Uses of Fats Affected by Their Chemical Structure

Address Before John Cass Technical Institute, London, as Reported by The Chemical Age

By T. P. Hilditch

THE utilization of fats in edible products (butter, margarine, cooking fats, confectionery), for soap making, in paints and varnishes, or for other purpose, involves at the present time the consumption of several million tons per annum of natural fats, and the existence of very large industries, employing large numbers of people, which are dependent on the natural fats as raw materials.

There are many different kinds of fats and fatty acids found both in the fruit of plants and in animals, some solid, some liquid and some semi-solid. Of the solid fats, some are hard and brittle; others, even though they melt at a higher temperature, are softer and more plastic in texture, and of the liquid fats (or oils) some will keep more or less unaltered on storage, whilst others become gummy or thicken on exposure to air. These varying properties make some fats especially suitable for butter or lard substitutes or for other edible ends; other fats make useful soap-making material, and yet others ("drying" oils) are adapted for use in the preparation of paints.

A number of more or less rapid analytical tests have been devised by means of which those engaged in the production of any of these commodities can readily assess the utility of any given natural fat for their particular service, but technical analytical methods of this nature do not, as a rule, tell us very much about the chemical structure of the fats. Nevertheless the usefulness of a particular fat depends ultimately on its fundamental chemical structure and it is, therefore, desirable to have as complete a knowledge as possible of the latter.

Industrial Uses of Natural Fats

UP TO the present some 1,400 different natural fats have been examined, of which number perhaps between 100 and 200 find technical use in one form or another. It has been known for more than a century that all fats are mixtures of chemical compounds known as glycerides, formed by union of glycerol with three groups or molecules of fatty acids, but it is only comparatively recently that the quantities and kinds of fatty acids characteristic of particular fats have received detailed attention, whilst the manner in which they are bound up with glycerol is only at present becoming clearly understood.

The reasons for this apparently slow development of knowledge do not lie in any particular complexity of the fatty acids (which, as organic chemical compounds go; are rather simple in structure), but in the fact that nearly 40 different fatty acids have been observed in one or other of these fats; that the number of different fatty acids in an yone fat is never less than 3 or 4 and may be as many as 15; that in the great majority of cases two or three different fatty acids are linked to the same glycerol molecule, so that the whole fat or mixture of glycerides is very complex; and that the different fatty acids are built up for the most part on very similar lines and are therefore not easy to separate quantitatively.

On the other hand, the specific utility of a fat depends ultimately on (*a*) the kinds and proportions of the individual fatty acids present in combination with glycerol and (*b*) the manner in which these are linked up with glycerol as natural glycerides. Consequently, there is considerable incentive to investigators in both these directions. Much progress has been made in the last 10-20 years in accumulating detailed analyses of the fatty acids present in numerous fats, and reliable data of this kind for 150 or more fats (including most of those in common use) are now available. The second problem (the structure of the glycerides themselves) is much more difficult, but definite advances have recently set in in this field.

The subject of fats is full of paradoxes. The constituent fatty acids are so simple in structure as to have proved relatively uninteresting to organic chemists, yet by reason of their simplicity and similarity and their complex mode of union with glycerol in nature, the resulting fats are usually most complicated mixtures which have proved singularly difficult for the chemist to unravel. Again, in the vegetable kingdom, which, from a biological standpoint, is in many ways simpler in functional mechanism than the animal, we find numerous specialized fatty acids which are never, or rarely, encountered in animals, and also the structure of the glycerides themselves in seed-fats appears to be oriented on more well defined and less haphazard lines than in many animal fats. Furthermore, the most complex forms of animal life appear to produce, or at all events to accumulate, fats containing the simplest group of fatty acids met with in nature, namely, palmitic, stearic, oleic and linoleic acids.

Comparison of Classifications

IT IS very interesting to classify the detailed data available at present for the fatty acid compositions of different natural fats according to the predominance, in a broad way, of one or more particular fatty acids, and to compare the resulting list with the classification adopted by the biologists for the plants or animals in which the fats originated. It is found that, so far as the existing information takes us, there is a remarkable connection between the two classifications.

Thus, in the fats present in seeds of various kinds, two acids, lauric and/or myristic, are especially prominent in seeds of the *Palmae, Myristicae* and *Simarubacae;* erucic in *Cruciferae;* petroselinic in *Umbelliferae* and *Araliaceae;* Chaulmoogric and hydnocarpic in *Flacourtiaceae;* arachidic and lignoceric in *Sapindaceae* and certain members of *Leguminosae;* whilst a few acids are even almost peculiar to certain genera or species — elaeostearic to *Aleurites Fordii* and *Montana,* ricinoleic to *Ricinus communis,* tariric to *Picramnia* species. The majority of seed-fats, however, have only four predominating acids — palmitic, stearic, oleic and linoleic; yet in these cases stearic is present in greater amount than palmitic in seed-fats of five botanical families, whilst the relative proportions are reversed in 13 other botanical families. In 11 other families, finally, the proportion of palmitic and stearic acids is very low, and oleic, linoleic (and linolenic) acids predominate. This group includes nearly all the more familiar "drying" oils used in the paint and varnish industries.

Again, in the animal kingdom, many of the common fish oils and even those of the ordinary whales contain similar mixtures of fatty acids, which are entirely differentiated from any vegetable or non-marine animal fatty oils by the presence of large quantities of peculiar unsaturated acids known as palmitoleic, doleic, cetoleic, clupanodonic, etc. The only exceptions met with so far are certain abnormal types of oil, such as that of the sperm whale, which contains higher fatty alcohols in place of glycerol, and those of the shark and ray group, the liver oils of which contain large amounts of hydrocarbon as well as fatty oil. In these cases the fatty acid composition, although still different from that of fats of non-aquatic origin, is also different from that of the average fish, the oil of which is practically all fatty or glyceridic in nature.

Finally, as already stated, the fats of carnivora, herbivora and man contain, for the most part, the simple mixtures of palmitic, stearic, oleic and linoleic acids.

To a large extent, therefore, and in general terms, the composition of the fatty acids of the natural fats is characteristic for particular biological families, genera, or even species; at the same time, within certain limits, there is variability in the actual amounts of any one acid present in a fat from the same species, such variations probably depending on factors such as climatic conditions, life history and habits, stage of development of the organism, etc.

The great differences in kind and amount of the various fatty acids present in these natural materials are not accompanied by parallel differences in the manner in which they are assembled into glycerides. So far as our present information goes (and it is still in a rudimentary condition) the structure of the glycerides seems to be determined solely by their place of origin in the plant or animal and to be of two sharply defined kinds:—

(*a*) Glycerides in which the fatty acid molecules are woven into combination with glycerol in such a way that a maximum even distribution of the fatty acids among the glycerol molecules has taken place. So far this has only been observed in vegetable seed fats, but within this category it appears to be a rule almost without exception.

(*b*) Glycerides in which the fatty acids are thrown into combination with glycerol in a more fortuitous fashion and, apparently, much on the lines on which probability would determine the combinations in which a number of differently coloured balls could be withdrawn, haphazard, three at a time, from a bag in which a large number were present. Animal body and milk fats, pericarp or fruit flesh oils of plants, and artificially prepared fats made by heating fatty acids and glycerol together fall into this class.

Experimental Data Lacking

IT SHOULD be noted that experimental data is yet lacking on this point for many fats, especially those of animal organs such as liver, etc., oils.

Sufficient is already known, however, to indicate the considerations, which, for example, broadly determine the characteristic consistency of butter-fat as contrasted with that of coconut fat or cacao butter. To simulate completely the physical texture of butter is not only a matter of having approximately the same proportions of mixed faty acids present, but of combining these in a similar manner to that of milk-fat, so that there are about 30 per cent. of fully saturated glycerides present, with a molecular ratio of about equal parts of saturated and unsaturated acids in the mixed saturated-unsaturated glycerides. Whilst it is probably economically unnecessary closely to approach this ideal, it may yet be pointed out that fats present in animal tallows are built up on these lines. So to a certain extent is palm oil, whilst coconut oil and palm kernel fats or soft oils such as cottonseed oil belong definitely to the other evenly distributed class of glycerides.

On the other hand, certain fats of which cacao butter is an outstanding example, contain substantial amounts of only three fatty acids, oleic, palmitic and stearic, and their proportions are not very far from equimolecular. Consequently, by reason of the "even distribution rule," they contain large proportions of oleopalmitostearin (as has been experimentally proved), and thus come closer in physical properties to those of an individual compound; they have a low but sharp melting point, and, for fats, are exceptionally hard and brittle. They are thus especially suited for use in confectionery.

In another class of oils, the "drying" or paint and varnish oils, both the nature of the fatty acids and the structure of the glycerides play an important part. All highly "unsaturated" fatty acids absorb oxygen from the air very readily, and become converted into thick, almost solid, gelatinous or horny substances. If the acids are extremely unsaturated, as in fish oils, the products are gummy and thick and do not cohere readily into solid films, but with less unsaturated acids, especially mixtures of linoleic and linolenic, the products of oxidation or "drying" are transparent coherent solid films.

Thus fatty oils containing mixed glycerides of these acids are most suited for paint oils, and such oils are found in various seeds, such as linseed, poppyseed, perilla, walnut seed, hemp seed and others. These seed oils, however, invariably also contain combined oleic acid, which is not a "drying" agent, its state of unsaturation being too low. Owing, however, to the operation of the "even distribution" rule in glyceride structure, it is probable that, so long as the more unsaturated acids are present well in excess of the oleic acid, each molecule of the latter is partnered by two of the more unsaturated components. In these circumstances the final oxidized product is a suitable solid film, in spite of the presence of more or less oleic acid in combination.

Choice of Raw Material

TO TRADES where the fats are broken up into their constituent acids and glycerol—soap-making being by far the most important—the structure of the original fat is of no great interest, and the main concern is the nature and the amount of the fatty acids present.

The variety of fatty acid mixtures in the hundreds of natural fats which are available (though only a fraction have yet been commercially exploited) may be found to satisfy the needs of practically all the industries concerned. Two ultimate developments of these lines of work suggest themselves: (*a*) To collect detailed fatty acid compositions of all fats likely to be of any industrial use, and, where necessary, to obtain sufficient analyses to cover any likely range of variability within the same species or variety of plant or animal; (*b*) to determine the particular strains or varieties of plant species which will give the best yield of fatty oil of desired composition under given conditions of climate, soil, etc. Combined efforts by chemists and agriculturists on scientific lines should, in the course of time, make great improvements in the standardization of fats as raw materials.

Cultivation of Oil-bearing Plants

INDICATIONS of what is likely to happen in this manner are afforded by comparison of plantation coconut and palm kernel and palm oils with the native-produced fats from the corresponding wild trees; these are already matters of course, but the scientific cultivation of other oil-bearing plants is also coming into being in various parts of the world, notably of late years in the United States, where soya beans, *Aleurites* (China wood) trees and *stillingia* oil trees are already in bearing on a practical scale.

Beginnings are also being made in parts of the British Empire, especially Malaya, Kenya and West Africa, and experimental crops of

(*Turn to page* 347)

Cottonseed Samples

(*From Page* 337)

The curved plate "F" (Fig. 1.) in the rear of the hopper beside preventing any back dropping of seed, apparently tends to cause a rolling of the seed in the hopper and possibly results in some mixing of the seed. As to size, the belts are ⅞ inch in width, the pulleys 3 inches in diameter and 7½ inches from center to center. The tacks protrude ⅛ inch through the belts. We operate the crank at a fairly constant rate of about 75 rpm. The apparatus is exceptionally simple and was constructed in this office by one of my assistants, Mr. F. S. Hubbard, from scrap material with the use of hack saw, a metal drill, pair of tin snips and a soldering iron.

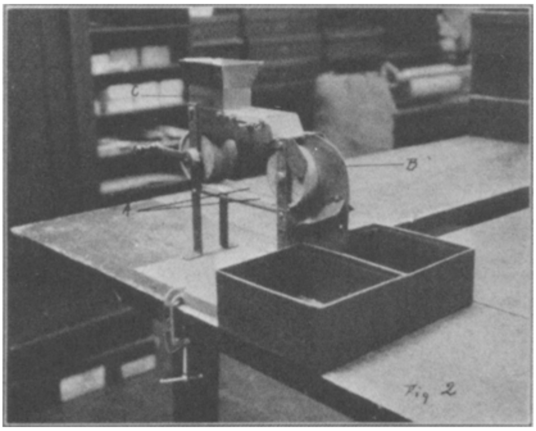

Fig. 2. COTTON SEED SAMPLE REDUCER.

Side view—showing machine in position for operation.

The machine is peculiarly adapted to the division of samples of cotton seed sent in under the revised rules of the National Cottonseed Products Association. These samples under the new rules are to weigh 1,000 grams. One-half or 500 grams is to be retained as a referee sample, a single division on the machine. Again dividing one half of the original sample gives two parts of 250 grams, a second division of one of these portions results in two parts of 125 grams each. One of these is available for Free Fatty Acid determinations and dividing the other results in two portions of approximately the size required under the rules for moisture and oil determinations.

The Lipeometer

(*From Page* 336)

The method as presented, has been thoroughly tested not only on a number of samples but on various portions of the same gross sample. The results are within 0.1 of 1% in the hands of various analysts. It is perhaps needless to point out that the simplicity of the manipulation permits the work to be done by a trained technician.

Acknowledgment is hereby made to Dr. C. P. Harris, of our Research Laboratory, for his work in the development of the process, and to his assistant, Mr. Manuel Horwitz, for his co-operation.

Fat Composition and Uses

(*From Page* 341)

China wood (tung oil) trees, rubber seed, perilla and some other plants are being systematically tested. Yet, bearing in mind the wide climatic and agricultural resources of the Empire and the opportunity for opening up fresh tracts of cultivated land on these lines, progress within the Empire is all too slow, and the efforts already made by the Government Departments concerned to promote these developments deserve encouragement, but also require to be intensified and fortified by the close co-operation of chemists, biologists and agricultural experts.

Tentative Official Oil Trier

THE Tentative Official Oil Trier (sampler) adopted at the meeting in New Orleans this year can be obtained complete from the Refinery Supply Company, Tulsa, Okla. at the price of $35.00.

The committee suggests that all companies who have any use for oil sampling devices, purchase at least one of these Tentative Official Triers in order to enable us to collect data and opinions during the coming season. At the next meeting of the Society, this matter will again come up for definite adoptions or recommendations.

We very much appreciate your cooperation in connection with the above and wish to refer you to the Sampling Committee's report printed in the May issue of *"Oil and Fat Industries,"* also the report of Uniform Methods Committee, *"Oil and Fat Industries,"* June, 1930. Further details concerning the sampler may be obtained from the chairman.

V. SERBELL,
P. O. Box 740,
Portsmouth, Va.