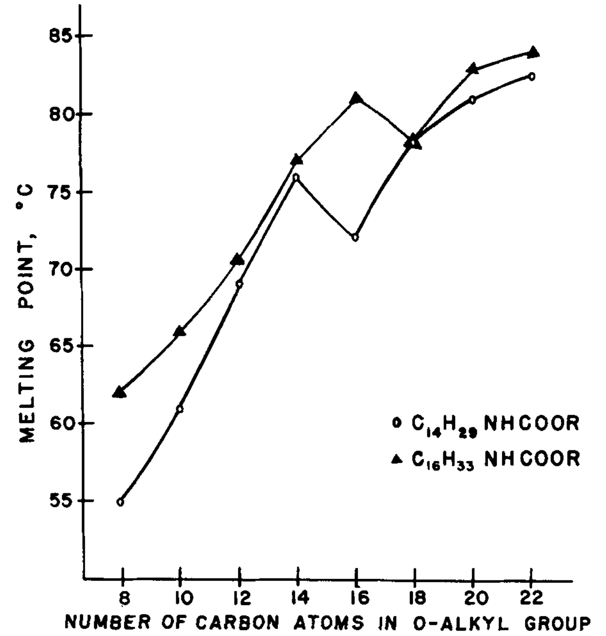

FIG. 3. Melting points of alkyl esters of N-n-tetradecyl and N-n-hexadecyl carbamic acid.

with transition points at symmetry were obtained for the other carbamates.

The urethanes give thixotropic liquids or nonflowing gels with soybean oil, solvent-thinned vehicles, ethanol, and other similar materials at concentrations as low as 0.5%. Better-defined crystal structure and poorer thixotropic properties were observed with an increase in symmetry. Best thixotropic behavior is observed when the N-alkyl group differs from the O-alkyl by 4 to 8 carbon atoms. For example, in the eicosyl series of N-alkyl carbamates the best thixotropic properties were observed when the N-alkyl group contained 14 to 16 carbon atoms.

It would be interesting to examine other fatty derivatives to determine whether a similar peaking at point of symmetry is observed. Systems which might demonstrate similar properties include N-alkyl fatty amides, N-N-dialkyl fatty amides, symmetrical and unsymmetrical disubstituted ureas, etc. There is scattered melting-point information available in the technical literature for several different classes of compounds, but questionable purity of the materials or paucity of data makes analyses of the information difficult. Possibly even simple alkyl esters might show such behavior, but again the literature information on compounds of known purity is inadequate for evaluation.

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REFERENCES

1. Hauser, E.A., U.S. 2,531,427 (1950).
2. I.G. Farbenindustrie A.G., Brit. 462,182 (1937).
3. "International Critical Tables of Numerical Data, Physics, Chemistry and Technology," First Ed., McGraw Hill Book Co., New York, 1926-1928.
4. Ralston, A.W., "Fatty Acids and Their Derivatives," John Wiley and Sons, New York, 1948.
5. Sasin, R., Ashley, W.F., Manning, I.W. Jr., Paolini, A. Jr., and Sasin, G.S., J. Am. Oil Chemists' Soc., *35*, 192-194 (1958).
6. Siggia, S., and Hanna, J.G., Ind. Eng. Chem., Anal. Ed., *20*, 1084 (1948).
7. Winkler, W.B., U.S. 2,663,649 (1953).

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Hydrogenation of Linolenate. II. Hydrazine Reduction[1]

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Observations by Aylward and Rao that hydrazine is a reducing agent for a number of unsaturated fatty acids were extended. The hydrazine reaction on linolenic acid was followed by periodic sampling until methyl esters prepared from the reduced acids had an iodine value of 162. These esters were shown by countercurrent distribution to consist of 26% triene, 43% diene, 26% monoene, and 5% stearate and by infrared analysis to contain no *trans* bonds.

Oxidation of the separated monoene and diene fractions by permanganate-periodate mixtures and gas chromatography of the dibasic acids showed that the double bonds were in the original 9, 12, and 15 positions and that the double bonds farthest from the carboxyl were reduced at a slightly faster rate. Gas chromatography of the monoene fraction indicated three components that were identified in the order of elution from the column as 9, 12, and 15 monoenes; in the diene fraction three components were identified in the order of elution as 9,12; 9,15; and 12,15 dienes. After alkali isomerization of this diene fraction, the conjugated material was reacted with maleic anhydride; the unreacted 9,15 diene isomer was separated by distillation.

THE REDUCTION of a number of unsaturated fatty acids with hydrazine has been described by Aylward and Rao (1-6). Their earlier work on the hydrazine reaction is summarized in their first paper. A detailed study of the reduction of linolenic acid seemed pertinent to research on the selective hydrogenation of linolenates (7) for two reasons.

First, catalytic hydrogenation of methyl linolenate produces a complex mixture of *cis* and *trans* monoene and diene isomers with widely different double bond locations. In work at this laboratory nine monoenes and four diene components were separated by gas chromatography (7). By contrast the all *cis* product of hydrazine reduction might be expected to provide a relatively simple mixture for the characterization and identification of the all *cis* monoenes and dienes present and thereby afford some insight into the composition of more complicated mixtures from catalytic reduction.

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Secondly, preliminary experiments indicated that reduction with hydrazine was first order with respect to linolenate. This reaction thus supplies a simple model by which to compare the more complicated kinetics of catalytic hydrogenation.

This paper reports the fractionation and characterization of the diene and monoene isomers formed from linolenic acid by hydrazine reduction. Kinetic studies will be reported elsewhere.

Experimental

Reduced Esters. Linolenic acid was prepared by saponification of pure methyl linolenate that had been isolated by countercurrent distribution (8).

In preliminary experiments several 0.6-g. samples of linolenic acid were successfully reduced by stirring with hydrazine in ethanol as described by Aylward and Rao (1). In larger preparations the rate of reduction was very slow. The suggestion that increased exposure to atmospheric oxygen resulted in a more rapid rate (1) was pursued. If air were blown through the mixture, a more rapid reduction was indeed obtained.

The influence of oxygen on the reaction is illustrated in the following preparation. A mixture of 16.6 g. of linolenic acid (iodine value 266), 166 ml. of 95% ethanol, and 14.4 ml. of hydrazine hydrate (Eastman practical grade) was stirred in an open Erlenmeyer flask at 50–56°C. by a magnetic stirrer. After 4 hrs. the iodine value of fatty acids recovered from a small portion of the reaction mixture was essentially unchanged. The mixture was again warmed to 50°C. In addition to stirring, a slow stream of compressed air was blown through the liquid. Under these conditions, after 3 hrs. and 40 min., the iodine value of fatty acids from a small portion was 184.7. After 4 hrs. the reaction was stopped, the mixture was made acid with dilute hydrochloric acid, and the acids were extracted with ether, washed with water, and dried over sodium sulfate. On evaporation of ether, 16.5 g. of acids were obtained which were refluxed 9 hrs. with 85 ml. of methanol and 0.2 ml. of sulfuric acid to form methyl esters. The esters were distilled at 144–155° and 0.07 mm. to yield 14.4 g. of product.

Infrared analysis showed that this product contained less than 1% of *trans* esters. Wijs iodine value was 161.7. Gas chromatography (4 ft. x ¼ in. column, packed with 10% polyvinylacetate on Chromosorb and operated at 163°C., 50 cc. per min. Argon flow) indicated the following composition: 24.4% triene, 47.9% diene, 23.5% monoene, and 4.2% stearate.

Countercurrent Distribution. A 13.7-g. portion of the esters prepared as described was fractionated in a 200-tube countercurrent distribution apparatus. The procedure was quite similar to that previously used for fractionating catalytically hydrogenated linolenate (7). Forty-milliliter portions of acetonitrile and 10-ml. portions of pentane-hexane were used per tube. Two fractions from the apparatus were combined in each collector tube. From areas under the weight curve (Figure 1) it is estimated that the reduced esters contain 26.6% triene, 43.1% diene, 25.6% monoene, and 4.7% stearates or amounts comparable to the analytical figures obtained by gas chromatography. Fractions in the collector tubes were combined as shown at the top of Figure 1 to give monoene, diene, and triene fractions for more detailed study.

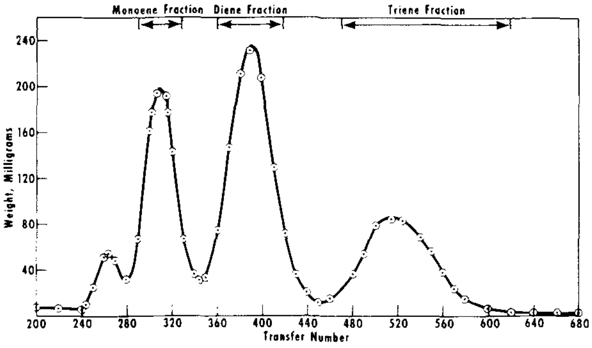

FIG. 1. Countercurrent distribution of hydrazine reduced linolenic acid (I.V.—161.7).

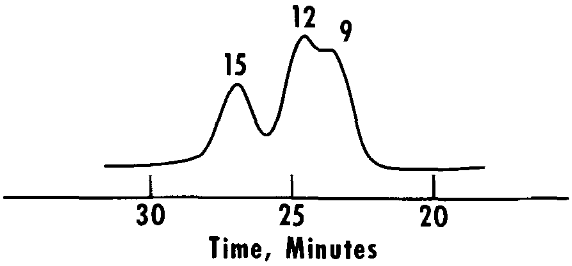

FIG. 2. Gas chromatogram of monoene fraction (4-ft. packed column).

Composition of Monoenes. The monoene fraction had a Wijs iodine value of 86.6 (theory 85.61). Gas chromatograms on a 4-ft. column, using 10% ethylene glycol succinate, are shown in Figure 2 and on a capillary Apiezon L column in Figure 3. Both chromatograms indicate the presence of three components, but the resolution is much greater on the capillary column. The three components were identified by "mixed chromatogram" technique, using methyl oleate and a mixture of methyl 9- and 12-octadecenoates prepared from linoleic acid as described below. In Figure 2 the third component, 15-octadecenoate, makes up 28.8% of the area; in Figure 3, it is 29.5%. The other areas in Figure 3 represent 34.9% 12-octadecenoate and 35.6% 9-octadecenoate.

Oxidation of the monoene mixture by the periodate-permanganate method of Jones and Stolp (10) and measurement of the resultant dibasic acid composition by liquid partition chromatography gave the following molar dibasic acid composition: C_{15}, 29.4%; C_{12}, 33.5%; C_{10}, 0.9%; C_9, 36.2%.

Composition of Dienes. The diene fraction had a Wijs iodine value of 170.1 (theory 172.4). Quantitative isomerization (9) gave a value of 64.1% diene, which was conjugated by alkali.

Gas chromatograms of the diene esters are shown for a 4-ft. column packed with 10% ethylene glycol succinate in Figure 4 and for a capillary Apiezon L column in Figure 5. The curves are quite similar in appearance to those for the monoene fraction; each indicates three components, but the capillary column gives much greater resolution. The three components were identified by the "mixed chromatogram" technique, using methyl linoleate and methyl-9,15-octadecadienoate prepared as described later. In Figure 4 the third component, 12,15-octadecadienoate, constitutes 28% of the area; in Figure 5 it is 29.8%. The

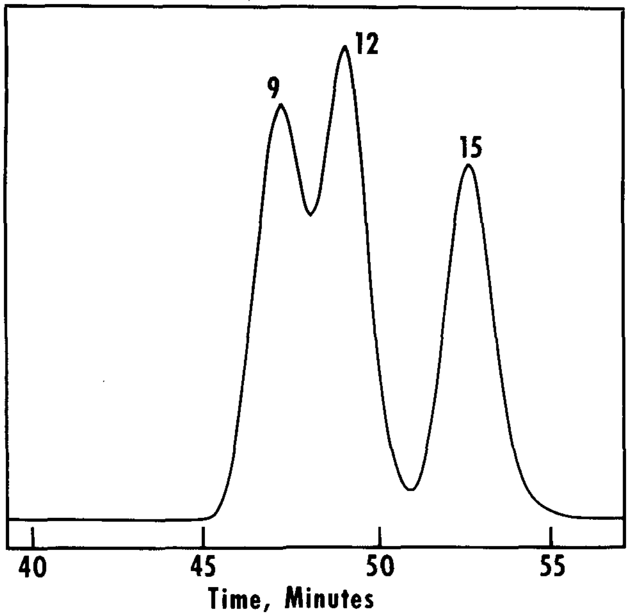

FIG. 3. Gas chromatogram of monoene fraction (200-ft. capillary column).

other areas in Figure 5 represent 33.6% 9,12-octadecadienoate and 36.6% 9,15-octadecadienoate.

Oxidation of the diene mixture by the periodate-permanganate method (10) and liquid partition chromatography of the dibasic acids gave the following molar composition: C_{15}, 1.5%; C_{12}, 23.3%; C_{10}, 1.1%; C_9, 52.3%; C_8, 2.3%; C_7, 0.6%; C_6, 18.9%.

Isolation of Methyl-9,15-Octadecadienoate. The solutions left after quantitative alkali isomerization of the diene fraction were used to isolate methyl-9,15-octadecadienoate. Solvents were evaporated under vacuum, the residue was diluted with water and made acid with sulfuric acid, and the acids were extracted with ether. Diazomethane was added to the ether solution, and the solvent was evaporated to yield methyl esters (Figure 6). To 0.18 g. of these esters was added 0.1 g. of maleic anhydride in 10 ml. of toluene and 1 ml. of iodine solution (1 mg. I_2/ml. toluene). The mixture was heated in a sealed tube for 20 hrs. at 110–120°C. This reaction is similar to that used by von Mikusch in his pandiene determination (11). Contents of the tube were transferred to a separatory funnel with pentane-hexane and washed five times with 15% potassium iodide to remove iodine. The solution was then washed with water and dried over sodium sulfate, and the solvent was evaporated. By vacuum distillation of the residue from a small flask, 0.04 g. of product was obtained. This product gave only one band in the gas chromatograph at the same position as the 9,15-octadecadienoate in Figure 6. Infrared measurement showed only traces of isolated *trans* and conjugated *trans,trans* double bonds. Oxidation and dibasic acid analysis gave equal amounts of azelaic and adipic acids. It was concluded that the material was the expected methyl-9,15-octadecadienoate.

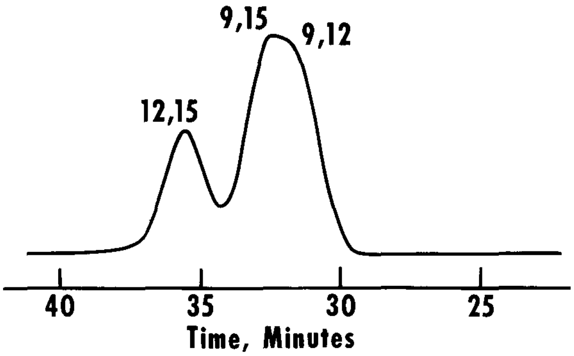

FIG. 4. Gas chromatogram of diene fraction (4-ft. packed column).

Composition of Triene. The triene fraction from the countercurrent distribution appeared to be unchanged after several days of storage at 0° under nitrogen. Quantitative alkali isomerization gave a value of 100.7% triene and no diene.

Reduction of Linoleic Acid by Hydrazine. To obtain a mixture of methyl 9- and 12-octadecenoates for identification of the 12-octadecenoate in the monoene fraction from linolenate. a reduction of linoleic acid was carried out. Air was bubbled through a mixture of 2.17 g. of linoleic acid, 22 ml. of 95% ethanol, and 2 ml. of hydrazine hydrate for 4 hrs., at 50°. Acids, recovered in the same way as in the linolenic acid reduction, had an iodine value of 56; they were crystallized from 25 ml. of acetone at −25°C. to remove saturates. Oxidation and dibasic acid analysis of a portion of the acids showed that nearly all the double bonds of these monoenes were in the original 9 and 12 positions. The remainder of the acids was converted to methyl esters with diazomethane for gas chromatographic standards.

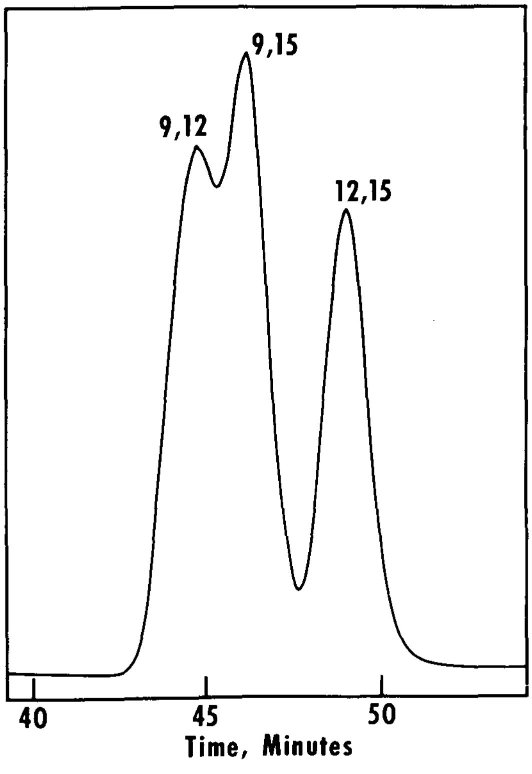

FIG. 5. Gas chromatogram of diene fraction (200-ft. capillary column).

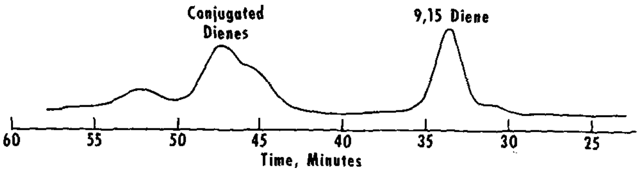

FIG. 6. Gas chromatogram of diene fraction after alkali conjugation and esterification.

Discussion

In contrast to catalytic hydrogenation, hydrazine reduction produces only those acids that would be formed by reduction of linolenate without shift in position or configuration of the double bonds. Dibasic acids resulting from double bonds in changed positions are produced only in minute amounts or reflect impurities in the original linolenate. The absence of *trans* bonds is in agreement with the observation of Rao (6).

The procedure used for fractionation of the reduced mixture was similar to that used for catalytically hydrogenated linolenate in the first paper of this series (7). Methyl esters of the reduced acids separated by countercurrent distribution into monoene, diene, and triene fractions possessed iodine values in good agreement with those calculated for pure esters. The composition of monoenes, dienes, and trienes was comparable to that determined on the unfractionated mixture by gas chromatography.

Oxidation of the monoene and diene fractions and analysis of the resulting dibasic acids showed that three monoenoic and three dienoic acids were present with double bonds in the same position as in the original linolenic acid.

Gas chromatography, using both a column packed with 10% ethylene glycol succinate and a capillary column packed with Apiezon L, also showed the presence of three monoene components and three diene components. The higher resolution of the capillary column is illustrated by the fact that three distinct peaks were found for both monoene and diene fractions; with the packed column the first two components were slightly separated or appeared as a single broad peak, and only the third was sufficiently defined for quantitative estimations.

On both the ethylene glycol succinate and Apiezon L columns the monoene isomers and diene isomers were eluted in the same order. In both monoene and diene mixtures the isomers with the double bond nearer the carboxyl were eluted first. The order for monoenes is 9, 12, 15; for the dienes, 9,12; 9,15; and 12,15.

Estimates of the amounts of the various monoene and diene isomers may be calculated. Monoene composition, based upon dibasic acid analysis and gas chromatographic data, is given in Table I.

TABLE I

Composition of Monoene Esters Formed by Hydrazine Reduction of Linolenic Acid

Monoenoate ester	Composition based on		
	Dibasic acid analysis	Gas chromatography	
		Packed column	Capillary column
	%	%	%
C_9	36.2	......	35.6
C_{10}	0.9	......	......
C_{12}	33.5	......	34.9
C_{15}	29.5	28.8	29.5

Diene composition, calculated from three independent methods of analysis, is given in Table II. Small amounts of other dibasic acids were combined with the C_6, C_9, and C_{12} acids in the calculations. Probably the value for 9,15-dienoate is low because adipic acid is lost during oxidation and isolation of the mixed dibasic acids. Except for this one value, the compositions calculated by the different methods agree well.

TABLE II

Composition of Diene Esters Formed by Hydrazine Reduction of Linolenic Acid

Dienoate ester	Composition based on			
	Dibasic acid analysis	Alkali isomerization	Gas chromatography	
			Packed column	Capillary column
	%	%	%	%
9.12+ 9,15	69.2 from $C_{8.9.10}$	......	......	......
9,15	24.3 from $C_{6.7}$	35.9 by difference	......	36.6
9,12	44.9 by difference	......	......	33.6
12,15	30.8 from C_{12}+C_{15}	......	28.0	29.8
9,12+12.15	......	64.1	......	......

From the composition of the monoenoic and dienoic esters it is apparent that any differences in the reactivity of the double bonds are small. The composition of the monoenoates suggests a slightly decreasing reactivity for the double bonds nearer the carboxyl.

Acknowledgments

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REFERENCES

1. Aylward, F., and Rao, C.V.N., J. Appl. Chem., *6*, 248 (1956).
2. *Ibid.*, *6*, 559 (1956).
3. *Ibid.*, *7*, 134 (1957).
4. *Ibid.*, *7*, 137 (1957).
5. Rao, C.V.N., J. Sci. Industrial Res., *17B*, 204 (1958).
6. *Ibid.*, *18B*, 131 (1959).
7. Scholfield, C.R., Jones, E.P., Nowakowska, J., Selke, E., Sreenivasan, B., and Dutton, H.J., J. Am. Oil Chemists' Soc., *37*, 579–582 (1960).
8. Scholfield, C.R., Nowakowska, J., and Dutton, H.J., *ibid.*, *37*, 27–30 (1960).
9. Brice, B.A., Swain, M.L., Herb, S.F., Nichols, P.L. Jr., and Riemenschneider, R.W., *ibid.*, *29*, 279–287 (1952).
10. Jones, E.P., and Stolp, J.A., *ibid.*, *35*, 71–76 (1958).
11. von Mikusch, J.D., Angew. Chem., *62*, 475 (1950).

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