Three New Sesquiterpenoid Glucosides of *Ficus pumila* Fruit

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As the glycosyl constituents of *Ficus pumila* L. fruits (Moraceae), three new sesquiterpenoid glucosides, pumilasides A, B and C were isolated together with benzyl β-D-glucopyranoside, (*E*)-2-methyl-2-butenyl β-D-glucopyranoside and rutin. Their structures were characterized as (1*S*,4*S*,5*R*,6*R*,7*S*,10*S*)-1,4,6-trihydroxyeudesmane 6-*O*-β-D-glucopyranoside, (1*S*,4*S*,5*S*,6*R*,7*R*,10*S*)-1,4-dihydroxymaaliane 1-*O*-β-D-glucopyranoside and 10α,11-dihydroxycadin-4-ene 11-*O*-β-D-glucopyranoside by spectral and chemical methods.

Key words *Ficus pumila* fruit; sesquiterpenoid glycoside; eudesmane; maaliane; cadinane; pumilaside

The fruit of *Ficus* (*F.*) *pumila* L. (Moraceae, ōhitabi in Japanese) has been used in Chinese folk medicine as antitumor, antiinflammatory and tonic medicament.[1)]

In previous papers,[2)] we reported on the sterol and triterpenoid components of this fruit. In this paper, we describe the isolation and characterization of three new sesquiterpenoid glucosides from the fruit, together with identification of the known glycosides.

The methanolic extract of the fresh fruit was suspended in water and then extracted with ether, ethyl acetate and *n*-butanol, successively. The *n*-butanol extract was treated as described in Experimental to isolate three new sesquiterpenoid glucosides, pumilaside A (**1**), pumilaside B (**2**) and pumilaside C (**3**), together with the known glycosides **4**—**6**, which were identified as benzyl β-D-glucopyranoside,[3)] (*E*)-2-methyl-2-butenyl β-D-glucopyranoside[4)] and rutin[5)] by comparison of ^{1}H- and ^{13}C-NMR spectra with those of authentic samples.

Pumilaside A (**1**, $C_{21}H_{38}O_8$, amorphous powder, $[\alpha]_D^{24}$ $-28°$) showed the $[M+K]^+$, $[M+Na]^+$, $[M+H]^+$ and $[M-C_6H_{12}O_6+H]^+$ ion peaks at *m/z* 457, 441, 419 and 239 on the positive FAB-MS. The ^{1}H-, ^{13}C- and ^{13}C–^{1}H correlation spectroscopy (COSY) NMR spectral data (Tables 1 and 2) showed the presence of one β-glucopyranosyl, two *tert*-methyls, two *sec*-methyls, four methylenes, five methines (two of them were oxygenated) and two quaternary carbons (one of them oxygenated). From the cross-peaks observed in the heteronuclear multiple bond correlation (HMBC) spectrum: H-1/C-9, C-10 and C-14; H-5/C-3, C-4, C-6, C-7, C-9, C-10 and C-14; H-6/C-7, C-10 and C-11; H-7/C-5 and C-12; H_2-9/C-5, C-7 and C-10; H_3-12/C-7, C-11 and C-14; H_3-13/C-7, C-11 and C-12; H_3-14/C-1, C-5, C-9 and C-10; H_3-15/C-3, C-4 and C-5, and ^{1}H–^{1}H COSY correlation data: H-1/H_2-2; H-6/H-5 and H-7; H-7/H-8 (δ 1.63) and H-11, a partial structure as described in Fig. 1 was obtained. Then, **1** was suggested to be a glucoside of eudesmane-type sesquiterpenoid having three hydroxyl groups at C-1, C-4 and C-6. The position of the glycosyl unit was ascertained to be C-6 from the HMBC correlation of glucosyl H-1/C-6, and from the observed nuclear Overhauser effect (NOE) interaction between the glucosyl H-1/H-6 in the nuclear Overhauser and exchange spectroscopy (NOESY) spectrum. The cross-peaks between H-6/H_3-14 and H_3-15; H_3-14/H_3-15 in the NOESY spectrum (Fig. 2) suggested that the orientation of H-6, H_3-14 and H_3-15 should be axial. Moreover, NOE interactions between H-5/H-1, H_3-12 and H_3-13 (Fig. 2), and the small coupling constant (4.5 Hz) between Hax.-6/H-7 suggested that the orientation of H-1, H-5 and the isopropyl group should be axial in the opposite direction to H-6, H_3-14 and H_3-15. So, **1** could be assumed to be a 6-*O*-β-D-glucopyranoside of 1α,4β,6β-trihydroxyeudesmane or its enantiomer. Enzymatic hydrolysis of **1** gave an aglycone (**1a**, $C_{15}H_{28}O_3$, amorphous powder, $[\alpha]_D^{24}$ $+6°$) and D-glucose, and the absolute configuration at C-6 of **1** was indicated as *R* by the values of the glycosylation shift of the α- and the β-pro-*S*-side-carbons, and the chemical shift of the glucosyl anomeric carbon as shown in Table 3.[6)] Thus, **1** was characterized as (1*S*,4*S*,5*R*,6*R*,7*S*,10*S*)-1,4,6-trihydroxyeudesmane 6-*O*-β-D-glucopyranoside as described in Fig. 2.

Pumilaside B (**2**, $C_{21}H_{36}O_7$, white powder [mp 195—197 °C (dec.)], $[\alpha]_D^{24}$ $-19°$) showed the $[M+K]^+$, $[M+Na]^+$, $[M-C_6H_{12}O_6+H]^+$ and $[M-C_6H_{12}O_6-H_2O+H]^+$ ion peaks at *m/z* 439, 423, 221 and 203 in the positive FAB-MS. The ^{1}H-, ^{13}C- and ^{13}C–^{1}H COSY NMR spectral data of **2** (Tables 1 and 2) showed the presence of one β-glucopyranosyl, four *tert*-methyls, four methylenes, four methines (one of them oxygenated), three quaternary carbons (one of them oxygenated). From the HMBC correlation data: H-5/C-1, C-3, C-4, C-6, C-9, C-10, C-11, C-14 and C-15; H-6/C-4, C-7, C-11, C-12 and C-13; H-7/C-5, C-6, C-9, C-11, C-12 and C-13; H_3-12/C-6, C-7, C-11 and C-13; H_3-13/C-6, C-7, C-11 and C-12; H_3-14/C-1, C-5, C-9 and C-10; H_3-15/C-3, C-4 and C-5, a partial structure as described in Fig. 1 was obtained and **2** was suggested to be a glucoside of maaliane-type sesquiterpenoid having two hydroxyl groups at C-1 and C-4. The position of the glycosyl unit was ascertained to be C-1 in the same way as described for **1**. As the NOE interactions between the signals of H_3-14/Hax.-2, H-6, H-7, Heq.-9 and H_3-15; H_3-15/Heq.-3 and H-6 were observed in the NOESY spectrum of **2** (Fig. 2), the orientation of H-6, H-7, H_3-14 and H_3-15 was concluded to be the same as **1**. Moreover, NOE interactions between H-5/H-1, Hax.-3 and H_3-12 were observed in its NOESY spectrum (Fig. 2), and the orientation of H-1 and H-5 was opposite to H-6, H-7, H_3-14 and H_3-15. So, **2** was considered to be 1-*O*-β-D-glucopyranoside of 1α,4β-dihydroxymaaliane or its enantiomer. Enzymatic hydrolysis of **2** gave an aglycone (**2a**, $C_{15}H_{26}O_2$, mp 172—175 °C, $[\alpha]_D^{24}$ $+10°$) and D-glucose, and the values of the glycosylation shift of the α- and the β-pro-*S*-side-carbons, and the chemical shift of the glucosyl anomeric carbon (Table 3) suggested the absolute configuration at C-1 of **2** was *S*.[6)] From these facts, **2** was determined as (1*S*,4*S*,5*S*,6*R*,7*R*,10*S*)-

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Table 1. ^{1}H-NMR Spectral Data for **1**, **2** and **3**

	1	2	3
H-1	3.69 (1H, t, J=7.0 Hz)	3.58 (1H, t, J=7.0 Hz)	1.71 (1H, ddd J=12.0, 10.0, 1.5 Hz)
H_2-2	1.90 (2H, m)[a]	1.98 (1H, br ddd, J=13.0, 7.0, 3.0 Hz, H-α)	2.56 (1H, br ddd, J=15.0, 4.0, 1.5 Hz, H-α)
		2.42 (1H, dddd, J=13.0, 12.0, 7.0, 3.0 Hz, H-β)	1.40 (1H, br ddd, J=15.0, 12.0, 5.5 Hz, H-β)
H_2-3	1.93 (2H, m)[a]	1.94 (1H, ddd, J=13.0, 12.0, 3.0 Hz, H-α)	2.11 (1H, br dd, J=15.0, 5.5 Hz, H-α)
		1.85 (1H, br dd, J=13.0, 3.0 Hz, H-β)	1.96 (1H, br dd, J=15.0, 4.0 Hz, H-β)
H-5	2.35 (1H, d, J=11.5 Hz)	1.38 (1H, d, J=6.0 Hz)	6.96 (1H, br s)
H-6	5.07 (1H, dd, J=11.5, 4.5 Hz)	0.85 (1H, dd, J=9.0, 6.0 Hz)	2.22 (1H, br dd, J=12.0, 10.0 Hz)
H-7	2.22 (1H, ddd, J=7.5, 4.5, 3.0 Hz)	0.56 (1H, t, J=9.0 Hz)	1.82 (1H, ddd, J= 12.5, 12.0, 4.0 Hz)
H_2-8	1.63 (1H, m, H-α)	1.55 (1H, dd, J=15.0, 7.5 Hz, H-α)	1.79 (1H, dddd, J=12.5, 4.0, 3.5, 3.5 Hz, H-α)
	1.77 (1H, ddd, J=12.5, 6.0, 3.0 Hz, H-β)	1.75 (1H, m, H-β)	1.13 (1H, dddd, J=12.5, 12.5, 12.5, 3.5 Hz, H-β)
H_2-9	1.98 (1H, ddd, J=12.5, 3.0, 3.0 Hz, H-α)	2.44 (1H, m, H-α)	1.85 (1H, ddd, J=12.5, 12.5, 3.5 Hz, H-α)
	1.56 (1H, m, H-β)	0.91 (1H, ddd, J=13.0, 13.0, 7.5 Hz, H-β)	2.02 (1H, ddd, J=12.5, 3.5, 3.5 Hz, H-β)
H-11	2.48 (1H, m)		
H_3-12	1.44 (3H, d, J=6.5 Hz)	1.04 (3H, s)	1.494 (3H, s)
H_3-13	1.01 (3H, d, J=6.5 Hz)	1.07 (3H, s)	1.489 (3H, s)
H_3-14	1.24 (3H, s)	1.17 (3H, s)	1.32 (3H, s)
H_3-15	1.75 (3H, s)	1.45 (3H, s)	1.75 (3H, s)
Glc-1	5.18 (1H, d, J=7.5 Hz)	4.90 (1H, d, J=7.5 Hz)	5.13 (1H, d, J=7.5 Hz)
Glc-2	4.02 (1H, dd, J=9.0, 7.5 Hz)	4.04 (1H, dd, J=7.5, 7.0 Hz)	4.05 (1H, dd, J=9.0, 7.5 Hz)
Glc-3	4.27 (1H, t, J=9.0 Hz)	4.26 (1H, t, J=7.0 Hz)	4.25 (1H, t, J=9.0 Hz)
Glc-4	4.17 (1H, t, J=9.0 Hz)	4.27 (1H, t, J=7.0 Hz)	4.19 (1H, t, J=9.0 Hz)
Glc-5	4.05 (1H, m)	3.98 (1H, m)	3.92 (1H, m)
Glc-6	4.38 (1H, dd, J=12.5, 6.0 Hz)	4.42 (1H, dd, J=12.0, 5.0 Hz)	4.29 (1H, dd, J=12.0, 6.0 Hz)
	4.61 (1H, dd, J=12.5, 2.5 Hz)	4.55 (1H, dd, J=12.0, 2.5 Hz)	4.48 (1H, dd, J=12.0, 3.5 Hz)

Solvent: pyridine-d_5 (500 MHz). δ in ppm from TMS [coupling constants (J) in Hz are given in parantheses]. *a*) Assignment may be reversed.

Table 2. ^{13}C-NMR Spectral Data for **1**, **1a**, **2**, **2a**, **3** and **3a**

		1	1a	2	2a	3	3a
Ag	C-1	79.25	79.22	88.94	78.12	50.76	50.69
	C-2	29.26	29.37	28.54	30.09	23.60	23.55
	C-3	40.94	41.30	41.66	41.89	31.27	31.32
	C-4	72.35	72.75	71.24	71.63	131.96	132.27
	C-5	51.25	51.02	48.67	48.63	127.81	127.51
	C-6	78.55	73.06	20.79	21.08	41.34	41.46
	C-7	41.78	47.88	18.81	18.99	51.67	53.01
	C-8	23.30	23.43	15.83	16.02	27.06	27.56
	C-9	36.47	36.78	37.04	37.83	43.48	43.42
	C-10	42.33	41.51	38.68	38.51	70.81	70.89
	C-11	25.85	25.83	17.44	17.53	81.12	73.20
	C-12	23.54	24.43	15.66	15.74	21.86	24.89
	C-13	22.93	22.65	29.57	29.61	27.98	32.43
	C-14	14.55	14.71	14.84	14.45	21.25	21.29
	C-15	24.49	25.10	23.61	23.74	24.00	24.30
Glc	C-1	100.30		106.69		98.43	
	C-2	75.73		75.74		75.50	
	C-3	78.87		78.69		79.21	
	C-4	72.09		71.69		72.01	
	C-5	78.57		78.21		77.77	
	C-6	63.14		62.91		63.27	

Solvent: pyridine-d_5 (125 MHz). δ in ppm from TMS.

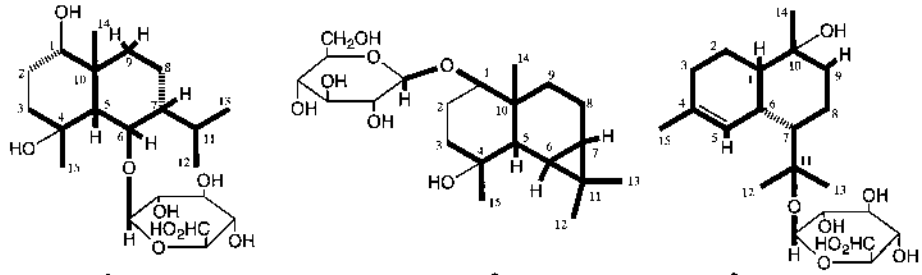
1,4-dihydroxymaaliane 1-*O*-β-D-glucopyranoside as described in Fig. 2.

Pumilaside C (**3**, $C_{21}H_{36}O_7$, amorphous powder, $[\alpha]_D^{24}$ $-17°$) showed the $[M+K]^+$, $[M+Na]^+$ and $[M-C_6H_{12}O_6+H]^+$ ion peaks at *m/z* 439, 423 and 221 in the positive FAB-MS. The ^{1}H-, ^{13}C- and ^{13}C–^{1}H COSY NMR spectral data of **3** (Tables 1 and 2) showed the presence of one β-glucopyranosyl, four *tert*-methyls, four methylenes, three methines, two oxygenated quaternary carbons and one trisubstituted double bond. The results of HMBC correlation: H-1/C-3, C-6, C-10 and C-14; H-5/C-1, C-3, C-6 and C-15; H-9 (δ 1.85)/C-1, C-7, C-8, C-10 and C-14; H_3-12/C-7, C-11 and C-13; H_3-13/C-7, C-11 and C-12; H_3-14/C-1, C-9 and C-10; H_3-15/C-3, C-4 and C-5, and the ^{1}H–^{1}H COSY spectrum: H-6/H-7 showed the presence of a structure which is described in Fig. 1. Then, **3** was suggested to be a glucoside of cadinane-type sesquiterpenoid having a double bond at C-4(5) and two hydroxyl groups at C-10 and C-11. The comparison of ^{13}C-NMR data with that of α-cadinol[7] supported this conclusion. The position of the glycosyl unit was ascertained to be C-11 in the same way as described for **1**. As the NOE interactions between the signals of H-6/H_3-12, H_3-14, and between the signals of H_3-14/Hax.-2, Hax.-8, Heq.-9, H_3-12 were observed in the NOESY spectrum of **3** (Fig. 2), the orientation of H_3-14, H-6 were suggested to be axial, the hydroxyisopropyl group attached to C-7 was equatorial, and the AB ring was indicated to be *trans*. Since D-glucose was obtained together with the aglycone **3a** by enzymatic hydrolysis, **3** was shown to have a 10α,11-dihydroxycadin-4-ene 11-*O*-β-D-glucopyranoside structure. But the absolute configuration of **3** could not be determined from available data.

Table 3. Glycosylation Shift and Glucosyl C-1 Chemical Shift of **1** and **2**

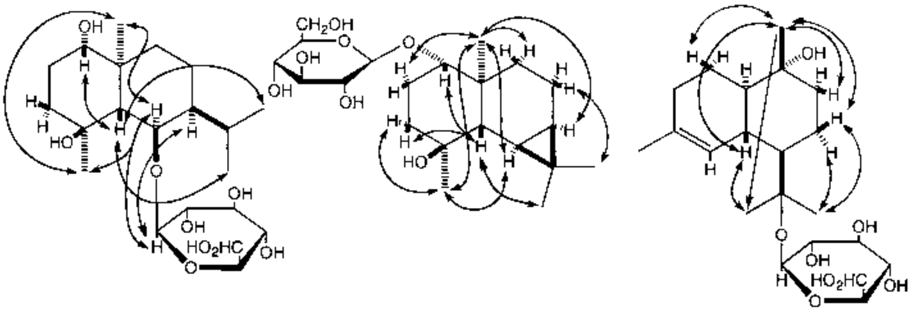
Glucoside and carbon	$\Delta\delta$ (δ glucosyl$-\delta$ aglycone) or δ
1 α-Carbon (C-6)	$\Delta\delta$ +5.49
	R-alcohols, about $\Delta\delta$ +5 to +8
2 α-Carbon (C-1)	$\Delta\delta$ +10.82
	S-alcohols, about $\Delta\delta$ +10 to +11
1 β-pro-*S*-side-carbon (C-7)	$\Delta\delta$ -6.10
	R-alcohols, about $\Delta\delta$ -4 to -5
2 β-pro-*S*-side-carbon (C-10)	$\Delta\delta$ +0.16
	S-alcohols, about $\Delta\delta$ 0 to -2
1 Glucosyl C-1	δ 100.30 *R*-alcohols, about δ 102
2 Glucosyl C-1	δ 106.69 *S*-alcohols, about δ 106

This is the first report of the isolation of sesquiterpenoid



1 2 3

Fig. 1. Partial Structures of **1** to **3** Solved by HMBC (heavy lines) and ^{1}H–^{1}H COSY (plot lines) Spectra



1 2 3 (rel. config.)

Fig. 2. Structures and NOE Interactions Observed in the NOESY Spectra of **1** to **3**

from plants of the *Ficus* genus.

Experimental

HPLC separation was carried out on a JASCO chromatography (980-system) with a JASCO 930 RI detector, JASCO OR-970 chiral detector and ODS-3251-D [Senshupak, column size, 8×250 mm], Symmetry Prep C_{18} [Waters, column size, 7.8×300 mm], Megapak SIL C_{18}-10 [JASCO, column size, 7.5×250 mm], carbohydrate analysis [Waters, column size, 3.9×300 mm] column. The other instruments used and the experimental conditions for the spectral data and for chromatography were the same as in the preceding paper.[2a)]

Extraction and Separation of 1 to 6 *F. pumila* L. was collected at Gushikawa City, Okinawa Prefecture, Japan, in March 1994. The fresh fruit (28 kg) was extracted with methanol (32 l) at room temperature. After evaporation of the solvent, the residue (987 g) was suspended with water and successively extracted with ether, ethyl acetate and *n*-butanol. Removal of the solvent from each phase gave an ether (43.1 g), ethyl acetate (6.5 g), *n*-butanol (35.1 g) and an aqueous (889 g) residue. The *n*-butanol residue was subjected to column chromatography on Amberlite XAD-II (H_2O→MeOH) to afford water eluate (14.4 g) and methanol eluate (20.6 g). The methanol eluate fraction was chromatographed on Sephadex LH-20 (MeOH) which furnished four fractions. Fraction 2 (5.7 g) was purified by silica gel [$CHCl_3$–MeOH (9 : 1→8 : 2)] chromatography to afford six fractions. From the second fraction, **4** (2 mg) and **5** (3 mg) were isolated by Sephadex LH-20 (MeOH), Lobar RP-8 column (25% MeOH) and silica gel [$CHCl_3$–MeOH (9 : 1)] chromatography, and HPLC using Symmetry Prep C_{18} (20% MeOH) and ODS-3251-D (10% MeOH). From the third fraction (140 mg), **1** (13 mg) was isolated by Sephadex LH-20 (MeOH), Lobar RP-8 column (30% MeOH) silica gel [$CHCl_3$–MeOH–H_2O (4 : 1 : 0.1)] chromatography and HPLC using carbohydrate analysis column (95% CH_3CN). From the fourth fraction (50 mg), **2** (22 mg) was isolated by Sephadex LH-20 (MeOH), silica gel [$CHCl_3$–MeOH–H_2O (4 : 1 : 0.1)] chromatography and HPLC using Megapak SIL C_{18} column (95% CH_3CN). From the fifth fraction (35 mg), **3** (11 mg) was isolated by Sephadex LH-20 (MeOH), silica gel [$CHCl_3$–MeOH–H_2O (4 : 1 : 0.1)] chromatography and HPLC using Megapak SIL C_{18} column (95% CH_3CN). Fraction **3** (3.2 g) was purified by Sephadex LH-20 (MeOH) and Lobar RP-8 column (40% MeOH) to get **6** (35 mg).

The following compounds were identified by comparison with authentic compounds.

Benzyl β-D-glucopyranoside (**4**), (*E*)-2-methyl-2-butenyl β-D-glucopyranoside (**5**) and rutin (**6**).

Pumilaside A (1) Amorphous powder, $[\alpha]_D^{24}$ −28° (c=1.0, MeOH). Positive FAB-MS *m/z*: 457 [M+K]$^+$, 441.2417 [M+Na]$^+$ (base, Calcd for $C_{21}H_{38}NaO_8$: 441.2465), 419.2663 [M+H]$^+$ (Calcd for $C_{21}H_{39}O_8$: 419.2645), 399 [M−H_2O+H]+ (base), 239 [M−$C_6H_{12}O_6$+H]$^+$.

Pumilaside B (2) White powder [mp 195—197 °C (dec.)], $[\alpha]_D^{24}$ −19° (c=1.8, MeOH). Positive FAB-MS *m/z*: 439 [M+K]$^+$, 423.2314 [M+Na]$^+$ (Calcd for $C_{21}H_{36}NaO_7$: 423.2359), 221 [M−$C_6H_{12}O_6$+H]$^+$, 203 [M−$C_6H_{12}O_6$−H_2O+H]$^+$ (base).

Pumilaside C (3) Amorphous powder, $[\alpha]_D^{24}$ −17° (c=0.9, MeOH). Positive FAB-MS *m/z*: 439 [M+K]$^+$, 423.2364 [M+Na]$^+$ (base, Calcd for $C_{21}H_{36}NaO_7$: 423,2359), 221 [M−$C_6H_{12}O_6$+H]$^+$.

Enzymatic Hydrolysis of 1, 2 and 3 Glycoside **1** (4 mg), **2** (6 mg) and **3** (3 mg) were each dissolved in water (5 ml) with hespiridinase (3 mg), and shaken in a water bath at 37 °C for 2 weeks. The mixtures were evaporated *in vacuo* to dryness and the residues were chromatographed on silica gel [$CHCl_3$–MeOH (9 : 1)→$CHCl_3$–MeOH–H_2O (7 : 3 : 0.5)] to give aglycone and the sugar fractions. The sugar fractions were passed through Sephadex LH-20 (MeOH) to give syrups. They were analyzed by HPLC [column, carbohydrate analysis (Waters: size, 3.9×300 mm), detector, JASCO RI-930 and OR-990 chiral detector: 85% CH_3CN, 2 ml/min; t_R 4.53 min] which revealed the presence of D-glucose. The aglycone fractions were purified by silica gel chromatography on silica gel [*n*-hexane–EtOAc (1 : 1)] to give aglycones (**1a**, 1.9 mg; **2a**, 2.0 mg; **3a**, 0.8 mg), respectively.

(1*S*,4*S*,5*R*,6*R*,7*S*,10*S*)-Trihydroxyeudesmane (1a) An amorphous powder, $[\alpha]_D^{24}$ +6° (c=0.2, MeOH). Positive FAB-MS *m/z*: 256 [M($C_{15}H_{28}O_3$)+H]$^+$. ^{1}H-NMR (pyridine-d_5) δ: 0.97 (3H, d, J=6.5 Hz, H_3-13), 1.24 (3H, s, H_3-14), 1.36 (3H, d, J=6.5 Hz, H_3-12), 1.62 (3H, s, H_3-15), 2.12 (1H, d, J=11.5 Hz, H-5), 2.29 (1H, ddd, J=7.5, 7.5, 4.5 Hz, H-7), 3.69 (1H, t, J=7.0 Hz, H-1), 4.67 (1H, dd, J=11.5, 4.5 Hz, H-6).

(1*S*,4*S*,5*S*,6*R*,7*R*,10*S*)-Dihydroxymaaliane (2a) Colorless needles, mp 172—175 °C, $[\alpha]_D^{24}$ +10° (c=0.2, MeOH). Positive FAB-MS *m/z*: 239 [M($C_{15}H_{26}O_2$)+H]$^+$. ^{1}H-NMR (pyridine-d_5) δ: 0.64 (1H, t, J=9.0 Hz, H-7), 0.91 (1H, dd, J=9.0, 6.0 Hz, H-6), 1.05 (3H, s, H_3-12), 1.10 (3H, s, H_3-13), 1.22 (3H, s, H_3-14), 1.42 (1H, d, J=6.0 Hz, H-5), 1.53 (3H, s, H_3-15), 3.59 (1H, t, J=7.0 Hz, H-1).

10α,11-Dihydroxycadin-4-ene (3a) Amorphous powder. ^{1}H-NMR (pyridine-d_5) δ: 1.34 (3H, s, H_3-14), 1.44 (6H, s, H_3-12 and H_3-13), 1.68 (3H, s, H_3-15).

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