analyzed several cocoa shell fats and poor quality cocoa butters. Such fats do not affect our method of analysis.

Nut oils from nuts added to chocolate will be detected and in most cases it is not possible to distinguish them from oils such as shea oil by this method. In this case slightly more sophisticated methods would have to be used if a correction for nut oils was required.

The accuracy and speed of this method for the detection and the determination of CBE in chocolate make it ideal for the routine analysis of chocolate for the purpose of minotoring the addition of CBE. In just a few cases, the method will not yield unequivocal results and supplementary analyses such as sterol or *trans* acid determination would be required.

ACKNOWLEDGMENT

J. Taylor helped with statistical interpretation of the data.

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Selective Hydrogenation with Copper Catalysts: V. Kinetics and Mechanism at High Pressure[1]

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ABSTRACT

The mechanism of hydrogenation at 900-950 psi with copper-chromite catalyst was investigated with pure methyl esters as well as their mixtures. A comparison of double bond distribution in *trans*-monoenes formed during hydrogenation of linoleate and alkali-conjugated linoleate revealed that 85-95% of the double bonds in linoleate conjugated prior to hydrogenation. The mode of hydrogen addition to conjugated triene and diene at high pressure is similar to that at low pressure but positional and geometric isomerizations of unreduced conjugated esters were less at high pressure. Geometric isomerization of methyl linoleate and linolenate was considerable at high pressure whereas it was negligible at low pressure. The absence of conjugated products during hydrogenation of polyunsaturated fatty acid esters resulted from their high reactivity. Conjugated dienes are 12 times more reactive than the triene, methyl linolenate, and 31 times more reactive than the diene, methyl linoleate. The products of methyl linolenate hydrogenation were the same as those predicted by the conjugation mechanism.

INTRODUCTION

Studies on the selective hydrogenation of soybean oil with copper catalysts at pressures between 500 and 3000 psi (1) revealed a number of features that are different from low-pressure hydrogenation. Minor amounts of conjugated dienes that appear in the product during low-pressure hydrogenation were eliminated at high pressures. The amount of *trans* isomers formed for each unit of iodine value drop was significantly greater at high pressures. Despite these differences, the selectivity for the reduction of linolenate remained the same. According to theory (2), increased pressure decreases linoleate selectivity (S_L) and *trans* isomerization. In the hope of explaining the anomalous behavior of copper catalysts at high pressures, the mechanism of hydrogenation was investigated with pure unsaturated fatty acid esters varying in number, position and geometric configuration of double bonds as model compounds. The relative reaction rates were determined by hydrogenating mixtures of fatty acid esters. The results of these studies were compared with those obtained at low pressure (3-5) where conjugation was shown to be an essential step prior to hydrogenation.

EXPERIMENTAL PROCEDURES

Preparation of Pure Methyl Esters

Methyl linolenate (6) and methyl linoleate (7) were prepared by counter double-current distribution of linseed and safflower oil esters, respectively. β-Eleostearic (*t*9,*t*11,*t*13-octadecatrienoic) acid was prepared from tung oil by low-temperature crystallization (8) and esterified with methanolic hydrochloric acid and 2,2-dimethoxy propane (9). Methyl *c*9,*t*11- and *t*10,*c*12-octadecadienoate mixture was obtained by conjugation of methy linoleate with alkali.

Hydrogenation. Reductions were carried out in a 150-ml, magnetically stirred, Magna-Dash autoclave. The fatty ester and 0.5% commercial copper chromite catalyst (Harshaw-CU 1106P) were heated electrically to 170 C under vacuum.

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With β-eleostearate reaction was carried out at 150 C. Hydrogen was admitted into the autoclave to 950 psi. When pressure dropped to 900 psi, hydrogen gas was readmitted to 950 psi. Samples were withdrawn at predetermined intervals.

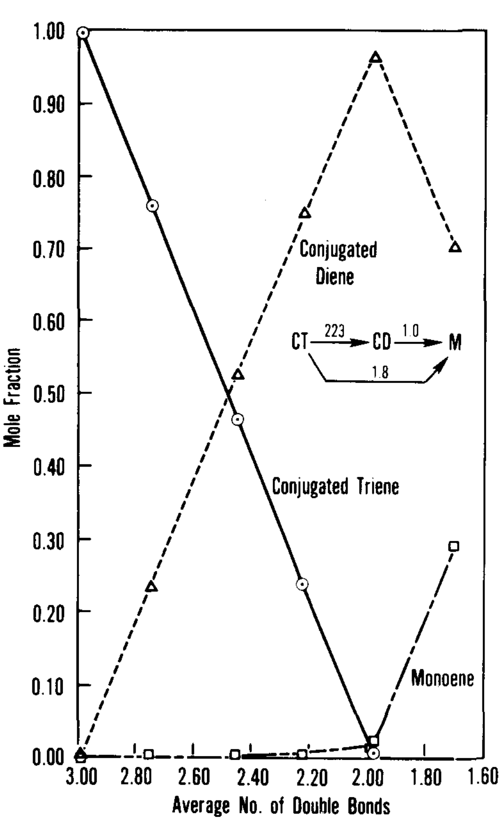
Analytical methods. Fatty acid compositions of partially hydrogenated methyl esters were determined isothermally at 190 C with a Varian Aerograph Model 1860 GC instrument equipped with dual 6 ft × 1/8 in. stainless-steel columns, packed with 15% EGSS-X on Gas-Chrom P, 100/120 mesh and with flame ionization detectors. Nitrogen carrier gas was used at a flow rate of 20 ml/min. The percentage of each ester was calculated as the percentage of the total area of all the peaks. Conjugatable dienes were determined by the official AOCS method (10) except that alkali-conjugation was carried out for 1 hr. The percentage of isolated *trans* unsaturation was measured by infrared (IR) absorption of methyl esters at 10.36 μm and by comparison with methyl elaidate standard. Methyl esters were separated into saturates, monoenes, dienes and trienes by high performance liquid chromatography (HPLC) (11). Conjugated dienes and conjugated trienes could not be separated by HPLC. Therefore, hydrogenated product from β-eleostearate was separated by reverse-phase chromatography on a rubber column (12). Further separation of monoenes into *cis*- and *trans*-fractions and conjugated dienes into *cis,trans*- and *trans,trans*-fractions was accomplished on a silver-exchanged resin column (13). Positional isomers of various monoene, conjugated diene and conjugated triene fractions were determined by reductive ozonolysis followed by gas liquid chromatography (GLC) analysis of the fragments (14). Relative reaction rate constants were calculated by a digital computer according to a DRATE program written by Butterfield (15).

RESULTS AND DISCUSSION

Hydrogenation of Conjugated Trienes

If polyunsaturates conjugate prior to hydrogenation, information on the composition of products formed from conjugated esters will be useful to better understand the mechanism. β-Eleostearate reduced exclusively to conjugated dienes (Fig. 1), which did not further hydrogenate until all the conjugated triene disappeared. From these results conjugated triene was calculated to be over 200 times more reactive than conjugated diene. This high selectivity implies that the reduction of β-eleostearate over conjugated diene is nearly absolute. This is quite evident from Figure 1,. where hardly any monoene was formed when conjugated triene disappeared completely. Similar high selectivity for conjugated triene over conjugated diene was observed with copper chromite catalyst during atmospheric hydrogenation (16).

When 54% of β-eleostearate was reduced, the double bond distribution in the products shown in Figure 2 resulted. Conjugated dienes are formed either by 1,2- or 1,6-addition of hydrogen to the double bonds in β-eleostearate. Equal amounts of $\Delta^{9,11}$ and $\Delta^{11,13}$ conjugated diene isomers result by 1,2-addition, whereas 1,6-addition yields the $\Delta^{10,12}$ isomer. Nearly equal amounts of these 3 isomers are formed which indicates that 1,2-addition is preferred over 1,6-addition. Similar results were obtained during atmospheric hydrogenation (5). All 3 isomers could result by 1,4-addition of hydrogen followed by conjugation of the resulting $\Delta^{9,12}$ and $\Delta^{10,13}$ methylene-interrupted dienes. This possibility was discounted since methylene-interrupted dienes were not found. It also might be argued that the $\Delta^{10,12}$ isomer was solely the result of 1,2-addition of hydrogen to the $\Delta^{8,10,12}$ and $\Delta^{10,12,14}$ trienes which were in turn formed by isomerization. This is unlikely because the $\Delta^{10,12}$ isomer was found in large amounts even during early stages of hydrogenation (5% reduction) when $\Delta^{8,10,12}$ and $\Delta^{10,12,14}$ isomers were insignificant compared to $\Delta^{9,11,13}$ triene (17). Furthermore, $\Delta^{10,12}$ was formed with nickel and Lindlar catalysts that did not isomerize unreduced conjugated triene (18).



$$CT \xrightarrow{223} CD \xrightarrow{1.0} M, \quad CT \xrightarrow{1.8} M$$

FIG. 1. Computer-drawn curves for the course of hydrogenation of β-eleostearate. CT = conjugated triene, CD = conjugated diene, M = monoene.

After 54% of β-eleostearate was reduced, 44% of the remaining conjugated trienes had double bonds in their original 9,11 and 13 positions. GLC analysis also indicated that geometric isomers formed. However, isomerization of β-eleostearate was much smaller at high pressure compared to atmospheric hydrogenation (5) where only 28% of the conjugated triene had double bonds at 9,11,13 positions after 50% reduction.

Hydrogenation of Conjugated Diene

During hydrogenation of alkali-conjugated linoleate (equimixture of *c*9,*t*11- and *t*10,*c*12-octadecadienoate), some *c,t*-conjugated diene isomerized to *t,t*-isomer (Table I). Positional isomers of conjugated diene also formed. For example, in the 5-min sample, only 68% of the double bonds were found in the original 9,11 and 10,12 positions, whereas 27% of the conjugated dienes had double bonds at 8,10 and 11,13 positions. The remainder had double bonds at 7,9 and 12,14 positions. Isomerization of conjugated dienes was, however, much less than that observed at atmospheric hydrogenation (5) where only 40% of the conjugated dienes had double bonds in the 9,11 and 10,12 positions after 50% reduction.

Hydrogenation of Linoleate

Hydrogenation of linoleate was accompanied by geometric isomerization (Table II). For example, after 58% reduction

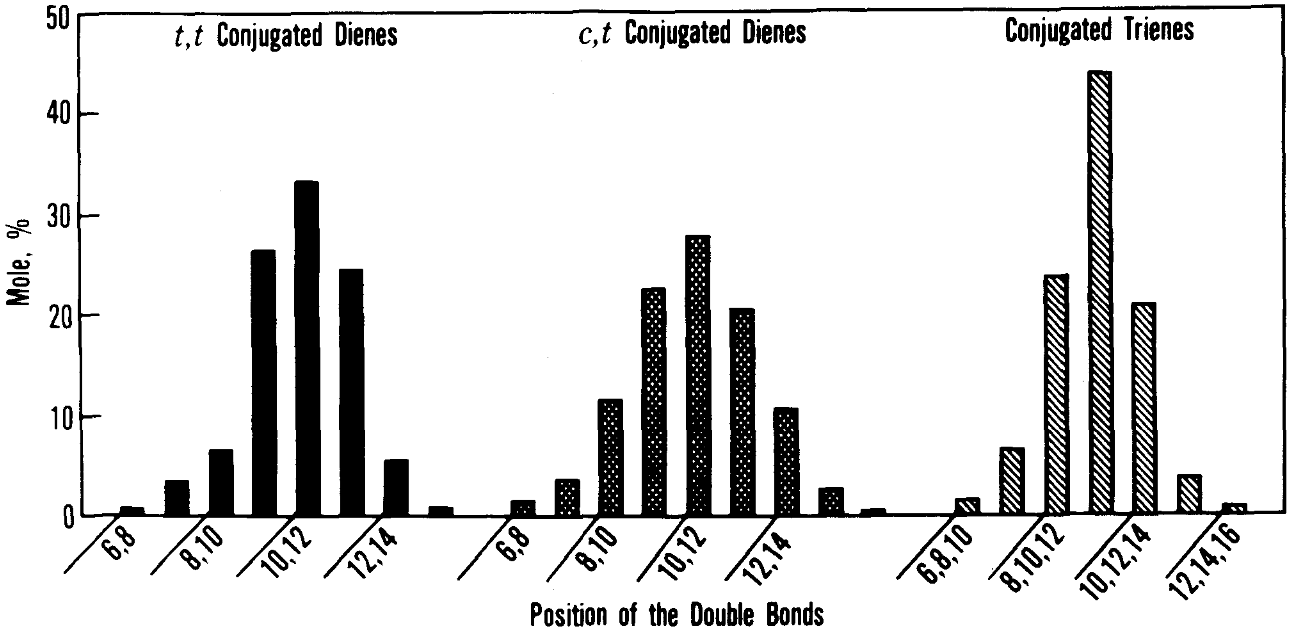


FIG. 2. Double bond distribution in various fractions formed during hydrogenation of β-eleostearate.

(59-min sample), 39% *trans* unsaturation was found in the remaining diene. In contrast, no *trans*-isomers of linoleate were formed at 30 psi (19). Some nonconjugatable diene was also formed during hydrogenation at high pressure. About 12% of the remaining diene in the 100-min sample (Table II) was not conjugatable. At low pressures (19), all remaining diene was conjugatable. Conjugated diene was not found in the products at high pressure, but up to 4% conjugated diene was found at 30 psi (19).

When methyl linoleate and alkali-conjugated linoleate were hydrogenated to the same extent (5- and 59-min samples of Tables I and II, respectively), the double bond distribution of the *trans*-monoenes (Fig. 3) was quite similar, which strongly suggests that the double bonds in linoleate conjugated prior to hydrogenation. The percentage of linoleate hydrogenated through a conjugated intermediate can be estimated by comparing the proportions of Δ^{10} and Δ^{11} *trans*-monoenes formed from linoleate to those from alkali-conjugated linoleate. According to this criterion, 95% of the double bonds in linoleate conjugated prior to hydrogenation. Recently Van Der Plank and Van Oosten (20) suggested plotting the sum of Δ^{10} and Δ^{11} isomers against the sum of Δ^{9} and Δ^{12} isomers from linoleate and alkali-conjugated linoleate and comparing the slopes. By this method, 85% of the double bonds in linoleate conjugated prior to hydrogenation.

TABLE I

Fatty Acid Composition of Products from Hydrogenation of Alkali-conjugated Linoleate with Copper-chromite Catalyst[a]

Me ester	Time (min)			
	0	2	5	8
Monoene	0.4	24.8	54.6	76.5
% *trans* in monoene	-	69.8	69.0	71.7
Diene	3.5[b]	3.4	3.8	3.2
c,t-Conjugated diene	93.2	48.9	15.4	7.1
t,t-Conjugated diene	2.8	22.9	26.1	13.2

[a] Catalyst (0.5%) at 170 C and 900-950 psig.
[b] Unreacted methyl linoleate.

TABLE II

Hydrogenation of Methyl Linoleate with Copper-chromite Catalyst[a]

Me ester	Time (min)		
	25	59	100
Monoene	39.2	57.8	69.2
% *trans* in monoene	56.1	58.8	59.2
Diene	60.8	42.2	30.8
% *trans* in diene	20.9	38.9	51.8
% Diene, conjugatable	95.5	94.1	88.1

[a] Catalyst (0.5%) at 170 C and 900-950 psig.

Hydrogenation of Methyl Linolenate

Hydrogenation of methyl linolenate with copper-chromite

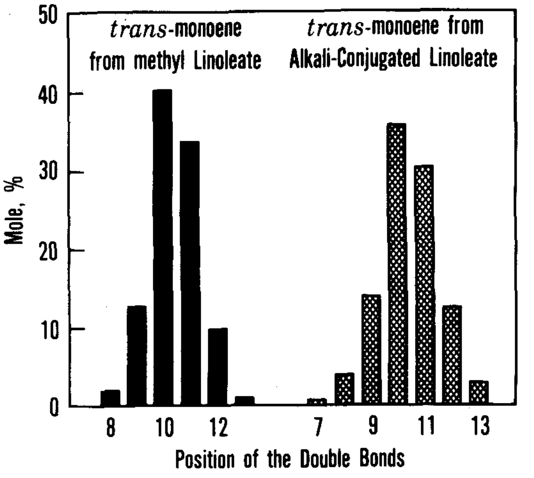


FIG. 3. Double bond distribution in *trans*-monoenes formed during hydrogenation of methyl linoleate and alkali-conjugated linoleate. Monoenes from 5- and 59-min samples, respectively, of Tables I and II.

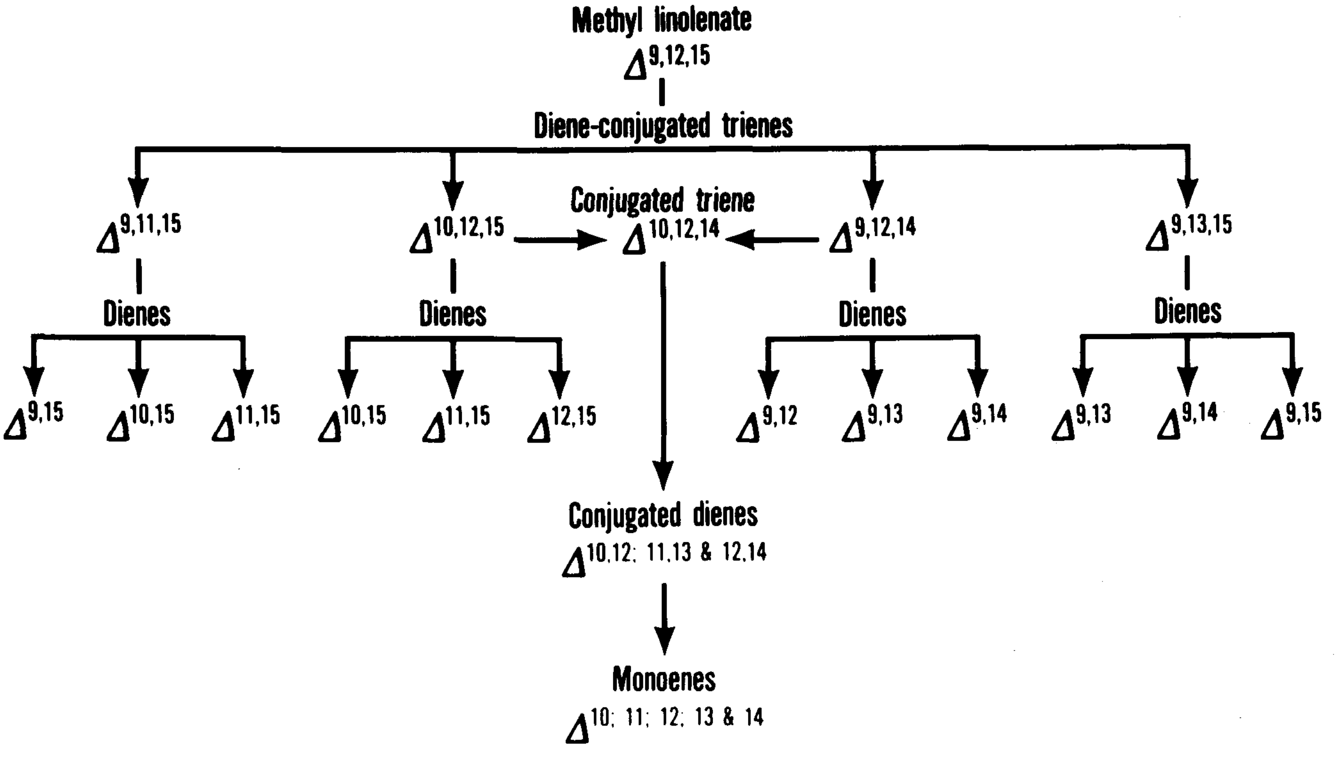
TABLE III

Fatty Acid Composition of Products Formed during Hydrogenation of Methyl Linolenate with Copper-chromite Catalyst[a]

Me ester	Time (min) 0	2	4	7	13	30
Palmitate	0.3	0.3	0.3	0.3	0.3	0.3
Stearate	0.1	0.2	0.2	0.2	0.1	0.3
Monoene	1.0	5.6	11.8	16.3	21.3	30.1
% *trans* in monoene	-	-	-	70.8	65.2	66.8
Diene	1.3	14.4	27.9	40.8	56.9	66.1
% *trans* in diene	-	-	-	49.3	50.3	62.9
% Diene, conjugatable	-	23.6	28.0	26.2	26.5	21.9
Triene	97.3	79.5	59.8	42.4	21.5	3.2
% *trans* in triene	-	-	-	23.8	48.2	-

[a]Catalyst (1%) at 170 C and 900-950 psig.

at high pressure (Table III) was accompanied by geometric isomerization. In 7- and 13-min samples, 24 and 48%, respectively, of the remaining triene had *trans*-unsaturation. Geometric isomerization was negligible during hydrogenation at atmospheric pressure (3). Conjugated dienes were absent at high pressure and conjugatable and nonconjugatable dienes were the major products. When all the triene disappeared (30 min), 30% monoene and 67% diene were formed. At low pressure, on the other hand, conjugated diene was the major product (3). After complete hydrogenation of triene at low pressure, 83% monoene and 16% diene were formed (4). Even though the products formed at high pressure were different from those at low pressure, conjugation prior to hydrogenation must still be the basic mechanism as shown in Scheme I. This scheme envisions the formation of conjugated intermediates that do not desorb from the catalyst surface until hydrogenated to nonconjugated products. Hydrogenation of diene-conjugated trienes results in both conjugatable and nonconjugatable dienes. Also, this mechanism predicts that a large proportion of the dienes should have their first double bond located at the 9,10-position. In fact, ozonolysis of the diene fraction from the 30-min sample (Table III) showed 62% of the dienes had their first double bond at the 9,10-position. The remainder of the dienes had their first double bond at 10,11- (12%), 11,12- (14%) and 12,13-positions (11%). Monoenes could form only through conjugated triene intermediates. It is true that conjugatable diene intermediates ($\Delta^{9,12}$ and $\Delta^{12,15}$) also form monoenes through conjugation. But since these dienes are much less reactive than triene ($K_{Le}/K_{Lo} = 10$), the monoenes contributed by conjugatable dienes compared to conjugated intermediates would not be significant. This mechanism predicts the formation of monoene isomers whose double bonds are at 10,11- through 14,15-positions. The double bond distribution in *trans*-monoenes (Fig. 4) from linolenate hydrogenation is consistent with the conjugation mechanism. The conjugation mechanism further predicts the formation of



SCHEME I

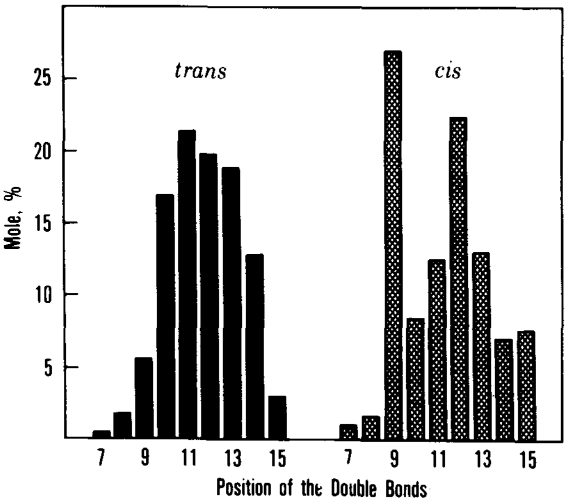


FIG. 4. Double bond distribution in *cis* and *trans* monoenes from methyl linolenate–7-min sample, Table III.

Δ^9, Δ^{12} and Δ^{15} *cis*-monoenes from conjugatable dienes. Surprisingly, Δ^{15}-*cis*-monoene was much smaller than the Δ^9 and Δ^{12} isomers (Fig. 4). This can be explained if we assume that $\Delta^{9,12}$ diene isomer is more reactive than the $\Delta^{12,15}$ isomer or that 1,2-addition of hydrogen to conjugated intermediates is preferential at the 15,16-position. Of course, no evidence exists for these assumptions.

Hydrogenation of methyl linolenate was simulated on a digital computer according to the scheme shown in Figure 5. The computer-drawn curves represent the best fit for the experimental points when the summed, squared error was at a minimum. The relative reaction rates shown in the inset were obtained. The scheme assumes the formation of monoene directly from linolenate without the conjugated triene and conjugated diene intermediates desorbing from the catalyst surface. Similarly, diene-conjugated triene is formed on the catalyst surface and will hydrogenate to either nonconjugatable (polymethylene interrupted) or conjugatable (single methylene interrupted) diene. The proposed scheme in Figure 5 is consistent with the conjugation mechanisms of Scheme I. The scheme in Figure 5 is, for the most part, similar to that proposed for low-pressure hydrogenation (4) except that at high pressure conjugated diene intermediates do not desorb from the catalyst surface because they are assumed to be much more reactive than single methylene-interrupted polyunsaturated fatty acids. The validity of this assumption was confirmed from the relative reaction rates of polyunsaturated fatty acids and their conjugated counterparts (Figs. 6-8).

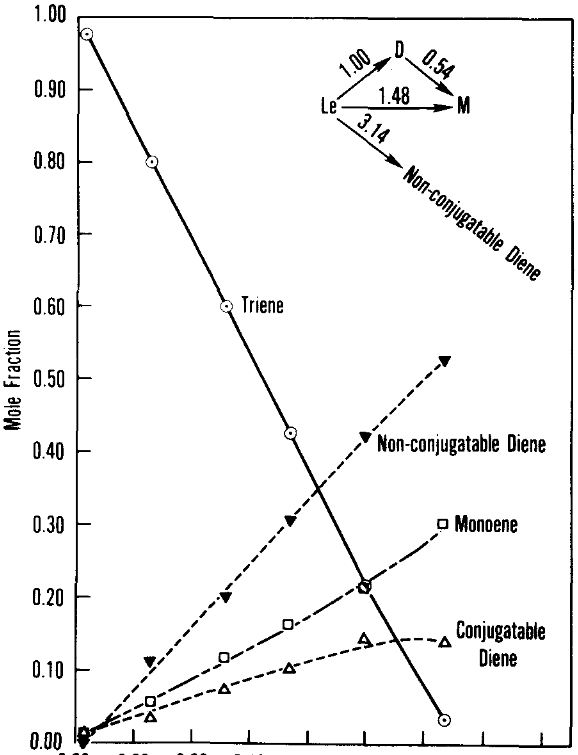


FIG. 5. Computer-drawn curves for the course of hydrogenation of methyl linolenate.

Hydrogenation of Conjugated and Unconjugated Ester Mixtures

Computer simulation of the hydrogenation of conjugated diene and linoleate (Fig. 6) indicated that conjugated diene is 31 times more reactive than linoleate. At atmospheric pressure (4), where the concentration of hydrogen is lower at the catalyst surface, the relative rates were 9:1. Conjugated triene is over 100 times more reactive than methyl linolenate (Fig. 7) and similar high selectivity for conjugated triene was observed for low-pressure hydrogenation (4). Even conjugated dienes are 12 times more reactive than the triene, methyl linolenate (Fig. 8). At atmospheric pressure (4), conjugated diene was less than half as reactive as methyl linolenate.

The results of our study indicate that, with few exceptions, the mechanism of hydrogenation at high pressure (900-950 psi) is similar to that at low pressure (0-30 psi). Polyunsaturated fatty esters conjugate prior to hydrogenation both at low and high pressures. The same conjugation mechanism, therefore, explains the high selectivity at

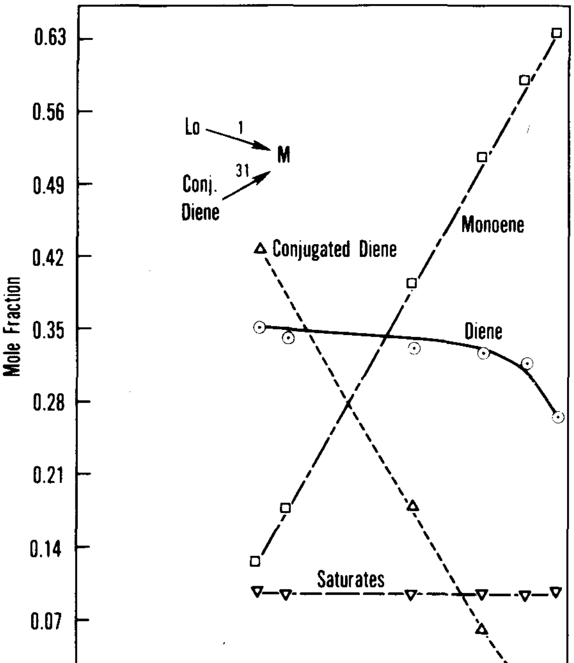


FIG. 6. Hydrogenation of methyl ester mixture of safflower and alkali-conjugated safflower oil.

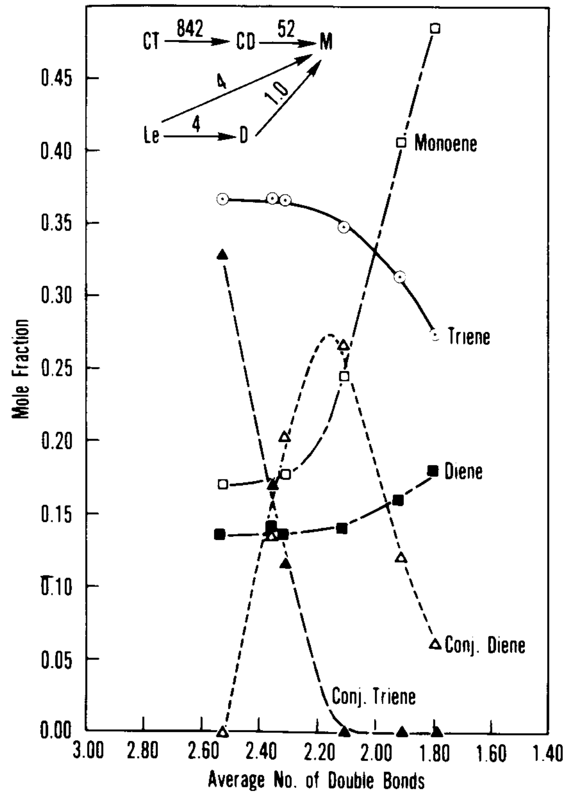


FIG. 7. Hydrogenation of methyl ester mixture of tung and linseed oil.

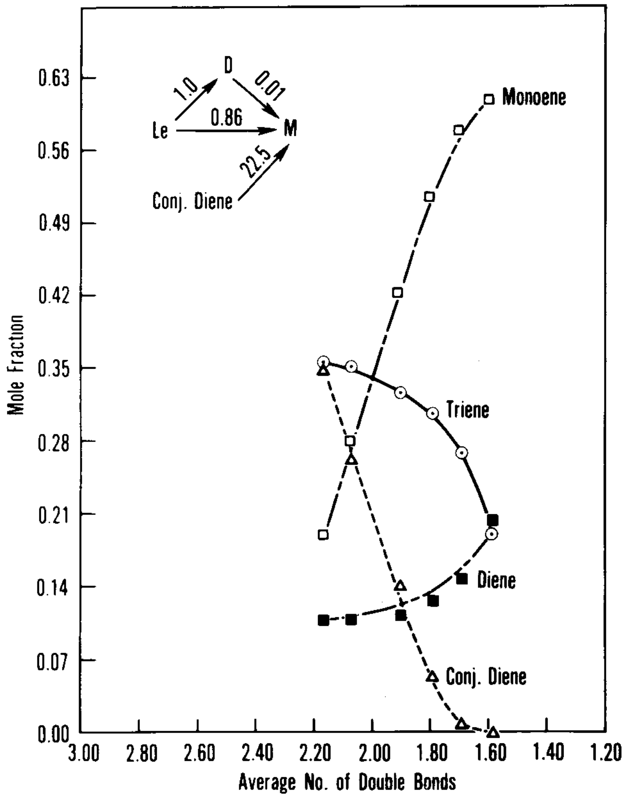


FIG. 8. Hydrogenation of methyl ester mixture of linseed and alkali-conjugated safflower oil.

high pressure (1). The mode of hydrogen addition to conjugated esters is similar at both pressure ranges although isomerization of conjugated esters was less at high pressure. Conjugated esters are preferentially hydrogenated over unconjugated esters at low and high pressures but more so at the higher pressure compared to the low pressure. In light of this observation, it is not surprising that conjugated dienes are absent from soybean oil hydrogenated at high pressures (1,21). One dissimilarity observed at the higher pressure is the isomerization of polyunsaturated esters to *trans* isomers. The increase in percentage of *trans* isomers at high pressures (21) primarily resulted from this isomerization reaction which was absent at the low pressure.

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