Synthesis and Relative Structure of Conocephalenol, a Sesquiterpene Alcohol isolated from the European Liverwort *Conocephalum conicum*

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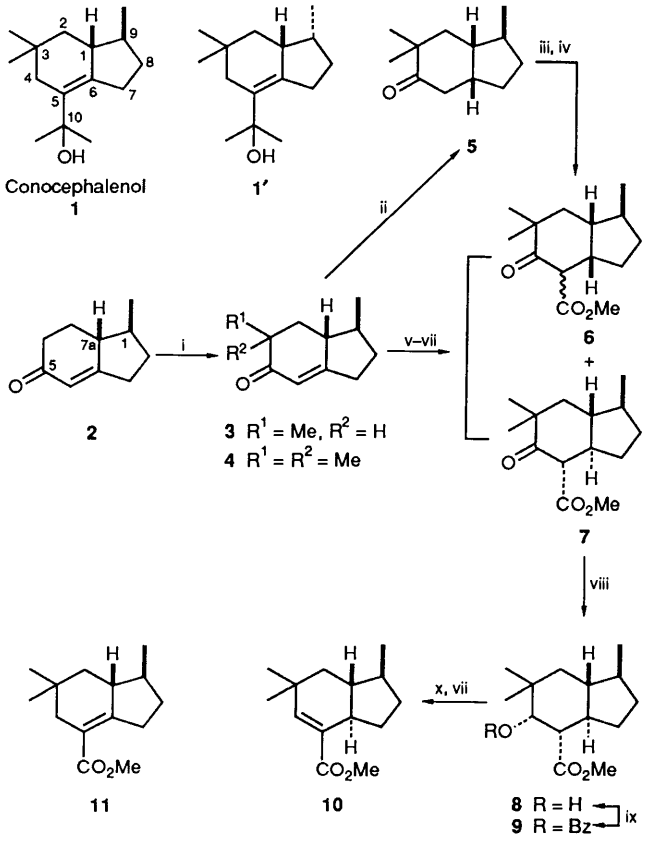
Conocephalenol, isolated from the European liverwort *Conocephalum conicum*, has been synthesized from (1*R**,7a*S**)-1-methyl-7,7a-dihydroindan-5(6*H*)-one and the relative stereostructure has been shown to have the 1*R**,9*S** configuration.

Liverworts produce various kinds of terpenoids and aromatic compounds.[1] A sesquiterpene alcohol, conocephalenol **1**, has been isolated from the European liverwort *Conocephalum conicum* and its structure was determined by the extensive analysis of high-field NMR spectra including 2D techniques by Connolly and his associates.[2] Although the planar structure (**1** or **1'**) was clarified by the 2D INADEQUATE method, the relative configuration has not been determined, due to severe overlap of the proton signals. As the structure of conocephalenol **1** resembles that of tamariscol[3] and pacifigorgiol,[4] we planned to synthesize conocephalenol **1** having the 1*R**,9*S** configuration,† starting from the known hydrindenone **2**, whose relative structure has been confirmed by the synthesis of pacifigorgiol[4] and tamariscol.[5]

The enone **2** was methylated in the usual manner [$LiNPr^i_2$ (LDA)–MeI, twice]. The dimethylated enone **4** was carboxylated under reductive conditions (Li–liq. NH_3, then solid CO_2) followed by reaction with CH_2N_2 to afford *cis*- **6** and *trans*-β-keto esters **7**.[5] Since we have reported reductive carboxylation of the compound without a methyl group at the C-3 position,[5] the stereochemistry of these products was deduced by comparison of the spectral data of these compounds. The *trans*-keto ester **7** was then reduced (L-Selectride), benzoylated (BzCl–Py), treated with base (Bu^tOK–PhH, reflux), and methylated (CH_2N_2) to afford an α,β-unsaturated ester **10**. When this ester **10** was subjected to isomerization under acid or metal catalysis conditions, the rearranged unsaturated ester **11** was not produced in acceptable yield (Scheme 1).



Scheme 1 *Reagents:* i, LDA, MeI (either once or twice); ii, H_2, Pd/C; iii, LDA; iv, $NCCO_2Me$; v, Li, liq.NH_3; vi, CO_2; vii, CH_2N_2; viii, L-Selectride, ix, BzCl, pyridine; x, Bu^tOK, PhH

Since the yield of reductive carboxylation product of the enone **4** was not always very high, the hydrindanone **5**, obtained by hydrogenation of enone **4**, was methoxycarbonylated with LDA–$NCCO_2Me$ to afford the desired *cis*-keto ester **6** in 70% yield. The *cis*-keto ester **6** was converted into the allylic alcohol **13** in five steps [i, $NaBH_4$; ii, Ac_2O; iii, Bu^tOK–tetrahydrofuran (THF); iv, CH_2N_2; v, $LiAlH_4$]. The alcohol **13** was epoxidized [*m*-chloroperbenzoic acid (MCPBA)], reduced ($LiAlH_4$–THF, reflux), acetylated (Ac_2O–Py) and dehydrated ($SOCl_2$–py) without separation of the diastereoisomers. The olefin acetates were converted into the corresponding allylic alcohols ($LiAlH_4$–Et_2O) and the mixture was separated by HPLC (Chemcopak; 20% EtOAc–hexane) to give a tetrasubstituted allylic alcohol **17** as well as the trisubstituted alcohol **13** in the ratio 1:1.6. The tetrasubstituted alcohol **17** was oxidized [pyridinium dichromate (PDC)], methylated (MeLi), and then again oxidized (PDC) to afford a methyl ketone **20**. Methylation (MeLi) of the ketone **20** completed the synthesis of conocephalenol **1** (Scheme 2), whose spectral data were identical with those of the natural product.‡ This study has established the relative stereochemistry of the liverwort sesquiterpene alcohol conocephalenol **1** as 1*R**,9*S**.

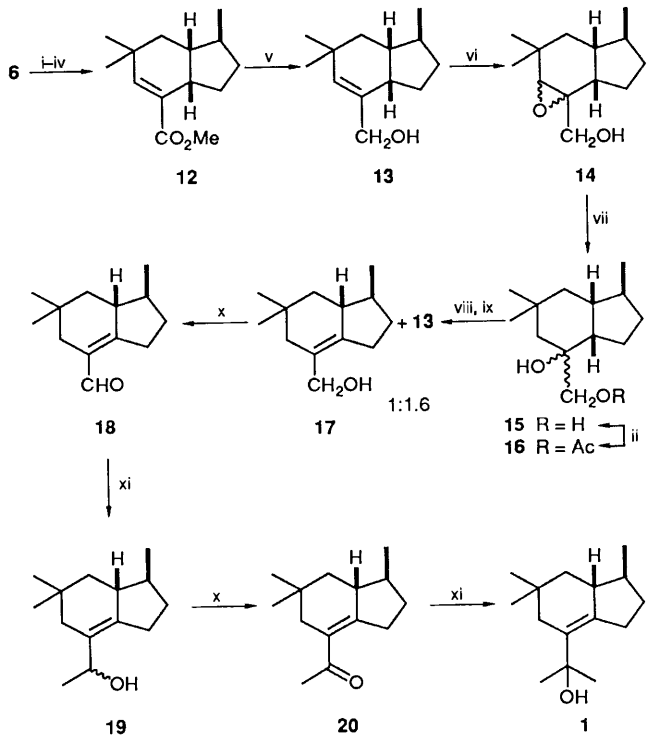
Experimental

General.—IR spectra were measured on a Shimadzu IR-408 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM GS-400 or FX-90Q spectrometer. The solvent used for NMR spectra was $CDCl_3$ unless otherwise stated, and *J*-values are given in Hz. Mass spectra were measured on a JEOL JMS HX-100 spectrometer. A Chemcopak Nucleosil 50-5 (10 × 250 mm) or Develosil 60-3 (4.6 × 150 mm) column was used for HPLC (JASCO pump system). Silica gel 60 for column chromatography was purchased from Merck.

Methylation of the Enone **2**.—To a stirred solution of diisopropylamine (1.1 cm^3) in dry THF (16 cm^3) was added

† The numbering system is that used for brasilenol.[6]

‡ Since conocephalenol **1** was rapidly decomposed in a solution of $CDCl_3$, the NMR spectra were taken in C_6D_6. We thank Dr. J. D. Connolly, University of Glasgow, for sending us the authentic spectra.



Scheme 2 *Reagents and conditions:* i, $NaBH_4$, MeOH; ii, Ac_2O, pyridine; iii, Bu'OK, THF; iv, CH_2N_2; v, $LiAlH_4$; vi, MCPBA; vii, $LiAlH_4$, THF, reflux; viii, $SOCl_2$, pyridine; ix, $LiAlH_4$, Et_2O (then HPLC); x, PDC; xi, MeLi, Et_2O

Bu^{n}Li (1.6 mol dm^{-3}; 4.4 cm^3) at −78 °C. The solution was stirred at 0 °C for 0.5 h, and then cooled to −78 °C before addition of a solution of the enone **2** (1 g) in THF (2 cm^3). The mixture was stirred at the same temperature for 1 h and then MeI (1.25 cm^3) was added slowly. The mixture was stirred at the same temperature for 1 h and then at 0 °C for 10 min before being quenched with water. The solvent was removed and the mixture was extracted with diethyl ether. The extract was washed successively with dil. HCl and brine, dried over $MgSO_4$, filtered and evaporated to afford a monomethylated enone **3** (911 mg, 83%). The crude material was used for the next reaction without further purification. An analytical sample was purified by silica gel column chromatography (hexane–EtOAc, gradient), ν_{max}(film)/cm^{-1} 1660; δ_H 1.11 (3 H, d, *J* 5.1), 1.18 (3 H, d, *J* 7) and 5.80 (1 H, m); δ_C 16.2 (Me), 17.7 (Me), 30.5 (CH_2), 32.5 (CH_2), 33.7 (CH_2), 39.6 (CH), 41.1 (CH), 45.0 (CH), 121.2 (CH), 174.3 (C) and 203.2 (C); *m/z* 164 (M$^+$), 136, 122 and 107 (base).

A solution of the monomethylated enone **3** (911 mg) in THF (2 cm^3) was added to LDA prepared from diisopropylamine (1.2 cm^3) and Bu^{n}Li (1.6 mol dm^{-3}; 4.5 cm^3) in THF (17 cm^3) at −78 °C. MeI (1 cm^3) was added and the mixture was stirred for 2 h at the same temperature. Then the temperature was kept at 0 °C for 10 min. The usual work-up afforded a residue (945 mg), which was purified by silica gel column chromatography (hexane–EtOAc, gradient) to give a dimethyl enone **4** (480 mg, 49%) as well as recovered enone **3** (187 mg). For *compound* **4**: ν_{max}(film)/cm^{-1} 1660; δ_H 1.10 (3 H, d, *J* 6.5), 1.10 (3 H, s), 1.13 (3 H, s) and 5.77 (1 H, m); δ_C 17.7 (Me), 24.0 (Me), 26.0 (Me), 30.3 (CH_2), 32.4 (CH_2), 40.6 (C), 41.2 (CH), 41.7 (CH_2), 46.8 (CH), 121.1 (CH), 173.0 (C) and 204.4 (C); *m/z* 178 (M$^+$), 163, 149, 136 and 121 (base) (Found: M$^+$, 178.1372. $C_{12}H_{18}O$ requires M, 178.1358).

Hydrogenation of the Dimethyl Enone **4**.—The enone **4** (2.4 g) was hydrogenated in the presence of 10% Pd–C (200 mg) in MeOH (50 cm^3). The solvent was evaporated off after filtration of the catalyst to afford the *ketone* **5** (2.3 g, 95%), ν_{max}(film)/cm^{-1} 1705; δ_H 0.94 (3 H, d, *J* 6.5), 1.05 (3 H, s) and 1.09 (3 H, s); δ_C 18.8 (Me), 23.7 (Me), 25.9 (Me), 32.8 (CH_2), 34.1 (CH_2), 36.0 (CH), 40.8 (CH_2), 41.4 (CH), 41.6 (CH), 42.3 (C), 42.5 (CH_2) and 216.7 (CO); *m/z* 180 (M$^+$), 162, 151, 147, 136 (base), 121, 109, 95, 86, 81, 70 and 55 (Found: M$^+$, 180.1471. $C_{12}H_{20}O$ requires M, 180.1514).

Reductive Carboxylation of the Enone **4**.—Lithium (76 mg) was dissolved in liq. NH_3 (40 cm^3) and a solution of the enone **4** (651 mg) and Bu'OH (0.28 cm^3) in THF (20 cm^3) was introduced at −78 °C. The mixture was stirred for 15 min at the same temperature. Isoprene was added until the blue colour disappeared. Ammonia and THF were evaporated off under reduced pressure and THF (20 cm^3) was added to the residue at −78 °C. Solid CO_2 (large excess) was added in one portion. The mixture was left overnight. HCl was added (to pH 1) and the mixture was extracted with diethyl ether. The aqueous layer was extracted with diethyl ether and the combined organic layers were washed with brine, and dried over $MgSO_4$. Evaporation of the solvents afforded a residue, which was treated with CH_2N_2 in diethyl ether. Evaporation of the ether afforded a residue (904 mg), which was separated by column chromatography over silica gel (hexane–EtOAc, gradient) to give the *cis*-keto ester **6** (362 mg) and the *trans*-keto ester **7** (345 mg). For cis-*keto ester* **6**: ν_{max}(film)/cm^{-1} 1740, 1705, 1640 and 1605; δ_H 1.03 (3 H, d, *J* 7.0), 1.15 (3 H, s), 1.18 (3 H, s), 3.75 (3 H, s) and 12.53 (1 H, s); *m/z* 238 (M$^+$), 206, 191, 180, 162, 147 and 136 (base) (Found: M$^+$, 238.1568. $C_{14}H_{22}O_3$ requires M, 238.1569. For *trans*-keto ester **7**: ν_{max}(film)/cm^{-1} 1740 and 1700; δ_H 1.02 (3 H, d, *J* 6.6), 1.09 (3 H, s), 1.20 (3 H, s), 3.45 (1 H, d, *J* 12.9) and 3.75 (3 H, s); *m/z* 238 (M$^+$), 220, 207, 191, 180 and 136 (base) (Found: M$^+$, 238.1532).

Preparation of the trans-α,β-*Unsaturated Methyl Ester* **10**.—A solution of the *trans*-keto ester **7** (170 mg) in dry THF (2 cm^3) at −78 °C was added L-Selectride (0.71 cm^3). The mixture was stirred for 2 h at this temperature. Water was added and the mixture was extracted with diethyl ether. The extract was washed successively with water and brine, dried over $MgSO_4$, filtered and evaporated to afford a residue (190 mg). An analytical sample was purified by column chromatography over silica gel (hexane–EtOAc, gradient) to afford the *axial alcohol* **8**, ν_{max}(film)/cm^{-1} 3500, 1710 and 1200; δ_H 0.92 (3 H, s), 0.95 (3 H, d, *J* 5.3), 1.05 (3 H, s), 2.49 (1 H, dd, *J* 13.6 and 2.0), 3.61 (1 H, d, *J* 2.0) and 3.70 (3 H, s); *m/z* 240 (M$^+$), 222, 212 (base), 193, 179, 163, 155 and 136 (Found: M$^+$, 240.1757. $C_{14}H_{24}O_3$ requires M, 240.1725).

The residue (115 mg) was treated with benzoyl chloride (0.17 cm^3) in pyridine (3 cm^3) in the presence of 4-dimethylaminopyridine (DMAP) (10 mg) at room temperature overnight. Water was added and the mixture was stirred for 1 h to decompose excess of benzoyl chloride. The mixture was extracted with diethyl ether and the extract was washed successively with HCl, aq. $NaHCO_3$, and brine, dried over $MgSO_4$, filtered and evaporated to afford the *benzoate* **9** (157 mg, 95%), ν_{max}(film)/cm^{-1} 1740, 1600 and 1450; δ_H 0.97 (3 H, s), 1.00 (3 H, d, *J* 5.7), 1.09 (3 H, s), 2.67 (1 H, dd, *J* 10.8 and 2.3), 3.54 (3 H, s), 5.45 (1 H, d, *J* 2.3) and 7.3–8.2 (5 H, m); *m/z* 344 (M$^+$), 313, 239, 222, 211, 179, 162, 148, 137, 121 and 105 (base) (Found: M$^+$, 344.2004. $C_{21}H_{28}O_4$ requires M, 344.1988).

The benzoate **9** (157 mg) thus formed was treated with Bu'OK (511 mg) in dry benzene (10 cm^3) for 2 h under reflux. Water was added and the pH of the mixture was adjusted to 1 by addition of HCl. The mixture was extracted with diethyl ether. The extract was washed successively with HCl and brine, dried

over $MgSO_4$, filtered and evaporated to afford a residue (141 mg), which was treated with CH_2N_2 to give another residue. This second residue was purified by column chromatography over silica gel (hexane–EtOAc, gradient) to afford the *methyl ester* **10** (87 mg, 86%), ν_{max}(film)/cm^{-1} 1715; δ_H 0.98 (3 H, d, *J* 6.4), 1.06 (3 H, s), 1.09 (3 H, s), 3.71 (3 H, s) and 6.50 (1 H, s); *m/z* 222 (M^+), 207, 191, 175 and 163 (base) (Found: M^+, 222.1639. $C_{14}H_{22}O_2$ requires M, 222.1620).

Methoxycarbonylation of the Ketone **5**.—The ketone **5** (2.3 g) was added to a solution of LDA, prepared from diisopropylamine (3.9 cm)[3] and Bu^nLi (1.6 mol dm^{-3}; 17 cm^3), in dry THF (18 cm^3) at −78 °C under Ar. The mixture was stirred for 1 h before addition of methyl cyanoformate (1.5 cm^3). The mixture was allowed to reach room temperature overnight. The usual work-up afforded a residue (4.6 g), which was purified by column chromatography over silica gel (hexane–EtOAc, gradient) to give the *cis*-keto ester **6** (2.12 g, 70%).

Preparation of the cis-α,β-*Unsaturated Methyl Ester* **12**.—The keto ester **6** (3.7 g) was reduced by $NaBH_4$ (588 mg) in MeOH (50 cm^3) at room temperature for 1 h. The usual work-up afforded a residue, which was further treated with a solution of Ac_2O (6 cm^3) in pyridine (15 cm^3). The usual work-up gave a residue, which was purified by column chromatography over silica gel (hexane–EtOAc, gradient) to afford an acetate (1.86 g). The acetate was treated with Bu^tOK (7.4 g) in dry benzene (110 cm^3) for 30 min. The pH of the solution was adjusted to 1 by addition of HCl. The usual work-up afforded a residue, which was treated with CH_2N_2 in diethyl ether. Evaporation of the ether afforded a residue (1.68 g). The product was purified by column chromatography over silica gel (hexane–EtOAc, gradient) to afford the cis-α,β-*unsaturated methyl ester* **12** (745 mg), ν_{max}(film)/cm^{-1} 1710; δ_H 1.00 (3 H, s), 1.03 (3 H, d, *J* 6.0), 1.06 (3 H, s), 3.73 (3 H, s) and 6.68 (1 H, s); δ_C 21.9 (Me), 27.2 (Me), 30.2 (Me), 32.0 (CH_2), 33.2 (CH_2), 33.5 (C), 37.6 (CH), 40.0 (CH), 40.6 (CH_2), 42.3 (CH), 51.3 (Me), 131.1 (CH), 148.2 (C) and 168.4 (CO); *m/z* 222 (M^+), 207, 191, 180, 175, 163 (base), 147, 133, 128, 107, 95, 91, 81, 69 and 59 (Found: M^+, 222.1617. $C_{14}H_{22}O_2$ requires M, 222.1620).

Reduction of the cis-*Methyl Ester* **12**.—The methyl ester **12** (745 mg) was treated with $LiAlH_4$ (300 mg) in dry diethyl ether (50 cm^3) for 30 min at room temperature. Water (0.3 cm^3), 15% aq. NaOH (0.3 cm^3) and water (0.9 cm^3) were added successively. The mixture was filtered and the solvent was evaporated off to afford the *allylic alcohol* **13** (638 mg, 98%), ν_{max}(film)/cm^{-1} 3300; δ_H 0.95 (3 H, s), 0.98 (3 H, s), 1.02 (3 H, d, *J* 6.5), 4.03 (2 H, br s) and 5.41 (1 H, t, *J* 1.3); δ_C 21.7 (Me), 27.7 (Me), 31.2 (CH_2), 31.4 (CH_2), 32.5 (C), 33.9 (CH_2), 39.0 (CH), 40.5 (CH), 42.0 (CH_2), 42.4 (CH), 66.7 (CH_2), 132.8 (CH) and 138.0 (C); *m/z* 194 (M^+), 179, 163 (base), 147, 133, 119, 107, 93, 81, 69 and 55 (Found: M^+, 194.1674. $C_{13}H_{22}O$ requires M, 194.1671).

Epoxidation of the Allylic Alcohol **13**.—A solution of the alcohol **13** (638 mg) in dichloromethane (100 cm^3) at 0 °C was treated with MCPBA (2.13 g) for 2 h. The mixture was extracted with CH_2Cl_2 and the organic layer was washed successively with aq. Na_2SO_3, aq. $NaHCO_3$, and brine. Evaporation of the solvent afforded a mixture of *epoxides* **14** (677 mg), ν_{max}(film)/cm^{-1} 3420; δ_H 0.95 (3 H, d, *J* 7), 0.96 (3 H, s), 1.05 (3 H, s), 2.93 (1 H, s) and 3.66 (2 H, s); δ_C 20.1 (Me), 22.8 (Me), 27.8 (CH_2), 27.9 (Me), 30.8 (C), 33.8 (CH_2), 36.0 (CH), 37.9 (CH_2), 40.2 (CH), 41.7 (CH), 63.3 (CH_2), 63.9 (C) and 65.1 (CH); *m/z* 210 (M^+), 192, 179, 161, 149, 141, 136, 121, 109, 95, 81 (base), 69 and 55 (Found: M^+, 210.1643. $C_{13}H_{22}O_2$ requires M, 210.1620).

Preparation of the Allylic Alcohol **17**.—A solution of the epoxide **14** (677 mg) in THF (100 cm^3) was treated with $LiAlH_4$ (1.2 g) under reflux for 1.5 h. Water (1.2 cm^3), 15% aq. NaOH (1.2 cm^3) and water (3.6 cm^3) were added successively after decomposition with EtOAc. Filtration and evaporation afforded a mixture of diols **15** (752 mg), ν_{max}(film)/cm^{-1} 3450; *m/z* 181 ($M - CH_2OH$), 163 (base), 147, 137, 121, 115, 107, 95, 81, 69 and 55.

The residue was acetylated with acetic anhydride (5 cm^3) and pyridine (5 cm^3) for 1 h. The usual work-up and purification by column chromatography over silica gel (hexane–EtOAc, gradient) afforded a mixture of acetates **16** (590 mg, 72%), ν_{max}(film)/cm^{-1} 3500 and 1730; δ_H 0.89 (3 H, s), 0.97 (3 H, d, *J* 7.0), 1.11 (3 H, s), 2.05 (3 H, s) and 3.83 and 3.93 (each 1 H, ABq, *J* 12); δ_C 20.9 (Me), 22.9 (Me), 25.6 (CH_2), 26.7 (Me), 30.7 (C), 31.0 (CH_2), 34.4 (Me), 38.6 (CH), 41.3 (CH), 41.6 (CH_2), 41.7 (CH_2), 44.8 (CH), 72.4 (CH_2), 73.4 (C) and 171.2 (CO); *m/z* 181 ($M - CH_2OAc$), 163, 147, 137, 121, 107, 95, 81, 69 and 55.

The acetate was dissolved in pyridine (10 cm^3) and the solution was treated at 0 °C with $SOCl_2$ (0.75 cm^3) for 30 min. Water was added and the usual work-up afforded a residue (515 mg).

The unsaturated acetates were treated with $LiAlH_4$ (950 mg) in diethyl ether (100 cm^3). The usual work-up afforded a residue (279 mg), which was separated by HPLC (Chemcopak 10 × 250; 20% hexane–EtOAc, 5 cm^3 min^{-1}) to give the trisubstituted olefinic alcohol **13** (52 mg) and a *tetrasubstituted olefinic alcohol* **17** (87 mg). For compound **17**: ν_{max}(film)/cm^{-1} 3300; δ_H 0.88 (3 H, s), 1.01 (3 H, s), 1.02 (3 H, d, *J* 6.4) and 4.06 (2 H, s); δ_C 18.0 (Me), 26.4 (Me), 26.5 (CH_2), 30.0 (C), 32.2 (Me), 33.2 (CH_2), 40.4 (CH_2), 41.0 (CH), 41.0 (CH_2), 46.5 (CH), 66.8 (CH_2), 125.8 (C) and 140.6 (C); *m/z* 194 (M^+), 179, 163 (base), 147, 133, 120, 107, 91, 81, 69 and 55 (Found: M^+, 194.1628. $C_{13}H_{22}O$ requires M, 194.1671).

Oxidation of the Allylic Alcohol **17**.—A solution of the alcohol **17** (42 mg) in dichloromethane (10 cm^3) was treated with PDC (100 mg) and powdered molecular sieves (3 Å; 100 mg) for 1 h. Dry diethyl ether was added and the mixture was passed through a short column of silica gel to afford the *aldehyde* **18** (32 mg), ν_{max}(film)/cm^{-1} 2700 and 1660; δ_H 0.87 (3 H, d, *J* 6.4), 1.05 (6 H, s) and 9.93 (1 H, s); *m/z* 192 (M^+, base), 177, 163, 149, 136, 121, 107, 91, 79, 69, 65 and 55 (Found: M^+, 192.1498. $C_{13}H_{20}O$ requires M, 192.1514).

Preparation of the Methyl Ketone **20**.—To a stirred solution of the aldehyde **18** (32 mg) in dry diethyl ether (2 cm^3) at 0 °C was added MeLi (0.34 cm^3). The mixture was stirred for 20 min at the same temperature. Water was added and the mixture was extracted with diethyl ether. The extract was washed successively with water and brine, dried over $MgSO_4$, filtered and evaporated to afford a mixture of alcohols **19** (33 mg), δ_H 0.90 (3 H, d, *J* 6.2), 1.01 (6 H, s), 1.20 (3 H, d, *J* 6.4) and 4.61 (1 H, m); *m/z* 208 (M^+), 190, 175 (base), 161, 157, 147, 133, 119, 105, 91, 79, 69 and 55.

The alcohol was then treated with PDC (180 mg) and powdered molecular sieves (3 Å; 100 mg) in dichloromethane (20 cm^3) overnight. The work-up as before afforded a residue (20 mg), which was purified by column chromatography over silica gel (hexane–EtOAc, gradient) afforded the *enone* **20** (9 mg), ν_{max}(film)/cm^{-1} 1695, 1670, 1635 and 1600; δ_H 0.87 (3 H, s), 0.91 (3 H, d, *J* 7.3), 1.05 (3 H, s) and 2.22 (3 H, s); δ_H (90 MHz; C_6D_6) 0.78 (3 H, s), 0.94 (3 H, s) and 1.96 (3 H, s); *m/z* 206 (M^+), 191 (base), 177, 163, 149, 135, 121, 107, 91, 79, 69, 65 and 55 (Found: M^+, 206.1655. $C_{14}H_{22}O$ requires M, 206.1671).

Preparation of Conocephalenol **1**.—To a stirred solution of the enone **20** (9 mg) in dry diethyl ether (2 cm^3) at 0 °C was

added MeLi (0.05 cm^3). The mixture was stirred for 20 min at the same temperature. Work-up as before afforded a residue (13 mg), which was purified by HPLC (Develosil 60-3; 5% EtOAc–hexane) to give conocephalenol **1** (3.6 mg), ν_{max}(film)/cm^{-1} 3450; δ_H (C_6D_6) 0.90 (3 H, s), 1.00 (3 H, s), 1.01 (3 H, d, *J* 6.4) and 1.25 (6 H, s); δ_C (C_6D_6) 18.1, 26.6, 29.3, 29.5, 29.99, 30.04, 32.5, 34.1, 40.5, 40.8, 41.5, 48.3, 74.0, 132.7 and 135.9; *m/z* 222 (M^+), 204, 189, 175, 161, 149, 133, 127, 119, 105, 91, 84, 69, 59 and 55 (Found: M^+, 222.2009. Calc. for $C_{15}H_{26}O$: M, 222.1984).

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