Conversion of Methyl 9(10)-Formylstearate to Carboxymethylstearate

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ABSTRACT

Methyl 9(10)-formylstearate was converted to methyl 9(10)-carboxymethylstearate. The reactions to prepare the intermediates methyl 9(10)-hydroxymethyl-, 9(10)-acetoxymethyl-, 9(10)-methylene-, and 9(10)-formylmethylstearate are described. Methyl 9(10)-hydroxymethylstearate readily loses methanol and forms a trimeric polymer. The acetate of the primary alcohol when pyrolyzed gives 59% yield of methyl 9(10)-methylenestearate. Hydroformylation of the methylene compound followed by permanganate oxidation gave methyl carboxymethylstearate. Evidence is presented to show that pyrolysis of the acetate ester and hydroformylation of the pyrolysis product produce, respectively, only the methylene and formylmethylstearates. Rates of esterification-transesterification of methyl 9(10)-carboxymethylstearate show that the carboxymethyl group is 2-3 times as active as the carboxyl group in methyl 9(10)-carboxystearate and that the terminal carboxyl group is about 10 times more active towards esterification than the branched carboxymethyl group.

INTRODUCTION

An authentic sample of methyl 9(10)-carboxymethylstearate (MCMS) was required for use in recent studies (1,2) of reactions and uses of methyl 9(10)-formylstearate (MFS). Selective hydroformylation of methyl oleate (3) gives high yields of MFS. An obvious route to prepare MCMS from MFS seemed feasible, and the following series of reactions was proposed: (a) reduction of MFS to methyl 9(10)-hydroxymethylstearate (MHMS); (b) dehydration to methyl 9(10)-methylenestearate (MMS); (c) hydroformylation of MMS to methyl 9(10)-formylmethylstearate (MFMS); and (d) oxidation with permanganate to MCMS. Although the reaction conditions were not optimized to obtain the highest yields, this article reports the preparation and some properties of MCMS and the intermediate compounds obtained from the above proposed reaction sequence.

RESULTS AND DISCUSSION

Methyl 9(10)-Hydroxymethylstearate

This compound has been prepared by reduction of MFS with Raney nickel (3). Although some properties have been reported, no mention of polymeric MHMS has been made. MHMS can be distilled in vacuo using a molecular still. However, during pot distillation of large quantities of MHMS, vacuum is lost rapidly, and methanol is evolved. Three moles of product loses 2 moles of methanol and is converted to a trimeric MHMS, $\mathrm{H(OCH_2\text{-}\overset{C_9H_{19}}{CH}(CH_2)_7COO)_3CH_3}$, and estolide with an observed mol wt of 858. The calculated mol wt is 920. Saponification of the trimer gave near quantitative yields of hydroxymethylstearic acid. On standing at room temperature for over 1 year, a similar viscous product was obtained from MHMS. Possibly, the viscous residues encountered by Miller (4) from methyl *bis*(hydroxymethyl)stearate have similar structures. Polymeric esters with a terminal acid group are also obtained from hydroxymethylstearic acid (MHSA) on standing at room temperature. Estolides with mol wt of 1500 obtained by heating ricinelaidic acid in vacuo for several hours have

TABLE I

Pyrolysis of 9(10)-Acetoxymethylstearic Acid and Ester

Product (g)	Temperature (°C)	Passes No.	Time (min)	N_2 (ml/min)	MMS[a] Yield Crude (g)	MMS[a] Yield GLC[b] (%)	MMS[a] Yield Distilled (wt %)
Methyl 9(10)-acetoxymethylstearate							
			On glass helices				
10	400	1	20	None	9.8	20	---
10	400	5	120	None	9.0	79	46
10	450	1st	20	None	8.1	63	
		2nd	20	None	7.5	88	32
10	500	1	20	None	8.2	92	32
			On 40-60 mesh ground glass				
10	400	1	45	None	9.8	86	59
10	400	1st	25	30	9.3	67	
		2nd	25	30	8.7	92	43
10	425	1	60	None	8.2	92	27
10	430	1	12	15	8.4	90	56
43	425-430	1	60	30	40.5	88	55
9(10)-Acetoxymethylstearic acid							
10	400	1	30	50	8.1	89	48
10	430	1	12	30	8.2	92	52

[a] MAMS = Methyl acetoxymethylstearate; MMS = methyl 9(10)-methylenestearate; GLC = gas liquid chromatography.

[b] Based only on MMS and MAMS peaks. One mg sample treated with diazomethane before GLC analysis.

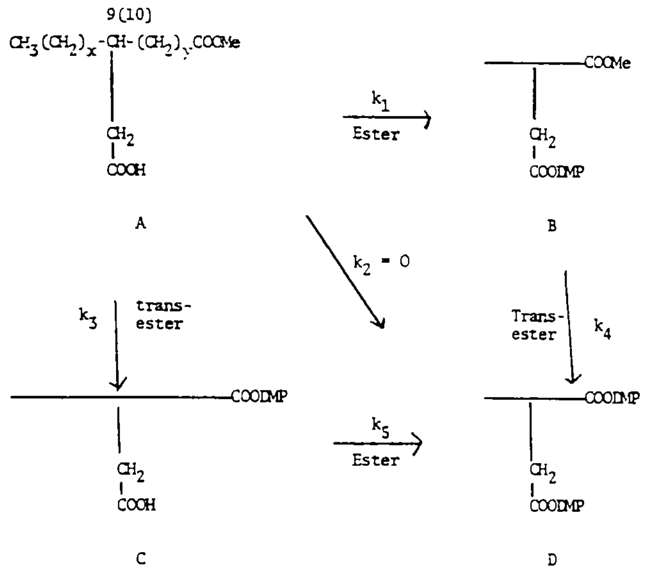

FIG. 1. Scheme of esterification and transesterification of 0.133 molar methyl 9(10)-carboxymethyl stearate (MCMS) with 4.2 molar 2,2-dimethyl-1-pentanol [(DMP)OH] in benzene at 95 C using 79 mg sulfuric acid. Assume $k_2 = 0$. (A) M 9(10)-CMS; (B) M 9(10)-carbo(DMP)-MS; (C) DMP 9(10)-CMS; (D) DMP 9(10)-carbo(DMP)MS.

been used to prepare 9,11-*trans,trans*-octadecadienoic acid (5).

Freshly prepared MHMS when treated with acetic anhydride is readily converted to the easily distillable methyl 9(10)-acetoxymethylstearate (MAMS). Acetoxymethylstearic acid (AMSA) was also obtained when trimeric MHMS was refluxed with acetic acid and sulfuric acid catalyst.

Methyl 9(10)-Methylenestearate

Pyrolysis of acetates of primary alcohols is reported to yield only terminal olefins (6). For example, 3-methylbutyl acetate is converted exclusively to 3-methyl-1-butene. Thus, methyl 9(10)-acetoxymethylstearate should yield only MMS. Attempts to pyrolyze MAMS at 400, 450, and 500 C using pyrex helices gave 63 to 92% conversion by gas liquid chromatography (GLC) analysis based only on MMS and starting product. Large amounts of low mol wt compounds, however, were formed as evidenced by the 32-46 wt % yield of pure MMS obtained by fractional distillation (Table I).

Pyrolysis of MAMS on 30-60 mesh ground glass at 400 to 430 C with and without nitrogen increased yields on distillation up to 59% (Table I). Polymeric MHMS and acetoxy stearic acid gave 19 and 48% of MMS and methylenestearic acid, respectively. Attempts to dehydrate the borate ester of MHMS as described for dehydration of ricinelaidic acid were unsuccessful (5).

Methyl 9(10)-Formylmethylstearate

MMS, when treated with H_2 and CO using rhodium on alumina and triphenylphosphine catalyst, readily undergoes the oxo reaction to yield MFMS. The other possible product of hydroformylation, methyl 9(10)-methyl 9(10)-formylstearate, was not formed. The NMR spectra of MFMS were consistent with the structure. The following peaks were observed: at δ0.8-1.0, for terminal CH_3 of long alkyl chains; two peaks at δ2.2-2.4, for $-CH_2-$ of $-CH_2CHO$ and $-CH_2COOR$; at δ3.62 for CH_3 of methyl esters; and at δ9.8 for CHO. The sharp peak expected at δ1.1 for the branched methyl group of $-C(CHO)(CH_3)-$ was not present. Thus, hydroformylation takes place only at the unsubstituted methylene carbon of MMS, and pyrolysis of the acetate ester (MAMS) produces only MMS.

Methyl 9(10)-Carboxymethylstearate

Oxidation of MFMS with potassium permanganate (7) gave MCMS. A kinetic study of the rate of esterification-transesterification with 2,2-dimethyl-1-pentanol was carried out as previously reported (8). The reaction scheme is shown in Figure 1.

A ratio of esterification rates (average of k_1 and k_5) of the branched acid groups of MCMS and methyl carboxystearate (MCS), $\frac{\text{-COOH}_{MCMS}}{\text{-COOH}_{MCS}}$, is 0.109/0.047 which indicates that the $-CH_2COOH$ is about 2-3 times as active as the branched -COOH of MCS (8). This agrees favorably with a value of 4-5 obtained by Roe et al. (9) by determining reduction of acid number during esterification of an isomeric mixture of methyl carboxymethylstearates. The reported rate of esterification of the terminal carboxyl of carboxystearic acid (CSA) is 1.09 hr^{-1} (8). This value would be expected to be the same for the terminal carboxyl of MCMS. Under almost identical conditions the rate of esterification of the branched $-CH_2COOH$ is 0.109 (average k_1 and k_5 in Table II). Thus, the terminal -COOH of carboxymethylstearic acid is about 10 times as active as the branched $-CH_2COOH$. For CSA containing a branched -COOH, the value is 26-27 (8).

Transesterification rates of terminal methyl ester k_3 and k_4 for MCMS are 0.075 and 0.054 hr^{-1} which agree favorably with the values of 0.096 and 0.063 hr^{-1}, respectively, for transesterification of the methyl ester moiety of methyl carbodimethylpentoxymethylstearate and methyl carbomethoxy stearate (8).

Another possible route to the desired carboxymethylstearic acid is hydrolysis of methyl 9(10)-cyanomethyl stearate. However, one attempt to prepare the intermediate, methyl 9(10)-bromomethylstearate, by adding an equal

TABLE II

Rates of Esterification and Transesterification with Dimethylpentanol[a]

Ester-acid	Conc. M/1	Temperature	Rates,[b] (hr^{-1}) k_1	k_3	k_4	k_5
MCMS[c]	0.133	95	0.118	0.075	0.054[d]	0.099
M(DMP)MS[c]	0.130	93			0.067[d]	
MCS[a,c]	0.139	101	0.047	0.111	0.096	0.045

[a] See Ref. 8, Table II, experiment 18, for procedures and additional rates.

[b] In Figure 1, assume $k_2 = 0$.

[c] MCS = methyl 9(10)-carboxystearate; MCMS = methyl 9(10)-carboxymethylstearate; M(DMP)MS = methyl 9(10)-carbodimethylpentoxymethylstearate.

[d] Transesterification rate B→D in Figure 1.

molar amount of phosphorus tribromide to MHMS gelled on standing. Attempts to prepare the cyanohydrin of MFS by addition of sodium bisulfite to MFS followed by cyanide resulted in recovery of MFS.

EXPERIMENTAL PROCEDURES

Methyl 9(10)-Formylstearate (MFS)

MFS was prepared by hydroformylation of methyl oleate using rhodium on alumina-triphenylphosphine catalyst (3).

Methyl 9(10)-Hydroxymethylstearate (MHMS) and Its Polymer

MFS (950 g) was reduced with Raney Ni (75 g) and H_2 at 900 psi and 100 C for 2 hr. After filtration, 952 g of water-white oil were obtained. Distillation of 125 g of product at 0.05 mm yielded 25-30 g of MHMS b.p. 185-195 C. The residue was a viscous polymeric material. Anal. Calc. for trimer of MHMS less 2 methanol, $C_{58}H_{112}O_7$: C, 75.8; H, 12.3; CH_3O, 3.4. Found: C, 76.93, H, 12.62, CH_3O, 3.53. Molecular wt: 920. Found 858. A sample was saponified to HMSA. Neutral equivalent Calc.: 314. Found 313. On standing at room temperature for 1 year, a similar viscous polymeric material was obtained from MHMS.

Methyl 9(10)-Acetoxymethylstearate (MAMS)

MHMS (32.8 g; 0.1*M*) was refluxed for 2 hr with acetic anhydride (15 g; 0.14*M*) on a steam bath with magnetic stirring. Acetic acid and excess anhydride were removed in vacuo and the MAMS distilled to give 34.3 g (92.7%); b.p. 170-174 (0.25 mm).

9(10)-Acetoxymethylstearic Acid (AMSA)

AMSA was prepared from freshly prepared HMSA and acetic anhydride as described above for MAMS. The acidic product distilled at 199-201 C (0.025 mm). Anal. Calc. for $C_{21}H_{40}O_4$: C, 70.76; H, 11.02; neutral equivalent (NE), 356. Found: C, 70.66; H, 11.38; NE, 350.

AMSA was also prepared by refluxing polymeric MHMS (125 g) with acetic acid (250 ml) containing sulfuric acid (5 ml). After normal workup and distillation, 102 g of product were obtained.

Methyl 9(10)-Methylenestearate (MMS)

A pyrolysis column was constructed as previously reported by Froemsdorf et al. (6) and List et al. (10). Two nichrome wire heaters and thermocouples were used to control heat input more accurately. A thermocouple was placed in the center of each heater. An initial rapid flow at the top of the column cools the packing rapidly; thus the initial starting temperature at the top heater was always 5 to 6 C above the desired run temperature taken at the middle of the bottom heater. The compound to be pyrolyzed was placed in a pressure-equalized vacuum addition funnel which was fitted with a nitrogen inlet tube. The column was flushed with nitrogen before all reactions. Pyrolyses were carried out as described previously (10), and the results are summarized in Table I.

Methyl 9(10)-methylenestearate was distilled, b.p. 126-129 C at 0.02 mm. Anal. Calc. for $C_{20}H_{38}O_2$: C, 77.35; H, 12.33; CH_3O, 9.99; iodine value 83.8. Found: C, 76.89; H, 12.49; CH_3O, 9.88; IV, 81.8.

Methyl 9(10)-Formylmethylstearate (MFMS)

MMS (19.5 g) was dissolved in toluene (50 ml) and hydroformylated at 105 C with H_2 and CO at 900 psi with rhodium on alumina (200 mg) triphenylphosphine (110 mg) catalyst (1). The product (20.8 g) was filtered and fractionally distilled. The yield was 14.0 g; b.p. 164-169 C (0.15 mm). Anal. Calc. for $C_{21}H_{40}O_3$: C, 74.07; H, 11.84. Found: C, 73.99; H, 12.20.

Methyl Carboxymethylstearate (MCMS) and Its Dimethylpentyl Ester

MFMS (10.9 g) was oxidized with potassium permanganate as described (7). The product was first passed through a small silicic acid column to remove some saponified product and then distilled, b.p. 197-200 C (0.05 mm). Neutral equivalent calcualted, 356.5. Found 358.1. The product (MCMS) was converted to the acid chloride with phosphorus trichloride (8,11) and then to methyl 9(10)-carbodimethylpentoxymethylstearate using dimethylpentanol and pyridine (8). The boiling point was 200-203 C (0.035 mm).

2,2-Dimethylpentyl 9(10)-Carbo(2,2-dimethylpentoxy)methylstearate

This compound was prepared in 90% yield by esterification of carboxymethyl stearic acid with 2,2-dimethylpentanol using sulfuric acid catalyst and benzene to azeotropically remove the water. Anal. Calc. for $C_{34}H_{66}O_4$: C, 75.78; H, 12.34. Found: C, 75.21; H, 12.38.

KINETIC STUDY

The procedure reported previously (8) to study the rates of esterification-transesterification of methyl carboxystearate was used to determine the rate of esterification of MCMS. The rates of reaction were determined by a digital computer program (12). The scheme and rates are shown in Figure 1 and Table II.

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