FATTY ACIDS

Their Chemistry, Properties, Production and Uses

Edited by **KLARE S. MARKLEY**

PART I

FATTY ACIDS

Their Chemistry, Properties, Production, and Uses

**Second Completely Revised
and Augmented Edition**

1960
INTERSCIENCE PUBLISHERS, INC., NEW YORK
INTERSCIENCE PUBLISHERS LTD., LONDON

Library of Congress Catalog Card Number 60-10162

INTERSCIENCE PUBLISHERS, INC., 250 Fifth Avenue, New York 1, N. Y.
For Great Britain and Northern Ireland:
INTERSCIENCE PUBLISHERS LTD., 88–90 Chancery Lane, London, W. C. 2

PRINTED IN THE UNITED STATES OF AMERICA BY MACK PRINTING CO., EASTON, PA.

PREFACE TO THE SECOND EDITION

This second edition of *Fatty Acids* follows the general outline and format of the first edition, but is considerably broader with respect to the subject matter covered, and the treatment of prior subjects is more comprehensive than was that of the earlier edition. This broader treatment has been necessitated, in part, by the marked advances that have occurred in this field since the publication of the first edition in 1947.

Considerable expansion of the present work resulted from the more comprehensive treatment of the lower members of the fatty acid series, the hydroxy-, keto-, branched-chain, and polycarboxylic acids and their derivatives. The industrial production and utilization of fatty acids, which were treated only superficially in the first edition, are stressed throughout the present work and also are the subjects of specific chapters.

With few exceptions the present work represents a complete rewriting and not merely a revision of the former edition. To some extent this has resulted from the development of certain specializations in the field which have made it impossible for a single author to treat all phases of the subject with equal degrees of adequacy. In order to provide the reader with the information he desires and needs, a number of outstanding specialists in various fields were invited to participate in the preparation of the present edition. This device introduces certain difficulties, such as variations in style, unevenness of emphasis, breadth of treatment, duplication of subject matter, and other problems. It has been the policy in the present work to allow the individual authors a maximum of freedom in preparing their respective contributions and to defer to the technical editor the responsibility of bringing the completed work into a unified treatise of maximum value to the prospective reader. The result has been, what is believed to be, the most comprehensive work devoted to this subject and is entirely in keeping with the other monographs of this series.

The editor of the present volumes on the chemistry, properties, production, and uses of fatty acids acknowledges the great debt he owes to the contributing authors, without whose assistance such a comprehensive work could not have been prepared. He also wishes to acknowledge the assistance of a number of individuals in preparing his own contributions.

Foremost among these is Mrs. Evald L. Skau who verified and often contributed to the hundreds of references which have been cited. He is also greatly indebted to Mrs. Lygia Bastos de Lemos for the difficult task of typing the numerous tables accompanying the text, and to Miss Yolanda de Castro Sampaio for typing the final draft of this author's manuscripts.

All of the authors of the present work join in thanking the editors of the many journals and the authors and publishers of various books for permission to reproduce certain illustrations; and also those firms and organizations which generously supplied illustrations, data, and technical information for these volumes.

KLARE S. MARKLEY

Rio de Janeiro, Brazil
January, 1960

Publisher's Note

The second edition of *Fatty Acids* was planned originally to contain two parts; the vastness of the subject, however, and the extensive illustrative material make it desirable to extend the size to several volumes. To facilitate using this comprehensive work, the pagination is consecutive from the first to the last volume. Although the last volume contains a cumulative subject and author index for the entire edition, each separate volume contains its own table of contents, list of contributors, and subject index.

CONTRIBUTORS TO PART 1

Klare S. Markley, International Cooperation Administration, U.S.A. Operation Mission to Brazil, Río de Janeiro, Brazil. Chapter I, *Historical and General.* Chapter II, *Nomenclature, Classification, and Description.* Chapter III, *Isomerism.*

Robert T. O'Connor, Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture, New Orleans, Louisiana. Chapter IV, *X-Ray Diffraction and Polymorphism.* Chapter V, *Spectral Properties.*

W. S. Singleton, Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture, New Orleans, Louisiana. Chapter VI, *Properties of the Liquid State.* Chapter VII, *Solution Properties.*

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Part 1

CHAPTER 1

HISTORICAL AND GENERAL

KLARE S. MARKLEY
Rio de Janeiro, Brazil

1. Introduction

The group of compounds referred to as *fatty acids* were designated thus because they were originally found to be constituents of animal and vegetable fats and fatty oils. The term was originally applied principally to the saturated monobasic carboxylic acids and especially to the long-chain acids, although Chevreul isolated such short-chain acids as butyric as early as 1814 and valeric, caproic, and impure oleic acid between 1818 and 1823 (1). As our knowledge of the natural fats increased, polyunsaturated acids, hydroxy, keto, and branched-chain acids were also found as constituents of these substances, and even acids containing alicyclic substituents.

The term fatty acids has come to be applied more broadly and loosely to include the saturated and unsaturated monobasic carboxylic acids and several series of substituted acids having carbon skeletons identical with the normal saturated acids.

The number of unsaturated and substituted acids found to date in natural fats is limited by comparison with the number of normal saturated acids, but the various series have been extended by synthesis or isolation from nonfat natural sources (waxes, essential oils, fruit essences, fossiliferous materials, etc.). Other representatives have been found as products of destructive distillation, pulping wood, oxidation of petroleum, and as by-products of processing various natural products. They have also been found as constituents of the phosphatides, sterol and vitamin esters, and other lipid materials which are present in natural fats or which accompany them as produced by modern methods of processing.

Moreover, the fatty acids per se and the substances of which they are natural components undergo spontaneously certain reactions (oxidation, scission, polymerization, etc.) to produce other acids such as aldehydic, keto, and dibasic acids.

Because of these and other considerations, any exposition of the fatty acids must be broader in scope than that encompassed within the original concept of this group of compounds, but the question arises as to where the line should be drawn between the included and the excluded. The answer can probably never be entirely satisfactory to either the author or reader; hence the material selected and treated herein must be considered merely as a compromise devised by the authors and editor to make this exposition as broad as possible and yet remain within the limitation of the allotted space.

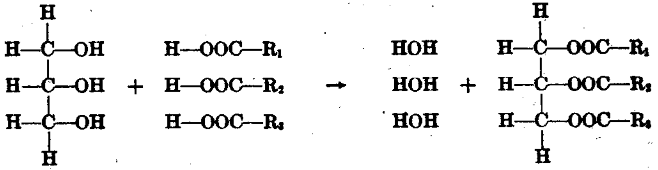
The present work, like its predecessor edition, is concerned primarily with the fatty acids and their derivatives rather than with the fats, waxes, fruit essences, essential oils, and other products of which they are components. Nevertheless, reference is made to these substances wherever this has seemed to be desirable or pertinent.

2. Definitions

(a) *Fats and Oils*

The words *fats* and *oils* have been applied with so many different meanings that it is necessary to define them to avoid misunderstanding in the present usage. As commercial products *fats* and *oils* refer to that class of lipid materials consisting of the glyceride esters of the fatty acids and their associated phosphatides, alcohols, hydrocarbons, pigments, etc., which are obtained from plants or animals by such processes as cooking with water or steam, pressing, extraction with organic solvents, or any combination thereof.

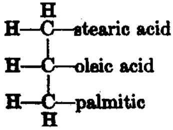
Except for minor quantities of associated or accompanying lipids, some of which are removed by refining, fats and oils consist of triglycerides or esters of fatty acids formed by the reaction between glycerol and three molecules of fatty acids, as shown below.



$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{H} \end{array} + \begin{array}{c} \mathrm{H{-}OOC{-}R_1} \\ \mathrm{H{-}OOC{-}R_2} \\ \mathrm{H{-}OOC{-}R_3} \end{array} \rightarrow \begin{array}{c} \mathrm{HOH} \\ \mathrm{HOH} \\ \mathrm{HOH} \end{array} + \begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H{-}C{-}OOC{-}R_1} \\ | \\ \mathrm{H{-}C{-}OOC{-}R_2} \\ | \\ \mathrm{H{-}C{-}OOC{-}R_3} \\ | \\ \mathrm{H} \end{array}$$

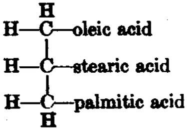
Glycerol Fatty acids Water Triglyceride

In the equation R_1, R_2, and R_3 may be the same or different fatty acid radicals. The large number and the complexity of the natural fats and oils have their origins in two sources, namely, the number, kind, and mode of arrangement of the individual fatty acids which are attached to the glycerol skeleton to form specific glycerides, and in the number and relative proportions of such glycerides which are mixed or mutually dissolved to form the specific fat or oil. For example, a natural fat or oil might be composed of the following three triglycerides in different proportions.



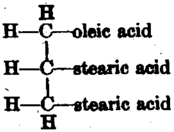
$$\begin{array}{c} \mathrm{H} \\ \mathrm{H{-}C{-}stearic\ acid} \\ | \\ \mathrm{H{-}C{-}oleic\ acid} \\ | \\ \mathrm{H{-}C{-}palmitic} \\ \mathrm{H} \end{array}$$

β-Oleopalmitostearin



$$\begin{array}{c} \mathrm{H} \\ \mathrm{H{-}C{-}oleic\ acid} \\ | \\ \mathrm{H{-}C{-}stearic\ acid} \\ | \\ \mathrm{H{-}C{-}palmitic\ acid} \\ \mathrm{H} \end{array}$$

β-Stearopalmitoolein



$$\begin{array}{c} \mathrm{H} \\ \mathrm{H{-}C{-}oleic\ acid} \\ | \\ \mathrm{H{-}C{-}stearic\ acid} \\ | \\ \mathrm{H{-}C{-}stearic\ acid} \\ \mathrm{H} \end{array}$$

α-Oleodistearin

In contrast to the natural product, a synthetic one consisting of a single triglyceride containing only one kind of fatty acid residue may also be considered to be a fat or oil. This is also true of a pure triglyceride containing two or even three different fatty acid residues attached to the same glycerol skeleton. Thus a simple triglyceride such as tristearin, oleodipalmitin, or oleopalmitostearin may be considered as a fat or oil.

Whether any one of the foregoing triglycerides or mixture of triglycerides, natural or synthetic, may be referred to as a fat or oil depends on its physical state, that is, whether it is a solid or a liquid, because of the common practice of referring to a solidified oil as a fat and to a liquified fat as an oil. This usage has little scientific foundation because many of the more familiar fats are in reality plastic solids or at least semisolids, consisting at ordinary temperatures of a liquid in intimate admixture with many very small, often microcrystalline, solid particles. At 70° F. (21° C.), for example, only about one-third of the glycerides of natural lard are in the solid state. However, at a sufficiently low temperature any liquid oil will become completely solidified and at a sufficiently elevated temperature any fat will become a liquid oil. The difference between a fat and oil may, therefore, be considered merely as a difference in physical state which is reversible by altering the temperature in the proper degree and in the required direction.

Changes in state can be effected by means other than a change in temperature. By means of hydrogenation a liquid oil at ambient temperature can be changed into a plastic (semisolid) fat or a completely solid fat at the same temperature. Naturally liquid (α-form) tung or oiticica oil can be converted into a solid fat (β-form) by the action of a trace of iodine or sulfur. These transformations of state are, however, not reversible, and each of the products, either original or transformed, will still exhibit changes of state (liquid$\rightleftharpoons$solid) with the appropriate change in temperature.

In view of the foregoing, the term *fat* is now quite generally used to include both *fats and oils* where specification of the physical state is of no importance and where the repetitious use of the phrase *fats and oils* becomes monotonous.

(b) Essential Oils and Fruit Essences

The essential or ethereal oils differ in composition and properties from the glyceride oils. They are odoriferous substances of an oily nature obtained largely from vegetable sources; generally liquids, but may be semisolid or solid at ordinary temperatures. They are often thought, erroneously, to consist largely of esters of fatty acids. Most essential oils are composed of terpenes, oxygenated constituents, sesquiterpenes, and a small amount of nonvolatile residue; of these the terpenes and sesquiterpenes are most characteristic. The oxygenated compounds include alcohols, aldehydes, ketones, esters, phenols, phenolic ethers, acids, lactones, oxides, coumarins, etc.

The distillation waters of essential oils contain small quantities of fatty acids, especially lower fatty acids, such as formic, acetic, propionic, butyric, and valeric. Most probably they do not occur as such in the oils but are formed by hydrolysis of esters in the course of distillation. Only a few essential oils consist largely of some ester, such as methyl salicylate (wintergreen and sweet birch oils) or linalyl acetate (bergamot, lavender, petitgrain, and clary oils). Orris root oil consists chiefly of myristic acid (83–96%) which accounts for the consistency of the oil but contributes nothing to the odor. Oil of ambrette seed consists principally of palmitic acid but it likewise contributes nothing to the odor of the oil.

Fatty acid esters are often found as constituents of fruit essences, for example, isoamyl isovalerate in bananas; and a large number of simple esters are used in formulating artificial fruit flavors, for example, ethyl and isoamyl butyrates, which are used in making artificial essences of pineapple, banana, strawberry, raspberry, red-currant and peach. Such esters are usually formed by the reaction of short-chain fatty acids.

(c) Waxes

The term wax was originally applied to the secretion of the glands on the underside of the abdomen of the worker bee of the genus *Apis*. The bee uses the material to construct its so-called honeycombs. Beeswax appears to be the first substance of this type with which man became familiar; it was clearly different from fats by being harder, more stable, and possessed of a high luster, especially when applied in thin layers and rubbed vigorously. Eventually, other substances having the same or similar properties were discovered and these too were called waxes in analogy to beeswax.

When these substances were subjected to chemical analysis they were found to consist essentially of esters of long-chain monohydric alcohols and monobasic acids admixed with various amounts of the same or similar long-chain alcohols and acids in unesterified form, hydrocarbons, sterols, resins, and other minor constituents. Waxes, therefore, came to be defined as esters of long-chain monohydric alcohols and long-chain fatty acids, but with the passage of time the word assumed a broader significance and came to be applied to various substances, natural and synthetic, which had little or nothing in common with true waxes, except such physical attributes as hardness, luster, chemical stability, etc. Solids such as paraffin hydrocarbons, long-chain alcohols, acids and esters of dihydric alcohols, which were hard and lustrous and which had a waxy feel and appearance, were referred to as waxes, especially in trade literature.

Moreover, various oily (sperm and jojoba oils) and greasy (wool grease) substances, which in nowise resembled beeswax or other hard waxes, were found to consist essentially of esters of monohydric alcohols and monobasic fatty acids. Some waxes (Japan waxes) were also found to consist essentially of esters of dibasic acids, but despite the general broadening of the term, the majority of the natural plant and insect waxes still conform to the original chemical distinction between fats and waxes.

3. History

Man has been familiar with fats since prehistoric time. Long before he had any knowledge of the chemical nature of these substances he recognized differences in their properties and employed them in a variety of ways. The use of fats as foods was probably instinctive but other applications no doubt resulted from observations of the properties and behavior of these substances under various environmental conditions. When and how man first became familiar with these substances and their manifold uses is lost in antiquity, but certainly fats, as well as waxes, were employed by primitive peoples of all climes as medicinals, in cosmetics, in religious ceremonies, as illuminants and lubricants, and for other purposes.

The ancient Egyptians and Phoenicians used vegetable oils for food and for anointing their bodies, but not for illumination. From them, knowledge of the application of fats and oils spread to the Hebrews, and thence to the Greeks.

Friedel (2) analyzed the contents of a number of earthen vases found in the interior of Egyptian tombs believed to predate the First Dynasty (ca. 3200 B.C.). One of these vases contained several kilograms of a pale brown, porous, granular substance which was found to consist of palmitic acid mixed with less than 51% of tripalmitin, indicating that the original material was a palm oil that had undergone oxidation and partial saponification. Another vase contained a firmer, more granular, paler mass consisting of stearic acid with about 30% tristearin and was probably beef or mutton tallow. A third vase, containing material similar to the first-mentioned, contained palmitic acid and 41% tripalmitin. These materials were probably intended as provisions for the dead. Other smaller vases contained unidentifiable fatty material mixed with galena which was probably used as a cosmetic.

Klemgard (3) mentions the fact that the Egyptians used olive oil as a lubricant for moving large stones, statues, and building materials and that axle greases consisting of a fat and lime together with other materials were used in lubricating Egyptian chariots as early as 1400 B.C.

Sarton's (4) *Introduction to the History of Science* contains many references to the use of fats and oils in the arts, technology, and medicine from the dawn of Greek and Hebrew knowledge (9th to the 8th centuries B.C.) to the Middle Ages. The Homeric poems contain a reference to the use of oil in weaving. Candles, made of beewax and tallow, were known to the Romans and prorbably were used by others in pre-Roman times.

According to Davidsohn, Better, and Davidsohn (5), soap was made by the Phoenicians as early as 600 B.C.; they used it as an article of barter with the Gauls. These authors state that it is not known whether the Romans learned the use of soap from the ancient Mediterranean peoples or from the Celtic inhabitants of Britannia who produced soap from fats and plant ashes and gave the product the name "saipo" from which the word soap is derived.

Soap, both as a medicinal and as a cleansing agent, was known to Pliny (23–79 A.D.) who mentions both hard and soft soap, and it may be inferred that soaps were known considerably prior to Pliny's time. According to Pliny, soap appears to have been made by boiling goat's tallow with causticized wood ashes to produce a soft soap which was converted to hard soap by repeatedly treating the pasty mass with salt or sea water. Excavations of Pompeii, which was destroyed in 79 A.D., has revealed at least two buildings equipped as soap factories.

The Greek physician Galen (ca. 130–200 A.D.) mentions soap as a medicant and body-cleansing agent and the physician Theodorus Priscianus (ca. 385 A.D.) mentions it as a shampooing agent. Geber (Jabir ibn Hayyan), the famed Arab chemist who lived about 800 A.D., repeatedly mentions soap in his writings.

Waxes, as well as resins, were used as protection against moisture, especially in shipbuilding and in some forms of wall painting. An early form of painting known as *encaustic,* actual specimens of which are known in the form of portraits on late Egyptian mummy cases and which was certainly used before then on wall decorations, employed a mixture of pigments in natural waxes. Another early form of painting known as *tempera* employed an emulsion of wax or oil, water, pigments, and an emulsifying agent such as a vegetable gum or egg yolk.

Varnishes were certainly used in Egypt on mummy cases of the New Empire. Many of these varnishes are insoluble, but their method of preparation is not known with certainty. The earliest mention of the use of a drying oil in a process connected with painting is given by Aetius about the 6th century A.D., who stated that nut oils dry and form a protective varnish. From this time on, the use of drying oils and varnishes seems to be well established and recipes dating from the 8th or 9th century A.D. are known for transparent varnishes composed of linseed oil and natural resins.

Theophilus Presbyter, an unknown craftsman, who lived about the end of the 11th and the beginning of the 12th century, devoted many chapters of his *Diversarum artium schedula* to the preparation and use of oil colors.

Theophilus used linseed oil together with some kind of resin, probably amber, copal, or sandarac. He gives many recipes for the preparation of paints, varnishes, and dyes. However, the discovery of the effect of driers in linseed oil paints, which is accredited to the brothers van Eyck, was not made until the first half of the 15th century.

The extensibility of oil upon the surface of water appears to have been known by Greek sailors and was applied by them to subduing waves during a storm. This phenomenon of surface tension or extension of oil upon the surface of water, was investigated by the great Hindu mathematician Bhāskara who is presumed to have lived about 1114 to 1178 A.D.

The American Indian apparently was long familiar with many oil-producing plants and employed them as food, medicine, cosmetics, and illuminants. Standley and Steyermark (6) state that the Indians of Panama strung the oil-rich nuts of a species of *Virola* on thin splinters of wood and used them as candles. In Belém, Brazil, the author was told that the natives of the Amazon followed a similar practice with the nuts of *Virola surinamensis* and *V. sebifera* (ucuhuba nuts). Elsewhere in South American the nuts of various species of oilpalms appear to have been similarly used.

As animal and vegetable fats were used from the time of the earliest records, methods for their separation must have been devised before the dawn of history. Probably the first fats used by man were of animal origin—tallows and greases—which were separated from other tissue simply by heating or boiling with water. Certain oily fruits, for example, the olive and the African oilpalm in the Old World and the avocado in the New, as well as certain oil-rich nuts may likewise have been made to yield their oils in the same manner. In the oilpalm (*Elaeis guineensis*) belt of west Central Africa, as well as in Brazil, the natives still produce oil by boiling the fruit of the oilpalm with water after preliminary fermentation and maceration of the pulp. Long before the advent of Europeans in the Western Hemisphere, the natives in many parts of South and Central America produced oils from various palm and other oil-rich nuts by crushing the kernels, roasting the crushed mass, and boiling it with water. This process is still practiced in isolated parts of South America and was observed by the author (7) in the interior of the State of Bolivar, Venezuela, south of Caicara, where it was being applied to the kernels of the coroba palm (*Scheelea macrolepis*).

Recovery of oil from small seeds with extremely hard seed coats required the development of more vigorous methods of processing and probably gave rise to cooking, grinding, and pressing processes. However, these too are of very ancient origin. Cotton was manufactured and cottonseed crushed for oil and cake by the Hindus as early as the 5th century B.C. and possibly earlier. Old medical books of the Hindus recommended cottonseed oil for external applications and described the method of extracting it by pounding the seed and then boiling it with water. It is believed that about this same time cottonseed oil was produced in China by grinding in edge runner mills followed by heating and pressing in wedge presses.

The Hebrews possessed oil mills powered by treads that were usually operated by prisoners. According to Blank (8), sesame, linseed and castor oils were produced in Egypt by pressing as early as 259 B.C., and that as early as 184 B.C. screw and wedge presses, filters, and edge runner mills were used in Rome for the production of oil.

Pliny the Elder (23–79 A.D.) described olive, rice, almond, sesame, grapeseed, walnut, and palm oils. He also described an olive oil mill which resembled the edge runner, the stones being flat on the inner side and convex on the outer side. The Greeks and Romans are said to have employed screw presses similar to wine presses for recovering olive oil.

The wedge press was used in very early times in the Orient, particularly in China, where it is still operated. Another type of extractor, known as ghani, chekku, or kolhu, was developed long ago in India. It operates on the principle of a pestle rotating in a mortar and is often powered by bullocks. The ghani is still used in remote areas of India (9).

Ample evidence exists to attest the fact that the peoples of all early civilizations were acquainted with a variety of fats and waxes, various methods for producing them, and a considerable number of uses and applications. Aside from their use as food, they were used in the manufacture of protective and decorative coatings, soaps, and cosmetics, as illuminants, medicinals, lubricants, and in religious ceremonies. The primary applications of these substances are very much the same today as those which prevailed in antiquity. However, in addition to the uses prevailing since remote times they are now employed in numerous ways unknown to the ancients.

The uses of fats and oils which were known prior to the beginning of the 19th century were based on empirical knowledge that had accumulated slowly over many centuries, whereas many of the present-day uses have stemmed largely from a knowledge of the composition, structure, properties, and reactions of these substances, and of their component fatty acids and derivatives, obtained through the application of scientific methods of research.

A number of important discoveries concerning the chemical nature of fats were made almost at the birth of modern organic chemistry. Scheele obtained glycerol by heating olive oil with litharge in 1779 and in 1813 Chevreul began his researches on fats which culuminated in the classical work, *Recherches chimiques sur les corps gras d'origine animale.* In 1814 he isolated butyric acid from butter; in 1816 established the glyceride nature of fats; in 1817 he prepared stearic acid; and between 1818 and 1823, valeric, caproic, and impure oleic acid.

In 1819 Poutet converted oleic acid to elaidic acid by treatment of the former with the oxides of nitrogen, but the acid was not isolated until 1832 by Boudet. In 1828 Gusserow differentiated oleic and other unsaturated acids from palmitic and stearic on the basis of the differential solubility of the lead salts of these acids. A year later Lefèvre observed that tallow could be treated with sulfuric acid to yield fatty acids. In 1834 Runge prepared the first "sulfonated" oil by the action of sulfuric acid on olive oil; in 1841 Varrentrapp observed that the fusion of oleic acid with caustic soda gave palmitic and acetic acids; in 1844 Pelouze and Gélis synthesized tributyrin by the direct esterification of glycerol and butyric acid; and in 1849 Darby isolated erucic acid. Only the classical study of esterification by M. Bertholet between 1853 and 1862 can be compared with Chevreul's contribution to the chemistry of fatty acids.

Among Bertholet's contributions was the demonstration in 1854 of the trihydric nature of glycerol, the synthesis of the first non-glycerol polyhydric alcohol esters in 1855, the synthesis of mono-, di-, and triglycerides, and the suggestion that natural fats consisted of mixtures of heteroglycerides rather than mixtures of homoglycerides.

During the remainder of the century little progress was made in the fundamental chemistry of fats and fatty acids, but many useful analytical tests were developed and many practical developments occurred which were to continue at an accelerated pace during the first half of the 20th century. New and more efficient methods of saponification were introduced, as well as the vacuum-distillation of fatty acids and glycerol and the solvent extraction of fats; Turkey red oil was prepared by sulfonation of castor oil (1875); margarine and linoleum were invented and commercial manufacture of these products was begun in various countries.

Various factors appear to have retarded the chemists' interest in natural fats during the second half of the 19th century. Foremost of these, no doubt, was man's long familiarity with these products, and the fact that over a period of centuries a considerable empirical knowledge concerning them had been acquired, permitting the establishment of numerous