Medicinal Foodstuffs. XII.[1] Saponin Constituents with Adjuvant Activity from Hyacinth Bean, the Seeds of *Dolichos lablab* L. (1): Structures of Lablabosides A, B, and C

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From the glycoside mixture with adjuvant activity obtained from the hyacinth bean, the seeds of *Dolichos lablab* L., six new oleanane-type triterpene bisdesmosides, lablabosides A, B, C, D, E, and F, were isolated together with chikusetsusaponin IVa. The structures of lablabosides A, B, and C were determined on the basis of chemical and physicochemical evidence as follows: 3-*O*-[α-L-rhamnopyranosyl (1→2)-β-D-galactopyranosyl (1→2)-β-D-glucopyranosiduronic acid]-28-*O*-(β-D-glucopyranosyl) oleanolic acid (lablaboside A), 3-*O*-[α-L-rhamnopyranosyl (1→2)-β-D-galactopyranosyl (1→2)-β-D-glucopyranosiduronic acid]-28-*O*-(β-D-glucopyranosyl) 24-*epi*-hederagenin (lablaboside B), 3-*O*-[α-L-rhamnopyranosyl (1→2)-β-D-galactopyranosyl (1→2)-β-D-glucopyranosiduronic acid]-28-*O*-[α-L-rhamnopyranosyl (1→2)-β-D-glucopyranosyl] 24-*epi*-hederagenin (lablaboside C).

Key words hyacinth bean; lablaboside; *Dolichos lablab*; adjuvant activity; oleanane-type triterpene bisdesmoside; medicinal foodstuff

The Leguminosae plant *Dolichos lablab* L. (Hyacinth bean, Japanese name "ingenmame or fujimame") has been widely cultivated as a vegetable in Asian countries. In Chinese traditional medicine, the white seeds of *D. lablab* ("白扁豆" in Chinese) have been prescribed for stomachic, antidote, and anti-alcoholism purposes. As the chemical constituents of *D. lablab*, several sterols with plant growth-regulatory activity,[2] gibberellin glycoside,[3] and aminopropylaminoalcohols[4] were isolated from the seeds, while pyridine alkaloids,[5] amino-butyric acid,[6] and triterpene glycoside[7] have been reported from other parts of this plant.

During the course of our characterization studies on bioactive constituents in medicinal foodstuffs[1,8] and natural medicines,[9] we have found a number of triterpene and sterol oligoglycosides having inhibitory effects on alcohol and sugar absorption,[10] as well as anti-inflammatory,[11] antiallergic,[12] and hepatoprotective activity.[13] In a continuing study, we have found that the glycoside mixture obtained from the white seeds of *D. lablab* showed potent adjuvant activity.[14] From the glycosidic fraction with this adjuvant activity, six new oleanane-type triterpene bisdesmosides called lablabosides A (**1**), B (**2**), C (**3**), D, E, and F were isolated together with chikusetsusaponin IVa (**4**). In this paper, we describe the isolation of these saponins and the structural elucidation of lablabosides A (**1**), B (**2**), and C (**3**).

The white seeds of *D. lablab* L. cultivated in China were extracted with methanol under reflux. The methanolic extract was partitioned into an ethyl acetate–water mixture and the water phase was further extracted with 1-butanol. The 1-butanol-soluble portion was subjected to normal- and reversed-phase silica gel column chromatography and, finally, HPLC to afford lablabosides A (**1**, 0.00023% from the seeds), B (**2**, 0.00038%), C (**3**, 0.00014%), D (0.00030%), E (0.00065%), and F (0.00043%) and chikusetsusaponin IVa[15] (**4**, 0.00044%).

Lablaboside A (1) Lablaboside A (**1**) was isolated as colorless fine crystals of mp 184.0—185.5 °C from aqueous methanol. The IR spectrum of **1** showed absorption bands at 1716 and 1736 cm^{-1} ascribable to ester and carboxyl groups and strong absorption bands at 3419 and 1076 cm^{-1} suggestive of its oligoglycosidic structure. In the positive-ion FAB-MS of **1**, a quasimolecular ion peak was observed at *m/z* 1125 $(M+Na)^+$, while the negative-ion FAB-MS showed a quasimolecular ion peak at *m/z* 1101 $(M-H)^-$. Furthermore, fragment ion peaks at *m/z* 939 $(M-C_6H_{11}O_5)^-$ and *m/z* 793 $(M-C_{12}H_{21}O_9)^-$, which were derived by cleavage of the glycosidic linkage at the 28- and 2′-positions, were observed in the negative-ion FAB-MS of **1**. The molecular formula $C_{54}H_{86}O_{23}$ of **1** was determined by high-resolution MS measurement of the quasimolecular ion peak $(M+Na)^+$. Methanolysis of **1** with 9% hydrogen chloride in dry methanol liberated oleanolic acid (**5**)[10c,d] as a sapogenol and methyl glycosides of glucuronic acid, galactose, rhamnose, and glucose in

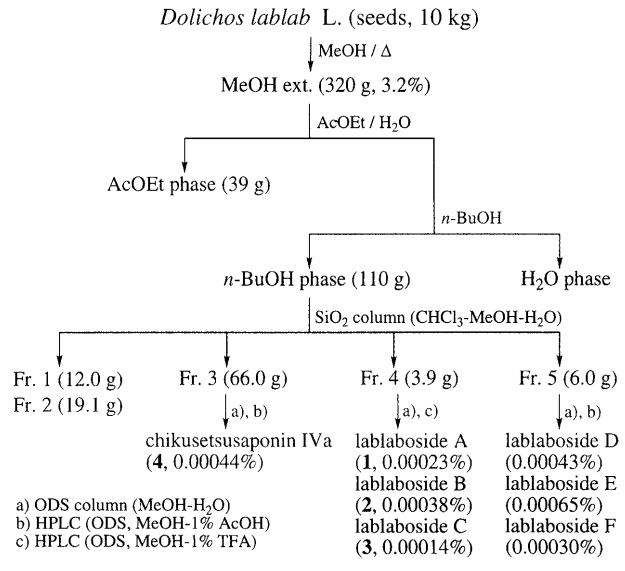

Chart 1

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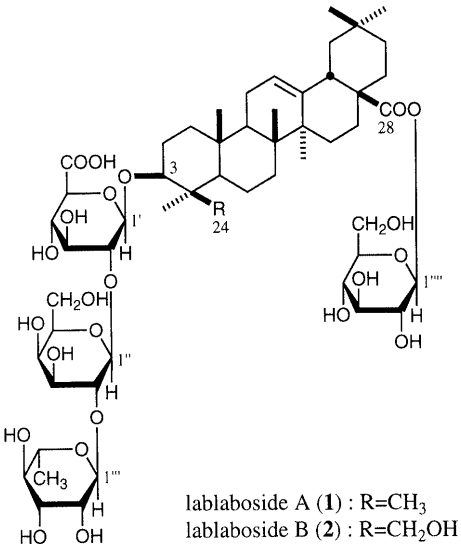
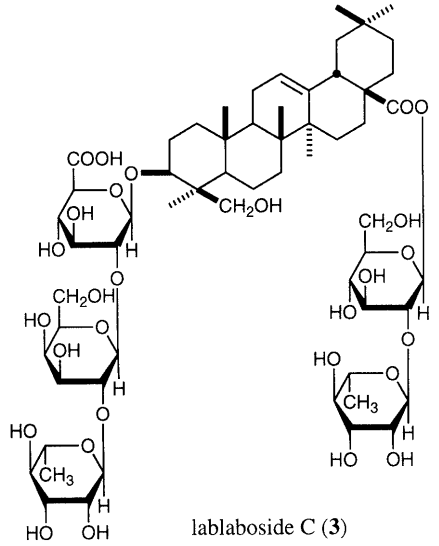
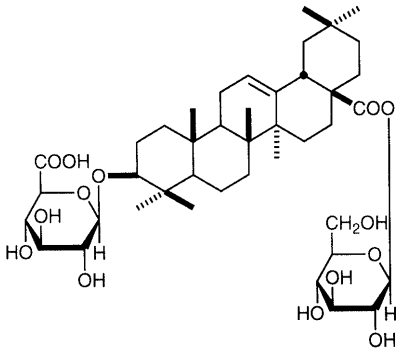


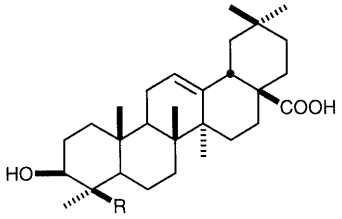
lablaboside A (**1**) : R=CH_3
lablaboside B (**2**) : R=CH_2OH



lablaboside C (**3**)



chikusetsusaponin IVa (**4**)



oleanolic acid (**5**) : R=CH_3
24-*epi*-hederagenin (**6**) : R=CH_2OH

Chart 2

a 1 : 1 : 1 : 1 ratio.[16] In order to determine the absolute configuration of the component monosaccharides, **1** was subjected to acid hydrolysis with 5% aqueous sulfuric acid–dioxane (1 : 1, v/v) to furnish D-glucuronic acid, D-galactose, L-rhamnose, and D-glucose, which were identified by gas-liquid chromatography (GLC) analysis of their trimethylsilyl (TMS) thiazolidine derivatives.[17]

The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 1) spectra of **1**, which were assigned by means of various NMR experiments,[18] showed signals assignable to an oleanolic acid moiety [δ 3.17 (dd, J=3.1, 14.7 Hz, 18-H), 3.30 (dd, J=4.6, 12.2 Hz, 3-H), 5.39 (br s, 12-H)], a β-D-glucuronic acid moiety [δ 5.03 (d, J=7.3 Hz, 1′-H)], a β-D-galactopyranosyl moiety [δ 5.66 (d, J=7.7 Hz, 1″-H)], a α-L-rhamnopyranosyl moiety [δ 1.74 (d, J=5.8 Hz, 6‴-H_3), 6.25 (br s, 1‴-H)], and a β-D-glucopyranosyl moiety [δ 6.28 (d, J=8.0 Hz, 1⁗-H)]. The carbon signals due to the 3-*O*-triglycosidic moiety in the ^{13}C-NMR spectrum of **1** were found to be superimposable on those of the α-L-rhamnopyranosyl (1→2)-β-D-galactopyranosyl (1→2)-β-D-glucuronic acid moiety in kaikasaponin III.[19] Finally, the glycosidic structure of **1** was characterized by a heteronuclear multiple bond correlation (HMBC) experiment, in which long-range correlations were observed between the 1‴-proton of the α-L-rhamnopyranosyl moiety and the 2″-carbon (δ_C 76.7) of the β-D-galactopyranosyl moiety, between the 1″-proton and the 2′-carbon (δ_C 79.4) of the β-D-glucuronic acid moiety, between the 1′-proton and the 3-carbon (δ_C 90.0) of the oleanolic acid moiety, and between the 1⁗-proton of the β-D-glucopyranosyl moiety and the 28-carboxyl carbon (δ_C 176.4) of the oleanolic acid moiety. Consequently, the structure of lablaboside A was assigned as 3-*O*-[α-L-rhamnopyranosyl (1→2)-β-D-galactopyranosyl (1→2)-β-D-glucopyranosiduronic acid]-28-*O*-(β-D-glucopyranosyl) oleanolic acid (**1**).

Lablaboside B (2) Lablaboside B (**2**) was also isolated as colorless fine crystals of mp 219.6—220.5 °C from aqueous methanol and its IR spectrum was very similar to that of **1**. The molecular formula $C_{54}H_{86}O_{24}$ was determined from the positive-ion and negative-ion FAB-MS and by high-resolution MS measurement. A quasimolecular ion peak was observed at m/z 1141 $(M+Na)^+$ in the positive-ion FAB-MS of **2**, while the negative-ion FAB-MS showed a quasimolecular ion peak at m/z 1117 $(M-H)^-$ in addition to the fragment ion peaks at m/z 955 $(M-C_6H_{11}O_5)^-$ and m/z 809 $(M-C_{12}H_{21}O_9)^-$. Methanolysis of **2** liberated 24-*epi*-hederagenin (**6**)[20] together with the methyl glycosides of glucuronic acid, galactose, rhamnose, and glucose in a 1 : 1 : 1 : 1 ratio.[16] On acid hydrolysis of **2** followed by GLC analysis of the TMS thiazolidine derivatives,[17] D-

Table 1. ^{13}C-NMR Data of Lablabosides A (**1**), B (**2**), and C (**3**)

	1	2	3		1	2	3
1	38.8	38.6	38.6	GlcA-1′	105.3	105.4	105.6
2	26.5	26.7	26.7	2′	79.4	77.0	76.6
3	90.0	91.3	91.3	3′	78.8	78.5	78.5
4	39.7	43.9	43.9	4′	73.4	73.8	73.9
5	56.0	56.2	56.2	5′	77.4	77.6	77.7
6	18.6	18.6	18.6	6′	172.5	172.3	172.4
7	33.2	33.3	33.3	Gal-1″	102.8	101.8	101.7
8	40.0	39.9	39.9	2″	76.7	77.7	77.9
9	48.1	47.9	47.9	3″	76.1	76.6	76.6
10	37.0	36.6	36.6	4″	70.6	71.3	71.2
11	23.5	24.0	24.0	5″	76.3	76.4	76.4
12	122.9	122.8	122.8	6″	62.0	61.8	61.6
13	144.1	144.1	144.1	Rha-1‴	102.0	102.3	102.5
14	42.2	42.2	42.2	2‴	72.4	72.4	72.5
15	28.3	28.3	28.3	3‴	72.7	72.8	72.8
16	23.8	23.5	23.4	4‴	74.4	74.4	74.4
17	47.0	47.1	47.1	5‴	69.5	69.4	69.5
18	41.8	41.8	41.8	6‴	18.9	18.9	19.0
19	46.2	46.3	46.3	Glc-1⁗	95.8	95.8	94.9
20	30.8	30.8	30.8	2⁗	74.2	74.2	75.6
21	34.1	34.1	34.1	3⁗	78.9	78.9	79.9
22	32.6	32.6	32.6	4⁗	71.3	71.3	71.4
23	28.5	23.0	23.0	5⁗	79.2	79.2	79.0
24	16.8	63.6	63.6	6⁗	62.4	62.4	62.1
25	15.5	15.7	15.7	Rha-1⁗′			101.4
26	17.5	17.4	17.4	2⁗′			72.3
27	26.1	26.0	26.0	3⁗′			72.6
28	176.4	176.4	176.4	4⁗′			73.9
29	33.1	33.1	33.1	5⁗′			69.8
30	23.7	23.7	23.7	6⁗′			18.7

125 MHz in pyridine-d_5.

glucuronic acid, D-galactose, L-rhamnose, and D-glucose were identified. The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 1) spectra[18] of **2** showed signals due to the 24-*epi*-hederagenin moiety [δ 3.15 (dd, J=4.3, 13.8 Hz, 18-H), 3.22, 4.22 (both d, J=11.3 Hz, 24-H$_2$), 3.39 (dd, J=4.0, 11.6 Hz, 3-H), 5.38 (br s, 12-H)], a β-D-glucuronic acid moiety [δ 4.96 (d, J=7.4 Hz, 1′-H)], a β-D-galactopyranosyl moiety [δ 5.72 (d, J=7.4 Hz, 1″-H)], a α-L-rhamnopyranosyl moiety [δ 1.75 (d, J=6.1 Hz, 6‴-H$_3$), 6.21 (br s, 1‴-H)], and a β-D-glucopyranosyl moiety [δ 6.27 (d, J=7.9 Hz, 1⁗-H)]. The carbon signals of the glycosidic moiety in the ^{13}C-NMR spectrum of **2** were superimposable on those of soyasaponin I[21] and dehydrosoyasaponin I[22] having a 24-hydroxyl group and a 3-*O*-[α-L-rhamnopyranosyl (1→2)-β-D-galactopyranosyl (1→2)-β-D-glucuronic acid] moiety. The glycosidic structure of **2** was confirmed to be the same as that of **1** from the HMBC experiment, which showed long-range correlations between the following protons and carbons: 1‴-H and 2″-C, 1″-H and 2′-C, 1′-H and 3-C, 1⁗-H and 28-C. On the basis of the above evidence, the structure of lablaboside B is 3-*O*-[α-L-rhamnopyranosyl (1→2)-β-D-galactopyranosyl (1→2)-β-D-glucopyranosiduronic acid]-28-*O*-(β-D-glucopyranosyl) 24-*epi*-hederagenin (**2**).

Lablaboside C (3) Lablaboside C (**3**), obtained as colorless fine crystals of mp 222.0—223.5 °C from aqueous methanol, showed absorption bands due to hydroxyl, ester, and carboxyl groups at 3409, 1736, 1718, and 1076 cm^{-1} in the IR spectrum. The molecular formula $C_{60}H_{96}O_{28}$ was determined from the quasimolecular ion peaks [m/z 1287 $(M+Na)^+$ and m/z 1263 $(M-H)^-$] in the positive-ion and negative-ion FAB-MS and by high-resolution MS measurement. In addition, fragment ion peaks at m/z 1117 $(M-C_6H_{11}O_4)^-$ and m/z 955 $(M-C_{12}H_{21}O_9)^-$ were observed in the negative-ion FAB-MS of **3**. Methanolysis of **3** liberated **6** and the methyl glycosides of D-glucuronic acid, D-galactose, L-rhamnose, and D-glucose in a 1:1:2:1 ratio,[16] and their absolute configuration was determined by acid hydrolysis of **3** followed by GLC analysis of the TMS thiazolidine derivatives.[17]

The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 1) spectra[18] of **3** showed signals assignable to a 24-*epi*-hederagenin moiety [δ 3.10 (dd, J=4.9, 14.0 Hz, 18-H), 3.13, 4.19 (both d, J=11.0 Hz, 24-H$_2$), 3.34 (dd, J=4.9, 12.2 Hz, 3-H), 5.41 (br s, 12-H)], a β-D-glucuronic acid moiety [δ 4.98 (d, J=7.4 Hz, 1′-H)], a β-D-galactopyranosyl moiety [δ 5.80 (d, J=7.3 Hz, 1″-H)], two α-L-rhamnopyranosyl moieties [δ 1.79 (d, J=5.2 Hz, 6⁗′-H$_3$), 1.81 (d, J=5.8 Hz, 6‴-H$_3$), 6.28, 6.66 (both br s, 1‴-H, 1⁗′-H)], and a β-D-glucopyranosyl moiety [δ 6.19 (d, J=8.3 Hz, 1⁗-H)]. The carbon signals in the ^{13}C-NMR spectrum of **3** were very similar to those of **2**, except the signals due to the 28-terminal α-L-rhamnopyranosyl moiety. The glycosidic structure was confirmed by the detailed HMBC experiment, which showed long-range correlations between the following protons and carbons: 1‴-H and 2″-C, 1″-H and 2′-C, 1′-H and 3-C, 1⁗′-H and 2⁗-C, 1⁗-H and 28-C. On the basis of this evidence, the structure of lablaboside C was assigned as 3-*O*-[α-L-rhamnopyranosyl (1→2)-β-D-galactopyranosyl (1→2)-β-D-glucopyranosiduronic acid]-28-*O*-[α-L-rhamnopyranosyl (1→2)-β-D-glucopyranosyl] 24-*epi*-hederagenin (**3**).

We are currently engaged in characterization studies involving the structure elucidation of other lablabosides and their adjuvant activity which will be reported in our forthcoming paper.[14]

Experimental

The following instruments were used to obtain physical data: melting points, Yanagimoto micro-melting point apparatus MP-500D (values are uncorrected); specific rotations, Horiba SEPA-300 digital polarimeter (l=5 cm); UV spectra, Shimadzu UV-1200 spectrometer; IR spectra, Shimadzu FTIR-8100 spectrometer; FAB-MS and high-resolution MS, JEOL JMS-SX 102A mass spectrometer; ^{1}H-NMR spectra, JEOL EX-270 (270 MHz) spectrometer and JNM-LA500 (500 MHz) spectrometer; ^{13}C-NMR spectra, JEOL EX-270 (68 MHz) spectrometer and JNM-LA500 (125 MHz) spectrometer with tetramethylsilane as an internal standard.

The following experimental conditions were used for chromatography: ordinary-phase silica gel column chromatography, Silica-gel BW-200 (Fuji Silysia Chemical, Ltd., 150—350 mesh); reversed-phase silica gel column chromatography, Chromatorex ODS DM1020T (Fuji Silysia Chemical, Ltd., 100—200 mesh); TLC, pre-coated TLC plates with Silica-gel 60F$_{254}$ (Merck, 0.25 mm) (ordinary phase) and Silica-gel RP-18 60F$_{254}$ (Merck, 0.25 mm) (reversed phase); reversed-phase HPTLC, pre-coated TLC plates with Silica-gel RP-18 60WF$_{254S}$ (Merck, 0.25 mm); detection was achieved by spraying with 1% Ce(SO$_4$)$_2$–10% aqueous H_2SO_4 and heating.

Isolation of Lablabosides A (1), B (2), C (3), D, E, and F and Chikusetsusaponin IVa (4) from the White Seeds of *Dolichos lablab* L. The air-dried seeds of *Dolichos lablab* L. (10 kg, cultivated in China and purchased from Honzou Pharmaceutical Co., Ltd., Nagoya) were minced and extracted three times with MeOH under reflux. Evaporation of the solvent from the extract under reduced pressure gave the MeOH extract (320 g, 3.2% from the seeds). This extract (300 g) was partitioned in an AcOEt–H_2O (1:1) mixture. The H_2O-soluble portion was further

extracted with *n*-BuOH. Removal of the solvent under reduced pressure from the AcOEt-soluble and *n*-BuOH-soluble portions yielded 39 g (0.39%) and 110 g (1.1%), respectively. The *n*-BuOH extract (110 g) was separated by normal-phase silica gel column chromatography [BW-200 (Fuji Silysia Chemical Ltd., 2 kg), $CHCl_3$–MeOH–H_2O (65 : 35 : 10, lower layer→6 : 4 : 1)→MeOH] to give five fractions [fr. 1 (12.0 g), fr. 2 (19.1 g), fr. 3 (66.0 g), fr. 4 (3.9 g), fr. 5 (6.0 g)]. Fraction 3 (66.0 g) was separated by reversed-phase silica gel column chromatography [1 kg, MeOH–H_2O (65 : 35→70 : 30→75 : 25, v/v)→MeOH] and HPLC [MeOH–1% aq. AcOH (75 : 25, v/v)] to give chikusetsusaponin IVa (**4**, 41.0 mg, 0.00041%). Fraction 4 (3.9 g) was subjected to reversed-phase silica gel column chromatography [Chromatorex ODS DM1020T (Fuji Silysia Chemical Ltd., 100 g), MeOH–H_2O (30 : 70→60 : 40→80 : 20, v/v)→MeOH] to give six fractions [fr. 4-1 (1.32 g), fr. 4-2 (0.047 g), fr. 4-3 (0.23 g), fr. 4-4 (0.28 g), fr. 4-5 (1.34 g), fr. 4-6 (0.34 g)]. Fraction 4-3 (0.23 g) was purified by HPLC [YMC-Pack ODS (YMC Co., Ltd., 250 × 20 mm i.d.), MeOH–1% aq. trifluoroacetic acid (TFA) (65 : 30, v/v)] to give lablabosides A (**1**, 22.8 mg, 0.00023%), B (**2**, 38.2 mg, 0.00038%), and C (**3**, 13.8 mg, 0.00014%). Fraction 5 (6.0 g) was subjected by reversed-phase silica gel column chromatography [180 g, MeOH–H_2O (30 : 70→50 : 50→80 : 20, v/v)→MeOH] to give four fractions [fr. 5-1 (3.4 g), fr. 5-2 (0.7 g), fr. 5-3 (1.1 g), fr. 5-4 (0.2 g)]. Fraction 5-3 (1.1 g) was separated by HPLC [MeOH–1% aq. AcOH (70 : 30, v/v)] to give eight fractions [fr. 5-3-1 (595.5 mg), fr. 5-3-2 (85.9 mg), fr. 5-3-3 (94.9 mg), fr. 5-3-4 (19.4 mg), fr. 5-3-5 (24.0 mg), fr. 5-3-6 (14.5 mg), fr. 5-3-7 (43.2 mg), fr. 5-3-8 (13.3 mg)]. Fraction 5-3-2 (85.9 mg) was purified by HPLC [MeOH–1% aq. AcOH (65 : 35, v/v)] to give lablaboside E (65.0 mg, 0.00065%). Fraction 5-3-3 (94.9 mg) was purified by HPLC [1) MeOH–1% aq. AcOH (65 : 35, v/v); 2) CH_3CN–1% aq. AcOH (35 : 65, v/v)] to give lablaboside F (26.1 mg, 0.00026%). Fraction 5-3-7 (43.2 mg) was purified by HPLC [MeOH–1% aq. AcOH (70 : 35, v/v)] to give lablaboside D (43.2 mg, 0.00043%). Chikusetsusaponin IVa (**4**) was identified by TLC, ^{1}H-NMR (pyridine-d_5), and ^{13}C-NMR (pyridine-d_5) spectral comparisons with an authentic sample.[10e,15]

Lablaboside A (**1**): Colorless fine crystals from MeOH–H_2O, mp 184.0—185.5 °C, $[\alpha]_D^{26}$ −9.3° (c = 1.2, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{54}H_{86}O_{23}Na$ $(M+Na)^+$: 1125.5458; Found: 1125.5436. IR (KBr): 3419, 2943, 1736, 1716, 1676, 1076 cm^{-1}. ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: 0.82, 0.88, 0.91, 1.06, 1.13, 1.25, 1.36 (3H each, all s, 25, 30, 29, 26, 24, 27, 23-H_3), 1.74 (3H, d, J = 5.8 Hz, 6‴-H_3), 3.17 (1H, dd, J = 3.1, 14.7 Hz, 18-H), 3.30 (1H, dd, J = 4.6, 12.2 Hz, 3-H), 5.03 (1H, d, J = 7.3 Hz, 1′-H), 5.39 (1H, br s, 12-H), 5.66 (1H, d, J = 7.7 Hz, 1″-H), 6.25 (1H, br s, 1‴-H), 6.28 (1H, d, J = 8.0 Hz, 1⁗-H). ^{13}C-NMR (pyridine-d_5, 125 MHz) δ_C: given in Table 1. Negative-ion FAB-MS (m/z): 1101 $(M-H)^-$, 939 $(M-C_6H_{11}O_5)^-$, 793 $(M-C_{12}H_{21}O_9)^-$ Positive-ion FAB-MS (m/z): 1125 $(M+Na)^+$.

Lablaboside B (**2**): Colorless fine crystals from MeOH–H_2O, mp 219.6—220.5 °C, $[\alpha]_D^{25}$ −10.4° (c = 2.2, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{54}H_{86}O_{24}Na$ $(M+Na)^+$: 1141.5407; Found: 1141.5385. IR (KBr): 3409, 2942, 1736, 1716, 1676, 1075 cm^{-1}. ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: 0.65, 0.88, 0.90, 1.01, 1.26, 1.41 (3H each, all s, 25, 30, 29, 26, 27, 23-H_3), 1.75 (3H, d, J = 6.1 Hz, 6‴-H_3), 3.15 (1H, dd, J = 4.3, 13.8 Hz, 18-H), 3.22, 4.22 (1H each, both d, J = 11.3 Hz, 24-H_2), 3.39 (1H, dd, J = 4.0, 11.6 Hz, 3-H), 4.96 (1H, d, J = 7.4 Hz, 1′-H), 5.38 (1H, br s, 12-H), 5.72 (1H, d, J = 7.4 Hz, 1″-H), 6.21 (1H, br s, 1‴-H), 6.27 (1H, d, J = 7.9 Hz, 1⁗-H). ^{13}C-NMR (pyridine-d_5, 125 MHz) δ_C: given in Table 1. Negative-ion FAB-MS (m/z): 1117 $(M-H)^-$, 955 $(M-C_6H_{11}O_5)^-$, 809 $(M-C_{12}H_{21}O_9)^-$. Positive-ion FAB-MS (m/z): 1141 $(M+Na)^+$.

Lablaboside C (**3**): Colorless fine crystals from MeOH–H_2O, mp 222.0—223.5 °C, $[\alpha]_D^{24}$ −22.9° (c = 0.97, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{60}H_{96}O_{28}Na$ $(M+Na)^+$: 1287.5986; Found: 1287.5996. IR (KBr): 3409, 2940, 1736, 1718, 1676, 1076 cm^{-1}. ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: 0.63, 0.80, 0.89, 0.99, 1.28, 1.35 (3H each, all s, 25, 30, 29, 26, 27, 23-H_3), 1.79 (3H, d, J = 5.2 Hz, 6⁗′-H_3), 1.81 (3H, d, J = 5.8 Hz, 6‴-H_3), 3.10 (1H, dd, J = 4.9, 14.0 Hz, 18-H), 3.13, 4.19 (1H each, both d, J = 11.0 Hz, 24-H_2), 3.34 (1H, dd, J = 4.9, 12.2 Hz, 3-H), 4.98 (1H, d, J = 7.4 Hz, 1′-H), 5.41 (1H, br s, 12-H), 5.80 (1H, d, J = 7.3 Hz, 1″-H), 6.19 (1H, d, J = 8.3 Hz, 1⁗-H), 6.28 (1H, br s, 1‴-H), 6.66 (1H, br s, 1⁗′-H). ^{13}C-NMR (pyridine-d_5, 125 MHz) δ_C: given in Table 1. Negative-ion FAB-MS (m/z): 1263 $(M-H)^-$, 1117 $(M-C_6H_{11}O_4)^-$, 955 $(M-C_{12}H_{21}O_9)^-$. Positive-ion FAB-MS (m/z): 1287 $(M+Na)^+$.

Methanolysis of Lablabosides A (1), B (2), and C (3) A solution of lablabosides (**1**, **2**, **3**, 1.0 mg each) 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 samples [oleanolic acid (**5**) from **1**; 24-*epi*-hederagenin (**6**) from **2**, **3**] by TLC [$CHCl_3$–MeOH (10 : 1), benzene–acetone (3 : 1), *n*-hexane–AcOEt (1 : 2)] and HPLC [YMC-Pack ODS-A (YMC Co., Ltd., 250 × 4.6 mm i.d.), MeOH–1% aq. AcOH (85 : 15, v/v)]. The sugar composition of the product was analyzed by GLC. After removal of the solvent from the filtrate *in vacuo*, each residue was dissolved in pyridine (0.01 ml) and the solution was treated with *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA, 0.02 ml) for 1 h. The reaction solution was then subjected to GLC analysis to identify the TMS derivatives of methyl glycoside [methyl glucuronide (i), methyl galactoside (ii), methyl rhamnoside (iii), and methyl glucoside (iv), from **1**, **2**, and **3**; GLC conditions: CBR-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 (18.4, 18.6 min), ii (18.9, 19.4 min), iii (11.5, 13.9 min), iv (17.8, 18.2, 19.2 min)].

Acid Hydrolysis of Lablabosides A (1), B (2), and C (3) A solution of lablabosides (**1**, **2**, **3**, 2.0 mg each) in 5% aqueous H_2SO_4–1,4-dioxane (1 : 1, v/v, 1.0 ml) was heated under reflux for 1 h. After cooling, the reaction mixture was neutralized with Amberlite IRA-400 (OH^- form) and the resin was removed by filtration. After removal of the solvent from the filtrate *in vacuo*, the residue was transferred to a Sep-Pak C_{18} cartridge with H_2O and MeOH. The H_2O eluate was concentrated and the residue was treated with L-cysteine methyl ester hydrochloride (3.0 mg) in pyridine (0.5 ml) at 60 °C for 1 h. After reaction, the solution was treated with BSTFA (0.02 ml) at 60 °C for 1 h. The supernatant was then subjected to GLC analysis to identify the derivatives of D-glucuronide (i), D-galactoside (ii), L-rhamnoside (iii), and D-glucoside (iv), from **1**, **2**, and **3**; GLC conditions: Supelco™-1, 0.25 mm (i.d.) × 30 m capillary column, column temperature 230 °C, He flow rate 15 ml/min, t_R: i (26.4 min), ii (13.8 min), iii (15.5 min), iv (24.2 min).

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