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Pregnane Glycosides from *Trachelospermum asiaticum*[1)]

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Eight bisdesmosidic pregnane glycosides were isolated from *Trachelospermum asiaticum* NAKAI (Apocynaceae). The glycosides have a common structure of 3-*O*-*β*-D-digitalosyl-3*β*,17*α*,20*α*-trihydroxy-5*α*-pregn-6-ene, and three sugars at most are linked to the 20-hydroxyl group.

Keywords——Apocynaceae; *Trachelospermum asiaticum*; pregnane; bisdesmosidic pregnane glycoside; 3*β*,17*α*,20*α*-trihydroxy-5*α*-pregn-6-ene; teikagenin; teikaside; 3-*O*-*β*-D-digitalosyl-teikagenin

During our studies on the constituents of *Trachelospermum asiaticum* NAKAI, we have described teikaside A, a bisdesmosidic pregnane glycoside,[2)] lignan glycosides,[3)] and trachelosperosides, glucosides of ursane-type and oleanane-type polyhydroxy-triterpenoids.[1,4)]

This paper deals with a further investigation on pregnane glycosides, resulting in the isolation and structure determinations of eight bisdesmosidic glycosides composed of 3-*O*-*β*-D-digitalosyl-teikagenin (3*β*,17*α*,20*α*-trihydroxy-5*α*-pregn-6-ene), common to teikaside A[2)] (teikagenin-3-*O*-*β*-D-digitalosyl-20-*O*-*β*-D-glucosyl-*β*-D-sarmentosyl-*β*-D-sarmentoside, renamed teikaside A-IIIa), and teikasides A-Ia (**1**), A-Ib (**2**), A-IIa (**3**), A-IIb (**4**), A-IIc (**5**), A-IIIb (**6**), A-IIIc (**7**), and A-IIId (**8**).

The pregnane glycosides were obtained in small amounts from the $CHCl_3$-soluble fraction of the MeOH percolate.

The fast atom bombardment (FAB) mass spectra (MS) of **1** and **2** afforded $M^+ + Na$ peaks at *m/z* 647.376 and *m/z* 661.393, respectively, suggesting **1** and **2** to be biosides. Upon hydrolysis with 0.05 N H_2SO_4–50% dioxane, teikagenin-3-*O*-*β*-D-digitaloside (Tr-1)[2)] was observed from **1** and **2**, besides canarose from **1** and oleandrose from **2**. In the proton nuclear magnetic resonance (^{1}H-NMR) spectra, the coupling constants of the anomeric protons of the canarose and oleandrose were observed to be 9 Hz (br d) and 10 Hz and 1 Hz (dd), respectively, indicating that these sugars retain *β*-linkages. The sugars were allocated to the 20 hydroxyl group based on the downfield shifts of C-20 in **1** (+11.0 ppm) and **2** (+11.1 ppm) in comparison with the signal of Tr-1 in the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectra. Since all the signals due to the canarose and oleandrose moieties in the ^{1}H- and ^{13}C-NMR spectra were identical with those of a *β*-D-canaroside[5)] and a *β*-D-oleandroside,[6)] the structures of **1** and **2** were determined to be teikagenin-3-*O*-*β*-D-digitalosyl-20-*O*-*β*-D-canaroside and teikagenin-3-*O*-*β*-D-digitalosyl-20-*O*-*β*-D-oleandroside, respectively.

Based on the $M^+ + Na$ peaks at *m/z* 823 (**3** and **4**) and *m/z* 809 (**5**), **3**, **4**, and **5** seemed to be triosides having an additional hexose as compared with teikagenin biosides such as **1** or **2**, and the terminal hexose was assignable as glucose from the ^{13}C-NMR spectra. Although the glucosyl linkage in **3** was not cleaved by cellulase, acid hydrolysis provided Tr-1 and a biose which was identified as *β*-D-glucosyl-D-diginose by comparison with an authentic sample, by thin layer chromatography (TLC). Upon further hydrolysis of the biose, diginose

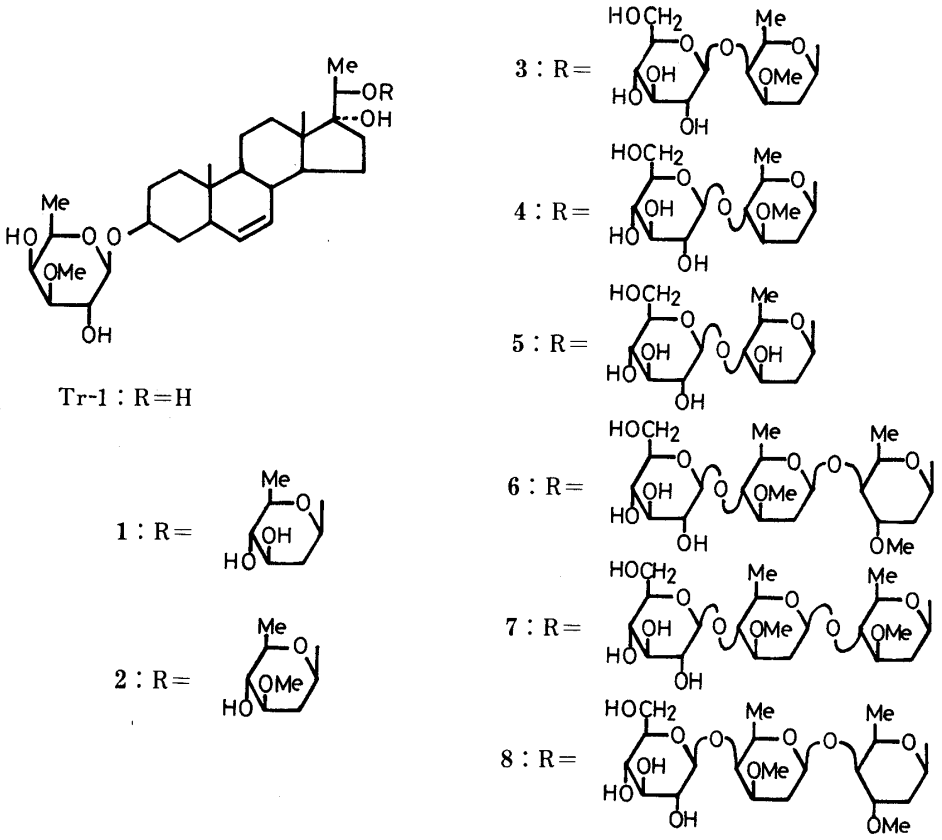

Chart 1

and glucose were detected. The structure of **3** was finally determined to be teikagenin-3-*O*-*β*-D-digitalosyl-20-*O*-*β*-D-glucosyl-*β*-D-diginoside by comparison of the ^{13}C-NMR signals with those of Tr-1, and with the signals due to the sugar moiety of oleagenin-*β*-D-glycosyl-*β*-D-diginoside.[7] Compound **4** was hydrolyzed with 0.05 N H_2SO_4–50% dioxane to Tr-1 and a biose which was not identical with *β*-D-glucosyl-L-oleandrose on TLC. Upon enzymic hydrolysis of **4** with *β*-glucosidase, the product showed the same *Rf* value as **2** on TLC. In order to confirm it to be **2**, the product was further hydrolyzed under acidic conditions to yield Tr-1 and oleandrose. The presence of the *β*-D-glucosyl moiety at 4-hydroxyl of the *β*-D-oleandrose was shown by the ^{13}C- and ^{1}H-NMR signals. Compound **4** was therefore characterized as teikagenin-3-*O*-*β*-D-digitalosyl-20-*O*-*β*-D-glucosyl-*β*-D-oleandroside. The terminal glucose of **5** was hydrolyzed enzymically to afford **1**. Since glycosylation shifts were observed in C-4 of the canarose (+10.7 ppm) and C-20 of the aglycone (+11.2 ppm) in comparison with **1** and Tr-1, respectively, the presence of the *β*-D-glucosyl-(1→4)-*β*-D-canarosyl moiety at the 20-hydroxyl group was established in **5**.

Compounds **6**, **7**, and **8** seemed to be tetraosides based on the $M^+ + Na$ peaks at *m/z* 967, as well as the signals of four anomeric carbons and four anomeric protons, of which two were observed as a doublet of doublets, indicating the presence of two 2-deoxy sugars. All the glycosidic linkages were assignable as *β* based on the coupling constants. Upon acid hydrolysis of **6**, sarmentose and *β*-D-glucosyl-D-oleandrose were detected along with Tr-1, suggesting the sugar sequence of glucose–oleandrose–sarmentose. The location of the triose moiety at the 20-hydroxyl group was assignable based on a comparison of the ^{13}C-NMR spectra with those of **1** and Tr-1. Since the *β*-linkage of the sarmentose was shown by the ^{1}H-NMR spectrum, the sarmentose was considered to retain D-form, and the structure of **6** is concluded to be as shown in Chart 1. Compound **7** provided, on acid hydrolysis, Tr-1, oleandrose, and *β*-D-glucosyl-D-oleandrose, which was identified by comparison with the biose from **4** and **6**. Since

TABLE I. ^{13}C Chemical Shifts of Pregnane Glycosides, δ (ppm) from TMS in Pyridine-d_5

Carbon No.	Tr-1[a]	1[a]	2	3	4	5	6	7	8
1	34.9	34.9	34.9	34.9	34.9	34.9	34.9	34.9	34.8
2	30.0	30.0	30.1	30.0	30.0	30.0	30.0	30.0	29.9
3	77.6	77.6	77.7	77.7	77.6	77.7	77.7	77.7	77.7
4	32.9	33.0	33.0	32.9[d]	33.0	33.0	32.9	33.0	32.9
5	45.1	45.1	45.2	45.1	45.1	45.2	45.2	45.2	45.1
6	129.5	129.5	129.6	129.5	129.5	129.5	129.5	129.4	129.5
7	131.1	131.1	131.2	131.1	131.1	131.1	131.1	131.2	131.1
8	38.2	38.2	38.3	38.3	38.3	38.3	38.3	38.3	38.2
9	52.7	52.7	52.7	52.7	52.7	52.7	52.7	52.7	52.6
10	34.6	34.6	34.6	34.6	34.6	34.6	34.6	34.6	34.5
11	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0
12	38.5	37.9	38.1	37.9	37.9	37.9	37.9	38.0	37.9
13	47.0	47.0	47.1	47.0	47.0	47.0	47.0	47.1	47.0
14	49.5	49.1	49.2	49.1	49.1	49.1	49.2	49.2	49.1
15	23.5	23.5	23.6	23.5	23.5	23.5	23.5	23.5	23.4
16	32.0	31.9	32.0	32.0	31.9	31.9	31.9	31.9	31.9
17	85.3	85.0	85.0	84.9	84.9	84.9	85.0	85.0	84.9
18	11.5	11.5	11.5	11.5	11.5	11.5	11.5	11.5	11.5
19	14.5	14.7	14.7	14.7	14.7	14.7	14.7	14.7	14.7
20	71.8	82.8	82.9	83.2	82.9	83.0	82.9	83.1	83.2
21	19.4	18.1	18.1	18.2[e]	18.0	18.1	18.0[d]	18.1	17.9[d]
3-*O*-dgt.[b]									
1′	102.6	102.7	102.8	102.7	102.7	102.7	102.6	102.7	102.6
2′	70.8	70.8	70.9	70.8[f]	70.8	70.8	70.7	70.9	70.7[e]
3′	85.0	85.0	85.1	85.0	85.0	85.0	85.5	85.1	85.4
4′	68.6	68.6	68.7	68.6	68.6	68.6	68.1	68.6	68.1
5′	71.0	71.0	71.1	71.0	71.0	71.0	71.4	71.1	71.4
6′	17.4	17.4	17.5	17.4	17.4	17.5	17.3	17.5	17.3
OMe	57.2	57.2	57.3	57.2	57.2[d]	57.2	56.4[e]	57.2[d]	56.4[f]
20-*O*-sug.[c]		(can.)	(ole.)	(dgn.)	(ole.)	(can.)	(sar.)	(ole.)	(sar.)
1″		102.5	102.2	103.0	101.9	102.2	99.8	100.1	99.8
2″		41.1	37.3	33.0[d]	37.4	39.9	31.1	37.6[e]	31.1
3″		72.1	81.7	73.4	79.5	70.3	80.2	79.3	80.2[g]
4″		78.5	76.4	80.1	83.5	89.2	75.0	83.1[f]	74.9
5″		72.9	72.9	70.7[f]	72.0[e]	71.5[d]	70.2	72.1[g]	70.2[e]
6″		18.8	18.8	17.9[e]	19.0	18.6	17.9[d]	18.9	17.9[d]
OMe			57.0	56.1	57.1[d]		58.7	57.2[d]	58.7
							(ole.)	(ole.)	(dgn.)
1‴							101.9	102.1	102.9
2‴							37.5	37.7[e]	32.9
3‴							79.6	79.6	73.4
4‴							83.4	83.3[f]	80.1[g]
5‴							72.0	72.0[g]	70.5[e]
6‴							19.0	18.9	18.2[d]
OMe							57.1[e]	57.3[d]	56.1[f]
term. glc									
1⁗				104.7	104.5	105.7	104.4	104.5	104.7
2⁗				75.9	75.7	75.1	75.7	75.7	75.9
3⁗				78.5[g]	78.6[f]	78.4	78.6[f]	78.7[h]	78.5[h]
4‴				71.9	71.9[e]	71.6[d]	72.0	71.5[g]	71.9
5⁗				78.3[g]	78.0[f]	78.4	78.1[f]	78.1[h]	78.3[h]
6⁗				63.1	63.1	62.5	63.1	63.1	63.1

a) Signal assignments were done based on the two-dimension (2D) NMR (^1H–^{13}C COSY) spectra. *b*) dgt. = β-D-digitalose. *c*) can. = β-D-canarose, ole. = β-D-oleandrose, dgn. = β-D-diginose, sar. = β-D-sarmentose, and glc. = β-D-glucose. *e*—*h*) Signal assignments marked *d*—*h*) in each column may be reversed.

TABLE II. ^{1}H Chemical Shifts of Pregnane Glycosides, δ (ppm) from TMS in Pyridine-d_5[a]

	Tr-1[b]	1[b]	2	3	4	5	6	7	8
H-3α	3.99 (m)	3.99 (m)	4.00 (m)	3.99 (m)					
H-6	5.58 (br d, 10)	5.58 (br d, 10)	5.60 (br d, 10)	5.59 (br d, 10)	5.59 (br d, 10)	5.58 (br d, 10)	5.58 (br d, 9)	5.60 (br d, 10)	5.58 (br d, 10)
H-7	5.35 (br d, 10)	5.37 (br d, 10)	5.38 (br d, 10)	5.38 (br d, 10)	5.38 (br d, 10)	5.37 (br d, 10)	5.37 (br d, 9)	5.38 (br d, 10)	5.36 (br d, 10)
H-18	0.76	0.76	0.77	0.77	0.75	0.74	0.74	0.76	0.74
H-19	0.80	0.78	0.79	0.77	0.77	0.76	0.75	0.77	0.77
H-20	4.13 (q, 6)	4.01 (q, 6)	4.02 (q, 6)	3.98 (q, 6)	3.95 (q, 6)	3.94 (q, 6)	3.95 (q, 6)		
H-21	1.50 (d, 6)	1.65 (d, 6)	1.64[c] (d, 6)	1.63[c] (d, 6)	1.61[c] (d, 6)	1.61[c] (d, 6)	1.61[c] (d, 6)	1.64[c] (d, 6)	1.63[c] (d, 6)
H-1′	4.84 (d, 8)	4.83 (d, 7)	4.84 (d, 7)	4.84 (d, 8)	4.84 (d, 7)	4.84 (d, 7)	4.79 (d, 8)	4.86 (d, 8)	4.78 (d, 8)
H-2′	4.36 (dd, 8, 9)	4.35 (dd, 7, 8)	4.36 (dd, 7, 8)	4.36 (t, 8)	4.36 (t, 8)			4.39 (t, 8)	
H-3′	3.54 (dd, 9, 3)	3.54 (dd, 8, 3)	3.54 (dd, 8, 3)	3.54 (dd, 8, 3)		3.54 (dd, 9, 3)			
H-4′	4.09 (d, 3)	4.09 (br s)	4.09 (br s)	4.10 (br s)	4.09 (d, 3)	4.09 (d, 3)		4.11 (d, 3)	
H-5′	3.82 (q, 7)	3.82 (q, 6)	3.82 (q, 6)	3.82 (q, 6)		3.82 (q, 6)		3.83 (q, 6)	
H-6′	1.60 (d, 7)	1.60 (d, 6)	1.60[c] (d, 6)	1.60[c] (d, 6)	1.60[c] (d, 6)	1.60[c] (d, 6)	1.60[c] (d, 6)	1.61[c] (d, 6)	1.59[c] (d, 6)
3′-OMe	3.60	3.60	3.60	3.61	3.60	3.60	3.68	3.61	3.68
H-1″		4.96 (br d, 9)	4.89 (dd, 10, 1)	4.77 (br d, 10)	4.82 (br d, 10)	4.89 (br d, 10)	5.32 (dd, 8, 2)	4.83 (br d, 10)	5.33 (dd, 8, 2)
H-3″		4.14 (m)	3.52 (m)	3.49 (br d, 10)					
H-4″		3.56 (t, 9)	3.52 (m)	4.21 (br s)		3.48 (t, 9)			
H-6″		1.65 (d, 6)	1.61[c] (d, 6)	1.54 (d, 6)	1.76 (d, 6)	1.77 (d, 6)	1.52 (d, 6)	1.47 (d, 6)	1.52 (d, 6)
3″-OMe			3.48	3.41	3.54		3.31	3.52	3.31
Others				5.16 (d, 8, H-1‴)	5.13 (d, 8, H-1‴)	4.97 (d, 8, H-1‴)	4.82 (dd, 9, 1, H-1‴)	4.92 (br d, 10, H-1‴)	4.73 (br d, 9, H-1‴)
							3.54 (3‴-OMe)	3.54 (3‴-OMe)	3.41 (3‴-OMe)
							1.76 (3H, d, 6, H-6‴)	1.74 (3H, d, 6, H-6‴)	1.54 (3H, d, 6, H-6‴)
							5.13 (d, 8, H-1⁗)	5.14 (d, 8, H-1⁗)	5.17 (d, 8, H-1⁗)

a) Signal pattern and *J* value (Hz) are given in parentheses. *b*) Signal assignments were based on ^{1}H–^{1}H COSY spectra. *c*) Signal assignments marked *c*) in each column may be reversed.

all of the sugars retain β-linkages based on the coupling constants of the anomeric protons, each oleandrose was considered to retain D-form and the ^{13}C-NMR signals due to oleandrose were in good agreement with those of **6**. As described for other glycosides, a downfield shift at C-20 (+11.3 ppm) was observed, and the structure of **7** was assigned as teikagenin-3-*O*-β-D-digitalosyl-20-*O*-β-D-glucosyl-β-D-oleandrosyl-β-D-oleandroside. Upon acid hydrolysis, **8**

afforded Tr-1, sarmentose, and β-D-glucosyl-D-diginose, which were identified by comparison with authentic samples on TLC and from ^{13}C-NMR considerations. As described in the case of **6**, the sarmentose was considered to retain D-form. The structure of **8** was therefore assigned as teikagenin-3-*O*-β-D-digitalosyl-20-*O*-β-D-glucosyl-β-D-diginosyl-β-D-sarmentoside.

In this paper, we describe eight bisdesmosidic pregnane glycosides including biosides to tetraosides, isolated from the plants collected in the suburbs of Fukuoka City (Shiibaru district). Of the component sugars at the 20-hydroxyl group, three 2,6-dideoxy-3-*O*-methylhexoses, D-sarmentose, D-oleandrose and D-diginose, and one 2,6-dideoxyhexose, D-canarose were identified along with terminal D-glucose. The number and kinds of the component sugars vary depending upon the collecting area, from biosides such as **1** and **2**, to heptaosides having six sugars at the C-20 hydroxyl group. Teikaside A was not isolated from the plants in this study. The structures of the glycosides having more sugars will be presented elsewhere.

Experimental

Melting points were taken on a hot stage apparatus and are uncorrected. ^{1}H- and ^{13}C-NMR spectra were recorded on a JEOL GX-400 spectrometer in pyridine-d_5. Chemical shifts are given in δ values referred to internal tetramethylsilane, and the following abbreviations are used: s=singlet, d=doublet, t=triplet, m=multiplet, dd=doublet of doublets, br d=broad doublet. The following solvent systems were applied for silica gel column chromatography and TLC: solv. 1, $CHCl_3$–MeOH–H_2O (bottom layer); solv. 2, EtOAc–MeOH–H_2O (upper layer). Detection of the spots was carried out by spraying diluted H_2SO_4 onto the TLC plates followed by heating the plates. For detection of the deoxy sugars a mixture of equal volumes of 1% vanillin in EtOH and 3% aqueous perchloric acid was applied.

Extraction and Isolation of Teikasides——Air-dried whole plants of *Trachelospermum asiaticum* NAKAI (11 kg) collected in the Shiibaru district of Fukuoka City in April 1986, were powdered and percolated with MeOH. The MeOH percolate (100 l) was concentrated *in vacuo* to 5 l and diluted with 5 l of H_2O. The deposit was filtered off, and the filtrate was extracted with benzene and then with $CHCl_3$. The $CHCl_3$ extract (118 g) was dissolved in 30% MeoH and passed through an MCI gel (CHP-20-P, Mitsubishi Chem. Ind. Ltd.) column, elution was done with H_2O–MeOH, with increasing MeOH concentrations. The eluate with 60—100% MeOH was chromatographed on a silica gel column with solv. 1 (7:2:1—7:3:1). The fractions containing the glycosides were further chromatographed on a silica gel column with solv. 2 (4:1:5—4:1:3), and then on an ODS-column (RQ-1, Fuji-gel) and further by high-performance liquid chromatography (HPLC) in some cases with CH_3CN–H_2O (30—40%) to yield **1**—**8**. Yields of the glycosides: **1**, 68 mg; **2**, 19 mg; **3**, 75 mg; **4**, 16 mg; **5**, 40 mg; **6**, 16 mg; **7**, 27 mg; **8**, 16 mg.

MeOH and passed through an MCI gel (CHP-20-P, Mitsubishi Chem. Ind., Ltd.) column, elution was done with

Teikaside A-Ia (Teikagenin-3-*O*-β-D-digitalosyl-20-*O*-β-D-canaroside) (1)——mp 205—213 °C from MeOH, $[\alpha]_D^{26}$ −122.3° (c=0.60, MeOH), FAB-MS m/z: 647.376 (Calcd for $C_{34}H_{56}O_{10}$+Na: 647.377).

Teikaside A-Ib (Teikagenin-3-*O*-β-D-digitalosyl-20-*O*-β-D-oleandroside) (2)——mp 207—211 °C from MeOH, $[\alpha]_D^{18}$ −117.2° (c=1.00, MeOH), FAB-MS m/z: 661.393 (Calcd for $C_{35}H_{58}O_{10}$+Na: 661.393).

Teikaside A-IIa (Teikagenin-3-*O*-β-D-digitalosyl-20-*O*-β-D-glucosyl-β-D-diginoside) (3)——mp 265—280 °C (dec.) from MeOH, $[\alpha]_D^{26}$ −113.1° (c=0.50, MeOH), *Anal.* Calcd for $C_{41}H_{68}O_{15}\cdot 0.5H_2O$: C, 60.80; H, 8.59. Found: C, 60.73; H, 8.69, FAB-MS m/z: 823 ($C_{41}H_{68}O_{15}$+Na). Compound **3** (5 mg) was dissolved in 20% EtOH (2 ml) and shaken with cellulase (Sigma Chem. Co., Ltd.) (15 mg) for 3d at 38 °C. The mixture was diluted with H_2O and extracted with BuOH. The BuOH extract showed only **3** on TLC (Rf 0.5, solv. 1 7:3:1).

Teikaside A-IIb (Teikagenin-3-*O*-β-D-digitalosyl-20-*O*-β-D-glucosyl-β-D-oleandroside) (4)——mp 250—260 °C (dec.) from MeOH, $[\alpha]_D^{27}$ −44.8° (c=0.60, MeOH), *Anal.* Calcd for $C_{41}H_{68}O_{15}\cdot 4.5H_2O$: C, 55.83; H, 8.80. Found: C, 55.59; H: 9.09, FAB-MS m/z: 823 ($C_{41}H_{68}O_{15}$+Na). Compound **4** (5 mg) was dissolved in 20% EtOH (1 ml) and treated with cellulase (15 mg) in the same manner as described for **3**. The BuOH extract showed a spot identical with **2** on TLC (Rf 0.37, solv. 1 7:2:1, Rf 0.29, solv. 2 9:1:0.1).

Teikaside A-IIc (Teikagenin-3-*O*-β-D-digitalosyl-20-*O*-β-D-glucosyl-(1→4)-β-D-canaroside) (5)——mp 285—295 °C (dec.) from MeOH, $[\alpha]_D^{19}$ −95.9° (c=0.40, MeOH), *Anal.* Calcd for $C_{40}H_{66}O_{15}\cdot 3H_2O$: C, 57.13; H, 8.63. Found: C, 57.07; H, 8.40, FAB-MS m/z: 809 ($C_{40}H_{66}O_{15}$+Na). Compound **5** (5 mg) was dissolved in 10% EtOH (2 ml) and treated with cellulase (10 mg) for 1 day in the same manner as described above. The BuOH extract showed a spot identical with **1** on TLC (Rf 0.32, solv. 1 7:2:1, Rf 0.25, solv. 2 9:1:0.1).

Teikaside A-IIIb (Teikagenin-3-*O*-β-D-digitalosyl-20-*O*-β-D-glucosyl-β-D-oleandrosyl-β-D-sarmentoside) (6)——A solid, $[\alpha]_D^{32}$ −35.0° (c=0.55, MeOH), FAB-MS m/z: 967 ($C_{48}H_{80}O_{18}$+Na).

Teikaside A-IIIc (Teikagenin-3-*O*-*β*-D-digitalosyl-20-*O*-*β*-D-glucosyl-*β*-D-oleandrosyl-*β*-D-oleandroside) (7)——A solid, $[\alpha]_D^{27}$ −64.2° (c=1.90, MeOH), FAB-MS m/z: 967 ($C_{48}H_{80}O_{18}$+Na). The hexaacetate of **7** was obtained by usual acetylation, mp 194—197 °C from MeOH, FAB-MS m/z: 1219 ($C_{60}H_{92}O_{24}$+Na).

Taikaside A-IIId (Teikagenin-3-*O*-*β*-D-digitalosyl-20-*O*-*β*-D-glucosyl-*β*-D-diginosyl-*β*-D-sarmentoside) (8)——A solid, $[\alpha]_D^{28}$ −102.2° (c=0.25, MeOH), FAB-MS m/z: 967 ($C_{48}H_{80}O_{18}$+Na). Hexaacetate, mp 228—240 °C (dec.), *Anal.* Calcd for $C_{60}H_{92}O_{24}\cdot H_2O$: C, 59.29; H, 7.80. Found: C, 59.11; H, 7.86.

Acid Hydrolysis of the Glycosides——The glycosides (5—10 mg) were dissolved in 0.05 M H_2SO_4–50% dioxane (2 ml) and the solution was refluxed for 30 min. The dioxane was evaporated off *in vacuo* and the residue was diluted with H_2O. The mixture was extracted with $CHCl_3$. The $CHCl_3$ layer was concentrated *in vacuo* to dryness after being washed with H_2O and dried over Na_2SO_4. The residue was examined by TLC in comparison with authentic teikagenin-3-*O*-*β*-D-digitaloside (Tr-1). The hydrolysates from **1**—**8** showed the same *Rf* value as Tr-1 (*Rf* 0.35, solv. 1 7:2:1; *Rf* 0.28, solv. 2 9:1:0.1). After extraction with $CHCl_3$, the H_2O layer was deacidified with IRA-410 and the H_2O was evaporated off *in vacuo*. The residue was examined by TLC (solv. 1, 7:3:1 and solv. 2, 4:1:0.5). *Rf* values of the sugars from each glycoside are as follows: **1**, 0.32 (solv. 1) and 0.53 (solv. 2); **2**, 0.56 and 0.66; **3**, 0.21 and 0.30; **4**, 0.18 and 0.26; **5**, 0.11 and 0.26; **6**, 0.61, 0.18 and 0.62, 0.26; **7**, 0.56, 0.18 and 0.66, 0.26; **8**, 0.61, 0.21 and 0.62, 0.30. D-Canarose, 0.32 and 0.53; D-diginose, 0.58 and 0.56; D-oleandrose, 0.56 and 0.66; D-sarmentose, 0.61 and 0.62; *β*-D-glucosyl-D-diginose, 0.21 and 0.30; *β*-D-glucosyl-D-glucosyl-D-oleandrose, 0.18 and 0.26; *β*-D-glucosyl-(1→4)-D-canarose, 0.11 and 0.26.

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