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STUDIES IN SESQUITERPENES—LIII

DEODARONE AND ATLANTOLONE, NEW SESQUITERPENOIDS FROM THE WOOD OF *CEDRUS DEODARA* LOUD†‡

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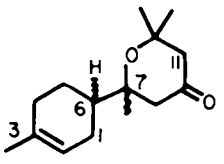
Abstract—Isolation and structure determination of a novel bisabolane-based tetrahydro-γ-pyrone from the essential oil from the wood of *Cedrus deodara* Loud. is described. The compound, which has been named deodarone, has been chemically correlated with the sesquiterpene ketone, atlantone. An hydroxy ketone, designated as atlantolone, has also been isolated. This compound appears to be the precursor of the new C_{15}-ketone, recently described as a component of the essential oil of *Cedrus atlantica* Manet.

In extension of our earlier investigations[1] on the essential oil from the wood of *Cedrus deodara* Loud., we report on the isolation and structure determination of a novel bisabolane-based tetrahydro-γ-pyrone (1), now named deodarone, and, the hydroxy ketone (2), which we designate atlantolone.



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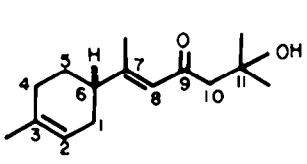

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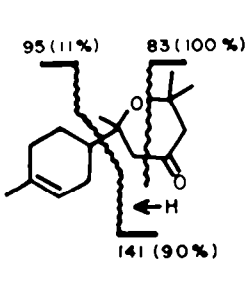
Deodarone[2]

The early atlantone-containing cuts from the fractional distillation[1] of *Cedrus deodara* essential oil contain deodarone, which is readily separated by silica gel column chromatography. With respect to deodarone, *cis*- and *trans*-atlantone[3] have RRT of 0.77 and 1.13 respectively (column: 300 × 0.6 cm, 5% diethyleneglycol polysuccinate on Chromosorb W; 185°). Deodarone is present to the extent of ~2% in the essential oil and has an intense odour characteristic of the wood.

Deodarone analyses for $C_{15}H_{24}O_2$ (M^+, *m/e* 236) and displays in its IR spectrum absorptions for C=O (1725 cm^{-1}) and C=C (1625 cm^{-1}), but no OH band. The compound remains unaffected by 10% alc. KOH (3 hr, reflux; N_2) and hence, an ester or δ-lactone grouping is ruled out. Its PMR spectrum displays signals assignable to: three Me–$\overset{|}{C}$–O (3H, s, 1.16 ppm; 6H, s, 1.28 ppm), Me–$\overset{|}{C}$=C (3H, bs, 1.62 ppm), –$\overset{|}{C}$–CH_2–C=O (~2H, s, 2.28 ppm), Me–$\overset{|}{C}$=$\overset{|}{C}$H–CH_2– (1H, ill-resolved m, 5.26 ppm, W_H = 8 Hz). Since, the PMR spectrum does not show any signal for HC=O, deodarone must be a ketone and, from the intensity of absorption for C=O in the IR[4] (ε, 335; CCl_4) or UV (λ_{max}, 285 nm, ε, 20), only one such group is present. Hence, the second oxygen function must occur as an ether.

From its UV absorption (no strong absorption above 220 nm) it is clear that deodarone is not an αβ-unsaturated ketone. That, in all likelihood, the ethylenic linkage is also not located βγ to the carbonyl, became evident from the fact that, deodarone remained unchanged (UV) on exposure to 1% t-BuOK in t-BuOH (reflux, 7 hr; attempted equilibration with αβ-isomer). Deodarone undergoes no change on treatment with Zn and AcOH,[5] and hence, the ether linkage cannot be located α to the carbonyl. On deuterium exchange (MeOK in MeOD, reflux, 10 min; five successive treatments), deodarone incorporated 4D atoms (M^+, *m/e* 240, PMR: loss of 4H signals in the 2.10–2.40 ppm region), revealing the presence of the unit: –CH_2–CO–CH_2–.

All the known constituents of the *Cedrus deodara* wood essential oil appear to have been derived from *cis*-farnesyl pyrophosphate, either by a 1,6-cyclization (bisabolane type) or 1,11-cyclization (himachalane, longibornane types). Arguing, that deodarone also may belong to either one of these types, it was found that, only on the basis of a bisabolane skeleton (1,6-cyclization), can one draw up a working structure (1), meeting all the structural requirements disclosed earlier. This structure (1) is clearly supported by electron-impact-induced fragmentation of deodarone, the main features of which are depicted in 3. This fragmentation is borne out by the mass spectrum of deodarone-d_4, which displays in its mass spectrum these fragment ions at *m/e* 84, 95 and 145, as required.



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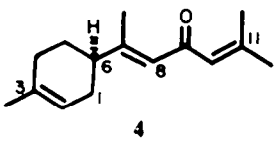

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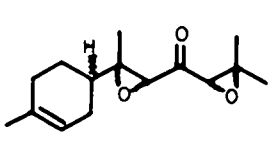

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†Communication No. 2014, National Chemical Laboratory, Poona, India.

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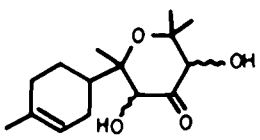

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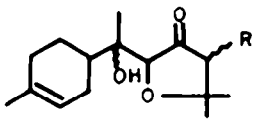
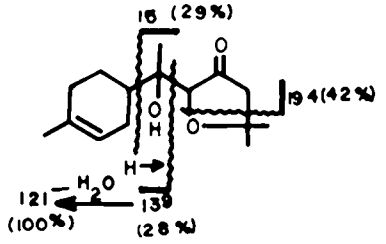


7: R = OH
8: R = H



9

Chemical evidence in favour of **1** was obtained by a direct correlation with *trans*-atlantone (**4**)[1,6] in two ways.

In the first sequence of reactions, atlantone was exposed to alkaline H_2O_2[7] to yield the expected diepoxide **5**; this product is possibly a mixture of diastereoisomers, though its PMR spectrum is unexpectedly clean (Experimental). It is reasonable to expect that in the presence of a strong aq acid, compound **5** will first cleave to an α-glycol, hydroxyls of which are well-placed for participation during the second oxirane ring opening, thus, hopefully generating a tetrahydropyran (and/or tetrahydrofuran) ring-system.[8] In practice, compound **5**, on being stirred with 10% H_3PO_4 aq at ~60° for 18 hr, yielded a complex mixture of keto alcohols from which a TLC pure fraction, analysing for $C_{15}H_{24}O_4$ (M^+, *m/e* 268), could be isolated. However, from its spectral data (IR, PMR, Mass) it is clear that this product is a mixture of **6** and **7** (IR: C=O 1755,[9] 1720 cm^{-1}) in which **7** predominates. This material was acetylated (Ac_2O, pyridine, 80°, 6 hr) and then subjected to the action of Ca in liquid NH_3 (for removal of OAc functions α to C=O).[10] The product, which was a mixture of two major compounds, was separated (column chromatography) to furnish a compound identical (PMR, Mass) with deodarone (**1**). The second compound, $C_{15}H_{24}O_3$ (M^+, *m/e* 252), arising from **7**, must be **8**. This structure is borne out by IR (C=O 1752 cm^{-1};[9] OH 3448 cm^{-1}), PMR (-O-CH-C=O: s, 3.57 ppm; see Experimental for other signals) and mass spectral fragmentation (see **9**).

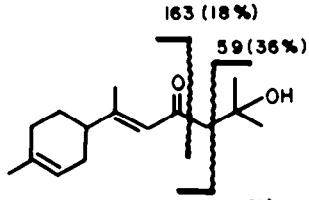
The second route, which is patterned after its possible biogenesis, proved more effective and is discussed below in connection with the structure of atlantolone (**2**). The question of stereochemistry of deodarone and its possible mode of origin in the essential oil are also briefly discussed there.

It may be pointed out here that since the publication of our preliminary communication,[2] deodarone has been isolated from the essential oil of *Cedrus atlantica* Manet[11] and its more formal syntheses have been reported.[12]

Atlantolone; stereochemistry of deodarone and its possible genesis

From the hydrocarbon-free essential oil,[1] an hydroxy ketone ($C_{15}H_{24}O_2$; M^+, *m/e* = 236. RR_f 0.31 with respect to *trans*-atlantone; solvent: 5% EtOAc in C_6H_6; temp. 32°) has been isolated and this has the following structural features: $-\underset{|}{\overset{|}{C}}-OH$ (IR: 3390, 1145 cm^{-1}. PMR), $-\underset{|}{C}=CH-$ (Me), C=O (λ_{max} 245 nm, ϵ 13110. IR: C=O 1662 cm^{-1}; C=C 1600 cm^{-1}, absorption more intense than that of C=O, see Ref. 13. PMR: Me, 3H, bs, 2.13 ppm; C=CH, 1H, bs, 5.93 ppm), $Me_2C(-O-)$ (PMR: 6H, s, 1.19 ppm), Me-C= (PMR: 3H, bs, 1.65 ppm), $-C=CH-CH_2$ (PMR: 1H, broad unresolved signal, 5.37 ppm, W_H = 9 Hz). Bearing in mind the occurrence of atlantone (**4**) in the essential oil, these structural features suggested structure **2** for the hydroxyketone, which we name atlantolone. This structure appears to be supported by its mass spectral fragmentation (see **10**). That this is indeed the structure is borne out by the results of acid-catalyzed hydration of atlantone, discussed below.

The isolation of atlantolone from the same essential oil suggested that this hydroxyketone and/or its isomer (**11**), which may also be present in the essential oil of *Cedrus deodara* (see below) and which is known[14] to occur in nature (in *Chrysanthemum flosculosum* Linn.), may be the immediate progenitor of deodarone, as conceivably, under acid catalysis, intramolecular hydroxyl addition to the enone moiety should generate the tetrahydropyran system. Thus, it appeared of considerable interest to study acid-catalyzed hydration of atlantone, in the hope of obtaining hydroxyketones such as **2**/**11** and deodarone (**1**). As a matter of fact, divinyl ketones (cf. atlantone) have been converted to tetrahydro-γ-pyrones with $HgSO_4$–H_2SO_4 in aq. acetone.[15]



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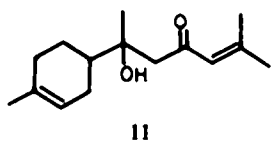

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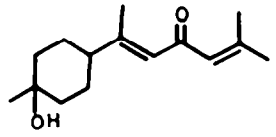

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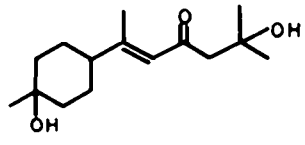

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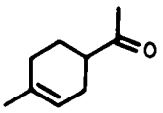

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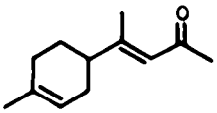


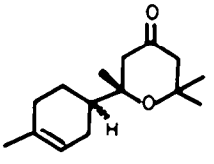
15

We find that hydration of *trans*-atlantone is best effected by $HClO_4$ aq in acetone. This system yielded a complex mixture of at least seven products having RR_f of 1.00 (deodarone), 0.88, 0.67, 0.53, 0.42, 0.30 and 0.27 (solvent: 5% EtOAc in C_6H_6; 25°), besides unchanged (~40%) atlantone (RR_f 1.17). Compounds of RR_f 1.00 and 0.67 were readily identified (IR, PMR, Mass) as deodarone and atlantolone respectively. Compounds with RR_f 0.53 and 0.42 have been assigned structures **12** and **13** respectively, on the basis of spectral and analytical data (Table 1). The material with RR_f 0.88, is clearly a mixture (~1:1) of C_7-epimers corresponding to structure **11** (Table 1). The other two compounds (RR_f 0.30 and 0.27) could not be completely separated from each other. As already stated, one of the constituents of *Chrysanthemum flosculosum* has the gross structure **11**,† now shown to be formed by the hydration of atlantone.

During this work it was found that both hydroxyketones (**2**, **11**) fragment[16] on GLC (Al column, packed with 5% diethyleneglycol polysuccinate on Chromosorb W; 160°). Thus, injection of pure **11** gave two sharp peaks, identified as mesityl oxide and Δ^1-tetrahydroacetophenone (**14**) by co-injection. Likewise, fragmentation to acetone (identified by mixed GLC) and presumably **15** occurred on GLC of pure **2**. It is conceivable that the recently isolated C_{12}-ketone (**15**)[11] arises in the essential oil from fragmentation of atlantolone (**2**) during steam-distillation and thus, may be an artefact.

Deodarone obtained by the hydration of *trans*-atlantone has $[\alpha]_D$ of the same sign and order of magnitude as that of the product isolated from the essential oil. Thus (+)-deodarone must have the same absolute stereochemistry at C_6 (as depicted in **1**) as has been established[6] for (+)-*trans*-atlantone; this is as it should be on the basis of Absolute Stereochemistry Biogenetic Rule.[17] However, since *trans*-atlantone as occurring in the essential oil is essentially racemic[6] with only a small excess (~2%) of the (+)-antipode, it is obvious that deodarone prepared from this material, and consequently the deodarone isolated from the essential oil of *Cedrus deodara* (as the two products are identical in every respect) should be racemic to the same extent.

Two stereostructures (**16**, **17**) are possible for (+)-deodarone. From a study of models (Dreidings) it is clear (cf. the most probable conformations **16a**, **17a** of the two diastereoisomers) that these stereostructures are of very comparable energy‡ and hence, during the formation of deodarone from *trans*-atlantone (under essentially equilibrating conditions) both isomers should be formed in similar quantities. And, since, the synthetic material is entirely identical with the product isolated from the essential oil, this material also should be a similar mixture§ of **16** and **17**.



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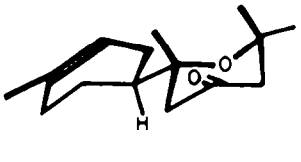


16a

†The naturally occurring compound, α-bisabololon, is levorotatory and its stereochemistry has not yet been defined.[14]

‡In fact, dihydro derivatives of **16**, **17** (assuming hydrogenation from the same face in both cases) have mirror-image relationship.

§The PMR spectrum of deodarone does not give any indication of the product being a mixture. However, it has been concluded[11] from the CMR spectrum of deodarone isolated from *Cedrus atlantica* that the material was a mixture of two stereoisomers

Table 1. Spectroscopic characteristics of keto-alcohols from hydration of atlantone

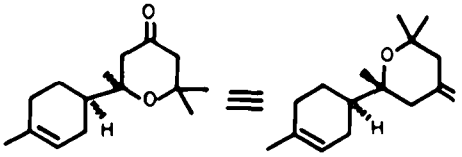
Compd.	Mol. formula	UV	IR			PMR					
		λ_{max} (nm), ε	ν_{max} (cm^{-1})			δ (ppm)					
			OH	C=O	C=C	C_{11}-Me's (s)	C_7-Me (s)	C_3-Me (s)	C_{10}-H (bs)	C_8-H (bs)	C_2-H
2 (Atlantolone)	$C_{15}H_{24}O_2$	245‡ 13,110	3390	1662	1600	1.19 1.19	2.13	1.65	-	5.93	5.37
11*	$C_{15}H_{24}O_2$	243; 10,500	3400	1670	1620	2.17 1.90	(1.11)* (1.06)*	1.60	5.96	-	5.33
12‡	$C_{15}H_{24}O_2$	266; 11,700	3400	1670	1620	2.11 1.87	2.11	1.20	5.97	5.97	-
13#	$C_{15}H_{26}O_3$	245‡ 6,090	3350	1675	1610	1.20 1.20	2.10	1.30	-	6.00	-
4 (Atlantone)[1]	$C_{15}H_{22}O$	266‡ 16,900	-	1670	1630 1610	2.10 1.85	2.10	1.63	5.90	5.90	5.33

*Unresolved multiplet.

*Epimeric pair, see text.

‡Purity ~90%.

#Purity ~70%.



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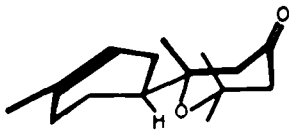

17a

The $[\alpha]_D$ of atlantolone from the essential oil is very close to the value obtained for the material prepared from atlantone, which is mostly racemic. This fact, along with the knowledge that deodarone is also considerably racemised, suggests that either these compounds are artefacts produced during steam-distillation or racemisation occurs during this process. Racemisation of **1** is readily rationalised by reversible ring-opening to **2**, followed by enolisation.

EXPERIMENTAL

All b.pts are uncorrected. Light petrol refers to the fraction b.p. 60–80°. All solvent extracts were washed with brine before drying over Na_2SO_4. Optical rotations were measured in $CHCl_3$ at room temp. (30 ± 2°) on a Perkin-Elmer Polarimeter model 141.

UV spectra were taken on a Perkin-Elmer spectrophotometer, model 350, in 95% EtOH. IR spectra were recorded as smears (liquids), on a Perkin-Elmer Infracord model 137E. PMR spectra were taken in 10% soln in CCl_4 on a Varian A-60 spectrometer; signals are recorded in δ (ppm) relative to TMS as zero. Mass spectra were determined on a CEC mass spectrometer, model 21-110B using an ionizing voltage of 70 eV and a direct inlet system; besides the molecular ion, ten most abundant ions, above *m/e* 40, are reported with their relative intensities.

GLC analyses were carried out on "Aerograph" model A-350-B using Al columns (300 × 0.6 cm) packed with 20% diethyleneglycol polysuccinate on Chromosorb W (60–80 mesh), unless stated to the contrary; H_2 was used as the carrier gas.

SiO_2-gel for column chromatography (~100, ~200 mesh) was activated at 125–130°/6–8 hr and standardised.[18] TLC was carried out on 0.3 mm layers of SiO_2-gel containing 15% gypsum (spray reagent: 1% vanillin in 30% H_3PO_4 aq or conc. H_2SO_4, heating at 120°/10 min).

Isolation of new ketones

Deodarone (**1**). The higher boiling fractions[1] (b.p. 137°/4.5 mm, n_D^{25} 1.5115–1.5120, $[\alpha]_D$ + 17 to + 8) of the essential oil from the wood of *Cedrus deodara*, which contain amongst other constituents, himachalol and some atlantone, are relatively rich in deodarone. Such a fraction (2.0 g) was chromatographed over SiO_2-gel/III (34 × 2.5 cm) with TLC monitoring (solvent: 5% EtOAc in C_6H_6):

Frac. 1	light petrol	50 ml × 15	0.723 g, mixture
Frac. 2	25% C_6H_6 in light petrol	50 ml × 8	0.101 g, *trans*-atlantone, R_f 0.52
Frac. 3	50% C_6H_6 in light petrol	50 ml × 10	0.131 g, mixture
Frac. 4	C_6H_6	50 ml × 6	0.627 g, deodarone, R_f 0.34
Frac. 5	2% MeOH in C_6H_6	50 ml × 9	0.360, mixture of alcohols

Fraction 4 was distilled to give pure deodarone: b.p. 145–148° (bath)/1.7 mm, n_D^{30} 1.4951, $[\alpha]_D$ + 6.3° (c, 0.9%). Mass: *m/e* 236 (M⁺, 4%), 141 (90%), 134 (12%), 119 (11%), 95 (11%), 85 (21%), 83 (100%), 67 (13%), 55 (20%), 43 (90%), 41 (28%). (Found: C, 76.52; H, 10.01. $C_{15}H_{24}O_2$ requires: C, 76.22; H, 10.24%).

Atlantolone (**2**). The hydrocarbon-free essential oil[1] (200 g) in light petrol (100 ml) was partitioned with 80% MeOH aq (150 ml × 5) to give a fraction (1.0 g) rich in atlantolone (TLC). This material was chromatographed on SiO_2-gel/IIB (35 × 2.5 cm) using C_6H_6 as a solvent. Initial fractions (80 ml × 20) were mixtures of atlantone and deodarone, containing increasing amounts of the new hydroxyketone. Later C_6H_6 cuts (80 ml × 4) furnished 150 mg of pure atlantolone, which was distilled: b.p. 150–155° (bath)/1 mm, n_D^{31} 1.5027, $[\alpha]_D$ + 2.87° (c, 0.49%). (Found: C, 75.93; H, 10.30. $C_{15}H_{24}O_2$ requires: C, 76.22; H, 10.24%).

Atlantone diepoxide (**5**)

To a mixture of H_2O_2 aq (30%, 10.3 ml) and atlantone (6.76 g, 0.029 mole) in MeOH (80 ml) at 0°, NaOH aq (1.2 N, 14 ml) was introduced (15 min) with stirring such that the temp. did not exceed 10°. After completion of addition, the mixture was stirred for an additional 2 hr at 15–20°, after which it was diluted with water (50 ml) and extracted with ether (50 ml × 4). Removal of solvent gave a product (7.0 g), part (3.3 g) of which was purified by IDCC[19] (SiO_2 gel/IIIB, 400 g, 45 cm × 4 cm; solvent, 5% EtOAc in C_6H_6) to give pure **5** (2.1 g): b.p. 140–145° (bath)/0.8 mm, n_D^{30} 1.4935, λ_{max} 289 nm (ϵ, 145)[20]. IR: C=O 1725 cm⁻¹, C——C[21] 1225, 913, 840 cm⁻¹. PMR: three -O-C-Me (3H singlets at 1.22, 1.32, 1.43 ppm), C-C-Me (3H, bs, 1.62 ppm), two -C(O)-CH- (2H, overlapping singlet due to diastereoisomers, 3.39 ppm), -C=CH- (1H, unresolved m, 5.27 ppm). Mass: *m/e* 250 (M⁺, 13%), 235 (42%), 123 (30%), 121 (100%), 95 (42%), (94) (40%), 93 (60%), 81 (28%), 55 (36%), 43 (92%), 41 (55%). (Found: C, 71.55; H, 8.76. $C_{15}H_{22}O_3$ requires: C, 71.97; H, 8.86%)

Conversion of **5** *into deodarone*

The above diepoxide (2.0 g) in light petrol (35 ml) was stirred at 60° for 18 hr with 10% H_3PO_4 aq (65 ml). After cooling to room temp. the mixture was diluted with water (25 ml), the organic layer separated and the aqueous phase extracted with light petrol (40 ml × 3). The combined extract, which contains essentially diols, was washed with 5% $NaHCO_3$ aq and freed of solvent to furnish a product (0.97 g), which was chromatographed over SiO_2-gel/IIA (100 × 1.8 cm) with TLC monitoring (solvent: 20% EtOAc in C_6H_6). After eluting with C_6H_6 (60 ml × 30) and 5% EtOAc in C_6H_6 (60 ml × 40), 10% EtOAc in C_6H_6 (60 ml × 12) eluted a mixture of **6**, **7**: b.p. 160–165° (bath) /1 mm, 0.24 g. PMR: -O-C-Me (3H, s, 1.03 ppm; 6H, s, 1.23 ppm), O=C-CH-C- (singlets at 3.53, 3.97 ppm), -C-CH-CH₂ (unresolved m, 5.33 ppm). Mass: *m/e* 268 (M⁺, 18%), 121 (100%). (Found: C, 67.53; H, 8.96. $C_{15}H_{24}O_4$ requires: C, 67.13, H, 9.02%). This material (0.15 g) was acetylated (Ac_2O, 6 ml; pyridine, 6 ml; 80°, 5 hr) and then subjected to reduction cleavage as follows.

Ca metal (0.3 g) was added with stirring, under anhyd conditions, to liquid NH_3 (50 ml) and after stirring for ~10 min, the above crude acetate dissolved in toluene (2 ml) was added to the deep blue soln. After stirring for a total of 8 min, the excess reagent was destroyed[9] by the addition of bromobenzene (1 ml) followed by cautious addition of water (10 ml) and NH_3 was allowed to evaporate. The mixture was acidified with 15% H_3PO_4 aq (15 ml) and the product extracted with ether (30 ml × 3). The extract was dried and freed of solvent to give a material (0.12 g; two major spots on TLC, solvent: 5% EtOAc in C_6H_6) which was separated by chromatography (SiO_2 gel/IIA, 30 × 0.8 cm).

Deodarone (8 mg) was obtained from C_6H_6 (10 ml × 4) eluates and was identified by PMR, Mass. 2% EtOAc in C_6H_6 (10 ml × 3) eluted **8** (25 mg). PMR: three –O–C(Me)– (6H, s, 1.17 ppm; 3H, s, 1.27 ppm), O–C–CH–C– (s, 3.57 ppm), –C=CH–CH$_2$– (unresolved m, 5.30 ppm). Mass: *m/e* 252 (M^+, 6%), 194 (42%), 121 (100%), 119 (78%), 117 (82%), 93 (52%), 78 (52%), 59 (65%), 55 (39%), 43 (100%), 41 (78%). (Found: C, 70.82; H, 9.42. $C_{15}H_{24}O_3$ requires: C, 71.39; H, 9.59%).

Hydration of atlantone

Atlantone (5.0 g) in acetone (200 ml) was mixed with cooling (ice-water) with 10% $HClO_4$ aq (150 ml) and the clear soln left aside at room temp. (25–32°) for 50 hr, with occasional swirling, during which period the soln became dark yellow. The mixture was diluted with water (100 ml), saturated with $(NH_4)_2SO_4$ and extracted with ether (80 ml × 5). The extract was washed with 5% $NaHCO_3$ aq (80 ml × 2) and the solvent stripped off to furnish a dark residue (5.4 g), which (5.0 g) was chromatographed over SiO_2-gel/IIA (100 × 3 cm) with TLC monitoring (solvent: 5% EtOAc in C_6H_6):

Frac. 1	C_6H_6	80 ml × 9	1.92 g, R_f 1.17, atlantone
		80 ml × 3	
Frac. 2	C_6H_6		0.1 g, mixture
	5% EtOAc in C_6H_6	80 ml × 1	
Frac. 3	5% EtOAc in C_6H_6	80 ml × 2	1.08 g, R_f 1.00, deodarone (**1**)
Frac. 4	5% EtOAc in C_6H_6	80 ml × 3	0.17 g, mixture
Frac. 5	5% EtOAc in C_6H_6	80 ml × 1	50 mg, R_f 0.88 (**11**)
Frac. 6	5% EtOAc in C_6H_6	80 ml × 4	0.1 g, mixture
Frac. 7	5% EtOAc in C_6H_6	80 ml × 14	0.90 g, R_f 0.67, atlantolone (**2**)
Frac. 8	5% EtOAc in C_6H_6	80 ml × 15	0.26 g, mixture: R_f 0.53, 0.42
Frac. 9	30% EtOAc in C_6H_6	80 ml × 4	0.2 g, mixture
	5% MeOH in ether	500 ml × 2	

Deodarone (**1**). Fraction 3 was distilled: b.p. 130–133° (bath)/0.8 mm n_D^{30} 1.4910, $[\alpha]_D$ + 7.9° (c, 0.5%). (Found: C, 76.07; H, 10.36. $C_{15}H_{24}O_2$ requires: C, 76.22; H, 10.24%).

7-*Hydroxy*-7,8-*dihydro*-*atlantone* (**11**). Fraction 5 was distilled: b.p. 135–140° (bath) 0.8 mm, n_D^{30} 1.5050, $[\alpha]_D$ + 0.7° (c, 0.58%). Mass: *m/e* 236 (M^+, 3%), 141 (17%), 138 (9%), 123 (8%), 120 (13%), 119 (12%), 95 (12%), 83 (100%), 67 (7%), 55 (22%), 43 (22%). (Found: C, 75.75; H, 10.02. $C_{15}H_{24}O_2$ requires: C, 76.22; H, 10.24%).

11-*Hydroxy*-10,11-*dihydro*-*atlantone* (**2**: *atlantolone*). Fraction 7 was distilled: b.p. 135–140° (bath)/0.8 mm, n_D^{30} 1.5018, $[\alpha]_D$ + 1.58° (c, 0.57%). Mass: *m/e* 236 (M^+, 12%), 163 (18%), 134 (14%), 119 (14%), 95 (33%), 79 (17%), 69 (27%), 67 (25%), 59 (36%), 43 (100%), 41 (100%). (Found: C, 75.49; H, 9.84. $C_{15}H_{24}O_2$ requires: C, 76.22; H, 10.24%).

3-*Hydroxy*-2,3-*dihydro*-*atlantone* (**12**). Fraction 8 (0.20 g) was rechromatographed over SiO_2 gel/IIA (50 × 1.5 cm) and eluted with increasing amounts of EtOAc in C_6H_6.

10% EtOAc in C_6H_6 (40 ml × 3) eluted 60 mg of **12**: n_D^{30} 1.5019, $[\alpha]_D$ + 1.09° (c 0.55%). Mass: *m/e* 236 (M^+, 7%), 135 (9%), 123 (12%), 93 (8%), 91 (8%), 83 (100%), 79 (12%), 55 (30%), 53 (13%), 43 (38%), 41 (20%). (Found: C, 75.90; H, 9.92. $C_{15}H_{24}O_2$ requires: C, 76.22; H, 10.24%).

3,11-*Dihydroxy*-2,3,10,11-*tetrahydro*-*atlantone* (**13**). In the above chromatography, 15% EtOAc in C_6H_6 (40 ml × 4) eluted 56 mg of ~70% pure **13**: n_D^{30} 1.4964. Mass: *m/e* 254 (M^+, 0.5%), 178 (13%), 141 (58%), 139 (17%), 95 (18%), 83 (60%), 73 (16%), 55 (16%), 45 (20%), 43 (100%), 41 (20%). (Found: C, 70.13; H, 10.31. $C_{15}H_{26}O_3$ requires: C, 70.83; H, 10.30%)

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