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DAMMARANE TRITERPENOIDS FROM RHIZOMES OF *PYRROSIA LINGUA*

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Key Word Index—fern; *Pyrrosia lingua*; Polypodiaceae; triterpenoid; dammarane.

Abstract—Hexane extract of fresh rhizomes of *Pyrrosia lingua* (Thunb.) Farwell. yielded five new dammarane triterpenoids, designated as octanordammarane (**1**), (18*S*)-18-hydroxydammar-21-ene (**3**), (18*S*)-pyrrosialactone (**5**), (18*S*)-pyrrosialactol (**7**) and 3-deoxyocotillol (**8**), along with known dammara-18(28),21-diene (**2**). Structures of **1**, **3**, **5**, **7** and **8** were elucidated by mainly 2D NMR and other spectroscopic analyses and chemical correlations.

INTRODUCTION

The dried whole plant of *Pyrrosia lingua* (Thunb.) Farwell (Polypodiaceae) has been used as a diuretic in folk medicine in Japan [1]. This fern grows on trees or rocks in shaded place and its fronds are simple, rarely palmately or hastately lobed and covered with stellate hairs, especially when young. Having stellate hair is peculiar to the genus *Pyrrosia*. Ferns of this group are morphologically different from other polypodiaceous ferns. Only hop-22(29)-ene has, so far, been reported from this species as the triterpenoid constituent [2]. In continuation of our chemotaxonomic studies on polypodiaceous ferns, we investigated this plant for its triterpenoid constituents and recently reported five oxygenated hopane derivatives [3] along with hop-22(29)-ene (**9**, 0.18% yield of dried plant material estimated) from fresh rhizomes of this species. However, migrated hopane triterpenoid hydrocarbons, commonly encountered in the other ferns of this family, could only be isolated in trace amounts. A thorough reinvestigation on the triterpenoid constituents of this species was therefore taken up, resulting in the isolation of five new dammarane triterpenoids, *viz.* octanordammarane (**1**), (18*S*)-18-hydroxydammar-21-ene (**3**), (18*S*)-pyrrosialactone (**5**), (18*S*)-pyrrosialactol (**7**) and 3-deoxyocotillol (**8**) besides known dammara-18(28),21-diene (**2**). We report herein the isolation and structure elucidation of the new compounds.

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RESULTS AND DISCUSSION

All of the five dammarane triterpenoids (**1**, **3**, **5**, **7** and **8**) were isolated from the *n*-hexane extract of fresh rhizomes on repeated CC over Si gel followed by prep. HPLC. The low-resolution EIMS of all the compounds showed an intense peak at *m/z* 191 ($C_{14}H^{+}_{23}$, **a**) (Fig. 1) indicating the presence of an intact A/B/C ring system of hopane triterpenoids [4]. The spectra of **3**, **5**, **7** and **8** also invariably exhibited a very low intensity peak at *m/z* 301 ($C_{22}H^{+}_{37}$, **b**) due to the loss of the entire side chain, demonstrating that these compounds belong to tetracyclic triterpenoid. In order to unambiguously elucidate the carbon skeleton of the compounds, 2D NMR, *viz.* ^{1}H–^{1}H COSY, ^{1}H–^{13}C COSY, HSQC, HMBC and NOESY spectra were recorded for all the five compounds. The multiplicity of the ^{13}C signals in their PND spectra were determined by DEPT experiments. Detailed analyses of the ^{1}H–^{13}C COSY (or HSQC) and HMBC spectra of the compounds not only revealed the presence of the part structures as shown by heavy lines in structures **1a**, **3a**, **5a**, **7a** and **8a** in Fig. 2, but also the chemical shifts of all the protons and carbons of the compounds could be assigned unambiguously and these are summarised in Tables 1 and 2.

The molecular formula of compound **1** was deduced to be $C_{22}H_{38}$ by high resolution EIMS. Its ^{1}H NMR spectrum exhibited signals for five tertiary methyl groups (Table 1). Its ^{13}C NMR spectrum displayed signals for 22 carbons, of which five are CH_3, ten CH_2, three CH and four quaternary carbons. The back-bone structure of the compound

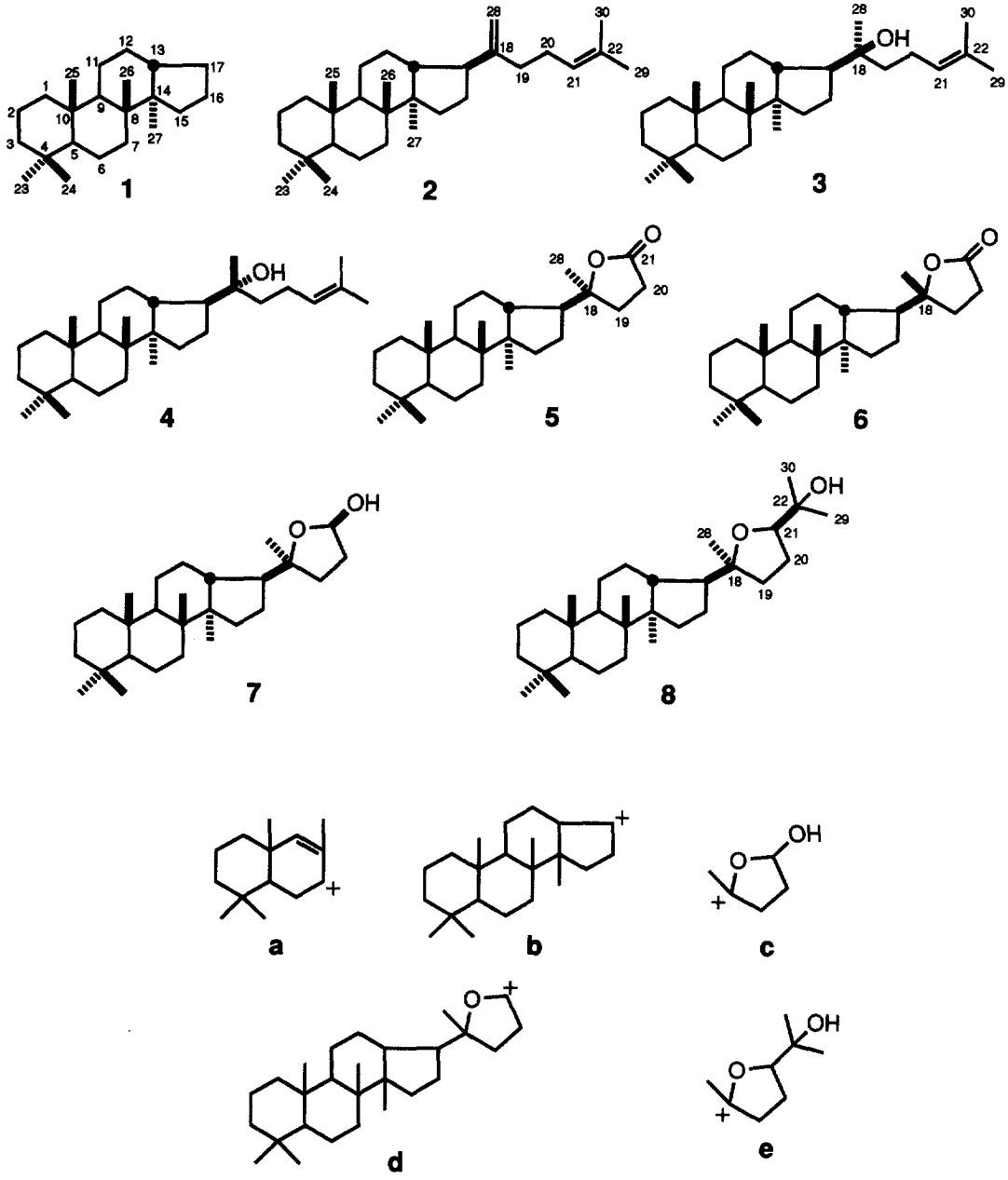

Fig. 1.

(*cf.* **a**) could be easily determined from the two- and three-bond correlations observed for the methyl proton signals with those of the neighbouring carbons in its HMBC spectrum (Fig. 2). The remaining carbon–carbon connectivities shown by the broken lines in **1a** were determined from ^{1}H–^{1}H COSY and HSQC spectra of the compound. That the ring system of **1**, including the methyl substitutions, is identical with that of the co-occurring dammara-18(28),21-diene (**2**) was clearly evident from the very close ^{13}C chemical shifts of all the carbons of **1** with those of **2** (Table 2) except C-13, C-16 and C-17, which were shielded by ~4, ~8 and ~20 ppm due to the absence of the side chain at C-17. The compound was, therefore, represented by octanordammarane structure (**1**).

Compound **2** was earlier isolated from *Lemmaphyllum microphyllum* var. *obovatum* and characterised as dammara-18(28),21-diene [5]. However, no ^{13}C NMR data was reported. During the present study, unambiguous assignments of its ^{1}H and ^{13}C chemical shifts (Tables 1 and 2) have been done through detailed analyses of its 2D NMR spectra.

Compound **3** did not show the molecular ion peak in its EIMS. Instead, the spectrum exhibited

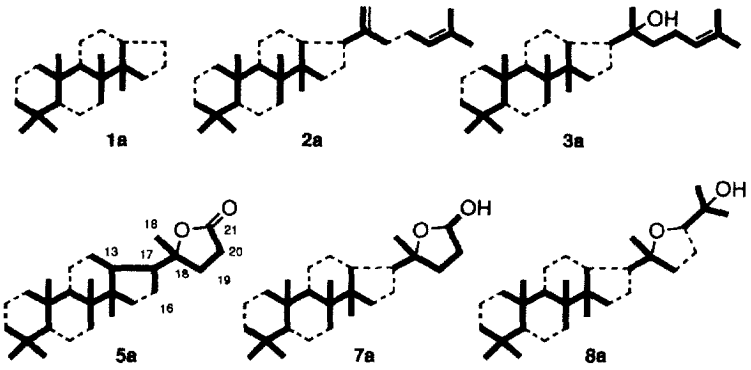

Fig. 2. Partial structures (shown by heavy lines) derived from HMBC spectra.

an intense peak at *m/z* 410 (HR–MS: *m/z* 410.3899, $C_{30}H_{50}$) due to the elimination of a molecule of H_2O from the M^+. Its ^{13}C NMR spectrum (Table 2) showed the presence of 30 carbons, of which eight are CH_3, eleven CH_2, five CH and six quaternary carbons, including two olefinic carbons of a trisubstituted double bond and one quaternary carbinyl carbon (δ 75.44 s), thereby substantiating the molecular formula of $C_{30}H_{50}O$ for the molecule. The ^1H NMR spectrum (Table 1) of the compound displayed signals for eight tertiary methyl groups, two of which are vinylic in nature (δ 1.625 and 1.689). The spectrum also showed the signal for a trisubstituted vinylic proton. Analysis of the HMBC spectrum of the compound revealed the presence of two part structures, as shown by heavy lines in **3a** (Fig. 2) which clearly showed that the $\Delta^{18(28)}$ double bond of **2** is converted to $>C(OH)–CH_3$ in **3**. This was indeed supported by the very close ^{13}C chemical shifts of C-13 to C-22 and C-27 to C-30 of **3** with those of hydroxydammarenone II. It is important to mention here that hydroxydammarenone I (18*R*) and II (18*S*) can be easily distinguished from each other by their C-(18)–Me (C-28) carbon chemical shifts (δ 23.61 in 18*R*-isomer and δ 25.48 in 18*S*-isomer). Since **3** showed a C-28 signal at δ 25.37, it must have 18*S* configuration. Both **3** and its 18*R*-isomer (**4**) were prepared from hydroxydammarenones I (**10**) and II (**11**), respectively, by Wolff–Kishner reduction for comparison and it was found that **3** was identical with the one obtained from **11**, thereby confirming its structure. Thus, **3** can be represented by (18*S*)-18-hydroxydammar-21-ene structure.

The high resolution EIMS of pyrrosialactone (**5**) showed the molecular formula to be $C_{27}H_{44}O_2$ (M^+, *m/z* 400.3350). Its IR spectrum showed the presence of a γ-lactone chromophore (1760, 1770 cm^{-1}) in the molecule. The ^1H NMR spectrum of the compound displayed signals for six tertiary methyl groups. Its ^{13}C NMR spectrum exhibited signals for C-1 to C-17 and C-23 to C-28 very close to those of **3** (Table 2) indicating that the A/B/C/D ring system of **5**, including the methyl substituents, is identical to that of **3**. The two- and three-bond correlations (Table 3) observed for the H_2-19 protons (δ 1.913 and 2.12) with C-17, C-18 (δ 90.25), C-20, C-21 (δ 176.83) and C-28 in its HMBC spectrum clearly demonstrated that the γ-lactone moiety is attached to C-17 as shown in **5**. The structure was finally confirmed by its preparation from **3** by oxidation with CrO_3–AcOH.

Compound **7** did not show any peak for M^+ in its mass spectrum. However, an intense peak at *m/z* 384 ($C_{27}H_{44}O^+$) was observed. Its ^{13}C NMR spectrum displayed signals for 27 carbons, of which one methine carbon signal at δ 99.88 and a quaternary carbon signal at δ 88.03 indicated that the compound might contain a lactol ring in the molecule. A comparison of the ^{13}C NMR spectrum of the

Table 1. ^1H chemical shifts* (δ ppm, $CDCl_3$, 500 MHz) of compounds **1–8**, **10** and **11**

Compd.	H_3-23	H_3-24	H_3-25	H_3-26	H_3-27	H_3-28/H_2-28	H_3-29	H_3-30	H-21
1	0.850	0.806	0.844	0.934	0.787				
2	0.852	0.808	0.847	0.975	0.879	4.704, 4.742	1.693	1.620	5.134 (*dd* 7.1, 7.1)
3	0.848	0.804	0.841	0.960	0.888	1.139	1.689	1.625	5.122 (*dd* 7.1, 7.1)
4	0.848	0.805	0.843	0.965	0.887	1.117	1.680	1.621	5.114 (*dd* 7.1, 7.1)
5	0.848	0.803	0.835	0.958	0.894	1.361			
6	0.848	0.805	0.843	0.963	0.888	1.337			
7	0.841	0.799	0.831	0.938	0.857	1.264			5.376 (*dd* 4.3, 4.0)
8	0.846	0.801	0.834	0.953	0.881	1.128	1.118	1.209	
10	1.081	1.039	0.946	1.007	0.888	1.130	1.688	1.627	5.120 (*dd* 7.1, 7.1)
11	1.081	1.039	0.945	1.001	0.888	1.150	1.692	1.627	5.120 (*dd* 7.1, 7.1)

* Figures in the parentheses are the coupling constants in Hz. Assignments were done on the basis of 2D NMR spectral analyses.

Table 2. ^{13}C Chemicals shifts (δ, $CDCl_3$, 125 MHz) of compounds **1**–**8**, **10** and **11**

Carbon	1	2	3	4	5	6	7	8	10	11
1	40.75	40.71	40.64	40.62	40.61	40.62	40.63	40.66	39. 89	39.89
2	18.75	18.73	18.72	18.70	18.68	18.68	18.70	18.72	34. 12	34.11
3	42.19	42.17	42.19	42.16	42.14	42.15	42.18	42.19	218.15	218.11
4	33.39	33.38	33.38	33.33	33.36	33.37	33.36	33.38	47. 43	47.42
5	56.97	56.98	56.98	56.94	56.92	56.94	56.92	56.98	55.36	55.35
6	18.62	18.62	18.60	18.58	18.56	18.57	18.59	18.60	19.65	19.65
7	35.67	35.42	35.22	35.23	35.18	35.24	35.27	35.28	34.56	34.54
8	40.37	40.68	40.58	40.59	40.57	40.63	40.57	40.60	40.31	40.27
9	51.08	51.04	50.73	50.69	50.64	50.73	50.78	50.88	50.00	50.00
10	37.55	37.53	37.44	37.41	37.43	37.45	37.43	37.47	36.83	36.83
11	21.39	21.24	21.40	21.33	21.28	21.15	21.44	21.43	21.93	22.03
12	26.64	25.05	27.61	27.59	26.88	26.53	27.18	27.44	27.51	27.52
13	41.53	45.22	42.25	42.10	43.14	42.58	43.07	42.91	42.32	42.38
14	48.93	49.53	50.39	50.08	50.25	50.14	50.01	50.07	50.00	50.26
15	32.07	31.36	31.14	31.00	31.16	31.00	31.03	31.42	31.04	31.16
16	20.84	28.91	24.81	25.31	25.06	25.02	26.03	26.13	25.31	24.80
17	27.79	47.88	49.87	49.62	49.40	49.51	49.75	49.57	49.51	49.81
18		152.84	75.44	75.71	90.25	90.05	88.03	86.47	75.75	73.36
19		34.10	40.52	41.79	31.18	32.99	31.95	35.72	41.84	40.46
20		27.00	22.55	22.28	29.23	28.70	33.84	25.72	22.29	22.56
21		124.50	124.77	124.75	176.83	176.99	99.88	83.32	124.64	124.68
22		131.40	131.56	131.43				71.44	131.64	131.64
23	33.45	33.45	33.43	33.42	33.41	33.42	33.43	33.43	26.70	26.70
24	21.58	21.57	21.55	21.54	21.54	21.54	21.55	21.54	21.03	21.01
25	16.25	16.20	16.20	16.16	16.16	16.18	16.19	16.20	16.02	16.02
26	15.59	15.70	15.57	15.59	15.53	15.53	15.56	15.51	15.25	15.21
27	14.80	15.96	16.49	16.39	16.27	16.25	16.19	16.50	16.26	16.34
28		107.43	25.37	23.59	25.35	22.37	28.95	23.50	23.61	25.48
29		25.72	25.76	25.74				27.49	25.75	25.75
30		17.72	17.71	17.70				24.27	17.73	17.72

Chemical shifts were assigned to specific carbons on the basis of detailed analyses of 2D NMR *viz.* ^1H–^1H COSY, ^1H–^{13}C COSY, HSQC, HMBC and NOESY spectra.

compound with that of **5** (Table 2) revealed that the chemical shifts of all the carbons of **7** except C-18, C-20, C-21 and C-28 were very close to those of **5**. The shielding of C-18 and C-21 by ~2 and 77 ppm, and deshielding of C-20 and C-28 by ~5 and 3.5 ppm, respectively, were found to be in excellent agreement with the lactol structure **7** for the compound. The base peak in its mass spectrum at *m/z* 101 ($C_5H_9O_2^+$, **c**), due to cleavage of the bond between C-17 and C-18, supported the above structural assignment. The assigned structure was fully corroborated by the HMBC spectrum of the compound (Table 4). Finally, the stereochemistry at the chiral centres C-18 and C-21 could be deduced from the NOE interactions, *viz.* H-21 ↔ H_3-28 ↔ H-17 ↔ H_3-27, observed in its NOESY spectrum.

The high resolution EIMS of compound **8** showed its molecular formula to be $C_{30}H_{52}O_2$ (M^+, *m/z* 444.4085). Its low resolution mass spectrum exhibited intense peaks at *m/z* 385 (M^+–C_3H_7O, **d**) and 143 ($C_8H_{15}O_2^+$, **e**) besides the peak at *m/z* 191 (**a**), indicating that one oxygen is attached to the terminal three carbon unit and the second oxygen must be in the remaining five carbon unit. The ^{13}C NMR spectrum of the compound (Table 2) displayed three down-field signals at δ 71.44 s, 83.32 d and 86.47 s, indicating that one tertiary hydroxyl group must be attached to the terminal isopropyl unit and one oxygen forms an ether linkage between C-18 and C-21. This was indeed supported by the HMBC spectrum (Table 5) of the compound. The stereochemistry at C-18 and C-21 could be determined from the NOE interactions. *viz.*

Table 3. One-bond (^1H–^{13}C COSY) and multiple bond (HMBC) correlation data of **5**

δ_H	One-bond correlation δ_C	Multiple bond correlation δ_C			
0.848 (H_3-23)	33.41 (C-23)	21.54 (C-24)	33.36 (C-4)	42.14 (C-3)	56.92 (C-5)
0.803 (H_3-24)	21.54 (C-24)	33.36 (C-4)	33.41 (C-23)	42.14 (C-3)	56.92 (C-5)
0.835 (H_3-25)	16.16 (C-25)	37.43 (C-10)	40.61 (C-1)	50.64 (C-9)	56.92 (C-5)
0.958 (H_3-26)	15.53 (C-26)	35.18 (C-7)	40.57 (C-8)	50.25 (C-14)	56.64 (C-9)
0.894 (H_3-27)	16.27 (C-27)	31.16 (C-15)	40.57 (C-8)	50.25 (C-14)	43.14 (C-13)
1.361 (H_3-28)	25.35 (C-28)	31.18 (C-19)	49.40 (C-17)	90.25 (C-18)	
1.989 (H-17)	49.40 (C-17)	25.06 (C-16) 90.25 (C-18)	26.88 (C-12)	31.18 (C-19)	43.14 (C-13)
1.913 (Ha-19)	31.18 (C-19)	25.35 (C-28)	29.23 (C-20)	49.40 (C-17)	90.25 (C-18)
2.12 (Hb-19)		176.83 (C-21)			

Table 4. One-bond (^1H–^{13}C COSY) and multiple bond (HMBC) correlation data of **7**

δ_H	One-bond correleation δ_C	Multiple bond correlation δ_C			
0.842 (H_3-23)	33.43 (C-23)	21.55 (C-24)	33.36 (C-4)	42.18 (C-3)	56.92 (C-5)
0.799 (H_3-24)	21.55 (C-24)	33.36 (C-4)	33.43 (C-23)	42.18 (C-3)	56.92 (C-5)
0.831 (H_3-25)	16.19 (C-25)	37.43 (C-10)	40.63 (C-1)	50.78 (C-9)	56.92 (C-5)
0.938 (H_3-26)	15.56 (C-26)	35.27 (C-7)	40.57 (C-8)	50.01 (C-14)	50.78 (C-9)
0.857 (H_3-27)	16.19 (C-27)	31.03 (C-15)	40.57 (C-8)	50.01 (C-14)	43.07 (C-13)
1.264 (H_3-28)	28.95 (C-28)	31.95 (C-19)	49.75 (C-17)	88.03 (C-18)	

H-21 ↔ H_3-28 ↔ H_3-27, observed in the NOESY spectrum of the compound. Based on these observations, compound **8** was characterised as deoxyocotillol [6].

EXPERIMENTAL

General

Mps: uncorr.; NMR: JEOL ALPHA 500 (500 MHz for ^1H, 125 MHz for ^{13}C) with TMS as int. standard; HR–EIMS (JEOL D-300) and LR–EIMS (JEOL HX-110): 30 eV, direct inlet; HPLC: SENSHU PAK C_{18} column (8 mm × 250 mm, 5μ), **A**, MeOH–$CHCl_3$ (8:2), **B**, MeCN–$CHCl_3$ (9:1) as mobile phase and detector RI; GC: 1.4% SE-30 on Chromosorb HP glass column (1 m × 4 mm i.d.) at 260°; cholestane was used as int. standard and its R_t was set at 3 min. for hydrocarbons. HPTLC: precoated Si gel plates (E. Merk) were used.

Plant material

Fresh rhizomes of *Pyrrosia lingua* were collected at Matsuzaki in Shizuoka in December, 1991. The voucher specimens (# 911202) have been deposited in the herbarium of Showa College of Pharmaceutical Sciences, Tokyo.

Extraction and isolation

Sliced fresh rhizomes (2.03 kg) were extracted with hot *n*-hexane to afford the extract (22 g) with H_2O (936 ml). The extract was subjected to silica gel CC to give the following fractions: fr. 1–3 [eluted with *n*-hexane], fr. 4–9 [*n*-hexane–benzene (8:2)], fr. 10–17 [*n*-hexane–benzene (1:1)], fr. 18–26 [benzene], fr. 27–33 [benzene–ether (1:1)], fr. 34 [ether] and fr. 35 [MeOH]. Each fraction was further purified by repeated silica gel CC and HPLC to furnish **1** (1.5 mg) from fr. 1, **2** (19.7 mg) from fr. 2, **3** (320 mg) from fr. 16 and 17, **5** (8.7 mg) from fr. 26, **7** (0.6 mg) from fr. 13, and **8** (0.6 mg) from fr. 16 in pure form.

Octanordammarane (**1**). Recrystallized from Me_2CO as colourless needles, mp 63–66°, $[\alpha]_D$ + 29.5° (*c* 0.1, $CHCl_3$), GC *RR*$_t$ 0.32; HPLC R_t 16.5 (**A**, flow 4 ml/min.); EIMS *m/z*: (rel. int.): 302.2952 $[M]^+$ (18), 287 $[M-CH_3]^+$ (18), 192 (27), 191 (100), 123 (29), 108 (30); ^{13}C NMR (δ): Table 1; ^1H NMR (δ): Table 2.

Dammara-18(28),21-*diene* (**2**). Recrystallized from Me_2CO as colourless needles, mp 51–52°, $[\alpha]_D$ + 57.1° (*c* 0.8, $CHCl_3$); GC *RR*$_t$ 1.54; HPLC R_t 22.9 (**A**, flow 3 ml/min.); EIMS *m/z*: (rel. int.): 410.3861 $[M]^+$ (23), 395 $[M-CH_3]^+$, (3), 341 (1), 301 (4), 299 (7), 218 (18), 204 (30), 191 (100), 189 (39), 109 (91), 69 (71); ^1H NMR Table 1; (δ): ^{13}C NMR (δ): Table 2.

(18S)-18-*Hydroxydammar*-21-*ene* (**3**). Recrystallized from Me_2CO as colourless needles, mp 76–78°, $[\alpha]_D$ + 38.4° (*c* 1.1, $CHCl_3$); HPLC R_t 14.7 (**B**, flow 2.5 ml/min.); EIMS *m/z*: (rel. int.): 410.3899 $[M-H_2O]^+$ (31), 395 $[M-CH_3]^+$, (9), 367 (2), 345 (13), 341 (23), 328 (12), 301 (16), 299 (14), 231 (14), 218 (18), 205 (24), 204 (23), 191 (100), 189 (13), 109 (61), 69 (5); ^1H NMR Table 1; (δ): ^{13}C NMR (δ): Table 2.

(18S)-*Pyrrosialactone* (**5**). Recrystallized from Me_2CO as colourless plates, mp 192–193° $[\alpha]_D$ + 45.0° (*c* 0.4, $CHCl_3$); HPLC R_t 10.2 (**B**, flow 2.8 ml/min.); EIMS *m/z* (rel. int.): 400.3350 $[M]^+$ (6), 385 $[M-CH_3]^+$, (12), 301 (17), 299 (5), 231 (3), 218 (4) 208, (15), 205 (11), 204 (10), 192 (95), 191 (100), 177 (15), 137 (14), 123 (18), 109 (10), 69 (4); ^1H NMR Table 1; (δ): ^{13}C NMR (δ): Table 2.

Pyrrosialactol (**7**). Recrystallized from Me_2CO as colourless plates, mp 255–257°, $[\alpha]_D$ + 103.8° (*c* 0.05, $CHCl_3$); EIMS *m/z*: (rel. int.): 384 $[M-H_2O]^+$ (15),

Table 5. One-bond (^1H–^{13}C COSY) and multiple bond (HMBC) correlation data of **8**

δ_H	One-bond correlation δ_C	Multiple bond correlation δ_C			
0.846 (H_3-23)	33.43 (C-23)	21.54 (C-24)	33.38 (C-4)	42.19 (C-3)	56.98 (C-5)
0.801 (H_3-24)	21.54 (C-24)	33.38 (C-4)	33.43 (C-23)	42.19 (C-3)	56.98 (C-5)
0.834 (H_3-25)	16.20 (C-25)	37.47 (C-10)	40.66 (C-1)	50.88 (C-9)	56.98 (C-5)
0.953 (H_3-26)	15.51 (C-26)	35.28 (C-7)	40.60 (C-8)	50.07 (C-14)	50.88 (C-9)
0.881 (H_3-27)	16.50 (C-27)	31.42 (C-15)	40.60 (C-8)	50.07 (C-14)	42.91 (C-13)
1.128 (H_3-28)	23.50 (C-28)	35.72 (C-19)	49.57 (C-17)	86.47 (C-18)	
1.209 (H_3-29)	24.27 (C-29)	27.49 (C-30)	71.44 (C-22)	83.32 (C-21)	
1.118 (H_3-30)	27.49 (C-30)	24.27 (C-29)	71.44 (C-22)	83.32 (C-21)	

369 $[M-H_2O-CH_3]^+$, (9), 340 (6), 327 (4), 299 (9), 273 (8), 231 (7), 218 (3), 205 (18), 204 (9), 191 (80), 189 (8), 101 (100), 69 (10); ^1H NMR Table 1; (δ): ^{13}C NMR (δ): Table 2.

3-Deoxyocotillol (**8**). White powders from Me_2CO, $[\alpha]_D$ +19.3°(*c* 0.05, $CHCl_3$); HPLC R_t 30.4 (B, flow 3.0 ml/min.); EIMS *m/z*: (rel. int.): 444.4085 $[M]^+$ (15), 429 $[M-CH_3]^+$, (14), 411 $[M^+-H_2O-CH_3]$ (3), 385 (100), 367 (12), 299 (3), 231 (6), 205 (10), 204 (23), 193 (24), 191 (52), 175 (12), 143 (100), 125 (18), 109 (6), 69 (4); ^1H NMR Table 1; (δ): ^{13}C NMR (δ): Table 2.

Isolation of hydroxydammarenone I (**10**) *and II* (**11**). Powdered dammar resin (270 g) was refluxed with MeOH (3 l). The process was repeated three times to get the extract (141 g). The extract was dissolved in 5% KOH–EtOH–H_2O and extracted with ether to give neutral fraction (127 g) which, on repeated column chromatography over silica gel, yielded **10** (4.3 g) and **11** (1.4 g).

Hydroxydammarenone I (**10**). Recrystallized from MeCN as white powder, mp 145–147°; $[\alpha]_D$ +60.0° (*c* 1.3, $CHCl_3$); EIMS *m/z*: (rel. int.): 424 $[M-H_2O]^+$ (87), 409 $[M-H_2O-CH_3]^+$, (10), 381 (4), 359 (14), 355 (63), 341 (29), 316 (24), 315 (22), 313 (50), 311 (18), 301 (14), 299 (14), 298 (12), 256 (15), 245 (15), 205 (56), 189 (21), 109 (100).

Hydroxydammarenone II (**11**). Recrystallized from MeCN as colourless plates, mp 134–136°; $[\alpha]_D$ +66.0° (*c* 1.2, $CHCl_3$), EIMS *m/z*: (rel. int.): 424 $[M-H_2O]^+$ (83), 409 $[M-H_2O-H_3]^+$, (11), 381 (3), 355 (68), 341 (25), 316 (24), 315 (24), 313 (31), 311 (16), 301 (13), 298 (13), 245 (16), 219 (12), 205 (60), 189 (22), 109 (100).

Synthesis of (18S)-18-*hydroxydammar*-21-*ene* (**3**) *and* (18R)-18-*hydroxydammar*-21-*ene* (**4**). Compounds **11** (400 mg) and **10** (550 mg) were subjected to Wolff–Kishner reduction to afford compound **3** (368 mg) and **4** (392 mg) respectively.

(18R)-18-*Hydroxydammar*-21-*ene* (**4**). Recrystallized from $CHCl_3$–MeOH as colourless needles, mp 87–89°; $[\alpha]_D$ +31.8° (*c* 1.3, $CHCl_3$); EIMS *m/z*: (rel. int.): 428 $[M]^+$ (0.4), 410 $[M-H_2O]^+$ (47), 395 $[M-H_2O-CH_3]^-$, (1), 367 (2), 345 (18), 341 (26), 328 (12), 301 (15), 299 (14), 297 (11), 287 (8), 284 (7), 231 (10), 218 (19), 205 (22), 204 (21), 191 (100), 177 (16), 163 (16), 149 (20), 137 (23), 127 (38), 109 (97), 95 (23), 69 (12); ^1H NMR (δ); 0.848 (H_3-23), 0.805 (H_3-24), 0.843 (H_3-25), 0.967 (H_3-26), 0.888 (H_3-27), 1.122 (H_3-28), 1.685 (H_3-29), 1.626 (H_3-30), 5.119 (H_3-21); ^{13}C NMR (δ): 40.63 (C-1), 18.72 (C-2), 42.19 (C-3), 33.37 (C-4), 56.96 (C-5), 18.60 (C-6), 35.24 (C-7), 40.63 (C-8), 50.71 (C-9), 37.44 (C-10), 21.35 (C-11), 27.61 (C-12), 42.12 (C-13), 50.13 (C-14), 31.02 (C-15), 25.34 (C-16), 49.64 (C-17), 75.80 (C-18), 41.79 (C-19), 22.30 (C-20), 124.73 (C-21), 131.57 (C-22), 33.44 (C-23), 21.55 (C-24), 16.17 (C-25), 15.61 (C-26), 16.40 (C-27), 23.65 (C-28), 25.75 (C-29), 17.23 (C-30).

Synthesis of (18S)-*pyrrosialactone* (**5**) *and* (18R)-*pyrrosialactone* (**6**). To a solution of compound **3** (180 mg) in benzene (18 ml) and AcOH (20 ml) mixture, the solution of CrO_3 (150 mg) in AcOH (15 ml) was added drop by drop and the solution was refluxed for 1 hr. Ice water was added into the reaction mixture and it was extracted with ether, washed with sat. $NaHCO_3$ solution and water to afford an oily product which was purified by silica gel CC to give compound **5** (108 mg), identical in all respect with the one obtained from the natural source. Similarly, compound **4** (200 mg) on oxidation yielded compound **6** (69 mg).

(18R)-*Pyrrosialactone* (**6**). Recrystallized from Me_2CO as colourless plates, mp 235–238°; $[\alpha]_D$ +49.9° (*c* 0.8, $CHCl_3$); EIMS *m/z*: (rel. int.): 400 $[M]^+$ (18), 385 $[M-CH_3]^-$ (12), 357 (3), 344 (1), 331 (1), 301 (17), 299 (5), 276 (5), 263 (4), 231 (3), 218 (5), 208 (14), 205 (12), 204 (11), 192 (95), 191 (100), 190 (18), 177 (15), 163 (11), 149 (10), 137 (14), 123 (18); ^1H NMR (δ): 0.848 (H_3-23), 0.850 (H_3-24), 0.843 (H_3-25), 0.963 (H_3-26), 0.888 (H_3-27), 1.337 (H_3-28); ^{13}C NMR (δ): 40.62 (C-1), 18.68 (C-2), 42.15 (C-3), 33.37 (C-4), 56.94 (C-5), 18.57 (C-6), 35.24 (C-7), 40.63 (C-8), 50.73 (C-9), 37.45 (C-10), 21.15 (C-11), 26.53 (C-12), 42.58 (C-13), 50.14 (C-14), 31.00 (C-15), 25.02 (C-16), 49.51 (C-17), 90.05 (C-18), 32.99 (C-19), 28.70 (C-20), 176.99 (C-21), 33.42 (C-23), 21.54 (C-24), 16.18 (C-25), 15.53 (C-26), 16.25 (C-27), 22.37 (C-28).

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