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TERPENOIDS FROM THE JAPANESE LIVERWORTS *JACKIELLA JAVANICA* AND *JUNGERMANNIA INFUSCA*

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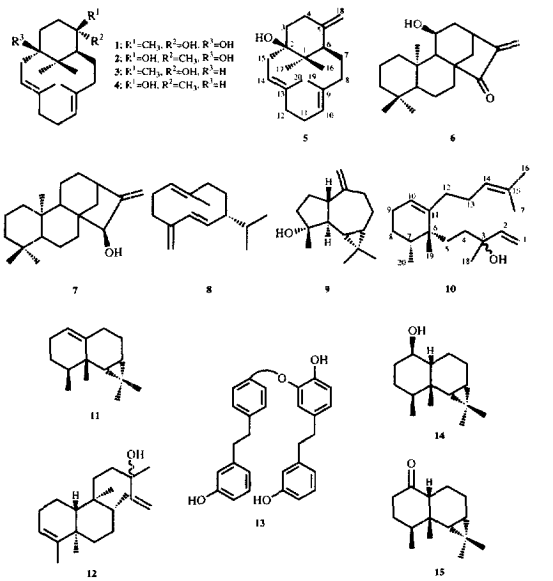
Key Word Index—*Jungermannia infusca*; *Jackiella javanica*; Jungermanniaceae; Adelanthaceae; Hepaticae; infuscatrienol; aristolane-type; germacrane-type; clerodane-type; *ent*-verticillane-type; *ent*-kaurane-type; sesquiterpenoid; diterpenoid; *bis*-bibenzyl.

Abstract—Five *ent*-verticillane-type diterpenoids have been isolated from the Japanese liverwort *Jackiella javanica*, along with previously known sesqui- and di-terpenoids. The chemical shifts of the ^1H and ^{13}C NMR spectra of *ent*-verticillane-type diterpenoids are given. A new monocyclic diterpenoid, infuscatrienol, three known sesqui- and di-terpenoids, and a *bis*-bibenzyl derivative have been isolated from the Japanese *Jungermannia infusca*. © 1997 Elsevier Science Ltd

INTRODUCTION

As part of a search for biologically active substances of the Hepaticae, we are studying the chemical constituents of liverworts [1, 2]. *Jackiella javanica* grows on wet rock and is distributed in South-East Asia, Taiwan and Japan. We have reported the presence of unique *ent*-verticillane-type diterpenoids with a carbon skeleton similar to that of taxane-type diterpenoids [3, 4]. The stereostructure of *ent*-verticillanediol (**1**) was established by X-ray crystallographic analysis [3]. However, the ^1H and ^{13}C NMR spectral data of the *ent*-verticillanes **1–5** have not been reported before. The liverwort *Jungermannia infusca*, which grows on wet soil and distributes in Japan, contains many types of diterpenoids, such as clerodane-, *ent*-kaurane-, labdane-and pimarane-type [2]. Since *J. infusca* exists in different chemo-types [5], we reinvestigated the chemical constituents of *J. infusca* collected in Kochi, Japan. This species contains a new monocyclic diterpenoid named infuscatrienol (**10**) [6] and the known *bis*-bibenzyl compound **13** which had not been found in a previous study of the same plant [5]. In this paper, we report the assignments of the ^1H and ^{13}C NMR chemical shifts of *ent*-verticillanes **1–5** isolated from *J. javanica*, the structure elucidation of **10** in detail, and the distribution of sesqui- and di-terpenoids and aromatic compounds in *J. infusca*.



RESULTS AND DISCUSSION

A combination of column chromatography on silica gel, Sephadex LH-20 and preparative HPLC of the ether extract of *J. javanica* gave five *ent*-verticillane-type diterpenoids, *ent*-verticillanediol (**1**) [3, 4], *ent*-5-*epi*-verticillanediol (**2**) [3, 4], *ent*-verticillol (**3**) [3, 4, 7], *ent*-5-*epi*-verticillol (**4**) [3, 4] and *ent*-isoverticillenol (**5**) [3, 4], two kaurane-type diterpenoids, *ent*-11α-hydroxy-16-kauren-15-one (**6**) [8] and *ent*-15α-hydroxy-16-kaurene (**7**) [9], and two sesquiterpenoids, (+)-germacrene D (**8**) [10–12] and *ent*-spathulenol (**9**) [1, 2].

The ^1H NMR spectrum (Table 1) of **1**, $C_{20}H_{34}O_2$

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Table 1. ^{1}H NMR data of compounds **1**–**5** and **10** (400 MHz, $CDCl_3$)

H	**1**	**2**	**3**	**4**	**5**	**10***
1						
2						4.95 *dd* (10.7, 1.7)†
3	1.69–1.90 2H, *m*	1.56–1.66 *m*	1.42–1.49 *m*	1.49–1.53 *m*		5.18 *dd* (17.3, 1.7)
		1.94–2.20 *m*	1.61 *br s like*	1.41–1.47 *m*		5.79 *dd* (17.3, 10.7)
4	1.69–1.90 *m*	1.56–1.66 *m*	1.93–2.11 *m*	2.18–2.29 *m*	1.81–1.94 2H, *m*	
	1.98–2.16 *m*	1.94–2.20 *m*	1.70 *dt like*	1.49–1.53 *m*		
5			1.79–1.88 *m*	1.79–1.87 *dt like*	2.31 *ddd* (14.2, 6.4, 2.0)	1.26 *ddd* (12.7, 12.7, 4.2)
6	2.40 *m*	1.94–2.20 *m*			2.54 *m*	1.45–1.57 *m*
7	1.35 *m*	1.37 *m*	2.19–2.28 *m*	1.96–2.12 *m*		1.45–1.57 2H, *m*
	1.47 *m*	1.46 *m*	1.30 *m*	1.34 *ddd* (13.7, 13.7, 4.4)	2.96 *d* (10.3)	
8	1.98–2.16 2H, *m*	1.94–2.20 2H, *m*	1.42–1.49 *m*	1.41–1.47 *m*	1.33 *br t*	1.70 *m*
			1.93–2.11 *m*	1.96–2.12 *m*	1.48 *m*	
9			2.19–2.28 *m*	2.18–2.29 *m*	1.81–1.94 2H, *m*	1.42 2H, *m*
10	4.89 *d* (10.8)	4.79 *d* (11.7)	4.89 *d* (10.7)	4.80 *d* (11.2)		1.99 2H, *m*
11	1.98–2.16 *m*	1.94–2.20 *m*	1.93–2.11 *m*	1.96–2.12 *m*	4.69 *d* (10.7)	5.54 *br s*
	2.30 *ddd* (12.7, 12.7, 4.4)	2.40 *q like*	2.39 *q like*	2.38 *q like*	1.98–2.10 *m*	
12	1.98–2.16 2H, *m*	1.94–2.20 2H, *m*	1.93–2.11 *m*	1.96–2.12 2H, *m*	2.46 *m*	
			2.19–2.28 *m*		1.98–2.10 2H, *m*	2.05 2H, *t like*
13						
14	5.65 *d* (13.2)	5.45 *d* (12.7)	5.67 *d* (12.2)	5.48 *d* (12.7)		2.24 2H, *br s like*
15	1.98–2.16 *m*	1.94–2.20 *m*	1.79–1.88 *m*	1.79–1.87 *dt like*	5.60 *br d*	5.30 *t like*
	2.66 *ddd* (14.6, 14.6, 2.9)	2.65 *ddd* (14.7, 12.7, 2.9)	2.70 *ddd like*	2.70 *dt like*	1.98–2.10 *m*	
16	0.80 3H, *s*	0.97 3H, *s*	0.79 3H, *s*	0.98 3H, *s*	2.76 *ddd* (14.2, 12.7, 2.9)	
17	0.74 3H, *s*	0.72 3H, *s*	0.72 3H, *s*	0.68 3H, *s*	0.72 3H, *s*	1.68 3H, *d* (1.2)
18	1.29 3H, *s*	1.22 3H, *s*	1.26 3H, *s*	1.21 3H, *s*	0.89 3H, *s*	1.59 3H, *s*
					4.61 *d* (2.0)	1.12 3H, *s*
19	1.51 3H, *s*	1.51 3H, *s*	1.51 3H, *s*	1.50 3H, *s*	4.86 *d* (2.0)	
20	1.57 3H, *s*	1.57 3H, *s*	1.54 3H, *s*	1.54 3H, *s*	1.56 3H, *s*	0.91 3H, *s*
					1.58 3H, *s*	0.87 3H, *d* (6.8)

* 600 MHz (in C_6D_6).

† Parenthesis coupling constants (*J*, Hz).

Table 2. ^{13}C NMR data of compounds **1**–**5**, **10**, **11**, **14** and **15** (100 MHz, $CDCl_3$)

C	1	2	3	4	5	10†	11	14	15
1	41.7	41.7	37.2	36.4	42.1	111.8	120.3	74.1	217.1
2	76.8	77.0	43.3	43.8	76.8	146.2	25.7	29.9	38.84
3	37.2	35.4	28.8	26.9	38.9	73.3	27.2	25.0	28.8
4	39.9	38.2	41.3	38.8	34.5	37.4	36.7	32.02	31.3
5	75.2	73.0	75.8	73.7	147.3	31.1	36.8	36.4	38.81
6	45.0	42.9	44.8	42.1	42.8	41.1	33.5	34.3	31.9
7	21.4	20.8	20.8	20.3	19.8	34.3	19.6	19.9	19.3
8	40.7*	40.1	41.2*	41.3	37.7	27.6	20.9	21.9	20.3
9	133.2	133.0	133.0	133.0*	133.9	26.2	30.0	26.2	24.6
10	129.8	129.7	129.9	129.9	128.1	122.6	144.2	48.5	58.4
11	26.6	26.6	26.6	26.6	26.3	143.6	18.5	18.9	18.8
12	40.8*	40.9	41.1*	40.3	40.7	31.2	16.5	31.96	31.5
13	134.5	134.5	133.3	133.1*	134.3	28.3	29.9	16.9	17.0
14	124.6	124.5	127.7	127.7	124.3	125.9	23.0	27.4	25.6
15	43.1	42.7	34.1	34.1	42.0	131.4	16.1	17.0	16.2
16	23.2	21.2	26.0	26.5	19.2	18.2			
17	21.1	22.4	28.0	27.9	22.1	26.3			
18	24.3	31.8	24.1	32.2	106.7	28.5			
19	15.9	16.1	15.9	16.2	15.6	22.1			
20	15.4	15.4	15.2	15.2	15.1	16.6			

* May be interchanged in vertical column.
† in C_6D_6.

(*m/z* 306.2554), showed the presence of five tertiary methyls (δ 0.74, 0.80, 1.29, 1.51 and 1.57 each 3H, *s*) and two olefinic protons (δ 4.89 *d*, J = 10.8 Hz, 5.68 *d*, J = 13.2 Hz). This spectrum was identical with that of authentic *ent*-verticillanediol (**1**) [3, 4]. The ^{13}C NMR (Table 2) and DEPT spectra of **1** also displayed two trisubstituted olefinic carbons (δ 124.6, 129.8 each *d*, 133.2, 134.5 each *s*) and two quaternary carbons (δ 75.2 and 76.8) bearing a tertiary hydroxyl group, along with five methyls, seven methylenes, a methine and a quaternary carbon. The connectivity of each proton and carbon of **1** was clarified by the ^1H-^1H, C-H COSYs and HMBC spectra (Fig. 1). Thus, the

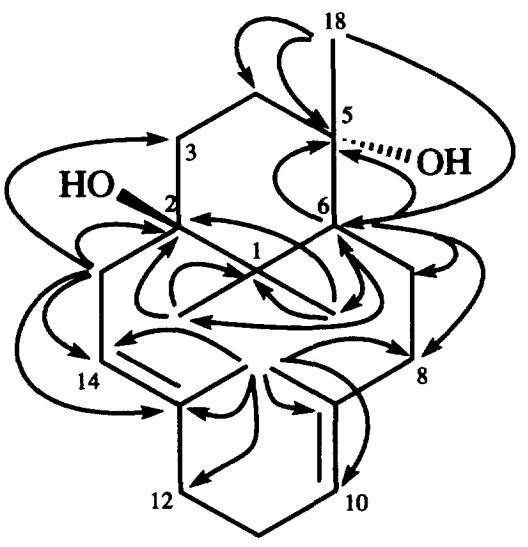

Fig. 1. The long range C-H correlations by the HMBC spectrum of **1**.

assignments of the ^1H and ^{13}C NMR of **1** were accomplished by these spectral analysis.

The ^1H NMR spectra of the other compounds **2**–**5** were identical with those of authentic spectra. The complete assignments of the ^1H and ^{13}C NMR spectra (Tables 1 and 2) of **2**–**5** were carried out by using the same NMR techniques as used for **1**. This is the first report on the assignments of the chemical shifts of ^1H and ^{13}C NMR of *ent*-verticillane-type compounds **1**–**5**.

Previously, the presence of germacrene D in liverworts was confirmed by GC-mass spectrometry [1, 2]. Recently, König *et al.* [13] confirmed the presence of the unusual (+)-enantiomer of germacrene D from the liverwort, *Preissia quadrata*, by GC. The isolation of (+)-germacrene D (**8**) [10–12] is the first record from the liverwort. The previous [3, 4] and the present experiments showed that *J. javanica* produced *ent*-verticillane-type diterpenoids as main components. *Ent*-verticillanes are significant chemical markers of *J. javanica*, since no verticillanes have been detected in or isolated from 800 species of liverworts so far chemically examined [1, 2].

Column chromatograph of the ether extract of *J. infusca* yielded a new monocyclic diterpenoid, infuscatrienol (**10**) [6], together with the known aristolane-type sesquiterpenoid (−)-1(10)-aristolene (**11**) [14, 15], clerodane-type diterpenoid, (−)-kolavelool (**12**) [16] and *bis*-bibenzyl, perrottetin E (**13**) [17].

The ^{13}C NMR and IR spectra of **10**, $C_{20}H_{34}O$ (HRMS *m/z* 290.2610 $[M]^+$), showed the presence of a tertiary hydroxyl group (3450 cm^{-1}, δ_C 73.3 *s*). The ^1H NMR (C_6D_6) spectrum (Table 1) contained the signals of a secondary methyl, two tertiary methyls,

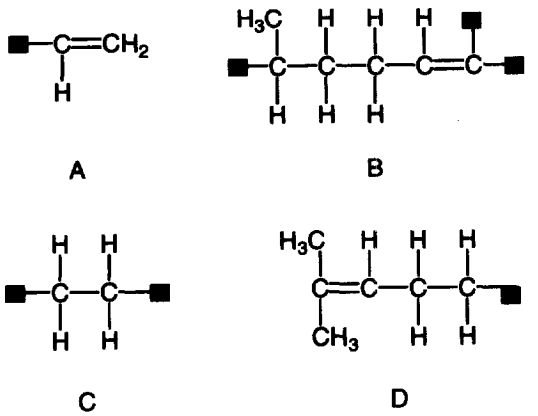

Fig. 2. The partial segments of **10**.

two olefinic methyls, two olefinic protons (δ 5.30 *t like*, 5.54 *br s*) and vinyl protons (δ 4.95 *dd*, 5.18 *dd*). Analysis of the ^{13}C NMR (Table 2) and DEPT spectra (C_6D_6) of **10** showed the presence of two tri-substituted olefinic carbons (δ 131.4, 143.6 each *s*, 122.6, 125.9 each *d*) and a vinyl carbon (δ 146.2 *d*, 111.8 *t*) and also showed six methylenes, a methine and a quaternary carbon. The four degrees of unsaturation and the IR, ^1H and ^{13}C NMR spectra suggested that **10** was a monocyclic diterpene with a tertiary hydroxyl group. The analysis of the ^1H-^1H, ^{13}C-^1H COSYs and totally correlated spectroscopy (TOSCY) indicated the presence of four partial segments A–D (Fig. 2). The connectivity of each partial structure was confirmed by the HMBC spectrum (Fig. 3). Nuclear Overhauser and exchange spectroscopy (NOESY) of **10** showed NOEs between (i) H-20 and H-5, (ii) H-20 and H-8, (iii) H-19 and H-2, and (iv) H-12 and H-5. The stereochemistry of H-19 and 20 was supported as shown in **10**. Thus, the structure of infuscatrienol (**10**) was established to be a monocyclic diterpene alcohol. However, the stereochemistry of the tertiary alcohol and the absolute configuration remain to be clarified. Many types of diterpenoids have been found in liverworts [1, 2], however, this is the first report of the isolation of a six-membered ring monocyclic diterpenoid from bryophytes. The distribution of monocyclic diterpenoids is rare in nature. It is known that same species belonging to the Umbelliferae elaborate monocyclic diterpenoids [18–20]. Possible biogenetic pathways for the formation of the new diterpene alcohol **10** are shown in Fig. 4. Compound **10** might be biosynthesized from geranylgeranyl pyrophosphate *via* methyl migration and deprotonation (route A) or from a labdane-type intermediate *via* methyl migration, cleavage of a single bond and protonation (route B).

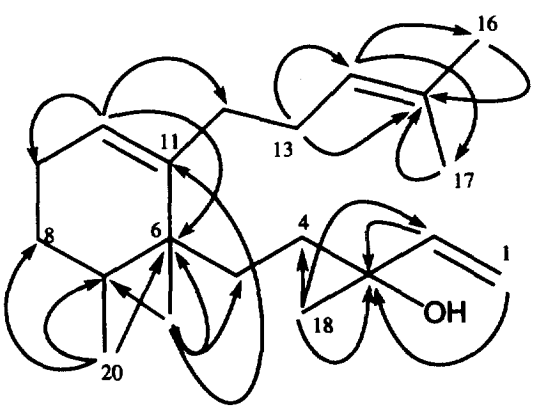

Fig. 3. The long range C-H correlations by the HMBC spectrum of **10**.

The structure of (−)-1(10)-aristolene (**11**) [14, 15] was elucidated by the ^1H-^1H, ^{13}C-^1H COSYs and HMBC spectra. These spectral data were in agreement with those of reference data [15]. Furthermore, the chemical degradation of **11** to **15** was carried out in order to confirm its stereochemistry. Hydroboration of **11** and subsequent reaction of the product with hydroperoxide gave the alcohol **14**, which on oxidation with pyridinium chlorochromate–aluminium oxide (PCC–Al_2O_3) gave the ketone **15**. The NOESY spectra of **14** and **15** clarified the stereochemistry of **11**. The complete assignments of the ^1H and ^{13}C NMR chemical shifts of **11** are reported for the first time (see Tables 2 and 3).

J. infusca exists in three chemo-types; (i) kaurane-type, (ii) kaurane-type glucoside, and (iii) clerodane- and labdane-type [5]. The present *J. infusca* which contained a new monocyclic diterpenoid, infuscatrienol (**10**) [6], and a *bis*-bibenzyl, perrottetin E (**13**) [17] which is the major component (24% yield of the crude extract), is classified as a new chemo-type.

EXPERIMENTAL

^1H and ^{13}C NMR. 400 and 600 MHz (^1H NMR) and 100.16 MHz (^{13}C NMR). Chemical shift values were expressed in δ (ppm) downfield from TMS as an int. standard (^1H NMR) and δ 77.03 (ppm) from $CHCl_3$ as a standard (^{13}C NMR). TLC: visualized under UV (254 nm) light and by spraying with 10% H_2SO_4 or Godin reagent [21] followed by heating. MeOH–CH_2Cl_2 (1:1) was used for Sephadex LH-20. $[\alpha]_D$: $CHCl_3$.

Plant material. Jackiella javanica Schiffn. and *Jungermannia infusca* (Mitt.) Steph. were collected in Kagoshima, Japan, November, 1993 and Kochi, Japan, July, 1994, respectively. These species were identified by Dr M. Mizutani (The Hattori Botanical Laboratory, Miyazaki, Japan). The voucher specimens were deposited at the Institute of Pharmacognosy, Tokushima Bunri University.

Extraction and isolation. The Et_2O extract (3.3 g) of *J. javanica* (490 g) was divided into 10 frs by CC on silica gel using a *n*-hexane–EtOAc gradient solvent system. Fr. 3 was chromatographed on silica gel (*n*-pentane and *n*-hexane) to afford (+)-germacrene D (**8**) (9.6 mg) ($[\alpha]_D$ +243.5° *c* 8.00) [10–12]. Fr. 6 was chromatographed on Sephadex LH-20, silica gel (*n*-hexane–Et_2O 9:1) and MPLC (Lobar^R column; RP-18, MeCN) and finally purified by prep. HPLC

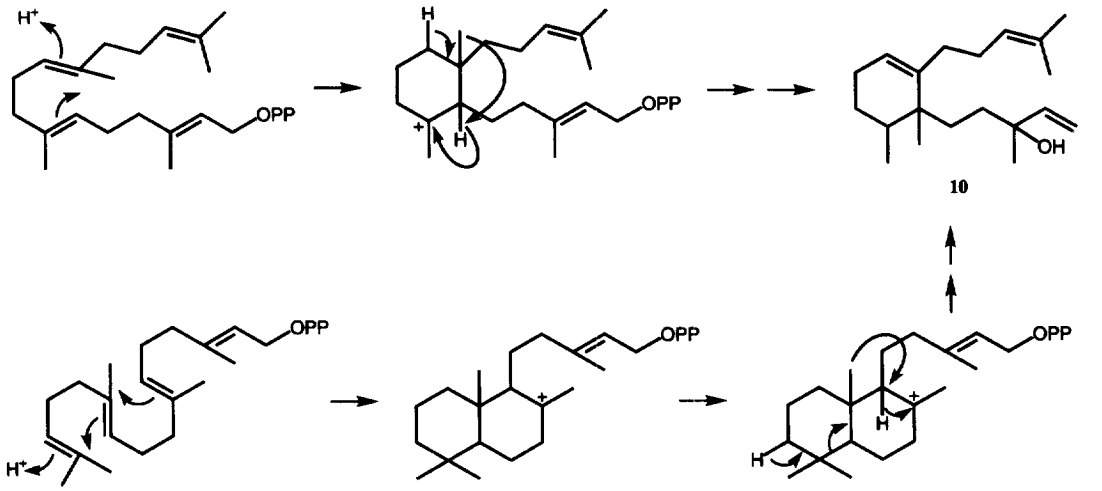

Fig. 4. Tentative biogenetic pathways of **10**.

Table 3. ^{1}H NMR data of compounds **11**, **14** and **15** (400 MHz, $CDCl_3$)

H	**11**	**14**	**15***
1	5.24 *br s*	3.80 *br s*	
2	1.89–2.01 2H, *m*	1.51–1.62 2H, *m*	2.22 *dddd* (14.9, 4.6, 1.7, 1.7)†, β 2.31 *ddd* (14.9, 13.5, 6.8), α
3	1.35–1.47 2H, *m*	1.14–1.30 *m* 1.51–1.62 *m*	1.49–1.57 *m*, β 1.68 *dddd* (13.5, 6.9, 3.9, 2.2), α
4	1.70–1.79 *m*	1.68 *m*	2.06 *m*
6	0.56 *d* (9.3)	0.29 *d* (9.8)	0.36 *d* (9.5)
7	0.74 *ddd* (9.3, 9.3, 3.4)	0.62 *m*	0.67 *m*
8	1.35–1.47 *m* 1.89–2.01 *m*	1.80 2H, *m*	1.79 2H, *m*
9	1.70–1.79 *m* 2.21 *m*	1.14–1.30 2H. *m*	1.43 *m*, α 1.49–1.57 *m*, β
10		1.14–1.30 *m*	1.82 *m*
12	1.02 3H, *s*	0.99 3H, *s*	1.03 3H, *s*
13	0.98 3H, *s*	1.18 3H, *s*	1.21 3H, *s*
14	1.07 3H, *s*	1.26 3H, *s*	1.01 3H, *s*
15	0.97 3H, *d* (7.8)	0.93 3H, *d* (6.8)	1.03 3H, *d* (6.3)

* Measured at 600 MHz.
† Parentheses coupling constants (*J*, Hz).

(CHEMCOSORB 5-ODS-H MeCN) to give *ent*-15α-hydroxy-16-kaurene (**7**) (14.6 mg) [9] and *ent*-5-*epi*-verticillol (**4**) (26.4 mg) ([α]$_D$ −141.6°, *c* 2.22) [3, 4]. Fr. 7 was chromatographed on Sephadex LH-20, silica gel (*n*-hexane–EtOAc 9:1) and MPLC (Lobar® column, *n*-hexane–EtOAc 9:1) to give *ent*-verticillol (**3**) (45.7 mg) ([α]$_D$ −106.3°, *c* 2.79) [3, 4, 7] and a mixt. of terpenoids. Rechromatography on prep. HPLC (NUCLEOSIL, *n*-hexane–EtOAc 9:1) of this mixt. gave *ent*-spathulenol (**9**) (33.3 mg) [1, 2] and *ent*-isoverticillenol (**5**) (45.7 mg) ([α]$_D$ −116.5°, *c* 5.40), [3, 4]. Fr. 9 was rechromatographed on Sephadex LH-20, silica gel (*n*-hexane–EtOAc 4:1 or 7:3) and MPLC (Lobar® column, *n*-hexane–EtOAc 4:1) to afford *ent*-11α-hydroxy-16-kauren-15-one (**6**) (16.4 mg) [8] and *ent*-verticillanediol (**1**) (6.6 mg) ([α]$_D$ −97.5°, *c* 0.92) [3, 4]. Fr. 10 was rechromatographed on Sephadex LH-20, silica gel (*n*-hexane–EtOAc 7:3) and MPLC (Lobar® column; Diol, CH_2Cl_2–Et_2O 9:1) and finally purified by prep. HPLC (Cosmosil 5C_{18}, MeOH) to give *ent*-5-*epi*-verticillanediol (**2**) (83.8 mg) ([α]$_D$ −115.7°, *c* 11.01) [3, 4].

Air dried *J. infusca* (806 g) was extracted with Et_2O and the crude extract (8.3 g) was chromatographed on silica gel (*n*-hexane–EtOAc gradient) to give 13 frs. Fr. 2 gave (−)-1(10)-aristolene (**11**) (166.8 mg) ([α]$_D$ −53.5°, *c* 10.6) [14, 15]. Fr. 5 was rechromatographed on silica gel impregnated with 10% $AgNO_3$ (*n*-hexane–Et_2O 19:1 and 97:3) to give (*E*)-β-farnesene (17.8 mg). Rechromatography on Sephadex LH-20 silica gel (*n*-hexane–Et_2O 9:1) of fr. 8 gave infuscatrienol (**10** (59.2 mg) [6] and (−)-kolavelool (**12**) (225.8 mg) [16]. Fr. 12 was chromatographed on Sephadex LH-20 and silica gel (*n*-hexane–Et_2O 9:1) to give perrottetin E (**13**) (2.00 g) [17].

Infuscatrienol (**10**). [α]$_D$ +29.2° (*c* 0.90); FTIR ν_{max}

cm^{-1}: 3450 (OH); HREIMS; *m/z* 290.2610. Calcd for $C_{20}H_{34}O$: 290.2609; ^1H and ^{13}C NMR: Tables 1 and 2; EIMS *m/z* (rel. int.): 290 $[M]^+$ (2), 272 (9), 243 (5), 229 (9), 203 (6), 191 (100), 175 (17), 147 (25), 135 (40), 121 (50), 107 (49), 95 (54), 81 (39), 69 (63), 55 (28), 41 (45).

Preparation of alcohol **14**. To a stirred soln of compound **11** (42 mg) in dry THF (0.5 ml) was added $BH_3 \cdot THF$ (1.5 ml) and the mixt. stirred for 1 hr. H_2O (0.5 ml), 3 mol NaOH (0.75 ml) and 30% H_2O_2 (1 ml) were added successively and stirred for 1 hr. Et_2O was added to the reaction mixt. and washed with H_2O and satd NaCl and dried over $MgSO_4$, then filtered and evapd to give a residue which was chromatographed on silica gel (*n*-hexane–EtOAc 19:1 and 9:1) to afford alcohol **14** (33 mg): $[\alpha]_D + 116.5°$ (*c* 0.4); HREIMS: Found $[M]^+$ 222.1995; $C_{15}H_{26}O$ requires 222.1984; FTIR ν_{max} cm^{-1}: 3400 (OH); ^{13}C and ^1H NMR: Tables 2 and 3; EIMS *m/z* (rel. int.): 222 $[M]^+$ (30), 204 (45), 189 (19), 179 (11), 165 (48), 138 (28), 122 (64), 107 (47), 93 (58), 82 (100), 67 (40), 55 (39), 41 (38).

Oxidation of **14**. To alcohol **14** (18 mg) in CH_2Cl_2 (3 ml) was added PCC–Al_2O_3 (40 mg) and the mixt stirred for 2 days at room temp. The resulting mixt. was filtered through a short column of silica gel to give the ketone **15** (15 mg): $[\alpha]_D - 32.9°$ (*c* 3.57); HREIMS: Found $[M]^+$ 220.1799; $C_{15}H_{24}O$ requires 220.1837; FTIR ν_{max} cm^{-1}: 1709 (C=O); CD: $\Delta\varepsilon_{295} - 0.97$ (*c* 2.76×10^{-3}, EtOH); ^{13}C and ^1H NMR: Tables 2 and 3; EIMS *m/z* (rel. int.): 220 $[M]^+$ (66), 205 (37), 187 (5), 177 (30), 138 (53), 125 (100), 107 (13), 93 (33), 67 (17), 55 (14), 41 (17).

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