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Affinoside A and Companion Glycosides from the Stem and Bark of *Anodendron affine*[1] (*Anodendron* II)[2]

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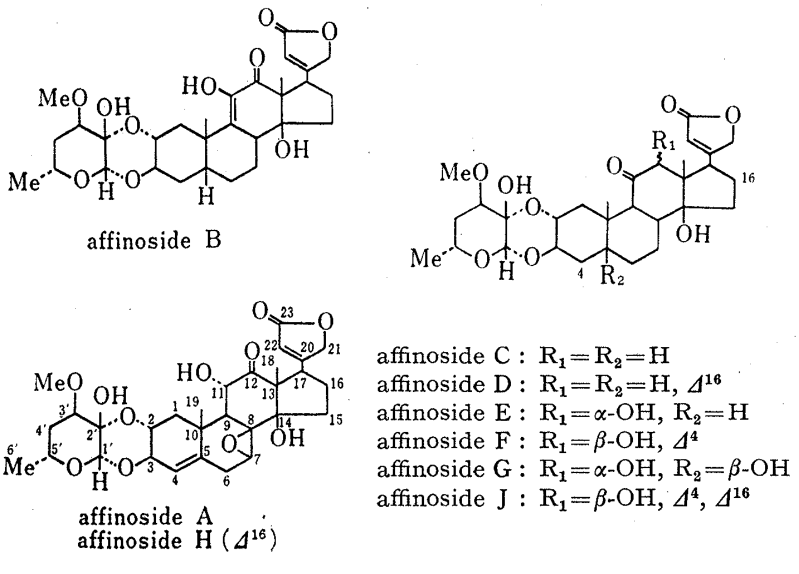
Cardenolide glycosides, affinosides A, C, D, E, F, G, H and J, were isolated from the stem and bark of *Anodendron affine* Druce, and their structures were elucidated. They have the same sugar moiety as affinoside B, 4,6-dideoxy-3-*O*-methyl-D-glycero-D-glycero-2-hexosulopyranose, which is doubly linked to the 2α- and 3β-hydroxyl groups of the aglycone with 2′-acetal and 1′-anomeric hydroxyl groups, respectively. The aglycone of A was identified as 2α,3β,11α,14-tetrahydroxy-12-oxo-14β-carda-4,20(22)-dienolide-7β,8β-epoxide. The others were found to be 2α,3β,14-trihydroxy-11-oxo-, 2α,3β,12α,14-tetrahydroxy-11-oxo-, and 2α,3β,5,12α,14-pentahydroxy-11-oxo-5β,14β-card-20(22)-enolide (C, E, and G, respectively), and 2α,3β,12β,14-tetrahydroxy-11-oxo-14β-carda-4,20(22)-dienolide (F). H, D, and J were Δ^{16}-derivatives of A, C, and F, respectively. C was hydrolyzed to the aglycone by preliminary splitting of the 2-*O*-2′ linkage by $NaBH_4$ reduction, followed by treatment with HCl/acetone.

Keywords——*Anodendron*; Apocynaceae; cardenolide; cardiac glycoside; affinoside; 3′-*O*-methyl-4′,6′-dideoxy-2′-hexosulopyranoside; doubly linked cardenolide glycoside; 11-oxo-cardenolide; 12-oxo-cardenolide; 7,8-epoxy-cardenolide

Among many cardiac glycosides, 2′-hexosulopyranosides or 2′-pentosulopyranosides have been found in Asclepiadaceae,[3] Apocynaceae,[4] and Celastraceae.[5] So far in Apocynaceae plants, *Anodendron* is the only genus containing glycosides of this type, and anodendrosides A, E_1, E_2, F, and G were isolated from *A. paniculatum* by Polonia *et al.*[4a] and their structures were proposed by Lichti *et al.*[4b] In Japan, one species, *A. affine* Druce (Japanese name: sakaki-kazura) grows principally in the coastal areas of Kyushu, Shikoku, and the Ryukyu Islands. Shima *et al.*[6] reported β-sitosterol glucoside, glucosyringic acid, 2,2-dimethyl-2*H*-1-benzopyran-6-carboxylic acid, two flavonoids, and dambonitol as constituents of this plant, and Sasaki and Hirata[7] isolated two pyrrolizidine alkaloids, anodendrine and alloanodendrine.



affinoside C : $R_1=R_2=H$
affinoside D : $R_1=R_2=H$, Δ^{16}
affinoside E : $R_1=\alpha$-OH, $R_2=H$
affinoside F : $R_1=\beta$-OH, Δ^4
affinoside G : $R_1=\alpha$-OH, $R_2=\beta$-OH
affinoside J : $R_1=\beta$-OH, Δ^4, Δ^{16}

Chart 1

Table I. ^{1}H Chemical Shifts of Affinosides and Their Acetates[a]

	B[b]	A	A-I	A-II	H	H-I	C[b]	D	E	E-I	F	F-I	J	J-I	G[b]	G-I
18, 19-Me	1.20 1.54	1.07 1.42	1.14 1.26	1.14 1.23	1.24 1.46	1.22 1.28	1.02 1.06	1.03 1.36	0.94 1.09	1.03 1.12	0.69 1.39	0.82 1.35	1.07 1.43	1.23	1.18 1.35	1.24
21-CH$_2$	5.01 5.28 (18)	4.82 (bs)	4.77 (bs)	4.78 (bs)	4.88 5.10 (17, 2)	4.83 5.06 (16, 2)	4.95 (2)	4.93 (bs)	4.59 5.11 (17, 2)	4.66 5.11 (17, 2)	4.83 (bs)	4.81 (2)	4.72 4.99 (2)	4.96 (bs)	4.83 5.48 (18, 2)	4.63 4.93 (18, 2)
22-H	6.26 (bs)	5.98 (bs)	5.94 (bs)	5.94 (bs)	5.95 (bs)	5.89 (bs)	6.09 (2)	5.93 (bs)	5.88 (t, 2)	5.86 (t, 2)	5.94 (bs)	5.84 (2)	6.24 (bs)	6.09 (bs)	6.15 (t, 2)	5.87 (t, 2)
3α-H		4.50 (9, 2, 1)	4.52[d] (9, 2, 1)	4.56 (9, 2, 1)	4.51 (8)	4.53 (9)					4.55 (9, 2)	4.51 (9, 2, 1)	4.58 (8, 2, 1)	4.56 (8)		
4-H		5.33 (bs)	5.36 (bs)	5.38 (bs)	5.38 (bs)	5.38 (bs)					5.29 (bs)	5.23 (bs)	5.31 (bs)	5.29 (bs)		
12-H									4.07 (3→s)[c]	5.04 (s)	3.84 (3, 2→s)[c]	4.76 (s)	3.86 (bs)	4.79 (s)	4.65 (2)	5.08 (s)
1′-H	5.36 (s)	4.68 (s)	4.69 (s)	4.78 (s)	4.59 (s)	4.70 (s)	5.30 (s)	4.63 (s)	4.65 (s)	4.59 (s)	4.71 (s)	4.65 (s)	4.71 (s)	4.70 (s)	5.31 (s)	4.59 (s)
3′α-H	3.61 (bs)	3.28 (bs)	3.30 (bs)	4.31 (bs)	3.29 (bs)	3.29 (bs)	3.62 (bs)	3.26 (bs)	3.29 (bs)	3.24 (bs)	3.30 (bs)	3.25 (bs)	3.30 (bs)	3.28 (bs)	3.64 (bs)	3.23 (bs)
3′-OMe	3.50	3.39	3.40	3.29	3.40	3.40	3.48	3.42	3.40	3.36	3.42	3.38	3.41	3.40	3.49	3.37
6′-Me	1.32	1.20	1.22	1.20	1.21	1.21	1.30	1.24	1.24	1.24	1.22	1.19	1.20	1.21	1.36	1.16
others	6.42 (-OH)	3.47 (5) (7α-H) 4.82 (11, 2) (11β-H) 3.63 (-OH)	3.52 (5) (7α-H) 5.70 (13) (11β-H) 2.22 (-OAc)	3.53 (5) (7α-H) 5.71 (14) (11β-H) 2.09 2.26 (-OAc)	3.51 (5) (7α-H) 4.78 (12, 3) (11β-H) 6.22 (5, 3) (16-H)	3.56 (5) (7α-H) 5.65 (13) (11β-H) 6.18 (bs) (16-H) 2.20 (-OAc)	4.80 5.74 (-OH)	6.06 (t, 3) (16-H)	3.65 (-OH) 3.74 (3) (12α-OH)	2.18 (-OAc)	3.68 (-OH)	2.17 (-OAc)	6.29 (bs) (16-H)	6.34 (bs) (16-H) 2.11 (-OAc)	6.74 (2) (12α-OH)	2.17 (-OAc)

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[a] δ (ppm) in CDCl$_3$, unless otherwise mentioned (J/Hz values in parentheses).
[b] Dissolved in pyridine-d_5.
[c] Treated with D$_2$O.
[d] Transformed into dd ($J=9$ and 2 Hz) by irradiation of the 4-H peak.

Table II. ^{13}C Chemical Shifts of Affinosides and Their Acetates, δ (ppm) from TMS in Pyridine-d_5

	B	A	A-I	A-II	H	C	D	E	E-I	F	F-I	J	G	G-I	dx$^{c)}$
C-1	34.0$^{a)}$	44.7	43.9	43.2	44.6	41.0	40.6	40.6	40.5	40.8	40.5	40.8$^{a)}$	42.8$^{a)}$	45.5	30.6
C-2	68.4	67.3	67.1	69.3	67.3	68.0	68.2	68.3	68.2	66.9	66.8	66.8	68.2	68.1	24.9
C-3	69.2	70.5	70.0	69.3	70.4	69.4	69.4	69.3	69.3	70.5	70.4	70.5	69.3	69.2	70.3
C-4	31.2	123.2	123.9	123.1	123.1	31.9	32.2	32.2	32.2	120.3	120.4	120.2	43.4$^{a)}$	43.2	30.5
C-5	36.7	140.0	138.8	139.4	140.0	38.6	36.5	34.8	35.1	144.7	144.3	144.6	74.9	75.0	33.5
C-6	24.7	30.3	30.1	30.1	30.1	25.1$^{a)}$	24.9	24.9$^{a)}$	24.9	31.3	31.2	31.2	31.3	31.3	26.6
C-7	22.3	53.9	54.2	54.1	54.0	24.5$^{a)}$	24.9	24.7$^{a)}$	24.9	30.1	30.0	30.1	22.6	22.8	22.3
C-8	39.1	64.6	65.1	65.2	63.5	38.6	38.9	39.0	39.3	43.2	42.9	42.8	34.3	34.7	40.6
C-9	137.5	49.1	46.1	46.0	49.2	57.1	58.2	56.4	56.8	57.9	57.6	57.2	57.7	58.1	37.5
C-10	40.2	41.3	40.8	41.0	41.1	38.3	38.6	38.9	39.3	40.2	40.2	40.1	43.4	43.9	35.6
C-11	141.9	74.6	75.8	75.8	73.6	212.6	213.0	214.2	207.7	209.4	202.7	209.2	214.8	208.1	37.4
C-12	199.0	212.7	205.0	205.0	213.0	54.3	51.3	82.7	84.8	79.8	81.3	81.6$^{b)}$	82.9	84.5	212.0
C-13	60.5	63.6	63.5	63.5	67.3	51.3	56.3	56.1	54.2	60.6	57.7	64.0	56.3	54.3	64.8
C-14	82.1	82.0	81.8	81.8	82.4	83.3	83.2	83.8	84.4	83.1	83.3	83.8	84.2	84.8	85.9
C-15	33.5$^{a)}$	36.5	36.2	36.1	43.6	34.8	42.6	34.2	34.2	33.6	33.4	41.2$^{a)}$	33.7	33.8	32.9
C-16	26.8	28.6	28.6	28.6	136.0	26.6	135.3	27.9	28.3	27.5	27.4	135.8	28.1	28.5	27.2
C-17	43.4	42.4	41.8	41.8	137.5	49.9	139.9	45.6	45.9	46.2	46.5	143.8	45.6	45.9	41.4
C-18	15.9	18.5	17.7	17.7	17.6	20.0	21.2$^{a)}$	20.0	19.2	11.0	11.8	10.7	19.7	19.3	16.8
C-19	23.1	21.3	21.4$^{a)}$	21.9$^{a)}$	21.4	21.8	21.6$^{a)}$	21.4	21.7$^{a)}$	20.3	20.5$^{a)}$	20.3	17.4	17.8	23.2
C-20	173.8	173.1	172.8	172.9	160.2	171.8	158.3	173.2	171.6	174.4	173.6$^{b)}$	160.3	173.5	171.8	174.8
C-21	73.5	73.9	73.8	73.8	72.1	73.6	72.0	75.3	74.8	73.7	73.5	72.0	75.3	74.8	73.8
C-22	118.5	118.7	118.8	118.9	114.4	117.4	112.5	117.6	118.3	118.2	118.7	114.8	117.4	118.3	118.5
C-23	173.9	174.1	173.9	173.9	174.5	173.9	174.4	174.4	174.0	174.9	174.1$^{b)}$	174.7	174.5	174.0	174.3
C-1′	96.0	96.2	96.1	94.2	96.1	95.8	95.8	95.8	95.8	96.2	96.1	96.2	95.6	95.6	
C-2′	91.7	92.0	92.0	97.4	91.9	91.5	91.4	91.5	91.5	92.0	92.0	91.9	91.6	91.6	
C-3′	81.3	81.4	81.3	76.8	81.3	81.4	81.4	81.4	81.3	81.4	81.3	81.3$^{b)}$	81.3	81.3	
C-4′	35.3	35.1	35.0	33.0	35.0	35.0	35.0	35.1	35.1	35.1	35.1	35.1	35.1	35.1	
C-5′	66.4	66.4	66.3	66.4	66.3	66.4	66.4	66.4	66.4	66.3	66.3	66.3	66.5	66.5	
C-6′	21.3	21.3	21.2$^{a)}$	21.3$^{a)}$	21.4	21.4	21.4$^{a)}$	21.3	21.4$^{a)}$	21.5	21.4	21.5	21.4	21.4	
-OMe	58.4	58.3	58.3	56.9	58.3	58.3	58.2	58.3	58.3	58.4	58.4	58.4	58.3	58.3	
-OAc			169.6 20.8	169.7 169.3 21.1$^{a)}$ 20.8$^{a)}$					169.6 20.7$^{a)}$		170.3 20.2$^{a)}$			169.6 20.7	

a), b) Assignments marked a or b in any column may be reversed.
c) dx: 12-keto-digitoxigenin acetate.

In 1979, we reported on the pregnanes of this plant⁸⁾ including neridienone A⁹⁾ and its derivatives. In the preceding paper of this series,²⁾ the structure of affinoside B (B), one of the minor constituents, was determined by means of X-ray crystallography; it is a cardiac glycoside composed of an aglycone with a diosphenol system in ring C and a 4,6-dideoxy-3-*O*-methyl-D-glycero-D-glycero-2-hexosulopyranose moiety which is doubly linked to the 2α-, and 3β-hydroxyl groups of the aglycone. This paper deals with the structure elucidation of affinoside A (A), a major glycoside, and affinosides C—H, and J (C—H, and J, respectively), which are companion glycosides having the same sugar moiety as B from the same plant.

The methanol percolate of the stem with bark was partitioned successively with benzene, $CHCl_3$, $CHCl_3$–EtOH (2 : 1), and then BuOH. The $CHCl_3$ extractives were chromatographed on silica gel columns with benzene–acetone, hexane–EtOAc, and $CHCl_3$–MeOH–H_2O. A and B were obtained from the least polar fraction on column chromatography with benzene–acetone, and were followed by F, H, J, C, D, and E, in turn. G was isolated from the most polar effluent on chromatography of these glycosides. In the ^1H-nuclear magnetic resonance (PMR) spectra of A—J (Table I), the anomeric protons are observed as a singlet at δ 4.59—4.71 in $CDCl_3$ (δ 5.30 in C; 5.31 in G in pyridine-d_5), in addition to the 3′-*O*-methyl protons at δ 3.39—3.49 and the 6′-methyl protons at δ 1.20—1.36, suggesting these glycosides to be 4′,6′-dideoxy-3′-*O*-methyl-2′-hexosulopyranosides like B. In the ^{13}C-nuclear magnetic resonance (CMR) spectra (Table II), resonances due to the carbons from the sugar moieties are quite coincident with those of B, indicating these glycosides to have the same component sugar and probably the same linking mode to the aglycone as in B.

Affinosides A and H

A shows a molecular formula of $C_{30}H_{38}O_{11}$ on the basis of elementary analysis and a molecular peak (M^+) at m/z 574 in the mass spectrum (MS), and forms a monoacetate (A-I) or a diacetate (A-II) on acetylation with Ac_2O and pyridine at room temp. or elevated temp., respectively. Three oxygens in the molecule seem to belong to the sugar moiety, that is, a hemiacetal hydroxyl at C-2′, a methoxyl at C-3′, and a pyranoside ring, two to a dioxane ring between the aglycone and the sugar, two to a butenolide ring, and one to a 14-hydroxyl residue. In the downfield region of the CMR spectrum the presence of a trisubstituted olefinic linkage is indicated by the signals at δ 123.2 (d) and 140.0 (s), in addition to one carbonyl carbon at δ 212.7 and the carbons due to the butenolide ring. In the PMR spectrum of A, an olefinic proton, corresponding to the CMR signals of the olefinic carbons, is observed at δ 5.33 as a broad singlet. The linkage was assigned to Δ^4 since the signal of 3α-H, which appears as a doublet of double doublets at δ 4.50 (J=9, 2, 1 Hz), is transformed into a doublet of doublets (J=9, 2 Hz) by irradiation of the δ 5.33 peak in A-I.

The carbinyl proton at δ 4.82 seen as a doublet with a coupling constant of 12 Hz in A shows an acetylation shift to δ 5.70 in A-I or δ 5.71 in A-II, while shielding is observed on the carbonyl carbon (−7.7 ppm) and on C-9 (−3.0 ppm) of A-I. The acylable hydroxyl residue is therefore assigned to C-11, the next carbon to the carbonyl moiety and to C-9, forming an α-ketol with an 11α-hydroxy-12-oxo structure.

The CMR peaks at δ 53.9 (d) and 64.6 (s) and the PMR signal at δ 3.47 (d, J=5 Hz) of A are considered to be due to an epoxide moiety. Its location and orientation were tentatively assigned as 7β,8β, on the basis of the PMR comparison with the known 7β,8β-epoxycardenolide, *e.g.* sarverogenin,¹⁰⁾ deacetyltanghinin,¹¹⁾ or desglucosyrioside.³ᵃ⁾ As a result of spectral analyses, the aglycone moiety of A was considered to be 2α,3β,11α,14-tetrahydroxy-12-oxo-14β-carda-4,20(22)-dienolide-7β,8β-epoxide, and the following reactions were examined in order to confirm the structure.

When A-I was treated with 1% hydrochloric acid in acetone, a product (A-III) showed a positive Beilstein test, indicating the introduction of a chlorine atom in the molecule. The doublet peak at δ 3.52 ascribable to 7α-H in A-I is shifted downfield to δ 4.33, being transformed from a doublet of 5 Hz into a broad singlet (Tables I and III). In the CMR of A-III, the signals due to C-7 and C-8 are deshielded from δ 54.2 to 60.9, and from δ 65.1 to 79.7, respectively, as are those of the neighboring carbons, C-6 (+7.4 ppm), C-9 (+0.9 ppm), and C-14 (+4.0 ppm) (Tables II and IV). Based on the PMR and CMR evidence, A-III was regarded as the 7α-chloro-8β-hydroxyl derivative of A-I, formed by opening of the epoxide ring with HCl.

On the reaction of A-II with $SOCl_2$ in pyridine, a product (A-IV) exhibited unusual less-polar behavior on thin layer chromatography (TLC). Since the Beilstein test was positive, the epoxide ring seems to have been cleaved to yield a 7α-chloro-8β-hydroxyl compound such

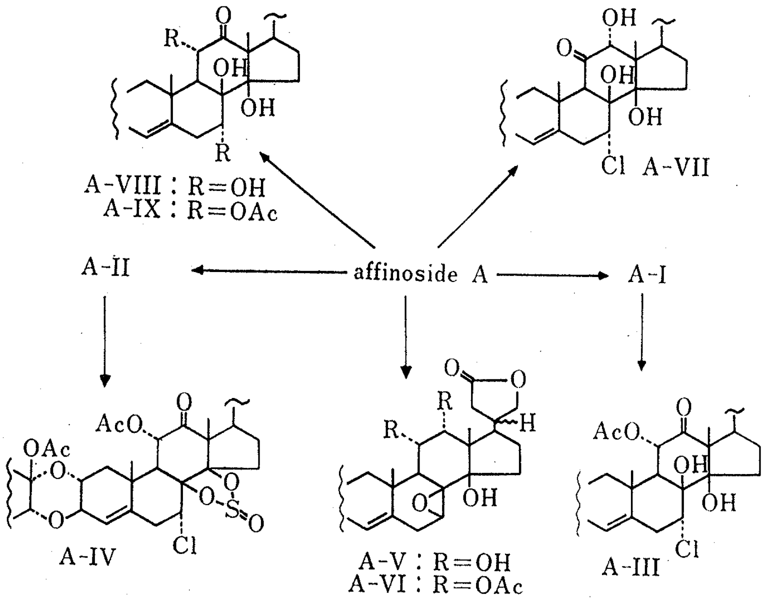

Chart 2

Table III. ¹H Chemical Shifts of Affinoside A Derivatives[a]

	A-Ⅲ	A-IV	A-V	A-VI	A-Ⅶ[b]	A-Ⅷ[b]	A-IX
18,19-Me	1.32 1.43	1.12 1.37	1.00 1.35	1.17 (6H)	1.46 1.55	1.48 1.82	1.31 1.44
21-CH_2	4.88 (bs)		4.74 (bs)		5.15(20) 5.54(20)	5.39 (bs)	4.85 (bs)
22-H	5.97	5.96			6.15	6.17	5.95
3α-H	4.65			4.49 (9)	5.28 (9, 2)		4.57 (9, 2, 2)
4-H	5.38(bs)	5.47(bs)	5.30(bs)	5.32(bs)	5.77(bs)	5.70(bs)	5.28(bs)
7-H	4.33(bs)	5.07 (t, 2)	3.30(6)	3.36(6)	4.87 or 4.90	4.50 (bs)	4.99 (bs)
11β-H	6.03(12)	5.75(12)		5.42 (12, 2)		5.52(12)	6.07(12)
12β-H			3.61(2)	5.14(2)	4.90 or 4.87		
1′-H	4.71(s)	4.83(s)	4.71(s)	4.68(s)	5.41(s)	5.35(s)	4.71(s)
3′α-H	3.31(bs)	4.35(bs)	3.28(bs)	3.29(bs)		3.63(bs)	3.33(bs)
3′-OMe	3.32	3.32	3.40	3.40	3.47	3.50	3.43
6′-Me	1.25(6)	1.25(6)	1.24(6)	1.25(6)	1.34(6)	1.24(6)	1.26(6)
others	2.21 (-OAc)	2.12 2.25 (-OAc)		2.00 2.18 (-OAc)			3.78 2.03 3.86 2.22 (-OH) (-OAc)

[a] δ (ppm) in $CDCl_3$, unless otherwise mentioned (J/Hz values in parentheses).
[b] Dissolved in pyridine-d_5.

TABLE IV. ^{13}C Chemical Shifts of Affinoside A Derivatives, δ (ppm) from TMS in pyridine-d_5c)

	A-III	A-IV	A-V	A-VII	A-VIII
C-1	43.7	42.3	44.9	42.9	44.5
C-2	66.8	68.4	67.5	66.8	67.2
C-3	70.5	69.4	70.5	71.0	70.9a)
C-4	125.0	126.7	122.1	125.6	123.7
C-5	140.1	138.0	141.0	139.5	143.1
C-6	37.5a)	37.8	30.8	38.0a)	37.3b)
C-7	60.9	59.5	52.6	60.8	71.0a)
C-8	79.7	91.9	64.6	79.6	79.0
C-9	47.0	45.1	47.5	54.0	50.8
C-10	42.6	43.4	40.6	43.2	42.9
C-11	74.8	72.1	70.5	211.6	73.1
C-12	205.6	203.9	80.3	82.0	213.9
C-13	65.9	62.2	53.2	57.7	64.6
C-14	85.8	106.8	81.0	85.6	86.1
C-15	37.3a)	36.5	35.9	38.7a)	37.2b)
C-16	27.8	28.1	33.3	29.3	28.3
C-17	41.3	43.4	44.5	45.2	42.3
C-18	18.9	21.9	17.7	19.2	19.1
C-19	21.1	21.9	21.7	24.0	22.7
C-20	173.5	168.7	39.1	173.5	174.0
C-21	73.5	74.3	73.7	75.5	73.6
C-22	119.2	119.2	48.1	117.9	118.7
C-23	174.0	173.5	177.5	174.4	171.4

a), b) Assignments marked a or b in any column may be reversed.
c) Carbons of the sugar moiety and acetyl residue are omitted.

as A-III. A marked downfield shift is observed not only in C-8 by +26.7 ppm but also in C-14 by +25.0 ppm. The $M^{+}+1$ peak at m/z 741, in addition to the CMR evidence, shows A-IV to be a cyclosulfite derivative of an 8,14-glycol. The orientation of the 14-hydroxyl group was also proved to be β by the formation of A-IV.

The presence of the α-ketol in ring C was confirmed by the catalytic reduction of A with PtO_2. While the olefinic linkage was retained, reduction of the α-ketol proceeded to yield an 11,12-glycol, in addition to the saturation of the butenolide ring. A diacetate of A-V (A-VI) shows two carbinyl protons at δ 5.14 (d, J=2 Hz) and 5.42 (dd, J=2 and 12 Hz), which are considered to be the 12β- and 11β-protons, respectively, on the basis of their coupling constants.

On reflux of A with 0.25 N HCl–50% EtOH, a product (A-VII) was obtained which afforded a positive reaction on the Beilstein test. The 11α-proton found at δ 4.82 in A is no longer apparent and broad singlets are observed at δ 4.87 and 4.90, one of which is considered to be 7β-H on the carbon bearing chlorine. The remaining proton seems to be the 12β-carbinyl proton which appears as a result of the isomerization of A into an 11-oxo-12α-hydroxyl derivative in the acidic medium. The rearrangement of the 12-oxo-11-hydroxyl in A to 11-oxo-12-hydroxyl is well supported by the downfield and upfield shifts, respectively, found in the C-9 (+4.9 ppm) and C-13 (−5.9 ppm) signals of A-VII in comparison with those of A. An α-orientation of the 12-hydroxyl is indicated not only by the deshielding of the carbinyl proton to δ 4.87 or 4.90, but also by comparison of the C-13 (δ 57.7) and C-18 (δ 19.2) signals with those of E (11-oxo-12α-hydroxyl) and F (11-oxo-12β-hydroxyl) as described below. In F, these two carbons are observed at δ 60.6 and 11.0, respectively. Wide splitting of the H_a and H_b signals of the 21-methylene at δ 5.15 and 5.54 is also considered to be caused by the steric interaction between the 12α-hydroxyl and 21-methylene groups.

A was transformed into a pentahydroxyl derivative (A-VIII) on reflux with 0.05 N H_2SO_4–50% EtOH. A 7,8-glycol structure is supported by the formation of a 7,11-diacetate (A-IX) upon acetylation at room temp., in addition to the M^+ peak at m/z 592 and the CMR spectrum of A-VIII.

Hence, the structure of A was established as represented in Chart 1, on the basis of the chemical evidence as well as the spectral considerations.

H was isolated as a solid and considered to be a Δ^{16}-derivative of A on the basis of its absorption maximum at 266 nm, $M^+ +1$ signal at m/z 573, and the similarity of the CMR spectrum to that of A except for the carbons affected by the Δ^{16} function. Among these carbons, the olefinic C-16 and C-17, and the neighboring C-13 and C-15 are deshielded, while those of the butenolide ring, C-20, C-21, and C-22, show shielding by −12.9, −1.8, and −4.3 ppm, respectively. On the catalytic reduction of H, two products were obtained and the minor product (H-II) was identified as A. The major one (H-III) is considered to be the 17α-derivative of A.

Affinosides C and D

C and D show similar CMR spectrum, except for the resonances due to Δ^{16} in D. Deshielding of C-13, C-15, C-16, and C-17, and shielding of C-20, C-21, and C-22 in D are consistent with the corresponding shifts in H. One carbonyl carbon (δ 212.6 in C; δ 213.0 in D) is observed and is considered to be located at C-11 or C-12 in view of the oxygen function in A and B. By comparison of the resonances of C-9 (δ 57.1 in C; δ 58.2 in D) and C-13 (δ 51.3 in C; δ 56.3 in D) with those of 12-keto-digitoxigenin acetate (dx) (C-9: δ 37.5; C-13: δ 64.8), the carbonyl group was assigned to C-11. In the CMR of C and D, four signals originating from the carbons bearing oxygen are found in the region between δ 60 and δ 100, in addition to the signals due to the sugar moiety, and they were respectively assigned to C-2, C-3, C-14, and C-21. The catalytic reduction of D with Pd-carbon afforded a mixture of products, from which a small amount of C was isolated and identified by comparison with an authentic sample.

The reduction of C with $NaBH_4$ in EtOH provided two major products (C-I and C-II), both of which clearly show an anomeric proton as a doublet of 5 Hz (C-I) or 8 Hz (C-II), suggesting conversion into the normal glycosides by splitting of the linkage between 2 and 2′. Upon acid hydrolysis with hydrochloric acid in acetone, the same aglycone was obtained from C-I and C-II as a major product, and was identified as affinogenin C, 2α,3β,14-trihydroxy-11-oxo-5β,14β-card-20(22)-enolide, obtained from the leaves of this plant as one of the cardenolides free from the component sugar.[1,12)] Thus, the structures of C and D were confirmed. Water layers of the hydrolyzates from C-I and C-II afforded two different sugars, suggesting that C-I and C-II are epimers of the 2′-hydroxyl group.

Affinosides E, F, and J

Upon acetylation at room temp., E, F, and J afforded monoacetates (E-I, F-I, and J-I), indicating the presence of one acylable hydroxyl group in the aglycone moieties. As shown in C and D, one carbonyl carbon is apparent in the CMR of E, F, and J. Since shielding was observed at the carbonyl carbon (−6.5 ppm in E-I; −6.7 ppm in F-I) and at C-13 (−1.9 ppm in E-I; −2.9 ppm in F-I) on acetylation, the acylable hydroxyl group is that of an 11-oxo-12-hydroxyl moiety. An α-orientation of the hydroxyl in E and a β-orientation in F were determined on the basis of the evidence that the carbinyl proton at C-12 in E was observed at lower field (δ 4.07) than that of F (δ 3.84), and that H_a and H_b of the 21-methylene in E appeared at widely separated chemical shifts of δ 4.59 and 5.11, as observed in A-VII. Shielding of C-18 in F in comparison with that of C (−9.0 ppm) is consistent with the fact that an introduction of 12β-hydroxyl causes an upfield shift of C-18 of digitoxigenin by −6.7 ppm.[13)] The presence of Δ^4 in F is also apparent in the PMR and CMR spectra. C-7 and C-8 in F show deshielding by +5.4 ppm and +4.2 ppm, respectively, in comparison with those of E, and these shifts seem to be due to the conformational difference of ring B in the two compounds, since B, having saturated rings A and B, is known to retain the boat conformation of ring B,[2)] which appears to be influenced by the introduction of a Δ^4 linkage.

Upon oxidation of E with pyridinium chlorochromate in CH_2Cl_2, E was transformed into the enolic form of an 11,12-dioxo compound, which was in good agreement with B on direct comparison.

J was found to have two trisubstituted olefinic linkages on the basis of olefinic protons at δ 5.31 and 6.29, and four CMR signals at δ 120.2 (d), 135.8 (d), 143.8 (s), and 144.6 (s). One of them is assigned to a Δ^{16}-linkage, since an absorption maximum was observed at 267 nm. The PMR signal at δ 5.31 and a pair of CMR peaks at δ 120.2 and 144.6 are considered to be due to Δ^4, by comparison with the resonances corresponding to Δ^4 in F. A characteristic blue staining of J and F by $SbCl_3$ reagent on TLC suggested that the compounds have similar structures. J-I shows a carbinyl proton at δ 4.79 as a sharp singlet; the chemical shift is rather closer to that of F-I (δ 4.76) than to that of E-I (δ 5.04). Therefore, J was identified as the Δ^{16}-derivative of F. As in H and D, deshielding and shielding of the carbons surrounding the Δ^{16} linkage are also observed in J. Unusual deshielding of the 22-H at δ 6.24 in the PMR of J seems to arise as a combinational effect due to the 12β-hydroxyl and Δ^{16}-functions, since neither function alone shows the deshielding.

Affinoside G

In the CMR spectra of G and its monoacetate (G-I), the presence of an 11-oxo-12α-hydroxyl moiety is suggested on the basis of the resonances at δ 214.8 (s) and 82.9 (d) in G, and δ 208.1 (s) and 84.5 (d) in G-I, since the chemical shifts of these two carbons were nearly identical with those of E and E-I. Signals of two tertiary carbinol carbons are observed at δ 74.9 and 84.2, the latter of which is assignable to C-14; the other signal is considered to be due to C-5, C-8, or C-9. On the reaction of G-diacetate with $SOCl_2$ in pyridine, a less polar product (G-II) was obtained and found to be a dianhydro compound on the basis of the $M^+ + 1$ peak at m/z 627 and two olefinic protons at δ 5.48, one of which is ascribable to the 15-H. Since an absorption maximum of G-I is observed only at 210 nm but not in the 7,14- or 8,14-diene region, the second olefinic linkage is located at Δ^5 or Δ^4. By comparison of the chemical shift of the 4-H with that in A (δ 5.33) or F (δ 5.29), Δ^5 seems preferable to Δ^4 in G-II. Consequently, one of the tertiary hydroxyl groups is assigned to C-5.

By comparison of the CMR signals with those of B, the rings A and B of C, D, and E, and probably of G are considered to form chair and boat conformations, respectively, retaining 5β-fusion as shown in B.[2)]

The structures of eight affinosides were thus established. Hydrolysis to give the native aglycone proceeded in the case of affinoside C. The reductive cleavage of the dioxane ring with $NaBH_4$ is in contrast to the reaction of *Calotropis* glycosides, in which the 2'-keto group seems to resist $NaBH_4$ or $LiAlH_4$ reduction.[14)] The results of studies on the cardenolides free from the component sugar, and on several glycosides with or without doubly linked sugar will be presented shortly.

Experimental

Melting points were taken on a hot stage apparatus and are uncorrected. PMR and CMR were recorded on Hitachi R-22 and JEOL FX-100 spectrometers, respectively. Samples for CMR measurements were dissolved 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, bs=broad singlet. MS and FD-MS were recorded on JEOL-01SG and JEOL D-300-FD spectrometers, respectively. UV spectra were taken in MeOH on a Shimadzu 200S double beam spectrometer. The following solvent systems were used for silica gel column, thin layer, and DCC chromatographies: Solv. 1: benzene–acetone (15:1—1:1), Solv. 2: hexane–EtOAc (1:3—1:5), Solv. 3: EtOAc–MeOH (9:1), Solv. 4: $CHCl_3$–MeOH (10:1—5:1), Solv. 5: $CHCl_3$–MeOH–H_2O (7:1:5—7:2:0.7, bottom layer), Solv. 6: (5:6:4, for DCCC). As a spray reagent for TLC, a) 1:1 mixture of 2% 3,5-dinitrobenzoic acid in MeOH and 2 N NaOH (Kedde's reagent), b) 15% $SbCl_3$ in $CHCl_3$, and c) 5% H_2SO_4 were used. When b) or c) was used, TLC plates were charred for detection of the spots.

Extraction and Isolation of Affinosides A—J——Dried stem with bark (22 kg), collected at Madara-Jima, Saga Pref., during 1979—1980, was powdered and percolated with MeOH (total volume: 100 l). The MeOH percolate was concentrated *in vacuo* to 10 l. To the concentrate, 10 l of water was added and the deposit was filtered off. The filtrate was extracted successively with benzene, $CHCl_3$, $CHCl_3$–EtOH (2: 1), and BuOH. The $CHCl_3$ extract (60 g) was subjected to column chromatographies with Solv. 1, 2, and 5. Each effluent was monitored by TLC using the Kedde reagent. The fractions showing a homogeneous spot on TLC with Solv. 1 (2: 1—1: 1), 2 (1: 3), 3 (9: 1), and 5 (7: 2: 0.7), were each concentrated and the residue was crystallized from EtOAc–hexane. The yields of affinosides except for A were between 0.0005% and 0.0001%.

Affinoside A (A)——A was obtained from the effluent with Solv. 1 (6: 1) and crystallized from EtOAc–hexane to give prisms (0.005%), mp 248—253°C, $[\alpha]_D^{17}$ $-23.0°$ ($c=0.34$, MeOH), λ_{max} nm (ε): 208 (19000). *Anal.* Calcd for $C_{30}H_{38}O_{11}$: C, 62.70; H, 6.67. Found: C, 62.61; H, 6.80. MS *m/z*: 574 (M^+), 556, 432, 414, 396, 142, 127. FD-MS *m/z*: 574 (M^+).

A-I: To a solution of 100 mg of A in 3 ml of pyridine, 2 ml of Ac_2O was added. The mixture was allowed to stand overnight at room temp. The solution was then poured into ice-water and the mixture was extracted with $CHCl_3$. The $CHCl_3$ ext. was purified on a silica gel column with Solv. 1 (7: 1) to give 92 mg of A-I as a solid.

A-II: To a solution of 90 mg of A in 3 ml of pyridine, 1.5 ml of Ac_2O was added. The mixture was heated at 85°C for 1.5 h. The solution was then poured into ice-water and worked up as in the case of A-I. On crystallization from EtOAc–hexane, A-II was obtained as a crystalline powder (27 mg), mp 250—260°C, MS *m/z*: 658 (M^+, $C_{34}H_{42}O_{13}$), in addition to 50 mg of A-I.

A-III: A-I (46 mg) was dissolved in 4 ml of 1% HCl in acetone. The solution was allowed to stand at room temp. for 6 d then the acetone was evaporated off *in vacuo* at room temp. The residue was diluted with water and extracted with $CHCl_3$. The $CHCl_3$ ext. (30 mg) was crystallized from EtOAc–hexane to give needles, mp 227—231°C (dec.). A green flame was observed when the sample was placed on a copper wire and burned in the flame of a Bunsen burner (Beilstein test).

A-IV: To a solution of A-II (100 mg) in pyridine (3 ml), 0.2 ml of $SOCl_2$ was added dropwise at 0°C. The mixture was allowed to stand at room temp. for 2 h, then poured into ice-water and extracted with $CHCl_3$. The $CHCl_3$ ext. was chromatographed on a column with Solv. 1 (15: 1). A-IV (64 mg) was crystallized from EtOAc–hexane to give needles, mp 210—212°C. FD-MS *m/z*: 741 (M^++1, $C_{34}H_{41}ClO_{14}S$).

A-V: A solution of A (150 mg) in 20 ml of EtOH was shaken with 50 mg of PtO_2 under an atmosphere of hydrogen for 2.5 h, then filtered. The filtrate was concentrated to dryness *in vacuo* and the residue was subjected to column chromatography with Solv. 1 (7: 1). A-V (75 mg) was crystallized from EtOAc–hexane to give a crystalline powder, mp 240—245°C. FD-MS *m/z*: 579 (M^++1, $C_{30}H_{42}O_{11}$), MS *m/z*: 418 (genin−18).

A-VI: A-V (50 mg) was acetylated with 2 ml of pyridine and 1 ml of Ac_2O at room temp. for 20 h, and worked up in the same manner as described for A-I. A-VI was obtained as a solid (35 mg).

A-VII: A (120 mg) was refluxed with 16 ml of 0.25 N HCl–50% EtOH for 1 h, and the EtOH was evaporated off *in vacuo*. The solution was diluted with water and extracted with BuOH. The BuOH ext. was subjected to column chromatography with Solv. 1 (6: 1). The first fraction (36 mg) was crystallized from MeOH to give A-VII as prisms, mp 212—218°C (dec.), MS *m/z*: 469 (genin+1). The second fraction (49 mg) was found to be A-VIII.

A-VIII: A (170 mg) was refluxed with 20 ml of 0.05 N H_2SO_4–50% EtOH for 1 h, and the EtOH was evaporated off *in vacuo*. The residue was diluted with water and extracted with BuOH. The BuOH ext. was purified by column chromatography with Solv. 1 (5: 1). A (*ca.* 60 mg) was recovered from the first fraction. The second fraction (71 mg) was crystallized from EtOAc to give A-VIII as a crystalline powder, mp 215—220°C, MS *m/z*: 592 (M^+, $C_{30}H_{40}O_{12}$).

A-IX: A-VIII (40 mg) was acetylated with pyridine and Ac_2O to give 35 mg of A-IX, which was crystallized from EtOAc–hexane to give a crystalline powder, mp 230—245°C (dec.), MS *m/z*: 598 (M^+-AcOH–H_2O).

Affinoside B (B)[2]——B was obtained in a yield of 0.0001% from the mother liquor fraction of A, after silica gel column chromatography with Solv. 2. It was crystallized as prisms from MeOH or EtOAc–hexane.

Affinoside H (H)——H was contained in the same fraction as F on chromatography with Solv. 1 (5: 1), and was isolated as a solid by repeated chromatographies with Solv. 2 (2: 1) and Solv. 5 (7: 1: 3). $[\alpha]_D^{30}$ $+43.9°$ ($c=0.43$, MeOH), λ_{max} nm (ε): 266 (10000). MS *m/z*: 573 (M^++1, $C_{30}H_{36}O_{11}$). H-monoacetate (H-I) was prepared in the same manner as described for A-I, FD-MS *m/z*: 615 (M^++1, $C_{32}H_{38}O_{12}$).

H (50 mg) was dissolved in 3 ml of MeOH and the solution was shaken with 30 mg of PdO as a catalyst under an atmosphere of hydrogen. After filtration, the methanolic solution was concentrated *in vacuo* and the residue was subjected to column chromatography with Solv. 5, followed by crystallization from EtOAc–hexane to give 1 mg of H-II as prisms, and 7 mg of H-III as prisms. H-II: mp 240—250°C. On admixture with authentic A, no melting point depression was observed and the *Rf* values of the two samples were identical on TLC with Solv. 1, 2, and 5. H-III: mp 250—255°C, FD-MS *m/z*: 574 (M^+, $C_{30}H_{38}O_{11}$), PMR ($CDCl_3$): 1.23 (3H, d, $J=6$ Hz, 6′-CH_3), 1.40 and 1.44 (3H of each, s, 18 and 19-CH_3), 3.31 (1H, bs, 3′-H), 3.41 (3H, s, 3′-OCH_3), 3.49 (1H, d, $J=5$ Hz, 7-H), 4.71 (1H, s, 1′-H), 4.90 (1H, d, $J=2$ Hz, 21-H_a, 5.04 (1H, d, $J=2$ Hz, 21-H_b), 5.37 (1H, bs, 4-H), 5.83 (1H, d, $J=2$ Hz, 22-H).

Affinoside C (C)——C was found in the fraction following F on column chromatography with Solv. 1 (5: 1). After successive chromatographies with Solv. 2 (2: 1), followed by crystallization from EtOAc–hexane, C was obtained as prisms, mp 254—258°C, $[\alpha]_D^{23}$ −41.1° (c=0.37, MeOH). λ_{max} nm (ε): 212 (20300). *Anal.* Calcd for $C_{30}H_{42}O_9 \cdot 1/2H_2O$: C, 64.84; H, 7.80. Found: C, 64.77; H, 7.58.

Hydrolysis of C——A solution of 70 mg of C in 18 ml of EtOH was stirred at room temp. with 90 mg of $NaBH_4$ for 2 h. The solution was diluted with water and extracted with BuOH. The BuOH ext. was subjected to column chromatography with Solv. 1 and then with Solv. 2 to give C-I (solid, 12 mg) and C-II (solid, 18 mg). C-I: $[\alpha]_D^{22}$ −12.8° (c=0.63, MeOH), FD-MS m/z: 549 ($M^+ + 1$, $C_{30}H_{44}O_9$), PMR ($CDCl_3$): 0.89 and 1.03 (3H of each, s, 18 and 19-CH_3), 1.17 (3H, d, J=6 Hz, 6′-CH_3), 3.36 (3H, s, 3′-OCH_3), 4.20 (1H, d, J=5 Hz, 1′-H), 4.77 (2H, J=2 Hz, 21-H_2), 5.86 (1H, bs, 22-H). C-II: $[\alpha]_D^{22}$ −21.0° (c=0.62, MeOH), FD-MS m/z: 549 ($M^+ + 1$, $C_{30}H_{44}O_9$), PMR ($CDCl_3$): 0.90 and 1.03 (3H of each, s, 18 and 19-CH_3), 1.19 (3H, d, J=6 Hz, 6′-CH_3), 3.40 (3H, s, 3′-OCH_3), 4.61 (1H, d, J=8 Hz, 1′-H), 4.77 (2H, d, J=2 Hz, 21-H_2), 5.88 (1H, bs, 22-H).

C-I and C-II were dissolved in 2 ml each of 1% HCl in acetone. The solutions were allowed to stand at room temp. for 2 d, then diluted with MeOH, and deacidified with IR-410. The MeOH was evaporated off *in vacuo*. The residues were dissolved in water and extracted with BuOH The BuOH layers from C-I and C-II were each subjected to DCCC with Solv. 6 and the major products were crystallized from EtOAc–hexane to give prisms, mp 275—282°C (from C-I) and mp 270—275°C (from C-II). On comparison of melting point and IR, they were found to be in good agreement with authentic affinogenin C (mp 275—285°C, $[\alpha]_D^{23}$ +34.0° (c=0.57, MeOH))1,12) isolated from the leaves of this plant. The water layers, after extraction with BuOH, were examined by TLC with Solv. 5 (7: 3: 1), and one spot was detected from each sample, $R_{digitoxose}$: 1.59 (from C-I), 1.41 (from C-II) (L-oleandrose: 1.41, D-diginose: 1.41, D-sarmentose: 1.68, D-cymarose: 1.68, D-digitalose: 0.91).

Affinoside D (D)——D was accompanied by C in the fraction from column chromatography with Solv. 1 (5: 1) and was separated from C on a column with Solv. 2 (2: 1), followed by recrystallization from EtOAc–hexane as prisms, mp 239—245°C, $[\alpha]_D^{23}$ −24.7° (c=0.34, MeOH), λ_{max} nm (ε): 263 (14000). *Anal.* Calcd for $C_{30}H_{40}O_9 \cdot 1/2H_2O$: C, 65.08; H, 7.46. Found: C, 64.89; H, 7.28. D (100 mg) was dissolved in 20 ml of MeOH and the solution was shaken with 150 mg of Pd-carbon for 1 h. The catalyst was filtered off and the MeOH was evaporated off *in vacuo*. The residue was chromatographed on a column with Solv. 2 (2: 1). The fraction showing the same *Rf* as C on TLC was collected and crystallized from EtOAc–hexane to give 3 mg of prisms, mp 249—251°C. On admixture with authentic C, no melting point depression was observed and the IR spectra of the two samples were in good agreement.

Affinoside E (E)——E was eluted following D on a column with Solv. 1 (4.5: 1) and was crystallized as prisms, mp 225—228°C, $[\alpha]_D^{23}$ −78.7° (c=0.45, MeOH), λ_{max} nm (ε): 213 (14000), *Anal.* Calcd for $C_{30}H_{42}O_{10} \cdot 1/2H_2O$: C, 63.03; H, 7.58. Found: 63.32; H, 7.53. MS m/z: 562 (M^+), 544, 420 (genin), 402, 142. E-monoacetate (E-I) was prepared in the same manner as described for A-I with pyridine and Ac_2O at room temp.

Oxidation of E——E (30 mg) was dissolved in 10 ml of CH_2Cl_2 and a small amount of pyridinium chlorochromate was added portionwise. The mixture was stirred for 5 h at room temp. and diluted with $CHCl_3$. The whole solution was washed with water several times and the $CHCl_3$ was evaporated off *in vacuo*. The residue was chromatographed on a column with Solv. 1 (6: 1). The first fraction was crystallized from EtOAc–hexane to give 4 mg of prisms, mp 295—302°C, λ_{max} nm: 213, 284. On admixture with authentic B, no melting point depression was observed, and the *Rf* values of the two samples were in good agreement on TLC with Solv. 1, 2, and 5.

Affinoside F (F)——F was obtained following A and B on a column with Solv. 1 (5: 1), and was crystallized from EtOAc–hexane as prisms, mp 270—280°C (dec.), $[\alpha]_D^{30}$ +49.3° (c=0.15, MeOH), λ_{max} nm (ε): 214 (20300). *Anal.* Calcd for $C_{30}H_{40}O_{10} \cdot H_2O$: C, 62.27; H, 7.32. Found: C, 61.62; H, 7.01. FD-MS m/z: 560 (M^+). When heated on a TLC plate, after spraying $SbCl_3$ reagent, F showed a blue spot. F-monoacetate (F-I) was obtained as a solid in the usual manner as described above.

Affinoside J (J)——J appeared following F on a column with Solv. 1 (5: 1) and was obtained as crystals after several chromatographies with Solv. 1, 2 (2: 1), and 5 (7: 1: 3), mp 240—245°C, $[\alpha]_D^{30}$ +144.1° (c=0.14, MeOH), λ_{max} nm (ε): 267 (14800). *Anal.* Calcd for $C_{30}H_{38}O_{10} \cdot 1/2H_2O$: C, 63.48; H, 6.93. Found: C, 63.59; H, 6.87. Blue staining was observed on a TLC plate when $SbCl_3$ reagent was sprayed and the plate was heated. J-monoacetate (J-I) was prepared in the same manner as described above.

Affinoside G (G)——G was fractionated on a column with Solv. 1 (3.5: 1) and Solv. 5 (7: 1: 1), by DCCC (Solv. 6), and finally on a column with EtOAc. Crystallization from EtOAc–hexane gave a crystalline powder, mp 199—203°C, $[\alpha]_D^{30}$ −84.4° (c=0.18, MeOH), λ_{max} nm (ε): 212 (17100). *Anal.* Calcd for $C_{30}H_{42}O_{11} \cdot 3/2H_2O$: C, 59.49; H, 7.49. Found: C, 59.67; H, 7.09. FD-MS m/z: 578 (M^+). G-monoacetate (G-I) was prepared in the same manner as described above.

Diacetyl G Dianhydride (G-II)——G (100 mg) was heated at 85°C with pyridine (3 ml) and Ac_2O (1.5 ml) for 1.5 h. The solution was poured into ice-water and the deposit was extracted with $CHCl_3$. The $CHCl_3$ ext. (75 mg) was dissolved in 2 ml of pyridine and 0.2 ml of $SOCl_2$ was added dropwise at 0°C. The mixture was allowed to stand at room temp. for 30 min and was then poured into ice-water. The deposit was extracted with $CHCl_3$ and the $CHCl_3$ ext. was subjected to column chromatography with Solv. 1 (15: 1). G-II (45 mg) was obtained as a solid, FD-MS *m/z*: 627 ($M^+ + 1$, $C_{34}H_{42}O_{11}$). λ_{max}: 210 nm. PMR ($CDCl_3$): 1.09 and 1.30 (3H of each, s, 18 and 19-CH_3), 1.21 (3H, d, $J=6$ Hz, 6'-CH_3), 2.11 and 2.15 (3H of each, s, –OAc), 3.28 (3H, s, 3'-OCH_3), 4.27 (1H, bs, 3'-H), 4.68 (1H, dd, $J=17$, 2 Hz, 21-H_a), 4.72 (1H, s, 1'-H), 4.95 (1H, dd, $J=17$, 2 Hz, 21-H_b), 5.03 (1H, s, 12-H), 5.48 (2H, bs, 6-H and 15-H), 5.93 (1H, d, $J=2$ Hz, 22-H).

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References and Notes

1) This work was presented at the 23rd Symposium on "Chemistry of Natural Products," Nagoya, Oct., 1980.
2) *Anodendron* I: T. Yamauchi, K. Miyahara, F. Abe, and T. Kawasaki, *Chem. Pharm. Bull.*, **27**, 2463 (1979).
3) *a*) P. Brown, J.v. Euw, T. Reichstein, K. Stöchel, and T.R. Watson, *Helv. Chim. Acta*, **62**, 412 (1979); H.T.A. Cheung, T.R. Watson, N. Seiber, and C. Nelson, *J. Chem. Soc.* I, **1980**, 2169; *b*) H.T.A. Cheung, R.G. Coombe, W.T.L. Sidwell, and T.R. Watson, *J. Chem. Soc.*I, **1981**, 64; D.H.G. Crout, C.H. Hassall, and T.L. Jones, *J. Chem. Soc.*, **1964**, 2187; G. Hesse, and G. Ludwig, *Ann.*, **632**, 158 (1959); and references cited therein.
4) *a*) J. Polonia, H. Jäger, J.v. Euw, and T. Reichstein, *Helv. Chim. Acta*, **53**, 1253; *b*) H. Lichti, J.v. Euw, J. Polonia, and T. Reichstein, *Helv. Chim. Acta*, **53**, 1696 (1970).
5) S.M. Kupchan, J. Uchida, K. Shimada, B. Yu Fei, D.M. Stevens, A.T. Sneden, R.W. Miller, and R.F. Bryan, *Chem. Commun.*, **1977**, 255; K. Shimada, T. Nambara, and I. Uchida, *Heterocycles*, **12**, 1445 (1979); K. Shimada, T. Kyuno, T. Nambara, and I. Uchida, *Heterocycles*, **15**, 355 (1981).
6) T. Inagaki, S. Hisada, and K. Shima, *Yakugaku Zasshi*, **91**, 1133 (1971); K. Shima, S. Hisada, and T. Inagaki, *Yakugaku Zasshi*, **91**, 1121, 1124 (1971); *ibid.*, **92**, 507 (1972).
7) K. Sasaki and Y. Hirata, *Tetrahedron Lett.*, **1969**, 4065.
8) T. Yamauchi, F. Abe, Y. Nishishita, H. Okabe, K. Shima, and S. Nishibe, *Phytochemistry*, **18**, 1240 (1979).
9) F. Abe and T. Yamauchi, *Phytochemistry*, **15**, 1745 (1976); T. Yamauchi, F. Abe, Y. Ogata, and M. Takahashi, *Chem. Pharm. Bull.*, **22**, 1680 (1974).
10) H. Fuhrer, R.F. Zürcher, and T. Reichstein, *Helv. Chim. Acta*, **52**, 616 (1969).
11) F. Abe and T. Yamauchi, *Chem. Pharm. Bull.*, **25**, 2744 (1977).
12) The details will be presented in subsequent papers.
13) K. Tori, H. Ishii, Z.W. Wolkowski, C. Chachaty, M. Sangaré, F. Piriou, and G. Lukacs, *Tetrahedron Lett.*, **1973**, 1077.
14) F. Brünschweiler, K. Stöchel, and T. Reichstein, *Helv. Chim. Acta*, **52**, 2276 (1969).