to the present time, while Chapters VI and VII refer more particularly to the component glycerides present, respectively, in individual vegetable and animal fats.

Chapter VIII, which formerly surveyed some aspects of the general biochemistry of fats, has been restricted to consideration of the possible means whereby fats may be synthesised in living tissues and, in the case of animals, how they may be derived from fat already present in the diet.

Very great advances have been made in recent years in our knowledge of the constitution of individual natural fatty acids. On the one hand, a remarkable number of general methods of formal synthesis of long-chain acids, unsaturated as well as saturated, have appeared in the past few years, and many of the natural unsaturated members have now been prepared synthetically, often by more than one route. On the other hand, the constitutions of a number of the rarer and lesser known unsaturated acids have been settled by recent work, so that it is possible to write with more certainty than hitherto on this subject. Consequently Chapter IX has been largely rewritten and, although new matter is appearing actively on both the synthetical and constitutive aspects of this field, it is hoped that this Chapter (and also the book as a whole) includes most of the relevant results published up to the end of 1954. The individual unsaturated acids in Chapter IX have been grouped for discussion, as far as possible, according to their structural resemblances to each other and (in many instances) to *oleic acid* itself.

Chapter XI, which deals with experimental techniques used in the study of fats, has been altered to give more emphasis to the most recently developed procedures, especially the use of crystallisation from solvents at low tem-

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peratures, and of spectrophotometric determination of certain unsaturated acids (notably linoleic, linolenic, and elaeostearic).

Many fresh records of the component acids of fats have been added to the tables of data in Chapters II, III and IV. A measure of the activity in this branch of the subject since 1940 is given by comparing the approximate number of component acid records in the present edition with those (given in parentheses) in the original edition: about 600 (400) fats from plant species, about 200 (80) fats from land animals, and about 200 (100) fats of aquatic origin. (Many authors persist in publishing fat component acid figures as percentages of fatty acids in the original *fat*, or as percentages of "glycerides" in the original fat, instead of as a percentage of the total fatty acids present, which is the only rational basis of comparison: the time occupied in converting the former data into the form necessary for comparative purposes is considerable, and one is tempted to ignore results which authors refuse to present in a logical form.)

The indexing of the book is not easy, and I believe that some readers have found difficulty here. After discussing the matter with a number of friends I decided to make certain alterations to the existing indexes, in the hope that reference may be facilitated. Cursorry or incidental references to individual fats, fatty acids, or glycerides, which are very unlikely to be sought in the indexes, have been largely omitted in the present edition (this applies especially to the inevitably continuous mention of the more common fatty acids); "selective" indexing of this nature has its dangers, but it is hoped that the indexes as a whole will thus be more useful. The individual fats and fatty oils are now listed together alphabetically, and not subdivided according to their biological origin as formerly. Pages where details of component acid* or of component glyceride† compositions will be found are distinguished respectively by asterisks or daggers (as indicated).

Several of the Figures added in the present edition are taken from our papers in various scientific journals, whilst I am indebted to Mr. D. N. Grindley for permission to reproduce Fig. 15 from his paper in the *Journal of the Science of Food and Agriculture*. My thanks are offered to the governing bodies and Editors of the following Journals for permission to reproduce the Figures mentioned: *Proceedings of the Royal Society* (Figs. 13, 14, 17); *Journal of the Chemical Society* (Fig. 24); *Biochemical Journal* (Figs. 5, 16, 19); *Journal of the Science of Food and Agriculture* (Figs. 15, 20, 23); and *Journal of the Oil and Colour Chemists' Association* (Fig. 4).

Through the kindness of several investigators in the field (including Dr. F. D. Gunstone, Dr. J. Holmberg, Dr. R. P. Linstead, C.B.E., F.R.S., Dr. M. L. Meara, Dr. F. B. Shorland, and workers at the Paint Research Station, Teddington), who have kept me informed of some of their papers in course of publication, I have been able to bring the volume more up-to-date than would otherwise have been possible.

I have again had the assistance of much helpful criticism and many useful suggestions from a number of my former co-workers and other friends, to all of whom I would express my thanks. I am also most grateful to Dr. M. L. Meara for further revision of the synthetic glyceride section of Chapter X, to Dr. R. V. Crawford, who prepared the drawings for the blocks of Figs. 6-11, and to Dr. F. D. Gunstone and Dr. J. P. Riley, who independently checked all the proofs of this Edition.

Especially, however, I offer my thanks to my wife, for her assistance in

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preparing the typescript for the new Edition, in reading the proofs and in checking the numerous literature references; without her constant interest and efficient help it would have been much more difficult to complete a rather complicated and tedious undertaking.

Oxton, Birkenhead.
July, 1955.

T. P. H.

PREFACE TO THE SECOND EDITION

THE FIRST EDITION of this book has been out of print for a longer time than could have been wished. As in many other cases, it suffered to some degree by enemy action, whilst production of the present edition has been hindered by the prolonged delays which unavoidably have afflicted the publishing and printing industries during and since the war of 1939-1945. Study of the fats does not appear to have been so much impeded by the prevailing unrest as might have been supposed; at all events a great deal of new matter has appeared during the six or seven years which have elapsed between the two editions of this book. In consequence it has expanded by about a hundred pages, and in places the story can be presented in a much more complete form than before. Endeavour, not wholly successful, has been made to mention all the more important contributions published before the end of 1945.

The more notable advances (contributed to prominently from the United States and from India, although workers in England, Holland and France have still made opportunities to continue their researches) include the addition of numerous *component acid* data in the groups of land animal and vegetable fats (Chapters III and IV); a large number of additional seed fat data have been contributed, and in the animal group the depot fats from a wider range of wild animals have been studied, whilst that of the human species has also been examined. Work on *component glycerides*, although not so extensive, has been notable for the development of methods which enable the more liquid and unsaturated fats to be more adequately investigated, for the more complete development of the glyceride picture in animal depot and milk fats, and for some insight into empirical methods whereby glyceride composition can be roughly predicted from that of the component acids of a fat (Chapters VI and VII). A good deal of fresh information on individual fatty acids (Chapter IX) has been worthy of record, whilst the welcome extended to the discussion of experimental technique has led me to revise and expand Chapter XI, especially in regard to the methods of interpretation of ester-fractions involved in the determination of component acids.

The arrangement of the indexes may have given some trouble to readers of the first edition, and I have endeavoured to make this more clear. The nature of the subject-matter requires treatment by means of several indexes, the use of which will, it is hoped, be facilitated by the indications given on pp. xiii and 529.*

Many friends were good enough to give me the advantage of helpful criticism of the first edition, of which I have made much use during the present revision. It is not possible to refer to all who have thus helped me, but amongst them I might mention Professor A. C. Chibnall, F.R.S., Dr. H. Jasperson, Mr. H. M. Langton, Dr. J. A. Lovern, Dr. F. B. Shorland, Mr. P. N. Williams and other colleagues in the Central Research Laboratories at Port Sunlight. In the preparation of the present edition I owe very much to the

* Second edition ; pp. xix and 633 in present edition.

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patient and assiduous help of my colleague, Dr. M. L. Meara, at all stages—revision, addition, final scrutiny of both manuscript and proofs (in the latter we were also assisted by Mrs. M. L. Meara). I wish to express my appreciative thanks to Dr. Meara, and to all who have given me the benefit of their advice or comments.

T. P. H.

University of Liverpool,

July, 1946.

P R E F A C E

IT HAS SEEMED opportune for some time past to write a monograph on the natural fats in such a form that their inter-relationships as a group of naturally occurring organic compounds should be developed as completely as possible, and without primary reference either to their physiological functions or to their technical applications. The many detailed data on the acids combined in natural fats which have been published during the past twenty years or so have made more and more evident the existence of a close connection between the component acids in a fat and its biological source. Therefore, I decided to make some sort of biological classification the basis for the order in which the various natural fats are considered. To those familiar with the more customary sequence of "vegetable fats, animal fats, marine animal fats" the change may seem inconvenient or even unnecessary; but assurance may be given that contemplation of the fats and their component acids in the sequence developed in Chapters II-IV of this book soon presents itself as the logical and consistent method of approach to their study. This, it is hoped, will be realised by perusal of Chapter I, which is mainly devoted to a general summary of the data discussed in fuller detail in the six chapters which follow.

Whilst acknowledging all responsibility for the method I have adopted, it is right to add that the first use of this principle was made ten years ago by Grün and Halden (*Analyse der Fette und Wachse*, vol. II), who, when describing the usual chemical and physical characteristics of plant and animal fats, arranged them mainly according to their biological origin, in the general order vegetable, marine animal, animal fats. These authors (*op. cit.*, p. 10) were, however, at that time unable to accept my view that there were sufficient parallelisms between the component acids of seed fats and the families of the parent plants to justify a comprehensive generalisation.

In postponing discussion of the chemical constitution and properties of individual fatty acids until a late stage of the book—indeed, until its main objects have been dealt with—I have followed the example of my friend Dr. G. S. Jamieson, who adopted this plan (I think very usefully) in his "Vegetable Oils and Fats," published in 1932.

The aim has been to include as much as possible of relevant data on the subject published up to the end of 1938, whilst some work which has appeared during 1939 has also been considered. It is hoped that not many investigations have been overlooked which ought to have been mentioned, because one of the chief uses of a volume of this kind should be to stimulate research, to draw the attention of investigators to what has already been done, and to the lacunæ which still exist. For the latter reason, also, some of the more recent work has been discussed more fully than might otherwise have been deemed necessary.

With few exceptions, only those fats whose component acids have been defined in some detail by modern methods are considered in this book. Actually, it will be found that about 420 fats from plant species, about 80 fats from land animals, and about 100 fats of aquatic origin are men-

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tioned; in several instances these numbers include fats from different parts of the same animal or plant. These figures illustrate on the one hand the disproportion between the number of plant and of animal fats studied, and on the other, that those fats so far adequately studied are drawn from only a minute proportion of the hundreds of thousands of natural species.

I have received much help in the preparation of the book, especially in verifying numerical data and textual references and in correction of proofs from Miss M. Tadman, M.Sc. Dr. M. L. Meara read the book in manuscript and also contributed the part of Chapter X which deals with synthetic glycerides. To these, and to Dr. J. A. Lovern and others with whom I was able to discuss various parts of the work, I offer my warm thanks. I take this opportunity, moreover, to express my great appreciation of my co-workers in this laboratory who, during the past fourteen years, have done very much to encourage and maintain my interest in research on fats by their own keenness and assiduity in the investigations which we have pursued together.

T. P. H.

University of Liverpool.

December, 1939.

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CHAPTER I

INTRODUCTORY SURVEY OF THE NATURAL FATS

THIS book is planned to give as complete an account as possible of the constitution of the fats, and more especially the glycerides, which are produced naturally in plant and animal life. It is intended to treat the natural fats as a group of organic chemical compounds, in exactly the same way as it has been found helpful to have separate monographs dealing with other natural groups such as, for example, the carbohydrates, terpenes, alkaloids, or flavone derivatives. This method of approach is stressed, because it naturally follows that the fats are considered, primarily, neither from the standpoint of their utility as raw materials for any industrial purpose nor with regard to their biochemical functions in the organisms in which they are produced. References will, it is true, be found to these and other aspects in the course of the work; but its first objective is the descriptive presentation of the organic chemistry of the natural fats, so far as our present knowledge takes us.

It is probable that many readers will be already familiar with the subject from the biochemical or the technological side; this circumstance warrants some further explanations. First of all, it will be found that much less reference than usual is made to the many "characteristics" of fats (whether physical, such as density or refractivity, or chemical, such as saponification, acid, iodine or acetyl values, etc.) which have been so widely elaborated and which are indispensable in the routine or rapid characterisation, and even determination, of fatty materials in technical practice. This is, of course, owing to the circumstance that these "characteristics," applied to an entire fat, give in general merely average figures which by no means serve to indicate its detailed composition (although saponification equivalents, iodine values, and occasionally other analytical characteristics, are indispensable in collecting the detailed experimental data upon which knowledge of the chemical structure of fats is ultimately based). The individual fats discussed in this book, with few exceptions, have been investigated so far that the proportions of the separate component acids, and in many cases the chief component glycerides, can be stated with some degree of accuracy; and for the most part the compositions of the fats are given in these forms alone. Many tables illustrating the component acids present in natural fats have been included in the book, and it might have been interesting to have incorporated some of the more important physical and chemical analytical "characteristics" of each fat mentioned. To do so would, however, have greatly increased the size and complexity of these tables (already cumbersome enough). To add separate compilations of the customary analytical characteristics would also have involved considerable increase in the size of the volume and, since full details of the analytical characteristics of individual fats have been collected in a number of excellent technological or general treatises on fats, it seemed unnecessary to repeat them in a work