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TRANSFORMATIONS OF MONOTERPENOIDS IN AQUEOUS ACIDS

THE REACTIONS OF LINALOOL, GERANIOL, NEROL AND THEIR ACETATES IN AQUEOUS CITRIC ACID

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Abstract—The fate of linalool, geraniol and nerol and their acetates in aqueous citric and hydrochloric acids has been investigated. Linalool and linalyl acetate yield predominantly α-terpineol and 3,7-dimethyloct-1-en-3,7-diol (6). Geraniol and nerol afford α-terpineol, linalool and the isomeric 3,7-dimethyloct-2-en-1,7-diols (7 and 8). While both neryl and geranyl acetate give α-terpineol and linalool, the former affords Z-1-acetoxy-3,7-dimethyloct-2-en-7-ol (8a), and the latter the E-isomer 7a and 2β-acetoxymethyl-1α,3,3-trimethylcyclohexanol (13).

While it is commonly recognised that the acyclic monoterpene alcohols linalool (1), geraniol (2) and nerol (3) together with their esters undergo a variety of transformations in acidic media the majority of studies have however focused on the products derived from reactions in strong mineral acids[1-3] and at elevated temperatures.[3-11] In view of the importance of these compounds as flavourings[12] their transformations in dilute acidic solutions are of intrinsic interest. As recently reported investigations of the reactions of citral in aqueous citric[13] and hydrochloric acids[14] at room temperature have shown the major products to be different from those reported by earlier workers we were prompted to examine the reactions of the monoterpene alcohols and their acetates under similar mild conditions.

RESULTS AND DISCUSSION

Solutions of the alcohols (1–3) and their acetates (1a–3a) in aqueous citric acid (0.025M), stored for varying periods of time, were extracted with dichloromethane and the extracts subsequently analysed by gas liquid chromatography. The identity of the products formed was established, in the case of known compounds, by comparison of their spectra and retention data with those of authentic samples.

Examination of the product mixtures arising from the reactions of linalool and linalyl acetate (Table 1) showed the presence of a polar major product. Isolation by successive column and tlc on silica afforded compound 6($C_{10}H_{20}O_2$). A strong band at 3400 cm^{-1} in its IR spectrum coupled with lack of significant absorption in the CO region indicates at least one OH function, while a major peak at *m/e* 59 in the mass spectrum suggested the presence of a hydroxyisopropyl group in the molecule. Singlet resonances at δ 1.21 (6H) and 1.29 (3H) in the NMR spectrum together with an ABX pattern typical of an ethylidene group δ 5.04 (dd, *J* 10.5, 2 Hz), 5.19 (dd, *J* 18, 2 Hz), 5.93 (dd, *J* 18, 10.5 Hz) confirmed assignment

Table 1. Products of the reactions of linalool and linalyl acetate, in aqueous citric acid (0.025M) at 24°

Products[a,b]	linalool		linalyl acetate	
	time in days			
	10	20	10	20
linalool (1)	63.4	44.0	49.5	29.3
linalyl acetate (1a)	-	-	0.5	-
α-terpineol (4)	17.3	31.0	26.4	35.0
geraniol (2)	2.2	0.6	9.1	5.6
3,7-dimethyloct-1-en-3,7-diol (6)	10.2	17.3	4.0	14.9
trans-1,8-terpin (5)	-	2.8	0.3	3.5

[a]In order of increasing retention time on Carbowax 20M.
[b]Concentrations are expressed as % of initial substrate concentration.

as 3,7 - dimethyloct - 1 - en - 3,7 - diol (6). A diol of this structure has been suggested as a component of the glycol mixture formed in the reaction of linalool in refluxing tartaric acid.[8] The isolation of 6 in significant amounts indicates that under mild acidic conditions simple hydration of the 6,7-double bond is competitive with allylic rearrangement.

A minor polar product formed from geraniol (Table 2) was tentatively assigned the structure 7 on the basis of its mass spectrum [*m/e* 157 ($M-CH_3$), 154 ($M-H_2O$) and 59 (100%, hydroxyisopropylium ion)] and the stereochemistry of the starting material. Similarly a minor product detected by glc-ms of the mixture of products derived from nerol was assigned the structure 8.

Synthesis of the two isomers confirmed these assignments. Treatment of geraniol with 3-chloroperbenzoic acid afforded a mixture from which the 6,7-epoxy derivative was separated by tlc on silica. Reduction of the 6,7-epoxide 9 with LAH yielded the oily diol 7 in fair yield.[15] The Z-isomer 8 was prepared from nerol in an analogous manner. The compounds 7 and 8 were shown by glc, IR and mass spectral comparison to be identical with the products from the citric acid reaction. The corresponding acetates 7a and 8a, isolated by successive column and tlc of the acid mixtures formed from geranyl and neryl acetates respectively, were identified on the basis of mass (both show major peaks at *m/e* 59), NMR and IR spectra and their identity confirmed by comparison with the monoacetyl derivatives of 7 and 8.

An additional polar product of the geranyl acetate reaction mixture was isolated as a colourless oil, $C_{12}H_{22}O_3$, by column and tlc. Absorption bands at 3460 and 1736 cm^{-1} in the IR spectrum suggested both OH and OAc groups were present in the molecule. The NMR spectrum showed two singlet resonances (each 3H) at δ 0.88 and 1.03 indicative of two alkyl Me groups, singlets (each 3H) at δ 1.21 and 2.08 corresponding to a $\underline{CH_3}C(OH)$– and an acetate Me group respectively and a doublet (2H, *J* 3 Hz) at δ 4.32 assignable to the methylene of an acetoxymethyl function. These data are indicative of the formulae 12 or 13 for this compound. In order to confirm the structure of this product and to assign stereochemistry, both the 1α, 2α- and 1α,2β-isomers of 2 - acetoxymethyl - 1,3,3 - trimethylcyclohexanol (12 and 13 respectively) were prepared by the following route.

Epoxidation of α-cyclogeranyl acetate (15) afforded a mixture of the isomeric epoxides 10 and 11 (6/1) which were separated by tlc. It was predicted that the major product should be the 1α,2α-isomer 10 and this was confirmed on examination of the NMR spectra of the two epoxides formed. The spectrum of the major product shows singlet signals for the *gem*-dimethyl groups at δ 0.87 and 0.92 and a multiplet at δ 4.16 corresponding to the methylene protons of the acetoxymethyl group. In contrast in the spectrum of the minor product the C_3Me resonances appear at δ 0.75 and 0.99 and the methylene protons give rise to a doublet of doublets (*J* 6, 6 Hz) at δ 4.01 and a doublet (*J* 6 Hz) at δ 4.30. The non-equivalence of both the C_3Me groups and the methylene protons of the actoxymethyl group in the spectrum of the minor product can be attributed to the interactions between the epoxide oxygen and the substituents at positions 1 and 5 in the structure 11.

Reduction of the epoxides 10 and 11 with LAH followed by acetylation of the resultant diols afforded 12

Table 2. Products of the reactions of geraniol, geranyl acetate, nerol and neryl acetate in aqueous citric acid (0.025M) at 24°

Products[a,b]	geraniol		geranyl acetate		nerol		neryl acetate	
	time in days							
	10	20	10	20	10	20	10	20
linalool (1)	42.4	35.0	17.6	39.0	19.0	14.5	12.6	11.7
α-terpineol (4)	13.8	29.9	4.2	11.1	43.7	55.8	5.2	7.5
neryl acetate (3a)	-	-	-	-	-	-	52.1	29.9
geranyl acetate (2a)	-	-	36.0	13.9	-	-	-	-
nerol (3)	-	-	-	-	30.2	10.5	12.6	11.7
geraniol (2)	11.8	1.6	11.0	1.8	-	-	-	trace
3,7-dimethyloct-1-en-3,7-diol (6)	10.0	17.9	6.6	7.5	1.1	5.3	1.1	3.8
trans-1,8-terpin (5)	-	1.5	-	trace	-	3.8	-	1.4
Z-1-acetoxy-3,7-dimethyloct-2-en-1-ol (8a)	-	-	-	-	-	-	8.1	12.0
2β-acetoxymethyl-1α,3,3-trimethylcyclohexanol (13)	-	-	3.9	5.5	-	-	-	-
E-1-acetoxy-3,7-dimethyloct-2-en-1-ol (7a)	-	-	8.9	10.3	-	-	-	-
Z-3,7-dimethyloct-2-en-1,7-diol (8)	-	-	-	-	5.0	4.3	-	trace
E-3,7-dimethyloct-2-en-1,7-diol (7)	7.1	6.0	-	trace	-	-	-	-

[a]In order of increasing retention time on Carbowax 20M.
[b]Concentrations are expressed as % of initial substrate concentration.

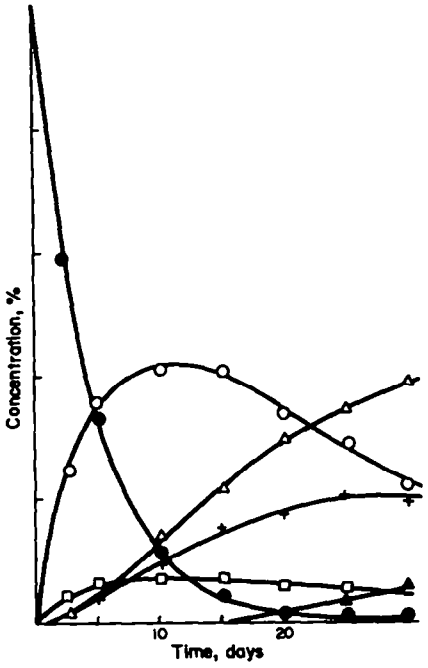


Fig. 1. Reaction of geraniol in aqueous citric acid; ●, geraniol; ○, linalool (1); △, α-terpineol (4); +,3,7 dimethyloct - 1 - en - 3,7 - diol (6); □, *E* 3,7 dimethyloct - 2 - en - 1,7 - diol (7); ▲, *trans* 1,8 terpin (5).

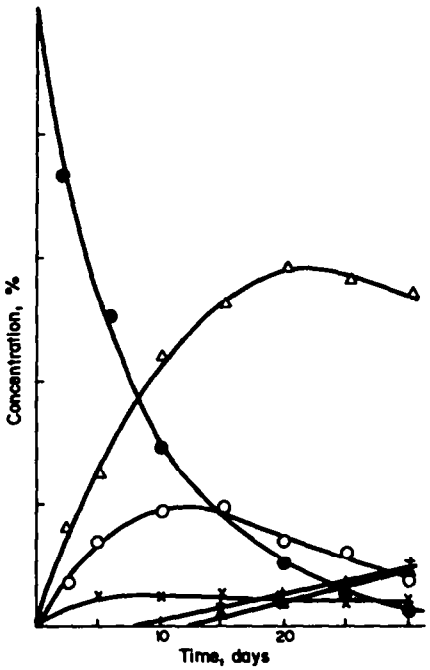
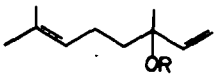
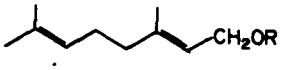


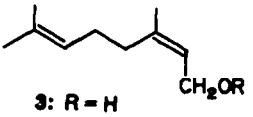
Fig. 2. Reaction of nerol in aqueous citric acid; ●, nerol; ○, linalool (1); △, α-terpineol (4); +, 3,7 - dimethyloct - 1 - en - 3,7 - diol (6); ×, *Z* 3,7 - dimethyloct - 2 - en - 1,7 - diol (7); ▲, *trans* 1,8 terpin (5).



1: R = H
1a: R = Ac



2: R = H
2a: R = Ac



3: R = H
3a: R = Ac

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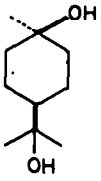

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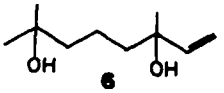

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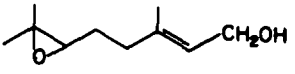

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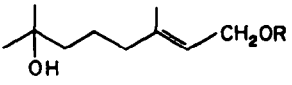
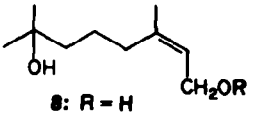
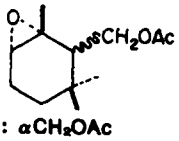


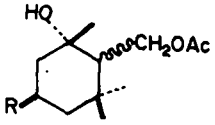
7: R = H
7a: R = Ac



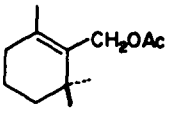
8: R = H
8a: R = Ac



10: αCH₂OAc
11: βCH₂OAc



12: αCH₂OAc, R = H
13: βCH₂OAc, R = H
14: αCH₂OAc, R = Br



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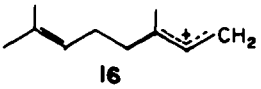

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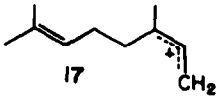

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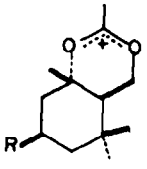
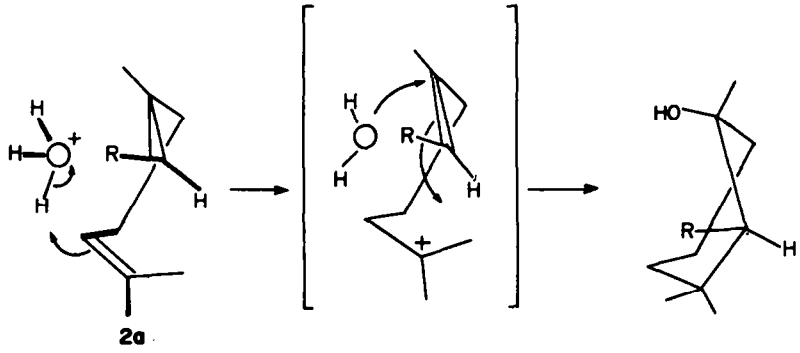


18: R = Br
19: R = H



2a

and 13 respectively. The latter compound was shown to be identical with the product isolated from the geranyl acetate reaction mixture. Neither 12 nor 13 were detected in the reaction mixtures derived from neryl acetate.

The courses of the reactions of nerol and geraniol in aqueous citric acid at pH 2.4 are shown in Figs. 1 and 2. Similar data were obtained for the reactions in hydrochloric acid at this pH and are comparable with the relative rates of cyclisation and allylic substitution obtained by Valenzuela and Cori.[16] These results indicate that whereas in the case of nerol both cyclisation and 1,3 allylic rearrangement are involved, geraniol undergoes the latter transformation almost exclusively and that α-terpineol formed in this reaction is derived from the primary product, linalool.[17] This is contraindicatory to the hypothesis[18,11] that equilibrium between the carbonium ions 16 and 17 accounts for the formation of cyclised products from geraniol. Although an equilibrium between such species may be involved under conditions of higher acidity and temperature, in dilute acids it is probable that no such equilibrium is involved.

The formation of the 1α,2β-hydroxyacetate 13 from geranyl acetate is of considerable interest. While this compound might be expected to arise, together with its 1α,2α-diastereomer, by hydration of α- and β-cyclogeranyl acetate neither of the latter compounds was detected in the citric acid reaction mixture; moreover α-cyclogeranyl acetate was recovered unchanged when treated with aqueous acids under a variety of conditions. Wolinsky and Faulkner[19] have invoked the intermediate bicyclic ion 18 in the bromination of geranyl acetate under anhydrous conditions. Hydrolysis of this intermediate would be expected to yield the alcohol 14. While a similar mechanism might be proposed in this case via nucleophilic inversion of the C_1 centre of 19, it is unlikely that the alcohol 13 would be the exclusive product. Additionally neryl acetate might be expected to yield the isomer 12 under the same conditions. An alternative explanation (Scheme) would involve protonation of the 6,7-double bond to afford an intermediate C_7 carbonium ion. Ring closure with concerted *syn*-addition of a molecule of water associated with the C_7 carbonium ion to the C_3 position would afford the alcohol 13. Steric interaction between the acetoxymethyl and terminal methyl groups would forbid adoption of such a conformation by neryl acetate.

EXPERIMENTAL

General. Glc was carried out on a Perkin-Elmer F30 Chromatograph fitted with a flame ionisation detector and coupled to a CSI Supergrator 2 digital integrator. Glc-MS studies were performed on a Perkin-Elmer 990 Chromatograph coupled via a Biemann Separator to a Hitachi-Perkin Elmer RMU-6L Mass Spectrometer and data analysed with the aid of a VG 2040 Datasystem. Both packed (4 m × 1.75 mm, 10% Carbowax 20M/Diatomite CLQ) and SCOT (30 m × 0.5 mm, Carbowax 20M) glass columns were used for glc analyses. IR spectra were recorded on a Perkin–Elmer 157G Spectrophotometer and NMR spectra on a Varian HR220 Spectrometer in $CDCl_3$ using TMS as internal standard. M.ps were determined on a Gallenkamp micro-m.p. apparatus. Elemental analyses were performed by Dr. F. B. Strauss, Microanalytical Laboratory, Oxford.

Materials. Linalool, linalyl acetate, geraniol and geranyl acetate were supplied by Bush, Boake, Allen & Co. Ltd., London; nerol and neryl acetate by Givaudan Ltd., Mitcham, Surrey. These were purified to ≥99% by preparative glc as required. Tlc plates were supplied by Anachem Ltd., Luton.

Analysis of reaction mixtures. Typically the terpene alcohol or ester (20–30 mg) in MeOH (2 ml) was added with vigorous stirring to aqueous citric acid (0.025 M, pH 2.4, 11) with diethyl pyrocarbonate (Bayer, 20 μl) as a sterilant, or to dil. HCl (0.2M KCl-HCl, pH 2.40, 1 l), and the solns stored at 24° in the dark. At predetermined intervals aliquots of soln (100 ml) were saturated with NaCl and extracted with freshly distilled CH_2Cl_2 (25 ml × 2). The combined organic extracts were washed with sat. NaClaq (10 ml) and dried by passage through a short column of Na_2SO_4 (1 g). 2-Phenylethanol (10 μl of a 0.82 M soln in CH_2Cl_2) was added as internal standard to the extract which was partially evaporated at 30° under vacuum on a rotary evaporator fitted with a dry ice/isopropanol cold trap. Samples were analysed directly by glc.

Products (Tables 1 and 2) were isolated by preparative glc of each of the mixtures and identified by spectroscopic (IR, MS) and chromatographic (glc, tlc) comparison with authentic samples. In the mixtures formed from geranyl and neryl acetates the compounds 5 and 7, and 2 and 8 respectively, present only in trace amounts, were identified on the basis of glc-MS comparison with authentic materials.

Relative rates of reaction (citric acid, HCl): linalool (1.0: 1.0); linalyl acetate (11.6: 11.2); geraniol (5.3: 5.3); geranyl acetate (2.4: 2.5); nerol (2.9: 3.0); neryl acetate (1.5: 1.6).

Isolation of acid-reaction products of linalool. Linalool (550 mg) in MeOH (5 ml) was added to aqueous citric acid (0.025 M, 2.5 l) and stored in the dark at 24° for 4 weeks. The soln was extracted with CH_2Cl_2 (500 ml × 2), the organic layer dried (Na_2SO_4) and evaporated. Tlc of the residue (310 mg) on 10 silica (G) plates (0.25 × 200 × 200 mm) eluted with 50% EtOH-light petroleum (40–60°) afforded 5 (5.2 mg), as needles from CH_2Cl_2, m 100–2° (lit.[20]m 104°) and an oily less polar fraction which was rechromatographed on 2 silica (G) plates (0.25 × 200 × 200 mm) eluted with 50% ether-toluene to give 3,7 - *dimethyloct* - 1 - *en* - 3,7 - *diol* (6, 70 mg) as colourless needles, m 44–45°: IR (KBr) max 3400 (br), 2950, 1370, 997, 914 cm^{-1}, NMR see text; MS *m/e* (rel int) 157 (M-15, 0.5), 154 (5), 139 (20), 121 (3), 93 (45), 81 (60), 71 (100), 59 (35). (Found: C, 69.76; H, 11.76. $C_{10}H_{20}O_2$ requires: C, 69.76; H, 11.62%).

Isolation of acid-reaction products of geranyl and neryl acetates. Geranyl acetate (1 g) in MeOH (20 ml) was added to aqueous citric acid (0.025M, 5 l) and stored in the dark at 24° for 4 weeks. The soln was extracted as described in the case of

linalool and the extract subjected to column chromatography on silica (100–200 mesh, 13g) eluting with increasing amounts of EtOAc in light petroleum (30–40°). Fractions eluted with 20–40% EtOac–light petroleum were combined and evaporated to give a residue (90 mg) which was subjected to tlc on 3 silica (GF) plates (0.5 × 200 × 200 mm) using 2% MeOH–CH_2Cl_2 as eluant to give two fractions. The more polar material, *E* - 1 - *acetoxy* - 3,7 - *dimethyloct* - 2 - *en* - 7 - *ol* (**7a**, 47 mg), isolated as an oil, had: IR (film) max 3440 (br), 2942, 1736, 1670, 1235, 1103, 1025, 948 cm^{-1}; NMR δ 1.21 (6H, s, $C(CH_3)_2$), 1.79 (3H, brs, $=C-CH_3$), 2.04 (3H, s, $-CO-CH_3$), 4.58 (2H, d, J = 7 Hz, $-CH_2OAc$), 5.34 (1H, brt, J 7 Hz, $-CH=$); ms *m/e* (rel int) 154 (M-60, 1), 139 (35), 136 (30), 121 (40), 93 (95), 81 (99), 59 (100). (Found: C, 67.73; H, 10.60. $C_{12}H_{22}O_3$ requires: C, 67.29; H, 10.28%).

The less polar fraction (16 mg) was resubmitted to tlc on 2 (0.25 × 200 × 200 mm) silica (CF) poates eluted with 2% MeOH–CH_2Cl_2 to give 2β - *acetoxymethyl* - 1α,3,3 - *trimethylcyclohexanol* (**13**, 4 mg); IR (film) max 3460 (br), 2935, 1736, 1245, 1170, 1105, 1081, 970, 915 cm^{-1}; NMR see text, ms *m/e* (rel int) 154 (13), 139 (15), 136 (65), 121 (90), 96 (65), 93 (80), 69 (100). (Found: C, 67.47; H, 10.64. $C_{12}H_{22}O_3$ requires: C, 67.29; H, 10.28%).

Treatment of neryl acetate (1 g) with aqueous citric acid (0.025 M, 5 l.) for 4 weeks, followed by extraction and chromatography as above, afforded *Z* - 1 - *acetoxy* - 3,7 - *dimethylcot* - 2 - *en* - 7 - *ol* (**8a**, 52 mg) as an oil: IR (film) max 3440 (br), 2940, 1730, 1667, 1235, 1087, 1022, 948 cm^{-1}; NMR δ1.21 (6H, s), 1.76 (3H, s) 2.05 (3H, s), 4.56 (2H, d, J 7 Hz), 5.37 (1H, brt, J 7 Hz); ms *m/e* (rel int) 139 (23), 136 (25), 121 (33), 93 (76), 81 (100), 59 (69). (Found: C, 67.26; H, 10.58. $C_{12}H_{22}O_3$ requires: C, 67.29; H, 10.28%).

E - 3,7 - *Dimethyloct* - 2 - *en* - 1,7 - *diol* (**7**). To a soln of geraniol (154 mg) in $CHCl_3$ (5 ml) at −10°, 3-chloroperbenzoic acid (173 mg) in $CHCl_3$ (5 ml) was added with stirring and the soln left the room temp. for 18 hr. The soln was washed with sat. $NaHCO_3$aq (5 ml × 2), water (5 ml × 2), dried (Na_2SO_4) and evaporated. The resultant residue (150 mg) was subjected to tlc on 3 silica (G) plates (0.5 × 200 × 200 mm) eluted with 2% isopropanol–CH_2Cl_2 affording the epoxide **9** (80 mg): IR (film) max 3420 (br), 2925, 1667, 1250, 1118, 1001, 870, 678 cm^{-1}; ms *m/e* (rel int) 152 (M-18, 3), 109 (30), 85 (66), 84 (38), 81 (98), 71 (80), 67 (56), 59 (76), 41 (100); NMR δ 1.28, 1.30 (6H, 2s, $C(CH_3)_2$), 1.72 (3H, s, $=C-CH_3$), 2.73 (1H, t, J 7 Hz, $-C(O)H$), 4.18 (2H, d, J 8 Hz, $-CH_2OH$), 5.48 (1H, brt, J 8 Hz, $=C-H$).

The epoxide **9** (20 mg) in dry ether (5 ml) at 0° was treated with LAH (6 mg) and the stirred soln allowed to warm to room temp. over 1 hr. After a further 1 hr Na_2SO_4aq (2 ml) was added, the aqueous layer acidified with dil HCl and extracted with Ch_2Cl_2 (5 ml × 2). The combined organic layers were dried (Na_2SO_4), evaporated, and the residue subjected to tlc on a silica (G) plate (0.25 × 200 × 200 mm) eluted with 4% isopropanol–CH_2Cl_2 to give **7** (7.8 mg) as an oil: IR (film) max 3320 (br), 2940, 1667, 1205, 1150, 1000, 910 cm^{-1}; NMR δ 1.16 (6H, s, $-C\cdot(CH_3)_2$), 1.65 (3H, s, $=C-CH_3$), 4.02 (2H, d, J 7.5 Hz, $-CH_2-OH$), 5.34 (1H, brt, J 7.5 Hz, $=CH-$); ms *m/e* (rel int) 154 (M-18, 0.5), 139 (30), 136 (25), 121 (50), 93 (90), 81 (95), 59 (100).

Using the above procedure nerol (120 mg) afforded the isomeric epoxide (34 mg) which was reduced with LAH in ether to give *Z* - 3,7 - *dimethyloct* - 2 - *en* - 1,7 - *diol* (**8**, 20 mg) as an oil: IR (film) max 3440 (br), 2940, 1665, 1215, 1183, 1150, 1000, 910 cm^{-1}; ms *m/e* (rel int) 139 (20), 136 (26), 121 (39), 93 (69), 81 (84), 69 (80), 59 (100).

1 - *Acetoxy* - 3,7 - *dimethyloct* - 2 - *en* - 7 - *ols* (**7a** *and* **8a**). To a soln of **7** (10 mg) in pyridine (0.5 ml), Ac_2O (0.1 ml) was added, the soln left for 18 hr at room temp., diluted with HCl (1M, 1 ml) and extracted with ether (2 ml × 2). The ethereal extract was washed with water (2 ml), dried (Na_2SO_4) and evaporated. The residue was chromatographed on a silica (GF) plate (0.25 × 200 × 200 mm) using 2% MeOH–CH_2Cl_2 as eluant to afford **7a** (8 mg) identical (IR, tlc, glc–ms) with material described previously. Acetylation of **8** (16 mg) as above afforded **8a** (15 mg) identical (IR, tlc, glc-ms) to material described previously.

6 - *Acetoxymethyl* - 1,2 - *epoxy* - 1,5,5 - *trimethylcyclohexanes* (**10** *and* **11**). α - Cyclogeranyl acetate[21] (300 mg) in $CHCl_3$ (10 ml) was treated with 3-chloroperbenzoic acid (330 mg), as described above, to give a viscous oil (305 mg) which was separated by tlc on 6 silica (GF) plates (0.5 × 200 × 200 mm) using $CHCl_3$ as eluant to give the 1α,2α-*epoxide* **10** (115 mg): IR (film) max 2938, 1739, 1231, 1158, 1036, 874, 774 cm^{-1}; NMR δ 0.86, 0.92, 1.40, 2.07 (12H, 4s), 2.98 (1H, brs, $-C(O)H$), 4.16 (2H, s, $-CH_2-OAc$); ms *m/e* (rel int)153 (M-59, 15), 152 (14), 137 (30), 124 (25), 109 (27), 43 (100): and the 1α,2β-*epoxide* **11** (30 mg): IR (film) max 1935, 1739, 1240, 1183, 1149, 1035, 890, 789 cm^{-1}; NMR δ 0.74, 0.99, 1.34, 2.08 (12H, 4s), 2.93 (1H, brs, $-C(O)H$), 4.01 (1H, dd, J 6, 6 Hz, $-CH_2-OAc$); ms *m/e* (rel int) 153 (M-59, 6), 152 (12), 124 (78), 109 (78), 43 (100).

2α - *Acetoxy* - 1α,3,3 - *trimethylcyclohexanol* (**12**). The epoxide **10** (30 mg) in dry ether (10 ml) was treated with LAH (10 mg) at 0°, the stirred soln allowed to warm to room temp. over 2 hr and then heated at reflux for a further 0.5 hr. Work up as described above gave a viscous oil (20 mg) which was acetylated in pyridine (0.5 ml)–Ac_2O (0.1 ml) for 18 hr at room temp. Dilution of the mixture with dil. HCl, extraction with ether (2 ml × 2) and evaporation of the ethereal layer gave an oil (18 mg) which was subjected to tlc on a silica (GF) plate (0.25 × 200 × 200 mm) eluted with 2% MeOH–$CHCl_3$ affording **12** (12.5 mg), as colourless prisms m 54–56°: IR (KBr) max 3510 (br), 2940, 1725, 1250, 1188, 1038, 975 cm^{-1}; NMR δ 0.99, 1.01, 1.24, 2.06, 2.06 (12H, 4s), 4.29 (1H, dd, J 3, 13 Hz, $-CH_2-OAc$), 4.42 (1H, dd, J 6, 13 Hz, $-CH_2-OAc$); ms *m/e* (rel int) 154 (M-60, 25), 139 (25), 136 (45), 121 (55), 96 (45), 69 (70), 43 (100). (Found: C, 67.34; H, 9.75. $C_{12}H_{12}O_3$ requires: C, 67.29; H, 10.28%).

Treatment of the isomeric epoxide **11** (20 mg) in alike manner afforded 2β - *acetoxymethyl* - 1α,3,3 - *trimethylthylcyclohexanol* (**13**, 4.5 mg), identical (IR, tlc, glc–ms) to the material described previously.

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