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CAESPITENONE, A NEW CYCLOPROPANOID PSEUDOGUAIANE AND *ENT*-SESQUITERPENES FROM *PORELLA* SPECIES

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Key Word Index—*Porella caespitans* ssp. *setigera*; *P. stephaniana*; *P. acutifolia* ssp. *tosana*; *P. fauriei*; *P. grandiloba*; *P. japonica*; *Macvicaria ulophylla*; Hepaticae; caespitenone; pseudoguaiane; (+)-aristolone; (−)-α-eudesmol; *ent*-sesquiterpenoids; diterpene dialdehyde; monoterpenoids.

Abstract—Six *Porella* species and one *Macvicaria* species have been investigated and a new cyclopropane pseudoguaiane was isolated and its structure elucidated by chemical and spectral evidence. *Macvicaria ulophylla* and the *Porella* species, except *P. caespitans* ssp. *setigera*, contain the diterpene dialdehyde, perrottetianal A. (+)-Aristolone, (−)-α-eudesmol, and related sesquiterpene hydrocarbons and alcohols, enantiomeric to those found in higher plant, have been isolated from the *Porella* species.

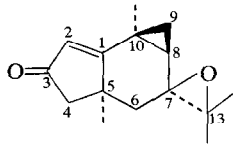
INTRODUCTION

The *Porella* species of liverworts produce various sesqui- and diterpenoids [1–11]. There are two types of *Porella* species, one containing a sharp pungent substance, polygodial and one containing no pungent substance [7]. Recently, we have reported the isolation and structures of the unique diterpene dialdehydes, perrottetianal A (**12**) and perrottetianal B from *Porella perrottetiana* which belongs to the latter type of *Porella* [11]. The present paper reports the isolation and structure of caespitenone, a new cyclopropanoid pseudoguaiane-type sesquiterpene ketone from non-pungent *Porella* species, together with the previously known sesquiterpenoids enantiomeric to those found in higher plants.

RESULTS AND DISCUSSION

Caespitenone (**1**)

Compound **1** is the major component of *P. caespitans* ssp. *setigera*. The same substance was also isolated from *P. japonica*, as a minor component. The high resolution MS established the molecular formula $C_{15}H_{20}O_2$. The IR and UV spectra showed absorption bands at 1725 cm^{-1} and 277 nm respectively, suggesting the presence of a cyclopentenone conjugated with another unsaturated group. The ^1H NMR and double resonance spectra (NMDR) contained signals of four tertiary methyl groups (δ 1.01, 1.15, 1.26 and 1.43), one vinylic proton (5.83) appeared as a sharp singlet, one proton (0.55) on a cyclopropane ring, and one methylene group (2.13 and 1.46, each *d*, $J = 15$ Hz) located between a carbonyl group and a quaternary sp^3 carbon atom. In the IR spectrum, the absorption bands of a hydroxyl group could not be observed, indicating the additional oxygen to be an ether. Treatment of **1** with $NaBH_4$ or $LiAlH_4$ gave a labile allylic alcohol (**2**), $C_{15}H_{22}O_2$ (M^+ 234), which was applied to a Si gel column and eluted with $CHCl_3$ to afford a cyclopentadiene derivative (**3**) (262 nm; 1630 and 1510 cm^{-1}) [12]. Hydrogenation of **1** in the presence of Pd–C gave a cyclopentanone (**4**) ($C_{15}H_{22}O_2$ (M^+ 234); 1745 cm^{-1}) and a cyclopentanol derivative (**5**) ($C_{15}H_{24}O_2$ (M^+ 236); 3620 and 3430 cm^{-1}). The bathochromic absorption bands at 277 nm in the UV spectrum of **1** indicated that **1** may possess a cyclopropyl enone system [13, 14]. The ^1H NMR spectrum of **4** contained a pair of triplet-like signals at δ 0.17 and 0.56, assignable to the methylene protons of cyclopropane ring. From the above chemical and spectral evidence, coupled with the molecular formula, caespitenone was suggested to be a tricyclic sesquiterpene containing a cyclopentenone conjugated with a cyclopropane ring and an oxirane ring. The presence of a tetrasubstituted ethylene oxide group in **1** was



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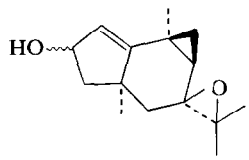

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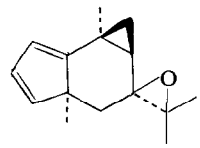

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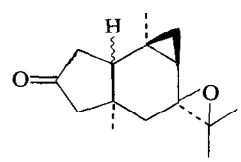

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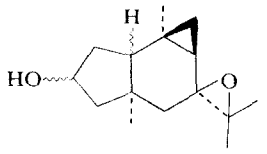

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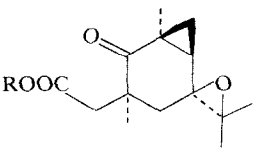


6 R = H
7 R = Me

confirmed by two singlet signals at δ 66.8 and 61.1 in the ^{13}C NMR spectrum. In addition, the ^{13}C NMR spectrum contained the signals of three carbon atoms assignable to a typical β-substituted cyclopentenone (200.7 (*s*), 180.5 (*s*) and 128.8 (*d*)) [15], two quaternary sp^3 carbons (34.7 (*s*) and 21.6 (*s*)), three methylenes, one methine and four tertiary methyl groups. Ozonolyzis of **1** gave an acid (**6**) (1700 cm^{-1}), followed by methylation with CH_2N_2 to afford a keto ester (**7**) ($C_{15}H_{22}O_4$ (M^+ 266); 1720 and 1670 cm^{-1}) conjugated with a cyclopropyl group. The ^1H NMR spectrum of **7** indicated the presence of four tertiary methyl groups and an AB-type doublet signal located between a carbomethoxyl group and a quaternary sp^3 carbon atom. The position of one of the four tertiary methyl groups at C-10 was established by the lowest field signal at δ 1.64. The ^1H NMR spectrum of **7** further displayed a doublet signal ($J = 11$ Hz) at 2.11, due to one of the AB-type methylene protons located between two quaternary sp^3 carbons.

On the above chemical and spectral evidence, the gross structure of caespitenone is most favourably represented as cyclopropanoid pseudoguaiane (**1**). The stereochemistry at C-5 and of the cyclopropyl group has been tentatively assigned by the negative Cotton effect of **1** and by the positive Cotton effect of the keto ester (**7**). The configuration of the isopropyl group might be α from biogenetic considerations of (+)-aristolone (**8**) isolated from the same species.

Pseudoguaiane-type sesquiterpenoids have generally been found in higher plants, paritculàrly in members of the Compositae. This is the first report of the isolation of a pseudoguaiane-type sesquiterpene from a species of the Hepaticae. The similar cyclopropanoid guaianolide to caespitenone has been isolated from *Iva* species [14, 16].

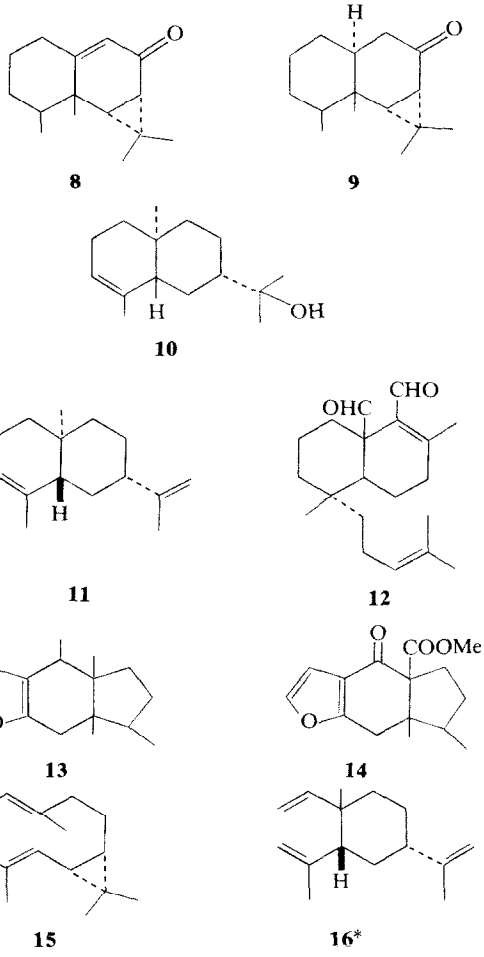
(+)-*Aristolone* (**8**) *and* (−)-α-*eudesmol* (**10**)

In addition to caespitenone (**1**), aristolone (**8**) has been isolated from *P. caespitans* ssp. *setigera* as the minor component. The same compound was also isolated from the pungent *P. fauriei*. From *P. stephaniana*, α-eudesmol was obtained as the major component. The structures of the above two oxygenated sesquiterpenes deduced from the spectral and chemical transformation of **8** to **9** and **10** to **11** were confirmed by the identity of spectra with those of aristolone [17–19], α-eudesmol and their derivatives [20]. However, the optical rotation of each compound was opposite to that for the corresponding compound isolated from higher plants.

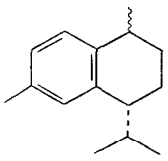
P. acutifolia ssp. *tosana*, *P. stephaniana*, *P. grandiloba*, *P. japonica* and *Macvicaria ulophylla*, which belongs to the Porellaceae, commonly produce a unique diterpene dialdehyde, perrottetianal A (**12**), recently isolated from *P. perrottetiana*. *P. japonica* elaborates the previously known deoxopinguisone (**13**) [21] and norpinguisone methyl ester (**14**) [4]. The latter furanosesquiterpene has also been obtained from *P. grandiloba*. Thus, *P. japonica* and *P. grandiloba* resemble the *P. vernicosa* complex, although the former two taxa do not produce the pungent sesquiterpene dial, an important chemosystematic marker of the Porellaceae. The present *Porella* samples contain various kinds of sesquiterpene hydrocarbons and oxygenated sesquiterpenes. (−)-Bicyclogermacrene (**15**) was isolated from *P. stephaniana*. β-Elemene (**16**) was detected in *P. acutifolia* ssp. *tosana*, *P. japonica*, *P. stephaniana*, and *P. grandiloba*. Calamenene (**17**), elemol (**18**) from *P. caespitans setigera*, *trans*-β-farnesene (**19**) from *P. stephaniana*, and β-caryophyllene (**20**) from *P. grandiloba* were detected by GC–MS. Calamenene was also found in *P. japonica* and *M. ulophylla*.

Porella species generally emit a fragrant odor when they are crushed. This is mainly due to the presence of the monoterpene hydrocarbons. All *Porella* species so far examined contain the same monoterpene hydrocarbons as those found in the higher plants.

Recently, various sesquiterpenoids including ones with a new skeleton have been isolated from the



* The configurations of the sesquiterpenes (**16–18** and **20**) have been tentatively assigned by the biogenetic consideration of the sesquiterpenes of **8**, **10** and **15**.



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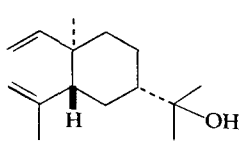

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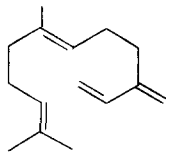

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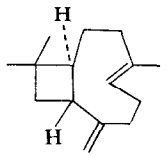

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Hepaticae. Many of these are the same sesquiterpenes or have the same skeleton as those found in higher plants. One of the most significant chemical properties of the Hepaticae is the elaboration of the sesquiterpenes enantiomeric to those found in higher plants [8, 22–25], although there are several exceptions as seen in the sesquiterpenoids of *Porella* [4, 6, 8], *Frullania* [26], *Conocephalum* [27] and *Wiesnerella* [28]. The present sesquiterpenoids found in the *Porella* species possess the former characteristics.

EXPERIMENTAL

All mps are uncorr. The solvents used for spectral determinations were: TMS–$CDCl_3$ (^{1}H NMR 60, 90 and 100 MHz; ^{13}CNMR 22.6 MHz); $CHCl_3$ (IR); MeOH ($[\alpha]_D$, CD and ORD); 95% EtOH (UV), unless otherwise stated. TLC and PLC: precoated Si gel plates (0.25 mm) F_{254}, *n*-hexane–EtOAc (4:1), C_6H_6–EtOAc (4:1 and 1:1). Spots were detected in UV light (254 nm) and by spraying with 30% H_2SO_4, 2,4-DNP of Ehrlich reagent. GC–MS: 70 eV, column SE-30, 1% 2 m × 2 mm, temp. programme, 50–270° at 5°/min. He 30 ml/min.

Extraction and isolation. P. caespitans ssp. *setigera* collected in Kizawa-son, Tokushima Prefecture in December 1978 was air-dried for 5 days. The ground material (117 g) was extracted with Et_2O for 2 weeks. The green bitter fragrant oil (3.319 g) was directly chromatographed on Si gel using *n*-hexane-EtOAc gradient. The first fraction eluted (*n*-hexane) contained mono- and sesquiterpene hydrocarbon mixtures (60 mg) in which camphene, β-pinene and calamenene (**17**) were detected by GC–MS. The second fraction eluted with *n*-hexane gave the pure sesquiterpene hydrocarbon, caespitene (257 mg), $C_{15}H_{22}$, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1640 (C=C), 1610 (C=C), 1430, 1375, 1365, 970, 845, 820, 765, 755; UV λ_{max} nm (ε): 251 (2362); ^{1}H NMR δ 0.90 (3H, *s*), 1.00 (3H, *s*), 1.10 (3H, *s*), 1.60 (3H, *m*), 2.13 (2H, *m*), 5.23 (1H, *t*, *J* = 4), 5.72 (1H, *d*, *J* = 4), 5.76 (1H, *bs*); MS *m/e* (rel. int.): 202 (56), 187 (39), 159 (base), 145 (56), 131 (50), 117 (54), 105 (23), 91 (27). The third fraction (*n*-hexane–EtOAc, 19:1) gave yellow fragrant oil (1.5 g) which was rechromatographed on Si gel using *n*-hexane–EtOAc gradient to afford caespitenone (**1**) (825 mg). $[\alpha]_D$ −34° (*c*, 0.2); UV λ_{max} nm (ε): 204.5 (6333), 277 (3150); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1725 (C=O), 1605 (C=C), 1380, 1370, 1345, 1335, 1290, 1245, 1180, 1140, 1105, 1085, 950, 905, 885, 865, 720, 705; ^{13}C NMR: 42.9 (*t*), 34.7 (*s*), 34.4 (*t*), 31.4 (*q*), 31.0 (*q*), 29.1 (*q*), 26.7 (*t*), 23.6 (*d*), 21.6 (*s*), 19.8 (*q*); MS *m/e* (rel. int.): 232.1392 (M^+, $C_{15}H_{20}O_2$, calc. 232.1464, base), 204.1528 (M^+ − 15, calc. 204.1513, 38), 189.1254) (M^+–CO, calc. 189.1277, 83), 161.1045 ($C_{11}H_{13}O$, calc. 161.0965, 89), 175 (43), 147 (56), 133 (59), 119 (51), 105.0716 (C_8H_8, calc. 105.0705, 79), 91 (50), 77 (39), 43.0183 (C_2H_3O, calc. 43.0183, 95), 41.0393 (C_3H_5, calc. 41.0392, 31); $CD_{320\ nm}$ Δε −2.26, $_{345\ nm}$ Δε −2.46. The fourth fraction (4:1) gave a sterol mixture (campesterol, stigmasterol and sitosterol) (81 mg). The fifth fraction (4:1) gave a sesquiterpene ketone which was purified by PLC to afford (+)-aristolone (**8**) (8 mg). $[\alpha]_D$ +253° (*c*, 0.4); $CD_{323\ nm}$ Δε +0.94; MS *m/e* (rel. int.): 218 (M^+ $C_{15}H_{22}O$, base), whose spectral data (NMR, IR and UV) were identical to those of (−)-aristolone [17–19]. The sixth fraction contained sesquiterpene alcohols in which elemol (**18**) was detected by GC–MS.

P. stephaniana collected in Monobe-mura, Kochi prefecture in August 1978 was treated with the same manner as described above and the crude extract (461 mg) obtained from the ground material (12 g) was chromatographed on Si gel using *n*-hexane–EtOAc gradient. The first fraction contained mono- and sesquiterpene hydrocarbons (87 mg) in which β-pinene, β-phellandrene, β-elemene (**16**), bicyclogermacrene (**15**) and *trans*-β-farnesene (**19**) were detected by GC–MS. The preparative GLC of the above hydrocarbon mixtures resulted in the isolation of (−)-bicyclogermacrene [6]. The second fraction (19:1) afforded a yellow oil (30 mg) which was not identified. The third fraction (9:1) gave perrottetianal A (**12**) (15 mg) and (−)-α-eudesmol (**10**) (167 mg), as colourless needles. mp 77–78° (lit. 75° [20]); $[\alpha]_D$ −35° (*c*, 1.5) (lit. +28.6° [20]). The structure of (−)-α-eudesmol was further confirmed by the transformation of **10** to α-selinene (see later). The fifth fraction (4:1) contained a sterol mixture (campesterol, stigmasterol and sitosterol) (32 mg).

Air-dried and ground *P. fauriei* (10 g) collected in Hokkaido, in Sept. 1974, *P. japonica* (110 g) in Kaifu-cho, Tokushima prefecture, Sept. 1977, *P. acutifolia* ssp. *tosana* (32 g) in Kizawa-son Tokushima prefecture, in June 1977, *P. grandiloba* (40 g) in Hokkaido, April 1979, and *Macvicaria ulophylla* (950 mg) in Kaifu-cho, Tokushima prefecture, August 1978, were treated in the same manner as described for *P. caespitans* ssp. *setigera*, and the following sesqui- and diterpenes were isolated. *P. fauriei*: (+)-aristolone (**8**) (10 mg). *P. japonica*: deoxopinguisone (**13**) (15 mg), caespitenone (5 mg), norpinguisone methyl ester (**14**) (85 mg) and perrottetianal A (**12**) (67 mg). *P. grandiloba*: norpinguisone methyl ester (**14**) (12 mg) and perrottetianal A (**12**) (80 mg). The following mono- and sesquiterpenes were detected in each species by GC–MS. *P. acutifolia* ssp. *tosana*: α-pinene, camphene, sabinene, β-phellandrene, α-terpinene, *p*-cymene, terpinolene and β-elemene. *P. japonica*: α-pinene, camphene, β-pinene, limonene, β-phellandrene, *p*-cymene, caespitene and β-elememe. *P. grandiloba*: α-pinene, camphene, α-phellandrene, β-elemene and β-caryophyllene (**20**). *M. ulophylla*: β-pinene, β-phellandrene, myrcene and calamenene. All species contained a small amount of sterol mixture.

Reduction of caespitenone (**1**) *with* $NaBH_4$. To an EtOH soln of **1** (72 mg) was added $NaBH_4$ (40 mg) with stirring at 0° for 1 hr. The excess $NaBH_4$ was decomposed with dil HOAc and the solvent evapd. The reaction mixture dissolved in $CHCl_3$ was passed through a short column packed with Si gel and eluted with $CHCl_3$ to afford a labile allylic alcohol (**2**) (5 mg) and a dehydrated product (**3**) (10 mg). Compound **2**, $C_{15}H_{22}O_2$ (M^+ 234); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450 (OH), which was also obtained by the reduction of **1** with $LiAlH_4$. Compound **3**: UV λ_{max} nm (ε): 262 (8500); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1630, 1510 (cyclopentadiene), 1480, 1390, 1370, 1340, 1330, 1280,

1255, 1230, 1215, 1165, 1120, 1080, 1035, 1000, 980, 840, 785, 760, 725, 685, 665, 640.

Reduction of **1** *with* $LiAlH_4$. To $LiAlH_4$ in dry Et_2O (2 ml) was added **1** (105 mg) with stirring at 0° for 2 hr. The excess $LiAlH_4$ was decomposed with H_2O. The product was filtered and the solvents evapd to afford a labile allylic alcohol (**2**) (67 mg). IR ν_{max}^{Liquid} cm^{-1}: 3450 (OH), 1380, 1365, 1290, 1240, 1160, 1100; MS *m/e* (rel. int.): 234 (M^+, $C_{15}H_{22}O_2$, 51), 219 (M^+-15, base), 217 (M^+-17, 52), 218 (M^+-18, 23), 191 (95), 175 (53), 161 (67), 149 (64), 135 (68), 121 (50), 119 (60), 107 (62), 105 (87), 91 (69), 41 (45).

Hydrogenation of **1**. Compound **1** (170 mg) in EtOH (4 ml) was hydrogenated in the presence of 5% Pd–C (60 mg). Work-up as usual gave a viscous oil which showed two spots on TLC. It was purified by PLC to afford dihydrocaespitanone (**4**) (45 mg) and caespitanol (**5**) (20 mg). Dihydrocaespitanone (**4**): $[\alpha]_D$ −22° (*c*, 1.8); UV λ_{max} nm (ε): 207.5 (2872), 235 sh (613); IR ν_{max}^{liquid} cm^{-1}: 1745 (cyclopentanone), 1400, 1380, 1365, 1150, 1090, 1065; ^1H NMR: δ 0.17 (1H, *t*, $J=4$), 0.56 (1H, *t*, $J=4$), 0.90 (3H, *s*), 1.00 (3H, *s*), 1.13 (3H, *s*), 1.30 (3H, *s*), 1.4–3.0 (complex *m*); MS *m/e* (rel. int.): 234 (M^+, $C_{15}H_{22}O_2$, 18), 219 (M^+-15, 16), 206 (M^+-CO, 21), 191 (M^+-MeCO, 43), 163 (77), 149 (34), 123 (38), 121 (56), 107 (74), 91 (41), 43 (base), 41 (36); $CD_{337\ nm}$ $\Delta\varepsilon$ +0.07. Caespitanol (**5**): IR ν_{max}^{liquid} cm^{-1}: 3620, 3430, 1060 (OH), 1370, 1360, 1320, 1020, 970, 940, 920, 880, 835; ^1H NMR: δ 0.83 (3H, *s*), 1.00 (3H, *s*), 1.03 (3H, *s*), 1.11 (3H, *s*), 3.90 (1H, *bt*, $J=7$, CH_2-CHOH-CH_2); MS *m/e* (rel. int.): 236 (M^+, $C_{15}H_{24}O_2$, 38), 221 (M^+-15, 62), 218 (M^+-H_2O, 25), 203 ($M^+-15-18$, 62), 175 (base), 163 (70), 161 (62), 147 (64), 133 (50), 121 (64), 119 (92), 109 (30), 105 (48), 93 (34), 91 (55), 43 (91), 41 (39).

Reduction of **4** *with* $LiAlH_4$. To an Et_2O soln of $LiAlH_4$ (20 mg) was added **4** (45 mg) with stirring at 0° for 1 hr. Work up as usual gave caespitanol (**5**) (7.2 mg).

Ozonolysis of **1**. A stream of ozonized oxygen was passed through an EtOAc (3 ml) soln of **1** (120 mg) at −78° for 30 min. To the reaction mixture was added 30% H_2O_2 (1.7 ml), HOAc (13.3 ml), H_2O (0.7 ml) and one drop of conc HCl and then stirred for 24 hr. Work-up as usual gave a carboxylic acid (**6**) (34 mg). IR ν_{max}^{Liquid} cm^{-1}: 3550–2650 (COOH); ^1H NMR: δ 7.5 (*bs*, 1H, COOH), 1.00 (3H, *s*), 1.06 (3H, *s*), 1.30 (3H, *s*), 1.63 (3H, *s*), 2.36 (1H, *d*, $J=11$).

Methylation of the acid (**6**). Compound **6** in dry Et_2O was methylated with CH_2N_2 to afford a keto ester (**7**) (20 mg) after PLC. $[\alpha]_D$ +21° (*c*, 0.3); UV λ_{max} nm: 202 (ε 1911); IR ν_{max}^{Liquid} cm^{-1}: 1720 (COO), 1670 (O=C-cyclopropy), 1390, 1370, 1330, 1290, 1220, 1195, 1155, 1125, 1110, 1060, 985, 905, 890, 880, 820, 785, 750; ^1H NMR: δ 0.85 (1H, *m*), 1.00 (3H, *s*), 1.05 (3H, *s*), 1.30 (3H, *s*), 1.61 (3H, *s*), 1.30 (1H, *d*, $J=15$), 2.46 (1H, *d*, $J=15$), 2.11 (1H, *d*, $J=11$); MS: *m/e* (rel. int.): 267 ($M^+ + 1$, 4), 266 (M^+, $C_{15}H_{22}O_4$, 2), 251 (M^+-15, 22), 207 (42), 165 (70), 153 (50), 139 (50), 123 (45), 109 (base), 95 (92), 83 (50), 69 (42), 59 (27), 43 (50), 41 (39); CD_{300nm} $\Delta\varepsilon$, +0.58, $_{345nm}$ $\Delta\varepsilon$, −0.07.

Hydrogenation of (+)*-aristolone* (**8**). An EtOH soln of **8** (8 mg) was hydrogenated in the presence of prereduced 5% Pd–C for 48 hr. Work-up as usual afforded dihydroaristolone (**9**) (5 mg). $[\alpha]_D$ −92° (*c*, 0.2); UV λ_{max} nm (ε): 208 (2249); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1660 (C=O), 1420 (CO-CH_2), 1375, 1355, 910; ^1H NMR: δ 0.95 (3H, *d*, $J=6$), 1.16 (3H, *s*), 1.37 (3H, *s*); MS *m/e* (rel. int.): 220 (M^+, $C_{15}H_{22}O$, 15), 110 (18) 109 (base), 96 (42); $CD_{288\ nm}\Delta\varepsilon$ −21.2. The spectral data (IR and UV) were identical to (+)-dihydroaristolone[17].

Dehydration of (−)*-α-eudesmol* (**10**). To a Py soln of **10** (50 mg) was added redistilled $SOCl_2$ (0.4 ml) at 0° and the mixture allowed to stand 1 hr. After the reaction mixture was diluted with excess Et_2O, a few drops of H_2O were added. Work-up as usual gave a sesquiterpene hydrocarbon which was purified by preparative GLC to afford α-selinene (**11**) (8 mg) whose physical and spectral data were identical to those reported for (+)-α-selinene [29].

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REFERENCES

1. Asakawa, Y., Aratani, T. and Ourisson, G. (1976) *Misc. Bryol. Lichenol.* **7**, 99.
2. Asakawa, Y., Toyota, M., Uemoto, M. and Aratani, T. (1976) *Misc. Bryol. Lichenol.* **7**, 124.
3. Asakawa, Y., Toyota, M. and Aratani, T. (1976) *Tetrahedron Letters* 3619.
4. Asakawa, Y. et Aratani, T. (1976) *Bull. Soc. Chim. Fr.* 1469.
5. Asakwa, Y., Toyota, M., Uemoto, M. and Aratani, T. (1976) *Phytochemistry* **15**, 1929.
6. Asakawa, Y., Toyota, M. and Takemoto, T. (1978) *Phytochemistry* **17**, 457.
7. Asakawa, Y., Toyota, M., Takemoto, T. and Suire, C. (1979) *Phytochemistry* **18,** 1007.
8. Asakawa, Y., Tokunaga, N., Toyota, M., Takemoto, T. and Suire, C. (1979) *J. Hattori Bot. Lab.* **45,** 395.
9. Asakawa, Y., Huneck, S., Toyota, M., Takemoto, T. and Suire, C. (1979) *J. Hattori Bot. Lab.* **46,** 163.
10. Asakawa, Y., Tokunaga, N., Toyota, M., Takemoto, T., Hattori, S., Mizutani, M. and Suire, C. (1979) *J. Hattori Bot. Lab.* **46,** 67.
11. Asakawa, Y., Toyota, M. and Takemoto, T. (1979) *Phytochemistry* **18,** 1681.
12. Mironov, V. A., Sobolev, E. V. and Elizarova, A. N. (1963) *Tetrahedron* **19,** 1939.
13. Scott, A. I. (1964) *Interpretation of the Ultraviolet Spectra of Natural Products*, p 344. Pergamon Press, Oxford.
14. Herz, W., Sudarsanam, V. and Schmid, J. (1966) *J. Org. Chem.* **31,** 3232.
15. Marr, D. H. and Stothers, J. B. (1965) *Can. J. Chem.* **43,** 596.
16. Anderson, G. D., McEwen, R. C. and Herz, W. (1972) *Tetrahedron Letters* 4423.
17. Furukawa, S. and Soma, N. (1961) *J. Pharm. Soc. Jpn.* 81,559.
18. Berger, C., Franck-Neuman, M. and Ourisson, G. (1968) *Tetrahedron Letters* 3451.
19. Piers, E., Britton, R. W. and De Wall, W. (1969) *Can. J. Chem.* **47,** 831.
20. Ruzicka, L., Wind, A. H. and Koolhaas (1931) *Helv. Chim. Acta* **14,** 1132.
21. Krutov, S. M., Samek, Z., Benesova, V. and Herout, V. (1973) *Phytochemistry* **12,** 1405.
22. Huneck, S. and Klein, E. (1967) *Phytochemistry* **6,** 383.
23. Hayashi, S. and Matsuo, A. (1975) *Kagaku No Ryoiki* **29,** 46.

24. Andersen, N. H., Tseng, C.-L. W., Moor, A. and Ohta, Y. (1978) *Tetrahedron* **34,** 47.
25. Asakawa, Y., Muller, J.-C. Ourisson, G., Foussereau, J. and Ducombs, G. *Bull. Soc. Chim. Fr.* 1465.
26. Knoche, H., Ourisson, G., Perold, G. W., Foussereau, J. and Maleville, J. (1969) *Science* **166,** 239.
27. Asakawa, Y. and Takemoto, T. (1979) *Phytochemistry* **18,** 285.
28. Asakawa, Y., Matsuda, R. and Takemoto, T. (1980) *Phytochemistry* **19,** 567.
29. Andersen, N. H., Shunk, B. and Costin, C. R. (1973) *Experientia* **29,** 645.