FATTY ACIDS

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THEIR CHEMISTRY AND PHYSICAL PROPERTIES

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PREFACE

The higher fatty acids have been the subject of continuous research and investigation since about 1815, when Chevreul established the constitution of natural fats as the glycerol esters of these long chain aliphatic compounds. During the interval of nearly one and a half centuries which has elapsed since Chevreul's discovery a vast literature has accumulated dealing with the chemical and physical properties of the fatty acids and their simple derivatives. Moreover, the increment of this knowledge during the past twenty-five years has exceeded that of the entire preceding history of these substances. This accumulated literature is not only voluminous but it is widely scattered and relatively unorganized. Although all books and monographs on fats, oils, or waxes devote some space to a description of the more common properties and reactions of the fatty acids as a background to the main subject, none has been devoted solely to an exposition of our knowledge of the fatty acids *per se.*

The purpose of this volume has been to bring together in an organized and readily accessible form as much as possible of the present accumulation of facts and data pertaining to the chemical reactions and physical properties of the fatty acids and, especially, of the long chain fatty acids which comprise the building stones of all natural fats, oils, and waxes. The material thus made available should obviate many hours of searching the literature by the large and growing body of chemists, physicists, engineers, and technologists who are interested in the fatty acids and their numerous products and by-products.

While it has not been the primary purpose to discuss the lower members of the fatty acid series at length, it has nevertheless been impossible to ignore them entirely. Although the lower members of this series are not generally encountered as components of the fatty glycerides or the solid waxes, they do occur as simple esters in fruit essences and many ethereal oils. Furthermore, many of the reactions and derivatives of the fatty acids have been investigated only for the lower members of the series. This is especially true with respect to various physical properties of these acids and their derivatives. Moreover, it is only when the reactions and properties of the complete series are examined that it becomes apparent to what extent additional work is necessary to fill the missing gaps in our knowledge of these substances. It has likewise not been the primary purpose to discuss the chemical and physical properties of the glyceride esters and natural fats, because a comprehensive treatment of these subjects would require a volume at least the same size and scope as the present one. Here too, however, it has been impossible to ignore them entirely.

In the process of assembling the data with respect to the physical properties of the fatty acids and their derivatives, a number of anomalies has come to light. For example, many of the most useful and important properties were determined twenty-five or more years ago when it was most improbable that even moderately pure fatty acids were available. Also, very many of the reported constants have been obtained incidentally and not as a result of planned or systematic investigations. Owing to the incidental manner in which many physical properties have been determined, there is often no way of selecting the most reliable value from among several which may have been recorded by different investigators for the same compound. However, an effort has been made to include only the most accurate values available for the various properties, but in some instances these may be in error. Where no choice appeared to be preferable, two or more values are sometimes given without comment.

It is hoped that, in addition to the purposes mentioned above, the present work will result in the stimulation of qualified individuals to undertake investigations designed to fill the missing gaps in our knowledge of the subject and to re-examine those reactions and properties which obviously are in need of review.

While the plan and contents of the present volume are the author's and any defects found therein are attributable to him alone, he has had the assistance of many individuals in its preparation and desires to make grateful acknowledgment to them. For their invaluable assistance in reading and criticizing the individual chapters, he is deeply indebted to A. M. Altschul, A. E. Bailey, S. T. Bauer, F. G. Dollear, Mrs. M. G. Lambou, R. T. O'Connor and E. L. Skau. Sincere thanks are also expressed to R. O. Feuge who prepared many of the original drawings, to C. H. Billett for assistance in preparing photographs for illustrations, to B. Ashby Smith who checked the calculated molecular weights, neutralization values, iodine values, etc., of the many tables of such data, to Mrs. E. L. Skau for checking and verifying all literature citations, to M. E. Jefferson and Mrs. F. B. Kreeger for preparation of the original x-ray photographs, and to Mrs. Calla L. Markley and Mrs. Ruth R. Warren for an inordinate amount of typing of the various drafts of the manuscript. The author also wishes to thank the editors of *The Journal of the American Oil Chemists' Society* and *Industrial and Engineering Chemistry* as well as various industrial concerns and publishing houses for permission to reproduce illustrations from their publications.

K. S. Markley

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CHAPTER I

HISTORICAL AND GENERAL

1. Introduction

The three most important classes of compounds which occur in nature are the proteins, the carbohydrates, and the fats. All vital processes are involved primarily in the elaboration or degradation of these substances, assisted or activated by various natural catalysts such as enzymes, vitamins, hormones, and other vital agents. Each of these classes of compounds is represented by numerous and varied individual members which are elaborated by nature from a small number of simpler compounds. The proteins, no matter how complex, are all built up from simple amino acids, the carbohydrates from glucose residues or other simple monosaccharides, and the fats and waxes from a small number of fatty acids.

The fats differ from the proteins and carbohydrates by the fact that the latter consist solely of condensation products of similar structural units, whereas in the fats the component acids are attached to a common skeleton, namely, the trihydric alcohol, glycerol. The natural fats also differ from proteins and carbohydrates by virtue of the fact that their complexity is due, in part, to mechanical admixture or mutual solubility of several components of relatively low molecular weight rather than to the existence of highly condensed systems.

The large number and complexity of the natural fats have their origin in two sources, namely, in 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 in the mixture or solution comprising the fat. The natural waxes likewise consist of mixtures of esters of fatty acids, but these esters are derived, not from one polyhydroxy alcohol, but from a number of alcohols having relatively long hydrocarbon chains and only one replaceable hydroxyl group. Their complexity is due, therefore, to the variety of combinations which may result from esterifying different fatty acids with different monohydroxy alcohols, and from the relative proportions of these esters in the mixture comprising the wax.

Although the present volume is concerned primarily with the fatty acids and their derivatives rather than with the natural fats and waxes, nevertheless, the latter represent the natural source of these substances and provide the stimulus for investigating their chemical and physical properties. Consequently, in discussing the fatty acids, frequent references to and comparisons with the natural fats and waxes will be made throughout the text and, especially in the introductory chapter, where the related histories of the two are set forth against a common background.

2. Definitions

The words *fats and oils* have been applied both in the technical and lay literature with so many different meanings that it is necessary to define them at the outset to avoid subsequent misunderstanding regarding their usage in the present instance. Throughout this work, the term *fats and oils* will be used to refer to that class of lipoidal materials consisting of the glycerol esters of the fatty acids and their associated phosphatides, sterols, alcohols, hydrocarbons, pigments, etc., which are obtained from plants and animals by such industrial processes as pressing, cooking with steam and water, extraction with organic solvents, or any combination of these processes.

No chemical distinction exists between *fats and oils*, and by an oil is meant a liquid fat, and by a fat is meant a solidified oil. These changes in physical state may occur more or less spontaneously as a result of change in environment (temperature, light, etc.), or as a result of chemical treatment (hydrogenation, isomerization, etc.). For example, a liquid oil at room temperature may be hydrogenated to produce a hard fat at the same temperature, but on elevation of the temperature a few degrees it will again resume the liquid state. Naturally occurring tung and oiticica oils exist as liquid fats (α-form) but are readily isomerized by the action of light or suitable catalysts into geometrically isomeric solid fats (β-form).[1] By raising the temperature of these solid fats, they again become liquid although the geometrical isomerism is not reversed. The difference, therefore, between a fat and oil is one of physical state which is reversible merely by changing the surrounding environment. Furthermore, as pointed out by Bailey[2] the designation of fats as solids is somewhat misleading since at ordinary temperatures fats are actually plastic solids, and consist of a liquid in intimate mixture with many very small solid particles. At 70°F., for instance, only about one-third of the glycerides of lard are in the solid state.

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 constant use of the phrase *fats and oils* becomes monotonous and repeti-

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[1] R. S. Morrell and W. R. Davis, *J. Oil Colour Chem. Assoc.*, **19**, 264–272 (1936).

[2] A. E. Bailey, in *The Chemistry and Technology of Food and Food Products.* Vol. I, M. B. Jacobs, ed., Interscience, New York, 1944, p. 567.

tious. This practice will be followed here for the reasons that have just been mentioned.

3. History

Man has been familiar with fats since prehistoric time. Long before he had any knowledge of the nature of these substances he recognized differences in their properties and employed them in a variety of ways. Their use as foods was probably instinctive but their other applications no doubt resulted from observation of their properties and their behavior 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.

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. Friedel[4] analyzed the contents of a number of earthen vases found in the interior of Egyptian tombs believed to predate the First Dynasty. 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 palm oil which 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.

Sarton's[5] *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. 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. Candles, made from beeswax and tallow, were known to the Romans and probably were used by others in pre-Roman times.

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[3] E. N. Klemgard, *Lubricating Greases: Their Manufacture and Use.* Reinhold, New York, 1937, p. 14.

[4] C. Friedel, *Compt. rend.*, **124**, 648–653 (1897).

[5] G. Sarton, *Introduction to the History of Science.* 2 vols., Carnegie Inst. Wash. Pub. No. 376, Williams & Wilkins, Baltimore, 1927–31.

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.

Ample evidence exists which attests the fact that the peoples of all early civilizations were acquainted with numerous uses of fats and waxes and strangely enough, the primary applications of these substances are today much the same as those which prevailed in antiquity. Aside from their uses as foods, they are consumed in the production of protective coatings (paints, varnishes, and finishes of various types), cosmetics and pharmaceuticals, soaps, lubricants, fuels, and illuminants. However, in addition to these uses, fats and oils serve today as the raw materials for the production of such products as textile assistants and synthetic resins, fibers and rubbers, as flotation agents for the separation of the mineral constituents of ores, as de-emulsifiers in the production of petroleum oil, insecticides, weed killers, and in many other products and processes. In fact, the number of products derived from natural fats and oils becomes increasingly larger year by year. This increased and diversified application of natural fats and oils has stemmed primarily from the advances which have been made in the knowledge of the composition, structure, and properties of these substances during the present century.

A number of important discoveries concerning the chemical nature of natural fats were made almost simultaneously with the birth of modern organic chemistry. Scheele obtained glycerol by heating olive oil with litharge in 1779 and about 1815 Chevreul established the fact that the common animal and vegetable fats and oils were composed of glycerol and the higher fatty acids. In 1819 Poutet converted oleic acid to elaidic acid by treatment of the former with the oxides of nitrogen. In 1828 Gusserow differentiated oleic and other unsaturated acids from palmitic and stearic acids on the basis of the differential solubilities of the lead salts of these acids. Following these discoveries little progress was made in the fundamental chemistry of fats and oils until after the beginning of the 20th century, and this despite the fact that during the 19th century the most brilliant and far-reaching discoveries were being made in many fields of organic chemistry.

Various factors appear to have operated to retard the chemists' interest in natural fats. 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 industries devoted to the processing of these products for consumption as food, in soapmaking, and in the manufacture of paints, varnishes, and related products. Generally, there were no burdensome surpluses of fats and oils and they did not accumulate as by-products in the manufacture of other products as was the case with coal tar, hence they presented no disposal problem and they were not a source of cheap raw material.

From the academic point of view, fats were not attractive research materials as they were not readily crystallizable and few crystalline derivatives could be prepared from them. Furthermore, they were considered to be very simple substances, or at best, more or less complex mixtures of simple triglycerides of fatty acids. They were assumed to possess few characteristic chemical or physical properties, and they could not be separated into definite chemical entities by any simple method such as crystallization or distillation.

The process of saponification by means of which fats can be broken down to produce fatty acids has been known for about 20 centuries, but the mixtures of fatty acids produced by saponification apparently were no more attractive to the organic chemist than were the original natural fats. Here again, simplicity of structure of the individual acids, the difficulty of isolating them in pure form, and, in the case of the unsaturated acids, the difficulty of converting them to crystalline derivatives appear to have been among the chief reasons for their neglect. The fatty acids were known to consist of a relatively long, saturated or unsaturated, hydrocarbon chain with a terminal carboxyl group. It was assumed that such simplicity of structure afforded little opportunity for applying newly discovered ingenious reactions which were being applied so effectively in other directions in preparing hitherto unknown organic compounds. During this period of development of classical organic reactions, hydrocarbon chemistry, based on petroleum, was in its infancy, and the chemistry of high molecular weight polymers was unknown. However, the development of numerous products from petroleum hydrocarbons, followed by the application of polymerization reactions to many simple organic molecules, undoubtedly stimulated the chemist to turn to the natural fats and their derived fatty acids as a source of raw materials for the production of similar products.

As late as 1924, Armstrong[6] in a Presidential address entitled, *A Neglected Chapter in Chemistry,* presented at the annual meeting of the Society of Chemical Industry, stated: "This account of our knowledge of the fats and of some of the many problems needing study, particularly in the organic branch of chemistry, is mainly written with the hope of reviving interest in them as, apart from physical and analytical investigations, *no other province of chemistry has been so little studied in recent years.*"

Strangely enough, about this time a renaissance in the chemistry of fats had its inception, and at the present time the tempo of research in this field is increasing at a continuously accelerating rate. The increased interest in the chemistry of fats and fatty acids is evident not only in the expansion and diversification of the literature on the subject, but also in the appearance of a number of scientific journals devoted solely to publication of research in this field. Bull[7] has referred to the fact that in 1932, *Chemical Abstracts* contained approximately 800 abstracts on various phases of lipid chemistry compared to approximately 150 in 1917. It should be noted that a very considerable proportion of the recent expansion in the literature relating to fats and fatty acids has had its origin in the multiplication of research laboratories in the United States which are devoted to many phases of research in this field. With the influx of many additional workers in this field there has come a realization that the chemistry of the fats and fatty acids is not as simple as was heretofore supposed and, consequently, many preconceived ideas concerning their nature and reactivity have undergone revision.

It has been found that the glycerides, and/or the fatty acids, are capable of undergoing many types of reactions including condensation and polymerization, halogenation, oxidation, dehydration, isomerization, etc., as well as conversion into numerous derivatives such as amides, amines, ni-

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[6] E. F. Armstrong and J. Allan, *J. Soc. Chem. Ind.*, **43**, 207–218T (1924).

[7] H. B. Bull, *The Biochemistry of the Lipids.* Wiley, New York, 1937.