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

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Abstract

A series of esters of α-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 α-decyloctadecanoate have been studied. The structure of methyl α-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 α-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 α-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 α-position under similar conditions.

The purpose of our work was to synthesize methyl esters of α-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

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

TABLE I

Free Radical Catalyzed Synthesis of α-Branched Esters

Starting materials		Product $\mathrm{CH_3(CH_2)_x \diagdown \overset{O}{\overset{\Vert}{}}}$ $\mathrm{CH_3(CH_2)_y \diagup CHCOCH_3}$		Yield %	mp °C	n_D^{60}
Ester	Olefin	x	y			
Methyl laurate	1-Hexadecene	15	9[a]	58	38.0	1,4385
Methyl palmitate	1-Dodecene	13	11	65	35.0	1.4398
Methyl stearate	1-Decene	15	9	66	37.0	1.4388
Methyl laurate	1-Docosene	21	9[b]	47	51.0	1.4313
Methyl palmitate	1-Octadecene	17	13	60	48.0	1.4478
Methyl stearate	1-Hexadecene	15	15	64	53.0	1.4470
Methyl palmitate	1-Docosene	21	13	63	56.0	1.4474
Methyl stearate	1-Eicosene	19	15[c]	50	55.0	1.4472

[a] Anal. Calcd. C, 79.38%; H, 13.32; mol. wt., 439. Found: C, 79.52; H, 13.27; Mol. wt., 445.
[b] Anal. Calcd. C, 80.39; H, 13.49. Found: C, 80.45; H, 13.15.
[c] Anal. Calcd. C, 80.89; H, 13.58. Found: C, 81.29; H, 13.55.

gas-liquid chromatography (GLC) and thin-layer chromatography (TLC). Commercial methyl palmitate (Neofat) was purified by repeated distillation until 99+% pure (by GLC analysis). Methyl stearate, prepared by esterification of stearic acid was 95% pure by GLC. Impurities in the practical grade methyl laurate and methyl stearate were homologs of up to two carbon atoms less and up to four carbon atoms more than the principal component.

Olefins. Straight-chain terminal olefins of the series decene-1 to eicosene-1 were complimentary samples of the Gulf Oil Corporation. Purities ranged from about 92% to about 98%. Docosene-1, purchased from Humphrey-Wilkinson, was approximately 87% pure.

Di-tertiary butyl peroxide was purchased from Monomer-Polymer Laboratories and was used as received.

Experimental Procedures

Addition of Methyl Esters to Terminal Olefins. The following typical procedure was used for the preparation of α-alkyl esters listed in Table I. The appropriate methyl ester, terminal olefin and di-tertiary butyl peroxide were used in the molar ratio of 40:4:1, respectively. Two-thirds of the methyl ester was placed in a reaction flask equipped with heater, stirrer, thermometer and addition funnel. The remaining methyl ester and the olefin and peroxide were mixed and the mixture placed in the addition funnel. The flask content was heated to and maintained at 160 ± 2C with stirring while the mixture in the funnel was added slowly over a period of 6 hr. Some olefin-ester mixtures required slight warming to prevent solidification in the addition funnel. After the addition was complete the reaction mixture was subjected to distillation at reduced pressure to remove excess starting materials. The distillation residue contained the principal product (50–70%) and by-products. Purification procedures varied depending on the degree of purification desired.

Isolation and Purification of Methyl α-Decyloctadecanoate. Methyl α-decyloctadecanoate was prepared by the addition of methyl laurate to hexadecene-1 in the manner described above. Various isolation and purification procedures were applied to the reaction product in order to test these methods, and in order to isolate relatively pure methyl α-decyloctadecanoate.

a) Isolation.

1) Removal of Excess Methyl Laurate by Molecular Distillation: The reaction mixture, 118.0 g, was introduced into a brush-type molecular still and distilled in vacuo at 135C. The distillate 85.9 g, contained 5.2% product while the still residue (crude product) 10.1 g, contained approximately 1% methyl laurate. The darkened still residue, dissolved in hexane, was passed through a Florisil column (Florisil to sample weight ratio 5:1) to remove colored impurities.

2) Removal of Excess Methyl Laurate by Distillation: The reaction mixture, 119.0 g, was distilled in vacuo at 110C taking the distillate directly from the reaction flask and using no column, just a still head. The distillate, 97.2 g, contained no product or by-product. The residue (crude product), 19.5 g, was free of methyl laurate. The procedure was repeated to prepare additional amounts of crude product.

b) Purification.

1) Crude product was recrystallized from 200 parts methanol at 0C to obtain semi-refined methyl α-decyloctadecanoate purity approximately 90% as estimated from a combination of GLC and TLC.

2) Crude product, 30.0 g, was charged to an 18 in. long spinning band column equipped with reflux control. Material distilling at 145–155C at 0.01 mm was collected (11.6 g) and was estimated to contain about 95% methyl α-decyloctadecanoate.

3) Crude product, 5.0 g, was charged to a chromatography column loaded with 200 g silica gel (Davison #923, 100–200 mesh, 5.3% moisture). Elution with redistilled Skellysolve B gave 0.56 g of methyl α-decyloctadecanoate, purity 99%. Recovered material having a purity of about 95% or greater totaled 2.20 g.

4) Crude product, 0.100 g, dissolved in benzene was streaked on a TLC plate coated with Adsorbosil-1 (0.75 mm thick) and developed with benzene/hexane 50/50 mixture. The plate was sprayed with 2′, 7′-dichlorofluorescein and viewed under ultraviolet light. The band containing the principal product was scraped off and eluted with ether. Evaporation of the solvent gave 0.066 g methyl α-decyloctadecanoate, purity about 98%.

Preparation of α-Methylstearic Acid. A 100 ml round-bottom flask was fitted with an addition funnel, magnetic stirrer and reflux condenser equipped with a calcium sulfate drying tube. The latter was connected to a 500 ml eudiometer. Into the flask was placed 0.46 g (0.01 mole) of a sodium hydride suspension and 25 ml toluene previously dried over sodium. To the stirred suspenion at room temperature was slowly added a solution of 3.84 g (0.01 mole) diethyl cetylmalonate (11) in 15 ml dried toluene. After about one-half of the ester solution was added, the addition was stopped and the temperature of the reaction mixture was raised to 45C. Hydrogen evolution, which was slow initially, increased with warming. The balance of the ester was added at 45C. Upon

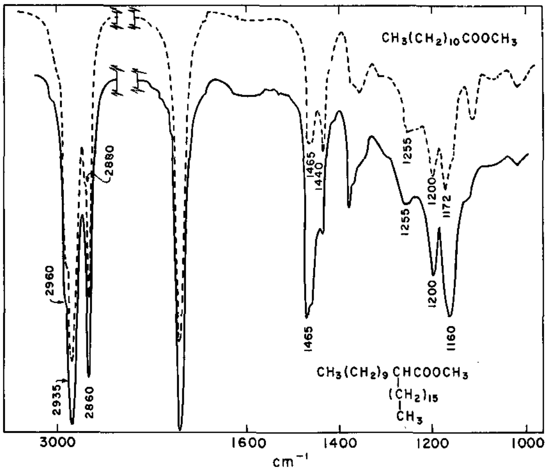

Fig. 1. IR spectra of methyl laurate and methyl α-decyloctadecenoate. Liquid films taken on a Perkin-Elmer Model 237B Spectrophotometer.

completion of addition and when about 83% of the theoretical amount of H_2 had been evolved, the mixture was cooled to room temperature and 1.42 g (0.01 mole) of iodomethane was added. Stirring at room temperature was continued overnight and was accompanied by separation of sodium iodide. The reaction mixture was heated at 70C for 2 hr, with stirring.

The reaction mixture was cooled to room temperature, diluted with ether and extracted with water until neutral. The ether solution was dried and evaporated to obtain 3.48 g light yellow residue. The latter was saponified with 25 ml alcoholic potassium hydroxide (10%), and the resulting mixture was acidified and extracted with ether. Drying of the ether solution and evaporation of the solvent under nitrogen gave 2.54 g of a white solid, mp 81–100C, having the typical IR spectrum of a carboxylic acid. The solid (2.29 g) was heated at 180C for 2 hr at 8 mm pressure and was finally heated for a brief period at 200C and 8 mm pressure. Cooling gave 2.02 g of a solid, mp 43–53C. Recrystallization from Skellysolve B at −5C gave α-methylstearic acid, mp 54–55C.

GLC Analyses. All GLC analyses were carried out on an F & M No. 810 dual column gas chromatograph equipped with thermal conductivity and flame detectors. The columns used were 8 ft × ¼ in. O.D. stainless steel columns packed with 10% silicone gum rubber (SE-30) on 60–80 mesh Diatoport S, or packed with 10% diethylene glycol succinate on 60–80 mesh Gas-Chrom P and 2 ft × ¼ in. O.D. stainless steel columns packed with 4% nitrile silicone gum rubber (XE-60) on 60–70 mesh Gas-Chrom Z. The XE-60 columns, which were used for the α-branched esters, were aged for two days at 300C with a gas flow of 250 ml per minute so that the actual amount of XE-60 left after aging was probably less than 1%.

Results and Discussion

The products listed in Table I can be divided into three groups by the number of carbon atoms which they contain. The first three products each contain 28 carbon atoms in the acid portion of the ester, the next three each contain 34 carbon atoms and the final two each contain 38 carbon atoms. The yields presented in Table I were calculated from analytical thin-layer chromatograms of the crude materials and relate to products which give single spots by TLC but which are not necessarily pure. In cases where the starting materials contained homologue impurities, the single-spot products were contaminated by materials resulting from the reactions of the impurities. These contaminants could not be separated by TLC but were readily visible by GLC. The yields are mostly in the 60–65% range, and in the three runs where this level was not quite reached, the discrepancy is due to operating problems rather than to causes related to the reaction itself.

Compared to the well-known (10, 12–14) resistance of hindered esters toward hydrolysis, the products of the present addition reaction, while more resistant than straight-chain esters, were saponified with relative ease. It was therefore considered desirable to establish that the reaction, as carried out in our laboratory, was indeed producing α-branched esters as principal products.

The first and third examples in Table I were chosen to prepare the same product, methyl α-decyloctadecanoate, from two different sets of starting materials. Proof of identity of the two principal components would constitute partial proof of structure. The melting points of the two products were indeed very similar, and the two compounds did not depress each other's melting point, while they did depress the melting point of the third member of the C_{28} series. The two compounds also had identical TLC R_f values and GLC retention times.

Pure methyl α-decyloctadecanoate, obtained by the addition of methyl laurate to 1-hexadecene, was studied further to obtain further evidence for its assumed structure. Both the molecular weight, determined by the thermistor method, and elemental analysis agreed well with calculated values. Saponification of the ester in 10% alcoholic potassium hydroxide led to the free carboxylic acid which gave the expected neutralization equivalent. Re-esterification of the acid with BF_3-methanol gave the ester in 75% yield.

The NMR spectrum of methyl α-decyloctadecanoate indicated the presence of a single α-proton at 2.35 ppm with respect to TMS. This compares with a 2.45 ppm location of the equivalent hydrogen of α-methyl stearic acid prepared via diethyl cetylmalonate. Cason (15) gives 2.38 ppm as the location for the single proton in the 2-position. The hindered ester was saponified and it and α-methyl stearic acid were both brominated by the Hell-Volhard-Zelinsky method. The bromine of both compounds was then replaced by ethoxide and the resulting products analyzed by NMR. Complete absence of absorption in the 2.4 ppm region of the ethoxides indicated that the single protons which had now been removed were originally in the α-position.

The infrared absorption bands of the α-branched esters are essentially identical. A comparison of the neat spectra of methyl laurate and methyl α-decyloctadecanoate is seen in Figure 1. Aside from the expected difference in band intensities, there is a change in the relative intensities of the methylene bending vibration at 1465 cm^{-1} and 1440 cm^{-1} and a shift in the 1172 cm^{-1} C-O-C band to 1160 cm^{-1}.

The preparation of methyl α-decyloctadecanoate is accompanied by the formation of impurities containing three major components as identified by TLC. These byproducts move faster on the TLC plates than the principal component and comprise about 25–30% of the crude reaction product. The three components which were separated with difficulty by preparative TLC occur in relative amount of 3:5:5. All three materials had a very high GLC retention times relative to the principal ester and thus were not detectable by standard techniques.

The fastest moving (on TLC) component is a waxy solid melting near room temperature. It contains no ester function, is hydrocarbon in nature and presumably is a product of olefin self-condensation.

The second of the three by-products is also a waxy solid, but this material contains an ester group, and, judging from NMR and IR spectra, it is an α-branched ester. Saponification of the ester with 10% alcoholic potassium hydroxide gave a carboxylic acid having a neutralization equivalent of 671. Theoretical neutralization equivalent for an acid formed from one mole lauric acid plus two moles 1-hexadecene is 648.

The slowest of the three byproducts is a liquid. Its IR spectrum indicates the presence of a carboxylic ester function and its NMR spectrum indicates a hydrogen in the 2-position. Saponification of the ester results in an acid having a neutralization equivalent of 683. Thus it appears that the slowest by-product is a slightly more polar isomer of the second by-product and that both resulted from the condensation of one mole of methyl laurate with two moles of 1-hexadecene.

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Cyclopropenoid Fatty Acid Content and Fatty Acid Composition of Crude Oils from Twenty-Five Varieties of Cottonseed

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Abstract

The cyclopropenoid acid content of oils extracted from 22 commercial varieties and 3 botanical species of cottonseed have been determined. The malvalic acid content determined by HBr titration varied from a low of 0.56% to a high of 1.17%. Iodine values of the oils ranged from 96.8 to 111.6. No definite correlation could be established between iodine value and malvalic acid content. Equations for regression lines for the major acids have been calculated from plots of fatty acid composition vs. iodine value. The high degree or correlation suggests that for commercial oils the fatty acid composition can be estimated from the iodine value. Oils of the 3 experimental types of different species showed wide variations in fatty acid composition and represented many of the maximum and minimum values reported.

Introduction

THERE HAVE BEEN NUMEROUS reports dealing with the fatty acid composition of cottonseed oil. Stansbury and Hoffpauir (1) made a systematic study of the relationship between iodine value and fatty acid composition of oils from a number of native varieties and types. Cattaneo et al. (2) reported on the physical-chemical characteristics and fatty acid composition of a number of Argentine cottonseed oils. Harwalkar, Achaya and Saletore (3,4) reported on the fatty acid composition of a number of Indian cottonseed oils. The various methods of analysis employed in these studies are now known to be unreliable. With the advent of modern gas-liquid chromatographic techniques (GLC) more accurate and complete analyses have been reported (5–8). However, these analyses in general were limited to but a few random cottonseed oils. The only reported GLC analyses of a series of cottonseed oils was in connection with the detection of cottonseed oil as an adulterant in olive oil, and no attempt was made to correct for detector response differences. In none of the analyses was there mention of the cyclopropenoid constituents present in cottonseed oil, namely, malvalic or sterculic acid. The recently developed stepwise HBr titration method (9) now makes it possible to determine cyclopropenoid fatty acid moieties to the nearest 0.01%. These factors and the availability of ideally suitable sample material have prompted us to investigate the fatty acid composition of cottonseed oils extracted from a number of cottonseed varieties and species.

Apparatus and Methods

Gas-liquid chromatograms of the cottonseed methyl esters were obtained with the Aerograph Autoprep

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