

The Chemical Constitution of Natural Fats

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Preface to the Fourth Edition

Since the first appearance of this book in 1940, revised editions have been published in 1947 and in 1956. At the time of this last (Third) Edition, determination of component fatty acids by gas-liquid chromatography was in its infancy but in the following years it has become of great value and abundant use; in study of component glycerides in natural fats, partial (selective) hydrolysis of triglycerides by pancreatic lipase has similarly proved a most important technique, leading already to considerable fresh understanding of their structure; whilst knowledge of the mechanisms operative in the biosynthesis of (saturated) higher fatty acids has been much enlarged. These three topics, with the discovery of a number of natural fatty acids, especially conjugated unsaturated acids which had not previously been characterised, have again necessitated a major revision during the preparation of the present Fourth Edition.

Meanwhile the main objective of this volume remains as outlined in the Preface to the First Edition: "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". Whilst much discussion of the biological relationships of natural fats is included as a matter of course, and whilst specific references are also made to the particular uses, edible or technical, of not a few of the fats usually employed in either of these respects, attention is predominantly focussed upon their *specific chemical constitution*.

The number and variety of natural fats from both vegetable and animal sources becomes increasingly bewildering, and the reader is strongly recommended to study carefully the general outline given in the "Introductory Survey of the Natural Fats" (Chapter I) in order to obtain a true idea of the scope of the subject.

Many fresh records of the component acids of fats have been added to the tables of data in Chapters II, III and IV. The advance of knowledge in this fundamentally important branch of the subject since this book first appeared in 1940 is illustrated by the following approximate figures:

| COMPONENT ACIDS OF FATS FROM | 1st EDITION 1940 | 3rd EDITION 1956 | PRESENT EDITION 1964 |
|---------------------------------|---------------------|---------------------|-------------------------|
| Plant species | 400 | 600 | 900 |
| Land animal species | 80 | 200 | 300 |
| Aquatic animal species | 100 | 200 | 250 |
| | 580 | 1000 | 1450 |

It was pointed out in the Preface to the Third Edition that "many authors persist in publishing fat component acid figures as percentages of fatty acids in

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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". This bad practice has continued to be followed by many (but not all) of the contributors of results which have appeared since the last edition was published. These results, when not ignored, have been too numerous to warrant the time and trouble needed to convert them (as was done in the earlier editions of the book) to the correctly comparative *percentages of each acid in the total component acids*; to this extent, therefore, some of the recent results now added are not fully comparable with the rest.

The arrangement of the large main tables of component acids of vegetable fats in Chapter IV has been improved by placing each of these tables at the end of the text of the sub-section of fats which it covers. To facilitate reference, the bibliographical references to the items in these tables now immediately follow each table (instead of being placed at the end of the chapter).

Major revisions have been required in several of the later chapters, some of which have been largely rewritten. Recent developments in the experimental study and in the understanding of the structure of natural glycerides have been fully considered in the general survey of this subject (Chapter V). The important recent advances in study of some of the biosynthetic processes whereby carbohydrates are transformed *in vivo* into fats *via* the intermediaries of C_2 (or C_3) units, and the intervention of acetyl- (or malonyl-) co-enzyme A, have led to major alterations in Chapter VIII. The section in Chapter X on synthetic glycerides has been much abbreviated and is now confined to the bearing of synthetical work on glycerides upon the configuration of the more important naturally-occurring members of this group. Finally, Chapter XI, dealing with experimental techniques used in quantitative studies of fats, has been completely rewritten. The very detailed treatment in previous editions of the older "ester-fractionation" procedure (now largely superseded by gas-liquid chromatography) has been much curtailed, and this chapter is now devoted very largely to accounts (necessarily somewhat brief) of the various chromatographic methods which are finding increasing use and value in the investigation of natural fats.

There is still abundant scope for much additional factual information on the detailed composition of individual component acids and component glycerides in natural fats. Some suggestions of the chief lacunae in our knowledge of these are given at the end of the introductory Chapter I (p. 24).

A detailed list of the contents of the book follows this preface, while attention should be drawn to the five indexes at the conclusion of the book. The first of these is a general subject index from which individual fats, fatty acids and glycerides are excluded. Individual fats (and waxes) are indexed alphabetically in a separate index, which is followed by an index of botanical families mentioned in the text. There remain two more separate indexes, one of individual fatty acids and one of individual glycerides. cursory and incidental references to individual fats, fatty acids or glycerides, which are very unlikely to be sought in the indexes, are for the most part not included therein; this applies especially to the almost continuous mention of the more common fatty acids. "Selective"

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indexing of this kind has its dangers, but we believe it is preferable to overload the indexes with page numbers which will probably never be required.

Furthermore, the pages in which a topic or individual fat or fatty acid or glyceride is mainly discussed are indicated by numbers in **heavy type**; and pages where details of component acid* or of component glyceride† compositions will be found are distinguished respectively by asterisks or daggers (as indicated).

Our thanks are offered to Dr F. D. Gunstone and to Mr D. N. Grindley for allowing us to reproduce Figs. 9a, 9b and Fig. 13 respectively from their original papers; to the governing bodies and Editors of a number of Journals for permission to reproduce the following Figures: *Proceedings of the Royal Society* (Figs. 11, 12), *Journal of the Chemical Society* (Fig. 17), *Biochemical Journal* (Figs. 4, 14, 15), and *Journal of the Science of Food and Agriculture* (Figs. 13, 16); and to Dr R. V. Crawford, who prepared the drawings for the blocks of Figs. 5-8. We are much indebted to the Information Section of the Unilever Research Department, Port Sunlight, for access to some items of published information and to Messrs. Prices (Bromborough) Ltd., for permission to quote some information from their "Analysis of Fatty Acids and Fatty Alcohols" (1960) in connection with gas-liquid chromatographic analysis of fatty acids.

We are greatly indebted to Mrs T. P. Hilditch and Mrs P. N. Williams for much help in the preparation of the typescript and of the indexes, and in checking the proofs (especially the many tables and bibliographical references) of this fourth edition.

January 1964

T.P.H.
P.N.W.

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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 lipids, 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, carbohydrates, terpenes, or alkaloids. It 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 because 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 frequently 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

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a number of excellent technological or general treatises on fats, it seemed unnecessary to repeat them in a work which is primarily a guide to the chemical structure of natural fats and is concerned only with the data relevant thereto.

In the next place, the arrangement of this volume may be found unusual. Logically, perhaps, the individual fatty acids, their properties and constitutions, should be discussed before proceeding to their combined forms, the glycerides, etc., whilst the experimental and analytical methods employed in the elucidation of their composition should also precede the essential part of the work. It is a great advantage, on the other hand, to come to the main business of the book as soon as possible; and since most readers are doubtless familiar with the fundamental chemistry of the fatty acids, it has been thought feasible to attempt this. The chapters immediately following therefore deal at once with the component acids and glycerides which have been found to occur throughout the vegetable and animal kingdoms, without undue detail as to the evidence upon which, for example, the constitution of any particular fatty acid is based. Later in the book, however, chapters will be found in which the constitution and specific features of individual fatty acids are considered, and in which accounts are given of the chief experimental and analytical methods referred to in the more general portion of the work.

SOME GENERAL CONSIDERATIONS ON THE STUDY OF NATURAL DERIVATIVES OF THE HIGHER FATTY ACIDS

Unanimity has not yet been reached in the terminology to be adopted in classifying the various types of naturally occurring compounds in which higher fatty acids are present. Even a collective title for the whole group is not completely settled. These types are broadly as follows:

- (I) *Compounds containing only carbon, hydrogen, and oxygen:*
 - (i) Esters of higher fatty acids with glycerol (triglycerides).
 - (ii) Esters of higher fatty acids with alcohols other than glycerol (higher aliphatic alcohols, sterols, etc.).
- (II) *Compounds containing other elements (phosphorus, nitrogen) in addition to carbon, hydrogen and oxygen:*
 - (i) Compounds containing glycerophosphoric acid coupled with a nitrogen base or with inositol (phospholipids).
 - (ii) Compounds derived from the long-chain hydroxy-amino alcohol sphingosine (sphingolipids):
 - (a) phosphoric acid derivatives (sphingomyelin);
 - (b) not containing phosphorus (cerebrosides).

In the present book the terms used have the following significance:

Lipids. The collective title for the whole group of natural products in which the higher fatty acids are present as essential components.

Fats. Natural triglycerides, solid or liquid.

Waxes (type I (ii)). These will be most frequently referred to as ester-waxes or, more specifically, as sterol, higher aliphatic alcohol, etc., esters.

Phospholipids or Phosphatides. Derivatives of α -glycerophosphoric acid in which the two

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remaining hydroxyl groups of the glycerol are combined with higher fatty acids (as in glycerides), whilst the phosphoryl group is united as an ester with:

- (a) a nitrogen base which may be choline (*phosphatidyl choline*, lecithin), ethanolamine (*phosphatidyl ethanolamine*), or serine (*phosphatidyl serine*):



where R' and R'' are higher fatty acid groups and B is the nitrogenous base;

- (b) the cyclic hexose inositol (*phosphoinositides*).

Phosphatidic acids. Glycerophosphoric acid derivatives of the structure



or their metallic (calcium, magnesium) salts.

Plasmalogens. Glycerophosphoric acid derivatives of the structure



where the group R' . CH : CH . O— is a vinyl ether derivative of a higher fatty acid (with R'' and B as in the phosphatides above).

Sphingolipids. In these lipids the fatty acids are present as amido-derivatives of the unsaturated C₁₈ alcohol *sphingosine*, 1,3-dihydroxy-2-amino-octadec-4-ene:



In *sphingomyelins* the terminal, primary alcoholic group is combined with a phosphoryl choline ester (as in glycerophosphatides):



In the *cerebrosides* the sphingosine is present in the form of a glycoside of a hexose (usually galactose but sometimes also glucose):



In this book attention is focussed on the natural fats (triglycerides) and some ester-waxes (higher fatty acid esters of higher fatty alcohols), but in addition some notice is given to the component acids present in phospholipids when the latter accompany the glycerides in specific tissues and organs. The complete chemistry of the phospholipids and the sphingolipids, however, falls beyond the scope of this volume, and for a full account of lipids which include phosphorus and/or nitrogen or carbohydrate groups in their molecules the reader is recommended to consult works on the general biochemistry of lipids (such as those of Deuel¹ or Lovern²), or monographs on specific lipid groups such as the phospholipids (Wittcoff,³ Desnuelle⁴), the sterols (Bergmann⁵), etc.

The constitution of the fats (triglycerides), or for that matter of the ester-waxes or of the phosphatides, may be considered in two distinct ways, namely: (i) with respect to the amounts of the various individual esters present, or (ii) with reference to the proportions of the various *fatty acids* which are present in combination in the natural product as a whole. We may with advantage here confine the discussion to the fats or triglycerides themselves. Very few natural fats have been found to contain only two or even three different acids united with glycerol; more usually five, six, or seven such acids are present and this number may often be much exceeded. Many common fats,

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notably milk fats and the fats of fishes, contain a dozen or more component acids. If it were the invariable rule that each natural triglyceride molecule contained only one species of fatty acid (e.g. triolein, tripalmitin), there would be no need for the distinction just mentioned. Expressed on a molar (not weight) percentage basis,* the proportions of component fatty acids and of component glycerides would be the same. Most unfortunately, this is exactly what does *not* happen in nature. As will be seen later, the overwhelming tendency is towards the production of mixed triglycerides,† in which at least two, and often three, species of fatty acids are combined; simple triglycerides (i.e., triglycerides containing three identical acyl groups) are the exception, and are only produced, apparently, when no other course is open. It therefore follows that the proportions of the component acids in a natural fat, and those of its component glycerides, are by no means the same thing; and accordingly we have to differentiate at the outset between the *component fatty acids* and the *component glycerides* present in a fat.

Here and there (especially in vegetable seed fats), some natural fats, or fats from a group of biologically related organisms, are found to contain in combination some particular fatty acid which is rarely or never found elsewhere in nature; but this is on the whole decidedly exceptional. The general case is that a few higher fatty acids occur continually throughout nature. The consequence is that the differences between one fat and another depend very largely on the varying proportions of the fatty acids in combination in the different fats, as well as upon the particular acids which happen to be components. The study of the natural fats is therefore somewhat differently placed from that of many other groups of naturally occurring organic compounds in that it must be conducted on a quantitative, rather than solely upon a qualitative, basis. Accepting the necessity for quantitative treatment of the subject, we may therefore consider, as has already been said, either the proportions of the *component triglycerides* in a fat, or of the *component acids* in the total fatty acids present in combination with glycerol.

A practical difficulty next presents itself: whilst the component acids of a fat or other natural lipid can be determined quantitatively with a considerable degree of accuracy (frequently to within, at all events, one unit per cent. of the

* The molar composition is frequently more informative than composition by weight in discussing the fats, because it expresses the relative number of molecules of each type of acid, or component glyceride, present in a fat. The difference in the two modes of expression becomes especially significant when fatty acids of widely different molecular weight are present in the same fat. Thus, for instance, the presence of 3 per cent. by weight of butyric acid in the mixed acids of butter fat really means that, out of every 100 mols. of fatty acids, about 10 mols. are butyric acid.

The composition of natural fatty acids being so familiar in the form of weight-percentages, this mode is used to a considerable extent in this book. In many cases, however, it is desirable (as in the milk fats mentioned) to present the facts on a molecular basis of comparison; and in quantitative work on component glycerides this is indeed the only rational course.

† It is unfortunate, from this point of view, to express the composition of a fat (from its detailed fatty acid analysis) as "glycerides of oleic acid", "glycerides of palmitic acid", etc., etc. The only logical and comparable method is to give, in the first place, the component acids as a *percentage (wt. or mol.) of the total fatty acids present*.

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total fatty acids), the quantitative determination of the individual component glycerides in a fat is a matter of much greater difficulty. At present, indeed, fats in which the component glycerides have been determined in anything approaching full detail form only a very small proportion of those for which we have accurate measures of their component fatty acids. Our knowledge of the individual glycerides present in many natural fats is therefore still far from complete. A good deal of knowledge of the general build of the mixed glycerides in the more important groups of natural fats is becoming available, but we cannot yet (except in a very few cases) define the nature and proportion of each individual mixed glyceride present with anything approaching the accuracy with which it is possible to state the total proportions of each fatty acid present in combination in the whole fat.

Nevertheless it has so far become evident that the mode of union – or interweaving, as it were – of the fatty acids in a natural triglyceride is fundamentally similar in wide sectors of both vegetable and animal kingdoms. In other words, the kinds and proportions of the individual fatty acids combined in a fat often seem to have little influence upon the general mode of construction or assembly of the acids into triglycerides; the latter are assembled on principles which operate, to a considerable degree, independently of the particular fatty acids which happen to be present.

On the other hand, the amounts and kinds of the component fatty acids in natural fats vary extremely widely, whilst, as we shall see, these variations run strikingly parallel in most cases with the biological sources of the materials. A great amount of information becomes available, therefore, by consideration of the composition of the total fatty acids, as distinct from the component glycerides. For the reasons which have already been given, the natural fats are considered in detail in this book, first of all, with reference to their *component fatty acids* (Chapters II–IV) and, subsequently, in terms of what is known of their *component glycerides* (Chapters V–VII). Similarly, in endeavouring to present a preliminary survey of the whole field in the present chapter, we shall consider the subject first with reference to the component acids and then with reference to glyceride structure.

The rather impressive rate at which new studies of the *component acids* of natural fats have been made since this book was first published in 1940 is well indicated by tabulating the approximate numbers of species of which the component acids were recorded in the first (1940), third (1956) and present (1964) editions:

| | 1940 | 1956 | 1964 |
|---------------------|------|------|------|
| Vegetable fats | 400 | 600 | 900 |
| Land animal fats | 80 | 200 | 300 |
| Aquatic animal fats | 100 | 200 | 250 |

These figures also illustrate how much less attention has been given to collecting comprehensive data for fats from different animal species than to those from vegetable sources, whilst the latter are of course only an exceedingly small fraction of the total number of plant species.