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Epoxidation of Methyl Linoleate. I. The Question of Positional Selectivity in Monoepoxidation[1]

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Abstract

The mixture of compounds resulting from the epoxidation of one of the double bonds of methyl linoleate has been examined to determine possible positional selectivity in monoepoxidation. The analysis, which depended on periodic acid cleavage of saturated epoxides or saturated vicinal glycols, has revealed that the two monoepoxidation products, methyl vernolate and methyl coronarate, are produced in essentially equal amounts.

Introduction

EPOXIDATION OF LINOLEIC ACID or its esters has been carried out repeatedly and successfully in the past (1,2). Our aim in reexamining epoxidation of methyl linoleate with the aid of modern analytical tools was two-fold: (a) to determine whether monoepoxidation of methyl linoleate proceeds with any degree of selectivity at either the 9,10- or the 12,13-double bond, and (b) to seek and perhaps isolate and purify a previously unreported stereoisomer of the known methyl *cis, cis,* 9,10:12,13-diepoxystearate.

The current paper is concerned with the monoepoxidation of methyl linoleate, and all alkyl groups attached to double bonds or oxirane groups have a *cis* relationship. The examination of the diepoxides will be reported in a later paper.

Epoxidation of methyl linoleate with sufficient peroxy acid to oxidize only one of the two double bonds should result, in the absence of limiting factors, in the formation of equal amounts of the two possible monoepoxides (Fig. 1). Epoxidation of the 9,10 double bond only gives rise to methyl 9,10-epoxy-12-octadecenoate, the methyl ester of coronaric acid which was the first reported by Smith (3,4). Epoxidation of the 12,13 double bond of methyl linoleate yields methyl 12,13- epoxy-9-octadecenoate, methyl vernolate. The latter is an ester of the naturally occurring vernolic acid which was first described by Gunstone (5) and which has been investigated extensively by Krewson (6,8). The determination of any selectivity in epoxidation of one of the two double bonds of methyl linoleate depends upon the quantitative analysis of the monoepoxide product for relative amounts of methyl coronarate and methyl vernolate present. Methyl coronarate has not been reported in the literature, but fortunately trivernolin was available to us in ample supply through the generosity of Dr. Krewson, so that we were able to use methyl vernolate as a model compound for our studies.

Experimental

Methyl Linoleate

The material used for epoxidation studies had the following characteristics: Saponification No., 190.0 (theory 190.0) acid No., 1.24, iodine value; 172.4 (theory 172.4) gas-liquid chromatography (GLC) showed a single peak with trace impurities amounting to less than 1%.

Methyl Vernolate

Prepared by the method of Luddy and Barford (9,10) with modifications as reported previously (11).

Column chromatography on silica gel gave methyl 12,13-epoxy-9-octadecenoate; oxirane oxygen, 4.97% (theory 5.15%). GLC indicated that a small amount of residual solvent was the principal impurity.

Dimethyl Sebacate

This material was required as internal standard for GLC analyses. Sebacic acid was esterified according to the method of Lough (12).

Methyl 9,10-Epoxystearate

Prepared by epoxidation of methyl oleate as reported previously (13).

Caproic Aldehyde

The material purchased from Fluka, A. G., had a purity of 95+% by GLC and was used as received.

Pelargonic Aldehyde

The aldehyde purchased from Aldrich Chemical Company was distilled through a 2-foot packed column and the heartcut reserved (bp 14 mm 76.5C; n_D^{20} 1.4231; purity by GLC: 94.8%).

Methyl Azelaaldehydate

To 5 g (0.0160 mole) of methyl 9,10-epoxystearate dissolved in 75 ml purified 1,4-dioxane was added a solution of 12.5 g (0.0548 mole) paraperiodic acid in a mixture of 20 ml water and 25 ml dioxane (11). The reaction mixture was agitated for 15 min at

[1] Presented at AOCS Meeting in Cincinnati, October 1965.
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TABLE I

Acetoxylation of Methyl 12,13-Epoxy-9-Octadecenoate

Methyl vernolate moles × 10^{-3}	Additional reagent		Reaction time, hr	Reaction temp, °C	Estimated product[c] yield	Starting material remaining[d]
	Reagent	Amount moles × 10^{-3}				
2.9[a]	Sodium acetate (Trihydrate)	14.7	18	25	50.0	50
2.9[a]	Sodium acetate Phosphoric acid 85%	14.7 0.9	18	25	37.5	62.5
8.7[b]	Sodium acetate (Trihydrate)	44.1	2	75	87.5	Nil
2.9[a]	Sodium acetate (Anhyd.)	24.4	2	80	98.0	Nil

[a] Dissolved in 10 ml glacial acetic acid.
[b] Dissolved in 30 ml glacial acetic acid.
[c] Product methyl 12(13)-acetoxy-13(12)-hydroxy-9-octadecenoate estimated by GLC and IR.
[d] Estimated from GLC and oxirane analysis.

room temperature and was then poured into 1000 ml water containing 3.0 g potassium hydroxide. The aqueous mixture was washed with eight 50 ml portions of petroleum ether (bp 40–60C) and the combined extracts were washed with 25 ml water, dried over sodium sulfate, filtered and evaporated under nitrogen to obtain an oily residue (6.77 g) which contained, according to GLC analysis 2.03 g nonanal and 2.02 g methyl azelaaldehydate. The oil was further blown with nitrogen on the steam bath to approximately constant weight of a light yellow oil which contained almost no nonanal and was about 85% pure methyl azelaaldehydate. This crude ester was chromatographed on silica gel (Davison No. 923) to obtain methyl azelaaldehydate, purity >99% by GLC and TLC, n_D^{30} 1.4360 [lit (14): n_D^{30} 1.4344].

Methyl Brassylaldehydate

The methyl ester of the semialdehyde of brassylic acid was prepared by the periodate oxidation of methyl 12,13-epoxystearate in a manner analogous to that used to prepare methyl azelaaldehydate from methyl 9,10-epoxystearate. Methyl 12,13-epoxystearate (1.0 g, 95% pure) dissolved in 10 ml 1,4-dioxane was treated with paraperiodic acid (1.25 g) dissolved in 2 ml water. After treatment for 15 min. at room temperature the product mixture was worked up in the same manner as described for methyl azelaaldehydate. The crude aldoester thus obtained was approximately 95% pure. It was chromatographed on silica gel to obtain pure methyl brassylaldehydate (purity by GLC, 99.0%).

Methyl 9(10)-Acetoxy-10(9)-Hydroxystearate

A mixture of methyl 9,10-epoxystearate (1.0 g, 98.4% pure, 0.0031 mole), anhydrous sodium acetate (2.0 g, 0.0244 mole) and glacial acetic acid (10 ml) was heated at 85 ± 2C for two hours with stirring. The reaction mixture was poured into 200 ml water and the resulting mixture was extracted with five 25 ml portions petroleum ether (bp 25–60C). The combined extracts were washed successively with 25 ml water, 20 ml $NaHCO_3$ solution (0.5%) and 2 × 25 ml water, and were then dried over Drierite, filtered and evaporated to obtain a water-white oil (1.0 g; oxirane oxygen, nil) which solidified to a white solid on standing. GLC and infrared (IR) analysis indicated this product to be approximately 95% pure methyl 9(10)acetoxy-10(9)-hydroxystearate.

Methyl 12(13)-Acetoxy-13(12)-Hydroxy-9-octadecenoate

Acetoxylation of methyl vernolate was carried out analogously to the acetoxylation of methyl 9,10-epoxystearate. Variations in procedures and reagents are shown in Table I together with yields obtained.

Hydrogenation of Methyl 12,13-Epoxy-9-octadecenoate

Palladium on Carbon. Crude methyl vernolate (1.0 g; oxirane oxygen, 4.65%) was dissolved in 10 ml purified 1,4-dioxane, some 10% Pd on carbon catalyst was added and the mixture was shaken at 36 lbs gauge pressure H_2 for 15 minutes at 26C. Filtration and solvent stripping gave 0.97 g oil; oxirane oxygen, 3.37%. GLC and IR analysis demonstrated disappearance of the C-C double bond and formation of a significant amount of byproduct, possibly methyl 9(10)-hydroxystearate and/or methyl 9(10)-ketostearate.

The hydrogenation was repeated under analogous conditions with PtO_2 catalyst, and with Pd on carbon at atmospheric pressure for varying periods of time. In all cases the results were approximately the same as shown above.

Sodium Borohydride. The published procedure of Brown (15) for the analytical reduction of unsaturated materials with sodium borohydride was modified by Miwa (16). Pure methyl vernolate (0.72 g; oxirane oxygen, 5.09%) was hydrogenated by the Miwa procedure. The hydrogenation mixture was poured into 200 ml water, filtered, and the filtrate was extracted repeatedly with ether. The combined ether extracts were washed with water, dried over Drierite, filtered, and evaporated to yield an oil (0.64 g; oxirane oxygen, 4.60%) which crystallized on standing. GLC and IR analysis indicated methyl 9(10)-hydroxystearate was the principle by-product.

Methyl 12,13-Epoxystearate

Crude methyl 12,13-epoxystearate, obtained by the sodium borohydride reduction of methyl 12,13-epoxy-9-octadecenoate was recrystallized once from acetone at −20C and three times from methanol at −20C to obtain methyl 12,13-epoxystearate mp 30.5–31.5C, oxirane oxygen, 5.02% (theory 5.12%), Sap. Equiv. 320.8 (theory 312.5).

Anal. Calcd. for $C_{19}H_{36}O_3$: C, 73.04; H, 11.61
Found: C, 73.02; H, 11.57.

Hydration of Methyl 12,13-Epoxy-9-octadecenoate

Methyl vernolate (2.5 g) dissolved in purified 1,4-dioxane was treated with 16% fluoboric acid according to a procedure described previously (13). The hydration products were hydrogenated and then treated with periodic acid in dioxane, and the cleavage products as well as the hydration products were analyzed by GLC and IR spectroscopy. Results indicate that more than 50% of the unsaturated epoxide

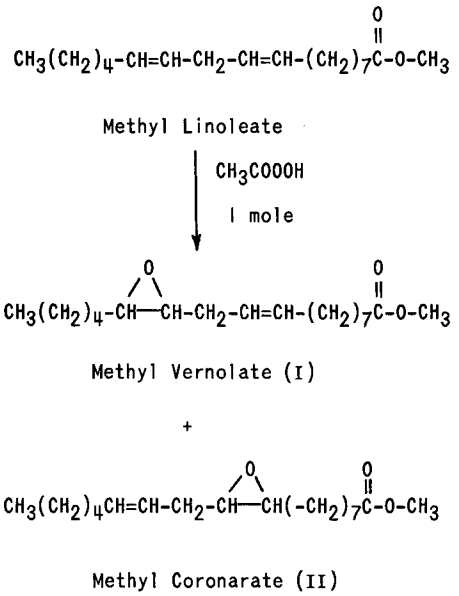

FIG. 1. Monoepoxidation of methyl linoleate.

was hydrated to the expected dihydroxide, but that during the hydration about 43% of the starting material rearranged to methyl 12(13)-ketoöctadecenoate.

Reaction of Methyl 12,13-Epoxy-9-octadecenoate with Periodic Acid

Periodic acid cleavage of methyl vernolate was described previously (11). GLC and IR analysis of the product indicated the presence of caproic aldehyde, two products related to methyl 11-formyl-9-undecenoate, and hydroxylated materials.

GLC Analyses

Procedures reported previously (11) were again employed.

Partial Epoxidation of Methyl Linoleate

To a solution of 35.0 g (0.119 mole) methyl linoleate in 250 ml chloroform was added a mixture of 26.0 g (0.119 mole) of a solution of peracetic acid (41.4%) in acetic acid and 1.3 g sodium acetate trihydrate. The addition was carried out with stirring over a period of 10 min. Very little cooling was required to maintain the temperature at about 24C. Stirring was continued for 2½ hr after completed addition. The reaction was then stopped by washing the mixture successively with 2 × 200 ml water, 130 ml sodium bicarbonate (2%), and again 200 ml water. The chloroform solution was dried over Drierite, filtered, and the solvent was removed by evaporation to obtain a light yellow oil (33.7 g). GLC analysis indicated the oil to consist of 6% unreacted methyl linoleate, 69% methyl epoxyoctadecenoates and 25% methyl diepoxystearates. A portion of the oil (28.0 g) was dissolved in 140 ml acetone, and solution cooled at −38C overnight and filtered cold. The filtrate was evaporated to obtain 23.8 g of oil which, according to GLC analysis, contained methyl linoleate 5%, monoepoxidized methyl linoleate, 75%, and methyl diepoxystearates, 20%. Column chromatography on silica gel resulted in the isolation of pure monoepoxidized methyl linoleate, oxirane oxygen, 5.11% (theory 5.15%). GLC analysis indicated a single component.

Composition of Monoepoxidized Methyl Linoleate

Determination via Hydrogenation. Pure monoepoxidized methyl linoleate (1.03 g; 0.00332 mole; oxirane oxygen, 5.11%) in diglyme-isopropanol was treated with 0.05 M sodium borohydride dissolved in diglyme-isopropanol, and the hydrogenation mixture was poured into 200 ml water and filtered. The filtrate was extracted with three 50 ml portions of ether, and the combined ether extracts were washed with two 25 ml portions water, dried over Drierite and evaporated under N_2 to a semi-solid residue (0.96 g, GLC indicated the presence of approximately 10% methyl ketostearate or methyl hydroxystearate) of crude methyl epoxystearate. The latter epoxide, dissolved in 10 ml dioxane, was treated with 1.25 g paraperiodic acid in 2 ml water at room temperature for 15 minutes. Work-up by the usual procedure gave a liquid (1.56 g) which by GLC analysis was shown to contain solvent, hexanal, nonanal, methyl azelaaldehydate, methyl brassylaldehydate, methyl keto- (or hydroxy-) stearate and minor impurities. Duplicate analysis of the cleavage product containing a measured amount of dimethyl sebacate demonstrated the presence of 0.00129 moles of methyl azelaaldehydate (stemming from an equal amount of methyl coronarate) and 0.00144 moles of methyl brassylaldehydate (stemming from an equal amount of methyl vernolate). Based on a recovery of a total of 0.00273 moles (82.2%) the composition of the monoepoxidized methyl linoleate was therefore 47.3% methyl coronarate and 52.7% methyl vernolate.

Determination via Acetoxylation. Monoepoxidized methyl linoleate (1.0 g; 0.0032 mole; purity, 99.0%), anhydrous sodium acetate (2.0 g) and glacial acetic acid (10 ml) were heated at 85 ± 2C for 2 hours. The cooled reaction mixture was transferred to a hydrogenation flask and 15 ml glacial acetic acid and a catalytic quantity of 10% palladium on charcoal was added. The mixture was shaken at 35 psi hydrogen at room temperature for 2 hours and was then filtered. The filtrate was evaporated on a rotary evaporator to solid residue. The latter was dissolved in 15 ml 95% ethanol, and the solution was rendered alkaline by dropwise addition of 50% aqueous potassium hydroxide solution. Alcoholic potassium hydroxide (50 ml) was added and the solution refluxed gently for 2 hours. The cooled solution was acidified with concentrated HCl, diluted with 100 ml water, and filtered. The filtrate was cooled at 2C, refiltered, and the filter cakes were combined. The solids were dried under vacuum to obtain 0.95 g dry residue, presumably mainly a mixture of isomeric dihydroxystearic acids.

To the solids was added BF_3-methanol reagent (5 ml), prepared by dissolving 10.6 g boron trifluoride etherate in sufficient methanol to make 100 ml solution, and the mixture was refluxed for 10 minutes. The excess reagent was then removed by blowing with N_2 on the steam bath. Treatment of the residue (0.99 g) with H_5IO_6 as described above, work-up of the products, and addition of dimethyl sebacate gave 1.46 g cleavage products and solvent. Duplicate GLC analyses demonstrated the presence of 0.000704 mole methyl azelaaldehydate and 0.000854 moles of methyl brassylaldehydate. Based on a recovery of 0.00156 moles (42.9% of starting material), the composition of the monoepoxidized methyl linoleate was, therefore, 45.2% methyl coronate and 54.8% methyl vernolate.

Analysis of Known Mixtures of Methyl Vernolate and Methyl 9,10-Epoxystearate

Determination via Hydrogenation. A mixture containing 46.1% methyl vernolate and 53.9% methyl 9,10-epoxystearate was hydrogenated according to the Miwa procedure and treated with periodic acid, as described for the monoepoxidized methyl linoleate. GLC analysis by the method of Anders (14) using dimethyl sebacate as internal standard indicated that the aldoesters, recovered in 74.4% yield, contained 42.9% methyl brassylaldehydate and 57.1% methyl azelaaledehydate.

Determination via Acetoxylation. A mixture containing 51.6% methyl vernolate and 48.4% methyl 9,10-epoxystearate was subjected to the reaction sequence described for monoepoxidized methyl linoleate and illustrated in Figure 1, i.e., acetoxylation, hydrogenation, saponification, reesterification and cleavage. GLC analysis indicated that the aldoesters, recovered in 59.6% yield contained 51.0% methyl brassylaldehydate and 49.0% methyl azelaaldehydate.

Discussion

In order to measure the relative amounts of methyl coronarate and methyl vernolate present in monoepoxidized methyl linoleate, a procedure for distinguishing between the two isomeric epoxy esters had to be devised. It was apparent from the beginning that the chromatographic procedures available to us would be insufficient to distinguish between the two isomers, let alone to measure their relative amounts in a mixture. It was therefore decided to use methyl vernolate as a model compound to test possible chemical modification procedures.

Direct periodate cleavage (11) of the unsaturated epoxy ester followed by GLC measurement of the aldehydes and aldoesters produced seemed to be the most direct approach to the solution of our problem. Periodate cleavage of methyl vernolate, however, could not be accomplished without partial isomerization of the double bond, so that the cleavage product mixture was complex and did not lend itself readily to quantitation by GLC. Similar double bond isomerizations were encountered by Gunstone (5) and by Smith (4) in the periodate oxidation of unsaturated vicinal glycols. Since a mixture of methyl vernolate and methyl coronarate could be expected to give an even more complex mixture of cleavage products, direct cleavage was abandoned.

A more circuitous route to the saturated aldehydes and aldoesters consists of hydration of the unsaturated epoxyesters, followed by hydrogenation of the resulting unsaturated vicinal glycols and finally periodate oxidation. Hydration of methyl vernolate, however, led to isomerization to the unsaturated ketoester in 43% of the starting material. By contrast, the saturated methyl 9,10-epoxystearate isomerized only to the extent of about 5% under identical conditions. The abnormally great extent of byproduct formation made the hydration route impractical in the solution of this problem.

Since the difficulties in the application of both the cleavage and the hydration reaction to methyl vernolate were caused by the presence of the double bond, removal of the latter seemed desirable.

The hydrogenation of carbon-carbon double bonds in the presence of oxirane groups has been reported for alicyclic systems (17) and for steroids (18), but to our knowledge no procedure applicable to aliphatic systems has been published. The Miwa modification

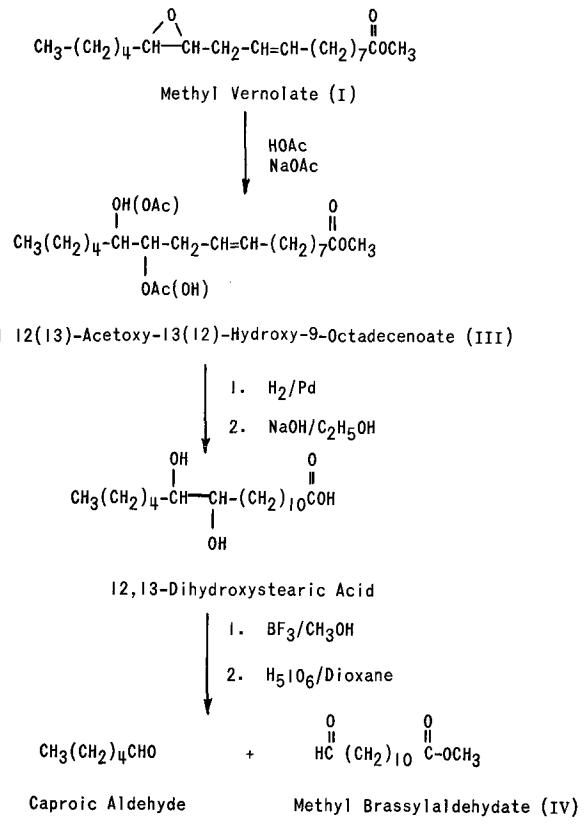

FIG. 2. Cleavage of methyl vernolate-acetoxylation route.

(16) of the Brown sodium borohydride analytical method accomplished this task, however, with loss of less than 10% of the oxirane oxygen functionality. S. C. Sethi (19) working in Professor Brown's laboratory analyzed our sample of pure methyl vernolate and found the amount of sodium borohydride consumed to be slightly greater than theoretical. Undoubtedly this excess is used up in reducing the byproduct methyl 9(10)-ketostearate to methyl 9(10)-hydroxystearate.

Catalytic hydrogenation of the unsaturated epoxyester, using either palladium on carbon or platinum oxide as catalyst, proceeded with unexpected ease. Bubbling hydrogen gas through a solution of methyl vernolate in dioxane at room temperature for a period of 30 minutes was sufficient to reduce the double bond, when either suspended platinum oxide or palladium on carbon was present. Unfortunately, 20–30% of oxirane oxygen was lost, and therefore this hydrogenation method was rejected.

The classical initial step in the determination of structures of unsaturated epoxides, namely acetoxylation of the epoxide ring, was tested on methyl vernolate (Fig. 2). Best yields were obtained with a mixture of acetic acid and anhydrous sodium acetate. Use of trihydrated sodium acetate led to formation of some methyl dihydroxyoctadecenoate as byproduct. The acetoxyhydroxy octadecenoate was hydrogenated in essentially quantitative yield, the saturated ester was saponified, and the resulting glycol acid was reesterified. The resulting methyl dihydroxystearate was then oxidized with periodic acid to produce aldehydes and aldoesters dissolved in a mixture in petroleum ether and dioxane.

The GLC analysis of aldehydes and aldoesters obtained by reductive ozonolysis of unsaturated fatty materials has been described by Ackman (30) and Privett (21), and aspects of quantitation were dis-

cussed by Anders (14). In analyzing the aldehydes and aldoesters obtained as periodate cleavage products of epoxides and glycols we sought to demonstrate that (a) as a result of periodate treatment equimolar amounts of aldehyde and aldoester are obtained and (b) the ratio of C_9 and C_{12} aldoesters found by GLC analysis is the same as the ratio of 9,10-epoxide and 12,13-epoxide present in the original mixture of epoxyesters.

For the cleavage of methyl 9,10-epoxystearate it was readily established that pelargonic aldehyde and methyl azelaaldehydate are produced in equimolar amounts. This was demonstrated by analyzing known mixtures of the two components and comparing the relative peak areas with those obtained from a cleavage product. The actual amount of methyl azelaaldehydate present was confirmed by addition to the sample of a known amount of dimethyl sebacate as internal standard. It was not possible to establish molar equivalence for the cleavage products of methyl 12,13-epoxystearate since some hexanal was lost during the work-up, and the hexanal peak was incompletely separable from the solvent peak in the system used. There is no reason to suppose, however, that the cleavage of methyl 12,13-epoxystearate is less complete than that of methyl 9,10-epoxystearate.

Both procedures for converting the unsaturated epoxyesters to aldehydes and aldoesters were utilized to test the composition of monoepoxidized methyl linoleate. Both methods, borohydride hydrogenation as well as acetoxylation plus associated transformations, were first tested on known mixtures of methyl vernolate and methyl 9,10-epoxystearate, the latter being used since pure methyl coronarate was not available, to establish that neither method favored or discriminated against one component selectively. Application of these methods to monoepoxidized methyl linoleate indicated it to be composed of 46.3% (45.2% and 47.3%) methyl coronarate and 53.7% (54.8% and 52.7%) methyl vernolate. The slight deviation from randomness which these figures seem to indicate is considered insignificant and well within the experimental error. Thus it is concluded that epoxidation of methyl linoleate with peracetic acid in chloroform occurs with equal ease at the two double bonds.

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Helpful discussions regarding TLC techniques by S. F. Herb and P. Magidman; samples of methyl azelaaldehyde; samples of trivernolin by C. F. Krewson.

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Synthesis and Isolation of Methyl Esters of *a*-Branched Acids[1]

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Abstract

A series of esters of *a*-branched fatty acids containing 28–38 carbon atoms has been synthesized by free radical-catalyzed addition of saturated aliphatic esters to terminal aliphatic olefins. Methods of purification of methyl *a*-decyloctadecanoate have been studied. The structure of methyl *a*-decyloctadecanoate has been established by nuclear magnetic resonance and by independent synthesis.

Introduction

THE FREE-RADICAL-INDUCED addition of saturated carboxylic acids and esters to terminal olefins to give *a*-alkylated acids and esters has been the subject of much recent interest (1–9). Most investigators assumed without proof that the principal 1:1 addition product was the *a*-branched acid or ester exclusively, but at least some workers (2,6,8) proved that some principal products had the expected structure. The investigation of most of the byproducts of this reaction has not been undertaken, but Wheeler (10) demonstrated that methyl oleate and methyl stearate undergo some coupling in the *a*-position under similar conditions.

The purpose of our work was to synthesize methyl esters of *a*-branched carboxylic acids containing 28–38 carbon atoms and to study methods by which such compounds can best be purified.

Experimental Procedures and Data

Materials

Methyl Esters of Fatty Acids. Methyl laurate, Eastman practical grade (95%), was used as received or was fractionally distilled at reduced pressure to attain a heart cut purity of 99+% as measured by

[1] Presented at AOCS Meeting, Houston, April 1965.
[2] E. Utiliz. Res. Dev. Div., ARS, USDA.