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ENANTIOMERIC TYPE SESQUITERPENOIDS OF THE LIVERWORT *MARCHANTIA POLYMORPHA*

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Key Word Index—*Marchantia polymorpha*; Hepaticae; Bryophyte; biogenesis; *ent*-type sesquiterpenoids; optical antipodes; new compounds.

Abstract—A series of *ent*-sesquiterpenoids corresponding to the optical antipodes of those in higher plants have been isolated from the liverwort *Marchantia polymorpha*. These sesquiterpenoids provide yet another example of the peculiar stereospecificity of the biogenesis of the liverwort sesquiterpenoids and suggest a special taxonomic position of the liverworts in the plant kingdom.

INTRODUCTION

Liverworts are morphologically placed in a special group considered to be at an early stage of the evolution of terrestrial green plants. They contain several oil bodies characteristic of the species in each cell of the gametophytes. They usually elaborate sesquiterpenoids and diterpenoids as well as esters of fatty acids and aromatic acids as their major lipophilic constituents. Interestingly, we found that almost all the liverwort sesquiterpenoids are either enantiomers or similar to the enantiomers of sesquiterpenoids of higher plants (e.g. [1–4]). This observation has also been made by other workers [5, 6]. The liverworts are, therefore, akin to fungi and marine invertebrates [7–9] with respect to the metabolism of sesquiterpenoids. All of the drimane-type compounds obtained from the liverworts, however, consist of normal structures, not the enantiomeric forms, and the chirality is the same even in drimanoids of the fungi and marine invertebrates [7–10]. This is because the drimanoids are biosynthesized by an alternative pathway having some similarity to that of the triterpenoids and steroids, although the formation of carbon skeletons of most sesquiterpenoids is the result of initial displacement of the pyrophosphate anion from farnesyl pyrophosphate followed by an attack of the distal or central double bond.

The thalloidal liverwort *Marchantia polymorpha* L. is one of the most common species of bryophytes, upon which many phytochemical and biochemical investigations have been performed [11–13]. The sesquiterpenoids which have been isolated from *M. polymorpha* are β-cedrene, β-chamigrene, (+)-costunolide, cuparene, β-elemene, δ-elemene, eremophilene, α-himachalene and (−)-δ-cuparenol [14–18], although their absolute configurations had not been established except for (+)-costunolide and (−)-δ-cuparenol.

In the course of our study on sesquiterpenoid constituents of the liverworts, we have isolated ten kinds of sesquiterpenoids including three new compounds from the liverwort *M. polymorpha*, the structures and absolute configurations of which have been shown to be (−)-gymnomitrene (**1**), (−)-cuparene (**2**), (+)-β-chamigrene (**3**), (+)-thujopsene (**4**), (−)-δ-cuprenene (**5**), (+)-ε-cuprenene (**6**), (−)-widdrol (**7**), (−)-δ-cuparenol (**8**), (−)-β-herbertenol (**9**) and (−)-thujopsenone (**10**), although the structures of the two hydrocarbons, **5** and **6**, were tentatively assigned. These results establish that the liverwort sesquiterpenoids are the antipodal forms of those found in higher plants.

RESULTS AND DISCUSSION

M. polymorpha was extracted with methanol and the neutral fraction (soluble in ethyl acetate) was subjected to chromatography over a silica gel column. From the least polar fraction, six sesquiterpene hydrocarbons including two new compounds were isolated by a combination of column chromatography (CC) and preparative TLC using silica gel impregnated with silver nitrate. Their structures were established by IR, NMR and mass spectroscopy.

(−)-Gymnomitrene (**1**), $C_{15}H_{24}$, $[\alpha]_D$ −22°, and (−)-cuparene (**2**), $C_{15}H_{22}$, $[\alpha]_D$ −63°, two compounds which are distributed widely in liverworts [11–13], were identified as the enantiomeric forms by the perfect agreement of both the spectral data and the specific optical rotations with those of the *ent*-type compounds isolated from other liverworts [19, 20]. The spectral data of (+)-β-chamigrene (**3**), $C_{15}H_{24}$, $[\alpha]_D$ +66°, and (+)-thujopsene (**4**), $C_{15}H_{24}$, $[\alpha]_D$ +74°, were also in agreement with the reported data [21, 22]. However, the values of the optical rotations showed an opposite sign to those of the sesquiterpenoids from higher plants [21, 22]. This is the first report of the isolation of enantiomeric forms of these two sesquiterpenoids.

The first new hydrocarbon, (−)-δ-cuprenene (**5**), $C_{15}H_{24}$, $[\alpha]_D$ −40°, was characterized as a bicyclic compound with three tertiary methyl groups, a disubstituted double bond and an exocyclic double bond (see Experimental). Its UV spectrum (λ 232 nm) revealed a heteroannular diene system of two double bonds [23]. When hydrocarbon **5** was treated with DDQ, cuparene

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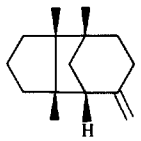

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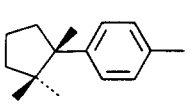

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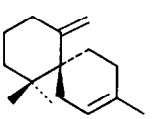

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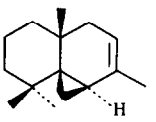

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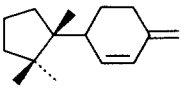

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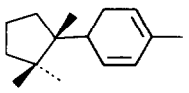

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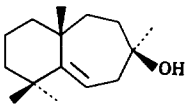

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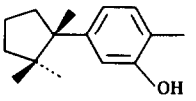

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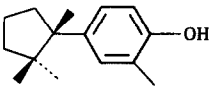

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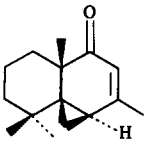

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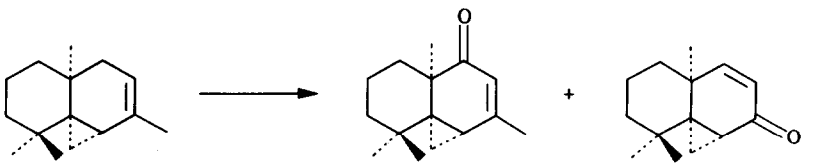
was produced. Thus the carbon skeleton of compound **5** consisted of the cuparane (= cuprenane) framework, and the gross structure was assigned as the fourth cuprenene, i.e. δ-cuprenene (**5**) with a conjugated diene system made up of the *exo*-methylene and the disubstituted double bond, in the isomeric series of α-, β- and γ-cuprenene [24].

The second new sesquiterpene hydrocarbon, (+)-ε-cuprenene (**6**), $C_{15}H_{24}$, $[\alpha]_D$ +168°, had a disubstituted double bond, a trisubstituted double bond and three tertiary methyl groups as well as two quaternary carbons, four methylenes and a methine carbon. Thus, it was a bicyclic compound, and the two double bonds were in conjugation with each other as a part of a homoannular diene system (λ 253 and 248 nm) [23]. The structure was tentatively assigned as that of a fifth cuprenene, ε-cuprenene (**6**), on the basis of the spectroscopic evidence, especially that based on the similarity of its mass spectrum to that of α-cuprenene [25] and by a consideration of the biogenesis of all of the sesquiterpenoids found in this liverwort.

From a polar fraction, four oxygenated compounds were isolated as a sesquiterpene ketone, a sesquiterpene alcohol and two sesquiterpene phenols by CC followed by preparative TLC. The spectral data of the alcohol (**7**), $C_{15}H_{26}O$, $[\alpha]_D$ −91°, were identical with those of (+)-widdrol [26]. The optical rotation suggested the enantiomeric structure having an opposite configuration to the corresponding compound obtained from higher plants [26]. The two isomers of the sesquiterpene phenols were identified by their spectroscopic properties and optical rotations as (−)-δ-cuparenol (**8**), $C_{15}H_{22}O$, $[\alpha]_D$ −43°, and (−)-β-herbertenol (**9**), $C_{15}H_{22}O$, $[\alpha]_D$ −39°. The first had been isolated from certain liverworts including *M. polymorpha*, whilst the second had been obtained from *Herberta adunca* [20, 27].

The spectroscopic data of the last new compound, (−)-thujopsenone (**10**), $C_{15}H_{22}O$, $[\alpha]_D$ −80°, revealed it to be a tricyclic sesquiterpene ketone having three tertiary methyl groups and a β, β'-disubstituted α, β-unsaturated ketone function; the patterns of all the spectra were similar to those of thujopsene (**4**) except for information about the carbonyl group. Only one of the three tertiary methyl groups showed a solvent effect, suggesting the carbonyl group was on a neighbouring position of the angular methyl group. This was supported by the UV spectrum (λ 262 nm) which showed further conjugation of the α,β-unsaturated ketone to a cyclopropane ring. To confirm the deduced structure and its absolute configuration, the normal hydrocarbon (not the enantiomeric form), (−)-thujopsene (**11**), $[\alpha]_D$ −85°, obtained from cedar wood oil was oxidized with Collins reagent in methylene chloride to give an α,β-unsaturated ketone, (+)-thujopsenone (**12**), $[\alpha]_D$ +85°, which was an enantiomer of natural (−)-thujopsenone (**10**), although (+)-mayurone (**13**), $C_{14}H_{20}O$, $[\alpha]_D$ +229°, which had been isolated as a natural product from certain species of the Coniferales [28, 29], was obtained as a major product. Accordingly, the structure and absolute configuration of the new α,β-unsaturated ketone was determined to be (−)-*ent*-thujopsenone (**10**).

On the basis of the experimental results just described, the structures and absolute configurations of eight sesquiterpenoids were established as the enantiomers or the enantiomeric forms of those found in higher plants. However, β-cedrene, β-elemene, δ-elemene, eremophilene, α-himachalene and (+)-costunolide, the occurrence of which in *M. polyanthus* had previously been reported, were not isolated from this specimen. These enantiomeric sesquiterpenoids may be biosynthesized from *cis*-farnesyl pyrophosphate (*cis*-FPP) by the routes shown in Scheme 1. The stereoselective process is due to the unique enzyme-catalysed stereospecific cyclizations of the mono-



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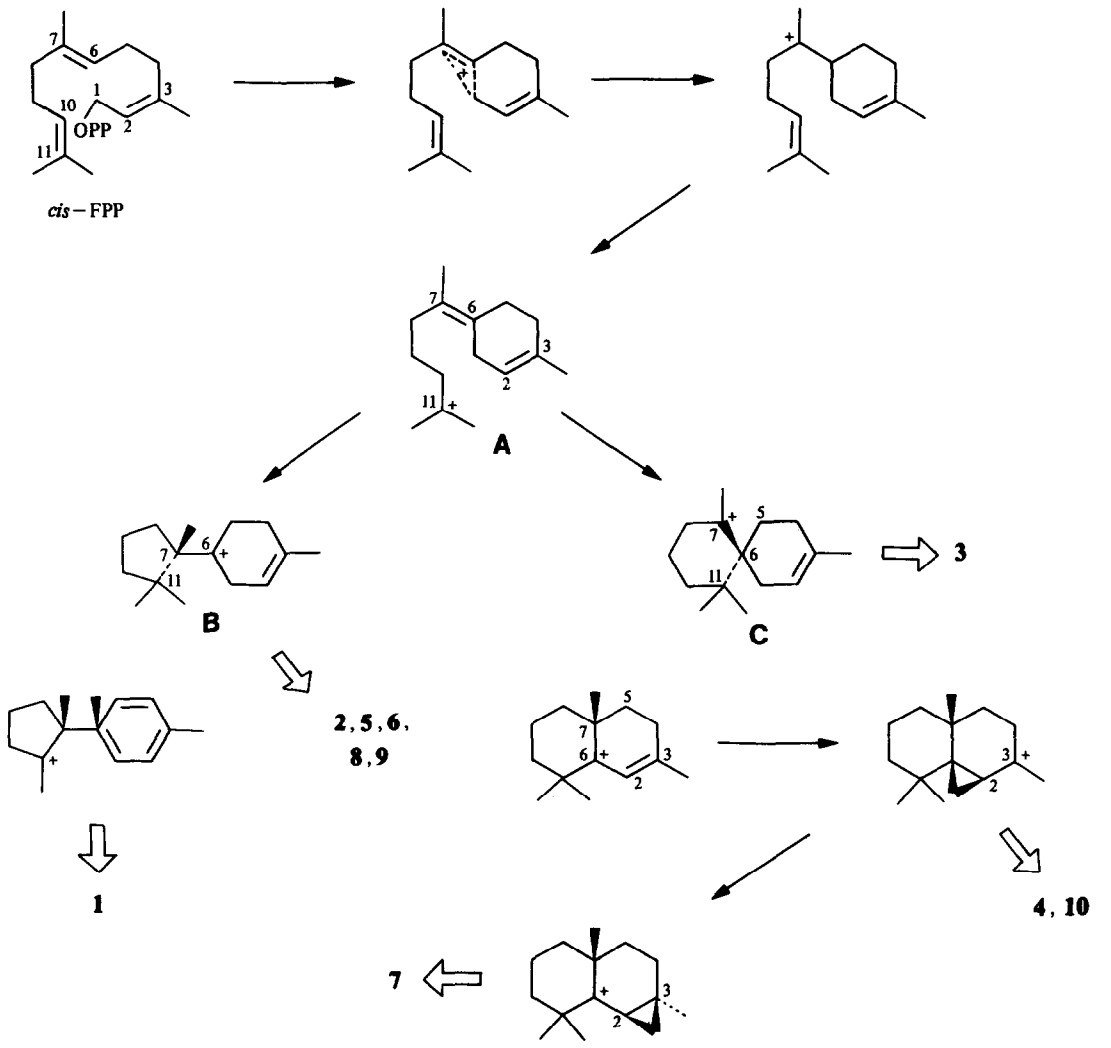

Scheme 1. A survey of the biogenetic routes leading to *ent*-sesquiterpenoids.

cyclic intermediate cation **A** to the bicyclic intermediates **B** and **C**: ring formation from the bisabolane cation **A** of the cuparane **B** and chamigrane **C** cations proceed in the reverse direction compared with the cyclizations catalysed by the enzyme of higher plants. These intermediate cations (**B** and **C**) produce the individual *ent*-sesquiterpenoids (**1**–**10**) through further reactions of methyl migration, cyclization, homoallyl-cyclopropylcarbinyl rearrangement, deprotonation and oxygen functionalization [30]. By considering the biogenetic sequence of sesquiterpenoid formation in this liverwort, the two new sesquiterpene hydrocarbons, (−)-δ-cuprenene and (+)-ε-cuprenene, whose gross structures were tentatively assigned by spectroscopic evidence, may be shown by the stereostructures **5** and **6**, respectively. These results support the peculiar stereospecific cyclizations involved in the biogenesis of most of the liverwort sesquiterpenoids [1–4], and suggest a special taxonomic position of the liverworts in the plant kingdom.

EXPERIMENTAL

General procedures. Mps: uncorr.; IR and $[\alpha]_D$: $CHCl_3$; ^1H NMR (60 or 90 MHz) and ^{13}C NMR (22.63 MHz): CCl_4, unless otherwise stated, with TMS as the internal standard; EIMS: 70 eV; UV: EtOH; GLC: glass columns (3 mm × 2 m) packed with 3% SE-30 and 3% OV-1 on 80–100 mesh Chromosorb AW, N_2 40 ml/min; CC: Merck Kieselgel 60; TLC and prep. TLC: Merck Kieselgel 60 PF_{254}; spots were visualized under UV radiation or sprayed with 10% H_2SO_4 in EtOH and heated at 100°.

Material and its extraction. M. polymorpha was collected in Miyajima-cho, an island near Hiroshima city. The whole plant (2.4 kg), after washing with H_2O and drying in the shade for several days, was extracted with MeOH for 1 week at room temp. The solvent was distilled off under reduced pressure to afford a viscous, dark green oil. The extract dissolved in EtOAc was washed with 5% aq. NaOH to yield a neutral fraction (20.3 g).

Isolation of the constituents. The neutral fraction was chro-

matographed over a column of silica gel using a mixture of C_6H_{14} and EtOAc to separate 7 fractions. From fraction 1, the six sesquiterpene hydrocarbons, (−)-gymnomitrene (**1**) (10 mg), (−)-cuparene (**2**) (450 mg), (+)-β-chamigrene (**3**) (150 mg), (+)-thujopsene (**4**) (31 mg), (−)-δ-cuprenene (**5**) (27 mg), (+)-ε-cuprenene (**6**) (24 mg), were isolated by a combination of CC and prep. TLC using silica gel–$AgNO_3$ (9:1). Fraction 3 gave the following oxygenated sesquiterpenes: (−)-widdrol (**7**) (25 mg), (−)-δ-cuparenol (**8**) (11 mg), (−)-β-herbertenol (**9**) (9 mg) and (−)-thujopsenone (**10**) (57 mg). The physical and spectroscopic properties of these compounds are listed below.

(−)-Gymnomitrene (**1**). $C_{15}H_{24}$; $[\alpha]_D$ −22° (*c* 0.5) (lit. −26° [19]); IR ν_{max} cm^{-1}: 3060, 1635, 1385, 1372, 892; ^{1}H NMR: δ0.85, 0.92 and 1.05 (each 3H, *s*), 4.55 (2H, *s* (*br*)); MS *m/z* (rel. int.): 204 $[M]^+$ (16), 189 (13), 175 (5), 161 (18), 147 (6), 133 (12), 119 (14), 108 (90), 96 (100), 93 (83), 81 (62), 69 (39), 55 (37), 41 (42).

(−)-Cuparene (**2**). $C_{15}H_{22}$; $[\alpha]_D$ −63° (*c* 1.6) (lit. +64° [31]); UV λ_{max} nm: 264 and 217 (ε 780 and 7600); IR ν_{max} cm^{-1}: 1510, 1380, 1371, 1360, 818; ^{1}H NMR: δ0.55, 1.06, 1.23 and 2.28 (each 3H, *s*), 6.91 and 7.19 (each 2H, *d*, *J* = 8.5 Hz); MS *m/z* (rel. int.): 202 $[M]^+$ (25), 187 (5), 159 (7), 145 (34), 132 (100), 119 (21), 105 (18), 91 (16), 77 (6), 69 (7), 55 (9), 41 (18).

(+)-β-Chamigrene (**3**). $C_{15}H_{24}$; $[\alpha]_D$ +66° (*c* 1.0) (lit. −53° [21]); IR ν_{max} cm^{-1}: 3095, 1634, 1385, 1375, 1365, 898, 855, 820; ^{1}H NMR: δ0.82 and 0.87 (each 3H, *s*), 1.55 (3H, *s* (*br*)), 4.47 and 4.82 (each 1H, *d*, *J* = 2.0 Hz), 5.22 (1H, *m*); MS *m/z* (rel. int.): 204 $[M]^+$ (54), 189 (100), 176 (6), 161 (23), 147 (20), 133 (41), 121 (48), 105 (63), 93 (81), 79 (55), 69 (35), 55 (43), 41 (73).

(+)-Thujopsene (**4**). $C_{15}H_{24}$; $[\alpha]_D$ +74° (*c* 1.3) (lit. −91° [22]); IR ν_{max} cm^{-1}: 3080, 1680, 1400, 1388, 1375, 1362, 880, 818; ^{1}H NMR: δ0.63, 1.14 and 1.14 (each 3H, *s*), 1.78 (3H, *s* (*br*)), 4.98 (1H, *d* (*br*), *J* = 7.0 Hz); ^{1}H NMR (C_6H_6): δ0.57, 1.13 and 1.13 (each 3H, *s*), 1.83 (3H, *s* (*br*)), 5.13 (1H, *d* (*br*), *J* = 6.0 Hz); ^{13}C NMR: δ134.7, 34.6, 33.6 and 31.2 (each *s*), 114.3 and 22.0 (each *d*), 41.0, 40.2, 36.3, 19.4 and 11.0 (each *t*), 28.9, 28.4, 26.6 and 23.3 (each *q*); MS *m/z* (rel. int.): 204 $[M]^+$ (43), 189 (16), 175 (5), 161 (14), 147 (15), 133 (40), 119 (100), 105 (66), 93 (63), 81 (34), 69 (43), 55 (43), 41 (66).

(−)-δ-Cuprenene (**5**). $C_{15}H_{24}$; $[\alpha]_D$ −40° (*c* 1.3); UV λ_{max} nm: 232 (ε 21 000); IR ν_{max} cm^{-1}: 3090, 1665, 1634, 1593, 1386, 1374, 1364, 885; ^{1}H NMR: δ0.80, 1.00 and 1.02 (each 3H, *s*), 4.63 (2H, *s* (*br*)), 5.60 (1H, *d* (*br*), *J* = 10.0 Hz), 6.04 (1H, *dd*, *J* = 10.0 and 2.0 Hz); ^{13}C NMR: δ142.5 (*s*), 134.1 and 129.9 (each *d*), 109.5 (*t*); MS *m/z* (rel. int.): 204 $[M]^+$ (5), 189 (2), 161 (3), 133 (5), 119 (10), 111 (96), 94 (38), 69 (100), 55 (28), 41 (30).

(+)-ε-Cuprenene (**6**). $C_{15}H_{24}$; $[\alpha]_D$ +168° (*c* 1.1); UV λ_{max} nm: 253 and 248 (ε 6700 and 6600); IR ν_{max} cm^{-1}: 1615, 1380, 1360, 978, 870; ^{1}H NMR: δ0.82, 0.88 and 0.96 (each 3H, *s*), 1.77 (3H, *s* (*br*)), 5.2–5.8 (3H, complex); ^{13}C NMR: δ130.5, 35.7 and 35.1 (each *s*), 131.7, 129.9, 126.0 and 58.8 (each *d*), 42.8, 42.4, 39.7 and 18.7 (each *t*), 33.5, 30.8, 26.4 and 22.5 (each *q*); MS *m/z* (rel. int.): 204 $[M]^+$ (35), 189 (14), 161 (29), 133 (26), 119 (100), 105 (64), 93 (48), 77 (24), 69 (21), 55 (35), 41 (49).

(−)-Widdrol (**7**). $C_{15}H_{26}O$; mp 96–97° (lit. 98° [26]); $[\alpha]_D$ −91° (*c* 1.2) (lit. +104° [26]); IR ν_{max} cm^{-1}: 3605, 3430, 1382, 1100, 902, 890, 865, 840; ^{1}H NMR: δ1.08, 1.08, 1.14 and 1.19 (each 3H, *s*), 5.47 (1H, *dd*, *J* = 9.0 and 6.0 Hz); MS *m/z* (rel. int.): 222 $[M]^+$ (14), 189 (5), 164 (8), 151 (100), 135 (18), 123 (18), 109 (35), 95 (53), 81 (42), 69 (45), 55 (34), 43 (78).

(−)-δ-Cupranenol (**8**). $C_{15}H_{22}O$; $[\alpha]_D$ −43° (*c* 0.5) (lit. −74° [20]); IR ν_{max} cm^{-1}: 3615, 3390, 1622, 1505, 1410, 1385, 1375, 1364, 1188, 995, 868, 820; ^{1}H NMR: δ0.55, 1.03, 1.18 and 2.16 (each 3H, *s*), 4.83 (1H, *s* (*br*), exchangeable with D_2O), 6.6–6.8 (3H, complex); MS *m/z* (rel. int.): 218 $[M]^+$ (43), 203 (5), 175 (7), 161 (29), 148 (91), 136 (100), 121 (27), 107 (10), 91 (18), 77 (13), 69 (11), 55 (15), 41 (33).

(−)-β-Herbertenol (**9**). $C_{15}H_{22}O$; $[\alpha]_D$ −39° (*c* 0.3) (lit. −47° [27]); IR ν_{max} cm^{-1}: 3610, 3325, 1605, 1505, 1380, 1372, 1360, 1260, 1115, 895, 820; ^{1}H NMR: δ0.55, 1.05, 1.20 and 2.18 (each 3H, *s*), 4.65 (1H, *s* (*br*), exchangeable with D_2O), 6.45–7.0 (3H, complex); MS *m/z* (rel. int.): 218 $[M]^+$ (43), 203 (10), 175 (6), 161 (48), 148 (100), 135 (55), 121 (15), 105 (5), 91 (10), 77 (8), 69 (7), 55 (7), 41 (13).

(−)-Thujopsenone (**10**). $C_{15}H_{22}O$; $[\alpha]_D$ −80° (*c* 1.1) (Found: $[M]^+$, 218.1639. $C_{15}H_{22}O$ requires: 218.1668) UV λ_{max} nm: 262 (ε 6700); IR ν_{max} cm^{-1}: 3060, 1645, 1405, 1390, 1373, 1245, 1175, 1143, 1035, 875; ^{1}H NMR: δ0.68, 1.15 and 1.38 (each 3H, *s*), 2.03 (3H, *d*, *J* = 1.5 Hz), 5.38 (1H, *s* (*br*)); ^{1}H NMR (C_6H_6): δ0.44, 1.00 and 1.58 (each 3H, *s*), 1.70 (3H, *d*, *J* = 1.5 Hz), 5.63 (1H, *s* (*br*)); ^{13}C NMR: δ198.8, 160.0, 45.5, 34.1 and 32.5 (each *s*), 118.1 and 29.0 (each *d*), 39.9, 36.8, 24.7 and 18.2 (each *t*), 27.0, 23.8, 23.8 and 21.2 (each *q*); MS *m/z* (rel. int.): 218.1639 $[M]^+$ ($C_{15}H_{22}O$ requires: 218.1668) (71), 203.1441 $[M-Me]^+$ ($C_{14}H_{19}O$ requires: 203.1435) (16), 190.1672 $[M-CO]^+$ ($C_{14}H_{24}$ requires: 190.1720) (9), 175.1518 ($C_{13}H_{19}$ requires: 175.1486) (20), 161 (48), 147 (100), 135 (49), 119 (64), 105 (61), 91 (48), 77 (40), 67 (40), 55 (53), 41 (97).

Treatment of (−)-δ-cuprenene (**5**) *with DDQ*. A mixture of hydrocarbon **5** (15 mg) and DDQ (2,3-dichloro-5,6-dicyano-*p*-benzoquinone) (70 mg) in dry C_6H_6 (15 ml) was refluxed for 5.5 hr. To the cooled soln petrol (35–45°) (10 ml) was added and the ppt. filtered off. The filtrate was concd and the formation of cuparene was certified by GC/MS methods.

Collins oxidation of (−)-thujopsene (**11**) *to (+)-thujopsenone* (**12**). CrO_3–$(C_5H_5N)_2$ complex was prepared by the usual manner from dry C_5H_5N (40 ml) and dry CrO_3 (4 g) [32]. To a mechanically stirred soln of (−)-thujopsene (**11**) (350 mg) in dry CH_2Cl_2 (20 ml) was added at 0° the CrO_3–$(C_5H_5N)_2$ complex as a slurry in dry CH_2Cl_2 (20 ml). After 16 hr of stirring at room temp., the CH_2Cl_2 soln was passed through a Florisil column and was then washed with 5% aq. HCl. The crude product was subjected to prep. TLC to isolate (+)-thujopsenone (**12**) (28 mg) and (+)-mayurone (**13**) (110 mg) together with unreacted (−)-thujopsene (**11**) (13 mg).

(+)-Thujopsenone (**12**). $C_{15}H_{22}O$; $[\alpha]_D$ +85° (*c* 0.6). The IR, NMR and mass spectra of the ketone were identical with those of natural (−)-thujopsenone (**10**).

(+)-Mayurone (**13**). $C_{14}H_{20}O$; mp 68° (lit. 70° [29]); $[\alpha]_D$ +229° (*c* 1.1) (lit. +259° [29]); UV λ_{max} nm: 216 (ε 8000); IR ν_{max} cm^{-1}: 1662, 1624, 1405, 1380, 1370, 1297, 1107, 872; ^{1}H NMR: δ0.68, 1.17 and 1.37 (each 3H, *s*), 5.47 (1H, *dd*, *J* = 10.0 and 1.5 Hz), 6.05 (1H, *d*, *J* = 10.0 Hz); ^{13}C NMR ($CDCl_3$): δ198.1, 38.0, 36.1 and 32.2 (each *s*), 157.9, 121.2 and 31.3 (each *d*), 39.4, 39.0, 17.4 and 16.6 (each *t*), 28.1, 26.7 and 25.4 (each *q*); MS *m/z* (rel. int.) 204 $[M]^+$ (84), 189 (69), 176 (29), 161 (63), 147 (41), 135 (67), 122 (92), 107 (93), 91 (100), 79 (48), 69 (38), 55 (49), 41 (98).

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