Composition of Fatty Acids Obtained by Decomposition of Castor Oil Fatty Acid Estolides

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ABSTRACT

The composition (wt %) of the fatty acids obtained by decomposition of castor oil fatty acid estolides and distillation was determined by a combination of spectroscopic (ultraviolet, nuclear magnetic resonance, infrared), chromatographic (thin layer on Silica Gel G modified with silver nitrate and ammonium hydroxide, gas liquid) and chemical (partial reduction and periodate/permanganate oxidation) techniques and found to be 16:0, 2.7; 18:0, 2.6; 18:1, 5.2; conjugated *cis,trans* (*trans,cis*)-18:2, 34.4; conjugated *cis,cis*-18:2, 9.7; conjugated *trans,trans*-18:2, 3.9; 9-*cis*,12-*trans*-18:2, 20.8; 9-*trans*,12-*cis*-18:2, 2.3; and 9-*cis*,12-*cis*-18:2, 18.4.

INTRODUCTION

Octadecadienoic acids rich in conjugated unsaturation are used in the manufacture of dimer acids (1). Catalytic dehydration of castor oil (2) or methyl ricinoleate (3) gives a low content of conjugated unsaturation. Decomposition of estolides derived from castor oil fatty acids gives a high content of diene conjugation (4-6). The proportions of geometrical and positional isomers in the dienoic fatty acids also depend on the mode of preparation (3,7). This report deals with the detailed composition of the fatty acids obtained by a process developed in this laboratory (8) and released to the National Research and Development Corp., Government of India, New Delhi, for commercial exploitation, which involves autoclave splitting of castor oil, formation and decomposition of estolides and distillation of the resulting fatty acids.

MATERIALS AND METHODS

Castor oil had hydroxyl value 163.5, iodine value 83.8 and acid value 1.5, as determined by AOCS methods (9). The fatty acid composition (wt %) was determined by gas liquid chromatography (GLC) using trimethylsilyl ether derivatives of methyl esters and was found to be 16:0, 1.3; 18:0, 1.3; 18:1, 3.1; 18:2, 3.3; 18:3, 0.8; and ricinoleic, 90.2. The dihydroxystearic acid content, reported to be 1.3% for an Indian sample (10), was not estimated. Castor oil was split (97%) with water in an autoclave under pressure (8). The sweet water was drawn off. The split product was heated and distilled under vacuum. The yield of the dehydrated castor oil (DCO) fatty acids was 72%.

Methyl esters of DCO fatty acids were prepared by esterification with methanol at room temperature using sulfuric acid as catalyst and purified by Silica Gel G (ACME Synthetic Chemicals, Bombay) thin layer chromatography (TLC) using a mixture of diethyl ether and *n*-hexane (5:95, v/v). Diene conjugation was determined according to the AOCS method (9). The methyl esters were analyzed using a Toshniwal gas chromatograph equipped with a flame ionization detector (FID) and a stainless steel column (2.4 m × 3.2 mm) packed with 15% EGSS-X/Gas Chrom Q (80-100 mesh). The column, injection port and detector were maintained at 210, 260 and 260 C, respectively. The flow rate of carrier gas, nitrogen, was 60 mL/min. The peak area was measured by multiplying peak height with width at half-height.

For TLC, Silica Gel G (50 g) was slurried with ammonium hydroxide/silver nitrate solution which was prepared by adding 28-30% ammonium hydroxide solution (ca. 9 mL) to silver nitrate (12 g) dissolved in 50 mL water and diluting to 100 mL (11). For analytical separations, 0.3-mm- and for preparative work, 1-mm-thick layers were used. A mixture of benzene and *n*-hexane (30:70) was used for development. 2′,7′-Dichlorofluorescein was used to locate the separated components of the DCO fatty acid esters which were scraped off and extracted with ethyl ether. The separations were checked by TLC and GLC. The samples were preserved under nitrogen at -10 C until further analysis.

Proton nuclear magnetic resonance (NMR) spectra were recorded in CCl_4 solution using a Varian A-60A spectrometer. Tetramethylsilane was used as an external standard. Infrared (IR) spectra were recorded in CS_2 solution using a Perkin-Elmer Model 21 spectrometer.

Partial reduction of nonconjugated dienoates was done with hydrazine (12). Oxidation of monoenoates obtained by partial reduction was done with periodate/permanganate (13). The products were esterified with diazomethane and analyzed by GLC using methyl esters of pure C_8-C_{12} dicarboxylic acids as standards.

RESULTS AND DISCUSSION

A typical sample of DCO fatty acids, obtained from castor oil via estolide route by a process developed in this laboratory, was converted to methyl esters and found to contain 48% diene conjugation by ultraviolet (UV) spectrophotometry. The GLC of the methyl esters showed 5 peaks (Table I), with retention times, RRT (relative to that of 16:0), given in parentheses, corresponding to 16:0 (1.00), 18:0 (1.77) 18:1 (2.00), nonconjugated 18:2 (2.38) and conjugated 18:2 (3.04, 3.24 and 3.33). The isomers of conjugated 18:2 were poorly resolved and the resulting unsymmetrical peak could not be quantified. The total area due to the other peaks was considered equal to 52% because the content of conjugated 18:2 was 48% as obtained by UV spectrophotometry. The percentages (wt) of 16:0, 18:0, 18:1 and nonconjugated 18:2, were 2.7, 2.6, 5.2 and 41.5, respectively.

TLC on Silica Gel G modified with silver nitrate and ammonium hydroxide resolved the methyl esters into 5 fractions having retention factors relative to that of 16:0 (RR_f) 1.00, 0.61, 0.50, 0.30 and 0.13 (Table I). The GLC of these fractions showed them to consist of 16:0 and 18:0 (RR_f 1.00), 18:1 (RR_f 0.61), conjugated 18:2 (RR_f 0.50) and nonconjugated 18:2 (RR_f 0.30 and 0.13). As there was slight overlapping of the 18:1 (RR_f 0.61) with conjugated 18:2 (RR_f 0.50) in preparative TLC, these fractions were combined for determination of the components. The combined fraction was free of nonconjugated dienoates as found by GLC. The contents of conjugated *cis,trans*- and

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TABLE I

Relative Retention Times and Factors of Methyl Esters of Fatty Acids Obtained by Decomposition of Castor Oil Fatty Acid Estolides[a]

Fatty acid ester	RRT[b] on 15% EGSS-X column in GLC	RR_f[b] on Silica Gel G modified with NH_4OH and $AgNO_3$ in TLC
16:0	1.00	1.00
18:0	1.77	1.00
18:1	2.00	0.61
18:2-nonconjugated	2.38	0.30, 0.13
18:2-conjugated	3.04, 3.24, 3.33	0.50

[a]See Results and Discussion for details.

[b]Relative retention time (RRT) and factor (RR_f) with respect to that of 16:0.

trans,trans-dienoates in this fraction were estimated by IR spectroscopic technique according to Chipault and Hawkins (14) by using absorptivity values 0.288 and 0.187 (948 and 990 cm^{-1}), and 1.33 (990 cm^{-1}), respectively. As the content of monoenoate was also known, by GLC analysis, the proportion of conjugated *cis,cis*-dienoate was determined by difference. Thus, the percentages (wt) of *cis,trans*-, *trans,trans*- and *cis,cis*-conjugated octadecadienoates in the DCO fatty acid esters were 34.4, 3.9 and 9.7, respectively. To determine the position of double bonds in these isomers, which were not resolved, total conjugated dienoates, after separation from 18:1 by analytical TLC, were oxidized with periodate/permanganate and the resulting fragments were analyzed as methyl esters by GLC using authentic methyl esters of C_8-C_{12} dicarboxylic acids as standards. The data indicated that the 9,11-isomers were predominant (62%) whereas 8,10-, 7,9- and 10,12-isomers were present to the extent of 33, 3 and 2%, respectively. The double bond at the ninth carbon atom could be assumed to be predominantly of *cis* configuration because it is not involved in the dehydration reaction, unlike the double bond created at eleventh carbon atom. The low percentage of *trans* double bonds at the ninth carbon atom in the nonconjugated dienoates (as can be seen in the subsequent discussion) also supports this assumption.

The nonconjugated dienoate TLC fractions (RR_f 0.30 and 0.13) were estimated gravimetrically and amounted to 23.1 and 18.4%, respectively, in the DCO fatty acid esters.

The proton NMR spectrum of the dienoate (RR_f 0.30) showed a multiplet at 5.4 ppm (δ) corresponding to 4 olefinic protons. It also showed signals for characteristic diallylic methylene protons (2.8 ppm, δ) confirming that it is a nonconjugated dienoate. The IR spectrum of the dienoate in CS_2 showed a band at 960 cm^{-1}, confirming the presence of isolated *trans* unsaturation. Nonconjugated *cis,trans*- and *trans,trans*-octadecadienoates are resolvable by TLC on Silica Gel G modified with silver nitrate and ammonium hydroxide. However, even rechromatography of the dienoate gave a single spot. Thus, this could be a *cis,trans*- or *trans,trans*-dienoate, but partial hydrogenation of the dienoate using hydrazine gave *cis*- and *trans*-monoenoates which confirmed that it was a *cis,trans*-dienoate. Further, periodate/permanganate oxidation of the respective monoenoates followed by GLC analysis of the resulting dicarboxylic acid fragments as methyl esters showed that the dienoate fraction was a mixtue of 9-*cis*,12-*trans*- and 9-*trans*,12-*cis*-octadecadienoates. The proportion of each isomer in the mixture was calculated from the proportion of the C_9 and C_{12}-dicarboxylic acid fragments resulting from the oxidation of the *cis*- and *trans*-monoenoate fractions. Thus, the 9-*cis*,12-*trans*- and 9-*trans*,12-*cis*-octadecadienoates were found to be 20.8 and 2.3%, respectively, in the DCO fatty acid esters.

The proton NMR spectrum of the other dienoate (RR_f 0.13) in CCl_4 showed a multiplet at 5.3 ppm (δ) corresponding to 4 olefinic protons. It also showed signals for characteristic diallylic methylene protons (2.8 ppm, δ) confirming that it is a nonconjugated dienoate. The dienoate did not show any absorption at 960 cm^{-1} for *trans* unsaturation. Thus, the NMR and IR data prove that it was a nonconjugated *cis,cis*-dienoate. Partial hydrogenation of the dienoate provided only *cis*-monoenoates, as shown by silver ion TLC. Periodate/permanganate oxidation of the monoenoate fraction gave only C_9 and C_{12} dicarboxylic acid fragments, as shown by GLC, proving that the dienoate was 9-*cis*,12-*cis*-18:2.

The composition of the dehydrated castor oil fatty acid methyl esters prepared from castor oil fatty acids via the estolide route was thus computed from the data obtained by chromatographic, spectral and chemical methods and is recorded in Table II. The saturates amounted to 5.3% and the monoenoates to 5.2%. The conjugated octadecadienoates amounted to 48%, consisting mainly of *cis,trans* (*trans,cis*)-dienoates. The remainder (41.5%) consisted of mainly 9-*cis*,12-*trans*- and 9-*cis*,12-*cis*-octadecadienoates. Based on 90.2% ricinoleic acid in castor oil fatty acids the percentage of dienoic acids expected in DCO fatty acids, including the amount of 18:2 originally present, is 93.1%. This compares reasonably well with that found (89.5%) in DCO fatty acids. The percentages of conjugated and nonconjugated dienoates arising from ricinoleic acid were 48 and 38%, respectively, in the DCO fatty acids, giving an approximate ratio of 5:4.

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TABLE II

Composition of Fatty Acids Obtained by Decomposition of Castor Oil Fatty Acid Estolides

Fatty acid methyl ester	Wt %
16:0	2.7
18:0	2.6
18:1	5.2
18:2-conjugated *cis,trans* (*trans,cis*)	34.4
18:2-conjugated *trans,trans*	3.9
18:2-conjugated *cis,cis*	9.7
18:2-9-*cis*,12-*trans*	20.8
18:2-9-*trans*,12-*cis*	2.3
18:2-9-*cis*,12-*cis*	18.4

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Sodium Santalbate-Dimethyl Sulfate Inclusion Complex

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ABSTRACT

A molecular inclusion complex has been obtained from the major acetylenic acid, santalbic acid (octadec-11-en-9-ynoic acid or *trans*-11-octadecen-9-ynoic acid) of the seed oil of *Santalum album* L. by a simple treatment of its sodium salt with dimethyl sulfate. Aqueous solutions (0.5-1%) of the complex produce good lather and have efficient cleansing (detergent) action on grease and dirt particles.

INTRODUCTION

The seed oil of *Santalum album* L. is a drying oil obtained in about 55-60% yield by hot petrol extraction (1). The chemical aspects of the oil have been extensively studied earlier by many workers (2-4). The viscous oil contains 88% of santalbic glyceride and, by chromatography of the mixed fatty acids, about 60% of santalbic acid could be obtained.

The chemical reaction involving dimethyl sulfate and the sodium salt of a carboxylic acid is normally expected to give the methyl ester of the acid (5,6). It is also known that alkyl sulfates are of interest as sulfating and sulfonating reagents (7). But, in the case of sodium santalbate, the reaction with dimethyl sulfate furnished a molecular inclusion complex that had cleansing action on greasy and dirty particles.

EXPERIMENTAL PROCEDURES

Isolation of Santalbic Acid

The seed oil (50 g) was saponified by boiling with ethanolic potassium hydroxide (10 g in 200 mL) for 1 hr. Alcohol was distilled off and the solution was acidified; the mixed fatty acids (42 g) were extracted with ether. After the removal of solvent, the acids were passed through a silica gel (1:30) column with benzene as eluent (1,500 mL). The benzene eluate (37 g) was chilled in 200 mL of petroleum ether (boiling range 60-80 C) overnight at -10 C, when shining white plates of santalbic acid (mp 38-39 C) separated out (30 g, yield 60%).

Alternatively, santalbic acid may also be obtained by direct chilling of mixed fatty acids in petroleum ether or by direct treatment of crushed sandal seeds with alcoholic potash, followed by ether extraction of acids and chilling the ether solubles in petroleum ether. But, the yields by these methods are only 50 and 40%, respectively (8).

Preparation of Complex

Santalbic acid (10 g) was boiled with ethanolic sodium hydroxide solution (2.5 g in 100 mL) for 10 min. Alcohol was distilled off under vacuum, when a white solid mass of sodium santalbate was obtained, to which was added 3.5 mL of freshly distilled dimethyl sulfate (bp 186 C). The reaction, which was exothermic, was set aside for 30 min and then heated on a boiling water bath for 45 min with occasional swirling. A pasty mass was formed, which gradually solidified. Volatile material, if any, was removed under vacuum (15 mm Torr). The product was crushed into powder, washed with acetone (5 x 40 mL) and finally dried under suction, when a pale yellow amorphous powder (12 g) was obtained: IR γ_{max}^{Nujol} cm^{-1}: 2925-2800 (C-H), 1640 (conjugated C=C), 1560 (-C-O$^-$), 1450, 1380, 1250-1220 (S=O), 1070, 1000 (C-O), 950 (=C-H), 770 (S-O), 720.

The complex gave a positive Lassaigne's test for elemental sulfur and, upon burning, it gave a sooty flame, leaving aside a black residue. A 0.5-1% aq solution of the complex was found to give good lather and had cleansing action on dirty and greasy materials.

Hydrolysis with Acid

The complex (3 g) was added to 100 mL of 6 N HCl. The mixture was heated on a boiling water bath for 3 hr. The solution was cooled and then extracted with 3 x 100 mL of ether. The ether-soluble matter (2.1 g) was chilled in petroleum ether overnight at -10 C. The white solid (1.4 g) was filtered off and was identified as santalbic acid by mp, mmp, Co-TLC and Co-IR.

Hydrolysis with Aqueous Acetone

The complex (5 g) was refluxed with aq acetone (150 mL, 0.5%) for 10 hr. The acetone was distilled off and the product was dissolved in 100 mL of distilled water, then extracted with ethyl acetate (3 x 75 mL). The ethyl acetate-soluble matter (0.4 g) gave santalbic acid (0.23 g) upon chilling with petroleum ether.

Alkylation of Phthalic Anhydride

A mixture of the complex (10 g) and phthalic anhydride (3.6 g) was heated to reflux with sodium-dry benzene