THE CHEMICAL CONSTITUTION OF NATURAL FATS

The Chemical Constitution of Natural Fats. By T. P. Hilditch. (Chapman & Hall, Ltd., London), 1940. Pp. xi + 438. Price 35*sh.* net.

WORKERS on the technical and biochemical aspects of the fats will already be acquainted with the fruitful results which have come from Professor Hilditch's school of research at Liverpool, represented by over a hundred papers from his laboratory during the past fifteen years, and they will keenly welcome his new book on this group of natural substances.

It is fitting at this stage to look back to the establishment of the Campbell Brown Professorship at Liverpool University in 1926, and the reviewer cannot do better than quote Dr. E. F. Armstrong's introduction to Professor Hilditch's earlier work *"Fats and Waxes"* (1927):

"In Liverpool, thanks to the generosity of one of its most prominent Professors of Chemistry, the late J. Campbell Brown, F.R.S., there has been established recently a Professorship in Industrial Chemistry, with special reference to Oils and Fats, to which Dr. T. P. Hilditch has been elected. In my opinion, not only is the choice of subject highly appropriate itself, but, further, no better geographical situation for a Chair of Research in relation to the industry in question could have been chosen. Liverpool as a port ranks high in the import of oil-bearing seeds and fats . . . .; a large group of industries based on bulky materials brought from overseas are all grouped round the port of entry to minimize transport; industries indeed which in many cases manufacture largely for export and pay for their raw materials by the manufactured goods which they send away from the same port.

The industries mentioned all have this in common, a need of precise and complete knowledge of the materials they use: in this case, the fats.

The scientific problems in such a field cannot profitably be solved by individual and isolated effort—they require mass attack by the whole staff of a research school, working to a definite programme during a number of years, before any real measure of success can be obtained. The experimental difficulties are considerable and a special manipulative technique has to be acquired."

Seldom can there have been so close a correspondence between initial aims and ultimate achievements as that attained by Professor Hilditch's research school.

Apart from technology, the chemistry of the fats had been a strangely neglected field. Indeed from the time that Chevreul established the fundamental nature of fats as compounds of glycerol with fatty acids, there was little essential development for about a century. Chevreul's collected work *"Recherches chimiques sur les Corps Gras d'Origine animale"* appeared in 1823. In Chapter V of the second part of his Book V Chevreul had already considered the quantitative aspect of alkali saponification, this chapter being headed *"De la quantité de graisse qu'un poids donné de potasse peut saponifier"*. It is all the more curious that not for nearly another sixty years was the chemical analysis of fats put on a really quantitative basis. It was early apparent that elementary analysis afforded little information since the carbon and hydrogen contents of most fats are similar.

A text-book of 1864, T. Chateau's *"Guide pratique de la Connaissance et de l' Exploitation des Corps Gras industriels"* may be taken as typical of the later years of this period. The analytical section refers to the determination of density (with a considerable variety of "oleometers"); an electric "diagnometer" based on conductivity measurements; the rise in temperature when different fats are mixed with sulphuric acid (the Maumené thermal value, which still finds a limited technical application), and an amazing variety of colour tests. Saponification is referred to as a possible method of quantitative examination. Trials are described of a large number of reagents including iodine solutions and it is clear that more or less settled procedures emerged later out of a considerable welter of empiricism.

There followed a period during which technical fat analysis developed fairly satisfactory standard methods for such purposes as the detection of adulteration of industrial fats, the determination of quality, and the assessment of potential raw materials. The two fundamental "characteristics", Saponification value (Köttstorfer, 1879) and Iodine value (Hübl, 1884) may be regarded as roughly dating the beginning of this period. Development of suitable instruments added the refractometer to the service of industry, and methods for special purposes such as those of Reichert, Meissl, Polenské, and Kirschner came into use.

The mass of literature which arose round these technical methods may conveniently be surveyed in the pages of J. Lewkowitsch's

well-known *"Chemical Technology and Analysis of Oils, Fats and Waxes"* (6th Edition, 1921), which may in fact be regarded as an epitome of fat chemistry before what the reviewer would term the "Hilditch era".

In general it may be said that the "characteristics" determined by such methods, developed mainly for technical purposes, represent a summation of the properties of the constituents of a fat under examination, and do not provide any information on the proportion of individual constituents. From this generalization may be excepted Kaufmann's thiocyanometric method (1925), and to some extent the Hexabromide value, and the Elaidin transformation which Professor Hilditch himself has placed on a semi-quantitative basis.

The problem of investigating the chemical constituents of a fat falls into two parts, the determination of the constituent fatty acids and of the manner in which these are combined with glycerol.

The first part of the problem had been attacked from time to time, for example by procedures involving the fractional crystallization of magnesium and other salts. These methods were tedious and only successful to a limited extent. The fractional distillation of methyl or ethyl esters was used by Haller (1906) and others. Professor Hilditch has adopted this method as a standard procedure, and has demonstrated that it is capable of giving reproducible results with an accuracy of about one per cent. Preliminary separation of the mixed fatty acids into saturated and unsaturated by Twitchell's method is advised, as well as a partial separation of lower acids in such cases as butter fat. The full experimental details which Professor Hilditch gives of the procedures he has found satisfactory will be especially welcomed by other workers.

A word may be added at this point on the important and often unconsidered role played in the development of chemistry by improvements in mechanical technique. The brilliant progress made in recent years in the field of vitamin and hormone research would hardly have been possible without improved microchemical methods. Similarly Professor Hilditch has pointed out that the development of ester-fractionation technique was greatly assisted by the availability of excellent electrically-driven rotary pumps which will maintain a steady vacuum for hours of running.

The second part of the problem—that of determining glyceride structure—had been attacked by physical methods prior to 1927. The main lines of attack were the fractional crystallization of fats, of brominated unsaturated fats, of hydrogenated fats; and the vacuum distillation of fats. Of this often extremely tedious work (involving, for example, in Bömer's studies, hundreds of crystallizations) an adequate account is given in the book under review, and Professor Hilditch sums it up with the observation that "the results were almost wholly qualitative in character nevertheless they are sufficient to demonstrate conclusively that seed fats are mixtures of mixed triglycerides, and that the occurrence of simple triglycerides is quite exceptional."

The modern methods of investigation developed particularly by Professor Hilditch need not be detailed here. The reader is referred to the book itself. Suffice it to say that these methods have proved capable of giving a fairly detailed picture of the major glyceride components of a variety of fats.

The emphasis here laid on the work of the Liverpool School is natural in a review of Professor Hilditch's book; this is not to discount the value of the data which has accumulated during the last fifteen years from other sources, of which may be mentioned the associates of Dr. G. S. Jamieson in the United States, Japanese workers on fish fats, the Dutch school at Delft, and various German investigators. Professor Hilditch includes in his book only those fats whose component acids have been adequately defined by modern methods; about 420 fats from plant species, about 80 fats from land animals, and about 100 fats of aquatic origin are mentioned. The number of fats whose glyceride structures have been at all satisfactorily defined is of course much smaller. The account which Professor Hilditch contributed to Schönfeld's *"Chemie und Technologie der Fette und Fettprodukte"* (Bd. I, 1936) has here been brought up to date to include data published to the end of 1938. Some 1939 publications also receive notice.

The available material has been sufficient to indicate the existence of a close connection between the component acids in a fat and its biological source. The fats of the most primitive organisms are usually made up of a very complex mixture of fatty acids, whilst as evolutionary development

has proceeded, the major component acids have progressively become fewer in number. In the depot fats of the higher animals, oleic, palmitic and stearic acids are the major components.

In a number of plant families, specific fatty acids are often found such as petroselinic (associated with the *Umbelliferæ*) and erucic (with the *Cruciferæ*).

Professor Hilditch has, on account of these associations, adopted a biological classification of the fats in his book. Similar biological relationships have attracted much attention in other fields, notably those of the terpenes and of the alkaloids, and it is of interest to refer to certain features of the latter group of compounds. Whilst there are such obvious chemical relationships as those of the *Papaveraceæ* group of alkaloids, there is an increasing number of anomalies in distribution. Sparteine is a case in point; this, formerly regarded as a typical alkaloid of the *Papilionaceæ*, has been recorded in association with piperidine type alkaloids from *Anabasis aphylla* (*Chenopodiaceæ*) and also with chelidonine in *Chelidonium majus* (*Papaveraceæ*). Professor Hilditch refers to the occurrence of eleostearic acid in the three distinct families *Euphorbiaceæ*, *Rosaceæ* and *Cucurbitaceæ*, and similar apparent anomalies could be quoted among the terpenes.

T. A. Henry in the latest (1939) edition of "*The Plant Alkaloids*" remarks that "Nature does not manage the production of alkaloids to meet the requirements of the chemical systematist, or, indeed, those of his botanical equivalent", and in the field of the fats, the interesting biological relationships already apparent should not be too rigidly interpreted.

With the existing data in all these fields, only a very small sample of the whole biological kingdom is open for inspection, and that a very uneven sample. The investigation of more animal fats is obviously desirable, since for these much less reliable data are available than for the vegetable fats.

Much earlier work on the fats has been valueless by reason of faulty identification of raw material. There is a necessity to refer to systematists questions of botanical and zoological classification. The not infrequent changes of nomenclature sometimes causes embarrassment to the chemist. The *Madhuca* fats form an illuminating example, and to the chemist it seems unfortunate that the rules of nomenclature could not have been modified in such a case, since these fats had for a long time been known to the technical world under the name *Bassia*.

Professor Hilditch has obviously taken care to ensure the correctness of the identification of the fats detailed in his book, though the reviewer has noticed at least one minor duplication. *Litsea zeylanica*, quoted (in a supplementary list) from Jumelle's "*Les Huiles Végétales*" (1921) is synonymous with *Neolitsea involucrata* (Lamk.), Merrill, a Ceylon sample of which was investigated in detail by Gunde and Hilditch last year.

Where systematists themselves disagree, chemists must hope for the best. There is a temptation to expect that the chemist may soon be able to come to the assistance of the botanist by supplementing morphological with chemical characteristics. The cases quoted of sparteine and of elæostearic acid show, however, the danger of making deductions on the basis of similarity of chemical constituents.

It is not the least of the merits of Professor Hilditch's book that it will give a tremendous impetus to future research. In fact the reviewer is acquainted with few monographs of recent years which perform so well this essential duty of stimulating further work, and so clearly indicates promising lines of study. The field opened up is a wide one, and the subject is in an active state of development. Professor Hilditch's enthusiasm has inspired workers all over the world, including many in India and Ceylon, where a wealth of raw material, both animal and vegetable, awaits investigation.

There is no doubt that the present work represents in the chemical history of the fats a milestone as notable as Chevreul's "*Récherches*"; but unlike that classic work it is improbable that it will be followed by a comparatively sterile period of sixty years. The reviewer may be permitted to hope that, in spite of the inevitable dislocation of research by war, progress in the next decade or so will be even more rapid, and that in 1950 Professor Hilditch will be still so ably reporting it.

It remains to congratulate the publisher on the excellent printing, especially of the extensive tabulated data, and on the general get-up of the book. If there are any serious typographical defects the reviewer has failed to find them.

R. CHILD.