New *ent*-Verticillane Diterpenoids from the Japanese Liverwort *Jackiella javanica*

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Three new *ent*-verticillane diterpenoids have been isolated from the Japanese liverwort *Jackiella javanica*, together with known sesqui- and diterpenoids. Their absolute configurations were established by X-ray crystallographic analysis and circular dichroism spectroscopy.

Key words *Jackiella javanica*; liverwort; *ent*-verticillane; diterpenoid; absolute configuration

In our search for novel compounds possessing biological activity, we are currently studying the chemical constituents of Japanese, European, New Zealand and Argentine liverworts.[1,2] To date, we have reported a number of novel carbon skeletal, sesqui- and diterpenoids or bisbibenzyl compounds, and enantiomers of known terpenoids. Some of them show interesting biological activities.[3] Moreover these compounds are often valuable as chemosystematic and genetic markers.[1,2]

The sesqui- and diterpenoids of *Jackiella javanica* SCHIFFN., that is known as only one genus and one species in Japan, have previously been reported by our group.[4,5] Reinvestigation of the Japanese *J. javanica* resulted in the isolation of the very rare natural products, *ent*-verticillane diterpenoids **1**—**8** as main components, together with known sesquiterpenoids and *ent*-kaurane diterpenoids.[6] Recently, Coates *et al.*[7] reported that the absolute configuration of (+)-verticillol which had been isolated from *Sciadopitys verticillata*[8] should be corrected from structure **9** to **1** by X-ray crystallographic analysis of the *p*-iodobenzoate derivative. Inevitably, the absolute configuration of *ent*-verticillol, the enantiomer of (+)-verticillol, must be corrected from structure **1** to **9**. Furthermore, the absolute structures of the other *ent*-verticillanes might also be reversed. Continuing the study of the chemical constituents of *J. javanica* resulted in the isolation of three additional new *ent*-verticillanes **10**—**12**, together with the four known sesquiterpenoids **13**—**16** and a known *ent*-verticillene diterpenoid **17**.

Here, we report on the isolation and structural characterization of the new compounds from *J. javanica* and revision of their absolute configurations.

Results and Discussion

A combination of chromatography on silica gel, Sephadex LH-20 and preparative HPLC of the ether extract of *J. javanica* afforded three new *ent*-verticillanes **10**—**12** as well as known sesquiterpenoids, *ent*-ledene (**13**),[9] *ent*-4,10-aromadendrandiol (**14**),[10] (1*R*,7*R*)-germacra-4(15),5*E*,10(14)-trien-1-ol (**15**)[4] and *ent*-11-hydroxy-5-guaien (**16**),[11] and a diterpene hydrocarbon, *ent*-*exo*-verticillene (**17**).[12—14] The structures of the known compounds were determined by comparison of authentic ^{1}H- and ^{13}C-NMR spectra and/or reference data.

The IR spectrum of compound **10** showed the presence of hydroxy and carbonyl groups (3466, 1709 cm^{-1}). Electron impact mass spectrometry (EI-MS) showed a molecular ion peak at *m*/*z* 304 $[M]^+$ and the molecular formula was confirmed as $C_{20}H_{32}O_2$ by high resolution EI-MS (HR-EI-MS). The ^{1}H-NMR spectrum (Table 1) showed the presence of an aldehyde proton (δ 10.11 s), two olefinic protons (δ 4.78 d, 5.54 br d), two tertiary methyls and two olefinic methyls. The ^{13}C-NMR (Table 2) and distortionless enhancement by polarization transfer (DEPT) spectra indicated the presence of two trisubstituted olefinic carbons (δ 124.3, 128.9 each CH, 132.9, 134.3 each C), a carbonyl carbon (δ 205.7) originating from the aldehyde group, a quaternary carbon (δ 76.6) bearing a hydroxy group, and also four methyls, seven methylenes, two methines and a quaternary carbon. These spectral data are similar to those of verticillene-type diterpenoids. The analysis of ^{1}H–^{1}H correlated spectroscopy (^{1}H–^{1}H COSY) confirmed the presence of three segments, i) –CH_2–CH_2–CH(CHO)–CH–CH_2–CH_2–, ii) –C=CH–CH_2–, and iii)

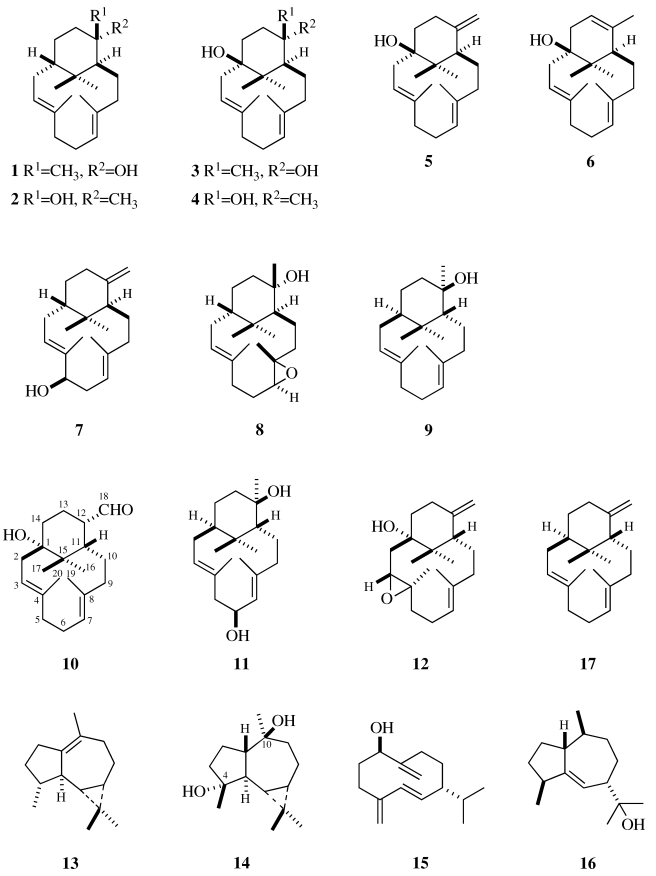

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Table 1. ^{1}H-NMR Data for **10**—**12** (600 MHz, $CDCl_3$)

H	**10**	**11**	**12**
1		1.46 br s	
2	2.69 t (13.5) α	2.69 dddd (14.8, 12.9, 6.3, 1.6) α	1.87—1.96 m
	2.00—2.09 m β	1.85 m β	2.01 br d (14.3)
3	5.54 br d (12.4)	5.76 d (12.9)	3.33 d (10.4)
5	2.21 br d (9.9) α	2.48 br d (11.8) α	2.17 dt (13.7, 3.8) α
	2.00—2.09 m β	2.18 t (11.5) β	1.20 ddd (13.7, 13.7, 4.1) β
6	2.47 m α	4.58 ddd (11.6, 9.9, 3.8)	2.32 m α
	2.00—2.09 m β		2.08 m β
7	4.78 d (11.5)	5.04 d (9.9)	4.77 d (9.9)
9	2.16 br d (13.5) α	2.09 dt (13.1, 3.6) α	1.87—1.96 m
	1.99 ddd (13.2, 13.2, 3.0) β	2.36 ddd (13.1, 13.1, 4.2) β	2.04 m
10	1.49 ddd (14.3, 14.3, 3.0) α	1.32 ddd (14.2, 14.2, 3.6) α	1.43 br t (14.5) α
	1.81 m β	1.51 m β	1.60 m β
11	2.73 dd (10.2, 5.8)	2.15 d (7.1)	2.23 br d (10.4)
12	2.36 t (5.8)		
13	2.32 d (8.5) α	1.71 ddd (12.9, 4.4, 3.0) α	2.39 ddd (14.6, 6.7, 1.6) α
	1.85—1.88 m β	1.83 m β	2.45 br dd (14.8, 6.9) β
14	1.74 d (8.5)	1.98 m α	1.87—1.96 m
	1.85—1.88 m	1.62 m β	2.02 m
16	0.76 s	0.78 s	0.76 s
17	0.84 s	0.70 s	0.88 s
18	10.11 s	1.27 s	4.68 d (1.4)
			4.93 d (1.4)
19	1.57 s	1.61 s	1.65 t (1.6)
20	1.57 s	1.59 s	1.23 s

Table 2. ^{13}C-NMR Data for **10**—**12** (100 MHz, $CDCl_3$)

C	**10**[a)]	**11**	**12**
1	76.6	43.9	76.8
2	42.2	34.0	42.2
3	124.3	129.8	62.8
4	134.3	130.0	63.7
5	40.6	50.0	39.5
6	26.4	67.6	24.4
7	128.9	132.2	127.3
8	132.9	137.7	134.4
9	37.4	41.2	37.0
10	20.6	20.9	20.8
11	40.0	44.8	43.6
12	45.6	75.8	145.9
13	22.0	41.3	34.7
14	35.0	28.7	38.1
15	41.3	37.0	41.9
16	20.2	25.9	18.8
17	22.2	28.0	22.5
18	205.7	24.3	108.1
19	15.2	16.4	16.2
20	15.5	16.4	15.8

a) Measured at 150 MHz.

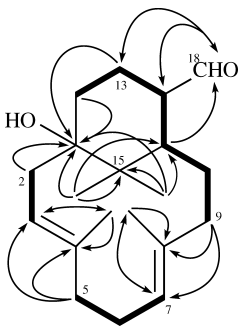


Fig. 1. ^{1}H–^{1}H Correlations (Bold Line) and Long-Range ^{1}H–^{13}C Correlations (Arrows) of **10**

–C=CH–CH_2–CH_2–. The heteronuclear multiple quantum coherence (HMQC) and heteronuclear multiple bond correlation (HMBC) spectra of **10** clarified that the structure of **10** is verticillene-type with a hydroxy group at C-1 and an aldehyde group at C-12 as shown in Fig. 1. The stereochemistry of **10** was determined by the phase sensitive nuclear Overhauser enhancement and exchange spectroscopy (NOESY) spectrum. NOEs were observed between i) the aldehyde proton at H-18 and H-16 methyl and H-14α, ii) H-12β and H-9β and H-11, iii) H-11 and H-3, H-7, H-12β and H-17 methyl, iv) H-17 methyl and H-2α, H-19 methyl and H-20 methyl, as shown in Fig. 2. Thus, it was found that the tertiary hydroxy group at C-1 and the aldehyde group at C-12 both have the α-configuration.

The EI-MS spectrum of **11** showed *m*/*z* 288 as the M-18 ion peak, and its fast atom bombardment (FAB) MS (FAB-MS) spectrum confirmed the quasimolecular ion peak at *m*/*z* 329 $[M+Na]^+$. Therefore, the molecular weight of **11** was revealed to be 306. The IR and ^{13}C-NMR spectra exhibited the presence of secondary and tertiary hydroxy groups (δ_C 67.6 CH, 75.8 C). The ^{1}H- and ^{13}C-NMR spectra (Tables 1, 2) of **11** closely resembled those of compound **10**. Moreover the DEPT spectrum of **11** showed two trisubstituted olefinic carbons (δ 129.8, 132.2 each CH, 130.0, 137.7 each C), a methine and quaternary carbon bearing hydroxy groups as well as five methyls, six methylenes, two methines and a quaternary carbon. The detailed analyses of ^{1}H–^{1}H COSY, HMQC and HMBC spectra as shown in Fig. 3 confirmed that the structure of **11** is a verticillene diterpenoid with hydroxy groups at C-6 and C-12. The stereochemistry was determined by a NOESY spectrum shown in Fig. 4 in which NOEs were observed between i) H-18 methyl and H-13α, H-14α, and H-16 methyl, ii) H-6α and H-5α, H-19 methyl, and

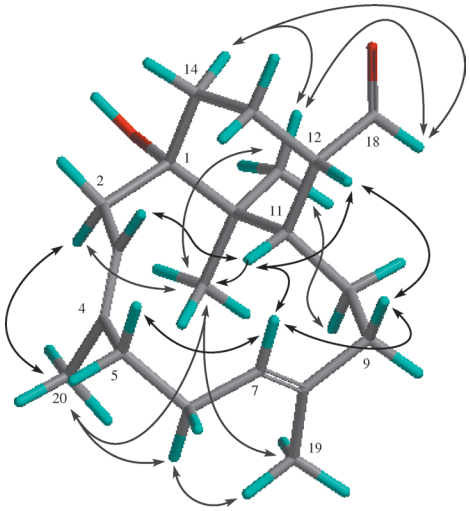


Fig. 2. NOE Correlations of **10**

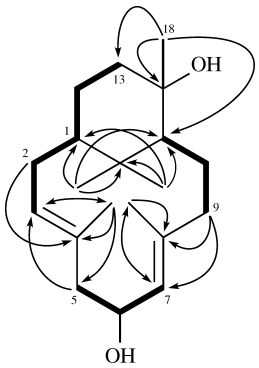


Fig. 3. ^{1}H–^{1}H Correlations (Bold Line) and Long-Range ^{1}H–^{13}C Correlations (Arrows) of **11**

H-20 methyl, iii) H-17 methyl and H-10α, H-19 methyl, and H-20 methyl. Thus, the stereochemistry of **11** is verticilla-3,7-diene-6β,12β-diol.

The EI-MS spectrum of compound **12** showed a molecular ion peak at *m/z* 304 $[M]^{+}$, and its IR spectrum displayed the presence of a hydroxy group (3474 cm^{-1}). The ^{1}H- and ^{13}C-NMR spectra (Tables 1, 2) were similar to those of compounds **10** and **11** except for the absence of a double bond between C-3 and C-4. The DEPT spectrum of **12** showed the presence of an *exo*-methylene (δ 108.1 CH_2, 145.9 C), trisubstituted olefinic carbons (δ 127.3 CH, 134.4 C), one methine and two quaternary carbons bearing oxygen atoms (δ 62.8 CH, 63.7, 76.8 each C) as well as four methyls, seven methylenes, one methine and one quaternary carbon. The IR, ^{13}C-NMR and HR-EI-MS ($C_{20}H_{32}O_2$ Calcd for 304.2402) spectra suggested that compound **12** possessed a tertiary hydroxy and an epoxy ring in the molecule. Furthermore, the detailed analysis of the ^{1}H–^{1}H COSY, HMQC, HMBC and NOESY spectra revealed that the structure of **12** is verticillene-type with the hydroxy group at C-1, epoxy ring at C-3–C-4 and *exo*-methylene at C-12. Its stereochemistry was confirmed by a NOESY experiment as shown in drawing **12** (Fig. 5).

The absolute configurations of the *ent*-verticillanes had originally been established by comparison with the optical

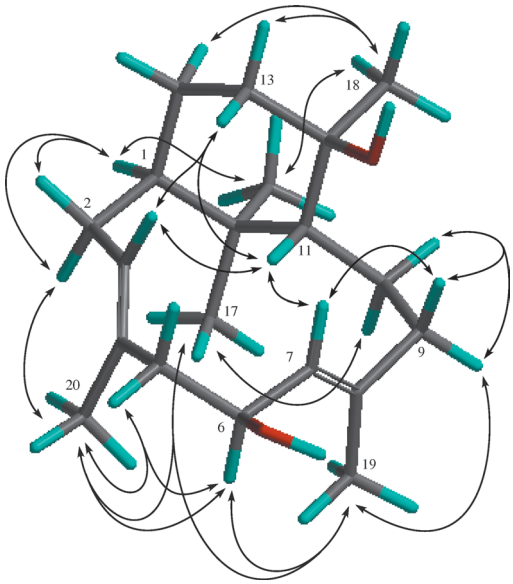


Fig. 4. NOE Correlations of **11**

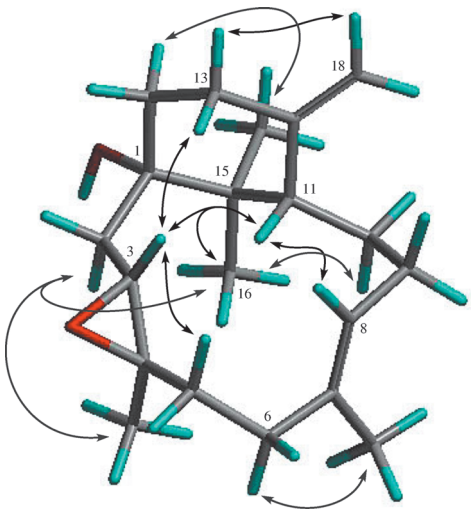


Fig. 5. NOE Correlations of **12**

rotations of their enantiomeric compounds. However, Coates *et al.*[7] reported the revision of the absolute configuration of (+)-verticillol as the structure **1** depicted as *ent*-verticillol. Therefore, we reexamined the absolute configuration of the *ent*-verticillanes using X-ray crystallographic analysis of *ent-epi*-verticillol *p*-iodobenzoate **18** obtained as a crystal by benzoylation. The ORTEP drawing of **18** in Fig. 6 clearly shows that the absolute configurations at C-1 and C-11 are both of the *R* configuration. Thus, *ent-epi*-verticillol should be revised from structure **2** to (12*S*)-*ent*-verticilla-3*E*,7*E*-dien-12-ol (=*ent*-12-*epi*-verticillol) (**19**). The CD spectra of **18** and **19** both showed a negative sign at λ_{max} 206 nm. Additionally, the CD spectrum of *ent*-verticillol (**9**) also exhibited a negative sign, while (+)-verticillol (**1**) showed a positive sign at λ_{max} 206. Furthermore, the CD spectra (Table 3) of other *ent*-verticillenes **3**—**7** and **11** were also negative like **9**, **18** and **19** although those of **10** and **17** were not measured. Accordingly, the absolute structure of **11** was established as (6*S*,12*R*)-*ent*-verticilla-3*E*,7*E*-diene-6,12-diol. Further-

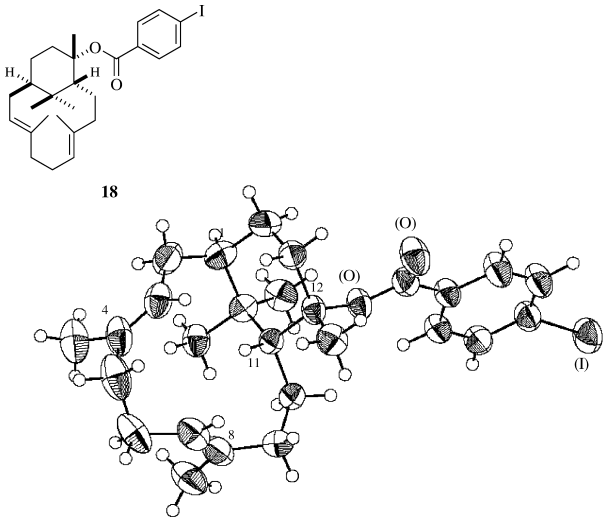


Fig. 6. The ORTEP Drawing of **18**

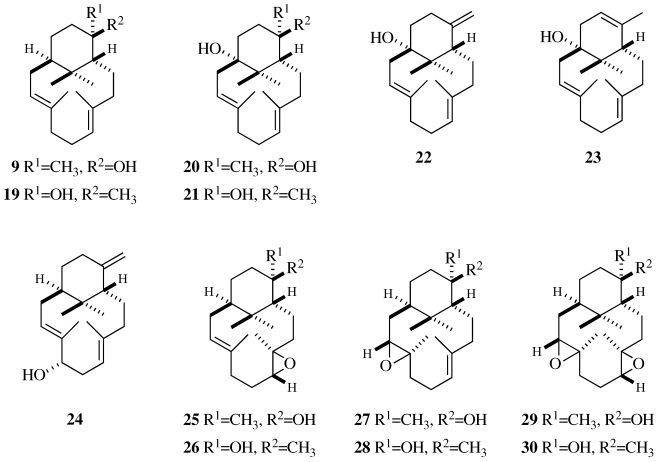
Table 3. The Cotton Effect (CE) Sign of CD Spectra of **1**, **9**, **11** and **18**—**24**[a)]

Comp.	λ_{max} (nm)	CE sign	Comp.	λ_{max} (nm)	CE sign
1	206	Positive	**20**	206	Negative
9	206	Negative	**21**	206	Negative
11	205	Negative	**22**	210	Negative
18	206	Negative	**23**	207	Negative
19	206	Negative	**24**	204	Negative

a) All compounds were measured in EtOH, and the solvent spectrum (EtOH) was subtracted from the sample spectrum in all cases.

more, the absolute structures of **3**—**7** should be revised to (1*S*,12*R*)-*ent*-verticilla-3*E*,7*E*-diene-1,12-diol (=*ent*-verticillanediol) (**20**), (1*S*,12*S*)-*ent*-verticilla-3*E*,7*E*-diene-1,12-diol (=*ent*-12-*epi*-verticillanediol) (**21**), (1*S*)-*ent*-verticilla-3*E*,7*E,*12(18)-trien-1-ol (=*ent*-isoverticillenol) (**22**), (1*S*)-*ent*-verticilla-3*E*,7*E,*12-trien-1-ol (**23**) and (5*S*)-*ent*-verticilla-3*E*,7*E,*12(18)-trien-5-ol (**24**). Moreover, the absolute structures of **10** and **12** also were determined to be the same absolute configuration as **21** based on the presence of *ent*-verticillanes **9**, **11** and **19**—**24** in the present species. The absolute structure of **8**, which has been reported as the epoxy derivative given by the oxidation of **9**,[6)] was also revised to (7*R*,8*R*,12*R*)-*ent*-7,8-epoxy-3*E*-verticillen-12-ol (**25**). Additionally, the previously reported epoxy derivatives[6)] from the oxidation of **9** and **19** were also corrected to (7*R*,8*R*,12*S*)-*ent*-7,8-epoxy-3*E*-verticillen-12-ol (**26**), (3*R*,4*R*,12*R*)-*ent*-3,4-epoxy-7*E*-verticillen-12-ol (**27**), (3*R*,4*R*,12*S*)-*ent*-3,4-epoxy-7*E*-verticillen-12-ol (**28**), (3*R*,4*R*,7*R*,8*R*,12*S*)-*ent*-3,4:7,8-diepoxyverticillan-12-ol (**29**), and (3*R*,4*R*,7*R*,8*R*,12*R*)-*ent*-3,4:7,8-diepoxyverticillan-12-ol (**30**), respectively.

The verticillane-type diterpenoids, which are known as precursors to taxanes, have been isolated from the conifer *Sciadopitys verticillata*,[8)] the soft coral *Cespitularia hypotentaculata*,[15)] and the dicotyledons *Bursera suntui*,[14)] *B. kerberi*[14)] and *Boswellia carterii*.[16)] However, the *ent*-verticillanes have been isolated as the main components only in the liverwort *J. javanica*. *ent*-Verticillanes might be useful as chemical markers of *J. javanica*. The results of the present study clearly revealed that the absolute configuration of the *ent*-verticillanes should be revised.



Experimental

Optical rotations were measured on Jasco DIP-1000 or P-1030 polarimeters. IR spectra were recorded on a Shimadzu FTIR-8400S infrared spectrophotometer. CD spectra were recorded on a Jasco J-725 spectropolarimeter (sol. EtOH). The ^{1}H- and ^{13}C-NMR spectra were measured on Varian Unity-600 (^{1}H; 600 MHz, ^{13}C; 150 MHz) and JEOL Eclipse-400 (^{1}H; 400 MHz, ^{13}C; 100 MHz) instruments. Chemical shift values are expressed in δ (ppm) downfield from tetramethylsilane as an internal standard (^{1}H-NMR), and in δ 77.03 (ppm) from $CDCl_3$ as a standard (^{13}C-NMR). Mass spectra were obtained on a JEOL Mstation JMS 700 instrument. X-ray crystallographic analysis was carried out on a Mac Science DIP-2020 instrument. TLC was carried out using Silica gel 60F_{254} plates (Merck). Column chromatography was performed on Silica gel 60 (Merck, 230—400, 35—70 mesh) and Sephadex LH-20 (Amersham Pharmacia Biotech, sol. CH_2Cl_2–MeOH 1 : 1). TLC plates were examined under UV (254 nm) light, and by spraying with Godin reagent[17)] and 30% H_2SO_4 followed by heating.

Plant Material *Jackiella javanica* SCHIFFN. was collected in Kagoshima, Japan, in 1993 and identified by Dr. M. Mizutani (Hattori Botanical Laboratory, Miyazaki, Japan). Their voucher specimens were deposited at the Faculty of Pharmaceutical Sciences, Tokushima Bunri University.

Extraction and Isolation The fractionation of the ether extract (23.6 g) of *J. javanica* has been reported previously in detail.[5,6)] The hydrocarbon fraction was chromatographed on silica gel and silica gel impregnated with 15% $AgNO_3$ to afford *ent*-ledene (**13**, 42.5 mg) and *ent*-*exo*-verticillene (**17**, 36.8 mg). Fr. 4, which included the sesquiterpenoids, was chromatographed on Sephadex LH-20, silica gel and preparative HPLC (Chemcosorb 5Si-U, *n*-hexane–EtOAc 9 : 1) to yield *ent*-11-hydroxy-5-guaien (**16**, 13.2 mg). (1*R*,7*R*)-Germacra-4(15),5*E*,10(14)-trien-1-ol (**15**, 95.8 mg) was isolated from fr. 7 by CC on Sephadex LH-20, silica gel and prep. HPLC (Nucleosil 50-5, *n*-hexane–Et_2O 49 : 1). (1*S*,12*S*)-*ent*-1-Hydroxyverticilla-3*E*,7*E*-dien-18-al (**10**, 3.7 mg) and (1*S*,3*R*,4*R*)-*ent*-3,4-epoxyverticilla-7,12(18)-dien-1-ol (**12**, 3.7 mg) were obtained from fr. 8 by CC on Sephadex LH-20, silica gel and prep. HPLC (Zorbax BP-SIL, *n*-hexane–EtOAc 4 : 1). Fr. 12, the sesqui- and diterpenoids fraction, was chromatographed on Sephadex LH-20, silica gel and preparative HPLC (Cosmosil 5SL-II, *n*-hexane–EtOAc 1 : 1) to yield (6*S*,12*R*)-*ent*-verticilla-3,7-diene-6,12-diol (**11**, 15.7 mg) and *ent*-4,10-aromadendrandiol (**14**, 4.7 mg).

(1*S*,12*S*)-*ent*-1-Hydroxyverticilla-3*E*,7*E*-dien-18-al (**10**): $[\alpha]_D^{21}$ −50.5° (*c*=0.21, $CHCl_3$). FT-IR cm^{-1}: 3466, 1709. ^{1}H- and ^{13}C-NMR: Tables 1 and 2. HR-EI-MS *m/z*: 304.2400 (Calcd for $C_{20}H_{32}O_2$: 304.2402). EI-MS *m/z* (int.): 304 $[M]^+$ (12), 287 (3), 235 (9), 217 (10), 205 (13), 189 (7), 163 (9), 159 (9), 149 (17), 135 (21), 123 (50), 119 (17), 107 (28), 95 (100), 81 (64), 69 (45), 55 (44), 43 (42).

(6*S*,12*R*)-*ent*-Verticilla-3,7-diene-6,12-diol (**11**): $[\alpha]_D^{21}$ −86.2° (*c*=0.20, $CHCl_3$). FT-IR cm^{-1}: 3474. CD (EtOH): $\Delta\varepsilon_{205\,nm}$ −33.12 (*c*=1.28×10^{-3}). ^{1}H- and ^{13}C-NMR: Tables 1 and 2. FAB-MS (*m*-NBA) *m/z* 329 $[M+Na]^+$; (*m*-NBA+KCl) *m/z* 345 $[M+K]^+$, HR-EI-MS *m/z*: 304.2406 (Calcd for $C_{20}H_{32}O_2$: 304.2402). EI-MS *m/z* (int.): 304 $[M]^+$ (11), 289 (18), 286 (21), 271 (18), 261 (15), 243 (21), 177 (14), 161 (13), 149 (22), 137 (31), 135

(41), 133 (30), 123 (100), 121 (39), 109 (38), 107 (34), 97 (67), 95 (43), 84 (39), 81 (42), 69 (45), 55 (27), 43 (33).

(1*S*,3*R*,4*R*)-*ent*-3,4-Epoxyverticilla-7,12(18)-dien-1-ol (**12**): $[\alpha]_D^{22}$ −86.2° (c=0.20, $CHCl_3$). FT-IR cm^{-1}: 3474. ^{1}H- and ^{13}C-NMR: Tables 1 and 2. HR-EI-MS *m/z*: 304.2406 (Calcd for $C_{20}H_{32}O_2$: 304.2402). EI-MS *m/z* (int.): 304 $[M]^+$ (11), 289 (18), 286 (21), 271 (18), 261 (15), 243 (21), 219 (16), 201 (28), 188 (24), 175 (22), 173 (28), 161 (38), 147 (48), 137 (46), 133 (58), 123 (48), 121 (79), 119 (54), 107 (100), 93 (87), 81 (97), 67 (88), 55 (71), 43 (93).

CD Spectral Data of Compounds 1, 9 and 19—24 Solvent data (EtOH) were subtracted from sample data in all cases. **1**: $\Delta\varepsilon_{206\,nm}$ +26.59 ($c=2.06\times10^{-3}$). **9**: $\Delta\varepsilon_{206\,nm}$ −46.48 ($c=1.39\times10^{-3}$). **19**: $\Delta\varepsilon_{206\,nm}$ −44.90 ($c=1.73\times10^{-3}$). **20**: $\Delta\varepsilon_{206\,nm}$ −35.73 ($c=2.89\times10^{-3}$). **21**: $\Delta\varepsilon_{206\,nm}$ −37.95 ($c=1.53\times10^{-3}$). **22**: $\Delta\varepsilon_{210\,nm}$ −45.09 ($c=3.20\times10^{-3}$). **23**: $\Delta\varepsilon_{207\,nm}$ −53.48 ($c=2.27\times10^{-3}$). **24**: $\Delta\varepsilon_{204\,nm}$ −42.33 ($c=1.89\times10^{-3}$).

***p*-Iodobenzoylation of 19** A mixture of **9** and **19** (60 mg) in THF (1 ml) was stirred at 0 °C, and then *n*-BuLi (120 μl) was added dropwise. After 60 min at 0 °C, *p*-iodobenzoyl chloride (73 mg) in THF (2 ml) was added.[7] The reaction mixture was stirred overnight at room temperature. The reaction mixture was quenched by adding saturated NH_4Cl, and extracted with Et_2O. The reaction mixture was purified by CC on silica gel (*n*-hexane–EtOAc 19 : 1) to afford *ent-epi*-verticillol *p*-iodobenzoate **18** (48 mg), which was then recrystallized from MeOH.

ent-epi-Verticillol *p*-iodobenzoate **18**: $[\alpha]_D^{21}$ −40.0° (c=1.04, $CHCl_3$). CD (EtOH): $\Delta\varepsilon_{206\,nm}$ −70.09 ($c=1.12\times10^{-3}$). ^{1}H-NMR (400 MHz, C_6D_6): δ 0.65 (3H, s), 1.02 (3H, s), 1.25—1.34 (m, overlapped signals), 1.43 (3H, s), 1.45 (3H, s), 1.64 (3H, s), 1.61—1.68 (m, overlapped signals), 1.75—1.94 (m, overlapped signals), 1.97—2.07 (m, overlapped signals), 2.29 (1H, br q, J=13.2 Hz), 2.61 (1H, ddd, J=14.3, 14.3, 6.6 Hz), 3.24 (1H, d, J=14.6 Hz), 4.74 (1H, d, J=11.0 Hz), 5.41 (1H, d, J=12.8 Hz), 7.45 (2H, d, J=8.4 Hz), 7.74 (2H, d, J=8.4 Hz). ^{13}C-NMR (100 MHz, C_6D_6): δ 15.3, 16.4 (each CH_3) 21.0 (CH_2), 26.9 (C), 27.0 (CH_3), 27.1 (CH_2), 27.7, 28.0 (each CH_3), 32.9, 34.2 (each CH_2), 36.6 (C), 40.5, 41.5 (each CH_2), 43.6, 44.7 (each CH), 87.5, 100.2 (each C), 127.8, 130.4 (each CH), 131.3 (CH, ×2), 132.5, 132.9, 133.3 (each C), 137.9 (CH, ×2), 164.9 (C). FAB-MS (*m*-NBA) *m/z*: 519 $[M-1]^+$; (*m*-NBA+KCl) *m/z* 519 $[M-1]^+$, 559 $[M+K]^+$. EI-MS *m/z* (int.): 273 $[M-C_7H_4O_2I]^+$(8), 257 (66), 248 (100), 231 (58), 203 (17), 189 (19), 175 (12), 161 (24), 147 (17), 134 (36), 121 (42), 107 (30), 93 (36), 81 (29), 65 (25), 55 (18), 41 (21). Crystal data: $C_{27}H_{37}IO_2$, Mr=520.495, Monoclinic, $P2_1$, a=15.2870 (8) Å, b=7.2130 (3) Å, c=23.493 (2) Å, α=90.00°, β=105.206 (2)°, γ=90.00°, V=2499.8 (2) Å, Z=4; Mo$K\alpha$ radiation, λ=0.71073, refinement on F^2, full matrix least squares refinement, R(gt)=0.0399, wR(gt)=0.1018, S(ref)=1.073; 7386 reflections, 537 parameters; only coordinates of H atoms refined; data collection: DIP Image plate; cell refinement: Scalepack (HKL); data reduction: maXus; program used to solve structure: *SIR92*; program used to refine structure: *SHELXL-97*.

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