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Hydrogenation of Methyl Linolenate. I. The Formation of Methyl Isolinoleate on the Hydrogenation of Methyl Linolenate[1]

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"ISOLINOLEIC acid" is the name applied to the octadecadienoic acids formed during the hydrogenation of polyunsaturated acids (1, 2). These acids are non-conjugable on alkali isomerization with ethylene glycol potassium hydroxide solution and are therefore not capable of determination by the spectrophotometric method of Mitchell, Kraybill, and Zschiele (3).

Although the formation of two isomers of isolinoleic acid was first demonstrated by van der Veen (4) in his studies on the hydrogenation of methyl linolenate using a nickel-kieselguhr catalyst, it was Lemon (1, 5), who recognized that the double bonds in isolinoleic acid were separated by more than one methylene group. This acid therefore could not be isomerized and estimated by the spectral method.

The problem of the structure of the non-conjugable isomeric octadecadienoic acids was not completely solved in the investigations to date (1, 4). By definition 15 positionally isomeric isolinoleic acids are possible on the saturation of one double bond of the linolenic (9, 12, 15-octadecatrienoic) acid molecule, assuming a shift by one carbon atom of each of the remaining two unsaturated bonds. The position of the double bonds in these isolinoleic acids is indicated as follows:

9:10 15:16; 8:9, 15:16; 10:11, 15:16;
9:10 14:15; 8:9, 14:15; 10:11; 14:15;
9:10 16:17; 8:9, 16:17; 10:11; 16:17;
9:10 13:14; 8:9, 12:13; 12:13, 16:17;
11:12 15:16; 8:9, 13:14; 11:12, 16:17.

Van der Veen (4) hydrogenated methyl linolenate, using a nickel-kieselguhr catalyst, at 180° C. and demonstrated the formation of 9,15- and 10,14-octadecadienoic acids. He thereby showed that the 12:13- or middle double bond saturated preferentially to the 9:10- and 15:16- double bonds, which underwent a partial shift to the 10:11 and 14:15 positions respectively.

Lemon (1, 5) obtained isolinoleic acid by a partial hydrogenation of linseed oil. The concentration of isolinoleic acid was shown to reach a maximum of 15% at an iodine value of 120. Lemon assumed the formation of only one isomer, the 9,15-octadecadienoic acid, and presumed it to be the cause of flavor reversion in hydrogenated linseed oil.

Daubert and Filer (6) hydrogenated methyl linolenate and soybean oil, using palladium black supported on barium sulphate as the catalyst. These workers demonstrated the presence of an isolinoleic acid in the hydrogenated product. This acid, according to these workers, could arise only by a partial shift of one or both of the double bonds in the 9:10- and 12:13 positions, resulting in a greater degree of separation of the two unsaturated bonds.

Bailey and Fisher (2) hydrogenated linseed and soybean oils under selective and non-selective conditions of hydrogenation, using dry, electrolytically precipitated nickel as the catalyst. From the results of their work the relative reactivities of the various polyunsaturated acids towards hydrogen absorption were approximately represented by the following whole numbers, under selective conditions of hydrogenation: oleic 1, isoleic 1, isolinoleic 3, linoleic 20, and linolenic 40. Under non-selective conditions the reactivities of linoleic and linolenic acids were affected, being as low as 5 for the linoleic acid.

According to Bauer and Ermann (7) the 9:10-double bond of the linolenic acid molecule saturates more readily than the 15:16-double bond, which in its turn saturates more readily than the 12:13-double bond, resulting in the formation of a 12,15-octadecadienoic acid.

In a recent investigation Lemon (8) attempted the concentration of an isolinoleic acid by chromatographic procedures. The methyl esters of hydrogenated linseed oil (iodine value 75-70) were subjected initially to two low temperature crystallizations at —18° and —70° C., using hexane as the solvent. The fraction soluble at —70° C. was adsorbed on silica gel and eluted with hexane and chloroform. The methyl isolinoleate concentrates isolated had iodine values of 172 and 173 (theory 172.5). The linoleic and linolenic acid content of these concentrates on a fatty acid basis were of the order of 1.0 and 0.1% respectively.

The purpose of the present investigation was initially to study the relative reactivities of the various polyunsaturated acids towards hydrogen absorption during the hydrogenation of methyl linolenate. The next part of the investigation was an attempt at the concentration of an isolinoleic acid fraction and the determination of the structure of the fatty acids in this fraction.

Experimental

Hydrogenation of Methyl Linolenate. Calculation of the Fatty Acid Composition. Methyl linolenate was prepared from linolenic acid, obtained by the debromination of hexabromostearic acid (m.p. 184-5° C.). Hexabromostearic acid was obtained by the bromination of the linseed oil-fatty acids, according to the method of Rollet (9). Determination of the

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[1] Contribution No. 798 from the Department of Chemistry, University of Pittsburgh.

TABLE I

Separation of "Solid" and "Liquid" Acids by the Twitchell Lead Salt-Alcohol Method

Sample	Wt. g.	I.V.	Fatty Acid Composition					
			Linolenic	Linoleic	Isolinoleic	Oleic	Stearic	Total
Hydrog. ester	7.05[a]	119.0	0.0	0.6	41.2	48.2	5.2[b]	95.2
"Solid" acids	2.79	94.4	0.0	0.0	17.2	69.7[c]	13.1	100.0
"Liquid" acids	4.21	144.4	0.0	0.9	56.1	43.0[d]	0.0	100.0

[a] Wt. of fatty acids from the ester. [b] Interpolated from the hydrogenation curve for methyl stearate (Figure 1). [c] As isooleic acids. [d] As *n*-oleic acid.

hexabromide was carried out according to the method of Frankel and Brown (10).

All hydrogenations were conducted at room temperature and atmospheric pressure, using a modification of the apparatus described by Noller and Barusch (11). Palladium black, supported on barium sulphate, prepared according to the method of Schmidt (12), was used as the catalyst. Ethyl acetate, purified by treatment with calcium chloride and potassium carbonate and subsequent distillation, was used as the solvent. Hydrogenations were conducted on 10 g. samples of methyl linolenate in 60 ml. of ethyl acetate, using 0.33 g. of the catalyst (5% palladium). Samples were withdrawn at various intervals, indicating progressive stages of hydrogenation.

The samples of hydrogenated ester were analyzed for total unsaturation, using the Wijs iodine absorption (I.V.) method. Methyl linoleate (L) and methyl linolenate (Ln) were determined by a modification of the spectral method as suggested by the Spectroscopy Committee of the American Oil Chemists' Society (13). Methyl stearate (S) was determined for four representative samples, (10 g.) hydrogenated to requisite iodine values. The Bertram's oxidation method was employed for the purpose. The values for the methyl stearate content of other hydrogenated samples were interpolated from a plot of these data (Figure 1).

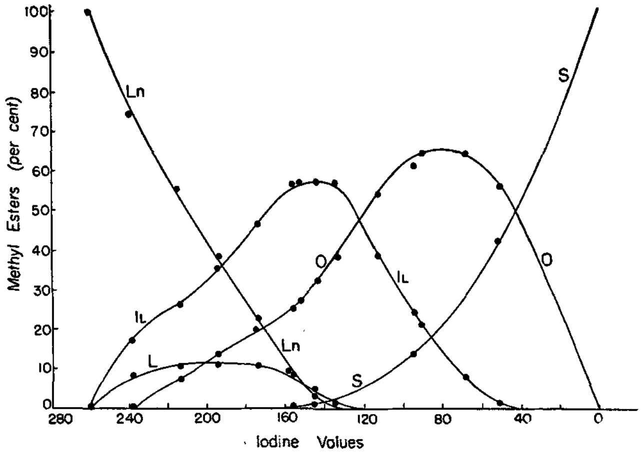

FIG. 1. Composition of methyl esters produced on hydrogenation of methyl linolenate. Ln: Me-linolenate; O: Me-oleate; L: Me-linoleate; S: Me-stearate; Il: Me-isolinoleate.

The amount of methyl isolinoleate (Il) present in the fraction was evaluated by a method of calculation using the equation:

$$\mathrm{Il} = 1.152\ \mathrm{I.V.} - 98.62 - 1.0\mathrm{L} - 2.014\ \mathrm{Ln} + 0.9862\ \mathrm{S}$$

This equation was derived in a similar way to the one employed by Bailey and Fisher (2) in their studies on the hydrogenation of linseed oil.

The amount of methyl oleate and isooleate (O) were evaluated by difference, i.e., 100 minus the aggregate sum of the methyl esters of the remaining unsaturated acids. Results of the hydrogenation are graphically represented in Figure 1.

Isolation of an Isolinoleic Acid. Efficient isolation of an isolinoleic acid was considered practical only from samples hydrogenated to an iodine value between 121 and 124. Methyl linolenate is completely absent in this interval and methyl linoleate is present in a very small concentration (less than 1%) (Figure 1). This range was designated the optimum iodine value range. Hydrogenations were conducted on 10 g. samples of methyl linolenate, hydrogenated to an optimum iodine value. Studies on the concentration of an isolinoleic acid fraction were made on these hydrogenated samples.

An initial Twitchell lead salt-alcohol separation into "solid" and "liquid" acids was performed on a 10 g. sample of hydrogenated ester (I.V. 119.0) having the composition as given in Table I. The "solid" acids were found to contain 17.2% of isolinoleic acid and the "liquid" acids, 56.1% isolinoleic acid.

An attempt at a large scale isolation of an isolinoleic acid fraction (diagramatically represented in Figure 2) is as follows: An initial lead salt-alcohol separation was performed on a 56 g. sample of hydrogenated methyl linolenate, (I.V. 112.8) hydrogenated in six batches of 10 g. each. The method of separation employed was the modified method of Hilditch (14). Another fraction was obtained by cooling the lead soaps of the "liquid" acids to 4° C. The fatty acids of the lead soaps soluble at 4° C. were regenerated (28.3 g. I.V. 149.8) and subjected to a low temperature crystallization.

All the low temperature crystallizations were carried out in a small crystallization bath of 800 ml. capacity. The crystallization bath consisted of a large four-liter beaker insulated by means of rock wool. A wire framework capable of supporting a one-liter beaker was fitted inside the larger 4-liter beaker. The solution of fatty acids or their esters in solvent, to be crystallized, were placed in the one-liter beaker and were cooled from the outside by means of a mixture of dry ice and acetone contained in the larger beaker.

The general procedure employed consisted in the dissolution of the fatty acids in an appropriate solvent (methanol or methyl-ethyl-ketone), such that a concentration of about 6% of fatty acids was obtained. The solution was cooled slowly by additions of small amounts of dry ice to the acetone. Continuous stirring was maintained. The crystallization was allowed to continue for half an hour to one hour after the crystallization temperature was attained. The crystals were filtered off *in situ* using a sintered glass filter stick (1.5 cm. in diameter) covered with a coarse filter paper. Recrystallizations were carried out by the addition of the solvent to the crystals in the beaker and cooling the resultant solution to the desired temperature.

The liquid acids, soluble at 4° C., obtained above, were crystallized at the following temperatures of —40°, —62 to —63°, and —65 to —66° C., using methyl-ethyl-ketone as the solvent (Figure 2). The solids which separated out at each of the above temperatures were refractionated and the filtrate added to the initial filtrate. The fractions obtained at —63° C. (A-5) and —65 to —66° C. (A-7) were refractionated from methanol, (b.p. 64.5° C.) as the solvent (Figure 2). A fraction (A-9, I.V. 161.0) containing 76.6% isolinoleic acid was obtained. Further crystallization of this concentrate did not lead to an appreciable increase in the concentration of isolinoleic acid. The solid and liquid fractions obtained by crystallizatons at —59 to —60° C. were mixed and esterified with methanol. The esters were subjected to a distillation under reduced pressure.

A fraction (A-15, I.V. 161.1) containing 85.4% methyl isolinoleate was obtained by crystallization of the distilled methyl esters from methanol as solvent at —60 to —61° C. The methyl linoleate content of this fraction on an ester basis was of the order of 1.6%; and methyl linolenate was completely absent.

A second attempt at a large scale isolation of an isolinoleic acid differed from the first in that the initial lead salt-alcohol separation was not performed. The procedure adopted (illustrated diagramatically in Figure 3) is as follows:

The hydrogenated ester (95.0 g. I.V. 112.6) was crystallized at temperatures of —22°, —30°, —40°, —50°, —60°, —62°, and —70° C. The solids which separated out at each of the above temperatures were recrystallized three or four times, using a smaller amount of solvent in each successive recrystallization. The filtrates from the recrystallization were pooled with the filtrate from the initial crystallization at the operated temperature of crystallization. Two fractions, rich in methyl isolinoleate, were obtained by a double distillation under reduced pressure of the fractions crystallized at —70°. In both cases the temperature of distillation was between 143 and 148° C. The redistilled product (B-10-1 and B-12-1) had iodine values of 168.6 and 170.1 respectively (Figure 3). The methyl isolinoleate content of the two redistilled fractions were respectively of the order of 94.6

TABLE II

Composition of Methyl Ester-Fractions Obtained by Low Temperature Crystallization of Hydrogenated Methyl Linolenate

Fraction	Wt. g.	I.V.	Fatty Acid Composition as Methyl Esters				
			Lino-leate	Isolin-oleate	Oleate	Stearate	Total
B-1	95.0	122.6	0.7	46.9	47.3	5.1	100.0
B-2	41.0	88.4					
B-2a	32.2	84.4	0.0	8.5	76.5	15.0[a]	100.0
B-3	10.1	99.7	0.2	16.0	83.8	0.0	100.0
B-4	8.0	123.0	0.8	52.3	46.9	0.0	100.0
B-5	11.1	148.0	1.1	70.8	28.1	0.0	100.0
B-6	9.5	139.0	1.2	60.4	38.4	0.0	100.0
B-7	8.5	153.4	1.4	76.7	21.9	0.0	100.0
B-7a	6.2	148.2	1.4	70.8	27.8	0.0	100.0
B-8	16.0	166.3	1.7	91.3	7.0	0.0	100.0
B-10	7.0	165.6					
B-11	3.2	160.3	1.6	84.5	13.9	0.0	100.0
B-12	6.5	169.5					
B-10-1	4.9	168.6	1.6	94.1	4.3	0.0	100.0
B-10-1	5.0	170.0	1.4	95.8	2.8	0.0	100.0

[a] Calculated value assuming all methyl stearate as being in this fraction. Methyl linolenate was absent in all the fraction.

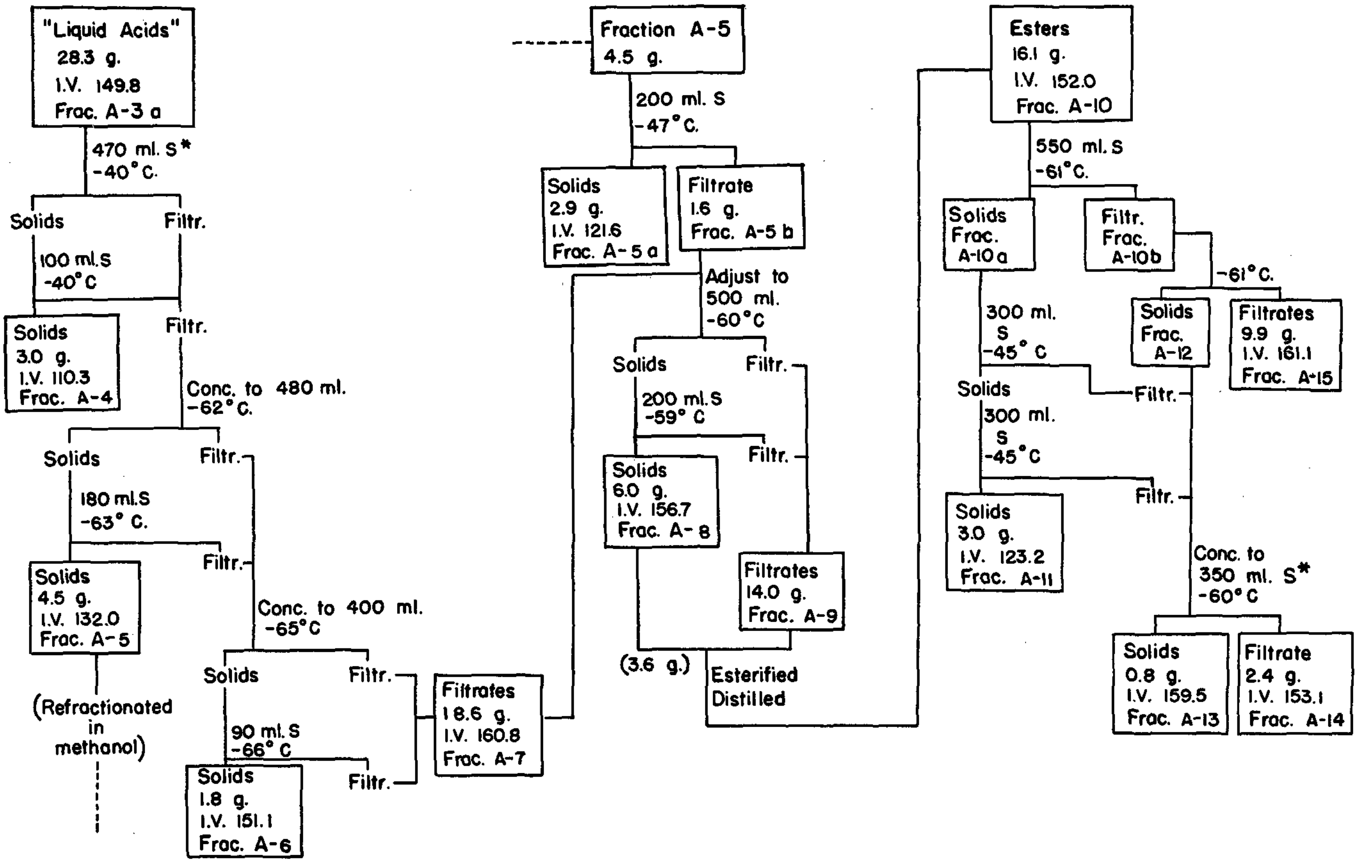

FIG. 2. Diagramatic representation of the crystallization of methyl isolinoleate. S: solvent to A-7, methyl ethyl ketone; S*: solution from A-5, methanol.

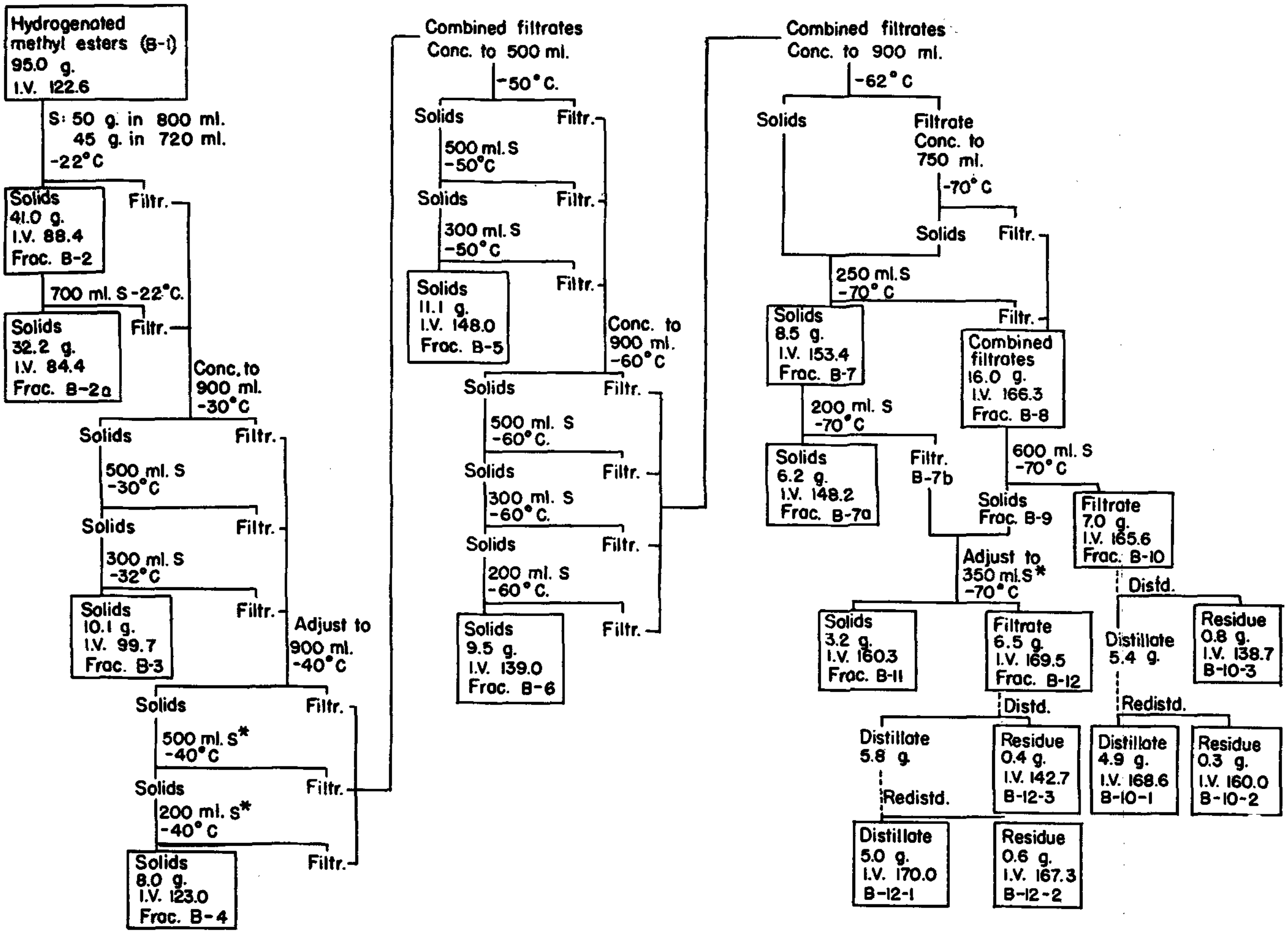

FIG. 3. Diagramatic representation of the crystallization of methyl isolinoleate. S: solvent, methanol; S*: solution, methanol.

and 95.8%. The fatty acid composition of the various fractions, as methyl esters are given in Table II.

Infrared Studies. Infrared spectral transmission curves were obtained for the concentrates of methyl isolinoleate (A-15, 85.4% ester; B-12-1, 95-8% ester) using a Baird Double Beam Spectrophotometer.[2] The absorption peak at 10.3 μ characteristic of a *trans*-configuration for a double bond in a straight chain molecule was obtained in both cases.

Discussion

Isolation of an Isolinoleic Acid. The concentration of a fraction rich in methyl isolinoleate has been carried out by means of low temperature solvent-crystallization procedures, employing temperatures as low as —70° C. (1, 5, 8). Solvent crystallization of methyl esters at low temperatures have been known to give highly pure fractions of linoleic acid (15, 16, 17, 18).

In the present work the low temperature solvent crystallization procedures were found satisfactory in obtaining a concentration of 95.8% methyl isolinoleate. It was not possible to remove the last traces of octadecenoic acids and conjugable dienoic acids by the crystallization procedure. Lemon's (8) work on the concentration of an isolinoleic acid fraction by chromatographic procedures has given more satisfactory results. Chromatographic procedures have been adopted by Reimenschneider and co-workers (19) in the isolation of highly pure linoleic and linolenic acids. These studies therefore indicate that concentration of a fatty acid or its ester by chromatographic procedures gives more satisfactory results than those employing low temperature solvent crystallization methods. In view of the large number of non-conjugable octadecadienoic acids that are possible, it is difficult to ascertain the identity of the various isolinoleic acids which may be present in the methyl isolinoleate-rich fraction without resorting to structure-determination methods. In the present investigation it is conclusively proved that the methyl isolinoleate concentrate isolated is a mixture of isomeric non-conjugable octadecadienoic acids.

Saturated Acids and the Lead Salt-Alcohol Method. The Twitchell lead salt-alcohol method (20) cannot be used for the estimation of saturated acids in a hydrogenated sample, where linolenic acid is a constituent of the original sample. The presence of a "solid isolinoleic" acid in the "solid" fraction, obtained by a lead salt separation of the mixed fatty acids, formed in the hydrogenation of linolenic acid, will offset the calculation of stearic acid content from iodine value data. Hence methods whereby stearic acid is determined directly, as in the case of the Bertram oxidation method (21), are the ones that can be employed with safety for the estimation of this acid.

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The Concept of Affinity Constants. The relative reactivities of the various polyunsaturated acids formed during the hydrogenation of methyl linolenate have been determined according to the method of Bailey and Fisher (2). These values are valid under the conditions of hydrogenation in this study and will be subject to change under different conditions of temperature and pressure of hydrogenation as well as with the nature of the catalyst and the catalyst-oil ratio.

According to Bailey and Fisher the reactivity of one unsaturated acid A, compared to another unsaturated B, as standard is given by the relation:

$$K_A/K_B = H_A\ B_m/H_B\ A_m$$

where K_A and K_B represent respectively the affinities of A and B for hydrogen. H_A and H_B represent the fraction of hydrogen absorbed by A and B respectively in an interval of hydrogenation. A_m and B_m represent the average concentrations of A and B respectively over the interval. The ratio K_A/K_B therefore measures the relative readiness with which A and B undergo hydrogenation.

Relative Production of Conjugable Dienoic and Isolinoleic Acids. During the initial part of the hydrogenation of methyl linolenate (I.V. 260.6) to an iodine value of 238.5 (Figure 1) methyl linolenate was the only ester hydrogenated, with the formation of esters of conjugable dienoic and isolinoleic acids. Further the amount of methyl isolinoleate formed was approximately twice the amount of the methyl esters conjugable dienoic acids. If the production of methyl isolinoleate is assumed to arise from the hydrogenation of the 12:13-double bond of methyl linolenate (which may not be entirely correct, according to Daubert and Filer [6]), then, from the hydrogenation data the 12:13-double bond of methyl linolenate hydrogenates with twice the rapidity compared to either of the two and (9:10- and 15:16-) double bonds of this fatty acid ester.

Assuming no shift of double bonds, two isomeric conjugable dienoic acids are possible: the 9,12- or *n*-linoleic acid and the 12,15-linoleic acid. These two acids will be referred to, in the discussion that follows, as "linoleic acid." It is not certain as to which of these two acids is formed in predominance. However it is reasonable to assume that the 9,12- or *n*-linoleic acid predominates because the 9:10-double bond is the more sluggish of the two (9:10 and 15:16) towards hydrogenation, in lieu of its proximity to the carboxylic group (Hilditch and Vidyarthi [22]).

The hydrogenation of linolenic acid thus occurs twice as rapidly in the production of isolinoleic acid, than in the production of linoleic acid.

Relative Reactivities of Linolenic and Isolinoleic Acids. The maximum amount of isolinoleic acid, methyl ester, formed is 57.4%, at an iodine value of 144.7 (Figure 1). This also represents the maximum amount that can be formed under the conditions of hydrogenation employed. At this point (I.V. 144.7) the production of methyl isolinoleate (Il) from methyl linolenate (Ln) and its desorption into methyl oleate takes place at equal rates. Hence by equation given above the ratio of affinity constants K_{Ln}/K_{Il}, taking into account that the desorption of methyl linolenate produces methyl linoleate and methyl isolinoleate, is given by:

$$k_{Ln}/k_{Il} = \frac{\text{conc. methyl isolinoleate}}{⅔\ \text{conc. methyl linolenate}} = 57.4/⅔(3.5)$$

$$\text{i.e.,}\quad k_{Ln}/k_{Il} = 25$$

Linolenic acid is thus 25 times more reactive than isolinoleic acid.

Relative Reactivities of Linolenic and Linoleic Acids. The amount of methyl linoleate formed during the hydrogenation of methyl linolenate is half the amount of methyl isolinoleate formed in the same process (Figure 1). The concentration of methyl linoleate reaches a maximum of 11.4%, at an iodine value of 194.4. At this point the rates at which methyl linoleate is formed and desorbed into methyl oleate are equal, provided there is no positional shift of double bonds to a non-conjugable position. Such a shift (1) would make the acid impossible of determination by the spectrophotometric method (3, 23).

The concentration of methyl linoleate (L) and methyl linolenate (Ln) at the iodine value of 194.4 and 11.4 and 38.9 respectively. Accordingly:

$$k_{Ln}/k_L = \frac{\text{conc. methyl linoleate}}{⅓\ \text{conc. methyl linolenate}} = 11.4/⅓(38.9)$$

$$k_{Ln}/k_L = 0.9$$

The hydrogenation of linolenic acid to linoleic acid occurs at approximately the same rate as the hydrogenation of linoleic acid to oleic acid.

Relative Reactivities of Isolinoleic and Oleic Acids. The relative reactivities of isolinoleic and oleic acids (including isooleic acid) may be obtained in exactly the same way as in the preceding section. The maximum concentration of methyl oleate (O) (65.8%, Figure 1) occurs at an iodine value of 79.0. At this iodine value the concentration of methyl isolinoleate (Il) is 12.5%, methyl linolenate and methyl linoleate being absent.

The relative affinity of isolinoleic acid to oleic acid is given by:

$$k_{Il}/k_O = \frac{\text{conc. methyl oleate}}{\text{conc. methyl isolinoleate}} = 65.8/12.5$$

$$k_{Il}/k_O = 5.3\ \text{(approx.)}$$

Approximating this value to a whole number, isolinoleic acid hydrogenates five times as readily as oleic acid.

Relative Reactivities of Linoleic and Oleic Acid. The determination of the relative reactivities of linoleic and oleic acids offers some difficulty because of the presence of linolenic and isolinoleic acids. But the data and method outlined in Table III serve as a possible approximation in the calculation of this ratio. Methyl stearate does not appear until an iodine value

TABLE III

Calculation of Relative Reactivities (Expressed As Ratio of Affinity Constants) of Linoleic and Oleic Acids

	Interval (I.V. 153.7-144.7)
Decrease in methyl linolenate	3.5 units
Decrease in methyl linoleate	2.9 units
Increase in methyl oleate	5.4 units
Increase in methyl stearate	0.7 unit
H_O	0.7 unit
H_L	2.9 + ⅓ (3.5) = 4.05 units
$(O)_m$	30.0 units
$(L)_m$	6.45 units
k_L/k_O*	27.0

The ratio* k_L/k_O was calculated by the use of equation (4):

$$k_L/k_O = H_L(O)_m/H_O(L)_m = 4.0 \times 30.0/0.7 \times 6.45$$

$$\text{i.e.,}\quad k_L/k_O = 27.0$$

of about 162.0 is reached and below the iodine value of 118.0, methyl linoleate is absent. Therefore the range best suited for the calculation of relative reactivities of linoleic and oleic acid is between iodine values of 153.7 and 144.7.

The hydrogenation of linolenic acid occurs 27 times as readily as oleic acid.

In the calculation outlined for k_L/k_O the increase in the amount of methyl stearate is taken as the amount of methyl oleate hydrogenated to methyl stearate. The amount of methyl linoleate hydrogenated to methyl oleate is given by the decrease in methyl linoleate, plus one-third of the amount of methyl linolenate hydrogenated, since the hydrogenation of three moles of methyl linolenate produces one mole of methyl linoleate and two moles of methyl isolinoleate, as indicated previously.

Under the conditions of hydrogenation employed in the present investigation, the relative reactivities of the various fatty acids may be represented by the following whole numbers: oleic (including isooleic), 1; isolinoleic, 5; linoleic, 27; and linolenic, 27. With a change in conditions and the nature of the catalyst these values will change and are thus not to be regarded in the absolute sense.

Bailey and Fisher (2) have determined the relative reactivities of the unsaturated fatty acids under selective and non-selective conditions of hydrogenation. According to these workers the relative reactivities of the various unsaturated fatty acids have been represented by the following whole numbers: a) under selective conditions: oleic, 1; isooleic, 1; isolinoleic, 3; linoleic, 20; linolenic, 40; and b) under non-selective conditions: oleic, 1; isooleic, 1; linoleic, 5.

The data for the relative reactivities of the various polyunsaturated acids compare well with the data obtained by Bailey and Fisher. The reactivity of linolenic acid in comparison with the reactivity of linoleic acid (of 2.0) in the work of Bailey and Fisher has been calculated from data on the hydrogenation studies on soybean oil. A similar calculation from data on the hydrogenation of linseed oil has given a ratio of 0.5, which would indicate that linolenic acid is less reactive than linoleic acid. There is some degree of uncertainty in the latter calculation due to the high percentage of isolinoleic acid in the interval and due to the fact that an indeterminate small proportion of oleic acid produced was actually derived from this acid. Therefore the former value of 2.0 was selected as expressive of the relative reactivity of linolenic to linoleic acid.

In the present work the calculation of the relative reactivity of linolenic to linoleic acid has been much facilitated as the concentration of methyl linoleate reaches a maximum (11.4%) and remains constant over a small interval of hydrogenation. The value of 1.0 therefore seems reasonable, thereby showing that linolenic and linoleic acids have equal reactivities in comparison with oleic acid and as standard.

The relative low reactivity of isolinoleic acid towards hydrogen is to be expected on the basis of its widely separated double bonds. Isolinoleic acid is non-conjugable on alkali isomerization and hence does not contain the reactive methylene group $-CH=CH-CH_2-CH=CH-$, which is present in the linoleic and linolenic acids. According to Hilditch (21), the presence of such a group in a fatty acid increases its reactivity 12 to 20 times over that for a monoenoic acid e.g. oleic acid. The two double bonds in isolinoleic acid may be compared with the double bond of oleic acid, due to their wide separation. This would therefore account for the low reactivity of isolinoleic acid compared to linoleic acid.

Summary

A highly purified sample of methyl linoleate was prepared from linolenic acid obtained by debromination of hexabromostearic acid. The methyl linolenate was hydrogenated to varying degrees of saturation, using palladium on barium sulfate as the catalyst. Ethyl acetate was used as the solvent and all hydrogenations were conducted at room temperature and atmospheric pressure. The hydrogenated samples were analyzed for their fatty acid composition (as methyl esters).

The relative reactivities of the various polyunsaturated acids towards hydrogenation were calculated and may be represented by the following whole numbers: oleic (including isooleic) acid, 1; isolinoleic acid, 5; linoleic, 27; linolenic, 27.

A procedure was outlined for effecting a concentration of an isolinoleic acid (methyl ester) by low temperature crystallization. The fraction isolated contained 95.8% methyl isolinoleate.

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