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

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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

partial catalytic hydrogenation of highly purified methyl linoleate, methyl linolenate, mixtures of methyl stearate and methyl linoleate, and soybean oil, and to emphasize further the complicating factors involved in the selective hydrogenation of fats and oils.

Experimental

All hydrogenations were carried out at room temperature and atmospheric pressure using a modification of the apparatus described by Noller and Barusch (3). Palladium black supported on barium sulfate (4) was used as the catalyst in all experiments. Ethyl acetate purified by treatment with potassium carbonate and distillation was used as the solvent for the hydrogenation of soybean oil. The hydrogenations of all esters and mixtures of esters were carried out in 95% ethyl alcohol, purified by distillation over zinc and sodium hydroxide. The quantity of catalyst added to the reaction flask was 0.100 g. per sample weight (0.250 to 0.500 g.) of ester or oil. The size of sample was selected so that adequate quantities of partially hydrogenated material could be recovered to permit duplicate analyses of iodine values and spectrophotometric examinations.

Methyl stearate was prepared from a stearic acid purified by fractional distillation and crystallization. The methyl linoleate was prepared from linoleic acid obtained by debromination in ether of tetrabromostearic acid (m.p. 115° C.) (5). The methyl linolenate was prepared from linolenic acid obtained by debromination in ether of hexabromostearic acid (m.p. 185° C.) (6). The constants for the distilled esters are given in Table I.

TABLE I

Constants for Distilled Esters

| Methyl Ester | Iodine Values | | | E $\frac{1\%}{1 \text{ cm.}}$ (Alkali Isomerized) | |
	Wijs	Calc. from H₂ Absorption	Theory	234 mμ	270 mμ
Stearic...............	0.0	0.0	0.0	......	......
Linoleic...............	171.7	172.7	172.4	829	......
Linolenic...............	259.0	260.0	260.4	516	443

Two commercially hydrogenated soybean oils of iodine value 80 and 100, respectively, were fractionated using a lead salt separation of the fatty acids and low temperature fractional crystallization of the glycerides. The lead salt separation was carried out by a modification of the Twitchell procedure (7). Fractions of the fatty acids so obtained were subjected to bromination-debromination procedures.

Low temperature solvent crystallization methods were applied to the partially hydrogenated methyl linoleate.

Iodine values were determined using Wijs reagent for a 30-minute reaction time. The spectrophotometric analyses on the alkali isomerized acids or esters were

carried out according to the modification by Baldwin and Longenecker (8) of the method of Mitchell, et al. (2).

Results and Discussion

In view of the results obtained by Lemon (1) that indicated a decrease in saturated acids during the hydrogenation of linseed oil it was considered worthwhile to investigate the partial hydrogenation of known mixtures of purified methyl stearate and methyl linoleate. The results of these hydrogenation studies are summarized in Tables II and III. From

TABLE III

Data for Partially Hydrogenated Ester Mixtures

| Mixture * | Iodine Value Wijs | Iodine Value Calc.** | Composition Calculated from I. V. and Spectral Data | | |
			Methyl Linoleate	Methyl Oleate	Methyl Stearate
			%	%	%
1	64.8	62.7	22.7	30.0	47.3
	47.8	45.7	3.9	48.0	48.1
2	96.4	94.6	35.9	40.3	23.8
	80.0	76.0	14.5	64.3	21.2
	50.9	65.8	2.7	54.0	43.3
3	105.7	102.3	42.8	37.3	19.9
	92.7	88.5	27.0	54.0	19.0
	87.8	87.9	25.8	50.2	24.0

* Mixtures 1, 2, and 3 of Table II.
** Calculated upon Constant Methyl Stearate Content and all Linoleate Yielding Oleate.

the data in Table III the percentage of methyl stearate appears to decrease during hydrogenation. This erroneous conclusion would arise if a double bond acid were formed during the catalytic hydrogenation of methyl linoleate which did not conjugate upon alkali isomerization. The unsaturated acid may be similar to that reported by Lemon (1) to be formed during the catalytic hydrogenation of methyl linolenate or the linolenic acid found in linseed oil glycerides. This effect is also reflected in the iodine value calculated upon the assumption that the methyl stearate content of the mixture remained constant during the hydrogenation while the loss of spectroscopically active methyl linoleate could be accounted for by formed methyl oleate. When the hydrogenation was carried too far, the effect of the presence of the iso-acid was not easily discernible.

Partial catalytic hydrogenation of purified methyl linoleate should indicate the same effect as was observed in the case of the methyl stearate-linoleate mixture. If a compound were produced during the hydrogenation that had unsaturation greater than methyl oleate and was spectroscopically inactive, the total unsaturation as accounted for by methyl linoleate and oleate should total more than 100%. The data supporting this hypothesis are given in Table IV. These data serve to emphasize the production of an iso-linoleic acid upon the catalytic hydrogenation of methyl linoleate. In an effort to concentrate this iso-acid, low temperature crystallization of the par-

TABLE II

Composition of Methyl Stearate-Linoleate Mixtures Prior to Hydrogenation

| Mixture | Composition | | | | Iodine Values | | |
| | By Weight | | Calc. from Spectral Data | | | | |
	Methyl Stearate	Methyl Linoleate	Methyl Stearate	Methyl Linoleate	Wijs	Calc. from Spectral Data	Calc. from Weight Composition
	%	%	%	%			
1	49.7	50.3	49.7	50.3	85.7	86.7	86.7
2	25.6	74.4	25.9	74.1	127.3	127.7	128.3
3	23.7	76.3	23.9	76.1	131.0	131.2	131.5

TABLE IV
Partially Hydrogenated Methyl Linoleate

Sample	Source	Iodine Value	Methyl Linoleate	Methyl Oleate	Total Unsaturated Acids
			%	%	%
1	Original ester	138.7	54.9	51.5	106.4
2	Original ester	109.0	21.2	84.8	105.9
3	Original ester	89.4	2.5	99.4	101.9
4	Original ester	146.0	65.8	38.3	104.1
4	Soluble —60° C.	157.7	72.9	38.1	111.0
4	Insol. —60° C.	139.5	63.7	35.5	99.2

tially hydrogenated ester (sample 4) was carried out at —60° C. in methanol. The data in Table IV seem to indicate a concentration of the acid in the fraction soluble at —60° C.

Partial hydrogenation of methyl linolenate has been implied by Lemon (1) to take place preferentially at the 12, 13 position under the conditions of catalytic hydrogenation encountered in commercial practice. To determine whether room temperature, atmospheric pressure, and palladium black catalytic hydrogenation of methyl linolenate produced the same type of spectral absorption phenomena that he observed, samples of purified methyl linolenate were subjected to partial hydrogenation. The results of these experiments are summarized in Table V. It is evident from

TABLE V
Partial Hydrogenation of Methyl Linolenate

Sample	Approximate Extent of Hydrogenation	Iodine Value	Methyl Linolenate	Methyl Linoleate	Methyl Oleate	Total Unsaturated Acids
1	½ Δ	212.6	67.6	7.0	29.2	103.8
2	1 Δ	179.0	42.4	7.6	65.4	115.4
3	1½ Δ	128.0	6.7	5.6	118	130.3
4	1½ Δ	127.0	3.5	5.8	125	134.3

these data that an iso-acid non-conjugated by alkali is formed during the hydrogenation of methyl linolenate. Examination of the spectral curve for sample 4 dissolved in purified iso-octane indicated that no conjugation had been induced in the methyl linolenate as a direct result of the catalytic hydrogenation.

From the results obtained on purified methyl esters it seemed likely that soybean oil partially hydrogenated under the conditions used in the ester study would yield similar data. Since it has been demonstrated that methyl linoleate and methyl linolenate may produce an acid that resists conjugation by alkali, it is difficult to establish the precursor of this acid in hydrogenated soybean oil or linseed oil. Evidence for the formation of an iso-acid in partially hydrogenated soybean oils may be observed in Table VI. That these laboratory hydrogenations produce

TABLE VI
Hydrogenation of Soybean Oil

Sample	Method Hydrogenation	Iodine Value	Methyl Linolenate	Methyl Linoleate	Methyl Oleate	Per Cent Saturated
1	Original oil	134.7	9.5	61.3	5.0	24.2
2	Pd on BaSO₄	104.9	4.0	31.7	46.5	17.8
3	Pd on BaSO₄	90.1	1.6	17.3	65.5	15.6
4	Pd on BaSO₄	84.4	1.3	16.1	62.1	20.5
5	Commercial	100.1	1.9	24.4	62.0	11.7
6	Commercial	78.9	....	5.0	82.1	12.9

an effect comparable to those obtained in commercial hydrogenations may also be observed when the data for commercially hydrogenated samples are compared with the data obtained upon palladium black hydrogenated soybean oil. This evidence emphasizes the difficulties of selecting a catalyst and conditions of hydrogenation to minimize the production of iso-linoleic acids.

In an effort to effect concentration of the iso-acid. fractionations of the commercially hydrogenated soybean oil fatty acids were made using a lead salt separation with subsequent solvent crystallization. Certain of the fractions so isolated and suspected of containing quantities of the iso-acid were subjected to bromination-debromination procedures.

The data in Table VII were obtained on two independent fractions of the same sample of soybean oil partially hydrogenated to an iodine value of 100. Comparison of these data with those in Table VIII seems to indicate that the lead salt separation of the fatty acids is the better method for effecting the concentration of the iso-acid in a particular fraction. Attempts to date to concentrate further the iso-acid for the purpose of its isolation have not been successful.

Summary

Spectroscopic evidence has been obtained to indicate that a double bond acid which resists conjugation on alkali isomerization is produced on the partial hydrogenation of methyl linoleate. This iso-acid is found in methyl linoleate subjected to hydrogenation at room temperature, atmospheric pressure, using a supported palladium black catalyst. The acid may be identical with that which arises from a preferential hydrogenation of 9,12,15-linolenic acid.

Soybean oil hydrogenated under similar conditions contains an iso-diene acid that resists conjugation by alkali. The source of this acid has not been determined.

Lead salt separations of soybean oil fatty acids and low temperature solvent crystallizations of soybean

TABLE VII
Lead Salt Fractionation of Partially Hydrogenated Soybean Oil Acids *

Sample	Fraction	Iodine Value Wijs	Methyl Linolenate	Methyl Linoleate	Methyl Oleate	Total Unsaturated Acids
			%	%	%	%
1	Acids from Liquid Pb Salts.	130.2	2.9	35.1	72.5	110.5
		133.1	3.1	36.2	73.1	112.4
2	Acids of (1) Insoluble Acetone —45° C.	116.6	1.8	25.0	80.0	107.2
		107.9	1.4	18.3	85.0	104.7
3	Acids of (1) Soluble Acetone —45° C.	142.1	3.6	43.8	66.8	114.2
		155.9	5.9	51.0	61.4	118.3
4	Acids from Bromides (3) Soluble in Pet. Ether.	114.5	3.9	25.3	70.9	100.1
		136.1	6.0	34.9	70.4	111.3

* Commercially hydrogenated to an Iodine Value of 100. Corresponds to sample 5 of Table VI.

TABLE VIII

Low Temperature Crystallization of Soybean Oil Glycerides in Acetone

Sample	Fraction	Iodine Value	Methyl Linolenate	Methyl Linoleate	Methyl Oleate	Methyl Stearate	Total Unsaturated Acids
			%	%	%	%	%
1	Original	100.1	1.9	24.4	62.0	11.7	88.3
2	—30° C. insoluble	85.5	1.4	16.8	61.8	20.0	80.0
3	—30° C. soluble	132.6	4.5	39.4	61.9	......	105.8
4	—60° C. insoluble of fraction 3	133.0	4.7	39.4	61.7	......	105.8
5	—60° C. soluble of fraction 3	129.3	8.5	38.0	48.7	......	95.2

oil fatty acids and glycerides resulted in some concentration of the iso-acid. Further work involving bromination and/or oxidation of these concentrates is necessary before the structure of the iso-acid can be established with certainty.

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Fractionation of Tallow Fatty Acids.

Preparation of Purified Oleic Acid and an Inedible Olive Oil Substitute

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THE starting material usually employed in the laboratory preparation of purified oleic acid (oleic acid content, over 95%) is olive oil (1) since it not only contains a high percentage of oleic acid, but, what is probably more important, it also has a high ratio of oleic to linoleic acid (about 10:1). For the industrial preparation of purified oleic acid, however, olive oil is too expensive, and only relatively small quantities are available for non-edible uses. In a recent publication from this laboratory (2) we described a procedure for the preparation of purified oleic acid from red oil (commercial oleic acid) by low-temperature, solvent crystallization. Although red oil is inexpensive and readily available and is rich in oleic acid, its ratio of oleic to linoleic acid is rather low (usually less than 5:1). When such a large proportion of linoleic acid is present, its solubilizing effect causes considerable loss of oleic acid during the low-temperature crystallization. A more satisfactory starting material is one which is not only inexpensive and readily available in large quantities but which also has a high ratio of oleic to linoleic acid (at least 8:1). An examination of the fatty acid composition of various common fats and oils reveals that tallow meets these requirements.

Superficially, it would appear that tallow would be unsatisfactory as a starting material for the preparation of purified oleic acid since it usually contains only 45 to 50% oleic acid and its content of saturated acids is rather high (about 50%). Fortunately, the major proportion of the saturated acids can be

separated from the mixed fatty acids of tallow by crystallization from a suitable solvent under proper temperature conditions. Our experience indicates that this separation can best be accomplished with acetone at 0° to —20° C. The iodine number of the solid acids obtained in this way ranges from 4 to 12. These iodine values result mainly from incomplete removal of occluded mother liquor from the precipitate, but apparently at lower crystallization temperatures some unsaturated material, probably iso-oleic acid, is precipitated. The saturated acids obtained by crystallization at 0° C. usually have an iodine number of about 4 whereas the acids obtained by crystallization at —20° C. usually have an iodine number of about 12. Approximately 90% of the saturated acids in the tallow may be obtained in this fraction; this yield is considerably higher than can be obtained by conventional cold and hot pressing. These acids, obtained as glistening crystalline solids, correspond to "double- or triple-pressed stearic acid."

When crystallization of the saturated acids is conducted at —20° C., the filtrate acids have approximately the same fatty acid composition as an olive oil rich in oleic acid. These acids, which are pale yellow and have iodine numbers which range from 84 to 88, contain approximately 83 to 86% oleic acid, 4 to 7% polyunsaturated acids, and 7 to 11% saturated acids. By reaction with glycerol these acids yield a synthetic triglyceride which resembles olive oil in fatty acid composition. The preparation of a synthetic olive oil in this way offers certain obvious advantages over crystallization processes that involve fractional crystallization of natural triglycerides in which two

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