Electrolytic Acetoxylation of Methyl Oleate

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The electrolysis of methyl oleate in acetic acid solution with $LiClO_4$ as the supporting electrolyte was studied. Both stirred and pumped undivided cells were used with Pt electrodes. Constant current at 6, 8, 16 and 24 ma/cm² current densities was used. The amount of acetoxyl substitution appeared to be independent of the current density. With 4 Faradays of charge, about 1.1 acetoxy groups were introduced/mole at a current efficiency (i.e., net chemical reaction/net charge) of 50 to 60%. The acetoxylated octadecenoates exhibit thermal instability upon molecular distillation with the formation of conjugated unsaturation by loss of acetic acid. Catalytic hydrogenation of the acetoxylated product yielded distillable acetoxylated methyl octadecanoates. The unsaturated acetoxylated products gave 25–47% undistillable material upon molecular distillation, while the saturated acetoxy derivatives had as little as 1%. From the corresponding alcohols of the unsaturated acetoxy products, *t*-butyldimethylsilyl ethers were prepared and analyzed by mass spectrometry. This analysis supported the hypothesis that the principal points of acetoxyl substitution in the mono-acetoxylated esters were at C-8,9,10 and 11, while the acetoxylation in the poly-acetoxylated esters was more widely dispersed.

The application of electrochemistry to the synthesis of organic chemicals has had a renaissance (1). Relatively few studies have been directed toward the field of fatty acids, however. The anodic acetoxylation of methyl oleate has been reported (2). In that study, three preparative experiments were carried out in acetic acid solution with $LiClO_4$ electrolyte, which demonstrated that high conversion of methyl oleate to a mixture of mono- and di-acetoxy substituted methyl octadecenoates could be achieved. An undivided cell with rotating Pt anode and Hg cathode was used (3). From the mass spectra of the products, it was deduced that oxidation occurred principally, but not exclusively, in the allylic positions of the C9-10 double bond together with the double bond isomerized to C8-9 and 10-11. Because of our continued interest in the functionalization of unsaturated vegetable oils and their constituent acids, we have investigated this electrolysis further.

MATERIALS AND METHODS

Electrolyses were performed in undivided cells of either a simple magnetically stirred type with two Pt foil electrodes (2.5 × 2 cm) at a separation of 2.5 cm or a pumped cell that was machined from polypropylene. The Pt electrodes in the stirred cell were connected to Pt wires that were sealed through glass tubes that in turn passed through fittings mounted in a three-necked glass cell top. The cell top and electrodes were purchased from Electrosynthesis Co., East Amherst, New York. The pumped cell is shown schematically in Figure 1. The electrodes for this cells were fabricated from two Pt foils, 2.5 cm square, by spot welding no. 26 gauge Pt wires to one side of the foil. The wires then passed out through fitting seals in the end of the cell. The liquid was passed through the cell with a metering pump (Metering Pumps Ltd., London, England).

All electrolyses were carried out at constant current which was supplied by an electrophoresis-type (Bio-Rad Laboratories, Richmond, California) or lab-constructed power supply. Somewhat better constancy of current was obtained with the lab-constructed supply, but owing to its smaller power transformer, its use was limited to lower current experiments, i.e., lower power operation. The lab-constructed supply was made by assembling the modular units: power supply and booster (4), oper-

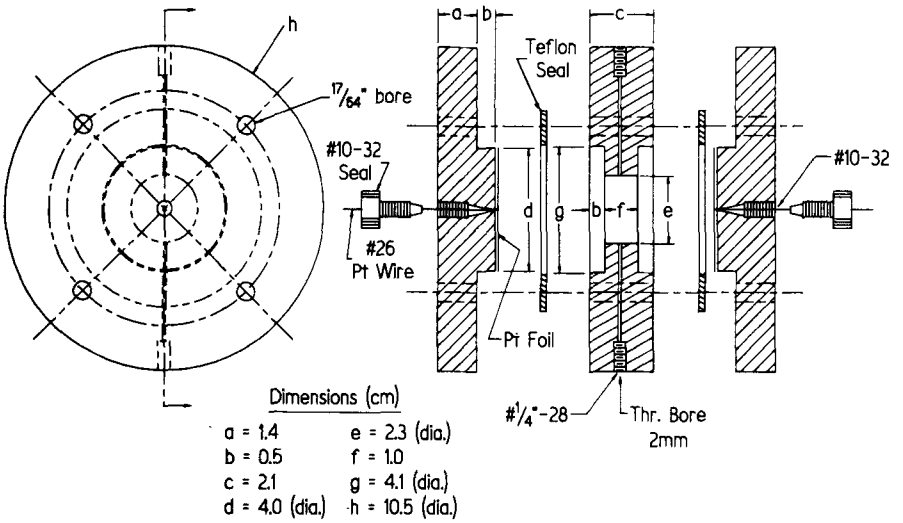

FIG. 1. Schematic drawing of pumped cell (not to scale).

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ational amplifier power supply kit (Jameco Electronics, Belmont, California) and operational amplifier constant current controller, which was based upon the circuit of Jung (5). The whole system could be constructed for less than $100, but a more powerful transformer than that described would have made the supply useful at the higher cell resistances encountered in this work.

Electrolysis experiments in both cell types were carried out in a similar manner and will be described by example.

Stirred cell. In a glass cylindrical vessel with round bottom of ca. 100 ml capacity was placed a solution of 6.0 g (20.3 mmol) methyl oleate in 50 ml of 0.1 M $LiClO_4$ in acetic acid. A glass top supporting a pair of Pt electrodes was fitted to the vessel. The system was flushed with N_2, and the third neck of the top was loosely closed with a plug of glass wool so that H_2 might escape. While the solution was magnetically stirred, constant current at 40 ma (8 ma/cm²) was passed from a power supply. The power supply was operated through a time switch set for 54 hr 20 min so that the total charge supplied was 4 F (i.e., 4 Faradays)/mol. After completion of the electrolysis, the dark solution was rinsed with a small amount of methanol into a 100-ml round bottom flask containing 1 g 5% Pd-on-carbon. The mixure was then hydrogenated at atmospheric pressure until hydrogen absorption ceased. Approximately 14.5 mmol H_2 were taken up. The product was filtered through a pad of filter aid with suction, and the solids were washed with methanol combined with the filtrate. The filtrate was diluted with saturated NaCl solution (400 ml), and the product was extracted with 3 × 100 ml ether. The combined extracts were washed successively with 400-ml portions of saturated NaCl solution, water and saturated $NaHCO_3$ solution, dried over $MgSO_3$ and filtered. The ether was removed on the rotary evaporator to yield 6.91 g of clear oil (82% of theory for substitution of two acetoxy groups and addition of one H_2).

The oil was distilled in a falling film still at 0.05 Torr and 184 C to yield 5.96 g of distillate and 0.08 g residue (1.3%). The distillate was analyzed by GC, and the ester equivalent weight was determined by saponification using a modification of AOCS method Cd 3b-76 (no toluene and methanolic rather than ethanolic alkali was used). From the ester equivalent weight, E, the average degree of acetoxylation was computed by the equation: X = (296-E)/(E-58), where X is the number of acetoxy groups substituted/mol.

Pumped cell. The cell was connected to the pump and a four-necked flask, so that the flow was from the flask to the pump upward through the cell and back to the flask. Polypropylene 1/8″ tubing and suitable fittings were used to form the liquid path. The flask was fitted with a thermometer, and through the stoppered fourth neck a sampling port was available. The pump was adjusted to a flow of ca. 22 ml/min. Both the pump and power supply were operated through a time switch connected to a thermal switch monitoring the temperature in the four-necked flask. In this way, should the flow be stopped by a pump failure while unattended, the system would be shut down by the fall of the temperature in the flask. In operation the flask was charged with a solution of 6.0 g (20.3 mmol) methyl oleate in 50 ml 0.1 M $LiClO_4$ in acetic acid. The pump was started independently of the time switch until a circulation of the solution was obtained, and then the pump was connected through the time switch. The current (33.2 ma, 8 ma/cm²) was then passed into the solution until a total of 5 F/mol had been introduced. Samples were removed after addition of each F, taken up in ether, washed successively with water twice and saturated $NaHCO_3$, dried over $MgSO_4$ and analyzed by capillary GC on SPB-1 or SP 2330 (Supelco Inc., Bellefonte, Pennsylvania). The final reaction mixture was hydrogenated and isolated, as were the products from the stirred cell.

High performance liquid chromatography (HPLC) on two coupled C18 reversed phase, 2 × 25 cm stainless steel columns packed with 7 μm particles (Rainin Instrument Co., Woburn, Massachusetts) was used to separate two mixtures of conjugated dienes: one *c,t* and *t,c*-, and the other *t,t*-conjugated from the methylated sample of acids that resulted from saponification of a distilled acetoxylated sample (no. 5, Table 1). This sample contained ca. 26 and 44% of these dienes, respectively. From three injections of 70–80 mg each on the HPLC columns, there were obtained 72 mg of the *t,t*-conjugated diene mixture of 96% purity. By rechromatographing the first eluting peak, 50 mg of 94% pure *c,t* and *t,c*-conjugated diene mixture was obtained. Eluent was H_2O/methanol (15:200, v/v) at 10 ml/min flow with detection at 215 nm. NMR spectra were obtained with a Bruker instrument WM 300 (Bruker Instruments, Billerica, Massachusetts) and tetramethylsilane as internal standard: *t,t*-conjugated diene mixture ^{1}H NMR ($DCCl_3$) δ .88 ppm (t, 3H, CH_3CH_2), 1.27 (m, 16H, $-(CH_2)_8-$), 1.62 (m, 2H, $-CH_2CH_2CO_2CH_3$), 2.03 (m, 4H, $CH_2-C=$), 2.30 (t, 2H, $CH_2CH_2C=O$), 3.66 (s, 3H, $-CO_2CH_3$), 5.56 (m, 2H, HC=), 5.96 (m, 2H, HC=, J = 14); ^{13}C NMR ($DCCl_3$) δ 14.11 ppm (CH_3-CH_2); 22.67 (CH_3CH_2-); 24.83, 24.90, 24.95 ($-CH_2CH_2CO_2CH_3$); 28.67–29.72 [10 signals, $-(CH_2)_n$]; 31.78, 31.84, 31.90 ($CH_3CH_2CH_2-$); 32.35, 32.50, 32.56, 32.62 (*t*, $CH_2-CH=$); 34.04, 34.09 ($CH_2CO_2CH_3$); 51.40 (CO_2CH_3); 130.26, 130.42, 130.50, 130.60 ($-CH^t=CHCH^t=CH-$); 131.79, 132.01, 132.15, 132.42, 132.49, 132.58 ($-CH^t=CHCH^t=CH-$); 174.18 ($-CO_2CH_3$).

c,t- and *t,c*-conjugated diene mixture ^{1}H NMR ($DCCl_3$) δ .88 ppm (t, 3H, CH_3CH_2-), 1.30, [m, 16H, $-(CH_2)_8-$], 1.62 (m, 2H, $-CH_2CH_2CO_2CH_3$), 2.10 (m, 4H, $CH_2-C=$), 2.30 (t, 2H, $-CH_2CO_2CH_3$), 3.66 (s, 3H, $-CO_2CH_3$), 5.32 (m, 1H, HC=), 5.66 (m, 1H, HC=), 5.94 (m, 1H, HC=), 6.28 (m, 1H, HC=); ^{13}C NMR ($DCCl_3$) δ 14.11 ppm (CH_3CH_2-); 22.69 (CH_3CH_2-); 24.86, 24.93 ($-CH_2CH_2CO_2CH_3$), 27.50, 27.62, 27.74 ($-CH_2C^c=$); 28.79–29.74 [11 signals, $-(CH_2)_n$]; 31.78, 31.87 ($CH_3CH_2CH_2-$); 32.80, 32.86, 32.92 (*t* $-CH_2C=$); 34.11 ($-CH_2CO_2CH_3$); 51.43 (CH_3O_2C); 125.48, 125, 53, 125.77 ($-HC^c=CHCH^t=CH-$); 128.54, 128.76, 128.86 ($-HC^c=CHCH^t=CH-$); 129.52, 129.76, 130.15, 130.21 ($-HC^c=CHCH^t=CH-$); 134.34, 134.47, 134.82, 134.91 ($-CH^c=CHCH^t=CH-$); 174.25 ($-CO_2CH_3$).

t-Butyldimethylsilylation of methyl hydroxyesters from the electrolytic acetoxylation and saponification was achieved by treatment with the *t*-butyldimethylchlorosilane-imidazole-dimethylformamide combination (6, 7). A sample of methyl ricinoleate was also con-

verted to *t*-butyldimethylsilyl (TBDMS) ethers for comparison of mass spectra.

Gas chromatography/mass spectrometry (GC/MS) was carried out on a Finnegan (San Jose, California)/MAT GC/MS Quadrupole 1020 instrument which incorporated a 30 m × 0.24 mm SP2330 (Supelco, Inc. Bellefonte, Pennsylvania) fused silica capillary column. The GC column was operated in the temperature programming mode from 170 to 266 C at 5 C/min. The mass spectra were obtained with 70 ev impact ionization. The spectrum of methyl ricinoleate TBDMS ether showed, m/z (% rel. abundance): 337(6), 230(12), 229(68), 173(15), 73(100). The data for the mass spectrum of TBDMS ethers derived from the products of acetoxylation are in Table 2.

RESULTS AND DISCUSSION

The results of the electrolysis experiments are shown in Table 1. Most experiments were performed with the stirred cell (nos. 1-12). In early experiments (nos. 1-5), distillation and/or reduction of the product acetoxy derivatives were not performed. The product yields and degree of acetoxy substitution were independent of the current density with 4 Faradays of charge.

When the products were distilled in the low thermal-hazard falling film molecular still (nos. 6-9, Table 1), without prior catalytic hydrogenation, large amounts of nondistillable substances (polymer in Table 1) were present. These polymers were either in the crude products or were formed in the distillation process. The amount of acetoxy substitution in the distillate material was reduced by 80% or more compared to non-distilled material. Comparison of data from GC analyses of the products before and after molecular distillation indicated the probable formation of conjugated dienes in the distillation.

Conjugated diene was confirmed by NMR analyses of two mixtures isolated by HPLC. The fraction with shortest retention time was identified as a mixture of *c,t* and *t,c*- conjugated dienoates. The ^{1}H NMR showed four olefinic protons but the ^{13}C NMR was definitive. Thus, at δ 27.50, 27.62 and 27.74 were observed signals for three methylenes attached to a *c*-double bond, while at δ 32.80, 32.86 and 32.92 are found signals for three methylenes on a *t*-double bond (8). The multiplicity of the signals is due to the presence of positional isomers, probably with double bonds moved one or two carbon positions. The double bonds are seen to be conjugated from the signals for the olefinic carbon atoms. Thus, the internal *c*-olefinic carbon atom of a 1-3 diene system is shown by signals: 125.48, 125.53 and 125.77. The external *c*-olefinic carbon atoms are indicated by signals: 129.52, 129.76, 130.15 and 130.21. The internal and external olefinic carbons of a *t*-double bond in a conjugated diene are shown by the signals: 128.54, 128.76, 128.86 and 134.34, 134.47, 134.82, 134.91, respectively (9). Similar analysis, applied to the ^{13}C NMR of the later-eluting HPLC peaks, confirmed them as a mixture of *t,t*-conjugated dienoates.

From the NMR data, it may further be deduced that the conjugated double bond system is probably greater than ω-5, because the methylene at ω-3 is sensitive to the double bond proximity, and it is in its normal range of ca. 31.8-31.9 in both conjugated isomer mixtures. Further, the signal for the methylene beta to the carbonyl at 24.83-24.90 suggests a double bond at C-5,6 or 7 (8).

TABLE 1

Results of Electrolyte Acetoxylation of Methyl Oleate

No.	Reactor system[a]	Oleate concentration (g/ml)	Electrolyte concentration	Current density[b] (ma/cm^2)	Reduced[c]	Percent yields[d]		Acetoxyls/mol[e]
						Product	Polymer	
1	S	0.08	0.1 M $LiClO_4$	6	N	89	-	1.0
2	S	0.08	0.1 M $LiClO_4$	8	N	89	-	1.1
3	S	0.08	0.1 M $LiClO_4$	16	N	89	-	1.0
4	S	0.08	0.1 M $LiClO_4$	24	N	88	-	1.1
5	S	0.06	0.1 M $LiClO_4$	8	N	86	-	1.2
6	S	0.12	0.1 M $LiClO_4$	8	N	45	25	0.1
7	S	0.12	0.1 M $LiClO_4$	8	N	34	47	0.2
8	S	0.12	0.1 M $LiClO_4$	24	N	40	40	0.2
9	S	0.12	0.1 M $(C_4H_9)_4NClO_4$	24	N	48	34	-
10	S	0.12	0.1 $LiClO_4$	8	Y	72	1	1.0
11	S	0.12	0.1 $LiClO_4$	8	Y	62	3	1.1
12	S	0.12	0.1 $LiClO_4$	24	Y	59	8	1.1
13	P	0.12	0.1 $LiClO_4$	8	Y	36[f]	17	1.4
14	P	0.12	0.2 M $LiClO_4$	8	Y	31	36	1.1
15	P	0.12	0.2 M $LiClO_4$	8	Y	45	17	1.2

[a]S = stirred cell, P = pumped cell.

[b]No. 1-12 received 4 F, no. 13-15 5 F of charge.

[c]Hydrogenated over Pd/C, N = No, Y = Yes.

[d]Polymer yields calculated from molecular distillation fraction weights, product yields from undistilled product, no. 1-5, but distilled product, nos. 6-15. Nos. 1-5 were not distilled.

[e]Computed from saponification; see Experimental.

[f]Five GC samples removed from no. 13-15 during electrolysis.

TABLE 2

GC/MS Analysis of *t*-Butyldimethylsilyl Ethers from Product Methyl Esters

Relative retention[a]	% Total[b]	Ions: M/Z (% relative abundance)
2.3	4	369(23), 337(19), 313(10), 283(22), 269(11), 75(100).
2.4	34	369(8), 337(20), 327(7), 313(6), 299(13), 75(100).
3.3	4	375(14), 331(15), 317(28), 263(17), 257(18), 245(18), 243(21), 229(20), 147(100).
3.4	17	499(7), 325(5), 311(3), 287(2), 273(4), 243(5), 73(100).
3.9	5	301(30), 279(6), 263(12), 257(41), 245(11), 75(100).

[a]Retention relative to methyl stearate.
[b]Of total integrated ion current.

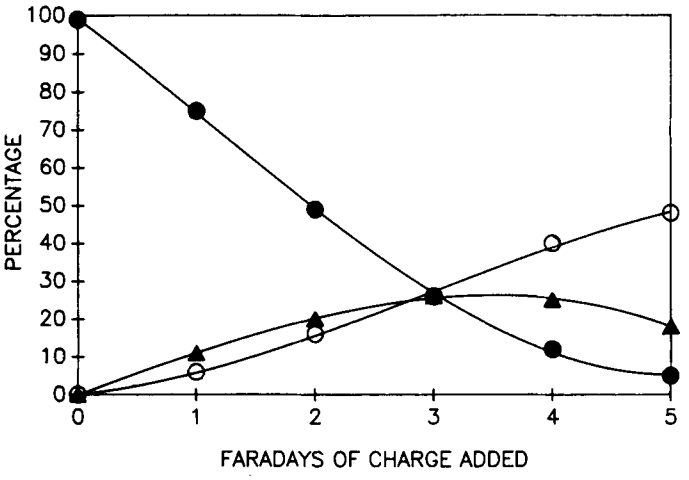

FIG. 2. Product formation (▲, mono-acetoxylated methyl oleate; ○, di-acetoxylated methyl oleate) and disappearance of starting material (●, methyl oleate) as function of charge added. Data were derived from GC analysis of Exp. #15, Table 1.

Thus, it is probable that the conjugated diene system is near the center of the carbon chain.

When the products were saturated with H_2 prior to molecular distillation, the yield of polymer fell to low levels (nos. 10–12, Table 1), and the degree of acetoxylation was similar to what had been observed in undistilled products. Little formation of methyl stearate by reduction of oleate at the cathode was observed. The principal reaction occurring at the cathode during the electrolysis appears to be H_2 evolution. The stabilization of the acetoxy function in the products by reduction indicates that the acetoxy group is probably in the allylic position as deduced by Adams et al. (2) from study of the mass spectrum of the TMS ethers of the alcohols derived from acetoxylated methyl oleate.

It appears that the formation of conjugated dienes (as well as possibly more highly unsaturated olefins) through the loss of acetic acid and subsequent polymerization of these unsaturates accounts for most of the polymer observed in no. 6–9. Frankel et al. (10) observed thermal instability in acetoxylated methyl oleate produced by Pd-catalyzed oxidation.

The results from the pumped cell electrolyses (nos. 13–15, Table 1) showed a markedly high level of polymer formation in the electrolysis and/or subsequent distillation despite hydrogenation prior to distillation. These reactions were carried out with input of 5 F rather than 4 to reduce the level of unreacted methyl oleate to that obtained in the stirred cell runs (<5%). Samples were removed after each F of added charge for GC analysis. The data for no. 15, Table 1, are plotted in Figure 2. Comparison with similar plots for nos. 13 and 14 shows similar shaped curves, but no advantage for doubling the electrolyte concentration from 0.1 to 0.2 M is indicated except for reduction of the cell voltage from 100 to 30 V.

GC/MS was applied to characterize more fully products that were produced in the electrolytic acetoxylation of methyl oleate. The mass spectrum of the acetoxylated derivatives themselves provided little information with electron impact MS owing to the great loss of acetic acid and the extensive fragmentation of the ions. Therefore, we prepared the TBDMS ethers of the methyl esters of the hydroxy acids that were isolated from the saponifications. The TBDMS ethers yield pseudo-molecular ions, i.e. ions reflecting the loss of a *t*-butyl group (M-57), that can be useful in deducing structure (11). We also prepared the TBDMS ether of methyl ricinoleate to examine its mass spectrum under the same conditions.

In the mass spectrum of the TBDMS ether of methyl ricinoleate, the expected ion at m/z M-57 is found at 337 reflecting the loss of methanol from the ester function. A diagnostic, intense peak at 229 shows the highly preferential cleavage between C11-12 to the virtual absence of cleavage between C12-13 or between either of the olefinic carbons and the allylic carbons. Cleavage between the oxygenated carbon and the adjacent carbon is well known (2, 11) but is apparently highly preferential with ricinoleate TBDMS ether.

The GC/MS of the TBDMS ethers of the methyl hydroxyesters from the acetoxylated metyl oleate obtained in our experiments (no. 5, Table 1) confirms the GC results showing complexity. Table 2 shows the m/z of the principal loss from the TBDMS ethers while in Table 3 are listed possible m/z values for the ionic fragments (structures A-F) where "n" assumes the values in column 1. Table 3 is useful in suggesting possible fragments for the m/z of the ions of Table 2 and will be referred to by the column coordinate A-F followed by the row coordinate n in the following discussion.

In addition to the GC/MS peaks reflecting the presence of TBDMS ether derivatives of hydroxyoleate (Table 2), minor constituents were identified as methyl esters of 18:0, 18:1 and 18:2. It can be seen in the mass data for ricinoleate and in Table 2 that base ions from the GC peaks are either 73, 75 or 147. This is to be expected because in the mass spectra of TBDMS ethers the silyl ions of m/z 73, 75 and 147 have been observed

TABLE 3

Mass Fragments Possible from TBDMS Ethers

	M/Z Structures[a]							
n	A	B	C	(C-32)	D	(D-32)	E	F
1	159	185	217	185	243	211	289	347
2	173	199	231	199	257	225	303	361
3	187	213	245	213	271	239	317	375
4	201	227	259	227	287	253	331	389
5	215	241	273	241	299	267	345	
6	229	255	287	255	313	281	359	
7	243	269	301	269	327	295	373	
8	257	283	315	283	341	309	387	
9	271	297	329	297	355	323		
10	285	311	343	311	369	337		
11	299	325	357	325	383	351		
12	313	339	371	339	397	365		
13	327	353		353				
14	341	381		367				

[a]Structures:

A = $H(CH_2)_nCHO(TBDMS)+$

B = $H(CH_2)_nCH{=}CHCHO(TBDMS)+$ or $H(CH_2)_nCHCH{=}\overset{(TBDMS)}{\overset{|}{O}}CH+$

C = $(TBDMS)OCH(CH_2)_nCO_2CH_3+$

D = $(TBDMS)OCHCH{=}CH(CH_2)_nCO_2CH_3+$ or $CH{=}CHCH(CH_2)_nCO_2CH_3+$ ($\overset{(TBDMS)}{\overset{|}{O}}$)

E = $(TBDMS)O(CH_2)_nCHO(TBDMS)+$

F = $+CH(\overset{(TBDMS)}{\overset{|}{O}})(CH_2)_x CH(\overset{(TBDMS)}{\overset{|}{O}})(CH_2)_yCO_2CH_3$ $\quad x + y = n$

commonly and assigned as $(CH_3)_3Si+$, $(CH_3)_2SiOH+$ and $(CH_3)_3SiOSi(CH_3)_2+$, respectively (12). The GC peaks at 2.3 and 2.4 relative retention (rel. retention to methyl 18:0, Table 2) represent TBDMS ethers of mono-hydroxyesters as seen from pseudo-molecular ions at m/z 369 (M-57) and 337 (M-57-32). It also seems likely that the first of these GC peaks represents the isomer pair resulting from acetoxylation of methyl oleate at C-8 and/or C-10 while the larger following GC peak is due mainly to products derived from acetoxylation at C-9 and/or C-11. The respective ion pairs have the m/z of D6 and B8, and D7 and B7. This is, of course, a comforable speculation because these fragment ions sum to a C-18 mono-ether methyl ester and at logical points of oxygenation (2, 10), but it may also be seen that columns B and (C-32) in Table 3 have the same m/z values.

The GC peaks at relative retention 3.3 and 3.4 appear to represent TBDMS ethers of products that were derived from di-acetoxylated esters. The GC peak at 3.4 relative retention (Table 2) has a pseudo-molecular ion at 499 (M-57). The peak at 3.3 relative retention has ions corresponding to E3, E4 and F3. Homologous substitution is suggested by the mass 14 differences seen.

The GC peaks grouped at relative retention 3.9 probably are tri-TBDMS ethers based upon their retention and the ions from them. The ions of m/z 301 and 245 suggest ester ions C7 and C3 (Table 3), while 257 suggests A8 and/or D2.

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