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Minor Cardenolide Glycosides and a Cardenolide from the Leaves of *Anodendron affine* (Anodendron. VIII)[1)]

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Minor cardenolide glycosides, including 3-*O*-(4,6-dideoxy-3-*O*-methyl-Δ^3-D-hexosulosyl)-affinogenin L_d (affinoside O), 3-*O*-(4,6-dideoxy-3-*O*-methyl-D-allosyl)-affinogenin H (affinoside N), and Δ^{16}-affinoside M (affinoside I) were isolated along with the 3,16-diacetate of 2β,3β,14,16β-tetrahydroxy-11-oxo-5β,14β-card-20(22)-enolide (affinogenin D-VI), from the leaves of *Anodendron affine* DRUCE. The conformations of rings A and B in the doubly linked glycosides and free aglycones are discussed.

Keywords——Apocynaceae; *Anodendron affine*; cardenolide glycoside; 4,6-dideoxy-3-*O*-methyl-Δ^3-2-hexosulosyl affinogenin L_d; 4,6-dideoxy-3-*O*-methyl-D-allosyl affinogenin H; Δ^{16}-affinoside M; doubly linked glycoside; Δ^{16}-cardenolide; 16-*O*-acetyl-cardenolide

In the preceding paper of this series, isolation of the cardenolide glycosides from the leaves of *Anodendron affine* DRUCE and structure elucidation of affinosides L_a—L_e, the major cardenolide glycosides, were described.[1)] This paper deals with affinosides O, N, I, and affinogenin D-VI, the minor cardenolide glycosides and a cardenolide, from the same source.

Affinoside O (**1**), mp 145—150 °C, afforded a diacetate (**2**) on acetylation. In the proton nuclear magnetic resonance (^{1}H-NMR) spectra of **1** and **2**, the C-18 methyl group was observed as a singlet peak at δ 0.64 (**1**) or 0.81 (**2**), in the upper field in comparison with the cardenolides which have no oxygen function in C-12 or which have a 12α-hydroxyl group.[2)] A singlet peak ascribable to H-12α was observed at δ 4.34, suggesting the presence of an 11-oxo-12β-hydroxyl moiety such as that in affinoside L_d[1)] (Table I). In the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum, the peaks of carbonyl carbons in **1** were found at δ 211.2 and 186.1, of which the former was shifted upfield by 8.1 ppm in **2** on acetylation, and was assigned to C-11 (Table II). The presence of 2α- and 3β-hydroxyl groups, found in the other cardenolides in this plant, was also suggested by the carbinyl protons at δ 5.03 (br s) (H-2β) and 3.95 (br s) (H-3α) in **2**, and by the signals of carbinyl carbons at δ 69.1 (d, C-2) and 78.1 (d, C-3) in **1**. Based on the peaks of C-2 and C-3 which were observed at almost the same chemical shifts as those of affinoside S-I[3)] (3-*O*-β-D-digitalopyranoside of 2α,3β,14-trihydroxy-11-oxo-5β,14β-card-20(22)-enolide) in this plant, the sugar moiety seemed to be attached to the C-3 hydroxyl group as a normally linked glycoside. The peaks due to C-1 to C-10 and C-11 to C-23 were in good agreement with those of affinosides S-I and L_d, respectively. The aglycone was therefore characterized as 2α,3β,12β,14-tetrahydroxy-11-oxo-5β,14β-card-20(22)-enolide (affinogenin L_d).

On the basis of the ultraviolet (UV) absorption maximum at 262 nm, the remaining one carbonyl group and olefinic linkage were considered to be conjugated in the sugar moiety. Since the anomeric proton was observed as a singlet, the location of the enone group was assigned as 3′-en-2′-one. The olefinic proton of H-4′ was observed at δ 5.91 as a doublet of 3 Hz, which was consistent with a doublet of quartets (J=3 and 7 Hz) at δ 4.70, due to H-5′.

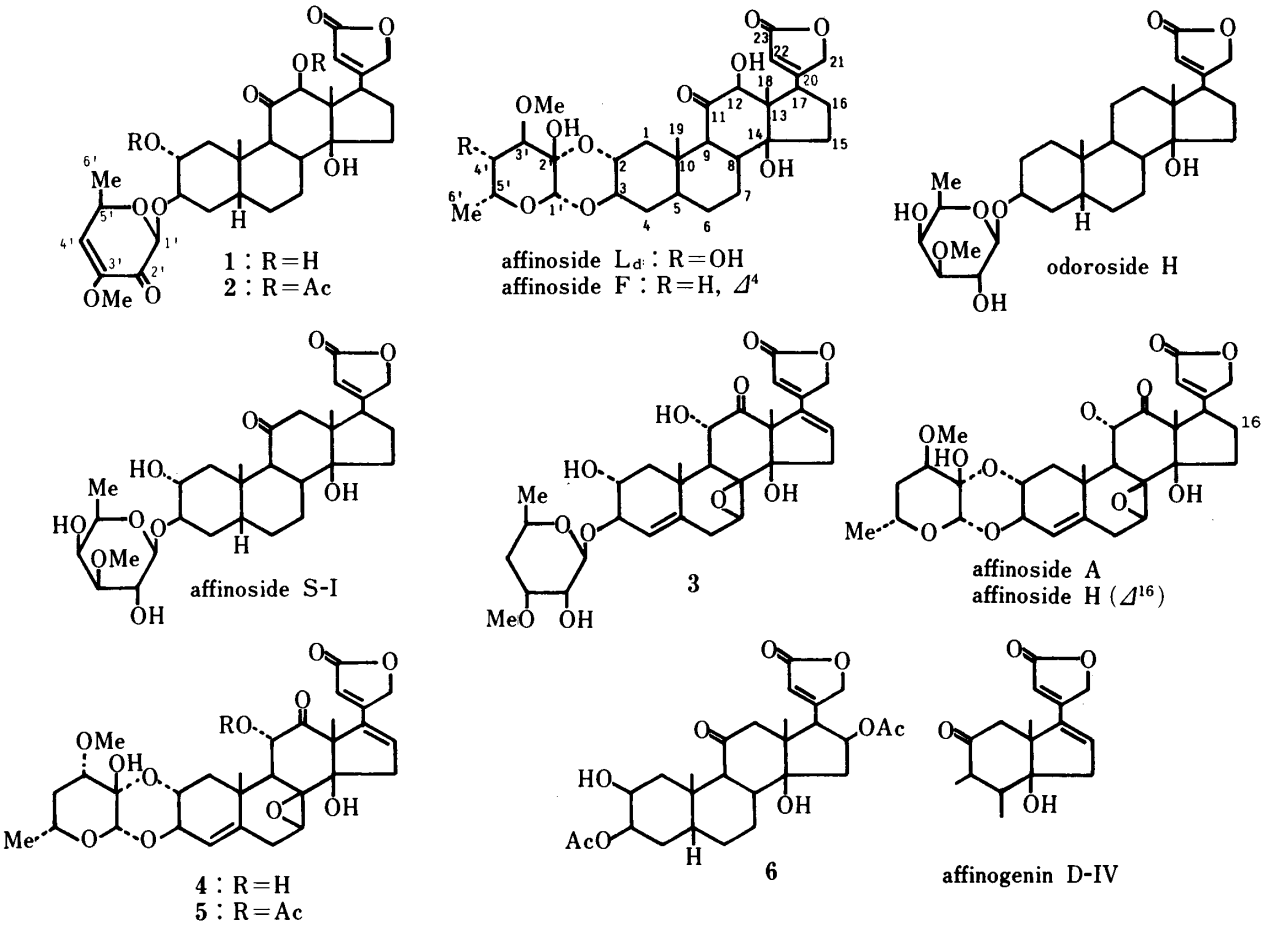

Chart 1

The 3′-en-2′-one system was also suggested by the peaks at δ 186.1 (s, C-2′), 148.2 (s, C-3′), and 119.4 (d, C-4′), along with C-1′, C-5′, C-6′, and the 3′-methoxyl carbon. The component sugar was therefore determined to be 4,6-dideoxy-3-*O*-methyl-Δ^3-2-hexosulose.

In a comparison of **1** with the digitoxigenin glycoside having the same sugar moiety, which was prepared from digitoxigenin β-D-digitaloside (odoroside H) according to the modified procedure of Cruz *et al.*,[4] the ^{1}H-chemical shifts of the peaks due to the sugar moieties of the two compounds were in good agreement.

Affinoside N (**3**) was isolated as a solid in a small amount. The fast atom bombardment (FAB) mass spectrum (MS) of **3**, afforded the same molecular ion peak at *m/z* 597 $(M+Na)^+$ as that of affinoside A. The ^{13}C-NMR spectrum, however, showed the peaks of three trisubstituted olefins. Two of them seemed to be located at C-16 and C-20(22) on the basis of the chemical shifts of the carbons in ring D and the side chain,[2] and the remaining one was considered to be Δ^4, as in affinosides A and H. A doublet peak at δ 5.25 with a characteristically large coupling constant (J=13 Hz), and one carbonyl carbon peak at δ 213.1 suggested the presence of an 11α-hydroxy-12-oxo-structure.[2] A 7β,8β-epoxide moiety was also found on the basis of the doublet peak at δ 3.84 with a coupling constant of 4 Hz, due to 7α-H, and the ^{13}C-NMR peaks at δ 53.8 (d, C-7) and 63.5 (s, C-8).[2] The ^{13}C-NMR chemical shifts of the aglycone moiety were in good agreement with that of affinoside H (Δ^{16}-affinoside A)[2] within a range of 0.5 ppm, except for the carbons in ring A. The aglycone of **3**, therefore, was considered to be 2α,3β,11α,14-tetrahydroxy-12-oxo-14β-carda-4,16,20(22)-trienolide-7β,8β-epoxide (affinogenin H).

In the ^{1}H-NMR spectrum, an anomeric proton was observed as a doublet at δ 5.21

TABLE I. ^{1}H-Chemical Shifts of **1**—**6**[a]

	1	**2**[b]	**3**	**4**	**5**	**6**
18,19-H_3	1.02, 1.33[c]	0.81, 1.19	1.68, 1.73	1.43, 1.68	1.26, 1.54	1.08, 1.13
21-H_2	4.97, 5.22	4.86	4.91, 5.14	4.90, 5.20	4.85, 5.05	4.84
	(dd, 2, 17)	(br s)	(dd, 1, 17)	(dd, 2, 16)	(dd, 2, 16)	(br s)
22-H	6.18	5.89	6.33	6.28	5.90	6.01
	(br s)	(br s)	(br s)	(br s)	(br s)	(br s)
16-H			6.30	6.36	6.18	5.38
			(t, 2)	(br s)	(t, 3)	(dt, 2, 6)
12-H	4.34	4.80				
	(s)	(s)				
11-H			5.25	5.12	5.65	
			(d, 13)	(d, 14)	(d, 13)	
7α-H			3.84	3.79	3.56	
			(d, 4)	(d, 5)	(d, 5)	
3α-H	4.40	3.95	4.33		4.63	5.20
	(br s)	(br s)	(br d, 7)		(br d, 10)	(br s)
2β-H		5.03				
		(br s)				
1′-H	5.36	4.97	5.21	5.02	5.44	
	(s)	(s)	(d, 8)	(s)	(s)	
3′-H			3.83		4.37	
			(t, 2)		(dd, 12, 5)	
4′-H	5.91	5.82				
	(d, 3)	(d, 3)				
5′-H	4.70	4.74				
	(dq, 3, 7)	(dq, 3, 7)				
6′-H_3	1.41	1.52	1.18	1.32	1.30	
	(d, 7)	(d, 7)	(d, 6)	(d, 6)	(d, 6)	
3′-OMe	3.47	3.63	3.50	3.50	3.39	
–OAc		2.10, 2.20			2.16, 2.24	2.08, 2.10

a) δ (ppm) in pyridine-d_5 from tetramethylsilane (TMS), unless otherwise mentioned (*J*/Hz values in parentheses). *b*) Dissolved in $CDCl_3$. *c*) Observed at δ 0.64 and 1.19 ppm in $CDCl_3$.

(J=8 Hz), suggesting **3** to be a glycoside of a 2′-hydroxy-sugar with a normal glycosidic linkage. On the basis of the coupling constant of the anomeric proton (J=8 Hz), H-1′ and H-2′ retain a *trans* diaxial relation, the glycosidic linkage being β. In a comparison of the ^{1}H- and ^{13}C-NMR spectra of **3** with those of tetrahydro affinoside A (3-*O*-(4,6-dideoxy-3-*O*-methyl-D-allosyl)-2α,3β,11α,12α,14-pentahydroxy-7β,8β-epoxy-14β-carda-4,20(22)-dienolide),[5] which was prepared by the $NaBH_4$ reduction of the C-12 and C-2′ carbonyl groups of affinoside A, the peaks due to the sugar moieties of the two samples were in good agreement.[5] Furthermore, **3** and tetrahydro affinoside A were subjected to acid hydrolysis to afford the sugars. The acetates of these two sugars were confirmed to be identical on gas liquid chromatography (GLC). Thus, the component sugar of **3** was determined to be 4,6-dideoxy-3-*O*-methyl-D-allose, linked to the 3β-hydroxyl group of the aglycone.

In the previous paper of this series, the unusual boat conformation of ring B in affinoside B was disclosed on the basis of X-ray analysis.[6] Affinosides C, D, E,[2] L_a, and L_e,[1] the doubly linked glycosides of affinogenins C, D-I, and E, were also considered to retain the same conformation in rings A and B as those of affinoside B, since they show the same ^{13}C-chemical shifts of the carbons of rings A and B. The carbons of rings A and B in affinogenins C and D-I were unequivocally distinct from those of their doubly linked glycosides in terms of the chemical shifts, so that the free aglycones and also their singly linked glycosides seem to retain the usual 5β chair/chair conformation of rings A and B. In affinosides A, H, and M,

TABLE II. ^{13}C-Chemical Shifts of **1**—**6** and Related Compounds[a)]

	1	**2**	S-I[b)]	L_d[c)]	**3**	**4**	**6**	D_g-IV[d)]
C-1	35.0	30.8	37.3	41.7	46.6	44.6	39.8	40.0
C-2	69.1	71.1	69.9	67.0	67.1	66.9	66.0	65.9
C-3	78.1	74.3	78.4	69.7	68.5	70.5	73.5	73.6
C-4	27.5[e)]	27.5[e)]	27.2[e)]	30.8	124.2	122.0	31.2	31.2
C-5	37.4	36.7	37.3	37.3	140.2	140.0	37.4	37.4
C-6	26.0[e)]	26.3[e)]	27.2[e)]	25.4[e)]	29.9	30.2	26.1	26.2
C-7	23.4	23.2	23.1	24.1[e)]	53.8	54.0	22.0	22.1
C-8	43.4	42.9	43.3	38.6	63.5	63.5	43.9	42.9
C-9	48.0	47.6	50.4[f)]	54.0	48.7	49.2	48.2	48.5
C-10	35.0	34.7	35.3	36.6	39.8	41.1	37.8	37.8
C-11	211.2	203.1	211.2	209.8	73.8	73.5	211.5	211.4
C-12	80.0	81.6	55.6	79.6	213.1	213.0	54.0	51.8
C-13	60.9	57.9	53.4	59.8	67.4	67.3	53.3	56.9
C-14	83.6	83.5	83.7	83.2	82.4	82.4	82.1	82.8
C-15	33.7	33.6	33.6	33.9	43.6	43.6	41.2	41.8
C-16	26.7[e)]	26.6[e)]	26.8[e)]	27.3	136.0	136.0	75.3	135.5
C-17	46.4	46.4	50.6[f)]	46.2	137.5	137.5	53.7	141.3
C-18	11.0	11.8	17.6	11.1	17.7	17.6	19.4	19.7
C-19	22.8	23.0	23.9	22.0	21.1	21.5[e)]	24.0	24.0
C-20	175.2	173.5	174.1	175.0	160.3	160.2	167.5	158.5
C-21	73.7	73.5	73.6	73.7	72.1	72.1	75.4	71.9
C-22	117.9	118.7	118.0	118.1	114.4	114.5	120.8	112.6
C-23	174.5	174.1	174.2	174.4	175.0	174.5	173.8	174.5
C-1′	98.1	98.3	103.7	96.9	101.6	97.5		
C-2′	186.1	185.5	70.7	93.2	78.9	93.0		
C-3′	148.2	148.0	85.0	83.2	82.5	82.9		
C-4′	119.4	119.5	68.6	68.0	37.0	35.2		
C-5′	69.1	69.4	71.1	71.6	72.1	68.4		
C-6′	24.1	23.8	17.4	17.2	21.4	21.4[e)]		
3′-OMe	54.8	54.8	57.2	56.9	58.2	57.9		
–OAc		20.5					21.0	21.4
		21.3					21.3	170.7
		169.8					170.2	
		170.4					170.7	

a) δ (ppm) in pyridine-d_5 from TMS. *b*) S-I = affinoside S-I. *c*) L_d = affinoside L_d. *d*) D_g-IV = affinogenin D-IV. *e*, *f*) Signal assignments marked *e*) and *f*) in each column may be reversed.

however, the conformations of rings A and B were ambiguous, since these cardenolides have Δ^4- and 7β,8β-epoxy functions, and a direct comparison with affinoside B in terms of ^{13}C-NMR was inappropriate. In the 400 MHz ^{1}H-NMR spectra (Table III), affinogenin A, **3**, and affinoside A showed almost the same coupling constants of the proton signals in rings A and B, suggesting that the Δ^4-7β,8β-epoxy cardenolides retain the same conformation in the free aglycone and in the doubly linked glycosides.

Affinoside I (**4**), was found to be a Δ^{16}-cardenolide glycoside on the bases of the UV absorption at λ_{max} 260 nm, the broad singlet peak at δ 6.36 due to the olefinic H-16 in the ^{1}H-NMR spectrum, and the shielding of C-20, C-21, and deshielding of C-13, C-15, C-16, C-17 in the ^{13}C-NMR spectrum. The presence of Δ^4, 7β,8β-epoxide and 11α-hydroxy-12-oxo moieties in affinoside A[2)] and M[5)] was also apparent from the ^{1}H- and ^{13}C-NMR spectra. A singlet peak due to an anomeric proton at δ 5.02 and two 3H signals due to 6′-CH_3 and 3′-OCH_3 were observed, as in the known doubly linked 4,6-dideoxy-3-*O*-methyl-hexosuloside.[2)] Since the H-3′ signal was seen at δ 4.37 as a doublet of doublets (J=5, 12 Hz) in the **4**-diacetate (**5**), as observed in affinoside M (3′-*epi*-affinoside A) diacetate (δ 4.35, J=4, 12 Hz),[5)] and the ^{13}C-

TABLE III. ^{1}H-Chemical Shifts of Affinoside A and Its Homologues[a]

	Affinoside N	Affinogenin A	Affinoside A
H-1β	3.27 (dd, 3.9, 13.7)	3.32 (dd, 3.4, 13.7)	2.90 (dd, 3.2, 13.4)
H-2β	4.10 (m)	4.22 (ddd, 3.4, 6.8, 11.9)	4.66 (ddd, 3.2, 9.0, 12.7)
H-3α	4.33 (br d, 6.8)	4.53 (br d, 6.8)	4.94 (dd, 2.7, 9.0)
H-4	5.56 (br s)	5.73 (br s)	5.53 (br s)
H-6β	2.88 (d, 18.5)	2.90 (td, 2.5, 17.4)	2.77 (td, 2.7, 17.1)
H-6α	2.59 (dd, 3.4, 18.5)	2.61 (dd, 5.5, 17.4)	2.50 (dd, 5.6, 17.1)
H-7α	3.84 (d, 3.4)	3.80 (d, 5.5)	3.74 (d, 5.6)
H-9	2.47 (d, 12.2)	2.46 (d, 12.7)	2.37 (d, 12.7)

a) δ (ppm) in pyridine-d_5 from TMS, at 400 MHz (J/Hz values in parentheses).

NMR peaks due to the sugar moiety in **4** coincided with those of affinoside M, the structure of **4** was assigned as Δ^{16}-affinoside M.

Affinogenin D-VI (**6**) was also obtained as a solid in a small amount. FAB-MS showed the $(M+1)^+$ peak at m/z: 505, suggesting **6** to be a free cardenolide. In the ^{1}H-NMR spectrum of **6**, the presence of two acetyl groups was observed as 3H singlet peaks at δ 2.08 and 2.10. Carbinyl protons were found at δ 5.38 (dt), 5.20 (br s), and 3.62—4.06 (m). A similar acetylated cardenolide from the leaves, affinogenin D-IV (3-*O*-acetyl affinogenin D-II) has already been reported.[7] In a comparison of the ^{13}C-NMR spectra of **6** and affinogenin D-IV, the carbon signals ascribable to rings A, B, and C were in good agreement in the two compounds. Instead of the olefinic linkage in affinogenin D-IV, **6** showed the peak at δ 5.38, which is in good agreement with H-16α of 16β-acetoxy-digitoxigenin (δ 5.48, dt, J=2, 7 Hz). The structure of **6** was therefore considered to be 3,16-di-*O*-acetyl-2β,3β,14,16β-tetrahydroxy-5β,14β-card-20(22)-enolide. Upon reaction with NaOTs and NaOAc in dimethylformamide,[8] **6** was transformed into 2-*O*-acetyl affinogenin D-II, as a result of acyl migration from 3β-OH to 2β-OH, along with the formation of the 16-olefinic linkage. Hence, the structure of **6** was confirmed.

When hexosulose is attached to 2α,3β-dihydroxy-cardenolides, the aglycone and the sugar are known to form double linkages between the hydroxyl groups at C-3 and C-1′, and C-2 and C-2′. In **1**, however, the doubly linked structure is prevented by the olefinic linkage at C-3′, conjugated to the carbonyl group.

Affinogenin D-VI is the only example of a 16-*O*-acetyl cardenolide to be isolated from this plant, although many Δ^{16}-cardenolides were isolated in the free and glycoside forms.

Experimental

The physical and spectral data were obtained with the same machines and in the same manner as described in the preceding paper.[1] The following abbreviations for NMR peaks are used: s=singlet, d=doublet, t=triplet, m=multiplet, br s=broad singlet, br d=broad doublet, dd=doublet of doublets, dt=doublet of triplets, dq=doublet of quartets. The following solvent systems were used for silica gel column and thin layer chromatographies (TLC): solv. 1, benzene–acetone; solv. 2, $CHCl_3$–MeOH–H_2O (lower layer). Each spot on the TLC plate was detected by spraying 10% H_2SO_4 and heating the plate, or by spraying a 1 : 1 mixture of 2% 3,5-dinitrobenzoic acid in MeOH and 2 N NaOH (Kedde's reagent). Isolation of the glycosides and cardenolide was described in the preceding paper.[1]

Affinoside O (1)——On crystallization from MeOH or hexane–EtOAc, **1** was obtained as prisms, mp 145—150 °C, $[\alpha]_D^{18}$ +8.6° (c=1.75, MeOH). UV λ_{max}^{MeOH} nm (ε): 219 (18500), 262 (7600). Electron impact (EI)-MS m/z: 402 ($C_{23}H_{30}O_6$, genin-H_2O), 384, 366, 332, 267, 249, 231, 222. *Anal.* Calcd for $C_{30}H_{40}O_{10}\cdot 2H_2O$: C, 60.34; H, 7.43. Found: C, 59.60; H, 7.51. Upon acetylation of **1** (20 mg) in 1 ml each of Ac_2O and pyridine at room temperature for 24 h, a diacetate of **1** (**2**) was obtained as a solid (10 mg).

Digitoxigenin β-4,6-Dideoxy-3-*O*-methyl-Δ^3-D-hexosuloside——Odoroside H diacetate (mp 224—227 °C, 2 g)

was saponified with 250 ml of 0.8% $KHCO_3$ in 80% MeOH at room temperature for two weeks. The mixture was diluted with H_2O and extracted with $CHCl_3$. The $CHCl_3$ extract was fractionated on a silica gel column with solv. 1 (4:1). The 2′-monoacetate thus obtained was crystallized from EtOAc–hexane to give needles (170 mg), mp 222—224 °C, $[\alpha]_D^{23}$ +10.0° (c=0.18, MeOH). The 2′-monoacetate (200 mg) was dissolved in pyridine (4 ml) and 2 ml of benzoyl chloride was added. The mixture was allowed to stand at 0 °C for 2 h. The benzoate was crystallized from EtOAc–hexane to give needles, mp 164—167 °C. The 2′-*O*-acetyl-4′-*O*-benzoyl-orodoside H (500 mg) was deacetylated with $KHCO_3$ (1 g of $KHCO_3$ in 250 ml of 80% MeOH) for 1 week at room temperature. The 4′-benzoate was obtained as a solid (70 mg), which was dissolved in 3 ml of HOAc and stirred with a solution of 70 mg of CrO_3 in H_2O–HOAc (3 ml) for 2 h. The mixture was diluted with H_2O and extracted with $CHCl_3$. The $CHCl_3$ extract was subjected to silica gel column chromatography with solv. 1 (10:1). The 2′-oxo-$\Delta^{3'}$-derivative of odoroside H was obtained as a solid (5 mg) and showed identical chemical shifts with those of the same compound prepared from neriifolin (digitoxigenin α-L-thevetoside) by Cruz *et al.*[4] ^{1}H-NMR ($CDCl_3$) δ: 0.87, 0.92 (3H each, s, 18 and 19-methyl), 1.53 (3H, d, J=6 Hz, 6′-methyl), 3.64 (3H, s, 3′-methoxyl), 4.11 (1H, br s, H-3), 4.73 (1H, m, H-5′), 4.77, 5.00 (1H each, dd, J=16, 2 Hz, H-21), 4.97 (1H, s, H-1′), 5.78 (1H, d, J=3 Hz, H-4′), 5.87 (1H, br s, H-22).

Affinoside N (3)——Affinoside N was obtained as a solid, $[\alpha]_D^{18}$ +49.7° (c=0.83, MeOH). A mixture of **3** (6 mg) with 1 ml of HCl in acetone was allowed to stand at room temperature for 5 h. The mixture was diluted with H_2O and deacidified with IR-410. The solution was extracted with BuOH, and the water layer was concentrated to dryness *in vacuo*. The residue was acetylated with pyridine and Ac_2O at room temperature. The sugar acetate from tetrahydro affinoside A was prepared in the same manner as described for **3**. GLC t_R: 4.49 (minor), 4.81 (from **3**); 4.48 (minor), 4.82 (from tetrahydro affinoside A) (column OV-17 (capillary), 150 °C, N_2 1.0 kg/cm^2).

Affinogenin A——A solution of 50 mg of affinoside A in 2 ml of EtOH was treated with 0.05 ml of phenylhydrazine and 0.02 ml of HOAc. The mixture was refluxed for 2 h and the EtOH was evaporated off *in vacuo*.[1,9] The residue was subjected to silica gel chromatography with solv. 2 (7:2:2—7:2:1). Affinogenin A was obtained as a solid (9 mg), $[\alpha]_D^{24}$ +5.15° (c=1.63, MeOH), EI-MS m/z: 432 (M^+), 414.1663 ($M^+ - H_2O$, Calcd for $C_{23}H_{26}O_7$: 414.1678).

Affinoside I (4)——Affinoside I was obtained as a solid, $[\alpha]_D^{15}$ +50.0° (c=1.00, MeOH), FAB-MS m/z: 595 ($(M+Na)^+$, $C_{30}H_{36}O_{11}$: m/z: 572), UV λ_{max}^{MeOH} nm (ε): 260 (11000). Affinoside I diacetate (**5**) was prepared from 10 mg of **4** and 1 ml each of Ac_2O and pyridine by heating at 60 °C for 5 h, and 4 mg of **5** was obtained as a solid, FAB-MS m/z: 679 ($(M+Na)^+$, $C_{34}H_{40}O_{13}$: M_r 656).

Affinogenin D-VI (6)——Affinogenin D-VI was obtained as a solid, $[\alpha]_D^{18}$ +3.3° (c=0.97, MeOH). FAB-MS m/z: 505 ($(M+1)^+$, $C_{27}H_{36}O_9$).

Conversion of 6 into 2-*O*-Acetyl-affinogenin D-II——A solution of 10 mg of **6** in 1 ml of dimethylformamide was treated with 30 mg of NaOTs and 10 mg of NaOAc, and the mixture was heated at 125 °C for 30 min. The mixture was diluted with H_2O, and extracted with BuOH, then the BuOH extract was subjected to silica gel column chromatography with solv. 1 (4:1) to afford a homogeneous product as a solid. The NMR spectrum was identical with that of 2-*O*-acetyl-affinogenin D-II; ^{1}H-NMR (pyridine-d_5) δ: 1.20, 1.31 (3H each, s, 18 and 19-methyl), 2.06 (3H, s, –OAc), 4.13 (1H, br s, H-3α), 4.86 (1H, br d, J=10 Hz, H-2α), 4.92, 4.97 (1H each, J=16, 1 Hz, H-21), 5.98 (1H, br s, H-22), 6.17 (1H, br s, H-16).

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