Hydroformylation of Unsaturated Fatty Esters[1]

E. N. FRANKEL,[2] S. METLIN,[3] W. K. ROHWEDDER[2] and I. WENDER,[3]
Northern Regional Research Laboratory,[2] Peoria, Illinois 61604, and Pittsburgh Coal Research Center,[3] Pittsburgh, Pennsylvania 15213

Abstract

Unsaturated fatty esters and vegetable oils were hydroformylated with H_2 and CO (3500–4600 psi) and $Co_2(CO)_8$ to give fatty aldehydes at 100–110 C and fatty alcohols at 175–190 C. Yields of distillable C_{19} oxo products varied from 42% to 84%. Distilled products contained from 50% to 90% branched isomers and from 4% to 16% linear isomers. The proportion of linear isomers increased at higher reaction temperatures and in the presence of tributylphosphine-cobalt carbonyl complex. Linear and branched hydroxy products were separated by silicic acid column, thin-layer, and gas-liquid chromatography. The linear hydroxy product (from oleate and linoleate) was identified as methyl 19-hydroxynonadecanoate by nuclear magnetic resonance and mass spectrometry. Isomeric branched products were analyzed by mass spectrometry as the diester derivatives. They were identified as a mixture of 5- to 13-carbomethoxy methyl octadecanoate.

Introduction

The oxo reaction is one of the most important industrial routes to primary alcohols. Olefins react with CO and H_2 in the presence of a metal carbonyl catalyst, usually $Co_2(CO)_8$. This reaction is known as hydroformylation because aldehydes are the primary products derived by the addition of the elements of formaldehyde (H-CHO) (1). Although the oxo process is relatively old (1938), it has not been exploited in the fatty acid chemical industry. The patent literature cites samples of the hydroformylation of oleate (4,5,9,16), olive oil (16) and tall oil fatty acids (2). In one report (14), 75% to 85% hydroformylation was obtained with camellia oil containing oleate. With linoleate- and linolenate-containing oils (soybean, linseed and cuttlefish oils), one double bond was hydroformylated and the other double bonds were hydrogenated. The products of the oxo reaction of unsaturated fats have not been well characterized.

Our researches in homogeneous catalysis have shown that $Co_2(CO)_8$ is an effective hydrogenation and isomerization catalyst of unsaturated fats (13). These studies have now been extended to other reactions of possible industrial interest. The present work was undertaken to characterize the oxo products from pure fatty esters and vegetable oils. Factors affecting the relative proportion of branched to linear oxo products were also explored.

Experimental Procedures

Materials

Soybean, linseed and safflower oils used were commercially refined. Their methyl esters were obtained by transesterification with methanol and potassium methoxide and by vacuum distillation. Methyl oleate came from The Hormel Institute. Methyl linoleate and linolenate were purified from safflower and linseed esters, respectively, by counter double current distribution (6), and found by gas-liquid chromatography (GLC) to be 99% to 99.5% pure. The cobalt carbonyl was prepared as described previously (21). It was dissolved in hexane and stored in a pressure bottle under synthesis gas (H_2 and CO). Tributylphosphine was purchased from Carlisle Chemical Works, Inc., Reading, Ohio. Pure standards for GLC and mass spectrometry included methyl 16-hydroxypalmitate (L. L. Wallen, Northern Laboratory), methyl 18-hydroxystearate (A. P. Tulloch, Prairie Regional Laboratory, Saskatoon, Saskatchewan, Canada), and 8- to 13-carbomethoxy methyl octadecanoate (J. Klein, Hebrew University, Jerusalem, Israel).

Methods

GLC analyses were carried out in an Aerograph, Model 1520 (Varian Aerograph, Walnut Creek, Calif.) equipped with a flame ionization detector. The column (5 ft × ⅛ in. stainless steel) was packed with 25% DEGS on Chromosorb W 60/80 mesh. Temperature was programmed from 150 to 215 C at 4°/min and the nitrogen flow was 30 ml/min.

Thin-layer chromatography (TLC) was done on glass plates (20 × 20 cm) spread with a 0.2 mm layer of Silica Gel G (Brinkmann Instruments, Inc., Westbury, N.Y.) and activated for 30 min at 110 C. The developing solvent was a mixture of diethyl ether and hexane. Spots were visualized with 50% H_2SO_4 followed by heat.

Infrared (IR) analyses were made in CCl_4 solution with a Perkin-Elmer spectrophotometer, Model 621 (Perkin-Elmer Corp., Norwalk, Conn.).

Nuclear magnetic resonance (NMR) analyses were carried out in $CDCl_3$ solution with a Varian A-60 and with trimethylsilane as the internal standard.

Mass spectra were measured on a Nuclide 12-90G mass spectrometer (Nuclide Analysis Assoc., State College, Pa.) equipped with an all-glass inlet; inlet temperature, 192 C; source temperature, 200 C; and 70 V electron energy.

Procedures

All experiments were performed in a 200 ml or 500 ml rocked Aminco bomb (American Instrument Co., Silver Spring, Md.). In a typical run (run 8, Table I) 150 g of soybean oil (0.43 equivalent of unsaturates) was charged into a 500 ml autoclave together with 7.1 g $Co_2(CO)_8$ (0.02 mole) and 100 ml methylcyclohexane. The sealed autoclave was pressurized with synthesis gas (H_2:CO, 2:1) to 3550 psi. The reaction mixture was heated to 180 C in 1.5 hr. After the reaction started at 100 C, the pressure reached a maximum of 4200 psi and then decreased to 1850 psi at 175 C. At this point the autoclave was recharged with synthesis gas to a pressure of 4000 psi and heating (175–180 C) was continued for 5 hr. The autoclave was then allowed to cool overnight. The reaction mixture was transferred with methylcyclohexane into a round-bottomed flask. It was refluxed 2 hr to decompose unreacted catalyst. Almost

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[2] No. Utiliz. Res. Dev. Div., ARS, USDA.
[3] Bureau of Mines, U.S. Dept. of Interior.

TABLE I

Hydroformylation of Unsaturated Fatty Esters[a]

Reaction parameters and analyses	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10
Oils	MeOl	MeOl	MeOl	MeLo	MeLo	MeLn	SBO	SBO	MeSFO	MeLSO
Conditions										
Catalyst	$Co_2(CO)_8$	$Co_2(CO)_8$	$Co_2(CO)_8/Bu_3P$	$Co_2(CO)_8$	$Co_2(CO)_8/Bu_3P$	$Co_2(CO)_8$	$Co_2(CO)_8$	$Co_2(CO)_8$	$Co_2(CO)_8$	$Co_2(CO)_8$
Catalyst conc., mole %	0.015	0.02	0.015/0.04	0.02	0.01/0.03	0.03	0.01	0.02	0.02	0.015
Solvent	Benzene	Benzene	Benzene	Benzene	Benzene	Benzene	Benzene	Mecyclo	None	None
Temp., C	105–110	175–180	200	180	180–185	175	100–110	175–180	175–180	180–190
Pressure,[b] psi	4100	3500	3500	3500	3500	3600	4400	4200	4500	4600
Time,[c] hr	4.5	5.5	5.5	4	5	4	5.5	5	4	4
Analyses										
Distillation,[d] %	95	89	74	76	51	66	90	87	82	52
GLC[e] (acetates)										
Palmitate	.....	.....	.....	.....	.....	.....	15.6	16.6	9.9	11.2
Stearate	11.0	9.9	9.1	2.2	14.4	1.5	6.4	13.9	12.6	14.7
Monoene	0.5	0.7	5.0	0.1	1.7	0.3	4.7	1.0	0.8	0.1
Diene	.....	.....	.....	.....	.....	.....	0.6	1.1	1.3	0.2
Aldehydes	10.0	2.7	2.0	3.0	0.5	0.6	12.6	5.3	1.9	0.8
Alcohols										
Branched (1,2)	71.7	71.3	67.5	86.9	68.4	85.4	49.6	54.0	62.8	62.2
Linear (3)	6.8	15.0	15.9	7.8	14.3	12.2	4.2	7.7	10.7	10.8
Unidentified (4,5)	.....	0.4	0.5	.....	0.7	.....	6.3	.....	.....	.....
Total oxo products[f]	88.5	89.4	85.9	97.7	83.4	98.2	85.1	78.4	84.2	81.2
Distillable oxo products[g]	84	80	64	74	43	65	77	68	69	42

[a] Abbreviations: MeOl, methyl oleate; MeLo, methyl linoleate; MeLn, methyl linolenate; SBO, soybean oil; MeSFO, safflower oil methyl esters; MeLSO, linseed oil methyl esters; Bu_3P, tributylphospine; Mecyclo, methyl cyclohexane.
[b] At reaction temperature. Initial pressure: 3500 psi; after pressure drop at 100–110 C, autoclave was repressurized to 3500–4600 psi.
[c] Does not include heating time which varied from 60 to 90 min.
[d] At 145–220 C/0.015 mm Hg with a Claisen microstill. Formyl products (runs 1 and 7) were distilled as the dimethylacetals, and the hydroxy products (runs 2–6, 8–10) as the acetates. Yields were based on weights of distilled products.
[e] After distillation. Formyl products (runs 1 and 7) were reduced to hydroxy esters, then acetylated and distilled before GLC analyses (see Experimental section). Gas chromatograms of runs 1 and 2 are shown in Figure 1.
[f] From GLC analyses for total aldehydes and alcohols, based on unsaturated fatty ester content in original oils: SBO, 85.4%; MeSFO, 89.6%; MeLSO, 90.8%.
[g] Total oxo products times percentage of distilled product.

all the solvent was then removed on a rotating evaporator under vacuum. The mixture was then transferred into a separatory funnel with diethyl ether. It was repeatedly washed with dilute HCl (2:1) to decompose the catalyst until no blue color appeared in the aqueous phase. The ether solution was washed with water until neutral and dried over Na_2SO_4. A viscous light yellow product resulted (153 g).

In run 1, Table I, 50 g methyl oleate (0.17 mole) was charged into a 200 ml bomb with 2.5 g $Co_2(CO)_8$ (0.015 mole) and 60 ml benzene. The autoclave was pressurized with 3500 psi synthesis gas (H_2:CO, 2:1). It was heated to 110 C in 90 min, and the mixture was allowed to react at that temperature for 4.5 hr. Since the unreacted cobalt carbonyl catalyst in the formyl product was difficult to decompose with heat and acid, the crude product was processed directly without decomposition.

Preparation of Derivatives

Alcohols. The formyl crude products from hydroformylation at 100–110 C (runs 1 and 7, Table I) were reduced to primary alcohols with sodium borohydride (18). Completeness of reduction was verified by TLC.

Dimethyl Acetals. A portion of crude formyl product (4.5 g; run 1, Table I; containing undecomposed cobalt carbonyl) was refluxed in 30 ml of methanol-BF_3 solution (0.3 g BF_3/ml) for 1 hr. The cooled solution was neutralized with $NaHCO_3$, extracted with diethyl ether, washed and dried (Na_2SO_4) to yield 4.5 g of product.

Acetates. The hydroxy products were acetylated by refluxing with excess acetic anhydride (1 g sample plus 1.5 ml acetic anhydride, refluxed 1 hr, ice water was added and mixture extracted into petroleum ether). Some crude oxo products were also treated directly, and the cobalt carbonyl catalyst was decomposed during acetylation.

Carboxy Esters. Oxidation of crude formyl product (run 1, Table I) was carried out by bubbling air in acetic acid solution at 60 C in the presence of undecomposed $Co_2(CO)_8$ catalyst. TLC indicated completion of oxidation after 6 hr.

Methyl Esters. Hydroxytriglyceride products (run 8, Table I) were transmethylated with potassium methoxide and methanol. The carboxy ester from oxidation of formyl products was converted to the dicarboxylic methyl esters with BF_3-MeOH or diazomethane.

Separations

Vacuum Distillation. The hydroxy methyl esters were distilled as the acetates, and the formyl esters as the dimethyl acetals.

Column Chromatography. Partition chromatography with Mallinckrodt silicic acid treated with methanol and benzene (12) was used to separate both hydroxyl methyl esters and carbomethoxy methyl esters. Adsorption chromatography was carried out with Adsorbosil silicic acid and mixtures of ethyl ether and hexane as eluting solvents (8).

Preparative TLC. Fractions of hydroxy esters from column chromatography were further purified by TLC on plates coated with 0.2 mm Silica Gel G. A sample load of 15 to 20 mg was used on several plates and the developing solvent was diethyl ether-hexane (3:2). Dichlorofluorescein served as a nondestructive indicator. Also, 50% H_2SO_4 was used as a marker on one narrow vertical edge of the plates. Fractions (20–25 mg) were large enough for mass spectral and NMR analyses.

Preparative GLC. Two systems were used. For separation of hydroxy esters, an Aerograph Autoprep Model A-700 was used isothermally with a 10 ft × ¼ in. column packed with 20% Carbowax 20M on 60/80 mesh Chromosorb W at 198 and 215 C and flow rate of 200 ml/min. Also, a programmed-temperature instrument was used (Aerograph Model 1520) with a 10 ft × ¼ in. column packed with 25% DEGS on 60/80 mesh Chromosorb W. The program was 175 to 230 C at 10°/min with a flow of 50 ml/min. The procedure for collection of fractions was described previously (10).

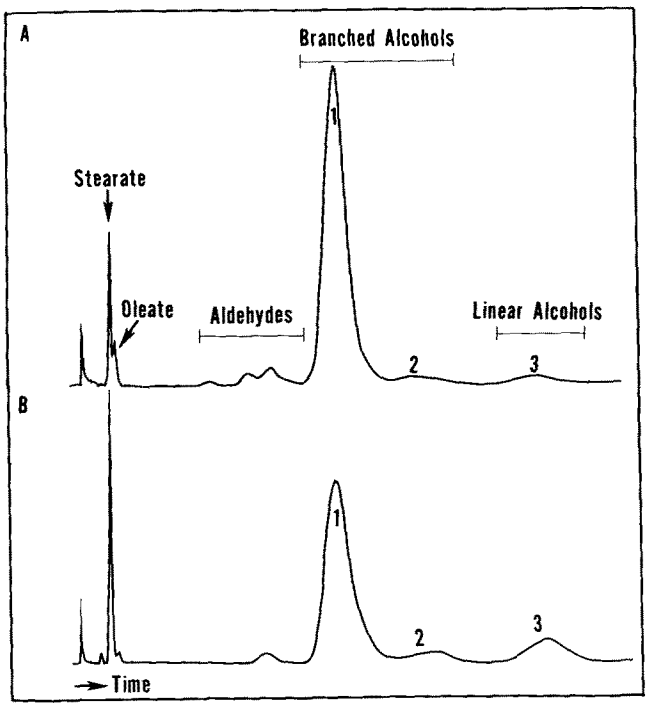


FIG. 1. GLC of hydroformylated methyl oleate, as acetates: (A) run 1, Table I; (B) run 2, Table I.

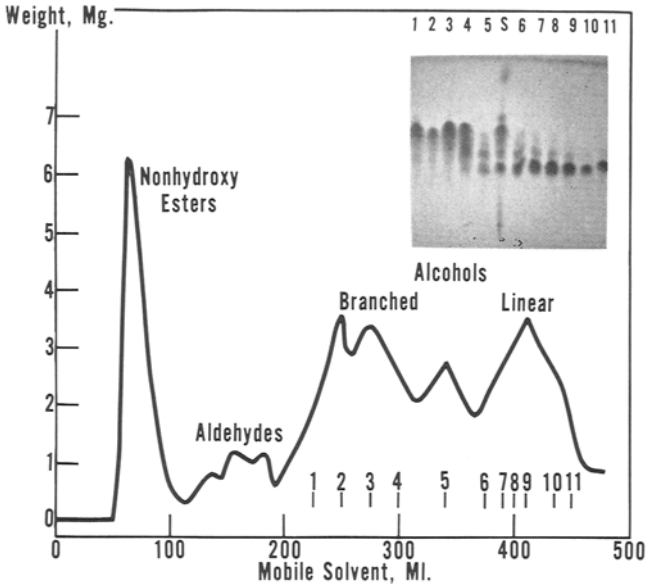


FIG. 2. Partition silicic acid column chromatography of hydroformylated methyl linoleate as alcohols. [Run 5, Table I; Column: silicic acid, 50 g; stationary phase, 9.6 ml MeOH; mobile solvent, 1% MeOH in benzene. TLC of fractions: mobile solvent, diethyl ether-hexane (3:2 v/v) S = original sample.]

Results

Analysis

Reaction parameters, yields of oxo products and GLC analyses are recorded in Table I. A mixture of formyl esters was obtained at 100–110 C, and of hydroxy esters at 175–190 C. Yields of distilled products ranged from 51% to 95% and decreased from oleate to linoleate to linolenate. Runs at 100–110 C gave better yields than corresponding runs at 175–190 C. Linseed esters and methyl linolenate produced large amounts of nonvolatile products (34–48%). Some hydrogenation to stearate occurred. Conversion of fatty esters into oxo products (aldehydes plus alcohols) varied from 42% to 84%. Distilled products contained from 50% to 87% branched isomers and from 4% to 16% linear isomers. Runs made at 175–190 C gave higher yields of linear oxo products (8–16%) than those at 100–110 C (4–7%). Yields of distilled products decreased at the higher temperature range. Although addition of tributylphosphine-cobalt carbonyl complex increased the proportion of linear product (runs 4 and 5, Table I), the yield of distilled product decreased.

Individual components separated by GLC (Fig. 1 and Table I) were identified by comparison of retention times with those of known hydroxy fatty esters and by isolation of components by preparative GLC followed by mass spectrometric analyses. Methyl 16-hydroxypalmitate and methyl 18-hydroxystearate were chromatographed together with oxo products either as free alcohols or as acetates with a polar (DEGS) and a nonpolar column (Silicone SE-30). Preliminary characterization was made by plotting retention time vs. carbon number. The polar hydroxy ester component of oxo products (acetate component number 3 by GLC, Fig. 1A and 1B) corresponded to methyl 19-hydroxynonadecanoate. The less polar hydroxy components (acetates 1 and 2) were identified as branched by isolation and mass spectral analyses. The formyl components were identified by comparison of gas chromatograms before and after reduction of a formyl oxo product (run 1, Table I).

Separation

Oxo products were separated by column chromatography, preparative TLC and GLC. Partition column chromatography separated hydroxy oxo products into fatty esters, formyl esters and hydroxy esters (Fig. 2). Final elution with diethyl ether yielded polar acidic products. TLC showed partial separation between branched and linear hydroxy methyl esters. The linear hydroxy esters were the more polar components. The branched hydroxy esters (combined fractions 1 to 4, Fig. 2) were 99% functionally pure by GLC after acetylation. The linear hydroxy esters (combined fractions 6 to 11) were only 73% pure. Silicic acid partition chromatography was also used to separate monocarboxylic and dicarboxylic esters from oxidized formyl oxo products (runs 1 and 7, Table I). Some gross fractionation of isomers of diesters was indicated by TLC. Adsorption column chromatography (Adsorbosil silicic acid, diethyl ether-hexane) was equivalent to the partition chromatographic system in providing separation between fatty esters, formyl esters, branched and linear hydroxy esters and polar acidic products. Column chromatographic fractions of linear hydroxy esters were further purified by preparative TLC. Functionally pure linear and branched isomeric alcohols were obtained by this technique. Preparative GLC afforded some fractionation of hydroxy and diester oxo products. However, qualitative TLC showed that the linear hydroxy fractions were not so pure as those obtained by preparative TLC.

For further characterization the branched hydroxy and carbomethoxy esters were obtained either by column chromatography (partition or adsorption) or by preparative GLC. The linear hydroxy esters were obtained by preparative TLC either directly or after preliminary concentration by partition column chromatography.

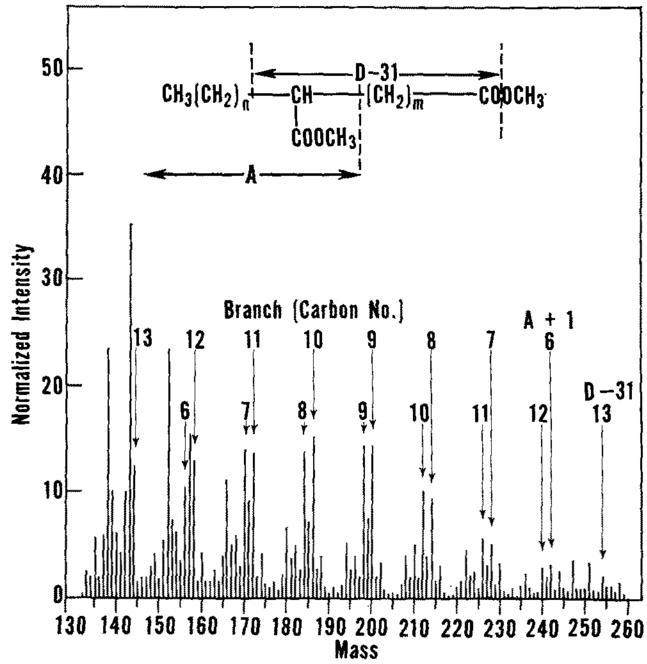


FIG. 3. Partial mass spectrum of branched diesters from hydroformylated methyl oleate. (Run 1, Table I, preparative GLC fraction).

Characterization

Characterization of oxo products was achieved by IR, NMR, chemical analyses and mass spectrometry. A linear hydroxy fatty ester fraction (run 5, Table I) gave an IR spectrum which was identical with that of methyl 18-hydroxystearate. The corresponding branched hydroxy fatty ester fraction had much stronger bands at 1440 (C–C–CH_3 asymmetric band) and 1460 cm^{-1} (CH_2 band) than the linear isomers. The position of the C-O stretch band indicates branching. With the branched hydroxy isomers the C-O band appeared at 1030 cm^{-1}, whereas with the linear hydroxy products it appeared at 1040 to 1050 cm^{-1}. With linear primary alcohols this band is known to be reduced 10 to 15 cm^{-1} when branching occurs in the α-carbon position (19). Attempts were made to estimate hydroxy content by measuring the intensity of the hydroxy band at 3450 cm^{-1}. Since the hydroxy esters were highly associated even with 1% solutions in CCl_4, this band was quantitatively unreliable.

The NMR spectrum of the oxo hydroxy esters is relatively simple. Unfractionated alcohols showed the following bands: 9.1τ (relative to 10τ for tetramethylsilane; CH_3), 8.7τ (CH_2), 8.25τ (OH), 7.7τ (CH_2 α to $COOCH_3$), 6.5τ (CH_2 α to OH) and 6.3τ (OCH_3). The OH proton signal was assigned by the D_2O exchange technique. The spectrum of a branched hydroxy isomer fraction (run 5, Table I) was almost identical to that of the unfractionated product. The corresponding linear hydroxy isomer showed unique features as follows: Absence of CH_3 absorption at 9.1τ; the OH peak was at 8.1τ; the signal due to CH_2 α to OH was a triplet centered at 6.38τ but overlapped with the OCH_3 band at 6.30τ. The spectrum of this linear hydroxy isomer was qualitatively identical to that of standard methyl 16-hydroxypalmitate and methyl 18-hydroxystearate. Although the linear hydroxy isomers were distinguished from the branched isomers by the absence of CH_3 absorption, it was not possible to detect the α CH_2 signal at 6.38τ and to determine linear hydroxy isomers in a mixture containing branched hydroxy isomers predominantly. NMR was therefore only useful in the identification of the purified isomers.

Various purified branched oxo products gave correct elemental analyses (Table II). Molecular weights of the hydroxy esters deviated from 1% to 10% of expected value. These branched hydroxy esters were liquid. A pure linear oxo fraction, identified as methyl 19-hydroxynonadecanoate, melted at 57 C.

Mass spectral analysis provided definite identification of the linear hydroxy C_{19} esters and permitted an estimate of the isomeric composition of branched C_{19} diesters. The linear hydroxy oxo product was identified as methyl 19-hydroxynonadecanoate. When the difference in chain length was accounted for, purified linear hydroxy products (preparative TLC and GLC, runs 1 and 2, Table I) gave similar mass spectra with those of authentic methyl 18-hydroxystearate and methyl 16-hydroxypalmitate. These samples have the following characteristics: No parent peak, M-18 peak from loss of H_2O, M-30 peak probably from loss of $CH_2{=}O$ including the terminal carbon atom, M-32 peak probably from loss of CH_3OH including the terminal carbon atom, M-50 peak from loss of terminal OH as H_2O and the methoxy group as CH_3OH and M-92 peak from loss of terminal OH as H_2O and $CH_3OC(=O)CH_2$ plus H. The linear diester from oxidized formyl oxo product (run 1, Table I) was identified as methyl nonadecane-1,19-dioate by comparison with the spectrum reported for methyl octadecane-1,18-dioate (17).

The branched hydroxy ester fractions gave mass spectra, which were almost identical with those of the linear isomers except that the linear compounds have a small peak due to loss of 32 along with the large peak due to loss of 30. Loss of CH_2OH, leaving a radical ion with subsequent degradation, results in many peaks that provide no information as to location of the branched CH_2OH groups. The branched diesters (from oxidation of oxo formyl products, run 1, Table I) provided the most distinct spectrum for location of the branch. Fig. 3 shows the partial spectrum of diesters from hydroformylated methyl oleate. A small molecular peak appeared at 356. A fragmentation scheme and qualitative data for a series of known C_{19} branched diesters with branch in the C-8 through C-13 positions are recorded in Table III. Mass of other isomers (C-5 to C-7) were extrapolated. The spectra are dominated by cleavage around the tertiary carbon atom, simple cleavage to form 297 peak and rearrangement of an H to form fragments A and D. Fragments A-31 and D-31 are due to the loss of CH_3O from A and D ions. Although fragment B was intense, it was unimportant in interpretation

TABLE II

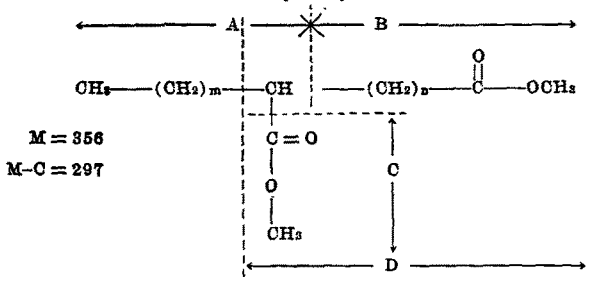
Elemental Analyses of Purified Hydroformylation Products

Samples[a] (source)	Purification technique	Per cent C	Per cent H	Molecular weight[b]
Branched hydroxy esters				
Run 2 (oleate)	Preparative TLC	72.5	12.0	312
Run 5 (linoleate)	Preparative TLC	72.7	12.2	349
Run 8 (soybean oil)	SiO_2 column	72.3	12.2	333
Calculated ($C_{20}H_{40}O_3$)		72.2	12.7	316
Branched carbomethoxy esters				
Run 1 (oleate)	SiO_2 column	70.9	11.3	356
Calculated ($C_{21}H_{40}O_4$)		69.8	11.6	356

[a] See Table I.
[b] Determined by osmometry for alcohols and by mass spectrometry for diester.

TABLE III
Mass Spectral Analysis of Branched Diesters
Fragmentation Scheme

Carbomethoxy methyl octadecanoate



Branch C No.	n	m	Major fragments, mass A+1	A−31	D+1	D−31	B	D−31–32	Unidentified
8	6	9	214	182	216	184	143	152	171
9	7	8	200	168	230	198	157	166	
10	8	7	186	154	244	212	171	180	170,152
11	9	6	172	140	258	226	185	.....	
12	10	5	158	126	272	240	199	208	184
13	11	4	144	112	286	254	213	222	181

because the series 59+ $(14)_n$ from $CH_3OC(CH_2)_n$ (O above C) is found in all long-chain methyl esters. A peak at D-31-32 occurred for most of the compounds. Estimation of the branched isomeric composition was based on the relative intensity of the A + 1 fragments of the standard 8- to 13-carbomethoxy methyl octadecanoate (Table III). Estimates of the other isomers (branched on C-5 to C-7) were made by extrapolation.

Analysis of a branched fraction from hydroformylated methyl oleate (Fig. 4A) shows that the branch is distributed between the C-6 and C-13 positions and peaks at the C-11 position. Fractions obtained by preparative TLC showed separation of branched isomers (Fig. 4B). Diester isomers with a branch between C-5 and C-6 positions were most polar, and those with a branch between C-10 and C-13 were least polar on TLC.

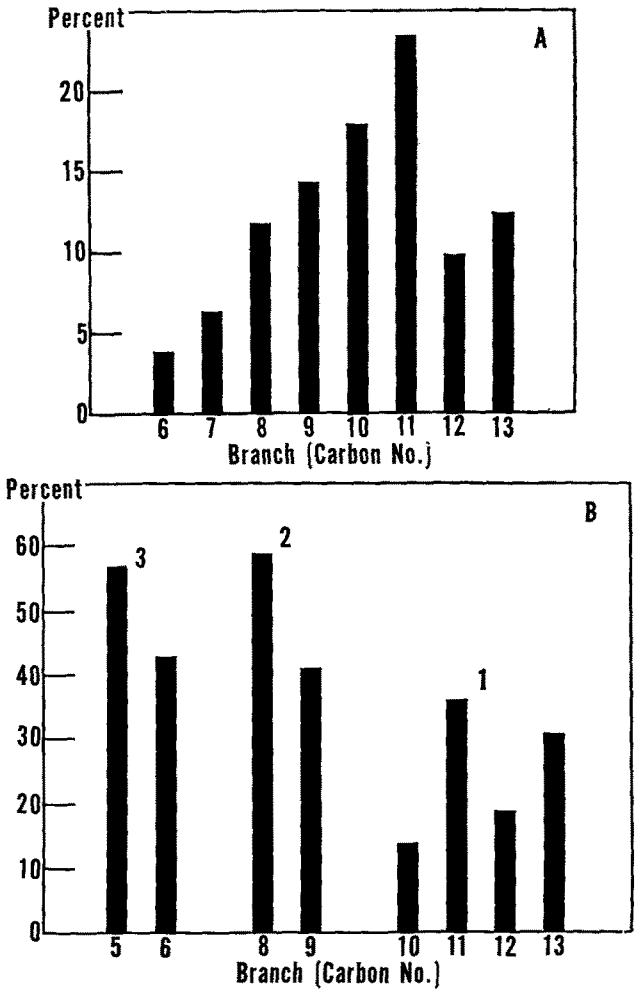


FIG. 4. Distribution of branched diesters by mass spectrometry: hydroformylated methyl oleate, run 1, Table I, oxidized, (A) Preparative GLC fraction; (B) preparative TLC fractions; order of increasing polarity, 1–3.

Discussion

Detailed characterization of the oxo products from oleate and linoleate showed a complexity of formyl and hydroxy C_{19}-fatty esters. The more highly unsaturated fats underwent side reactions, such as condensations, which contributed to the nondistillable products. These products may include acetals, hemiacetals and ethers (11). The branched isomers were the major oxo products and of the type: $CH_3-(CH_2)_x-CH(Z)-(CH_2)_y-COOCH_3$, where Z = –CHO or $-CH_2OH$, and x + y = 15. Branch Z was distributed between C-6 and C-13 of the C-18 chain. The isomeric composition was similar to that previously found for the double bond positions in monoenoic products from unsaturated fats hydrogenated with $Co_2(CO)_8$ (13). It is known that homogeneous hydrogenation and double bond migration occur concurrently with hydroformylation (3,11,20). In polyunsaturated fatty esters the probable formation of conjugated diene intermediates would hinder hydroformylation (15) and contribute to side reactions. Better yields of oxo products were indeed obtained from oleate than from linoleate, linolenate and polyunsaturated vegetable oils.

The linear isomers were minor oxo products and of the type: $Z-(CH_2)_{17}COOCH_3$, where Z = –CHO or $-CH_2OH$. The formation of these linear isomers would depend on migration of the double bond to the terminal C_{17}-C_{18} position. Therefore higher yields of linear products would be expected under conditions promoting double bond migrations; thus, higher reaction temperatures resulted in higher yields of linear products. However, more side reactions occurred under these conditions. Further work is needed to determine how to maximize double bond migration with a minimum of side reactions. There was an indication that tributylphosphine complex with cobalt carbonyl also increased the proportion of linear oxo produlct. The Shell low pressure process (7) uses a complex metal catalyst, of which the tributylphosphine complex of cobalt carbonyl is an example. This complex is an effective hydrogenation and hydroformylation catalyst and allows the reaction to proceed to the hydroxy product at low pressure. In our work we suggest that the tributylphosphine cobalt carbonyl complex stabilizes the hydride catalyst-fatty ester intermediates so that, initially, double bond migration is favored over hydroformylation. When the double bond reaches the terminal position, then hydroformylation proceeds.

Our work has pointed a way to isomerize double bonds and to introduce oxygen functionality throughout a fatty acid chain, including the terminal position. Chemical modification of vegetable oils by the oxo reaction, which involves the unsaturated fatty acid components, should provide an efficient outlet for industrial utilization. The high-molecular weight of the C_{19} hydroxy esters and diesters derived from unsaturated fats may provide unique properties for special uses. These oxo products would have low volatility, resistance to oxidation and high electric resistivity. These properties are particularly important for electrical cables and for lubrication (11).

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REFERENCES

1. Adkins, H., and G. Krsek, J. Amer. Chem. Soc. *71*, 3051–3055 (1949).
2. Alm, R. M., and J. W. Shepard (Standard Oil Co.), U.S. Patent 2,891,084 (1959).
3. Bird, C. W., "Transition Metal Intermediates in Organic Synthesis," Logos Press-Academic Press, London-New York, 1967, p. 117–148.
4. Birum, G. H., and T. M. Patrick, Jr. (Monsanto Chemical Co.), U.S. Patent 2,965,598 (1960).
5. Büchner, K., O. Roelen, J. Meis and H. Langwald (Ruhrchemie Aktiengesellschaft), U.S. Patent 3,043,871 (1962).
6. Butterfield, R. O., H. J. Dutton and C. R. Scholfield, Anal. Chem. *38*, 86–88 (1966).
7. Cannell, L. G., L. H. Slaugh and R. D. Mullineaux (Shell Internationale Research, Maatschappig, N.V.), French Patent 1,300,404 (1962).
8. Dolev, A., W. K. Rohwedder and H. J. Dutton, Lipids *1*, 231–233 (1966).
9. duPont de Nemours and Co., E. I., British Patent 614,010 (1948).
10. Emken, E. A., C. R. Scholfield, V. L. Davison and E. N. Frankel, JAOCS *44*, 373–375 (1967).
11. Ferguson, G. V., Chem. Ind. (London), *1965*, 451–456.
12. Frankel, E. N., C. D. Evans, H. A. Moser, D. G. McConnell and J. C. Cowan, JAOCS *38*, 130–134 (1961).
13. Frankel, E. N., E. P. Jones, V. L. Davison, E. Emken and H. J. Dutton, Ibid. *42*, 130–134 (1965).
14. Kodama, S., I. Taniguchi, S. Yuasa, A. Watanabe and I. Yoshida, J. Chem. Soc. Jap., Ind. Chem. Sect. *57*, 395–397 (1954); Chem. Abstr. *49*, 5005 (1955).
15. Macho, V., M. Marko, M. Ciha and J. Strešinka, Czech. Patent 104,691; Chem. Abstr. *59*, 11261a (1963).
16. Natta, G., and E. Beati, British Patent 646,424 (1950).
17. Ryhage, R., and E. Stenhagen, Ark. Kemi *14*, 497–509 (1959).
18. Shechter, H., D. E. Ley and L. Zeldin, J. Amer. Chem. Soc. *74*, 3664–3668 (1952).
19. Silverstein, R. M., and G. C. Bassler, "Spectrometric Identification of Organic Compounds," Wiley & Sons, Inc., New York, 1963, p. 61.
20. Wender, I., S. Metlin, S. Ergun, H. W. Sternberg and H. Greenfield, J. Amer. Chem. Soc. *78*, 5401–5405 (1956).
21. Wender, I., H. W. Sternberg, R. A. Friedel, S. J. Metlin and R. E. Markby, U.S. Bur. Mines, Bull. 600 (1962).

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