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NEW DITERPENES FROM *PORELLA PERROTTETIANA*

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Key Word Index—*Porella perrottetiana*; Jungermanniales; Hepaticae; perrottetianal A; perrottetianal B; diterpene dialdehydes; *ent*-labdane-type diterpene diol; sacculatane.

Abstract—Perrottetianal A and perrottetianal B, two new diterpene dialdehydes and a new *ent*-labdane-type diterpene diol have been isolated from the liverwort *Porella perrottetiana* and their structures have been elucidated by the chemical and spectral evidence.

INTRODUCTION

The liverworts, *Porella* species belonging to Jungermanniales, produce various sesquiterpenes. Recently, we have reported the isolation and structures of several drimane-, pinguisane- and aromadendrane-type sesquiterpenes from *Porella vernicosa* complex [1–3], *P. densifolia* [4], *P. japonica* [5] and *P. platyphylla* [6] and the intense pungency of *P. vernicosa* complex was due to a sesquiterpene dial, polygodial [1–3]. In our continuation of studies of terpenoid constituents of the liverworts, we investigated *Porella perrottetiana* which proved to be a rich source of diterpenoids with an aldehyde group. We now report the isolation and structures of two new diterpene dialdehydes named perrottetianal A (**1**) and perrottetianal B (**6**), and a new *ent*-labdane-type diol (**9**) from *Porella perrottetiana*.

RESULTS AND DISCUSSION

Column chromatography and PLC on Si gel of the combined ether extract of the air-dried material resulted in the isolation of three main diterpenes, perrottetianal A (**1**), perrottetianal B (**6**) and an *ent*-labdane-type diol (**9**).

Perrottetianal A (**1**)

The main component (**1**), $C_{20}H_{30}O_2$ (M^+ 302.2254), showed the intense positive 2,4-DNP test and the presence of a simple aldehyde (1715 cm^{-1}; δ 9.83 (*s*, 1H)) and an α,β-unsaturated aldehyde group (λ_{max} 245 nm; 1668 cm^{-1}; δ 10.13 (*s*, 1H)). The ^1H NMR spectrum also contained the signals for one tertiary methyl (δ 0.72), one vinylic methyl (2.16) and a dimethyl allyl group (1.66 and 1.70, each *bs*, 3H and 5.10, *bt*, J = 7, 1H). The dimethyl allyl group was further confirmed by the base peak at *m/e* 69 in the high resolution MS. The lower chemical shift of one aldehyde proton and of the vinylic methyl group, and the absorption maximum of the UV spectrum were very similar to those of authentic β-cyclocitral, indicating that **1** contained a Me–C=C–CHO group. The arrangement of two aldehyde groups as shown in **1** was confirmed by chemical transformation. Treatment of **1** with $LiAlH_4$ gave diol **2** (3300 cm^{-1}) whose IR spectrum indicated the presence of intramolecular hydrogen bonding between two hydroxyl groups. Treatment of **2** with acetone–$CuSO_4$ under mild conditions easily resulted in the formation of an acetonide (**4**), $C_{23}H_{38}O_2$ (M^+ −58, *m/e* 288). Acetylation of **2** with Ac_2O–Py afforded diacetate **3** (1740, 1240 cm^{-1}; δ 2.08, *s*, 6H), followed by oxidation with CrO_3–Py to afford an α,β-unsaturated ketone **5** (1740, 1670 cm^{-1}). The above results, coupled with the molecular formula, showed **1** to be a bicyclic diterpene dialdehyde with a dimethyl allyl group. The ^1H NMR, IR and MS patterns of **1** resembled those of sacculatal (**8**), recently isolated from the liverworts *Trichocoleopsis sacculata* [7] and *Pellia endiviaefolia* [8], suggesting that **1** might possess the same sacculatane skeleton* as that of sacculatal with two aldehyde groups and one vinylic methyl group located at C-9, C-10 and C-8, respectively and one tetrasubstituted double bond placed between C-8 and C-9. This assumption was further confirmed by the ^{13}C NMR spectrum of **1** which was also quite similar to that of sacculatal (**8**) as shown in Table 1. It contained the signals of 20 carbon atoms with two aldehyde groups (191.3 (*d*) and 204.5 (*d*)), tetrasubstituted ethylenic carbons (157.9 (*s*) and 138.6 (*s*)), assignable to C-8 and C-9, trisubstituted ethylenic carbons (131.5 (*s*) and 124.7 (*d*)) attributable to C-18 and C-17, four methyl groups, seven methylene groups, one methine group (51.4 (*d*)) assigned to C-5 and two quaternary sp^3 carbon atoms. The above chemical and spectral data showed that the structure of perrottetianal A was most favourably represented by formula **1**. The stereochemistry was tentatively shown by biogenetic considerations of the drimane-type sesquiterpenes commonly elaborated in *Porella* species [1–3, 9] and by the same Cotton effect of polygodial and its related sesquiterpene dial [10].

Perrottetianal B (**6**)

Compound **6**, $C_{20}H_{30}O_3$ (M^+ 318), exhibited the presence of a hydroxyl group (3500 cm^{-1}), a simple aldehyde (1710 cm^{-1}; δ 9.91 (*s*, 1H)) and an α,β-unsaturated aldehyde (1665 cm^{-1}; δ 10.20 (*s*, 1H)). The UV and

* The name sacculatane is proposed for the drimane skeleton in which one isoprene unit is attached to C-15 (eq.).

Table 1. ^{13}C NMR chemical shifts of perrottetianal A (ppm from internal TMS)*

	1	2	3	9
C-1	42.1	35.9	44.2	39.7
C-2	19.5†	30.4†	20.6†	23.5
C-3	36.0	75.7	39.4	41.8
C-4	35.7	39.6	36.6	32.7
C-5	51.4	47.8	46.9	55.7
C-6	18.8†	18.6‡	21.8†	26.1
C-7	31.8	29.8	154.3	73.9†
C-8	157.9	158.6	138.3	73.3†
C-9	138.6	138.5	60.5	46.3
C-10	50.5	50.5	35.9	32.7
C-11	191.3	190.4	201.9	23.5
C-12	16.7‡	16.4	193.3	136.0
C-13	204.5	204.6	15.7	132.8
C-14	21.8	18.6§	17.8‡	141.7
C-15	36.4	31.4†	37.3	110.5
C-16	21.8	19.5‡	25.0	11.8
C-17	124.7	121.5	124.4	18.5
C-18	131.5	136.3	131.4	14.9
C-19	17.6‡	18.0§	17.6‡	23.2
C-20	25.7	25.9	25.7	21.5

* The spectra were obtained at 22.6 MHz in Fourier transform mode in $CDCl_3$ solutions.
†‡§ Values within any vertical column may be reversed.

Table 2. NMR chemical shifts* (ppm from internal TMS) and UV spectra† of **9** and *cis*- and *trans*-labda-12,14-dienes and the related compounds [14, 15]

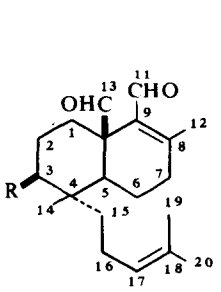
	H-15	H-15′	H-14	H-12	λ_{max} nm	ε
9	4.91	4.80	6.23	5.46	239	26500
trans-Biformene	4.93	4.84	6.26	5.37	231	26000
trans-Methyl communate	5.02	4.89	6.28	5.40	232	27600
trans-β-Ocimene	5.00	4.87	6.30	5.39	232	27600
Methyl zanzibarate [20]	—	—	6.25	—	232.5	26600
					240 sh	18000
cis-Abienol	5.07	5.00	6.85	5.45	235	19800
cis-Biformene	5.10	5.03	6.83	5.25	236	20500
cis-β-Ocimene	5.11	5.03	6.73	5.28	237.5	21000
cis-Methyl communate	5.07	5.00	6.82	5.20	235	—

* In CCl_4 solution.
† In EtOH solution.

CD spectra were almost identical to that of perrottetianal A (**1**). The signal pattern of the ^1H NMR spectrum was also consistent with that of **1**, except for the presence of a carbinyl proton at δ 3.47 (*bt*, J = 6 Hz), indicating that perrottetianal B has the same structure as **1** in which one secondary hydroxyl group was located on the cyclohexane rings or C-4 cyclohexenyl side chain. Oxidation of **6** with CrO_3–Py gave a saturated ketone **7** ($C_{20}H_{28}O_3$ (M^+ 316); 1710 cm^{-1}). In the ^1H NMR spectrum of **7**, one quaternary methyl group was largely shifted to the lower field (δ 1.09) in comparison with that of the original alcohol, showing that the resulting carbonyl group was placed at C-3, hence the original hydroxyl group was at C-3. The configuration of the secondary hydroxyl group was confirmed to be β by the splitting pattern of H-3 (*bt*, J = 6 Hz). Thus, the above results, together with the ^{13}C NMR (Table 1) and biogenetic considerations of the drimane-type sesquiterpenes [9, 11] led to the structure of **6** for perrottetianal B. Compound B was unstable in comparison with perrottetianal A and gradually polymerized, even in the refrigerator. A possible reason for this instability is the formation of a hemiacetal between the hydroxyl group at C-3 and the aldehyde group at C-10, which may facilitate the oxidation. However, the mechanism remains to be confirmed.

Ent-*labdane-type diterpene diol* (**9**)

From the most polar fraction a crystalline diterpene was obtained. Compound **9**, $C_{20}H_{34}O_2$ (M^+ 306), had a conjugated double bond (λ_{max} 239 nm), a vinyl group (990 and 910 cm^{-1}; δ 4.90 (*d*, J = 11, 1H), 5.06 (*d*, J = 17, 1H), 6.40 (*dd*, J = 11, 17, 1H)) and a trisubstituted ethylenic bond [830 cm^{-1}; δ 5.63 (*bt*, J = 7, 1H)]. The IR and ^1H NMR spectra indicated the presence of a hydroxyl group (3520 cm^{-1}) and four tertiary methyl groups, one of which was located on a carbon bearing a hydroxyl group, a carbinyl proton (δ 3.70) and a vinyl methyl group (δ 1.80). In the ^{13}C NMR spectrum (Table 1) 20 carbon atoms could be observed. The off-resonance spectrum showed the presence of five methyl groups, five methylene groups, three methine groups (one of which possessed a hydroxyl group), three quaternary sp^3 carbons (one of which possessed a hydroxyl group), trisubstituted ethylenic carbons and a vinyl group. Acetylation of **9** with Ac_2O–Py gave a monoacetate **10** (1730 cm^{-1}; δ 1.97 (*s*, 3H)) whose IR spectrum exhibited the presence of a hydroxyl group (3590 cm^{-1}), indicating that **9** had certainly one tertiary and one secondary hydroxyl group. Treatment of **9** with *m*-chloroperbenzoic acid afforded the diepoxide **11**, $C_{20}H_{34}O_4$ (M^+ 338). Hydrogenation of **9** in the presence of PtO_2 gave a tetrahydro derivative **12**, $C_{20}H_{38}O_2$ (M^+ 310). The above spectral and chemical data, together with the molecular formula, suggested that **9** was a typical labda-12,14-diene having two hydroxyl groups. On oxidation of **12** with CrO_3–Py, it gave a saturated ketone **13**, $C_{20}H_{36}O_2$ (M^+ 308; 1713 cm^{-1}), followed by dehydration with *p*-TsOH in benzene to give an α,β-unsaturated ketone **14**, $C_{20}H_{34}O$ (M^+ 290, 1680 cm^{-1}), which was treated with DDQ to afford a cross-conjugated ketone **15**, $C_{20}H_{32}O$ (M^+ 288). On the basis of the above reactions, the positions of the two hydroxyl groups were established to be at C-7 and C-8, respectively, and the structure to be that represented by formula **9**. The configurations of the tertiary and the secondary hydroxyl groups were determined to be α and β, respectively, by the facile hydration of **13** with acid and by the broad singlet signal of a carbinyl proton ($W_{\frac{1}{2}}$ = 7 Hz) at C-7 [12]. The negative Cotton effect of the ketone (**13**) was in agreement with the depicted structure [13]. In structure **9**, there are *cis*- and *trans*-isomers with respect to the Δ^{12} bond. The chemical shift of H-14 has been used to determine *cis*- and *trans*-isomers of the Δ^{12} bond in labda-12,14-diene [14, 15]. The values of H-12, H-14, H-15 and H-15′ of **9** and those of the related labda-12,14-dienes are shown in Table 2. The value for H-14 indicates that **9** has the *trans* configuration, however, the UV maximum was very close to that of the *cis* series. Therefore, it is dangerous to use the UV maximum for the determination of *cis*- and *trans*-isomers of the Δ^{12} bond. Thus, the new diterpene diol was established to be *trans*-(5*R*, 7*S*, 8*S*, 9*S*, 10*S*)-labda-12,14-dien-7,8-diol (**9**). Recently, the stereoisomer of **9**, (5*S*, 7*S*, 8*S*, 9*R*, 10*R*)-labda-12,14-dien-7,8-diol has been isolated from *Nidrella* species (Compositae) [16].



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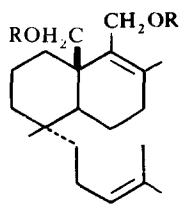

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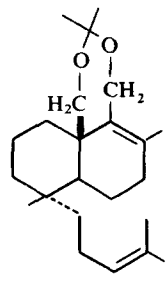

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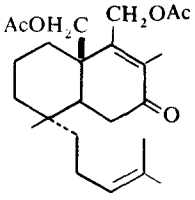

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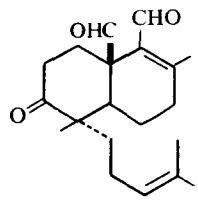

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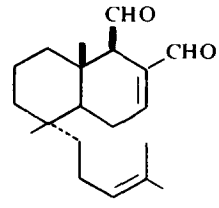

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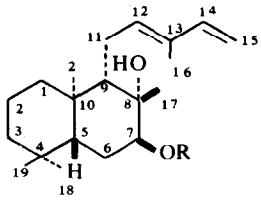

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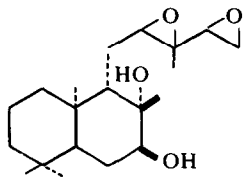
10 R = Ac



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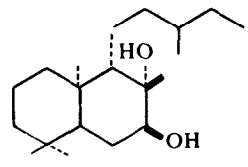

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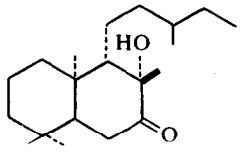

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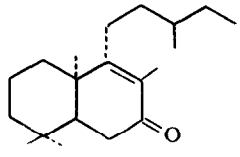

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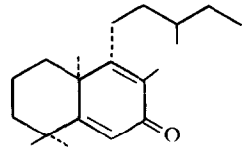

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Perrottetianal A and B are interesting from the biogenetic view point. Like sacculatal (**8**), the perrottetianals might be derived from geranyl-geranyl pyrophosphate by cyclization analogous to that of farnesyl pyrophosphate for the drimane-type sesquiterpenes. Perrottetianal A has also been isolated from the liverwort *Makinoa crispata* [5]. Polygodial, sacculatal (**8**), ugandensidial [17, 18] and warburganal [10] have an enal and simple aldehyde groups responsible for the intense pungency. The present perrottetianals do not show such pungency, but perrottetianal A has a bitter taste which is a characteristic of this species. Perrottetianals inhibited the germination of rice in the husk at *ca* 500 ppm.

EXPERIMENTAL

The solvents used for spectral determination were: TMS–$CDCl_3$ (^{1}H NMR, 60 or 90 MHz; ^{13}C NMR, 90 MHz); $CHCl_3$ (IR and $[\alpha]_D$); 95% EtOH (UV); MeOH (CD). TLC and PLC: precoated Si gel (0.25 mesh) F_{254}, *n*-hexane–EtOAc (4:1) and C_6H_6–EtOAc (4:1 and 1:1). Spots were detected by 2,4-DNP, 30 or 50% H_2SO_4 and UV light (254 and 360 nm). MS: EI-MS (DI method), 70 eV; GC–MS, OV-17, SE-30 1 or 5‰ glass column, 3 m × 2 mm, He 30 ml/min, temp. programme, 50–250° at 5°/min. High resolution MS: 30 eV, chamber temp. 160–220°, sample temp. 80–100°; CI-MS: 500 eV, reaction gas, *iso*-C_4H_{10}.

Extraction and isolation. Porella perrottetiana collected in Katsuura, Tokushima prefecture in January, 1977 was air-dried for 1 week. The ground material (900 g) was extracted with Et_2O for 2 weeks. The crude green oil (25 g) which showed 2 intense yellow spots on TLC after spraying with 2,4-DNP, was directly chromatographed on Si gel using *n*-hexane–EtOAc gradient in the dark condition. The first fraction (*n*-hexane 100%) gave a colourless liquid (2.80 g) in which α-pinene, β-pinene, camphene, limonene and camphor, unidentified sesqui- and diterpene hydrocarbons and *n*-paraffins were detected by GC–MS. The second fraction (*n*-hexane–EtOAc, 19:1) contained carotenoids

together with unknown oxygenated sesquiterpenes (1.805 g). The third fraction (7:3) contained a 2,4-DNP positive compound which was carefully rechromatographed on Si gel using the same solvent to afford perrottetianal A (**1**) (867 mg) as colourless crystals, mp 68–69°; $[\alpha]_D$ +282° (*c*, 2.0); $C_{20}H_{30}O_2$; $\Delta\varepsilon$ 304 nm (+3.00), 343 (−1.35); UV λ_{max} nm: 204 (ε, 6290), 245 (6480); IR ν_{max} cm^{-1}: 2750, 1715 (CHO), 1668 (C=C − CHO), 1620 (C=C), 1135, 1250; MS *m/e* (rel. int.): 303.2304 (M^+ +H, calc. 303.2324, 2.0), 302.2254 (M^+, calc. for $C_{20}H_{30}O_2$, 302.2245, 4), 274.2259 (M^+ −CO, calc. 274.2296, 37), 191 (94), 161 (35), 133 (44), 121 (50), 119 (38), 107 (43), 95 (81), 81 (55), 69.0703 ($C_5H_9^+$, calc. 69.0704, base). Mono2,4-DNP, mp 151–152°; UV λ_{max} nm: 377 (ε, 15200); IR ν_{max} cm^{-1}: 3320, 3120, 2740, 1710 (CHO), 1601, 1597, 1510, 1380, 1334, 1313, 1275, 1140, 970, 833; ^1H NMR: δ 0.97 (*s*, 3H), 1.71 (*bs*, 3H), 1.77 (*bs*, 3H), 2.13 (*s*, 3H), 5.13 (*bt*, 1H), 7.85 (*d*, *J* = 8, 1H), 7.86 (*s*, 1H), 8.35 (*dd*, *J* = 8, 2, 1H), 9.15 (*d*, *J* = 2, 1H), 10.10 (*s*, 1H, C<u>H</u>O), 11.80 (*bs*, 1H, N<u>H</u>). The fourth fraction (7:3) contained sterol mixtures (450 mg) in which campesterol, stigmasterol and sitosterol were detected by GC–MS (SE-30, 1%). The fifth fraction (3:2) gave perrottetianal B (**6**) which was purified by PLC to give a colourless liquid (98 mg). $[\alpha]_D$ +250° (*c*, 0.85); UV λ_{max} nm: 207 (ε, 1710), 246 (1399); $\Delta\varepsilon$, 309 nm (+4.77), 346 (−0.89); IR ν_{max} cm^{-1}: 3500 (OH), 2750, 1710 (CHO), 1665 (C=C − CHO), 1620 (C=C), 1380, 1050, 880, 735; ^1H NMR: δ 0.73 (*s*, 3H), 1.68 (*bs*, 3H), 1.80 (*bs*, 3H), 2.18 (*s*, 3H), 3.47 (*bt*, *J* = 6, 1H, C<u>H</u>OH), 5.20 (*bt*, *J* = 7, 1H, =CH), 9.91 (*s*, 1H, C<u>H</u>O), 10.20 (*s*, 1H, C=C − C<u>H</u>O); MS *m/e* (rel. int.): 318 (M^+, $C_{20}H_{30}O_3$, 1), 290 (M^+ −CO, 17), 272 (M^+ $-H_2O$ − CO, 35), 249 (M^+ −69, 39), 221 (28), 219 (36), 203 (base), 191 (63), 189 (59), 175 (56), 173 (56), 105 (62), 69 (40). The sixth fraction (1:1) gave a mixture of diterpene diols which were rechromatographed on Si gel using the same solvent to give a diterpene diol (**9**) (945 mg). Mp 111–112°; $[\alpha]_D$ −11° (*c*, 1.1); $C_{20}H_{34}O_2$; UV λ_{max} nm: 239 (ε, 8843); IR ν_{max} cm^{-1}: 3520 (OH), 1635 (C=C), 1605 (C=C), 1440, 1390, 1365, 1065, 990, 970, 950, 910; ^1H NMR: δ 0.80 (*s*, 3H), 0.83 (*s*, 3H), 0.88 (*s*, 3H), 1.17 (*s*, 3H), 1.80 (*bs*, 3H), 3.70 (*bs*, $W_{\frac{1}{2}}$ = 7 Hz, 1H), 3.25 (*s*, OH), 2.63 (*s*, OH); MS *m/e* (rel. int.): 306 (M^+, 1), 288 (M^+ $-H_2O$, 9), 270 (M^+ $-H_2O$ − H_2O, 18), 177 (15), 150 (base), 123 (43), 121 (33), 119 (24), 109 (32), 95 (38), 93 (40), 81 (92), 69 (56), 55 (40), 41 (33). CI–MS: (no parent peak), 289 (M^+ +1 − H_2O, base), 271 (M^+ +1 $-H_2O$ − H_2O, 86). 3,5-Dinitrobenzoate: $[\alpha]_D$ −51° (*c*, 7.1); IR $\nu_{max}^{liq.}$ cm^{-1}: 3560 (OH), 1730, 1280 (COO), 1630, 1603 (C=C), 1550 (Ar), 1392, 1348, 1170, 1080, 1015, 920, 830, 775, 730, 720; ^1H NMR: δ 0.85 (*s*, 6H), 0.97 (*s*, 3H), 1.37 (*s*, 3H, C<u>H</u>$_3$ − COH), 1.82 (C<u>H</u>$_3$ − C=) 2.37 (*bt*, 2H, H-11, 11′), 4.88 (*d*, *J* = 11, 1H), 5.08 (*d*, *J* = 17, 1H), 5.28 (*bs*, 1H, H-7), 5.58 (*bt*, 1H, H-12), 6.35 (*dd*, *J* = 11, 17, 1H), 9.20 (*m*, 3H, Ar-H).

Reduction of **1** *with* $LiAlH_4$. To $LiAlH_4$ (30 mg) in dry Et_2O (4 ml) was added perrottetianal (**1**) (80 mg) in dry Et_2O with stirring at 0° for 2 hr. Work-up as usual gave a diol which was purified by PLC to afford **2** (78 mg). IR $\nu_{max}^{liq.}$ cm^{-1}: 3300, 1030 (OH), 985; IR $\nu_{max}^{CCl_4(0.007\ mol)}$ cm^{-1}: 3610 (free OH), 3450 (ε, 51.4, intramolecular hydrogen bond), 3280 (ε, 53.5 intermolecular hydrogen bond), IR $\nu_{max}^{CCl_4(0.003\ mol)}$ cm^{-1}: 3610 (free OH), 3450 (ε, 53.3), 3280 (ε, 36.4); ^1H NMR: δ 0.88 (*s*, 3H), 1.60 (*s*, 3H), 1.70 (*bs*, 3H), 1.78 (*bs*, 3H), 3.95 (*d*, *J* = 10, 1H, H-11), 3.73 (*bs*, 2H, H-13, 13′), 4.33 (*d*, *J* = 10, 1H, H-11′), 5.16 (*bt*, *J* = 7, 1H).

Acetylation of **2**. The diol (**2**) (30 mg) was acetylated with Ac_2O–Py at 0° and allowed to stand overnight. Evapn of solvents, followed by PLC to give a diacetate **3** (25 mg). IR $\nu_{max}^{liq.}$ cm^{-1}: 1740, 1240 (OAc), 1385, 1120, 1030, 958; ^1H NMR: δ 0.83 (*s*, 3H), 1.64 (*bs*, 3H, =C − Me), 1.73 (*bs*, 6H, 2 × =C − Me), 2.08 (*bs*, 6H, 2 × OAc), 4.75 (*d*, *J* = 11, 1H), 4.48 (*d*, *J* = 11, 1H), 4.66 (*bs*, 2H), 5.10 (*m*, 1H); MS *m/e* (rel. int.): (no parent peak), 258 (base), 187 (30), 173 (50), 69 (35).

Formation of acetonide (**4**) *from* **2**. To the diol **2** (45 mg) in Me_2CO (3 ml) was added $CuSO_4$ (50 mg) and the mixture refluxed for 5 min. Filtration of $CuSO_4$ through a short column packed with Si gel and evapn of the solvent gave a colourless liquid, purified by PLC to afford an acetonide **4** (40 mg). IR ν_{max} cm^{-1}: 1380, 1160, 1100, 1065, 1035, 1010, 890, 875, 840; ^1H NMR δ 0.80 (*s*, 3H), 1.33 (*s*, 6H, O − CMe_2), 1.63 (*bs*, 3H), 1.68 (*bs*, 3H), 1.73 (*bs*, 3H), 3.73 (*bs*, 2H), 4.73 (*bs*, 2H), 5.13 (*bt*, *J* = 7, 1H); MS *m/e* (rel. int.): (no molecular peak), 288 [M^+ − O − CMe_2, 14], 243 (33), 215 (35), 204 (97), 147 (base), 133 (55), 119 (79), 105 (73), 69 (63), 41 (62).

Oxidation of **3** *with* CrO_3–Py. To CrO_3–Py complex prepared by Dauben's method [19] was added diacetate **3** (25 mg) in CH_2Cl_2 (3 ml) with stirring at room temp. The reaction mixture, after filtration of the excess reagent, was purified by PLC to afford an α,β-unsaturated ketone **5** (10 mg). IR ν_{max} cm^{-1}: 1740, 1240 (OAc), 1670 (C=C − C=O), 1380, 1040; ^1H NMR: δ 2.00 (*s*, 3H, H-12), 2.10 (*s*, 6H, 2 × OAc), 4.21 (*d*, *J* = 11, 1H), 4.57 (*d*, *J* = 11, 1H), 4.80 (*bs*, 1H), 5.00 (*bt*, *J* = 7, 1H).

Oxidation of perrottetianal B (**6**). The dial **6** (40 mg) was treated with the same manner described above to give a saturated ketone **7**. $\Delta\varepsilon$ 310 nm (+0.51); IR ν_{max} cm^{-1}: 1710 (C=O), 1700 (CHO), 1665 (C=C − CHO), 1620 (C=C), 930; ^1H NMR δ 1.09 (*s*, 3H, H-14), 1.63 (*bs*, 3H), 1.76 (*bs*, 3H), 2.19 (*s*, 3H, H-12), 3.23 (*m*, 2H), 5.36 (*bt*, *J* = 7, 1H), 10.03 (*s*, 1H, C<u>H</u>O), 10.18 (*s*, 1H, C<u>H</u>O); MS *m/e* (rel. int.): 316 (M^+, 10), 205 (base), 105 (76), 69 (50).

Acetylation of **9**. To Py soln of **9** (50 mg) was added Ac_2O (1 ml) and the mixture allowed to stand overnight. Work-up as usual gave the monoacetate **10** (45 mg). IR ν_{max} cm^{-1}: 3590 (OH), 1730, 1250 (OAc), 1640 (C=C), 1608 (C=C), 1075, 1030, 996, 953, 900; UV λ_{max} nm: 240 (ε, 9083); ^1H NMR: δ 0.78 (*s*, 6H), 0.83 (*s*, 3H), 1.22 (*s*, 3H), 1.80 (*bs*, 3H), 1.97 (*s*, 3H, OAc), 4.85 (*bs*, $W_{\frac{1}{2}}$ = 7 Hz, 1H), 4.93 (*d*, *J* = 10, 1H), 5.09 (*d*, *J* = 17, 1H), 5.60 (*bt*, *J* = 7, 1H), 6.41 (*dd*, *J* = 10, 17, 1H); MS *m/e* (rel. int.): 348 (M^+, 1), 330 (M^+ $-H_2O$, 5), 270 (M^+ $-H_2O$ − 60, 37), 192 (28), 150 (90), 81 (base), 69 (61), 43 (95).

Epoxidation of **9**. To a $CHCl_3$ soln of **9** (50 mg) was added *m*-chloroperbenzoic acid (40 mg) with stirring at 0°. After 2 hr, the reaction mixture was filtered. The filtrate showed 2 spots on TLC. The major epoxide **11** (30 mg) was isolated by PLC. Epoxide (**11**), IR ν_{max} cm^{-1}: 3550 (OH), 1100, 1060, 1040, 1005, 975, 920, 900, 840; ^1H NMR: δ 0.83 (*s*, 6H), 1.20 (*s*, 3H), 1.40 (*s*, 3H), 2.85 (*m*, 3H), 3.10 (*bs*, 1H), 3.98 (*m*, 1H); MS *m/e* (rel. int.): 338 (M^+, 16), 277 (M^+ $-C_2H_3O$ − H_2O, 10), 251 (29), 208 (21), 189 (37), 123 (66), 109 (57), 95 (43), 81 (50), 69 (83), 43 ($C_2H_3O^+$, base).

Hydrogenation of **9**. Compound **9** (100 mg) in EtOAc soln was hydrogenated in the presence of prereduced PtO_2 (30 mg) for 3 hr. Work-up as usual gave a tetrahydro derivative **12** (80 mg). IR ν_{max} cm^{-1}: 3370 (OH), 1385, 1375, 1240, 1110, 1066, 1056, 1031, 970, 950, 920, 855, 770, 720; ^1H NMR δ 0.80 (*bs*, overlapped 12H), 0.88 (*s*, 3H), 1.15 (*s*, 3H), 2.20 (*bs*, 1H, OH), 2.80 (*bs*, 1H, OH), 3.68 (*bs*, $W_{\frac{1}{2}}$ = 7 Hz, 1H). MS *m/e* (rel. int.): 310 (M^+, 36), 123 (44), 109 (46), 97 (46), 95 (40), 83 (59), 71 (65), 69 (base), 57 (63), 55 (62), 43 (55), 41 (43).

Oxidation of **12**. To CrO_3–Py complex (50 mg) was added **12** (50 mg) in CH_2Cl_2 soln. Work-up as usual afforded a saturated ketone **13** (30 mg). $[\alpha]_D$ −51° (*c*, 0.4); $\Delta\varepsilon$ 286 nm (−0.20); IR ν_{max} cm^{-1}: 3500 (OH), 1713 (C=O), 1395, 1380, 1270, 1165, 1120, 1070, 1045; ^1H NMR δ 0.90 (*s*, 12H), 1.07 (*s*, 3H), 1.32 (*s*, 3H), 3.97 (*s*, 1H, OH); MS *m/e* (rel. int.): 308 (M^+, 61), 291 (M^+ $-H_2O$, 73), 221 (58), 123 (89), 109 (base) 95 (71).

Dehydration of **13**. To a C_6H_6 soln of **13** (30 mg) was added *p*-TsOH (4 mg) and the mixture warmed at 50° with stirring. After evapn of the solvent, the reaction products were purified

by PLC to give an α,β-unsaturated ketone **14** (28 mg). $[\alpha]_D$ +22° (*c*, 0.34); UV λ_{max} nm: 247 (ε, 8146); Δε 292 nm (−0.69), 334 (+0.43); IR ν_{max} cm^{-1}: 1680 (C=C − C=O), 1610 (C=C), 1390, 1380, 1335, 1258, 1215, 1155, 1080; ^1H NMR δ 0.90–1.10 (overlapped 12H), 1.10 (s, 3H), 1.78 (s, 3H); MS *m/e* (rel. int.): 290 (M^+, 5), 205 (90), 135 (base), 128 (88).

Dehydrogenation of **14**. To a C_6H_6 soln of **14** (15 mg) was added DDQ (5 mg) and the mixture refluxed for 12 hr. Work-up as usual afforded a cross-conjugated ketone **15** (4 mg). ^1H NMR: δ 6.40 (s, 1H, H-6); GC–MS: *m/e* (rel. int.): 288 (M^+, 33), 273 (M^+ −15, 33), 245 (65), 204 (75), 203 (61), 189 (base).

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