Synthesis of Dimer and Oligomers from (*R*)-Methyl Hydnocarpate

Navdeep B. Malkar[a,*], Ashish A. Vaidya[b], and V.G. Kumar[c]

[a]Florida Atlantic University, Department of Chemistry and Biochemistry, Boca Raton, Florida 33431,
[b]Lehigh University, Chemical Engineering Department, Bethlehem, Pennsylvania 18015,

and [c]Hindustan Lever Research Centre, Andheri,
Mumbai - 400 099, India

ABSTRACT: We report synthesis and characterization of dimer and oligomer acids from chaulmoogra oil. (*R*)-Methyl hydnocarpate (methyl ester of the major fatty acid component of chaulmoogra oil) was brominated to give *threo*-2,3-dibromocyclopentane-1-methyl undecanoate. Formation of two diastereoisomers, *viz.*, *threo*-2(*R*),3(*R*)-dibromocyclopentane-1(*R*)-methyl undecanoate and *threo*-2(*S*),3(*S*)-dibromocyclopentane-(*R*)-1-methyl undecanoate, was observed. Dehydrobromination of bromo derivatives using alcoholic KOH gave a cyclopentadiene derivative as intermediate, which underwent Diels-Alder reaction to give dimer and oligomer fatty acids. The products were characterized by ultraviolet, direct exposure probe–mass spectroscopy, ^{1}H nuclear magnetic resonance (NMR), and ^{13}C NMR spectroscopic techniques.

Paper no. J9477 in *JAOCS 77,* 1101–1105 (October 2000).

KEY WORDS: Dimer and oligomer acids, Flacourtiaceae, *Hydnocarpus wightiana,* hydnocarpic acid, ^{13}C NMR, ^{1}H NMR.

Chaulmoogra oil obtained (1) from seeds of *Hydnocarpus wightiana* and *H. anthelmintica* is a triglyceride of fatty acids containing the cyclopentenyl (Cy) group. The fatty acids obtained from this oil are a mixture of 2-cyclopentene-1-undecanoic acid (hydnocarpic acid, 50%), 13-(2-cyclopentene-1-yl) 6-tridecenoic acid (gorlic acid, 10%) and 2-cyclopentene-1-tridecanoic acid (chaulmoogric acid, 32%) (2,3). Chaulmoogra oil and its derivatives show biological activity (4,5) and have great medicinal value (6), especially in the treatment of leprosy (7,8). Some derivatives are also used as an intermediate in the preparation of perfumery compounds (9,10). Our goal was to synthesize novel dimer or oligomer acids from chaulmoogra oil.

Dimer acids obtained by dimerization (11) of various fatty acids (conjugated and nonconjugated) are known in the literature. The fatty acid precursors used for the dimerization (12–14) and oligomerization (15) are generally tall oil, soybean oil, rapeseed oil, or dehydrated castor oil fatty acids. These dimer acids reportedly show biological activity (16) and are industrially important. They are used in preparation of such things as nonreactive and reactive polyamide resin (17), corrosion inhibitors, and lubricants (18,19). Most of the present-day processes involve use of tall oil fatty acids as a precursor for formation of dimer and oligomer acids.

We report a synthesis of novel *endo*-1,4-bis (methyl undecanoate)-tricyclo [5,2,1,$0^{2,6}$]deca-4,8-diene (methyl ester of dimer acid) from 2-cyclopentene-1(*R*)-methyl undecanoate (methyl hydnocarpate). Methyl hydnocarpate was obtained from chaulmoogra oil. We also report a synthesis of *threo*-2(*R/S*), 3(*R/S*)-dibromocyclopentane-1(*R*)-methyl undecanoate (bromo derivative of methyl hydnocarpate) from methyl hydnocarpate. The stereoisomers of dibromo derivatives were characterized using ^{1}H and ^{13}C nuclear magnetic resonance (NMR). The cyclopentene moiety present in methyl hydnocarpate provided an opportunity to prepare a 1,3-cyclopentadiene-1-undecanoic acid (diene intermediate). The dibromo-derivative on dehydrobromination gave an diene intermediate that underwent a further Diels-Alder reaction to form the novel *endo*-1,4-bis (undecanoic acid)-tricyclo [5,2,1,$0^{2,6}$]deca-4,8-diene (dimer) and oligomer acids. The dimer acid obtained was structurally different from the dimer acids prepared from tall oil, soybean oil, and rapeseed oil or dehydrated castor oil fatty acids. Owing to these structural differences, dimer acid prepared from chaulmoogra oil may show different properties as compared to conventional dimer acids.

EXPERIMENTAL PROCEDURES

Fourier transform infrared (FT-IR) spectra were recorded using a Bomem infrared spectrophotometer (Québec City, Canada). The ^{1}H and ^{13}C NMR spectra were taken in $CDCl_3$ using tetramethylsilane as an internal standard using 200.13 MHz Bruker spectrometer (Karlsruhe, Germany). Chemical shifts are reported in δ-units. In addition, Distortionless Enhancement by Polarization Transfer (DEPT) pulse sequence was used for ^{13}C NMR experiment. Ultraviolet (UV) spectroscopy (20) was carried out on a Shimadzu Ultraviolet Spectrophotometer (Kyoto, Japan). A sample aliquot (0.1 g) taken from reaction mixture was dissolved in 50 mL methanol in a volumetric flask. The UV spectrum of the sample solution was recorded over a range of 200 to 400 nm using methanol as a blank. Absorbance of the sample at 239 nm was monitored. Uerjeeta Jain's Herbals (Mumbai, India) supplied chaulmoogra oil. Gas–liquid chromatography (GLC) was car-

*To whom correspondence should be addressed at Florida Atlantic University, Department of Chemistry and Biochemistry, 777 Glades Rd., Boca Raton, FL 33431. E-mail: nmalkar@fau.edu

ried out on Shimadzu 14A and 14B gas chromatographs using the following columns: DB-1 (J&W Scientific, Folsom, CA), capillary column, internal diameter: 0.5 mm; length 30 m and 3% OV-17 liquid phase, adsorbent: Chromosorb WHP, 80–100 mesh (Chrompack, Middelburg, The Netherlands), packed stainless steel column, 2 mm i.d., 1 ft length, with flame-ionization detector. Mass spectral studies of the methyl ester of dimer acid were carried out by Direct Exposure Probe–Mass Spectroscopy (DEP–MS). The following program was used: start at 25 mA current and hold for 30 s; increase at a rate of 1 mA/s to 800 mA and hold for 30 s. Thin-layer chromatography (TLC) was carried out on Whatman 60 Å Silica Gel precoated TLC plates (2.5 × 5.5 cm in size and 200 µm in thickness; Maidstone, United Kingdom). Preparative chromatography was carried out on Whatman 60 Å Silica Gel precoated TLC plates (20 × 20 cm in size and 500 µm in thickness). Preparative TLC plates were activated before use by heating them at 120°C for 2 h.

*Synthesis of 2-cyclopentene-1(*R*)-methyl undecanoate (methyl hydnocarpate).* Chaulmoogra oil (200 g) and 5% alcoholic KOH (2 L) were refluxed for 3 h. After complete hydrolysis, the reaction mixture was neutralized with 10% HCl, and excess ethanol (1.8 L) was distilled off. The reaction mixture was diluted with water (1 L) and then extracted with hexane (3 × 1 L). The hexane layer was dried over anhydrous Na_2SO_4. The chaulmoogra fatty acids (175 g, yield: 92%) were obtained by distilling hexane completely.

These chaulmoogra fatty acids were then subsequently dissolved in methanol (1.5 L), and concentrated H_2SO_4 (0.1% vol/vol) was added. The reaction mixture was refluxed for 4 h and was monitored using TLC. After completion of reaction, 70% of the methanol was distilled off. The reaction mixture was diluted with water, and crude methyl ester was extracted in hexane. The hexane layer was washed with water to ensure complete removal of acid. The organic layer was dried over anhydrous Na_2SO_4. The crude methyl ester (179 g, 97% yield) was obtained after distilling off hexane under vacuum. The methyl ester was then analyzed by GLC. GLC analysis showed 50.8% of 2-cyclopentene-1-methyl undecanoate (methyl hydnocarpate), 10.2% of 13-(2-cyclopentene-1-yl)-6-methyl tridecenoate (methyl gorlate) and 32.1% of 2-cyclopentene-1-methyl tridecanoate (methyl chaulmoograte). The crude methyl ester was fraction-distilled using a 1-ft glass column packed with dixon rings using a perkin triangle. Methyl hydnocarpate (78.7 g, 88% yield) was collected at 144–146°C at 1-mm vacuum. The temperature of the oil bath was maintained at 230°C. The product was characterized using FT-IR, NMR, and gas chromatography–mass spectrometry (GC–MS).

^{1}H NMR ($CDCl_3$): δ 5.68 (*m*, 2H, –C*H*=C*H*– in cyclopentenyl ring), 2.6 (*bs*, 1H, –CH=CH–C*H*–(–CH_2–)–(CH_2)$_{10}$–$COOCH_3$, in cyclopentenyl ring), 2.30 (*m*, 2H, –CH=CH–CH_2–CH_2, in cyclopentenyl ring), 2.02 (*m*, 2H, –CH=CH–CH_2–CH_2–CH–, in cyclopentenyl ring), 3.66 (*s*, 3H, –$COOCH_3$), 2.30 (*t*, 2H, –CH_2–$COOCH_3$), 1.61 (*s*, 2H, CH_2–CH_2COOCH_3), 1.27 (*s*, 16H, –CH_2–).

^{13}C NMR: δ 174 (–*C*$OOCH_3$), 136 (–CH_2–CH=*C*H–CH– in cyclopentenyl ring), 130 (–CH_2–*C*H=CH–CH– in cyclopentenyl ring), 52 (–COO*C*H_3), 46 (–CH_2–CH=CH–*C*H– in cyclopentenyl ring), 32 (–*C*H_2–CH=CH–CH– in cyclopentenyl ring), 30 (–*C*H_2–CH_2–CH=CH–CH– in cyclopentenyl ring), 37 (–CH–*C*H_2–CH_2–), 30 (–CH–CH_2–*C*H_2–), 28 (–CH–CH_2–CH_2–*C*H_2–), 34 (–*C*H_2–$COOCH_3$), 25 (–*C*H_2–CH_2–$COOCH_3$), 28–30 (5C, –*C*H_2–).

Synthesis of threo-*2(*R/S*),3(*R/S*)-dibromo cyclopentane-1(*R*)-methyl undecanoate.* A solution of 2-cyclopentene-1(*R*)-methyl undecanoate (methyl hydnocarpate, 50 g, 0.19 mmol) in chloroform (200 mL) was cooled to 0–5°C. A solution of bromine (33 g, 0.2 mmol) in chloroform (100 mL) was added dropwise to methyl hydnocarpate solution, until bright yellow color of excess bromine appeared. The reaction mixture was stirred for 3 h at 0–5°C. The excess bromine was removed by washing the reaction mixture with water. The chloroform layer was separated and dried over anhydrous Na_2SO_4 *threo*-2(*R/S*),3(*R/S*)-dibromo cyclopentane-1(*R*)-methyl undecanoate (76 g, 95% yield) was obtained by distilling off chloroform. The product was then characterized using FT-IR, NMR, and GC–MS.

^{1}H NMR ($CDCl_3$): δ 3.9–4.9 (*m*, 2H, *J* = 5.2, 12 Hz, –C*H*(Br)–C*H*(Br)– in cyclopentane ring), 3.66 (*s*, 3H, –$COOCH_3$), 2.30 (*t*, 2H, –CH_2–$COOCH_3$), 2.09 (*bs*, 1H, –CHBr-CHBr–C*H*(–CH_2–)–(CH_2)$_{10}$–$COOCH_3$, in cyclopentane ring), 2.03 (*m*, 4H, –CHBr–CHBr–CH_2–CH_2–CH–, in cyclopentane ring), 3.66 (*s*, 3H, –$COOCH_3$), 1.61 (*s*, 2H, –CH_2–CH_2COOCH–), 1.27 (*s*, 16H, –CH_2–).

^{13}C NMR ($CDCl_3$): δ 174 (–*C*$OOCH_3$), 50, 57, 62, and 66 (–*C*HBr–*C*HBr– in cyclopentane ring), 52 (–COO*C*H_3), 43 (–CHBr–CHBr–*C*H– in cyclopentane ring), 28 (–*C*H_2–CHBr–CHBr– in cyclopentane ring), 27 (–*C*H_2–CH_2–CHBr–CHBr– in cyclopentane ring), 33 (–CH–*C*H_2–CH_2–), 28 (–CH–CH_2–*C*H_2–), 27 (–CH–CH_2–CH_2–*C*H_2–), 34 (–*C*H_2–$COOCH_3$), 25 (–*C*H_2–CH_2–$COOCH_3$), 28–30 (5C, –*C*H_2–).

Synthesis of endo *1,4-bis(methyl undecanoate)-tricyclo [5,2,1,0^{2,6}]deca-4,8-diene* via *diene intermediate*. *Threo*-2(*R/S*),3(*R/S*)-dibromo cyclopentane-1(*R*)-methyl undecanoate (50 g) was added to 10% alcoholic KOH solution (200 mL) with constant stirring at 60°C. 1,3-Cyclopentadiene-1-undecanoic acid (diene intermediate) obtained during the reaction underwent self Diels-Alder reaction to give dimer and oligomers. The reaction mixture was stirred further for 11 h and then cooled to 25°C. It was then acidified with 2 N HCl and diluted with diethylether (200 mL). The stirring was further continued for 20 h. The diethylether layer was separated and further washed with water to ensure complete removal of acid. This was then dried over anhydrous Na_2SO_4. The orange-yellow product was obtained by distilling off diethylether completely (43 g, 69% yield). The crude dimer and oligomer acids were esterified using methanol in the presence of H_2SO_4 and purified by preparative chromatography. A solution of 100 mg of crude methyl esters of dimer and oligomer acid dissolved in diethylether (1 mL) was loaded

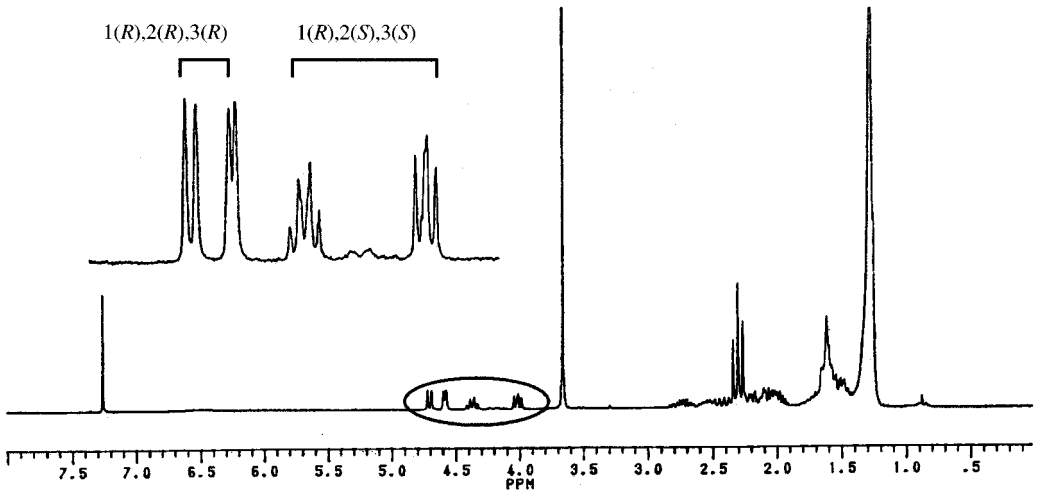


FIG. 1. ^{1}H Nuclear magnetic resonance spectrum of *threo*-2,3-dibromocyclopentane-1-methyl undecanoate.

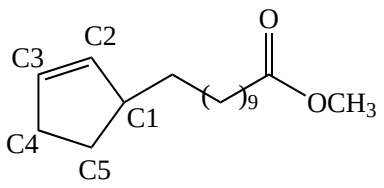
onto preparative TLC plates by means of a 100-μL syringe. Preparative chromatography was carried out using hexane/diethylether/acetic acid in 7.0:2.9:0.1 proportions. Plates were developed in an iodine chamber. The colored bands obtained were separated and extracted in diethylether. Diethylether was evaporated under vacuum to yield 58 mg of pure methyl ester of dimer acid. The *endo* 1,4-bis(methyl undecanoate)-tricyclo [5,2,1,$0^{2,6}$]deca-4,8-diene thus obtained was characterized by FT-IR and NMR.

^{1}H NMR ($CDCl_3$; Fig. 1): δ 5.9 (*m*, 3H, –C*H*=C*H*– in ring), 3.66 (*s*, 6H, –COOCH_3), 3.5 (*m*, 2H, >C*H*–CH=CH– in ring), 2.5–3.1 (*m*, 2H, –CH_2–CH=CH– in ring), 2.30 (*t*, *J* = 7.3 Hz, 4H, –CH_2–COOCH_3), 2.17–2.0 (*m*, 3H, >CH–CH_2– and –C*H*–CH_2–CH=CH– in ring), 1.60 (*m*, 8H, ≥C–CH_2–CH_2– and –CH_2–CH_2–CH_2–COOCH_3), 1.27 (*m*, 28H, –CH_2–).

^{13}C NMR ($CDCl_3$, Fig. 4): δ 147.2 (–CH=*C*≤ in ring), 132 (–*C*H=*C*H– in ring), 120 (–*C*H=C≤ in ring), 52 (–COO*C*H_3), 47.3 (>*C*< in ring), 37 (≥C–*C*H_2–CH_2–), 31 and 37.2 (>*C*H–CH=CH– in ring), 34 (–*C*H_2–COOCH_3), 31.5 (–*C*H_2–CH=CH– in ring), 30 (≥C–CH_2–*C*H_2–), 28–30 (–*C*H_2–), 28.2 (–*C*H–CH_2–CH=CH– in ring), 28 (≥C–CH_2–CH_2–*C*H_2–), 25 (–*C*H_2–CH_2–COOCH_3).

RESULTS AND DISCUSSION

Alkaline hydrolysis of chaulmoogra oil gave a mixture of cyclopentene fatty acids, which on subsequent esterification gave methyl esters. GLC analysis of methyl esters showed the presence of 51.3% methyl hydnocarpate [Scheme 1, 2-cyclopentene-1(*R*)-methyl undecanoate; 16:1 Cy], 34.7% methyl chaulmoograte (18:1 Cy) and 9.8% methyl gorlate (18:2 Cy). These methyl esters were separated by fractional distillation.

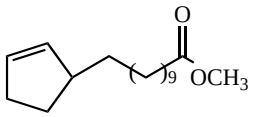


SCHEME 1

To form a dimer acid (*via* Diels-Alder reaction) it is necessary to have a conjugated diene moiety in the precursor. Conjugation in methyl hydnocarpate was achieved by bromination followed by subsequent dehydrobromination. Bromination of methyl hydnocarpate gave a *threo*-2,3-dibromocyclopentane-1-methyl undecanoate (dibromo methyl hydnocarpate), which on dehydrobromination gave 1,3-cyclopentadiene-1-undecanoic acid (cyclopentadiene derivative). The cyclopentadiene derivative further underwent Diels-Alder reaction to give a dimer and oligomer acids. The crude dimer and oligomer acids were esterified and purified to give novel *endo* 1,4-bis(methyl undecanoate)-tricyclo [5,2,1,$0^{2,6}$]deca-4,8-diene. The reaction sequence is given in Scheme 2.

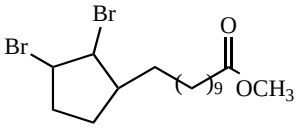
Bromination of methyl hydnocarpate gave two diastereoisomers in 1:1 proportion. Methyl hydnocarpate possesses one chiral center at C1 (Scheme 1), with *R*-configuration. Bromination generates two more chiral centers at the C2 and C3 atoms. The configuration of C2, C3 were assigned to be *R,R* and *S,S,* respectively. Hence the diastereoisomers of dibromo derivative possess *R,R,R* or *R,S,S* configuration at C1, C2, and C3 atoms, respectively. The structures of the two diastereoisomers are given in Scheme 3.

The ^{1}H NMR spectra (Fig. 1) of dibromo methyl hydnocarpate indicates two different sets of peaks in the region of δ 3.9 to 4.9 due to –BrC*H*–C*H*Br– protons. This was because of two diastereoisomers (*R,R,R* and *R,S,S*) of dibromo methyl hydnocarpate. In the case where both –BrC*H*–C*H*Br– protons were equatorial (Scheme 3A), Ha and Hb can couple only with one adjacent axially oriented proton (axial-equatorial coupling, *J* = 5 Hz) giving a doublet for each at δ 4.79 and 4.58, respectively. When both –BrC*H*–C*H*Br– protons were axial (Scheme 3B), Ha can couple with two axially oriented protons (axial-axial coupling, *J* = 12 Hz) giving a triplet at δ 4.0, while Hb can couple with two axially oriented protons



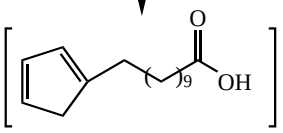
2-cyclopentene-1(*R*)-methyl undecanoate

Br_2 in $CHCl_3$



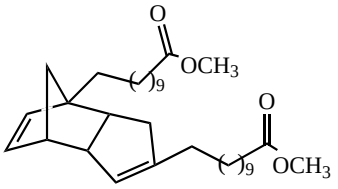
threo-2*(R/S)*,3*(R/S)*-dibromo cyclopentane-1*(R)*-methyl undecanoate

(i) Alcoholic KOH 60°C, 11.5 h (ii) 2 N HCl



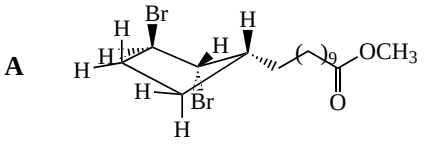
1,3-cyclopentadiene-1-undecanoic acid

CH_3OH, 0.1% H_2SO_4

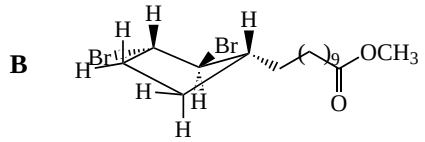


endo 1,4-bis(methyl undecanoate)-tricyclo [5,2,1,$0^{2,6}$]deca-4,8-diene

SCHEME 2

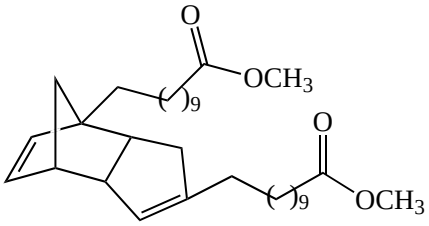


threo-2(*R*),3(*R*)-dibromocyclopentane-1(*R*)-methylundecanoate



threo-2(*S*),3(*S*)-dibromocyclopentane-1(*R*)-methylundecanoate

SCHEME 3



SCHEME 4

and one equatorially oriented proton (axial-axial and axial-equatorial coupling, $J = 5$ to 12 Hz) giving a quartet at δ 4.36.

In ^{13}C NMR spectra, four peaks were observed at δ 50, 57, 62, and 66 for –BrCH–CHBr– carbons of dibromo methyl hydnocarpate. ^{13}C DEPT NMR experiment was carried out to simplify the ^{13}C NMR spectra. It showed inversion of peaks due to $–CH_2–$ (secondary) carbon atoms while there was no inversion of peaks due to –*C*H– (primary) and $–CH_3$ (tertiary) carbon atoms at δ 50, 57, 62, 66 (of –*C*HBr–), δ 43 (of –*C*H– in cyclopentane ring) and δ 52 (of $–COOCH_3$). The carbons directly attached to the bromine of dibromo methyl hydnocarpate showed two different sets of peaks in ^{13}C NMR and ^{13}C DEPT NMR experiments (as in the case of ^1H NMR), thus confirming the presence of two diastereoisomers.

The dehydrobromination of dibromo methyl hydnocarpate to cyclopentadiene derivative was monitored using UV spectroscopy. The product was characterized using FT-IR and ^1H NMR. Peaks at 1606 and 722 cm^{-1} (in FT-IR) and in the region of δ 5.8–6.5 (in ^1H NMR) were observed for conjugated *cis*-double bonds. The dimer content was analyzed by GLC and found to be 60%, along with 36% of oligomers. The DEP-MS analysis of dimer acid methyl ester showed a molecular ion peak at *m/z* 528. The fragmentation pattern showed a peak at $m/z = M - 31 = 497$ (loss of $–OCH_3$ group). The retro-Diels-Alder fragment at *m/z* 264 was also observed, confirming the bicylic nature of the dimer acid. A prominent peak due to β-cleavage (β- to the cyclopentadiene) was observed at $m/z = M - 185 = 79$. The base peak was observed at *m/z* 81, and this was attributed to C_6H_9 (containing cyclopentene ring). On further loss of CH_2 this gave *m/z* 67, C_5H_7 (cyclopentene ring). The peak at $m/z = M - 199 = 329$ was observed and was explained as loss of one of the side chains, $–C_{10}H_{20}COOCH_3$. Further loss of a second side chain gave a peak at *m/z* 130 confirming the structure as a tricyclic dimer acid (Scheme 4).

ACKNOWLEDGMENTS

This work was supported by research grants from Hindustan Lever Research Foundation, Mumbai, India. We are thankful to Dr. V.K. Gore (research scientist, Hindustan Lever Research Center) for his valuable suggestions.

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[Received December 3, 1999; accepted July 28, 2000]