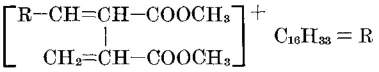
A peak at 380 is explainable from the same intermediate losing only one R with hydrogen transfer to give



$$\left[\begin{array}{c}\mathrm{R{-}CH{=}CH{-}COOCH_3}\\ |\\ \mathrm{CH_2{=}CH{-}COOCH_3}\end{array}\right]^{+}\quad \mathrm{C_{16}H_{33}} = \mathrm{R}$$

Discussion

While the intensity of various fragmentation peaks relative to the base peak cannot be related strictly quantitatively to the amt of structures in different dimers giving rise to the peaks, the mass spectrographic data given above, taken as a whole, are an elegant confirmation and extension of the chemical evidence for considerable α-linkage, and for the identity of the α-,α'-linked dimer isolated via the cyclic anhydride. Linkage at positions other than α- appears to be random.

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The Geometric Isomers of Conjugated Octadecadienoates from Dehydrated Methyl Ricinoleate

D. R. BODY and F. B. SHORLAND, Fats Research Division, Department of Scientific and Industrial Research, Wellington, New Zealand

Abstract

The dehydration of methyl ricinoleate by heating *in vacuo* in the presence of $KHSO_4$ resulted in the formation of the following conjugated octadecadienoates expressed as a percentage of the final product: *cis, trans (trans, cis)*, 14.3; *cis, cis*, 11.2; *trans, trans*, 7.3. The isomers contained the double bonds predominantly in the 9,11 position but the possible presence of traces of 8,10 and other conjugated isomers is not excluded. Using urea "inclusion" fractionation and low temp crystallization from acetone methyl, *cis*-9, *cis*-11-octadecadienoate was isolated.

The methyl esters of commercially dehydrated castor oil fatty acids on the other hand, contained the following percentages of conjugated octadecadienoate isomers: *cis, trans (trans, cis)*, 20.3; *cis, cis*, 8.0; *trans, trans*, 5.4. From these mixtures conc of *cis, trans (trans, cis)*- and *trans, trans*-octadecadienoates were prepared by fractional distillation and low temp crystallization. It was found that the conjugated octadecadienoates consisted of mixtures of positional isomers with double bonds mainly in the 8,10 and 9,11 positions with lesser amounts in the 7,9 and 10,12 positions.

Introduction

CONJUGATED *cis, cis*-octadecadienoic acids have not been reported as constituents of natural products, but *cis*-9, *cis*-11- and *cis*-10, *cis*-12-octadecadienoic acids (1) as well as the methyl esters of the latter (2) have been synthesised using acetylenic intermediates. In addition, we have shown that during dehydration of methyl ricinoleate, not only are *trans, trans*- and *cis, trans (trans, cis)*-octadecadienoates produced in agreement with the results of previous investigations by Jackson, Paschke, Tolberg, Boyd and Wheeler (3), using dehydrated castor oil, but there also are formed *cis, cis* conjugated isomers (4). The purpose of the work now reported was to elucidate the position of the double bonds in the conjugated *cis, cis* isomers and to reinvestigate in the light of the new techniques and knowledge the related conjugated isomers previously examined by other investigators (3,5,6).

Our interest in the present work stems from a general project to investigate more closely the wide range of isomeric octadecadienoic acids found in ruminant fats. Using Reiser's observation (7) that sheep rumen contents hydrogenate linolenic acid in linseed oil to linoleic acid, workers in the Fats Research Division have shown (8) that in pasture fed ruminants, the main dietary fatty acid, linolenic acid, is converted into *trans* and positional isomers of linoleic acid, as well as into oleic acid isomers and stearic acid.

Procedures

Gas-Liquid Chromatography. The GLC analyses were made at 207C using packed columns (254 x 0.65 cm I.D.) with argon as carrier gas in conjunction with the ionising detector described by Lovelock, James and Piper (9). The determination of the retention times relative to methyl stearate was as described by Gerson (10). (Throughout the composition of the methyl esters is expressed as moles % on the assumption that the detector response is proportional to the mol wt.) As a guide to the composition of the fractions obtained during the separation of the conjugated octadecadienoates, the relative retention volumes given by Farquhar, Insull, Rosen, Stoffel and Ahrens (11) were generally used. In addition, the data provided by Beerthuis, Dijkstra, Keppler and Recourt (12) assisted in locating the peaks corresponding to the *cis, trans (trans, cis)*- and *trans, trans*-octadecadienoates. Two types of liquid phase comprising a) 20% (w/w) diethylene glycol adipate (DEGA), and b) 5% (w/w) Apiezon L (ApL) were applied with 30–80 mesh celite (British Drug Houses Ltd., Poole, England) as the solid support.

Infrared Spectrophotometry. Pure methyl elaidate prepared as described by Jart (13) was used as a standard in the determination of the amt of *trans* double bonds. The melting point of the purified elaidic acid used to prepare methyl elaidate was 43.6–43.8C as compared with 43.8–44.0C recorded by Jart (13). An approx measure of the concn of conjugated *trans, trans* isomers was obtained by comparing the ratios of *trans* absorption at 986 cm^{-1} (3) to the absorption at 1450 cm^{-1} corresponding to the deformation fre-

TABLE I
The Composition of the Fractions Obtained by Urea 'Inclusion' Precipitation of Dehydrated Methyl Ricinoleate Using GLC *

Fraction	Composition (moles %)					
	D_{12} (original	$D_{12}S_1$ †	$D_{12}S_2$	$D_{12}S_3$	$D_{12}S_4$	$D_{12}L$
Recovered wt (g)	56	11.3	15.2	14.0	10.6	3.9 ‡
Methyl esters						
16:0	0.7	3.9	0.1	......	......	
18:1/18:2	64.8	49.9	59.5	73.3	63.8	
18:0	1.0	3.7	......	......	......	
18:2(c.t)(t,c) §	14.3	11.1	10.7	16.5	26.8	
18:2(c,c)	11.2	16.6	19.7	6.8	3.4	
18:2(t,t)	7.3	14.1	9.1	3.4	2.4	
Ricinoleate	0.7	0.7	0.9	......	3.6	

* Column: (w/w) ApL on celite at 207C.
† Throughout all Tables and the Figure recorded in this paper, S = precipitate, L = filtrate.
‡ Discarded.
§ c = *cis*, t = *trans*.

quency of $-C-CH_3$ (14) using as a basis the corresponding values obtained for methyl elaidate and allowing for the shift in frequency of the *trans* double bond. For routine assays, the measurements were made on an Infracord 137 (Perkin Elmer) but for the standards and purified fractions the Perkin Elmer Model 21 instrument was used. The absorptions were measured throughout as films on KBr discs.

Ultraviolet Spectrophotometry. The UV absorption measurements were determined on a Beckman model DU spectrophotometer using a 1-cm quartz cell with absolute alcohol (E. Merck, A.G., Darmstadt, Germany) as solvent.

Determination of the Position of the Double Bonds. The oxidation procedure of Armstrong and Hilditch (15) as modified by Haverkamp Begemann, Keppler and Boekenoogen (16) was used. However, whereas Haverkamp Begemann et al. (16) oxidized the methyl esters for several hr we have adhered to a 2-hr period because as shown below increasing the time results in secondary oxidation products. The method of extraction of the oxidation products was also varied to suit the preparations of the methyl esters of the dibasic acids required for the determination of their composition by GLC in place of partition chromatography used by Haverkamp Begemann et al. (16). Instead of extracting with aqueous sodium carbonate the ether extract was washed with distilled water (1/10 vol) five times. The ether layer was evaporated on the water bath, dried *in vacuo,* and the residue methylated with diazomethane as described by Schlenk and Gellerman (17).

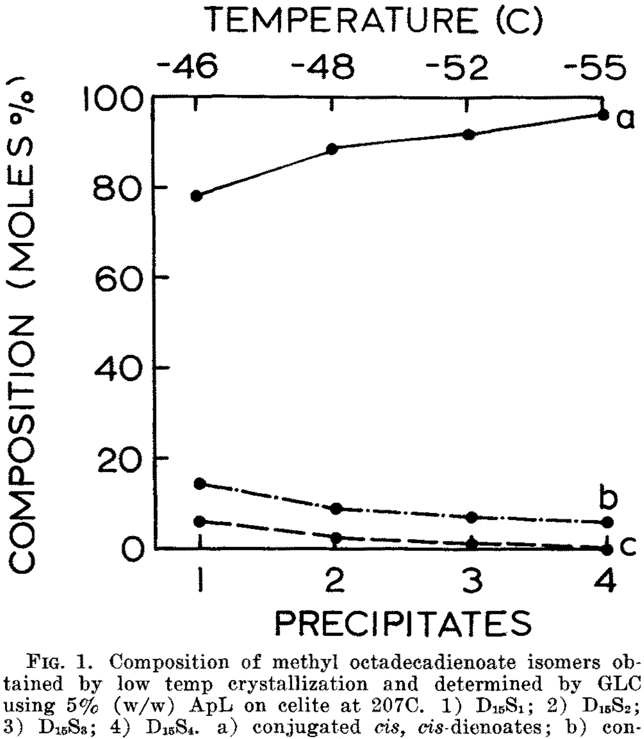

FIG. 1. Composition of methyl octadecadienoate isomers obtained by low temp crystallization and determined by GLC using 5% (w/w) ApL on celite at 207C. 1) $D_{15}S_1$; 2) $D_{15}S_2$; 3) $D_{15}S_3$; 4) $D_{15}S_4$. a) conjugated *cis, cis*-dienoates; b) conjugated *trans, trans*-dienoates; c) conjugated *cis, trans(trans, cis)*-dienoates.

TABLE II
Fractional Distillation *in vacuo* of the Methyl Esters of Commercial Dehydrated Castor Oil Fatty Acids. The Composition Was Determined by GLC *

Fractionation			Composition (moles %)					
			Conjugated					
Fraction	bp at 0.07 mm Hg (c)	Wt (g)	18.1/ 18:2	18:2 (c,t) (t,c) †		18:2 (c,c)	18:2 (t,t)	Remainder
Commercial dehydrated castor oil fatty acids	....	34.0	28.4	20.3		8.0	5.4	37.9
Distillates								
A_1	76–100	1.07	......	......		......	......	100 ‡
A_2	100–115	0.67	49.9	......		......	......	53.1
A_3	115–119	4.31	88.6		6.8	......	......	4.6
A_4	120–122	2.42	71.4	14.3		8.9	tr	5.4
A_5	122–123	2.16	26.6	50.6		18.1	0.9	3.8
A_6	123–124	2.36	4.4	67.8		19.0	8.3	0.5
A_7	124–125	2.25	1.3	52.4		20.4	25.6	0.3
A_8	125–126	2.36	0.9	18.3		14.2	63.9	2.8
A_9	126–140	9.68	0.7		5.1		3.7	90.5 §
A_R	>140	6.34 ‖						
		33.62						

* Column; 5% ApL on celite at 207C.
† c = *cis*, t = *trans*.
‡ Represents mainly methyl undecenoate.
§ Represents methyl ricinoleate.
‖ Polymerised material not detected by GLC.

To test the effectiveness of the method, pure methyl linoleate prepared by the method of Johnson and Ali (18) was oxidized for two hr at 50C. The sample (102.0 mg) yielded 87.5 mg of oxidation products, which were methylated and the solvents removed *in vacuo* at room temp. The methyl esters of monocarboxylic acids also were removed during evaporation as the residue (70.0 mg) on GLC using a 20% (w/w) DEGA on celite packing at 207C, yielded dimethyl azelate (96.6%) and dimethyl suberate (3.4%) with only a trace of methyl linoleate. A longer oxidation period produced increasing amt of secondary oxidation products. For example, methyl linoleate when oxidized for four hr yielded dimethyl pimelate (1.1%). Repetition of these experiments gave similar results. For two hr, the standard deviations for the yields of dibasic acid were low (±0.1%) but over four hr they were increased (±0.5%) together with the range of secondary oxidation products. The applicability of this technique to conjugated isomers is supported to some extent by the results (Table IV) for the purified methyl *cis*-9, *cis*-11-octadecadienoate isolated as described below. The determination of the positions of the double bonds in the series of the methyl octadecadienoate isomers investigated in this study was therefore based on the 2-hr period.

Results

Methyl cis-9, cis-11-Octadecadienoate. Using the well known dehydration procedure [cf Ralston (19)], methyl ricinoleate (93 g) supplied by the Nutrition Biochemical Corp., USA was distilled *in vacuo* over potassium hydrogen sulfate (10 g) using a Vigreaux column (8 x 2.2 cm). The pot was heated gently under reduced pressure to remove the water formed during dehydration. When this phase had been completed the temperature was raised and a distillate D_{12} (56 g bp 135–152C at 0.17 mm Hg) collected. The purification of the conjugated *cis, cis*-octadecadienoate fraction was based on the work of Allen (2). The

TABLE III

Physical Properties of the Methyl Esters of the Conjugated Octadecadienoates Isolated in the Present Investigation

Fraction	Isomer	mp (c)	Infrared *		Ultraviolet		Gas-liquid chromatography ‡	
			CH=CH region (cm^{-1})	*Trans* region (cm^{-1})	λ max (mμ)	k †	ECL § (3)	Purity
BS$_2$	*cis,trans* (*trans,cis*)	—20 to 2	1651 Weak, ill defined	981 and 946 strong doublet	232	107.3	18.24	95.2
B$_1$L$_1$	*cis,trans* (*trans,cis*)	—61 to —57	1651 Weak, ill defined	981 and 946 strong doublet	232	84.4	18.24	79.2
CS$_2$	*trans,trans*	8.5 to 9.5	1621 Weak, ill defined	986 strong	230	115.5	18.72	94.5
D$_{14}$S$_5$	*trans,trans*	—3 to 3.6	1621 very weak, ill defined	986 strong	231	76.3	18.72	68.2
D$_{15}$S$_1$	*cis,cis*	—8 to —7	1598 weak, well defined	986 ‖ weak	235	90.8	18.46	94.2

* KBr disc film phase used.
† Specific extinction coefficient (1 cm 1 g/litre).
‡ Column; 5% (w/w) ApL on celite at 270C.
§ Equivalent carbon length using methyl stearate as standard; see reference (24) for explanation of ECL determination.
‖ Due to 5.8% conjugated *trans,trans* isomer present.

distillate D$_{12}$ was dissolved in 600 ml methanol containing 60 g urea and the precipitate was fractionated as indicated in Table I.

To conc the *cis, cis* conjugated isomer, fractions D$_{12}$S$_1$ and D$_{12}$S$_2$ were bulked, denoted D$_{14}$ and crystallized eight times from 10–20 vol acetone at temp ranging from —46 to —75C, using in each instance the insoluble fraction. The last two precipitates were also bulked, denoted D$_{15}$ and further purified by low temp crystallization as shown in Figure 1. The final precipitate, D$_{15}$S$_4$(0.31 g), showed a very low infrared absorption in the *trans* region, together with a weak but well defined absorption peak at 1598 cm^{-1}. The UV spectrum exhibited an absorption maximum at 235 mμ (2).

The dibasic acid formed on oxidation was almost entirely azelaic acid indicating that fraction D$_{15}$S$_4$ is methyl *cis*-9, *cis*-11-octadecadienoate. (See Tables III and IV).

Conjugated Methyl cis, trans (trans, cis)-Octadecadienoates. Following the observations of Terry and Wheeler (20) that nonconjugated and conjugated methyl octadecadienoates may be separated by fractional distillation *in vacuo,* the methyl esters (34 g) of commercial dehydrated castor oil fatty acids were fractionated using a coiled spring column E [Shorland (21)]. The results in Table II show that fractions A$_6$ and A$_8$ are rich in different types of conjugated octadecadienoates. Fraction A$_6$ contained mainly *cis, trans (trans, cis)* isomers as judged by the retention volume data given by Beerthuis et al. (12). This fraction denoted B (1.99 g) was therefore subjected to low temp crystallization from methanol (10 vol) at —40C. The precipitate BS$_1$(0.73 g) was redissolved in methanol (10 vol) at —40C and the precipitate BS$_2$ (0.37 g) collected to provide a conc of *cis, trans (trans, cis)* isomers. Both soluble fractions from BS$_1$ and BS$_2$ were bulked, denoted B$_1$(1.59 g) and recrystallized from acetone (10 vol) at —70C. The soluble fraction B$_1$L$_1$(1.30 g) was found by GLC to have the same relative retention volume as BS$_2$ indicating the presence of mainly *cis, trans (trans, cis)* isomers. Fractions BS$_2$ and B$_1$L$_1$ (Table III) both show a strong doublet at 981 and 946 cm^{-1} indicating the presence of *cis, trans (trans, cis)* conjugated double bonds (3) which is also supported by the UV absorption maximum at 232 mμ (22). The oxidation results given in Table IV indicate that fraction BS$_2$ consists mainly of 8,10 *cis, trans (trans, cis)* isomers whereas the more soluble fraction B$_1$L$_1$ contains more 9,11 *cis, trans (trans, cis)* isomers.

Conjugated Methyl trans, trans-Octadecadienoates. From the GLC retention volume data of Beerthuis et al. (12) fraction A$_8$ (Table II) appeared to contain mainly conjugated *trans, trans* isomers. This fraction, denoted C, (1.48 g) was therefore crystallized from methanol (10 vol) at —40C. The precipitate, CS$_1$ (0.52 g) was recrystallized as described giving a precipitate CS$_2$ (0.49 g) which was found to be the purified conjugated *trans, trans* isomer, as shown by a strong single peak at 986 cm^{-1} together with an ultraviolet absorption maximum at 230 mμ (3,5). The oxidation data show that CS$_2$ consists mainly of equal parts of methyl *trans*-8, *trans*-10 and methyl *trans*-9, *trans*-11-octadecadienoates. The melting point of CS$_2$ (8.5 to 9.0C) is lower than that of 24C given by Jackson et al. (3) for methyl *trans*-10, *trans*-12-octadecadienoate and is therefore consistent with the presence of the positional isomers indicated in Table IV, and also with von Mikusch's (23) data for mixtures of 10,12; 8,10 and 9,11; 8,10 *trans, trans*-octadecadienoic acids in which he found that the melting points of 10,12- and 9,11-octadecadienoic acids were reduced by 12 and 10C respectively.

Trans, trans-octadecadienoates formed during dehydration of methyl ricinoleate with potassium hydrogen sulfate (D$_{12}$, Table I)were also examined. In concentrating the *cis*-9, *cis*-11-octadecadienoate already described the second precipitate (D$_{14}$S$_2$, 6.32 g) obtained by low temp crystallization of D$_{14}$ was found by GLC to contain 30.5% of *trans, trans* conjugated isomers. Low temp crystallization of D$_{14}$S$_2$ twice at —40C from 10 vol methanol and once from acetone under the same conditions, using in each instance the precipitate, yielded an insoluble fraction (D$_{14}$S$_5$, 0.75 g). The composition of this fraction (moles %) measured by GLC, using 5% ApL on celite, was as follows: Conjugated *trans, trans*-octadecadienoate, 68.2; conjugated *cis, cis*-octadecadienoate, 10.0; conjugated *cis, trans (trans, cis)*-octadecadienoate, 7.1 non-conjugated octadecadienoate, 2.3; methyl palmitate, 10.5; methyl stearate, 1.9. Oxidation of D$_{14}$S$_5$ (Table IV) gave azelaic as the main (96.2%) dibasic acid formed.

The purified methyl esters of the conjugated octadecadienoic acids were hydrogenated in absolute al-

TABLE IV

GLC * Analyses of the Dimethyl Esters of Dibasic Acids Obtained by the Oxidation of Fractions of Conjugated Methyl Octadecadienoate Isomers

Fraction	Composition (moles %)				
	C$_6$	C$_7$	C$_8$	C$_9$	C$_{10}$
BS$_2$	2.7	12.1	60.0	17.4	7.8
B$_1$L$_1$	1.6	10.0	22.2	56.6	9.6
CS$_2$	1.3	6.1	38.9	41.6	12.1
D$_{14}$S$_5$	....	1.4	2.4	96.2	......
D$_{15}$S$_4$	....		4.5	95.5	.....
A$_6$	tr	17.5	38.0	37.5	7.0
A$_8$	tr	8.3	38.8	41.7	11.2
D$_{12}$	...	3.3	9.8	86.9	......
Alkali isomerized methyl linoleate	....	tr	7.3	59.4	33.3

* Column; 20% (w/w) DEGA on celite at 207C.

cohol at 50C using activated platinum oxide as catalyst. GLC analysis of the hydrogenated isomers of the conjugated methyl octadecadienoates showed in all instances the presence of methyl stearate only.

Discussion

Apart from fraction $D_{14}S_5$, which contained only 68.2% of the *trans, trans* isomer, the remaining conjugated methyloctadecadienoates were found by GLC to be 94.2–95.2% pure and to yield on hydrogenation pure methyl stearate. The geometrical isomers were distinguishable from each other by their ECL value (24). The presence of mainly conjugated double bonds is indicated by the strong UV absorption bands at 230–235 mμ. It is shown that GLC, with packed columns as used in the present work, does not separate methyl esters of positional isomers of conjugated octadecadienoic acids having the same geometrical configuration nor distinguish between *cis, trans* and *trans, cis* conjugated isomers. However, Litchfield et al. (25) using capillary columns resolved to some extent methyl *cis*-9, *trans*-12 and *trans*-9, *cis*-12-octadecadienoates.

Terry and Wheeler (20) have already shown that the methyl esters of non-conjugated octadecadienoic acids appear during fractional distillation *in vacuo* before those of the conjugated isomers. In the present work we also found some separation of the conjugated isomers: the order of volatility being *cis, trans (trans, cis)* > *cis, cis* > *trans, trans.* In agreement with Allen (2) urea 'inclusion' fractionation was found to proceed according to the linearity of the geometric molecular structure of conjugated methyl octadecadienoates; *trans, trans* precipitated first followed by *cis, cis* and then *cis, trans (trans, cis)* isomers. Low temp crystallization showed that the order of solubility of conjugated isomers in acetone is *cis, trans (trans, cis)* > *cis, cis* > *trans, trans.* Recently, Schofield et al. (26) using counter-current distribution between silver nitrate in 90% methanol and hexane found that conjugated and non-conjugated isomers were separated as well as to some extent the conjugated *cis, trans (trans, cis)*- and *trans, trans*-octadecadienoates.

The formation of the conjugated positional isomers appeared to depend on the conditions of the reaction used. von Mikusch (23) was unable to find *trans*-8, *trans*-10-octadecadienoic acid following the dehydration of castor oil fatty acids by sodium hydrogen sulfate. In support of this observation we have shown that similar catalytic dehydration of methyl ricinoleate (D_{12}) gives conjugated geometrical isomers with double bonds predominantly in the 9,11 position, as indicated by the oxidation data for fraction D_{12} (Table IV). As, however, conjugated dienes comprise only ca. 33% of this fraction it cannot be stated with certainty that these dienes belong entirely to the 9,11 series. Nevertheless, there is a high degree of probability of the predominance of 9,11 isomers as the conc of *cis, cis* conjugated and *trans, trans* conjugated octadecadienoates yielded respectively dimethyl azelate almost exclusively. This means that under the conditions used there was some geometrical isomerization, but no migration, of the 9,10 double bonds of methyl ricinoleate. The production of *trans*-9, *trans*-11-octadecadienoate (Mangold's ester) during dehydration of methyl ricinoleate by potassium hydrogen sulfate suggests the possibility of the formation of unconjugated methyl *trans*-9, *trans*-12-octadecadienoate but Litchfield et al. (25) using capillary GLC failed to locate this isomer in the products formed by this reaction. On the other hand, they found that methyl *trans*-9, *trans*-12-octadecadienoate was formed during the dehydration of methyl ricinelaidate. From the results it appears that elaidination of the 9 position occurs only in conjugated isomers. On the other hand, von Mikusch reported the presence of *trans*-8, *trans*-10-octadecadienoic acid in castor oil fatty acids after dehydration by commercial distillation. In the present work (Tables III and IV) the commercial preparation of dehydrated castor oil fatty acids contain mixtures of conjugated and positional isomers consisting mainly of 9,11; 8,10 together with lesser amt of 10,12- and 7,9-octadecadienoates. This indicates that the question of migration of the double bonds depends on the conditions under which the dehydration reaction occurs.

Mixtures of isomeric octadecadienoates have likewise been found by other investigators using alkali isomerized linoleic acid. For example, Nichols et al. (5) demonstrated the presence of *cis*-9, *trans*-11 and *trans*-10, *cis*-12- as well as von Mikusch's *trans*-10, *trans*-12-ocatdecadienoic acid. These results are supported by GLC retention volume data of Beerthuis et al. (12) for methyl *cis, trans (trans, cis)*- and *trans, trans*-octadecadienoates. More recently Schofield et al. (26) using GLC with capillary columns also obtained retention volume data for the *cis, trans; trans, cis* (which were partly separated from each other) and *trans, trans* isomers found in alkali isomerized linoleic acid. In addition, evidence for the occurrence of conjugated *cis, cis*-octadecadienoic acid was obtained. In the Fats Research Division our investigations on alkali isomerized linoleic acid using the method of Brice and Swain (22) generally confirm the work of previous investigators in showing the occurrence of conjugated positional isomers (8,10; 9,11 and 10,12) and of the conjugated geometrical (including *cis, cis*) isomers (27) (Table IV).

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