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DITERPENE CHEMISTRY—IV[1]

TRANSFORMATIONS OF 8(17),14-LABDADIEN-13-OL

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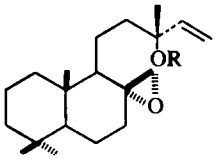
Abstract—The origin of the long range coupling in exocyclic epoxides with quasi-axial methylenes has been established by the synthesis of specifically deuterated analogues. Use was made of paramagnetic shift reagents in distinguishing between the epoxide protons.

Huntrakul,[2] in an investigation of the extractives of *Dacrydium kirkii*, isolated a compound $C_{20}H_{32}O_2$ which he formulated as 8,17-epoxy-14-labden-13-ol **1** from spectral evidence. This compound had been synthesised previously[3,4] but in both cases had been reduced with lithium aluminium hydride without the PMR spectrum being recorded. Authentic 8,17-epoxy-14-labden-13-ol **1**, synthesised by the action of m-chloroperbenzoic acid in dichloromethane at 0° on 8(17),14-labdadien-13-ol (manool) **2**, was identical to the naturally occurring sample. In addition a small quantity of 14*RS*,15-epoxy-8(17)-labden-13-ol **3** was produced on epoxidation.

An interesting feature of the PMR spectrum of 8,17-epoxy-14-labden-13-ol **1** was the presence of a substantial long range coupling (1·4 Hz) in the down field spin pair of the epoxidic AB system. Similar long-range couplings in exocyclic epoxides have been reported for several positions throughout the steroid nucleus[5,6] but no attempts have been made to establish the origin or the stereochemical requirements, apart from the observation[6] that exocyclic epoxides with quasi-axial methylenes show long-range coupling (as evidenced by the increased half-band width of the down field spin pair) whereas those with quasi-equatorial methylenes do not.

In an attempt to establish the origin of the



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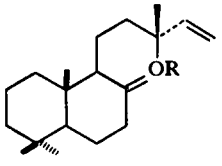
7: R = Ac



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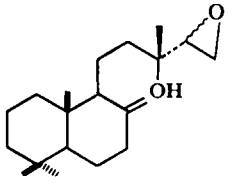

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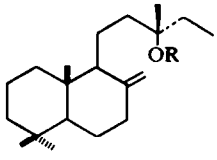

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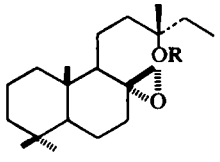

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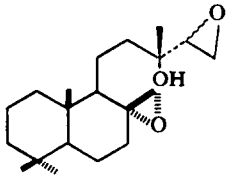
9: R = Ac



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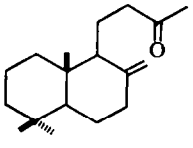

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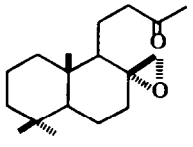

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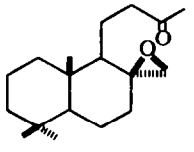

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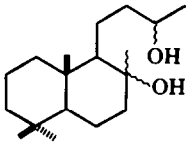
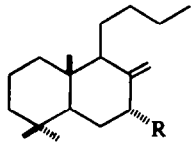


14: βCH_3, αOH
15: αCH_3, βOH



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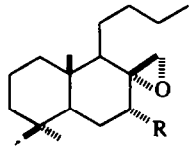

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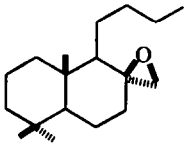

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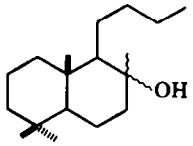
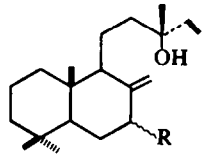


19: βCH_3, αOH
20: αCH_2, βOH



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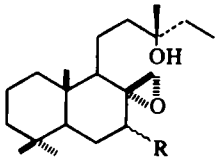
25: R = αOAc
27: R = βOH



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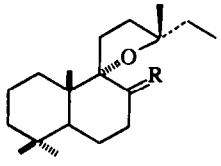
26: R = αOAc
28: R = βOH



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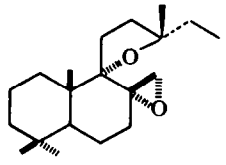
42: R = O



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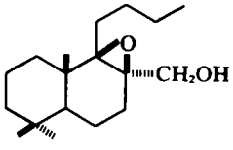

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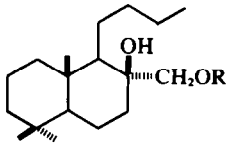

32: R = H
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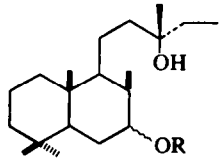
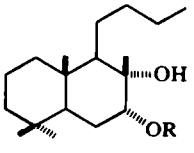


34: R = αOH
44: R = αOTs
58: R = βOH



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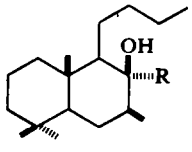

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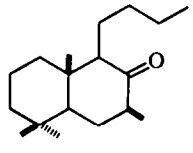

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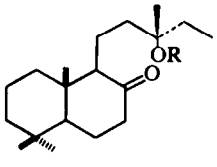

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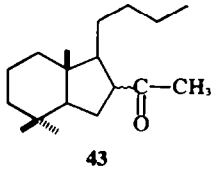

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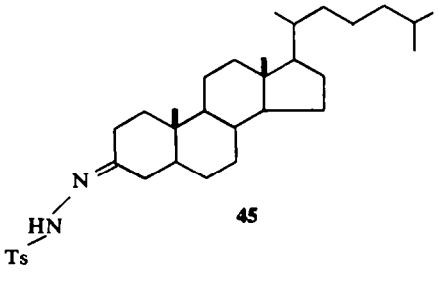

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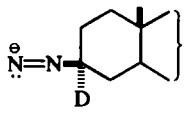
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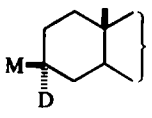
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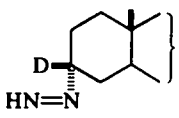
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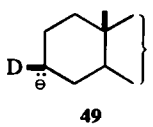
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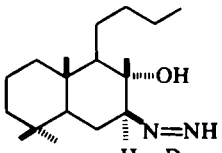
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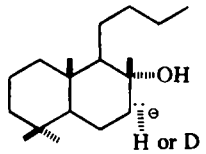
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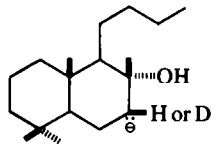
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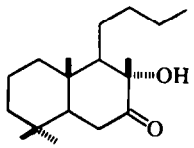
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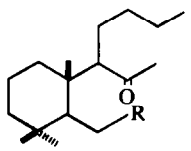
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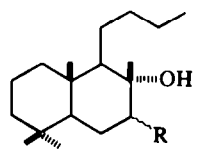
55: R = COOH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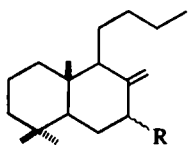
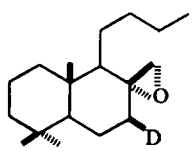

57: R = βD
61: R = αD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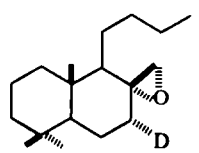
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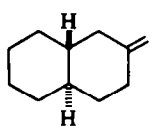
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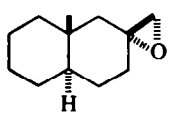
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long-range coupling a series of 8,17-epoxylabdanes was synthesised (Table 1). All the α-epoxides (quasi-axial methylenes) unsubstituted in ring B exhibited long-range coupling but the two β-epoxides **13** and **18** were not long-range coupled. The ring B substituted α-epoxides **22**, **24**, **26** and **28**, through which it was hoped to establish the origin of the coupling, did not show long-range coupling. This is attributed to substituent-induced variations. The synthesis of deuterated epoxides was thus undertaken. When epoxidation gave both the α- and β-epoxides, assignments were made from an examination of the LAH reduction products. The reduction product of the β-epoxide showed the typical low field 10β methyl signal due to the 8β-hydroxyl group. In view of the very low yield of β-epoxides, 8β,17-epoxy-14,15-dinorlabdane **18** was synthesised by an alternative route. 8β,9β-Epoxy-14,15-dinorlabdan-17-ol **31** which was shown[9] to be a minor product from the SeO_2/H_2O_2 oxidation of **16** was reduced with LAH to the diol, 14,15-dinorlabdane-8β,17-diol **32**. Base treatment of the monotosylate **33** gave 8β,17-epoxy-14,15-dinorlabdane **18** in good yield.

The most direct method of introducing a deuterium at the 7 position appeared to be the hydrogenolysis of a 7-tosylate with lithium aluminium deuteride, a reaction known to proceed with inversion.[7,8] However, treatment of 8(17)-labdene-7α,13-diol **23** or 8(17)-labdene-7β,13-diol **27** with tosyl chloride in pyridine produced none of the required tosylates despite the fact that labdane-

Table 1. Chemical shifts of epoxide protons

Compound	C-17 Protons	
	H_A	H_B
8,17-Epoxy-14-labden-13-ol **1**	2·76*	2·46
8,17-Epoxylabdan-13-ol **5**	2·80*	2·49
13-Acetoxy-8,17-epoxy-14-labden-13-ol **7**	2·69*	2·43
13-Acetoxy-8,17-epoxylabdan-13-ol **9**	2·71*	2·47
8,17;14RS,15-Diepoxylabdan-13-ol **10**	?	2·49
8,17-Epoxy-14,15-dinorlabdan-13-one **12**	2·79*	2·47
8β,17-Epoxy-14,15-dinorlabdan-13-one **13**	2·52	2·31
8,17-Epoxy-14,15-dinorlabdane **17**	2·70*	2·45
8β,17-Epoxy-14,15-dinorlabdane **18**	2·51	2·26
8,17-Epoxy-14,15-dinorlabdan-7α-ol **22**	2·83	2·54
8,17-Epoxylabdane-7α,13-diol **24**	2·91	2·59
7α-Acetoxy-8,17-epoxylabdan-13-ol **26**	2·83	2·52
8,17-Epoxylabdane-7β,13-diol **28**	3·05	2·71
8,17;9,13-Diepoxylabdane **30**	2·58	2·58

*Long-range coupling present.

7α,13-diol **34** gave a tosylate readily. It was then decided to synthesise the tosylate of an 8α-hydroxy compound, thus preserving the potential exocyclic double bond. In order to facilitate this the side chain was completely defunctionalised.

8(17),14-Labdadien-13-ol **2** was oxidised to 14,15-dinorlabd-8(17)-en-13-one **11** using potassium permanganate in acetone at 0°. Wolff Kishner reduction of this ketone gave 14,15-dinorlabd-8(17)-ene **16** in good yield. Allylic oxidation of the alkene with selenium dioxide–hydrogen peroxide gave the expected 14,15-dinorlabd-8(17)-en-7α-ol **21** as the major product which was epoxidised to 8,17-epoxy-14,15-dinorlabdan-7α-ol **22**. Lithium aluminium hydride reduction of the epoxide gave 14,15-dinorlabdane-7α,8-diol **35** which tosylated readily to the monotosylate **36**. Hydrogenolysis of the monotosylate with lithium aluminium deuteride took an unexpected course, giving a rearrangement product formulated as 8-deuterio-14,15-dinor-17(8→7β)-abeolabdan-8β-ol **37**. Lithium aluminium hydride reduction of the tosylate **36** gave the corresponding rearranged alcohol **38**, $C_{18}H_{34}O$. It showed hydroxyl absorption (3650, 3500 cm^{-1}) and in the PMR the ring A methyl signals appeared at δ 0·84, 0·84, 0·94, the C-13 methyl triplet at δ 0·90 and a methyl doublet at δ 0·99 (J 7 Hz). The one proton multiplet at δ 3·71 ($W_{\frac{1}{2}}$ 6 Hz), typical of an axial hydroxyl group, was absent in the deuterated product **37**. Mass spectra of the two products were consistent with the incorporation of one deuterium. The alcohols **37** and **38** arise from a 1,2-nucleophilic rearrangement followed by reduction. This was confirmed when treatment of the tosylate **36** with aqueous potassium hydroxide in dioxan gave a ketone, 14,15-dinor-17(8→7β)abeolabdan-8-one **39** $C_{18}H_{32}O$ (1713 cm^{-1}). PMR data were similar to those of other labdan-8-ones (Table 2) and the methyl doublet at δ 1·02 (J 6·5 Hz) was consistent with a methyl in the deshielding zone of a carbonyl group.[10] Aromatic solvent induced shifts[11,12] confirmed the equatorial orientation of the methyl group (Table 2) and the negative CD curve was in accord with the octant rule prediction.[13] A further rearrangement product, the ring B contracted ketone, 14,15-dinor-9(8→7)-abeolabdan-8-one **43**, $C_{18}H_{32}O$ (1711 cm^{-1}) was isolated, corresponding to the non-planar rearrangement of participating centres. The PMR spectrum showed ring A methyls at δ 0·75, 0·84, 0·86, the C-13 triplet at δ 0·83 and a methyl resonance at δ 2·17, typical of a methyl ketone. The methyl ketone **43** was the major product when base

Table 2. Chemical shifts and solvent shifts of some labdan-8-ones

Compound	Solvent	Methyls			
		4α	4β	10	7(d)
13-Hydroxy-17-norlabdan-8-one **40**	$CDCl_3$	0·96	0·85	0·71	—
13-Acetoxy-17-norlabdan-8-one **41**	$CDCl_3$	0·96	0·86	0·72	—
9,13-Epoxy-17-norlabdan-8-one **42**	$CDCl_3$	0·92	0·82	0·72	—
14,15-Dinor-17(8→7β)-abeolabdan-8-one **39**	$CDCl_3$	0·97	0·83	0·65	1·02
	C_6H_6	0·86	0·71	0·57	1·02
	CCl_4	0·97	0·83	0·63	0·98
	C_5H_5N	0·92	0·76	0·61	1·03

treatment was carried out using methanol as the solvent and the minor product using dioxan, consistent with greater charge separation in the former case, allowing more random alkyl migration (*cf* base catalysed eliminations[14]). Lithium aluminium hydride reduction of 14,15-dinor-17(8→7β)-abeolabdan-8-one **39** gave 14,15-dinor-17(8→7β)-abeolabdan-8β-ol **38**, identical in all respects to that obtained from the hydrogenolysis of the tosylate **36**.

Since experiments with lithium aluminium hydride reduction of 7α-tosyloxylabdan-13-ol **44** showed that rearrangements occurred even in the absence of an 8α-hydroxyl group the reduction of tosylates as a route to 7-deuterio derivatives was abandoned.

It has been reported that reduction of tosylhydrazones with lithium aluminium deuteride takes place with incorporation of one deuterium, the remaining hydrogen coming from the water added at the end of the reaction.[15] Similar observations have been noted with sodium borodeuteride reduction,[15] the reduction proceeding via an intermediate which decomposes on treatment with water to give the desired alkane.[16] Higher yields are generally obtained with this latter reagent.

Djerassi[15] studied the reduction of 5α-cholestane-3-tosylhydrazone **45** with lithium aluminium hydride, sodium borohydride and the deuterated analogues of both reagents. Reduction with lithium aluminium deuteride followed by work up with water gave 3α and 3β-deuteriocholestanes in the ratio 7:3, but with sodium borodeuteride the ratio of α:β epimers obtained was 3:7. This latter ratio was also obtained using lithium aluminium hydride followed by workup with D_2O. The results of the lithium aluminium hydride reduction were interpreted in terms of an initial attack by a hydride species from the α-face to give species **46**, followed by carbanion formation. Predominant retention of configuration of this species was accounted for by the formation of a metallic derivative **47** which on treatment with water gave the alkane, still essentially with retention of configuration. On the other hand reduction with sodium borohydride was assumed to proceed via initial hydride attack from the β-face giving the α-diimide **48** which decomposed as before, with predominant retention of configuration.

In view of the fact that sodium borohydride reduction of cholestan-3-one gives a product composition fairly comparable to that obtained with lithium aluminium hydride,[17] attack from the β-face seems an unlikely course. It is more likely that the borohydride reduction proceeds in a similar manner to that with lithium aluminium hydride. The difference in observed product ratio can be explained by the amount of inversion of the carbanion formed in each case. Inversion of carbanions tends to be more pronounced in polar solvents[18] and as the borohydride reduction was carried out in methanol, the carbanion produced is more likely to invert to the stable species **49** than that produced by lithium aluminium hydride reduction in tetrahydrofuran. Although boron is a more efficient acceptor than aluminium.[19] the size of the boron-containing species in methanol is large thus preventing interaction with the carbanion from the β-face. A mechanism invoking a similar inversion process has been proposed to explain the formation of 3β-methyl-5α-cholestane from the methyl lithium treatment of 5α-cholestane-3-tosylhydrazone.[20]

With the more hindered labdane-7-tosylhydrazone, the reduction would be expected to be more stereospecific. Initial reduction would be expected to give the 7β-diimide **50** which would decompose to the carbanion **51**. As the result of steric hindrance to β-face attack complete inversion to the more stable and more accessible carbanion **52** would be expected to occur, resulting in a 7β-deuterium with a deuterated reducing reagent.

Formation of 8-hydroxy-14,15-dinorlabdan-7-one **53** presented difficulties. Oxidation of the diol **35** using Jones reagent, Collins reagent or the 2-phase modification of Jones oxidation gave cleavage products **54** and **55**. The transformation was finally achieved using aqueous N-bromosuccinimide in dioxan.[21]

Treatment of the ketol **53** with tosyl hydrazine followed by sodium borodeuteride in methanol with a water workup gave the monodeuterio derivative 7β-deuterio-14,15-dinorlabdan-8-ol **56** (*m/e* 269, 91% deuterium incorporation), the IR spectrum showing bands at 2175 and 2140 cm^{-1} consistent with an equatorial C—D bond[22] (i.e. a 7β-deuterium). Dehydration with thionyl chloride/pyridine gave the 8(17)-alkene **57** (*m/e* 251). The IR again showed bands consistent with an equatorial C—D bond and in addition the PMR spectrum did not possess a multiplet at δ 2·35 which occurs in the spectrum of the non-deuterated alkene **16** and which can be assigned to the 7β-proton on the following grounds: (a) In 14,15-dinorlabd-8(17)-ene **16**, apart from the C-17 protons the allylic protons would be expected to resonate at lowest field; (b) The multiplet is absent in both 8(17)-labdene-7α,13-diol **23** and 8(17)-labdene-7β,13-diol **27** but is present in 9,13-epoxy-8(17)-labdene **29**; (c) In the epimeric alcohols 8(17)-labdene-7α,13-diol **23** and 8(17)-labdene-7β,13-diol **27**, the 7β proton is observed 1·13 ppm downfield from the 7α proton, consistent with the former being in the deshielding zone of the double bond. In the corresponding saturated compounds **34** and **58** the 7β proton is only 0·16 ppm downfield from the 7α proton.

Epoxidation of the alkene **57** gave 7β-deuterio-8,17-epoxy-14,15-dinorlabdane **59** (*m/e* 265) which showed equatorial C–D stretching in the IR and still retained long-range coupling in the epoxide system in the PMR spectrum.

Treatment of 8-hydroxy-14,15-dinorlabdan-7-one **53** with tosyl hydrazine, followed by sodium borohydride in pre-dried dioxan in the presence of deuterium oxide gave 7α-deuterio-14,15-dinorlabdan-8-ol **60**. The mass spectrum showed incorporation of one deuterium (*m/e* 269, 87% incorporation) and the IR spectrum possessed axial C–D bands (2130, 2115 cm^{-1}). Dehydration with thionyl chloride in pyridine gave the 7α-deuterio alkene **61** which showed axial C–D stretching in the IR (2130, 2110 cm^{-1}). The PMR spectrum showed a multiplet at δ 2·35 ($W_{\frac{1}{2}}$8 Hz) considerably sharper than that observed in the non-deuterated alkene **16** ($W_{\frac{1}{2}}$19 Hz). This is consistent with removal of geminal coupling by deuteration in the 7α-position. The 7α-deuterio α-epoxide **62**, produced on m-chloroperbenzoic acid treatment of 7α-deuterio-14,15-dinorlabd-8(17)-ene **61**, also showed axial C–D stretching (2125, 2110 cm^{-1}). The PMR spectrum exhibited an epoxide AB system without long-range coupling in the downfield spin pair, thus establishing that the long-range coupling in 8,17-epoxides involves the 7α-proton.

To analyse completely the long-range coupling it was necessary to establish which of the epoxide protons was involved. This could not be solved directly but substantial indirect evidence indicated that the proton involved was the *exo*-proton.

PMR solvent shift studies using benzene and pyridine (Table 3) and europium shift reagent techniques (Fig 1) showed quite conclusively that the high-field C-17 proton in 8(17)-labden-13-ol **4** was that nearer the side chain, i.e. the endo proton. However with the 13-hydroxy-8,17-epoxide **5** no conclusive results could be obtained. In this case there is strong hydrogen bonding between the C-13 hydroxyl and the epoxide grouping as evidenced by the C-13 methyl resonance in the PMR spectrum (δ 1·08) and by hydroxyl absorption in dilute CCl_4 solution IR studied (3510 cm^{-1}). This hydrogen bonding apparently prevents any accumulation of solvent molecules or europium complex around the side chain, accumulation being in the vicinity of the epoxide function instead, the results obtained being very similar to those observed in the case of 8,17-epoxy-14,15-dinorlabdane **17** (Fig 2).

The PMR spectrum of 2 methylene-*trans*-decalin **63** shows equivalence of the olefinic proton signals.[5] Introduction of an angular 9β methyl substituent produces a slight non-equivalence but introduction of an equatorial side chain adjacent to the exocyclic methylene as in the labdane series results in substantial non-equivalence. Similarly in 2α,2'-epoxy-9β-methyl *trans*-declin **64**, the epoxide protons are equivalent[5] whereas in the labdane derivative **5** with a 9β side chain non-equivalence is

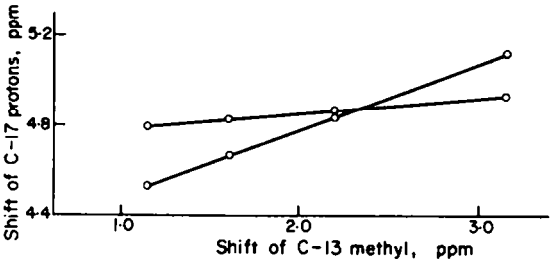

Fig 1. Europium shift reagent on 8(17)-labden-13-ol **4**.

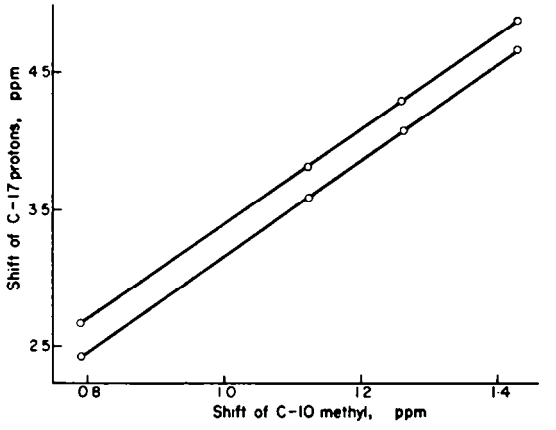

Fig 2. Europium shift reagent on 8(17)-epoxy-14,15-dinorlabdane **17**.

Table 3. Solvent shifts of 8,17-epoxides

Compound	Solvent	Methyls (δ)					C-17 H's (δ)	
		4α	4β	10β	13	14 (t)	H_A	H_B
8,17-Epoxylabdan-13-ol **5**	$CDCl_3$	0·89	0·83	0·81	1·08	0·87	2·80	2·49
	C_6H_6	0·82	0·77	0·67	1·24	0·92	2·59	2·19
	C_5H_5N	0·84	0·78	0·65	1·14	0·99	2·72	2·40
8,17-Epoxy-14,15-dinorlabdane **17**	$CDCl_3$	0·89	0·83	0·79	0·85 (t)	—	2·70	2·45
	C_6H_6	0·81	0·77	0·66	0·91 (t)	—	2·47	2·16
	C_5H_5N	0·84	0·78	0·73	0·93 (t)	—	2·65	2·39
8(17)-Labden-13-ol **4**	$CDCl_3$	0·87	0·80	0·69	1·14	0·88	4·81	4·53
	C_6H_6	0·85	0·79	0·72	1·06	0·86	4·90	4·70
	C_5H_5N	0·84	0·77	0·71	1·29	1·02	4·85	4·79

again observed. The non-equivalence in the exocyclic olefins and epoxides in the labdane series is thus the result of the anisotropy of the 9β-side chain. Although the C-17 protons do not have exactly the same spatial relationship to the C-9 substituent in the epoxides as they do in the olefins, the difference is only small. Thus although the magnitudes of shifts induced in these protons by the introduction of a 9β-side chain might be expected to differ slightly, the overall trends would be expected to be similar, i.e. that the low field (and long-range coupled) signal would arise from the *exo* proton in the exocyclic epoxides as in the parent alkenes.

Shifts in position of the exocyclic methylene protons of 209 to 213 ppm on epoxidation of decalin exocyclic olefins[5] are quite consistent with the shifts observed for the labdane derivatives provided there is no reversal of proton position (Table 4) even for those cases where additional functional group interactions, not present in the alkene, are known to occur (e.g. 8,17-epoxylabdan-13-ol **5**).

An interesting consequence of this study is that the long-range coupling observed does not require the W arrangement characteristic of long-range coupled systems in the alkane series.[23] No such arrangement is possible in the 8,17-epoxylabdanes, in fact any near planar arrangement of bonds involved results in an axially orientated side chain, a highly destabilised system. Neither is the arrangement obtained that experienced for allylic coupling in alkenes, but is in fact more like this type of situation.

There is strong evidence for considerable delocalised electron density above the C–C bond in epoxides.[24–26] Interaction between this delocalised system and the tails of the sp^3 orbitals of the interacting C–H bonds, in a manner similar to that proposed to account for the favourability of the W arrangement in alkanes could explain the observed long range coupling.

In the case of allylic coupling in exocyclic alkenes with an exocyclic methylene $|J_{cisoid}|$ is generally greater than $|J_{transoid}|$[27] when the double bond is exocyclic to a 6-membered ring. The relative magnitudes of J_{cisoid} and $J_{transoid}$ are highly dependent on the dihedral angle and consequently on the ring system to which the double bond is exocyclic.[27] To date studies on such systems have been largely empirical. In the case of the 8,17-epoxylabdanes $|J_{cisoid}|$ is again greater than $|J_{transoid}|$ but no particular significance can be attached to this.

In view of the symmetrical siting of the 7α and 9α protons relative to the exocyclic epoxide grouping it is contrary to expectation that substantial coupling should exist between the 7α and the *exo*-epoxidic protons and not between the 9α and the *endo*-epoxidic protons. The half band width observed for the equivalent epoxidic protons in the 2-exocyclic epoxide of 9β-methyl-*trans*-decalin **64**[5] (1·61 Hz) is more consistent with long-range coupling to both epoxidic protons (assuming a coupling of 1·4 Hz as in the labdane series) than with long-range coupling to only one epoxidic proton. It would appear that the absence of any substantial coupling between the 9α and *endo*-proton is due to some effect of the labdane side chain. This may be due to a conformational change, although it is likely that changes in conformation at C-9 would produce similar changes at C-7, or to an electronic effect, redistribution of charge destroying the favorable interaction previously existing.

Other known examples of long-range coupled exocyclic epoxides possess a similar environment to that existing in the 8,17-epoxylabdanes. The cases cited by Carlson[5] and by Hartshorn[6] all possess a pseudo axial methylene and at least one axial hydrogen on one of the "allylic" carbons.

EXPERIMENTAL

For general experimental details see Part 1.[28]

Epoxidations. All epoxidation reactions were worked up by washing the reaction mixture with 10% NaOH, then water and the solvent removed under vacuum.

Selective epoxidation of 8(17),14-*Labdadien*-13-*ol* **2**. To a solution of **2** (1 g) in CH_2Cl_2 (10 ml), cooled to − 5°, was added, over a period of 12 min, m-chloroperbenzoic

Table 4. Shifts in C-17 proton positions on epoxidation

Compound	Shift (ppm) H_A	H_B
8(17),14-Labdadien-13-ol **1**	2·01(2·31)	2·02(1·71)
13-Acetoxy-8(17),14-labdadiene **7**	2·10(2·36)	2·06(1·80)
8(17)-Labden-13-ol **4**	2·00(2·37)	2·04(1·73)
13-Acetoxy-8(17)labdene **8**	2·09(2·34)	2·06(1·81)
14,15-Dinorlabd-8(17)-ene **16**	2·09(2·34)	2·05(1·80)
14,15-Dinorlabd-8(17)-en-7α-ol **21**	1·78(2·13)	1·82(1·47)
8(17)-Labdene-7α,13-diol **23**	1·77(2·09)	1·79(1·47)
8(17)-Labdene-7β,13-diol **27**	2·08(2·44)	1·97(1·31)
9,13-Epoxy-8(17)-labdene **29**	2·18(2·18)	2·07(2·07)

The figures in brackets correspond to cross-over of proton positions.

acid (1·8 g, 85%) in CH_2Cl_2 (10 ml) and stirring continued for a further 30 min. The product purified by PLC (3 × 30% ether/hexane) gave: (i) The upper band, unchanged 8(17),14-labdadien-13-ol **2** (200 mg). (ii) The middle band, 14RS,15-epoxy-8(17)-labden-13-ol **3** (20 mg), b.p. 101°/0·02 mm. ν_{max} 3429 (OH); 3080, 1640, 886 (C=CH_2); 3065, 1485, 975, 914, 868, 819, 716 (epoxide); 1199, 1134, 1069, 1033 (CO) cm^{-1}. PMR: methyls at δ 0·68, 0·81, 0·87, 1·25; epoxide protons as a complex multiplet 2·50–3·00; C=CH_2 4·52, 4·80; 7β H 2·36 (multiplet). (Found: C, 78·4; H, 11·2. $C_{20}H_{34}O_2$ requires C, 78·4; H, 11·2%). (iii) The lower band, 8,17-epoxy-14-labden-13-ol **1**. (438 mg) distilled 90°/0·02 mm identical I.R.; PMR with the naturally occurring compound. ν_{max} 3450 (OH); 3080, 1640, 1410, 990, 918 (CH=CH_2); 3030, 1485, 968, 912, 888, 828, 802, 746, 734 (epoxide); 1199, 1150, 1112, 1072, 1035, 989 (CO) cm^{-1}. PMR: methyls at δ 0·80, 0·83, 0·89, 1·21; epoxide protons as an AB system H_A 2·76 (long range coupled, J_{LR} 1·5 Hz), H_B 2·46 (J_{AB} 4 Hz); CH=CH_2 as an ABX system H_X 5·88, H_A 5·20, H_B 4·95 (J_{AX} 17·5, J_{AB} 1·5, J_{BX} 10·5 Hz). (Found: C, 78·4; H, 11·6. $C_{20}H_{34}O_2$ requires C, 78·4; H, 11·2%).

m-Chloroperbenzoic acid on 8(17)*labden*-13-*ol* **4**. Treatment of **4** (1 g) in CH_2Cl_2 (10 ml) with m-chloroperbenzoic acid (1 g, 85%) in CH_2Cl_2 (20 ml) at r.t. overnight and PLC (75% ether/hexane) gave 8,17-epoxylabdan-13-ol **5** (920 mg), distilled 120°/0·02 mm. ν_{max} 3400 (OH), 3025, 1480, 969, 937, 913, 884, 825, 799 (epoxide); 1192, 1143, 1120, 1041 (CO) cm^{-1}. PMR: methyls at δ 0·81, 0·83, 0·87 (triplet, J 7 Hz), 0·89, 1·08; epoxide protons as an AB system H_A 2·80 (long range coupled, J_{LR} 1·6 Hz), H_B 2·49 (J_{AB} 4·1 Hz). PMR (C_6H_6): methyls at δ 0·67, 0·77, 0·82, 0·92 (triplet), 1·09; epoxide protons H_A 2·59, H_B 2·19. (Found: C, 77·9; H, 11·9. $C_{20}H_{36}O_2$ requires C, 77·9; H, 11·8%).

Epoxidation of 13-*acetoxy*-8(17),14-*labdadiene* **6**. m-Chloroperbenzoic acid (300 mg, 85%) in chloroform (10 ml) was added slowly to a stirred solution of **6** (300 mg) in chloroform (7 ml) stirring continued at 0° for 1 h. PLC (20% ether/hexane) gave 13-acetoxy-8,17-epoxy-14-labdene **7** (280 mg), distilled 85°/0·02 mm. ν_{max} 1730, 1245 (acetate); 3080, 1640, 1410, 992, 921 (CH=CH_2); 3040, 1490, 992, 973, 921, 900, 833, 812, 759. 690 (epoxide) cm^{-1}. PMR: methyls at δ 0·78, 0·81, 0·88, 1·49; acetate methyl 1·98; epoxide protons as an AB system H_A 2·69 (long range coupled, J_{LR} 1·5 Hz), H_B 2·43 (J_{AB} 4 Hz); CH=CH_2 as an ABX system H_X 5·90, H_A 5·14, H_B 5·06 (J_{AX} 17·5, J_{AB} 1·5, J_{BX} 10·5 Hz). (Found: C, 75·7; H, 10·6. $C_{22}H_{36}O_3$ requires C, 75·4; H, 10·9%).

Epoxidation of 13-*acetoxy*-8(17)-*labdene* **8**. 8 (200 mg) in CH_2Cl_2 (10 ml) was stirred with m-chloroperbenzoic acid (200 mg, 85%) in CH_2Cl_2 (10 ml) at R.T. for 12 h gave 13-acetoxy-8(17)-epoxylabdane **9** (185 mg), distilled 86°/0·03 mm. ν_{max} 1720, 1246 (acetate); 3025, 1484, 969, 932, 891, 829, 801, 758, 706 (epoxide) cm^{-1}. PMR: methyls at δ 0·79, 0·82, 0·82 (triplet, J 7 Hz), 0·88, 1·35; acetate methyl at 1·94; epoxide protons as an AB system H_A 2·71 (long range coupled, J_{LR} 1·5 Hz), H_B 2·47 (J_{AB} 4 Hz). (Found: C, 75·5; H, 11·0. $C_{22}H_{38}O_3$ requires C, 75·4; H, 10·9%).

Epoxidation of 8,17-*epoxy*-14-*labden*-13-*ol* **1**. 1 (50 mg) in chloroform (5 ml) was treated overnight at r.t. with m-chloroperbenzoic acid (60 mg, 85%) in chloroform (5 ml) and gave 8,17;14RS,15-diepoxylabdan-13-ol **10** (50 mg), distilled 110°/0·02 mm. ν_{max} 3450 (OH); 3065, 3045, 1490, 972, 910, 894, 872, 832, 812, 801, 752 (epoxide); 1152, 1074 (CO) cm^{-1}. PMR: methyls at δ 0·82, 0·83, 0·86 (triplet, J 7 Hz), 0·90, 1·23; epoxide protons as a complex multiplet 2·66–3·00 with H_B of the C-17 protons 2·49 (J_{AB} 4 Hz). (Found: C, 74·3; H, 10·7. $C_{20}H_{34}O_3$ requires C, 74·5; H, 10·6%).

14,15-*Dinorlabd*-8(17)-*en*-13-*one* **11**. 8(17),-14-Labdadien-13-ol **2** (60 g) in acetone (1 l) was cooled to 0° and $KMnO_4$ (30 g) in acetone (1 l) at 0° added. After 30 min at 0°, a further portion of $KMnO_4$ (30 g) in acetone (1 l) was added. The reaction mixture was maintained at 0° for 7 days with 28 additions of finely powdered $KMnO_4$ (each 5 g) over the intervening period. Work up by filtering off the MnO_2 produced and removal of solvent gave crude oil (19·9 g) which, on filtration through alumina with 15% ether–hexane gave 14,15-dinorlabd-8(17)-en-13-one **11** (17 g), identical (IR; PMR) with an authentic compound. ν_{max} 3075, 1638, 886 (C=CH_2); 1709 (ketone); 1405 (perturbed methylene) cm^{-1}. PMR: methyls at δ 0·69, 0·80, 0·86, 2·09; perturbed methylene 2·2–2·6; C=CH_2 4·44, 4·81.

Epoxidation of 14,15-*dinorlabd*-8(17)-*en*-13-*one* **11**. To a stirred solution of **11** (0·45 g) in $CHCl_3$ (25 ml) was added m-chloroperbenzoic acid (0·30 g; 85%) in $CHCl_3$ (10 ml) and stirring continued for 19 h at r.t. PLC (30% ether–hexane) gave the upper band, 8,17-epoxy-14,15-dinorlabdan-13-one **12** (0·365 g) distilled at 70°/0·02 mm. ν_{max} 1710 (C=O), 975, 895, 840, 800, (epoxide) cm^{-1}. PMR: methyls at δ 0·82, 0·82, 0·89, 2·08; epoxide protons as an AB system H_A 2·79 (long range coupled J_{LR} 1·8 Hz), H_B, 2·47 (J_{AB} 4 Hz). (Found: C, 77·6, H, 10·9. $C_{18}H_{30}O_2$ requires C, 77·6, H, 10·9%). The lower band, 8β,17-epoxy-14,15-dinorlabdan-13-one **13** (0·02 g) distilled at 58°/0·01 mm. ν_{max} 1716 (C=O) 895, 830 (epoxide) cm^{-1}. PMR: methyls at δ δ 0·86, 0·89, 0·90 and 2·10 (CH_3CO); epoxide protons as an AB system H_A 2·52; H_B 2·31 (J_{AB} 4 Hz). (Found: C, 77·3; H, 11·1. $C_{18}H_{30}O_2$ requires C, 77·6; H, 10·9%).

LAH Reduction of 8,17-*Epoxy*-14,15-*dinorlabdan*-13-*one* **12**. The ketone 12 (0·82 g) in dry ether (100 ml) was refluxed with excess LAH for 24 h. Excess LAH was destroyed by the addition of wet ether and then water. The complex was hydrolysed with H_2SO_4 (10 ml, 10%) and the mixture ether extracted. PLC (ether) gave two bands, the diols epimeric at C-13. The upper band was 14,15-dinorlabdane-8,13RS-diol **14** (0·21 g) m.p. 96–97°, sublimed 90°/0·02 mm. ν_{max} 3400 (OH); 1120, 1070 (CO) cm^{-1}. PMR: methyls at δ 0·78, 0·81, 0·87, 1·15, 1·17, (doublet, J 7 Hz), –CHOH 3·90 (broad). (Found: C, 76·4; H, 12·4. $C_{18}H_{34}O_2$ requires C, 76·5; H, 12·1%). The lower band gave 14,15-dinorlabdane-8,13RS-diol **14** (0·55 g) m.p. 106–107°, sublimed 81°/0·01 mm. ν_{max} 3220 (OH); 1120, 1070 (CO) cm^{-1}. PMR: methyls at δ 0·78, 0·78, 0·85, 1·15, 1·16 (doublet, J 7 Hz), CHOH 3·68, (sextet, J 7 Hz). (Found: C, 76·2; H, 12·3. $C_{18}H_{34}O_2$ requires C, 76·5; H, 12·1%).

LAH Reduction of 8β,17-*epoxy*-14,15-*dinorlabdan*-13-*one* **13**. **13** (0·24 g) in dry ether (30 ml) was stood at r.t. with excess LAH for 18 h. Work-up as above gave an inseparable mixture (multiple run PLC) of C-13 epimers, 14,15-dinorlabdan-8β,13RS-diol **15** (0·23 g) distilled at ν_{max} 104°/0·02 mm. 3350 (OH); 1128, 1040 (CO) cm^{-1}. PMR: methyls at δ 0·86, 0·86, 1·04, 1·11 (doublet, J 7 Hz), 1·08 (doublet, J 7 Hz), CHOH 3·93 (broad). (Found: C, 76·3; H, 12·1. $C_{18}H_{34}O_2$ requires C, 76·5; H, 12·1%).

14,15-*Dinorlabd*-8(17)-*ene* **16**. 14,15-Dinorlabd-8(17)-en-13-one **11** (6 g), diethylene glycol (150 ml) and hydrazine hydrate (30 ml, 98%) were heated at 120° for 1 h, KOH (10 g) was then added and the temperature raised slowly to 205° under distillation conditions. This temperature was maintained for 3 h. The reaction was worked up

by pouring material from distillation and receiver flasks into water and extracting with ethyl acetate. Evaporation of solvent and chromatography (200 g alumina) gave, on elution with hexane, 14,15-dinorlabd-8(17)-ene **16** (5·3 g). An analytical sample was prepared by $AgNO_3$–PLC (hexane) followed by distillation at 65°/0·6 mm. ν_{max} 3077, 1636, 1401, 887 (C=CH_2) cm^{-1}. PMR: methyls at δ 0·68, 0·81, 0·84 (triplet, J 7 Hz), 0·88; C=CH_2 4·50, 4·79; 7βH 2·35 (multiplet, $W_{\frac{1}{2}}$ 19 Hz) *m/e* 250 (M^+). (Found: C, 87·1; H, 12·9. $C_{18}H_{32}$ requires C, 87·0; H, 13·0%).

Epoxidation of 14,15-*dinorlabd*-8(17)-*ene* **16**. To a stirred solution of **16** (500 mg) in chloroform (3 ml) was added m-chloroperbenzoic acid (650 mg, 85%) in chloroform (5 ml) and stirring continued at r.t. for 10 h. Work up gave a mixture of 8,17-epoxy-14,15-dinorlabdane **17** and 8β,17-epoxy-14,15-dinorlabdane **18** (495 mg). Repeated PLC (6×15% ether–hexane) gave pure 8,17-epoxy-14,15-dinorlabdane **17** (30 mg) (the 8β,17-isomer was not isolated pure and was assigned from the PMR spectrum of the mixture by comparison with that of an authentic α-epoxide), distilled 50°/0·02 mm. ν_{max} 3030, 1485, 970, 930, 890, 830, 800 (epoxide) cm^{-1}. PMR: methyls at δ 0·79, 0·83, 0·85 (triplet, J 7 Hz). 0·89; epoxide protons as an AB system H_A 2·70 (long range coupled, J_{LR} 1·5 Hz), H_B 2·45 (J_{AB} 4 Hz). (Found: C, 81·7; H, 12·2. $C_{18}H_{32}O$ requires C, 81·8; H, 12·2%).

Lithium aluminium hydride reduction of epoxide mixture **17** *and* **18**. The mixture of epoxides **17** and **18** (200 mg) in dry ether (20 ml) was refluxed with excess LAH for 7 h. Work up, followed by PLC (30% ether–hexane) gave: (i) The upper band, 14,15-dinorlabdan-8β-ol **20** (52 mg), distilled 85°/0·02 mm. ν_{max} 3490 (OH); 1180, 1095, 1070, 1018 (CO) cm^{-1}. PMR: methyls at δ 0·85, 0·87, 0·90 (triplet, J 7 Hz), 0·96, 1·13. (Found: C, 81·0; H, 12·7. $C_{18}H_{34}O$ requires C, 81·1; H, 12·9%). (ii) The lower band, 14,15-dinorlabdan-8-ol **19** (104 mg) sublimed 80°/0·02 mm, m.p. 74–76°. ν_{max} 3450. (OH); 1150, 1129, 1096, 1074 (CO); additional peaks at 966, 933, 903 cm^{-1}. PMR: methyls at δ 0·79, 0·86, 0·89 (triplet, J 7 Hz), 1·14. *m/e* 268 (M^+). (Found: C, 81·1; H, 12·7. $C_{18}H_{34}O$ requires C, 81·1; H, 12·9%).

14,15-*Dinorlabd*-8(17)-*en*-7α-*ol* **21**. **16** (5·4 g) in dioxan (100 ml) was stirred with SeO_2 (2·5 g) and H_2O_2 (20 ml, 30%) at r.t. for 2½ days. Work up by dilution and ether extraction gave crude material (6·1 g) which was chromatographed on alumina (180 g). Elution with 20% ethyl acetate–hexane gave 14,15-dinorlabd-8(17)-en-7α-ol **21** (2·9 g) distilled 74°/0·03 mm, m.p. 43–45°. ν_{max} 3340 (OH); 3080, 1635, 1408, 895 (C=CH_2); 1198, 1163, 1140, 1117, 1080, 1045, 1033, 994 (C–O) cm^{-1}. PMR: methyls at δ 0·65, 0·80, 0·88, 0·93 (triplet, J 7 Hz); C=CH_2 4·35, 4·62, CHOH as a multiplet 5·02 ($W_{\frac{1}{2}}$ 3 Hz). (Found: C, 81·5; H, 12·1. $C_{18}H_{32}O$ requires C, 81·8; H, 12·2%).

8,17-*Epoxy*-14,15-*dinorlabdan*-7α-*ol* **22**. 14,15-Dinorlabd-8(17)-en-7α-ol **21** (2·9 g) in CH_2Cl_2 (50 ml) was treated at r.t. for 24 h with m-chloroperbenzoic acid (3·6 g, 85%) in CH_2Cl_2 (50 ml). PLC (50% ether/hexane) gave 8,17-epoxy-14,15-dinorlabdan-7α-ol **22** (2·5 g), distilled 85°/0·02 mm, m.p. 69–70°. ν_{max} 3400 (OH); 3030, 1480, 963, 943, 914, 886, 842, 811, 880, 720 (epoxide); 1105, 1054, 1034 (CO) cm^{-1}. PMR: methyls at δ 0·78, 0·82, 0·85 (triplet, J 7 Hz), 0·91; epoxide protons as AB system H_A 2·83, H_B 2·54 (J_{AB} 4 Hz); CHOH as a multiplet 3·44 ($W_{\frac{1}{2}}$ 4 Hz). (Found: C, 77·1; H, 11·5. $C_{18}H_{32}O_2$ requires C, 77·1; H, 11·5%).

8,17-*Epoxylabdane*-7α,13-*diol* **24**. 8(17)-Labdene-7α,13-diol **23** (250 mg) in CH_2Cl_2 (45 ml) was treated at r.t. for 10 h with m-chloroperbenzoic acid (250 mg, 85%). PLC (ether) gave 8,17-epoxylabdane-7α,13-diol **24** (250 mg), sublimed 113°/0·015 mm, m.p. 125–127°. ν_{max} 3480 (OH); 3020, 1490, 979, 920, 900, 885, 853, 845, 820, 779, 723 (epoxide); 1187, 1118, 1056, 1030, 979 (CO) cm^{-1}. PMR: methyls at δ 0·79, 0·81, 0·88 (triplet, J 7 Hz), 0·90, 1·07. Epoxide protons as an AB system H_A 2·91, H_B 2·59 (J_{AB} 4·0 Hz); CHOH as a broadened singlet 3·45 ($W_{\frac{1}{2}}$ 6 Hz). (Found: C, 74·1; H, 11·1. $C_{20}H_{36}O_3$ requires C, 74·0; H, 11·2%).

7α-*Acetoxy*-8,17-*epoxylabdan*-13-*ol* **26**. 7α-Acetoxy-8(17)-labden-13-ol **25** (250 mg) in CH_2Cl_2 (25 ml) was treated with m-chloroperbenzoic acid (165 mg, 85%) at r.t. for 8 h. PLC (90% ether–hexane) gave 7α-acetoxy-8,17-epoxylabdan-13-ol **26** (150 mg), distilled at 105°/0·02 mm. ν_{max} 3450 (OH), 1730, 1240 (AcO), 1200, 1025, 852, 824 (CO) cm^{-1}. PMR: methyls at δ 0·80, 0·80, 0·80, 0·86 (triplet, J 7 Hz) 2·06 (CH_3COO). Epoxide protons as an AB system H_A 2·83, H_B 2·52 (J_{AB} 4 Hz); CHOAc 4·51 ($W_{\frac{1}{2}}$ 5 Hz). (Found: C, 72·1; H, 10·5. $C_{22}H_{38}O_4$ requires C, 72·1; H, 10·45).

8,17-*Epoxylabdane*-7β,13-*diol* **28**. 8(17)-Labdane-7β,13-diol **27** (50 mg) in CH_2Cl_2 (6 ml) was treated at r.t. for 7 h with m-chloroperbenzoic acid (50 mg, 85%). PLC (ether gave 8,17-epoxylabdane-7β,13-diol **28** (50 mg) distilled 115°/0·015 mm, m.p. 105–107°. ν_{max} 3265 (OH), 3035, 1485, 977, 917, 904, 894, 866, 847, 820 (epoxide); 1182, 1145, 1094, 1066, 1015, 977 (CO) cm^{-1}. PMR: methyls at δ 0·79, 0·84, 0·86 (triplet, J 7 Hz), 0·91, 1·08; epoxide protons as an AB system H_A 3·05, H_B 2·71 (J_{AB} 4·6 Hz); CHOH as a multiplet 3·77 ($W_{\frac{1}{2}}$ 18 Hz). (Found: C, 73·8; C, 11·1. $C_{20}H_{36}O_3$ requires C, 74·0; H, 11·2%).

8,17;9,13-*Diepoxylabdane* **30**. 9,13-Epoxy-8(17)-labdene **29** (690 mg) in chloroform (5 ml) was treated at r.t. with m-chloroperbenzoic acid (800 mg, 85%) in chloroform (5 ml) for 48 h. PLC (5% ether–hexane) gave 8,17;9,13-dipoxylabdane **30** (300 mg), distilled 100°/0·06 mm. ν_{max} 3040, 1490, 984, 974, 941, 903, 870, 849, 818, 778 (epoxide); 1115, 1054, 1037, 1030 (CO) cm^{-1}. PMR: methyls at δ 0·81, 0·86, 0·89, 0·93 (triplet, J 7 Hz), 1·21: C-17 protons 2·58. PMR (C_6H_6): methyls at δ 0·71, 0·80, 0·87, 0·93 (triplet, J 7 Hz), 1·35; C-17 protons as an AB system H_A 2·31, H_B 2·28 (J_{AB} 4·5 Hz). (Found: C, 78·7; H, 11·3. $C_{20}H_{34}O_2$ requires C, 78·4; H, 11·2%).

14,15-*Dinorlabdane*-8β-17-*diol* **32**. 8β,9β-Epoxy-14,15-dinorlabdan-17-ol **31** (180 mg) was refluxed with excess LAH for 6 h. Work up followed by PLC (70% ether–hexane) gave 14,15-dinorlabdane-8β,17-diol **32** (160 mg), sublimed 96°/0·02 mm, m.p. 123–124°. ν_{max} 3395 (OH), 1179, 1053, 1040 (CO) cm^{-1}. PMR: methyls at δ 0·85, 0·87, 0·88 (triplet, J 7 Hz), 0·98; C-17 protons as an AB system H_A 3·52, H_B 3·23 (J_{AB} 11 Hz). (Found: C, 76·8; H, 12·1. $C_{18}H_{36}O_2$ requires C, 76·5; H, 12·1%).

17-*Tosyloxy*-14,15-*dinorlabdan*-8β-*ol* **33**. 14,15-Dinorlabdan-8β,17-diol **32** (135 mg) was treated with excess tosyl chloride in dry pyridine (3 ml) for 24 h at r.t. Work up by pouring into dil. HCl and ether extracting, washing the ethereal layer with water (2x), followed by PLC (50% ether–hexane) gave 17-tosyloxy-14,15-dinorlabdan-8β-ol **33** (150 mg). ν_{max} 3540 (OH); 1595, 1487, 1182, 1166, 960, 836, 800, 650 (tosylate); 1087 (CO) cm^{-1}. PMR: methyls at δ 0·81, 0·84, 0·86 (triplet, J 7 Hz), 0·93; CH_3–Ar 2·43; C-17 protons 3·74; p-disubstituted benzene as an AB system H_A 7·78, H_B 7·33 (J_{AB} 8·5 Hz).

8β,17-*Epoxy*-14,15-*dinorlabdane* **18**. 17-Tosyloxy-14,15-dinorlabdan-8β-ol **33** (150 mg) in MeOH was treated with KOH (0·25 g) in water (3 ml) for 2 h at r.t. Work up

by dilution and ether extraction followed by PLC (5% ether/hexane) gave 8β,17-epoxy-14,15-dinorlabdane **18** (105 mg), distilled 80°/0·015 mm, m.p. 65–66°. ν_{max} 3055, 1487, 972, 932, 901, 853, 831, 804, 775, 731, 699 (epoxide) cm^{-1}. PMR: methyls at δ 0·87, 0·89, 0·89, 0·86 (triplet, J 7 Hz); epoxide protons as an AB system H_A 2·51, H_B 2·26 (J_{AB} 4·4 Hz). PMR (C_6H_6): methyls at δ 0·83, 0·85, 0·86 (triplet, J 7 Hz) 0·97; epoxide protons H_A 2·34, H_B 2·03. PMR (C_5H_5N): methyls at δ 0·81, 0·86, 0·92 (triplet, J 7 Hz), 0·94; epoxide protons H_A 2·48, H_B 2·22. (Found: C, 82·0; H, 12·3. $C_{18}H_{32}O$ requires C, 81·8; H, 12·2%).

LAH reduction of **18** gave 14,15-dinorlabdan-8β-ol **20** identical with a product isolated from the LAH reduction of the α,β-epoxide mixture.

7α-Tosyloxylabdan-13-ol **44**. Labdane-7α,13-diol **34** (500 mg) in dry pyridine (5 ml) was treated with excess tosyl chloride at r.t. for 48 h. Work up by dilution, ether extraction, and washing of the ethereal extract with 10% HCl and water, followed by PLC (80% ether–hexane) gave 7α-tosyloxylabdan-13-ol **44** (510 mg) ν_{max} 3450 (OH); 1600, 1494, 1189, 1177, 888, 809, 692, 663 (tosylate); 1097 (CO) cm^{-1}. PMR: methyls at δ 0·73, 0·79, 0·84 (doublet, J 7 Hz), 0·87 (triplet, J 7 Hz), 1·11; C$\underline{H}_3$–Ar 2·42; 7β$\underline{H}$ 4·66 (multiplet, W/2 6 Hz); p-disubstituted benzene as an AB system H_A 7·78, H_B 7·27 (J_{AB} 9 Hz).

14,15-Dinorlabdane-7α,8-diol **35**. 8,17-Epoxy-14,15-dinorlabdan-7α-ol **22** (2·5 g) in dry ether (50 ml) was refluxed with excess LAH for 5 h. Work up as before followed by chromatography (120 g alumina) gave, on elution with 70% ether–hexane, 14,15-dinorlabdane-7α,8-diol **35** (1·5 g), sublimed 85°/0·01 mm, m.p. 121–122°. ν_{max} 3405 (OH), 1159, 1141, 1100, 1081, 1062, 1044, 1028 (CO) cm^{-1}. PMR: methyls at δ 0·79, 0·79, 0·87, 0·89 (triplet, J 7 Hz), 1·13; C$\underline{H}$OH as a multiplet 3·66 (W ½ 7 Hz). (Found: C, 76·4; H, 12·3. $C_{18}H_{34}O_2$ requires C, 76·5; H, 12·1%).

7α-Tosyloxy-14,15-dinorlabdan-8-ol **36**. 14,15-Dinorlabdane-7α,8-diol **35** (750 mg) in dry pyridine (5 ml) was treated with excess tosyl chloride at r.t. for 48 h. Work up as before followed by PLC (60% ether–hexane) gave 7α-tosyloxy-14,15-dinorlabdan-8-ol **36** (936 mg). ν_{max} 3560 (OH); 1602, 1480, 1190, 1176, 903, 839, 809, 657 (tosylate); 1120, 1096, 1041, 1003 (CO) cm^{-1}. PMR: methyls at δ 0·65, 0·70, 0·74, 0·85 (triplet, J 7 Hz), 1·08; CH_3–Ar 2·42; C$\underline{H}$OTs as a broadened singlet 4·54 (W ½, 6 Hz); p-disubstituted benzene as an AB system H_A 7·82, H_B 7·31 (J_{AB} 8·5 Hz).

8-Deuterio-14,15-dinor-17(8→7β)-abeolabdan-8β-ol **37**. 7α-Tosyloxy-14,15-dinorlabdan-8-ol **36** (100 mg) in dry ether (15 ml) was added dropwise to a refluxing solution of $LiAlD_4$ (100 mg) in dry ether (5 ml) over a period of ½ h. After refluxing for a further 2 h the reaction mixture was worked up as before. PLC (20% ether–hexane) gave 8-deuterio-14,15-dinor-17(8→7β)-abeolabdan-8β-ol **37** (50 mg) ν_{max} 3650, 3505 (OH); 2100, 1378 (CD); 1206, 1186, 1001, 971, 954, 930, 914 (fingerprint region) cm^{-1}. PMR: methyls at δ 0·84, 0·87, 0·90 (triplet, J 7 Hz), 0·94, 0·99 (doublet, J 7 Hz). *m/e* 267 (M^+). By following the same procedure using LAH in place of $LiAlD_4$ 14,15-dinor-17(8→7β)-abeolabdan-8β-ol **38** was obtained, distilled 90°/0·06 mm. ν_{max} 3650, 3500 (OH); 1260, 1164, 1120, 995, 985, 970, 930 (fingerprint region) cm^{-1}. PMR: methyls at δ 0·84, 0·87, 0·895 (triplet, J 7 Hz), 0·94, 0·99 (doublet, J 7 Hz); C$\underline{H}$OH as a multiplet 3·71 (W ½ 6 Hz). *m/e* 266 (M^+). (Found: C, 81·2; H, 12·7. $C_{18}H_{34}O$ requires C, 81·1; H, 12·9%).

Base treatments of 7α-Tosyloxy-14,15-dinorlabdan-8-ol **36**. (a) **36** (100 mg) in MeOH (40 ml) was refluxed with KOH (0·29 g) in water (4 ml) for 24 h. Dilution, ether extraction and drying followed by PLC (10% ether–hexane) gave: (i) The upper band, 14,15-dinor-9(8→7)-abeolabdan-8-one **43** (24 mg), distilled 94°/0·06 mm. ν_{max} 1711 (ketone); 1425 (perturbed methylene) cm^{-1}. PMR: methyls at δ 0·75, 0·83 (triplet, J 7 Hz), 0·84, 0·86, 2·12. (Found: C, 82·0; H, 12·3. $C_{18}H_{32}O$ requires C, 81·8; H, 12·2%). (ii) The lower band, 14,15-dinor-17(8→7β)-abeolabdan-8-one **39** (10 mg), distilled 85°/0·02 mm. ν_{max} 1713 (ketone); 1420 (perturbed methylene) cm^{-1}. PMR: methyls at δ 0·65, 0·83, 0·86 (triplet, J 7 Hz), 0·97, 1·02 (doublet, J 6·5 Hz); perturbed methylene 1·90–2·40. PMR (CCl_4): methyls at δ 0·63, 0·83, 0·87 (triplet), 0·97, 0·98 (doublet). C.D. (C, 0·150; MeOH) $[\theta]_{247}$ O, $[\theta]_{292}$ − 8840 (Γ38 nm), $[\theta]_{327}$ O. (Found: C, 81·5; H, 12·0. $C_{18}H_{32}O$ requires C, 81·8; H, 12·2%). (b) **36** (315 mg) in dioxan (25 ml) was refluxed with KOH (1·05 g) in water (5 ml) for 24 h. Work up by dilution, ether extraction and drying, followed by PLC (10% ether–hexane) gave: (i) The upper band, 14,15-dinor-9(8→7)-abeolabdan-8-one **43** (28 mg) identical (IR) with an authentic sample. (ii) The lower band, 14,15-dinor-17(8→7β)-abeolabdan-8-one **39** (81 mg), identical (IR) with an authentic sample.

Lithium aluminium hydride reduction of 14,15-dinor-17(8→7β)-abeolabdan-8-one **39**. **39** (40 mg) in dry ether (10 ml) was refluxed with excess LAH for 6 h. Work up as before, followed by PLC (20% ether–hexane) gave 14,15-dinor-17(8→7β)-abeolabdan-8β-ol **38** (35 mg), identical (IR; PMR) with an authentic sample.

Lithium aluminium hydride reduction of 7α-tosyloxylabdan-13-ol **44**. **44** (100 mg) in dry ether (15 ml) was refluxed with excess LAH for 6 h. Work up as before followed by $AgNO_3$–PLC (50% ether–hexane) gave: (i) The upper band, rearrangement product (32 mg). ν_{max} 3390 (OH); 1145, 1132, 1060 (CO) cm^{-1}. PMR: methyls at δ 0·82, 0·83, 0·85 (triplet, J 7 Hz), 0·90, 0·96 (doublet, J 7 Hz), 1·16. (ii) The middle band, unchanged 7α-tosyloxylabdan-13-ol **44** (5 mg), identical (IR) with an authentic sample. (iii) The lower band, labdane-7α,13-diol (15 mg), identical (IR; PMR) with an authentic sample.

Jones oxidation of 14,15-dinorlabdane-7α,8-diol **35**. **35** (150 mg) in acetone (5 ml) was swirled with Jones reagent (0·2 ml) at 0° for 2 min. Dilution, ether extraction, washing the ethereal extract with aq Na_2CO_3 and water followed by PLC (50% ether–hexane) gave: (i) The upper band, 8-hydroxy-14,15-dinorlabdan-7-one **53** (26 mg) (contaminated (contaminated with a trace of an impurity of the same R_f, characterised by comparison with the PMR of an authentic sample). (ii) The middle band, keto aldehyde **54** (20 mg) (attempts to distil a sample for analysis at 100°/0·01 mm produced the keto-acid **56**). ν_{max} 2610, 1728 (aldehyde); 1714 (ketone), 1449, 1422 (perturbed methylene). PMR: methyls at δ 0·69, 0·77, 0·77, 0·83 (triplet, J 7 Hz), 2·00; perturbed methylene 2·00–2·40; aldehydic proton 9·77. (iii) The lower band, keto acid **56** (26 mg), distilled 98°/0·01 mm. ν_{max} 3400–2500 (broad), 1710 (carboxylic acid); 1710 (ketone); 1419 (perturbed methylene). PMR: methyls at δ 0·86 (triplet, J 7 Hz), 0·92, 0·92, 0·92, 2·13. (Found: C, 73·1; H, 11·1. $C_{18}H_{32}O_3$ requires C, 73·0; H, 10·9%).

8-Hydroxy-14,15-dinorlabdan-7-one **53**. 14,15-Dinorlabdane-7α,8-diol **35** (290 mg) was treated at r.t. for 24 h with NBS (300 mg) and H_2O (1 ml). Dilution, ether extraction, drying and removal of solvent followed by PLC (50% ether–hexane) gave 8-hydroxy-14,15-dinorlabdan-7-one **53** (250 mg), distilled 95°/0·04 mm. ν_{max} 3480 (OH);

1709 (ketone); 1157, 1104, 1060, 1036 (CO) cm^{-1}. PMR: methyls at δ 0·86, 0·88, 0·89 (triplet, J 7 Hz), 1·02, 1·27; perturbed methylene as the AB portion of an ABX system centred at 2·53. (Found: C, 77·1; H, 11·6. $C_{18}H_{32}O_2$ requires C, 77·1; H, 11·5%).

7β-Deuterio-14,15-dinorlabdan-8-ol **56**. 8-Hydroxy-14,15-dinorlabdan-7-one **53** (340 mg) in EtOH (200 ml) was refluxed with tosylhydrazine (400 mg) for 1 h. The reaction mixture was cooled and $NaBD_4$ (400 mg) was added slowly. After a further 2 h reflux the reaction mixture was diluted with water and ether extracted. PLC (2 × 30% ether–hexane) gave 7β-deuterio-14,15-dinorlabdan-8-ol **56** (70 mg). ν_{max} 3420 (OH); 2175, 2140 (CD); 1152, 1079, 1022, 954, 928, 913 (fingerprint region) cm^{-1}. PMR: methyls at δ 0·79, 0·79, 0·86, 0·89 (triplet, J 7 Hz), 1·14. *m/e* 269 (M^+).

7β-Deuterio-14,15-dinorlabd-8(17)-ene **57**. 7β-Deuterio-14,15-dinorlabdan-8-ol **56** (30 mg) in pyridine (1·5 ml) was treated at r.t. for 15 min with thionyl chloride (1 drop). Work up by pouring into iced-water, ether extraction and washing the ethereal layer with dil HCl and water, followed by drying, gave an oil which was purified on $AgNO_3$–PLC (hexane) to give 7β-deuterio-14,15-dinorlabd-8(17)-ene **57** (20 mg). ν_{max} 3075, 1635, 1401, 888 ($C=CH_2$); 2175, 2135 (CD) cm^{-1}. PMR: methyls at δ 0·68, 0·81, 0·84 (triplet J 7 Hz), 0·88; $C=CH_2$ 4·50, 4·79; there was no multiplet at δ 2·37. *m/e* 251 (M^+).

7β-Deuterio-8,17-epoxy-14,15-dinorlabdane **59**. 7β-deuterio-14,15-dinorlabd-8(17)-ene **57** (10 mg) in $CHCl_3$ (5 ml) was treated with m-chloroperbenzoic acid (10 mg, 85%) in $CHCl_3$ (2 ml) for 4 h at r.t. PLC (5% ether–hexane) gave 7β-deuterio-8,17-epoxy-14,15-dinorlabdane **59** (8 mg) ν_{max} 3030, 1485, 973, 831, 792 (epoxide); 2175, 2145 (CD) cm^{-1}. PMR: methyls at δ 0·79, 0·83, 0·85 (triplet, J 7 Hz), 0·89, epoxide protons as an AB system H_A 2·70 (long range coupled, $J_{1,H}$ 1·5 Hz), H_B 2·45 (J_{AB} 4 Hz). *m/e* 267 (M^+).

7α-Deuterio-14,15-dinorlabdan-8-ol **60**. 8-Hydroxy-14,15-dinorlabdan-7-one **53** (190 mg) was refluxed with tosylhydrazine (190 mg) in dioxan (40 ml, dried over sodium, refluxed with LAH and distilled there from) for 1 h. The reaction mixture was cooled and D_2O (1 ml) added. $NaBH_4$ (200 mg) was then added portionwise and the mixture refluxed for a further 2 h. Work up as for the previous tosylhydrazone reduction followed by PLC (2 × 30% ether–hexane) gave: 7α-deuterio-14,15-dinorlabdan-8-ol **60** (20 mg). ν_{max} 3390 (OH); 2130, 2115 (CD); 1153, 1079, 966, 932, 911 (CO) cm^{-1}. PMR: methyls at δ 0·79, 0·79, 0·86, 0·89 (triplet, J 7 Hz), 1·14. *m/e* 269 (M^+).

7α-Deuterio-14,15-dinorlabd-8(17)-ene **61**. 7α-Deuterio-14,15-dinorlabdan-8-ol **60** (18 mg) was dehydrated as for 7β-deuterio-14,15-dinorlabdan-8-ol **56**. Purification on $AgNO_3$–PLC (hexane) gave 7α-deuterio-14,15-dinorlabd-8(17)ene **61** (12 mg). ν_{max} 3080, 1639, 1401, 884 ($C=CH_2$); 2130, 2110 (CD) cm^{-1}. PMR: methyls at δ 0·68, 0·81, 0·84 (triplet, J 7 Hz), 0·88: $C=CH_2$ 4·50, 4·79; 7β H 2·34 (multiplet, W ½ 8 Hz). *m/e* 251 (M^+).

7α - Deuterio - 8,17 - epoxy - 14,15 - dinorlabdane **62**. Epoxidation of 7α-deuterio-14,15-labd-8(17)-ene **61** (10 mg) as for 7β-deuterio-14,15-labd-8(17)-ene **57** followed by PLC (5% ether–hexane) gave 7α-deuterio-8,17-epoxy-14,15-dinorlabdane **62** (5 mg). ν_{max} 3030, 1485, 970, 830, 798 (epoxide); 2125, 2110 (CD) cm^{-1}. PMR: methyls at δ 0·79, 0·83, 0·85 (triplet, J 7 Hz), 0·89; epoxide protons as an AB system H_A 2·70, H_B 2·45 (J_{AB} 4 Hz). *m/e* 267 (M^+).

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