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STUDIES IN SESQUITERPENES—XLVII*

CIS- AND *TRANS*-ATLANTONES FROM *CEDRUS DEODARA* LOUD†

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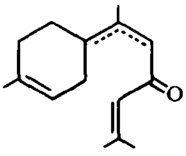
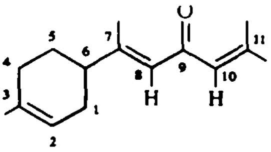
Abstract—Isolation and characterisation of pure atlantone is reported for the first time, and has been found to have *trans*-geometry. A minor constituent of the essential oil from *Cedrus deodara* Loud is shown to be its *cis*-isomer. Interconversion of the isomers is reported.

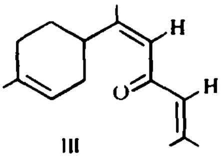
Atlantones,[1] the major ketones of the essential oil from *Cedrus libanotica* Link., *C. atlantica* Manet. and *C. deodara* Loud., have not been obtained pure to date and are considered to be an inseparable mixture of isomers, indicated in formula I.[2] While working[3] on the constituents of *Cedrus deodara*, we became interested in obtaining pure atlantone. We now find that at least the essential oil from *Cedrus deodara* contains essentially one atlantone, which is now shown to have the structure and geometry depicted in II. The only other isomer, which occurs in only minor amounts, is shown to be the *cis*-isomer III. The two isomers can be separated by chromatography on silica gel.



I



II



III

The major isomer‡ (R_f 0·275) displays in its PMR spectrum four vinylic methyls (1·63, 1·85, 2·10 and 2·10 δ), the precise assignments of which are best made[4] in terms of geometry II: δ 1·63 (C_3-Me), 1·85 (C_{11}-*trans*§-Me), 2·10 ppm (C_7-Me and C_{11}-*cis*§-Me); the 1H multiplet centred at 5·33 δ is assignable to olefinic proton at C_2, while the 2H signal (essentially a singlet) at 5·90 δ is clearly due to the C_8 and C_{10}

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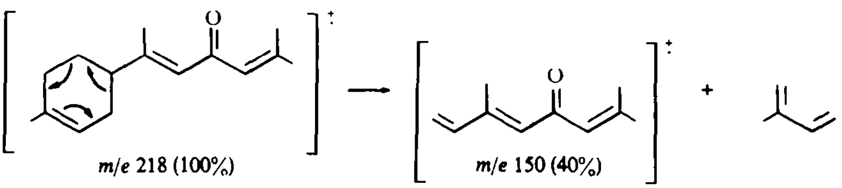
‡ The major ketone from the essential oil of *Cedrus deodara* has been earlier identified[3a] as atlantone (I) by its base-catalysed cleavage into acetone and p-methyl-Δ^3-tetrahydroacetophenone.

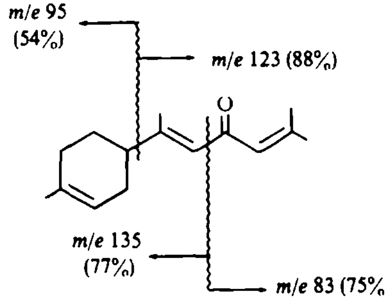
§ *Trans*- or *cis*-prefixes for methyls are with respect to the CO group.

protons. On the other hand, the second isomer (R_f 0·365) shows the four vinylic methyls, the chemical shifts of which, are best rationalised in terms of structure and geometry depicted in III: δ 1·66 broad singlet (C_3-Me), two doublets centred at 1·80 ($J = 2$ c/s) and 1·89 with $J = 1$ c/s (C_7-Me and C_{11}-*trans*-Me), and 2·16 ppm doublet with $J = 1$ c/s (C_{11}-*cis*-Me); the three olefinic protons virtually occur at the same field strengths as in the *trans*-isomer (unresolved 1H multiplet at 5·40 δ; 2H multiplet centred at 5·95 δ).

The UV (II: λ_{max}^{EtOH} 266 mμ, ε 16,900; III: λ_{max}^{EtOH} 266 mμ, ε 10,210) and IR absorptions (both isomers: ν_{max} 1670 (low intensity), 1630, 1610 cm^{-1}) of both the isomers are as expected.* The two isomers display virtually identical mass spectra; the important fragments are readily rationalised in terms of fragmentations depicted in IV and V.



IV



V

The *cis*-isomer (III) is quite unstable and on distillation (bath temp: ~140°) gives a product containing as much as 75–80% *trans*-isomer (II). As expected,[5] irradiation of *trans*-isomer results in isomerisation to the *cis*-isomer.

EXPERIMENTAL

UV spectra were taken on a Perkin-Elmer spectrophotometer, model 350. IR spectra were taken on a Perkin-Elmer Infracord model 137E. PMR spectra were measured in 10–20% soln in CCl_4 with TMS as internal standard, on a Varian A-60 spectrometer; signals are recorded in δ (ppm) relative to TMS as zero. Mass spectra were measured on a CEC mass spectrometer, model 21-110B, using an ionizing voltage of 70 eV and a direct inlet system.

Silica gel for column chromatography (−100, +200 mesh) was activated at 125–130°/6–8 hr and standardised according to Hernandez *et al.*[6] TLC was carried out on silica gel layers (0·3 mm) containing 15% gypsum; visualisation of the spots was carried out with 1% vanillin-in-H_3PO_4 aq (30%) spray, followed by heating at ~100°/10 min.

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*e.g. cf. phorone[4b]: λ_{max}^{EtOH} 265 mμ, ε 19,400, $\nu_{max}^{CCl_4}$ 1678, 1637, 1619 cm^{-1}.

GLC was carried out on Aerograph model A-350-B using 300 cm × 0·6 cm column packed with 20% diethyleneglycol polysuccinate on Chromosorb W (60–80 mesh) with H_2 as carrier gas.

Isolation of trans- *and* cis-*atlantones*

The essential oil* (1·84 kg in 20 litre light petroleum, b.p. 40–60°) from the wood of *Cedrus deodara* Loud. was partitioned with 90% aq EtOH (20 l.) in a continuous-type extractor† to finally give a hydrocarbon fraction (520 g) and a hydrocarbon-free oxygenated terpenes cut (400 g), besides a mixture of the two (870 g). The oxygenated terpenes fraction (25 g) was chromatographed (silica gel/IIa, 50 cm × 5 cms) to get two gross cuts: (I) C_6H_6 eluate, 500 ml × 9, 14·68 g; (ii) ether cut, 500 ml × 6, 9·89 g. The C_6H_6 eluted material (5·0 g), which contains atlantone was rechromatographed on silica gel/IIA (70 cm × 1·6 cm) with TLC monitoring (solvent: C_6H_6, two irrigations, 12 cm each time):

Fract. 1	light petroleum 50% C_6H_6 in light petroleum C_6H_6	500 ml × 2 500 ml × 3 300 ml × 4	negligible.
Fract. 2	C_6H_6	300 ml × 9	1·6 g, components with R_f 0·4 and 0·32 (trace).
Fract. 3	C_6H_6	300 ml × 2	0·735 g, components with R_f 0·32 and 0·28.
Fract. 4	C_6H_6	300 ml × 5	1·2 g, component with R_f 0·28.
Fract. 5	C_6H_6 5% acetone in C_6H_6	300 ml × 3 300 ml × 3	1·1 g, component with R_f 0·28 and 0·18 (trace).
Fract. 6	5% acetone in C_6H_6	300 ml × 3	0·277 g, component with R_f 0·18 and 0·16.

Fraction 4, which was essentially atlantone (TLC: single spot; a characteristic green colour. GLC, one major component with retention time 6·4 min; temp 165°; gas: 100 ml/min) resolved into a minor and a major component on TLC with another solvent system (10% $CHCl_3$ in pet. ether). This fraction (4·3 g) was recharged on silica gel/II (100 cm × 3·6 cm) using 10% $CHCl_3$ in light petroleum as the only eluent to finally yield *trans*-isomer II [1·26 g; R_f 0·275, b.p. 142–145° (bath)/1 mm, n_D^{30} 1·5342, $[\alpha]_D$ +1·2° (*c* 0·83% in $CHCl_3$)] and the *cis*-isomer III [0·20 g; R_f 0·365, n_D^{30} 1·5228]. Mass spectrum (*trans*-isomer): important ions at *m/e* 218 (M^+, 100%), 203 (M^+-15, 33%), 150 (40%), 135 (77%), 123 (88%), 107 (61%), 105 (48%), 95 (54%), 91 (50%), 83 (75%), 79 (44%), 77 (42%), 67 (38%) and 55 (45%).

Photoisomerisation of trans-*atlantone*

trans-Atlantone (0·5 g) in heptane (130 ml) was irradiated (100 watts, 'Hanovia' high-pressure, quartz Hg vapour lamp) at room temp with TLC (solvent: 10% $CHCl_3$ in light petroleum) monitoring. After ~1·5 hr irradiation, sufficient amount of *cis*-isomer had been formed and other compounds started appearing (TLC). At this stage the irradiation was stopped, the solvent flashed off at room temp under vacuum and the product (475 mg) chromatographed on silica gel/II (71 cm × 1·4 cm) using 10% $CHCl_3$ in light petroleum as eluent to finally give 120 mg pure *cis*-isomer, 100 mg (~90% pure) *trans*-isomer.

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* Supplied by Standard Essential Oil Distillers, Kanpur (UP).

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