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Affinoside B, a Cardiac Glycoside with a Diosphenol System in the Aglycone, from *Anodendron affine* (*Anodendron*. I)[1]

Tatsuo Yamauchi,[2a] Kazumoto Miyahara,[2b] Fumiko Abe[2a] Toshio Kawasaki[2b]

Faculty of Pharmaceutical Sciences, Fukuoka University[2a] *and Faculty of Pharmaceutical Sciences, Kyushu University*[2b]

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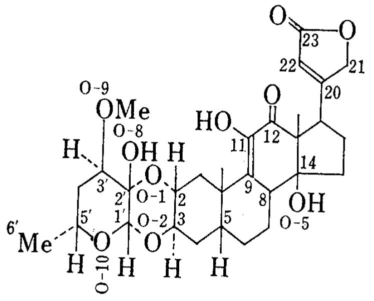
Affinoside B, a novel cardiac glycoside with a diosphenol system in ring C of the aglycone and with a doubly linked 3-O-methyl-4,6-dideoxy-2-hexosulose sugar moiety, was isolated from *Anodendron affine* Druce and the structure was determined by direct single crystal X-ray analysis.

Keywords——cardiac glycoside; Apocynaceae; *Anodendron*; X-ray analysis; 3-O-methyl-4,6-dideoxy-2-allohexosuloside; $\Delta^{9(11)}$-11-hydroxy-12-oxo-cardenolide; diosphenol

Several cardiac glycosides, anodendrosides A—G, were isolated from *Anodendron paniculatum* by Polonia *et al.*[3a] and structures having 3-O-methyl-4,6-dideoxy-2-hexosulose as a sugar moiety were proposed by Lichti *et al.*[3b] We had previously identified pregnane derivatives such as neridienone A and its homologs[1,4] from *Anodendron affine* Druce, indigenous to the south-western part of Japan. This paper deals with the isolation and structure determination of a cardiac glycoside with a diosphenol system in ring C and with a 2-hexosulose residue doubly conjugated to the aglycone, from the same plant.

The methanol extracts of the bark were partitioned between chloroform and methanol–water, and the chloroform layer was subjected to column chromatography on silica gel, using benzene–acetone as an eluent. One of the fractions reacting positively to Kedde and $SbCl_3$ reagents was crystallized from EtOAc–hexane to give a compound as prisms in a yield of 0.005%; this was named affinoside A (A) (mp 250—255°).



affinoside B

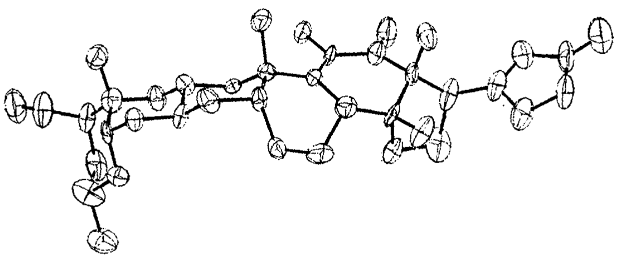


Fig. 1. An ORTEP Drawing of the Molecular Structure of Affinoside B

From the mother liquor of crystallization of A, a small amount (0.0001%) of another constituent, named affinoside B (B), was obtained as prisms, mp 307—310° (dec.), which showed ultraviolet (UV) absorption peaks at 211 nm and 282 nm. Elementary analysis and field desorption mass spectrometry (FD–MS) (M^+: 560) of B indicated the molecular formula

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[1] Preceding paper of this series: T. Yamauchi, F. Abe, Y. Nishishita, H. Okabe, K. Shima, and S. Nishibe, *Phytochemistry*, **18**, 1240 (1979).

[2] Location: *a*) *11 Nanakuma, Nishi-ku, Fukuoka*; *b*) *3-1-1 Maedashi, Higashi-ku, Fukuoka.*

[3] *a*) J. Polonia, H. Jäger, J.v. Euw, and T. Reichstein, *Helv. Chim. Acta*, **53**, 1253 (1970); *b*) H. Lichti, J.v. Euw, J. Polonia, and T. Reichstein, *Helv. Chim. Acta*, **53**, 1696 (1970).

[4] F. Abe and T. Yamauchi, *Phytochemistry*, **15**, 1745 (1976); T. Yamauchi, F. Abe, Y. Ogata, and M. Takahashi, *Chem. Pharm. Bull.* (Tokyo), **22**, 1680 (1974).

$C_{30}H_{40}O_{10}$. In the proton magnetic resonance (PMR) spectrum, 21-methylene, 22-olefin and two angular methyls of the cardenolide nucleus as well as 6′-methyl, 3′-methoxyl and an anomeric proton (sharp singlet at 5.36 ppm) in the sugar moiety were observed. The above data suggest that B is a cardenolide with 3-O-methyl-4,6-dideoxy-2-hexosulose, as seen in the anodendrosides.[3] In the carbon nuclear magnetic resonance (CMR) spectrum, the presence of sixteen signals in the region from 55 to 200 ppm supports the presence of a butenolide moiety (C-21: 73.5, C-22: 118.5, C-20 and C-23: 173.8), one tetrasubstituted double bond (137.5, 141.9), one carbonyl (199.0), one methoxyl (58.5), one quaternary carbon (60.5) probably adjacent to the carbonyl, and seven carbons bearing oxygen functions. The positive color reaction with $FeCl_3$ and the UV absorption at 282 nm suggested the presence of a diosphenol system in ring B or C. Due to the very small amount of the material available, and the difficulty in splitting off the sugar moiety, the structure of B was determined by direct single crystal X-ray analysis.

The structures of its aglycone and sugar moieties were found to be 2α,3β,11-trihydroxy-12-oxo-5β-carda-9(11),20(22)-dienolide and 3-O-methyl-4,6-dideoxy-D-allo-2-hexosulose, respectively. However, unlike the reported anodendrosides,[3] B is a glycoside in which the aglycone is doubly linked at 2α- and 3β-hydroxyl groups to C-2′ acetal and C-1′ hemiacetal of the sugar moiety to form a dioxane ring. Ring A has a chair conformation in which the 2α- and 3β-hydroxyl groups are both oriented equatorial, preserving *trans* fusion of the dioxane ring, and hence ring B takes an unusual boat conformation. The junction of the sugar and dioxane rings is *cis*.

In contrast to other glycosides so far isolated from Apocynaceae plants, B is rather similar, in the mode of glycosidic linkage, to the glycosides found in the genera *Calotropis*, *Asclepias* and *Pergularia* of Ascrepiadaceae[5] and to elaeodendroside A in Celastraceae.[6]

As for other cardiac glycosides having 11,12-dioxo functions in the aglycone moiety, chryseoside[7a] and decoside[7b] have been reported. These compounds were derived from natural 11α-hydroxy-12-oxo- or 12α- (and β)-hydroxy-11-oxo-cardenolides by CrO_3 or $Cu(OAc)_2$ oxidation.

Table I. Fractional Atomic Coordinates ($\times 10^4$) and Anisotropic Thermal Parameters ($\times 10^3$)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C (1)	7175 (7)	5174 (7)	8285 (7)	52 (7)	29 (5)	22 (5)	−9 (5)	−10 (5)	8 (5)
C (2)	7203 (6)	4070 (7)	8157 (8)	29 (6)	40 (6)	29 (6)	−8 (5)	10 (5)	−5 (5)
C (3)	7479 (7)	3833 (7)	7095 (8)	43 (6)	19 (5)	49 (7)	2 (5)	13 (6)	6 (5)
C (4)	8353 (8)	4159 (9)	6908 (10)	57 (8)	50 (7)	43 (7)	−7 (6)	8 (7)	−15 (6)
C (5)	8429 (7)	5277 (7)	7041 (8)	50 (7)	29 (5)	29 (5)	−14 (5)	18 (6)	−2 (5)
C (6)	8039 (9)	5756 (8)	6086 (9)	94 (10)	38 (7)	35 (7)	−25 (7)	−12 (7)	−2 (6)
C (7)	7821 (10)	6812 (10)	6229 (9)	115 (12)	65 (9)	34 (7)	−4 (9)	−21 (8)	2 (7)
C (8)	8325 (8)	7282 (8)	7162 (9)	63 (8)	39 (6)	44 (7)	3 (6)	−5 (6)	−1 (6)
C (9)	8018 (6)	6734 (7)	8102 (7)	36 (5)	33 (5)	22 (5)	−12 (5)	2 (5)	7 (5)
C (10)	8057 (7)	5633 (7)	8078 (8)	34 (6)	39 (6)	32 (6)	−9 (5)	−4 (5)	8 (5)
C (11)	7776 (7)	7236 (7)	8952 (8)	45 (6)	14 (5)	53 (7)	−4 (5)	−12 (6)	14 (5)
C (12)	7877 (7)	8284 (8)	9076 (9)	54 (7)	28 (6)	53 (7)	4 (6)	2 (7)	3 (6)

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Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C (13)	8356 (7)	8862 (7)	8231 (9)	46 (6)	13 (4)	64 (8)	0 (5)	−8 (6)	6 (5)
C (14)	8184 (7)	8390 (7)	7198 (9)	44 (7)	28 (5)	56 (8)	−6 (5)	3 (6)	29 (5)
C (15)	7278 (9)	8734 (8)	6936(11)	86(10)	31 (6)	77 (9)	3 (7)	−18 (9)	17 (7)
C (16)	7266 (8)	9810(10)	7242(14)	29 (7)	68 (9)	140(15)	−1 (7)	8 (9)	11(10)
C (17)	7906 (7)	9888 (8)	8145(11)	49 (8)	32 (6)	88(10)	5 (6)	29 (8)	18 (7)
C (18)	9269 (7)	8872 (8)	8551(11)	45 (7)	32 (6)	92(11)	3 (6)	−8 (7)	−8 (7)
C (19)	8681 (8)	5343 (8)	8950 (9)	59 (8)	33 (6)	48 (7)	8 (6)	−4 (6)	1 (6)
C (20)	8527 (7)	10735 (7)	8037(11)	43 (7)	26 (5)	82 (9)	16 (5)	20 (7)	9 (6)
C (21)	8913 (8)	11068 (9)	7046(12)	53 (8)	58 (8)	87(10)	−8 (7)	26 (8)	21 (8)
C (22)	8769 (8)	11301 (9)	8767(10)	62 (8)	45 (7)	68 (9)	−5 (7)	6 (8)	−9 (7)
C (23)	9340 (9)	12030 (8)	8371(12)	79(10)	23 (6)	97(11)	−11 (6)	1 (9)	1 (6)
C (1′)	6622 (7)	2428 (6)	7097 (8)	49 (6)	14 (4)	35 (6)	−7 (4)	9 (5)	−12 (4)
C (2′)	6332 (7)	2676 (8)	8194(10)	42 (7)	43 (6)	62 (8)	5 (6)	4 (6)	0 (6)
C (3′)	5415 (8)	2372 (8)	8356(10)	60 (8)	27 (5)	61 (8)	−4 (5)	28 (7)	0 (6)
C (4′)	4883 (7)	2715 (9)	7497(12)	25 (6)	51 (7)	111(11)	−12 (6)	7 (7)	−4 (8)
C (5′)	5215 (7)	2414(11)	6473(11)	28 (7)	101(12)	72 (9)	10 (7)	7 (7)	−23 (9)
C (6′)	4715 (8)	2854(11)	5582(12)	52 (9)	86(11)	79(11)	13 (9)	−15 (8)	−7 (9)
C (7′)	4765(12)	911(11)	8966(13)	128(15)	59 (9)	84(12)	−39(10)	14(11)	−8 (9)
O (1)	6372 (5)	3690 (5)	8363 (6)	51 (5)	34 (4)	46 (5)	−3 (4)	11 (4)	−10 (4)
O (2)	7430 (4)	2800 (5)	6907 (6)	36 (4)	32 (3)	47 (4)	−1 (4)	8 (4)	−3 (4)
O (3)	7425 (5)	6783 (5)	9788 (5)	63 (5)	28 (4)	35 (4)	−5 (4)	5 (4)	5 (4)
O (4)	7659 (7)	8661 (6)	9859 (7)	114 (8)	35 (4)	59 (6)	−11 (5)	20 (6)	−3 (4)
O (5)	8732 (6)	8799 (6)	6416 (7)	84 (6)	50 (5)	68 (6)	7 (5)	25 (5)	25 (5)
O (6)	9450 (6)	11850 (5)	7341 (7)	74 (6)	36 (4)	87 (7)	−17 (5)	28 (6)	6 (5)
O (7)	9696 (7)	12715 (7)	8779 (8)	111 (8)	62 (6)	93 (8)	−26 (6)	20 (7)	−12 (6)
O (8)	6872 (5)	2197 (6)	8901 (6)	66 (6)	46 (5)	52 (5)	−3 (5)	3 (5)	7 (5)
O (9)	5449 (6)	1348 (6)	8417 (8)	80 (6)	46 (5)	105 (8)	−17 (5)	25 (6)	5 (5)
O (10)	6073 (5)	2823 (6)	6373 (6)	50 (5)	51 (5)	45 (5)	−7 (4)	−11 (4)	4 (4)

The anisotropic thermal parameters are expressed in the form: $\exp[-2\pi(U_{11}h^2a^{*2}+\cdots+2U_{23}klb^*c^*)]$.
The standard deviation for the last digit is given in parentheses.

TABLE II. Bond Lengths and Their Standard Deviations (Å)

C (1)-C (2)	1.529(14)	C (14)-C (15)	1.548(17)
C (1)-C (10)	1.557(15)	C (14)-O (5)	1.452(14)
C (2)-C (3)	1.488(15)	C (15)-C (16)	1.534(19)
C (2)-O (1)	1.441(12)	C (16)-C (17)	1.557(21)
C (3)-C (4)	1.476(16)	C (17)-C (20)	1.534(15)
C (3)-O (2)	1.446(11)	C (20)-C (21)	1.500(20)
C (4)-C (5)	1.554(15)	C (20)-C (22)	1.288(18)
C (5)-C (6)	1.536(16)	C (21)-O (6)	1.426(15)
C (5)-C (10)	1.554(15)	C (22)-C (23)	1.447(18)
C (6)-C (7)	1.504(19)	C (23)-O (6)	1.376(18)
C (7)-C (8)	1.591(18)	C (23)-O (7)	1.221(16)
C (8)-C (9)	1.519(15)	C (1′)-C (2′)	1.540(16)
C (8)-C (14)	1.541(15)	C (1′)-O (2)	1.401(12)
C (9)-C (10)	1.518(14)	C (1′)-O (10)	1.391(13)
C (9)-C (11)	1.360(14)	C (2′)-C (3′)	1.525(17)
C (10)-C (19)	1.555(16)	C (2′)-O (1)	1.415(14)
C (11)-C (12)	1.460(14)	C (2′)-O (8)	1.417(14)
C (11)-O (3)	1.373(13)	C (3′)-C (4′)	1.477(19)
C (12)-C (13)	1.557(16)	C (3′)-O (9)	1.413(14)
C (12)-O (4)	1.196(14)	C (4′)-C (5′)	1.493(21)
C (13)-C (14)	1.520(16)	C (5′)-C (6′)	1.528(20)
C (13)-C (17)	1.583(14)	C (5′)-O (10)	1.478(14)
C (13)-C (18)	1.502(16)	C (7′)-O (9)	1.431(19)

The standard deviation for the last digit is given in parentheses.

Experimental

Melting points were taken on a hot stage apparatus and are uncorrected. PMR and CMR were run on JEOL PS-100 and JEOL FX-100 machines, respectively. FD-MS was recorded on a JEOL D-300-FD spectrometer.

Extraction and Isolation of Affinoside B (B)——Dried bark (3 kg) was powdered and percolated with MeOH. The MeOH extracts were concentrated *in vacuo* to 3 l and diluted with an equal volume of water. The mixture was extracted successively with hexane, benzene, $CHCl_3$ and then $CHCl_3$–EtOH (2: 1). The $CHCl_3$ extracts were subjected to column chromatography on silica gel with benzene–acetone as an eluent. The fraction containing the least polar and Kedde-positive compounds was found to be composed of neridienone A and its homologs.[1,4] The fraction eluted next to the above pregnane derivatives was positive to both Kedde and $SbCl_3$ reagents; it was further fractionated by column chromatography in the same way as above, followed by crystallization from EtOAc–hexane to give prisms (affinoside A), mp 250—255°, $[\alpha]_D^{17}$ $-23.0°$ ($c=0.34$, MeOH), yield: 0.005%. From the mother liquor of crystallization, a small amount of prisms was obtained (affinoside B), mp 307—310° (dec.), $[\alpha]_D^{17}$ $+2.0°$ ($c=0.86$, MeOH), yield: 0.0001%, Kedde-reaction: positive, $SbCl_3$-test: negative; UV λ_{max}^{MeOH} nm (ε): 211 (14000), 282 (8400), *Anal.* Calcd. for $C_{30}H_{40}O_{10}$: C, 64.27; H, 7.19. Found: C, 63.83; H, 7.12. FD-MS: 560 (M^+). PMR (pyridine-d_5) δ (ppm): 1.20 and 1.54 (3H of each, s, 18- and 19-CH_3), 1.32 (3H, d, $J=7$ Hz, 6′-CH_3), 2.9—3.3 (2H, m), 3.50 (3H, s, $-OCH_3$), 3.61 (1H, bs), 4.30 (2H, m), 5.01 and 5.28 (1H of each, d, $J=18$ Hz, 21-CH_2), 5.36 (1H, s, 1′-H), 6.26 (1H, s,

TABLE III. Bond Angles and Their Standard Deviations (°)

C(2)-C(1)-C(10)	111.1(8)	C(8)-C(14)-O(5)	106.0(9)
C(1)-C(2)-C(3)	109.1(8)	C(13)-C(14)-C(15)	103.3(9)
C(1)-C(2)-O(1)	108.5(8)	C(13)-C(14)-O(5)	110.4(8)
C(3)-C(2)-O(1)	111.2(8)	C(15)-C(14)-O(5)	106.4(9)
C(2)-C(3)-C(4)	111.3(9)	C(14)-C(15)-C(16)	104.4(10)
C(2)-C(3)-O(2)	108.9(8)	C(15)-C(16)-C(17)	104.9(11)
C(4)-C(3)-O(2)	108.9(8)	C(13)-C(17)-C(16)	106.4(10)
C(3)-C(4)-C(5)	111.0(9)	C(13)-C(17)-C(20)	113.4(9)
C(4)-C(5)-C(6)	107.6(9)	C(16)-C(17)-C(20)	113.7(11)
C(4)-C(5)-C(10)	112.3(9)	C(17)-C(20)-C(21)	125.0(12)
C(6)-C(5)-C(10)	114.7(9)	C(17)-C(20)-C(22)	125.7(11)
C(5)-C(6)-C(7)	113.8(10)	C(21)-C(20)-C(22)	109.2(11)
C(6)-C(7)-C(8)	112.0(11)	C(21)-C(21)-O(6)	104.0(11)
C(7)-C(8)-C(9)	104.6(9)	C(20)-C(22)-C(23)	110.1(12)
C(7)-C(8)-C(14)	110.8(10)	C(22)-C(23)-O(6)	107.6(10)
C(9)-C(8)-C(14)	114.9(9)	C(22)-C(23)-O(7)	132.1(14)
C(18)-C(9)-C(10)	117.8(9)	O(6)-C(23)-O(7)	120.4(12)
C(8)-C(9)-C(11)	119.6(9)	C(2′)-C(1′)-O(2)	110.8(8)
C(10)-C(9)-C(11)	122.4(9)	C(2′)-C(1′)-O(10)	110.8(8)
C(1)-C(10)-C(5)	111.2(8)	O(2)-C(1′)-C(10)	107.9(8)
C(1)-C(10)-C(9)	111.5(8)	C(1)-C(2′)-C(3′)	110.6(9)
C(1)-C(10)-C(19)	109.8(9)	C(1′)-C(2′)-O(1)	110.5(9)
C(5)-C(10)-C(9)	110.4(8)	C(1′)-C(2′)-O(8)	108.7(9)
C(5)-C(10)-C(19)	108.3(9)	C(3′)-C(2′)-O(1)	107.1(9)
C(9)-C(10)-C(19)	105.4(8)	C(3′)-C(2′)-O(8)	110.8(9)
C(9)-C(11)-C(12)	124.2(10)	O(1′)-C(2′)-O(8)	109.2(9)
C(9)-C(11)-O(3)	121.9(9)	C(2′)-C(3′)-C(4′)	110.5(10)
C(12)-C(11)-O(3)	113.9(9)	C(2′)-C(3′)-O(9)	104.3(9)
C(11)-C(12)-C(13)	118.7(9)	C(4′)-C(3′)-O(9)	112.4(10)
C(11)-C(12)-O(4)	119.5(10)	C(3′)-C(4′)-C(5′)	112.8(10)
C(13)-C(12)-O(4)	121.5(10)	C(4′)-C(5′)-C(6′)	112.8(11)
C(12)-C(13)-C(14)	108.6(8)	C(4′)-C(5′)-O(10)	107.3(10)
C(12)-C(13)-C(17)	106.7(9)	C(6′)-C(5′)-O(10)	104.9(11)
C(12)-C(13)-C(18)	106.2(10)	C(2)-O(1)-C(2′)	111.9(8)
C(14)-C(13)-C(17)	103.8(9)	C(3)-O(2)-C(1′)	112.4(7)
C(14)-C(13)-C(18)	114.9(10)	C(21)-O(6)-C(23)	108.9(10)
C(17)-C(13)-C(18)	116.2(9)	C(3′)-O(9)-C(7′)	114.8(10)
C(8)-C(14)-C(13)	115.2(9)	C(1′)-O(10)-C(5′)	111.4(9)
C(8)-C(14)-C(15)	115.3(9)		

The standard deviation for the last digit is given in parentheses.

22-H), 6.42 (1H, bs). CMR (pyridine-d_5) (ppm): 15.9, 21.4, 22.3, 23.1, 24.7, 26.8, 31.2, 33.5, 34.0, 35.0, 36.7, 39.1, 40.2, 43.4, 58.4, 60.5, 66.4, 68.4, 69.2, 73.5, 81.2, 82.2, 91.7, 96.0, 118.5, 137.5, 141.9, 173.8×2, 199.0.

X-Ray Analysis——Crystal data: $C_{30}H_{40}O_{10}$ (M.W. 560.65), orthorhombic, Space group: $P2_12_12_1$, $a=15.829(4)$ Å, $b=13.765(7)$ Å, $c=13.027(4)$ Å, $V=2838(2)$ Å^3, $D_{\text{obs}}=1.305$ g/cm^3 (in aqueous KI solution), $D_{\text{calcd.}}=1.312$ g/cm^3, $Z=4$.

Lattice constants and diffracted intensities were derived from measurements carried out on a Syntex $P\bar{1}$ automated four-circle diffractometer using a crystal with approximate dimensions of $0.15\times0.15\times0.2$ mm. Intensity data were collected by $2\theta-\theta$ scanning with graphite-monochromated Mo Kα radiation ($\lambda=0.71069$ Å) within the limit $2\theta\leq60°$ to yield 3997 unique reflections, among which 1406 were regarded as significant ($I\geq2.0\sigma_I$). The intensities were corrected for the usual Lorentz and polarization factors. No absorption correction was applied.

The phase problem was solved by the direct method[8] and 21 plausible atomic positions were obtained on an E-map from 178 reflections with $E\geq1.8$. The structure was determined by successive difference Fourier syntheses and refined by block-diagonal least-squares techniques to an R-value of 0.063 for the observed reflections. Anisotropic thermal parameters were used for nonhydrogen atoms, and isotropic thermal parameters[9] for hydrogen atoms other than the three hydroxyl hydrogen atoms. The weights were taken as $w=40.0/|F|$, if $Fa>40.0$. The atomic scattering factors were taken from International Tables for X-ray Crystallography.[10]

An ORTEP[11] drawing of the structure, the final atomic parameters, the bond lengths, and the bond angles for nonhydrogen atoms are shown in Fig. 1 and Tables I, II and III, respectively.

All the calculations were performed on a FACOM M-190 computer at the Computer Center of Kyushu University using the UNICS II[12] and the MULTAN[8] programs.

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