Medicinal Foodstuffs. I. Hypoglycemic Constituents from a Garnish Foodstuff "Taranome," the Young Shoot of *Aralia elata* SEEM.: Elatosides G, H, I, J, and K

Masayuki YOSHIKAWA,* Satoshi YOSHIZUMI, Takahiro UENO, Hisashi MATSUDA, Toshiyuki MURAKAMI, Johji YAMAHARA, and Nobutoshi MURAKAMI

Kyoto Pharmaceutical University, 5 Nakauchi-cho, Misasagi, Yamashina-ku, Kyoto 607, Japan.
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Five new saponins named elatosides G, H, I, J, and K were isolated from a garnish foodstuff "Taranome," the young shoot of *Aralia elata* SEEM., together with hederagenin-3-*O*-glucuronopyranoside and elatoside C. Their chemical structures were elucidated on the basis of chemical and physicochemical evidence. Elatosides G, H, and I were found to exhibit potent hypoglycemic activity in the oral glucose tolerance test in rats.

Key words elatoside; *Aralia elata*; medicinal foodstuff; hypoglycemic activity; oleanene-type triterpene glycoside; oral glucose tolerance test

The bark and root cortex of *Aralia elata* SEEM. (Taranoki in Japanese, Araliaceae) have been used in Japanese and Chinese traditional medicines as a tonic, antiarthritic, and antidiabetic agent. The young shoot of this medicinal plant, which is commonly called "Taranome" in Japanese, is used as a garnish foodstuff in Japanese-style dishes. Many saponins have been isolated from the leaves of this plant, and were reported to exhibit a cytoprotective effect on carbon tetrachloride-induced hepatic injury.[1]

In the course of our studies on the bioactive constituents of natural medicines,[2] several saponin constituents from *Camellia japonica* (seed),[3] *Aesculus hippocastanum* (seed),[4] and *Polygara senega* var. *latifolia* (root)[5] were found to inhibit ethanol absorption and to show a hypoglycemic effect. In addition, their saponin structure–activity relationships were elucidated by comparison of the activities with those of sapogenols, prosapogenols, and related glycosides. We have also isolated six bioactive oleanolic acid oligoglycosides designated as elatosides A, B, C (**10**), D, E, and F from the bark and root cortex of *Aralia elata* SEEM., together with many known oleanolic acid glycosides, and elucidated their structures.[6] Recently, we have found that the saponin fraction from the young shoot of *Aralia elata* shows a potent hypoglycemic effect in the oral glucose tolerance test in rats. By bioassay-guided separation, five new saponins named elatosides G (**5**), H (**7**), I (**8**), J (**9**), and K (**11**), were isolated from the young shoot of this plant. This paper describes the structure elucidation of **5**, **7**, **8**, **9**, and **11**, and their hypoglycemic activity.[7]

The saponin constituents of the young shoot were separated through the procedure shown in Chart 1. Thus, the aqueous methanolic extract of the young shoots was first subjected to reversed-phase silica gel column chromatography. The methanol eluate, designated as the saponin fraction, showed potent hypoglycemic activity (Table 2), and was separated by normal silica gel column chromatography to provide three fractions. The HPLC separation of fractions 1 and 2 furnished elatosides G (**5**), H (**7**), I (**8**), and J (**9**) and hederagenin 3-*O*-*β*-D-glucuronopyranoside (HN-saponin K, **6**).[8] The reversed-phase silica gel column chromatography of fraction 3

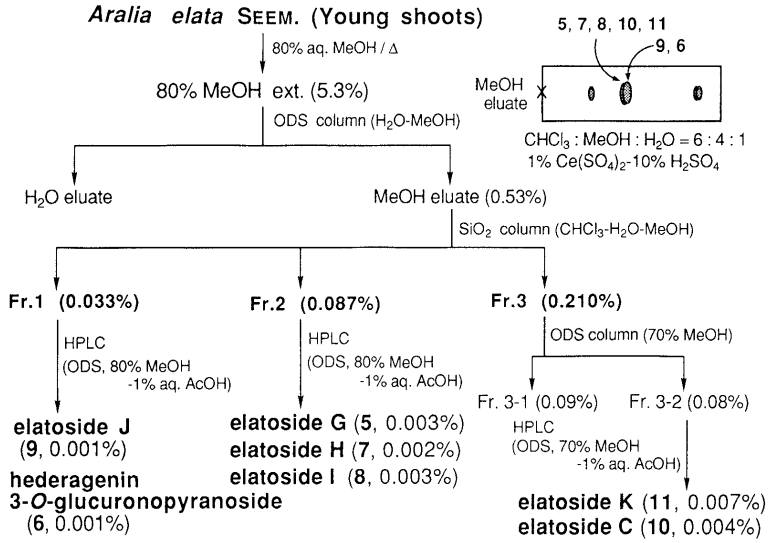

Chart 1. Isolation Procedure for Elatosides

* To whom correspondence should be addressed.

followed by HPLC separation yielded elatosides C (**10**)[6a] and K (**11**).

Chemical Structures of Elatosides G (5), H (7), I (8), J (9), and K (11) Elatoside G (**5**) was obtained as colorless fine crystals of mp 246.8—249.2 °C. The IR spectrum of **5** showed absorption bands (1719 and 1701 cm^{-1}) ascribable to carboxyls and broad bands (3432 and 1080 cm^{-1}) suggestive of glycosidic structure. In the negative and positive mode FAB-MS of **5**, quasimolecular ion peaks were observed at *m/z* 663 $(M-H)^-$ and *m/z* 687 $(M+Na)^+$, and high-resolution MS analysis revealed the molecular formula of **5** to be $C_{36}H_{56}O_{11}$. The ^{1}H-NMR spectrum (pyridine-d_5) of **5** showed signals [δ 5.26 (br s, 16-H) and δ 1.82 (s, 28-H_3)] characteristic of an oleanene-type triterpene bearing a 16α-hydroxyl group.[9] The ^{13}C-NMR spectrum (Table 1) of **5** was closely similar to that of hederagenin 3-*O*-β-D-glucuronopyranoside (**6**) except for some signals due to the 16-hydroxyl group of **5**. Finally, detailed comparison of the ^{13}C-NMR (Table 1) data for **5** with those for caulophyllogenin (**1**) and its glycosides[10] led us to formulate the structure of elatoside G as caulophyllogenin 3-*O*-β-D-glucopyranosiduronic acid (**5**).

Elatoside H (**7**) was also obtained as colorless fine crystals of mp 214.8—217.3 °C and its IR spectrum showed absorption bands due to hydroxyl and carboxyl groups (3432, 1719, 1702, and 1078 cm^{-1}). The negative and positive mode FAB-MS of **7** showed quasimolecular ion peak at *m/z* 809 $(M-H)^-$ and 833 $(M+Na)^+$, and the molecular formula $C_{42}H_{66}O_{15}$ was determined by high-resolution MS measurement. Furthermore, a fragment ion peaks at *m/z* 647 $(M-C_6H_{11}O_5)^-$ was observed in the negative mode FAB-MS. Methanolysis of **7** with 9% HCl–dry methanol liberated echinocystic acid (**2**) as a sapogenol and methyl glycosides of D-glucuronic acid and D-glucose. The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 1) spectra[11] of **7** showed signals assignable to an echinocystic acid moiety [δ 3.65 (dd-like, 18-H), 3.40 (dd-like, 3-H), 5.28 (br s, 16-H), 5.64 (br s, 11-H)], a β-D-glucuronic acid moiety [δ 5.03 (d, J=7.6 Hz, 1′-H)], and a β-D-glucopyranosyl moiety [δ 5.39 (d, J=7.9 Hz, 1″-H)]. The oligosaccharide structure bonding to the 3-position of **2** was characterized by an HMBC experiment. Namely, long-range correlations were observed between the 1″-proton of the glucopyranosyl moiety and the 3′-carbon of the glucuronic acid moiety and between the 1′-proton of the glucuronic acid moiety and the 3-carbon of the echinocystic acid moiety. Based on the above-mentioned evidence and comparison of the ^{13}C-NMR data for **7** with those for echinocystic acid glycosides,[12] the structure of elatoside H was elucidated as echinocystic acid 3-*O*-β-D-glucopyranosyl (1″-3′)-β-D-glucuronic acid (**7**).

Elatoside I (**8**), obtained as colorless fine crystals of mp 262.8—265.1 °C, showed absorption bands due to hydroxyl and carboxyl groups at 3432, 1721, 1701, and 1078 cm^{-1} in the IR spectrum. The negative mode FAB-MS of **8** showed a quasimolecular ion peak at *m/z* 955 $(M-H)^-$ in addition to the fragment ion peak at *m/z* 793 $(M-C_6H_{11}O_5)^-$. The molecular formula $C_{48}H_{76}O_{19}$ of **8** was clarified from the quasimolecular ion peak by high-resolution MS measurement. The methanolysis of **8** gave oleanolic acid (**4**) and methyl glycosides of D-glucose and D-glucuronic acid. The ^{1}H-NMR (pyridine-d_5) spectrum[11] of **8** showed signals assignable to an oleanolic acid moiety [δ 3.30 (dd-like, 3-H), 5.43 (br s, 12-H)] together with three anomeric protons [δ 4.97 (d, J=6.9 Hz, 1′-H), 5.72 (d, J=7.6 Hz, 1″-H), and 5.40 (d, J=8.2 Hz, 1‴-H)]. Comparison of the ^{13}C-NMR (Table 1) data[11] for **8** with those for oleanolic acid 3-*O*-monodesmosides such as elatosides A, B, and E[6] led us to presume a triglycoside structure with a D-glucopyranosiduronic acid and two D-glucopyranosyl moieties. The connectivity of the oligosaccharide structure was clarified by an HMBC experiment, in which long-range correlations were observed between the 1‴-proton and 3′-carbon, between the 1″-proton and 2′-carbon, and between the 1′-proton and 3-carbon. Consequently, the structure of elatoside I was formulated as oleanolic acid 3-*O*-{β-D-glucopyranosyl (1″-2′)-[β-D-glucopyranosyl (1‴-3′)]}-β-D-glucopyranosiduronic acid (**8**).

Elatoside J (**9**) was also isolated as colorless fine crystals of mp 231.1—235.6 °C. The IR spectrum of **9** showed hydroxyl and carboxyl absorption bands and the molecular formula $C_{48}H_{78}O_{19}$ was determined from its positive and negative mode FAB-MS and by high-resolution MS measurement. Thus, in the positive mode FAB-MS of **9**, the quasimolecular ion peak was observed at *m/z* 981 $(M+Na)^+$, while the negative mode FAB-MS of **9** showed the quasimolecular ion peak at *m/z* 957 $(M-H)^-$ in addition to fragment ion peaks at *m/z* 795 $(M-C_6H_{11}O_5)^-$ and *m/z* 633 $(M-C_{12}H_{21}O_{10})^-$. The methanolysis of **9** liberated hederagenin (**3**) and methyl glucosides. The ^{1}H-NMR (pyridine-d_5) spectrum[11] of **9** showed signals due to the hederagenin moiety together with three anomeric protons [δ 5.00 (d, J=7.9 Hz, 1′-H), 5.71 (d, J=7.9 Hz, 1″-H), 5.28 (d, J=7.6 Hz, 1‴-H)]. Comparison of the ^{13}C-NMR data (Table 1)[11] for **9** with those for hederagenin glycosides[1,10] led us to presume the hederagenin triglucoside structure (**9**) of elatoside J. Furthermore, HMBC correlations were observed between the following protons and carbons: 1‴-H and 3′-C; 1″-H and 2′-C; 1′-H and 3-C. Based on the above evidence, the structure of elatoside J was characterized to be hederagenin 3-*O*-{β-D-glucopyranosyl (1″-2′)-[β-D-glucopyranosyl (1‴-3′)]-β-D-glucopyranoside (**9**).

Elatoside K (**11**), isolated as colorless fine crystals of mp 219.2—222.4 °C, showed absorption bands of hydroxyl and carboxyl groups in the IR spectrum. Here again, the molecular formula $C_{53}H_{84}O_{23}$ of **11** was clarified from the quasimolecular ion peaks observed in the positive and negative mode FAB-MS and by high-resolution MS measurement. Namely, quasimolecular ion peaks were observed at *m/z* 1133 $(M+2Na-H)^+$ and *m/z* 1111 $(M+Na)^+$ in the positive mode FAB-MS of **11**, while the negative mode FAB-MS showed the quasimolecular ion peak at *m/z* 1087 $(M-H)^-$ and fragment ion peaks at *m/z* 955 $(M-C_5H_9O_4)^-$, *m/z* 925 $(M-C_6H_{11}O_5)^-$, and *m/z* 793 $(M-C_{11}H_{19}O_9)^-$. The methanolysis of **11** furnished oleanolic acid, methyl glucoside, methyl glucuronide, and methyl xyloside. The ^{1}H-NMR (pyridine-d_5)[11] spectrum of **11** showed signals assignable to an oleanolic acid moiety together with three

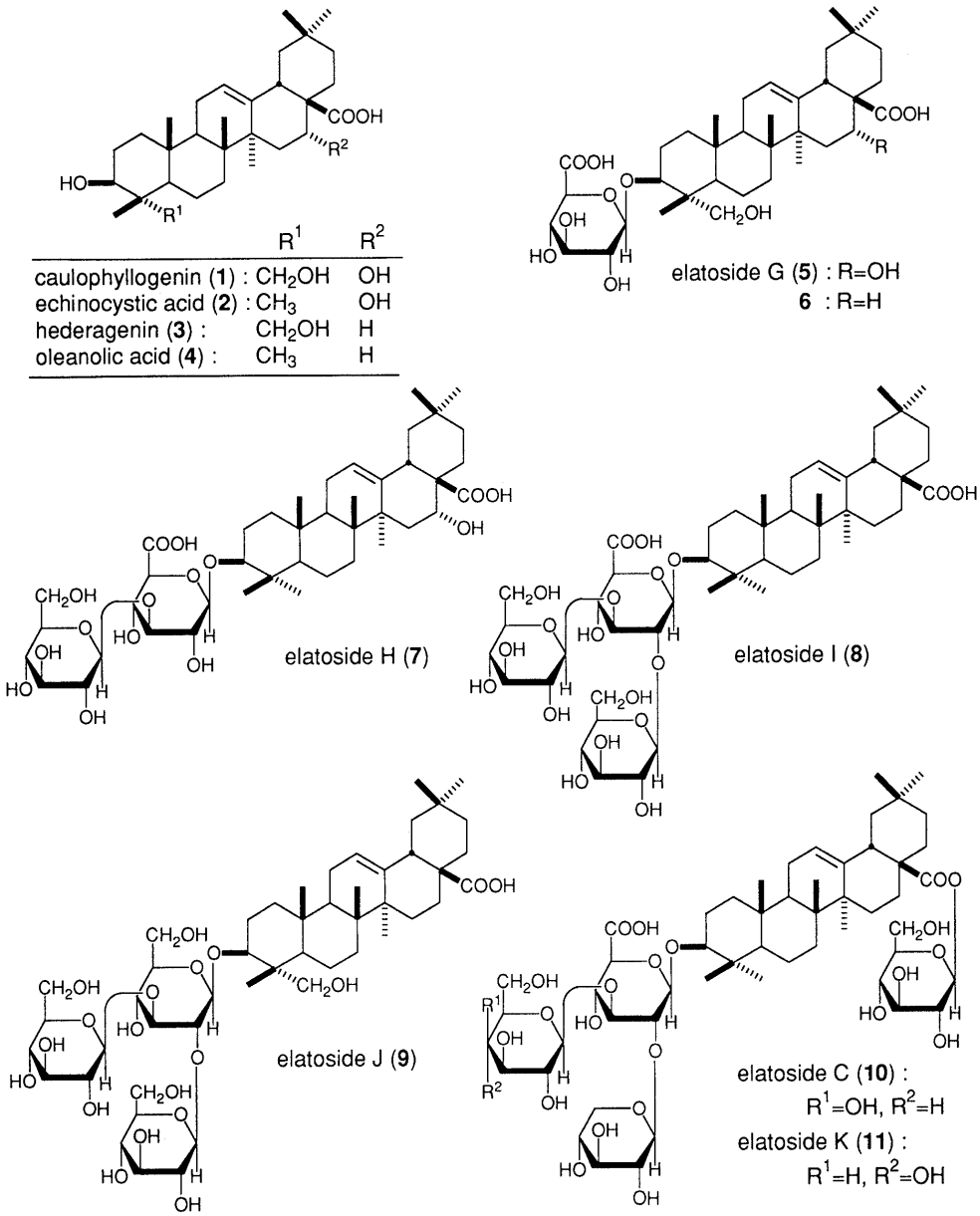

Chart 2. Structures of Elatosides and Their Sapogenols

anomeric protons [δ 4.96 (d-like, 1′-H), 5.59 (d, $J=7.3$ Hz, 1″-H), 5.40 (d, $J=7.3$ Hz, 1‴-H)] and an anomeric proton of an ester glucoside linkage [δ 6.32 (d, $J=7.9$ Hz, 1⁗-H)]. In the HMBC experiment, long-range correlations were observed between the following protons and carbons: 1‴-H and 3′-C; 1″-H and 2′-C; 1′-H and 3-C; 1⁗-H and 28-C. Comparison of the ^{13}C-NMR (Table 1) data[11] for **11** with those for oleanolic acid 3, 28-*O*-bisdesmosides such as elatosides C (**10**), D, and F[6] led us to formulate the structure of elatoside K as 3-*O*-{β-D-glucopyranosyl (1‴-3′)-[β-D-xylopyranosyl (1″-2′)]-β-D-glucopyranosiduronic acid oleanolic acid 28-*O*-β-D-glucopyranoside (**11**).

Hypoglycemic Activity of Saponin Fractions and Elatosides G, H, I, and K Inhibitory effects of the saponin fraction and elatosides G (**5**), H (**7**), I (**8**), and K (**11**) from the young shoot of *Aralia elata* on the elevation of plasma glucose level in the oral glucose tolerance test in rats are summarized in Table 2. The saponin fraction from the shoot was found to exhibit inhibitory activity after a single oral administration of 200 mg/kg. In the same bioassay, elatosides G (**5**), H (**7**), and I (**8**) showed potent activity at a lower dose (100 mg/kg). We have reported that oleanolic acid 3-*O*-monodesmoside structure is required for hypoglycemic activity by examination of structure–activity relationships.[6] This time, the 3-*O*-monodesmosides of caulophyllogenin (**1**) and echinocystic acid (**2**), such as elatosides G (**5**) and H (**7**), were also found to exhibit potent hypoglycemic activity similar to that of oleanolic acid 3-*O*-monodesmosides including elatoside I (**8**). On the other hand, the 3,28-*O*-bisdesmoside of oleanolic acid, elatoside K (**11**), showed little activity.

Experimental

The instruments used for obtaining physical data and experimental conditions for chromatography were the same as described in our previous paper.[2]

Isolation of Elatosides C (10), G (5), H (7), I (8), J (9), and K (11) and Hederagenin 3-*O*-Glucuronide (6) from the Young Shoots of *Aralia elata* The fresh young shoots of *Aralia elata* (3 kg, collected in Nagano Prefecture at 1994) were cut finely and then extracted with 80% aqueous

Table 1. ^{13}C-NMR Data for Elatosides G (**5**), H (**7**), I (**8**), J (**9**), and K (**11**)

	Elatoside G (**5**)	Elatoside H (**7**)	Elatoside I (**8**)	Elatoside J (**9**)	Elatoside K (**11**)		Elatoside G (**5**)	Elatoside H (**7**)	Elatoside I (**8**)	Elatoside J (**9**)	Elatoside K (**11**)
C-1	38.7	38.7	38.5	38.8	38.6	3-GlcA-1′	106.3	106.8	105.2	103.9	105.3
C-2	26.1	26.6	26.5	26.0	26.6	(Glc) 2′	75.5	74.3	78.9	79.4	79.1
C-3	82.2	89.2	89.6	83.2	89.8	3′	78.1	87.6	87.4	89.0	87.9
C-4	43.5	39.6	39.6	43.6	39.7	4′	73.4	71.8	71.8	70.0	71.9
C-5	47.3	55.8	55.7	48.1	55.8	5′	77.9	77.2	77.2	77.7	77.2
C-6	18.2	18.5	18.4	18.3	18.5	6′	172.8	172.2	171.9	63.3	171.8
C-7	33.2	33.5	33.3	33.3	33.1	2′-Glc-1″			103.8	103.8	104.7
C-8	39.9	39.9	39.7	39.8	39.9	(Xyl) 2″			76.3	76.3	76.2
C-9	47.7	47.2	47.9	48.2	48.0	3″			78.5	78.7	78.6
C-10	37.0	37.0	36.9	36.9	36.9	4″			72.5	72.3	71.4
C-11	23.8	23.8	23.7	23.8	23.6	5″			77.9	77.7	67.2
C-12	122.4	122.4	122.5	122.6	122.5	6″			62.3	62.4	
C-13	145.1	145.1	144.8	144.9	144.1	3′-Glc-1‴		105.9	104.6	104.6	104.7
C-14	42.1	42.1	42.1	42.2	42.1	2‴		75.7	75.4	75.5	75.4
C-15	36.2	36.2	28.3	28.4	28.2	3‴		78.8	78.5	78.7	78.9
C-16	74.7	74.8	23.7	23.8	23.4	4‴		71.6	71.5	71.7	71.6
C-17	48.8	48.9	44.6	46.5	47.0	5‴		78.3	78.5	78.6	78.6
C-18	41.4	41.4	41.9	42.0	41.7	6‴		62.5	63.3	62.6	62.2
C-19	47.3	47.3	46.4	46.7	46.2	28-Glc-1⁗					95.8
C-20	31.0	31.1	30.9	31.0	30.8	2⁗					74.1
C-21	36.2	36.5	34.2	34.3	34.0	3⁗					78.9
C-22	32.9	32.9	33.3	33.0	33.1	4⁗					71.1
C-23	64.5	28.1	27.9	64.6	27.7	5⁗					79.3
C-24	13.7	17.0	16.6	13.4	16.4	6⁗					62.2
C-25	16.2	15.6	15.4	16.0	15.5						
C-26	17.5	17.5	17.3	17.5	17.4						
C-27	27.2	27.3	26.2	26.2	26.1						
C-28	180.0	180.0	180.2	180.1	176.4						
C-29	33.3	33.4	33.3	33.3	33.1						
C-30	24.7	24.7	23.7	23.8	23.6						

GlcA, β-D-glucopyranosiduronic acid; Glc, β-D-glucopyranosyl; Xyl, β-D-xylopyranosyl.

Table 2. Hypoglycemic Activity of the Saponin Fraction and Elatosides G (**5**), H (**7**), I (**8**), and K (**11**)

	Dose (mg/kg, *p.o.*)	*n*	Plasma glucose concentration (mg/dl)		
			0.5 h	1.0 h	2.0 h
Control (normal)	—	5	68.4± 3.4**	95.6±4.3**	91.4± 3.2
Control	—	8	146.0± 5.3	130.3±6.8	102.4± 1.5
(D-Glucose tolerance)			(77.6± 5.3)	(34.7±6.8)	(11.0± 1.5)
The saponin fraction	200	5	95.5± 6.5**	117.3±9.1	111.7± 8.9
			(27.1± 6.5**)	(21.7±9.1)	(20.3± 8.9)
Elatoside G (**5**)	100	4	97.8±10.1**	114.0±8.6	111.0± 9.3
			(29.4±10.1**)	(18.4±8.6)	(19.6± 9.3)
Elatoside H (**7**)	100	3	89.3± 4.3**	129.7±7.9	124.0±21.1
			(20.9± 4.3**)	(34.1±7.9)	(32.6±21.1)
Elatoside I (**8**)	100	5	86.2± 6.7**	118.2±5.8	113.8± 6.9
			(17.8± 6.7**)	(22.6±5.8)	(22.4± 6.9)
Elatoside K (**11**)	100	5	134.6± 6.7	124.6±5.3	95.8± 4.8
			(66.2± 6.7)	(29.0±5.3)	(4.4± 4.8)

** $p<0.01$.

MeOH three times under reflux. After removal of the solvent from the aqueous MeOH solution under reduced pressure, the extract (160 g) was subjected to reversed-phase silica gel column chromatography [Chromatorex DM1020T (Fuji Silysia Chemical Ltd., 1.2 kg), $H_2O\rightarrow$ MeOH] followed by evaporation to furnish the MeOH eluate (16 g, 0.53%). Normal-phase silica gel column chromatography {Silica gel G (Merck, 1.5 kg), $CHCl_3$–MeOH–H_2O [65 : 35 : 10 (lower layer)→6 : 4 : 1]} of the MeOH eluate afforded three fractions [fraction 1 (1.0 g, 0.033%), 2 (2.6 g, 0.087%), 3 (6.3 g, 0.210%)]. Fraction 1 was further purified by HPLC [YMC-ODS-A (YMC Co., Ltd.), 80% aqueous MeOH–1% AcOH] to give elatoside J (**9**, 31.4 mg, 0.001%) and hederagenin 3-*O*-glucuronide (**6**, 30.2 mg, 0.001%). Fraction 2 was also separated with HPLC (the same conditions as the case of fraction 1) to give elatosides G (**5**, 73.7 mg, 0.003%), H (**7**, 62.4 mg, 0.002%), and I (**8**, 84.7 mg, 0.003%). Reversed-phase silica gel column chromatography (Chromatorex DM1020T, 70% aqueous MeOH) of fraction 3 followed by HPLC separation (YMC-ODS-A, 70% aqueous MeOH–1% AcOH) afforded elatosides C (**10**, 126.1 mg, 0.004%) and K (**11**, 203.4 mg, 0.007%).

Hederagenin 3-*O*-glucuronopyranoside (**6**) and elatoside C (**10**) were identified by TLC, ^{1}H-NMR (pyridine-d_5), and ^{13}C-NMR (pyridine-d_5) spectral comparisons with authentic samples.

Elatoside G (**5**): mp 246.8—249.2 °C, (colorless fine crystals from $H_2O\rightarrow$MeOH), $[\alpha]_D^{28}$ −5.1° (c=0.1, MeOH). High-resolution FAB-MS: Calcd for $C_{36}H_{56}O_{11}Na$ $(M+Na)^+$, 687.3721. Found: 687.3785. IR γ_{max}^{KBr} cm^{-1}: 3432, 1719, 1701, 1649, 1080. ^{1}H-NMR (pyridine-d_5) δ: 0.94,

0.97, 1.04, 1.05, 1.17, 1.82 (3H each, all s, tertiary-CH_3 × 6), 3.61 (1H, dd-like, 18-H), 5.26 (1H, br s, 16-H), 5.29 (1H, d, J=7.6 Hz, 1′-H), 5.63 (1H, br s, 12-H). ^{13}C-NMR: see Table 1. Negative mode FAB-MS (*m/z*): 663 $(M-H)^-$. Positive mode FAB-MS (*m/z*): 687 $(M+Na)^+$.

Elatoside H (**7**): mp 214.8—217.3 °C, (colorless fine crystals from H_2O→MeOH), $[\alpha]_D^{29}$ −2.4° (*c*=0.1, MeOH). High-resolution FAB-MS: Calcd for $C_{42}H_{66}O_{15}Na$ $(M+Na)^+$, 833.4300. Found: 833.4277. IR γ_{max}^{KBr} cm^{-1}: 3432, 1719, 1702, 1649, 1078. ^{1}H-NMR (pyridine-d_5) δ: 0.89, 0.99, 1.03, 1.07, 1.19, 1.29, 1.90 (3H each, all s, 25, 24, 26, 29, 30, 23, 27-H_3), 3.40 (1H, dd-like, 3-H), 3.65 (1H, dd-like, 18-H), 5.03 (1H, d, J=7.6 Hz, 1′-H), 5.28 (1H, br s, 16-H), 5.39 (1H, d, J=7.9 Hz, 1″-H), 5.64 (1H, br s, 12-H). ^{13}C-NMR: see Table 1. Negative mode FAB-MS (*m/z*): 809 $(M-H)^-$, 647 $(M-C_6H_{11}O_5)^-$. Positive mode FAB-MS (*m/z*): 833 $(M+Na)^+$.

Elatoside I (**8**): mp 262.8—265.1 °C, (colorless fine crystals from H_2O→MeOH), $[\alpha]_D^{29}$ +17.4° (*c*=0.1, MeOH). High-resolution FAB-MS: Calcd for $C_{48}H_{75}O_{19}$ $(M-H)^-$, 955.4903. Found: 955.4918. IR γ_{max}^{KBr} cm^{-1}: 3432, 1721, 1701, 1648, 1078. ^{1}H-NMR (pyridine-d_5) δ: 0.77, 1.01, 1.07, 1.25, 1.31 (3H each, all s, 25, 30, 24, 23, 27-H_3), 0.96 (6H, s, 26, 29-H_3), 3.30 (2H, dd-like, 3, 18-H), 4.97 (1H, d, J=6.9 Hz, 1′-H), 5.40 (1H, d, J=8.2 Hz, 1‴-H), 5.43 (1H, br s, 12-H), 5.72 (1H, d, J=7.6 Hz, 1″-H). ^{13}C-NMR: see Table 1. Negative mode FAB-MS (*m/z*): 955 $(M-H)^-$, 793 $(M-C_6H_{11}O_5)^-$.

Elatoside J (**9**): mp 231.1—235.6 °C, (colorless fine crystals from H_2O→MeOH), $[\alpha]_D^{25}$ +25.7° [*c*=0.1, $CHCl_3$–MeOH–H_2O (6:4:1)]. High-resolution FAB-MS : Calcd for $C_{48}H_{78}O_{19}Na$ $(M+Na)^+$, 981.5035. Found: 981.5029. IR γ_{max}^{KBr} cm^{-1}: 3432, 1702, 1638, 1078. ^{1}H-NMR (pyridine-d_5) δ: 0.89, 0.93, 1.06, 1.24 (3H each, all s, 25, 29, 24, 27-H_3), 1.00 (6H, s, 26, 30-H_3), 3.27 (1H, dd-like, 18-H), 4.10 (1H, dd-like, 3-H), 5.00 (1H, d, J=7.9 Hz, 1′-H), 5.28 (1H, d, J=7.6 Hz, 1‴-H), 5.46 (1H, br s, 12-H), 5.71 (1H, d, J=7.9 Hz, 1″-H). ^{13}C-NMR: see Table 1. Negative mode FAB-MS (*m/z*): 957 $(M-H)^-$, 795 $(M-C_6H_{11}O_5)^-$, 633 $(M-C_{12}H_{21}O_{10})^-$. Positive mode FAB-MS (*m/z*): 981 $(M+Na)^+$.

Elatoside K (**11**): mp 219.2—222.4 °C, (colorless fine crystals from H_2O→MeOH), $[\alpha]_D^{26}$ +2.0° (*c*=0.1, MeOH). High-resolution FAB-MS: Calcd for $C_{53}H_{84}O_{23}Na$ $(M+Na)^+$, 1111.5301. Found: 1111.5298. IR γ_{max}^{KBr} cm^{-1}: 3432, 1728, 1638, 1075. ^{1}H-NMR (pyridine-d_5) δ: 0.82, 0.88, 0.91, 1.27, 1.28 (3H each, all s, 25, 30, 29, 23, 27-H_3), 1.08 (6H, s, 24, 26-H_3), 3.24 (1H, dd-like, 3-H), 3.25 (1H, dd-like, 18-H), 4.96 (1H, d-like, 1′-H), 5.40 (1H, d, J=7.3 Hz, 1‴-H), 5.40 (1H, br s, 12-H), 5.59 (1H, d, J=7.3 Hz, 1″-H), 6.32 (1H, d, J=7.9 Hz, 1⁗-H). ^{13}C-NMR: see Table 1. Negative mode FAB-MS (*m/z*): 1087 $(M-H)^-$, 955 $(M-C_5H_9O_4)^-$, 925 $(M-C_6H_{11}O_5)^-$. Positive mode FAB-MS (*m/z*): 1133 $(M+2Na-H)^+$, 1111 $(M+Na)^+$.

Methanolysis of Elatosides H (7), I (8), J (9), and K (11) A solution of elatoside (2 mg of **7**, **8**, **9** or **11**) in 9% HCl–dry MeOH (0.5 ml) was heated under reflux for 2 h. After cooling, the reaction mixture was neutralized with Ag_2CO_3 and the insoluble portion was removed by filtration. The sapogenol constituent of each product, which was obtained from the filtrate by removal of the solvent under reduced pressure, was shown to be identical with an authentic sample (**2** from **7**; **4** from **8** and **11**; **3** from **9**) by TLC [$CHCl_3$–MeOH (10:1), benzene–acetone (3:1), hexane–AcOEt (1:2)] and HPLC [YMC-Pack ODS-A, 85% MeOH–1% AcOH] comparisons. The sugar composition of the product was analyzed by GLC. A solution of each product in pyridine (0.1 ml) was treated with *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA, 0.2 ml) for 1 h. The reaction solution was then subjected to GLC analysis to identify trimethylsilyl (TMS) derivatives of methyl glycoside [methyl glucoside (i) and methyl glucuronide (ii) from **7** and **8**; ii from **9**; i, ii and methyl xyloside (iii) from **11**; GLC conditions: CBR1-M25-025, 0.25 mm (i.d.) × 25 m capillary column, column temperature 140—280 °C, He flow rate 15 ml/min, t_R: i 17.7 min, 17.9 min, ii 18.4 min, 18.6 min, iii 15.7 min, 16.2 min].

Bioassay for the Hypoglycemic Activity in Rats Male Wistar rats (Kiwa Laboratory Animals Ltd., Wakayama, Japan) weighing 125—155 g were starved for 20—24 h but allowed water *ad libitum*. The test samples were dissolved in water (5 ml/kg) and orally administered to the rats at each dose. At 30 min thereafter, a water solution (5 ml/kg) of D-glucose (0.5 g/kg) was orally administered. Blood (0.4 ml) was collected from the carotid at 0.5, 1.0, and 2.0 h after D-glucose administration and the plasma glucose concentration was assayed by the enzymatic glucose oxidase method. Statistical significance of differences was estimated by analysis of variance (ANOVA) followed by Dunnett's test. Results were expressed as the mean ± S. E. (Table 2).

References and Notes

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