

Antisweet Natural Products. XI.¹⁾ Structures of Sitakisosides VI—X from *Stephanotis lutchuensis* KOIDZ. var. *japonica*

Kazuko YOSHIKAWA,* Hitomi TANINAKA, Yukiko KAN, and Shigenobu ARIHARA

Faculty of Pharmaceutical Sciences, Tokushima Bunri University, Yamashiro-cho, Tokushima 770, Japan.

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From the fresh stem of *Stephanotis lutchuensis* var. *japonica*, five new oleanane-type triterpenoid glycosides named sitakisosides VI—X (1—5) were isolated. Their structures were determined on the basis of spectroscopic data and chemical evidence. Sitakisosides VI and VII are 3-*O*- β -D-xylopyranosyl(1 $\rightarrow$ 6)- β -D-glucopyranosyl(1 $\rightarrow$ 6)- β -D-glucopyranosido-21-*O*-(6-*N*-methylantranilyl)- β -D-glucopyranosyl and 3-*O*- β -D-xylopyranosyl(1 $\rightarrow$ 6)- β -D-glucopyranosyl(1 $\rightarrow$ 6)- β -D-glucopyranosido-21-*O*-(4-*N*-methylantranilyl)- β -D-glucopyranosyl sitakisogenin, respectively. Sitakiside VIII is 3-*O*- β -D-xylopyranosyl(1 $\rightarrow$ 6)- β -D-glucopyranosyl(1 $\rightarrow$ 6)- β -D-glucopyranosido-21-*O*-*N*-methylantranilyl-3 β ,16 β ,21 β ,28-tetrahydroxyolean-12-ene-22-one. Sitakiside IX is 3-*O*- β -D-xylopyranosyl(1 $\rightarrow$ 6)- β -D-glucopyranosyl(1 $\rightarrow$ 6)- β -D-glucopyranosido-21-*O*-(6-*N*-methylantranilyl)- β -D-glucopyranosyl gymnastrogenin. Sitakiside X is 3-*O*- β -D-xylopyranosyl(1 $\rightarrow$ 6)- β -D-glucopyranosyl(1 $\rightarrow$ 6)- β -D-glucopyranosyl longispinogenin.

Keywords *Stephanotis lutchuensis* var. *japonica*; Asclepiadaceae; sitakiside; sitakisogenin; antisweet substance; *N*-methylantranilic acid

In the preceding paper¹⁾ of this series, we reported the isolation and structure determination of five antisweet principles named sitakisosides I—V, from the stem of *S. lutchuensis* var. *japonica* (Asclepiadaceae). Sitakisosides I, III, IV and V are 3-*O*- β -D-xylopyranosyl(1 $\rightarrow$ 6)- β -D-glucopyranosyl(1 $\rightarrow$ 6)- β -D-glucopyranosido-22-*O*-*N*-methylantranilyl, 3-*O*- β -D-xylopyranosyl(1 $\rightarrow$ 6)- β -D-glucopyranosyl(1 $\rightarrow$ 6)- β -D-glucopyranosido-28-*O*-*N*-methylantranilyl, 3-*O*- β -gentiotriosido 22-*O*-*N*-methylantranilyl and 3-*O*- β -D-xylopyranosyl(1 $\rightarrow$ 6)- β -D-glucopyranosyl(1 $\rightarrow$ 6)- β -D-glucopyranosido-22-*O*-tigloyl chichipegenin, respectively. Sitakiside II is 3-*O*- β -D-xylopyrano-

syl(1 $\rightarrow$ 6)- β -D-glucopyranosyl(1 $\rightarrow$ 6)- β -D-glucopyranosido-21-*O*-*N*-methylantranilyl marsglobiferin. In this paper, we report the isolation and structural elucidation of five additional novel saponins, sitakisosides VI—X (1—5), having an oleanene skeleton. Their structures were elucidated by chemical and spectral methods, two dimensional NMR (2D-NMR) techniques being especially helpful.

The EtOH extract obtained from the fresh stem of *S. lutchuensis* var. *japonica* was subjected to Amberlite XAD-2 column chromatography to give a saponin fraction. Repeated separation of the saponin fraction by HPLC gave five new compounds named sitakisosides VI (1), VII (2), VIII (3), IX (4) and X (5). ¹H-¹H correlation spectroscopy (¹H-¹H COSY), ¹H-¹³C COSY, total correlation spectroscopy (TOCSY), heteronuclear multiple-bond correlation (HMBC) and rotating frame Overhauser enhancement spectroscopy (ROESY) experiments provided sufficient information to enable us to construct the complete structures of 1—5, inclusive of the sequence of the sugar moieties and the positions of attachment of the acyl moiety and the sugar chains to the aglycone.

Sitakisosides VI (1) and VII (2) showed an intense blue fluorescence in methanol solution. An alkaline treatment with CH₃ONa-MeOH (1 : 3) of 1 and 2 released a methyl

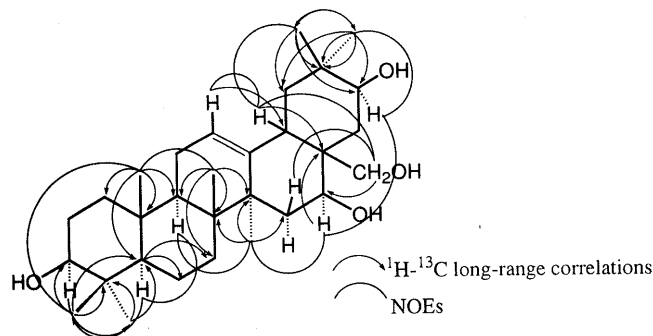


Fig. 1. Significant Correlations Observed in HMBC and NOEs of Sitakisogenin (7)

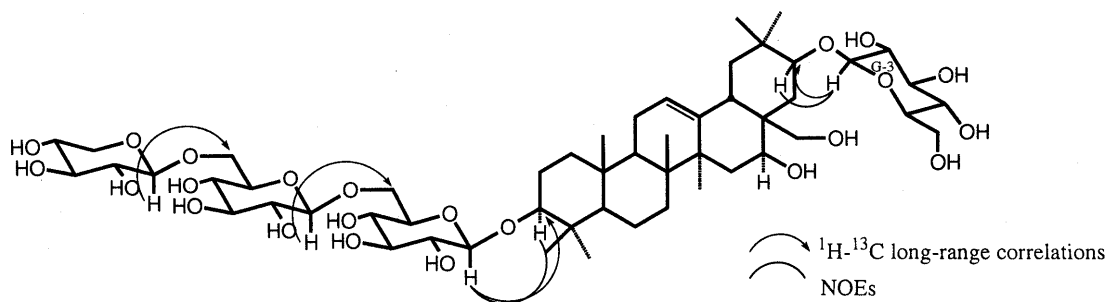


Fig. 2. Most Significant Correlations Observed in HMBC and NOEs of Compound 6

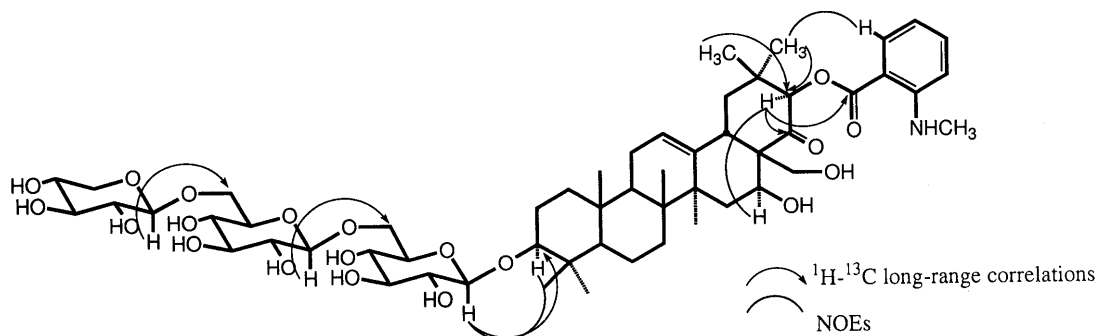


Fig. 3. Most Significant Correlations Observed in HMBC and NOEs of Shitakisoside VIII (3)

N-methylantranilate, which was shown to be identical with an authentic sample by TLC and NMR spectroscopy, and prosapogenin I (6). On acid hydrolysis, 6 afforded sitakissogenin (7) as an aglycone, besides D-glucose and D-xylose in molar ratio of 3:1, confirmed by specific rotation measurement using HPLC with chiral detection.

Sitakissogenin (7) showed an $[M - H_2O]^+$ ion peak at m/z 456.3628 in the HR-MS, suggesting the molecular formula to be $C_{30}H_{50}O_4$. The ^{13}C -NMR (DEPT) and 1H -NMR (D_2O exchange) spectra indicated the presence of seven methyls, eight methylenes, three methines, six quaternary carbons, one oxygen-bearing methylene, three oxygen-bearing methines and one double bond. The 1H - 1H COSY and TOCSY spectra of 7 revealed isolated spin systems (H-1—3, H-5—7, H-9—12, H-15—16, H-18—19, H-21—22). The gross structure of 7 was determined by analysis of NMR data including 1H - 1H COSY, 1H - ^{13}C COSY, HMBC and ROESY experiments (Fig. 1), and by referring to the data for gymnastrogenin (8).^{2,3} Thus, 7 is shown to be olean-12-ene-3 β ,16 β ,21 β ,28-tetrol.

Prosapogenin I (6) was deduced to have the molecular formula $C_{53}H_{88}O_{23}$ based on elemental analysis. The 1H - and ^{13}C -NMR spectra of 6 indicated the presence of three β -glucopyranosyl units [H-1: δ 4.86 (d, $J=7.8$ Hz), C-1: δ 107.0, H-1: δ 5.05 (d, $J=7.6$ Hz), C-1: δ 105.4, H-1: δ 5.08 (d, $J=7.6$ Hz), C-1: δ 106.5], and one β -xylopyranosyl unit [H-1: δ 4.94 (d, $J=7.3$ Hz), C-1: δ 106.0]. A ^{13}C -NMR spectral comparison of 6 with 7 showed glycosylation shifts^{4,5} of +10.6 ppm at the C-3 signal and 9.8 ppm at the C-21 signal, demonstrating the sugar linkages to be located at C-3-OH and C-21-OH. The sugar sequences were determined as follows. The negative FAB-MS of 6 showed the fragment ion peaks m/z 959 $[M - C_5H_8O_4 - H]^-$ and 797 $[M - C_5H_8O_4 - C_6H_{10}O_5 - H]^-$, disclosing a xylose to be terminal. In the ^{13}C -NMR spectrum of 6, the C-6 positions of each of two glucoses were shifted to δ 70.0 and 70.4 by the glycosylation shifts, showing that the sugar sequences were Xyl⁶Glc⁶Glc-O and Glc⁶Glc-O, or Glc⁶Glc-O, and Xyl⁶Glc1-O. In the HMBC experiment on 6, long-range correlations were observed between H-1 (δ 4.86) of the glucose (G-1) and C-3 (δ 89.0) of the aglycone, H-1 (δ 5.05) of the glucose (G-2) and C-6 (δ 70.4) of the glucose (G-1), and H-1 (δ 4.94) of the xylose and C-6 (δ 70.0) of the glucose (G-2), and H-1 (δ 5.08) of the glucose (G-3) and C-21 (δ 82.9) of the aglycone. Furthermore, NOEs were observed between H-1

(δ 4.86) of the glucose (G-1) and C-3-H (δ 3.34) of the aglycone, and H-1 (δ 5.08) of the glucose (G-3) and C-21-H (δ 4.16) of the aglycone (Fig. 2). Hence, 6 was formulated as 3-*O*- β -D-xylopyranosyl(1 $\rightarrow$ 6)- β -D-glucopyranosyl(1 $\rightarrow$ 6)- β -D-glucopyranosido-21-*O*- β -D-glucopyranosyl sitakissogenin.

Sitakissoside VI (1) had the molecular formula $C_{61}H_{95}NO_{24}$ based on elemental analysis. Comparison of the 1H - and ^{13}C -NMR spectra of 1 with those of 6 showed the 6 position of glucose joined to C-21-OH to be the acylation site in the former [$+0.77$ ppm, from δ 4.10 to 4.87 and $+0.56$ ppm, from δ 4.61 to 5.17 (C6-H2), $+0.6$ ppm, from δ 64.0 to 64.6 (C-6), -2.9 ppm, from δ 78.2 to 75.3 (C-5)]. Accordingly, 1 was formulated as 3-*O*- β -D-xylopyranosyl(1 $\rightarrow$ 6)- β -D-glucopyranosyl(1 $\rightarrow$ 6)- β -D-glucopyranosido-21-*O*-(6-*N*-methylantranilyl)- β -D-glucopyranosyl sitakissogenin.

Sitakissoside VII (2) had the same molecular formula, $C_{61}H_{95}NO_{24}$ (positive FAB-MS m/z 1226 $[M + H]^+$), as 1. Comparison of the 1H - and ^{13}C -NMR spectra of 2 with those of 6 showed the 4 position of glucose joined to C-21-OH to be the acylation site in the former [$+1.46$ ppm, from δ 4.20 to 5.66 and $+0.42$ ppm (C4-H), $+0.3$ ppm, from δ 72.6 to 72.9 (C-4), -2.3 ppm, from δ 78.5 to 76.2 (C-3), -1.8 ppm, from δ 78.2 to 76.4 (C-5)]. This was further confirmed by an HMBC experiment. A long-range correlation was seen between H-4 (δ 5.66) of the glucose (Glc-3) and the carbonyl carbon (δ 168.3) of the *N*-methylantranilyl group in the HMBC spectrum. Hence, 2 was formulated as 3-*O*- β -D-xylopyranosyl(1 $\rightarrow$ 6)- β -D-glucopyranosyl(1 $\rightarrow$ 6)- β -D-glucopyranosido-21-*O*-(4-*N*-methylantranilyl)- β -D-glucopyranosyl sitakissogenin.

Sitakissoside VIII (3) had the molecular formula $C_{55}H_{83}NO_{20}$ (negative FAB-MS, m/z 1076 $[M - H]^-$), i.e., 2 H less than that of sitakissoside II (9). On acid hydrolysis, 3 afforded several unresolved aglycone components, besides D-glucose and D-xylose in the ratio 2:1, confirmed by HPLC with chiral detection. The 1H - and ^{13}C -NMR spectra indicated that 3 was composed of 1 mol each of the aglycone, *N*-methylantranilic acid and xylose, and 2 mol of glucose. A ^{13}C -NMR spectral comparison of 3 with 9, showed that 3 differs structurally from 9 only in its E ring, though the same sugar units and the same acyl unit are affixed to the C-3 and E ring, respectively. The long-range correlation between a singlet signal at δ 6.20 and C-29/C-30 in the HMBC spectrum,

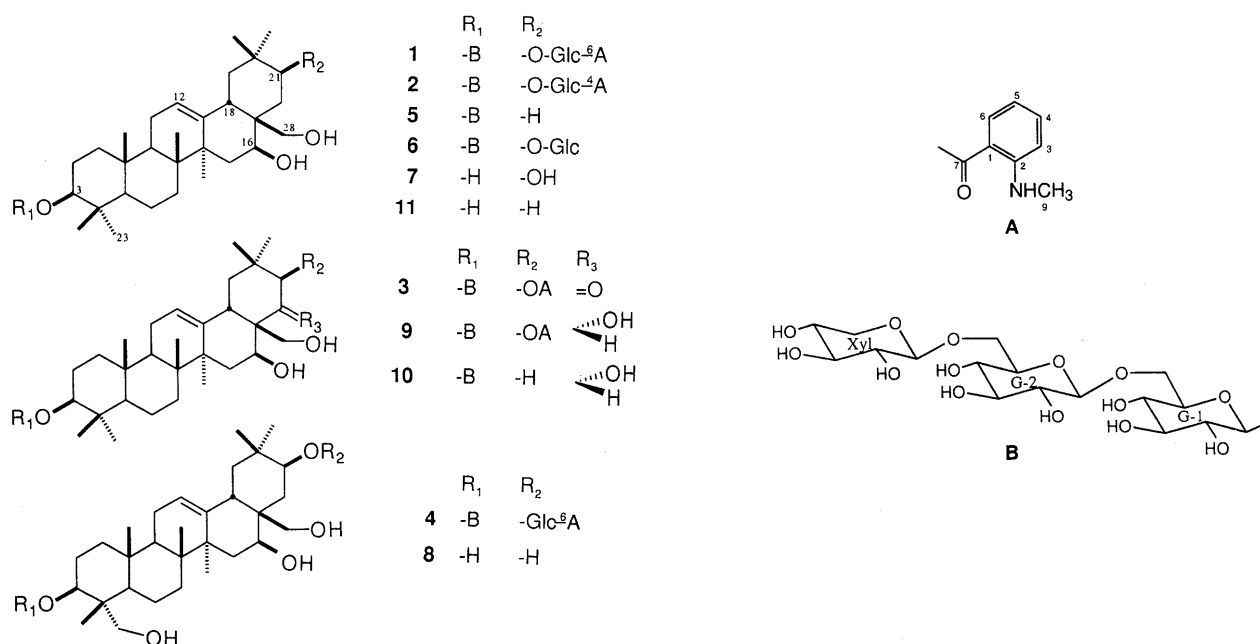


Chart 1

and an NOE between the former and H-29 at δ 1.09 in the ROESY spectrum of **3** (Fig. 3), indicated the presence of 21 β -OH. A long-range correlation between H-21 and carbonyl carbon at δ 206.6 established the site of the carbonyl at C-22. Hence, the aglycone of **3** was formulated as 3 β ,16 β ,21 β ,28-tetrahydroxyolean-12-ene-22-one, which has not been reported before. The HMBC experiment of **3** revealed that H-21 was coupled to the carbonyl of the acyl group, indicating the acyl group to be at C-21-OH. Further, reduction of **3** with lithium borohydride gave sitakissoside II (**9**). Accordingly, **3** was formulated as 3-*O*- β -D-xylopyranosyl(1 $\rightarrow$ 6)- β -D-glucopyranosyl(1 $\rightarrow$ 6)- β -D-glucopyranosido-21-*O*-*N*-methylantranilyl-3 β ,16 β ,21 β ,28-tetrahydroxyolean-12-ene-22-one.

Sitakissoside IX (**4**) had the molecular formula C₆₁H₉₅NO₂₅ (positive FAB-MS, m/z 1242 [M+H]⁺), i.e., one oxygen atom less than that of **1**. The ¹H- and ¹³C-NMR spectra indicated that **4** was composed of 1 mol each of the aglycone, *N*-methylantranilic acid and xylose, and 3 mol of glucose. On acid hydrolysis, **4** afforded gymnastrogenin (**8**), besides D-glucose and D-xylose in the ratio of 3:1, confirmed by HPLC with chiral detection. The C-3 and C-21 signals in the ¹³C-NMR spectrum of **4** appeared at lower field by 9.5 ppm and 11.4 ppm, respectively, than those of **8** because of the glycosylation shifts, demonstrating that sugar units are located at C-3-OH and C-21-OH of the aglycone. The carbon signals due to the sugar moieties and *N*-methylantranilyl group are superimposable on those of **1**, indicating that the sugar moieties are the same. Hence, the structure of sitakissoside IX (**4**) was established as 3-*O*- β -D-xylopyranosyl(1 $\rightarrow$ 6)- β -D-glucopyranosyl(1 $\rightarrow$ 6)- β -D-glucopyranosido-21-*O*-(6-*N*-methylantranilyl)- β -D-glucopyranosyl gymnastrogenin.

Sitakissoside X (**5**) had the molecular formula C₄₇H₇₈O₁₇ (FAB-MS, m/z 915 [M+H]⁺), i.e., one oxygen atom less than that of prosapogenin II (**10**) derived from sitakissoside I and showed no intense fluorescence in

methanol solution. The ¹H- and ¹³C-NMR spectra indicated that **5** was composed of 1 mol each of the aglycone and xylose, and 2 mol of glucose. On acid hydrolysis, **5** afforded longispinogenin (**11**),^{6,7} besides D-glucose and D-xylose in the ratio of 2:1, confirmed by HPLC with chiral detection. A ¹³C-NMR spectral comparison of **5** with **11** showed a glycosylation shift of +9.8 ppm at C-3, demonstrating sugar moieties to be located at C-3-OH. The carbon signals due to the sugar moieties are superimposable on those of **1**, indicating that the sugar moieties are the same. Hence, the structure of sitakissoside X (**5**) was established as 3-*O*- β -D-xylopyranosyl(1 $\rightarrow$ 6)- β -D-glucopyranosyl(1 $\rightarrow$ 6)- β -D-glucopyranosyl longispinogenin.

A 1 mM solution of any of sitakissosides VI–IX led to complete suppression of the sensation of sweetness induced by 0.2 M sucrose. Compound **5** was not active at all. The activities of sitakissosides VI–IX were half those of gymnemic acids III and IV.

Experimental

Melting points were measured with a Yanagimoto micromelting point apparatus, without correction. Optical rotations were taken on a JASCO DIP-140 digital polarimeter. IR and UV spectra were measured with JASCO FT/IR-5300 and Shimadzu UV-160. NMR spectra were recorded on Varian UNITY 200 and 600 spectrometers in C₅D₅N solution using TMS as an internal standard. NMR experiments included ¹H-¹H-COSY, ¹³C-¹H-COSY, DEPT, HMBC (512 $\times$ 1024 data matrix size, 128 scans, recycle delay=1.16 s), TOCSY and ROESY. Coupling constants (*J* values) are given in hertz (Hz). The high resolution-electron impact MS (HR-EI-MS) and the FAB-MS (Xe gun, 10 kV, *m*-nitrobenzyl alcohol as the matrix) were measured on JEOL JMS-HX-100 and JEOL JMS-PX303 mass spectrometers, respectively. For column chromatography, Kiesel gel 60 (230–400 mesh, Merck), and for TLC, Silica gel 60F-254 (Merck) were used. HPLC was carried out on a Waters ALC/GPC 244 instrument.

Isolation of Saponins The fresh stems (8.5 kg) of *S. lutchuensis* var. *japonica* collected in Tokushima Prefecture, in June 1993, were extracted with absolute EtOH at room temperature for 3 weeks. The ethanolic extract (540 g) was partitioned between H₂O and EtOAc. The water layer was passed through an Amberlite XAD-2 column. The column was

TABLE I. ^{13}C -NMR Spectral Data for 1–11 (in Pyridine- d_5 , 150 MHz)

Carbon	1	2	3	4	5	6	7	8	9	10	11
1	38.9	38.8	38.8	38.9	39.0	38.8	39.3	39.0	38.8	38.9	39.3
2	26.8	26.7	26.7	26.1	26.9	26.8	28.1	27.7	26.7	26.7	28.1
3	89.1	88.9	89.0	82.9	89.1	89.0	78.4	73.4	89.0	89.1	78.3
4	39.6	39.5	39.6	43.5	39.7	39.6	39.6	42.9	39.5	39.6	39.6
5	55.8	55.7	55.8	47.7	55.9	55.8	56.0	48.6	55.7	55.8	55.9
6	18.5	18.4	18.4	18.3	18.6	18.4	18.9	18.6	18.4	18.5	18.9
7	33.0	32.8	32.9	32.8	33.1	33.0	33.2	32.8	32.9	33.0	33.2
8	40.2	40.1	40.1	40.2	40.3	40.2	40.3	40.2	40.2	40.4	40.3
9	47.2	47.0	47.0	47.2	47.2	47.1	47.4	47.3	47.0	47.2	47.4
10	36.9	36.8	36.8	36.8	36.9	36.9	37.4	36.9	36.8	36.8	37.3
11	24.0	23.9	23.9	24.0	24.0	24.0	24.1	24.0	23.9	24.0	24.1
12	124.0	123.9	123.9	124.0	123.9	123.9	123.1	123.1	124.0	123.9	122.8
13	143.1	142.7	142.2	143.1	143.9	142.8	143.4	143.2	142.2	143.0	144.1
14	43.9	43.8	43.7	43.9	43.9	43.8	44.0	43.9	42.6	42.7	44.0
15	36.8	36.2	36.5	36.8	36.9	36.4	36.8	36.8	36.2	36.0	36.8
16	67.6	67.9	68.6	67.5	66.9	68.0	67.9	67.7	68.1	67.0	66.9
17	43.8	43.9	59.3	43.8	41.1	44.0	43.9	43.7	47.3	45.2	41.2
18	43.6	43.5	44.0	43.6	44.6	43.6	44.0	44.0	42.0	43.2	44.6
19	48.0	47.7	46.0	47.9	47.2	48.0	48.0	47.7	46.4	46.7	47.3
20	37.0	36.7	39.2	37.0	31.3	36.9	37.1	37.0	36.8	32.3	31.3
21	84.1	83.0	81.3	84.1	34.5	82.9	73.1	72.7	79.6	44.2	34.4
22	33.5	33.9	206.6	33.3	26.4	34.0	35.0	35.1	71.2	69.6	26.3
23	28.3	28.2	28.2	65.0	28.4	28.3	29.0	67.9	28.2	28.3	28.9
24	17.2	17.1	17.1	13.8	17.2	17.2	16.8	13.1	17.1	17.2	16.7
25	15.8	15.7	15.7	16.4	15.9	15.8	16.0	16.2	15.6	15.8	15.9
26	17.0	16.9	16.9	17.1	17.1	17.0	17.2	17.0	17.0	17.1	17.1
27	27.2	27.0	26.8	27.2	27.3	27.2	27.3	27.1	27.4	27.7	27.3
28	68.2	67.9	60.3	68.2	69.1	68.2	68.6	68.5	58.2	58.9	69.0
29	29.9	29.2	28.5	29.8	33.7	29.4	30.2	30.0	29.7	33.7	33.6
30	18.9	18.4	20.1	18.8	24.3	18.6	18.2	17.9	20.1	25.2	24.3
3-O-Glc (G-1)											
1	107.0	107.0	106.9	106.1	107.0	107.0			107.0	107.0	
2	75.0	75.0	75.0	75.0	75.0	75.0			75.0	75.0	
3	78.4 ^{a)}	78.4 ^{a)}	78.4 ^{a)}	78.4 ^{a)}	78.3 ^{a)}	78.3 ^{a)}			78.4 ^{a)}	78.3 ^{a)}	
4	71.5	71.5 ^{b)}	71.6	71.5	71.5	71.5			71.6	71.5	
5	77.1	77.0	77.0	77.1	77.0	77.1			77.0	77.0	
6	70.4	70.4	70.4	70.12	70.4	70.4			70.4	70.4	
Glc (G-2)											
1	105.4	105.4	105.4	105.4	105.4	105.4			105.4	105.4	
2	75.6	75.6	75.6	75.7	75.6	75.6			75.6	75.6	
3	78.6 ^{a)}	78.6 ^{a)}	78.5 ^{a)}	78.6 ^{a)}	78.6 ^{a)}	78.5 ^{a)}			78.6 ^{a)}	78.5 ^{a)}	
4	71.5	71.6 ^{b)}	71.6	71.5	71.5	71.5			71.6	71.5	
5	77.1	77.0	77.0	77.1	77.0	77.1			77.0	77.0	
6	69.9	69.8	69.9	79.9	69.9	70.0			69.9	69.9	
Xyl											
1	106.1	106.1	106.0	106.0	106.0	106.0			106.0	106.0	
2	74.9	74.9	74.9	74.9	74.9	74.9			74.9	74.9	
3	78.2	78.2	78.1	78.2	78.1	78.1			78.1	78.1	
4	71.1	71.1	71.2	71.2	71.2	71.2			71.2	71.2	
5	67.1	67.1	46.1	67.1	67.1	67.1			67.1	67.1	
21-O-Glc (G-3)											
1	106.5	106.5		106.4		106.5					
2	75.8	75.8		75.4		75.9					
3	78.6 ^{a)}	76.2		78.6		78.5 ^{a)}					
4	71.5	72.9		71.5		72.6					
5	75.3	76.4		75.8		78.2					
6	64.6	63.2		64.7		64.0					
Acyl moieties											
1	110.7	110.2	110.5	110.7					111.2		
2	152.3	152.6	152.6	152.3					152.6		
3	111.2	111.2	111.4	111.1					111.3		
4	135.1	135.7	135.3	135.1					134.8		
5	115.0	114.6	114.8	114.9					114.7		
6	132.6	132.0	132.2	132.6					132.0		
7	168.8	168.3	168.0	168.8					169.0		
9	29.6	29.4	29.4	29.6					29.5		

a, b) Assignments may be interchanged in each column.

washed with water, and the adsorbed materials were eluted with 100% MeOH to obtain the MeOH eluate (143 g). The MeOH eluate was chromatographed on Bondapak C₁₈ with 20–80% MeOH to give four fractions (frs. 1–4). Fraction 3 (20.0 g) was subjected to HPLC on ODS (Develosil Lop ODS, 60% CH₃OH) to give four fractions (frs. 3-1–4). Fraction 3-3 and fr. 3-4 were purified by preparative HPLC (YMC, ODS S-5, 27% CH₃CN) to afford sitakissosides VI (1, 480 mg), VII (2, 540 mg), IX (4, 150 mg) and X (5, 300 mg). Fraction 4 (22.5 g) was subjected to HPLC on ODS (Develosil Lop ODS, 70% CH₃OH) to give five fractions (frs. 4-1–5). Fraction 4-3 was purified by preparative HPLC (YMC, ODS S-5, 37% CH₃CN) to afford sitakissoside VIII (3, 210 mg). Fraction 4-2 was purified by preparative HPLC (YMC, ODS S-5, 27% CH₃CN) to afford 1 (140 mg), 2 (430 mg), 4 (75 mg) and 5 (460 mg). Sitakissosides I–V had been obtained from fr. 4-4 and fr. 4-5.

Sitakissoside VI (1). An amorphous powder, $[\alpha]_D^{20} -30.1^\circ$ ($c=7.7$, MeOH). IR (film) cm^{-1} : 3460, 1680, 1090. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 204 (4.11), 222 (4.27), 255 (3.86), 353 (3.61). Positive FAB-MS m/z : 1226 $[\text{M}(\text{C}_{61}\text{H}_{95}\text{NO}_{24})+\text{H}]^+$, 1094 $[\text{M}+\text{H}-\text{C}_8\text{H}_8\text{NO}_2]^+$. Anal. Calcd for $\text{C}_{61}\text{H}_{95}\text{NO}_{24}$: C, 59.74; H, 7.81; N, 1.14. Found: C, 60.00; H, 7.81; N, 1.54. ¹H-NMR (600 MHz, C₅D₅N) δ : 0.84 (H₃-25), 0.97 (H₃-26), 0.99 (H₃-24), 1.22 (H₃-30), 1.28 (H₃-23), 1.34 (H₃-27), 1.43 (H₃-29), 1.72 (1H, dd, $J=12.5, 4.3$ Hz, H_x-15), 2.06 (1H, dd, $J=12.5, 12.5$ Hz, H_p-22), 2.21 (1H, dd, $J=12.5, 11.0$ Hz, H_p-15), 2.52 (1H, dd, $J=11.5, 4.0$ Hz, H-18), 3.33 (1H, dd, $J=11.5, 4.5$ Hz, H-3), 3.56 (1H, dd, $J=12.5, 4.5$ Hz, H_x-22), 3.69, 4.34 (each 1H, d, $J=11.0$ Hz, H₂-28), ca. 4.18 (1H, m, H-21), 4.67 (1H, dd, $J=11.0, 4.3$ Hz, H-16), 5.24 (1H, m, H-12), ca. 4.30, 4.77 (each 1H, brd, $J=10.5$ Hz, H-6 of Glc-2), ca. 4.30, 4.89 (each 1H, brd, $J=11.0$ Hz, H-6 of Glc-1), 4.86 (1H, d, $J=7.8$ Hz, H-1 of Glc-1), 4.87, 5.17 (each 1H, brd, $J=10.5$ Hz, H-6 of Glc-3), 4.94 (1H, d, $J=7.6$ Hz, H-1 of Xyl), 5.04 (1H, d, $J=7.6$ Hz, H-1 of Glc-2), 5.09 (1H, d, $J=7.8$ Hz, H-1 of Glc-3). Acyl part: 2.67 (3H, d, $J=4.1$ Hz, N-CH₃), 6.56 (1H, dd, $J=8.0, 1.2$ Hz, H-3), 6.67 (1H, ddd, $J=8.0, 8.0, 1.2$ Hz, H-5), 7.33 (1H, ddd, $J=8.0, 8.0, 1.2$ Hz, H-4), 7.82 (1H, q, $J=4.1$ Hz, NH), 8.29 (1H, dd, $J=8.0, 1.2$ Hz, H-6). ¹³C-NMR: Table I.

Sitakissoside VII (2). Colorless needles from MeOH, mp 214–216°C $[\alpha]_D^{20} -36.0^\circ$ ($c=6.5$, MeOH). IR (film) cm^{-1} : 3460, 1680, 1090. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 222 (4.34), 254 (3.86), 356 (3.70). Positive FAB-MS m/z : 1226 $[\text{M}(\text{C}_{61}\text{H}_{95}\text{NO}_{24})+\text{H}]^+$, 1094 $[\text{M}-\text{C}_8\text{H}_8\text{NO}_2+\text{H}]^+$. Anal. Calcd for $\text{C}_{61}\text{H}_{95}\text{NO}_{24}$: C, 59.74; H, 7.81; N, 1.14. Found: C, 59.58; H, 8.10; N, 1.27. ¹H-NMR (600 MHz, C₅D₅N) δ : 0.84 (H₃-25), 0.94 (H₃-26), 0.99 (H₃-24), 1.20 (H₃-30), 1.24 (H₃-27), 1.26 (H₃-23), 1.40 (H₃-29), 1.67 (1H, dd, $J=12.1, 4.3$ Hz, H_x-15), 2.09 (1H, dd, $J=12.8, 12.8$ Hz, H_p-22), 2.16 (1H, dd, $J=12.1, 12.1$ Hz, H_p-15), 2.53 (1H, dd, $J=11.4, 4.3$ Hz, H-18), 3.34 (1H, dd, $J=11.4, 4.3$ Hz, H-3), 3.54 (1H, dd, $J=12.8, 4.0$ Hz, H_x-22), 3.73, 4.33 (each 1H, d, $J=10.3$ Hz, H₂-28), ca. 4.20 (1H, m, H-21), ca. 4.31, 4.79 (each 1H, brd, $J=10.0$ Hz, H-6 of Glc-2), ca. 4.31, 4.91 (each 1H, brd, $J=11.0$ Hz, H-6 of Glc-1), 4.48 (1H, dd, $J=9.5, 9.0$ Hz, H-4 of Glc-3), 4.66 (1H, dd, $J=12.1, 4.3$ Hz, H-16), 5.22 (1H, m, H-12), 4.88 (1H, d, $J=7.5$ Hz, H-1 of Glc-1), 4.96 (1H, d, $J=7.3$ Hz, H-1 of Xyl), 5.06 (1H, d, $J=7.8$ Hz, H-1 of Glc-2), 5.17 (1H, d, $J=7.8$ Hz, H-1 of Glc-3), 5.66 (1H, dd, $J=9.5, 9.5$ Hz, H-4 of Glc-3). Acyl part: 2.65 (3H, d, $J=4.9$ Hz, N-CH₃), 6.59 (1H, ddd, $J=8.0, 8.0, 1.5$ Hz, H-5), 6.61 (1H, dd, $J=8.0, 1.5$ Hz, H-3), 7.38 (1H, ddd, $J=8.0, 8.0, 1.5$ Hz, H-4), 7.81 (1H, q, $J=4.9$ Hz, NH), 8.11 (1H, dd, $J=8.0, 1.5$ Hz, H-6). ¹³C-NMR: Table I.

Sitakissoside VIII (3). An amorphous powder, $[\alpha]_D^{20} -8.0^\circ$ ($c=2.5$, MeOH). IR (film) cm^{-1} : 3400, 1700, 1680. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 224 (4.41), 254 (3.92), 349 (3.70). Negative FAB-MS m/z : 1076 $[\text{M}(\text{C}_{55}\text{H}_{83}\text{NO}_{20})-\text{H}]^-$. Anal. Calcd for $\text{C}_{55}\text{H}_{83}\text{NO}_{20}$: C, 58.81; H, 7.90; N, 1.25. Found: C, 58.78; H, 7.95; N, 1.53. ¹H-NMR (600 MHz, C₅D₅N) δ : 0.86 (H₃-25), 0.95 (H₃-26), 1.01 (H₃-24), 1.22 (H₃-29), 1.24 (H₃-30), 1.30 (H₃-23), 1.42 (H₃-27), 3.36 (1H, dd, $J=12.0, 5.0$ Hz, H-18), 3.38 (1H, dd, $J=12.0, 4.5$ Hz, H-3), 4.08, 4.75 (each 1H, d, $J=11.0$ Hz, H₂-28), 5.16 (1H, dd, $J=11.0, 4.8$ Hz, H-16), 5.44 (1H, m, H-12), 6.20 (1H, s, H-21), 4.89 (1H, d, $J=7.8$ Hz, H-1 of Glc-1), 4.96 (1H, d, $J=7.8$ Hz, H-1 of Xyl), 5.07 (1H, d, $J=7.8$ Hz, H-1 of Glc-2). Acyl part: 2.66 (3H, d, $J=5.4$ Hz, N-CH₃), 6.68 (1H, dd, $J=7.8, 1.7$ Hz, H-3), 6.74 (1H, ddd, $J=7.8, 7.8, 1.7$ Hz, H-5), 7.44 (1H, ddd, $J=7.8, 7.8, 1.7$ Hz, H-4), 7.87 (1H, q, $J=5.4$ Hz, NH), 8.35 (1H, dd, $J=7.8, 1.7$ Hz, H-6). ¹³C-NMR: Table I.

Sitakissoside IX (4). Colorless needles from MeOH, mp 209–211°C, $[\alpha]_D^{20} -25.1^\circ$ ($c=0.8$, MeOH). IR (film) cm^{-1} : 3400, 1680. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 203 (4.15), 222 (4.23), 255 (3.99), 349 (3.54). Positive FAB-MS m/z : 1242 $[\text{M}(\text{C}_{61}\text{H}_{95}\text{NO}_{25})+\text{H}]^+$, negative FAB-MS m/z : 1240

$[\text{M}-\text{H}]^-$, 1108 $[\text{M}-\text{H}-\text{C}_8\text{H}_8\text{O}_4]^-$. Anal. Calcd for $\text{C}_{61}\text{H}_{95}\text{NO}_{25}$: 3/2H₂O: C, 57.72; H, 7.78; N, 1.10. Found: C, 57.96; H, 7.97; N, 1.11. ¹H-NMR (600 MHz, C₅D₅N) δ : 0.93 (H₃-25), 0.98 (H₃-24), 1.00 (H₃-26), 1.20 (H₃-30), 1.25 (H₃-27), 1.38 (H₃-29), 2.52 (1H, dd, $J=11.5, 4.0$ Hz, H-18), ca. 2.06 (1H, m, H_p-22), 3.54 (1H, dd, $J=12.0, 4.5$ Hz, H_x-22), 3.68, 4.32 (each 1H, d, $J=10.5$ Hz, H₂-28), 3.70, 4.35 (each 1H, d, $J=10.8$ Hz, H₂-23), ca. 4.14 (1H, m, H-21), ca. 4.24 (1H, m, H-3), ca. 4.30, 4.78 (each 1H, brd, $J=10.5$ Hz, H-6 of Glc-2), ca. 4.30, 4.81 (each 1H, brd, $J=10.5$ Hz, H-6 of Glc-1), 4.62 (1H, dd, $J=11.0, 4.5$ Hz, H-16), 4.89 (1H, dd, $J=10.3, 4.5$ Hz, H-6 of Glc-3), 5.24 (1H, m, H-12), 4.93 (1H, d, $J=7.4$ Hz, H-1 of Xyl), 5.02 (1H, d, $J=7.8$ Hz, H-1 of Glc-2), 5.08 (1H, d, $J=7.6$ Hz, H-1 of Glc-1), 5.08 (1H, d, $J=7.6$ Hz, H-1 of Glc-3), 5.17 (1H, brd, $J=10.3$ Hz, H-6 of Glc-3). Acyl part: 2.67 (3H, d, $J=4.2$ Hz, N-CH₃), 6.56 (1H, dd, $J=8.0, 1.2$ Hz, H-3), 6.65 (1H, ddd, $J=8.0, 8.0, 1.2$ Hz, H-5), 7.32 (1H, ddd, $J=8.0, 8.0, 1.2$ Hz, H-4), 7.82 (1H, q, $J=4.2$ Hz, NH), 8.28 (1H, dd, $J=8.0, 1.2$ Hz, H-6). ¹³C-NMR: Table I.

Sitakissoside X (5). Colorless needles from MeOH, mp 213–215°C, $[\alpha]_D^{20} -16.7^\circ$ ($c=4.8$, MeOH). IR (film) cm^{-1} : 3400, 1680. Positive FAB-MS m/z : 915 $[\text{M}(\text{C}_{47}\text{H}_{78}\text{O}_{17})+\text{H}]^+$, 897 $[\text{M}+\text{H}-\text{H}_2\text{O}]^+$, 765 $[\text{M}+\text{H}-\text{H}_2\text{O}-\text{C}_5\text{H}_8\text{O}_4]^+$, 603 $[\text{M}+\text{H}-\text{H}_2\text{O}-\text{C}_5\text{H}_8\text{O}_4-\text{C}_6\text{H}_{10}\text{O}_5]^+$. Anal. Calcd for $\text{C}_{47}\text{H}_{78}\text{O}_{17}$ ·9/2H₂O: C, 56.67; H, 8.80. Found: C, 56.51; H, 8.64. ¹H-NMR (600 MHz, C₅D₅N) δ : 0.85 (H₃-25), 0.96 (H₃-26), 1.00 (H₃-24), 1.00 (H₃-29), 1.02 (H₃-30), 1.27 (H₃-23), 1.33 (H₃-27), ca. 1.75 (1H, m, H_x-15), 2.24 (1H, dd, $J=12.2, 10.5$ Hz, H_p-15), 2.81 (1H, d, $J=11.5, 4.0$ Hz, H-18), 3.32 (1H, dd, $J=11.5, 4.3$ Hz, H-3), 3.68, 4.42 (each 1H, d, $J=10.4$ Hz, H₂-28), 4.66 (1H, dd, $J=10.5, 4.5$ Hz, H-16), 5.23 (1H, m, H-12), 4.87 (1H, d, $J=7.5$ Hz, H-1 of Glc-1), 4.95 (1H, d, $J=7.5$ Hz, H-1 of Xyl), 5.05 (1H, d, $J=7.8$ Hz, H-1 of Glc-2). ¹³C-NMR: Table I.

Alkaline Hydrolysis of Sitakissoside VI (1) To a solution of 1 (100 mg) in MeOH (1.5 ml) was added dropwise 28% sodium methoxide (0.5 ml), under an N₂ atmosphere. The mixture was stirred for 4 h at room temperature. The reaction mixture was acidified with dilute HCl, and extracted with CHCl₃ and then 1-BuOH. From the CHCl₃ layer, methyl *N*-methylanthranilate (15 mg) was obtained. Methyl *N*-methylanthranilate, pale yellow oil. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 221 (4.24), 253 (3.72), 349 (3.57). IR (film) cm^{-1} : 3380, 2940, 1680, 1605, 1580, 1440, 1260, 1250. EI-MS m/z : 165 $[\text{M}]^+$. ¹H-NMR (200 MHz, C₅D₅N) δ : 2.73 (3H, d, $J=5.0$ Hz, N-CH₃), 3.76 (3H, s, COOCH₃), 6.67 (1H, ddd, $J=8.1, 8.1, 1.8$ Hz, H-5), 6.68 (1H, dd, $J=8.1, 1.8$ Hz, H-3), 7.43 (1H, ddd, $J=8.1, 8.1, 1.8$ Hz, H-4), 8.00 (1H, dd, $J=8.1, 1.8$ Hz, H-6). ¹³C-NMR (50 MHz, C₅D₅N) δ : 29.5 (N-CH₃), 51.5 (COOCH₃), 110.3 (C-1), 111.4 (C-3), 114.8 (C-5), 132.0 (C-6), 135.3 (C-4), 152.5 (C-2), 169.1 (C-7). The 1-BuOH layer was subjected to HPLC (YMC, ODS S-5, 20% CH₃CN) to provide 6 (60 mg). Compound 6, an amorphous powder, $[\alpha]_D^{20} -16.4^\circ$ ($c=5.3$, MeOH). IR (film) cm^{-1} : 3400, 3250. Negative FAB-MS m/z : 1091 $[\text{M}(\text{C}_{53}\text{H}_{88}\text{O}_{23})-\text{H}]^-$, 959 $[\text{M}-\text{H}-\text{C}_5\text{H}_8\text{O}_4]^-$, 797 $[\text{M}-\text{H}-\text{C}_5\text{H}_8\text{O}_4-\text{C}_6\text{H}_{10}\text{O}_5]^-$. Anal. Calcd for $\text{C}_{53}\text{H}_{88}\text{O}_{23}$ ·3/2H₂O: C, 57.75; H, 8.14. Found: C, 57.94; H, 8.37. ¹H-NMR (600 MHz, C₅D₅N) δ : 0.84 (H₃-25), 0.95 (H₃-26), 0.99 (H₃-24), 1.20 (H₃-30), 1.26 (H₃-23), 1.26 (H₃-27), 1.36 (H₃-29), 1.68 (1H, dd, $J=12.5, 4.3$ Hz, H_x-15), ca. 2.06 (1H, m, H_p-22), 2.17 (1H, dd, $J=12.5, 12.5$ Hz, H_p-15), 2.52 (1H, dd, $J=11.5, 4.0$ Hz, H-18), 3.34 (1H, dd, $J=11.5, 4.5$ Hz, H-3), 3.53 (1H, dd, $J=12.5, 4.5$ Hz, H_x-22), 3.73, 4.34 (each 1H, d, $J=11.0$ Hz, H₂-28), 4.68 (1H, dd, $J=12.5, 4.3$ Hz, H-16), 5.24 (1H, m, H-12), ca. 4.10 (1H, brd, $J=9.5$ Hz, H-6 of Glc-3), ca. 4.30 (2H, brd, $J=11.0$ Hz, H-6 of Glc-1 and Glc-2), 4.61 (1H, brd, $J=9.5$ Hz, H-6 of Glc-3), 4.78 (1H, brd, $J=11.0$ Hz, H-6 of Glc-2), 4.86 (1H, d, $J=7.8$ Hz, H-1 of Glc-1), 4.90 (1H, brd, $J=11.0$ Hz, H-6 of Glc-1), 4.94 (1H, d, $J=7.3$ Hz, H-1 of Xyl), 5.05 (1H, d, $J=7.6$ Hz, H-1 of Glc-2), 5.08 (1H, d, $J=7.6$ Hz, H-1 of Glc-3). ¹³C-NMR: Table I.

Acid Hydrolysis of Prosapogenin I (6) A solution of 6 (150 mg) in 5% H₂SO₄ was heated at 100°C for 8 h. The reaction mixture was extracted with EtOAc and purified by HPLC (YMC, ODS S-5, 37% CH₃CN) to provide sitakissogenin (7, 25 mg). Compound 7, colorless needles from MeOH, mp 333–335°C, $[\alpha]_D^{20} +57.0^\circ$ ($c=0.9$, CHCl₃:MeOH=1:1). HR-EI-MS Obsd for $[\text{M}(\text{C}_{30}\text{H}_{50}\text{O}_4)-\text{H}_2\text{O}]^+$ 456.3628, Calcd 456.3604. ¹H-NMR (400 MHz, C₅D₅N) δ : 0.93 (H₃-25), 1.04 (H₃-24), 1.06 (H₃-26), 1.25 (H₃-23), 1.29 (H₃-29), 1.29 (H₃-30), 1.35 (H₃-27), 2.13 (1H, dd, $J=13.2, 13.2$ Hz, H_p-22), 2.64 (1H, dd, $J=13.4, 4.1$ Hz, H-18), 3.28 (1H, dd, $J=13.2, 4.2$ Hz, H_x-22), 3.48 (1H, dd, $J=8.2, 8.2$ Hz, H-3), 3.80, 4.43 (each 1H, d, $J=10.6$ Hz, H₂-28), 4.18 (1H, dd, $J=13.2, 4.2$ Hz, H-21), 4.74 (1H, dd, $J=11.8, 4.8$ Hz, H-16), 5.38 (1H,

m, H-12). For ^{13}C -NMR: Table I. The aqueous layer was neutralized with Amberlite IR-35 and evaporated *in vacuo* to dryness. The sugar was determined by using refractive index (RI) detection (Waters 410) and chiral detection (Shodex OR-1) in HPLC (Shodex RSpak DC-613, 80% CH_3CN , 0.8 ml/min, 70 °C) by comparison with authentic sugars (10 mm each of D-Glc, L-Glc and D-Xyl, L-Xyl). The sugar part gave positive peaks at 8.80 min (D-Xyl, 8.78 min) and 13.40 min (D-Glc; 13.38 min).

Alkaline Hydrolysis of Sitakisoside VI (2) Alkaline hydrolysis of **2** (100 mg) was carried out in the same way as described for **1** to give methyl *N*-methylantranilate (13 mg) from the CHCl_3 layer, and **6** (60 mg) from the 1-BuOH layer.

Identification of Component Sugars of Sitakisoside VIII (3) A solution of compound **3** (3 mg) was examined in the same way as described for **6**. The sugar part gave D-Xyl and D-Glc.

LiBH_4 Reduction of Sitakisoside VIII (3) A solution of **3** (50 mg) and LiBH_4 (50 mg) in MeOH (5 ml) was stirred for 1 h at room temperature and worked up as usual. The reaction mixture (50 mg) was purified by HPLC (YMC, ODSS-5, 37% CH_3CN) to afford **8** (25 mg) and **3** (10 mg).

Acid Hydrolysis of Sitakisoside IX (4) A solution of **4** (100 mg) in 5% H_2SO_4 (10 ml) was heated at 100 °C for 2 h. The reaction mixture was extracted with EtOAc to provide an aglycone (**8**, 25 mg). Compound **8**, colorless needles from MeOH, mp 290–291 °C $[\alpha]_{\text{D}}^{20} + 53.1^\circ$ ($c = 2.4$, MeOH) was identified as gymnastrogenin (lit.²¹) mp 288–289 °C, $[\alpha]_{\text{D}}^{20} + 53.5^\circ$ ($c = 0.71$, MeOH) by comparison of spectral data with literature values.³⁾ EI-MS m/z 490 $[\text{M}]^+$. Anal. Calcd for $\text{C}_{30}\text{H}_{50}\text{O}_5 \cdot \text{H}_2\text{O}$: C, 70.83; H, 10.30. Found: C, 70.49; H, 10.12. ^1H -NMR (200 MHz, $\text{C}_5\text{D}_5\text{N}$) δ : 1.00 (H₃-25), 1.06 (H₃-24), 1.06 (H₃-26), 1.25 (H₃-29), 1.27 (H₃-30), 1.31 (H₃-27), 2.03 (1H, dd, $J = 14.0, 14.0$ Hz, H_x-19), 2.11 (1H, dd, $J = 13.0, 13.0$ Hz, H_β-22), 2.62 (1H, dd, $J = 14.0, 4.5$ Hz, H-18), 3.27 (1H, dd, $J = 13.0, 4.5$ Hz, H_x-22), 3.71, 4.18 (each 1H, d, $J = 10.2$ Hz, H₂-23), 3.78, 4.41 (each 1H, d, $J = 10.2$ Hz, H₂-28), 4.14 (1H, dd, $J = 13.0, 4.5$ Hz, H-21), ca. 4.20 (1H, m, H-3), 4.70 (1H, dd, $J = 10.5, 5.5$ Hz, H-16), 5.36 (1H, m, H-12). ^{13}C -NMR: Table I. The detection of the component sugars was carried out in the same way as described for **6**. The sugar

part gave D-Xyl and D-Glc.

Acid Hydrolysis of Sitakisoside X (5) A solution of **5** (100 mg) in 5% H_2SO_4 (10 ml) was heated at 100 °C for 2 h. The reaction mixture was extracted with EtOAc to provide an aglycone (**11**, 25 mg). Compound **11**, colorless needles from MeOH, mp 216–218 °C, $[\alpha]_{\text{D}}^{20} + 38.7^\circ$ ($c = 2.5$, CHCl_3) was identified as longispinogenin (lit.⁷⁾ mp 218–220 °C, $[\alpha]_{\text{D}}^{20} + 51^\circ$ (CHCl_3) by comparison of spectral data with literature values.^{7,8)} EI-MS m/z 458 $[\text{M}]^+$. HR-EI-MS Obsd for $\text{C}_{30}\text{H}_{50}\text{O}_3$ 458.3755, Calcd 458.3760. ^1H -NMR (200 MHz, $\text{C}_5\text{D}_5\text{N}$) δ : 0.95 (H₃-25), 0.95 (H₃-30), 1.03 (H₃-24), 1.06 (H₃-26), 1.06 (H₃-29), 1.25 (H₃-23), 1.36 (H₃-27), 3.47 (1H, dd, $J = 8.0, 8.0$ Hz, H-3), 3.71, 4.44 (each 1H, d, $J = 10.3$ Hz, H₂-28), 4.68 (1H, dd, $J = 12.0, 4.5$ Hz, H-16), 5.33 (1H, m, H-12). ^{13}C -NMR: Table I. The detection of the component sugars was carried out in the same way as described for **6**. The sugar part gave D-Xyl and D-Glc.

Bioassay of Antisweet Activity The antisweet activity of 1 mM solutions of **1**–**5** was tested on three volunteers. Each participant held the test solutions in the mouth for 3 min, spat, rinsed the mouth with distilled water and tasted a 0.2 M sucrose solution.

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