

Selective Hydrogenation With Copper Catalysts: I. Isolation and Identification of Isomers Formed During Hydrogenation of Linolenate¹

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Abstract

Methyl linolenate was hydrogenated with 10% copper chromite catalyst at 150 C and atmospheric hydrogen pressure. The product was separated into monoene, diene and triene fractions by countercurrent distribution. These fractions were further separated into various geometrical isomers. The double bond location in the various fractions was determined by reductive ozonolysis. Double bonds in both *cis* and *trans* monoene fractions, as well as in *cis,trans* and *trans,trans* conjugated dienes, were extensively isomerized. A monoene containing vinylic unsaturation was one of the major products. The nonconjugated dienes were mostly dienes whose double bonds were widely separated. Results are explained on the basis of conjugation of the double bonds in linolenate followed by hydrogen addition.

Introduction

Copper catalysts are by far more selective than nickel, platinum or palladium for reducing linolenate in soybean oil (1-3). Products formed from the hydrogenation of linolenate with nickel and platinum

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TABLE I
Analyses of Hydrogenated Methyl Linolenate

Catalyst	GLC, ^a %					<i>trans</i> , %	UV, a ₂₈₁
	M	D	T	CD	CDT		
Nickel (4)	37.2 ^b	40.8	21.1	37.2	0.5
Copper chromite	29.8	8.9	22.9 ^c	33.8	4.6	31.6	35.2

^a M, monoene; D, diene; T, triene; CD, conjugated diene; CDT, conjugated diene-triene.
^b Also 0.9% stearate.
^c Alkali isomerization.

TABLE II
Analyses of Countercurrent Distribution Fractions From
Hydrogenated Linolenate

Fraction	Wt, %	GLC, %	IR	UV
M ^a	29.9	100% M	63.4% <i>trans</i> ^b
MD	10.5	M = 46.4; D = 20.6; CD = 33.0
D	33.9	D = 16.5; CD = 83.5	a ₂₈₀ m μ = 86.8
DT	1.0	D = 3.6; T + CD = 86.1; CDT = 11.3	a ₂₃₀ m μ = 36.1; Linolenate ^c = 55.6%
T	24.8	T = 83.5; CDT = 16.5	6.0% <i>trans</i> ; a _{10.2} μ = 0.122; a _{10.6} μ = 0.021	a ₂₆₈ m μ = 0.22 a ₂₈₁ m μ = 15.5; Linolenate ^c = 85.5%

^a See Table I, Footnote a.

^b Also absorption bands due to vinyl group.

^c Alkali isomerization.

catalysts have already been characterized (4). Similar data with copper catalysts would be useful in explaining the mechanism of hydrogenation. The analysis, partial separation and characterization of the various isomers formed during hydrogenation of linolenate with copper chromite catalyst are described here.

Experimental Results

Methyl linolenate was prepared from the methyl esters of linseed oil by countercurrent distribution (CCD) between acetonitrile and hexane (5). Analysis by gas liquid chromatography (GLC) showed the linolenate to be better than 99% pure. UV and IR analyses showed the absence of conjugation and isolated *trans* bonds. Hydrogenation was carried out in a glass manometric apparatus (6) at 150 C and atmospheric pressure of hydrogen. Copper chromite (3 g) was heated to 350 C in air for 2 hr then cooled and placed in a hydrogenation flask. After the system was flushed with hydrogen gas, the temperature was increased to 150 C. The flask was evacuated and filled with fresh hydrogen. About 30 ml of methyl linolenate was then added and stirring was started. The rate of hydrogen uptake was measured from the drop in pressure in the hydrogen reservoir, which constantly fed hydrogen to the reactor at 0.5 psig. The reaction was stopped after 1 mole of hydrogen per mole of linolenate was added. Analytical data on the hydrogenated product and similar data from a nickel catalyst (4) are compared in Table I.

The copper chromite hydrogenated product was separated into monoene, diene and triene by CCD (Fig. 1). Analytical data on these fractions are given in Table II. The diene fraction was further fractionated by CCD with a silver nitrate system (7) as plotted in Figure 2; the analytical data for the various fractions are shown in Table III. The triene fraction was similarly fractionated. Since separation

TABLE III
 Analyses of Diene Fractions

Fraction	Wt, %	GLC, ^a %	IR	UV
A	80.3	100% CD; <i>trans,trans</i> <i>/cis,trans</i> \approx 2.3	$a_{10.15 \mu} = 0.851$; $a_{10.55 \mu} = 0.107$	$a_{230 m\mu} = 96.2$
B	2.4	D = 27.5; CD = 72.5	<i>trans</i> = 24.3%; $a_{10.15 \mu} = 0.211$; $a_{10.55 \mu} = 0.152$	$a_{234 m\mu} = 62.0$
C	9.0	100% D	<i>trans</i> = 64.4%	Conjugatable diene ^b = 27.2%
D	8.3	100% D	<i>trans</i> = 30.8% ^c	Conjugatable diene ^b = 2.7%

^a See Table I, Footnote a.

^b Alkali isomerization 1 hr.

^c Also absorption due to vinyl groups.

of components was poor, several transfers were combined to form individual fractions for analysis (Table IV).

The monoene fraction (Table II) was further separated into *cis* and *trans* fractions on a silver-saturated resin column (8). Monoene with a terminal double bond (Δ^{17} -octadecenoate) eluted as a separate peak after *cis* monoene. However for analytical purposes, Δ^{17} isomer was combined with the *cis* fraction. Conjugated dienes (Table III, Fraction A) were similarly separated into *trans,trans* and *cis,trans* fractions.

Various fractions from the hydrogenated product were ozonized in dichloromethane at -65°C and the ozonides reduced with triphenyl phosphine (9). The resulting aldehydes, aldehyde esters and dialdehydes were analyzed on a Model 810 F&M gas chromatograph equipped with a hydrogen flame detector and 4 ft \times $\frac{1}{4}$ in. dual aluminum columns packed with 10% EGSS-X on Gas-Chrom P, 100–120 mesh (organosilicon polyester packing obtained from Applied Science Laboratories, Inc., State College, Pa.). Column temperature was programmed at $6^\circ/\text{min}$ from 60–190 $^\circ\text{C}$ and held at 190 $^\circ\text{C}$ for the duration of the analysis (Fig. 3–5).

Methyl esters were analyzed with a Pye argon gas chromatograph, equipped with a 4 ft \times $\frac{1}{4}$ in. glass column packed with 10% EGSS-X on Gas-Chrom P, 100–120 mesh and with a Radium D ionization de-

tector. The column was held at 170 $^\circ\text{C}$ with a gas flow of 45 ml/min. The area under each peak was determined from an electronically integrated curve. UV and IR analyses were performed according to AOCS Official Methods (10). Alkali isomerization of diene fractions was carried out for 1 hr (11) to measure the total amount of conjugatable dienes.

Discussion

The dienes formed from the hydrogenation of linolenate with copper chromite consisted mostly of conjugated diene (Table I), whereas only traces of conjugated diene are formed with nickel catalyst. In the unreduced triene about 16% of the molecules had diene conjugation. GLC analysis showed several peaks for conjugated diene-triene, and all possible geometrical isomers are present as deduced from IR data (Table IV). Some conjugated diene-triene eluted after linolenate during CCD (transfers 800–911). This behavior indicates that the conjugated diene-triene in this fraction may have an all-*cis* configuration. The shifting of the maximum in the UV to longer wavelength (234 $m\mu$) is also indicative of *cis,cis* configuration (12). Apparently conjugated double bonds in conjugated diene-triene move away from the isolated double bond since ozonolysis (transfers 200–499; Table IV) showed dialdehydes with 4 to 8 carbon atoms. Only traces of conjugated trienes were found (Table II). Since conjugated trienes are selectively reduced by the catalyst (13), no appreciable accumulation is possible. Only a small amount (6%) of *cis* to *trans* isomerization of the double bonds occurred in the unreduced triene and the GLC and alkali-isomerization values for linolenate (Table IV) are in reasonable agreement. Ozonolysis of unreacted linolenate (transfers 640–799; Table IV) gave only one aldehyde ester with 9 carbon atoms which indicated that the double bonds remained in their original 9, 12 and 15 positions. Kinetic data

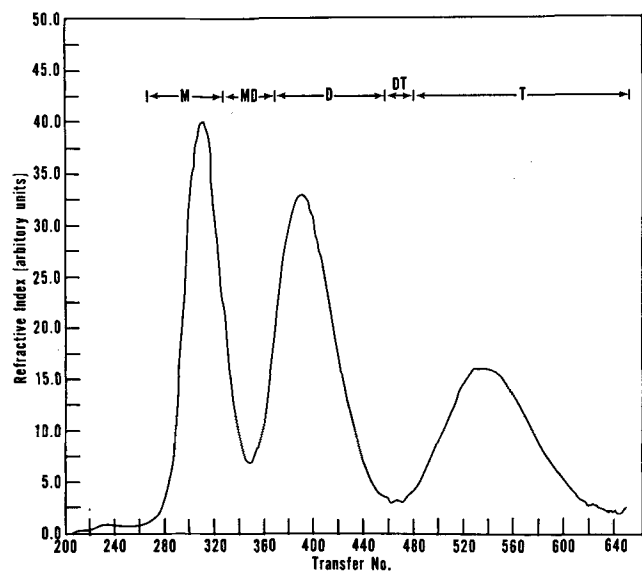


FIG. 1. Countercurrent distribution (CCD) of hydrogenated methyl linolenate between acetonitrile and hexane.

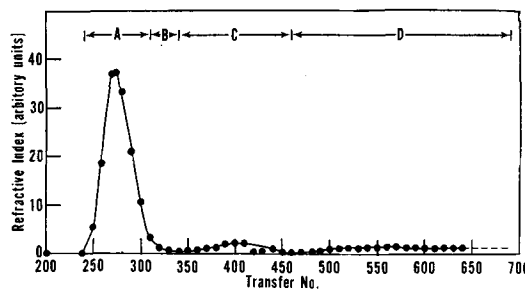


FIG. 2. CCD of diene fraction between 0.2 M silver nitrate in 90% methanol and hexane.

TABLE IV
Analyses of Triene Fractions

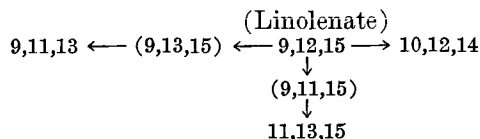
Transfer No.	Wt. %	GLC, ^a %	IR	UV
200-499	6.6	T = 12.4; CDT = 87.6	$a_{10.1 \mu} = 0.784$; $a_{10.5 \mu} = 0.044$; <i>trans</i> = 13.7%	$a_{268 m\mu} = 1.88$; $a_{280 m\mu} = 82.9$
500-589	5.5	T = 41.3; CDT = 58.7	$a_{10.1 \mu} = 0.361$; $a_{10.5 \mu} = 0.077$; <i>trans</i> = 31.5%	$a_{281 m\mu} = 55.7$; Linolenate ^b = 44.0%
590-639	14.1	T = 77.8; CDT = 22.2	<i>trans</i> = 2.7%	$a_{281 m\mu} = 20.1$; Linolenate ^b = 79.7%
640-799	89.4	T = 95.0; CDT = 5.0	<i>trans</i> = 1.1%	$a_{281 m\mu} = 4.5$; Linolenate ^b = 94.2%
800-911	4.4	T = 87.5; CDT = 12.5	<i>trans</i> = 0%	$a_{284 m\mu} = 12.5$; Linolenate ^b = 83.2%

^a See Table I, Footnote a.

^b Alkali isomerization.

(13) on the hydrogenation of linolenate indicate that the catalyst first conjugates the double bonds in linolenate to form conjugated triene and conjugated diene-triene. These are then hydrogenated to form conjugated dienes and nonconjugated dienes.

In conjugated diene (Table III) *trans,trans* isomer is the major product (*trans,trans/cis,trans* = 2.3). Only traces, if any, of the *cis,cis* isomers are found. These are concentrated in Fraction B (Table III) as indicated by GLC and the shift of the UV maximum to longer wavelength. In both *trans,trans* and *cis,trans* conjugated dienes, various positional isomers are found (Fig. 3) with the $\Delta^{10,12}$, $\Delta^{11,13}$ and $\Delta^{12,14}$ isomers predominating. These results are explained on the basis of conjugation of the double bonds in linolenate followed by hydrogenation. It was shown that β -eleostearate is reduced by 1,6 addition of hydrogen to form the 10,12 isomer of conjugated diene as the major product and that extensive isomerization of the unreduced conjugated triene occurred (14). On the basis of this finding, linolenate is first conjugated according to the following scheme:



Movement of the 9,10 and 15,16 double bonds towards the middle double bond in linolenate would result in $\Delta^{10,12,14}$ -octadecatrienoate, while movement of the middle double bond forms two conjugated diene-trienes ($\Delta^{9,11,15}$ and $\Delta^{9,13,15}$). The conjugated system in conjugated diene-triene would move towards the third double bond to form the other two conjugated trienes. The three conjugated triene isomers

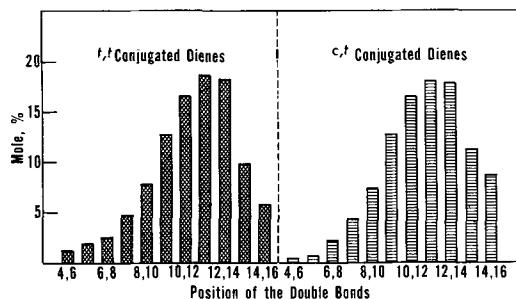


FIG. 3. Double bond distribution in conjugated dienes formed during hydrogenation of linolenate.

are then hydrogenated to form $\Delta^{10,12}$, $\Delta^{11,13}$ and $\Delta^{12,14}$ conjugated diene isomers. Isomerization of the three conjugated trienes followed by hydrogen addition will account for the other isomers formed.

The monoenes formed from linolenate are even more extensively isomerized (Fig. 4). According to the kinetic scheme postulated (13) monoenes are formed from conjugated diene. Figure 3 shows that conjugated dienes are extensively isomerized. Also, further isomerization occurs during hydrogenation of conjugated diene to monoenes (14). Hydrogen addition to conjugated diene seems to occur by both 1,2 and 1,4 addition with the latter being the preferred type of addition (14). Accordingly, Δ^{11} , Δ^{12} and Δ^{13} isomers should be formed from the three conjugated dienes that resulted from conjugated triene. These are indeed the major products, as seen in Figure 4, although extensive isomerization of conjugated systems during hydrogenation resulted in considerable scrambling of the double bonds up and down the chain. A large amount of Δ^{17} isomer (about 12% of monoene) accumulated during hydrogenation. This isomer eluted as a separate peak after the *cis* isomers during chromatography on a silver resin column. Identification of this isomer is based on IR, NMR and ozonolysis. This isomer has not previously been reported to form with other catalysts (4,15). It can be formed from a $\Delta^{15,17}$ isomer of conjugated diene by 1,2 addition. Since the $\Delta^{15,17}$ isomer is not found in conjugated dienes, it is apparently more reactive (due to terminal olefin) than the other isomers. Under the mild conditions of hydrogenation used, oleate did not isomerize (14). Thus, Δ^{17} monoene resulted from the hydrogenation of a diene and not by isomerization of monoenes.

The nonconjugated dienes formed from linolenate are mostly of the nonconjugatable type and are separated into two fractions by CCD (Table III, Fraction C and D). Their analyses by reductive ozonolysis (Fig. 5) are difficult to interpret. A large

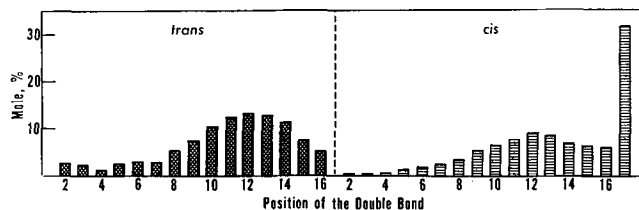


FIG. 4. Double bond distribution in *cis* and *trans* monoenes formed during hydrogenation of linolenate.

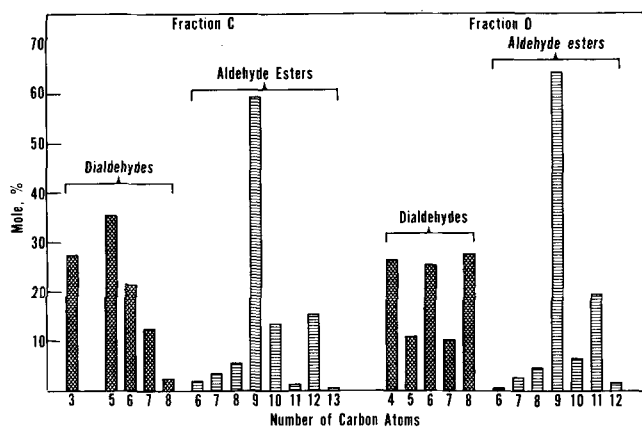


FIG. 5. Analysis by reductive ozonolysis of nonconjugated dienes formed during hydrogenation of linolenate.

number of diene isomers are possible. However, $\Delta^{9,17}$ -diene is inferred to be present in Fraction D. IR analysis indicated vinyl unsaturation. Reductive ozonolysis of a C_{18} diene could result in a C_8 dialdehyde fragment only if the first double bond in the diene is at or below the 9,10 position. The large amount of C_9 aldehyde ester together with minor amounts of aldehyde esters containing eight carbon atoms or less and the large amount of C_8 dialdehyde provide evidence for the presence of $\Delta^{9,17}$ -diene in Fraction D. The double bonds in dienes are separated by two to six carbon atoms, and a large amount of the diene has its first unsaturation at the 9,10 position. These dienes are formed from the two conjugated diene-trienes ($\Delta^{9,11,15}$ and $\Delta^{9,13,15}$) that are formed from linolenate. The conjugated systems in these molecules move extensively in both directions during hydrogenation (14). If the conjugated system moves towards the isolated double bond, then conjugated triene would result which will be hydrogenated to conjugated diene and then to monoene. However, if the conjugated double bonds move away

from the third double bond, then nonconjugatable dienes are formed by hydrogenation of these compounds. The nonconjugated diene formed from $\Delta^{9,13,15}$ isomer will have its first unsaturation at the 9,10 position. Therefore, a major portion of the nonconjugated diene formed should contain its first unsaturation at the 9,10 position. About 60% to 65% of the nonconjugated diene (Fig. 5) had its first unsaturation at the 9,10 position. The nonconjugated dienes formed during hydrogenation of a synthetic mixture of $\Delta^{9,11,15}$ and $\Delta^{9,13,15}$ -octadecatrienoates upon ozonolysis gave products similar to nonconjugated dienes in Figure 5 (14).

The formation of various isomers from linolenate with copper catalyst has been explained on the premise that conjugation of the double bonds precedes the hydrogenation step and that extensive isomerization of conjugated double bonds occurs during hydrogenation. The validity of this hypothesis will become more apparent from kinetic and mechanism data presented in Part II and III (13,14).

ACKNOWLEDGMENT

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