[Chem. Pharm. Bull. 36(11)4330—4336(1988)]

Pregnane Glycosides of Teikasides B and C Series, from *Trachelospermum asiaticum*[1)]

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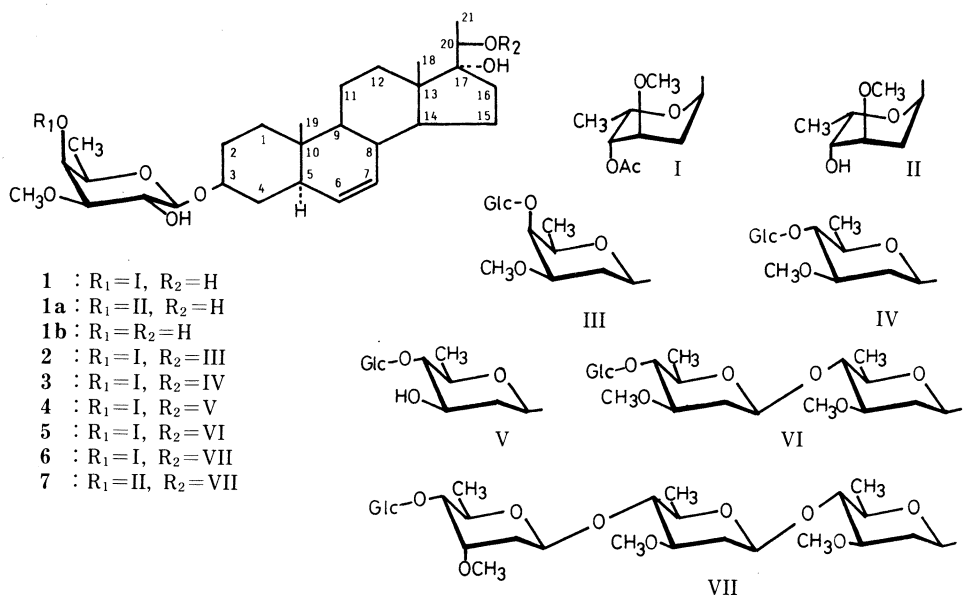
(Received May 2, 1988)

Seven pregnane glycosides including six bisdesmosidic glycosides of teikagenin were isolated and their structures were determined. L-Sarmentose, a new 2,6-dideoxy-3-*O*-methylhexose, was found as one of the component sugars.

Keywords——Apocynaceae; *Trachelospermum*; pregnane; pregnane bisdesmosidic glycoside; teikaside; L-sarmentose; 4-*O*-acetyl-α-L-sarmentosyl-(1→4)-β-D-digitaloside; teikagenin; 3β,17α,20-trihydroxy-5α,20*S*-pregn-6-ene

In the course of our studies on the constituents of Apocynaceae plants, we have described pregnanes from *Nerium*,[2)] *Anodendron*[3)] and *Apocynum*,[4)] and bisdesmosidic pregnane glycosides from *Trachelospermum*[1,5)] and *Apocynum*.[4)] In the preceding paper of this series, eight bisdesmosidic glycosides of teikagenin (3β,17α,20-trihydroxy-5α,20*S*-pregn-6-ene), having D-digitalose at the 3-OH and one or two 2,6-dideoxy-3-*O*-methylhexoses with one terminal glucose at the 20-OH, were described. This paper deals with teikasides B and C groups, seven teikagenin glycosides having an α-L-sarmentosyl-(1→4)-β-D-digitalosyl moiety at the 3-OH with or without one acetyl residue.

Seven glycosides (**1**—**7**) were obtained from plants collected separately in two different



1 : R_1=I, R_2=H
1a : R_1=II, R_2=H
1b : R_1=R_2=H
2 : R_1=I, R_2=III
3 : R_1=I, R_2=IV
4 : R_1=I, R_2=V
5 : R_1=I, R_2=VI
6 : R_1=I, R_2=VII
7 : R_1=II, R_2=VII

Chart 1

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

H	1b	1	2	3	4	5	6	7
6	5.58 (br d, 10)	5.56 (br d, 10)	5.58 (br d, 10)	5.58 (br d, 10)	5.58 (br d, 10)	5.58 (br d, 10)	5.60 (br d, 10)	5.59 (br d, 10)
7	5.35 (br d, 10)	5.34 (br d, 10)	5.37 (br d, 10)	5.37 (br d, 10)	5.36 (br d, 10)	5.37 (br d, 10)	5.37 (br d, 10)	5.37 (br d, 10)
18, 19	0.76, 0.80	0.74, 0.80	0.75, 0.77	0.74, 0.75	0.74 (×2)	0.75, 0.77	0.75, 0.77	0.75, 0.77
20	4.13 (q, 6)	4.12 (q, 6)	3.99 (q, 6)	3.95 (q, 6)	3.94 (q, 6)			
21	1.50 (d, 6)	1.48 (d, 6)	1.63 (d, 6)	1.61 (d, 6)	1.61 (d, 6)	1.63 (d, 6)	1.63 (d, 6)	1.63 (d, 6)
3-*O*-Sug.[b]								
1. (D-Digt.)	4.84 (d, 8)	4.77 (d, 7)	4.78 (d, 8)	4.79 (d, 7)	4.78 (d, 7)	4.79 (d, 7)	4.79 (d, 8)	4.80 (d, 8)
2	4.36 (dd, 8, 9)	4.27 (dd, 7, 10)	4.28 (dd, 8, 9)	4.29 (dd, 7, 9)	4.29 (dd, 7, 9)	4.29 (dd, 7, 9)		
3	3.54 (dd, 9, 3)	3.52 (dd, 10, 3)			3.53 (dd, 9, 2)	3.52 (dd, 9, 2)		
4	4.09 (d, 3)	4.14 (d, 3)	4.14 (d, 3)	4.15 (d, 3)	4.15 (d, 3)	4.15 (d, 3)	4.15 (d, 3)	4.22 (d, 3)
5	3.82 (q, 7)	3.79 (q, 6)	3.80 (q, 6)		3.81 (q, 6)	3.81 (q, 6)	3.81 (q, 6)	
6	1.60 (d, 7)	1.52 (d, 6)	1.52 (d, 6)	1.52 (d, 6)	1.52 (d, 6)	1.53 (d, 6)	1.53 (d, 6)	1.59[d] (d, 6)
OMe	3.60	3.65	3.66	3.66	3.66	3.66	3.66	3.66
1 (L-Sar.)		5.59 (t, 4)	5.60 (t, 4)	5.60 (t, 4)	5.60 (t, 4)	5.60 (t, 4)	5.61 (t, 4)	5.60 (t, 4)
3		3.56 (br s)	3.55 (br s)	3.54 (br s)	3.55 (br s)	3.56 (br s)		
4		5.13 (dd, 4, 2)	5.13 (dd, 4, 2)	5.13 (dd, 4, 2)	5.14 (dd, 4, 2)	5.13 (dd, 4, 2)	5.14 (dd, 4, 2)	4.15 (dd, 4, 2)
5		4.57 (qd, 7, 2)	4.58 (qd, 7, 2)	4.59 (qd, 6, 2)	4.59 (qd, 6, 2)	4.59 (qd, 6, 2)	4.59 (qd, 6, 2)	
6		1.24 (d, 7)	1.24 (d, 7)	1.25 (d, 6)	1.25 (d, 6)	1.25 (d, 6)	1.25 (d, 6)	1.50[d] (d, 6)
OMe		3.27	3.27	3.28	3.27	3.28	3.27	3.36
OAc		2.10	2.10	2.10	2.10	2.10	2.10	
20-*O*-Sug.[c]			(D-Dig.) 4.76 (br d, 10, H-1) 3.48 (br d, 10, H-3) 4.20 (br s, H-4) 1.53 (3H, d, 6, H-6) 3.41 (3H, s, OMe) (D-Glc.) 5.16 (d, 8, H-1) 4.35 (dd, 12, 6, H-6a) 4.56 (dd, 12, 1, H-6b)	(D-Ole.) 4.83 (br d, 10, H-1) 1.76 (3H, d, 6) 3.54 (3H, s, OMe) (D-Glc.) 5.14 (d, 8, H-1) 4.34 (dd, 12, 6, H-6a) 4.52 (dd, 12, 1, H-6b)	(D-Can.) 4.89 (br d, 9, H-1) 3.49 (t, 9, H-4) 1.77 (3H, d, 6, H-6) (D-Glc.) 4.98 (d, 8, H-1) 4.30 (dd, 12, 6, H-6a) 4.58 (dd, 12, 1, H-6b)	(D-Ole.) × 2 4.82, 4.91 (br d, 9, H-1) 1.46, 1.74 (3H, d, 6, H-6) 3.51, 3.56 (3H, s, OMe) (D-Glc.) 5.13 (d, 8, H-1) 4.34 (dd, 12, 6, H-6a) 4.52 (dd, 12, 1, H-6b)	(D-Ole.) × 2 4.82, 4.90 (br d, 9, H-1) 1.46, 1.62 (3H, d, 6, H-6) 3.53, 3.54[e] (3H, s, OMe) (D-Cym.) 5.27 (br d, 9, H-1) 1.43 (3H, d, 6, H-6) 3.52[e] (3H, s, OMe) (D-Glc.) 4.94 (d, 8, H-1) 4.40 (dd, 12, 6, H-6a) 4.58 (br d, 12, H-6b)	(D-Ole.) × 2 4.81, 4.90 (br d, 9, H-1) 1.46, 1.62 (3H, d, 6, H-6) 3.53, 3.54[e] (3H, s, OMe) (D-Cym.) 5.27 (br d, 10, H-1) 1.43 (3H, d, 6, H-6) 3.52[e] (3H, s, OMe) (D-Glc.) 4.94 (d, 8, H-1) 4.40 (dd, 12, 5, H-6a) 4.58 (br d, 12, H-6b)

a) Signal pattern and *J* value (Hz) are given in parentheses. *b*) D-Digt. = β-D-digitalose, L-Sar. = α-L-sarmentose. *c*) D-Dig. = β-D-diginose, D-Ole. = β-D-oleandrose, D-Can. = β-D-canarose, D-Cym. = β-D-cymarose, D-Glc. = β-D-glucose. *d*, *e*) Signal assignments marked *d*) or *e*) may be reversed.

TABLE II. ^{13}C Chemical Shifts of **1b**, **1**, **2** and Sugar Moieties of **3**—**7**, δ (ppm) from Tetramethylsilane in Pyridine-d_5

C	1b	1	2	C	1b	1	2	3	4	5	6	7
				3-*O*-Sug.[h]								
1	34.9	34.8	34.9	D-Digt. 1	102.6	102.6	102.6	102.7	102.6	102.6	102.6	102.7
2	30.0	29.9	30.0	2	70.8	71.3	71.3	71.3	71.3	71.3	71.3	71.3
3	77.6	77.7	77.8	3	85.0	86.2	86.2	86.2	86.2	86.2	86.2	86.3
4	32.9	32.9	32.9	4	68.6	72.7[a]	72.7[a]	72.7[a]	72.7[a]	72.7[a]	72.7[a]	72.3
5	45.1	45.1	45.1	5	71.0	70.5	70.5	70.5	70.5	70.5	70.5	70.7
6	129.5	129.5	129.5	6	17.4	17.5	17.6	17.6	17.6	17.6	17.6	17.7
7	131.1	131.1	131.1	OMe	57.2	58.8	58.8	58.8	58.8	58.8	58.8	58.7
8	38.2	38.2	38.3	L-Sar. 1		97.2	97.2	97.2	97.2	97.2	97.2	97.3
9	52.7	52.7	52.7	2		29.2	29.2	29.2	29.2	29.2	29.2	29.7
10	34.6	34.5	34.6	3		74.9	74.9	74.9	74.9	74.9	74.9	78.7
11	21.0	20.9	21.0	4		73.0[a]	73.0[a]	73.0[a]	73.0[a]	73.0[a]	73.0[a]	71.8[a]
12	38.5	38.5	37.9	5		63.3	63.3	63.4	63.3	63.3	63.3	65.9
13	47.0	47.0	47.0	6		16.0	16.0	16.0	16.0	16.0	16.0	16.3
14	49.5	49.5	49.1	OMe		56.1	56.1	56.1	56.1	56.1	56.1	56.2
15	23.5	23.5	23.5	OAc		170.4	170.4	170.4	170.4	170.4	170.4	
16	32.0	32.0	31.9			20.7	20.7	20.7	20.7	20.7	20.7	
17	85.3	85.3	84.9	20-*O*-Sug.[i]			D-Dig.	D-Ole.	D-Can.	D-Ole.	D-Ole.	D-Ole.
18	11.5	11.4	11.5	1			102.9	101.9	102.2	100.0	100.1	100.1
19	14.5	14.4	14.7	2			33.0	37.4	39.9	37.6[a]	37.7[a]	37.7[b]
20	71.8	71.8	83.2	3			73.4	79.5	70.3	79.2	79.1[b]	79.1[c]
21	19.4	19.4	18.2	4			80.0	83.5	89.3	83.2[b]	83.1[c]	83.1[d]
				5			70.7	72.0[b]	71.3	72.1[c]	71.8[d]	71.8[a]
				6			17.9	19.0	18.5	18.9	18.8[e]	18.8[e]
				OMe			56.0	57.0		57.1[d]	57.3[f]	57.3[f]
							D-Glc.	D-Glc.	D-Glc.	D-Ole.	D-Ole.	D-Ole.
				1			104.7	104.5	105.7	102.1	102.0	102.0
				2			75.9	75.7	75.1	37.7[a]	37.9[a]	37.9[b]
				3			78.5[b]	78.6[c]	78.4	79.6	79.2[b]	79.2[b]
				4			71.9	71.9[b]	71.6	83.4[b]	83.2[c]	83.2[d]
				5			78.3[b]	78.0[c]	78.4	72.0[c]	71.7[d]	71.6[a]
				6			63.1	63.1	62.5	18.9	18.7[e]	18.7[e]
				OMe						57.2[d]	57.4[f]	57.4[f]
										D-Glc.	D-Cym.	D-Cym.
				1						104.4	98.4	98.4
				2						75.7	36.7	36.7
				3						78.6[e]	78.1[g]	78.1[g]
				4						71.5	82.8[c]	82.8[d]
				5						78.3[e]	69.6	69.6
				6						63.1	18.6[e]	18.6[e]
				OMe							58.5	58.5
											D-Glc.	D-Glc.
				1							106.5	106.5
				2							75.4	75.4
				3							78.3[g]	78.4[g]
				4							71.5[d]	71.5
				5							78.3[g]	78.3[g]
				6							63.1	63.1

a—*g*) Signal assignments marked *a*—*g*) in each column may be reversed. *h*) D-Digt. = β-D-digitalose, L-Sar. = α-L-sarmentose. *i*) D-Dig. = β-D-diginose, D-Ole. = β-D-oleandrose, D-Can. = β-D-canarose, D-Cym. = β-D-cymarose, D-Glc. = β-D-glucose.

districts. We had reported in Part 1 of this series that teikagenin is the only pregnane in this plant,[5] and the aglycone of **1**—**7** was confirmed to be teikagenin, based on the characteristic signals in the proton and carbon-13 nuclear magnetic resonance (^{1}H- and ^{13}C-NMR) spectra.

Compound **1** afforded the $M^+ + Na$ peak at *m/z* 703.403 in the fast atom bombardment-mass spectrum (FAB-MS), suggesting the molecular formula to be $C_{37}H_{60}O_{11}$. The presence of one acetyl group was shown by ^{1}H-NMR, along with two anomeric proton signals as a doublet (δ 4.77, $J=8$ Hz) and a triplet (δ 5.59, $J=4$ Hz), two methoxyl proton signals and two 6-methyl proton signals of 6-deoxy-3-*O*-methylsugars. In a comparison of the ^{13}C-NMR spectrum with that of teikagenin 3-*O*-β-D-digitaloside (**1b**),[1,5] signals due to C-17, C-20 and C-21 were observed at the same chemical shifts, and two sugars having one acetyl residue were considered to be linked linearly at the 3-OH of teikagenin. One of the two deoxysugars in **1** was assignable as D-digitalose, the signals of C-4 of which showed a downfield shift (+4.1 ppm).

When **1** was subjected to alkaline hydrolysis, the acetyl residue was split off to afford a deacetyl derivative (**1a**), which was then hydrolyzed with 0.05 N H_2SO_4 in 50% dioxane to afford **1b** and sarmentose. Based on the ^{1}H–^{1}H COSY spectrum of **1**, the acetyl group was allocated to the 4-OH of the sarmentose. Since the anomeric proton signal of the sarmentose was observed as a triplet with a small coupling constant ($J=4$ Hz), the glycosidic linkage of the sarmentose to the digitalose was determined to be α, suggesting the sarmentose to be an L-sugar. The difference between the molecular rotations ($\Delta[M]_D$) of **1a** and **1b** was calculated as $-242°$, while the $[M]_D$ values of methyl α-D-sarmentoside and methyl β-D-sarmentoside were given as $+274°$ and $-69.3°$, respectively.[6] Since the acetylsarmentose (**1c**), obtained by acid hydrolysis of **1**, showed a negative specific rotation value ($[\alpha]_D$ $-15.0°$), the sarmentose was determined to be of L-type. Compound **1** was therefore elucidated as teikagenin 3-*O*-(4-*O*-acetyl-α-L-sarmentosyl-(1→4)-β-D-digitaloside), and is named teikaside C-0.

Compound **2** was suggested to be a tetraoside of teikagenin, based on four anomeric proton signals besides three secondary methyl and three methoxyl proton signals of 6-deoxy-3-*O*-methylhexose. The $M^+ + Na$ peak in the FAB-MS at *m/z* 1009 suggested the molecular formula to be $C_{50}H_{82}O_{19}$. Two of the four anomeric protons were observed as doublets, one as a broad doublet and one as a triplet. In a comparison of the ^{13}C-NMR spectra of **1** and **2**, the signals due to **1** corresponded to those in the spectrum of **2** with a downfield shift of the C-20 (+11.4 ppm). The remaining two sugars were considered to be one each of 2,6-dideoxy-3-*O*-methylhexose and glucose, being linked to the 20-OH. Signals at δ 4.76, 3.48, 4.20 and 1.53 (H-1, -3, -4 and -6, respectively) and one methoxyl proton signal were assignable to those of β-D-diginoside based on their coupling constants. The chemical shifts of the ^{13}C-NMR signals due to the β-D-glucosyl-β-D-diginosyl moiety at the 20-OH were in good agreement with those of teikaside A-IIa, a glycoside having the same sugar sequence at the 20-OH.[1] Upon acid hydrolysis of **2** with 4% HOAc in 50% EtOH, the products were identical with **1**, teikaside A-IIa, **1c**, and β-D-glucosyl-D-diginose on thin layer chromatography (TLC). The structure of **2** was thus determined to be teikagenin 3-*O*-(4-*O*-acetyl-α-L-sarmentosyl-(1→4)-β-D-digitalosyl)-20-*O*-(β-D-glucosyl-β-D-diginoside), and **2** is named teikaside C-IIa.

Compound **3** showed the M^+ peak at *m/z* 986, suggesting the same molecular formula as **2**, $C_{50}H_{82}O_{19}$. In the ^{13}C-NMR spectrum, the signals due to **1** were assignable with a downfield shift of the C-20. The sugar sequence at the 20-OH was determined to be β-D-glucosyl-β-D-oleandroside by comparison of the ^{13}C-NMR signals with those of teikaside A-IIb[1] and by direct comparison of the biose with authentic β-D-glucosyl-D-oleandrose on TLC after acid hydrolysis. The structure of **3** was established as teikagenin 3-*O*-(4-*O*-acetyl-α-L-sarmentosyl-(1→4)-β-D-digitalosyl)-20-*O*-(β-D-glucosyl-β-D-oleandroside), and **3** is named teikaside C-IIb.

Compound **4** afforded the $M^+ + Na$ peak at *m/z* 995, 14 mass units smaller than **2**. The

signals due to **1** were also assignable in the ^{13}C-NMR spectrum. The sugar sequence at the 20-OH seemed to be β-D-glucosyl-(1→4)-D-canarose from a comparison of the NMR signals with those of teikaside A-IIc.[1] After removal of the acetyl residue of **4** in alkaline medium, the deacetyl-**4** (**4a**) was hydrolyzed with acid to afford β-D-glucosyl-(1→4)-D-canarose and L-sarmentose along with **1b**. Compound **4** was thus determined to be teikagenin 3-*O*-(4-*O*-acetyl-α-L-sarmentosyl-(1→4)-β-D-digitalosyl)-20-*O*-(β-D-glucosyl-(1→4)-β-D-canaroside), and is named teikaside C-IIc.

In the ^{1}H-NMR spectrum of **5**, five anomeric proton signals were observed at δ 5.60, 5.13, 4.91, 4.82 and 4.79 along with one 3H singlet due to an acetyl residue, four 6-methyl proton signals and four methoxyl proton signals, and thus **5** was suggested to be a teikagenin pentaoside having one more 2,6-dideoxy-3-*O*-methylhexose than the monoacetyltetraosides mentioned above. The $M^+ + Na$ peak at *m/z* 1153 in the FAB-MS was also consistent with a pentaoside structure. The presence of **1** in the molecule of **5** was confirmed by the ^{13}C-NMR spectrum, and three sugars at the 20-OH were suggested to be one D-glucose and two D-oleandrose. Upon acid hydrolysis of **5**, β-D-glucosyl-D-oleandrose and D-oleandrose were detected on TLC. The sugar moiety at the 20-OH was also confirmed by comparison of the ^{13}C-NMR signals with those of teikaside A-IIIc.[1] The structure of **5** was therefore established as teikagenin 3-*O*-(4-*O*-acetyl-α-L-sarmentosyl-(1→4)-β-D-digitalosyl)-20-*O*-(β-D-glucosyl-β-D-oleandrosyl-β-D-oleandroside), and is named teikaside C-IIIa.

Compound **6** showed six anomeric proton signals, one as a triplet (J=4 Hz), three as broad doublets (J=9 Hz) and two as doublets (J=8 Hz), of which two doublet signals were assignable as those of β-linked D-digitalose and D-glucose. The presence of one acetyl group was suggested by a 3H singlet peak at δ 2.10. The FAB-MS peak at *m/z* 1297 ($C_{64}H_{106}O_{25}Na$) in **6** was also consistent with the NMR analysis. In the ^{13}C-NMR spectrum of **6**, the signals due to **1** were assignable. Upon acid hydrolysis of **6**, β-D-glucosyl-D-cymarose was detected besides D-oleandrose, **1c** and **1b**, suggesting the sugar sequence at the 20-OH to be glucosyl-cymarosyl-oleandrosyl-oleandrose. Since the sugar linkages at the 20-OH are β, based on the coupling constants of the anomeric protons, the component sugars at the 20-OH are regarded as being of D-type. The structure of **6** was therefore determined to be the 20-*O*-(β-D-glucosyl-β-D-cymarosyl-β-D-oleandrosyl-β-D-oleandroside) of teikaside C-0. Compound **6** is named teikaside C-IVa.

Unlike other glycosides in this series, **7** has no acetyl residue. In the FAB-MS, the $M^+ + Na$ peak was observed at *m/z* 1255, 42 mass units less than that of **6**. Six anomeric proton and carbon signals were observed in the ^{1}H- and ^{13}C-NMR spectra, and signals due to the sugar moiety at the 20-OH were in good agreement with those of **6**. Chemical shifts of the sugar moiety at the 3-OH were almost the same as those of **4a**. Since **7** was detected on alkaline deacetylation of **6**, **7** was identified as deacetyl-**6**, and is named teikaside B-IVa.

Six teikasides C, having a teikagenin 3-*O*-(4-*O*-acetyl-α-L-sarmentosyl-(1→4)-β-D-digitalosyl) moiety as the basic structure, and one non-acetylated glycoside, teikaside B-IVa, were obtained in this work. Recently L-cymarose was reported as a component sugar of pregnane glycosides from Asclepiadaceae plant.[7] To the authors' knowledge, this is the first report of the isolation of L-sarmentoside from a natural source. It should be noted that L-sarmentose is present exclusively in the sugar moiety at the 3-OH while D-sarmentose is contained in the sugar sequence at the 20-OH of teikasides A as described before.[1]

Experimental

Melting points, optical rotations, NMR and MS were measured in the same manner and with the same instruments as described in the preceding paper.[1] For column chromatography and TLC, the following solvent systems were applied; solv. 1, $CHCl_3$–MeOH–H_2O (bottom layer); solv.2, EtOAc–MeOH–H_2O (top layer); solv.3, benzene–acetone (3:2), solv.4, MeCN–H_2O.

Extraction and Isolation——Whole plants of *Trachelospermum asiaticum* Nakai collected at Beppu City in September, 1987, (sample 1) and at Wakasugi-yama in November, 1985 (sample 2) were air-dried and powdered. Sample 1 (14.8 kg) and sample 2 (3 kg) were each percolated with MeOH and the percolates were treated in the same manner as described in the preceding paper.[1] The following glycosides were obtained from samples 1 and 2 as a solid or as crystals. From sample 1: **1**, 50 mg; **2**, 45 mg; **4**, 47 mg; **1b**, 315 mg; teikasides A-Ia, 139 mg; A-Ib, 143 mg; A-IIa, 50 mg; A-IIb, 15 mg, A-IIc, 40 mg. From sample 2: **2**, 5 mg; **3**, 8 mg, **5**, 9 mg; **6**, 5 mg; **7**, 11 mg, teikaside A-IIIb, 3 mg.

Teikaside C-0 (1)——A solid, $[\alpha]_D^{29}$ −105.8° (c=1.00, MeOH), FAB-MS m/z: 703.403, (Calcd for $C_{37}H_{60}O_{11}Na$: 703.403). A mixture of a solution of **1** (50 mg) in MeOH (5 ml) and $KHCO_3$ (50 mg) in H_2O (1.25 ml) was allowed to stand for one week at room temperature, then diluted with H_2O and extracted with BuOH. The BuOH extract was purified by chromatography on a silica gel column with solv.1 (7 : 1 : 2) to give **1a** as a solid, $[\alpha]_D^{30}$ −120.6° (c=0.51, MeOH), $[M]_D$ −769° ($[M]_D$ of **1b**: −527°, $\Delta[M]_D$ −242°), FAB-MS m/z: 661.394 (Calcd for $C_{35}H_{58}O_{10}Na$: 661.393). Compound **1a** (5 mg) was refluxed with 0.05 N H_2SO_4 in 50% dioxane (1 ml) for 1 h. The mixture was diluted with MeOH and deacidified with IRA-410. The methanolic solution was then concentrated *in vacuo*, diluted with H_2O and extracted with $CHCl_3$. The $CHCl_3$ extract was examined by TLC in parallel with authentic **1b**. Solvent 1 (7 : 2 : 1): Rf 0.55 (**1b** 0.55). The H_2O layer was concentrated to dryness *in vacuo* and the residue was examined on TLC. Solvent 1 (7 : 2 : 1): Rf 0.58 (D-sarmentose 0.58), D-cymarose 0.60, D-oleandrose 0.53, D-diginose 0.57); solv.2 (9 : 1 : 0.1, homogeneous layer): Rf 0.57 (D-sarmentose 0.57, D-cymarose 0.64, D-oleandrose 0.66, D-diginose 0.55); solv.3: Rf 0.49 (D-sarmentose 0.49, D-cymarose 0.67, D-oleandrose 0.64, D-diginose 0.52).

Compound **1** (20 mg) was treated with 0.05 N H_2SO_4 in 50% dioxane in the same manner as described above. The hydrolysate was passed through a silica gel column with solv.1 (7 : 1 : 4) to afford **1c** as a solid showing a homogeneous spot on TLC with anilin hydrogen phthalate reagent or dilute H_2SO_4, $[\alpha]_D^{26}$ −15.0° (c=0.2, MeOH) (D-sarmentose: $[\alpha]_D$ +16.6°).[6] ^{1}H-NMR (pyridine-d_5) δ: 1.29 (3H, d, J=7 Hz, H-6), 2.03 (1H, m, H-2a), 2.07 (3H, s, CH_3CO-), 2.24 (1H, br d, J=15 Hz, H-2b), 3.34 (3H, s, 3-OMe), 3.76 (1H, t, J=4 Hz, H-3), 4.22 (1H, qd, J=7, 2 Hz, H-5), 4.95 (1H, dd, J=3, 1 Hz, H-4), 5.46 (1H, dd, J=10, 2 Hz, H-1).

Teikaside C-IIa (2)——A solid, $[\alpha]_D^{27}$ −93.5° (c=2.0, MeOH), FAB-MS m/z: 1009 ($C_{50}H_{82}O_{19}Na$). Upon usual acetylation of **2** with Ac_2O and pyridine, a pentaacetate of **2** was obtained, mp 244—248 °C, FAB-MS m/z: 1219 ($C_{60}H_{92}O_{24}Na$). Compound **2** (23 mg) was heated at 100 °C with 4% AcOH in 50% EtOH (2 ml) for 3 h. The solution was then neutralized with IRA-410 and concentrated to dryness *in vacuo*. The residue was passed through an ODS column with 30% MeCN to give two sugars, Rf 0.85, 0.21 (solv.1, 7 : 3 : 1): **1c** 0.85, D-sarmentose 0.61, D-cymarose 0.68, D-oleandrose 0.56, D-diginose 0.58, D-canarose 0.32, β-D-glucosyl-D-diginose 0.21, β-D-glucosyl-D-cymarose 0.15, β-D-glucosyl-D-oleandrose 0.18, β-D-glucosyl-L-oleandrose 0.25, β-D-glucosyl-(1→4)-D-canarose 0.11. Compound **1b**, teikaside A-IIa and **1** were also identified on TLC with solv.1 (7 : 2 : 1) and solv.2 (9 : 1 : 0.1).

Teikaside C-IIb (3)——A solid, $[\alpha]_D^{22}$ −65.8° (c=0.45, MeOH), FAB-MS m/z: 986 ($C_{50}H_{82}O_{19}$). Compound **3** (5 mg) was partially hydrolyzed with 4% AcOH in 50% EtOH (1 ml) as described above, and **1**, teikaside A-IIb, **1c** and β-D-glucosyl-D-oleandrose were identified on TLC (solv.1 and solv.2).

Teikaside C-IIc (4)——A solid, $[\alpha]_D^{19}$ −112.2° (c=0.60, MeOH), FAB-MS m/z: 995 ($C_{49}H_{80}O_{19}Na$). Compound **4** (20 mg) was treated with $KHCO_3$ according to the same procedure as described for **1**. The resultant solid (**4a**) showed a homogeneous spot on TLC. FAB-MS m/z: 953 ($C_{47}H_{78}O_{18}Na$). **4a**: ^{1}H-NMR (pyridide-d_5) δ: 0.74 (6H, s, H-18,19), 1.50, 1.59, 1.61, 1.77 (3 H each, d, J=6 Hz, H-21, $H_{digt.}$-6, $H_{sar.}$-6, $H_{can.}$-6), 3.36, 3.66 (3H, s, OMe), 4.79 (1H, d, J=7 Hz, $H_{digt.}$-1), 4.98 (1H, d, J=8 Hz, $H_{glc.}$-1) (one of the anomeric proton signals overlapped with the H_2O peak), 5.36, 5.58 (1H, each, br d, J=10 Hz, H-6,7), 5.60 (1H, t, J=4 Hz, $H_{sar.}$-1). ^{13}C-NMR (pyridine-d_5) δ: (sugar moieties) 105.7 (glc.-1), 102.7 (digt.-1), 102.2 (can.-1), 97.4 (sar.-1), 89.2 (can.-4), 86.3 (digt.-3), 78.7 (sar.-3), 78.5, 77.8 (glc.-3,5), 75.1 (glc.-2), 72.4 (digt.-4), 71.7, 71.6, 71.3, 70.7, 70.3 (digt.-2,5, sar.-4, can.-5, glc.-4), 65.8 (sar.-5), 62.5 (glc.-6), 58.7, 56.3 (OMe), 39.9 (can.-2), 29.7 (sar.-2), 18.6 (can.-6), 16.4 (digt.-6).

Upon 0.05N H_2SO_4 hydrolysis, **4a** afforded **1b**, β-D-glucosyl-(1→4)-D-canarose and sarmentose on TLC (solv.1, 7 : 3 : 1; solv.2, 4 : 1 : 0.5).

Teikaside C-IIIa (5)——A solid, $[\alpha]_D^{20}$ −85.9° (c=0.40, MeOH), FAB-MS m/z: 1153 ($C_{57}H_{94}O_{22}Na$). Upon 0.05 N H_2SO_4 hydrolysis, **5** afforded **1b**, **1c**, D-oleandrose and β-D-glucosyl-D-oleandrose on TLC (solv.1, 7 : 3 : 1; solv.2, 4 : 1 : 0.5).

Teikaside C-IVa (6)——A solid, $[\alpha]_D^{22}$ −83.7° (c=0.15, MeOH), FAB-MS m/z: 1297 ($C_{64}H_{106}O_{25}Na$). Upon partial hydrolysis with 0.05 N H_2SO_4 in 50% dioxane as described above, the following products were detected on TLC: **1b**, **1c**, D-oleandrose and β-D-glucosyl-D-cymarose (solv.1, 7 : 2 : 1, 7 : 3 : 1; solv.2, 4 : 1 : 0.5).

Teikaside B-IVa (7)——A solid, $[\alpha]_D^{20}$ −78.2° (c=0.55, MeOH), FAB-MS m/z: ($C_{62}H_{104}O_{24}Na$). Compound **6** (5 mg) was treated with $KHCO_3$/MeOH in the same manner as described for **1**. The Rf value of the product from **6** was identical on TLC with that of **7** (solv.1, 7 : 3 : 1; solv.2, 4 : 1 : 0.5).

Acknowledgement We thank Misses Y. Iwase and S. Hachiyama, of the Central Analysis Room in this University, for NMR and MS measurements.

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