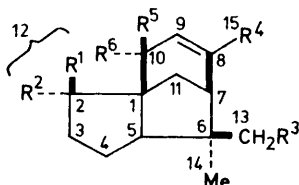


## Structural Investigation of Lac Resin. Part 14.<sup>1</sup> Model Esters related to Lac Resin

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Model esters formed from the 12- and 15-carboxy-functions of shellolic acid and its 2-epimer with the C-16-position of methyl *threo*-aleuritate are reported. While stearate esters involving the hydroxy-groups of the above two terpenes were readily obtained through the acid chloride or the mixed anhydride procedure, the corresponding mixed *threo*-aleuritic-carbonic anhydride failed to react. The results indicated the greater stability and preferential ester formation with mixed stearic-carbonic anhydride at C-13 rather than at C-10.

EARLIER work<sup>2</sup> of Sukh Dev *et al.* has projected a probable representation of the structure of lac resin involving ester linkages at some of the available centres in the terpene as well as the *threo*-aleuritic acid [(9*RS*,10*RS*)-9,10,16-trihydroxyhexadecanoic acid] moieties. The synthesis of one such ester (1) has been reported;<sup>3</sup> this utilises (9*RS*,10*RS*)-9,10,16-triformylaleuritoyl chloride, followed by deformylation. Evidence has already been presented<sup>2,4</sup> for the participation of the 9,10-



### Shellolate series

- (2)  $R^1 = R^4 = \text{CO}_2\text{Me}$ ,  $R^2 = R^6 = \text{H}$ ,  $R^3 = R^5 = \text{OH}$   
 (3)  $R^1 = R^4 = \text{CO}_2\text{Me}$ ,  $R^2 = R^6 = \text{H}$ ,  $R^3 = \text{OCO}[\text{CH}_2]_{16}\text{CH}_3$ ,  
 $R^5 = \text{OH}$   
 (12)  $R^1 = R^4 = \text{CO}_2\text{Me}$ ,  $R^2 = R^6 = \text{H}$ ,  $R^3 = R^5 = \text{OCOCF}_3$   
 (13)  $R^1 = R^4 = \text{CO}_2[\text{CH}_2]_6\text{CHOHCHOH}[\text{CH}_2]_7\text{CO}_2\text{Me}$ ,  $R^2 = R^6 = \text{H}$ ,  $R^3 = R^5 = \text{OH}$

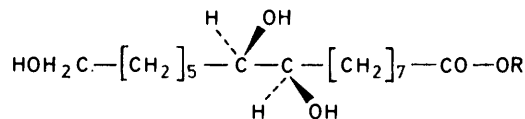
### 2-*epi*-Shellolate series

- (1)  $R^1 = R^6 = \text{H}$ ,  $R^2 = \text{CHO}$ ,  $R^3 = \text{OH}$ ,  $R^4 = \text{CO}_2\text{Me}$ ,  $R^5 = \text{OCO}[\text{CH}_2]_7\text{CHOHCHOH}(\text{CH}_2)_6\text{OH}$   
 (4)  $R^1 = R^6 = \text{H}$ ,  $R^2 = R^4 = \text{CO}_2\text{Me}$ ,  $R^3 = R^5 = \text{OH}$   
 (5)  $R^1 = R^6 = \text{H}$ ,  $R^2 = R^4 = \text{CO}_2\text{Me}$ ,  $R^3 = \text{OCO}[\text{CH}_2]_{16}\text{Me}$ ,  
 $R^5 = \text{OH}$   
 (6)  $R^1 = R^6 = \text{H}$ ,  $R^2 = R^4 = \text{CO}_2\text{Me}$ ,  $R^3 = R^5 = \text{OCO}[\text{CH}_2]_{16}\text{CH}_3$   
 (7)  $R^1 = R^6 = \text{H}$ ,  $R^2 = R^4 = \text{CO}_2\text{Me}$ ,  $R^3 = \text{OH}$ ,  $R^5 = \text{OCO}[\text{CH}_2]_{16}\text{CH}_3$   
 (8)  $R^1 = R^5 = \text{H}$ ,  $R^2 = R^4 = \text{CO}_2\text{Me}$ ,  $R^3 = \text{OAc}$ ,  $R^6 = \text{OH}$   
 (14)  $R^1 = R^6 = \text{H}$ ,  $R^2 = R^4 = \text{CO}_2[\text{CH}_2]_6\text{CHOHCHOH}[\text{CH}_2]_7\text{CO}_2\text{Me}$ ,  $R^3 = R^5 = \text{OH}$

hydroxy-functions of *threo*-aleuritic acid in resin formation. This paper presents some experiments directed towards ester formation, using *threo*-aleuritic acid without protection of the hydroxy-groups.

We have earlier made a detailed investigation<sup>5</sup> of the stereochemistry of substitution at the allylic position of the terpene skeleton and also of the acetylation of the allylic hydroxy-group. The comparative ease of acetate formation from the C-10 allylic hydroxy and the C-13 primary hydroxy was also reported. In view of the above work, ester formation from the terpenes of shellac and stearic acid or *threo*-aleuritic acid was attempted using different methods.

The condensation between dimethyl shellolate (2) and mixed stearic-carbonic anhydride was studied under conditions of both base and acid catalysis. The above reactions led to the formation of the 13-*O*-stearate (3) as a viscous gum (n.m.r.) unlike the acetate formation, where in a similar reaction, the 10,13-di-*O*-acetate was also obtained. The 10-*O*-stearate or the 10,13-di-*O*-stearate were absent in the reaction mixture. On the other hand, dimethyl 2-*epi*-shellolate (4) behaved differently and the ester condensation led to a mixture of three products with a trace of unchanged dimethyl 2-*epi*-shellolate. The mixture was separated by extensive column chromatography on silica gel. The major product was the 13-*O*-stearate (5) while the 10 $\beta$ -13-di-*O*-stearate (6) was obtained in lower yield. The third product (7), present in trace quantities, was the 10 $\beta$ -*O*-stearate ( $J_{9,10}$  2.5 Hz). All these were viscous gums and were characterised by elemental analysis, accurate mass measurements (see Experimental section), and n.m.r. spectra, the latter being closely similar to those of the well-characterised acetates.<sup>5</sup> Ester condensation with dimethyl 13-*O*-acetyl-2-*epi*-10-*epi*-shellolate (8) gave the corresponding 10 $\alpha$ -*O*-stearate ( $J_{9,10}$  4.5 Hz). The above results indicated a slight deviation from the ease of acetate formation noticed earlier,<sup>5</sup> in that the entry of the stearoyl group at the allylic position was somewhat hindered, especially in dimethyl shellolate (2). Stearoyl chloride gave results similar to those obtained by the anhydride method. Model compounds thus indicate greater stability and preferential formation of ester at a C-13-hydroxy rather than a C-10-hydroxy, while the structure projected for the natural resin involves an ester exclusively at C-10-hydroxy.



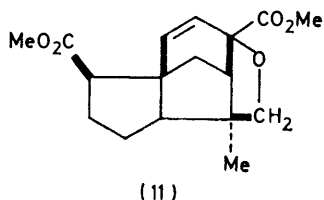
(9)  $R = \text{CO}_2\text{Et}$

(10)  $R = \text{CO}[\text{CH}_2]_7\text{CHOHCHOH}[\text{CH}_2]_5\text{CH}_2\text{OH}$

Mixed *threo*-aleuritic-carbonic anhydride (9) was readily prepared from the respective constituents, though it was difficult to remove the last traces of

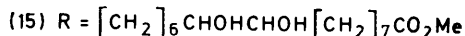
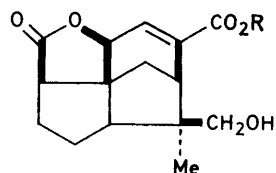
*threo*-aleuritic acid accompanying the mixed anhydride. The mixed anhydride reacted readily with ammonia to give the (9*RS*,10*RS*)-9,10,16-trihydroxyhexadecanamide as a crystalline solid. The mixed anhydride also gave the symmetrical *threo*-aleuritic anhydride (10) as a crystalline solid. However, attempts to prepare esters from dimethyl shellolate (or its 2-epimer) and the mixed *threo*-aleuritic-carbonic anhydride were unsuccessful under a variety of conditions. Steric factors may be involved.

We had earlier prepared<sup>5</sup> 10 $\alpha$ - and 10 $\beta$ -bromo-derivatives from dimethyl 2-*epi*-shellolate (5) and the 10 $\alpha$ -bromo-derivative from dimethyl shellolate (2). Condensation between these bromo-compounds and potassium *threo*-aleuritate or *threo*-aleuritic acid was also unsuccessful, no reaction taking place under anhydrous conditions, while under aqueous conditions, the bromo-compounds underwent solvolysis to give the corresponding 10 $\alpha$ -hydroxy-compounds. Attempts were also made to prepare the allylic esters in the presence of trifluoroacetic anhydride. With catalytic quantities, the anhydro-derivative (11) resulted, while with excess of reagent the 10 $\beta$ ,13-di-*O*-trifluoroacetate (12) was formed



( $M^{++}$  and n.m.r.). Transesterification, using the above 10 $\beta$ ,13-di-*O*-trifluoroacetate (12) and *threo*-aleuritic acid, was also unsuccessful.

On the other hand, esters involving 12 and/or 15-carboxy-functions of terpene acids and the C-16 position of *threo*-aleuritic acid were readily prepared. Thus shellolic acid in acetone solution reacted with methyl (9*RS*,10*RS*)-9,10-dihydroxy-16-iodohexadecanoate<sup>6</sup> in the presence of silver carbonate to give the 12,15-diester (13). Similar esters (14) and (15) were also prepared from 2-*epi*-shellolic acid and shellolic 12,10-lactone (16), respectively. The purity of these compounds was



established through their elemental analysis, spectra, and from estimation of the glycol group by the periodate method.

#### EXPERIMENTAL

T.l.c. of the methyl esters was carried out in chloroform-methanol (98:2) and of the free acids in toluene-ethyl

formate-formic acid (5:4:1) on silica gel plates. Spots were located by spraying with 50% aqueous sulphuric acid followed by charring.

#### Preparation of the 13-*O*-Stearate of Dimethyl Shellolate.—

(a) *In the presence of a base catalyst.* Dimethyl shellolate (2) (200 mg) and mixed stearic-carbonic anhydride<sup>7</sup> (600 mg) were dissolved in dry pyridine (2 ml) and stirred at room temperature for 15 h. The reaction mixture was diluted with ice-cold water (3 ml) and extracted into ether. The ether extract was washed with aqueous sodium hydrogen-carbonate followed by water and dried (anhydrous sodium sulphate). Removal of the solvent gave a gum which was chromatographed over silica gel (20 g). Elution with light petroleum (b.p. 60–80°)-benzene (1:1) gave *dimethyl 13-*O*-stearoylshellolate* (3) as a gum (150 mg) (Found: C, 70.7; H, 10.0.  $C_{35}H_{58}O_7$  requires C, 71.2; H, 9.9%),  $m/e$  ( $M^{++}$  not observed) 558.3925 ( $C_{34}H_{54}O_6$ ,  $M^{++} - CH_3OH$ ),  $\nu_{max}$  (KBr) 1 724 and 1 653  $cm^{-1}$ ,  $\delta$  1.20 (br, CMe,  $CH_2$ ), 3.69 (s,  $CO_2Me$ ), 3.73 (s,  $CO_2Me$ ), 4.5 (d,  $J$  2.5 Hz,  $CHOH$ ), and 6.53 (d,  $J$  2.5 Hz,  $CH=C$ ). The signal for  $CH_2-O-CO(q)$  partially overlapped with the signals for  $CO_2Me$ .

Elution with 1% ethyl acetate in benzene gave unchanged dimethyl shellolate (2) (30 mg), m.p. 152°.

(b) *In the presence of an acid catalyst.* Dimethyl shellolate (200 mg) and mixed stearic-carbonic anhydride (600 mg) were stirred in dioxan (2 ml) containing perchloric acid (0.01 ml) at room temperature for 8 h. The reaction mixture was extracted into ether, washed with aqueous sodium hydrogen carbonate and water, and dried ( $Na_2SO_4$ ). Removal of the solvent gave a gum which was chromatographed over silica gel. Light petroleum (b.p. 60–80°)-benzene (1:1) eluted the same ester as described in the previous experiment (i.r. and n.m.r. spectra).

Elution with 1% v/v ethyl acetate-benzene yielded unchanged dimethyl shellolate.

(c) *With stearoyl chloride.* Dimethyl shellolate (200 mg) in dry pyridine (2 ml) was kept in contact with stearoyl chloride (0.2 ml) at room temperature for 15 h. On work-up, the reaction mixture gave the 13-*O*-stearate (3) as the only product.

*Stearoylation of Dimethyl 2-epi-Shellolate.*—Dimethyl 2-*epi*-shellolate (4) (500 mg), on similar reaction with mixed stearic-carbonic anhydride (1.5 g) in dry pyridine (5 ml), gave a gummy product which showed, in addition to unchanged starting material, three spots on t.l.c. The components were separated on a silica gel column.

Elution with light petroleum (b.p. 60–80°)-benzene (3:1) gave as a gum, *dimethyl 10 $\beta$ ,13-di-*O*-stearoyl-2-epi-shellolate* (6) (100 mg) (Found: C, 73.8; H, 10.7.  $C_{33}H_{52}O_8$  requires C, 74.3; H, 10.7%),  $m/e$  [ $M^{++}$  (856) not observed] 825, 797, 769, 670, 590, 559, 560, 531, 532, 515, 514, 503, and 343,  $\nu_{max}$  (KBr) 1 745 and 1 639  $cm^{-1}$ ,  $\delta$  1.2 (br, CMe,  $CH_2$ ), 3.65 (s,  $CO_2Me$ ), 3.70 (s,  $CO_2Me$ ), 5.89 (d,  $J$  2.5 Hz,  $CHOCO$ ), and 6.59 (d,  $J$  2.5 Hz,  $CH=C$ ). The signal for  $CH_2OCO(q)$  partially overlapped with the signals for  $CO_2Me$ .

Light petroleum (b.p. 60–80°)-benzene (1:1) eluted *dimethyl 10 $\beta$ -*O*-stearoyl-2-epi-shellolate* (7) as a gum (30 mg) (Found: C, 70.8; H, 9.4.  $C_{35}H_{58}O_7$  requires C, 71.2; H, 9.9%),  $m/e$  590,4200 [ $M^{++}$  (0.13%)],  $\nu_{max}$  (KBr) 3 571, 1 724, and 1 639  $cm^{-1}$ ,  $\delta$  1.20 (br, CMe,  $CH_2$ ), 3.66 (s,  $CO_2Me$ ), 3.76 (s,  $CO_2Me$ ), 3.26 (br,  $CH_2OH$ ), 5.89 (d,  $J$  2.5 Hz,  $CHOCO$ ), and 6.6 (d,  $J$  2.5 Hz,  $CH=C$ ).

Elution with benzene yielded the major component, *dimethyl 13-*O*-stearoyl-2-epi-shellolate* (5) (250 mg) (Found: C, 70.8; H, 9.7.  $C_{35}H_{58}O_7$  requires C, 71.2; H, 9.9%),

*m/e* 590.4169 [ $M^{+}$  (0.07%)],  $\nu_{\max}$  (KBr) 3 571, 1 724, and 1 626  $\text{cm}^{-1}$ ,  $\delta$  1.21 (br, CMe,  $\text{CH}_2$ ), 3.70 (s,  $\text{CO}_2\text{Me}$ ), 3.73 (s,  $\text{CO}_2\text{Me}$ ), 4.8 (d,  $J$  2.5 Hz, CHOH), and 6.61 (d,  $J$  2.5 Hz,  $\text{CH}=\text{C}$ ). The signal for  $\text{CH}_2\text{OCO}(\text{q})$  partially overlapped with the signals for  $\text{CO}_2\text{Me}$ .

2% v/v Ethyl acetate–benzene eluted the unchanged dimethyl 2-*epi*-shellolate (4) (40 mg), m.p. 151°.

*Stearoylation of Dimethyl 13-O-Acetyl-2-epi-shellolate*.—Dimethyl 13-*O*-acetyl-2-*epi*-shellolate (200 mg) on similar reaction with mixed stearic–carbonic anhydride (600 mg) in dioxan and perchloric acid (0.01 ml) afforded a single product (gum) (t.l.c.) of dimethyl 13-*O*-acetyl-10 $\beta$ -*O*-stearoyl-2-*epi*-shellolate (150 mg),  $\nu_{\max}$  (KBr) 1 735 and 1 630  $\text{cm}^{-1}$ ,  $\delta$  1.20 (br, CMe,  $\text{CH}_2$ ), 2.0 (s,  $\text{OCOMe}$ ), 3.67 (6 H, s,  $\text{CO}_2\text{Me}$ ), 5.91 (d,  $J$  2.5 Hz, CHOCO), and 6.6 (d,  $J$  2.5 Hz,  $\text{CH}=\text{C}$ ). The signal for  $\text{CH}_2\text{OAc}(\text{q})$  partially overlapped with the signal for  $\text{CO}_2\text{Me}$ .

*Stearoylation of Dimethyl 13-O-Acetyl-2-epi-10-epi-shellolate* (8).—Compound (8) on similar reaction with mixed stearic–carbonic anhydride in dioxan and perchloric acid gave dimethyl 13-*O*-acetyl-10 $\alpha$ -*O*-stearoyl-2-*epi*-shellolate as a gum (t.l.c. pure),  $\nu_{\max}$  (KBr) 1 730 and 1 620  $\text{cm}^{-1}$ ,  $\delta$  1.19 (br, CMe,  $\text{CH}_2$ ), 1.95 (s,  $\text{OCOMe}$ ), 3.61 (s,  $\text{CO}_2\text{Me}$ ), 3.69 (s,  $\text{CO}_2\text{Me}$ ), 5.1 (d,  $J$  4.5 Hz, CHOCO), and 6.64 (d,  $J$  4.5 Hz,  $\text{CH}=\text{C}$ ). The signal for  $\text{CH}_2\text{OAc}(\text{q})$  partially overlapped with the signals for  $\text{CO}_2\text{Me}$ .

*Mixed threo-Aleuritic–Carbonic Anhydride*.—A solution of *threo*-aleuritic acid (500 mg) and triethylamine (0.28 ml) in chloroform (20 ml) was cooled to  $-5^\circ\text{C}$ . Into this mixture, a cooled solution of ethyl chloroformate (0.18 ml in 5 ml chloroform) was added dropwise with stirring. Stirring was continued for another 30 min at  $-5^\circ\text{C}$ . The mixture was diluted with chloroform, washed with water, and dried (anhydrous sodium sulphate). Removal of the solvent followed by repeated crystallisations from chloroform–light petroleum (b.p. 60–80°) afforded mixed *threo*-aleuritic–carbonic anhydride (9) as an amorphous solid, m.p. 58–60° (a trace of *threo*-aleuritic acid could not be removed),  $\nu_{\max}$  (KBr) 3 448, 1 802, 1 745, and 1 070  $\text{cm}^{-1}$ .

(9*RS*,10*RS*)-9,10,16-Trihydroxyhexadecanamide.—Aqueous ammonia (40%; 0.20 ml) in chloroform (5 ml) was added dropwise to the above reaction mixture of mixed *threo*-aleuritic–carbonic anhydride. After stirring for 3 h at 0 °C a solid separated out which was filtered off, washed with water and chloroform, and dried. Crystallisation from ethyl acetate–light petroleum (b.p. 60–80°) afforded (9*RS*,10*RS*)-9,10,16-trihydroxyhexadecanamide (300 mg), m.p. 123° (Found: C, 63.7; H, 10.5.  $\text{C}_{16}\text{H}_{33}\text{O}_4\text{N}$  requires C, 63.4; H, 10.9%),  $\nu_{\max}$  (KBr) 3 436–3 125 and 1 699  $\text{cm}^{-1}$ .

*Symmetrical threo-Aleuritic Anhydride* (10).—A cooled solution ( $-5^\circ\text{C}$ ) of *threo*-aleuritic acid (500 mg) and triethylamine (0.28 ml) in chloroform (20 ml) was added dropwise to a mixture of mixed-*threo* aleuritic–carbonic anhydride with stirring at  $-5$  to 0 °C. After the addition was complete, stirring was continued for another 10 h at room temperature. A solid separated out which was filtered off, washed repeatedly with excess of chloroform, and dried. Crystallisation from chloroform–light petroleum (b.p. 60–80°) afforded the symmetrical *threo*-aleuritic anhydride (10) (700 mg), m.p. 83° (Found: C, 65.5; H, 11.0.  $\text{C}_{32}\text{H}_{62}\text{O}_8$  requires C, 65.1; H, 10.5%),  $\nu_{\max}$  (KBr) 3 448, 1 802, 1 730, and 1 070  $\text{cm}^{-1}$ .

The above symmetrical *threo*-aleuritic anhydride, on stirring with aqueous ammonia (1 mol. equiv.) in chloroform

at 0 °C for 3 h, gave (9*RS*,10*RS*)-9,10,16-trihydroxyhexadecanamide, m.p. 123° (mixed m.p. and i.r.).

16-*O*-Methyl (7*RS*,8*RS*)-7,8-dihydroxyhexadecanedioic acid,<sup>6</sup> on similar reaction with ethyl chloroformate in chloroform solution, gave the mixed anhydride which gave the corresponding *amide* on treatment with aqueous ammonia, m.p. 100–101° (Found: C, 61.5; H, 9.7.  $\text{C}_{17}\text{H}_{33}\text{O}_5\text{N}$  requires C, 61.6; H, 9.9%),  $\nu_{\max}$  (KBr) 3 480–3 200, 1 735, and 1 640  $\text{cm}^{-1}$ .

Neither dimethyl shellolate nor dimethyl 2-*epi*-shellolate reacted with mixed *threo*-aleuritic–carbonic anhydride or the symmetrical *threo*-aleuritic anhydride, either in the presence of pyridine or perchloric acid, at room temperature or at reflux temperature (as shown by t.l.c. and the recovery of unchanged terpene).

*Dimethyl 10 $\beta$ ,13-Bis-O-trifluoroacetylshellolate* (12).—Dimethyl shellolate (2) (500 mg) was kept in contact with trifluoroacetic anhydride (1 ml) in dioxan (10 ml) at room temperature for 30 min. It was extracted into ether, washed with aqueous sodium hydrogen carbonate and water, and dried. Removal of the solvent yielded a gum which was chromatographed over silica gel.

Elution with 10% v/v light petroleum (b.p. 60–80°)–benzene afforded (12) (300 mg) as a gum (pure by t.l.c.), *m/e* 516.1228 [ $M^{+}$  (0.22%),  $\text{C}_{21}\text{H}_{22}\text{O}_8\text{F}_6$ ],  $\delta$  1.2 (s, CMe), 3.7 (s,  $\text{CO}_2\text{Me}$ ), 3.8 (s,  $\text{CO}_2\text{Me}$ ), 4.2 (q,  $J$  10.0 Hz,  $\text{CH}_2\text{-OCOCF}_3$ ), 5.9 (d,  $J$  3 Hz,  $\text{CHOCOCF}_3$ ), and 6.5 (d,  $J$  3 Hz,  $\text{CH}=\text{C}$ ).

Elution with benzene gave dimethyl anhydroshellolate (11) (50 mg), m.p. 63–64° (lit.,<sup>8b</sup> 65.5–66.5°).

*Attempted trans-Esterification of (12) with threo-Aleuritic Acid*.—Compound (12) (50 mg) and *threo*-aleuritic acid were heated under reflux for 10 h in acetone containing a trace of trifluoroacetic acid. Work-up of the reaction mixture yielded the unchanged starting materials.

12,15-*Di*-(16-*threo*-aleurityl)-esters.—(a) *From shellolic acid*. Shellolic acid (300 mg) and methyl (9*RS*,10*RS*)-9,10-dihydroxy-16-iodohexadecanoate<sup>6</sup> (1.0 g) were heated under reflux in dry acetone in the presence of silver carbonate (1.5 g) for 8 h. The reaction mixture was cooled, filtered, and washed with acetone. The combined filtrate, on evaporation of the solvent, gave a gum which was chromatographed over silica gel. Elution with 50% v/v ethyl acetate–benzene yielded the *diester* (13) as a gum (pure by t.l.c.) (200 mg) (Found: C, 65.9; H, 9.0.  $\text{C}_{46}\text{H}_{84}\text{O}_{14}$  requires C, 65.6; H, 9.4%), *m/e* [ $M^{+}$  (896) not observed] 879, 829, 716, 690, 673, 543, 526, 511, 391, 301, 269, 262, 261, and 260,  $\nu_{\max}$  (KBr) 3 500, 1 739, 1 714, and 1 604  $\text{cm}^{-1}$ ,  $\delta$  1.3 (br,  $\text{CH}_2$ , CMe), 3.3 (br,  $\text{CH}_2\text{OH}$ ,  $\text{CHOHCHOH}$ ), 3.6 (s, 6 H,  $\text{CO}_2\text{Me}$ ), 4.1 (br,  $\text{CH}_2\text{OCO}$ ), 4.5 (d,  $J$  2.5 Hz, CHOH), and 6.4 (d,  $J$  2.5 Hz,  $\text{CH}=\text{C}$ ).

*Periodate estimation*. The diester (13) (100 mg) in dioxan (5 ml) was treated with sodium periodate (0.1M; 10 ml) and kept for 40 min at 30 °C. The excess periodate was determined iodometrically; volume of sodium thiosulphate consumed: blank, 38.7 ml; with 100 mg of sample, 36.5 ml; observed thiosulphate equivalent, 114 mg; calculated thiosulphate equivalent for 100 mg of diester (13) of mol. wt. 896 containing two glycol units per molecule, 111.2 mg; % purity, 97.3.

(b) *From 2-epi-shellolic acid*. 2-*epi*-Shellolic acid (100 mg), on similar reaction with methyl (9*RS*,10*RS*)-9,10-dihydroxy-16-iodohexadecanoate (400 mg) in dry acetone containing silver carbonate gave the *diester* (14) (80 mg) as a gum which was estimated by the periodate method, showing the

presence of two glycol groups per molecule (Found: C, 65.5; H, 9.2.  $C_{49}H_{84}O_{14}$  requires C, 65.6; H, 9.4%),  $m/e$  [ $M^{+}$  (896) not observed] 821, 716, 715, 603, 579, 543, 542, 531, 530, 511, 392, 391, 262, 261, and 260,  $\nu_{\max.}$  (KBr) 3 509, 1 736, and 1 608  $\text{cm}^{-1}$ ,  $\delta$  1.12 (s, CMe), 1.3 (br,  $\text{CH}_2$ ), 3.3 (br,  $\text{CH}_2\text{OH}$ ,  $\text{CHOHCHOH}$ ), 3.6 (6 H, s,  $\text{CO}_2\text{Me}$ ), 4.1 (br,  $\text{CH}_2\text{OCO}$ ), 4.8 (d,  $J$  2.5 Hz,  $\text{CHOH}$ ), and 6.56 (d,  $J$  2.5 Hz,  $\text{CH}=\text{C}$ ).

(c) From shellolic 12,10-lactone (16). Shellolic 12,10-lactone <sup>8a</sup> (16) (100 mg), on heating under reflux with methyl (9*RS*,10*RS*)-9,10-dihydroxy-16-iodohexadecanoate (300 mg) in dry acetone containing silver carbonate (500 mg), yielded the monolactone ester (15) (100 mg) as the only product (confirmed by periodate estimation) (Found: C, 66.5; H, 9.0.  $C_{32}H_{50}O_9$  requires C, 66.4; H, 8.7%),  $\nu_{\max.}$  (KBr) 3 502, 1 780, 1 740, 1 680, and 1 608  $\text{cm}^{-1}$ ,  $\delta$  1.1 (s, CMe), 1.4 (br,  $\text{CH}_2$ ), 3.2 (br,  $\text{CH}_2\text{OH}$ ,  $\text{CHOHCHOH}$ ), 3.7 (s,  $\text{CO}_2\text{Me}$ ), 4.13 (br,  $\text{CH}_2\text{OCO}$ ), 5.0 (d,  $J$  2.5 Hz,  $\text{CHOCO}$ ), and 6.9 (d,  $J$  2.5 Hz,  $\text{CH}=\text{C}$ ).

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#### REFERENCES

- <sup>1</sup> Part 13, G. B. V. Subramanian, K. N. Ganesh, V. S. Chauhan, and V. K. Mahajan, *J.C.S. Perkin I*, 1978, 70.
- <sup>2</sup> A. N. Singh, A. B. Upadhye, V. V. Mhaskar, Sukh Dev, A. V. Pol, and V. G. Naik, *Tetrahedron*, 1974, **30**, 3687.
- <sup>3</sup> A. N. Singh, A. B. Upadhye, V. V. Mhaskar, and Sukh Dev, *Tetrahedron*, 1974, **30**, 867.
- <sup>4</sup> T. R. Seshadri, N. Sriram, and G. B. V. Subramanian, *Indian J. Chem.*, 1971, **9**, 524.
- G. B. V. Subramanian, U. Majumdar, V. S. Chauhan, K. N. Ganesh, and V. K. Mahajan, *J.C.S. Perkin I*, 1977, 1734.
- <sup>6</sup> S. V. Eswaran, T. R. Seshadri, N. Sriram, and G. B. V. Subramanian, *Indian J. Chem.*, 1971, **9**, 113.
- <sup>7</sup> J. S. Nelson, L. A. Goldblatt, and T. H. Applewhite, *J. Org. Chem.*, 1963, **28**, 1905.
- <sup>8</sup> (a) P. Yates and G. F. Field, *Tetrahedron*, 1970, **26**, 3135; (b) P. Yates, P. M. Burke, and G. F. Field, *Tetrahedron*, 1970, **26**, 3159.