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TRANSFORMATIONS OF 8(17), 14-LABDADIEN-13-OL—PART 2[1]

P. K. GRANT and R. T. WEAVERS*
Department of Chemistry, University of Otago, Dunedin, New Zealand

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Abstract—Aqueous permanganate oxidation of 8(17)-labden-13-ol gave two novel oxidation products by functionalisation of an unactivated carbon atom. The structures have been confirmed by degradative studies and a mechanism to account for their formation is proposed.

Aqueous permanganate treatment of 8(17),14-labdadien-13-ol **1** gave the odiferous ketal, 8,13:13,17-diepoxy-14,15-dinorlabdane **2** as the sole product from the neutral fraction.[2] A similar oxidation of 8(17)-labden-13-ol **3** gave labdane-8,13,17-triol **4** as the major product (39%) identical with a sample prepared from the osmylation of 8(17)-labden-13-ol **3**, together with 13-hydroxy-17-norlabdan-8-one **5** (2%), identical with the product of lead tetraacetate cleavage of triol **4**, and characterised as its hemi-ketal dehydration product, 8,13-epoxy-17-norlabd-8-ene **6**. In addition two novel oxidation products were isolated and characterised as 8,12s-epoxylabdane-13,17-triol **7** (25%) and 8,12R-epoxylabdane-13,17-triol **8** (2%).

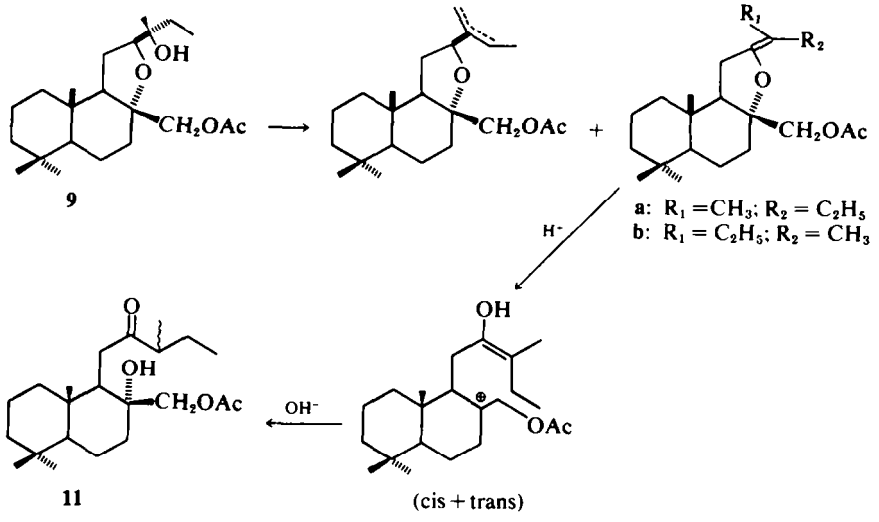
The major oxidation product **7** analysed for $C_{20}H_{36}O_3$ and showed $M—H_2O = 306$ as the highest mass peak with loss of CH_2OH, characteristic of a primary alcohol. IR showed hydroxyl absorption (3430, 3310 cm^{-1}) and extensive C—O absorption (1180–1000 cm^{-1}); PMR data for **7** and its derivatives are collected in the Table. The three ring-A methyls and the C-14 methyl triplet were consistent with the normal labdane derivatives prepared in these laboratories but the C-13 methyl signal appeared at unusually high field (δ 1·04). A two-proton singlet at δ 3·53 was consistent with a primary alcohol at C-17 and a one proton multiplet at δ 3·87 (W/2 16 Hz) indicated a secondary alcohol or ether function. Resistance to LAH reduction and the absence of reaction with lead tetra-acetate eliminated epoxide and vicinal diol functions respectively. Acetylation with pyridine/acetic anhydride gave the monoacetate **9**, $C_{22}H_{38}O_4$ [3645 cm^{-1} (OH); 1720, 1260 cm^{-1}; δ2·08 (acetate)] while treatment with isopropenyl acetate/toluene p-sulphonic acid gave the diacetate **10**, $C_{24}H_{40}O_5$ [1720, 1249 cm^{-1}, δ 1·96, 2·06 (acetate)]. These reactions established that **7** was a diol containing a primary and tertiary hydroxyl group at C-17 and C-13 respectively. Thus the remaining oxygen was in an oxide ring (not an epoxide) joining one tertiary and one secondary centre. Lack of evidence for a double bond to C-8 and the absence of a proton attached to C-8, together with mechanistic considerations, indicated that C-8 was the tertiary centre. The AB system of the monoacetate **9** was consistent with the acetylation of an axial hydroxymethyl group[3] and the absence of any ring A methyl signals in the δ 0·95–1·15 range confirmed the normal[4] labdane C-8 stereochemistry.

The secondary centre of the oxide ring was determined to be at C-12 as the low field multiplet was affected markedly by acetylation of the C-13 hydroxyl group in the diacetate **10** and C-14 was not functionalised as evidenced by the presence of the usual triplet for the C-14 methyl signal. Oxide ring opening attempts with acetyl tosylate[5] on the diacetate **10** and with boron trifluoride/acetic anhydride[6] on the diol **7** produced complex mixtures. Cleavage was finally achieved by dehydration of the hydroxy acetate **9** with toluene p-sulphonic acid/triethylorthoformate (a reagent which was found to dehydrate 13-hydroxy labdanes very efficiently) followed by hydrolysis of the enol ethers (a and b) formed (Scheme 1).

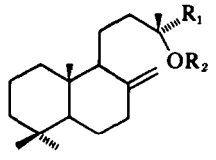
The product, 17-acetoxy-8-hydroxy-13αβH-labdan-12-one **11**, $C_{22}H_{38}O_4$ showed hydroxyl (3460 cm^{-1}), acetate (1730, 1230 cm^{-1}, δ 2·08) and ketone (1700 cm^{-1}) absorptions. PMR showed ring A methyls at δ 0·79, 0·82, 0·87 and the C-14 methyl triplet at δ 0·88. The C-13 methyl signal now appeared as a doublet (δ 0·98, J 7 Hz) consistent with a methyl adjacent to a ketone. Because of the mode of formation both C-13 epimers would be produced. This sequence confirms that the secondary ether linkage is attached to C-12.

Jones oxidation of the diol **7** at 0° slowly formed a lactone, 8,12s-epoxylabdano-13,17-lactone **12**, $C_{20}H_{32}O_3$ [1747 cm^{-1}(C=O)]. The absence of carboxylic acid and aldehyde peaks in the IR and PMR and the absence of the C-17 proton signal in the PMR further supported a lactone structure.

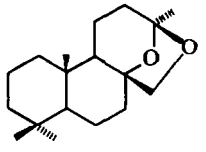
Thus the major oxidation product is formulated



SCHEME 1



1: $R_1 = CH{=}CH_2$; $R_2 = H$
3: $R_1 = C_2H_5$; $R_2 = H$
13: $R_1 = C_2H_5$; $R_2 = Ac$



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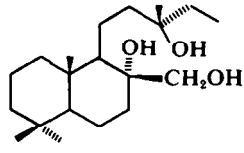

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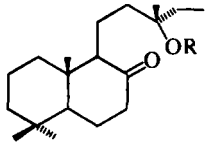
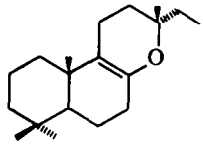


5: R = H
15: R = Ac



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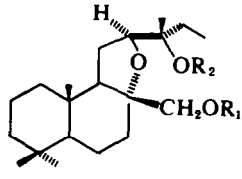
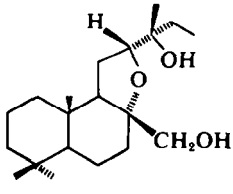


7: $R_1 = R_2 = H$
9: $R_1 = Ac$; $R_2 = H$
10: $R_1 = R_2 = Ac$



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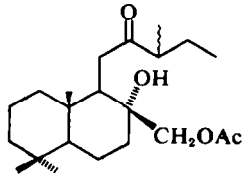

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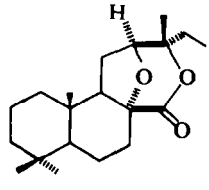

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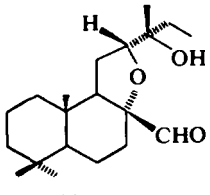

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as 8,12s-epoxylabdane-13,17-diol **7**. Models show that the two hydroxyl groups are in close proximity and strong intramolecular hydrogen bonding was confirmed by a dilute CCl_4 solution study[7] (3535, 3455 cm^{-1} bonded OH). This accounts for the unusually high-field position of the C-13 methyl resonance in both the diol **7** and the hydroxy acetate **9**, whereas in the diacetate **10** this signal had moved markedly downfield and was close to its position in 13-acetoxy-8(17)-labdene **13** (δ 1·41). Strong hydrogen bonding explains the resistance of the primary hydroxyl to oxidation and the ease of cyclisation in the lactonisation *via* the hemiacetal route.

The minor oxidation product **8**, $C_{20}H_{36}O_3$, showed hydroxyl absorption (3530, 3420 cm^{-1}) and extensive C—O stretching in the IR. Mass spectrum showed M—H_2O as the highest mass peak and loss of CH_2OH, consistent with a primary hydroxyl grouping. PMR (Table) showed the three ring A methyls and the C-14 methyl triplet. The C-13 methyl signal at δ 1·13 was in the normal position for C-13 hydroxylated labdanes. A two proton singlet at δ 3·45 was consistent with a primary hydroxyl attached to C-17 and a one proton multiplet was present at δ 3·89 (W/2 12 Hz). From the overall similarity to 8,12s-epoxylabdane-13,17-diol **7** this compound was assigned as its C-12 epimer, 8,12R-epoxylabdane-13,17-diol **8**. The fact that the band width of the C-12 proton signal in this case is smaller than is observed in the more abundant oxidation product **7** is consistent with the changes in dihedral angles measured from Dreiding models. This structure was confirmed by Jones oxidation which gave an aldehyde rather than a lactone. An unstable aldehyde, 13-hydroxy-8,12-epoxylabdan-17-al **14** which showed hydroxyl absorption (3500 cm^{-1}) and aldehyde peaks (2750, 1704 cm^{-1}; δ 9·78) was isolated. Models of 8,12R-epoxylabdane-13,17-diol **8** show that intramolecular hydrogen bonding is not possible, dilute CCl_4 solution IR studies showing only non-bonded hydroxyl group absorption[7] (3695 cm^{-1}). This accounts for the normal position of the C-13 methyl resonance and the observed rapid rate of oxidation.

C-13 Stereochemistry

In order to formulate a mechanism for the formation of the 8,12-epoxy compounds it was necessary to establish whether their formation had occurred with retention or epimerisation at C-13. The asymmetric shape of the C-12 proton signal in the oxidation products and their derivatives in all the solvents used ($CDCl_3$, C_6H_6, C_5H_5N) initially suggested the possibility of two different proton signals of very similar environments.

Several factors indicated that the shape of the multiplet was not produced by isomeric impurity. In the strongly hydrogen bonded diol **7** and the hydroxy acetate **9** and in the rigid lactone **12** the C-13 methyl would possess a very different environment if it were α than that experienced if it were β. Thus it would be highly unlikely that a mixture of 13α and 13β-epimers could not be detected by a difference in the C-13 methyl resonance in these compounds. PMR spectra in $CDCl_3$, C_6H_6, and C_5H_5N showed no multiplicity of the C-13 signal in any of the derivatives prepared. Nor was any multiplicity of this signal observed when the derivatives were examined in $CDCl_3$ with varying amounts of europium shift reagent [Eu (dpm)$_3$].[8] High temperature PMR studies on 8,12s-epoxylabdane-13,17-diol **7** showed no observable change in the shape of the multiplet up to 90° and ruled out the possibility of two different conformers contributing to the asymmetry of the C-12 proton signal.

That the C-12 proton multiplet did in fact result from only one proton environment was supported by the lack of evidence for epimerisation at any centre, the retention of asymmetry of the signal throughout several chemical transformations and the observation that the band width of the multiplet in any one compound was independent of the solvent used, despite the fact that the overall shape of the peak was altered markedly in some cases.

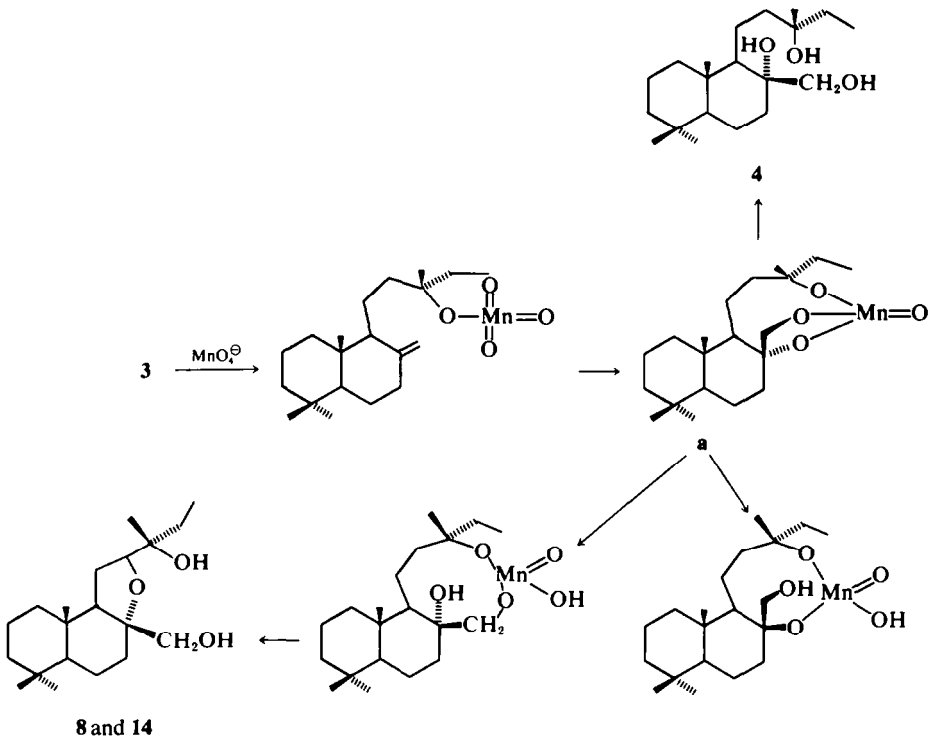
Alteration in peak shape without alteration in band width of the C-12 proton signal is attributed to virtual coupling[9] with the C-9 proton involving either or both of the C-11 protons. Change of solvent produces small changes in the relative positions of the C-11 protons, altering their interaction and thus the shape of the multiplet. The real coupling constants are unaltered and the band width remains constant.

Mechanism of aqueous permanganate oxidations

Reaction of neutral aqueous permanganate with an acetone solution of 13-acetoxy-8(17)-labdene **13** proceeded very slowly, the only product isolated being a small quantity of 13-acetoxy-17-norlabdan-8-one **15**. However with 8(17)-labden-13-ol **3** the reaction proceeded rapidly, thus indicating some participation by the side chain hydroxyl group, probably involving the formation of a manganate ester. Similar assistance by an hydroxyl group has been observed by Eastman and Quinn.[10]

A mechanism to account for the oxidation products of 8(17)-labden-13-ol **3** is proposed in Scheme 2. Initial formation of the C-13 manganate ester leads to an internal manganate ester **a**, as proposed for the cis hydroxylation of alkenes, which gives the triol **4** on hydrolysis. Cleavage of the vicinal diol grouping of the triol, a common side reaction in the cis hydroxylation[11] of alkenes, gives 13-hydroxy-17-norlabdan-8-one **5**.

The fact that one of the C-12 epimers predominates suggests that formation of the 8,12-oxide



8 and 14

SCHEME 2. Formation of Oxidation Products.

Table: PMR data (δ values; $CDCl_3$)

Compound	Methyl signals 4α	4β	10β	13	14	Low field signals	C-17		C-12	Band width of C-12H (Hz)
8,12S-Epoxylabdane-13, 17-diol **7**	0·88	0·83	0·81	1·04	0·93		3·53		3·87	16
17-Acetoxy-8.12S-epoxylabdan-13-ol **9**	0·87	0·84	0·85	1·00	0·91	4·39		4·14	3·87	15
13, 17-Diacetoxy-8, 12S-epoxylabdane **10**	0·88	0·84	0·88	1·38	0·92	4·34		3·96	4·12	16
8,12S-Epoxylabdano-13,17-lactone **12**	0·88	0·83	0·83	1·24	0·93				4·18	10
17-Acetoxy-8-hydroxy-13αβH-labdan-12-one **11**	0·87	0·82	0·79	0·98 (d)	0·88	4·35		3·95		
8,12R-Epoxylabdane-13,17-diol **8**	0·88	0·82	0·74	1·14	0·93		3·48		3·89	12
13-Hydroxy-8,12R-epoxylabdan-17-al **14**	0·89	0·80	0·73	1·15	0·93		9·78		4·34	11

bridge is formed at some stage when the side chain is held in a fixed position. Functionalisation of C-12 is regarded as proceeding through the internal manganate ester **a** proposed for the formation of the triol **4**. Permanganate has been shown to abstract hydride from tertiary centres, replacing these with hydroxyl groups with retention of configuration.[10] Models show that a manganate ester attached to carbons 8,13 and 17 would be moderately rigid but an ester attached to carbons 8 and 13 or 13 and 17 would be reasonably mobile and also very close to the C-12 hydrogens. Abstraction of a hydride from a secondary rather than from a less accessible tertiary centre gives a carbonium ion which undergoes nucleophilic attack by the C-8 oxygen. Hydrolysis of the manganate ester gives an 8,12-epoxy diol.

An alternative pathway to the 8,12-epoxy compounds, via dehydration of the C-13 hydroxyl to the Δ^{12}-olefin and subsequent hydroxylation by permanganate can be discarded as 8(17)-labden-13-ol **3** is dehydrated to mainly Δ^{13} isomers[12] and furthermore it would produce epimers at C-13 for which there is no evidence.

EXPERIMENTAL

For general experimental details see Part 1.[1]

8(17)-*Labden*-13-*ol* **3**—ν_{max} 3345 (OH); 3075, 1640, 885 (C=CH_2); 1140, 1129 (CO) cm^{-1}. PMR: methyls at δ 0·69, 0·80, 0·87, 0·88 (triplet, *J* 7 Hz), 1·14; C=C$\underline{H}_2$ 4·53, 4·81; 7 β$\underline{H}$ 2·35 (multiplet).

Aqueous permanganate on 8(17)-*Labden*-13-*ol* **3**—To a stirred soln of **3** (12 g) in acetone (490 ml) was added (with cooling to maintain T < 30°) over a period of 2 h, $KMnO_4$ (24 g) in water (960 ml). A further portion of acetone (250 ml) was then added and stirring continued for 3 h. MnO_2 was removed by filtration and washed with ether. Ether extraction of the filtrate gave an oil (10·8 g). MnO_2 was dissolved in acidic Na_2SO_3 and the resulting mixture ether extracted to give more oil (1·6 g). The two portions were combined and chromatographed (1000 g alumina, deactivated with 100 ml water) to give (i) with 25% ether/hexane, 8(17)-*labden*-13-*ol* **3** (0·27 g) identical to an authentic sample; (ii) with 35% ether/hexane, 13-*hydroxy*-17-*norlabdan*-8-*one* **5** (0·34 g). ν_{max} 3430 (OH); 1694 (C=O); 1426 (perturbed methylene); 1183, 1147, 1135, 1104, 1065, 1045, 968 (CO) cm^{-1}. PMR: methyls at δ 0·72, 0·86, 0·89 (triplet, *J* 7 Hz) 0·96, 1·13; perturbed methylene 1·80–2·50. This sample, on attempted distillation (70°/0·01 mm) on standing, or on contact with dilute acid, lost water to form 8,13-*epoxy*-17-*norlabd*-8-*ene* **6**, distilled 68°/0·01 mm ν_{max} 1664 (=C—O—); 1190, 1181, 1149, 1103, 1067, 1033 (C—O) cm^{-1}. PMR: methyls at δ 0·85, 0·86 (triplet, *J* 7 Hz), 0·89, 0·97, 1·15. (Found: C, 82·7; H, 11·9. $C_{19}H_{32}O$ requires: C, 82·5; H, 11·7%), (iii) with 65% ether/hexane, 8,12*s*-*epoxylabdane*-13,17-diol **7** (3·39 g), sublimed 110°/0·01 mm, m.p. 166–167° ν_{max} 3430, 3310 (OH); 1414 (perturbed methylene); 1179, 1164, 1116, 1094, 1063, 1046, 1018, 1000, 979 (CO) cm^{-1} $\nu_{max}^{CCl_4}$ 3535, 3455 (bonded OH). PMR: methyls at δ 0·81, 0·83, 0·88, 0·93 (triplet, *J* 7 Hz), 1·04; C-17 protons 3·53 (W/2 4 Hz); C-12α proton as a multiplet 3·87 (W/2 16 Hz); *m/e* 324 (M^+). (Found: C, 74·0; H, 11·1. $C_{20}H_{36}O_3$ requires: C, 74·0; H, 11·2%), (iv) with 70% ether/hexane, 8,12R-*epoxylabdane*-13,17-*diol* **8** (0·32 g), sublimed 115°/0·02 mm, m.p. 120–121°. ν_{max} 3530, 3420 (OH); 1174, 1141, 1099, 1080, 1009, 988, 972 (C—O) cm^{-1}. $\nu_{max}^{CCl_4}$ 3695 (non-bonded OH). PMR: methyls at δ 0·74, 0·82, 0·88, 0·93 (triplet, *J* 7 Hz), 1·14; C-17 protons 3·48 (W/2 4 Hz); C-12β proton as a multiplet 3·89 (W/2 12 Hz). *m/e* 324 (M^+). (Found: C, 74·3; H, 11·3; $C_{20}H_{36}O_3$ requires: C, 74·0; H, 11·2%), (v) with 5% MeOH/ether, *labdane*-8,13,17-*triol* **4** (5·07 g), identical (mmp, IR, PMR) with an authentic sample.

17-*Acetoxy*-8,12*s*-*epoxylabdan*-13-*ol* **9**—8,12*s*-epoxylabdane-13,17-diol **7** (50 mg) was acetylated with pyridine-acetic anhydride (2 ml, 1:1) at room temp. for 24 hr. Work up, followed by PLC (60% ether/hexane) gave 17-*acetoxy*-8,12*s*-*epoxylabdan*-13-*ol* **9** (45 mg), distilled 106°/0·04 mm ν_{max} 3465 (OH); 1720, 1260 (acetate); 1110, 1068, 1036, 1019, 1003, 982 (CO) cm^{-1}. PMR: methyls at δ 0·84, 0·85, 0·87, 0·91 (triplet, *J* 7 Hz), 1·00; acetate methyl 2·08; C-17 protons as an AB system H_A 4·39, H_B 4·14 (long range coupled, J_{LR} = 1 Hz) (J_{AB} 11 Hz); C-12α proton as multiplet 3·87 (W/2 14 Hz). (Found: C, 71·8; H, 10·3; $C_{22}H_{38}O_4$ requires: C, 72·1; H, 10·5%).

13,17-*Diacetoxy*-8,12*s*-*epoxylabdane* **(10)**—8,12*s*-epoxylabdane-13,17-diol **7** (50 mg) was treated at room temp for 24 hr with isopropenyl acetate (2 ml) and toluene p-sulphonic acid (5 mg). Dilution with ether, washing with dil NaOH and water, drying and removal of solvent gave a crystalline product (50 mg), which was purified by PLC (50% ether/hexane) to give 13,17-*diacetoxy*-8,12*s*-*epoxylabdane* **10** (45 mg), distilled 120°/0·02 mm, m.p. 101–102°. ν_{max} 1720, 1249 (acetate); 1143, 1113, 1074, 1040, 1025, 1010 (C—O) cm^{-1}. PMR: methyls at δ 0·84, 0·88, 0·88, 0·92 (triplet, *J* 7 Hz), 1·38; acetate methyls at 1·96, 2·05; C-17 protons as an AB system H_A 4·34, H_B 3·96 (long-range coupled, J_{LR} 1 Hz) (J_{AB} 11 Hz); C-12α proton as a multiplet 4·12 (W/2 14 Hz). (Found: C, 70·3; H, 10·2; $C_{24}H_{40}O_5$ requires: C, 70·6; H, 9·9%).

17-*Acetoxy*-8-*hydroxy*-13αβH-*labdan*-12-*one* **11**—17-acetoxy-8,12*s*-epoxylabdan-13-ol **7** (0·56 g) was refluxed for 15 min with triethylorthoformate (0·4 ml), toluene p-sulphonic acid (100 mg) and anhyd $NaHCO_3$ (1·25 g) in dry benzene (100 ml). The reaction mixture was filtered and the solvent removed. The remaining material was dissolved in methanol (50 ml) and treated at room temp with HCl (10 ml, 1%) for 12 hr. Work up by dilution with water, ether extraction, drying and removal of solvent gave an oil (0·5 g). PLC (45% ether/hexane) gave 17-*acetoxy*-8-*hydroxy*-13αβH-*labdan*-12-*one* **11** (0·13 g), distilled 92°/0·02 mm ν_{max} 3460 (OH); 1730, 1230 (acetate); 1700 (C=O); 1412 (perturbed methylene); 1180, 1074, 1033 (CO) cm^{-1}. PMR: methyls at δ 0·79, 0·82, 0·87, 0·88 (triplet, *J* 7 Hz), 0·98 (doublet, *J* 7 Hz; remained the same magnitude when recorded at 60 MHz); acetate methyl 2·08; perturbed methylene 2·00–2·70; C-17 protons as an AB system H_A 4·32, H_B 3·95 (J_{AB} 11 Hz). (Found: C, 71·9; H, 10·5; $C_{22}H_{38}O_4$ requires: C, 72·1; H, 10·5%).

8,12*s*-*Epoxylabdano*-13,17-*lactone* **12**—8,12*s*-epoxylabdane-13,17-diol **7** (50 mg) in acetone (5 ml) was treated overnight at 0° with Jones reagent (0·2 ml). Work up by pouring into sat $NaHCO_3$ and ether extraction, drying, removal of solvent and PLC (30% ether/hexane) gave **12** (45 mg), sublimed 100°/0·04 mm, m.p. 125–127°. ν_{max} 1720 (lactone), 1155, 1086, 1028, 1000, 954 (C—O) cm^{-1}; $\nu_{max}^{CCl_4}$ 1747 cm^{-1} (lactone). PMR: methyls at δ 0·83, 0·83, 0·88, 0·93 (triplet, *J* 7 Hz), 1·24; C-12α proton as a multiplet 4·18 (W/2 12 Hz). CD (c, 0·362; MeOH) $[\theta]_{217}$ 0; $[\theta]_{243}$ −2914 (Γ 24 nm); $[\theta]_{271}$ 0. (Found: C, 74·8; H, 10·0; $C_{20}H_{32}O_3$ requires: C, 75·0; H, 10·1%).

8,12R-*Epoxy*-13-*hydroxylabdan*-17-*al* **14**—8,12R-epoxylabdane-13,17-diol **8** (50 mg) in acetone (10ml) was treated with Jones reagent (0·2 ml) at 0° for 5 min. Work up as for oxidation of **7** followed by PLC (65% ether/hexane) gave the unstable aldehyde **14** (35 mg) ν_{max} 3500 (OH); 2750, 1704 (aldehyde); 1138, 1123, 1102, 1073, 1050, 1014, 990 (CO) cm^{-1}. PMR: methyls at δ 0·73, 0·80, 0·89, 0·93 (triplet, *J* 7 Hz), 1·15; C-12β proton as a multiplet 4·34 (W/2 12 Hz); —CHO 9·78.

Lead tetra-acetate oxidation of labdane-8,13,17-*triol* **4**—**4** (50 mg) was dissolved in dry benzene (20 ml) and a soln of $Pb(OAc)_4$ (150 mg) in dry benzene (20 ml) added, with stirring, at room temp over a period of 15 min. Stirring was continued for a further 15 min, excess $Pb(OAc)_4$ destroyed by addition of ethanediol (0·5 ml). Work up by filtration and evaporation of the solvent gave 13-*hydroxy*-17-*norlabdan*-8-*one* **5** (45 mg), identical (IR, PMR) with an authentic sample.

13-*Acetoxy*-8(17)-*labdene* **13**—8(17)-labden-13-ol **3** (1 g) was treated at room temp for 20 hr with isopropenyl acetate (1 ml) and toluene p-sulphonic acid (10 mg). Dilution with ether, washing with 0·5 M NaOH and water, drying and removal of solvent gave **13** (0·98 g), identical (IR, PMR) with an authentic sample.[13]

Aqueous permanganate oxidation of 13-*acetoxy*-8(17)-

labdene **13**–**13** (500 mg) in acetone (20 ml) was stirred with $KMnO_4$ (1 g) in water (60 ml) for 24 hr at room temp. Work up as for aqueous permanganate treatment of **3** gave an oil (450 mg) which on PLC (20% ether/hexane) gave: (i) as upper band, 13-*acetoxy*-8(17)-*labdene* **13** (300 mg), identical with an authentic sample, (ii) as lower band, 13-*acetoxy*-17-*norlabdan*-8-*one* **15** (27 mg) ν_{max} 1720, 1255 (acetate); 1702 (C═O); 1414 (perturbed methylene); 1170, 1124, 1011 (CO) cm^{-1}. PMR: methyls at δ 0·71, 0·85, 0·88 (triplet, J 7 Hz), 0·96, 1·40; acetate methyl 1·97; perturbed methylene 2·00–2·50. CD (c, 0·035; MeOH) $[\theta]_{252}$ 0; $[\theta]_{292}$ −5490 (Γ 33 nm); $[\theta]_{320}$ 0; (Found: C, 75·0; H, 10·5; $C_{21}H_{36}O_3$ requires: C, 74·95; H, 10·8%).

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