insolubility of the ethyl ester of 12-hydroxystearic acid in hydrocarbon solvents, one may obtain the pure material from which by de-hydroxylation via its halogeno derivative and recrystallization of the product from acetone there results exceptionally pure stearic acid. Yields of at least 40%, based on the weight of the castor oil used, are possible.

How the several steps outlined above were accomplished is described in the following paragraphs.

Experimental Procedure

12-Hydroxystearic Acid. A filtered, one-liter ethanol solution of castor oil (58 g.) completely saturated by catalytic hydrogenation over Raney nickel at 150° for 30 minutes was heated under a reflux for eight hours with sulfuric acid (20 g.). The solution was cooled and the ester removed by filtration. More ester was obtained from the filtrate upon the addition of 100 cc. of water. The combined ester crops were recrystallized from 300 cc. of petroleum ether (b.p. 60-69°) whereupon 45.8 g. of ethyl-12-hydroxystearate were obtained.

The hydroxy ester was saponified and the liberated acid recrystallized, first from benzene and then from petroleum ether. A marked tendency to form gels in solution made further purification desirable. The brownish solid (39 g.), comminuted in a mortar, was then washed with cold petroleum ether, a loss of only 0.1 g. per 12-gram portion resulting. A considerable improvement in color was noted. The 12-hydroxystearic acid thus purified had a melting point of 80.5-80.9°.

12-Iodostearic Acid. 12-hydroxystearic acid (11.9 g.), red phosphorus (.45 g.) and iodine (5.9 g.) were heated at 100 to 125° for three hours with vigorous stirring. The mixture was transferred to a separatory funnel with 300 cc. of warm petroleum ether, washed with water and 5% sodium sulfite solution, dried with calcium chloride and filtered. The solvent was removed by distillation.

Stearic Acid. The 12-iodostearic acid was not isolated but was converted to stearic acid by refluxing it with 250 cc. of glacial acetic acid with the addition of one-gram portions of zinc dust at half-hour intervals until four grams had been added. Unreacted zinc was filtered off after which the filtrate was diluted to four times its volume with water. After the solution had been cooled to room temperature, the precipitated white stearic acid (10.8 g. after being dried) was dissolved in 300 cc. of acetone, treated with charcoal, filtered, and crystallized. Eight grams of stearic acid having a solidification point (2) of 69.06° were obtained. Recrystallization of the product from 200 cc. of acetone resulted in a yield of 7.3 grams with a solidification point of 69.33°. Based on the weight of castor oil used, this represents a yield of approximately 40 per cent.

Summary

By de-hydroxylating the 12-hydroxystearic acid, which may be prepared in a pure state by the alcoholysis of fully hydrogenated castor oil, there may be obtained in at least 40% yield an exceptionally pure stearic acid whose solidification point is the same as that of a similar product previously reported by others (1). Avoided by the procedure described are recourse to the necessity of preparing lead soaps for the removal of unsaturated fatty acids and the drudgery of repeated crystallizations as prescribed by other published methods.

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Dilatometric Investigations of Fats

IV. Estimation of Solids and Liquid in Some Plastic Fats

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A PREVIOUS publication (3) from this laboratory has reported the results of a calorimetric estimation of solids and liquid in a plastic sample of hydrogenated cottonseed oil. As pointed out by Hofgaard (6), estimates of solids and liquid may be made equally well from dilatometric data since considerable changes in volume accompany melting or solidification of a fat. During the present investigation dilatometric estimates of the proportions of solids and liquid at different temperatures were made upon the sample of hydrogenated cottonseed oil previously examined in the calorimeter and also upon three additional plastic fats. These are believed to be the first reasonably reliable data of their kind. The previous data of Hofgaard (6) are rendered inaccurate by failure to work at temperatures low enough to attain complete solidification of the samples and by an assumption regarding the applicability of Tammann's rule to fatty materials which has been shown to be unjustified (4).

The Fat Samples

Each of the fats examined was a heterogeneous material which contained both solids and liquid over a wide range of temperature. The cottonseed oil was partially hydrogenated and was from the batch previously analyzed calorimetrically for solids and liquids at different temperatures. At ordinary room temperature it was slightly firmer in consistency than most commercial shortenings or margarine oils. The prime steam lard was a commercial sample, with no hardened

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lard added. The oleo oil was a commercial prime oil, which had a somewhat higher melting point than is usual in this product (42°-43°C.). An all-hydrogenated vegetable oil shortening (Crisco) was used as an example of this type of plastic fat.

The samples of fats were characterized by iodine values (included in Table 3) and by micropenetrations, according to the method of Feuge and Bailey (5).

Experimental

General information on the dilatometric method is contained in previous papers (2, 4, 7) of this series.

Each of the samples was quickly solidified in the form of a film on the interior of the dilatometer bulb. The dilatometers, of the gravimetric type, were then assembled and filled with mercury. The samples of fat in the filled dilatometers were tempered for 24 hours at approximately 29.0°C. and were then slowly cooled over a period of 1 hour to —60°C., to insure their complete solidification. After one hour at this temperature they were placed in a stirred, accurately controlled, low-temperature bath (4) at —38.65°C. The temperature was raised by increments of about 2°C., with time allowed at each temperature for the samples to reach equilibrium.

When the bath reached room temperature, the dilatometers were transferred to a thermostatically controlled oil bath (4) and the measurements continued until all samples had completely melted. In the case of one sample of the hydrogenated cottonseed oil the tempering operation described above was omitted.

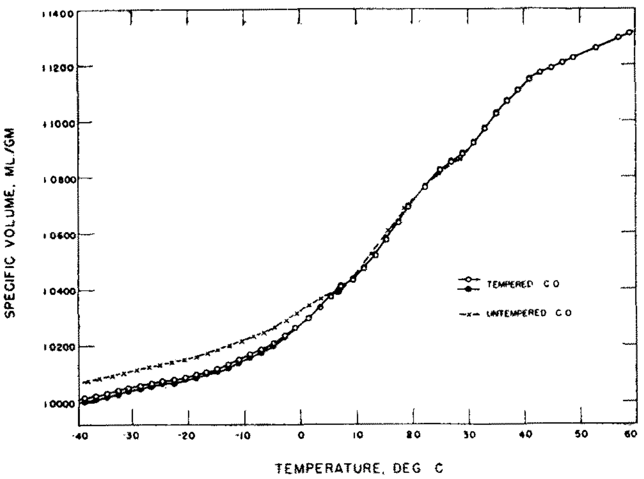

FIG. 1. Specific Volume *VS* Temperature of Hydrogenated Cottonseed Oil.

Specific volumes of the samples were calculated at each temperature from the dilatometric data and from density data on the liquid fats obtained with pycnometers. The method employed in making these calculations has been described in detail in a previous communication (4). The calculated specific volumes are tabulated in Table 1.

The dilatometric curves are plotted in Figures 1 and 2.

In the case of the tempered hydrogenated cottonseed oil measurements were made in duplicate and

TABLE 1

Specific Volumes in ml./g. of Plastic Fats at Different Temperatures

Tempered Samples						Untempered Sample	
Temp. °C.	Prime Steam Lard	Prime Oleo Oil	Crisco	Hydrogenated Cottonseed Oil		Temp. °C.	Hydrogenated Cottonseed Oil
				Run 2	Run 1		
—38.65	.9950	.9992	1.0025	1.0015	1.0000	—37.95	1.0075
—36.6	.9959	1.0000	1.0034	1.0021	1.0008	—36.0	1.0084
—34.6	.9971	1.0010	1.0044	1.0031	1.0017	—33.75	1.0091
—32.6	.9981	1.0020	1.0053	1.0041	1.0026	—31.6	1.0101
—30.7	.9994	1.0030	1.0065	1.0049	1.0037	—29.25	1.0113
—28.6	1.0005	1.0039	1.0074	1.0058	1.0045	—27.0	1.0123
—26.6	1.0017	1.0048	1.0084	1.0066	1.0054	—25.0	1.0132
—24.65	1.0031	1.0058	1.0096	1.0074	1.0064	—22.9	1.0142
—22.55	1.0041	1.0060	1.0097	1.0079	1.0065	—20.8	1.0149
—20.6	1.0057	1.0070	1.0109	1.0087	1.0078	—18.7	1.0160
—18.65	1.0077	1.0081	1.0125	1.0097	1.0086	—16.65	1.0173
—16.8	1.0094	1.0092	1.0144	1.0107	1.0098	—14.7	1.0187
—14.9	1.0115	1.0104	1.0169	1.0119	1.0108	—12.6	1.0202
—12.9	1.0140	1.0116	1.0196	1.0134	1.0121	—10.5	1.0217
—10.95	1.0169	1.0129	1.0226	1.0152	1.0139	— 8.45	1.0231
— 9.05	1.0200	1.0142	1.0255	1.0171	1.0158	— 6.45	1.0245
— 7.0	1.0209	1.0147	1.0282	1.0187	1.0175	— 4.55	1.0263
— 4.8	1.0237	1.0170	1.0311	1.0208	1.0198	— 2.55	1.0284
— 2.75	1.0277	1.0199	1.0346	1.0235	1.0228	— 0.7	1.0311
— 0.9	1.0319	1.0224	1.0382	1.0263	1.0260	+ 1.8	1.0337
+ 1.45	1.0365	1.0246	1.0418	1.0293	1.0295	3.7	1.0363
3.54	1.0439	1.0283	1.0461	1.0335	1.0341	6.75	1.0388
5.5	1.0532	1.0316	1.0497	1.0373	1.0375	9.7	1.0440
7.24	1.0576	1.0363	1.0531	1.0409	1.0410	12.65	1.0518
9.4	1.0599	1.0385	1.0558	1.0433	1.0437	15.7	1.0605
11.3	1.0625	1.0444	1.0595	1.0473	1.0476	18.7	1.0685
13.4	1.0656	1.0515	1.0638	1.0521	1.0525	21.8	1.0754
15.4	1.0686	1.0581	1.0680	1.0576	1.0580	24.8	1.0810
17.5	1.0720	1.0656	1.0722	1.0638	1.0640	28.5	1.0861
19.35	1.0752	1.0714	1.0757	1.0693	1.0697	31.5	1.0936
22.3	1.0796	1.0790	1.0800	1.0763	1.0765	34.5	1.1014
25.0	1.0845	1.0866	1.0835	1.0821	1.0824	37.5	1.1085
27.0	1.0890	1.0892	1.0856	1.0853	1.0855	40.5	1.1144
29.0	1.0949	1.0917	1.0877	1.0883	1.0885	41.5	1.1158
31.0	1.1001	1.0950	1.0901	1.0921	1.0924	44.0	1.1181
33.0	1.1025	1.0995	1.0933	1.0972	1.0976	46.0	1.1199
35.0	1.1050	1.1039	1.0966	1.1026	1.1029	48.0	1.1216
37.0	1.1071	1.1080	1.0999	1.1072	1.1075	50.0	1.1234
39.0	1.1094	1.1119	1.1031	1.1112	1.1114	52.0	1.1251
41.0	1.1118	1.1157	1.1057	1.1147	1.1150	57.0	1.1295
43.0	1.1144	1.1186	1.1085	1.1172	1.1173		
45.0	1.1169	1.1204	1.1116	1.1190	1.1193		
47.0	1.1186	1.1222	1.1149	1.1208	1.1208		
49.0	1.1204	1.1239	1.1179	1.1225	1.1226		
53.0	1.1238	1.1274	1.1215	1.1260	1.1259		
57.0	1.1273	1.1308	1.1251	1.1296	1.1296		
59.0	1.1290	1.1324	1.1267	1.1311	1.1314		

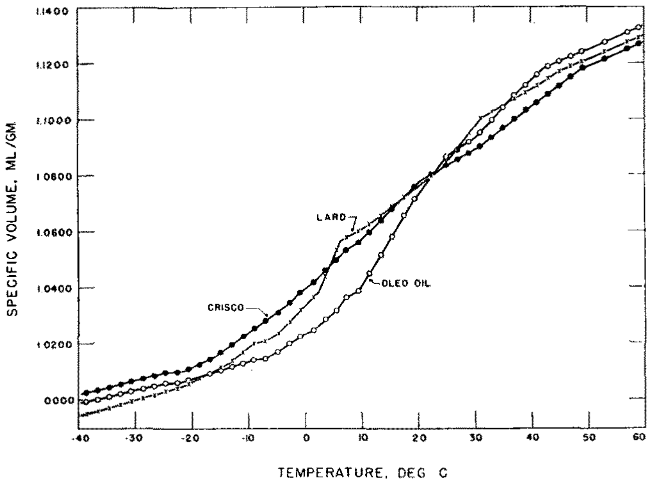

Fig. 2. Specific Volume *VS* Temperature of Three Plastic Fats.

yielded closely agreeing values for percentages of solids and liquid. Single dilatometric determinations were made in the case of the other fats.

Method of Calculating the Content of Solids and Liquid

The theoretical basis for dilatometric calculations of solids and liquid in a plastic fat has been outlined by Hofgaard (6). It may be best illustrated graphically, as in Figure 3.

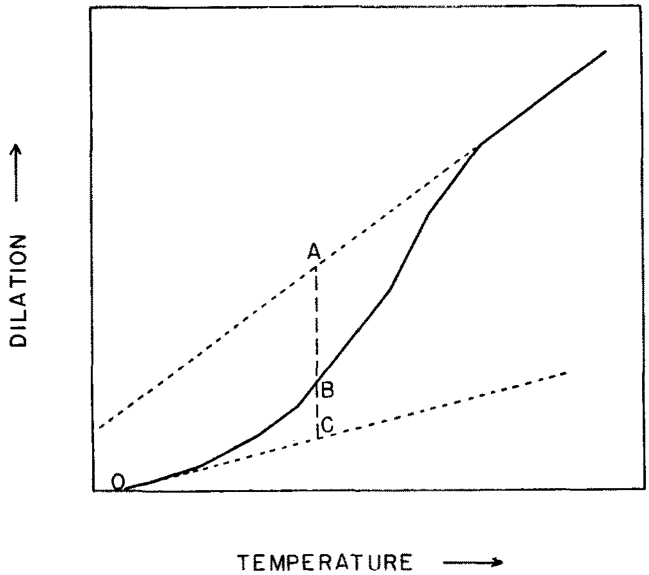

Fig. 3. Illustration of Method for Calculating Percentages of Solids and Liquid in a Plastic Fat.

This figure represents the dilation, or volume-temperature, curve of a typical plastic fat. *B* is the point on the curve which corresponds to the temperature, *t*. *A* and *C* are the points at which a vertical line through *B* intersects prolongations of the liquid- and solid-lines, respectively. The fraction of solids in the sample at the temperature *t* is equal to *AB/AC*; the fraction of liquid is equal to *BC/AC*.

For this calculation to be valid the sample must, of course, be completely solidified at the lowest temperature of the dilatometric run. Previous calorimetric examination (3) of the hydrogenated cottonseed oil revealed that this material is completely solid below —38°C. It was evident from preliminary dilatometric results (4) on this oil and on the lard that fats of the consistency of those examined can contain no considerable content of liquid oil at this low temperature.

The chief uncertainty in the calculation of content of solids and liquid lies in the choice of a slope for projection of the line representing thermal expansion in the solid state (*OC* of Figure 3). The dilatometric method is limited to temperatures above the freezing point of mercury (—38.87°C.) hence the expansibility of the sample in the solid form could not be determined directly. However, from previous dilatometric data on a variety of fats (4) it seems certain that the expansibility of the solid plastic fats must be somewhat less than the dilation observed for the hydrogenated cottonseed oil immediately above —38°C. (0.00038 to 0.00045 ml./g./°C.) and more than the thermal expansibility of tristearin (0.00023 ml./g./°C.). For the calculations reported here a

TABLE 2

Calculated Percentage of Solids in Hydrogenated Cottonseed Oil Using Different Values for Thermal Expansibility of the Solid Material

Temp. °C.	Thermal Expansibility of Solids, ml./g./°C.		
	0.00025	0.00030	0.00035
	percent	*percent*	*percent*
45	......	......	......
40	1.9	2.0	2.1
35	8.1	8.4	8.8
30	17.9	18.6	19.4
25	22.4	23.3	24.2
20	31.3	32.4	33.6
15	45.2	46.8	48.5
10	57.1	58.9	60.9
5	64.6	66.6	68.6
0	74.3	76.5	78.7
— 5	83.5	85.7	87.9
—10	88.1	90.2	92.3
—15	92.1	93.9	95.7
—20	94.4	96.0	97.7
—25	94.8	96.1	97.4
—30	96.7	97.4	98.2
—35	98.7	99.2	99.6

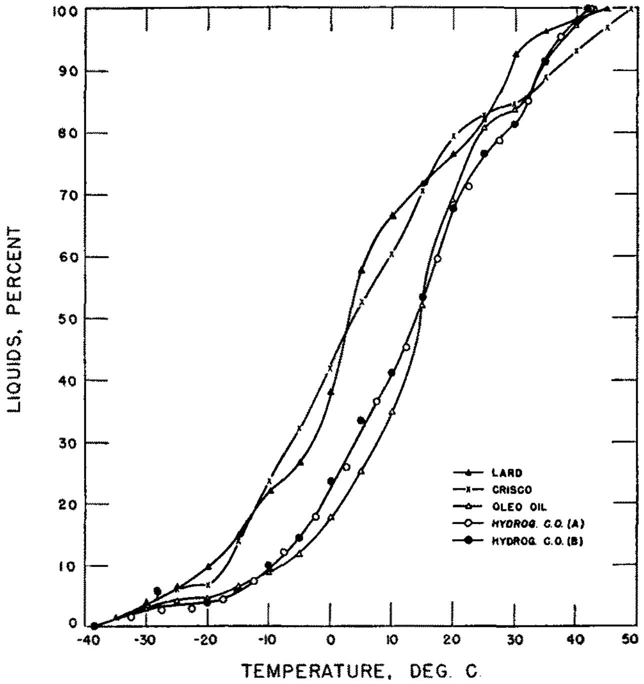

Fig. 4. Percentage of Liquid in the Fat Samples Over the Melting Ranges. Hydrogenated Cottonseed Oil (A) and (B) Are Duplicate Samples.

TABLE 3

Percentage of Solids and Micropenetrations of the Samples at Various Temperatures

Temp.	Lard		Hydrog. Cottonseed Oil		Crisco		Oleo Oil	
	Solids	Micropens.	Solids [1]	Micropens.	Solids	Micropens.	Solids	Micropens.
°C.	*percent*		*percent*		*percent*		*percent*	
10	33.6	41	59.8	15	39.8	16	65.2	13
15	28.4	73	47.0	19	29.6	24	47.8	15
20	23.2	105	33.1	28	20.6	45	31.0	29
25	17.7	137	23.7	63	17.2	101	19.3	78
30	7.2	378	19.0	154	15.4	212	16.3	197
35	3.6	......	8.9	380	10.9	336	8.6	386
40	1.7	......	2.0	......	6.8	......	2.4	......
Iodine Value..........	66.6		59.5		74.1		44.8	

[1] Average value of the two check samples.

value of 0.00030 ml./g./°C. has been assumed. An accurate value is essential for calculation of the percentage of liquid fat in the samples at the lower temperatures, but no large errors are introduced in the calculations of percent solids by errors in the solid expansibility value as great as 0.00005 ml./g./°C. As an indication of the possible errors occasioned by assumption of an erroneous value for expansibility of the solid fat Table 2 has been compiled. This table gives comparative calculations of percent solids in a typical plastic fat based upon solid expansibilities of 0.00025, 0.00030, and 0.00035 ml./g./°C., respectively.

Percentagese of Solids and Liquid in the Samples

The liquid content of each fat at temperature intervals of 5°C. is shown in Figure 4.

Both series of determinations made on the tempered, hydrogenated cottonseed oil sample are plotted in Figure 4 to show the close agreement obtained. In all of the samples rapid melting began at about —20°C.

The present dilatometric data on the proportions of solids and liquid in the hydrogenated cottonseed oil are compared in Figure 5 with data obtained previously (3) on the same oil by calorimetric means. The curves obtained by the two methods are in general agreement although over most of the diagram the calorimetric curve indicates a higher percentage of solids than does the dilatometric curve at any given temperature. This difference between the two is obviously the result of a condition of non-equilibrium in the sample examined calorimetrically. That equilibrium between solids and liquid was not attained in the calorimetric run is very apparent from the behavior of the sample toward the end of the run. In the calorimeter all crystals did not disappear from the fat until a temperature of 45.4°C. was reached. When melting was allowed to occur in a more leisurely manner in the dilatometer, the sample was completely melted at 41.4°C. The dilatometric data may accordingly be considered to represent more nearly the composition of the fat under ordinary storage conditions.

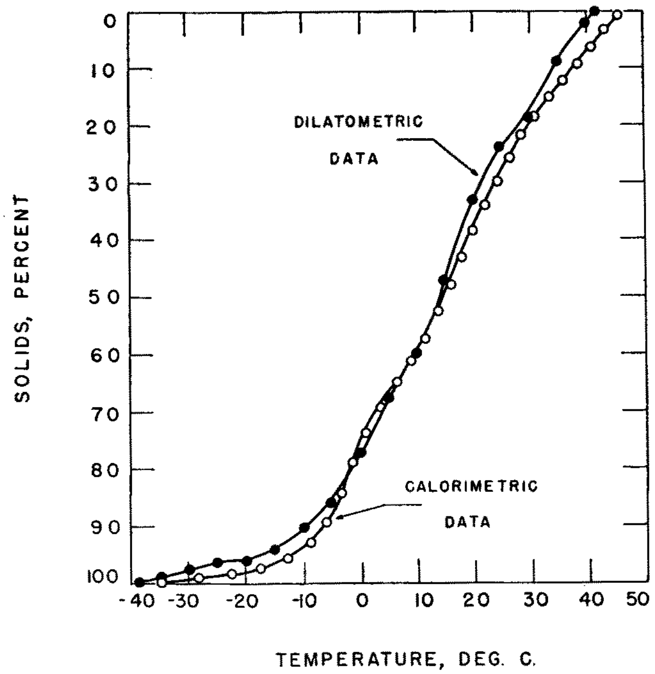

FIG. 5. Comparison of Calorimetric and Dilatometric Methods in Calculating the Percent Solids in Hydrogenated Cottonseed Oil.

In estimating the solids-liquid composition of a plastic fat dilatometrically, it is necessary to assume that all portions of the solids dilate equally upon melting, just as it is necessary to assume that all portions have a common heat of fusion in order to make this estimation calorimetrically. The dilatometric results cannot be expected to reveal any possible error in the calorimetric results due to actual differences in heats of fusion of low- and high-melting crystals. There appears to be a direct relationship between heat of fusion and melting dilation in triglycerides (4) hence a systematic error in the calorimetric estimates would be repeated in estimates made from the dilatometric results.

Relationship Between the Percentage of Solids and Micropenetration

The relationship between the percentage of solids and micropenetration in the samples at different temperatures is shown in Table 3 and Figure 6.

It is evident that the consistency of a plastic fat is not determined by its content of solids alone but must be influenced by other factors, including possibly the shape, rigidity, size, and size distribution of the crystal particles and the degree to which the particles tend to flocculate or become dispersed. The relative ineffectiveness of lard crystals in stiffening the fat has been noted previously (1) and attributed to the large size of the crystals.

Since different fats are stiffened to different degrees by the presence of a given amount of solids, the use of experimental data obtained on one fat to estimate the solids-liquid composition of others is not justified. Estimates (3) made previously of percentages of solids in certain commercial fats cannot, therefore, be relied upon. However, the present results fully confirm previous conclusions relative to the limited range of solids content within which fats are plastic and

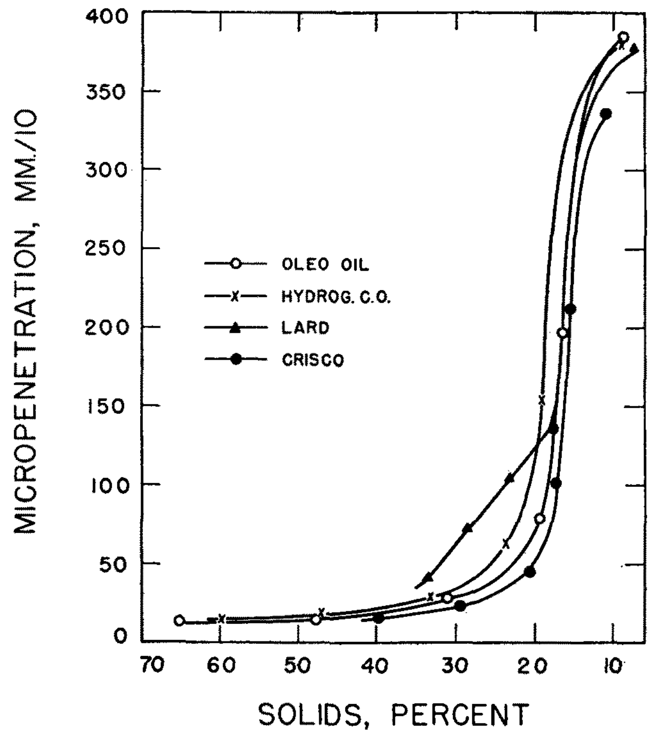

FIG. 6. Micropenetrations *VS* Solid Content in the Fat Samples, at Corresponding Temperatures.

workable and the large effect on consistency of small variations in the proportion of solids present.

Summary

1. Dilatometric curves have been determined over the complete melting range for samples of prime steam lard, oleo oil, all-hydrogenated vegetable shortening, and partially hydrogenated cottonseed oil. From the dilatometric data estimates have been made of the percentages of solids and liquid in the fats at different temperatures.

2. Estimates of the percentages of solids and liquid in the hydrogenated cottonseed oil agreed with those previously reported on the same oil from calorimetric data when allowance was made for a lack of equilibrium conditions in the calorimetric experiment. Since a condition of equilibrium between solids and liquid is attained in the dilatometer, this instrument is to be preferred to the calorimeter for determining the composition of fats in terms of the two phases.

3. The consistency of the fats, as measured by micropenetrations, was different for different fats which contained equal percentages of solids. The consistency, therefore, is not determined solely by the amount of solids present, but also by the character of the solid particles.

Acknowledgment

The authors wish to acknowledge the kind assistance of Frank C. Magne, who determined the densities of the various fats in the liquid state.

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Hydrogenation and Spectral Absorption Studies on Methyl Linoleate, Methyl Linolenate, and Soybean Oil[1, 2]

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IN A recent publication on flavor reversion in hydrogenated linseed oil Lemon (1) used the spectral absorption method of Mitchell, Kraybill, and Zscheile (2) for the study of the selectivity of catalytic hydrogenation. The results of the investigation indicated that the spectrophotometric method could not be used for the determination of unsaturated fatty acids in hydrogenated fats and oils because in the process of hydrogenation diene acids were produced which failed to conjugate upon alkali isomerization. He therefore postulated that an iso-linoleic acid (9,15-linoleic acid) was presumed to be produced by preferential hydrogenation of 9,12,15-linolenic acid. Lemon (1) has indicated further that the odors and flavors developed by heating fractions containing the iso-linoleic acid were similar to those odors and flavors developed in reverted hydrogenated linseed oil. However, the contribution of any iso-acid produced during the hydrogenation of soybean and linseed oil to flavor and odor reversion still remains to be determined. If it is found that iso-linoleic acids are directly or indirectly responsible for flavor and odor reversion of hydrogenated soybean and linseed oil, other iso-acids, in importance, may be equal to or greater than the 9,15-linoleic acid postulated by Lemon.

The possible spreading of double bonds in linoleic acid upon catalytic hydrogenation was not considered in the study of the hydrogenation of linseed oil. The production of 9,15- or 9,13-linoleic acid are two likely possibilities as a result of the shift of double bonds in normal linoleic acid.

It would seem that studies of the partial hydrogenation of methyl linoleate should yield some spectrophotometric evidence of these or other isolinoleic acids. The purpose therefore of this preliminary communication is to summarize the results obtained upon the

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[2] The generous financial assistance of the National Association of Margarine Manufacturers is gratefully acknowledged.