Structural Investigation of Lac Resin. Part 12.[1] 10-*epi*- and 2-*epi*, 10-*epi*-Shellolic Acids and Some Allylic Rearrangements

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The nature, reactivity, and acid-catalysed isomerisations of the allyl system in shellolic acid and its 2-epimer are discussed. The configurations of substituents at C-10 in these cedrene derivatives are correlated with their spectral characteristics. The relevance of the results to the complexity of shellac is indicated.

SHELLOLIC ACID (1), its 2-epimer, and 2-*epi*-jalaric acid (2) are obtained by alkaline hydrolysis as the main terpene acids of shellac.[1] During our work on lac resin it was realised that a considerable proportion of the terpene acids remained unidentified in a complex gummy mixture consisting of numerous fatty acids as well as terpene acids other than the primary ones reported earlier. Analysis of the gum was further complicated by the presence of cyclic acetals formed from the constituents of shellac and compounds of the type (3) and (4), either present originally or formed during the subsequent processing or degradative analysis.[1] Failure to separate this complex mixture led us to investigate the transformation products of the sensitive shellolic acid nucleus under acidic and basic catalysis. It was hoped that this investigation would assist in the preparation of modified commercial products.

A variety of Lewis acids (*e.g.* boron trifluoride–ether) directly converted shellolic acid or its dimethyl ester through allylic isomerisation into the cyclic ether (5), earlier obtained [2,3] by zinc-promoted debromination of the bromo-lactone (6). Hot dilute mineral acid or even catalytic amounts of trifluoroacetic anhydride under anhydrous conditions converted the ester of (1) smoothly into the ether (5) as the major product. The ether itself was converted readily with hydrogen bromide–glacial acetic acid at 30 °C into a 13-acetoxy-10-bromocedr-8-ene derivative (7) as the only product. The same bromo-derivative was obtained when dimethyl shellolate was treated with hydrogen bromide–glacial acetic acid. Dimethyl 2-*epi*-shellolate (8) exhibited a parallel behaviour pattern.

However, whereas dimethyl shellolate and the derived ether (5) gave a single crystalline bromo-derivative, the corresponding 2-epimers (8) and (9) gave a gummy product which could be separated into two non-crystalline bromine-containing components by careful column chromatography. An equilibrium mixture appears to be formed whether one starts with dimethyl 2-*epi*-shellolate or the derived cyclic ether. The configuration at C-10 in these products was assigned on the basis of n.m.r. spectra and the following series of experiments.

The bromo-derivatives reacted with potassium acetate–glacial acetic acid to give in each case a 10,13-diacetate as a single product. These diacetates were assigned the α-configuration at C-10 as they were different from the 10β,13-diacetates obtained from dimethyl shellolate and 2-*epi*-shellolate by the acetic anhydride–pyridine method. Alkaline hydrolysis of these diacetates gave 10-*epi*- (10) and 2-*epi*-, 10-*epi*- (11) shellolic acids, respectively. Two features are noteworthy in this series of reactions. The coupling constant of the vicinal protons at C-9 and C-10 in all the terpene acids isolated from the resin directly, where the C-10 substituents are known to be β, was 2.5 Hz, whereas all the α-isomers had a coupling constant of 4.0—4.5 Hz. Further, the chemical shift of the allylic proton in the α-series was generally to high field as compared with that in the β-series with the same substituents. On the basis of these data, the 13-acetoxy-10-bromo-derivative (7) from dimethyl shellolate was assigned the α-configuration at C-10. In the case of the mixture of bromo-acetates (12) and (13) from dimethyl 2-*epi*-shellolate, the one which had $J_{9,10}$ 2.5 Hz was assigned the β-configuration, the other, $J_{9,10}$ 4.5 Hz, the α-configuration. All the bromo-compounds irrespective of the configuration at C-10, formed exclusively the 10α-acetate, indicating preferential attack from the α-face, although the reagent generally attacks from the rear even in allylic systems.[4] Hence the β-face must be sterically crowded; and it is noteworthy that all the natural terpene acids of shellac have the β-configuration at C-10.

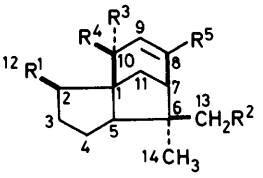
When the reaction with hydrogen bromide–glacial acetic acid was carried out at 0 °C, a mixture of products was obtained (Table). The initially formed acetates (both 10α- and 10β-) were readily converted exclusively into the 10α-bromo-derivative in the case of shellolate.

In the case of dimethyl 2-*epi*-shellolate, when the temperature of the same reaction mixture was raised to 30 °C or the pure acetates were treated independently with hydrogen bromide–glacial acetic acid, an equilibrium mixture of the 10α- and 10β-bromo-derivatives was obtained. Further, the pure bromo-acetate (13) underwent equilibration with hydrogen bromide–glacial acetic acid to give a mixture of both isomers, whereas the 10β-isomer was unaffected, thus indicating that the initial product was the α-isomer.

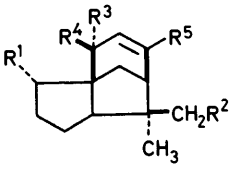
Whereas acetylation with acetic anhydride–pyridine gave the respective acetates without epimerisation at C-10, use of acetic anhydride–perchloric acid gave mixtures of the α- and β-isomers in various ratios (see Experimental section), analysable by n.m.r. spectroscopy.

[1] Part 11, G. B. V. Subramanian, J. Iqbal, K. N. Ganesh, and N. Sriram, *J.C.S. Perkin I*, 1976, 2045.
[2] R. C. Cookson, N. Lewin, and A. Morrison, *Tetrahedron*, 1962, **18**, 547.
[3] P. Yates, P. M. Burke, and G. F. Field, *Tetrahedron*, 1970, **26**, 3159.
[4] R. H. Dewolfe and W. G. Young, *Chem. Rev.*, 1956, **56**, 753.

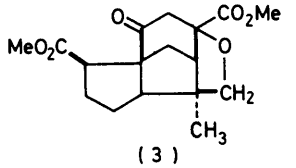
These products could be separated by a column chromatography over silica gel. The relevance of the preparation and behaviour of the 10-*epi*-acids to the properties of the parent lac resin is apparent. With such a susceptibility to acid-catalysed isomerisation, the presence of 10α-isomers in the complex gummy mixture might be



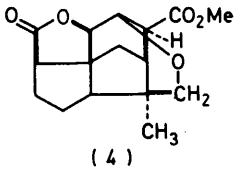
(1) $R^1 = R^5 = CO_2H$, $R^2 = R^4 = OH$, $R^3 = H$
(7) $R^1 = R^5 = CO_2Me$, $R^2 = OAc$, $R^3 = Br$, $R^4 = H$
(10) $R^1 = R^5 = CO_2H$, $R^2 = R^3 = OH$, $R^4 = H$



(2) $R^1 = CHO$, $R^2 = R^4 = OH$, $R^3 = H$, $R^5 = CO_2H$
(8) $R^1 = R^5 = CO_2Me$, $R^2 = R^4 = OH$, $R^3 = H$
(11) $R^1 = R^5 = CO_2H$, $R^2 = R^3 = OH$, $R^4 = H$
(12) $R^1 = R^5 = CO_2Me$, $R^2 = OAc$, $R^3 = H$, $R^4 = Br$
(13) $R^1 = R^5 = CO_2Me$, $R^2 = OAc$, $R^3 = Br$, $R^4 = H$



(3)



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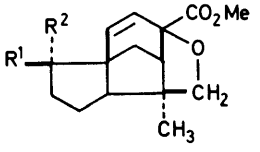
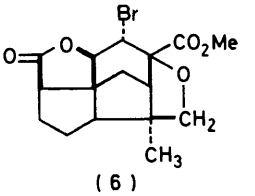


(5) $R^1 = CO_2Me$, $R^2 = H$
(9) $R^1 = H$, $R^2 = CO_2Me$



(6)

expected, though their isolation has not yet been reported. In general the α-isomers are more difficult to crystallise than the β-isomers in this series.

The isolation of the lactone (4) and its 8-epimer from the lac hydrolysate [5] indicated that these structures may arise by a base-catalysed Michael-type addition of the CH_2OH group to the 8,9-double bond. The action of sodium methoxide on dimethyl shellolate has already been studied.[2,3] In a repetition of this reaction, although a major part of the reaction mixture remained as a complex yellow gum, t.l.c. clearly indicated the presence of two minor components, identified as methyl laccolate γ-lactone and its 8-epimer through isolation by preparative t.l.c. followed by direct comparison with samples obtained from shellac (m.p., mixed m.p., and i.r. and n.m.r. spectra). The complexity of shellac samples may thus be a consequence in part of the various factors discussed above.

N.m.r. data (δ values; $CDCl_3$; J in Hz)

Compound	C*H*·C:C (1 H, d)	C:C*H* (1 H, d)
Dimethyl 13-acetoxy-10α-bromocedr-8-ene-12,15-dioate (7) [a]	5.32 (J 4.5)	6.87 (J 4.5)
Dimethyl 10,13-di-*O*-acetylshellolate [a]	5.58 (J 2.5)	6.48 (J 2.5)
Dimethyl 13-*O*-acetyl-10-*epi*-shellolate [a]	4.21 (J 4.5)	6.70 (J 4.5)
Dimethyl 13-*O*-acetylshellolate [a]	4.56 (J 2.5)	6.50 (J 2.5)
Dimethyl 13-acetoxy-10α-bromo-2β*H*-cedr-8-ene-12,15-dioate (13) [b]	4.62 (J 4.5)	6.80 (J 4.5)
Dimethyl 13-acetoxy-10β-bromo-2β*H*-cedr-8-ene-12,15-dioate (12) [b]	5.53 (J 2.5)	6.78 (J 2.5)
Dimethyl 10,13-di-*O*-acetyl-2-*epi*-shellolate [b]	5.89 (J 2.5)	6.63 (J 2.5)
Dimethyl 13-*O*-acetyl-2-*epi*,10-*epi*-shellolate [b]	3.8 (J 4.5)	6.68 (J 4.5)
Dimethyl 13-*O*-acetyl-2-*epi*-shellolate [b]	4.8 (J 2.5)	6.6 (J 2.5)
Dimethyl 10,13-di-*O*-acetyl-10-*epi*-shellolate	5.32 (J 4.5)	6.75 (J 4.5)
Dimethyl 10,13-di-*O*-acetyl-2-*epi*,10-*epi*-shellolate	5.14 (J 4.5)	6.66 (J 4.5)

[a] From the reaction of hydrogen bromide–glacial acetic acid with dimethyl shellolate at 0 °C for 5 h. [b] From the reaction of hydrogen bromide–glacial acetic acid with dimethyl 2-*epi*-shellolate at 0 °C for 5 h.

EXPERIMENTAL

T.l.c. of the methyl esters was carried out in chloroform–methanol (96 : 4) 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. Esterifications were carried out in methanolic solution with ethereal diazomethane. Crystallisations were carried out from ethyl acetate–petroleum unless otherwise mentioned.

Acid-catalysed Reactions of Dimethyl Shellolate and 2-epi-*Shellolate.*—(*a*) Dimethyl shellolate (200 mg) was treated with aqueous sulphuric acid (2N; 5 ml) at 70 °C for 3 h. The cooled mixture was neutralised and extracted with ethyl acetate (3 × 30 ml). Removal of solvent left a gum, which was esterified and chromatographed [silica gel (5 g)]. Elution with pure benzene gave a gum which on crystallisation afforded dimethyl 8,13-epoxycedr-9-ene-12,15-dioate (5) (45 mg), m.p. 63—64° (lit.,[3] 65.5—66.5°). Elution with 4% ethyl acetate–benzene gave unchanged dimethyl shellolate (40 mg).

Shellolic acid (1) (100 mg) on treatment with absolute methanol (20 ml) and concentrated sulphuric acid (0.2 ml) at reflux temperature for 24 h followed by esterification and chromatography gave the cyclic ether (5) (10 mg) and dimethyl shellolate (40 mg).

Dimethyl shellolate (300 mg) on treatment with boron trifluoride–ether (5 ml) in dry ether (30 ml) at reflux temperature for 30 min followed by chromatography gave the cyclic ether (5) (25 mg) and dimethyl shellolate (200 mg).

(*b*) Dimethyl 2-*epi*-shellolate (8) (200 mg) was treated

[5] G. B. V. Subramanian, N. Sriram, V. S. Chauhan, J. Iqbal, and K. N. Ganesh, *J.C.S. Perkin I*, 1976, 967.

with aqueous sulphuric acid (2N; 5 ml; 70 °C) for 3 h. The product was esterified and chromatographed on silica gel (7 g). Elution with pure benzene gave a solid, which on crystallisation from benzene–petroleum afforded plates of *dimethyl* 8,13-*epoxy*-2β*H*-*cedr*-9-*ene*-12,15-*dioate* (9) (25 mg), m.p. 115° (Found: C, 66.5; H, 7.1. $C_{17}H_{22}O_5$ requires C, 66.7; H, 7.2%), $\nu_{max.}$ (KBr) 1 748 and 1 730 cm^{-1}, δ 1.14 (s, CMe), 3.75 (s, CO_2Me), 3.82 (s, CO_2Me), and 5.6 (d, *J* 9.5 Hz) and 6.7 (d, *J* 9.5 Hz) (CH=CH; further split through long-range coupling).

Action of Hydrogen Bromide–Glacial Acetic Acid on Dimethyl Shellolate.—(a) *At* 0 °C. Dimethyl shellolate (1 g) was treated with hydrogen bromide–glacial acetic acid (48%; 18 ml) at 0 °C for 5 h. The excess of reagent was removed by a stream of nitrogen and the residue esterified. The product was chromatographed on silica gel (25 g). Pure benzene (10 × 100 ml) eluted *dimethyl* 13-*acetoxy*-10α-*bromocedr*-8-*ene*-12,15-*dioate* (7) (500 mg), m.p. 136—137°, $\lambda_{max.}$ (MeOH) 235 nm (ε 5 900) (Found: C, 53.3; H, 5.4. $C_{19}H_{25}BrO_6$ requires C, 53.1; H, 5.8%), $\nu_{max.}$ (KBr) 1 739, 1 709, and 1 653 cm^{-1}. Elution with 1% ethyl acetate–benzene (5 × 100 ml) gave dimethyl 10,13-di-*o*-acetylshellolate (50 mg), m.p. 125—126° (lit.,[3] 126—127.5°); 3% ethyl acetate–benzene (5 × 100 ml) eluted dimethyl 13-*O*-acetylshellolate (100 mg), m.p. 80—81° (lit.,[6] 80—81°); 3% ethyl acetate–benzene eluted dimethyl 13-*O*-acetyl-10-*epi*-shellolate, a gum (t.l.c.-pure), $[\alpha]_D$ (MeOH) −156°, $\nu_{max.}$ (KBr) 3 558, 1 709, and 1 634 cm^{-1}.

(b) *At* 30 °C. Dimethyl shellolate (200 mg) on similar treatment with hydrogen bromide–glacial acetic acid (48%; 3.5 ml) at 30 °C for 10 h followed by work-up and crystallisation gave the 10α-bromo-13-acetate (7) (160 mg), m.p. 136—137°.

Action of Hydrogen Bromide–Glacial Acetic Acid on the Cyclic Ether (5).—The ether (5) (100 mg) on treatment with hydrogen bromide–glacial acetic acid (48%; 2 ml; 30 °C; 15 h) followed by work-up and crystallisation gave the 10α-bromo-13-acetate (7) (80 mg), m.p. 136—137°.

Dimethyl 10,13-*Di*-O-*acetyl*-10-epi-*sheollolate.*—The 10α-bromo-13-acetate (7) (500 mg) was dissolved in glacial acetic acid (50 ml), potassium acetate (500 mg) was added, and the mixture was refluxed for 6 h. The clear solution was concentrated under reduced pressure and extracted with ethyl acetate (3 × 50 ml). Concentration of the extract yielded a gum (400 mg), which on crystallisation from hot petroleum gave dimethyl 10,13-*di*-O-*acetyl*-10-epi-*shellolate*, m.p. 108—109°, $[\alpha]_D$ (MeOH) −120° (Found: C, 62.0; H, 7.0. $C_{21}H_{28}O_8$ requires C, 61.8; H, 6.9%), $\nu_{max.}$ (KBr) 1 738, 1 720, and 1 639 cm^{-1}. This diacetate was different from dimethyl 10,13-di-*O*-acetylshellolate (10β,13-diacetate) obtained by acetylation of dimethyl shellolate (500 mg) with acetic anhydride–pyridine (1 : 1; 8 ml) at 30 °C for 20 h [m.p. 126—127° (lit.,[3] 126—127.5°)].

Acetylation of dimethyl shellolate (200 mg) with acetic anhydride (4 ml) and perchloric acid (78%; 0.05 ml) gave a gum which on chromatography (elution with benzene) afforded the 10β,13-diacetate (100 mg) followed by the 10α,13-diacetate (40 mg).

10-epi-*Shellolic acid* (10).—The 10α,13-diacetate (300 mg) was dissolved in ethanol (2 ml) and hydrolysed with aqueous sodium hydroxide (8%; 3 ml) at 30 °C for 15 h. The clear solution on acidification with ice-cold hydrochloric acid gave 10-epi-*shellolic acid* (10) (100 mg), which was recrystallised from chloroform–petroleum; m.p. 226—228°, $[\alpha]_D$ (MeOH) +88° (Found: C, 60.4; H, 6.9. $C_{15}H_{20}O_6$ requires C, 60.8; H, 6.8%), $\nu_{max.}$ (KBr) 3 447, 1 681, and 1 638 cm^{-1}. Esterification gave dimethyl 10-*epi*-shellolate as a gum (t.l.c.-pure) $[\alpha]_D$ (MeOH) −192°, $\nu_{max.}$ (KBr) 1 709, 1 693, and 1 640 cm^{-1}, δ 1.15 (s, CMe), 3.1br (CH_2OH), 3.66 (s, CO_2Me), 3.76 (s, CO_2Me), 4.19 (d, *J* 4.5 Hz, CHOH), and 6.76 (d, *J* 4.5 Hz, C=CH).

Acetylation with acetic anhydride–perchloric acid followed by esterification gave a mixture of 10α,13- and 10β,13-diacetates (4 : 3 by n.m.r.).

Solvolysis of the 10α-*Bromo*-13-*acetate* (7).—The 10α-bromo-13-acetate (7) (100 mg) was refluxed with dioxan–water (1 : 1; 5 ml) for 6 h. The mixture was concentrated under reduced pressure and extracted with ether (3 × 20 ml). Removal of solvent left a gum (t.l.c.-pure) (70 mg) identified as dimethyl 13-*O*-acetyl-10-*epi*-shellolate (n.m.r.). Hydrolysis of this gum with aqueous sodium hydroxide (10%; 2 ml) at 30 °C for 15 h gave 10-*epi*-shellolic acid.

The 10α-bromo-13-acetate (7) (100 mg) in dioxan (2 ml) was refluxed with aqueous sulphuric acid (2N; 5 ml) for 1 h. Esterification of the product gave the cyclic ether (5) (50 mg). Hydrolysis of the above bromo-acetate (150 mg) with aqueous sodium hydroxide (10%; 6 ml) at reflux temperature for 3 h, esterification, and chromatography gave the cyclic ether (5) (60 mg) followed by dimethyl 10-*epi*-shellolate (n.m.r. and i.r. spectra).

Oxidation of Dimethyl 10-epi-*Shellolate with Active Manganese Dioxide.*—Dimethyl 10-*epi*-shellolate (100 mg) was dissolved in dry chloroform (10 ml) and refluxed with freshly prepared active manganese dioxide (1 g) for 30 h. The mixture was filtered and the filtrate concentrated and chromatographed. Elution with 2% ethyl acetate–benzene gave dimethyl 8,13-epoxy-10-oxocedrane-12,15-dioate (3) (40 mg), m.p. 123—124° (lit.,[3] 124.5—125.5°).

Action of Hydrogen Bromide–Glacial Acetic Acid on Dimethyl 2-epi-*Shellolate.*—(a) *At* 0 °C. Dimethyl 2-*epi*-shellolate (500 mg) was treated with hydrogen bromide–glacial acetic acid (48%; 9 ml) at 0 °C for 5 h. The product was esterified and chromatographed [silica gel (12 g)]. Elution with 75% benzene–petroleum (5 × 100 ml) gave dimethyl 13-acetoxy-10β-bromocedr-8-ene-12,15-dioate (12) (100 mg), a gum (t.l.c.-pure), $[\alpha]_D$ (MeOH) −36°, $\nu_{max.}$ (KBr) 1 733, 1 709, and 1 622 cm^{-1}. Elution with 90% benzene–petroleum (5 × 100 ml) afforded dimethyl 13-acetoxy-10α-bromocedr-8-ene-12,15-dioate (13) (100 mg), a gum (t.l.c.-pure), $[\alpha]_D$ (MeOH) −130°, $\lambda_{max.}$ (MeOH) 233 nm (ε 13 835), $\nu_{max.}$ (KBr) 1 730, 1 709, and 1 627 cm^{-1}. Elution with 1% ethyl acetate–benzene (3 × 100 ml) yielded dimethyl 10,13-di-*O*-acetyl-2-*epi*-shellolate (30 mg), m.p. 112—113° (lit.,[3] 113—114°).

Elution with 3% ethyl acetate–benzene (4 × 100 ml) gave *dimethyl* 13-O-*acetyl*-2-epi,10-epi-*shellolate* (50 mg), m.p. 96—97°, $[\alpha]_D$ (MeOH) −80° (Found: C, 62.1; H, 7.1. $C_{19}H_{26}O_7$ requires C, 62.3; H, 7.2%), $\nu_{max.}$ (KBr) 3 571, 1 709, and 1 634 cm^{-1}. Elution with 5% ethyl acetate–benzene (4 × 100 ml) afforded *dimethyl* 13-O-*acetyl*-2-epi-*shellolate* (50 mg), m.p. 106° (Found: C, 62.1; H, 6.9. $C_{19}H_{26}O_7$ requires C, 62.3; H, 7.2%), $\nu_{max.}$ (KBr) 3 500, 1 720, 1 700, and 1 630 cm^{-1}.

Action of Hydrogen Bromide–Glacial Acetic Acid on the 2-epi-*Cyclic Ether* (9).—The ether (9) (100 mg) on treatment with hydrogen bromide–glacial acetic acid (48%; 2 ml) at 30 °C for 15 h gave a product which was chromatographed on silica gel (3 g). Elution with 75% benzene–petroleum (4 ×

[6] S. V. Eswaran, N. Sriram, T. R. Seshadri, and G. B. V. Subramanian, *Indian J. Chem.*, 1973, **11**, 991.

100 ml) afforded the 2-*epi*-10β-bromo-13-acetate (12) (20 mg), as a gum (t.l.c.-pure); 90% benzene–petroleum (5 × 100 ml) eluted the 2-*epi*-10α-bromo-13-acetate (13) (30 mg), as a gum, identified by n.m.r.

Dimethyl 10,13-*Di*-O-*acetyl*-2-epi,10-epi-*shellolate*.—The bromo-acetate mixture [(12) and (13)] (300 mg) was refluxed with glacial acetic acid (30 ml) and potassium acetate (300 mg) for 3 h. Work-up gave dimethyl 10,13-di-*O*-acetyl-2-*epi*,10-*epi*-shellolate (the 2-*epi*-10α,13-diacetate) as a gum (t.l.c.-pure), $[\alpha]_D$ (MeOH) −210°, $\nu_{max.}$ (KBr) 1 715 and 1 639 cm^{-1}. This was different from dimethyl 10,13-di-*O*-acetyl-2-*epi*-shellolate obtained by acetylation of dimethyl 2-*epi*-shellolate (250 mg) with acetic anhydride–pyridine (1 : 1; 5 ml). Acetylation with acetic anhydride–perchloric acid followed by esterification gave a 1 : 1 mixture of 2-*epi*-10α,13- and 2-*epi*-10β,13-diacetates (n.m.r.). The pure 2-*epi*-10α- and 10β-bromo-13-acetates treated independently with glacial acetic acid and potassium acetate gave the 2-*epi*-10α,13-diacetate as the only product.

2-epi,10-epi-*Shellolic Acid* (11).—Dimethyl 10,13-di-*O*-acetyl-2-*epi*-shellolate (200 mg) on hydrolysis with aqueous sodium hydroxide (8%; 2 ml) at 30 °C for 15 h gave 2-epi,10-epi-*shellolic acid* (11) (100 mg), m.p. 205—206°, $[\alpha]_D$ (MeOH) −45° (Found: C, 60.5; H, 6.9. $C_{15}H_{20}O_6$ requires C, 60.8; H, 6.8%), $\nu_{max.}$ (KBr) 3 389, 1 681, and 1 639 cm^{-1}. Esterification gave *dimethyl* 2-epi,10-epi-*shellolate*, m.p. 150—151°, $[\alpha]_D$ (MeOH) −121° (Found: C, 62.7; H, 7.5. $C_{17}H_{24}O_6$ requires C, 63.0; H, 7.5%), $\nu_{max.}$ (KBr) 3 383, 1 720, 1 684, and 1 626 cm^{-1}, δ 1.2 (s, CMe), 3.2 (s, CH_2·OH), 3.7 (s, CO_2Me), 3.8 (s, CO_2Me), 3.9 (d, *J* 4.5 Hz, C*H*OH), and 6.8 (d, *J* 4.5 Hz, C=CH).

Acetylation with acetic anhydride–perchloric acid followed by esterification gave mainly the 2-*epi*-10α,13-diacetate.

Action of Hydrogen Bromide–Glacial Acetic Acid on the 10,13-*Diacetates*.—Dimethyl 10,13-di-*O*-acetylshellolate (100 mg) and its 10-epimer (100 mg) each separately on treatment with hydrogen bromide–glacial acetic acid (48%; 2 ml) at 0 °C for 3 h and 30 °C for 15 h, respectively, gave the 10α-bromo-13-acetate (7) (50 mg).

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