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A NOVEL LIGNAN AND FLAVONOIDS FROM *POLYGONUM AVICULARE*

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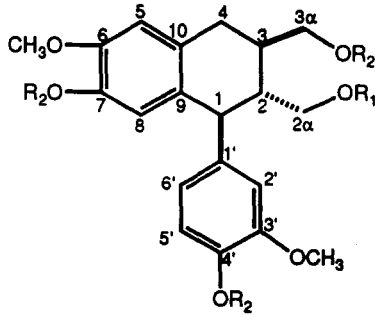
ABSTRACT.—A new lignan glycoside, aviculin [**1**], was isolated from the whole plant of *Polygonum aviculare* along with the known compounds juglanin [**2**], avicularin [**3**], astragalin [**4**], and betmidin [**5**]. The structure of the new compound was elucidated on the basis of spectroscopic and chemical evidence.

Polygonum aviculare L. (Polygonaceae) is a medicinal plant frequently employed in Korean traditional medicine. The whole plant has been used as an antipyretic, antiparasitic, and diuretic agent (1,2). This paper deals with the structural elucidation of a new lignan glycoside, aviculin [**1**], and the isolation from this plant of four flavonoid glycosides (3–5), juglanin [**2**], avicularin [**3**], astragalin [**4**], and betmidin [**5**].

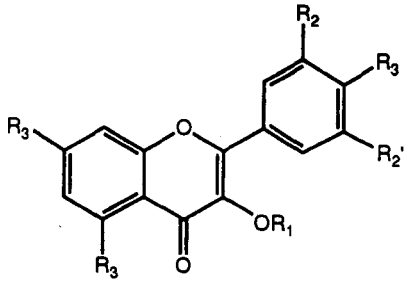
RESULTS AND DISCUSSION

The EtOAc-soluble fraction of the aqueous MeOH extract afforded **1**, $C_{26}H_{34}O_{10}$, amorphous powder, mp 155–157°, $[\alpha]^{25}D$ +20.27° (c=0.074, MeOH). On acetylation with Ac_2O and pyridine, compound **1** afforded a hexaacetate [**1a**], as an oily compound (6).

Acidic hydrolysis of compound **1** yielded L-rhamnose and an aglycone having identical specific rotation and eims data with those of (+)-isolariciresinol [**1b**] (7). The cd of the aglycone was a mirror image to that of (−)-isolariciresinol (8), with known absolute configuration (9), and also in agreement with published cd data of (+)-isolariciresinol dimethyl ether (10). The eims spectrum of compound **1** showed a molecular ion peak at *m/z* 506, besides significant fragment peaks at *m/z* 359 $[M-\text{rhamnose}]^+$, 341 $[M-\text{rhamnose}-H_2O]^+$, 311 $[M-\text{rhamnose}-H_2O-OCH_2]^+$,



1 R_1=α-L-Rhamnopyranosyl, R_2=H
1a R_1=Tri-*O*-acetyl-α-L-rhamnopyranosyl, R_2=Ac
1b R_1=R_2=H



2 R_1=α-L-Arabinofuranosyl, R_2=R_2'=H, R_3=OH
3 R_1=α-L-Arabinofuranosyl, R_2'=H, R_2=R_3=OH
3a R_1=Tri-*O*-acetyl-α-L-arabinofuranosyl, R_2'=H R_2=R_3=OAc
4 R_1=β-D-Glucopyranosyl, R_2=R_2'=H, R_3=OH
5 R_1=α-L-arabinofuranosyl, R_2=R_2'=R_3=OH
5a R_1=Tri-*O*-acetyl-α-L-arabinofuranosyl, R_2=R_2'=R_3=OAc

and 279 $[M-\text{rhamnose}-H_2O-2\times OCH_3]^+$. The ir spectrum of compound **1** showed characteristic absorption bands due to hydroxyl groups (3449 cm^{-1}) and aromatic double bonds (1598 and 1449 cm^{-1}).

The ^{1}H-nmr spectrum of compound **1** showed two peaks at δ 6.16 (1H, s) and 6.66 (1H, s) due to H-8 and H-5 of the tetrasubstituted aromatic ring, and peaks at δ 6.59 (dd, J=7.9 and 1.8 Hz, H-6′), 6.75 (d, J=7.9 Hz, H-5′), and 6.63 (d, J=1.8 Hz, H-2′), ascribable to the 3H ABX system of the 1-phenyl-3′,4′-disubstituted ring system (11,12). The peaks at δ 3.81 and 3.77 were attributed to the MeO groups at C-6 and C-3′. The signal of the anomeric proton was found at δ 4.51 (d, J=1.5 Hz) and the characteristic Me peak of rhamnose was observed as a doublet at δ 1.18 (J=6.0 Hz).

The structural assignment of **1** was further supported by 2D nmr studies using correlation spectroscopy (COSY). The signal at δ 3.34 (H-4″) showed a cross-peak with a methine signal at δ 3.51 (dd, J=6.0 and 9.0 Hz), which was assigned to H-5″. Cross-peaks between H-4″ and H-3″ were also observed. A ^{1}H-^{13}C HETCOR experiment on **1** indicated a carbon count of 26 carbons and a hydrogen count of 28 carbon-bound hydrogens. In order to determine the position of attachment and configuration of the L-rhamnose moiety, the ^{13}C-nmr spectra of **1** and **1a** were studied. Aviculin hexaacetate [**1a**] exhibited ^{13}C-nmr signals assignable to the carbons of the aglycone moiety at the δ values shown in Table 1; except for the $C_{2\alpha}$ carbon, each signal was essentially the same as the signal of the corresponding carbon of (+)-isolariciresinol tetraacetate (13), suggesting that the L-rhamnose moiety is attached at the $C_{2\alpha}H_2OH$ group as α-L-rhamnose. The glucosidation shifts (14,15) of tetra-*O*-acetyl glucopyranoside on the α-carbon of the R-CH_2OH group were reported as +6 ~ +7 ppm and the acetylation shift (16) on the α-carbon of the R-CH_2OH group has been reported as +1.6 ppm. On the assumption that the glucosidation shift is similar to the rhamnosidation shift, the calculated δ values of the ^{13}C-nmr chemical shift of the $C_{2\alpha}$ and $C_{3\alpha}$ carbons of (+)-isolariciresinol-2α,α-L-rhamnopyranoside hexaacetate could be δ 67.4 ~ 68.4 ppm

TABLE 1. ^{13}C-Nmr Data for **1** and **1a** (75.4 MHz, δ in ppm).[a]

C	(+)-Isolariciresinol[b]	**1**	**1a**	C	**1**	**1a**	Methyl-α-L-rha.[c]
1	47.4	48.3 (d)	47.0	1″	102.3 (d)	103.4	102.4
2	47.5	45.5 (d)	43.9	2″	72.3 (d)	69.2	71.9
3	39.5	40.0 (d)	35.3	3″	72.5 (d)	69.9	72.5
4	32.8	33.6 (t)	33.2	4″	73.8 (d)	70.9	73.6
5	110.6	112.4 (d)	111.9	5″	70.1 (d)	67.0	69.4
6	147.1	149.2 (s)	149.5	6″	17.9 (q)	17.3	18.4
7	144.1	146.1 (s)	138.1	$OCOCH_3$.	—	20.9, 20.7	
8	115.8	117.1 (d)	123.7	$OCOCH_3$.	—	168.9	
9	136.8	138.1 (s)	131.5			169.1	
10	127.2	128.9 (s)	134.1			169.9	
1′.....	132.6	133.9 (d)	138.5			170.0	
2′.....	112.0	113.4 (d)	113.3			170.1	
3′.....	145.2	147.2 (s)	151.3			171.1	
4′.....	143.5	145.2 (s)	142.8				
5′.....	114.5	116.1 (d)	123.0				
6′.....	121.9	123.2 (d)	121.5				
2α	62.1	67.9 (t)	67.2				
3α	65.7	65.3 (t)	66.0				
OMe ...	55.6	56.3 (q)	56.0				

[a]Multiplicities were determined from DEPT spectra. Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet. Solvent: compound **1** in CD_3OD, compound **1a** in $CDCl_3$.

[b]Data taken from Fonseca *et al.* (13).

[c]Data taken from Seo *et al.* (17).

[63.0–1.6+6 (or 7)] and δ 66.2 ppm, respectively, and the calculated ^{13}C-nmr chemical shift of the $C_{2\alpha}$ and $C_{3\alpha}$ carbons of (+)-isolariciresinol-3α,α-L-rhamnopyranoside hexaacetate could be δ 63.0 ppm and δ 70.6 ~ 71.6 ppm [66.2–1.6+6 (or 7)], respectively. Compound **1a** exhibited ^{13}C-nmr signals of the carbons of the CH_2OR groups at δ 67.2 ppm and at δ 66.0 ppm. Compound **1** also exhibited ^{13}C-nmr signals of the α-L-rhamnose moiety at the δ values shown in Table 1, each of which is equal to that of the corresponding carbon of methyl α-L-rhamnopyranoside (17), suggesting that the L-rhamnose moiety is present on the aglycone of **1** as α-L-rhamnopyranoside. The non-aromatic carbons of **1** were divided into two groups on the basis of their signal multiplicities from the distortionless enhancement by polarization transfer (DEPT) experiment, which showed triplets at δ 33.62, 65.32, and 67.90 and doublets at δ 40.02, 45.47, and 48.33. Among them, the signal at δ 33.62 was assigned to C-4 and the methine signals at δ 40.02, 45.47, and 48.33 were assigned by comparison with the literature values reported for (+)-isolariciresinol (13). The signal at δ 48.33, which is practically unaffected by shielding effects, can be assigned to C-1. Carbon-2 (C-2), which suffered an α-effect by C-2α, and two β-effects by C-3α and by the benzene ring, should be deshielded in comparison to C-3 (13); these carbons were assigned to the signals at δ 45.47 and 40.02, respectively. These spectroscopic and chemical results led us to propose the structure of **1** as isolariciresinol rhamnopyranoside, to which we have accorded the trivial name, aviculin.

The ^{13}C-nmr spectral data of four flavonoid glycosides [**2–5**] isolated from the EtOAc-soluble fraction of *P. aviculare* are also summarized in Tables 2 and 3. Among them, astragalin [**4**] and betmidin [**5**] were isolated from this plant for the first time.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Si gel (230–400 mesh, Merck) was used for cc, and Si gel F_{254} (Merck) plates were used for tlc. [Solvent systems: A, $CHCl_3$-MeOH (7:1); B, $CHCl_3$-Me_2CO-MeOH-H_2O (15:8:2:0.5); C, $CHCl_3$-MeOH-H_2O (6:1:0.1)]. ^{1}H-Nmr spectra were determined on a Varian 300 MHz Gemini Ft-nmr. Standard Varian pulse programs were used for homonuclear COSY. ^{13}C-Nmr and DEPT spectra were obtained on the same instrument at 75.4 MHz. The heteronuclear chemical shift correlation (C,H-COSY) experiment was performed with a Bruker 500 MHz. All nmr spectra were referenced to residual solvent as an internal standard: for CD_3OD, 3.33 ppm for ^{1}H, and 49.0 ppm for ^{13}C, and for $CDCl_3$, 7.26 ppm for ^{1}H. Mps were determined on an Electrothermal apparatus and are uncorrected. Optical

TABLE 2. ^{1}H-Nmr Data (in δ ppm) for Compounds **2–5**.[a]

Proton	Compound			
	2	**3**	**4**	**5**
H-6	6.17 d (1.8)	6.19 d (1.8)	6.18 d (1.8)	6.19 d (2.0)
H-8	6.36 d (1.5)	6.37 s	6.38 d (2.1)	6.37 d (1.8)
H-2′	7.92 d (8.7)	7.52 d (2.1)	8.05 d (9.0)	7.12 s
H-3′	6.89 d (9.0)	—	6.87 dd (2.1, 8.7)	—
H-5′	6.89 d (9.0)	6.89 d (8.4)	6.87 dd (2.1, 8.7)	—
H-6′	7.92 d (8.7)	7.48 dd (1.6, 8.4)	8.04 d (9.0)	7.12 s
H-1″	5.46 s	5.46 s	5.23 d (7.5)	5.45 s
H-2″	4.30 d (3.0)	4.33 d (2.7)	3.40 dd (7.2, 10.0)	4.34 s
H-3″	3.89 dd (3.0, 5.1)	3.89 dd (2.7, 4.8)	3.25–3.40 m	3.91 d (1.2)
H-4″	3.79 dd (4.2, 8.9)	3.80 dd (4.8, 9.6)	3.25–3.40 m	3.91 d (1.2)
H-5″	3.47 d (4.0)	3.30 dd (3.3, 1.5)	3.20 ddd (2.1, 5.1, 7.5)	3.51 d (1.2)
H-6″	—	—	3.50 dd (5.4, 11.7) 3.71 dd (2.1, 11.7)	—

[a]Data recorded in CD_3OD. Figures in parentheses are *J* values in Hz. The assignments were made by COSY.

TABLE 3. ^{13}C-Nmr Data for Flavonoids **2–5** (in CD_3OD, δ in ppm).

C	Compound							
	2	**3**	**4**	**5**	kaempferol[a]	quercetin[a]	Methyl-α-L-ara[b]	Methyl-β-D-glc[c]
2	158.5	159.3	158.6	158.6	146.8	146.9		
3	134.9	134.9	135.4	134.9	135.6	135.6		
4	179.8	179.9	179.4	180.0	175.9	175.7		
5	163.0	163.0	163.0	163.0	160.7	160.7		
6	99.9	99.9	100.2	100.0	98.2	98.2		
7	166.1	166.1	166.9	166.4	163.9	163.9		
8	94.8	94.8	95.1	94.9	93.5	93.4		
9	159.3	158.5	158.9	159.3	156.2	156.2		
10	105.6	105.6	105.5	104.9	103.1	103.0		
1′	122.8	122.9	122.8	122.1	121.7	122.0		
2′	131.9	116.8	132.3	109.5	129.5	115.3		
3′	116.5	146.3	116.0	146.8	115.4	145.0		
4′	161.5	149.8	161.5	138.0	159.2	147.6		
5′	116.5	116.4	116.0	146.9	115.4	115.6		
6′	131.9	123.1	132.3	109.5	129.5	120.0		
1″	109.6	109.5	104.2	109.4			109.2	105.4
2″	83.3	83.3	75.7	83.3			81.8	74.8
3″	78.6	78.7	78.4	78.9			77.5	78.1
4″	87.9	87.9	71.3	88.1			84.9	71.4
5″	62.5	62.5	78.0	62.6			62.4	78.1
6″			62.6					62.5

[a]Data taken from Markham *et al.* (18).
[b]Data taken from You *et al.* (19).
[c]Data taken from Seo *et al.* (17).

rotations were measured in a 3.5 mm×100 mm cell on a Jasco DIP-360 polarimeter, and cd data were obtained with a J-600 spectropolarimeter (Jasco). The ir spectra were performed on a Mattson Polakis (Mattson Instruments, Inc.), and eims were determined using a Hewlett-Packard 5890 GC/5988 mass spectrometer at 70 eV.

PLANT MATERIAL.—The whole plants of *P. aviculare* were collected in July 1991, in Taejon, Korea. Voucher specimens (No. 218-8) are deposited in the herbarium of the Korea Institute of Science and Technology.

EXTRACTION AND ISOLATION.—The fresh plants (840 g) were cut into small pieces and percolated three times with 70% MeOH at room temperature to yield 140 g of a dark green residue on removal of solvent under reduced pressure. The 70% MeOH extract was diluted with H_2O and extracted with Et_2O to remove unnecessary lipids. The H_2O solution was extracted with EtOAc followed by *n*-BuOH. The combined EtOAc layer was evaporated under reduced pressure to yield 5.4 g of a residue. This residue (5 g) was divided into ten fractions by cc on Si gel (solvent systems A→B). Fraction 3 was rechromatographed twice on Si gel to afford juglanin [**2**] and avicularin [**3**]. Fraction 5 was further fractionated by chromatography on Sephadex LH-20 with MeOH to give 9 fractions. Fraction 5b was further purified by chromatography on Si gel (solvent system C) to afford aviculin [**1**]. Fraction 5c was purified further by prep. RP-18 tlc (Kieselgel F_{254}S, 0.25 mm, 20×20 cm) using MeOH-H_2O (6:4) to afford astragalin [**4**]. Fraction 6 was further fractionated by cc on Sephadex LH-20 with MeOH to give 8 fractions. Fraction 6e was further purified by cc on Si gel (solvent system C) to give betmidin [**5**].

Aviculin [**1**].—Amorphous powder: mp 155–157°, $[\alpha]^{25}D$ +20.27° (*c*=0.074, MeOH); ir ν max (KBr) 3449, 2920, 1598, 1513, 1449, 1381, 1285, 1254, 1128, 1075 cm^{-1}; ^{1}H nmr (300 MHz, CD_3OD) δ 1.18 (3H, d, *J*=6.0 Hz, H-6″), 1.86 (1H, br t, *J*=10.2 Hz, H-2), 2.02 (1H, m, H-3), 2.83 (2H, d, *J*=7.8 Hz, H-4), 3.10 (1H, m, H_a-2α), 3.34 (1H, t, *J*=9.0 Hz, H-4″), 3.51 (1H, dq, *J*=9.0 and 6.0 Hz, H-5″), 3.62–3.63 (1H, H_a-3α, overlapping with H-3″), 3.63 (1H, dd, *J*=9.3 and 3.3 Hz, H-3″), 3.71 (1H, dd, *J*=11.0 and 3.7 Hz, H_b-3α), 3.77 (3H, s, OMe), 3.81 (3H, s, OMe), 3.80–3.82 (1H, H_b-2α, overlapping with OMe), 3.84 (1H, dd, *J*=3.4 and 1.6 Hz, H-2″), 3.85 (1H, d, *J*=10.4 Hz, H-1), 4.51 (1H, d, *J*=1.5 Hz, H-1″), 6.16 (1H, s, H-8), 6.59 (1H, dd, *J*=7.9 and 1.8 Hz, H-6′), 6.63 (1H, d, *J*=1.8 Hz, H-2′), 6.66 (1H, s, H-

5), 6.75 (1H, J=7.9 Hz, H-5′); ^{13}C nmr, see Table 1; eims *m/z* [M]$^+$ 506 (4), 359 (46), 341 (100), 311 (39), 279 (37), 189 (13), 175 (21), 137 (73).

ACID HYDROLYSIS OF **1**.—A solution of aviculin [**1**] (2.6 mg) in 2N HCl (2 ml) was heated at 90° for 2 h. The reaction mixture was diluted with H_2O (2 ml) and extracted with EtOAc (3×3 ml). The combined organic layers were evaporated to dryness. The residue was purified by prep. tlc [Kieselgel F_{254}, 1 mm, 20×20 cm, using $CHCl_3$-MeOH (7:1)] to afford isolariciresinol [**1b**] (R_f=0.43): [α]^{25}D +63.8° (c=0.000047, Me_2CO); eims (70 eV) *m/z* [M]$^+$ 360 (51), 311 (50), 284 (18), 255 (19), 241 (24), 211 (8), 187 (24), 175 (50), 137 (63), 91 (100), 55 (90). The aqueous layer was neutralized with KOH and extracted with *n*-BuOH (3×3 ml). The organic layer was washed with H_2O and evaporated to dryness, and L-rhamnose in the residue was identified by co-tlc with an authentic sample [$CHCl_3$-MeOH-H_2O (6:4:1)].

ACETYLATION OF **1**.—Treatment of **1** (3 mg) with freshly distilled Ac_2O (0.2 ml) and dry pyridine (0.2 ml) afforded **1a**, after stirring at 25° for 12–14 h. The reaction mixture was diluted with H_2O and extracted with EtOAc (3×3 ml). The combined organic layer was washed with saturated aqueous NaCl and dried with anhydrous Na_2SO_4. The crude product was purified by cc on Si gel to afford 4 mg of **1a**: oily compound; ir ν max (KBr) 2957, 2922, 2852, 1745, 1508, 1462, 1389, 1221, 1151, 1084, 1049, 910 cm^{-1}; ^{1}H nmr ($CDCl_3$, 300 MHz) δ 1.16 (3H, d, J=6.1 Hz, H-6″), 1.8–2.1 (2H, H-2 and H-3, overlapping with OAc), 1.99 (3H, s, OAc), 2.05 (3H, s, OAc), 2.09 (3H, s, OAc), 2.15 (3H, s, OAc), 2.23 (3H, s, OAc), 2.31 (3H, s, OAc), 2.93 (2H, d, J=7.7 Hz, H-4), 3.18 (1H, dd, J=2.8 and 9.9 Hz, H_a-2α), 3.6–3.7 (1H, m, H-5″, overlapping with OMe), 3.77 (3H, s, OMe), 3.81 (3H, s, OMe), 3.8–3.9 (1H, H_b-2α, overlapping with OMe), 4.06 (1H, d, J=10.9 Hz, H-1), 4.17 (1H, dd, J=6.0 and 11.2 Hz, H_a-3α), 4.29 (1H, dd, J=3.4 and 11.0 Hz, H_b-3α), 4.59 (1H, br s, H-1″), 5.05 (1H, dd, J=9.5 Hz, H-4″), 5.21–5.26 (2H, m, H-2″ and H-3″), 6.40 (1H, s, H-8), 6.71–6.74 (3H, m, H-2′, H-5, and H-6′), 6.98 (1H, d, J=8.4 Hz, H-5′); ^{13}C nmr, see Table 1.

Kaempferol-3-O-α-L-*arabinofuranoside (juglanin)* [**2**].—Mp 220–222°; [α]^{25}D −142° (c=0.00047, MeOH) [lit. (20), mp 223–225°; lit. (21), [α]^{20}D −127° (c=0.5, MeOH)]; ir ν max (KBr) 3300, 1654, 1608, 1506, 1100–1200 cm^{-1}; eims *m/z* [M−ara]$^+$ 286 (100), 229, 184, 148, 121 (28), 93 (10); ^{1}H nmr, see Table 2; ^{13}C nmr, see Table 3.

Quercetin-3-O-α-L-*arabinofuranoside (avicularin)* [**3**].—Mp 178°; [α]^{25}D −152° (c=0.00125, MeOH) [lit. (20), mp 213–214°; lit. (21), [α]^{20}D −109.7° (c=0.31, MeOH)]; ir ν max (KBr) 3300, 1656, 1606, 1571, 1509, 1446, 1362, 1240, 1168, 1088, 1004 cm^{-1}; eims *m/z* [M−ara]$^+$ 302 (100), 273, 245, 153 (11), 137 (17); ^{1}H nmr, see Table 2; ^{13}C nmr, see Table 3.

ACETYLATION OF **3**.—Compound **3** (8 mg) was acetylated with 2 ml of Ac_2O-pyridine (3:2) for 4 h at room temperature to afford **3a**: ir ν max (KBr) 2943, 1778, 1745, 1645, 1435, 1371, 1211 cm^{-1}; ^{1}H nmr ($CDCl_3$) δ 2.02 (3H, s, OAc), 2.09 (3H, s, OAc), 2.12 (3H, s, OAc), 2.32 (3H, s, OAc), 2.33 (3H, s, OAc), 2.35 (3H, s, OAc), 2.44 (3H, s, OAc), 3.73 (1H, m, H-4″), 3.98 (1H, dd, J=12.0 and 5.1 Hz, H_a-5″), 4.18 (1H, dd, J=12.0 and 3.3 Hz, H_b-5″), 4.97 (1H, dd, J=5.4 and 1.8 Hz, H-3″), 5.47 (1H, d, J=1.8 Hz, H-2″), 5.79 (1H, s, H-1″), 6.85 (1H, d, J=2.1 Hz, H-6), 7.29 (1H, d, J=2.1 Hz, H-8), 7.34 (1H, d, J=8.7 Hz, H-5′), 7.85 (1H, d, J=1.8 Hz, H-2′), 7.86 (1H, dd, J=8.7 and 1.8 Hz, H-6′).

Kaempferol-3-O-β-D-*glucopyranoside (astragalin)* [**4**].—Mp 231–233° [lit. (21), mp 175–178°]; ir ν max (KBr) 3406, 1745, 1654, 1608, 1498, 1362, 1209, 1179, 1073 cm^{-1}; eims *m/z* [M−glc]$^+$ 286 (100), 229 (11), 184, 153 (7), 121 (26); ^{1}H nmr, see Table 2; ^{13}C nmr, see Table 3.

Myricetin-3-O-α-L-*arabinofuranoside (betmidin)* [**5**].—Mp 158–160° [lit. (5), mp 240–242°]; [α]^{25}D −134° (c=0.00076, MeOH); ir ν max (KBr) 3400, 1653, 1608, 1506, 1354, 1308, 1200, 1024 cm^{-1}; eims *m/z* [M−ara]$^+$ 318 (100), 289 (9), 216, 166, 153 (41), 114 (34), 73 (48), 57 (76); ^{1}H nmr, see Table 2; ^{13}C nmr, see Table 3.

ACETYLATION OF **5**.—Compound **5** (10 mg) was acetylated with 2 ml of Ac_2O-pyridine (3:2) for 4 h at room temperature to afford **5a**: ir ν max (KBr) 2945, 1778, 1747, 1653, 1371, 1188, 1057 cm^{-1}; ^{1}H nmr ($CDCl_3$) δ 2.04 (3H, s, OAc), 2.09 (3H, s, OAc), 2.13 (3H, s, OAc), 2.32 (3H, s, OAc), 2.33 (3H, s, OAc), 2.36 (3H, s, OAc), 2.45 (3H, s, OAc), 3.91 (1H, d, J=3.3 Hz, H-4″), 4.05 (1H, dd, J=12.6 and 4.8 Hz, H_a-5″), 4.20 (1H, dd, J=12.0 and 3.0 Hz, H_b-5″), 5.00 (1H, dd, J=5.7 and 1.8 Hz, H-3″), 5.51 (1H, br s, H-2″), 5.79 (1H, s, H-1″), 6.86 (1H, d, J=2.1 Hz, H-6), 7.32 (1H, d, J=2.1 Hz, H-8), 7.73 (2H, s, H-2′ and H-6′).

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