Five New Triterpene Glycosides from *Wisteria brachybotrys* (Leguminosae)[1)]

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From the vines of *Wisteria brachybotrys* (Leguminosae), five new oleanene glycosides, called wistariasaponins $YC_{1,2}$, B_3 and $A_{2,3}$, together with four known ones were isolated. Their structures have been elucidated to be 3-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-xylopyranosyl-(1→2)-β-D-glucuronopyranosyl yunganogenin C 21-*O*-β-D-glucopyranoside (1), 3-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-galactopyranosyl-(1→2)-β-D-glucuronopyranosyl yunganogenin C 21-*O*-β-D-glucopyranoside (2), 3-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-xylopyranosyl-(1→2)-β-D-glucuronopyranosyl wistariasapogenol B 30-*O*-β-D-glucopyranoside (3), 3-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-xylopyranosyl-(1→2)-β-D-glucuronopyranosyl wistartiasapogenol A 30-*O*-β-D-glucopyranoside (4) and 3-*O*-β-D-galactopyranosyl-(1→2)-β-D-glucuronopyranosyl wistariasapogenol A 30-*O*-β-D-glucopyranoside (5), respectively.

Key words oleanene glycoside; triterpene; saponin; wistariasaponin; Leguminosae; *Wisteria brachybotrys*

The gall of *Wisteria brachybotrys* SIEB. *et* ZUCC. (Leguminosae), has been used as a folk medicine for gastric cancer in Japan. Recently, Konoshima *et al.* elucidated many triterpenoid saponins, together with isoflavonoids, from this folk medicine with the guidance of its anti-tumor promoting effect.[2)] Saito *et al.* have also isolated several isoflavones from the same source.[3)] Incidentally, this gall was formed on infection with the bacterium *Erwina milletiae*.[3)] Therefore, the constituents in the vine of this plant seemed to be different from those of the gall. During our course of studies on leguminous plants, we have examined the triterpenoidal constituents in the vines of this plant and isolated five new oleanene glycosides together with four known ones. This paper deals with the structural elucidation of these saponins.

The MeOH extract of the fresh vines was separated by MCI gel CHP 20P to give fractions 1 (H_2O), 2 (20% MeOH) and 3 (100% MeOH). The crude saponin fraction (fr. 3) was followed by various column chromatographies to yield compounds **1**—**9**. Compounds **6**—**9** were identified as astragaloside VIII (**6**),[4)] soyasaponin I (**7**),[5)] subproside V (**8**)[6)] and robinioside I (**9**)[7)] by comparison with the ^{1}H- and ^{13}C-NMR spectral data (Tables 1 and 2).

Wistariasaponin YC_1 (**1**), a white powder, $[\alpha]_D$ −50.2° (pyridine), showed a peak at *m/z* 1073 due to $[M-H]^-$ in the negative FAB-MS. The exact measurement under high resolution (HR) conditions showed that the composition is $C_{53}H_{86}O_{22}Na$ at *m/z* 1097.5508 $[M+H]^+$. The monosaccharide mixture obtained by acid hydrolysis of **1** revealed the presence of glucuronic acid, glucose, xylose, and rhamnose. Their absolute configurations were determined to be D-form except for rhamnose (L-form), according to the procedure developed by Hara *et al.*[8)] Although the sapogenol (**1a**) exhibited the same *Rf* value as soyasapogenol B[9)] on TLC, the colorlation of **1a** by sulfuric acid was different, although it was similar to that of kudzusapogenol C.[9b)] On the comparative study of ^{1}H- and ^{13}C-NMR spectral data (Tables 1 and 2), **1a** was identified with yunganogenin C,[10)] which was recently isolated from *Glycyrrhiza yunnanensis*. In the ^{13}C-NMR spectra, the signals due to a sugar moiety were in good agreement with those of **6** except for Glc A C-6 and additional hexosyl signals. The enzymatic hydrolysis of **1** with glycyrrhizinic acid hydrolase (GH)[11)] yielded a prosapogenin (**1b**), a white powder, $[\alpha]_D$ +20.6° (MeOH). Compound **1b** showed a peak at *m/z* 619 due to $[M-H]^-$ in the negative FAB-MS, indicating that it is yunganogenin C glycoside with a hexosyl unit. In the ^{1}H- and ^{13}C-NMR spectrum of **1b**, signals of the sugar component were assignable to the β-D-glucopyranosyl moiety. Since the signal at C-21 was shifted to a lower field by glycosylation,[12)] the structure of **1b** was elucidated as 21-*O*-β-D-glucopyranosyl yunganogenin C. Therefore, the full structure of **1** was characterized as 3-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-xylopyranosyl-(1→2)-β-D-glucuronopyranosyl yunganogenin C 21-*O*-β-D-glucopyranoside.

Wistariasaponin YC_2 (**2**), a white powder, $[\alpha]_D$ −31.9° (pyridine–H_2O), furnished **1a**, D-glucuronic acid, D-galactose, D-glucose and L-rhamnose in the same manner as above. In the negative and HR/positive FAB-MS, **2** showed a peak at *m/z* 1103 due to $[M-H]^-$ and at *m/z* 1127.5615 $[M+Na]^+$ ($C_{54}H_{88}O_{23}Na$), respectively. In the ^{13}C-NMR spectrum of **2** (Tables 1 and 2), the signals due to aglycone and β-D-glucopyranosyl residue were identical with those of **1**. On the other hand, the signals ascribable to the C-3 sugar chain were in accord with those of **7**. Consequently, **2** was concluded to be 3-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-galactopyranosyl-(1→2)-β-D-glucuronopyranosyl yunganogenin C 21-*O*-β-D-glucopyranoside.

Wistariasaponin B_3 (**3**), a white powder, $[\alpha]_D$ −2.0° (MeOH), showed a peak at *m/z* 1089 due to $[M-H]^-$ in the negative FAB-MS, and at *m/z* 1113.5470 $[M+Na]^+$ ($C_{53}H_{86}O_{23}Na$) in the HR/positive FAB-MS. By acid hydrolysis, **3** gave wistariasapogenol B (**3a**)[2b)] (the same as abrisapogenol E),[13)] D-glucuronic acid, D-glucose, D-xylose and L-rhamnose. In the ^{13}C-NMR spectrum of **3**, the signals for the aglycone with a C-30 glucopyranosyl moiety were superimposable on those of **8**, whereas the remaining sugar signals were identical with those of

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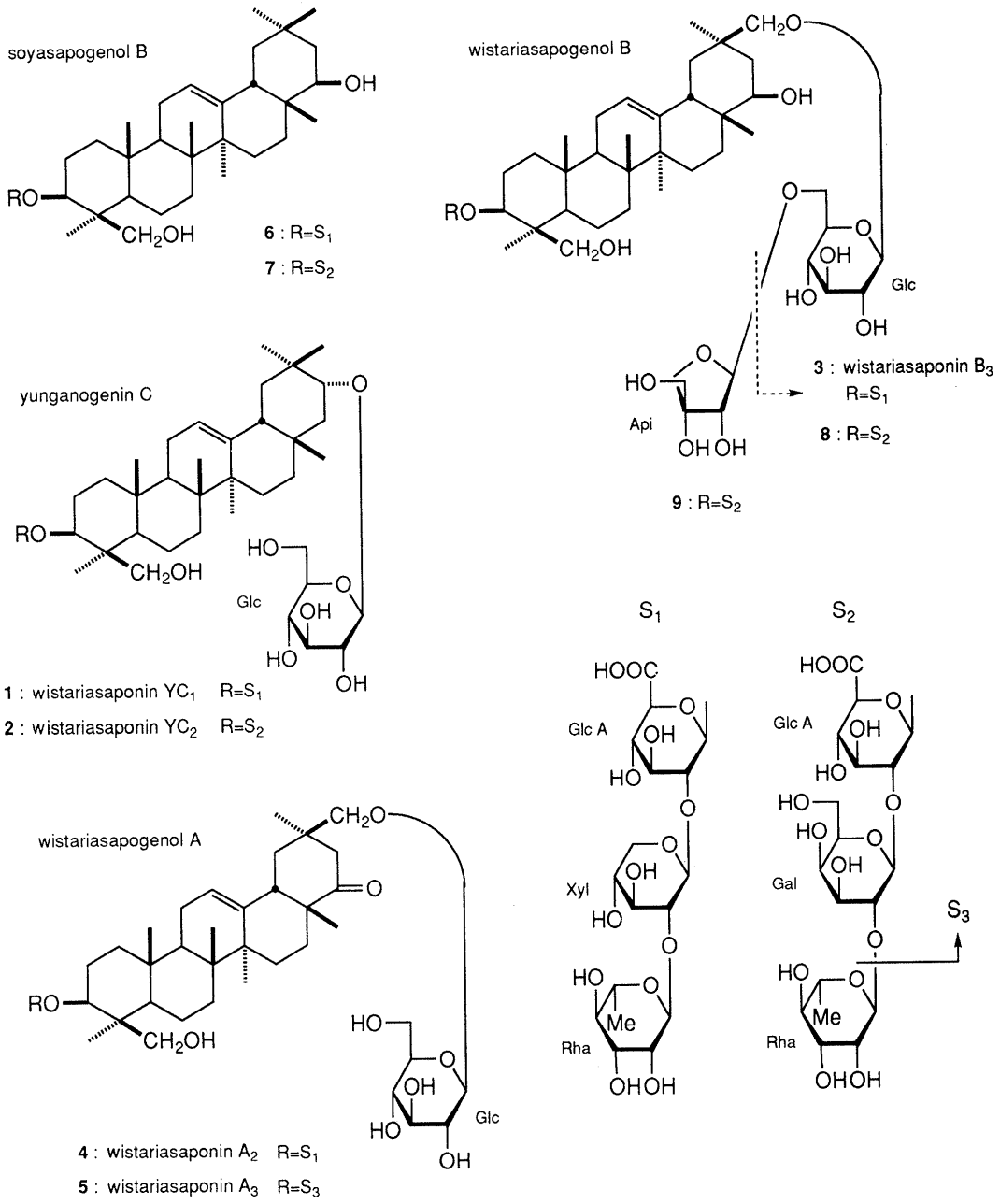

6. Therefore, the structure of **3** was established as 3-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-xylopyranosyl-(1→2)-β-D-glucuronopyranosyl wistariasapogenol B 30-*O*-β-D-glucopyranoside.

Wistariasaponin A_2 (**4**), a white powder, $[\alpha]_D$ −12.3° (MeOH), showed a peak at *m/z* 1087 due to $[M-H]^-$ in the negative FAB-MS, and at *m/z* 1111.5267 $[M+Na]^+$ ($C_{53}H_{84}O_{23}Na$) in the HR/positive FAB-MS. The sapogenol obtained by acid hydrolysis of **4** was identified with wistariasapogenol A[2b] (**4a**) by means of various spectral data. The component sugars were determined to be D-glucuronic acid, D-glucose, D-xylose and L-rhamnose. On the comparative analysis of the ^{13}C-NMR spectra of **4** and **4a**, the C-3 and C-30 signals of **4** appeared at a much lower field than that of **4a** due to glycosylation. Furthermore, signals due to the sugar region of **4** were in agreement with those of **3**. Consequently, the structure of **4** was elucidated as 3-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-xylopyranosyl-(1→2)-β-D-glucuronopyranosyl wistariasapogenol A 30-*O*-β-D-glucopyranoside.

Wistariasaponin A_3 (**5**), a white powder, $[\alpha]_D$ +11.2° (MeOH), showed a peak at *m/z* 972 due to $[M-H]^-$ in the negative FAB-MS, and at *m/z* 973.5015 $[M+H]^+$ ($C_{48}H_{77}O_{20}$) in the HR/positive FAB-MS. Compound **5** furnished **4a**, D-glucuronic acid, D-galactose and D-glucose under acid hydrolysis. In the ^{13}C-NMR spectrum of **5** (Tables 1 and 2), the signals for the aglycone with C-30 glucopyranosyl moiety were superimposable on those of **4**, and the remaining signals were identical with those of kaikasaponin I.[14b] Therefore, **5** was concluded to be 3-*O*-β-D-galactopyranosyl-(1→2)-β-D-glucuronopyranosyl wistariasapogenol A 30-*O*-β-D-glucopyranoside.

In the meantime, in comparison with Konoshima's work there were found some differences between vines and galls. Although the sugar moieties linked at C-3 were almost identical to each other, the former included bisdesmosides,

Table 1. ^{13}C-NMR Data for Compounds **1**—**9**, **1a** and **1b** (Aglycone Moieties)

	1a	1b	1	2	3	4	5	6	7	8	9
C-1	38.8	39.2	39.2	39.2	38.6	38.7	38.3	38.8	38.8	38.3	38.7
C-2	28.4	28.4	26.6	26.6	26.2	26.5	26.4	26.4	26.3	26.3	26.3
C-3	80.1	80.1	91.3	91.5	90.8	90.9	90.4	91.0	91.5	91.0	91.4
C-4	43.1	43.2	44.1	44.0	44.1	44.2	43.6	44.3	44.0	43.6	43.9
C-5	56.3	56.3	56.5	56.3	56.1	56.2	55.8	56.3	56.3	55.7	56.1
C-6	19.0	19.1	18.6	18.7	18.4	18.5	18.4	18.6	18.6	18.2	18.6
C-7	33.4	33.4	33.3	33.4	33.0	33.0	32.9	33.2	33.5	32.8	32.2
C-8	39.9	39.9	39.9	39.9	39.8	39.7	39.5	40.0	39.9	39.7	40.0
C-9	48.1	48.1	47.9	48.0	47.5	47.4	47.3	47.7	47.9	47.4	47.8
C-10	37.0	37.0	36.5	36.5	36.3	36.4	36.2	36.5	36.5	36.1	36.5
C-11	24.1	24.1	24.2	24.2	23.8	23.8	23.7	24.0	24.1	23.7	24.0
C-12	122.4	122.4	122.5	122.5	122.7	124.1	123.9	122.4	122.6	122.4	123.0
C-13	145.2	145.0	145.5	145.5	144.2	141.7	141.6	144.8	144.7	144.1	144.3
C-14	42.2	42.1	42.3	42.3	42.1	41.9	41.7	42.4	42.5	41.9	42.3
C-15	26.6	26.5	26.6	26.6	26.4	25.1	25.2	26.5	26.5	26.1	26.6
C-16	30.9	30.5	30.5	30.5	27.9	27.0	26.8	28.6	28.9	27.8	28.5
C-17	33.3	33.1	33.2	33.2	37.7	47.6	47.5	38.0	38.0	37.6	37.9
C-18	47.6	47.0	47.3	47.3	44.3	46.7	46.6	45.3	45.7	44.2	44.8
C-19	42.5	43.6	43.6	43.6	42.1	42.5	42.4	46.7	46.8	41.9	42.1
C-20	36.0	35.3	35.4	35.4	34.8	37.9	37.8	30.8	30.8	34.7	35.0
C-21	74.4	80.3	80.9	80.7	36.9	46.7	46.6	42.2	41.7	36.8	37.0
C-22	44.6	38.9	38.9	38.8	75.2	216.0	216.1	75.5	75.8	76.1	75.5
C-23	23.5	23.5	22.7	23.0	22.8	22.9	22.5	23.0	23.0	22.6	23.0
C-24	64.5	64.6	62.6	63.6	62.7	62.7	63.3	62.8	63.5	63.3	63.5
C-25	16.2	16.2	15.7	15.9	15.4	15.4	15.4	15.6	15.9	15.5	15.9
C-26	17.0	17.0	17.1	17.1	16.8	16.7	16.6	17.0	17.1	16.6	17.0
C-27	25.6	25.7	25.9	25.9	25.9	25.1	25.1	25.7	25.4	25.7	25.8
C-28	28.9	28.5	28.7	28.7	21.1	21.0	20.9	28.6	28.9	21.0	21.0
C-29	28.4	28.1	28.4	28.4	28.9	27.0	26.9	33.2	32.8	28.8	28.6
C-30	25.3	25.3	25.6	25.6	77.6	75.6	75.5	21.1	20.8	77.5	77.6

Chemical shifts (δ: ppm) were measured in pyridine-d_5.

whereas only monodesmosides were reported from the latter. Also, an oxidized saponin (wistariasaponin G), having a C-22 acetoxy and C-30 carboxy group, was isolated from the galls. These differences might be caused by the microorganism with which this plant was infected. These seemed to be interesting differences from the standpoint of biological action.

Experimental

The optical rotations were measured with a JASCO DIP-360 automatic digital polarimeter. IR spectra were recorded with a JEOL FT-IR spectrometer, JIR-6500W. ^{1}H- and ^{13}C-NMR spectra were measured with a JEOL JNM-GX 400 NMR spectrometer, and chemical shifts are given on a δ (ppm) scale with tetramethylsilane as an internal standard. The EI- and FAB-MS were measured with a JEOL DX-300 spectrometer. HR FAB-MS were measured with a JEOL DX-303 HF spectrometer and taken in a glycerol matrix containing NaI. TLC was performed on precoated Kieselgel 60 F_{254} plates (Merck). GC was performed by a Hewlett Packard HP5890A. The GC conditions were as follows: column, Ohio Valley OV-1 (0.5 μ film bonded, 0.32 × 30 m); colum oven temperature, 230 °C; injection port temperature, 270 °C; detection temperature, 270 °C; carrier gas, He (2.5 kg/cm^2). HPLC was carried out on a system of a pump: CCPM (Tosoh), UV detector: UV-970 (JASCO) and a column heater: U-620 (Sugai). Column chromatography was carried out on Kieselgel 60 (70—230 mesh, and 230—400 mesh, Merck), Sephadex LH-20 (Pharmacia), Bondapak C_{18} (Waters), Chromatorex ODS-DU 3050MT (Fuji Silysia) and MCI gel CHP 20P (Mitsubishi Chemical, Ind.).

Extraction and Isolation The vines (14 kg) of *Wisteria brachybotrys* collected in the medicinal garden of our department were extracted with MeOH. The extract (480 g) was subjected to MCI gel CHP 20P column chromatography using 0%→100% MeOH to give fractions 1 to 3. Fraction 3 (135 g) was further separated by Sephadex LH-20 (MeOH), Bondapak C_{18} (0%→100% MeOH, Chromatorex ODS (0%→100% MeOH) and silica gel ($CHCl_3$: MeOH : H_2O = 8 : 2 : 0.2→6 : 4 : 1) to provide compounds **1** (0.00047%, from fresh roots), **2** (0.00026%), **3** (0.00039%), **4** (0.00005%), **5** (0.00007%), **6** (0.00012%), **7** (0.00061%), **8** (0.00047%) and **9** (0.00012%).

Compound **1** (Wistariasaponin YC_1): A white amorphous powder, $[\alpha]_D^{25}$ −50.2° (c = 0.50, MeOH). IR (KBr): 3405 (ν_{O-H}), 1610 ($\nu_{C=O}$, COO^- form) cm^{-1}. HR FAB-MS m/z: 1097.5508 (Calcd for $C_{53}H_{86}O_{22}Na$: 1097.5508). Negative FAB-MS m/z: 1073 [M−H]$^-$, 927 [M−H−rha]$^-$, 795 [M−H−rha−xyl]$^-$, 619 [M−H−rha−xyl−glc A]$^-$. ^{1}H-NMR (in pyridine-d_6): 0.69, 0.87, 0.99, 1.08, 1.21, 1.24, 1.40 (each 3H, s, *tert*-Me × 7), 1.81 (3H, d, J = 5.5 Hz, rha H-6), 5.25 (1H, s, H-12), 6.05 (1H, s, rha H-1). ^{13}C-NMR: Tables 1 and 2.

Identification of Sapogenol and Sugars for 1 A sample of **1** (22 mg) was hydrolyzed in 2 N HCl/H_2O at 80 °C for 2 h. After filtration of the mixture, the precipitate was subjected to silica gel column chromatography with *n*-hexane–acetone (1 : 0→3 : 1) to yield **1a** (8 mg), $[\alpha]_D^{25}$ +64.9° (c = 0.40, pyridine : H_2O = 1 : 1). EI-MS m/z: 458 [M$^+$]. ^{1}H-NMR (in pyridine-d_5): 0.97, 1.00, 1.01, 1.06, 1.22, 1.32, 1.57 (each 3H, s, *tert*-Me × 7), 3.65 (1H, dd, J = 11.9, 5.0 Hz, H-3), 3.73, 4.55 (2H, ABq, J = 11.0 Hz, H-24), 3.74 (1H, br s, H-21), 5.35 (1H, br s, H-12). ^{13}C-NMR: Table 1. The fitrate was neutralized with 2 N KOH/H_2O. The sugar mixture was subjected to TLC analysis[15] [TLC, Kieselgel 60 (Merck Art 5553), *n*-PrOH–acetone–H_2O, 5 : 3 : 1, Rf: 0.75 (rhamnose), 0.67 (xylose), 0.51 (glucose), 0.11 (glucuronic acid); Reagent: *o*-aminobenzenesulfonic acid/2 M H_3PO_4].

D, L Determination of Sugars A sample of **1** (3 mg) was methylated in ethereal CH_2N_2. To a solution of the methylated sample for **1** was added $NaBH_4$ (*ca.* 5 mg), and the mixture was kept at r.t. for 30 min. The reaction mixture was worked up with MCI gel CHP 20P. The MeOH eluate was evaporated and heated in 2 N HCl/H_2O at 90 °C for 3 h. The precipitate was removed by filtration and the supernatant was neutralized with 2 N KOH/H_2O. After desalting with Amberlite MB-3, the sugar fraction was dissolved in pyridine (0.1 ml), then the mixture was added to a pyridine solution (0.2 ml) of L-cysteine methyl ester hydrochloride (0.1 mol/l) and warmed at 60 °C for 2 h. The mixture was then evaporated under N_2 stream and dried *in vacuo*. The obtained syrup was

Table 2. ^{13}C-NMR Data for Compounds **1**—**9** and **1b** (Sugar Moieties)

		1b	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Glc A	C-1		104.9	105.0	105.0	105.1	104.9[a]	105.3	104.9	105.4	105.1
	C-2		78.6[a]	78.2[c]	78.4[a]	78.7[a]	80.6	78.4	78.0	78.1[c]	78.0[c]
	C-3		76.8	76.5[a]	77.0	77.4	77.0[b]	77.4	76.5[a]	77.3[a]	76.4[a]
	C-4		73.8	73.8	73.7	73.8	73.4	73.9	73.7	73.5	73.6
	C-5		77.7	77.9	77.6	77.6	77.8	77.7	77.3	78.0	77.6
	C-6		176.3[d]	176.1[d]	173.7	172.4	172.5	172.9	176.2[d]	172.4	172.6
Gal	C-1			101.5			104.7[a]		101.8	101.4	101.7
	C-2			77.0[a]			72.8		76.9[a]	78.0[a]	76.9[a]
	C-3			75.9[a]			75.2		75.8[a]	76.2[a]	76.1[a]
	C-4			71.0			70.7		71.0	70.8	70.9
	C-5			77.4[a]			77.4[b]		76.7[a]	77.5[a]	76.7[a]
	C-6			61.9			62.3		61.8	61.2	61.5
Xyl	C-1		102.4		102.3	102.4		102.5			
	C-2		78.8		79.2	79.3		79.5			
	C-3		77.9[a]		78.2[a]	77.8[a]		78.4			
	C-4		70.5		70.6	70.8		70.8			
	C-5		66.4		66.6	66.7		66.8			
Rha	C-1		101.4	101.8	101.9	102.3		102.3	102.0	102.1	102.3
	C-2		71.9[b]	72.0[b]	72.1[b]	72.3[b]		72.3[a]	71.9[b]	72.1[b]	72.1[b]
	C-3		72.0[b]	72.1[b]	72.4[b]	72.6[b]		72.7[a]	72.0[b]	72.4[b]	72.3[b]
	C-4		73.8	73.9	74.1	74.3		74.3	73.9	74.0	74.1
	C-5		69.5	69.5	69.1	69.3		69.4	69.4	69.0	69.3
	C-6		18.6	18.7	18.7	18.8		18.6	18.6	18.6	18.8
Glc	C-1	101.9	102.0	102.1	105.5	105.4	105.1			105.1	105.3
	C-2	75.3	74.9	75.0	75.2	75.0	74.9			75.1	75.0
	C-3	78.3[a]	77.9[a]	77.9[c]	78.2[a]	78.3[a]	78.2[c]			78.1[c]	78.1[c]
	C-4	72.1	71.7	71.8	71.4	71.5	71.4			71.3	71.5
	C-5	79.0[a]	78.1[a]	78.0[c]	78.4[a]	78.5[a]	78.4[c]			78.3[c]	77.6
	C-6	63.1	63.0	62.7	62.5	62.7	62.6			62.4	68.9
Api	C-1										110.8
	C-2										77.6
	C-3										80.4
	C-4										65.1
	C-5										74.8

a—*c*) In each vertical column may be interchanged. *d*) Carboxylate form.

trimethylsilylated with trimethylsilylimidazole (0.1 ml) at 60 °C for 1 h. After the addition of *n*-hexane (0.1 ml) and H_2O (0.1 ml), the *n*-hexane layer was taken off and checked by GC. The retention time (t_R) of the peaks was at 11.9 min (D-xylose), 14.4 min (L-rhamnose), and 20.9 min (D-glucose).

Enzymatic Hydrolysis of **1**: To a solution of **1** (31 mg) in acetate buffer (pH 4.2, 30 ml) was added GH (100 μl) and the mixture was incubated at 37 °C for 2 d. When the hydrolysis had been completed, the hydrolysate was partitioned with 1-BuOH and H_2O. The 1-BuOH ext. was evaporated and purified over silica gel column chromatography with $CHCl_3$–MeOH–H_2O (1 : 0 : 0→8 : 2 : 0.2) to yield **1b** (3 mg), a white amorphous powder, $[\alpha]_D^{25}$ +20.6° (c=0.27, MeOH). IR (KBr): 3405 (ν_{O-H}). HR FAB-MS *m/z*: 643.4188 (Calcd for $C_{36}H_{60}O_8Na$: 643.4186). Negative FAB-MS *m/z*: 619 $[M-H]^-$. ^{1}H-NMR (in pyridine-d_5): 0.95, 0.97, 0.98, 1.03, 1.19, 1.22, 1.52 (each 3H, s, *tert*-Me×7), 3.64 (1H, dd, J=11.4, 5.1 Hz, H-3), 3.71, 4.52 (2H, ABq, J=11.0 Hz, H-24), 3.89 (1H, br s, H-21), 4.00 (1H, m, glc H-5), 4.06 (1H, t, J=8.2 Hz, glc H-2), 4.24 (1H, t, J=8.8 Hz, glc H-4), 4.30 (1H, t, J=8.8 Hz, glc H-3), 4.41 (1H, dd, J=11.7, 5.3 Hz, glc H-6), 4.58 (1H, dd, J=11.7, 2.6 Hz, glc H-6′), 4.97 (1H, d, J=7.7 Hz, glc H-1), 5.30 (1H, s, H-12). ^{13}C-NMR: Tables 1 and 2.

Compound **2** (Wistariasaponin YC_2): A white amorphous powder, $[\alpha]_D^{25}$ −31.9° (c=0.35, pyridine : H_2O=1 : 1). IR (KBr): 3400 (ν_{O-H}), 1610 ($\nu_{C=O}$, COO^- form) cm^{-1}. HR FAB-MS *m/z*: 1127.5614 (Calcd. for $C_{54}H_{88}O_{23}Na$: 1127.5614). Negative FAB-MS *m/z*: 1103 $[M-H]^-$, 957 $[M-H-rha]^-$, 795 $[M-H-rha-gal]^-$. 619 $[M-H-rha-gal-glc\ A]^-$. ^{1}H-NMR (in pyridine-d_5): 0.70, 0.89, 0.99, 1.07, 1.22, 1.25, 1.39 (each 3H, s, *tert*-Me×7), 1.80 (3H, d, J=5.9 Hz, rha H-6), 5.27 (1H, s, H-12), 6.03 (1H, s, rha H-1). ^{13}C-NMR: Tables 1 and 2.

Identification of Sapogenol and Sugars for 2 A sample of **2** was hydrolyzed in the above manner. The precipitate was identified as yunganogenin C (**1a**) by TLC. *Rf*, 0.24 ($CHCl_3$: MeOH = 19 : 1), 0.19 (*n*-hexane : acetone = 3 : 1). After neutralization, the sugar mixture was subjected to TLC analysis [TLC, Kieselgel 60 (Merck Art 5553), *n*-PrOH–acetone–H_2O, 5 : 3 : 1, *Rf*: 0.77 (rhamnose), 0.43 (galactose), 0.51 (glucose), 0.11 (glucuronic acid); Reagent: *o*-aminobenzenesulfonic acid/2 M H_3PO_4]

D, L Determination of Sugars A sample of **2** (3 mg) was treated in the same manner as above. The derivatives were analyzed by GC. The t_R of the peaks was at 14.1 min (L-rhamnose), 20.5 (D-glucose) and 21.8 min (D-galactose).

Compound **3** (Wistariasaponin B_3): A white amorphous powder, $[\alpha]_D^{28}$ −2.0° (c=0.34, MeOH). IR (KBr): 3405 (ν_{O-H}), 1725 ($\nu_{C=O}$) cm^{-1}. HR FAB-MS *m/z*: 1113.5470 (Calcd for $C_{53}H_{86}O_{23}Na$: 1113.5457). Negative FAB-MS *m/z*: 1089 $[M-H]^-$, 943 $[M-H-rha]^-$, 811 $[M-H-rha-xyl]^-$, 635 $[M-H-rha-xyl-glc\ A]^-$. ^{1}H-NMR (in pyridine-d_5): 0.74, 0.95, 1.18, 1.22, 1.30, 1.50 (each 3H, s, *tert*-Me×6), 1.80 (3H, d, J=5.0 Hz, rha H-6), 5.37 (1H, s, H-12), 6.33 (1H, s, rha H-1). ^{13}C-NMR: Tables 1 and 2.

Identification of Sapogenol and Sugars for 3 A sample of **3** was hydrolized in the same manner as above. The precipitate was identified as **3a** (wistariasapogenol B, 3.4 mg), $[\alpha]_D^{25}$ +50.7° (c=0.35, pyridine). Negative FAB-MS *m/z*: 473 $[M-H]^-$. ^{1}H-NMR (in pyridine-d_5): 0.95, 1.02, 1.19, 1.25, 1.29, 1.58 (each 3H, s, *tert*-Me×6), 3.64 (1H, br d, J=11.4 Hz, H-3), 3.73 (1H, d, J=11.0 Hz, H-24), 3.81 (1H, br s, H-22), 3.94 (2H, s, H-30, 30′), 4.53 (1H, d, J=11.0 Hz, H-24′), 5.35 (1H, s, H-12). ^{13}C-NMR (in pyridine-d_5): 38.9, 28.7, 80.1, 43.2, 56.3, 19.1, 33.5, 40.0, 48.1, 37.0, 23.5, 122.7, 144.6, 42.3, 26.4, 28.4, 38.1, 45.2, 42.0, 35.9, 38.7, 75.1, 23.5, 64.6, 16.2, 17.0, 25.8, 21.2, 28.5, 70.2 (C-1—30). After neutralization, the sugar mixture was subjected to TLC analysis [TLC, Kieselgel 60 (Merck Art 5553), *n*-PrOH–acetone–H_2O, 5 : 3 : 1, *Rf*: 0.75 (rhamnose), 0.67 (xylose), 0.51 (glucose), 0.11 (glucuronic acid); Reagent: *o*-aminobenzenesulfonic acid/2 M H_3PO_4]

D, L Determination of Sugars A sample of **3** (3 mg) was treated in the same manner. The derivatives were analyzed by GC. The t_R of the

peaks was at 11.7 min (D-xylose), 14.2 min (L-rhamnose), and 20.6 min (D-glucose).

Compound **4** (Wistariasaponin A_2): A white amorphous powder, $[\alpha]_D^{25}$ $-12.3°$ ($c=0.30$, MeOH). IR (KBr): 3400 (ν_{O-H}), 1695 ($\nu_{C=O}$) cm^{-1}. HR FAB-MS *m/z*: 1111.5267 $[M+Na]^+$ ($C_{53}H_{84}O_{23}Na$, Calcd for 1111.5301). Negative FAB-MS: *m/z* 1087 $[M-H]^-$, 941 [M−H−rha]$^-$, 809 [M−H−rha−xyl]$^-$, 471 [M−H−rha−gal−glc A]$^-$. ^{1}H-NMR (in pyridine-d_5): 0.74, 0.86, 1.10, 1.14, 1.27, 1.55 (each 3H, s, *tert*-Me × 6), 1.82 (3H, d, $J=6.4$ Hz, rha H-6), 5.40 (1H, br s, H-12), 6.37 (1H, s, rha H-1). ^{13}C-NMR: Tables 1 and 2.

Identification of Sapogenol and Sugars for 4 A sample of **4** (4 mg) was hydrolyzed in the same manner. The precipitate was identified as **4a** (wistariasapogenol A, 1.3 mg), $[\alpha]_D^{25}$ $+53.4°$ ($c=0.13$, pyridine). Negative FAB-MS *m/z*: 471 $[M-H]^-$. ^{1}H-NMR (in pyridine-d_5): 0.94, 0.94, 1.15, 1.23, 1.30, 1.58 (each 3H, s *tert*-Me × 6), 3.6—3.8 (5H, m, H-3, 24, 24′, 30, 30′), 4.54 (1H, d, $J=11.0$ Hz, H-24′), 5.39 (1H, br s, H-12). ^{13}C-NMR (in pyridine-d_5): 38.8, 28.4, 80.0, 43.2, 56.3, 19.0, 33.3, 39.8, 47.9, 37.0, 24.0, 122.9, 142.1, 42.0, 25.5, 27.3, 47.8, 47.4, 42.9, 38.9, 47.0, 216.1, 23.5, 64.5, 16.2, 16.8, 25.4, 21.3, 26.9, 68.2 (C-1—30). After neutralization, the sugar mixture was subjected to TLC analysis [TLC, Kieselgel 60 (Merck Art 5553), *n*-PrOH–acetone–H_2O, 5 : 3 : 1, *Rf*: 0.75 (rhamnose), 0.67 (xylose), 0.51 (glucose), 0.11 (glucuronic acid); Reagent: *o*-aminobenzenesulfonic acid/2 M H_3PO_4]

D, L Determination of Sugars A sample of **4** (1 mg) was treated in the same manner. The derivatives were analyzed by GC. The t_R of the peaks was at 11.8 min (D-xylose), 14.1 min (L-rhamnose), and 20.6 min (D-glucose).

Compound **5** (Wistariasaponin A_3): A white amorphous powder, $[\alpha]_D^{25}$ $+11.2°$ ($c=0.38$, MeOH). IR (KBr): 3390 (ν_{O-H}), 1695 ($\nu_{C=O}$) cm^{-1}. HR FAB-MS *m/z*: 973.5015 $[M+H]^+$ (Calcd for $C_{48}H_{77}O_{20}$: 973.5008). Negative FAB-MS: *m/z* 971 $[M-H]^-$, 809 [M−H−gal]$^-$. ^{1}H-NMR (in pyridine-d_5): 0.71, 0.84, 1.11, 1.14, 1.23, 1.37 (each 3H, s, *tert*-Me × 6), 5.40 (1H, br s, H-12). ^{13}C-NMR: Tables 1 and 2.

Identification of Sapogenol and Sugars for 5 A sample of **5** was hydrolyzed in the above manner. The precipitate was identified as wistariasapogenol A (**4a**) by TLC. *Rf*, 0.37 ($CHCl_3$: MeOH : H_2O = 9 : 1 : 0.1). After neutralization, the sugar mixture was subjected to TLC analysis [TLC, Kieselgel 60 (Merck Art 5553), *n*-PrOH–acetone–H_2O, 5 : 3 : 1, *Rf*: 0.51 (glucose), 0.43 (galactose), 0.11 (glucuronic acid); Reagent: *o*-aminobenzenesulfonic acid/2 M H_3PO_4]

D, L Determination of Sugars A sample of **5** (3 mg) was treated in the same manner. The derivatives were analyzed by GC. The t_R of the peaks was at 20.5 (D-glucose) and 21.8 min (D-galactose).

Compound **6** (Astragaloside VIII): A white amorphous powder, $[\alpha]_D^{25}$ $-10.5°$ ($c=0.50$, MeOH). IR (KBr): 3410 (ν_{O-H}), 1725 ($\nu_{C=O}$) cm^{-1}. Negative FAB-MS: *m/z* 911 $[M-H]^-$. ^{1}H-NMR (in pyridine-d_5): 0.77, 0.97, 1.00, 1.22, 1.29, 1.31, 1.54 (each 3H, s, *tert*-Me × 7), 1.82 (3H, d, $J=5.1$ Hz, rha H-6), 5.31 (1H, s, H-12), 6.37 (1H, s, rha H-1). ^{13}C-NMR: Tables 1 and 2.

Compound **7** (Soyasaponin I): A white amorphous powder, $[\alpha]_D^{25}$ $-8.5°$ ($c=1.0$, MeOH). IR (KBr): 3405 (ν_{O-H}), 1610 ($\nu_{C=O}$, COO^- form) cm^{-1}. Negative FAB-MS: *m/z* 941 $[M-H]^-$. ^{1}H-NMR (in pyridine-d_5): 0.70, 0.90, 1.02, 1.20, 1.21, 1.24, 1.43 (each 3H, s, *tert*-Me × 7), 1.81 (3H, d, $J=5.5$ Hz, rha H-6), 5.28 (1H, s, H-12), 6.05 (1H, s rha H-1). ^{13}C-NMR: Tables 1 and 2.

Compound **8** (Subproside V): A white amorphous powder, $[\alpha]_D^{25}$ $+2.1°$ ($c=0.40$, MeOH). IR (KBr): 3400 (ν_{O-H}), 1735 ($\nu_{C=O}$) cm^{-1}. Negative FAB-MS: *m/z*1119 $[M-H]^-$, 973 [M−H−rha]$^-$, 811 [M−H−rha−gal]$^-$, 635 [M−H−rha−gal−glc A]$^-$. ^{1}H-NMR (in pyridine-d_5): 0.68, 0.94, 1.17, 1.22, 1.28, 1.47 (each 3H, s, *tert*-Me × 6), 1.78 (3H, d, $J=5.9$ Hz, rha H-6), 5.34 (1H, s, H-12), 6.23 (1H, s, rha H-1). ^{13}C-NMR: Tables 1 and 2.

Compound **9** (Robinioside I): A white amorphous powder, $[\alpha]_D^{25}$ $-10.3°$ ($c=0.39$, MeOH). IR (KBr): 3405 (ν_{O-H}), 1735 ($\nu_{C=O}$) cm^{-1}. Negative FAB-MS: *m/z* 1251 $[M-H]^-$. ^{1}H-NMR (in pyridine-d_5): 0.70, 0.92, 1.21, 1.26, 1.34, 1.45 (each 3H, s, *tert*-Me × 6), 1.82 (3H, d, $J=6.2$ Hz, rha H-6), 5.40 (1H, s, H-12), 6.16 (1H, s, rha H-1). ^{13}C-NMR: Tables 1 and 2.

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References and Notes

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