# Fatty Acid Derivatives*

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The chemist's knowledge of the fats and fatty acids probably antedates that of any other group of organic compounds. Stearic acid was described by Chevreul before benzene was discovered and chemists were familiar with the general properties of oleic acid at a very early date in our chemical history. Soaps were known and used by the ancients long before man had any concepts of atoms and molecules, and fats and fatty acids were subjected to chemical reactions perhaps centuries before chemistry itself could be considered as being even a rudimentary science. If one browses through early chemical literature he will find many references to the constitution of fats as composed of earth, acid, fire, and water and also considerable discussion concerning the so-called "oil principle" which was supposed to be an integral part of all fatty substances. As early as 1797 Fourcroy described this "oil principle" in his book entitled "Elements of Natural History and Chemistry" and he considered it to be an inherent part of a fatty oil and also that pyrolysis of the fat separated this so-called "principle."

In spite of our very early familiarity with the fats and fatty acids and in spite of the intense interest of early chemists in them it is quite surprising to note that our knowledge concerning them is as yet rather meager. Both the chemist and the biologist have underestimated or neglected the importance of the fatty acids and their many possible derivatives. The chemist has not fully appreciated the many fascinating problems which are inherent in the physical chemistry of the fatty acids or their simple derivatives nor has he realized that in the fatty acids we have probably the greatest source of aliphatic compounds for chemical synthesis known to mankind. The biologist, on the other hand, has long considered the fats as simply a source of energy and has only recently attached any vital significance to them.

It might be of interest at this time to pause and speculate why for the past fifty years chemists have evidenced only a superficial interest either in the fatty acids themselves or in the products which can be prepared from them.

One of the major reasons why the fats and fatty acids have not received more attention is that chemists have been quite willing to accept what nature has provided. Thus linseed oil is known as a good drying oil and it has only been comparatively recently that serious attempts have been made to modify the structure of this oil in order to improve its drying properties. We are also very prone to think that a substance having drying properties should imitate linseed oil in its structure. Certain edible fats are known to possess desirable qualities but it has not been until the last years that much work has been done to correlate these properties with the actual chemical composition or configuration of the glyceride molecule. That such a study would be of great value has been indicated by some preliminary work which has already been done.

Another major factor which has contributed toward making the chemistry of the fats and the fatty acid derivatives an empirical rather than an exact science has been the lack of efficient methods for the separation of pure fatty acids from fatty acid mixtures. The synthetic organic chemist invariably prefers to work with pure compounds rather than with mixtures and major chemical advancements have resulted mainly when the organic chemist has had large amounts of pure organic compounds as the available starting material. Much of the advancement in the aromatic field can be attributed to the fact that the various starting materials such as benzene, toluene, anthracene, carbazole, etc., have been efficiently separated and have been made available to the chemist. Certainly much more work is indicated along this line in the fatty acid field. Distillation of the methyl or ethyl esters has served to efficiently separate the saturated acids one from another and the distillation of the acids themselves has made reasonably pure saturated fatty acids available in commercial quantities. When we come to the unsaturated fatty acids, such as oleic, linoleic, and linolenic acids, no satisfactory method has been developed for this separation on a commercial scale and those laboratory separations which are available are long and tedious and generally result in poor yields. These unsaturated fatty acids would be of much more interest to the organic chemist if they were available in higher degrees of purity. There is no problem of more importance to the fatty acid field as a whole than the development of effective methods for separating these unsaturated acids one from another. When this is accomplished they will probably be the parent substance for the production of many important organic chemicals.

Another reason why chemists, particularly organic chemists, have not chosen the fatty acids and their derivatives for investigation is because they have considered that in this field they would only be working with waxy compounds. We all know that the synthetic organic chemists delight in easily crystallizable compounds, sharp melting points and well defined derivatives. Such properties are generally found when one is dealing with aromatic chemicals. When one is working with high molecular weight aliphatic derivatives, such as the fatty acid derivatives, it must be admitted that frequently special techniques are required and well defined classifying derivatives are often difficult to obtain. It is true, however, that these features are often much overemphasized.

Still another reason why chemists have not entered enthusiastically into the fatty acid field is because they feel that aromatic compounds undergo many typical reactions which find no counterpart in aliphatic chemistry. Thus direct sulfonation, nitration, halogenation, and diazotization are thought to be type reactions which can be applied only to aromatic compounds. That this is not strictly true has been shown by the observations that, with the proper tech-

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nique, high molecular weight aliphatic compounds can be made to undergo many reactions, such as diazotization, which were formally classed as typical of aromatic compounds or specialized types of aliphatic compounds. Recent work has shown quite definitely that aromaticity is a relative term and that even a double bond in a hydrocarbon chain exhibits some aromatic properties. With this removal of any definite dividing line between aromatic and aliphatic compounds there comes a realization that the fatty acid derivatives may be reactive in many instances in which they were previously considered to be inert.

Many chemists are inclined to consider the fatty acids as relatively simple chemicals which differ only in molecular weight, boiling point, melting point, etc., but which are so similiar as to make individual acids essentially devoid of interest. Nothing could be further from the truth. Witness, for example, oleic acid which has the formula $C_{17}H_{33}COOH$ and which would be classed as one of the simplest of the unsaturated fatty acids. Oleic acid has its double bond in the 9,10-position and is, therefore, correctly termed 9,10-octadecenoic acid. A study of the structure of the octadecenoic acids shows that there are actually 16 possible acids of the general formula $C_{17}H_{33}COOH$, by reason of position isomerism, and a cis and trans isomer for each position of the double bond, except one, so that there are actually 31 acids of the above general formula. When we consider acids with two, three or more double bonds it becomes apparent that by virtue of their possible isomeric forms alone the fatty acids are compounds of extreme interest.

In spite of the several reasons which have deterred chemists from extensive investigations of the fatty acids it can be stated that they are the greatest source of pure aliphatic compounds of high molecular weight in existence. The last ten years has witnessed the production on a large scale of high molecular weight alcohols, amines, and amides and these will undoubtedly be followed by a large number of other simple derivatives. In addition many more complex substances such as polymers, plastics, elastomers, etc., will certainly be developed commercially using the fatty acids as the starting material.

Fatty acid derivatives can be roughly divided into two general groups: the simple derivatives and the complex derivatives. By a simple derivative we refer to a compound which can be prepared from the fatty acids and in which the alkyl or alkylene group retains its identity, either partially or totally. This is in contrast to a plastic or an elastomer where the alkyl or alkylene group is a portion of such a complex molecule that it loses its individual characteristics. The simple derivatives are all characterized by the long chain alkyl or alkylene group attached to one or more polar groups. They, therefore, possess interesting film forming characteristics, the ability to lower the surface tension of solutions, adsorption phenomena, etc. Their use in lubrication, flotation, emulsification, and many other fields is therefore indicated. The high molecular weight alcohols, amines, ketones, aldehydes, nitriles, hydroxy acids, etc., are examples of compounds of this type.

As an example let us consider for a moment the nitrogen derivatives of the fatty acids. Reaction of a fatty acid with ammonia first results in an ammonium soap which loses water at an elevated temperature and is converted into an amide. These are relatively high melting compounds useful as coating materials or impregnating agents. An amide of a fatty acid is simply a fatty acid in which the hydroxyl or OH group of the COOH group of the acid has been replaced by an amino or $NH_2$ group. Acid amides are, therefore, characterized by the presence of the group $—CONH_2$. Reactions such as sulfonation, bromination, etc., convert them into a wide variety of interesting and useful compounds.

When an amide is heated the $—CONH_2$ group loses a molecule of water and is converted into the nitrile or —CN group. These are either liquids or low melting solids and are in general quite chemically reactive. The nitriles have several interesting uses in themselves. For example, a number of them have been found to possess insect repellent properties; they are being used as plasticizers for synthetic rubber and as chemical intermediates. Hydrogenation of these nitriles results in the corresponding primary or secondary amines.

The amines have the general formula $RNH_2$, $R_2NH$, or $R_3N$ depending upon whether they are primary, secondary, or tertiary amines. They can, therefore, be considered as substituted ammonia in which the hydrogens of the ammonia are replaced by alkyl or alkylene groups. They form salts with acids and these salts can be looked upon as substituted ammonium compounds. One of the major points of interest in these compounds is that they differ from the usual fatty derivatives such as soaps, sulfuric acids, etc., in that the hydrocarbon group is in the positive portion of the molecule. Their adsorption characteristics, therefore, offer a fascinating study. Many uses have already been found for these amines and the number of such uses is increasing rapidly.

What is being done with these nitrogen derivatives of the fatty acids will undoubtedly be repeated with many types of derivatives.

When we come to the more complex products which can be prepared from the fatty acids we enter a field which is essentially limitless. There is no question but that many plastics, elastomers, and similar substances can be made wholly from the fatty acids.

A study of the configuration of the naturally occurring fatty acids offers many points of interest to the biologist and biochemist. For instance, why is it that palmitic and stearic acids constitute such an overwhelming proportion of the saturated acids found in nature, or that no acids containing an uneven number of carbon atoms are found? In the unsaturated series of acids nature appears to have worked out a very intricate picture. Oleic acid is the most abundant of all of the fatty acids and it is interesting to note that the position of its double bond between the ninth and tenth carbon atoms is repeated in linoleic, linolenic, and many other acids.

In this talk an attempt has been made to view the fatty acid derivative field in its broad aspects. It is certainly true that this is a branch of chemistry which will receive increased attention and that it cannot long be denied its rightful place.