Selective Hydroformylation of Polyunsaturated Fats With a Rhodium-Triphenylphosphine Catalyst[1]

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ABSTRACT

Soybean, safflower and linseed oils and their methyl esters were effectively hydroformylated with a rhodium and triphenylphosphine catalyst system. The product from safflower methyl esters, hydroformylated at 100 C and 1000 psi synthesis gas (H_2 + CO), proved to be a mixture of formylstearate, formyloleate and diformylstearate. At 150 C and 1500 psi synthesis gas the formyloleate was hydrogenated and the product formed was a mixture of mono- and diformylstearates. The unsaturated monoformyl fraction (100 C) was tentatively identified as a mixture consisting mainly of methyl 9(10)-formyl-*cis*-12- and methyl 12(13)-formyl-*cis*-9-octadecenoates. The saturated monoformyl fraction (150 C) was a more complex isomeric mixture of methyl formylstearate. The diformyl fractions from hydroformylated safflower and linseed esters were identified as mixtures consisting mainly of 9,12-(10,13)- and 10,12-(11,13)-diformyloctadecanoates. When hydroformlyation of polyunsaturated fats was interrupted, *cis*-unsaturated formyl oils resulted.

INTRODUCTION

Monoaldehydes and alcohols are formed by the conventional oxo reaction of conjugated (1,2) and nonconjugated diolefins (3) with synthesis gas (H_2 + CO) and cobalt carbonyl catalyst. These products result from the hydroformylation of one double bond and the hydrogenation of the other. Monoaldehydes and alcohols are similarly produced from methyl linoleate, linolenate and polyunsaturated vegetable oils hydroformylated with cobalt carbonyl, but the yields are diminished when the extent of unsaturation is increased (4).

The novel hydroformylation catalyst consisting of Rh_2O_3 and tri-*n*-butylphosphine, in 85 molar excess, permitted the conversion of butadiene to a mixture of mono- and dialdehydes (5). The dialdehyde fraction (42 mole %) was 87% branched and 9% linear. Pentenals were identified in the partially hydroformylated butadiene. A Rh complex catalyst in the presence of triarylphosphine or triarylphosphite was also claimed effective for the dihydroformylation of polycyclic nonconjugated diolefins (6).

A highly selective Rh-Ph_3P catalyst system was previously described (7) for the high yield hydroformylation of oleic oils into 9(10)-formyl acids, esters or triglycerides. Ph_3P was shown to inhibit double bond isomerization and hydrogenation and other side reactions. In this paper studies with the selective Rh-Ph_3P catalyst have been extended to the hydroformylation of polyunsaturated fats.

EXPERIMENTAL PROCEDURES

Materials and Methods

Soybean, safflower and linseed oils were commercially refined and bleached. Methyl esters were obtained by transesterification and distilled. Methods used for gas liquid chromatography (GLC), thin layer chromatography (TLC), infrared (IR) and mass spectrometry for monoformyl products and their derivatives were described previously (4,7). Diformyl- and dicarbomethoxystearate were analyzed by GLC on columns packed with 3% JXR on Gas Chrom Q 100/120 mesh and programmed from 150-240 C at 2-4 C/min. Methyl 9,12-dicarbomethoxystearate (8) was used as standard. Methyl carbomethoxystearate and dicarbomethoxystearate were separated by preparative TLC on commercial plates (Applied Science "PreKotes" Adsorbosil-5). A sample load of 0.1 g was applied on several plates with a sample streaker (Applied Science) and the developing solvent was diethyl ether-hexane 15:85. Dichlorofluorescein served as a nondestructive indicator. Carbonyl values were determined by oximation (9).

Hydroformylation

The procedure was similar to that described for oleic oils (7). One example is described here in detail. Safflower methyl esters (500 g) were charged in a 2 liter rocker-shaker autoclave with 10 g of 5% Rh on alumina, 5 g Ph_3P and 500 ml toluene. The sealed autoclave was purged three times and then pressurized to 1500 psi with synthesis gas (1:1 H_2 + CO). The reaction mixture was heated to 150 C in 35 min. Hydroformylation began in the range 95-150 C and during this period the pressure reached a maximum of 1800 psi and then decreased to 780 psi. The pressure was restored to 2000 psi with 1:1 synthesis gas. The temperature was controlled at 150 ± 3 C for 4 hr. During this period the pressure declined to 1190 psi and was restored to 1740 psi until it remained almost constant at 1400 psi for approximately 1 hr. The autoclave and contents were then cooled to room temperature and the gases were vented. The reaction mixture was transferred with benzene and filtered as before (7). The crude brown oil product (562 g) was analyzed by GLC and chemically for carbonyl (Table I, run 2). Molecular distillation (Consolidated Electrodynamic CMS-5 centrifugal) yielded clear, colorless fractions (Table II). Fractions 2, 4, 5 and 10 had respective carbonyl values of 2.4, 3.6, 4.2 and 4.7 me/g. Fractions 3 and 10 were used for further characterization by mass spectrometry.

RESULTS

Analysis

Safflower esters were hydroformylated with Rh-Ph_3P under various conditions. The products determined by GLC include a mixture of methyl formylstearate, formyloleate and diformylstearate (Table I). Total yields of formyl products varied from 63-90% (runs 1-10). Highest yields of formyloleate were obtained with Rh on alumina at 100-110 C and 1000 psi synthesis gas (run 1). Under these conditions methyl linoleate was partially conjugated. At 150 C and 1500 psi synthesis gas formyloleate was hydrogenated to formylstearate and further hydroformylated to diformylstearate. Although the Rh-Ph_3P system is ineffective for the hydrogenation of methyl oleate to stearate (7), it can catalyze under these conditions the hydrogenation of formyloleate to formylstearate. Conditions were sought to minimize this hydrogenation reaction which reduces the yields of diformyl-

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TABLE I

Hydroformylation of Polyunsaturated Fats With Rh-Ph_3P

Reaction conditions and analyses	Safflower methyl esters[a]										Soybean oil[b]		Linseed oil[c]		
	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10	Run 11	Run 12	Run 13	Run 14	Run 15[d]
Conditions[e]															
Catalyst[f]	Rh/Al	Rh/Al	Rh/C	Rh/C	Rh/C	Rh/C	Rh/C	Rh/C	Rh/C	Rh/C	$Rh/CaCO_3$	Rh/C	$Rh/CaCO_3$	Rh/C	$Rh/CaCO_3$
Catalyst conc., %	0.5	2.0	0.5	1.0	1.0	1.0	2.0	2.0	1.0	1.0	0.5	1.1	0.5	1.0	2.0
Ph_3P, %	0.25	1.0	0.25	0.5	1.0	1.0	1.0	2.0	0.5	0.5	0.5	0.7	0.4	0.6	0.9
Temperature, C	110	150	90	90	90	90	90	90	120	150	100-105	100	100	110	110
Pressure, psig	1000	1500	3500	3500	3500	3500[h]	3500	3500	3500	2000	2000	2000	2000	2000	2000
Time,[i] hr	6	4	6	6	6	6	6	6	2	1	5	3.5	6	4	6
Analyses															
GLC,[j] %															
Palmitate	7.0	7.0	7.0	7.0	7.0	7.0	6.9	6.9	7.0	7.0	12.8	13.2	6.6	13.0	8.5
Stearate	3.2	4.6	3.1	4.5	3.2	2.9	3.2	3.0	3.3	3.4	8.1	5.7	9.3	9.1	5.9
Unsaturates	26.9[k]	0.0	0.0	1.8	0.0	1.2	0.0	1.6	0.0	0.4	27.5	0.0	15.3	0.0	0.0
Formyloleate	33.0	0.8	10.0	1.8	4.5	10.3	0.8	1.3	0.0	1.0	33.5	0.0	36.1[l]	0.0	0.0
Formylstearate	12.2	36.4	17.1	20.3	16.0	17.0	17.7	17.1	19.1	28.1	12.2	34.1	4.2	35.7	29.7
Diformylstearate[m]	17.7	51.2	62.8	61.8	69.2	61.6	71.4	70.3	70.7	60.1	5.9	47.0	28.5	42.1	55.9
Carbonyl, me/g															
Chemical	2.76	3.84	4.35	4.22	4.43	4.26	4.36	4.24	4.19	4.21	2.00	3.34	3.43	5.13	5.05
GLC[n]	2.39	4.03	4.38	4.17	4.54	4.32	4.63	4.53	4.58	4.29	1.74	3.70	2.90	3.48	4.07

[a]Fatty acid composition: palmitate 7.0, stearate 2.7, oleate 14.3, linoleate 76.0%.

[b]Fatty acid composition: palmitate 10.4, stearate 3.3, oleate 23.0, linoleate 56.0, linolenate 7.2%.

[c]Fatty acid composition: palmitate 6.3, stearate 3.3, oleate 22.0, linoleate 15.1, linolenate 53.3%.

[d]Methyl esters.

[e]Runs 1 and 2 and 11-14 were made in a 2-liter rocker-shaker autoclave with 500 g methyl esters or oil and 500 cc toluene; runs 3-10 and 15 were made in a 250-ml rocker-shaker autoclave with 50 g methyl esters and 50 cc toluene. Runs 11 and 13 were interrupted at predetermined level by cooling with water.

[f]Rh/Al = 5% rhodium on alumina, Rh/C = 5% rhodium on carbon, $Rh/CaCO_3$ = 5% rhodium on calcium carbonate.

[g]Initial pressure of 1:1 H_2 + CO.

[h]1:2 H_2 + CO.

[i]Approximately when pressure leveled off.

[j]Analyses on JXR column.

[k]Includes 15.3% conjugated diene.

[l]Includes several components.

[m]Includes three peaks (see Fig. 2).

[n]Based on monoformyl = 3.07 me/g, diformyl = 5.65 me/g.

TABLE II

Molecular Distillation of the Crude Product From Hydroformylated Safflower Methyl Esters

Fraction	Temperature, C	P, μ	Weight, g	Composition (GLC),[a] %				
							Esters	
				Palmitate	Stearate	Oleate + linoleate	Formyl	Diformyl
1	100	16	43.2	55.9	14.4	2.4	25.6	1.7
2	100	6	29.6	17.7	14.9	2.7	53.2	11.5
3	102-106	6	95.3	2.3	5.8	1.2	70.5	20.2
4	112-115	6	46.9	—	0.4	—	63.3	36.2
5	120	7	33.6	—	0.8	—	46.5	52.7
6	115-125	5	52.4	—	0.2	—	29.7	70.1
7	125-127	5	47.5	—	—	—	10.4	89.6
8	128	5	19.0	—	—	—	6.2	93.8
9	129	5	29.9	—	—	—	3.3	96.7
10	130	5	20.0	—	—	—	2.1	97.9
11	130	5	18.2	—	—	—	1.2	98.8
12	138	5	32.2	—	—	—	0.7	99.3

[a]Gas liquid chromatography.

stearate were obtained at 90-120 C and 3500 psi H_2 + CO (Table I, runs 5-7). Changing the ratios of Rh catalyst to Ph_3P had no significant effect on the relative yields of mono- and diformyl products (runs 4-6). Increasing the proportion of CO in the synthesis gas decreased the yield of diformylstearate (run 6).

Soybean and linseed oils were hydroformylated at different levels of conversion (Table I). Formyloleate was the main product of partially hydroformylated soybean oil. In partially hydroformylated linseed oil (run 13) the product was a mixture of unsaturated and saturated monoformyl esters and diformylstearate. Although a small amount of conjugation was observed (GLC) in these partially hydroformylated oils, IR showed no evidence of isolated *trans* unsaturation. When the hydroformylation was carried out to completion both oils gave a mixture of mono- and diformylstearate.

Chemical carbonyl values agreed generally with those calculated from GLC analyses in hydroformylated safflower esters and soybean oils (Table I). In linseed oil these carbonyl values agreed in the partially hydroformylated oil (run 13) but not in the completely hydroformylated oils and esters (runs 14 and 15). This discrepancy may be attributed to polyformyl products derived from linolenate that do not emerge from the column under the GLC conditions used. The presence of these highly oxygenated compounds would account also for the low yields of distillable products in these fully hydroformylated linseed oils.

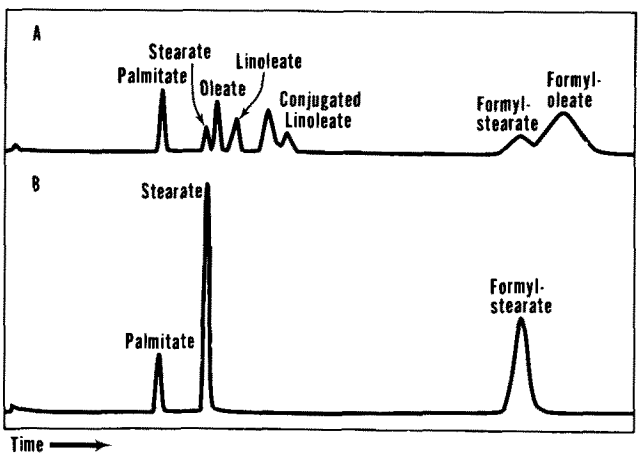

FIG. 1. Gas liquid chromatograms of partially hydroformylated safflower esters on a DEGS column. (A) Run 1, Table I; (B) after selective hydrogenation with $Pd/BaSO_4$.

Characterization

Preliminary identification of monoformyl components separated by GLC was made by comparing retention times with that of formylstearate from hydroformylated oleate (7). GLC of formyloleate on a DEGS column gave a peak of retention time 1.165 relative to 9(10)-formylstearate (Fig. 1A). Formyloleate in partially hydroformylated safflower esters was selectively hydrogenated to formylstearate with 10% Pd on $BaSO_4$ promoted with $FeCl_2$ in acetic acid solution (10). After hydrogenation the peak corresponding to formyloleate was shifted to the same retention as formylstearate (Fig. 1B). Although diformylstearate did not emerge on GLC from a DEGS column, it gave three peaks on a silicone JXR column (Fig. 2). One of these peaks was tentatively identified as methyl 9,12-diformylstearate by comparison with a known standard after conversion to the dicarbomethoxystearate. Further characterization was made by mass spectrometry (see below).

On TLC, monoformyl esters in hydroformylated safflower esters were separated into two components, the least polar of which corresponded to formylstearate. A third highly polar component giving a strongly positive carbonyl test, dinitrophenylhydrazine indicator spray, was also observed and later separated and identified as diformylstearate. After selective hydrogenation of formyloleate to formylstearate, three monoformyl components were separated by TLC, one partially resolved double spot having the same R_f as 9(10)-formylstearate and the third spot being less polar. TLC of the carbomethoxystearate derivatives showed also three components (Fig. 3, samples 4 and 8). The two partially separated polar components had the same R_f as 9(10)-carbomethoxystearate (7). The less polar

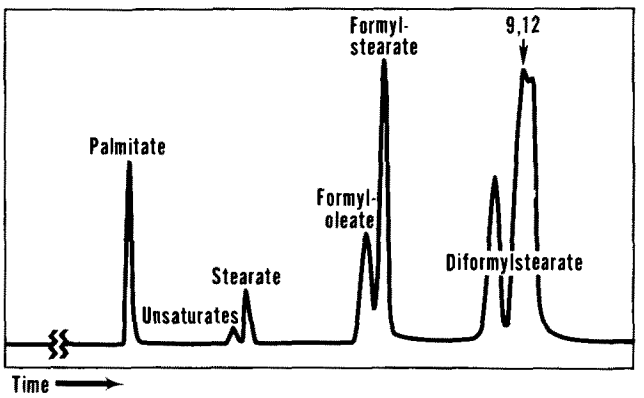

FIG. 2. Gas liquid chromatogram of hydroformylated safflower esters on a JXR silicone column (run 6, Table I).

TABLE III

Elemental Analyses of Mono- and Dicarbomethoxystearates From Hydroformylated Esters

Samples[a]	Purification technique	Per cent C	Per cent H
Methyl carbomethoxystearate			
Run 1	Prep. TLC[b]	69.57	10.98
Run 2	Distillation[c]	70.40	11.03
Run 15	Prep. TLC	70.50	11.40
Calculated ($C_{21}H_{40}O_4$)		70.74	11.31
Methyl dicarbomethoxystearate			
Run 2	Prep. TLC[d]	67.20	10.32
Run 15	Prep. TLC	66.06	10.36
Calculated ($C_{23}H_{42}O_6$)		66.63	10.21

[a]See Tables I and II: hydrogenated ($Pd/BaSO_4$), oxidized ($KMnO_4$), methylated (CH_2N_2).

[b]Preparative thin layer chromatography.

[c]Mol. distillation Fraction 3 (see Experimental), redistilled (pot 125 C/0.001 mm Hg) after oxidiaton and methylation.

[d]Mol. distillation Fraction 10 (see Experimental) purified by preparative TLC after oxidation and methylation.

component had an R_f corresponding to 12- and 13-carbomethoxystearate. Sample 10 in Figure 3 derived from safflower esters hydroformylated at 150 C (Table I, run 2) shows a greater mixture of isomers of R_f in the range corresponding to (9-13)-carbomethoxystearate.

Monoformyl and diformyl esters from hydroformylated safflower and linseed esters were further characterized by mass spectral and elemental analyses as the carbomethoxystearates. These derivatives were prepared by the reaction sequence: (1) selective hydrogenation of unsaturated formyl esters to saturated formyl esters with Pd on $BaSO_4$ (10); (2) oxidation of formyl esters to carboxy esters with $KMnO_4$ and air (7); and (3) methylation of carboxy esters to carbomethoxy esters with diazomethane. The mono- and dicarbomethoxystearate derivatives were separated by distillation and preparative TLC. Various purified mono- and dicarbomethoxystearates gave correct elemental analyses (Table III).

Mass spectral analysis of methyl carbomethoxystearates was based on the fragmentation pattern and standardization used previously (4,7). The monocarbomethoxystearates derived from formyloleate in safflower esters hydroformylated at 100 C/1000 psi synthesis gas were a mixture consisting mainly of the 9(10)- and 12(13)-isomers (Table IV, run 1). A greater mixture of isomers distributed mainly between C-9 and C-13 was determined in the carbomethoxy esters from formylstearate in safflower esters hydroformylated at 150 C/1500 psi synthesis gas (run 2). The carbomethoxystearates from linseed esters showed the branch to be located mainly on C-9 and C-10 (run 15).

The mass spectral analysis of dicarbomethoxystearate derived from diformylstearate was based in part on the fragmentation pattern established for methyl 9-12-dicarbomethoxystearate (8). Major peaks included M-257 and 271 corresponding to fragments $[CH_3OOC\text{-}(CH_2)_n\text{-}(CH\text{-}COOCH_3)\text{-}CH_2\text{-}CH_2]$, for n=7 and 8, and M-160 and 174 corresponding to fragments $[CH_3OOC\text{-}CH\text{-}(CH_2)_x\text{-}CH\text{-}COOCH_3 + 2H)$, for x=1 and 2. These results indicate the presence of two types of isomers: substituted 1,4-, e.g., 9,12-, and 1,3-, e.g., 10,12- dicarbomethoxystearates. The products from hydroformylated safflower and linseed esters were similar. They were identified as a mixture consisting mainly of two types of isomers: 9,12-(10,13)- and 10,12-(11,13)-dicarbomethoxystearate (Table IV).

DISCUSSION

Polyunsaturated vegetable oils and esters were effectively hydroformylated with the $Rh\text{-}Ph_3P$ catalyst system into saturated and unsaturated products containing one or more formyl groups. Dihydroformylation of methyl linoleate would be expected because of the high selectivity of the $Rh\text{-}Ph_3P$ system which does not catalyze double bond isomerization and hydrogenation (7). Indeed conditions were found with this catalyst to produce diformylstearate as the major product of hydroformylation of linoleate in safflower esters. However dihydroformylation was accompanied by the formation of formylstearate. This product would be derived from the hydrogenation of formyloleate formed as an intermediate. Since no hydrogenation of methyl oleate occurs with $Rh\text{-}Ph_3P$, these results suggest the formation of a Rh-carbonyl-formyloleate intermediate complex which can either hydrogenate or hydroformylate. Dihydroformylation of linoleate in safflower esters is favored at high pressures of synthesis gas, and hydrogenation is favored at high tempteratures (150 C). A greater mixture of branched isomers was also obtained at high temperatures, and the isomeric distribution observed be-

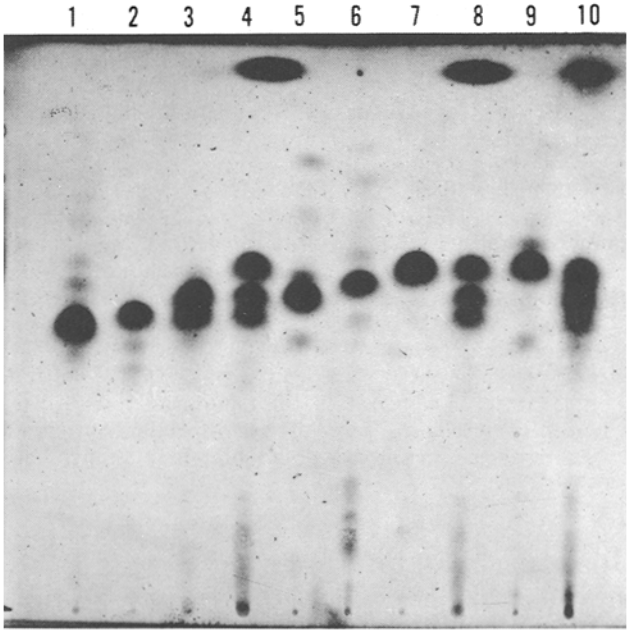

FIG. 3. Thin layer chromatogram of methyl carbomethoxystearate (MeCSA), 1: 8-MeCSA, 2: 9-MeCSA, 3: 9(10)-MeCSA, 4 and 8: MeCSA from run 1 (Table I), 5: 10-MeCSA, 6: 11-MeCSA, 7: 12-MeCSA, 9:13-MeCSA, 10: MeCSA from run 2 (Table I).

TABLE IV

Mass Spectral Analyses of Methyl Carbomethoxy and Dicarbomethoxystearate From Hydroformylated Safflower and Linseed Esters

Carbomethoxy-stearate compound	Branch, carbon no.	Hydroformylated esters: Safflower[a] Run 1	Safflower[a] Run 2	Linseed[b] Run 15
Methyl carbomethoxystearate,[c] relative %	7	—	1.9	—
	8	1.9	4.5	3.4
	9	20.7	15.8	35.1
	10	23.7	22.6	38.1
	11	3.0	14.3	5.3
	12	22.0	17.2	6.7
	13	24.4	12.8	5.8
	14	2.4	6.8	2.4
	15	1.8	4.2	1.9
	16	—	—	1.3
Methyl dicarbomethoxystearate,[d] relative %	8,10	1.3	2.3	0.9
	9,11	1.9	4.8	1.3
	10,12	8.9	15.2	7.5
	11,13	11.4	17.0	9.1
	12,14	1.1	3.9	0.9
	8,11	6.1	6.7	5.6
	9,12	28.7	21.2	32.1
	10,13	37.2	23.6	38.9
	11,14	3.5	5.4	3.7

[a]See Table I.

[b]See Table II.

[c]Based on relative intensity of fragment $[CH_3\text{-}(CH_2)_m\text{-}CH\text{-}COOCH_3 + H]^+$.

[d]Based on relative intensity of fragments $[CH_3OOC\text{-}(CH_2)_n\text{-}(CH\text{-}COOCH_3)\text{-}CH_2\text{-}CH_2\text{-}]$ and $[CH_3OOC\text{-}\dot{C}H\text{-}(CH_2)_x\text{-}\dot{C}H\text{-}COOCH_3 + 2H]$.

tween C-9 and C-13 suggests that conjugation of linoleate during hydroformylation becomes important (run 2, Table I).

The structure of formyloleate from hydroformylated safflower esters can be deduced from the GLC and TLC retention data relative to formylstearate before and after selective double bond hydrogenation and from mass spectral analyses. From these results formyloleate can be tentatively identified as a mixture of methyl 9(10)-formyl-12(13)- and 12(13)-formyl-9(10)-octacedenoate. More definitive identification will be reported elsewhere on the hydroformylation products of pure methyl linoleate. These studies show that there is no selectivity in the monohydroformylation of linoleate with $Rh\text{-}Ph_3P$. Dihydroformylation of safflower esters leads to a mixture consisting mainly of 9,12(10,13)- and 10,12(11,13)-diformylstearate. Therefore conjugation of linoleate is again indicated as a side reaction during hydroformylation.

Hydroformylation of linseed esters produced 9(10)-formylstearate and 9,12(10,13)-diformylstearate as main products (Table III). These results suggest stepwise hydroformylation of linolenate, i.e., formation of monoformyl at 9- or 10-positions, diformyl at 12- or 13-positions and triformyl (if formed) at 15- or 16-positions. The formation of triformylstearate has not been established, however. The selectivity of monohydroformylation of the 9(10)-position in linolenate is in contrast to the random monohydroformylation of linoleate. TLC of hydroformylated linseed esters showed the presence of polar components which have not been as yet identified. Further studies are needed with pure linolenate to determine whether or not monohydroformylation at the 12-13 and 15-16 positions results in unusual products.

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