Selective Homogeneous Hydrogenation of Triunsaturated Fats Catalyzed by Tricarbonyl Chromium Complexes

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ABSTRACT

The need for a selective catalyst to hydrogenate linolenate in soybean oil has prompted our continuing study of various model triunsaturated fats. Hydrogenation of methyl β-eleostearate (methyl *trans,trans,trans*-9,11,13-octadecatrienoate) with $Cr(CO)_3$ complexes yielded diene products expected from 1,4-addition (*trans*-9,*cis*-12- and *cis*-10,*trans*-13-octadecadienoates). With α-eleostearate (*cis,trans,-trans*-9,11,13-octadecatrienoate), stereoselective 1,4-reduction of the *trans,trans*-diene portion yielded linoleate (*cis,cis*-9,12-octadecadienoate). However, *cis,trans*-1,4-dienes were also formed from the apparent isomerization of α- to β-eleostearate. Hydrogenation of methyl linolenate (methyl *cis,cis,cis*-9,12,15-octadecatrienoate) produced a mixture of isomeric dienes and monoenes attributed to conjugation occurring as an intermediate step. The hydrogenation of α-eleostearin in tung oil was more stereoselective in forming the *cis,cis*-diene than the corresponding methyl ester. Hydrogenation of linseed oil yielded a mixture of dienes and monoenes containing 7% *trans* unsaturation. We have suggested how the mechanism of stereoselective hydrogenation with $Cr(CO)_3$ catalysts can be applied to the problem of selective hydrogenation of linolenate in soybean oil.

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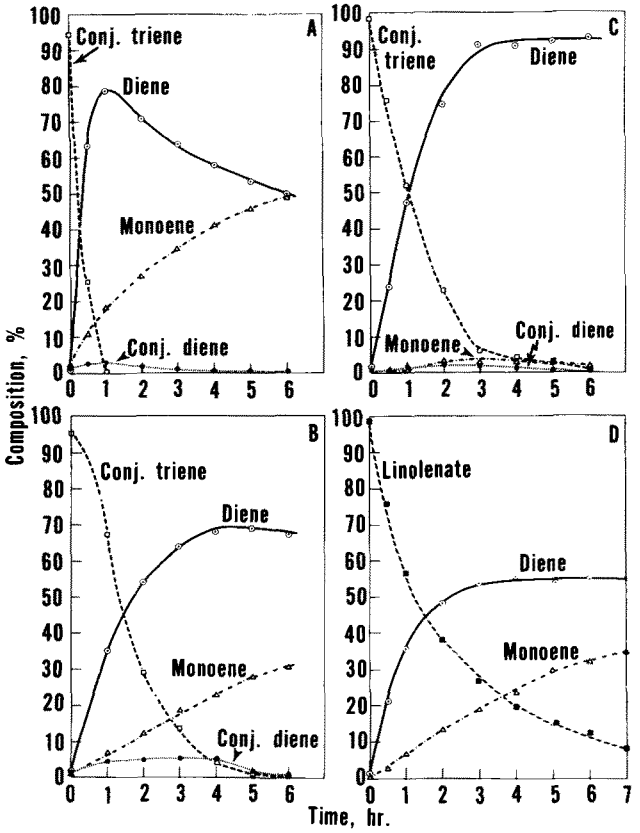


FIG. 1. Hydrogenation rate of: (A) methyl eleostearate with methyl benzoate-$Cr(CO)_3$ (Run 1, Table I); (B) methyl eleostearate with benzene-$Cr(CO)_3$ (Run 3, Table I); (C) methyl eleostearate with cycloheptatriene-$Cr(CO)_3$ (Run 6, Table I); and (D) methyl linolenate with methyl benzoate-$Cr(CO)_3$ (Run 9, Table I).

INTRODUCTION

Numerous metal complexes are known to catalyze the hydrogenation of olefins and unsaturated fats under homogeneous conditions. Our hydrogenation studies have been aimed at determining whether greater selectivity is possible with soluble organometallic catalysts than with the conventional heterogeneous metal catalysts. This work has been motivated by the need for a catalyst that will selectively hydrogenate linolenate constituents contributing to the flavor instability of soybean oil. Theoretically, soluble catalysts are good model systems and studying them has led to a better understanding of the mechanism of catalytic hydrogenation of unsaturated fats (1).

Soluble catalysts previously used to hydrogenate methyl linolenate include iron and cobalt carbonyl (2,3), nickel acetylacetonate (4) and triphenylphosphine complexes of platinum(II) and tin(II) (5). All these catalysts exhibited high selectivity for triene hydrogenation. Their selectivity can be attributed to the formation of isomeric dienes with isolated unconjugatable double bonds not readily reducible to monoenes. Unpublished work showed that pentacyanocobaltate(II) catalyzes the hydrogenation of eleostearic acid (6) and that in aqueous-methanol solution the product from α- and β-eleostearic acids consists of conjugated and unconjugated diene isomers (7).

Our previous work has shown that arene-$Cr(CO)_3$ complexes selectively catalyze the hydrogenation of conjugated fatty esters. In a mixture, conjugated methyl linoleate (mainly methyl *cis,trans*-9,11- and *trans,cis*-10,12-octadecadienoate) is reduced with methyl benzoate-$Cr(CO)_3$ 22 times faster than unconjugated methyl linoleate (8). However in the absence of conjugated fatty esters, benzene- and methyl benzoate-$Cr(CO)_3$ effectively catalyze the hydrogenation of linoleate and linolenate in soybean oil and esters with no formation of stearate (octadecanoate) (9,10). Of particular importance is the finding that monoene products are predominantly *cis* in configuration.

Earlier we showed that conjugated trienes in tung oil are reduced with arene-$Cr(CO)_3$ complexes into a mixture of methylene-interrupted or 1,4-dienes simulating the fatty acid composition of safflower oil (11). We report here details of this catalytic reaction with methyl α- and β-eleostearate, methyl linolenate, tung and linseed oils. We examined the stereoselectivity of this reaction to elucidate its mechanism and suggested how it can be applied to solving the problem of selective hydrogenation of linolenate in soybean oil.

PROCEDURES

All the catalysts used have been described previously (8,9). Methyl α- and β-eleostearates were prepared by the procedure of Hoffmann et al. (12). Methyl linolenate was prepared from linseed methyl esters by counter double-current distribution (13). The tung and linseed oils were commercially refined and laboratory deodorized. Hydro-

TABLE I

Catalytic Hydrogenation of Methyl Eleostearate and Methyl Linolenate With Chromium Tricarbonyl Complexes[a]

Run	Substrates	Catalysts	Catalyst conc.,[b] mole %	Temp., C	Time, hr	GLC analysis,[c] % M	D	CD[e]	CT[f]	T	*trans*,[d] %
1[g]	Methyl eleostearate[h]	Methyl benzoate-$Cr(CO)_3$	5.0	165	6	48.9	50.2	0.9	0.0	---	37.4
2	Methyl eleostearate[h]	Benzene-$Cr(CO)_3$	5.0	165	6	15.0	72.2	0.8	12.0	---	---
3[g]	Methyl eleostearate[h]	Benzene-$Cr(CO)_3$	10	165	6	28.7	67.5	2.9	0.9	---	---
4	Methyl eleostearate[h]	Benzene-$Cr(CO)_3$	2.5	175	4	8.8	91.2	0.0	0.0	---	46.1
5	Methyl eleostearate[h]	Benzene-$Cr(CO)_3$	10	175	2	34.7	62.9	2.4	0.0	---	45.9
6[g]	Methyl eleostearate[h]	Cycloheptatriene-$Cr(CO)_3$	10	120	6	2.1	96.8	0.6	0.5	---	40.3
7	Methyl α-eleostearate[i]	Cycloheptatriene-$Cr(CO)_3$	10	125	3	37.0	62.2	0.8	0.0	---	41.2
8	Methyl β-eleostearate[j]	Cycloheptatriene-$Cr(CO)_3$	10	125	4	7.2	79.2	5.6	7.9	---	89.7
9[g]	Methyl linolenate	Methyl benzoate-$Cr(CO)_3$	5	165	8	36.8	55.6	0.0	0.0	7.6	---
10	Methyl linolenate	Methyl benzoate-$Cr(CO)_3$	10	165	8	45.3	52.6	0.0	0.0	2.1	17.8
11	Methyl linolenate	Methyl benzoate-$Cr(CO)_3$	10	175	8	53.2	46.8	0.0	0.0	0.0	39.5

[a]Conditions: cyclohexane solvent 50 ml, 440 psi H_2, 150 ml autoclave.

[b]Based on substrate concentration.

[c]M, monoene; D, diene; CD, conjugated diene; CT, conjugated triene; T, triene.

[d]As methyl elaidate.

[e]Mixture of *trans,trans-*, *cis,trans-* and *cis,cis-* conjugated dienes.

[f]Includes small amounts of conjugated diene-trienes (trienes with two double bonds conjugated and one isolated).

[g]See rate curves in Figure 1.

[h]80% α + 20% β.

[i]92% α + 8% β.

[j]92% β + 8% α.

genations were carried out as described previously (8,9). Fractionations of hydrogenation products and analyses were also conducted as outlined earlier (2,3,9). Diene fractions from hydrogenated eleostearate were analyzed directly for isomeric composition (*cis,cis* and *cis,trans*) by capillary gas liquid chromatography (GLC) (14); methyl linoleate and methyl *cis*-9,*trans*-12-octadecadienoate were used as standards. Diene fractions from hydrogenated linolenate were too complex to be analyzed by this method.

RESULTS

Methyl eleostearate (a mixture of α and β) was effectively hydrogenated with various $Cr(CO)_3$ complexes at 120-165 C and 200-400 psi H_2, but methyl linolenate usually required temperatures above 165 C. We had observed previously that within this temperature range linoleate and linolenate undergo conjugation with these catalysts in the absence of H_2 (15). Also with 1,4-dienes, conjugation precedes H_2 addition (8). With methyl linolenate, conjugation is apparently necessary for hydrogenation (10). Typical rate curves are drawn in Figure 1. Methyl eleostearate was completely reduced with methyl benzoate-$Cr(CO)_3$ within 1 hr into diene, which is in turn reduced to monoene (Fig. 1A). Conjugated diene is a minor product. Reductions catalyzed by benzene- and cycloheptatriene -$Cr(CO)_3$ were much more selective because the major product was diene ranging from 70-90% (Figs. 1B and 1C). The slower reduction of methyl linolenate than of methyl eleostearate (Fig. 1D) can be attributed to conjugation being necessary before hydrogenation.

Hydrogenation data obtained with methyl eleostearate and linolenate are summarized in Table I. Conjugated trienes were completely hydrogenated to diene or monoene with methyl benzoate-$Cr(CO)_3$ at 165 C, with benzene-$Cr(CO)_3$ at 165 and 175 C and with cycloheptatriene-$Cr(CO)_3$ at 120 and 125 C. Methyl linolenate required a temperature of 175 C for complete reduction with methyl benzoate-$Cr(CO)_3$ (Run 11). With benzene-$Cr(CO)_3$, which is less active than methyl benzoate-$Cr(CO)_3$ (9), methyl linolenate could not be completely converted even at 175 C. Benzene-$Cr(CO)_3$ was more selective than methyl benzoate-$Cr(CO)_3$ for the conversion of conjugated trienes to dienes, but the reaction was not complete (Runs 1 and 2). This selectivity was higher at a low concentration of benzene-$Cr(CO)_3$ at 175 C than at a high concentration at 165 C (compare Runs 3 and 4). At the same concentration of benzene-$Cr(CO)_3$ the diene selectivity was higher at 165 than at 175 C (compare Runs 3 and 5). The best selectivity with a diene yield of 96.8% was achieved with cycloheptatriene-$Cr(CO)_3$ at 120 C (Run 6). Reduction of methyl linolenate with methyl benzoate-$Cr(CO)_3$ yielded a mixture of dienes and monoenes in approximately equal concentrations (Runs 10 and 11).

Hydrogenated products were separated by rubber, liquid-partition, column chromatography into diene and monoene fractions and were analyzed for isomeric composition (Table II). IR analyses gave values of 12.5-14.0% isolated *trans* in the monoenes from reduced eleostearate (Runs 1 and 4) and 14.3-31.6% in the monoenes from reduced linolenate (Runs 10 and 11). Diene fractions were analyzed by capillary GLC, by IR and after alkali conjugation by UV. Dienes from mixed α- and β-eleostearate and from α-eleostearate consisted of a mixture of *cis,cis-* and *cis,trans*-isomers which were 90-100% conjugatable with alkali (Runs 1, 4 and 7). The diene from β-eleostearate was nearly all *cis,trans* and 90% conjugatable (Run 8). Direct isomer analyses by capillary GLC were in fairly good agreement with indirect IR analyses for isolated *trans* unsaturation. $AgNO_3$-thin layer chromatography (TLC) confirmed these results qualitatively and showed also the absence of *trans,trans* dienes. In contrast to reduced eleostearate the diene fractions from reduced linolenate were only 25.3% and 1.7% conjugatable with alkali (Runs 10 and 11). These dienes contained 21.4% and 49.7% isolated *trans* double bond per diene molecule. Evidently the major products are *cis,cis-* and *cis,trans*-1,4-dienes from α-eleostearate, *cis,trans*-1,4-dienes from β-eleostearate and *cis,trans*-isolated dienes (with double bonds separated by more than one methylene group) from linolenate.

The double bond distribution in monoene and diene fractions was determined by reductive ozonolysis-GLC (Table II). Monoenes from reduced eleostearate have the double bond distributed between the C-8 and C-13 positions with a maximum of 44-45% in the C-12 position (Runs 1 and 4). Monoenes from reduced linolenate show more scattering and a double bond distribution between the

TABLE II

Analyses of Monoenes (M) and Diene (D) Fractions[a] From Hydrogenated Methyl Eleostearate and Methyl Linolenate

Analyses	Run 1[b]		Run 4		Run 7,	Run 8,	Run 10		Run 11	
	M	D	M	D	D	D	M	D	M	D
Capillary GLC,[c] %										
cis,cis-Diene	---	43.6	---	50.4	63.8	3.6	---	---	---	---
cis,trans-Diene	---	56.4	---	49.6	36.2	96.4	---	---	---	---
IR *trans*,[d] %	12.5	56.9	14.0	46.1	41.2	89.7	14.3	21.4	31.6	49.7
UV alkali conjugation[e]										
diene, %	---	89.1	---	100	87.2	90.1	---	25.3	---	1.7
O_3 cleavage; double bond position										
Aldehyde esters, M %										
C-8	2.8	2.3	2.4	1.6	1.5	0.7	2.3	5.6	2.6	---
C-9	10.6	44.4	10.5	49.7	53.7	44.5	13.2	52.7	12.2	---
C-10	19.3	51.0	19.6	45.0	43.7	53.0	12.8	25.9	13.5	---
C-11	19.0	2.3	18.4	3.7	1.1	1.8	13.6	7.4	14.7	---
C-12	43.9	---	45.4	---	---	---	19.8	8.4	19.0	---
C-13	4.3	---	3.7	---	---	---	15.1	---	16.8	---
C-14	---	---	---	---	---	---	12.5	---	13.0	---
C-15	---	---	---	---	---	---	10.7	---	8.2	---
Aldehydes, M %										
C-11	---	---	---	3.0	1.1	1.6	---	---	---	---
C-12	---	53.4	---	58.7	63.9	58.1	---	24.0	---	---
C-13	---	46.6	---	38.3	35.0	40.2	---	10.4	---	---
C-14	---	---	---	---	---	---	---	39.6	---	---
C-15	---	---	---	---	---	---	---	26.0	---	---

[a]Obtained in 95-100% purity by rubber, liquid partition, column chromatography.

[b]See Table I for description of individual runs.

[c]See Reference 14.

[d]As methyl elaidate.

[e]Absorbance at 232 mμ after alkali conjugation relative to that of methyl linoleate after alkali conjugation.

C-8 and C-15 positions with a maximum of 19-20% in the C-12 position (Runs 10 and 11). Diene fractions from reduced eleostearate had double bonds mainly on C-9,10 and C-12,13 positions (Runs 1, 4, 7 and 8). Since these dienes were shown by alkali conjugation to be of the 1,4-type, these fractions are therefore a mixture mainly of two isomers: 9,12- and 10,13-dienes. The diene fraction from reduced linolenate had a more complex distribution with double bonds centered on the C-9, C-12 and C-14 positions (Run 10). On the one hand the 1,4-diene components (which amount to 25% according to alkali-conjugation data) are those with double bonds centered either at C-9 and C-12 or at C-12 and C-15. On the other hand the remaining isolated diene components are those with double bonds at C-9,10 and at C-14,15 positions.

It was noted previously that hydrogenation of α-eleostearin in tung oil with $Cr(CO)_3$ complexes was more stereoselective for diene formation than for the corresponding methyl ester (11). Additional hydrogenations were carried out with tung oil, as well as with linseed oil, to determine conditions optimum for selectivity. On the basis of hydrogenation data in Table III, the highest yield of diene obtained from tung oil was with cycloheptatriene-$Cr(CO)_3$ at 125 C (Run 13). At higher temperatures and with methyl benzoate-$Cr(CO)_3$ partial hydrogenation produced the highest yield of diene. Further reaction resulted in hydrogenation of diene to monoene (Runs 14-16). Since monoenes from methyl eoeostearate contained from 12-14% *trans* (Table II) their contribution to total *trans* in the product is small. The *trans* isomeric composition can be

TABLE III

Catalytic Hydrogenation of Tung and Linseed Oils With Chromium Tricarbonyl Complexes[a]

Run	Catalysts	Temp., C	Time,[b] hr	GLC analysis,[c] %						*Trans*,[d] %
				P	S	M	D	T/CD	CT	
	Tung oil[e]									
12	Cycloheptatriene-$Cr(CO)_3$	115	6F	2.9	2.4	10.2	75.1	3.6	5.8	---
13	Cycloheptatriene-$Cr(CO)_3$	125	3	2.2	2.1	9.9	81.6	0.7	3.4	---
			4F	2.6	2.5	11.5	80.9	2.0	0.0	20.1
14	Cycloheptatriene-$Cr(CO)_3$	135	1	2.7	2.7	13.4	77.5	3.7	0.0	---
			4F	2.8	3.0	25.0	66.9	2.3	0.0	18.3
15	Methyl benzoate-$Cr(CO)_3$	160	1	3.2	2.8	15.1	77.1	1.8	0.0	---
			4F	3.3	2.5	37.5	55.0	1.7	0.0	22.1
16	Methyl benzoate-$Cr(CO)_3$	170	1	2.9	4.0	25.2	65.8	2.5	0.0	---
			4F	2.3	2.1	61.4	32.0	1.9	0.0	19.4
	Linseed oil[f]									
17	Methyl benzoate-$Cr(CO)_3$	175	3F	6.0	3.7	45.9	37.5	6.9	---	7.0

[a]Conditions: *n*-hexane solvent 30 ml, 220 psi H_2, 10 M % catalyst, 150 ml autoclave.

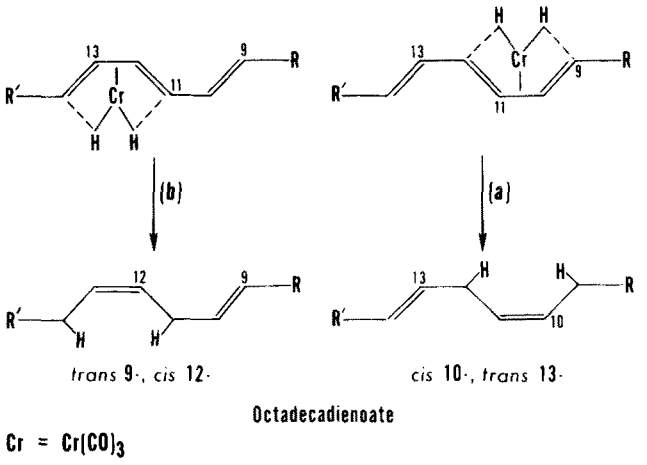
[b]Time at maximum diene concentration; F, final reaction time.

[c]P, palmitate; S, stearate; M, monoene; D, diene; T, triene; CD, conjugated diene; CT, conjugated triene.

[d]As methyl elaidate.

[e]Composition of starting material: 2.6% P, 2.5% S, 6.7% M, 7.0% D, 2.6% CD, 78.6% CT.

[f]Composition of starting material: 6.2% P, 3.9% S, 21.5% M, 16.0% D, 52.4% T. Hydrogenation carried out without solvent and with 5 M % catalyst.



SCHEME 1

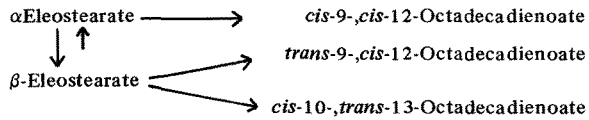
estimated in products by dividing the total *trans* by the concentration of monoene plus diene. Assuming an average of 13% *trans* in the monoene, then the isomeric composition of the product from Run 15 can be estimated as 2% *trans*-monoene, 60% *cis,cis*-diene and 20% *cis,trans*-diene. In the product from Run 16 it can be estimated as 7% *trans*-monoene, 18% *cis,cis*-diene and 32% *cis,trans*-diene.

In linseed oil about 90% of the linolenate was hydrogenated with methyl benzoate-$Cr(CO)_3$ to a mixture of dienes and monoenes. Cycloheptatriene-$Cr(CO)_3$ was ineffective for hydrogenation of linseed oil because it decomposed at temperatures above 150 C, which are necessary to conjugate polyunsaturated fats (10,15). The hydrogenated linseed oil had a lower *trans* value than the hydrogenated tung oils, and these triglycerides had significantly lower *trans* values than the corresponding methyl linolenate (Table I).

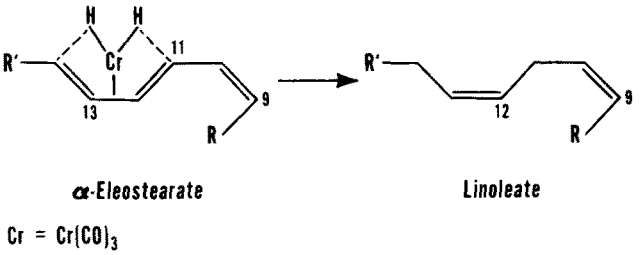
DISCUSSION

Studies of the hydrogenation of model compounds with $Cr(CO)_3$ complex catalysts have been reviewed (1,11). A 1,4-addition mechanism was supported by studies with various diene substrates and with deuterium as a tracer. Now Scheme 1, postulated earlier for β-eleostearate, has been confirmed.

The primary diene product of β-eleostearate is a mixture of *cis,trans/trans,cis*-9,12- and 10,13-octadecadienoates (Table II). These dienes were the products expected from 1,4-addition of H_2 at C-9 and C-12 and at C-11 and C-14 of β-eleostearate (Scheme 1). With conjugated linoleate, $Cr(CO)_3$ complexes are highly stereoselective toward *trans,trans*-dienes (8). These catalysts are therefore expected to favor stereoselective hydrogenation of the *trans*-11,*trans*-13-diene component of α-eleostearate as shown in Scheme 2. Although some stereoselective 1,4-reduction of the *trans,trans*-diene component occurs, a mixture of *cis,cis*- and *cis,trans*-1,4-dienes results from α-eleostearate (Run 7) and from mixtures of α- and β-eleostearate (Runs 1 and 4) (Table II). These results are consistent with a facile isomerization of α- to β-eleostearate during hydrogenation with $Cr(CO)_3$ catalysts:



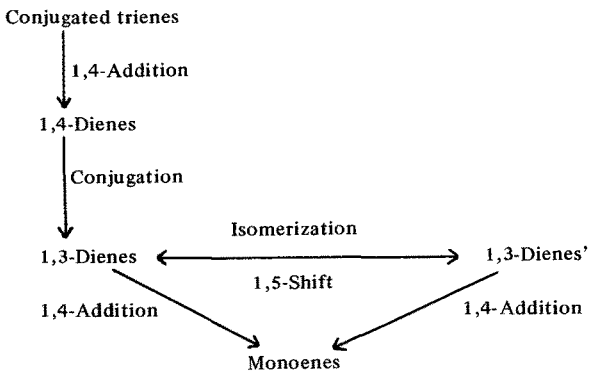
Although some stereoselectivity is lost by this geometric isomerization, linoleate is the major product formed from α-eleostearate and from tung oil (Tables II and III).



SCHEME 2

Still remaining is the problem of explaining the isomeric composition of the monoene products. The various positional monoene isomers, which can be derived from the dienes shown above, are listed in Table IV. Pathways postulated involve (a) conjugation of 1,4-dienes to 1,3-dienes; (b) isomerization of 1,3-dienes by 1,5-shift (8,15); e.g., *cis*-9,*trans*-11↔*trans*-8,*cis*-10; and (c) 1,4-addition; e.g., *trans*-11,*trans*-13→*cis*-12 monoene. The stereoselectivity of arene-$Cr(CO)_3$ complexes toward isomeric methyl 9,11-octadecadienoate was demonstrated to be in the order: *cis,cis* 1.0; *cis,trans* 8.0; and *trans,trans* 25 (8). Therefore the relative concentration of monoenes listed in Table IV would be expected in the following order: 10=12≫11>9. Although the 10- and 11-monoenes are important, the 12-monoene is the predominant isomer (Table II). This monoene isomer would be derived mainly from *trans*-11,*trans*-13-diene and a conjugation mechanism favoring it is indicated.

The diene and monoene products from methyl linolenate are much more complex than those of eleostearate. Although no conjugated products were detected, conjugation proved to be required for hydrogenation to take place with $Cr(CO)_3$ complex catalysts (8). Product analyses (Table II) support a hydrogenation mechanism involving conjugated diene-trienes (with two double bonds conjugated and one isolated) and conjugated trienes as important intermediates (1). Conjugated diene-trienes yield isolated dienes that do not reduce further, as was shown with pure methyl *cis*-9, *cis*-15-octadecadienoate (8), because they do not conjugate with $Cr(CO)_3$ catalysts. Conjugated trienes would yield monoenes by the same reaction sequence as postulated for eleostearate:



The wider distribution of positional monoene isomers from linolenate than from eleostearate indicates that conjugated trienes and conjugated dienes from which they are derived consist of a wider mixture of isomers, but their origin cannot yet be clearly determined by the results we have so far.

Selectivity for linolenate hydrogenation occurs with those catalysts favoring the formation of unreactive dienes having isolated unconjugatable double bonds. This type of

TABLE IV

Origin of Monoenes From Hydrogenated Methyl Eleostearate[a]

1,4-Dienes	1,3-Dienes	Monoenes (*cis*)
cis-9,*cis*-12-	*trans*-8,*cis*-10-	9
	cis-9,*trans*-11-	10
	trans-10,*cis*-12-	11
	cis-11,*trans*-13-	12
trans-9,*cis*-12-	*trans*-9,*trans*-11-	10
	cis-10,*cis*-12-	11
cis-10,*trans*-13-	*cis*-10,*cis*-12-	11
	trans-11,*trans*-13-	12

[a]Based on the following sequence:
(1) Conjugation: 1,4-diene→1,3-diene.
(2) 1,5-H shift; e.g., *cis*-9,*trans*-11↔*trans*-8,*cis*-10, see References 8,15.
(3) 1,4-Addition; e.g., *trans*-11,*trans*-13→*cis*-12-monoene.

selectivity has been achieved with most homogeneous and with some heterogeneous catalysts (1). However, it does not meet our goal of reducing only the Δ^{15} double bond of linolenate in soybean oil to convert it to linoleate. One approach to this problem becomes evident from the results reported here and from Scheme 2. If one could devise a way of selectively conjugating linolenate to α-eleostearate and of inhibiting the isomerization of α- to β-eleostearate, then these $Cr(CO)_3$ catalysts would permit conversion of linolenate to linoleate. Although this goal has not been achieved, our study points to the need of evaluating not only other selective hydrogenation catalysts, but also selective conjugation catalysts. Specific conjugation before hydrogenation may provide another means of increasing the selectivity of homogeneous and possibly heterogeneous catalysts.

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