

other patent issued to the latter [Fr. 809,363] was on a resin prepared by the reaction of a urea-formaldehyde resin on a fat acid ester. The Soc. française Beckacite [Fr. 810,073] in a similar process used a phenol-formaldehyde product instead of urea-formaldehyde resin.

Several reactions were carried out in the varnish oils or other liquid to make a finished coating material. C. Ellis [U. S. 2,101,791] heated a polyphenol with tung oil under controlled conditions so as to yield a liquid product. F. B. Root's [U. S. 2,082,515] invention dealt with reaction products between a drying oil and formaldehyde. J. B. Rust [U. S. 2,069,725] in a similar manner used a resorcinol-acetone resin with the drying oil. J. D. Murray [U. S. 2,099,570] combined cellulose esters with drying oils and dissolved the products in a solvent.

E. M. Williams [U. S. 2,082,371] prepared a gum which was miscible with oils, by heating and aerating tung oil with large quantities of menhaden oil in the presence of driers.

A fatty oil product suitable for use in nitrocellulose lacquers was prepared by J. S. Long and G. F. Beal [U. S. 2,059,260]. The oil was reacted with a phenol in the presence of aluminum chloride and the reaction products were hydrolyzed with weak acids and washed. A tung oil product that is compatible with nitrocellulose was prepared by B. S. Buchmaster [U. S. 2,061,829]

by heating the oil with sulfur monochloride in a non-oxidizing gas and then passing the inert gas through the product to reduce its sulfur content.

Several fat and oil products were used for moisture proofing textiles and fabrics. The impregnation of the textiles with resinous products derived from fats was patented by I. G. Farbenindustrie A.-G. [Brit. 463,300; Fr. 809,289] and Bakelite Ltd. [Brit. 461,649; 461,650]. Another patent issued to I. G. Farbenindustrie A.-G. [Brit. 451,300] describes a method of dispersing fat acid anhydrides with alkylolamines in water for use in waterproofing. L. Auer and P. Stamberger [U. S. 2,083,549] partially vulcanized an oil with sulfur and emulsified the product in ammoniacal casein solution to yield a composition suitable for impregnating textiles. The use of fat acid urethanes was patented for the same purpose by I. G. Farbenindustrie A.-G. [Fr. 806,944]. A composition suitable for automobile top fabrics, prepared by A. M. Alvarado [U. S. 2,078,921] comprised a mixture of asphalt, wood oil, and an antiwrinkling agent.

Experiments on pyrolysis of fatty oils to hydrocarbons were reported by J. Banzon [Philippine Agr. 25, 817-32], G. Manzella [Energia tecnica 4, 92-4], Y.-S. Chao [J. Chem. Eng. China 4, 169-72], F. Michot-Dupont [Bull. Assoc. Chem. 54, 438-48], N. M. Patel and M. S. Patel [J. Univ. Bombay 5, Pt. 2,

114-31], T.-S. Lo and L.-S. Tsai [J. Chinese Chem. Soc. 5, 44-50], E. C. Koo and S.-M. Cheng [J. Chem. Eng. (China) 3, 348-53] and M. Friedwald [Rev. pétrolière No. 734, 597-9]. The papers presented data on the yields of various hydrocarbon fractions from several oils and the method of pyrolysis used. D. Gardner [Fr. 801,991] patented the method of manufacture of hydrocarbons from fatty oils by heating in vacuum in the presence of calcium oxide and calcium carbide or calcium silicide. A patent issued to W. Schrauth [Ger. 642,590 Cl. 23a 4] concerned the production of hydrocarbons by the hydrogenation of waste fats and separating the product by fractional distillation.

Chrysalis, a waste product of the Chinese silk industry yields about 12 per cent oil on pressing. This oil which was described by S.-C. Chow [Ind. Research (China) 5, 475-80] and C.-C. Pan and K.-H. Sun [Chem. Ind. (China) 11, No. 2, 1-23] is high in fat acids, impurities and color. It was suggested that the oil be cracked to yield hydrocarbons.

This review will be continued in the May issue.

The committee which assisted the chairman in preparing this paper by reviewing and submitting additions, suggestions and corrections is composed of:

R. C. NEWTON  
H. A. MATTILL  
GEO. S. JAMIESON  
G. R. GREENBANK  
M. M. PISKUR, Chairman

## THE STRUCTURE AND CHEMICAL COMPOSITION OF FATS AND OILS\*

J. B. BROWN

FROM THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY, THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO

### Abstract

This is essentially a general review of progress during the past ten years both in the chemistry of the glycerides of fats and oils and in the chemistry and nature of their constituent fatty acids. Applications of some of the newer research methods are described and discussed.

OVER 120 years ago Chevreul showed that several of the common fats and oils were compounds of fatty acids with glycerol. If this is to be regarded as the beginning of our subject, its further development might be divided for convenience into three periods. During the first of these, from 1815 to about 1900, relatively

little of an exact nature was accomplished. This is not intended to imply, of course, that fats and oils were completely neglected scientifically, but rather to point out that fat research during this period was concerned mainly with the generalities of average analytical data. Many of the common fatty acids were discovered. The classic lead soap ether method was first described in 1825. Later two other classic procedures appeared, the saponification number and the iodine number. These two determinations have been of tremendous importance in characterizing fats and oils and in giving us infor-

mation about their average composition.

During the second period, 1900-1925, we observed a rapidly expanding chemistry of fats and oils. Some attempts were made to actually isolate and identify individual glycerides. Numerous fats and oils were examined, most of them by the accepted proximate methods, and many of them also in an attempt to evaluate quantitatively the composition of their component fatty acids. During this period, too, the chemistry of many of the individual fatty acids was intensively studied; the structures of acids such as oleic, linoleic and lin-

\*This paper was presented at the Symposium on the Chemistry & Metabolism of Fats, held at the Rochester meeting of the American Chemical Society. It is published here by special arrangement with the Division of Agricultural & Food Chemistry.

olenic, ricinoleic, chaulmoogric, and many others were worked out. Also we were given the classic in English reference books, namely, Lewkowitsch's "Technology of Fats, Oils, and Waxes," which has been of immense value to all workers in this field in spite of the great deal of erroneous information contained therein.

In the third period, beginning about 1925 and up to the present, chemists have become increasingly aware of the fact that fats contain more than a few common fatty acids, such as palmitic, stearic, and oleic, and where careful search has been made, they have found many other acids present. This search for new acids, the attempts to increase the accuracy of estimating the content of the various acids, and the development and use of new methods of studying glyceride structure, are typical of this period.

My object in this brief report is to review a very few of the important recent accomplishments during this third period and to suggest what seems to be some of the needs for future work in this field.

### Glyceride Structure

It is well known that several types of glycerides are theoretically possible;  $\alpha$ - and  $\beta$ -monoglycerides;  $\alpha$ - $\beta$  and  $\alpha$ - $\gamma$  diglycerides, both simple and mixed; and simple and mixed triglycerides. The mono and diglycerides rarely occur naturally, and when found, are usually regarded as partial hydrolysis products, rather than as incomplete products of synthesis. The simple triglycerides, commonly reported in the older literature, have been shown to be present only in relatively small amount unless one fatty acid is present in the fat in considerable excess. It should be pointed out that optically active glycerides are possible by virtue of glyceride structure, but the author is not aware of any naturally occurring optically active glyceride being reported, unless one of the component fatty acids possesses this property, for example, the glycerides of ricinoleic and chaumoogric acids.

Early studies of glyceride structure (1) were based primarily on repeated crystallization of glyceride mixtures from organic solvents, an extremely tedious process. By this method individual glycerides were occasionally isolated and their structure determined. Further information on the nature of the glycerides was furnished by Suzuki and Yokoyama (2) and by Eibner (3)

who fractionally crystallized the bromine addition products of some of the fish oils and linseed oil.

In the modern study of glyceride structure we are indebted primarily to the work of T. P. Hilditch and his co-workers in Liverpool. In the late twenties Hilditch (4) gave us his method of permanganate oxidation of fats and oils as a method of study. By this method the component glycerides could be grouped into two classes, the fully saturated glycerides, which were unaffected by the reaction and the unsaturated glycerides which were converted into acidic compounds by the permanganate and could be separated thus from the unaffected glycerides by alkali extraction. Since introducing the method, Hilditch has studied numerous fats and oils (5). It is impossible in this brief review more than to mention and to illustrate a few of his general findings (6).

(1) Nature favors the formation of mixed triglycerides. Exceptions are notable amounts of triolein in olive oil and trimyristin in nutmeg butter.

(2) Individual triglyceride molecules tend toward maximum heterogeneity in composition. (The so-called uniform distribution rule.)

(3) Fully saturated glycerides occur in large amounts in kernel fats, where the saturated acids make up more than 60 per cent of the total fatty acids. Example: (Table I.)

Kernel Fat	Saturated Fatty Acids	Saturated Glycerides
	Mol. %	Mol. %
Cocoanut .....	94	86
Dika nut .....	91.7	81
Nutmeg butter .....	90.2	73
Palm kernel .....	85.3	66

(4) Fully saturated glycerides occur in relatively small amounts in some fats, even though as much as half of the fatty acids are saturated. (See Table II.)

Fat	Saturated Acids	Fully Saturated Glycerides
	Mol. %	Mol. %
Borneo tallow .....	62.8	4.5
Cacao butter .....	59.8	2.5
Shea butter .....	45.1	2.5
Lard .....	45.4	5.6
Palm Oil .....	49.6	6.5

	Saturated Acid % by Wt.		Glycerides—Mol. %		
	C <sub>18</sub>	C <sub>16</sub>	Fully sat'd	Mono-oleo di-sat'd	di-oleo mono-sat'd
Borneo tallow .....	21.5	39	4.5	78	17.5
Palaquium oblongifolium* ..	5.9	54	2	77	21
Allanblackie S.* .....	3.1	52.6	1.5	62.5	36
Shea butter .....	85	35.9	2.5	29	68.5
Cacao butter** .....	24.4	34.5	2.5	73	24.5

\*65%  $\beta$ -oleo distearin.  
\*\*55%  $\beta$ -oleo palmitostearin; 25%  $\beta$ -oleo distearin.

(5) The uniform distribution rule may result in the formation of a fat with certain mixed triglycerides predominating. This triglyceride may determine the properties of the fat. The fats used in illustration are comparatively simple in fatty acid composition so that the mixed glycerides are relatively simple mixtures of individual compounds. (See Table III.)

The tendency toward formation of  $\beta$ -acyl glycerides is further shown by the fact that when palmitic acid is present in comparatively small amount with oleic acid predominating, the glyceride will be  $\beta$ -palmito-diolein.

(6) Much has been added to the knowledge of glyceride structure by studies of the hydrogenated and partially hydrogenated fats. Quantitative analysis of the composition of the fatty acid mixture during various stages of hydrogenation has led to many interesting conclusions. Apparently when a mixture of glycerides is hydrogenated, an unsaturated acid in the  $\beta$ -position is resistant to addition of hydrogen. A  $\beta$ -palmito-diolein, for example, would be selectively reduced before a  $\beta$ -oleo dipalmitin.

Anything approaching a satisfactory appreciation of Hilditch's work can be secured only by reference to and study of his numerous original articles.

### The Fatty Acids of Fats and Oils

During the past ten years progress in examining mixtures of fatty acids has been directed mainly toward refinement in the methods of separation, search for the so-called minor component acids and search for new types of acids. Regarding the methods of examination, it must be admitted that few new ones have been developed. Of the proximate procedures the iodine number is still universally used. Many new procedures and reagents for its determination have been proposed, but the *Hanus* and *Wijs* modifications are still the standard for most laboratories. Two new analytical procedures recently proposed are the "thiocyanogen" (7)

and "diene" (8) numbers. The thiocyanogen number, when used along with the iodine number, allows an indirect calculation of linoleic and linolenic acids in the presence of oleic acid. Only one of the two double bonds of linoleic acid and two of the three double bonds of linolenic acid react with thiocyanogen. The "diene" number, proposed by Kaufmann and Baltes, is based on the reaction of maleic anhydride with conjugate double bonds, and appears to be a specific means of estimating such groups. Some of the findings by this method will be referred to later.

With reference to methods for separating the fatty acids the lead soap-ether method is still widely used. Practically, however, many alcohol (9) method in its stead. A direct method for the estimation of saturated acids was proposed by Mottram (10); it was based on oxidation of the unsaturated acids with permanganate and isolation of the residual higher saturated acids. In our laboratory we have found (11) that subjecting an acetone solution of mixed fatty acids to a temperature of  $-20^{\circ}$  C. results in a separation of saturated and unsaturated acids with an efficiency approaching that of the lead soap method. We have also developed low temperature crystallization methods for the purification of certain of the unsaturated acids. With oleic (12) it is possible to prepare specimens of high purity by direct crystallization of the fatty acids of olive oil from acetone. No methods have been available hitherto for the separation of oleic and linoleic acids, except the complicated bromination-debromination procedure, which is far from satisfactory for quantitative purposes. By fractional crystallization (11) of the fatty acids of corn oil, it is possible to isolate linoleic acid of 92-94 per cent purity.

During the past decade we have seen the so-called ester fractionation method (13) (14) (15) refined to a point where it now becomes possible to evaluate the content of the major component acids in a given mixture much more accurately than before, perhaps to within 1-2 units per cent. Satisfactory accuracy of separation is certainly not yet attained with the drying and semi-drying oils and probably in the fish oils because of the difficulty in separating the unsaturated acids. Two general applications of the ester fractionation method are in general use—

(1) direct esterification and distillation of the resultant esters (usually methyl), and (2) separation into saturated and unsaturated acids, esterification of both, and separate fractional distillation and examination of the fractions of the two groups of esters. Highly efficient stills have been reported which are claimed to separate individual carbon series almost quantitatively. It seems likely that such stills will be extremely useful for separating saturated fatty acids, but there always remains the question of whether the two and more bond acids will undergo alteration (shift of bond, cis-trans) during the prolonged heating necessary for highly efficient separation.

One of our best annual reviews (18) on the subject includes for 1936 proximate analyses of about seventy specimens of fats and oils from widely distributed sources. Twenty of these report actual amounts of major component acids. Space permits here a review of recent work on the fatty acid composition of only a few of the more common and commercially important animal fats and oils.

Butter fat is perhaps our most important food fat. Since 1899, due to the work of C. A. Browne (19), we have known that butter contains the entire saturated series of fatty acids, from butyric to stearic, along with oleic acid and dihydroxystearic. Other fatty acids were mentioned from time to time. As early as 1930 Hilditch and Sleightholme (20) recorded the presence of linoleic acid. In 1931 we (21) reported the presence of highly unsaturated acids of the arachidonic type. Later in 1933 Bosworth and Brown (14) confirmed the presence of decenoic and tetradecenoic acids, previously found in much smaller quantity by Grün and Wirth (22). We also found acids of the arachidonic type and in addition, small amounts of behenic, tetracosanoic and cerotic acids. Bosworth and Sisson (23) later found positive evidence of arachidonic acid itself and Bosworth

and Helz (24) have recently isolated small amounts of an optically active acid, hydroxy-palmitic. Considerable attention has been directed to the possible occurrence of linoleic acid in butter fat. Hilditch reported it to be present in small amount, basing his evidence on high iodine numbers of the  $C_{18}$  fractions of the unsaturated acids. Likewise, Eckstein (25) claimed a small amount of it to be present. Bosworth and Brown could find no evidence for its presence, basing their conclusions on failure to isolate the characteristic petroleum-ether insoluble tetrabromide, the most conclusive and specific test for linoleic acid. The answer to this argument seems to be that ordinary linoleic acid does not occur in appreciable amounts in butter, but that other geometric or double bond position isomers of this acid probably do occur, i.e., other octadeca-dienoic acids of different cis-trans forms than ordinary linoleic acid. Bosworth has found ordinary linoleic acid in human milk fat (26). Riemenschneider and Ellis (27) found it in goat milk fat.

In the Table IV are listed the now recognized fatty acids of cow milk fat.

TABLE IV  
FATTY ACIDS OF BUTTER FAT

Saturated Fatty Acids		Observers
Butyric	.....	C. A. Browne
Caproic	.....	C. A. Browne
Caprylic	.....	C. A. Browne
Capric	.....	C. A. Browne
Lauric	.....	C. A. Browne
Myristic	.....	C. A. Browne
Palmitic	.....	C. A. Browne
Hydroxy palmitic	.....	Bosworth and Helz
Stearic	.....	C. A. Browne
Dihydroxy stearic	.....	C. A. Browne
Behenic	.....	Bosworth and Brown
Tetracosanoic	.....	Bosworth and Brown
Cerotic	.....	Bosworth and Brown
Unsaturated Fatty Acids		Observers
Decenoic	.....	Bosworth and Brown
Tetradecenoic	.....	Bosworth and Brown
Hexadecenoic	.....	Hilditch and Paul
Oleic	.....	C. A. Browne
Linoleic (not ordinary)	.....	Hilditch and Sleightholme
Arachidonic	.....	Bosworth and Sisson
Highly unsat'd acids	.....	Brown and Sutton

With further investigation, no doubt, other acids, especially of the highly unsaturated type, will be

TABLE V

Feeding Regime	Fat from	Iodine No.	Myristic	Palmitic	Stearic	Oleic	Linoleic
		mol. percent					
Brewer's Rice (28)	back	52.6	2.1	28.2	11.7	56.8	1.2
Soy beans (28)	back	90.7	0.9	18.7	9.2	39.6	31.4
Peanuts (28)	meat	84.1	0.5	16.8	7.3	55.9	19.3
Low fat (110 days) (29)	.....	61.2	1.4	27.4	8.2	56.5	6.5
Low fat (257) (29)	.....	55.1	0.9	27.2	10.7	59.9	1.3
Cottonseed—none	back	60.6	2.0	27.3	13.2	48.8	8.7
Cottonseed (4%) (30)	back	60.5	1.4	26.8	20.4	38.4	13.0
Cottonseed (8%) (30)	back	64.4	1.0	23.5	22.6	35.0	17.9
Cottonseed (12%) (30)	back	77.4	1.3	15.0	25.9	31.3	26.5
Control outer back (31)	.....	.....	2.4	26.3	10.2	51.8	9.3
Control inner back (31)	.....	.....	1.7	31.6	13.4	45.6	7.7
Control Parinephric (31)	.....	.....	4.4	30.2	20.5	39.9	5.0

found and identified.

From the standpoint of glyceride structure one might speculate on the possible complexity of this fat which is synthesized by the metabolic activity of the mammary glands. Certainly many hundreds and possibly thousands of compounds may occur. Butter fat is without doubt the most complex of all natural fats.

Lard is another extremely important food fat. The relative simplicity of its fatty acid mixture makes it a comparatively simple subject for investigating the effect of diet on the composition of depot fat. Results are summarized in Table V.

Concerning the minor component acids of normal lard, the occurrence of small amounts (less than 1 per cent) of arachidonic acid has been reported by Ellis and Isbell (28), and by Brown and Deck (32).

It is a curious fact that beef tallow, another of our important food fats, has been subjected to so few modern investigations. The only important recent references I can find concerning this fat are credited also to the Liverpool laboratory. Banks and Hilditch (49) studied the glyceride structure and fatty acid composition of four tallows. The fatty acids were as follows:

Fatty Acid	No. 1	No. 2	No. 3	No. 4
Myristic	6.3	4.5	7.8	5.7
Palmitic	27.4	30.6	27.7	23.7
Stearic	14.1	19.0	24.4	28.2
Arachidic	.....	0.1	.....	.....
Oleic	49.5	42.6	38.8	41.0
Linoleic	2.4	3.0	1.1	1.4

No detailed search for minor component acids other than linoleic and arachidic has been made.

It is impossible to discuss here work on the vegetable fats and oils on which numerous investigations have been made. The excellent book on Vegetable Fats and Oils by G. S. Jamieson appeared in 1932 and reviews work previous to that time, including the numerous researches of Dr. Jamieson and his co-workers. No comprehensive studies have appeared recently on such oils as olive, cottonseed, linseed and soybean, especially with regard to search for minor component acids. Difficulty in evaluating the composition of the semi-drying and drying oils arises from the fact that no quantitative methods are available for separating oleic, linoleic and linolenic acids

when present in a mixture. These acids are estimated by indirect calculation from the iodine and thiocyanogen numbers.

A large amount of work has been reported from several chemical laboratories in Japan on the composition of fish and marine animal oils. Several of the four and five bond acids have been purified and in some cases their structure studied. New high molecular weight unsaturated acids have been reported.

Concerning the chemistry of the individual unsaturated acids the following comments may be made. The low molecular weight unsaturated fatty acids are being increasingly recognized, especially hexadecenoic acid, which apparently occurs rather frequently—butter fat (50), fish oils (33), ox liver glycerides, lizard, tortoise, frog and rat depot fats (34). Decenoic and tetradecenoic acids have been reported in butter and in fish oils.

The structure of oleic acid has been definitely established as cis-9-10, octadecenoic. Only two or three of the numerous possible isomers of oleic acid have been shown to be naturally occurring. Although oleic acid is recognized as a universally occurring fatty acid, its geometric isomer, elaidic acid, has so far not been found in natural fats; however, Sinclair (35) has employed elaidic acid in studying certain aspects of fat metabolism, and has found that, if fed, it may be stored in depot fat. It is always of speculative interest to inquire why nature rejects elaidic acid so completely.

Linoleic acid has been studied in several laboratories, especially by West (36), Holde and Gentner (37) and Birosel (38). The question whether more than one isomeric linoleic acid occurs in fats and oils is still an open one. Ordinary linoleic acid has been shown by Burr (39) to be essential to life. It is most easily identified by isolation of its characteristic petroleum ether insoluble tetrabromide. Hilditch, on the other hand, has good evidence for the presence of isomeric octadecadienoic acids in butters. The origin of these is a question so far unsolved. Appreciable amounts of linoleic acid are found in beef tallow and lard, enough, in fact, to be of nutritional significance. Our isolation of linoleic acid by simple crystallization methods will help, we hope, in settling some of the problems concerning the chemistry of this acid.

Linolenic acid is still regarded as

unnatural fatty acid in animal depot fats and in fish oils, unless, of course, the animal has eaten linolenic acid at a time when it was storing fat. An interesting instance of the occurrence of this acid in animal fat is that of the western range horse (40); another is in fish oil when it was reported recently in carp oil (41), the oil having been taken from carp which had fed on grass.

Arachidonic acid, originally discovered in liver fat, has been shown to occur in adrenal fat (42) and in general in the lipids of the organs of animals. Traces of this acid along with other highly unsaturated acids occur rather generally in animal fats and oils (43). Acids of this type apparently do not occur in vegetable oils, although Farmer and Sunderland (44) recently reported an octadecatetrenoic acid in such a fat.

One of the unique acids reported in the last few years is that of licanic acid, a three double bond keto acid, in oiticica oil (45).

May I refer to two extremely interesting developments in the chemistry of the unsaturated fatty acids. First, in the spectroscopic examination of such acids, Dann and Moore (46) found in 1933 an increase in the absorption spectra during saponification of cod liver oil. Moore reported later (1937) (47) that acids with two or more double bonds were changed during saponification. In the case of the fish oils the suggestion of the formation of cyclic acids has been made. The acids of tung oil are highly absorptive before saponification. These findings make us question results in many of our previously reported investigations on fats and oils, especially in the semi-drying and drying groups.

Another recent development is the result of application of Kaufmann's "diene number" to which reference was made above. The diene number is specific for conjugate double bonds. In a very recent report Kaufmann, Baltes and Butes (48) describe an iodimetric method for the "diene number." Some of their results on various fats and oils follow:

Fat	Diene No.	Fat	Diene No.
Triolein	0.0	Cottonseed	4.7-5.0
Palm Kernel	0.0	Soy bean	8.5-8.9
Cacao butter	0.0	Linseed (fresh)	8.1-8.2
Peanut	4.8-5.3	Wood—I	67.3-67.8
Rapeseed	11.8-12.3	Wood—II	69.1-69.8
Almond	8.0-8.4		

Some evidence for change in diene numbers during saponifica-

tions of fats was given. It was suggested that the "diene numbers" in oils which by other methods had been shown not to contain conjugate system acids might be due either to unsaponifiable matter or to the presence of unsaturated labile substances, possibly acids, of a nature so far unknown. If further investigation proves the existence of fatty acids with conjugate bonds in many of these common oils, a new chapter in fatty acid chemistry will be opened. I am inclined to believe, however, that the data may simply be indications of hitherto unrecognized labile properties of unsaturated acids.

One cannot observe the voluminous literature in this field without realizing that fat chemistry, or more broadly speaking, lipid chemistry, is taking a foremost place as a branch of chemistry. What we need is further development and refinement of our available methods; new methods of study of glyceride mixtures as they occur naturally; new methods of separating fatty acids, especially the unsaturated acids; more study of the chemistry of the unsaturated acids and their isomers. To date relatively few fats and oils have been exhaustively studied by the best modern methods, and those that have been so studied do not include some of those of great commercial and biological importance; human fat, for example, has not been so studied. As such study progresses more and more of our favorite generalizations will undoubtedly fall and, in fact, are falling by the wayside. We will find, no doubt, fatty acids of uneven car-

bon series (as we already have in isolated instances). We will find new isomers of the unsaturated acids. We will find branched chain acids. We may find that it will be necessary to develop new methods of saponification before we examine fatty acids in order to avoid change while they are being investigated. There is an increasing amount of evidence of change during exposure to higher temperatures such as are used in vacuum distillation. Methods of avoiding this procedure are essential to further progress. Certainly it will be interesting to follow progress in the field of lipid chemistry during the years immediately before us.

## BIBLIOGRAPHY

1. A. Bömer. *Z. Unters. Nahr. Genussm.* **14**, 90 (1907).
2. J. Kilmont. *Monatsh.* **23**, 51 (1902); **33**, 441 (1912).
3. K. Amberger and J. Bauch, *Z. Nahr. Genussm.* **26**, 65 (1913); **48**, 371 (1924).
4. A. Bömer and K. Schneider. *Ibid.* **47**, 61 (1924).
5. B. Susuki and Y. Yokoyama. *Proc. Imp. Acad., Tokyo* **3**, 526, 529, 531 (1927).
6. B. Susuki and Y. Matsuda. *Ibid.* **4**, 165 (1928).
7. A. Eibner, L. Widenmeyer, and E. Schild. *Chem. Umschau.* **34**, 312 (1927).
8. G. Collin and T. P. Hilditch. *J. Soc. Chem. Ind.* **47**, 261T (1928).
9. T. P. Hilditch. *Allgem. Ol. Fettzt.* **27**, 93 (1930); *Fett chem. Umschau.* **42**, 105 (1935).
10. T. P. Hilditch. *J. Soc. Chem. Ind.* **54**, 139, 163, 184 (1935).
11. H. P. Kaufmann. *A. Untersuch. Lebensmittl.* **51**, 15 (1936).
12. H. P. Kaufmann and J. Baltes. *Fette U. Seifen* **43**, 93 (1936).
13. E. Twitchell. *J. Ind. Eng. Chem.* **13**, 806 (1921).
14. S. H. Mottram. *Z. Untersuch. Lebensmittl.* **55**, 179 (1928).
15. J. B. Brown and G. G. Stoner. *J. Am. Chem. Soc.* **59**, 3 (1937).
16. J. B. Brown and G. Y. Shinowara. *Ibid.* **59**, 6 (1937).
17. H. J. Channon, J. C. Drummond, and J. Golding. *Analyst.* **49**, 311 (1924).
18. A. W. Bosworth and J. B. Brown. *J. Biol. Chem.* **103**, 115 (1933).
19. T. P. Hilditch. *Biochem. J.* **28**, 779 (1934).
20. S. Lepkovsky, G. V. Peskov and H. M. Evans. *J. Am. Chem. Soc.* **58**, 978 (1936).
21. H. E. Longenecker. *J. Soc. Chem. Ind.* **56**, 199T (1937).
22. R. Schoenheimer and D. Rittenberg. *J. Biol. Chem.* **120**, 158 (1937).
23. R. C. Newton. *Oil and Soap* **14**, 59, 88 (1937).
24. C. A. Browne. *J. Am. Chem. Soc.* **21**, 807 (1899).
25. T. P. Hilditch and J. J. Sleightholme. *Biochem. J.* **24**, 1098 (1930).
26. J. B. Brown and T. S. Sutton. *J. Dairy Sci.* **14**, 125 (1931).
27. A. Grün and T. Wirth. *Ber.* **55**, 2197 (1922).
28. A. W. Bosworth and E. W. Sisson. *J. Biol. Chem.* **107**, 489 (1934).
29. A. W. Bosworth and G. E. Helz. *Ibid.* **112**, 489 (1936).
30. H. C. Eckstein. *Ibid.* **103**, 135 (1933).
31. A. W. Bosworth. *Ibid.* **106**, 225 (1934).
32. R. W. Riemenschneider and N. R. Ellis. *Ibid.* **113**, 219 (1936).
33. N. R. Ellis and H. S. Isbell. *Ibid.* **69**, 239 (1926).
34. N. R. Ellis and J. H. Zeller. *Ibid.* **89**, 185 (1930).
35. N. R. Ellis and C. S. Rothwell and W. O. Pool. *Ibid.* **92**, 385 (1931).
36. R. Bhattacharya and T. P. Hilditch. *Biochem. J.* **25**, 1954 (1931).
37. J. B. Brown and E. M. Deck. *J. Am. Chem. Soc.* **52**, 1135 (1930).
38. E. F. Armstrong and T. P. Hilditch. *J. Soc. Chem. Ind.* **44**, 180T (1925).
39. E. Klenk, F. Ditt and W. Diebold. *Z. Physiol. Chem.* **232**, 54 (1935).
40. E. Klenk. *Ibid.* **209**, 112 (1932); **221**, 259, 264 (1933); **232**, 47 (1935).
41. R. G. Sinclair. *J. Biol. Chem.* **111**, 297, 515 (1935).
42. A. P. West. *Philippine J. Sci.* **32**, 41 (1927); **42**, 251 (1930).
43. D. Holde and R. Gentner. *Ber.* **58**, 1067 (1925).
44. D. M. Biresel. *J. Am. Chem. Soc.* **59**, 689 (1937).
45. G. O. Burr and M. M. Burr. *J. Biol. Chem.* **82**, 345 (1929); **86**, 587 (1930).
46. H. A. Schuette, T. M. Garvin and E. J. Schwoegler. *J. Biol. Chem.* **107**, 635 (1934).
47. T. G. Green and T. P. Hilditch. *J. Soc. Chem. Ind.* **55**, 4T (1936).
48. J. B. Brown. *J. Biol. Chem.* **83**, 777 (1929).
49. J. B. Brown and C. C. Sheldon. *J. Am. Chem. Soc.* **56**, 2149 (1934).
50. E. H. Farmer and E. J. Sunderland. *J. Chem. Soc.* 759 (1935).
51. W. B. Brown and E. H. Farmer. *Biochem. J.* **29**, 631 (1935).
52. W. J. Dann and T. Moore. *Ibid.* **27**, 1166 (1933).
53. T. Moore. *Ibid.* **31**, 138 (1937).
54. H. P. Kaufmann, J. Baltes and H. Butes. *Ber.* **70B**, 903 (1937).
55. A. Banks and T. P. Hilditch. *Biochem. J.* **25**, 1168 (1931).
56. T. P. Hilditch and H. Paul. *Biochem. J.* **30**, 1905 (1936).

## ABSTRACTS

## Oils and Fats

Edited by

M. M. PISKUR and RUTH LINDAHL

**An improved Kreis test.** W. P. Walters, M. M. Muers and E. B. Anderson. *J. Soc. Chem. Ind.* **57**, 53-6 (1938).—An improved Kreis test is described in which the reaction occurs in a single phase, a soln. of trichloroacetic acid in amyl acetate being substituted for conc. HCl. The technic described gives reproducible quantitative results, and is much more sensitive than previous modifications of the Kreis test, especially in the very early stages of oxidation.

**Separation of phosphatides from the sediments in the hydration of vegetable oils.** I. Grabovskii. *Masloboino Zhirovnoe Delo* **13**, No. 5, 13-14 (1937).—In the acid hydration unfiltered oils give up to 5% and filtered oils up to 1% of sediment. The latter contains a max. of 70% oil and 2-8% phosphatides, based on the dry product. The lab. scheme for sepg. P compds.

(90%) consists in 2 alternate extns. with benzene or benzine. In this way, the water is removed with the partly escaping solvent. The latter is removed from the mixt. at 40-60° in vacuo. The mixt. of oil and P compds. is hydrated with HCl or H<sub>2</sub>SO<sub>4</sub> for 2-3 hrs. and then centrifuged. The aq. and oil layers are removed, and the phosphatide layer is dehydrated and defatted by distg. off the H<sub>2</sub>O with benzine, filtering, concg. and pptg. phosphatides with Me<sub>2</sub>CO. (*Chem. Abs.*)

**Isolation and properties of gorlic acid, and optically active liquid fatty acids.** H. I. Cose and H. T. Cardoso. *J. Amer. Chem. Soc.* **60**, 612-14 (1938).—A liquid fatty acid possessing a high optical activity has been isolated from 2 chaulmoogra oils, *Carpotroche brasiliensis* and *Oncoba echinata*.