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CLERODANE, KAURANE AND LABDANE DITERPENOIDS FROM THE LIVERWORT *JUNGERMANNIA INFUSCA**

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Key Word Index—*Jungermannia infusca*; *Jungermanniales*; Hepaticae; clerod-3, 13-(*Z*)-dien-15-al-17-oic acid; clerod-3, 13-(*E*)-dien-15-al-17-oic acid; clerod-3, 13-(*Z*)-dien-15, 17-dial; clerod-3,13-(*E*)-dien-15, 17-dial; clerod-3, 13(16), 14-trien-17-al; *ent*-15α-hydroxykaurene; *ent*-kaurene-15-one; (16*R*)-*ent*-kaurane-15-one; (16*R*)-*ent*-11α-hydroxykaurane-15-one; (16*S*)-*ent*-11α-hydroxykaurane-15-one; *ent*-11α-hydroxykaurene-15-one; clerodane-, kaurane- and labdane-type diterpenoids; chemosystematics.

Abstract—Five new clerodane-type diterpenoids were isolated from the liverwort *Jungermannia infusca* along with a known labdane-type diterpenoid, *iso*-abienol and six known *ent*-kaurane type diterpenoids and their structures determined by the extensive NMR examinations and some chemical reactions.

INTRODUCTION

The liverworts belonging to the Jungermanniaceae are rich sources of sesqui-and diterpenoids [1]. The liverwort *Jungermannia infusca* is taxonomically complex species as it is polymorphic. The kaurene-type diterpenoid [2–4] and its glucosides [5] have been isolated from *J. infusca*. As part of a chemosystematic study [6] and search for biologically active substances [7–9], we reinvestigated chemical constituents of *J. infusca* collected in Tokushima and Yakushima island. In this paper we report the isolation and characterization of five new clerodane-type diterpenoids of *J. infusca* and discuss its chemosystematics.

RESULTS AND DISCUSSION

A combination of column chromatography on silica gel and Sephadex LH-20 and on a Lobar column of the ethyl acetate extract of *J. infusca* resulted in the isolation of five new terpenoids (**1**–**5**) along with the previously known diterpene *iso*-abienol (**6**) [10]. The crude extract of *J. infusca* collected in Yakushima Island, 550 km from Tokushima was treated in the same manner as described above to afford the previously known six *ent*-kaurane-type diterpenoids, *ent*-15α-hydroxykaurene (**17**) [2], *ent*-kaurene-15-one (**18**) [2], (16*R*)-*ent*-kaurene-15-one (**21**) [2], (16*R*)-*ent*-11α-hydroxykaurane-15-one (**22**) [11, 12], (16*S*)-*ent*-11α-hydroxykaurane-15-one (**23**) [3] and *ent*-11α-hydroxykaurene-15-one (**24**) [11, 12].

Compound **1** had the molecular formula $C_{20}H_{30}O_3$ (*m/z* 318.2201) indicating six degrees of unsaturation. Its IR spectrum showed the presence of a carboxylic acid (3500–3000, 1700 cm^{-1}) and conjugated carbonyl group (1660 cm^{-1}). The ^1H NMR spectrum contained the signals of three tertiary methyl groups, two olefinic protons (δ5.13 and 5.78) and a formyl group (δ9.84). The ^{13}C NMR spectrum displayed 20 carbons (Table 1); four methyl, six methylene, two methine, four olefinic carbons (δ120.4, 127.9, 143.5 and 165.9), one formyl carbon (δ191.3), a carboxylic acid carbon (δ179.1) and two quarternary carbons. These spectral features disclosed a diterpenoid bearing formyl and carboxylic acid groups. The 2D ^1H–^1H and ^{13}C–^1H COSYs of **1** were extensively examined to clarify the connectivity of each proton in **1**. The formyl proton at δ9.84 coupled with an olefinic proton at δ5.78. Another olefinic proton at δ5.13 was coupled with a non-equivalent methylene proton and by long-range coupling with a poorly resolved non-equivalent methylene proton. These results led to the partial structures (A) –C(13)=CH(14)–CHO(15), (B) –C(4)–CH(3)–CH_2(2)–CH_2(1)–. Furthermore, the non-equivalent methylene proton at δ2.65 and 2.37 was coupled with a poorly resolved methylene proton. The methine proton at δ2.41 (H-8) was correlated with a poorly resolved nonequivalent methylene proton (H-7), which was coupled with a non-equivalent methylene proton (H-6). These results led to partial structures (C) –CH_2(11)–CH_2(12)–, (D) –CH(8)–CH_2(7)–CH_2(6)–. It was further possible to correlate each segment by the analyses of the long-range ^{13}C–^1H COSY of **1** (Table 2). The quarternary carbon signal at δ165.9(C-13) showed long-range coupling to both methyl (H-16) and methylene (H-12) protons. This methyl signal was found to be further correlated to the olefinic carbon (C-14). This olefinic carbon was correlated with the formyl proton (H-15). Moreover, the highest field tertiary methyl proton (H-20) showed long-range coupling to the quarternary carbon (C-9), two methine carbons (C-8 and C-10) and a methylene carbon (C-11). The second highest methyl proton (H-18) was found to be correlated with two quarternary carbons (C-4 and C-5), a methine carbon (C-10) and a methylene carbon (C-6). The third highest methyl proton (H-19) was correlated with a quarternary carbon (C-4) and an olefinic methylene carbon (C-3). The above spectral evidence, and comparison with the ^1H, ^{13}C NMR spectrum of **9** [4], disclosed that **1** was a clerodane-type diterpene with a carboxylic and formyl group. The relative stereochemistry of **1** was established by the difference NOE experiment. The NOEs were observed between (i) H-3 and H-19 and (ii) H-

*Part 30 in the series 'Chemosystematics of Bryophytes'. For part 29, see ref. [14].

Table 1. ^{13}C NMR data* of compounds **1**–**6** and **8**

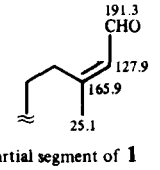
C	1†‡§	2‡§	3†‡§	4§	5§	8	6†‡§
1	18.0	17.8	17.4 (17.5)	17.2 (17.3)	17.3 (17.5)	18.0	39.7
2	26.5	26.5	26.6 (26.6)	26.4 (26.6)	26.5 (26.7)	26.6	18.4
3	120.4	120.6	120.7 (121.1)	120.7 (121.0)	120.7 (121.1)	120.7	41.9
4	143.5	143.6	143.4 (143.2)	143.4 (143.2)	143.7 (143.4)	143.8	33.2
5	37.7	37.7	37.7 (37.7)	37.7 (37.7)	37.7 (37.8)	37.9	56.1
6	35.3	35.4	35.0 (35.2)	35.1 (35.2)	35.2 (35.3)	35.6	20.5
7	21.3	21.4	19.0 (19.0)	19.0 (19.0)	19.0 (19.1)	21.7	44.5
8	48.8	49.0	54.7 (54.4)	54.7 (54.4)	54.8 (54.6)	49.1	74.1
9	38.9	38.6	39.2 (39.1)	38.8 (38.7)	38.9 (38.9)	38.9	62.2
10	46.2	46.3	46.4 (46.3)	46.4 (46.4)	46.4 (46.5)	46.4	39.1
11	39.1	37.7	39.1 (38.7)	37.6 (37.4)	39.3 (39.6)	39.5	24.5
12	26.5	34.2	26.4 (26.4)	34.2 (34.1)	24.9 (25.4)	24.8	35.1
13	165.9	165.2	164.6 (162.7)	164.2 (162.1)	146.6 (147.2)	147.1	147.4
14	127.9	127.4	128.0 (128.1)	127.5 (128.5)	138.7 (139.0)	139.0	138.8
15	191.3	191.5	190.5 (189.2)	191.2 (189.9)	113.3 (113.5)	113.2	113.5
16	25.1	17.7	25.2 (24.7)	17.7 (17.0)	116.1 (116.4)	115.9	115.5
17	179.1	180.4	206.1 (204.5)	206.1 (204.3)	206.2 (204.4)	181.0	24.0
18	19.76[a]	19.9[a]	19.5 (19.3)	19.6 (19.5)[a]	19.8 (19.7)[a]	20.1	33.4
19	17.8	17.9	17.9 (18.1)	17.9 (18.1)	18.0 (18.2)	18.0	21.5
20	19.84[a]	20.0[a]	19.9 (19.8)	19.9 (19.8)[a]	19.9 (19.9)[a]	20.1	15.4

*In $CDCl_3$ or C_6D_6 (in parentheses).
All assignments were confirmed by †^{13}C-^1H COSY,
‡Long-range ^{13}C-^1H COSY and §INEPT.
[a]Values in any vertical column may be interchanged.

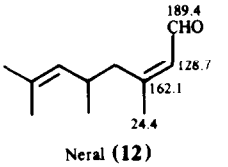
Table 2. Long-range correlations observed in the long-range ^{13}C–^1H COSY spectra of **1**

H (δ)	Correlated carbon
15 (9.84)	14
16 (1.92)	13, 14
18 (1.52)	4, 5, 6, 10
19 (0.99)	3, 4, 5
20 (0.87)	8, 9, 10, 11

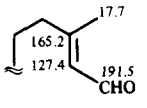
18 and H-20. The geometry of segment (A) was determined to be *Z*, not only from the comparison of ^{13}C NMR shifts of the partial segment in neral (**12**) (Fig. 1), but also from the detection of NOEs between the formyl proton and the olefine proton (H-14). Furthermore, the orientation of the carboxylic acid was evident from the following data. The NOE difference spectrum of a diol (**7**) obtained from reduction of **1** with lithium aluminium hydride exhibited the presence of NOE between H-20 and H-17. This result indicated that the carboxylic acid had an α-orientation. On the basis of the above spectral and difference NOE spectral examinations, the structure of **1** was established to be clerod-3, 13-(*Z*)-dien-15-al-17-oic acid.



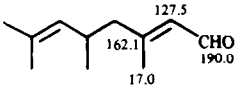
Partial segment of **1**



Neral (**12**)



Partial segment of **2**



Geranial (**13**)

High resolution mass spectrometry of compound **2** gave the same molecular formula $C_{20}H_{30}O_3$ (*m/z* 318.2190) as that of **1**. The ^1H NMR signals were very similar to those of **1**, except for the chemical shifts of the methyl proton (H-16), showing that **2** was the geometrical isomer on the $\Delta^{13,14}$ double bond found in **1**. This assumption was confirmed as follows. The ^{13}C NMR signals of segment (A) was in good accordance with those of the partial segment of geranial (**13**) (Fig. 1). Furthermore, NOEs were observed between methyl (H-16) and formyl proton (H-15), methyl H-18 and methyl H-20. On the basis of the above spectral data, the structure of **2** was established to be clerod-3, 13-(*E*)-dien-15-al-17-oic acid.

The IR spectrum of compound **3**, $C_{20}H_{30}O_2$ (*m/z* 302.2241), showed the presence of a carbonyl group (1730, 1680 cm^{-1}). The ^1H and ^{13}C NMR spectra resembled those of **1**, except for the presence of an additional formyl group in place of a carboxylic acid. This implied that the carboxylic acid group in **1** originated from the formyl group in **3**. This was confirmed by 2D COSY experiment which exhibited the presence of the partial structures OHC(15)–CH(14)=CMe(13)–CH_2(12)–CH_2(11)– and –OHCCH(8)–CH_2(7)–CH_2(6)–, and by comparison of ^1H and ^{13}C NMR spectra of **3** with those of **1** and **2**. NOEs were observed in the spectrum of **3** between (i) H-18 and H-20, (ii) H-20 and H-17 and (iii) H-16 and H-14. From

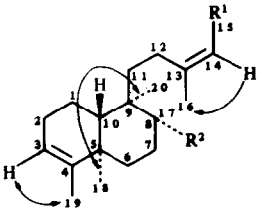
the above spectral data, the structure of **3** was established to be clerod-3,13-(*Z*)-dien-15,17-dial.

The ^1H and ^{13}CNMR signals for compound **4**, $C_{20}H_{30}O_2$ (*m/z* 302.2240), were very similar to those of **3** except for the chemical shift of a methyl proton (H-16), showing that **4** was the geometrical isomer on the $\Delta^{13,14}$ double bond in **3**. This assumption was confirmed by comparision of the ^{13}CNMR spectrum of **4** with that of **2** and by observation of NOEs between (i) H-16 and H-15, (ii) H-18 and H-20, and (iii) H-20 and H-17. Moreover, reduction of **2** with lithium aluminium hydride gave a diol, the spectral data of which were identical to those of a diol (**8**) obtained from reduction of **3** with lithium aluminium hydride. Accordingly, the structure of **4** was established to be clerod-3,13-(*E*)-dien-15,17-dial.

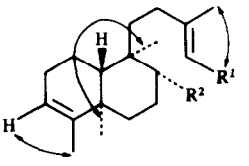
The IR spectrum of compound **5**, $C_{20}H_{30}O$ (*m/z* 286.2296) showed the presence of a carbonyl group (1715 cm^{-1}). The ^1H and ^{13}C NMR spectra resembled those of **9** [4], except for the presence of a formyl group in place of the carboxylic acid. This assumption was confirmed as follows. Reduction of **5** with lithium aluminium hydride gave a monoalcohol, the spectral data of which were identical with those of a monoalcohol (**11**) available from reduction of **10** [2]. Thus, the structure of **5** was represented as clerod-3,13(16),14-trien-17-al.

Among the six *ent*-kaurane-type diterpenoids (**17**, **18**, **21**–**24**) isolated from *J. infusca* collected in Yakushima Island, (16*S*)-*ent*-11α-hydroxykaurane-15-one (**23**) was the first naturally occuring compound although it was derived from **22** by the isomerization using alkali.

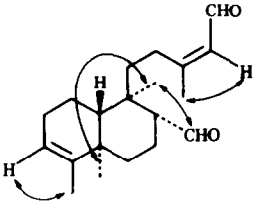
Jungermannia infusca is classified to three chemo-type (Table 3). The species belonging to the type I is intensely bitter. It elaborates the potent bitter kaurane-type diterpene glucosides (**25**–**29**) [5]. The species belonging to the types of II and III are tasteless. The former type produces *ent*-kaurane-type diterpenoids (**17**, **18**, **21**) [2], (**19**, **20**) [3], (**22**, **24**) [11, 12] and **23** [3]. The latter type biosynthesizes both clerodane-(**1**–**5**) and (**9**, **14**) [4] and labdane-type diterpenoids (**6**) [10] and (**15**, **16**) [4]. The present species collected in Yakushima Island and in Tokushima belong to chemotype II and III, respectively. These chemical data play a significant role in helping to understand the polymorphism of *J. infusca*.



1 R^1 = CHO, R^2 = COOH
7 R^1 = R^2 = CH_2OH



2 R^1 = CHO, R^2 = COOH
8 R^1 = R^2 = CH_2OH



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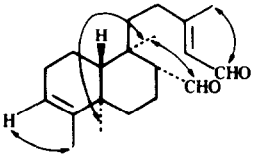
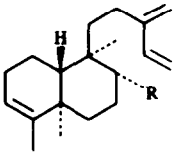
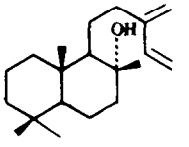


4



5 R = CHO
9 R = COOH
10 R = COOMe
11 R = CH_2OH



iso-abienol (**6**)

NOEs (⌒) observed by NOE difference spectra

EXPERIMENTAL

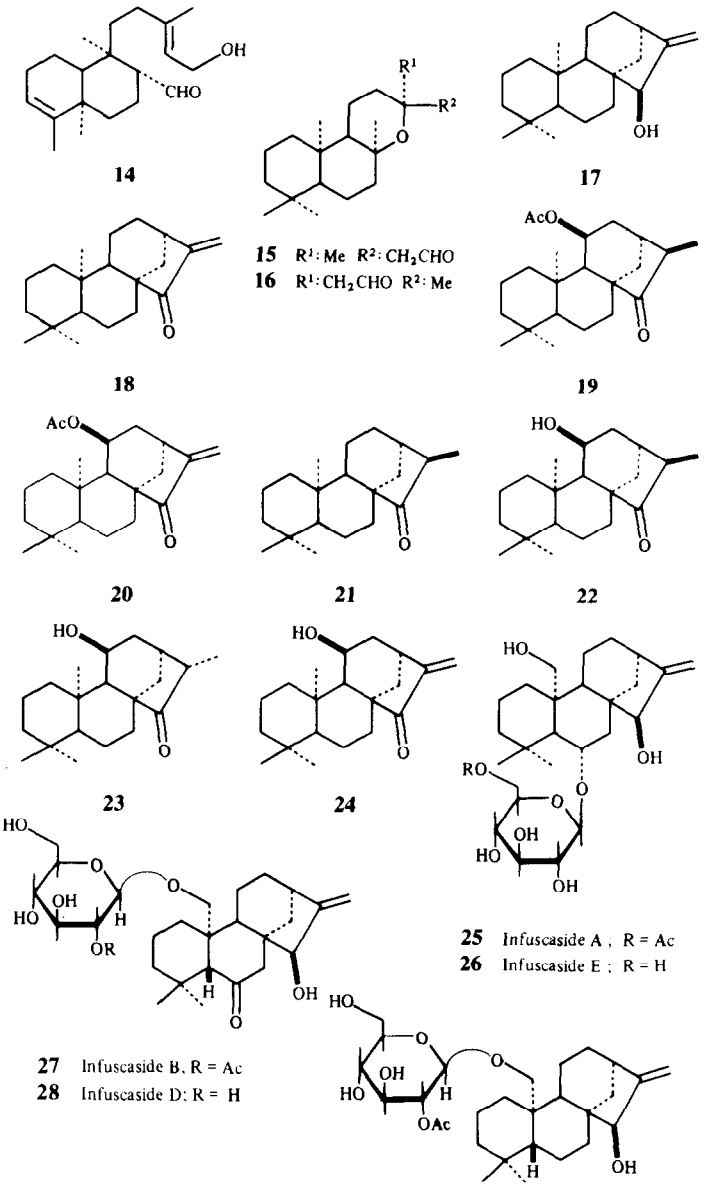
Mps: uncorr. The solvents used for spectral determinations were TMS–$CDCl_3$, [^1H NMR (400 MHz); ^{13}C NMR (100 MHz) unless otherwise stated]; $CHCl_3$ (IR and $[\alpha]_D$); EtOH(UV). A mixed solvent of MeOH and $CHCl_3$ (1:1) was used for Sephadex LH-20 column chromatography. TLC and GC were carried out as previously reported [13].

Plant material. Jungermannia infusca (Mitt.) Steph. was collected in Koutsuzan, Tokushima, in November 1987 and in Yakushima Island in October 1987 and identified by Dr M. Mizutani. The voucher specimen was deposited at the Institute of Pharmacognosy, Tokushima Bunri University.

Extraction and isolation. Fresh *Jungermannia infusca* was ground mechanically and extracted with EtOAc × 2 overnight at room temp. The crude extract (15g) was chromatographed on silica gel using *n*-hexane–EtOAc gradient to divide it into five fractions. Fr. 4 (7:3 and 1:1) (13 g) was rechromatographed on Sephadex LH-20, silica gel (*n*-hexane–EtOAc) and a Lobar column [Lichroprep Si 60 Type A, sol.; *n*-hexane–EtOAc

Table 3. Chemo-types of the liverwort *Jungermannia infusca*

Compounds	Type I	Type II	Type III
1			+
2			+
3			+
4			+
5			+
6 [10]			+
9 [4]			+
14 [4]			+
15 [4]			+
16 [4]			+
17 [2]	+	+	
18 [2]		+	
19 [3]		+	
20 [3]		+	
21 [2]		+	
22 [11, 12]		+	
23 [3]		+	
24 [11, 12]		+	
25 [5]	+		
26 [5]	+		
27 [5]	+		
28 [5]	+		
29 [5]	+		



(4:1)] to give **1** (171.1 mg) and **2** (146.5 mg). Compound **1**: mp 103–105°; $[\alpha]_D$: −48° (*c* 5.92); HRMS:Found:$[M]^+$ 318.2201; $C_{20}H_{30}O_3$ requires 318.2194; UV λ_{max} nm (log ε): 205 (3.82), 239 (4.30); IR ν_{max} cm^{-1}: 3550–3000, 1700, 1660, 1440, 1390; ^1H NMR: δ .87(3H, *s*, H-20), 0.99 (3H, *s*, H-18), 1.52 (3H, *s*, H-19), 1.92 (3H, *s*, H-16), 2.37 (1H, *m*, H-12), 2.41 (1H, *m*, *J* = 12.5, 3.0, H-8), 2.65 (1H, *ddd*, *J* = 12.5, 12.5, 3.7, H-12), 5.13 (1H, *br s*, H-3), 5.78 (1H, *d*, *J* = 8.1, H-14), 9.84 (1H, *d*, *J* = 8.1, H-15); ^{13}C NMR: Table 1; EIMS *m/z* (rel. int.): 318$[M]^+$(14), 219 (23), 175 (28), 173 (30), 145 (32), 121 (36), 119 (46), 109 (41), 107 (62), 105 (48), 95 (100), 93 (48), 91 (47), 81 (70), 69 (52), 55 (57). Compound **2**: oil; $[\alpha]_D$: −50° (*c* 6.15); UV λ_{max} nm (log ε): 204 (3.81), 240 (4.18); IR ν_{max} cm^{-1}: 3500–3000, 1710, 1680, 1430, 1380; HRMS: Found: $[M]^+$ 318.2190; $C_{20}H_{30}O_3$ requires 318.2195; ^1H NMR: δ 0.96 (3H, *s*, H-20), 1.07 (3H, *s*, H-18), 1.60 (3H, *s*, H-19), 2.20 (3H, *s*, H-16), 2.32 (1H, *ddd*, *J* = 12.5,12.5,3.7, H-12), 2.46 (1H, *dd*, *J* = 12.6,2.9, H-8), 5.21 (1H, *br s*, H-3), 5.90 (1H, *d*, *J* = 8.1, H-14), 9.97 (1H, *d*, *J* = 8.1, H-15); ^{13}C NMR: Table 1; EIMS *m/z* (rel. int.) 318 $[M]^+$ (43), 285 (33), 257 (25), 239 (32), 219 (67), 175 (43), 173 (72), 159 (37), 145 (60), 133 (49), 121 (45), 119 (62), 107 (91), 97 (50), 95 (100), 81 (64), 69 (38); Fr. 3 (1.8 g) was rechromatographed on Sephadex LH-20. The fraction containing diterpene was further rechromatographed on silica gel (*n*-hexane–EtOAc) and on a Lobar column to give *iso*-abienol (**6**) (103 mg) [12], **3** (27.9 mg), **4** (15.2 mg) and **5** (50.2 mg). Compound **3**: oil; $[\alpha]_D$: −62.7° (*c* 1.32): UV λ_{max} nm (log ε): 209 (3.50), 242 (3.02), 248 (3.08), 254 (3.07); IR ν_{max} cm^{-1}: 2950, 1730, 1680, 1390; HRMS: Found: $[M]^+$ 302.2241; $C_{20}H_{30}O_2$ requires 302.2246; ^1H NMR (C_6D_6): δ0.66 (3H, *s*, H-20), 0.86 (3H, *s*, H-18), 1.52 (3H, *s*, H-19), 1.55 (3H, *s*, H-16), 1.84–2.01 (4H, *m*, H-2, H-2′, H-8, H-12′), 2.12 (1H, *ddd*, *J* = 12.6, 12.6, 5.9, H-12), 5.14 (1H, *br s*, H-3), 5.80 (1H, *d*, *J* = 7.3, H-14), 9.44 (1H, *d*, *J* = 5.1, H-17), 9.97 (1H, *d*, *J* = 7.3, H-15); ^{13}C NMR: Table 1; EIMS *m/z* (rel. int.): 302 $[M]^+$ (15), 203 (22), 175 (43), 147 (23), 145 (35), 135 (21), 133 (75), 131 (24), 121 (40), 119

(58), 107 (77), 105 (62), 97 (52), 95 (100), 93 (60), 81 (75), 67 (45), 55 (70). Compound **4**: oil; $[\alpha]_D$: −72.8° (*c* 0.74); UV λ_{max} nm (log ε): 209 (3.61), 242 (3.14), 248 (3.17), 254 (3.15); IR ν_{max} cm^{-1}: 1715, 1690, 1395; HRMS: Found: $[M]^+$ 302.2240; $C_{20}H_{30}O_2$ requires 302.2246; ^1H NMR (C_6D_6): δ0.68 (3H, *s*, H-20), 0.87 (3H, *s*, H-18), 1.52 (3H, *s*, H-19), 1.63 (3H, *s*, H-16), 5.14 (1H, *br s*, H-3), 5.86 (1H, *br d*, *J* = 7.3, H-14), 9.43 (1H, *br s*, H-17), 9.89 (1H, *d*, *J* = 7.4, H-15); ^{13}C NMR: Table 1; EIMS *m/z* (rel. int.): 302 $[M]^+$ (13), 284 (3), 274 (7), 251 (4), 239 (8), 232 (17), 203 (24), 187 (12), 175 (44), 159 (22), 145 (42), 133 (100), 119 (73), 107 (89), 95 (96), 81 (95). Compound **5**: oil: $[\alpha]_D$: −63.7° (*c* 1.93); UV λ_{max} nm (log ε): 225 (3.44), 208 (3.55); IR ν_{max} cm^{-1}: 2930, 1715, 1450, 1380, HRMS: Found: $[M]^+$ 286.2296; $C_{20}H_{30}O$ requires 286.2297; ^1H NMR (C_6D_6): δ0.72 (3H, *s*, H-20), 0.88 (3H, *s*, H-18), 1.52 (3H, *s*, H-19), 4.98 (2H, *br s*, H-16), 5.04 (1H, *d*, *J* = 11.0, H-15), 5.14 (1H, *br s*, H-3), 5.32 (1H, *d*, *J* = 17.6, H-15[1]), 6.37 (1H, *dd*, *J* = 17.6, 11.0, H-14), 9.56 (1H, *d*, *J* = 2.9, H-17); ^{13}C NMR: Table 1; EIMS *m/z* (rel. int.): 286 $[M]^+$ (8), 175 (38), 159 (25), 145 (36), 133 (40), 119 (78), 107 (92), 95 (98), 81 (97), 67 (63), 55 (86), 41 (100).

The air-dried *J. infusca* (521 g) collected in Yakushima Island in October 1986 was treated in the same manner as described above to give the crude oil (3.93 g) which was chromatographed on silica gel using *n*-hexane–EtOAc gradient to afford **17** (58 mg), **18** (15 mg), **21** (10 mg), **22** (23 mg), **23** (13 mg) and **24** (73 mg), whose physical and spectral data were identical to those of reported data [2, 3, 11, 12].

Reduction of **1**. To a suspension of $LiAlH_4$ (15 mg) in Et_2O was added the mixture of **1** (12 mg) in Et_2O. The reaction mixture was stirred at 0° for 30 min. After work-up as usual, it was carefully purified by prep. TLC to furnish the diol (**7**) (1 mg). HRMS: Found $[M]^+$ 306.2564; $C_{20}H_{34}O_2$ requires 306.2558; ^1H NMR: δ0.75 (3H, *s*, H-20), 1.02 (3H, *s*, H-18), 1.60 (3H, *s*, H-19), 1.75 (3H, *s*, H-16), 2.18 (1H, *ddd*, *J* = 12.5,12.5,3.7, H-12), 3.33 (1H, *dd*, *J* = 11.0,7.3, H-17), 3.81 (1H, *dd*, *J* = 11.0,4.4, H-17′), 4.03 (1H, *dd*, *J* = 11.7,6.6, H-15), 4.17 (1H, *dd*, *J* = 11.7,8.1, H-15′), 5.20 (1H, *br s*, H-3), 5.41 (1H, *br t*, *J* = 7.3, H-14); EIMS *m/z* (rel. int.): 306 $[M]^+$ (17), 288 (32), 273 (10), 255 (10), 245 (4), 205 (49), 187 (25), 175 (15), 159 (25), 132 (33), 119 (55), 107 (56), 95 (100), 81 (52), 69 (30), 55 (35).

Reduction of **2**. To a suspension of $LiAlH_4$ (15 mg) in Et_2O was added **2** (10 mg) in Et_2O. The mixture was stirred at 0° for 40 min. Work-up as usual gave a diol (**8**) (4.2 mg): IR ν_{max} cm^{-1}: 3400, 2950, 1460, 1390; ^1H NMR: δ0.75 (3H, *s*, H-20), 1.02 (3H, *s*, H-18), 1.60 (3H, *s*, H-19), 1.69 (3H, *s*, H-16), 3.34 (1H, *dd*, *J* = 10.3,8.8, H-17), 3.83 (1H, *dd*, *J* = 10.7,3.4, H-17′), 4.14 (2H, *d*, *J* = 6.8, H-15), 5.20 (1H, *br s*, H-3), 5.41 (1H, *br t*, *J* = 6.8, H-14); EIMS *m/z* (rel. int.): 306 $[M]^+$ (5), 288 (8), 273 (6), 257 (4), 205 (29), 187 (16), 175 (14), 159 (18), 145 (21), 119 (44), 107 (51), 95 (100), 81 (44), 69 (24), 55 (31).

Reduction of **4**. Compound **4** (5.3 mg) was reduced in the same manner as described above to give a diol whose spectral data were identical to those of **8** prepared from **2**.

Reduction of **5**. Compound **5** (36.9 mg) was reduced in the same manner as described above to give a monoalcohol whose spectral data were identical to those of **11** prepared from **10** [4].

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