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Oils, Fatty—Pituitary Body

With an index by Dr. J. N. Goldsmith

WITH ILLUSTRATIONS

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NOTE.

Italicised words in inverted commas may be registered trade names.

ERRATUM.

In Vol. VIII, p. 644, Table I, last line, *for* −101° *read* 101°.

A DICTIONARY OF APPLIED CHEMISTRY.

O—*continued.*

OILS (FATTY) AND FATS. The materials to be considered are the natural fats produced in the vegetable and animal kingdoms, especially those which find important use in the production of edible fats, soaps, or other detergents, paints and varnishes, and in some other industries. The discussion is therefore broadly confined to the natural glycerides (esters of higher fatty acids with glycerol) which form the overwhelming bulk of the industrially useful fats. Other forms of fatty-acid derivatives are found in nature and may accompany the glyceridic fats. Such forms include phosphatides, in which a glycerol molecule is combined with two higher fatty-acid radicals, the remaining glyceryl hydroxyl group being united to phosphoric acid which in turn is linked with a nitrogenous base (chlorine or β-aminoethyl alcohol); wax esters, which are esters of higher fatty acids with some of the corresponding higher fatty alcohols, or with sterols (or vitamin-*A*), or (in a few instances) with a glyceryl higher acyl ether (batyl, selachyl, chimyl alcohols); and some other more complex substances such as sphingomyelin (cerebrosides, etc.). Although in most cases glyceridic fats (mixtures of mixed triglycerides, to which the term *fats* will be restricted throughout this article) are substantially the only lipid substances present in the materials here dealt with, a rigid line of demarcation cannot be drawn. In particular, some of the natural fats are accompanied by waxes of the ester type mentioned. This is notably the case in the sperm-whale oils and a few other fats of marine origin; whilst the small amounts of sterols which usually accompany natural fats, and of batyl, etc., alcohols which are sometimes present, frequently occur in the form of higher fatty esters in the natural state. These sterols and other alcohols, which are usually termed "unsaponifiable constituents," are thus mainly present in the form of wax esters (or ester-waxes). Ester-waxes in which glycerides are not present, such as the insect waxes (*e.g.*, beeswax) and vegetable waxes (*e.g.*, carnauba wax), are mainly esters of aliphatic alcohols and acids of higher molecular weight than those present in the glyceridic fats; they are outside the scope of this article.

Consideration of the natural fats (triglycerides) is thus complicated to a certain extent by the circumstance that they are frequently accompanied by some of the other lipid groups, usually in very small proportions, but occasionally in larger amounts. It has been complicated further until recently by the terminology applied to the glyceridic fats themselves. Originally, only those natural fats which happened to be solid at the usual temperatures were referred to as fats: those liquid at the usual temperatures were first termed "fixed oils," to distinguish them as a class from the volatile or essential oils (terpene derivatives, etc.) also found in the vegetable kingdom. Even later, the liquid fats have been usually termed oils, or fatty oils, and the usage in the case of well-known specific fats such as linseed oil or cottonseed oil has become so conventional that it must remain. Nevertheless it is desirable for systematic purposes to classify the entire group as "fats," distinguishing solely, if desired, between solid fats and liquid fats (the "fatty oils").

GENERAL NATURE OF NATURAL FATS.

Natural fats occur throughout the vegetable and animal kingdoms from the simplest organisms up to the most highly developed forms of vegetable and animal life, and are present in almost all tissues and organs. In the vegetable kingdom, fats are deposited in largest amounts in the seeds, usually in the endosperm where, with proteins and carbohydrates (starch), they serve as nourishment to the embryo. In some instances the fleshy fruit-coat (pericarp or receptacle) of the seed also contains notable proportions of fat, whilst in certain plants fat is present in some quantity in the tubers or rhizomes. In small proportions, it should be noted in passing, fats are found in all parts of the growing plant, roots, leaves, and fruits, but in most instances it is only in the seed that any high concentration of fat is observed. In animals, fats are usually stored in quantity in certain tissues, notably beneath the skin and around or in some of the intestinal organs. The kidneys are normally surrounded by a layer of fat, and in some animals (mainly fish) the liver serves as a fat-store as well as being, in all animals, the probable main site where fats are synthesised and elaborated by the animal. Fats also occur, but often only in minor proportions, in most of of the organs and tissues of animals. Finally, in mammals, the milk fats are important members of the group which may differ characteristically in composition from the rest of the animal fats.

From the technological standpoint, the fats of most interest are naturally those available in greatest quantity and concentration in the respective natural organisms. In the vegetable kingdom, therefore, it is the seed fats and a few fruit-coat fats which are of chief value, especially seed endosperms which are rich in fat and contain, *e.g.*, from 25 to 50% of fatty matter. In the animal kingdom, similarly, the main storage or depot fats are those of greatest industrial value—the adipose tissue fats from the back or rump of domestic animals such as the pig or ox, the blubber of whales, the perinephric fat surrounding the kidneys (lard, suet), and in fishes either flesh fats (*e.g.*, herring) or liver fats (*e.g.*, cod). To these must be added, as already mentioned, the mammalian milk fats (especially butter fat from the cow) on account of their dietetic importance.

METHODS OF INVESTIGATION OF THE COMPONENTS OF NATURAL FATS.

Natural fats are essentially mixtures of mixed triglycerides and resolution into their component glycerides by physical means is usually impracticable. A typical animal body fat, for example, may consist of large proportions of palmitodiolein and oleopalmitostearin, with lesser quantities of such mixed glycerides as oleodistearin, oleodipalmitin, palmitodistearin, dipalmitostearin, and triolein. The solubilities of many of these components are too similar to permit of any adequate resolution by crystallisation. Nevertheless, as shown below, other methods have been utilised whereby an approximate knowledge of the constituent mixed glycerides can be obtained, at all events when the mixture of fatty acids present in the whole fat is not too complex.

Component Fatty Acids.—Whilst the determination of the component glycerides of a fat is a difficult and laborious undertaking, that of the component fatty acids (*i.e.*, the mixture of fatty acids present in combination as glycerides and obtained by quantitative hydrolysis of the fat) can be effected with considerable accuracy, although here also the procedure is lengthy. The method hitherto usually employed has been first to separate the mixed fatty acids from a fat into two groups—those the lead salts of which are insoluble in 95% alcohol, and those the lead salts of which are soluble in this medium. (In the special case of milk fats, which may contain butyric, hexanoic, and octanoic acids, these are removed as far as possible by distillation of the mixed fatty acids in a current of steam before carrying out the lead-salt separation, the steam-volatile acids being recovered and dealt with separately by fractional distillation.) The lead salts of palmitic, stearic, and higher saturated fatty acids are insoluble in alcohol, those of myristic, lauric, decanoic, and octanoic sparingly (but increasingly) soluble, whilst of the unsaturated acids only the mono-ethenoid acids of the C_{20}, C_{22}, and C_{24} series, and to a minor extent oleic acid (together with "iso"-acids from hydrogenated fats) form lead salts sparingly soluble in alcohol. On the other side, monoethenoid acids of the C_{18} series or lower homologues and all natural polyethenoid acids yield lead salts which are freely soluble in alcohol, whilst, as stated, lead oleate is largely soluble. Consequently this preliminary separation gives (i) one group of fatty acids in which nearly all the palmitic and all the higher saturated acids are present, with part of any myristic or lower saturated acids, a small proportion of oleic and most of any higher monoethenoid acids, and (ii) another group of fatty acids containing, in addition to small amounts of palmitic and lower saturated acids, practically all the unsaturated acids from the original fat. The lead-salt separation has given excellent service although it is not fully effective when the saturated acids form 10% or less of the total acids in a fat, or when they consist largely of acids of lower molecular weight than myristic or palmitic. Furthermore, the conversion of the more unsaturated acids into salts and then back to free acids offers opportunities for oxidation or other chemical changes which are better avoided, *e.g.*, by the use of physical rather than chemical methods of separation.

Such a physical method, rapidly coming into use, is the resolution of a mixture of fatty acids into several groups (in which, respectively, saturated, monoethenoid, or polyethenoid acids will be largely concentrated) by crystallising it systematically from appropriate solvents over a range of temperatures, usually between −60° and 0°. Acetone is probably the best general solvent, although ether and light petroleum are preferred in specific instances. Crystallisation at −50° to −60° leaves in solution linolenic, linoleic, and other polyethenoid acids with minor amounts of oleic and saturated acids; a temperature of −30° serves as a rule to give fair separation of saturated from oleic and linoleic acids. The best conditions for different mixtures of fatty acids obtained from natural fats must be selected according to the general nature of the mixture and, where necessary, after preliminary trials have been made (*cf.* Foreman and Brown, Oil and Soap, 1944, **21**, 183; Hilditch and Riley, J.S.C.I. 1945, **64**, 204; 1946, **65**, 74; Gunstone and Hilditch, *ibid.* 1946, **65**, 8).

The saturated, oleic, linoleic, linolenic, and elæostearic acid contents of each group of acids thus obtained by low-temperature crystallisation from fatty oils containing one or more of these polyethenoid acids can be determined from (i) the extinction coefficient $E^{1\%}_{1\,\text{cm.}}$ at 268 mμ. (elæostearic) and (ii) the extinction coefficients of bands at 268 mμ. (linolenic) and 234 mμ. (linoleic) due to conjugated tri- or di-ethenoid acids produced by isomeric change when linolenic and linoleic acids are heated under standardised conditions with alkali (Mitchell, Kraybill, and Zscheile, Ind. Eng.

Chem. [Anal.], 1943, **15**, 1; Beadle and Kraybill, J. Amer. Chem. Soc. 1944, **66**, 1232; Hilditch, Morton, and Riley, Analyst, 1945, **70**, 68; Gunstone and Hilditch, Hilditch and Riley, *l.c.*).

Each group of acids is converted into methyl esters and the latter are distilled at low pressure (0·2–1 mm.) through a fractionating column. Longenecker (J.S.C.I. 1937, **56**, 199T), has described a suitable type of electrically-heated and packed column. The distillations can be so adjusted that, within very narrow limits, no resulting fraction will contain more than two saturated esters, or more than two homologous groups of unsaturated esters. From the mean molecular weight (saponification equivalent) and the mean unsaturation (iodine value) of each fraction its composition can in general be deduced, and therefrom the component acids present in each group of acids, and ultimately, the proportions of the component fatty acids present in the original fat. (For fuller details of the procedure, *cf.* T. P. Hilditch, "The Chemical Constitution of Natural Fats," Chapman and Hall, Ltd., 1947, Chapter XI.)

It should be observed that the above methods are intended to define the fats in terms of their ultimate chemical composition. For rapid evaluation of fats there exist an increasing number of specific determinations (*e.g.*, saponification value, acid value, iodine value, thiocyanogen value, acetyl value, Reichert–Meissl and Polenske values, etc.) which serve to define the analytical characteristics of a fat. These methods, many of which are indispensable in the routine examination of fats in industry, and by the Public Analyst, form the subject of a separate article (OILS (FATTY) AND FATS, TECHNICAL ANALYSIS OF, this Vol., p. 52c). It may here be remarked that these methods, valuable as they are for the purposes of control, merely give average values for the molecular size (equivalent), unsaturation, content of steam-volatile acids, or other characteristic of the fat as a whole, and are therefore rarely of use by themselves in elucidating the chemical composition of a fat or of its component fatty acids. For the latter purpose the more complete "ester-fractionation" technique is essential.

Component Glycerides.—From about 1895 onwards a number of investigators, notably Klimont, Bömer, and Amberger, attempted with little success to resolve a number of solid natural fats by crystallisation into their individual component glycerides. The general results of their exhaustive studies, although largely negative in character, served to establish the fact, long suspected, that simple triglycerides (triglycerides with three radicals of the same fatty acids) are of quite exceptional occurrence in natural fats and that the latter consist, often wholly, of mixed triglycerides.

Quantitative study of natural fat glycerides only began in 1927, when Hilditch and Lea (J.C.S. 1927, 3106) showed that triglycerides containing three saturated acid components can be isolated from and determined in a fat by oxidising it in acetone solution with potassium permanganate, when all unsaturated glycerides can be converted into acidic products of oxidation and subsequently removed from the unattacked, neutral fully-saturated triglycerides. Application of this procedure to a wide range of solid fats established that, as a general rule, the proportions of fully-saturated glycerides was negligible until the saturated acids present in the fat amounted to more than 60% of the total fatty acids, but that thereafter the proportion of fully-saturated glycerides rapidly increased in such a manner that in the mixed glycerides containing both saturated and unsaturated acids the ratio of saturated to unsaturated acids still remained at about 6:4. Definite exceptions to this generalisation were noted, however, in two groups of fats, (i) animal body-fats containing 10–30% of stearic acid, and (ii) animal milk-fats (*v. infra*).

Subsequently it was found, by study of partially-hydrogenated fats or of the tristearin content of completely hydrogenated fats, that liquid fats, in which oleic and linoleic acids were the chief components, contained proportions of tri-unsaturated glycerides which approached the minimum amount possible, *i.e.*, the unsaturated acids were linked in the form of mixed saturated-unsaturated glycerides with the saturated acids also present in the fat, almost as far as the proportion of the latter permitted.

This earlier quantitative work on glyceride structure led to more precise knowledge of the general tendency towards formation of the minimum possible proportions of mixed triglycerides in natural fats, and also of apparent exceptions, as mentioned above, to this general behaviour in a few groups of fats. Except when the number of component fatty acids was very small (two or three), however, examination of the fats as a whole by the quantitative methods indicated above still failed to give a very complete picture of the component glycerides present. More completely quantitative statements of the component glycerides in a natural fat have been found possible by resorting to the method, used by the earliest investigators, of physical separation of the fat by crystallisation from an appropriate solvent, acetone having been found most useful. Although it is very rarely possible to isolate individual glycerides from a fat by this means, it is comparatively easy to effect a separation into groups, usually of different degrees of unsaturation. Thus, glycerides containing three unsaturated acid groups are very freely soluble in cold acetone, those containing two unsaturated and one saturated acid group somewhat less so, whilst mono-unsaturated disaturated glycerides are as a rule but sparingly soluble, and glycerides with three saturated acid groups are usually almost insoluble in cold acetone. Thus, by a few systematic crystallisations of a fat, or of its partly-resolved components, from acetone at concentrations and temperatures which may be suitably varied, it is possible to divide it into four or five fractions, each of which will contain only two of the above groups in large proportions, accompanied by subordinate amounts, at most, of a third group. Determination of the component acids in each fraction, coupled where possible with determination of the fully-saturated glycerides and their component acids, or of the content of tri-unsaturated glycerides of the C_{18} acids (oleic, linoleic, etc.) leads in general to a close estimate of the main component glycerides in each fraction, and therefrom to a more or less detailed statement of the composition of the original fat.

With solid or semi-solid fats, crystallisation from acetone down to 0° suffices to give an adequate preliminary resolution of the fats. In the case of liquid fats such, for example, as olive, cottonseed, linseed, or whale oils a similar separation can be made by crystallising from acetone and solid carbon dioxide at progressively lowered temperatures down to $-40°$ or $-50°$. In such instances the only quantitative determination which can be made on the separated fractions is that of their component acids, but very frequently this then suffices to give a good indication of the probable quantitative composition of the mixed glycerides in the original fat.

In fats which contain only three or four major component acids, quantitative study by the procedure outlined in the preceding paragraphs usually affords a definite statement of the chief component glycerides to within 2 or 3 units per cent of the true figures. Where (as, for example, in milk fats or fish oils) the number of component acids is much greater, it is not in general possible to obtain so complete a statement, but the proportions of the chief groups of triglycerides present can be determined within fairly well-defined limits for each group.

Component Glycerides and Acids in Natural Fats.

It will be evident from what has been said already that, from the point of view of their constitution, the fats may be considered in terms of the actual glycerides present, or merely from the point of view of the nature and proportions of the fatty acids in combination in the whole fats. Whilst the mode of assemblage of fatty acids into the component mixed glycerides of natural fats appears to be governed by the same fundamental principles throughout almost the entire vegetable and animal kingdom, the nature of the particular fatty acids present in a fat is largely governed by biological factors and, indeed, a fairly close connection can be traced between the component acids of many fats and the place of the fat-producing organism, plant or animal, in the scale of evolutionary development (Hilditch and Lovern, Nature, 1936, 137, 478).

General Features of Glyceride Structure in Natural Fats.—The mode of assemblage of fatty acids in the triglycerides of fats which appears to hold almost universally throughout nature has often been termed the "rule of even distribution." By even distribution is meant the spreading throughout the triglyceride molecules of the fatty acids in a manner which tends to be as uniform as possible. It should be noted that this is not the same thing as "random distribution," *i.e.*, distribution according to the mathematical theory of probability; if the latter theory applied, indeed, the fats would contain in most instances higher proportions of the simple triglycerides than are in fact observed. The operation of the "even distribution" principle is perhaps most readily expressed in the following way. If any one acid forms one-third or more of the component acids of a natural fat, that acid will occur at least once in nearly all the triglyceride molecules; if it forms, for example, from 60–70% of the total acids, very many of the component triglyceride molecules will contain two radicals of the acid in question. On the other hand, if a particular acid is a minor component of a natural fat, amounting to perhaps 10% or less of the total fatty acids, it will of course not be present in all the triglyceride molecules, and will only contribute one acid radical to any triglyceride molecule in which it is present.

It follows from the preceding statement that if a fat contains, say, 35% or more of oleic acid, then this acid will be present in almost all the molecules of the fat glycerides—in other words, as has been demonstrated experimentally, such fats contain only very minor amounts of fully-saturated triglycerides. Similarly, in liquid fats such as olive oil, linseed oil, and other liquid vegetable seed-fats, the acids of which in many cases consist very largely of oleic and linoleic, with minor proportions of palmitic acid, all of the latter is present as monopalmitodiunsaturated glycerides, with the result that the proportion of oleo-linoleo-glycerides is the least possible.

This kind of evenly distributed type of natural mixed glycerides has been found to be present in almost all seed fats, solid or liquid, in many fruit-coat fats, in all marine-animal fats so far studied, and in all land-animal body fats in which the saturated acids present are mainly palmitic, with only minor proportions of stearic acid. The experimental evidence is most abundant in the case of solid seed-fats, but the liquid seed-fats which have been so far examined also conform closely with the rule. It is also followed closely in many fruit-coat fats, but in this class a few instances have been observed (especially palm oils) in which there is a tendency for the production of slightly more tripalmitin and triolein than is consistent with complete adherence to "even distribution." Again, those marine animal fats and land-animal body-fats low in stearic acid content which have been submitted to study by the quantitative methods have also been found to conform with the general rule, whilst qualitative studies by Eibner, Suzuki, and others of the crystalline bromo-additive products obtainable from the glycerides of linseed, soya-bean, whale, cod, herring, and some other oils lend full support to the view that the mixed glycerides of these oils are as heterogeneous a mixture as possible.

Many fats of the above types, containing not more than four major component acids, have now been studied experimentally and their chief component glycerides determined with some degree of certainty. It has been found possible (Hilditch and Meara, J.S.C.I. 1942, 61, 117), by a simple calculation based on arithmetical proportioning of one component acid among the rest, and subsequent arrangement of the resulting groups of acids into mixed glycerides, to obtain directly from the proportions of the component acids in the fat a "calculated" composition for its component glycerides which approximates to that observed by experimental analysis. It is notable that this accordance is not forthcoming unless the *unsaturated* acid (usually oleic) present in largest amount is arithmetically proportioned between the saturated and other acids of the fat. It is thus possible by an empirical calculation, based upon the fatty-acid composition of a fat, to predict with some likelihood of reasonable accuracy, when experimental determinations are lacking, the proportions of the chief component glycerides present.

As previously mentioned, there are two broad groups of natural fats which constitute apparent exceptions to (or, more probably, modifications super-imposed on) the "even distribution" principle, namely, animal body-fats, such as tallows, which are relatively rich in stearic acid, and animal milk-fats, which include about 20–25% of saturated acids of lower molecular weight than palmitic acid in their component acids. Broadly speaking, in all instances so far studied, the proportion of stearic acid or of lower saturated acids (as the case may be) seems to be closely connected with that of the oleic acid present, the sum of the latter and either of the former being of an approximately constant order. It has therefore been suggested that either of these forms of land-animal fats may arise by further modification of a preformed mixture of palmitodioleo- and similar glycerides built upon the usual "even distribution" principle. Partial saturation of such oleo-glycerides in the cases of depot fats, and transformation of such oleo-glycerides (by processes involving shortening of the oleic chain) in the case of milk fats, would account for the observed composition of the glycerides in these two classes of animal fats.

The component glycerides of a range of pig, sheep, and ox body-fats of varying stearic acid content have been determined experimentally (Hilditch *et al.*, Biochem. J. 1938, **32**, 1775; 1940, **34**, 971, 1301; 1941, **35**, 940). Since, as the result of the presumed bio-hydrogenation process, such fats contain much more fully-saturated triglycerides than fats of similar fatty-acid composition built up purely according to the "even distribution" rule, the empirical calculation described above fails to give results accordant with those observed when it is based on the fatty acids of the whole fat; but, if allowance is made for the palmitic and stearic acids present as palmitostearins (which can be approximately effected from a graph without actual determination of the proportion of fully-saturated glycerides) and the oleic acid of the fat is then proportioned between the remaining palmitic and stearic acids, the proportions of oleopalmitostearin, palmitodiolein, etc., thus calculated agree very closely with the observed values. This modified form of calculation thus permits the chief component glycerides of lards and tallows to be approximately computed from the proportions of fatty acids in the whole fats.

General Features of Component Acids in Different Types of Natural Fats.— The number of different acids combined in a natural fat varies from four or five in the simplest cases to as many as fifteen or twenty in the most complex fats. It is convenient to group the acids of any fat roughly into two categories, *major* and *minor* component acids. Such a grouping cannot be rigid, but broadly speaking an acid which forms anything from about 10% upwards of the total fatty acids falls into the category of a *major* component acid. *Minor component acids* are those which form less than 10% of the total fatty acids (down to traces of the order of 0·2–0·3% in some instances). The chief utility of roughly dividing fat component acids into these two groups is that it then at once becomes evident that, in a great many instances, fats from organisms which have been grouped together by biologists on morphological or anatomical grounds share the same acids as major components. At the same time, in a number of other groups, one or more of the minor component acids may be markedly characteristic of the particular fats concerned.

As detailed data for the fatty-acid compositions of fats have accumulated over a wide range of material, it has become more and more apparent that natural fats tend to align themselves, by their component acids, in groups according to their biological origin. Moreover, it has become clear that the fats of the simplest and most primitive organisms are usually made up from a very complex mixture of fatty acids whereas, as biological development has proceeded, the chief component acids of the fats of the higher organisms have become fewer in number. In the animal kingdom this change in type is remarkably consistent, and culminates, in the depot fats of the higher land mammals, in fats in which oleic, palmitic, and stearic acids are the only major components. In vegetable seed-fats, as a rule, similar simplicity is found in the major component acids which, in many families, are confined to oleic, linoleic, and palmitic; but here, in a number of other families, specific fatty acids occur which have been found nowhere else in nature. The systematic consideration of natural fat component acids is therefore best developed in relation to their biological sources, commencing with the fats of minute aquatic flora and fauna, proceeding to those of the larger aquatic denizens and then to those of the two broad groups of land fauna and land flora.

Component Acids of Fats of Aquatic Origin.— All fats of aquatic origin contain a wide range of combined fatty acids, mainly of the unsaturated series. The latter include acids containing 14, 16, 18, 20, 22 and sometimes 24 carbon atoms in the molecule, and are conveniently denoted as unsaturated C_{16}, C_{18}, C_{20}, etc., acids. These unsaturated acids are present in varying, but major, proportions and in different states of unsaturation. The unsaturation is greater with increasing chain-length: C_{18} acids may contain 4, C_{20} acids 4 or 5, and C_{22} acids 5 or 6 ethenoid bonds (*v. infra*). The only major-component saturated acid is palmitic acid (10–20% of the total acids), with myristic and stearic acid often present as minor components.

Relatively marked differences exist in the proportions of the component acids in fats from fresh-water and from sea-water organisms, respectively. In fats from all fresh-water life, plant or animal, minute or large, the type appears to be much the same, the component acids being relatively rich in unsaturated C_{16} and C_{18} acids, with low contents of unsaturated C_{20} and (especially) C_{22} acids. The unsaturated C_{16} acids may form as much as 30%, and the unsaturated C_{18} acids over 40–45% of the total fatty acids.

In the marine world, apart from the fats of marine diatoms and green algæ (which, in the few cases reported, belong to the fresh-water type as regards their component acids), there is a marked difference in the proportions of the unsaturated component acids of fats as compared with those from denizens of fresh water. In the fats of red and brown algæ and of marine plankton *Crustacea* the unsaturated C_{16} and C_{18} acids are less in amount, and the unsaturated C_{20} and, especially, C_{22} acids considerably increased as compared with fats of fresh-water organisms. This characteristic difference persists as a general background throughout almost the whole range of marine fish and mammalia, although it is in turn subject to subordinate modifications in fats from different families. Thus, in general, the fats of *Teleostid* fish of which the chief fat-depot is the liver (*e.g.*, cod, hake, halibut, and many others) have somewhat less C_{20} and C_{22} acids (of somewhat less average unsaturation) than those of *Teleostid* fish of which the fat is mainly deposited in the flesh-tissues (*e.g.*, herring, salmon, etc.); in herring fat nearly half of the total acids may be made up of unsaturated C_{20} and C_{22} acids. The salmon is interesting in that its body-fat alters progressively from the "fresh-water" to the "marine" type as the fish develops from a purely fresh-water to a marine animal (Lovern, *ibid.* 1934, **28**, 1955, 1961). In *Elasmobranch* fish the liver fats may be very similar to *Teleostid* liver-oils, or may contain unsaturated C_{20} and C_{22} acids of even higher mean unsaturation; or again, in certain families the liver fats are accompanied by unusually large proportions of the glyceryl ethers (batyl, etc., alcohols, *v. infra*) or by the hydrocarbon squalene, and in such cases it is invariably found that the unsaturation of all the acids in the glycerides is almost wholly monoethenoid, and that up to 10% of a monoethenoid C_{24} acid is also present.

Whale body-fats are very similar in general fatty-acid composition to many of the *Teleostid* fish oils, although the content of unsaturated C_{20} and C_{22} acids tends to be lower. Notably, the fats of Antarctic whales are relatively low in these acids and tend more to resemble in fatty-acid composition that of a freshwater fish. It has also been observed that fish fats from southern oceans (New Zealand) often appear to resemble fresh-water fish-fats rather than the more general type of sea-water fish-fats in their component acids.

Finally, the marine mammalia are marked in certain instances by quite exceptional variations in the composition of their fats. Thus the body and especially the head-cavity oils of the *Physeteridæ* (sperm whales) consist only of 30–35% of fats (glycerides), the remainder being ester-waxes formed by the union of cetyl (hexadecyl), oleyl (octadecenyl), and other higher aliphatic alcohols with higher fatty acids; the component acids, also, differ in type from the normal, unsaturated C_{22} acids being almost absent, and the unsaturation of the C_{20} and C_{18} acids being nearly all monoethenoid. The body fats of the *Delphinidæ* (porpoise, dolphin, white whale) also include a certain proportion of the above-mentioned ester-waxes, and are further notable (especially the fats of the head and jaw cavities) in that they contain large quantities of *iso*valeric acid combined in the form of mixed glycerides with the higher fatty acids (Lovern, *ibid.* 1934, **28**, 394). The occurrence of *iso*valeric acid in natural fats is quite exceptional, not only on account of its low molecular weight, but because it is the only known instance of a fat component acid containing an odd number of carbon atoms and a branched carbon-chain. (Other instances, however, are known amongst the wax acids of tuberculosis and other bacilli waxes, *e.g.*, tuberculostearic acid, 10-methylstearic acid, $C_{19}H_{38}O_2$, Spielman, J. Biol. Chem. 1934, **106**, 87).

Component Acids of Fats of Land Animals.—(*a*) *Depot Fats.*—On passing from depot fats of aquatic to those of land animals there is marked simplification in the composition of the mixed fatty acids. Most of the unsaturated acids, except oleic acid, of the former class disappear, still being present in some quantity in fats of amphibians and reptiles, and to a less extent in those of rodents and, perhaps, some birds; but in depot fats of the higher land-animals the proportion of highly unsaturated C_{20} and C_{22} acids is reduced to about 1% of the total acids, whilst that of unsaturated C_{16} (hexadecenoic) acid reaches a minimum at about 3%. In consequence, in the higher land-animals the most abundant component acids are always the monoethenoid oleic and the saturated palmitic acid, the latter being present in much larger quantities than in aquatic animal fats and approaching a more or less constant figure in the region of about 30% in the depot fats of widely different animals such as rat, rabbit, pig, ox, sheep horse, etc. The final result is that in most of the higher land-animals the major component acids of the depot fats are restricted to oleic, palmitic, and stearic, and, moreover, that about 60–65% of the acids belong to the C_{18} series, unsaturated or saturated. The major saturated component palmitic acid is usually accompanied by subordinate amounts (1–5%) of myristic acid.

In some groups of animals there is marked tendency to produce stearic as well as oleic acid in the depot fats, but in such cases the sum of all the C_{18} acids present remains approximately constant at between 60 and 65% of the total acids. It is in these fats alone that, in the component glycerides, a departure from the general rule of "even distribution" has been observed (*v. supra*), and that usually large proportions of fully-saturated glycerides (palmitostearins) are found. It seems probable that in these animals a mixture of palmito-oleo-glycerides or tri-olein initially synthesised may be partly reduced by a bio-hydrogenation process to more saturated products.

The progressive changes observed in the contents of palmitic, stearic, and unsaturated C_{16}, C_{18}, C_{20}, and C_{22} acids over a wide range of animal depot fats are illustrated by data taken from the observations of various investigators and collected in Table I.

TABLE I.—COMPONENT ACIDS (WT. %) OF TYPICAL ANIMAL DEPOT-FATS.

	Saturated.		Unsaturated.			
	C_{16}	C_{18}	C_{16}	C_{18}	C_{20}	C_{22}
Fish, fresh-water	13–15	1–2	20–30	40–45	10–12	0–5
Fish, marine	12–15	1–2	15–18	27–30	20–25	8–12
Whales	12–15	1–2	15–18	35–40	15–20	5–10
Frog	11	3	15	52	15	
Tortoise	14	4	9	65	7	
Lizard	18	7	10	56	5	
Domestic fowl	25–26	5–7	6–7	*ca.* 60	0·5–1	
Rat	24–28	2–3	7–8	*ca.* 60	0·3–0·5	
Bear	29	3	10	51	2	
Kangaroo	26	14	3	48	3	
Cat	29	17	4	43		
Lion	29	18	2	40	3	
Horse	28–29	5–7	?	64–67	?	
Pig	25–29	10–16	2–3	50–65	0·3–1	
Ox	27–30	13–25	2–3	40–50	0·2–0·5	
Sheep	24–28	14–28	1–2	40–50	0·5–1	
Baboon	19	6	4	67	0·5	

It will be seen that qualitatively the component acids of land-animal fats are an unusually simple mixture and, further, that up to the present no striking departures from the normal have been observed such as are encountered in marine-animal fats (*e.g.*, *iso*valeric glycerides in *Delphinidæ* fats, etc., *v. supra*) or in vegetable seed fats, where frequently quite specific and unusual higher fatty acids make their appearance (*v. infra*). The oleic acid of animal depot fats is usually accompanied by relatively small proportions of diethenoid octadecadienoic acid, $C_{18}H_{32}O_2$, which however in most cases is not identical with the linoleic acid of seed fats, but may probably be a geometrical isomer of the latter, since the unsaturation appears to be located in the 9:10 and 12:13 positions in the carbon chain.

All the above data for animal depot-fats refer as far as possible to animals which have received their natural diet, herbivorous or carnivorous, but in most cases comparatively low in fatty matter. By far the greater part of the depot fats therefore emanates from fat synthesised from carbohydrate or protein by the animal. It should of course be borne in mind that, in addition, most animals are able to ingest fats from fatty diets, and to assimilate and lay down in their fat depots many of the specific mixed glycerides which may be present in the dietary fats. Thus it has been notably shown that pigs are able to utilise as depot fat much of the fatty oils present in vegetable seeds on which they may be fed (*cf.*, *e.g.* Ellis *et al.*, *ibid.* 1926, **69**, 239; 1930, **89**, 185; 1931, **92**, 385).

(*b*) *Liver Fats.*—The liver is probably the main centre of animal-fat metabolism and the composition of liver lipids is thus of considerable, although not to any great extent industrial, interest. Both glycerides and phosphatides are found in animal livers and in the higher animals the component acids of both kinds of liver lipid differ considerably from those of the corresponding depot or body fats. In the lower land animals (*e.g.*, amphibians and reptiles) the liver glycerides and phosphatides are very similar to their depot fats (*v. supra*), so that the component acids bear considerable similarity to those of fats of wholly aquatic origin, but have less of the unsaturated C_{20} and C_{22} members, and to some extent of unsaturated C_{16} acids, compensated by a content of about 50–65% of unsaturated C_{18} acids.

In the pig, ox, and sheep the liver glycerides differ in composition both from the liver phosphatides and the corresponding depot fats, but the two classes of liver lipids share the characteristic of fairly high contents (10–25%) of highly unsaturated C_{20} and C_{22} acids of the marine-animal oil type. All the liver glycerides of pigs, ox, and sheep have as component acids about 22–30% palmitic, 5–20% stearic, 8–10% hexadecenoic, 40–48% unsaturated C_{18} (chiefly oleic), and 8–15% unsaturated C_{20} and C_{22} acids; the corresponding liver phosphatides have, on the other hand, less (12–20%) palmitic, more (15–30%) stearic, about 5% hexadecenoic, 30–40% unsaturated C_{18} (with more diethenoid acid than in the liver glycerides) and more (18–25%) unsaturated C_{20} and C_{22} acids.

Although the animal liver-fats have perhaps relatively little technical interest as fats, they are important as natural sources of vitamins-*A* and -*D*. Some fish-liver oils (especially cod-liver oil) are used medicinally for this purpose, whilst others (halibut-, whale-, soupfin shark-, and perhaps to a slight extent ox- and sheep-liver oils) are unusually high in vitamin-*A* and/or -*D* content and are worked up into vitamin concentrates, which serve both for increasing the vitamin potency of medicinal oils and for providing vitamins for addition to margarine, thereby making the latter equivalent in value to natural butter.

(*c*) *Mammalian Milk Fats.*—There is not so wide a range of detailed data here as for the depot fats. The component acids of whale milk-fat are almost quantitatively the same as those of its body fat, and there is reason to think (from the general analytical characteristics, which are the only data available) that the same may hold good for many of the land-animal milk-fats, such as those of the pig, dog, cat, and human milk-fat (*cf.* p. 28*b*). In other groups of land animals, more especially the ruminants, the C_{18} acids form a lower proportion of the total acids than in the corresponding depot fats, the differences being approximately balanced by the appearance of members of the lower saturated fatty acids (C_{10}, C_8, C_6 and most notably butyric acid). In the latter type of milk fat the component glycerides exhibit differences in structure from those of all other natural fats exactly similar to those shown by the stearic-rich animal body-fats (*v. supra*).

Of the milk fats in which the lower saturated acids are prominent, those of the cow and buffalo contain most butyric acid and hexanoic acid, the respective proportions amounting to about 4% and 2% (by weight), or 10% and 4% (molar). In sheep and goat milk-fats, the main lower acid present is decanoic (capric), which forms about 8% (wt.) or 10% (molar) of the total acids, and there is also present about 2–3% (wt.) each of butyric, hexanoic, and octanoic acids. In some other milk fats the relative proportions of the four lower saturated acids are much the same as in cow milk-fats, but the amount of each may be only half, or less than half, of that present in cow milk-fats. Milk fats, like that of the cow, which contain relatively large proportions of the lower saturated acids, also contain minor amounts of lower mono-ethenoid acids with the unsaturation in the same position (Δ^9-) as in oleic acid, from Δ^9-hexadecenoic, $C_{16}H_{30}O_2$ (about 3%) to Δ^9-decenoic, $C_{10}H_{18}O_2$ (about 0·2%).

Component Acids of Vegetable Fats.—It has been pointed out that the simplest forms of vegetable life (plankton, etc.) produce fats of similar complex and unsaturated nature to the rest of aquatic (animal) organisms, simple or highly developed. From the restricted data available, it seems that a somewhat similar type of fatty-acid mixture, especially rich however in Δ^9-hexadecenoic and oleic acids, is met with in the fats of many bacilli, of yeast and of the spores of cryptogams. As in the animal kingdom, hexadecenoic acid appears to persist throughout all vegetable fats, but in those of the seeds or fruit-coats of the more developed land plants it rarely amounts to more than about 0·5% of the total fatty acids.

The component acids of seed and fruit-coat fats of members of many plant families have been studied in greater or less detail and relatively much more information is at present available in this group than in most of the other realms of vegetable or animal life. As in animals, the most striking feature of the fats of land flora is great simplification in their component fatty-acid mixtures as compared with those of aquatic flora. As in land animals, palmitic and oleic become the most consistently prominent components; but a third acid, linoleic (diethenoid) must be added as a component which is so frequent as to be definitely characteristic for fats of land flora. Linoleic and the related, and still more unsaturated, linolenic acid are the typical constituents of the widely distributed class of " drying " seed oils.

Fruit-coat (*pericarp, etc.*) *fats* contain (so far with only one or two possible exceptions) palmitic and oleic acids as the only major components, irrespective of the plant family in which they occur; linoleic acid is also frequently present, but most often only in minor quantities. Fruit-coat fats exhibit a wide range of physical consistency, from the very hard Japan waxes or Chinese vegetable tallows through soft fats such as palm oil to fats, liquid at the ordinary temperature, such as olive oil. Their consistency is determined almost entirely by the relative proportions of palmitic and oleic acids present: thus Japan wax contains nearly 80%, and Chinese vegetable tallow about 65%, of palmitic acid, whilst palm oils contain about 40% each of palmitic and oleic, with up to 10% of linoleic acid, and the liquid olive-oil has amongst its component acids 75–80% of oleic, with only about 10% of palmitic and about 7% of linoleic acid.

Seed-fat component acids show a pronounced tendency to be, at least qualitatively, mixtures of the same acids throughout the same botanical family; but some botanical families produce seeds, the fats of which contain one or more acids which are found in no, or at most few, other families. This statement, although subject to occasional exceptions, has been found increasingly, with the collection of more and more data, to be broadly true for the seed fats of all land plants. In many *seed fats*, it is true, the main component acids are confined to palmitic, oleic, and linoleic in varying proportions; frequently, in these cases, seed fats of the same family exhibit considerable resemblance in the relative proportions of these three acids. Thus, seed fats of the *Malvaceæ* and *Bombacaceæ* are usually high in palmitic acid content (20–25%), and also often contain about 50% of linoleic acid; the component acids of *Gramineæ* seed-fats are usually made up of about 10–15% of palmitic, 30–60% of oleic, and 60–30% of linoleic acid. Linoleic acid is prominent in many coniferous seed fats, in those of the larger dicotyledonous trees and shrubs, and in shrubs and herbs of *Rosaceæ*, *Compositæ*, *Labiatæ*, *Linaceæ* and a number of other familiar and widely distributed plant families.

On the other hand, in many other families (and in this respect land plants differ from all other natural sources of fats) the seed fats include as major components a fatty acid (or acids) different from any of the above. In the saturated series, members of all the " even-numbered " acids from decanoic (capric, C_{10}) to tetracosanoic (lignoceric, C_{24}) are encountered as major components of one or other type of seed fats. Furthermore, similar cases are encountered in which a wide variety of unsaturated acids, differing in carbon content or in degree of unsaturation from the typical oleic acid of fats, occur specifically in certain groups of seed fats. Whilst most of the saturated acids referred to are found, at least as minor components, in some kinds of animal fats, the seed-fat unsaturated acids are restricted entirely to the vegetable kingdom and, indeed, almost always to the seed fats of a single family or, sometimes, of only one genus or even species within a botanical family. The distribution of these specific acidic components in seed fats is illustrated in Table II.

TABLE II.—OCCURRENCE OF SPECIFIC COMPONENT ACIDS IN SEED FATS.

Saturated acids.	Occurrence in seed fats.
Caprylic (Octanoic), $C_{8}H_{16}O_{2}$	*Palmæ* (minor component).
Capric (Decanoic), $C_{10}H_{20}O_{2}$	Elm (*Ulmaceæ*, major component; *Palmæ*, *Lauraceæ*, *Salvadoraceæ* (minor component).
Lauric, $C_{12}H_{24}O_{2}$	*Lauraceæ*, *Palmæ*, *Salvadoraceæ*, *Irvingia* sp. (Simarubaceæ), *Virola* sp. (Myristicaceæ); (major component in varying amounts).
Myristic, $C_{14}H_{28}O_{2}$	Although present in minor amounts in very many seed fats, accompanying major proportions of palmitic acid, myristic acid is only a major component in *Myristicaceæ*, *Salvadoraceæ*, *Irvingia* sp. (Simarubaceæ), and *Palmæ*.
Stearic, $C_{18}H_{36}O_{2}$	Although present in minor amounts in many seed fats, accompanying major proportions of palmitic acid, stearic acid is only found as a major component in seed fats of a few tropical families: *Guttiferæ*, *Sapotaceæ*, *Sterculiaceæ*, *Dipterocarpaceæ*.
Arachidic, $C_{20}H_{40}O_{2}$	Minor, but characteristic component in many *Leguminosæ* seed fats especially *Arachis* and *Soja* sp.; trace component in many other seed fats; major component in *Pentaclethra* sp. (Leguminosæ) and *Sapindaceæ*.
Behenic, $C_{22}H_{44}O_{2}$	Minor, but characteristic component in *Arachis* sp. (Leguminosæ) and in *Moringa* sp. (Moringaceæ).
Lignoceric, $C_{24}H_{48}O_{2}$	Minor, but characteristic component in *Arachis* sp., *Soja* sp., and other leguminous seed fats; trace component in many seed fats; major component in *Adenanthera pavonina* (Leguminosæ).
(*a*) Monoethenoid :—	
Δ^{9}-Tetradecenoic, $C_{14}H_{26}O_{2}$	*Pycnanthus kombo* (Myristicaceæ). (Major component.)
Δ^{6}-Octadecenoic (Petroselinic), $C_{18}H_{34}O_{2}$	Major component in all seed fats of *Umbelliferæ* and *Araliaceæ*; and of *Picrasma quassioides* (Simarubaceæ).
Δ^{11}-Eicosenoic, $C_{20}H_{38}O_{2}$	Major component in seed wax of *Simmondsia californica*.
Δ^{13}-Docosenoic (Erucic), $C_{22}H_{42}O_{2}$	Major component in seed fats of *Cruciferæ*, *Tropæolum* sp. and *Simmondsia californica* (seed box).
Δ^{17}-Hexacosenoic (Ximenic), $C_{26}H_{50}O_{2}$	Major component in seed fat of *Ximenia americana*.
Δ^{21}-Tricosenoic (Lumequic), $C_{30}H_{58}O_{2}$	Minor component in seed fat of *Ximenia americana*.
(*b*) Hydroxy-monoethenoid :—	
12-Hydroxy-Δ^{9}-octadecenoic (Ricinoleic), $C_{18}H_{34}O_{3}$.	Major component in *Ricinus* sp. and *Agonandra brasiliensis* (Olacaceæ).
(*c*) Ethynoid (or ethenoid-ethynoid) :	
Δ^{6}-Octadecinoic (Taririe), $C_{18}H_{32}O_{2}$	Major component in *Picramnia sow* and other sp. (Simarubaceæ).
Octadeca-Δ^{17}-en-di-ynoic (Erythogenic), $C_{18}H_{26}O_{2}$	Major component in *Ongokea* sp. (Olacaceæ).
(*d*) Cyclic mono- or di-ethenoid :	
Hydnocarpic, $C_{16}H_{28}O_{2}$ Chaulmoogric, $C_{18}H_{32}O_{2}$ Gorlic, $C_{18}H_{30}O_{2}$	Major components of *Hydnocarpus anthelmintica*, *H. kurzii*, *H. wightiana*, *Oncoba echinata* and some other species of the family *Flacourtiaceæ*.
(*e*) Tri- and tetra-ethenoid :	
(i) Non-conjugated :	
$\Delta^{9,12,15}$-Octadecatrienoic (Linolenic), $C_{18}H_{30}O_{2}$.	Major component in *Perilla* and *Salvia* sp. (Labiatæ), in *Linus* sp. (Linaceæ), *Cannabis* sp. (Moraceæ), some *Pinus* sp. (Coniferæ), *Juglans regia* (Juglandaceæ) and some other seed fats; minor component in *Papaveraceæ*, some *Leguminosæ* (*e.g.*, *Soja hispida*) and other seed fats.
$\Delta^{6,9,12}$-Octadecatrienoic, $C_{18}H_{30}O_{2}$	In *Œnothera biennis* (Œnotheraceæ).
(ii) Conjugated :	
$\Delta^{9,11,13}$-Octadecatrienoic (Elæostearic), $C_{18}H_{30}O_{2}$.	Major component in *Aleurites tordii*, *A. montana*, *A. cordata*, and *A. trisperma*, *Ricinodendron* sp. (Euphorbiaceæ); *Telfairia occidentalis* (Cucurbitaceæ); *Parinarium macrophyllum* (Rosaceæ).
4-Keto-$\Delta^{9,11,13}$-Octadecatrienoic (Licanic), $C_{18}H_{28}O_{3}$.	Major component in *Licania rigida* and *Parinarium sherbroense* (Rosaceæ).
$\Delta^{9,11,13,15}$-Octadecatetraenoic (Parinaric), $C_{18}H_{28}O_{2}$.	Major component in *Parinarium laurinium* and *P. glaberrimum* (Rosaceæ).

Although the occurrence of specific (especially unsaturated) fatty components places many of the families of land flora apart from the rest of nature as regards their fat types, it is clear that the incidence of these unusual features runs on the whole closely parallel with the groups into which morphologists have placed the parent plants. Throughout the seed fats it is evident that the fatty-acid mixtures present are closely connected with, and dependent upon, differences in biological species. At present this must be regarded as a broad generalisation, susceptible to extension and modification as more data and fats are accumulated.

It should be noted that natural fats must be liquid, or approximately so, at the temperature of the living organism in which they are produced or stored. Consequently the more saturated seed-fats, which are solid at the ordinary temperature of the temperature zones, are not produced in seeds indigenous to the latter climates, but only in sub-tropical or tropical regions where, in fact, they exist practically in the liquid state at the prevailing temperatures. It has frequently been stated that unsaturation tends to be greater in seed fats as the latter are produced in cooler regions (further from the equator). This is a confusion of ideas, for the non-occurrence of relatively saturated fats in cooler climates is simply the consequence of what has been pointed out in the preceding sentences, whilst the converse is not true: many seed fats of high unsaturation occur in plants which grow only in tropical regions, or are capable of growth in both hot and cold climates. In particular, the high degree of unsaturation of species of *Aleurites*, *Hevea*, *Perilla*, *Licania*, and *Parinarium*, to mention only a few tropical or sub-tropical seed fats, is only paralleled elsewhere in nature by the highly unsaturated C_{20} and C_{22} acids which are found most abundantly in cold-blooded aquatic-animal organisms.

At the same time, in those plants (*e.g.*, flax) which thrive in either hot or cold climates, Ivanow (Bull. Applied Botany, Leningrad, 1922–23, 13, No. 2) and others have shown by systematic experiments that when the plant is grown in a cold region higher proportions of the more unsaturated component acids characteristic of the particular seed-fat are produced than from seed produced in a hotter climate.

Structure of Individual Natural Fatty Acids.

The distribution of individual fatty acids throughout the natural fats will be apparent from the discussion of their component acids in the preceding paragraphs. Some notes may usefully be inserted at this point on structural and other features of the individual acids which merit attention.

Of all the natural fatty acids, two may be singled out as most widespread and characteristic: the monoethenoid oleic acid, $C_{18}H_{34}O_2$, which is probably present in all natural glyceride mixtures of vegetable or animal origin, and which must be regarded as a major component acid in the great majority of natural fats; and the saturated palmitic acid, $C_{16}H_{32}O_2$, which is similarly present, albeit generally in lesser proportions than oleic acid, in practically all known natural fats. In a considerable number of the more unsaturated seed fats palmitic acid may form only from, say, 2–5% of the total acids, but it is extremely rare to find it absent.

Other acids which are almost as ubiquitous as palmitic and oleic acid, but which are most frequently very minor components of natural fats, are the saturated myristic ($C_{14}H_{28}O_2$) and stearic ($C_{18}H_{36}O_2$) acids, and the monoethenoid hexadecenoic or palmitoleic acid, $C_{16}H_{30}O_2$. As already indicated, in certain groups of seed fats myristic and stearic acids also appear as specific major components, whilst hexadecenoic acid is similarly a major component of most fats of aquatic origin and fats of the more primitive land vegetable and animal organisms. All the remaining natural fatty acids, saturated and unsaturated, may be considered to be specific types which occur in fats of particular, and frequently quite restricted, groups of vegetable or animal species.

Saturated Fatty Acids.

As already indicated, the fatty acids of natural fats are straight-chain members of the aliphatic series, with the general formula $C_nH_{2n}O_2$ (or $C_{n-1}H_{2n-1}\cdot COOH$), where n is an even integer (from 4 to 24). The plant waxes contain still higher members of the same series, from $C_{26}H_{52}O_2$ to $C_{36}H_{72}O_2$, usually mixtures of two or three consecutive members of the "even-numbered" series, with one acid predominating. The straight-chain structure of the higher acids from C_{18} to C_{36} has been established by *X*-ray spectrum analysis (Müller and Shearer, J.C.S. 1923, 123, 2043, 3156; Piper, Malkin, and Austin, *ibid.* 1926, 2310; Chibnall, Piper *et al.*, Biochem. J. 1934, 28, 2175, 2189). All the saturated *n*-aliphatic acids have been prepared synthetically, proceeding from a lower member (C_n) to the next higher (C_{n+1}), up to *n*-hexatriacontanoic acid, $C_{36}H_{72}O_2$ (C_{18}–C_{26}, Levene and Taylor, J. Biol. Chem. 1924, 59, 905; C_{22}–C_{36}, Francis *et al.*, Proc. Roy. Soc. 1937, A, 158, 691; J.C.S. 1937, 999). More direct syntheses of lauric, myristic, palmitic, and stearic acids were not achieved until 1936, when polyene aldehydes ($CH_3\cdot[CH:CH]_5\cdot CHO$ and $CH_3\cdot[CH:CH]_7\cdot CHO$) were obtained by controlled polymerisation of crotonaldehyde, and were reduced to dodecyl and hexadecyl alcohols, which in turn yielded by oxidation lauric and palmitic acids. Condensation of the polyene aldehydes with malonic acid gave further products which, after hydrogenation and decarboxylation, furnished respectively myristic and stearic acids (Kuhn, *ibid.* 1938, 605).

The melting-points of the chief natural solid saturated acids are capric 31·3°, lauric 43·5°, myristic 54·4°, palmitic 62·9°, stearic 69·6°, arachidic 75·4°, behenic 80·0°, and lignoceric 84·2°. The stable (β) forms of simple triglycerides (trilaurin, etc.) melt in general about 2° higher than the corresponding fatty acids.

Unsaturated Fatty Acids.

With the exception of the few cyclic ethenoid acids and of hydroxyoleic or ricinoleic acid, all the naturally occurring unsaturated acids are converted by hydrogenation into the *n*-aliphatic acid of the same carbon content, thus demonstrating their straight-chain constitution. Oleic and linoleic acids, the most abundant of the natural unsaturated fatty acids, have been shown to occur in nature in the *cis*-form. The corresponding *trans*-geometrical isomers can be produced from them by chemical means, but have not been met with in any natural fat. It is probable, although not yet demonstrated in every instance, that the numerous other ethylenic acids of natural fats also occur predominantly in the less stable or *cis*-modifications. Syntheses of the unsaturated acids of natural fats have to date only been effected in the cases of oleic, linoleic, and chaulmoogric acids.

Oleic Acid, *cis*-Δ^9-octadecenoic Acid,

$CH_3{\cdot}[CH_2]_7{\cdot}CH{:}CH{\cdot}[CH_2]_7{\cdot}COOH$.

Naturally, in view of its abundant occurrence and simple degree of unsaturation, much more study has been given to oleic than to any other unsaturated higher fatty acid. Brief reference to its chief reactions will serve to illustrate the methods which are common to the study of oleic acid and its many analogues.

Oleic acid exists in two crystalline forms, melting-points respectively 13° and 16°. It may be purified by crystallising its barium salt from benzene containing 5% of alcohol or, better, its lithium salt from 80% alcohol. Alternatively, the acid itself may be crystallised from acetone at about −40°, admixed saturated acids being first separated from the solution at −20° (Brown, J. Amer. Chem. Soc. 1937, **59**, 6).

On treatment with oxides of nitrogen at room temperature, or with a small proportion of sulphur or selenium at 200° or above, oleic acid is converted into an equilibrium mixture consisting of about 34% of oleic acid and about 66% of the geometrically isomeric *trans*-modification, elaidic acid, m.p. 44°. Esters (including glycerides) of either acid are transformed under these conditions to equilibrium mixtures in which the elaidic form comprises about two-thirds of the total acid present. Analogous behaviour is shown by other naturally occurring unsaturated higher fatty acids. Evidence of various kinds, chemical and physical, leads to the conclusion that oleic and elaidic acids are respectively the *cis*- and *trans*- forms of Δ^9-octadecenoic acid; the physical evidence includes that deduced from X-ray spectra (Muller and Shearer, *l.c.*), from infra-red and Raman spectra (McCutcheon, Crawford, and Welsh, Oil and Soap, 1941, **18**, 9), from studies of unimolecular films on water (Marsden and Rideal, J.C.S. 1938, 1163; Harkins and Florence, Nature, 1938, **142**, 913), and from the systems formed with mixtures of either acid with stearic acid (Mascarelli, Atti. R. Accad. Lincei, 1914, [v], **23**, ii, 583, etc.).

The position of the ethenoid bond (Δ^9) was first established in 1894 by Baruch (Ber. 1894, **27**, 172) by a somewhat complicated sequence of reactions. More recently it has been confirmed by oxidative scission of oleic acid into *n*-nonanoic and azelaic acids by means either of ozone or of anhydrous potassium permanganate in acetone. Either or both of the latter methods have been used to establish the structure of most of the other unsaturated acids of natural fats.

Oleic acid was partly synthesised in 1925 by G. M. and R. Robinson (J.C.S. 1925, **127**, 175), who effected a complete synthesis of 10-ketostearic acid from acetoacetic ester, and also converted the acetylenic stearolic acid into oleic acid, but were unable to convert 10-ketostearic acid into the ethynoid acid; a complete synthesis of the *cis-trans* equilibrium mixture of oleic and elaidic acids was accomplished later by Noller and Bannerot (J. Amer. Chem. Soc. 1934, **56**, 1563), starting from 9-chlorononyl aldehyde, and by Baudart (Compt. rend. 1943, **217**, 399), starting from 1-methoxy-6-bromohexane and 1-ethoxy-1:2-dibromo-*n*-decane. Noller and Girvin (J. Amer. Chem. Soc. 1937, **59**, 606) subsequently carried out a similar synthesis of linoleic acid, which, however, was accompanied by other isomeric forms of octadecadienoic acids.

Like other long-chain unsaturated acids, oleic and elaidic acids unite additively with bromine to give two different dibromostearic acids, each of which on debromination with zinc reverts to the acid from which it was produced. On mild oxidation, isomeric 9:10-dihydroxystearic acids are produced: oleic acid yields a dihydroxy-acid, m.p. 132°, with aqueous alkaline permanganate, but an isomeric acid, m.p. 95°, when the oxidant is an acyl derivative of hydrogen peroxide (Caro's acid, peracetic or perbenzoic acids; in the latter case an oxidostearic acid is also formed). With elaidic acid the respective oxidising agents lead to production of the opposite acids, *i.e.*, respectively those melting at 95° and 132°. The stereochemical relationships underlying these transformations (in some of which a "Walden inversion" must take place) at present give rise to some conflict of opinion. Either 9:10-dihydroxystearic acid, on further oxidation with dilute alkaline permanganate, is broken down into *n*-octanoic, oxalic, and suberic acids (instead of *n*-nonanoic and azelaic acids).

Other *cis*- and *trans*-modifications of the higher monoethenoid fatty acids exhibit exactly similar behaviour to oleic and elaidic acids in their reactions with dilute alkaline permanganate and with acidic derivatives of hydrogen peroxide, yielding similar pairs of racemic forms of optically isomeric dihydroxy-fatty acids.

Other chemical changes characteristic of oleic and related unsaturated fatty acids will be considered later (pp. 47*a*, 51*b*) when discussing the action of various agents (*e.g.*, atmospheric oxygen, sulphuric acid) on natural fats.

Natural Monoethenoid Higher Fatty Acids.—The majority of these require little separate treatment, their occurrence in natural fats having already been indicated in a preceding section. It is useful to tabulate them here according to certain coincidences in their general chemical structure, which are worthy of notice although their precise significance is not apparent.

(*a*) *Monoethenoid acids of the general formula* $R\cdot CH:CH\cdot[CH_2]_7\cdot COOH$.

Composition.	Acid.	Structural formula.
$C_{10}H_{18}O_2$	Δ^{9}-Decenoic.	$CH_2:CH\cdot[CH_2]_7\cdot COOH$
$C_{12}H_{22}O_2$	Δ^{9}-Dodecenoic.	$CH_3\cdot CH_2\cdot CH:CH\cdot[CH_2]_7\cdot COOH$
$C_{14}H_{26}O_2$	Δ^{9}-Tetradecenoic, myristoleic.	$CH_3\cdot[CH_2]_3\cdot CH:CH\cdot[CH_2]_7\cdot COOH$
$C_{16}H_{30}O_2$	Δ^{9}-Hexadecenoic, palmitoleic, zoomaric.	$CH_3\cdot[CH_2]_5\cdot CH:CH\cdot[CH_2]_7\cdot COOH$
$C_{18}H_{34}O_2$	Δ^{9}-Octadecenoic, oleic.	$CH_3\cdot[CH_2]_7\cdot CH:CH\cdot[CH_2]_7\cdot COOH$
$C_{20}H_{38}O_2$	Δ^{9}-Eicosenoic, gadoleic.	$CH_3\cdot[CH_2]_9\cdot CH:CH\cdot[CH_2]_7\cdot COOH$

Of the above acids, all those below C_{18} are found, as has been observed, in some milk fats. Myristoleic, palmitoleic, and gadoleic acids are characteristic components of fish fats, and palmitoleic acid, it has already been pointed out, occurs in almost all fats, although in very small proportions in most of them (other than those of aquatic origin).

The existence of hexadecenoic acid has been recognised in fish oils for very many years; it has been variously termed palmitoleic and zoomaric acid at different times, and its constitution as Δ^{9}-hexadecenoic acid was not determined until 1925. Similarly, the structure of gadoleic acid, first noticed in cod-liver oil in 1906, was not determined until 1933.

(*b*) *Monoethenoid acids of the general formula* $CH_3\cdot[CH_2]_7\cdot CH:CH\cdot[CH_2]_x\cdot COOH$.

Composition.	Acid.	Structural formula.
$C_{14}H_{26}O_2$	Δ^{5}-Tetradecenoic.	$CH_3\cdot[CH_2]_7\cdot CH:CH\cdot[CH_2]_3\cdot COOH$
$C_{18}H_{34}O_2$	Δ^{9}-Octadecenoic, oleic.	$CH_3\cdot[CH_2]_7\cdot CH:CH\cdot[CH_2]_7\cdot COOH$
$C_{20}H_{38}O_2$	Δ^{11}-Eicosenoic.	$CH_3\cdot[CH_2]_7\cdot CH:CH\cdot[CH_2]_9\cdot COOH$
$C_{22}H_{42}O_2$	Δ^{13}-Docosenoic, erucic.	$CH_3\cdot[CH_2]_7\cdot CH:CH\cdot[CH_2]_{11}\cdot COOH$
$C_{24}H_{46}O_2$	Δ^{15}-Tetracosenoic, selacholeic.	$CH_3\cdot[CH_2]_7\cdot CH:CH\cdot[CH_2]_{13}\cdot COOH$
$C_{26}H_{50}O_2$	Δ^{17}-Hexacosenoic, ximenic.	$CH_3\cdot[CH_2]_7\cdot CH:CH\cdot[CH_2]_{15}\cdot COOH$
$C_{30}H_{58}O_2$	Δ^{21}-Tricosenoic, lumequic.	$CH_3\cdot[CH_2]_7\cdot CH:CH\cdot[CH_2]_{19}\cdot COOH$

Δ^{5}-Tetradecenoic acid is present in sperm-head oil, and selacholeic acid in some shark and other *Elasmobranch* fish acids, and also in brain cerebrosides (nervonic acid, Klenk). Erucic, ximenic, and lumequic acids are purely seed-fat acids, and a form of Δ^{5}-tetradecenoic acid occurs in a few Japanese seed-fats of the *Lauraceæ*; the C_{26} and C_{30} acids have so far only been reported in seed fat of one species of plant. The Δ^{11}-eicosenoic acid has only been encountered in the seed wax of *Simmondsia californica*.

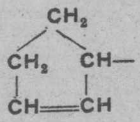
(*c*) *Monoethenoid acids of the general formula* $R\cdot CH:CH\cdot[CH_2]_9\cdot COOH$.

Composition.	Acid.	Structural formula.
$C_{18}H_{34}O_2$	Δ^{11}-Octadecenoic, vaccenic.	$CH_3\cdot[CH_2]_5\cdot CH:CH\cdot[CH_2]_9\cdot COOH$
$C_{22}H_{42}O_2$	Δ^{11}-Docosenoic, cetoleic.	$CH_3\cdot[CH_2]_9\cdot CH:CH\cdot[CH_2]_9\cdot COOH$

This group, in which the Δ^{11}-eicosenoic acid in (*b*) also belongs, is a small one, and all three acids are specific in occurrence. Vaccenic acid is a solid isomer of oleic acid which accompanies the latter in small quantities in the depot and milk fats of cows and sheep; Bertram, who discovered it, attributes to it the structure of a Δ^{11}-acid (Biochem. Z. 1928, **197**, 433). Cetoleic acid is the form of monoethenoid C_{22} acid which occurs in small proportions in most fish and other marine animal fats; its structure was determined by Toyama (J. Soc. Chem. Ind. Japan, 1927, **30**, 597).

(*d*) *Cyclic* (cyclo*Pentenyl-*) *mono- and diethenoid acids.*

A small group of acids, characterised chemically by the presence in the fatty acid chain of a *cyclo*pentenyl ring-system



is found in quantity in the seed fats of *Hydnocarpus* and a few other genera of the *Flacourtiaceæ*. These fats have specific therapeutic value in the treatment of leprosy and some other diseases. The chief acids of the group are as follows:

Composition.	Acid	Structural formula.
$C_{16}H_{28}O_2$	Hydnocarpic, 11-Δ^{2}-*cyclo*pentenyl-*n*-undecanoic.	$R\cdot[CH_2]_{10}\cdot COOH$
$C_{18}H_{32}O_2$	Chaulmoogric, 13-Δ^{2}-*cyclo*pentenyl-*n*-tridecanoic.	$R\cdot[CH_2]_{12}\cdot COOH$
$C_{18}H_{30}O_2$	Gorlic, 13-Δ^{2}-*cyclo*pentenyl-Δ^{6}-tridecenoic.	$R\cdot[CH_2]_5\cdot CH:CH\cdot[CH_2]_4\cdot COOH$
		(R, Δ^{2}-*cyclo*pentenyl.)

One carbon atom in the *cyclo*pentenyl group is asymmetric, and all the natural acids mentioned are strongly dextrorotatory ($[\alpha]_D$ $+56°$ to $+68°$). The chemical constitution of chaulmoogric and hydnocarpic acids was outlined by Power and Barrowcliff (J.C.S. 1905, **87**, 884; 1907, **91**, 557, 563) and confirmed and amplified by Shriner and Adams (J. Amer. Chem. Soc. 1925, **47**, 2727). Racemic chaulmoogric acid was synthesised by condensing Δ^{11}-cyano-undecanoic acid and Δ^{2}-chloro-*cyclo*pentene with acetoacetic ester and subsequent