

Terpenoids from Two *Dicranopteris* Species

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Two new compounds, (6*S*,13*S*)-6-[[β -D-glucopyranosyl-(1 \rightarrow 4)- α -L-rhamnopyranosyl]oxy]cleroda-3,14-dien-13-ol (**1**) and kadsuric acid 3-methyl ester (**2**), together with nine known compounds, (6*S*,13*E*)-6-[[β -D-glucopyranosyl-(1 \rightarrow 4)- α -L-rhamnopyranosyl]oxy]cleroda-3,13-dien-15-ol (**3**), (6*S*,13*S*)-6-[6-*O*-acetyl- β -D-glucopyranosyl-(1 \rightarrow 4)- α -L-rhamnopyranosyl]oxy]-13-[[α -L-rhamnopyranosyl-(1 \rightarrow 4)- β -D-fucopyranosyl]oxy]cleroda-3,14-diene (**4**), (6*S*,13*S*)-6-[6-*O*- β -D-glucopyranosyl-(1 \rightarrow 4)- α -L-rhamnopyranosyl]oxy]-13-[[α -L-rhamnopyranosyl-(1 \rightarrow 4)- β -D-fucopyranosyl]oxy]cleroda-3,14-diene (**5**), 15-hydroxydehydroabietic acid (**6**), 15-hydroxylabd-8(17)-en-19-oic acid (**7**), junicedric acid (**8**), (4 *β*)-kaur-16-en-18-oic acid (**9**), (4 *β*)-16-hydroxykauran-18-oic acid (**10**), and (4 *β* ,16 *β*)-16-hydroxykauran-18-oic acid (**11**) were isolated from the fronds of *Dicranopteris linearis* or *D. ampla*. Their structures were established by extensive 1D- and 2D-NMR spectroscopy. Compounds **1** and **3–8** showed no anti-HIV activities.

Introduction. – *Dicranopteris* species (ferns, family Gleicheniaceae) are widely distributed in China. In our previous research on *D. dichotoma*, we have reported the isolation and structural elucidation of two new highly oxygenated phenolic derivatives, dichotomains A and B, and of some tetranorclerodanes and clerodane-type diterpene glycosides, and some of them were tested for their anti-HIV activities [1][2]. To search for bioactive compounds from *Dicranopteris* species, we studied the fronds of *D. linearis* (BURM.) UNDERW and *D. ampla* CHING et CHIU, which led to the isolation of two new compounds, including a clerodane-type diterpene glycoside, (6*S*,13*S*)-6-[[β -D-glucopyranosyl-(1 \rightarrow 4)- α -L-rhamnopyranosyl]oxy]cleroda-3,14-dien-13-ol¹⁾ (**1**), and a 3,4-secolanostane triterpenoid, kadsuric acid 3-methyl ester¹⁾ (**2**), together with nine known compounds, (6*S*,13*E*)-6-[[β -D-glucopyranosyl-(1 \rightarrow 4)- α -L-rhamnopyranosyl]oxy]cleroda-3,13-dien-15-ol²⁾ (= (1*S*,3*R*,4*S*,4*aR*,8*aR*)-1,2,3,4,4*a*,5,6,8*a*-octahydro-4-[(3*E*)-5-hydroxy-3-methylpent-3-en-1-yl]-3,4,8,8*a*-tetramethylnaphthalen-1-yl 6-deoxy-4-*O*- β -D-glucopyranosyl- α -L-mannopyranoside; **3**) [2], (6*S*,13*S*)-6-[[6-*O*-acetyl- β -D-glucopyranosyl-(1 \rightarrow 4)- α -L-rhamnopyranosyl]oxy]-13-[[α -L-rhamnopyranosyl-(1 \rightarrow 4)- β -D-fucopyranosyl]oxy]cleroda-3,14-diene²⁾ (= (1*S*)-1-[2-[(1*S*,2*R*,4*S*,4*aR*,8*aR*)-4-[[4-*O*-(6-*O*-acetyl- β -D-glucopyranosyl)-6-deoxy- α -L-mannopyranosyl]oxy]-1,2,3,4,4*a*,7,

¹⁾ Trivial atom numbering; for systematic names, see *Exper. Part*.

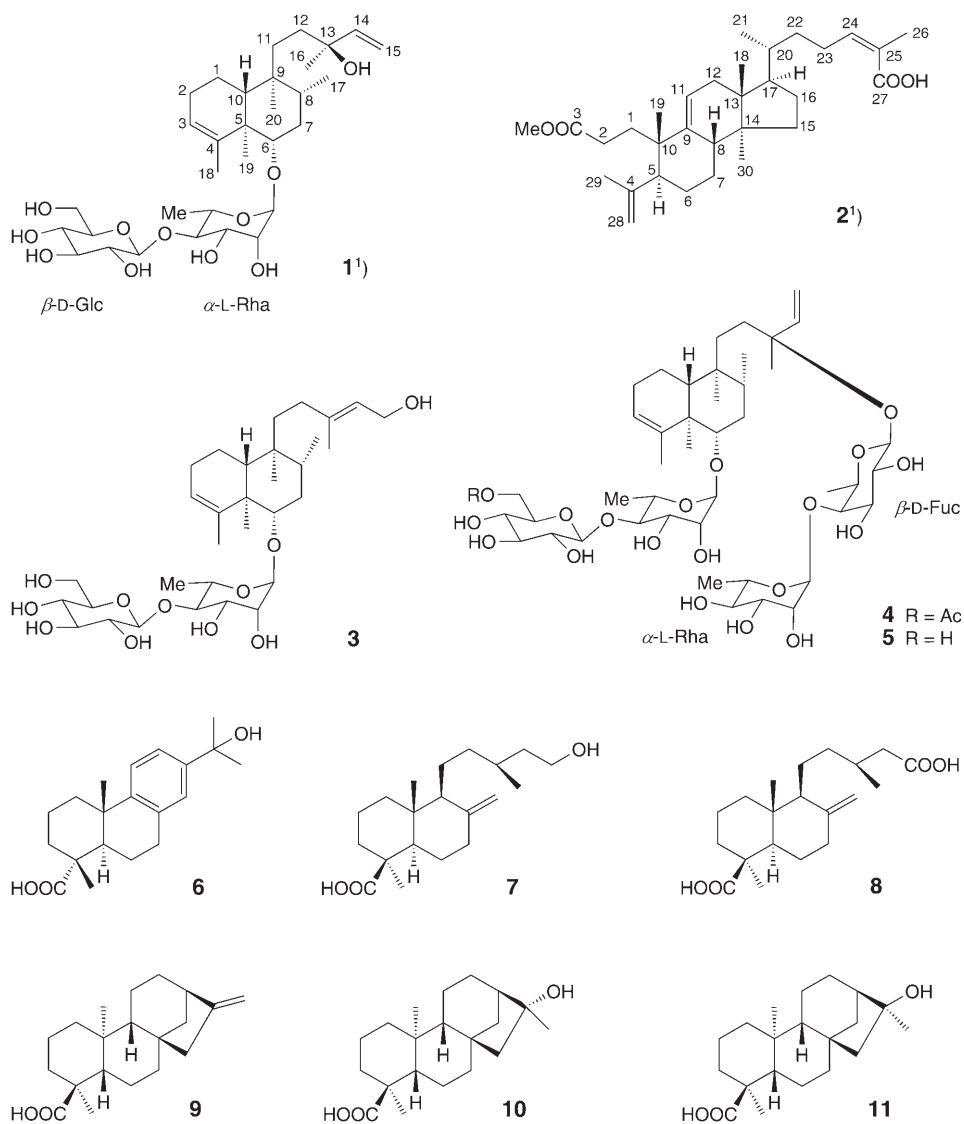
²⁾ Notice that here the systematic name (1*S*,2*R*,4*aS*,5*R*,8*aS*)-decahydro-1,2,4*a*,5-tetramethyl-1-[(3*S*)-3-methylpentyl]naphthalene is used for clerodane.

8,8a-octahydro-1,2,4a,5-tetramethylnaphthalen-1-yl}ethyl)-1-methylprop-2-en-1-yl 6-deoxy-4-*O*-(6-deoxy- α -L-mannopyranosyl)- β -D-galactopyranoside; **4**) [3], (6*S*,13*S*)-6-[[6-*O*- β -D-glucopyranosyl-(1 \rightarrow 4)- α -L-rhamnopyranosyl]oxy]-13-[[α -L-rhamnopyranosyl-(1 \rightarrow 4)- β -D-fucopyranosyl]oxy]cleroda-3,14-diene²) (**5**) [4], 15-hydroxydehydroabiatic acid (= (1*R*,4*aS*,10*aR*)-1,2,3,4,4*a*,9,10,10*a*-octahydro-1,4*a*-dimethyl-7-(1-hydroxy-1-methylethyl)phenanthrene-1-carboxylic acid; **6**) [5], 15-hydroxyabd-8(17)-en-19-oic acid (= (1*S*,4*aR*,5*S*,8*aR*)-Decahydro-5-[(3*S*)-5-hydroxy-3-methylpentyl]-1,4*a*-dimethyl-6-methylenenaphthalene-1-carboxylic acid; **7**) [6], junicedric acid (= (β *S*,1*S*,4*aR*,5*S*,8*aR*)-5-carboxydecahydro- β ,5,8*a*-trimethyl-2-methylenenaphthalene-1-pentanoic acid; **8**) [7], (4 *β*)-kaur-16-en-18-oic acid³) (**9**) [8], (4 *β*)-16 *α* -hydroxy-18-kauran-18-oic acid³) (**10**) [9], and (4 *β* ,16 *β*)-16-hydroxykauran-18-oic acid³) (**11**) [10] from *D. linearis* and *D. ampla*. In addition, compounds **1** and **3–8** showed no anti-HIV activities.

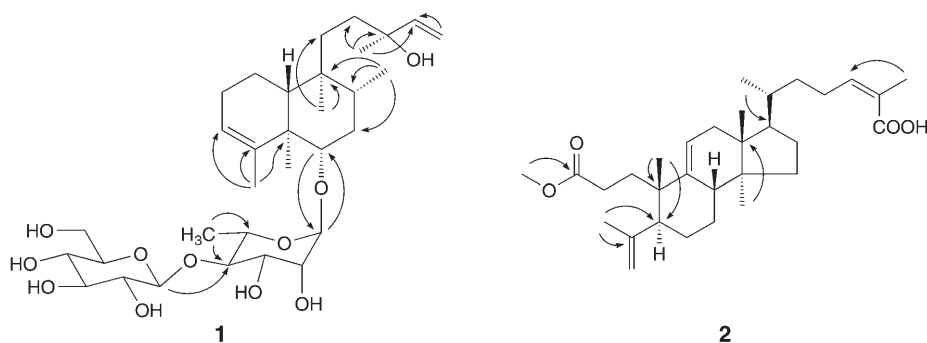
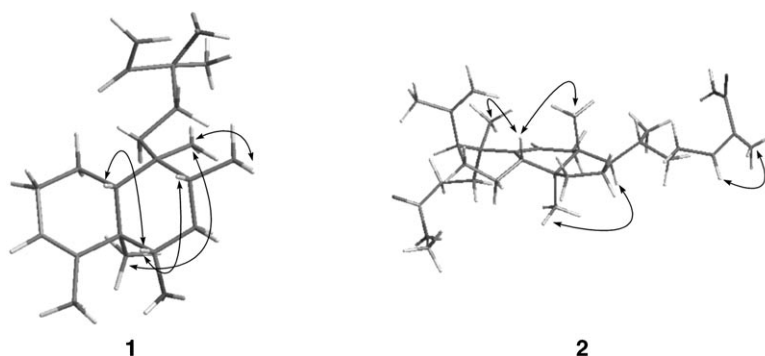
Results and Discussion. – Compound **1** was obtained as a pale yellow powder. Its molecular formula was determined as C₃₂H₅₄O₁₁ by HR-ESI-MS (*M*⁺ at *m/z* 613.3593), which revealed 6 unsaturation degrees. The ¹H- and ¹³C-NMR spectra of **1** (Table 1) showed the presence of a diterpene and two hexose moieties. Assignment of each glycoside was achieved by the analysis of ¹H, ¹H-COSY and HMBC experiments (Fig. 1). Acid hydrolysis of **1** by the method described in [2] led to decomposition of the aglycone, but gave a mixture of glucose and rhamnose. The two monosaccharides were identified as having D- and L-configuration, respectively, by comparison of their *R_f* values with those of authentic samples; comparisons of the ¹H- and ¹³C-NMR data of the glucopyranosyl unit with those of compound **3** [2] and considering that all glucose and rhamnose units in structures of compounds isolated from fern species have D- and L-configuration, respectively, confirmed these attributions. The relative configuration of **1** was determined by a ROESY experiment (Fig. 2). Thus, the structure of **1** was established as 6-[[β -D-glucopyranosyl-(1 \rightarrow 4)- α -L-rhamnopyranosyl]cleroda-3,14-dien-13-ol¹).

The diterpene moiety of **1** was composed by five Me groups (δ (C) 27.5, 23.2, 18.4, 16.6, and 16.2), five CH₂ groups (δ (C) 36.1, 36.1, 33.1, 27.5, and 18.7), four olefinic C-atoms (δ (C) 146.2, 144.5, 123.7, and 112.3), three CH groups (δ (C) 87.9, 47.0, and 35.3), and three quaternary C-atoms (δ (C) 72.6, 45.0, and 38.8) according to the ¹H- and ¹³C-NMR spectra. In the HMBC plot, the correlation of the anomeric H-atom (δ (H) 4.58) of the glucopyranosyl unit with C(4) (δ (C) 83.5) of the rhamnopyranosyl unit established a glucopyranosyl(1 \rightarrow 4)rhamnopyranosyl linkage. Moreover, the sugar chain was linked to C(6) of the aglycone by the correlation of the anomeric H-atom (δ (H) 4.77) of the rhamnopyranosyl unit with C(6) (δ (C) 87.9) of the aglycone. The rhamnopyranosyl and glucopyranosyl units were in α - and β -configurations as established by the coupling constants of their anomeric H-atoms (*J* = 1.3 and 7.8 Hz). The above evidence suggested that compound **1** was similar to (6*S*,13*S*)-6-[[6-*O*-acetyl- β -D-glucopyranosyl-(1 \rightarrow 4)- α -L-rhamnopyranosyl]oxy]cleroda-3,14-diene-13-ol, except for the absence of an Ac group in **1** [2]. The ROESY correlations of H–C(6) with H–C(8) and H–C(10) established that H–C(6) and H–C(10) were both β -oriented; accordingly, the glycosyloxy group at C(6) was α -oriented (Fig. 2). The ROESY correlation between Me(19) and Me(20) indicated that Me(20) was α -oriented.

³) The name kaurane implies (5 *β* ,8 *α* ,9 *β* ,10 *α* ,13 *α* ,16 *β*) configuration, according to *Chem. Abstr.*



Compound **2**, a colorless oil, had a molecular formula $C_{31}H_{48}O_4$, as deduced from, its HR-ESI-MS (M^+ at 485.3624), corresponding to eight unsaturation degrees. In the IR spectrum, the absorptions at 3424, 1740, 1689, and 1637 cm^{-1} indicated the presence of a COOH group and of C=C bonds. The ^1H - and ^{13}C -NMR spectra of **2** (Table 2) were very similar to those of kadsuric acid [11], except that the former possesses an additional MeO group, suggesting that **2** was a monomethyl ester derivative of kadsuric acid. The HMBC (Fig. 1) and ROESY data (Fig. 2) confirmed the structure of **2** as kadsuric acid 3-methyl ester.

Fig. 1. HMBC Data of compounds **1** and **2**Fig. 2. ROESY Correlations of the aglycone of compounds **1** and **2**

The ^1H -NMR spectrum of **2** shows the presence of an isopropenyl group at $\delta(\text{H})$ 4.87 and 4.71 (2s, 1 H each, $\text{CH}_2(28)$) and 1.77 (s, Me(29)), three tertiary Me groups at $\delta(\text{H})$ 0.66, 1.07, and 0.76 (3s, Me(18), Me(19), and Me(30)), besides an angelic acid-type terminal moiety at $\delta(\text{H})$ 6.10 (t, $J=6.7$ Hz, H-C(24)) and 1.93 (s, Me(26)), and a secondary Me group at $\delta(\text{H})$ 0.91 (d, $J=7.4$ Hz, Me(21)). Furthermore, the HMBC correlations between $\delta(\text{H})$ 3.67 (MeO) and $\delta(\text{C})$ 174.9 (C(3)) of **2** indicated that the methyl ester group was located at C(3). The relative configuration of **2** was determined by a ROESY experiment. The ROESY correlation H-C(8)/Me(19) suggested that H-C(8) was in β -orientation, the correlation H-C(17)/Me(30) indicated that H-C(17) was in α -configuration, and the correlation H-C(24)/Me(26) suggested that the C(24)=C(25) bond was in (Z) configuration.

Compounds **1** and **3–8** were tested for their anti-HIV activities. But none of them showed obvious activities.

Experimental Part

General. Column chromatography (CC): silica gel (100–200 mesh; Qingdao Marine Chemical Inc., China) and silica gel *H* (10–40 μm , Qingdao). TLC: silica gel; visualization by spraying with 10% H_2SO_4 in EtOH followed by heating. Optical rotations: Horiba-SEPA-300 spectro-polarimeter. UV Spectra: Shimadzu-210A double-beam spectrophotometer; λ_{max} log (ϵ) in nm. IR Spectra: Bio-Rad-FTS-135 spectrophotometer; KBr discs; $\tilde{\nu}_{\text{max}}$ in cm^{-1} . 1D- and 2D-NMR Spectra: Bruker-AM-400 and -DRX-500

Table 1. ^{13}C - and ^1H -NMR (CD_3OD) Assignments of Compound **1**¹). δ in ppm, J in Hz.

	δ (C)	δ (H)		δ (C)	δ (H)
$\text{CH}_2(1)$	18.7 (<i>t</i>)	1.57–1.59 (<i>m</i>)	Me(17)	16.2 (<i>q</i>)	0.80 (<i>d</i> , $J = 5.8$)
$\text{CH}_2(2)$	27.5 (<i>t</i>)	1.97–2.01 (<i>m</i>)	Me(18)	23.2 (<i>q</i>)	1.71 (<i>s</i>)
H–C(3)	123.7 (<i>d</i>)	5.11–5.15 (<i>m</i>)	Me(19)	16.6 (<i>q</i>)	1.05 (<i>s</i>)
C(4)	144.5 (<i>s</i>)		Me(20)	18.4 (<i>q</i>)	0.73 (<i>s</i>)
C(5)	45.0 (<i>s</i>)		Rha:		
H–C(6)	87.9 (<i>d</i>)	3.37–3.41 (<i>m</i>)	H–C(1')	103.3 (<i>d</i>)	4.77 (<i>d</i> , $J = 1.3$)
$\text{CH}_2(7)$	36.1 (<i>t</i>)	1.97–2.01 (<i>m</i>)	H–C(2')	72.5 (<i>d</i>)	3.87–3.93 (<i>m</i>)
H–C(8)	35.3 (<i>d</i>)	1.56–1.60 (<i>m</i>)	H–C(3')	72.6 (<i>d</i>)	3.79–3.83 (<i>m</i>)
C(9)	38.8 (<i>s</i>)		H–C(4')	83.5 (<i>d</i>)	3.61 (<i>t</i> , $J = 8.3$)
H–C(10)	47.0 (<i>d</i>)	1.29–1.33 (<i>m</i>)	H–C(5')	68.7 (<i>d</i>)	3.75–3.79 (<i>m</i>)
$\text{CH}_2(11)$	33.1 (<i>t</i>)	1.35, 1.32 (both overlapped)	Me(6')	17.9 (<i>q</i>)	1.30 (<i>d</i> , $J = 6.2$)
$\text{CH}_2(12)$	36.1 (<i>t</i>)	1.38–1.42, 1.28–1.32 (<i>2m</i>)	Glc:		
C(13)	72.6 (<i>s</i>)		H–C(1'')	105.7 (<i>d</i>)	4.58 (<i>d</i> , $J = 7.8$)
H–C(14)	146.2 (<i>d</i>)	5.86 (<i>dd</i> , $J = 9.8, 17.4$)	H–C(2'')	76.0 (<i>d</i>)	3.18–3.22 (<i>m</i>)
$\text{CH}_2(15)$	112.3 (<i>t</i>)	5.03 (<i>dd</i> , $J = 1.5, 7.3$), 5.17 (<i>dd</i> , $J = 1.5, 17.4$)	H–C(3'')	78.1 (<i>d</i>)	3.33–3.37 (<i>m</i>)
Me(16)	27.5 (<i>q</i>)	1.23 (<i>s</i>)	H–C(4'')	71.4 (<i>d</i>)	3.26–3.30 (<i>m</i>)
			H–C(5'')	74.0 (<i>d</i>)	3.84–3.88 (<i>m</i>)
			$\text{CH}_2(6'')$	62.7 (<i>t</i>)	3.85 (overlapped), 3.68 (<i>d</i> , $J = 11.0$)

Table 2. ^{13}C - and ^1H -NMR (CDCl_3) Assignments of Compound **2**¹). δ in ppm, J in Hz.

	δ (C)	δ (H)		δ (C)	δ (H)
$\text{CH}_2(1)$	32.2 (<i>t</i>)	1.99–2.01, 1.77–1.81 (<i>2m</i>)	$\text{CH}_2(16)$	28.8 (<i>t</i>)	1.28–1.32 (<i>m</i>)
$\text{CH}_2(2)$	28.8 (<i>t</i>)	2.46–2.50, 2.37–2.41 (<i>2m</i>)	H–C(17)	50.8 (<i>d</i>)	1.57–1.63 (<i>m</i>)
C(3)	174.9 (<i>s</i>)		Me(18)	14.6 (<i>q</i>)	0.66 (<i>s</i>)
C(4)	147.6 (<i>s</i>)		Me(19)	26.7 (<i>q</i>)	1.07 (<i>s</i>)
H–C(5)	49.3 (<i>d</i>)	2.06–2.10 (<i>m</i>)	H–C(20)	36.0 (<i>d</i>)	1.40–1.44 (<i>m</i>)
$\text{CH}_2(6)$	28.0 (<i>t</i>)	1.73–1.75, 1.63–1.67 (<i>2m</i>)	Me(21)	18.1 (<i>q</i>)	0.91 (<i>d</i> , $J = 7.4$)
$\text{CH}_2(7)$	27.9 (<i>t</i>)	1.54–1.56 (<i>m</i>)	$\text{CH}_2(22)$	35.8 (<i>t</i>)	1.50–1.54, 1.12–1.16 (<i>m</i>)
H–C(8)	42.5 (<i>d</i>)	2.08–2.12 (<i>m</i>)	$\text{CH}_2(23)$	26.9 (<i>t</i>)	2.55–2.59, 2.44–2.48 (<i>m</i>)
C(9)	142.4 (<i>s</i>)		H–C(24)	147.3 (<i>d</i>)	6.10 (<i>t</i> , $J = 6.7$)
C(10)	42.5 (<i>s</i>)		C(25)	125.8 (<i>s</i>)	
H–C(11)	118.5 (<i>d</i>)	5.33 (<i>d</i> , $J = 5.7$)	Me(26)	20.5 (<i>q</i>)	1.93 (<i>s</i>)
$\text{CH}_2(12)$	37.6 (<i>t</i>)	2.13–2.17, 1.93–1.97 (<i>2m</i>)	C(27)	173.2 (<i>s</i>)	
C(13)	43.9 (<i>s</i>)		$\text{CH}_2(28)$	113.7 (<i>t</i>)	4.87, 4.71 (<i>2s</i>)
C(14)	47.2 (<i>s</i>)		Me(29)	23.3 (<i>q</i>)	1.77 (<i>s</i>)
$\text{CH}_2(15)$	33.7 (<i>t</i>)	1.36–1.40 (<i>m</i>)	Me(30)	18.1 (<i>q</i>)	0.76 (<i>s</i>)
			MeO	51.5 (<i>s</i>)	3.67 (<i>s</i>)

instruments; chemical shifts δ in ppm rel. to residual solvent signals, J in Hz. ESI-MS and HR-ESI-MS: VG AutoSpec-3000 spectrometers; in m/z .

Plant Material. The fronds of *D. linearis* and *D. ampla* were collected from Hekou county, Yunnan Province, P. R. China, in March 2006. The specimens were identified by Prof. Xia Cheng and deposited in the Herbarium of the Department of Taxonomy, Kunming Institute of Botany, Chinese Academy of Sciences.

Extraction and Isolation. The dry fronds of *D. linearis* (12 kg) were ground and extracted 3 × with acetone (each time with 10 l for 24 h) at r.t. The acetone extract was concentrated and the crude extract suspended in H₂O/AcOEt. The AcOEt extract was subjected to CC (MCI, 95% EtOH). The fraction obtained with 95% EtOH was concentrated, and the residue (190 g) was subjected to CC (silica gel (200–300 mesh), CHCl₃/MeOH 1:0 → 0:1): *Fr. A–E*. *Fr. B* was subjected to repeated CC (silica gel) and semiprep. HPLC: **6** (16 mg), **7** (84 mg), and **8** (16 mg). *Fr. D* was subjected repeatedly to CC (*RP-18* and silica gel): **3** (2 g) and **4** (10 mg). Further purification by CC (*Sephadex LH-20*, *RP-18*) and semiprep. HPLC yielded **1** (4 mg) and **5** (1.5 mg).

The dry fronds of *D. ampla* (13 kg) were extracted and separated in the same manner as those of *D. linearis*. Compounds **2** (11 mg), **9** (6 mg), **10** (5 mg), and **11** (22 mg) were isolated from *Fr. B*. Compounds **4** (2 g) and **5** (11 mg) were obtained from *Fr. D*.

(1*S*,3*R*,4*S*,4*aR*,8*aR*)-1,2,3,4,4*a*,5,6,8*a*-Octahydro-4-[3*S*]-3-hydroxy-3-methylpent-4-en-1-yl]-3,4,8,8*a*-tetramethylnaphthalen-1-yl 6-Deoxy-4-O-β-D-glucopyranosyl-α-L-mannopyranoside (**1**): Pale yellow powder. M.p. 190–191°. $[\alpha]_D^{18} = -30.5$ ($c = 2.2$, MeOH). UV (MeOH): 202 (1.4). IR (KBr): 3420, 2965, 2920, 2873, 1641. ¹H- and ¹³C-NMR: Table 1. ESI-MS (neg.): 613 ($[M - H]^-$). HR-ESI-MS: 613.3593 (C₃₂H₃₃O₁₁; calc. 613.3587).

Acid Hydrolysis of 1. A soln. of **1** (3 mg) in 2M HCl (3 ml) was heated in a water bath at 70° for 6 h. After cooling, the mixture was neutralized with NaHCO₃ and extracted with CHCl₃. TLC Comparison (SiO₂, CHCl₃/MeOH 8:2) with authentic samples revealed the presence of glucose and rhamnose in the water layer (R_f 0.16 and 0.43, resp.). Unfortunately, the aglycone of **1** was not obtained because the TLC inspection of the water layer and the CHCl₃ part indicated that there were at least four products, which could not be identified due to their limited amount.

(3*R*,3*aR*,6*S*,7*S*,9*aS*,9*bS*)-3-[(1*R*,4*Z*)-5-Carboxy-1-methylhex-4-en-1-yl]-2,3,3*a*,4,6,7,8,9,9*a*,9*b*-decahydro-3*a*,6,9*b*-trimethyl-7-(1-methylethenyl)-1*H*-benz[e]indene-6-propanoic Acid Methyl Ester (**2**): Colorless oil. $[\alpha]_D^{24} = +50$ ($c = 0.240$, CHCl₃). UV (MeOH): 240 (0.30), 201 (0.13). IR (KBr): 3424, 2930, 1740, 1689, 1637, 1460, 1436, 1172, 895. NMR: Table 2. HR-ESI-MS: 485.3624 (C₃₁H₄₈O₄; calc. 485.3630).

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