disadvantage of these complexes is their instability to heat and the development of a typical burnt-hair or protein odor. As shown in Table VII, greater activity is obtained if the material is added on the cooling side of deodorization. The flavor scores of these oils were always low, and the use of such compounds in edible fat products appears questionable. The improvement in oxidative stability utilizing amino acid derivatives, like N-(carboxy methyl) *dl*-leucine, is sufficiently good however to warrant their use in stabilizing non-edible fat products. The α-amino acids have not given effective stability to edible oils when tested in the manner employed in our laboratory.

Table VIII shows that the amino acid derivatives did not have as great a stabilizing effect in cottonseed oil as did a number of the other complexing agents, such as chelidamic and iminodisuccinic acids.

Summary

Metal deactivating agents containing nitrogen as the coordinating atom have been developed for use in edible oils. The most effective compounds were those containing two carboxyl groups, α,α′ to the nitrogen. Those containing β,β′ carboxyls were less effective, and the efficiency of α,β carboxyls was intermediate. The activity is explained on the basis of the formation of metal chelation rings—complexes believed to be typical Werner's coordination complexes. The nitrogen atom may be an amine or a cyclic nitrogen. Complex coordination compounds can also be formed from acidic nitrogen compounds, such as hydroxamic acids, when the proper structure for metal chelation exists.

Chelidamic acid has been found to be a very efficient metal deactivating agent for both copper and iron. Imino α or β dicarboxylic acids show varying degrees of effectiveness toward the complexing of iron and copper. The greater the number of 5-membered chelation rings that are possible around the metal atom, the greater is the observed stability.

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A Method for the Determination of Linoleic Acid and Conjugated Dienoic Acids in Materials Containing Eleostearic Acids[1]

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THE scope of the American Oil Chemists' Society Tentative Method for polyunsaturated acids, Cd 7-48, is limited to the analysis of "... animal and vegetable fats containing only small amounts of preconjugated material ..." (1). For analyses such as the determination of linoleic acid in tung oil, it is apparent that the equations used must be corrected for the effect of the strong absorption of the naturally-occurring triene conjugated glyceride constituents (eleostearins) which interfere with measurements of absorption after the alkali isomerization.

Hilditch, Morton, and Riley (5) proposed methods for the analysis of fats containing various combinations of fatty acid constituents including oleic, linoleic, linolenic, and eleostearic acids, by first measuring the eleostearic acid content before isomerization. This value was "then to be taken into account in calculating the percentage of linolenic and linoleic acids from, respectively, $E^{1\%}_{1cm.}$ at 268 mμ after alkali-glycol treatment at 170°C. for 15 min., and $E^{1\%}_{1cm.}$ at 234 mμ after alkali-glycol treatment at 180°C. for 60 min." No details or equations for the proposed corrections were given. In a subsequent paper Hilditch and Riley (6) say that the method had been found to be unreliable. These workers describe a method they found satisfactory which involves separation of the mixed fatty acids by low temperature crystallization and subsequent analysis of each fraction. Low temperature crystallization separations are not considered suitable for routine analysis of a large number of samples.

The problem of deriving equations for calculations from spectrophotometric data, which would adequately correct for interfering trienoic absorption and permit direct determination after alkali isomerization, was reinvestigated. Samples of oils containing both linoleic and eleostearic acids, but no linolenic acids, were used. Hilditch and Riley (6) have shown that eleostearic and linolenic acids very probably never occur together in the same vegetable oil. The eleostearic acid isomers were determined by a previously described method (8), oleic acid was found by use of a recently described procedure using hydrogen-iodine values (10), and total saturated fatty acids were estimated by difference.

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Derivation of Equations

To achieve a satisfactory determination in the presence of eleostearic acids, the equation for calculating linoleic acid from spectrophotometric data must contain adequate correction factors for the absorption of these trienoic acids at 233 mμ, the region of dienoic absorption. The equation required for the calculation of linoleic acid from spectrophotometric data by the American Oil Chemists' Society tentative method, Cd 7-48, as derived by Brice and Swain (3), is sufficiently complicated to discourage any further correction factors. However in a recent paper O'Connor *et al.* (9) described considerable simplification of the equation for the linoleic acid content of normal vegetable oils in the absence of linolenic acid. This simplified equation, with the constant applying to natural acid standards, in accordance with Brice *et al.* (4), is:

1. Percentage of linoleic acid=1.086 ($K'_{233} - K_{233}$)

where K'_{233} and K_{233} are the measured extinction coefficients of the sample at 233 mμ after and before alkali isomerization, respectively. It is the basis for the proposed equation including a correction for eleostearic acids. The equation of the Tentative Method Cd 7-48, as derived by Brice and Swain (3) and also with the constant for natural acid standards (4),

2. Percentage of diene constituents=0.84 (K_{233} — 0.07)

is made the basis for a modified equation for dienoic acids in the presence of trienoic acids, where K_{233} has the same significance as in Equation 1.

To evaluate factors required to correct adequately for the absorption due to trienoic conjugation, a study was made of the absorption of pure samples of both alpha- and beta-eleostearic acids and of the effects of alkali isomerization on the absorption. Earliest workers, even predating the original proposal of Mitchell and his colleagues (7) which established the quantitative method based on alkali-produced isomerization, had observed that while treatment with alkali caused increased ultraviolet absorption of nonconjugated fatty acids, it decreased ultraviolet absorption of conjugated fatty acids. Bradley and Richardson (2) concluded: "When the isomerization process is applied to a mixture which contains a major proportion of a triple-conjugated component, such as tung oil, the normal effect is reversed and a net loss of conjugation results." This loss was attributed to "intramolecular and intermolecular addition" and to the "formation of polymer." Brice and Swain (3) have shown the decreased ultraviolet absorption of eleostearic acid isomers and of tung oil on alkali isomerization.

Eight samples of each of the pure alpha- and beta-isomers, each an independent preparation by methods previously described (8), were subjected to alkali isomerization by the procedures specified in Tentative Method Cd 7-48 (1). Examination of the data shows that:

a) There is a loss of about 10% of the total eleostearic acid during alkali isomerization, regardless of whether the original material is alpha- or beta-eleostearic acid.

b) When the alkali-isomerized beta-eleostearic acid is reanalyzed by means of the multicomponent equations (8), modified to eliminate any possible solvent effect by a redetermination of the extinction coefficients of each of the pure isomers in the alkali isomerization reagent, from 12 to 19% of the beta-isomer is found as the alpha-isomer.

c) Isomerization of the alpha-isomer and subsequent analysis revealed the conversion of from 21 to 27% of it to the beta-isomer.

The modified equations used for the analysis of alkali isomerized samples in the alkali-glycol reagent were:

3. Percentage of alpha-eleostearic acid = 1.774 $K_{270.6}$ — 1.469 $K_{267.5}$
4. Percentage of beta-eleostearic acid = 1.523 $K_{267.5}$ — 1.290 $K_{270.6}$

where $K_{270.6}$ and $K_{267.5}$ are the observed extinction coefficients of the sample at 270.6 and 267.5 mμ, respectively. These effects of alkali isomerization on alpha- and beta-eleostearic acids are illustrated in Figure 1.

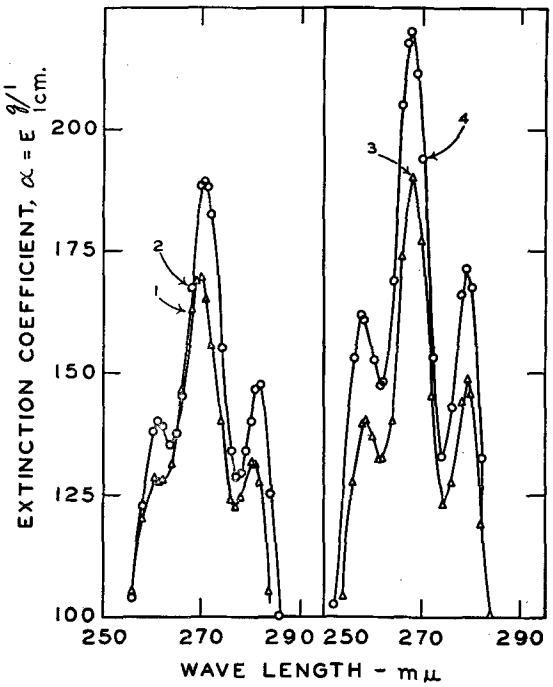

FIG. 1. Ultraviolet absorption spectra of eleostearic acids in methanol solutions of KOH-glycol isomerization reagent.
1. Alpha acid after isomerization.
2. Alpha acid before isomerization.
3. Beta acid after isomerization.
4. Beta acid before isomerization.

Incorporation of a constant for correction for the absorption of eleostearic acid or of constants for the somewhat different absorptions of alpha- and beta-eleostearic acids into the formula for calculating linoleic acid from spectrophotometric data would be the simplest procedure. The variability of the amount of isomerization and the fact that the effect of alkali treatment may depend upon the concentration of these acids in a particular sample however make such a simple correction appear unreliable. Therefore Equation 1 was corrected by the somewhat more complicated, but probably more reliable, manner of adding factors which require an evaluation of the alpha- and beta-eleostearic acids in the sample both before and after the alkali isomerization:

5. Percentage of linoleic acid = 1.086 $\left([K'_{233} - 15.8\,(\alpha') - 26.1\,(\beta')] - [K_{233} - 13.8\,(\alpha) - 17.5\,(\beta)] \right)$

where 15.8 and 26.1 are the average values for the extinction coefficients of pure nonisomerized alpha- and beta-eleostearic acids, respectively, at 233 mμ in the isomerization blank, and 13.8 and 17.5, the values for these constants in cyclohexane. α' and β' are the decimal fractions of alpha- and beta-eleostearic acids, respectively, found after isomerization (from Equations 3 and 4). α and β are these same values determined before isomerization by methods published previously (8). K'_{233} and K_{233} have the same significance as in Equation 1.

Equation 5 does not take into account polymeric-like material formed during alkali isomerization, which is approximately 10% of the total eleostearic acid. Studies of samples of known composition readily show that although this material does not exhibit triene conjugation absorption, its contribution to the total absorption in the diene region (233 mμ) cannot be completely ignored.

The portion of the absorption at 233 mμ attributed to the eleostearic acids can be computed from the determined percentages of the alpha- and beta-isomers (from Equations 3 and 4) and the established extinction coefficients of the pure acids at this wavelength in the alkali-glycol reagent, i.e., 15.8 and 26.1, respectively. The difference between this value and the measured absorption of the sample at 233 mμ is the absorption, at this wavelength, attributable to the material, probably polymeric, formed from the eleostearic acid during the alkali treatment. The amount of this material is merely the difference between the total eleostearic acid before and after isomerization. Knowing the absorption of a given quantity of the material, its extinction coefficient at 233 mμ can be computed. Repeated determinations gave an average value of 19.3.

From these data Equation 5 can be further corrected to eliminate absorption of this polymeric-like material.

6. Percentage of linoleic acid $= 1.086 \left(\begin{array}{l} [K'_{233} - 15.8\,(\%\ \text{alpha}') - 26.1\,(\%\ \text{beta}') - \\ 19.3\,(\%\ \text{gamma})] - \\ [K_{233} - 13.8\,(\%\ \text{alpha}) - 17.5\,(\%\ \text{beta})] \end{array} \right)$

where percentage of gamma is the apparent loss of total eleostearic acid during the alkali isomerization and all the other terms have the same meaning as in Equation 5.

Equation 2, corrected for the determination of the diene conjugation constituents in the presence of large quantities of triene conjugated components, becomes

7. Percentage of diene conjugated acids $=$ $0.84\,[K_{233} - 13.8\,(\%\ \text{alpha}) - 17.5\,(\%\ \text{beta}) - 0.07]$

In Tentative Method Cd 7-48 oleic acid is calculated from the determined polyunsaturated acid composition and the iodine value of the sample (1). However in tung oils or other materials containing large quantities of eleostearic acids, determinations of total unsaturation by iodine absorption are unreliable. Hilditch and Riley (6) say ". . . we have reached the conclusion that halogen addition methods are not, in the most favorable conditions, adapted for quantitative studies of this group of oils and that their use should be avoided in detailed analyses of their component acids." These workers determined total saturated acids by a modified Bertram method and then obtained oleic acid by difference. This procedure has the disadvantage that the Bertram method is neither simple, reliable, nor rapid when used for tung oils or similar products.

Recently Pack, Planck, and Dollear (10) proposed a method which they demonstrated to be satisfactory for the determination of total unsaturation of a tung oil or similar material by means of the hydrogen-iodine value. The method, as described in their paper, has been used and the oleic acid content calculated from the equation:

8. Percentage of oleic acid $= 1.113 \times$ H.I. value of sample $- 2.014$ (% linoleic acid) $- 3.043$ (% total eleostearic acid)

Total saturated fatty acids can then be determined by difference as in the Tentative Method Cd 7-48:

9. Percentage of total saturated acids (fatty acid basis) $= 95.7 -$ % oleic acid $-$ % linoleic acid $-$ % total eleostearic acids

Results and Discussion

Varying amounts of alpha, beta, and mixtures of alpha- and beta-eleostearic acids were added to a sample of cottonseed oil of known fatty acid composition to test the accuracy of results obtained by use of Equation 6. The alpha- and beta-eleostearic acid contents of these mixtures were determined by the previously described multicomponent method (8), and all samples were isomerized in duplicate by the procedure specified in Tentative Method Cd 7-48 (1). The alpha- and beta-contents of the alkali isomerized samples were determined by use of Equations 3 and 4, and from the data the linoleic acid content was calculated by use of Equation 6. Oleic acid and total saturated fatty acids were calculated from these values by means of Equations 8 and 9, respectively. The results of these analyses are given in Table I together with a comparison with values calculated from the known compositions of the cottonseed oil-eleostearic acid mixtures.

As fresh cottonseed oil contains only a negligible trace of diene conjugated acids, additional samples were prepared to test the use of Equation 7. Varying amounts of alpha, beta, and mixtures of alpha- and beta-eleostearic acids were added to a dehydrated castor oil of known composition, containing approximately 25% conjugated diene acids. These mixtures were measured spectrophotometrically with no isomerization and the data used to calculate the percentage of conjugated dienoic acids from Equation 7. The re-

TABLE II

Percentage of Conjugated Dienoic Acids in Dehydrated Castor Oil-Eleostearic Acid Mixtures

Dehydrated castor oil	Eleostearic acid		Conjugated dienoic acid		
	Alpha	Beta[a]	Found	Calculated	Δ
%	%	%	%	%	
100.0	0	0	23.9	.....	.....
79.3	20.7	.....	18.9	18.9	0
60.1	39.9	.....	13.7	14.4	−0.7
38.3	61.7	.....	8.5	9.1	−0.6
20.6	79.4	.....	4.4	4.9	−0.5
77.6	.....	21.9[a]	18.4	18.5	−0.1
58.0	.....	40.9[a]	13.5	13.8	−0.3
40.9	.....	57.7[a]	8.8	9.8	−1.0
18.7	.....	79.2[a]	4.5	4.5	0
50.5	26.6[b]	21.9[a]	11.2	12.1	−0.9
33.8	35.6[b]	29.3[a]	7.3	8.1	−0.8
26.0	27.3[b]	45.0[a]	6.1	6.2	−0.1
24.8	52.2[b]	21.5[a]	5.7	5.9	−0.2

[a] 97.5% pure. [b] 98.2% pure.

TABLE I

Determination of Linoleic Acid in Mixtures of Cottonseed Oil and Eleostearic Acids

Sample	Polyunsaturated acids									Monounsaturated acid (oleic)			Total saturated acids		
	Conjugated						Nonconjugated (linoleic)								
	Alpha-eleostearic			Beta-eleostearic											
	Found	Calc.	Δ	Found	Calc.	Δ	Found	Calc.	Δ	Found	Calc.	Δ	Found	Calc.	Δ
	%	%		%	%		%	%		%	%		%	%	
1	15.6	15.0	+0.6	6.5	7.0	−0.5	39.8	41.2	−1.4	13.8	12.7	+1.1	20.0	20.4	−0.4
							40.0	41.2	−1.2	13.4	12.7	+0.7	20.2	20.4	−0.2
2	52.3	50.0	+2.3	14.4	15.0	−0.6	18.9	18.5	+0.4	2.5	5.7	−3.2	7.6	9.2	−1.6
							18.6	18.5	+0.1	3.1	5.7	−2.6	7.3	9.2	−1.9
3	16.3	15.0	+1.3	5.9	7.0	−1.1	40.0	41.2	−1.2	13.3	12.7	+0.6	20.2	20.4	−0.2
							40.2	41.2	−1.0	12.9	12.7	+0.2	20.4	20.4	0
4	52.0	50.0	+2.0	14.5	15.0	−0.5	19.5	18.5	+1.0	1.5	5.7	−4.2	8.2	9.2	−1.0
							19.9	18.5	+1.4	0.8	5.7	−4.9	8.6	9.2	−0.6
5	1.8	0	+1.8	31.2	33.3	−2.1	33.3	35.2	−1.9	13.8	10.8	+3.0	15.6	17.4	−1.8
							33.4	35.2	−1.8	13.8	10.8	+3.0	15.6	17.4	−1.8
6	3.9	0	+3.9	63.6	66.7	−3.1	16.9	17.6	−0.7	5.5	5.4	+0.1	5.8	8.7	−2.9
							15.7	17.6	−1.9	8.0	5.4	+2.6	4.5	8.7	−4.2
7	1.8	0	+1.8	30.0	33.3	−3.3	34.3	35.2	−0.9	13.2	10.8	+2.4	16.3	17.4	−1.1
							34.1	35.2	−1.1	13.7	10.8	+2.9	16.1	17.4	−1.3
8	4.2	0	+4.2	63.5	66.7	−3.2	15.6	17.6	−2.0	8.0	5.4	+2.6	4.4	8.7	−4.3
							16.0	17.6	−1.6	7.2	5.4	+1.8	4.9	8.7	−3.8
9	66.7	66.7	0	0	0	0	16.7	17.6	−0.9	6.8	5.4	+1.4	5.4	8.7	−3.3
							16.7	17.6	−0.9	6.9	5.4	+1.5	5.4	8.7	−3.3
10	33.6	33.3	+0.3	0	0	0	35.0	35.2	−0.2	9.7	10.8	−1.1	17.4	17.4	0
							35.2	35.2	0	9.3	10.8	−1.5	17.6	17.4	+0.2
11	32.7	33.3	−0.6	1.4	0	+1.4	33.9	35.2	−1.3	11.3	10.8	+0.5	16.4	17.4	−1.0
							33.8	35.2	−1.4	11.5	10.8	+0.7	16.3	17.4	−1.1
12	65.8	66.7	−0.9	1.0	0	+1.0	22.6	17.6	+5.0	0(−5.1)	5.4	−5.4	6.3	8.7	−2.4
							19.2	17.6	+1.6	1.8	5.4	−3.6	7.9	8.7	−0.8

sults obtained and the differences between them and calculated values from known compositions of the dehydrated castor oil-eleostearic acid mixtures are given in Table II.

The data in Tables I and II have been subjected to some statistical treatment. The average differences and the standard deviation of these differences respectively, for each component (11) are:

	Average difference	Standard deviation
Diene conjugated acids	−0.43	0.36
Alpha-eleostearic acid	+1.39	1.33
Beta-eleostearic acid	−1.00	1.23
Linoleic acid	−0.50	0.82
Oleic acid	−0.06	1.40
Total saturated acids	−1.62	1.35

The agreement between results obtained by use of the proposed spectrophotometric method and the values calculated from known compositions are encouraging. The spectrophotometric procedure is therefore a reasonable method for the estimation of the fatty acid composition of normal vegetable oils containing large quantities of triene conjugation constituents. As the proposed procedure permits a determination of fatty acid composition with no treatment of the sample other than the alkali isomerization, it can be adapted to routine analyses. It extends the scope of the spectrophotometric method for the determination of polyunsaturated fatty acids to samples which contain large quantities of triene conjugated constituents. The method is however still applicable only to unhydrogenated animal and vegetable oils which contain only small amounts of color which might interfere with the determination of the individual fatty acids after isomerization (1).

To illustrate the applicability of the proposed procedure to oils containing large quantities of preformed conjugated constituents, a number of tung oils from different sources were analyzed. The alpha- and beta-isomers of eleostearic acid and linoleic acid contents of these samples obtained by use of the proposed equations are given in Table III.

TABLE III

Determination of Linoleic Acid in Tung Oils

Description	Eleostearic acids		Linoleic
	Alpha	Beta	
	%	%	%
Domestic	29.1	44.8	6.4
			6.6
Paraguayan	70.3	5.8	8.0
			8.8
Domestic	75.8	2.6	7.1
			7.4
Chinese	55.1	16.5	7.7
			7.5
Nyasaland Fordii	77.6	1.1	7.3
			9.8
Nyasaland Montana	64.7	2.7	15.5
			15.8

Summary

A procedure has been described which extends the scope of the spectrophotometric method for polyunsaturated acids to the determination of linoleic and conjugated acids in the presence of large quantities of conjugated trienoic acids.

Basis for the proposed method rests on equations which are offered to correct the "end" or "background" absorption of the highly absorbing triene conjugated acids at 233 mμ, the position of maximum absorption of conjugated dienoic acids and alkali isomerized linoleic acids. The method is limited to samples which do not contain nonconjugated trienoic acids (linolenic acids).

The method has been tested by the analysis of several mixtures of cottonseed and dehydrated castor oils of known composition, to which varying amounts of alpha, beta, and mixtures of alpha- and beta-eleostearic acids have been added. These samples have been used to demonstrate the application of the proposed

method for the determination of dienoic conjugated acids, alpha-eleostearic acid, beta-eleostearic acid, linoleic acid, oleic acid, and total saturated fatty acids.

Comparisons of the results obtained with similar values, calculated from the known composition of the mixtures, prove that the proposed method gives reasonable results. Standard deviations between determined and calculated results vary from 0.36 for diene conjugated acids to 1.40 for oleic acid.

The method has been applied to the analysis of foreign and domestic tung oils.

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On the Glyceride Composition of Animal Fats

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WHILE the glyceride composition of natural fats has received considerable attention, there are few cases where the composition is well-established, and general principles are not broadly or closely applicable. For many vegetable fats, especially seed fats, Hilditch and associates (1) have established an approximately "even distribution" of fatty acids in the glycerides, but there are many departures from perfect correspondence to the rule. For example, in a detailed study of corn oil Doerschuk and Daubert (2) observed a "partial random distribution."

There is less information on glycerides of animal fats than on those of vegetable origin. Evidence has been presented by Hilditch (3) that the glycerides of lard are largely 2-palmityl glycerides (and therefore non-random), but Norris and Mattil (4), in a study which included lard and tallow, concluded that "the results further substantiate the hypothesis that animal fats, in contradistinction to seed fats, are essentially randomly distributed." Kartha (5) has noted, on the basis of his own and others' results, that the trisaturated in animal fats is measurably less and the disaturated is measurably more than the "chance values."

The present authors propose to show that certain animal fats are quite non-random in their glyceride structure just as vegetable seed fats have been shown to be. The study involves a reexamination of lard, beef tallow, and mutton tallow by fractional crystallization and examination of fractions and products of their complete hydrogenation by familiar thermal techniques as well as by x-ray diffraction.

Experimental

A 50-lb. sample of edible lard (unhydrogenated) was obtained from E. Kahn's Sons (Cincinnati, O.). Approximately 10 lbs. of beef tallow were obtained from beef suet by dry rendering followed by a Super-filtrol bleach. Ten lbs. of mutton tallow were obtained from Swift and Company, Chicago, Ill. The original fats were analyzed and their methyl esters fractionated in a Podbielniak still. Data appear in Tables I and II.

TABLE I

Distillation Analysis of Methyl Esters

	Lard	Beef Tallow	Mutton tallow
% C_{14}	2.6	5	6.6
% C_{16}	27.9	30	24.4
% C_{18}	69.5	65	69.0

After analysis the fats were subjected to fractional solvent crystallization. In the case of the lard and mutton tallow a preliminary rough fractionation was followed by more careful detailed fractionation to obtain nearly representative S_3, S_2U, and SU_2 (and U_3) fractions. Two fractionations were performed for lard: one as a pilot run, therefore more detailed; the

TABLE II

Composition of Major Fractions

	Original	S_3	S_2U		SU_2	"U_3"
			Composite	Pure		
	From lard (large scale fractionation)					
I.V.	64.4	3.1[b]	35.8	33.4	62.2	
% Oleic	45.6[a]		25.4	24.5	53.3	
% Linoleic	10.6		6.3	5.2	6.9	
% Linolenic	1.2		0.25	0.15	0.31	
% Arachidonic	0.3		0.18	0.11	0.20	
% Conjugated	0.2		0.13	0.11	0.16	
% Saturated	37.8		63.3	65.5	34.7	
	From beef tallow					
I.V.	37.4	2.5	30.0		59.8	
% Oleic	35.8		29.2		55.2	
% Linoleic	1.8		0.86		3.4	
% Linolenic	0.22		0.10		0.71	
% Arachidonic	0.09		0.00		0.11	
% Conjugated	0.54		0.38		0.94	
% Saturated	57.1		64.6		35.3	
	From mutton tallow					
I.V.	42.6	8.5	33.5		59.3	79.2
% Oleic	40.8		32.5		50.8	62.0
% Linoleic	1.6		0.63		1.7	2.9
% Linolenic	1.1		0.51		1.8	2.6
% Arachidonic	0.34		0.03		0.48	1.2
% Conjugated	1.5		0.93		2.3	3.7
% Saturated	50.2		61.0		38.6	23.2

[a] 95.6% basis for total fatty acids.
[b] From original fractionation.