Eranthisaponins A and B, Two New Bisdesmosidic Triterpene Saponins from the Tubers of *Eranthis cilicica*

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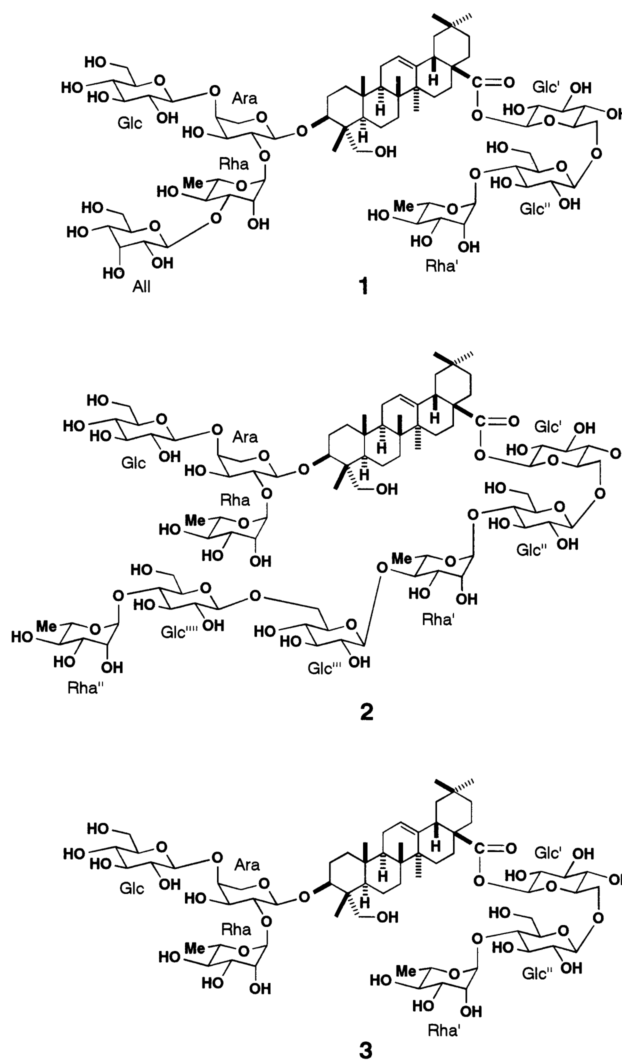
The present investigation aimed at the glycoside constituents of the tubers of *Eranthis cilicica* has resulted in the isolation of two new bisdesmosidic triterpene saponins based upon hederagenin, named eranthisaponins A (**1**) and B (**2**), along with four known triterpene saponins. The structures of the new saponins **1** and **2** were determined on the basis of spectroscopic analysis, including extensive 1D and 2D NMR data, and acid hydrolysis followed by chromatographic analysis. This is the first report concerning the secondary metabolites of *E. cilicica*.

The genus *Eranthis* belonging to the family Ranunculaceae is composed of two species, *Eranthis hyemalis* and *E. cilicica*, and is taxonomically related to the genus *Helleborus*.[1] The *Eranthis* plants, as well as some *Helleborus* species such as *Helleborus niger* and *H. orientalis*, are often described as poisonous plants due to the presence of cardiac glycosides.[2] Previous phytochemical studies disclosed the occurrence of a variety of chromenone derivatives,[2−4] a small amount of isoquinoline alkaloid,[5] and an *N*-acetylgalactosamine-specific lectin[6] in *E. hyemalis*, but failed to detect cardiac glycoside even in the cardioactive fractions prepared from *E. hyemalis* tubers.[3] As for *Eranthis cilicica* Schott et Kotschy, indigenous to Turkey and Afghanistan, a literature survey concerning its secondary metabolites showed that no chemical studies have been carried out on the plant, which prompted us to make a phytochemical screening of the tubers of *E. cilicica*. Cardiac glycosides could not be found; however, two new bisdesmosidic triterpene saponins based upon hederagenin, named eranthisaponins A (**1**) and B (**2**), along with four known triterpene saponins, were isolated. This paper deals with the structural determination of saponins **1** and **2** on the basis of spectroscopic analysis, including extensive 1D and 2D NMR data, and acid hydrolysis followed by chromatographic analysis.

The dry tubers of *E. cilicica* (1.3 kg) were extracted with hot MeOH, and the MeOH extract was passed through a porous-polymer resin (Diaion HP-20) column. The 80% MeOH eluate fraction was subjected to column chromatography over silica gel and octadecylsilanized (ODS) silica gel, as well as preparative HPLC, giving eranthisaponins A (**1**; 15.2 mg) and B (**2**; 20.0 mg), along with four known saponins.

Eranthisaponin A (**1**) was obtained as an amorphous solid, and its molecular formula $C_{71}H_{116}O_{36}$ was derived from a combination of the positive-ion FABMS (*m*/*z* 1567 [M + Na]$^+$), ^{13}C NMR spectral (71 carbon signals), and elemental analysis data. The IR spectrum of **1** showed a broad absorption band for hydroxyl groups at 3377 cm^{-1}, as well as absorption due to an ester carbonyl group at 1731 cm^{-1}. The ^{1}H NMR spectrum of **1** was typical of a triterpene saponin based upon an oleanolic acid derivative, showing signals for six tertiary methyl groups at δ 1.17, 1.10, 1.07, 0.93, 0.86, and 0.85, and an olefinic group at δ 5.38. In addition, signals for seven anomeric protons were observed



at δ 6.21, 6.19, 5.86, 5.83, 5.06, 4.99, and 4.90. The two three-proton doublet signals at δ 1.68 and 1.53 indicated the presence of two deoxyhexopyranosyl units in **1**. Acid hydrolysis of **1** with 1 M HCl in dioxane−H_2O (1:1) gave 3β,23-dihydroxyolean-12-en-28-oic acid (hederagenin), together with D-allose, L-arabinose, D-glucose, and L-rhamnose. The monosaccharides, including their absolute configurations, were identified by direct HPLC analysis of the hydrolysate, which was performed on an aminopropyl-

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Table 1. ^{1}H and ^{13}C NMR Spectral Data (δ) for the Glycoside Moieties of **2** in C_5D_5N at 318 K

	position	^{1}H	J (Hz)	^{13}C		position	^{1}H	J (Hz)	^{13}C
Ara	1	4.99 d	6.4	104.2	Rha′	1	5.76 br s		102.0
	2	4.45 dd	8.3, 6.4	76.5		2	4.61 br d	3.9	72.2
	3	4.09 dd	8.3, 4.4	74.3		3	4.60 dd	9.4, 3.9	72.5
	4	4.19 br s		79.8		4	4.40 t-like	9.4	84.4
	5a	4.39 br d	11.6	64.9		5	4.90 dq	9.4, 6.1	68.5
	b	3.68 br d	11.6			6	1.78 d	6.1	18.5
Rha	1	6.12 br s		101.7	Glc‴	1	5.17 d	7.8	106.0
	2	4.66 br d	3.9	72.1		2	3.99 dd	9.1, 7.8	76.1
	3	4.57 dd	9.3, 3.9	72.5		3	4.12 dd	9.7, 9.1	78.5
	4	4.23 t-like	9.3	74.1		4	4.10 dd	9.7, 9.1	71.5
	5	4.63 dq	9.3, 6.1	69.7		5	3.85 m		77.1
	6	1.63 d	6.1	18.5		6a	4.60 br d	10.5	70.1
						b	4.23 dd	10.5, 4.9	
Glc	1	5.07 d	7.8	106.4	Glc⁗	1	4.96 d	7.8	105.1
	2	3.98 dd	8.4, 7.8	75.5		2	3.91 dd	9.2, 7.8	75.4
	3	4.19 dd	9.2, 8.4	78.5		3	4.10 dd	9.2, 8.7	76.5
	4	4.16 dd	9.2, 8.5	71.4		4	4.32 t-like	8.7	78.5
	5	3.85 m		78.6		5	3.64 m		77.1
	6a	4.44 br d	11.0	62.6		6a	4.18 m		61.4
	b	4.33 dd	11.0, 4.4			b	4.05 m		
Glc′	1	6.19 d	8.1	95.7	Rha″	1	5.77 br s		102.6
	2	4.10 dd	8.9, 8.1	74.0		2	4.64 br d	3.8	72.5
	3	4.19 t-like	8.9	78.7		3	4.49 dd	9.1, 3.8	72.8
	4	4.27 dd	8.9, 8.3	71.0		4	4.27 t-like	9.1	73.9
	5	4.07 m		77.9		5	4.86 dq	9.1, 6.1	70.3
	6a	4.62 br d	10.9	69.4		6	1.67 d	6.1	18.5
	b	4.30 dd	10.9, 4.9						
Glc″	1	4.95 d	7.8	104.9					
	2	3.88 dd	8.9, 7.8	75.4					
	3	4.09 dd	8.9, 8.4	76.5					
	4	4.32 dd	9.4, 8.4	77.9					
	5	3.62 m		77.1					
	6a	4.18 m		61.5					
	b	4.05 m							

bonded silica gel column using MeCN–H_2O (17:3) as solvent system, with detection being carried out by using an optical rotation (OR) detector. Comparison of the ^{1}H and ^{13}C NMR spectra of **1** with those of 3β-[(*O*-β-D-glucopyranosyl-(1→4)-*O*-[α-L-rhamnopyranosyl-(1→2)]-α-L-arabinopyranosyl)oxy]-23-hydroxyolean-12-en-28-oic acid 28-*O*-α-L-rhamnopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→6)-β-D-glucopyranoside (**3**)[7] revealed that the aglycon whose C-3 hydroxyl and C-28 carboxyl groups were substituted by the sugar moieties and the triglycoside residue attached at C-28 of the aglycon were identical to those of **3**. However, significant differences were recognized in the signals from the rhamnosyl moiety linked to the inner arabinosyl group and the presence of the additional six carbon signals of a hexose at δ 104.2 (CH), 75.9 (CH), 73.0 (CH), 72.7 (CH), 68.9 (CH), and 62.8 (CH_2). The anomeric carbon signal at δ 104.2 was associated with the anomeric proton signal at δ 5.86 with a relatively large J value of 7.9 Hz by the HMQC spectrum. Analysis of the ^{1}H–^{1}H COSY and 2D TOCSY spectra, starting from the δ 5.86 anomeric resonance, allowed the sequential assignments of the signals from H-1 to CH_2-6 including their multiplet patterns and coupling constants, which were indicative of a β-D-allopyranosyl group.[8] In the HMBC spectrum, the anomeric proton of the allosyl moiety showed a long-range correlation with the δ 82.8 signal, assignable to C-3 of the rhamnosyl unit, of which the anomeric proton at δ 6.19, in turn, showed a $^{3}J_{C,H}$ correlation with C-2 of the arabinosyl at δ 75.8. An HMBC correlation from the anomeric proton of the terminal glucosyl at δ 5.06 to C-4 of the arabinosyl at δ 80.5 was also noted. All of these data were consistent with the structure 3β-[(*O*-β-D-allopyranosyl-(1→3)-*O*-α-L-rhamnopyranosyl-(1→2)-*O*-[β-D-glucopyranosyl-(1→4)]-α-L-arabinopyranosyl)oxy]-23-hydroxyolean-12-en-28-oic acid 28-*O*-α-L-rhamnopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→6)-β-D-glucopyranoside, which was assigned to **1**.

Eranthisaponin B (**2**) was isolated as an amorphous solid with a molecular formula $C_{83}H_{136}O_{45}$, as determined from data of the positive-ion FABMS (m/z 1875 $[M + Na]^+$), ^{13}C NMR spectrum (83 carbon signals), and elemental analysis. The ^{1}H NMR spectrum of **2** showed signals for nine anomeric protons at δ 6.19, 6.12, 5.77, 5.76, 5.17, 5.07, 4.99, 4.96, and 4.95, along with signals for six tertiary methyl groups at δ 1.18, 1.11, 1.06, 0.98, 0.89, and 0.87, and an olefinic group at δ 5.40 as observed for **1**. The three methyl doublet signals at δ 1.78, 1.67, and 1.63 were indicative of the presence of three 6-deoxyhexosyl units in **2**. Acid hydrolysis of **2** yielded hederagenin, L-arabinose, D-glucose, and L-rhamnose. The ^{13}C NMR shifts of C-3 at δ 81.1 and C-28 at δ 176.5 implied that the sugar linkages were at both C-3 and C-28. From the above data, **2** was assumed to be a hederagenin 3,28-bisdesmoside whose sugar moieties were composed of a total of nine monosaccharides. The severe overlapping of the proton signals for the sugar moieties excluded the possibility of a complete assignment in a straightforward way using the conventional 2D NMR methods such as the ^{1}H–^{1}H COSY, 2D TOCSY, and HSQC spectra in **2**. Analysis of the 1D TOCSY spectra followed by interpretation of the ^{1}H–^{1}H COSY, HSQC, HSQC-TOCSY, and HMBC spectra allowed us to solve the exact sugar sequences of the sugar moieties and their linkage positions to the aglycon. The ^{1}H NMR subspectra of individual monosaccharide units were obtained by using selective irradiation of the easily identifiable anomeric proton signals, as well as irradiation of other nonoverlapping proton signals in a series of 1D TOCSY experiments.[9] Subsequent analysis of the ^{1}H–^{1}H COSY spectrum resulted in the sequential assignments of all the proton

resonances due to the nine monosaccharides, including identification of their multiplet patterns and coupling constants as shown in Table 1. The HSQC and HSQC-TOCSY spectra correlated the proton resonances with those of the corresponding one-bond coupled carbons, leading to unambiguous assignments of the carbon shifts (Table 1). Comparison of the carbon chemical shift thus assigned with those of the reference methyl glycosides,[10,11] taking into account the known effects of *O*-glycosylation, indicated that **2** contained a β-D-glucopyranosyl unit (Glc) and two α-L-rhamnopyranosyl units (Rha and Rha″) as the terminal glycosyl moieties, and an α-L-arabinopyranosyl unit (Ara), four β-D-glucopyranosyl units (Glc′, Glc″, Glc‴, and Glc⁗), and an α-L-rhamnopyranosyl unit (Rha′) as the substituted sugar moieties. The relatively large *J* values of the anomeric protons of the arabinosyl (6.4 Hz) and glucosyl (7.8−8.1 Hz) moieties indicated an α anomeric orientation for the arabinosyl and β for the glucosyls. For the rhamnosyl moieties, the large $^{1}J_{C,H}$ values (>170 Hz) confirmed that the anomeric protons were equatorial (α-pyranoid anomeric form). In the HMBC spectrum, the anomeric proton signals at δ 6.12 (Rha) and 5.07 (Glc) showed long-range correlations with C-2 at δ 76.5 and C-4 at δ 79.4 of Ara, respectively, whose anomeric proton signal at δ 4.99, in turn, exhibited a long-range correlation with C-3 of the aglycon at δ 81.1, indicating that the branched triglycoside attached at C-3 of the aglycon was the same as that of **3**. Consequently, an oligoglycoside composed of six monosaccharides was presumed to be linked to C-28 of the aglycon. Further HMBC correlations from δ 5.77 (H-1 of Rha″) to C-4 of Glc⁗ at δ 78.5, δ 4.96 (H-1 of Glc⁗) to C-6 of Glc‴ at δ 70.1, δ 5.17 (H-1 of Glc‴) to C-4 of Rha′ at δ 84.4, δ 5.76 (H-1 of Rha′) to C-4 of Glc″ at δ 77.9, δ 4.95 (H-1 of Glc″) to C-6 of Glc′ at δ 69.4, and δ 6.19 (H-1 of Glc′) to C-28 of the aglycon at δ 176.5 confirmed the hexaglycoside sequence as Rha″-(1→4)-Glc⁗-(1→6)-Glc‴-(1→4)-Rha′-(1→4)-Glc″-(1→6)-Glc′, which was attached at C-28 of the aglycon. Accordingly, the structure of **2** was determined as 3β-[(*O*-β-D-glucopyranosyl-(1→4)-*O*-[α-L-rhamnopyranosyl-(1→2)]-α-L-arabinopyranosyl)oxy]-23-hydroxyolean-12-en-28-oic acid 28-*O*-α-L-rhamnopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→6)-*O*-β-D-glucopyranosyl-(1→4)-*O*-α-L-rhamnopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→6)-β-D-glucopyranoside.

This is the first report concerning the secondary metabolites of *E. cilicica*, and eranthisaponins A (**1**) and B (**2**) are newly described bisdesmosidic triterpene saponins. The branched tetraglycoside attached at C-3 of the aglycon in **1** and the linear hexaglycoside attached at C-28 of the aglycon in **2** have not been reported as sugars of either triterpene saponins or steroidal saponins. It is also notable that **1** has been found to contain D-allopyranose as a sugar component, which is rarely encountered in the plant saponins.[12,13]

Experimental Section

General Experimental Procedures. Optical rotations were measured using a JASCO DIP-360 (Tokyo, Japan) automatic digital polarimeter. IR spectra were recorded on a JASCO FT-IR 620 spectrophotometer. NMR spectra were recorded on a Bruker DRX-500 spectrometer (500 MHz for ^{1}H NMR, Karlsruhe, Germany) using standard Bruker pulse programs. Chemical shifts are given as δ values with reference to tetramethylsilane (TMS) as internal standard. MS were recorded on a Finnigan MAT TSQ-700 (San Jose, CA) mass spectrometer, using a dithiothreitol and dithioerythritol (3:1) matrix. Silica gel (200−400 mesh, Fuji-Silysia Chemical, Aichi, Japan), ODS silica gel (75 μm, Nacalai Tesque, Kyoto, Japan), and Diaion HP-20 (Mitsubishi-Chemical, Tokyo, Japan) were used for column chromatography. TLC was carried out on precoated Kieselgel 60 F_{254} (0.25 mm thick, Merck, Darmstadt, Germany) and RP-18 F_{254}S (0.25 mm thick, Merck) plates, and spots were visualized by spraying the plates with 10% H_2SO_4 solution, followed by heating. HPLC was performed using a system comprised of a Tosoh CCPM pump (Tokyo, Japan), a Tosoh CCP PX-8010 controller, a Tosoh RI-8010 detector, a Shodex OR-2 detector (Showa-Denko, Tokyo, Japan), and a Rheodyne injection port. Capcell Pak C_{18} UG80 columns (10 mm i.d. × 250 mm, 5 μm, Shiseido, Tokyo, Japan) were employed for preparative HPLC.

Plant Material. *Eranthis cilicica* was purchased from a nursery in Heiwaen, Japan, in October 2000, and was identified by one of the authors (Y.S.). A voucher specimen has been deposited in our laboratory (voucher No. 00-7-EC, Laboratory of Medicinal Plant Science).

Extraction and Isolation. Dry tubers of *E. cilicica* (1.3 kg) were extracted with hot MeOH (20 L). Following removal of MeOH, the residue (135 g) was passed through a Diaion HP-20 column (200 mm i.d. × 200 mm), eluted with 30% MeOH, 50% MeOH, 80% MeOH, MeOH, EtOH, and EtOAc. The 80% MeOH eluate portion (30 g) was subjected to column chromatography on silica gel (80 mm i.d. × 280 mm) and eluted with stepwise gradient mixtures of $CHCl_3$−MeOH (19:1; 9:1; 4:1; 2:1) and finally with MeOH to give 38 fractions. Fractions with the same TLC profile were combined, and nine fractions (I−IX) were recovered. Fraction IX was further divided by column chromatography on silica gel (65 mm i.d. × 280 mm) eluted with $CHCl_3$−MeOH−H_2O (14:8:1) into four subfractions (IX-1−IX-4). Fraction IX-1 was subjected to an ODS silica gel column (45 mm i.d. × 190 mm) eluted with MeCN−H_2O (2:5) to give 23-hydroxy-3β-[(*O*-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl)oxy]olean-12-en-28-oic acid 28-*O*-α-L-rhamnopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→6)-β-D-glucopyranoside (97.8 mg).[14] Fraction IX-2 was subjected to ODS silica gel column chromatography (45 mm i.d. × 190 mm) eluted with MeCN−H_2O (4:11) and preparative HPLC using MeCN−H_2O (2:5) to yield 3β-[(*O*-β-D-glucopyranosyl-(1→4)-α-L-arabinopyranosyl)oxy]-23-hydroxyolean-12-en-28-oic acid 28-*O*-α-L-rhamnopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→6)-β-D-glucopyranoside (10.5 mg).[15] Fraction IX-3 was chromatographed on ODS silica gel (45 mm i.d. × 190 mm) eluted with MeCN−H_2O (1:3) to give **3** (77.4 mg) and a mixture of two saponins, which was separated by preparative HPLC using MeCN−H_2O (1:3) to furnish **1** (15.2 mg) and 3β-[(*O*-β-D-glucopyranosyl-(1→2)-*O*-[β-D-glucopyranosyl-(1→4)]-α-L-arabinopyranosyl)oxy]-23-hydroxyolean-12-en-28-oic acid 28-*O*-α-L-rhamnopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→6)-β-D-glucopyranoside (42.5 mg).[15] Compound **2** (20.0 mg) was isolated from fraction IX-4 by subjecting it to preparative HPLC using MeCN−H_2O (1:3).

Eranthisaponin A (1): amorphous solid; $[\alpha]_D^{26}$ −22.0° (*c* 0.10, MeOH); IR (film) ν_{max} 3377 (OH), 2926 (C−H), 1731 (C=O), 1453, 1387, 1365, 1257, 1232, 1075, 1035, 913 cm^{-1}; ^{1}H NMR (pyridine-d_5) δ 6.21 (1H, d, *J* = 8.1 Hz, H-1 of Glc′), 6.19 (1H, br s, H-1 of Rha), 5.86 (1H, d, *J* = 7.9 Hz, H-1 of All), 5.83 (1H, br s, H-1 of Rha′), 5.38 (1H, t-like, *J* = 3.2 Hz, H-12), 5.06 (1H, d, *J* = 7.8 Hz, H-1 of Glc), 4.99 (1H, d, *J* = 7.8 Hz, H-1 of Glc″), 4.90 (1H, d, *J* = 7.1 Hz, H-1 of Ara), 4.71 (1H, t-like, *J* = 3.0 Hz, H-3 of All), 4.48 (1H, br dd, *J* = 8.7, 5.2 Hz, H-5 of All), 4.42 (1H, br d, *J* = 11.7 Hz, H-6a of All), 4.36 (1H, d, *J* = 11.7 Hz, H-23a), 4.28 (1H, dd, *J* = 11.7, 5.2 Hz, H-6b of All), 4.20 (1H, m, H-3), 4.18 (1H, dd, *J* = 8.7, 3.0 Hz, H-4 of All), 4.01 (1H, dd, *J* = 7.9, 3.0 Hz, H-2 of All), 3.57 (1H, d, *J* = 11.7 Hz, H-23b), 3.14 (1H, dd, *J* = 13.5, 3.8 Hz, H-18), 1.68 (3H, d, *J* = 6.2 Hz, Me-6 of Rha′), 1.53 (3H, d, *J* = 6.2 Hz, Me-6 of Rha), 1.17 (3H, s, Me-27), 1.10 (3H, s, Me-24), 1.07 (3H, s, Me-26), 0.93 (3H, s, Me-25), 0.86 (3H, s, Me-30), 0.85 (3H, s, Me-29); ^{13}C NMR (pyridine-d_5) δ 39.0, 26.4, 81.1, 43.5, 47.5, 18.0, 32.7, 39.8, 48.1, 36.8, 23.8, 122.8, 144.1, 42.1, 28.2, 23.3, 47.0, 41.6, 46.1, 30.7, 33.9, 32.5, 63.7, 14.0, 16.1, 17.5, 26.0, 176.5, 33.0, 23.6 (aglycon C-1−C-30), 104.7, 75.8, 74.9, 80.5, 65.9 (Ara C-1−C-5), 101.3, 71.5, 82.8, 72.7, 69.8,

18.5 (Rha C-1−C-6), 104.2, 73.0, 72.7, 68.9, 75.9, 62.8 (All C-1−C-6), 106.7, 75.4, 78.7, 71.2, 78.6, 62.4 (Glc C-1−C-6), 95.6, 73.8, 78.4, 70.8, 78.0, 69.1 (Glc′ C-1−C-6), 104.7, 75.3, 76.5, 78.2, 77.1, 61.2 (Glc″ C-1−C-6), 102.6, 72.5, 72.7, 73.9, 70.2, 18.5 (Rha″ C-1−C-6); FABMS (positive mode) *m*/*z* 1567 [M + Na]$^+$; *anal.* C 52.65%, H 7.86%, calcd for $C_{71}H_{116}O_{36}{\cdot}4H_2O$, C 52.71%, H 7.73%.

Acid Hydrolysis of 1. A solution of **1** (5.2 mg) in 1 M HCl (dioxane−H_2O, 1:1, 3 mL) was heated at 95 °C for 1 h under an Ar atmosphere. After the reaction mixture was diluted with H_2O (2 mL), it was extracted with Et_2O (5 mL × 3). The Et_2O extract was chromatographed on silica gel eluted with $CHCl_3$−MeOH (19:1) to give hederagenin (0.9 mg). The H_2O residue was neutralized using an Amberlite IRA-93ZU (Organo, Tokyo, Japan) column and passed through a Sep-Pak C_{18} cartridge (Waters, Milford, MA) eluted with H_2O−MeOH (3:2) to give a sugar fraction (2.6 mg). The sugar fraction was analyzed by HPLC under the following conditions: column, Capcell Pak NH2 UG80 (4.6 mm i.d. × 250 mm, 5 μm, Shiseido); solvent, MeCN−H_2O (17:3); flow rate, 0.9 mL/min; detection, RI and optical rotation (OR). Identification of D-allose, L-arabinose, D-glucose, and L-rhamnose was carried out by comparison of its retention time and OR with those of an authentic sample; t_R (min): 7.09 (negative optical rotation, L-rhamnose), 8.13 (positive optical rotation, L-arabinose), 10.31 (positive optical rotation, D-allose), 13.16 (positive optical rotation, D-glucose).

Eranthisaponin B (2): amorphous solid; $[\alpha]_D^{26}$ −36.0° (*c* 0.10, MeOH); IR (film) ν_{max} 3375 (OH), 2922 and 2852 (C−H), 1732 (C=O), 1451, 1387, 1365, 1255, 1232, 1063, 1034, 913 cm^{-1}; ^{1}H NMR (pyridine-d_5) δ 6.19 (1H, d, J = 8.1 Hz, H-1 of Glc′), 6.12 (1H, br s, H-1 of Rha), 5.77 (1H, br s, H-1 of Rha″), 5.76 (1H, br s, H-1 of Rha′), 5.40 (1H, t-like, J = 3.3 Hz, H-12), 5.17 (1H, d, J = 7.8 Hz, H-1 of Glc‴), 5.07 (1H, d, J = 7.8 Hz, H-1 of Glc), 4.99 (1H, d, J = 6.4 Hz, H-1 of Ara), 4.96 (1H, d, J = 7.8 Hz, H-1 of Glc⁗), 4.95 (1H, d, J = 7.8 Hz, H-1 of Glc″), 4.18 (1H, d, J = 10.5 Hz, H-23a), 4.17 (1H, m, H-3), 3.73 (1H, d, J = 10.5 Hz, H-23b), 3.16 (1H, dd, J = 13.9, 3.9 Hz, H-18), 1.78 (3H, d, J = 6.1 Hz, Me-6 of Rha′), 1.67 (3H, d, J = 6.1 Hz, Me-6 of Rha″), 1.63 (3H, d, J = 6.1 Hz, Me-6 of Rha), 1.18 (3H, s, Me-27), 1.11 (3H, s, Me-26), 1.06 (3H, s, Me-24), 0.98 (3H, s, Me-25), 0.89 (3H, s, Me-30), 0.87 (3H, s, Me-29); ^{13}C NMR (pyridine-d_5) δ 39.1, 26.2, 81.1, 43.5, 47.9, 18.2, 32.9, 40.0, 48.2, 36.9, 23.9, 123.0, 144.2, 42.2, 28.4, 23.5, 47.1, 41.8, 46.3, 30.7, 34.1, 32.6, 64.1, 13.9, 16.2, 17.6, 26.1, 176.5, 33.1, 23.7 (aglycon C-1−C-30), signals for the sugar moieties, see Table 1; FABMS (positive mode) *m*/*z* 1975 [M + Na]$^+$; *anal.* C 51.40%, H 7.46%, calcd for $C_{83}H_{136}O_{45}{\cdot}9/2H_2O$, C 51.52%, H 7.55%.

Acid Hydrolysis of 2. Compound **2** (7.6 mg) was subjected to acid hydrolysis as described for **1** to give hederagenin (1.2 mg) and a sugar fraction (3.5 mg). HPLC analysis of the sugar fraction under the same conditions as in the case of that of **1** showed the presence of L-arabinose, D-glucose, and L-rhamnose: t_R (min) 7.09 (L-rhamnose, negative optical rotation), 8.13 (L-arabinose, positive optical rotation), 13.25 (D-glucose, positive optical rotation).

Supporting Information Available: Spectroscopic data (^{13}C NMR, ^{1}H−^{1}H COSY, HSQC, HMBC, HSQC-TOCSY, and 1D TOCSY spectra) for compound **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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