Antisweet Natural Products. XII.[1] Structures of Sitakisosides XI—XX from *Stephanotis lutchuensis* KOIDZ. var. *japonica*

Kazuko YOSHIKAWA,* Aki MIZUTANI, Yukiko KAN, and Shigenobu ARIHARA

Faculty of Pharmaceutical Sciences, Tokushima Bunri University, Yamashiro-cho, Tokushima 770, Japan.
Received July 29, 1996; accepted October 5, 1996

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→6)-β-D-glucopyranosyl(1→6)-β-D-glucopyranosyl moiety and the aglycones of sitakisosides XI—XV, XVI and XVII, XVIII and XIX, and XX are sitakisogenin, chichipegenin, 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*-methylanthranilic 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**). ^{1}H–^{1}H correlation spectroscopy (^{1}H–^{1}H COSY), ^{1}H–^{13}C 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, $C_{53}H_{88}O_{23}$ was identified as deacylated sitakisoside VI[2] by direct comparison with an authentic sample.

Sitakisoside XIII (**3**) had the molecular formula $C_{61}H_{95}NO_{24}$ (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, $[\alpha]_D^{20}$ −57.0° (*c*=0.9, MeOH), $C_{30}H_{50}O_4$ (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 ^{1}H- and ^{13}C-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 CH_3ONa–MeOH (1:3) of **3** released a methyl *N*-methylanthranilate, which was identical with an authentic sample, and sitakisoside XIV (**4**). The location of the *N*-methylanthraniloyl 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*-methylanthraniloyl 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-

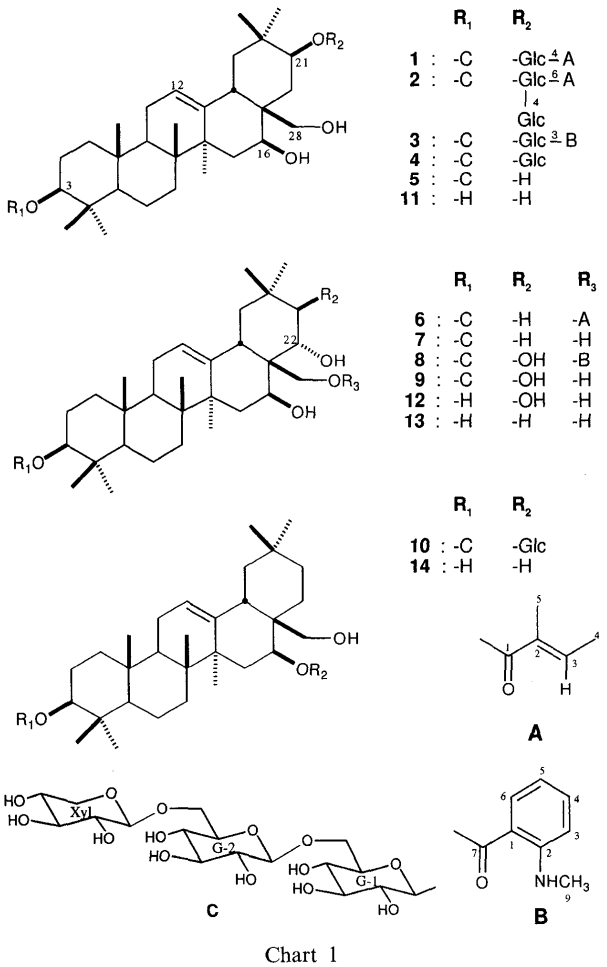

Chart 1

* To whom correspondence should be addressed.

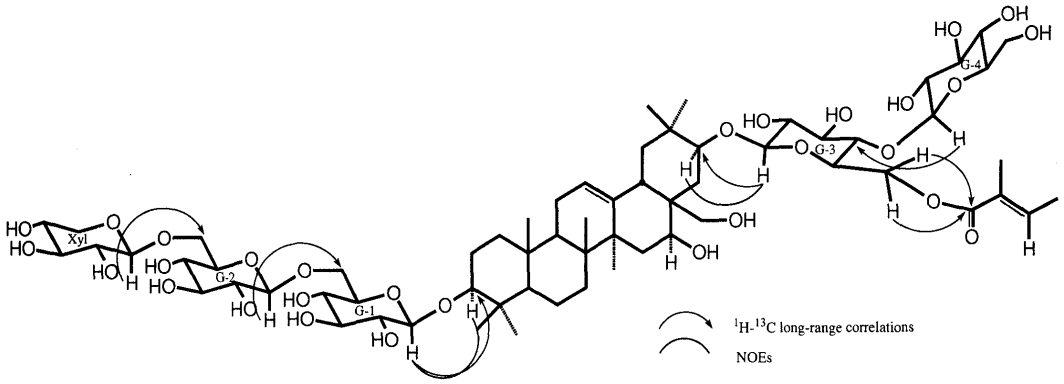

Fig. 1. Most Significant Correlations Observed in HMBC and ROESY Experiments for Sitakisoside XII (**2**)

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

Sitakisoside 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 ^{1}H- 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 sitakisogenin.

Sitakisoside 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 ^{1}H- and ^{13}C-NMR spectra indicated that **2** was composed of 1 mol each of sitakisogenin, 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 H_2-6 (*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 sitakisogenin.

Sitakisoside 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 ^{1}H- 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 sitakisogenin.

Sitakisoside XIX (**9**), an amorphous powder, $C_{47}H_{78}O_{19}$ was identified as deacylated sitakisoside II[1] by direct comparison with an authentic sample.

Sitakisoside 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 ^{1}H- 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*-methylanthranilate, and sitakisoside XIX (**9**). The location of the *N*-methylanthraniloyl 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 (H_2-28), −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*-methylanthraniloyl group at *δ* 169.0 was correlated with H_2-28 (*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*-methylanthraniloyl marsglobiferin.

Sitakisoside XVII (**7**), an amorphous powder, $C_{47}H_{78}O_{18}$ was identified as deacylated sitakisoside I[1] by direct comparison with an authentic sample.

Sitakisoside 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)									16-*O*-Glc (G-5)					
1	106.4	106.8	106.2	106.6						106.5				
2	76.0	75.1	73.8	76.0						75.7				
3	76.2	76.9	79.2	78.8						78.5				
4	73.3	81.9	70.4	72.7						71.9				
5	76.5	73.6	78.4	78.6						78.9				
6	63.2	64.7	63.4	64.1						78.9				
Glc (G-4)										63.0				
1		105.2												
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 sitakisoside 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 δ 4.12 to 4.71, 0.38 ppm, from δ 4.85 to 5.23 (H_2-28), −0.8 ppm, from δ 45.2 to 44.4 (C-17), and +3.7 ppm, from δ 58.9 to 62.6 (C-28)]. In the HMBC spectrum, the ester carbon signal of the tigloyl group at δ 168.1 was correlated with H_2-28 (δ 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→6)-β-D-glucopyranosyl(1→6)-β-D-glucopyranosyl 28-*O*-tigloyl chichipegenin.

Sitakisoside 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 (δ 4.86) of the glucose (G-1) and C-3 (δ 89.1) of the aglycone, H-1 (δ 5.06) of the glucose (G-2) and C-6 (δ 70.3) of the glucose (G-1), and H-1 (δ 4.95) of the xylose and C-6 (δ 69.8) of the glucose (G-2), and H-1 (δ 5.09) of the glucose (G-5) and C-16 (δ 77.1) of the aglycone. Hence, **10** was formulated as 3-*O*-β-D-xylopyranosyl(1→6)-β-D-glucopyranosyl(1→6)-β-D-glucopyranosyl 16-*O*-β-D-glucopyranosyl longispinogenin.

A 1 mM solution of any of sitakisosides XI—XIII, XVI and XVIII led to complete suppression of the sensation of sweetness induced by 0.2 M sucrose. Sitakisosides XIV, XV, XVII, XIX and XX, with no acyl group, had no activity. The activities of sitakisosides 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 ^{1}H–^{1}H-COSY, ^{13}C–^{1}H-COSY, DEPT, HMBC (512 × 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 Bondapack 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 sitakisosides 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 sitakisosides XI (**1**, 600 mg), XIV (**4**, 190 mg), XVI (**6**, 50 mg) and XIX (**9**, 70 mg). From Fr. 4-5, sitakisosides 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 sitakisoside XX (**10**, 80 mg).

Sitakisoside XI (**1**): Colorless needles from MeOH, mp 218—220 °C, $[\alpha]_D^{20}$ −21.8° (*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. ^{1}H-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_β-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_α-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 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.

Sitakisoside XII (**2**): Colorless needles from MeOH, mp 210—212 °C, $[\alpha]_D^{20}$ −24.9° (*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. ^{1}H-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_β-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_α-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.

Sitakisoside XIII (**3**): Colorless needles from MeOH, mp 208—210 °C, $[\alpha]_D^{20}$ −21.1° (*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. ^{1}H-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_β-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_α-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-CH_3), 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.

Sitakisoside XIV (**4**): An amorphous powder, $[\alpha]_D^{20}$ −16.4° (*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. ^{1}H-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_α-15), *ca.* 2.06 (1H, m, H_β-22), 2.17 (1H, dd, *J* = 12.5, 12.5 Hz, H_β-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_α-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, br d, 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}C-NMR: Table 1.

Sitakisoside XV (**5**): Colorless needles from MeOH, mp 231—232 °C, $[\alpha]_D^{20}$ −15.1° (c=2.2, MeOH). IR (film) cm^{-1}: 3400, 3250. Positive FAB-MS m/z: 953 $[M(C_{47}H_{78}O_{18})+Na]^+$, 969 $[M+K]^+$. *Anal.* Calcd for $C_{47}H_{78}O_{18}\cdot 7/2H_2O$: C, 56.78; H, 8.62. Found: C, 56.82; H, 8.24. ^{1}H-NMR δ: 0.86 (H_3-25), 1.00 (H_3-24), 1.00 (H_3-26), 1.27 (H_3-23), 1.27 (H_3-29), 1.27 (H_3-30), 1.34 (H_3-27), 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, H_2-28), 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}C-NMR: Table 1.

Sitakisoside XVI (**6**): Colorless needles from MeOH, mp 220—222 °C, $[\alpha]_D^{20}$ −10.0° (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). Negative FAB-MS m/z: 1011 $[M(C_{52}H_{84}O_{19})-H]^-$ *Anal.* Calcd for $C_{52}H_{84}O_{19}\cdot 2H_2O$: C, 59.74; H, 7.81; N, 1.42. Found: C, 59.60; H, 8.00; N, 1.30. ^{1}H-NMR δ: 0.81 (H_3-25), 0.97 (H_3-24), 1.05 (H_3-26), 1.05 (H_3-29), 1.14 (H_3-30), 1.26 (H_3-23), 1.37 (H_3-27), 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, H_2-28), 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, br s, H-5), 7.03 (1H, qq, J=7.0, 1.0 Hz, H-3). ^{13}C-NMR: Table 1.

Sitakisoside XVII (**7**): An amorphous powder, $[\alpha]_D^{20}$ −7.0° (c=9.3, MeOH). IR (film) cm^{-1}: 3400, 3250. Negative FAB-MS m/z: 929 $[M(C_{47}H_{78}O_{18})-H]^-$, 797 $[M-H-C_5H_8O_4]^-$, 635 $[M-H-C_5H_8O_4-C_6H_{10}O_5]^-$. *Anal.* Calcd for $C_{47}H_{78}O_{18}\cdot H_2O$: C, 59.48; H, 8.50. Found: C, 59.21; H, 8.41. ^{1}H-NMR δ: 0.82 (H_3-25), 0.93 (H_3-26), 0.99 (H_3-24), 1.02 (H_3-29), 1.11 (H_3-30), 1.26 (H_3-23), 1.37 (H_3-27), 3.31 (1H, dd, J=11.7, 4.4 Hz, H-3), 4.12, 4.85 (each 1H, d, J=10.0 Hz, H_2-28), 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}C-NMR: Table 1.

Sitakisoside XVIII (**8**): Colorless needles from MeOH, mp 203—205 °C, $[\alpha]_D^{20}$ −12.0° (c=2.5, 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: 1102 $[M(C_{55}H_{85}NO_{20})+Na]^+$, 1118 $[M+K]^+$. *Anal.* Calcd for $C_{55}H_{85}NO_{20}\cdot 2H_2O$: C, 59.74; H, 7.81; N, 1.42. Found: C, 59.60; H, 8.00; N, 1.30. ^{1}H-NMR δ: 0.83 (H_3-25), 0.97 (H_3-24), 1.10 (H_3-26), 1.26 (H_3-23), 1.34 (H_3-29), 1.37 (H_3-27) and 1.39 (H_3-30), 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, H_2-28), 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-CH_3), 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}C-NMR: Table 1.

Sitakisoside XIX (**9**): An amorphous powder, $[\alpha]_D^{20}$ −17.1° (c=1.6, MeOH). IR (film) cm^{-1}: 3400, 3250. Negative FAB-MS m/z: 945 $[M(C_{47}H_{78}O_{19})-H]^-$, 813 $[M-H-C_5H_8O_4]^-$, 651 $[M-H-C_5H_8O_4-C_6H_{10}O_5]^-$. *Anal.* Calcd for $C_{47}H_{78}O_{19}\cdot H_2O$: C, 58.49; H, 8.35. Found: C, 58.61; H, 8.61. ^{1}H-NMR δ: 0.82 (H_3-25), 0.93 (H_3-26), 1.00 (H_3-24), 1.27 (H_3-23), 1.32 (H_3-29), 1.34 (H_3-27), 1.36 (H_3-30), 3.33 (1H, dd, J=11.6, 4.4 Hz, H-3), 4.11, 4.76 (each 1H, d, J=10.5 Hz, H_2-28), *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}C-NMR: Table 1.

Sitakisoside XX (**10**): An amorphous powder, $[\alpha]_D^{20}$ −21.2° (c=2.2, MeOH). IR (film) cm^{-1}: 3460, 1090. Positive FAB-MS m/z: 1099 $[M(C_{53}H_{88}O_{22})+Na]^+$, 1115 $[M+K]^+$. *Anal.* Calcd for $C_{53}H_{88}O_{22}\cdot 9/2H_2O$: C, 54.96; H, 8.44. Found: C, 54.98; H, 7.63. ^{1}H-NMR δ: 0.76 (H_3-25), 0.80 (H_3-26), 0.93 (H_3-24), 0.93 (H_3-29), 1.04 (H_3-30), 1.21 (H_3-23), 1.27 (H_3-27), 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, H_2-28), 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 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}C-NMR: Table 1.

Acid Hydrolysis of Sitakisoside 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, $[\alpha]_D^{20}$ +57.0° (c=0.9, $CHCl_3$–MeOH=1:1). HREIMS obsd. for $[M\ (C_{30}H_{50}O_4)-H_2O]$ 456.3628, Calcd 456.3604. ^{1}H-NMR δ: 0.93 (H_3-25), 1.04 (H_3-24), 1.06 (H_3-26), 1.25 (H_3-23), 1.29 (H_3-29), 1.29 (H_3-30), 1.35 (H_3-27), 2.13 (1H, dd, J=13.0, 13.0 Hz, H_β-22), 2.64 (1H, dd, J=13.5, 4.0 Hz, H-18), 3.28 (1H, dd, J=13.0, 4.0 Hz, H_α-22), 3.48 (1H, dd, J=8.0, 8.0 Hz, H-3), 3.80, 4.43 (each 1H, d, J=10.5 Hz, H_2-28), 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}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 Sitakisoside 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*-methylanthranilate (8 mg), which was confirmed by comparison of ^{1}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 Sitakisoside 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}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 Sitakisosides 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}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 Sitakisoside 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}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 Sitakisoside 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*-methylanthranilate (6 mg), which was confirmed by comparison of ^{1}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 Sitakisoside 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}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 Sitakisoside 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

^{1}H-NMR data and by co-HPLC with an authentic sample. The 1-BuOH layer was subjected to HPLC (YMC, ODS S-5, 27% CH_3CN) 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 ^{1}H-NMR data and by co-HPLC with an authentic sample. From the H_2O 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.

Acknowledgment The authors are grateful to the Ministry of Education, Science, Sports and Culture for financial support (Grant No. 50006342).

References

1) Part X: Yoshikawa K., Taninaka H., Kann Y., Arihara S., *Chem. Pharm. Bull.*, **42**, 2023—2027 (1994).
2) Part XI: Yoshikawa K., Taninaka H., Kann Y., Arihara S., *Chem. Pharm. Bull.*, **42**, 2455—2460 (1994).
3) Qiu S.-X., Yong G., Cheung H. T. A., *Phytochemistry*, **34**, 1385—1387 (1993).
4) Khong P. W., Lewis K. G., *Aust. J. Chem.*, **28**, 165—172 (1975).
5) Mahato S. B., Pal B. C., *J. Chem. Soc., Perkin Trans. 1*, **1987**, 629—634.
6) Kazuo K., Yoshimura Y., Seo S. , Sakurai K., Tomita Y., Ishii H., *Tetrahedron Lett.*, **1976**, 4163—4166.
7) Tori K., Seo S., Yoshimura Y., Arita H., Tomita Y., *Tetrahedron Lett.*, **1977**, 179—182.
8) Kasai R., Ogihara M., Asakawa J., Mizutani K., Tanaka O., *Tetrahedron*, **35**, 1427—1432 (1979).