

Antisweet Natural Products. XII.¹⁾ Structures of Sitakisosides XI–XX from *Stephanotis lutchuensis* KOIDZ. var. *japonica*

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From the fresh stem of *Stephanotis lutchuensis* var. *japonica*, ten new oleanane-type triterpenoid glycosides, named sitakisosides XI–XX (1–10), were isolated. Their structures were determined on the basis of spectroscopic data and chemical evidence. The results show that all have a 3-*O*- β -D-xylopyranosyl(1 $\rightarrow$ 6)- β -D-glucopyranosyl(1 $\rightarrow$ 6)- β -D-glucopyranosyl moiety and the aglycones of sitakisosides XI–XV, XVI and XVII, XVIII and XIX, and XX are sitakisogenin, chichiogenin, marsglobiferin and longispinogenin, respectively. Sitakisosides XI–XIII, XVI and XVIII, having an acyl group, showed antisweet activity.

Key words *Stephanotis lutchuensis* var. *japonica*; Asclepiadaceae; sitakisoside; oleanane triterpene; antisweet substance; *N*-methylantranilic acid

In the preceding paper^{1,2)} of this series, we reported the isolation and structure determination of four antisweet principles named sitakisosides VI–IX, and of sitakisoside X, from the stem of *Stephanotis lutchuensis* KOIDZ. var. *japonica* (Asclepiadaceae). In this paper, we report the isolation, structural elucidation and antisweet activity of ten additional novel saponins, sitakisosides XI–XX (1–10), having an oleanene skeleton. Their structures were elucidated by chemical and spectral methods, 2D-NMR techniques having been specially helpful.

The EtOH extract obtained from the fresh stem of *Stephanotis lutchuensis* KOIDZ. var. *japonica* was subjected to Amberlite XAD-2 column chromatography to give a saponin fraction. Repeated separation of the saponin fraction by HPLC gave ten new compounds named sitakisosides XI (1), XII (2), XIII (3), XIV (4), XV (5), XVI (6), XVII (7), XVIII (8), XIX (9) and XX (10). 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 1–10.

Sitakisoside XIV (4), an amorphous powder, C₅₃H₈₈O₂₃ was identified as deacylated sitakisoside VI²⁾ by direct comparison with an authentic sample.

Sitakisoside XIII (3) had the molecular formula C₆₁H₉₅NO₂₄ (positive FAB-MS, *m/z* 1248 [M+Na]⁺) and showed an intense blue fluorescence in methanol solution. On acid hydrolysis, 3 afforded sitakisogenin (11)²⁾ mp 333–335 °C, [α]_D²⁰ –57.0° (*c*=0.9, MeOH), C₃₀H₅₀O₄ (positive FAB-MS *m/z*: 497 [M+Na]⁺) as an aglycone, besides D-glucose and D-xylose in a molar ratio of 3:1 (confirmed by specific rotation measurement using HPLC with chiral detection) as sugar components. The ¹H- and ¹³C-NMR spectra of 3 indicated the presence of three β -glucopyranosyl units [H-1: δ 4.88 (d, *J*=7.5 Hz), C-1: δ 107.0, H-1: δ 5.06 (d, *J*=8.0 Hz), C-1: δ 105.4, H-1: δ 5.14 (d, *J*=8.0 Hz), C-1: δ 106.2], and one β -xylopyranosyl unit [H-1: δ 4.95 (d, *J*=7.5 Hz), C-1: δ 106.0]. Alkaline treatment with CH₃ONa–MeOH (1:3) of 3 released a methyl *N*-methylantranilate, which was identical with an authentic sample, and sitakisoside XIV (4). The location

of the *N*-methylantraniloyl group in 3 was determined by spectral comparison of 3 and 4, and by an HMBC experiment on 3. Thus, acylation shifts were observed at the 3 position of glucose (G-3) joined to C-21-OH [+1.92 ppm, from δ 4.18 to 6.10 (H-3), –2.2 ppm, from δ 76.0 to 73.8 (C-2), +0.4 ppm, from δ 78.8 to 79.2 (C-3), and –2.3 ppm, from δ 72.7 to 70.4 (C-4)]. In the HMBC spectrum, the ester carbon signal of the *N*-methylantraniloyl group at δ 168.8 was correlated with H-3 (δ 6.10) of the G-3, establishing that in 3, H-3 of the C-21-*O*-glc was acylated. Accordingly, 3 was formulated as 3-*O*- β -D-

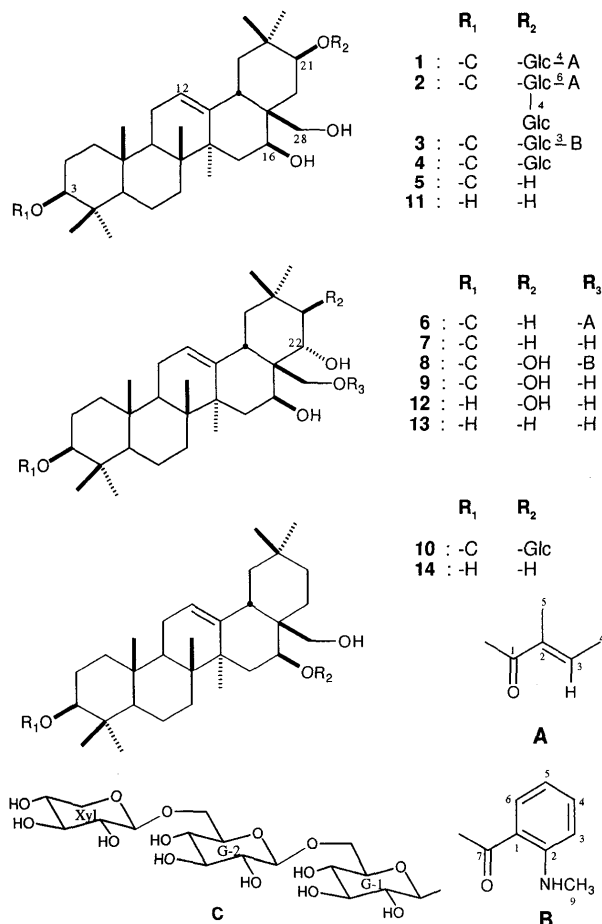


Chart 1

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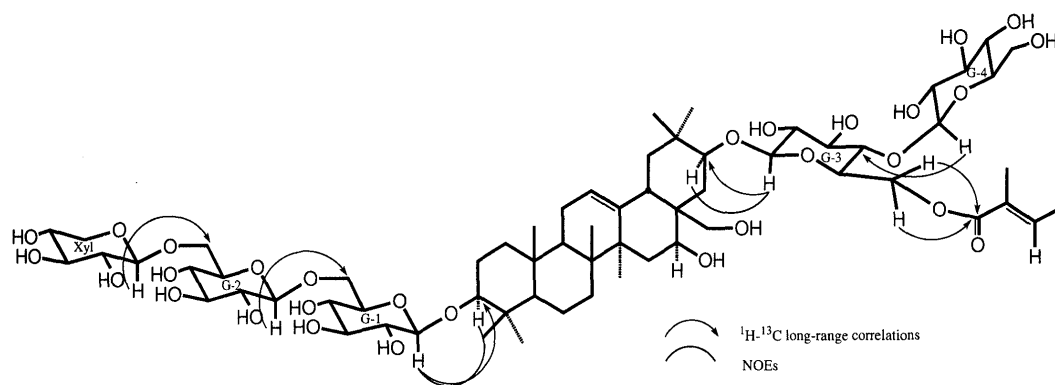


Fig. 1. Most Significant Correlations Observed in HMBC and ROESY Experiments for Sitakissoside XII (2)

xylopyranosyl(1→6)-β-D-glucopyranosyl(1→6)-β-D-glucopyranosido-21-*O*-3-*N*-methylantraniloyl-β-D-glucopyranosyl sitakissogenin.

Sitakissoside XI (**1**) had the molecular formula $C_{58}H_{94}O_{24}$ (positive FAB-MS, m/z 1197 $[M + Na]^+$), *i.e.*, 82 mass units (C_5H_6O) higher than that of **4**, and showed no intense fluorescence in methanol solution. Acid hydrolysis of **1** afforded **11**, and D-glucose and D-xylose in the ratio of 3:1. On alkaline hydrolysis, **1** gave **4** and tiglic acid, which was identical with an authentic sample. Comparison of the 1H - and ^{13}C -NMR spectra of **1** with those of **4** showed the 4 position of glucose (G-3) joined to C-21-OH to be the acylation site in the former [$+1.48$ ppm, from δ 4.00 to 5.48 (H-4), -2.6 ppm, from δ 78.8 to 76.2 (C-3), $+0.6$ ppm, from δ 72.7 to 73.3 (C-4), and -2.1 ppm, from δ 78.6 to 76.5 (C-5)]. This was further confirmed by an HMBC experiment. A long-range correlation was seen between H-4 (δ 5.48) of Glc-3 and the carbonyl carbon (δ 167.8) of the tigloyl group in the HMBC spectrum. Hence, **1** was formulated as 3-*O*-β-D-xylopyranosyl(1→6)-β-D-glucopyranosyl(1→6)-β-D-glucopyranosido-21-*O*-4-tigloyl-β-D-glucopyranosyl sitakissogenin.

Sitakissoside XII (**2**) had the molecular formula $C_{64}H_{104}O_{29}$ (positive FAB-MS, m/z 1359 $[M + Na]^+$), *i.e.*, 162 mass units higher than that of **1**. Acid hydrolysis of **2** afforded **11**, and D-glucose and D-xylose in the ratio of 4:1. The 1H - and ^{13}C -NMR spectra indicated that **2** was composed of 1 mol each of sitakissogenin, tiglic acid and xylose, and 4 mol of glucose. A ^{13}C -NMR spectral comparison of **2** with **1** showed that **2** differs structurally from **1** only in its C-21 substituents, though the sugar units are also affixed to the C-3 and C-21 positions. The HMBC spectrum (Fig. 1) of **2** showed long-range correlations between H-1 (δ 5.02) of the G-3 and C-21 (δ 84.2), H-1 (δ 5.05) of the G-4 and C-4 (δ 81.9) of G-3, and H₂-6 (δ 4.84 and 5.27) of the G-3 and C-1 (δ 168.4) of a tigloyl unit, indicating a glucosyl unit to be located at C-4-OH of G-3 and a tigloyl unit at C-6-OH of G-3. Hence, **2** was formulated as 3-*O*-β-D-xylopyranosyl(1→6)-β-D-glucopyranosyl(1→6)-β-D-glucopyranosido-21-*O*-(6-*O*-tigloyl)-[β-D-glucopyranosyl(1→4)]-β-D-glucopyranosyl sitakissogenin.

Sitakissoside XV (**5**) was deduced to have the molecular formula $C_{47}H_{78}O_{18} \cdot 7/2H_2O$ based on elemental analysis. Acid hydrolysis of **5** afforded **11**, and D-glucose and D-xylose in the ratio of 2:1. The 1H - and ^{13}C -NMR spectra

of **5** indicated the presence of two β-glucopyranosyl units [H-1: δ 4.87 (d, $J=8.0$ Hz), C-1: δ 107.0, H-1: δ 5.06 (d, $J=8.0$ Hz), C-1: δ 105.4], and one β-xylopyranosyl unit [H-1: δ 4.96 (d, $J=7.5$ Hz), C-1: δ 105.9]. The carbon signals due to the oligosaccharide moiety and the A ring part (3 position) are superimposable on those of **4**, indicating that **5** is 3-*O*-β-D-xylopyranosyl(1→6)-β-D-glucopyranosyl(1→6)-β-D-glucopyranosyl sitakissogenin.

Sitakissoside XIX (**9**), an amorphous powder, $C_{47}H_{78}O_{19}$ was identified as deacylated sitakissoside II¹⁾ by direct comparison with an authentic sample.

Sitakissoside XVIII (**8**) had the molecular formula $C_{55}H_{85}NO_{20}$ (positive FAB-MS, m/z 1102 $[M + Na]^+$) and showed an intense blue fluorescence in methanol solution. On acid hydrolysis, **8** afforded marsglobiferin (**12**)³⁾ as an aglycone, besides D-glucose and D-xylose in a molar ratio of 2:1. The 1H - and ^{13}C -NMR spectra of **8** indicated the presence of two β-glucopyranosyl units [H-1: δ 4.84 (d, $J=7.5$ Hz), C-1: δ 106.9, H-1: δ 5.04 (d, $J=8.0$ Hz), C-1: δ 105.4], and one β-xylopyranosyl unit [H-1: δ 4.94 (d, $J=7.5$ Hz), C-1: δ 106.0]. Alkaline treatment with CH_3ONa -MeOH (1:3) of **8** released methyl *N*-methylantranilate, and sitakissoside XIX (**9**). The location of the *N*-methylantraniloyl group in **8** was determined by spectral comparison of **8** and **9**, and by an HMBC experiment on **8**. Thus, acylation shifts were observed at the 28 position of the aglycone [$+0.75$ ppm, from δ 4.11 to 4.86, $+0.56$ ppm, from δ 4.76 to 5.32 (H₂-28), -0.8 ppm, from δ 46.6 to 45.8 (C-17), and $+4.2$ ppm, from δ 58.5 to 62.7 (C-28)]. In the HMBC spectrum, the ester carbon signal of the *N*-methylantraniloyl group at δ 169.0 was correlated with H₂-28 (δ 4.86 and 5.32), establishing that in **8**, C-28-OH of the aglycone was acylated. Hence, **8** was formulated as 3-*O*-β-D-xylopyranosyl(1→6)-β-D-glucopyranosyl(1→6)-β-D-glucopyranosyl 28-*O*-*N*-methylantraniloyl marsglobiferin.

Sitakissoside XVII (**7**), an amorphous powder, $C_{47}H_{78}O_{18}$ was identified as deacylated sitakissoside I¹⁾ by direct comparison with an authentic sample.

Sitakissoside XVI (**6**) had the molecular formula $C_{52}H_{84}O_{19}$ (negative FAB-MS, m/z 1011 $[M - H]^-$) and showed no intense fluorescence in methanol solution. On acid hydrolysis, **6** afforded chichipegenin (**13**)⁴⁾ as an aglycone, besides D-glucose and D-xylose in a molar ratio of 2:1. Alkaline treatment with CH_3ONa -MeOH (1:3)

Table 1. ^{13}C -NMR Spectral Data for **1**–**14** (in Pyridine- d_5 , 150 MHz)

Carbon	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	38.9	39.1	38.8	38.9	39.1	38.9	38.9	38.9	38.7	38.9	39.3	39.1	39.1	39.3
2	26.8	26.9	26.7	26.8	26.9	26.7	26.7	26.7	26.7	26.7	28.1	28.1	28.1	28.1
3	89.1	89.4	89.0	89.1	89.1	89.0	89.1	89.0	88.9	89.1	78.4	78.0	78.0	78.3
4	39.6	39.7	39.6	39.6	39.7	39.5	39.6	39.6	39.5	39.6	39.6	39.4	39.4	39.6
5	55.8	56.0	55.7	55.8	56.0	55.7	55.8	55.7	55.6	55.9	56.0	55.6	55.6	55.9
6	18.6	18.7	18.5	18.3	18.7	18.5	18.5	18.5	18.4	18.5	18.9	18.7	18.7	18.9
7	33.0	33.2	32.9	33.0	33.1	32.9	33.0	33.0	32.9	32.9	33.2	33.0	33.0	33.2
8	40.2	40.3	40.1	40.2	40.3	40.3	40.4	40.3	40.2	40.3	40.3	40.2	40.2	40.3
9	47.1	47.3	47.1	47.1	47.3	47.1	47.2	47.1	47.0	47.0	47.4	47.2	47.3	47.4
10	36.9	37.1	36.8	37.1	37.0	36.8	36.8	36.8	36.8	36.8	37.4	37.1	37.1	37.3
11	24.0	24.1	23.9	23.9	24.1	24.0	24.0	24.0	23.8	24.1	24.1	23.9	23.9	24.1
12	124.0	124.0	124.0	124.0	124.0	123.9	124.1	124.4	124.0	124.0	123.1	123.9	123.9	122.8
13	142.8	143.1	142.8	142.8	143.2	142.1	143.0	141.8	142.7	143.6	143.4	142.8	143.1	144.1
14	43.8	43.9	43.8	43.8	43.9	42.6	42.7	42.6	42.5	43.7	44.0	42.5	42.7	44.0
15	36.3	36.8	36.3	36.3	36.8	36.1	36.0	36.2	36.0	34.8	36.8	36.0	36.0	36.8
16	68.1	67.7	67.9	68.0	68.0	66.3	67.0	67.9	68.3	77.1	67.9	68.3	66.9	66.9
17	44.0	44.0	43.9	44.0	44.0	44.4	45.2	45.8	46.6	42.7	43.9	46.6	45.1	41.2
18	43.6	43.6	43.5	43.6	44.0	43.8	43.2	43.2	42.1	43.5	44.0	42.2	43.1	44.6
19	47.8	48.1	47.8	47.8	48.0	46.2	46.7	46.4	46.8	47.2	48.0	46.8	46.6	47.3
20	36.9	37.1	36.8	37.1	37.0	32.2	32.3	36.9	36.7	31.2	37.1	36.8	32.2	31.3
21	83.0	84.2	81.1	82.8	73.1	44.1	44.2	76.9	77.3	35.1	73.1	77.3	44.3	34.4
22	33.9	33.5	33.6	34.1	35.0	69.5	69.6	74.3	73.7	23.5	35.0	73.7	69.5	26.3
23	28.3	28.5	28.2	28.3	28.4	28.2	28.3	28.3	28.2	28.4	29.0	28.7	28.7	28.9
24	17.2	17.3	17.1	17.1	17.3	17.2	17.2	17.2	17.0	17.1	16.8	16.6	16.5	16.7
25	15.8	16.0	15.7	15.8	15.9	15.7	15.8	15.8	15.9	15.8	16.0	15.7	15.7	15.9
26	17.0	17.2	16.9	17.0	17.1	17.1	17.1	17.1	16.9	17.0	17.2	17.0	17.0	17.1
27	27.2	27.3	27.1	27.2	27.3	27.7	27.7	27.6	27.4	27.3	27.3	27.4	27.6	27.3
28	68.1	68.2	67.8	68.1	68.5	62.6	58.9	62.7	58.5	65.2	68.6	58.6	58.8	69.0
29	29.4	30.0	29.4	29.4	30.2	33.4	33.7	30.4	30.5	33.5	30.2	30.4	33.5	33.6
30	18.6	19.0	18.5	18.6	18.2	24.9	25.2	19.1	19.1	24.2	18.2	19.1	25.0	24.3
3-O-Glc (G-1)														
1	107.0	107.0	107.0	107.0	107.0	106.9	107.0	106.9	107.0	106.9				
2	75.0	75.0	75.0	75.0	75.1	75.0	75.0	75.0	75.0	75.0				
3	78.3	78.4	78.3	78.4	78.4	78.3	78.3	78.2	78.5	78.4				
4	71.5	71.5	71.5	71.5	71.6	71.6	71.5	71.6	71.6	71.5				
5	77.0	77.0	77.0	77.1	77.0	76.9	77.0	76.9	77.1	77.0				
6	70.4	70.4	70.4	70.5	70.4	70.4	70.4	70.4	70.5	70.3				
Glc (G-2)														
1	105.4	105.4	105.4	105.4	105.4	105.4	105.4	105.4	105.4	105.4				
2	75.7	75.6	75.7	75.6	75.8	75.6	75.6	75.6	75.8	75.6				
3	78.5	78.4	78.6	78.6	78.7	78.6	78.5	78.5	78.6	78.6				
4	71.5	71.5	71.5	71.5	71.6	71.6	71.5	71.6	71.6	71.6				
5	77.0	77.0	77.0	77.1	77.1	77.0	77.0	77.0	77.1	77.0				
6	69.9	69.9	69.9	69.9	70.0	69.9	69.9	69.9	70.0	69.8				
Xyl														
1	106.0	105.9	106.0	106.1	105.9	106.0	106.0	106.0	106.1	106.0				
2	74.9	74.9	74.9	75.0	75.0	74.9	74.9	74.9	74.9	74.9				
3	78.1	78.2	78.2	78.2	78.2	78.1	78.1	78.1	78.2	78.1				
4	71.2	71.3	71.2	71.2	71.3	71.2	71.2	71.2	71.1	71.2				
5	67.1	67.2	67.1	67.2	67.2	67.1	67.1	67.1	67.1	67.1				
21-O-Glc (G-3)														
1	106.4	106.8	106.2	106.6							16-O-Glc (G-5)			
2	76.0	75.1	73.8	76.0							106.5			
3	76.2	76.9	79.2	78.8							75.7			
4	73.3	81.9	70.4	72.7							78.5			
5	76.5	73.6	78.4	78.6							71.9			
6	63.2	64.7	63.4	64.1							78.9			
Glc (G-4)														
1		105.2									63.0			
2		74.7												
3		78.6												
4		71.8												
5		78.7												
6		62.8												
Acyl moieties														
1	167.8	168.4	111.1			168.1		111.5						
2	129.0	129.0	152.5			129.4		152.5						
3	138.1	138.2	111.0			137.1		110.6						
4	14.4	14.6	134.8			14.2		135.1						
5	12.4	12.5	114.5			12.3		114.8						
6			132.1					131.4						
7			168.8					169.0						
9			29.3					29.4						

of **6** released tiglic acid and sitakissoside XVII (**7**). The location of the tigloyl group in **6** was determined by spectral comparison of **6** and **7**, and by an HMBC experiment on **6**. Thus, acylation shifts were observed at the 28 position of aglycone [$+0.59$ ppm, from $\delta 4.12$ to 4.71 , 0.38 ppm, from $\delta 4.85$ to 5.23 (H_{2-28}), -0.8 ppm, from $\delta 45.2$ to 44.4 (C-17), and $+3.7$ ppm, from $\delta 58.9$ to 62.6 (C-28)]. In the HMBC spectrum, the ester carbon signal of the tigloyl group at $\delta 168.1$ was correlated with H_{2-28} ($\delta 4.71$ and 5.23), establishing that in **6**, C-28-OH of the aglycone was acylated. Hence, **6** was formulated as 3-*O*- β -D-xylopyranosyl(1 $\rightarrow$ 6)- β -D-glucopyranosyl(1 $\rightarrow$ 6)- β -D-glucopyranosyl 28-*O*-tigloyl chichipegenin.

Sitakissoside XX (**10**) had the molecular formula $C_{53}H_{88}O_{22}$ (positive FAB-MS, m/z 1099 $[M+Na]^+$). On acid hydrolysis, **10** afforded longispinogenin (**14**),^{5,6} besides D-glucose and D-xylose in a molar ratio of 3:1. The C-3 and C-16 signals in the ^{13}C -NMR spectrum of **10** appeared at lower field by $+10.8$ ppm and $+10.2$ ppm, respectively, than those of **14** because of the glycosylation shifts,^{7,8} demonstrating that sugar units are located at C-3-OH and C-16-OH of the aglycone. The HMBC spectrum of **10** showed long-range correlations between H-1 ($\delta 4.86$) of the glucose (G-1) and C-3 ($\delta 89.1$) of the aglycone, H-1 ($\delta 5.06$) of the glucose (G-2) and C-6 ($\delta 70.3$) of the glucose (G-1), and H-1 ($\delta 4.95$) of the xylose and C-6 ($\delta 69.8$) of the glucose (G-2), and H-1 ($\delta 5.09$) of the glucose (G-5) and C-16 ($\delta 77.1$) of the aglycone. Hence, **10** was formulated as 3-*O*- β -D-xylopyranosyl(1 $\rightarrow$ 6)- β -D-glucopyranosyl(1 $\rightarrow$ 6)- β -D-glucopyranosyl 16-*O*- β -D-glucopyranosyl longispinogenin.

A 1 mM solution of any of sitakissosides XI—XIII, XVI and XVIII led to complete suppression of the sensation of sweetness induced by 0.2 M sucrose. Sitakissosides XIV, XV, XVII, XIX and XX, with no acyl group, had no activity. The activities of sitakissosides XI—XIII, XVI and XVIII 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 instruments. NMR spectra were recorded on a Varian UNITY 600 spectrometer in C_5D_5N solution using TMS as an internal standard. NMR experiments included 1H - 1H -COSY, ^{13}C - 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 HREIMS 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, Kieselgel 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 *Stephanotis lutchuensis* KOIDZ. 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 H_2O and EtOAc. The water layer was passed through an Amberlite XAD-2 column. The column was washed with water, and the adsorbed materials were eluted with 100% MeOH. The MeOH eluate (143 g) was chromatographed on Bondapak C_{18} with 20–80% MeOH to give four fractions (Frs. 1–4). Fraction 4 (22.5 g) was subjected to HPLC on ODS (Develosil Lop ODS, 70% CH_3OH) to give five fractions (Frs. 4-1–5). Fraction 4-3 was purified by preparative HPLC (YMC, ODS S-5, 27% CH_3CN) to afford sitakissosides XVII (**7**, 230 mg) and XVIII (**8**, 760 mg).

Fraction 4-4 was subjected to HPLC (YMC, ODS S-5, 32% CH_3CN) to give sitakissosides XI (**1**, 600 mg), XIV (**4**, 190 mg), XVI (**6**, 50 mg) and XIX (**9**, 70 mg). From Fr. 4-5, sitakissosides XII (**2**, 90 mg), XIII (**3**, 3.2 g), XV (**5**, 660 mg) and a crude compound (120 mg) were obtained. The crude compound was further purified by preparative HPLC (YMC, ODS S-5, 37% CH_3CN) to afford sitakissoside XX (**10**, 80 mg).

Sitakissoside XI (**1**): Colorless needles from MeOH, mp 218–220 °C, $[\alpha]_D^{20} -21.8^\circ$ ($c=1.5$, MeOH). IR (film) cm^{-1} : 3460, 1680, 1090. UV λ_{max}^{EtOH} nm (log ϵ): 221 (4.07), 254 (3.66), 350 (3.20). Positive FAB-MS m/z : 1197 $[M(C_{58}H_{94}O_{24})+Na]^+$, 1213 $[M+K]^+$. Anal. Calcd for $C_{58}H_{94}O_{24} \cdot 2H_2O$: C, 57.51; H, 8.15. Found: C, 57.30; H, 8.35. 1H -NMR δ : 0.86 (H_{3-25}), 0.97 (H_{3-26}), 1.01 (H_{3-24}), 1.21 (H_{3-30}), 1.30 (H_{3-23}), 1.30 (H_{3-27}), 1.40 (H_{3-29}), 2.02 (1H, dd, $J=13.0$, 12.0 Hz, $H_{\beta-22}$), 2.52 (1H, dd, $J=11.5$, 4.0 Hz, H-18), 3.32 (1H, dd, $J=11.5$, 4.5 Hz, H-3), 3.43 (1H, dd, $J=13.0$, 4.0 Hz, $H_{\alpha-22}$), 3.72, 4.28 (each 1H, d, $J=11.0$ Hz, H_{2-28}), ca. 4.20 (1H, m, H-21), 4.68 (1H, dd, $J=12.0$, 4.5 Hz, H-16), 5.24 (1H, m, H-12), 4.85 (1H, d, $J=7.5$ Hz, H-1 of Glc-1), ca. 4.32 (1H, m, H-6 of Glc-1), 4.89 (1H, d, $J=11.0$, 2.5 Hz, H-6 of Glc-1), 5.02 (1H, d, $J=7.5$ Hz, H-1 of Glc-2), ca. 4.32 (1H, m, H-6 of Glc-2), 4.74 (1H, dd, $J=10.0$, 2.5 Hz, H-6 of Glc-2), 4.91 (1H, d, $J=7.5$ Hz, H-1 of Xyl), 5.13 (1H, d, $J=8.0$ Hz, H-1 of Glc-3), 5.48 (1H, t, $J=9.5$ Hz, H-4 of Glc-3), ca. 4.10 (1H, m, H-6 of Glc-3), 4.61 (1H, dd, $J=11.0$, 2.5 Hz, H-6 of Glc-3). Acyl part: 1.58 (3H, d, $J=7.0$ Hz, H-4), 1.78 (3H, s, H-5), 6.92 (1H, q, $J=7.0$ Hz, H-3). ^{13}C -NMR: Table 1.

Sitakissoside XII (**2**): Colorless needles from MeOH, mp 210–212 °C, $[\alpha]_D^{20} -24.9^\circ$ ($c=2.9$, MeOH). IR (film) cm^{-1} : 3420, 1685, 1080. UV λ_{max}^{EtOH} nm (log ϵ): 220 (4.09), 255 (3.64), 349 (3.19). Positive FAB-MS m/z : 1359 $[M(C_{64}H_{104}O_{29})+Na]^+$, 1375 $[M+K]^+$. Anal. Calcd for $C_{64}H_{104}O_{29} \cdot 2H_2O$: C, 55.97; H, 7.93. Found: C, 55.60; H, 8.02. 1H -NMR δ : 0.84 (H_{3-25}), 0.97 (H_{3-26}), 1.00 (H_{3-24}), 1.21 (H_{3-30}), 1.28 (H_{3-23}), 1.33 (H_{3-27}), 1.41 (H_{3-29}), 2.02 (1H, dd, $J=13.0$, 13.0 Hz, $H_{\beta-22}$), 2.52 (1H, dd, $J=11.5$, 4.0 Hz, H-18), 3.33 (1H, dd, $J=11.5$, 4.0 Hz, H-3), 3.43 (1H, dd, $J=13.0$, 4.0 Hz, $H_{\alpha-22}$), 3.68, 4.29 (each 1H, d, $J=9.5$ Hz, H_{2-28}), ca. 4.10 (1H, m, H-21), 4.60 (1H, dd, $J=12.0$, 4.0 Hz, H-16), 5.23 (1H, m, H-12), 4.87 (1H, d, $J=8.0$ Hz, H-1 of Glc-1), 4.33 (1H, m, H-6 of Glc-1), 4.90 (1H, dd, $J=11.0$, 2.5 Hz, H-6 of Glc-1), 5.06 (1H, d, $J=8.0$ Hz, H-1 of Glc-2), ca. 4.30 (1H, m, H-6 of Glc-2), 4.78 (1H, dd, $J=10.0$, 4.0 Hz, H-6 of Glc-2), 4.95 (1H, d, $J=7.5$ Hz, H-1 of Xyl), 5.02 (1H, d, $J=8.0$ Hz, H-1 of Glc-3), ca. 4.12 (1H, m, H-4 of Glc-3), 4.84 (1H, dd, $J=11.0$, 4.5 Hz, H-6 of Glc-3), 5.27 (1H, dd, $J=11.0$, 2.0 Hz, H-6 of Glc-3), 5.05 (1H, d, $J=8.0$ Hz, H-1 of Glc-4), 4.28 (1H, m, H-6 of Glc-4), 4.58 (1H, dd, $J=9.5$, 2.0 Hz, H-6 of Glc-4). Acyl part: 1.58 (3H, d, $J=7.0$ Hz, H-4), 1.81 (3H, s, H-5), 7.03 (1H, q, $J=7.0$ Hz, H-3). ^{13}C -NMR: Table 1.

Sitakissoside XIII (**3**): Colorless needles from MeOH, mp 208–210 °C, $[\alpha]_D^{20} -21.1^\circ$ ($c=3.4$, MeOH). IR (film) cm^{-1} : 3455, 1680, 1050. UV λ_{max}^{EtOH} nm (log ϵ): 222 (4.36), 255 (3.87), 356 (3.68). Positive FAB-MS m/z : 1248 $[M(C_{61}H_{95}NO_{24})+Na]^+$, 1264 $[M+K]^+$. Anal. Calcd for $C_{61}H_{95}NO_{24} \cdot 2H_2O$: C, 59.74; H, 7.81; N, 1.42. Found: C, 59.60; H, 8.00; N, 1.30. 1H -NMR δ : 0.84 (H_{3-25}), 0.95 (H_{3-26}), 1.00 (H_{3-24}), 1.19 (H_{3-30}), 1.27 (H_{3-23}), 1.27 (H_{3-27}), 1.34 (H_{3-29}), 2.12 (1H, t, $J=13.0$ Hz, $H_{\beta-22}$), 2.54 (1H, dd, $J=14.0$, 4.0 Hz, H-18), 3.35 (1H, dd, $J=11.5$, 4.5 Hz, H-3), 3.54 (1H, dd, $J=13.0$, 4.0 Hz, $H_{\alpha-22}$), 3.74, 4.34 (each 1H, d, $J=10.5$ Hz, H_{2-28}), ca. 4.14 (1H, m, H-21), 4.68 (1H, m, H-16), 5.24 (1H, m, H-12), 4.88 (1H, d, $J=7.5$ Hz, H-1 of Glc-1), ca. 4.32 (1H, m, H-6 of Glc-1), 4.91 (1H, dd, $J=9.5$, 2.5 Hz, H-6 of Glc-1), 5.06 (1H, d, $J=8.0$ Hz, H-1 of Glc-2), ca. 4.30 (1H, m, H-6 of Glc-2), 4.78 (1H, dd, $J=9.5$, 2.0 Hz, H-6 of Glc-2), 4.95 (1H, d, $J=7.5$ Hz, H-1 of Xyl), 5.14 (1H, d, $J=8.0$ Hz, H-1 of Glc-3), ca. 4.18 (1H, m, H-6 of Glc-3), 4.57 (1H, dd, $J=10.5$, 2.0 Hz, H-6 of Glc-3), 6.10 (1H, dd, $J=9.5$, 9.5 Hz, H-3 of Glc-3). Acyl part: 2.59 (3H, d, $J=5.0$ Hz, N-CH₃), 6.55 (1H, dd, $J=8.5$, 1.5 Hz, H-3), 6.57 (1H, ddd, $J=8.0$, 8.0, 1.5 Hz, H-5), 7.35 (1H, ddd, $J=8.0$, 8.0, 1.5 Hz, H-4), 7.93 (1H, q, $J=5.0$ Hz, NH), 8.13 (1H, dd, $J=8.0$, 1.5 Hz, H-6). ^{13}C -NMR: Table 1.

Sitakissoside XIV (**4**): 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 $[M(C_{53}H_{88}O_{23})-H]^-$, 959 $[M-H-C_5H_8O_4]^-$, 797 $[M-H-C_5H_8O_4-C_6H_{10}O_5]^-$. Anal. Calcd for $C_{53}H_{88}O_{23} \cdot H_2O$: C, 57.28; H, 8.16. Found: C, 57.54; H, 8.40. 1H -NMR δ : 0.84 (H_{3-25}), 0.95 (H_{3-26}), 0.99 (H_{3-24}), 1.20 (H_{3-30}), 1.26 (H_{3-23}), 1.26 (H_{3-27}), 1.36 (H_{3-29}), 1.68 (1H, dd, $J=12.5$, 4.3 Hz, $H_{\beta-15}$), ca. 2.06 (1H, m, $H_{\beta-22}$), 2.17 (1H, dd, $J=12.5$, 12.5 Hz, $H_{\beta-15}$), 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, $H_{\alpha-22}$), 3.73, 4.34 (each 1H, d, $J=11.0$ Hz, H_{2-28}), 4.16 (1H, m, H-21), 4.68 (1H, dd,

$J = 12.5, 4.3$ Hz, H-16), 5.24 (1H, m, H-12), 4.86 (1H, d, $J = 8.0$ Hz, H-1 of Glc-1), *ca.* 4.30 (2H, m, H-6 of Glc-1 and Glc-2), 4.90 (1H, dd, $J = 11.0, 2.0$ Hz, H-6 of Glc-1), 5.05 (1H, d, $J = 7.5$ Hz, H-1 of Glc-2), 4.78 (1H, dd, $J = 11.0, 2.5$ Hz, H-6 of Glc-2), 4.94 (1H, d, $J = 7.5$ Hz, H-1 of Xyl), 5.08 (1H, d, $J = 7.5$ Hz, H-1 of Glc-3), *ca.* 4.10 (1H, brd, $J = 9.5$ Hz, H-6 of Glc-3), 4.61 (1H, dd, $J = 9.5, 2.0$ Hz, H-6 of Glc-3). $^{13}\text{C-NMR}$: Table 1.

Sitakiside XV (5): Colorless needles from MeOH, mp 231–232 °C, $[\alpha]_{\text{D}}^{20} -15.1^\circ$ ($c = 2.2$, MeOH). IR (film) cm^{-1} : 3400, 3250. Positive FAB-MS m/z : 953 $[\text{M}(\text{C}_{47}\text{H}_{78}\text{O}_{18}) + \text{Na}]^+$, 969 $[\text{M} + \text{K}]^+$. *Anal.* Calcd for $\text{C}_{47}\text{H}_{78}\text{O}_{18} \cdot 7/2\text{H}_2\text{O}$: C, 56.78; H, 8.62. Found: C, 56.82; H, 8.24. $^1\text{H-NMR}$ δ : 0.86 (H₃-25), 1.00 (H₃-24), 1.00 (H₃-26), 1.27 (H₃-23), 1.27 (H₃-29), 1.27 (H₃-30), 1.34 (H₃-27), 2.50 (1H, dd, $J = 11.5, 4.0$ Hz, H-18), 3.35 (1H, dd, $J = 11.5, 4.5$ Hz, H-3), 4.18 (1H, dd, $J = 13.0, 4.0$ Hz, H-21), 3.80, 4.43 (each 1H, d, $J = 11.0$ Hz, H₂-28), 4.74 (1H, dd, $J = 12.0, 5.0$ Hz, H-16), 5.30 (1H, m, H-12), 4.87 (1H, d, $J = 8.0$ Hz, H-1 of Glc-1), 4.96 (1H, d, $J = 7.5$ Hz, H-1 of Xyl), 5.06 (1H, d, $J = 8.0$ Hz, H-1 of Glc-2). $^{13}\text{C-NMR}$: Table 1.

Sitakiside XVI (6): Colorless needles from MeOH, mp 220–222 °C, $[\alpha]_{\text{D}}^{20} -10.0^\circ$ ($c = 3.4$, MeOH). IR (film) cm^{-1} : 3455, 1680, 1050. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 222 (4.36), 255 (3.87), 356 (3.68). Negative FAB-MS m/z : 1011 $[\text{M}(\text{C}_{52}\text{H}_{84}\text{O}_{19}) - \text{H}]^-$. *Anal.* Calcd for $\text{C}_{52}\text{H}_{84}\text{O}_{19} \cdot 2\text{H}_2\text{O}$: C, 59.74; H, 7.81; N, 1.42. Found: C, 59.60; H, 8.00; N, 1.30. $^1\text{H-NMR}$ δ : 0.81 (H₃-25), 0.97 (H₃-24), 1.05 (H₃-26), 1.05 (H₃-29), 1.14 (H₃-30), 1.26 (H₃-23), 1.37 (H₃-27), 2.87 (1H, dd, $J = 14.0, 4.5$ Hz, H-18), 3.30 (1H, dd, $J = 11.5, 4.5$ Hz, H-3), 4.72 (1H, dd, $J = 12.5, 4.5$ Hz, H-22), 4.71, 5.23 (each 1H, d, $J = 11.0$ Hz, H₂-28), 5.12 (1H, dd, $J = 11.0, 5.0$ Hz, H-16), 5.35 (1H, m, H-12), 4.84 (1H, d, $J = 7.5$ Hz, H-1 of Glc-1), *ca.* 4.32 (1H, m, H-6 of Glc-1), 4.88 (1H, dd, $J = 10.5, 2.5$ Hz, H-6 of Glc-1), 5.04 (1H, d, $J = 8.0$ Hz, H-1 of Glc-2), *ca.* 4.30 (1H, m, H-6 of Glc-2), 4.77 (1H, dd, $J = 10.5, 2.0$ Hz, H-6 of Glc-2), 4.94 (1H, d, $J = 7.5$ Hz, H-1 of Xyl). Acyl part: 1.60 (3H, dq, $J = 7.0, 1.0$ Hz, H-4), 1.84 (3H, brs, H-5), 7.03 (1H, qq, $J = 7.0, 1.0$ Hz, H-3). $^{13}\text{C-NMR}$: Table 1.

Sitakiside XVII (7): An amorphous powder, $[\alpha]_{\text{D}}^{20} -7.0^\circ$ ($c = 9.3$, MeOH). IR (film) cm^{-1} : 3400, 3250. Negative FAB-MS m/z : 929 $[\text{M}(\text{C}_{47}\text{H}_{78}\text{O}_{18}) - \text{H}]^-$, 797 $[\text{M} - \text{H} - \text{C}_5\text{H}_8\text{O}_4]^-$, 635 $[\text{M} - \text{H} - \text{C}_5\text{H}_8\text{O}_4 - \text{C}_6\text{H}_{10}\text{O}_5]^-$. *Anal.* Calcd for $\text{C}_{47}\text{H}_{78}\text{O}_{18} \cdot \text{H}_2\text{O}$: C, 59.48; H, 8.50. Found: C, 59.21; H, 8.41. $^1\text{H-NMR}$ δ : 0.82 (H₃-25), 0.93 (H₃-26), 0.99 (H₃-24), 1.02 (H₃-29), 1.11 (H₃-30), 1.26 (H₃-23), 1.37 (H₃-27), 3.31 (1H, dd, $J = 11.7, 4.4$ Hz, H-3), 4.12, 4.85 (each 1H, d, $J = 10.0$ Hz, H₂-28), 5.10 (1H, dd, $J = 11.5, 5.0$ Hz, H-16), 5.08 (1H, dd, $J = 12.0, 4.5$ Hz, H-22), 5.29 (1H, m, H-12), 4.85 (1H, d, $J = 7.5$ Hz, H-1 of Glc), 5.03 (1H, d, $J = 8.0$ Hz, H-1 of Glc), 4.94 (1H, d, $J = 7.5$ Hz, H-1 of Xyl). $^{13}\text{C-NMR}$: Table 1.

Sitakiside XVIII (8): Colorless needles from MeOH, mp 203–205 °C, $[\alpha]_{\text{D}}^{20} -12.0^\circ$ ($c = 2.5$, MeOH). IR (film) cm^{-1} : 3455, 1680, 1050. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 222 (4.36), 255 (3.87), 356 (3.68). Positive FAB-MS m/z : 1102 $[\text{M}(\text{C}_{55}\text{H}_{85}\text{NO}_{20}) + \text{Na}]^+$, 1118 $[\text{M} + \text{K}]^+$. *Anal.* Calcd for $\text{C}_{55}\text{H}_{85}\text{NO}_{20} \cdot 2\text{H}_2\text{O}$: C, 59.74; H, 7.81; N, 1.42. Found: C, 59.60; H, 8.00; N, 1.30. $^1\text{H-NMR}$ δ : 0.83 (H₃-25), 0.97 (H₃-24), 1.10 (H₃-26), 1.26 (H₃-23), 1.34 (H₃-29), 1.37 (H₃-27) and 1.39 (H₃-30), 3.31 (1H, dd, $J = 11.5, 4.5$ Hz, H-3), 3.04 (1H, dd, $J = 14.0, 4.0$ Hz, H-18), 4.12 (1H, d, $J = 10.5$ Hz, H-21), 4.66 (1H, d, $J = 10.5$ Hz, H-22), 4.86, 5.32 (each 1H, d, $J = 12.0$ Hz, H₂-28), 5.15 (1H, dd, $J = 11.5, 5.5$ Hz, H-16), 5.34 (1H, m, H-12), 4.84 (1H, d, $J = 7.5$ Hz, H-1 of Glc-1), *ca.* 4.32 (1H, m, H-6 of Glc-1), 4.88 (1H, dd, $J = 12.5, 2.0$ Hz, H-6 of Glc-1), 5.04 (1H, d, $J = 8.0$ Hz, H-1 of Glc-2), *ca.* 4.30 (1H, m, H-6 of Glc-2), 4.77 (1H, dd, $J = 11.0, 2.0$ Hz, H-6 of Glc-2), 4.94 (1H, d, $J = 7.5$ Hz, H-1 of Xyl). Acyl part: 2.65 (3H, d, $J = 5.0$ Hz, N-CH₃), 6.60 (1H, ddd, $J = 8.5, 8.5, 1.5$ Hz, H-5), 6.62 (1H, dd, $J = 8.5, 1.5$ Hz, H-3), 7.37 (1H, ddd, $J = 8.5, 8.5, 1.5$ Hz, H-4), 8.15 (1H, dd, $J = 8.5, 1.5$ Hz, H-6). $^{13}\text{C-NMR}$: Table 1.

Sitakiside XIX (9): An amorphous powder, $[\alpha]_{\text{D}}^{20} -17.1^\circ$ ($c = 1.6$, MeOH). IR (film) cm^{-1} : 3400, 3250. Negative FAB-MS m/z : 945 $[\text{M}(\text{C}_{47}\text{H}_{78}\text{O}_{19}) - \text{H}]^-$, 813 $[\text{M} - \text{H} - \text{C}_5\text{H}_8\text{O}_4]^-$, 651 $[\text{M} - \text{H} - \text{C}_5\text{H}_8\text{O}_4 - \text{C}_6\text{H}_{10}\text{O}_5]^-$. *Anal.* Calcd for $\text{C}_{47}\text{H}_{78}\text{O}_{19} \cdot \text{H}_2\text{O}$: C, 58.49; H, 8.35. Found: C, 58.61; H, 8.61. $^1\text{H-NMR}$ δ : 0.82 (H₃-25), 0.93 (H₃-26), 1.00 (H₃-24), 1.27 (H₃-23), 1.32 (H₃-29), 1.34 (H₃-27), 1.36 (H₃-30), 3.33 (1H, dd, $J = 11.6, 4.4$ Hz, H-3), 4.11, 4.76 (each 1H, d, $J = 10.5$ Hz, H₂-28), *ca.* 4.12 (H-21), 4.93 (1H, d, $J = 9.5$ Hz, H-22), 5.12 (1H, dd, $J = 11.8, 5.2$ Hz, H-16), 5.32 (1H, m, H-12), 4.84 (1H, d, $J = 7.6$ Hz, H-1 of Glc-1), *ca.* 4.32 (1H, m, H-6 of Glc-1), 4.88 (1H, dd, $J = 12.5, 2.0$ Hz, H-6 of Glc-1), 5.04 (1H, d, $J = 8.0$ Hz, H-1 of Glc-2), *ca.* 4.30 (1H, m, H-6 of Glc-2), 4.77 (1H, dd, $J = 11.0, 2.0$ Hz, H-6 of Glc-2), 4.94 (1H, d, $J = 7.5$ Hz, H-1 of Xyl). $^{13}\text{C-NMR}$: Table 1.

Sitakiside XX (10): An amorphous powder, $[\alpha]_{\text{D}}^{20} -21.2^\circ$ ($c = 2.2$, MeOH). IR (film) cm^{-1} : 3460, 1090. Positive FAB-MS m/z : 1099 $[\text{M}(\text{C}_{53}\text{H}_{88}\text{O}_{22}) + \text{Na}]^+$, 1115 $[\text{M} + \text{K}]^+$. *Anal.* Calcd for $\text{C}_{53}\text{H}_{88}\text{O}_{22} \cdot 9/2\text{H}_2\text{O}$: C, 54.96; H, 8.44. Found: C, 54.98; H, 7.63. $^1\text{H-NMR}$ δ : 0.76 (H₃-25), 0.80 (H₃-26), 0.93 (H₃-24), 0.93 (H₃-29), 1.04 (H₃-30), 1.21 (H₃-23), 1.27 (H₃-27), 2.84 (1H, dd, $J = 13.5, 4.0$ Hz, H-18), 3.26 (1H, dd, $J = 11.5, 4.5$ Hz, H-3), 3.86, 4.21 (each 1H, d, $J = 10.0$ Hz, H₂-28), 4.84 (1H, dd, $J = 13.0, 4.5$ Hz, H-16), 5.20 (1H, m, H-12), 4.86 (1H, d, $J = 7.5$ Hz, H-1 of Glc-1), 4.26 (1H, dd, $J = 11.0, 4.5$ Hz, H-6 of Glc-1), 4.87 (1H, dd, $J = 11.0, 2.5$ Hz, H-6 of Glc-1), 5.06 (1H, d, $J = 8.0$ Hz, H-1 of Glc-2), 4.25 (1H, dd, $J = 11.0, 2.5$ Hz, H-6 of Glc-2), 4.76 (1H, d, $J = 10.0, 2.0$ Hz, H-6 of Glc-2), 4.95 (1H, d, $J = 8.5$ Hz, H-1 of Xyl), 5.12 (1H, d, $J = 8.0$ Hz, H-1 of Glc-3), 4.38 (1H, dd, $J = 11.0, 4.5$ Hz, H-6 of Glc-3), 4.52 (1H, dd, $J = 11.0, 2.0$ Hz, H-6 of Glc-3), 5.09 (1H, d, $J = 8.0$ Hz, H-1 of Glc-5). $^{13}\text{C-NMR}$: Table 1.

Acid Hydrolysis of Sitakiside XIV (4) A solution of **4** (30 mg) in 5% H_2SO_4 was heated at 100 °C for 2 h. The reaction mixture was extracted with EtOAc and purified by HPLC (YMC, ODS S-5, 37% CH_3CN) to provide sitakisogenin (**11**, 5 mg). Compound **11**, colorless needles from MeOH, mp 333–335 °C, $[\alpha]_{\text{D}}^{20} +57.0^\circ$ ($c = 0.9$, CHCl_3 -MeOH = 1:1). HREIMS obsd. for $[\text{M}(\text{C}_{30}\text{H}_{50}\text{O}_4) - \text{H}_2\text{O}]$ 456.3628, Calcd 456.3604. $^1\text{H-NMR}$ 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, $J = 13.0, 13.0$ Hz, H₂-22), 2.64 (1H, dd, $J = 13.5, 4.0$ Hz, H-18), 3.28 (1H, dd, $J = 13.0, 4.0$ Hz, H₂-22), 3.48 (1H, dd, $J = 8.0, 8.0$ Hz, H-3), 3.80, 4.43 (each 1H, d, $J = 10.5$ Hz, H₂-28), 4.18 (1H, dd, $J = 13.0, 4.0$ Hz, H-21), 4.74 (1H, dd, $J = 12.0, 5.0$ Hz, H-16), 5.38 (1H, m, H-12). For $^{13}\text{C-NMR}$: Table 1. The aqueous layer was neutralized with Amberlite IR-35 and evaporated *in vacuo* to dryness. The sugar was determined by using 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 Sitakiside XIII (3) A solution of **3** (50 mg) in MeOH (1.0 ml) was treated dropwise with 28% sodium methoxide (0.3 ml) under an N_2 atmosphere. The mixture was stirred for 4 h at room temperature. The reaction mixture was acidified with dilute HCl, and extracted with CHCl_3 and then 1-BuOH. The CHCl_3 layer gave methyl *N*-methylantranilate (8 mg), which was confirmed by comparison of $^1\text{H-NMR}$ data and by co-HPLC with an authentic sample. The 1-BuOH layer was subjected to HPLC (YMC, ODS S-5, 37% CH_3CN) to provide **4** (30 mg).

Alkaline Hydrolysis of Sitakiside XI (1) Alkaline hydrolysis of **1** (50 mg) was carried out in the same way as described for **3**. The CHCl_3 layer afforded tiglic acid (4 mg), which was confirmed by comparison of $^1\text{H-NMR}$ data and by co-HPLC with an authentic sample. The 1-BuOH layer was subjected to HPLC (YMC, ODS S-5, 37% CH_3CN) to provide **4** (35 mg).

Acid Hydrolysis of Sitakisides XI (1), XII (2), XIV (4) and XV (5) Acid hydrolysis of **1**, **2**, **4** and **5** (each 20 mg) was carried out in the same way as described for **4**. The EtOAc layer gave sitakisogenin (**11**, *ca.* 2 mg), which was confirmed by comparison of $^1\text{H-NMR}$ data and by co-HPLC with an authentic sample. From the H_2O layer, D-glucose and D-xylose were detected.

Acid Hydrolysis of Sitakiside XIX (9) Acid hydrolysis of **9** (25 mg) was carried out in the same way as described for **4**. The EtOAc layer provided marsglobiferin (**12**, 2 mg), which was confirmed by comparison of $^1\text{H-NMR}$ data and by co-HPLC with an authentic sample. From the H_2O layer, D-glucose and D-xylose were detected.

Alkaline Hydrolysis of Sitakiside XVIII (8) Alkaline hydrolysis of **8** (50 mg) was carried out in the same way as described for **3**. The CHCl_3 layer gave methyl *N*-methylantranilate (6 mg), which was confirmed by comparison of $^1\text{H-NMR}$ data and by co-HPLC with an authentic sample. The 1-BuOH layer was subjected to HPLC (YMC, ODS S-5, 32% CH_3CN) to provide **9** (35 mg).

Acid Hydrolysis of Sitakiside XVI (6) Acid hydrolysis of **6** (25 mg) was carried out in the same way as described for **4**. The EtOAc layer gave chichipegenin (**13**, 2 mg), which was confirmed by comparison of $^1\text{H-NMR}$ data and by co-HPLC with an authentic sample. From the H_2O layer, D-glucose and D-xylose were detected.

Alkaline Hydrolysis of Sitakiside XVI (6) Alkaline hydrolysis of **6** (25 mg) was carried out in the same way as described for **3**. The CHCl_3 layer gave tiglic acid (2 mg), which was confirmed by comparison of

¹H-NMR data and by co-HPLC with an authentic sample. The 1-BuOH layer was subjected to HPLC (YMC, ODS S-5, 27% CH₃CN) to provide **7** (20 mg).

Acid Hydrolysis of Sitakisoside XX (10) Acid hydrolysis of **10** (25 mg) was carried out in the same way as described for **4**. The EtOAc layer provided longispinogenin (**14**, 2 mg), which was confirmed by comparison of ¹H-NMR data and by co-HPLC with an authentic sample. From the H₂O layer, D-glucose and D-xylose were detected.

Bioassay of Antisweet Activity The antisweet activity of 1 mM solutions of **1**—**10** was tested on three volunteers. Each participant held the test solution 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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