# Structure and Synthesis of a New Ketone from *Cedrus* Species; Some New Constituents of *C. atlantica* Manet

By **David R. Adams, Surendra P. Bhatnagar,** and **Richard C. Cookson,** * Department of Chemistry, The University, Southampton SO9 5NH

Details are given of the structure and two syntheses of a new C_{12} ketone [4-(4-methylcyclohex-3-enyl)pent-3-en-2-one] isolated from the essential oils of *Cedrus atlantica* Manet and *C. deodara* Loud. The absolute configuration of the C_{12} ketone follows from the synthesis of the natural enantiomorph by acetylation of (+)-*p*-mentha-1,8-diene at C-9. The presence of deodarone [2.2.6-trimethyl-6-(4-methylcyclohex-3-enyl)tetrahydro-4-pyrone] in *Cedrus atlantica* is reported for the first time and clear proof of its structure is presented by dehydration to α-atlantone [2-methyl-6-(4-methylcyclohex-3-enyl)hepta-2.5-dien-4-one]. Other new constituents of *Cedrus atlantica* include α-caryophyllene alcohol. obtained for the first time as a natural product. epi-β-cubenol. α-ionone. and two new epoxides, epoxy-β-himachalene and *epi*-epoxy-β-himachalene (2.4a.5.6.7.8.9.9a-octahydro-3.5.5.9-tetramethyl-9,9a-epoxy-1*H*-benzocycloheptene).

IN a preliminary note [1] we described the structure and two syntheses of a new ketone (1) isolated from the essential oils of *Cedrus atlantica* Manet and *C. deodara* Loud. We now report the details of these syntheses and

(1)   (2)
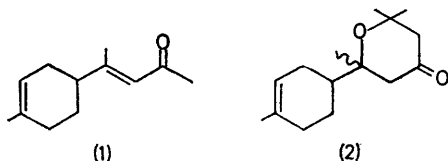
further results on the oxygenated fraction of the essential oil of *C. atlantica* Manet, widely used in the perfumery industry. The wood and oil of various *Cedrus* species have been investigated by several workers [2-4] and it has been suggested,[4] at least for *C. deodara*, that all the known sesquiterpene constituents have been derived from *cis*-farnesyl pyrophosphate, either by a 1,6-cyclisation (bisabolane type) or a 1,11-cyclisation (himachalane and

longibornane types). The isolation of deodarone with the suggested novel tetrahydro-γ-pyrone structure (2), drawn up on the basis of the bisabolane skeleton, prompted us to undertake an analysis of the oxygenated compounds of the essential oil of *C. atlantica* Manet, for reasons which will become clear.

Steam distillation of either the wood and stumps or sawdust of *C. atlantica* Manet, the so-called Atlas Cedar, affords 3—5% of essential oil, the commercial ' Atlas Cedarwood oil '. Chromatography of this oil (20.4 g) on silica gel gave four fractions including an oxygenated fraction (4.2 g) (see Experimental section). This fraction was shown to consist of *ca.* eleven components when subjected to analytical g.l.c. on a 5% SE 30 column (Figure), temperature programmed from 130 to 240 °C at 4° min⁻¹. The components shown in the Table were isolated by a combination of preparative t.l.c. and preparative g.l.c. (see Experimental section) and, where

[1] D. R. Adams, S. P. Bhatnagar, R. C. Cookson, and R. M. Tuddenham, *Tetrahedron Letters*, 1974, 3903.

[2] G. S. Krishna Rao, Sukh Dev, and P. C. Guha, *J. Indian Chem. Soc.*, 1952, **29**, 721.

[3] B. S. Pande, S. Krishnappa, S. C. Bisarya, and Sukh Dev, *Tetrahedron*, 1971, **27**, 841.

[4] R. Shankaranarayanan, S. Krishnappa, S. C. Bisarya, and Sukh Dev, *Tetrahedron Letters*, 1973, 427.

indicated, were identified from their spectral data, including when possible comparison with published values. The structure of component (b) was confirmed by two
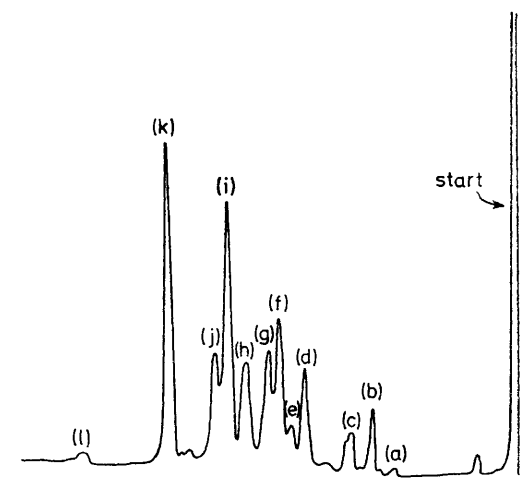
G.l.c. analysis of oxygenated terpene fraction 3 from Atlas Cedarwood oil; 5% SE 30 column; 130—240 °C at 4 min⁻¹

syntheses. Each component isolated gave a single peak on two different analytical columns (5% SE 30 and 5% Carbowax).

Peak	Compound	Approx. % in oil	Identified by (spectra)	Ref.
(a)	α-Ionone	0.1	mass	5
(b)	New ketone	0.8	mass, n.m.r., i.r.	
(c)	Unknown	1.0	(Mixture)	
(d)	Unknown	1.0		
(e)	α-Caryophyllene alcohol	0.4		8—10
(f)	Epoxy-β-himachalene	2.0		12
(g)	epi-Epoxy-β-himachalene	2.0		12
(h)	epi-β-Cubenol	2.2	mass, m.n.r., i.r.	13
(i)	Deodarone	3.8		4
(j)	cis-Atlantone	1.6		3
(k)	trans-Atlantone	4.6		3
(l)	Unknown	0.2		

Component (a) was tentatively identified as α-ionone on the basis of its mass spectrum [5] (see Experimental section). Component (b) ($[\alpha]_D^{20}$ +25° in CHCl₃) has M^+ 178 ($C_{12}H_{18}O$). Its n.m.r. spectrum (100 MHz) shows τ 4.04br (1H, s), 4.61br (1H, m), and 7.7—8.7br (m) on which are superimposed 7.95 (s) and 8.36br (s) (16H). Its i.r. spectrum shows absorptions characteristic of an αβ-unsaturated ketone (1 690 cm⁻¹) and a C=C bond (1 613 cm⁻¹). Its u.v. spectrum confirms the presence of an unsaturated ketone [$\lambda_{max.}$ (hexane) 237 nm (ε 9 500)]. These data, together with the mass spectrum (see Experimental section) support the assigned structure (1), which has been confirmed by two syntheses.

Low temperature acylation of isoprene with acetyl chloride in the presence of tin(iv) chloride and subsequent dehydrochlorination of the intermediate chloro-ketone furnished the dienone (3). Treatment of this crude dienone (3) with isoprene in the presence of aluminium chloride gave the mixture of cis- and trans-(±)-ketone (1) in the ratio 10 : 90, in 40% yield based on acetyl

[5] J. G. Grasselli, ' C.R.C. Atlas of Spectral Data and Physical Constants for Organic Compounds,' 1973, B-620.

chloride (Scheme 1). Selective addition at the terminal double bond of the dienone (3) had taken place without any evidence of the 1,3-substituted (' meta ') adduct nor of adducts formed by addition at the C-3 double bond of the dienone (3), through the combination of favourable electronic and steric factors.

An alternative synthesis involving acylation of (+)-p-mentha-1,8-diene (limonene) with acetyl chloride at low temperature and subsequent dehydrochlorination gave the (+)-ketone in an estimated yield of 30% (g.l.c.) (Scheme 2). The other major monoacylation products in this reaction were the non-conjugated ketone (6) (22%) and the conjugated ketone (7) (28%), identified by their spectral properties. This synthesis establishes the absolute configuration of the new ketone as (5), corresponding to that of (+)-p-mentha-1,8-diene (4). Pure samples of compounds (5)—(7) were obtained by preparative g.l.c., and although (5) had a pleasant odour
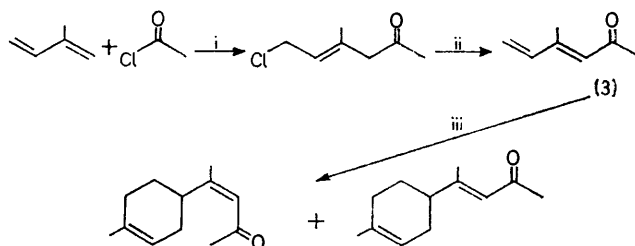
Scheme 1   Reagents: i, SnCl₄, CH₂Cl₂, −78 °C; ii, LiF, Li₂CO₃, Me₂N·CHO, 120 °C; iii, isoprene, AlCl₃, CH₂Cl₂, 20 °C

similar to that of the oil, (6) and (7) had intense rose-like odours.

The possibility that the C_{12} ketone (5) might have been formed from (+)-atlantone (8) during isolation of the
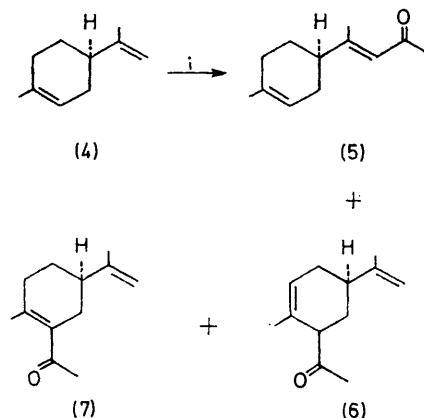

Scheme 2   Reagents: i, AcCl, SnCl₄, CH₂Cl₂, 100 °C; then LiF, Li₂CO₃, Me₂N·CHO, 120 °C

oil by steam distillation seemed to be supported by the claim [6] that ' acetyldipentene ' (1) is produced by treatment of atlantone with alcoholic alkali. However, in our hands, treatment of atlantone with alcoholic 3% potassium hydroxide for 10 min gave only methyl 4-methylcyclohex-3-enylketone (9), with no trace of (1).

[6] J. L. Simonsen and D. H. R. Barton, ' The Terpenes,' vol. 3, Cambridge University Press, 1952, p. 199.

Furthermore, the reported b.p. of ' acetyldipentene ' is lower than the b.p.s of our samples of this compound. Compound (9) showed spectral data identical with those of a synthetic [7] sample and had the same g.l.c. retention time (co-injection) on 5% SE 30 and 5% Carbowax columns (120 °C). The fact that the atlantone from the oil is largely racemised also tells against its partial conversion into (1) during isolation [unless the reverse aldol reaction is faster than enolisation of (8) and (9)].

(8)   (9)
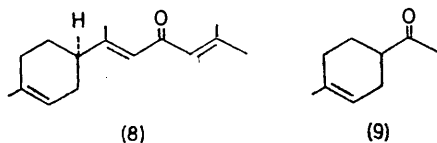
Component (e) was identified as α-caryophyllene alcohol (10) by a comparison of its m.p. and spectral data

(10)   (11)   (12)
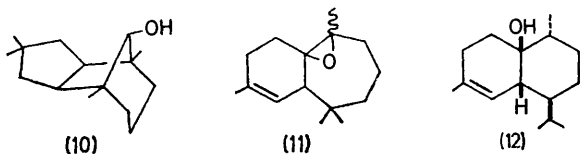
with those published.[8-10] Although this alcohol has been synthesised by several workers [8,9] and is obtained as a rearrangement product of humulene by treatment with aqueous sulphuric acid, it has not apparently, until now, been isolated as a natural product. It seems unlikely that the conditions of steam-distillation of the wood or chromatography of the oil on grade I silica gel would be acidic enough to induce rearrangement of humulene [8,9] to α-caryophyllene alcohol: indeed humulene has been reported [11] to be eluted from grade I silica gel without any mention of rearrangement. We suppose therefore that the alcohol (10) is present in the wood, rather than being formed from humulene during isolation.

Components (f) and (g) were shown to be isomers with almost identical spectral properties. Both had M^+ 220 ($C_{15}H_{24}O$) and similar fragmentation patterns (see Experimental section). The n.m.r. data indicated an olefinic proton (τ 4.71), a vinylic methyl at [8.28br (d)], a methyl group adjacent to oxygen (8.75), and two tertiary methyl groups [9.04 (s) and 9.15 (s)]. The i.r. spectrum indicated an oxiran system ($\nu_{max.}$ 800, 900, 910, and 1 230 cm^{-1}). These data are consistent with the structure (11). Treatment of compound (11) [either (f) or (g), named as epoxy-β-himachalene * and epi-epoxy-β-himachalene, respectively] with lithium aluminium hydride in ether at 25° furnished β-himachalene, identified by comparison of its mass spectrum with that published.[12]

Component (h) had spectral properties identical with those reported for epi-cubenol (12), isolated previously [13] from commercial cubeb oil.

* Isolation of an epoxyhimachalene was reported by P. Teisseire at the 5th International Congress on Essential Oils, Sao Paulo, October 1971.

[7] E. F. Lutz and G. M. Bailey, J. Amer. Chem. Soc., 1964, 86, 3899.

[8] E. J. Corey and S. Nozoe, J. Amer. Chem. Soc., 1965, 87, 5733.

Component (i) had spectral data identical with those reported for deodarone (2), a novel tetrahydro-γ-pyrone first isolated from C. deodara by Sukh Dev and his co-workers.[4] Although some chemical evidence for the structure (2) was presented [treatment of atlantone with alkaline hydrogen peroxide and exposure of the resultant diepoxide to aqueous 10% phosphoric acid at ca. 60 °C for 40 h gave a mixture of keto-alcohols which was acetylated; treatment of the product with calcium in ammonia was reported to give deodarone as one of the products], it seemed to us that more definite proof could be provided by an acid-catalysed double β-elimination of the ether oxygen from the tetrahydropyrone ring to form atlantone. In fact deodarone in methylene chloride with a catalytic amount of toluene-p-sulphonic acid at 20 °C was completely transformed into atlantone within 30 min. The ^{13}C n.m.r. spectrum of deodarone was in agreement with the proposed structure [4] (2) and showed the presence of two stereoisomers.

EXPERIMENTAL

I.r. spectra of solutions in carbon tetrachloride were recorded on a Perkin-Elmer 157 grating spectrometer. N.m.r. spectra were obtained at 60 MHz on a Perkin-Elmer R-12 spectrometer and at 100 MHz on a Varian HA 100 spectrometer for solutions in carbon tetrachloride with tetramethylsilane as internal standard. Mass spectra were obtained on an A.E.I. MS 12 instrument at 70 eV and from the P.C.M.U., Harwell. Analytical g.l.c. was performed on a Pye 104 chromatograph with (a) 2 m × 4 mm glass columns containing 5% silicone oil SE 30 on 80—100 mesh Diatomite C (for the oil, temperature programmed from 130 to 240 °C at 4° min^{-1}) and, (b) 5% Carbowax 20 M on 80—100 mesh Diatomite C, with nitrogen as carrier gas. Preparative g.l.c. was carried out on a Pye 105 preparative chromatograph with a 3 m × 6 mm glass column containing 15% SE 30 on 60—72 mesh Diatomite C (temperature programmed from 130 to 240 °C at 3° min^{-1}) with nitrogen as carrier gas. Silica gel used for column chromatography was B.D.H. grade I 60—120 mesh. Analytical t.l.c. was performed on 20 cm × 5 cm plates with 0.5 mm thickness Merck silica gel HF 256 + 366 (type 60). Preparative t.l.c. was performed on 20 cm × 20 cm plates with 1 mm thickness Merck silica gel PHF 254 + 366 and light petroleum–ethyl acetate (7 : 3) as solvent system. Light petroleum refers to the fraction of b.p. 40—60°.

Atlas Cedarwood oil (20.4 g) (supplied by R. C. Treatt & Co. Ltd., Bury St Edmunds) was chromatographed over silica gel (800 g) and eluted as follows: fraction 1, with light petroleum (500 ml × 5), 15 g (mainly hydrocarbons); fraction 2, with 10% chloroform–light petroleum and 20, 40, 60, and 80% chloroform (500 ml × 2 each), negligible; fraction 3, chloroform (500 ml × 2), 0.1 g; fraction 4, 10% ether–chloroform (500 ml × 2), 4.2 g; fraction 5, ether (500 ml × 4), 0.5 g. Fraction 4, which was essentially an oxygenated terpene fraction free of hydrocarbons, was shown to

[9] A. Nickon, T. Iwadare, F. J. McGuire, J. R. Mahajan, S. A. Narang, and B. Umezawa, J. Amer. Chem. Soc., 1970, 92, 1688.

[10] H. C. Hill, R. I. Reed, and M. T. Robert-Lopes, J. Chem. Soc. (C), 1968, 93.

[11] J. M. Greenwood, M. D. Solomon, J. K. Sutherland, and A. Torre, J. Chem. Soc. (C), 1968, 3004.

[12] Y. Hirose, Shitsuryo Bunseki, 1967, 15 (3—4), 162.

[13] Y. Ohta and Y. Hirose, Tetrahedron Letters, 1967, 2073.

consist of *ca.* eleven components when subjected to analytical g.l.c. on column (*a*). These components were isolated by a combination of preparative t.l.c. and preparative g.l.c. detailed in the Table.

Compound (*a*). This could not be isolated in sufficient quantity and was tentatively identified as α-ionone on the basis of its mass spectrum (similar to that of an authentic sample): *m/e* at 192 (18%, M^+), 177 (42%), 136 (40), 107 (31), 105, (35), 93 (100), 91 (28), 43 (85), and 41 (50).

Compound (*b*) (1). This showed $[\alpha]_D^{20}$ +25° in $CHCl_3$; *m/e* 178 (M^+, 39%), 43 (100%), 95, (95), 67 (53), 68 (52), 41 (52), 109 (45), 135 (42), 93 (40), 79 (39), and 120 (39%); for other spectra see main text. Microdistillation gave a sample of b.p. (bath temp.) 110° at 0.08 mmHg.

Synthesis of cis *and* trans-4-(4-*methylcyclohex-3-enyl*)*pent-3-en-2-one* (1) [*compound* (*b*)].

(*A*) 6-*Chloro-4-methylhex-4-en-2-one*. To acetyl chloride (7.8 g, 0.10 mol) in dry methylene chloride (60 ml) stirred in a nitrogen atmosphere was added anhydrous tin(IV) chloride (23.0 g, 0.09 mol) in methylene chloride (40 ml). After 15 min the solution was cooled to below −60 °C (acetone–solid carbon dioxide) and isoprene (8.5 g, 0.12 mol) in methylene chloride (50 ml) was added dropwise in 45 min. The mixture was kept at −60 °C for a further 30 min, then cold pyridine (35 ml, 0.40 mol) was added and the cold solution filtered. The filtrate was washed with 10% hydrochloric acid (5 × 100 ml), saturated sodium hydrogen carbonate solution (4 × 100 ml), and saturated brine (3 × 100 ml), and then dried (Na_2SO_4), filtered, and evaporated to give a clear yellow liquid (15.5 g), 6-chloro-4-methylhex-4-en-2-one [one peak on g.l.c. analysis, column (*a*), 130 °C; column (*b*), 130 °C] contaminated with isoprene polymer; *m/e* 148—146 (M^+, 28%), 133 (25%), 131 (75), 109 (8), 111 (23), 110 (66), 95 (21), 67 (63), 43 (100), and 41 (50); τ 8.36 (3H, d, *J* 1.4 Hz, 4-Me), 7.96 (3H, s, 1-H), 6.96 (2H, s, 3-H), 5.98 (2H, d, *J* 8.0 Hz, 6-H), and 4.51 (1H, t, *J* 8.0 Hz, 5-H); $\nu_{max.}$ 1 715s and 1 660m cm⁻¹.

4-*Methylhexa-3,5-dien-2-one* (3). 6-Chloro-4-methylhex-4-en-2-one (unpurified from the acylation of isoprene) (8.0 g) in dimethylformamide (DMF) (20 ml) was added to a stirred mixture of lithium carbonate (11.1 g, 0.15 mol) and lithium fluoride (3.9 g, 0.15 mol) in DMF (20 ml) maintained at 120 °C under nitrogen. The mixture was stirred for a further 1 h at this temperature, then cooled, poured into ice-cold 10% hydrochloric acid (5N; 200 ml), and extracted with ether (4 × 100 ml). The combined extracts were washed with dilute hydrochloric acid (5N; 3 × 100 ml), saturated sodium hydrogen carbonate solution (2 × 50 ml), and saturated brine (3 × 50 ml), dried (Na_2SO_4), and evaporated to yield an oil (5.7 g, 98%), b.p. 58—60° at 14 mmHg. G.l.c. analysis of this material [column (*a*); 100 °C] showed the presence of *cis*- and *trans*-isomers in the ratio 30 : 70, respectively; *m/e* 110 (M^+, 71%), 108 (37%), 95 (77), 67 (100), 65 (25), 43 (69), 41 (69), and 39 (45); τ (*trans*-isomer) 7.85br (6H, s, 1-H and 4-Me), 3.90—4.70 (3H, m, 3- and 6-H), and 3.65 (1H, dd, *J* 10 and 18 Hz, 5-H); τ (*cis-isomer*) 8.05br (3H, s, 4-Me), 7.87 (3H, s, 1-H), 4.0—4.7 (3H, m, 3- and 6-H), and 2.31 (1H, dd, *J* 10 and 18 Hz, 5-H); $\nu_{max.}$ 1 682s, 1 623m, and 1 580s cm⁻¹.

The ketone (1). To anhydrous powdered aluminium chloride (550 mg, 4 mmol) and dry methylene chloride (60 ml) stirred under nitrogen was added 4-methylhexa-3,5-dien-2-one (3) (600 mg, 5.5 mmol) in methylene chloride (60 ml) over 30 min. In 30 min the aluminium chloride dissolved and isoprene (1.87 g, 27 mmol) in methylene chlor-

ide (100 ml) was added over 8 h. The mixture was stirred for a further 8 h and poured into cold 10% hydrochloric acid (200 ml), and the aqueous mixture was extracted with light petroleum (5 × 100 ml). The combined extracts were washed with 10% hydrochloric acid (1 × 100 ml), saturated sodium hydrogen carbonate solution (3 × 100 ml), and saturated brine (2 × 100 ml), dried (Na_2SO_4), and evaporated to leave a yellow liquid (1.70 g), which was chromatographed on a silica gel column (100 g). Elution with 3.5% diethyl ether–light petroleum afforded a mixture of *cis*- and *trans*-isomers of the ketone (1) (580 mg, 3 mmol, 59%) in the ratio 10 : 90, respectively [g.l.c. analysis, column (*a*), 160 °C]. B.p. and spectral data were the same as for the natural product.

(*B*) Acetyl chloride (3.9 g, 0.05 mol) in methylene chloride (30 ml) was added to tin(IV) chloride (11.7 g, 0.045 mol) in methylene chloride (30 ml) under anhydrous conditions in an atmosphere of nigrogen; the solution was cooled to −78 °C after stirring for ½ h at room temperature, and then added dropwise to a solution of (+)-*p*-mentha-1,8-diene (9.0 g, 0.07 mol) in methylene chloride (40 ml) cooled to −100 °C in an atmosphere of nitrogen over a period of 2 h. After a further ½ h at this temperature, pyridine (20 ml) in ether (500 ml) was added, the cold mixture was filtered, and the residue was washed with ether. The filtrate was washed with 5N-hydrochloric acid (3 × 200 ml) and saturated brine until neutral, dried (Na_2SO_4), filtered, and evaporated to yield an oil (14.0 g).

This oil was taken up in DMF (20 ml) and added dropwise to a mixture of lithium fluoride (3.9 g, 0.15 mol) and lithium carbonate (11.1 g, 0.15 mol) in DMF (50 ml) stirred in nitrogen at 120 °C, and the resultant mixture was stirred at this temperature for 2 h and then at room temperature for 12 h. The mixture was filtered, the residue washed with ether, and the filtrate poured into ice-cold 5N-hydrochloric acid (300 ml) and then extracted with ether (4 × 100 ml). The extracts were combined, washed successively with dilute hydrochloric acid and saturated brine, dried (Na_2SO_4), filtered, and evaporated to yield an oil (12.6 g). This oil was shown to consist of three major components (5)—(7) [analytical g.l.c.; column (*a*); 130—200 °C at 4° min⁻¹] in the proportion of 30 : 22 : 28, respectively. Pure samples were separated by preparative g.l.c. on an SE 30 column (130—240 °C at 3° min⁻¹).

Component 1 (5), $[\alpha]_D^{20}$ +30° ($CHCl_3$) was found identical with the ketone (1). The b.p. and spectral data were similar to those of the natural product. This synthesis establishes the absolute configuration as shown in (5), corresponding to that of (+)-*p*-mentha-1,8-diene.

Component 2 (6) showed *m/e* 178 (M^+, very small), 93 (100%), 43 (89), 107 (50), 91 (39), 41 (41), 135 (39), 79 (30), 77 (30), 105 (19), 134 (13), 67 (11), and 119 (11); τ (100 MHz) 5.35br (2H, s), 4.45br (1H, s), and 7.7—8.7br(m) [on which is superimposed 7.95 (s), 8.28 (s), and 8.36 (s)] (15H); $\nu_{max.}$ 1 710s and 1 620m cm⁻¹.

Component 3 (7) showed *m/e* 178 (M^+, 15%), 43 (100%), 41 (36). 95 (36), 135 (32), 93 (29), 67 (27), 68 (24), 91 (24), 107 (24), 79 (21), 77 (18), 53 (18), 105 (15), and 121 (15); τ (100 MHz) 5.35br (2H, s) and 7.7—8.7br (m) [on which is superimposed 7.95 (s), 8.19 (s), and 8.25 (s)] (16H); $\nu_{max.}$ 1 691s and 1 613s cm⁻¹.

Treatment of atlantone (8) *with dilute alcoholic potassium hydroxide*. Atlantone (5 mg) was stirred in ethanol (5 ml) while alcoholic 3% potassium hydroxide (1 ml) was added. The reaction was stopped after 10 min and the product worked up as usual. The residue showed a single peak

[g.l.c. analysis columns (a) and (b) at 120 °C] and had spectral data identical with those of a synthetic sample [7] of 4-acetyl-1-methylcyclohex-1-ene (9); co-injection showed a single g.l.c. peak [columns (a) and (b) at 120 °C].

Component (e) (10). This was identified as α-caryophyllene alcohol by comparison of its m.p., and i.r., n.m.r.,[8,9] and mass spectral data [10] with those published.

Component (f) (11). This showed m/e 220 (M^+, 50%), 205 (11%), 177 (6), 163 (7), 159 (5), 151 (30), 150 (11), 137 (15), 135 (15) 121 (11), 119 (8), 111 (15), 110 (100), 95 (40), 94 (16), 93 (13), 91 (15), 81 (11), 79 (11), 77 (13), 69 (28), 55 (18), 43 (17), and 41 (19); τ 4.71 (1H), 8.28br (3H, d), 8.75 (3H, s) and 9.04 (s) and 9.15 (s) (6H); $ν_{max.}$ 800s, 900s, 910s, and 1 230 cm^{-1}.

Component (g) (11). This showed m/e 220 (M^+, 30%), 205 (8%), 161 (15), 151 (23), 150 (9), 137 (12), 135 (12), 121 (11), 119 (8), 111 (15), 110 (100), 109 (18), 95 (48), 94 (21), 93 (18), 91 (24), 81 (15), 79 (15), 69 (42), 67 (9), 55 (34), 53 (12), 43 (33), and 41 (36); n.m.r. and i.r. data were identical with those of component (f).

Treatment of components (f) and (g) with lithium aluminium hydride. Component (f) (4.4 mg, 0.02 mmol) in dry ether (1 ml) was added to lithium aluminium hydride (0.116 mg, 0.03 mmol) in dry ether (1 ml). The mixture was left at room temperature for 48 h; the excess of reagent was then destroyed with aqueous sodium sulphate and the organic layer separated, dried (Na$_2$SO$_4$), and evaporated. The residue showed a single peak on g.l.c. analysis [column (a); 150 °C] and was characterised as β-himachalene on the basis of the identity of its mass spectrum with the published one:[12] m/e 204 (M^+, 64.5%), 189 (10%), 168 (9), 161 (23), 148 (16), 147 (26), 135 (45), 134 (38), 121 (42), 119 (100), 105 (45), 93 (39), 91 (39), 77 (32), 69 (16), 55 (26), and 41 (42). A similar experiment with component (g) gave identical results.

Component (h) (12). This was characterised as *epi*-cubenol by comparison of its n.m.r. and i.r. spectral data with those published; [13] m/e 222 (M^+, very small), 204 (44%), 189 (6), 179 (20), 161 (83), 159 (23), 133 (41), 119 (100), 105 (67), 97

(8), 95 (18), 94 (6), 93 (26), 91 (30), 82 (21), 81 (25), 79 (18), 77 (18), 69 (20), 67 (12), 65 (8), 55 (28), 53 (12), 43 (25), and 41 (44).

Component (i) (2). This showed m/e 236 (M^+, very small), 218 (2%), 141 (42), 134 (11), 121 (12.6), 120 (12.6), 119 (10.5), 105 (8), 95 (15), 93 (10), 91 (7), 85 (23), 83 (100), 79 (11), 77 (8), 68 (8), 67 (12), 59 (10), 55 (15), 53 (8), 43 (72), and 41 (17); τ (100 MHz) 4.74br (1H, s), 8.84 (3H, s), 8.72 (6H, s), 8.38br (3H, s), 7.72 (2H, s), and 7.5—8.27 (9H, m); $ν_{max.}$ 1 725s, 1 020m, and 1 260—1 150 cm^{-1}; δ$_C$ (22.63 MHz, Fourier transform; CDCl$_3$ solution, p.p.m. to lower field than internal Me$_4$Si) 23.27 (q) and 23.79 (q) (4'-Me of the two stereoisomers), 23.53 (t, C-6' both isomers), 25.41 (t) and 26.00 (t) (C-2'), 26.32 (t) and 26.45 (t) (C-5'), 30.68 (q) and 30.94 (q) (6-Me), 32.17 (q, 2-Me$_2$), 45.88 (d) and 46.01 (d) (C-1'), 47.05 (t) and 47.70 (t) (C-5), 51.41 (t) and 51.54 (t) (C-3), 74.28 (s, C-6), 94.00 (s, C-2), 120.36 (d) and 120.56 (d) (C-3'), 133.81 (s) and 133.94 (s) (C-4'), and 209.01 (s, C-4). On addition of Eu(fod)$_3$ (100 mg) the main differences in the spectrum were in the signals from C atoms near the carbonyl oxygen: that from C-4 split into two at 208.42 and 222.14, those from C-3 moved to 55.57 and 55.83, and those from C-5 to 50.37 and 51.02 p.p.m.

Acid-catalysed opening of the γ-pyrone ring of deodarone (2). Deodarone (5 mg, 0.021 mmol) in dry methylene chloride (3 ml) was stirred at room temperature, and toluene-*p*-sulphonic acid (1 mg) was added. After 30 min the mixture was worked up as usual and the residue showed one single peak on g.l.c. analysis [column (a) at 168 °C]. The mass spectrum of this compound was identical with that of authentic atlantone. Co-injection with an authentic sample of atlantone gave a single peak on g.l.c. [column (a), 168 °C].