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NEW SECOIRIDOID DILACTONES FROM *FRAXINUS UHDEI*

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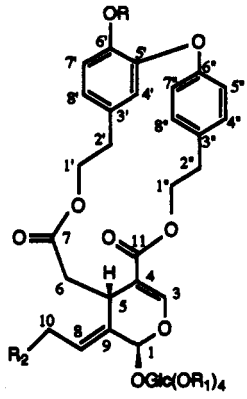
ABSTRACT.—Two new compounds, uhdosides A [**1**] and B [**4**], were isolated from the leaves of *Fraxinus uhdei* (Oleaceace). These cyclic dilactones of 5′-*O*-phenethyoxyl-6′-hydroxy-phenethoxyl secoiridoid glucosides were accompanied by the known phenylpropanoid glycoside verbascoside. The structures of these compounds have been elucidated on the basis of chemical methods and extensive 2D nmr analyses.

In recent papers (1–3) we reported the separation and structural elucidation of eight new secoiridoids from *Jasminum multiflorum* (Oleaceae). Some of them, such as multifloroside and jasmolactone D, showed potent coronary vasodilating activities. As part of our studies on the constituents of Oleaceous plants we have undertaken the phytochemical investigation of *Fraxinus uhdei* (Wenzig) Lingelsh. This ash with large opposite, feather-like, compound leaves of 7,9, or 11 leaflets is a tree native to Central America. It grows as a timber tree and as an ornamental. The flowers of *F. uhdei* open in October in dense clusters of yellow color. Its narrow, fattened and winged fruits appearing in February are about 3 cm long and 0.4 cm wide. Although the use of this plant is not clear in folk medicine, its leaves have a bitter taste. We describe here the isolation and structure elucidation of two new secoiridoids, uhdosides A [**1**] and B [**4**], from this species. Both new compounds contain an unusual cyclic dilactone ring system of 5′-*O*-phenethoxyl-6′-hydroxyphenethoxyl secoiridoid glucosides.

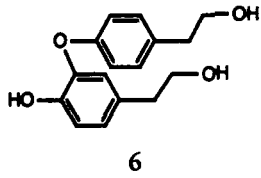
RESULTS AND DISCUSSION

The EtOH extract of fresh leaves of *F. uhdei* was fractionated on a charcoal column to yield secoiridoid glucosides. Further separation by a combination of LH-20, flash Si gel chromatography, and preparative tlc provided uhdoside A [**1**] (0.2%) and a minor compound, uhdoside B [**4**] (0.004%), as well as a major compound, verbascoside. The indentity of verbascoside was determined by spectral comparisons with an authentic sample (4).

Uhdoside A [**1**], $[\alpha]_D$ −72° (MeOH), was obtained as colorless crystals. The hr fabms spectrum of **1** showed the $[M+Na]^+$ ion at *m/z* 651.2054, consistent with a molecular formula of $C_{32}H_{36}O_{13}$, which was also supported by ^{13}C-nmr and DEPT data. The uv and ir spectra suggested the presence of a catecholic chromophore (273, 282 nm, 3400, 1618, 1565, 1508 cm^{-1}), the phenolic function of which was indicated by a bathochromic shift (282 nm to 300 nm) in base conditions. The ^1H-nmr spectrum of **1** (Table 1) displayed signals typical of a secoiridoid nucleus (5,6), including a hemiacetalic proton H-1 (δ 5.85), two vinylic protons, H-3 and H-8 (δ 7.53, 6.03), and ABX spin system consisting of H-6α, H-6β, and H-5 (δ 2.31, 2.15, and 3.78), and a methyl doublet H-10 (δ 1.60). An additional hemiacetalic proton at δ 4.78 was assignable to the anomeric proton of a β-D-glucopyranosyl moiety. The aromatic region revealed two spin patterns, A_2X_2 (δ 6.92, 7.18) and AMX (δ 6.51, 6.84, 6.75), suggesting the presence of a para-substituted phenolic and a catecholic ring. The relationships between protons in **1** were established by COSY and NOESY experiments. The complete assignment of the ^{13}C-nmr spectrum of **1** was performed on the basis of DEPT, HETCOR, and COLOC experiments. Two carbonyl resonances (δ 172.6, 167.9) were



1 R=R_1=R_2=H
2 R=R_1=Ac, R_2=H
3 R=Me, R_1=R_2=H
4 R=R_1=H, R_2=OH
5 R=R_1=Ac, R_2=OAc



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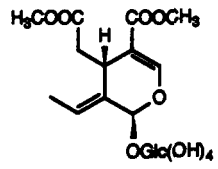

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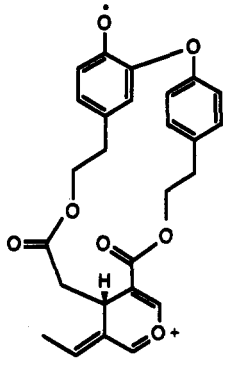
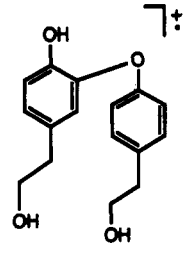
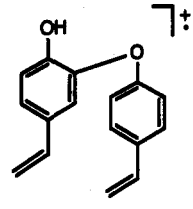


m/z 448 (4.5) from **1**
8



m/z 274 (2.4) from **1**
m/z 274 (43) from **4**
9



m/z 238 (100) from **1**
m/z 238 (9.1) from **4**
10

attributable to carbons at C-7 and C-11, respectively. Carbon signals at δ 155.3 (C-3), 109.6 (C-4), δ 125.1 (C-8), 129.9 (C-9), as well as the methyl carbon at δ 13.7 (C-10), indicated an oleoside-type secoiridoid nucleus (7,8) for compound **1**. In support of these structural features the eims spectrum of **1** exhibited base peak at *m/z* 238 (**10**) and an ion at *m/z* 274 (**9**), both indicating fragments from aromatic side chains, and the ion at *m/z* 448 (**8**), the fragment representing loss of a glucosyl moiety from the molecular ion.

Upon acetylation, compound **1** provided a pentaacetate **2**, the ^{1}H-nmr spectrum of which showed an aromatic acetyl singlet and four aliphatic acetyl singlets. As expected, the eims spectrum exhibited a significant peak at *m/z* 331, indicating a glucose tetraacetate fragment. Methylation of **1** yielded a monomethyl ether **3**, which showed an aromatic methoxyl singlet at δ 3.85. Irradiation of this methoxyl singlet significantly enhanced the signal intensity of H-7′ (9%) by nOe difference study. This located the methoxyl group at the C-6′ position in **3** and, in turn, implied a 5′-*O*-phenethoxyl-6′-hydroxyphenethoxyl moiety in **1**. The two partial structures, **A** and **B** (Figure 1), could account for 14 of the 15 unsaturations. Consequently, one more ring would be required, that leads to two alternative dilactone structures, **1** and **C**, for uhdoside A (Figure 1).

TABLE 1. ^{1}H nmr Spectral Data[a] (500 MHz, CD_3OD) for Compounds **1**, **3**, and **4**.

Proton	Compound		
	1	**3**	**4**
H-1	5.85 br s	5.85 br s	5.89 br s
H-3	7.53 s	7.53 s	7.54 s
H-5	3.78 dd (11, 3.7)	3.78 dd (11, 4.0)	3.78 dd (10, 4.5)
H-6α	2.31 dd (15, 3.7)	2.29 dd (15, 4.0)	2.27 dd (15, 3.6)
H-6β	2.15 dd (15, 11)	2.15 dd (15, 11)	2.22 dd (15, 10)
H-8	6.03 q (7.1)	6.04 q (7.0)	6.10 t (6.0)
H-10	1.60 d (7.1)	1.61 d (7.0)	4.24 dd (13.5, 7.6) 4.10 ddd (13.5, 7.6, 1.5)
H_a-1′	4.25 m	4.26 m	4.35 m
H_b-1′	3.99 m	4.03 m	3.96 m
H-2′	2.74 br t (5.2)	2.77 br t (5.5)	2.74 br t (4.8)
H-4′	6.51 d (2.0)	6.56 d (2.0)	6.51 d (1.8)
H-7′	6.84 d (8.1)	7.00 d (8.5)	6.85 d (8.2)
H-8′	6.75 dd (8.1, 2.0)	6.87 dd (8.5, 2.0)	6.76 dd (8.2, 1.8)
H_a-1″	4.48 m	4.49 m	4.48 t (6.0)
H_b-1″	4.48 m	4.49 m	4.48 t (6.0)
H_a-2″	2.99 m	3.00 m	2.98 m
H_b-2″	2.91 m	2.91 m	2.91 m
H-4″,-8″	7.18 d (8.3)	7.19 d (8.5)	7.18 d (8.7)
H-5″,-7″	6.92 d (8.3)	6.88 d (8.5)	6.91 d (8.7)
Glc H-1‴	4.78 d (7.6)	4.76 d (8.0)	4.79 d (8.1)
OMe		3.85 s	

[a]δ in ppm (*J* in Hz); TMS as internal standard.

Alkaline hydrolysis of **1** yielded the compound **6** and the secoiridoid glucoside moiety, which was methylated with CH_2N_2 to furnish the known dimethyl ether **7** (3). HMBC experiments provided the crucial structural linkage between the pair of signals C-7 and H-1′, as well as C-11 and H-1″, unambiguously establishing structure **1** for uhdoside A. Additional proof for this structural assignment was provided by nOe experiments on **1** and **3** (Figure 2). The stereochemistry of **1** was simultaneously determined based on the results of hydrolysis of **1** and the fact that all natural secoiridoids contain a β-oriented proton at the C-5 position (9). The signal of H-5 was enhanced by irradiation of the methylene proton at δ 2.15, which is obviously designated as H-6β. This allows the assignment of the coupled signal at δ 2.31 to H-6α. The latter signal was enhanced by irradiation of H-1 at δ 5.85, which, in turn, requires α orientation for H-1. Enhancement of the H-5 signal by irradiation of the C-10 methyl protons indicated an E geometry for the double bond between C-8 and C-9. Also, the mutual enhancement between the signals of H-1 and H-1‴, and the enhancement of both H-5″ and H-7″ by irradiation of H-4′, reflect their close relationship in space.

Uhdoside B [**4**] was obtained as a white powder, $[\alpha]_D$ −80° (MeOH). A molecular formula of $C_{32}H_{36}O_{14}$ was established by a quasi-molecular ion $[M+Na]^+$ at *m/z* 667 in its fabms spectrum, and by ^{13}C-nmr and DEPT spectra. The uv absorptions (273, 280 nm) and the ir bands (3404, 1706, 1622, 1508 cm^{-1}) resembled those of **1**. The presence

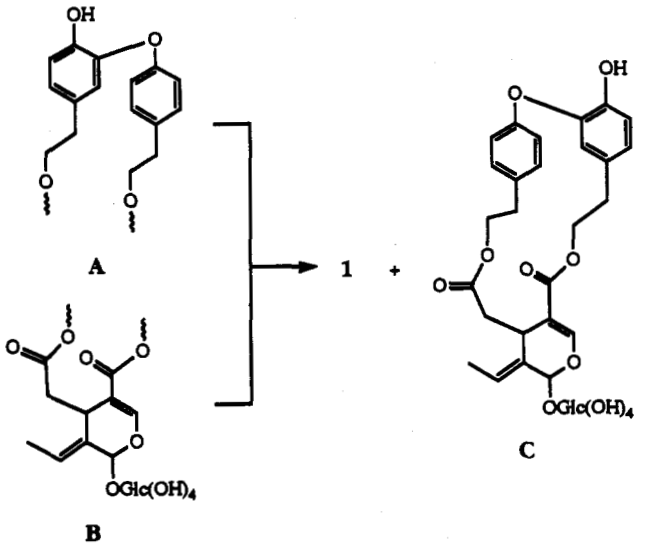


FIGURE 1. Two partial structures, **A** and **B**, and alternative structures, **1** and **C**, for uhdoside A.

of the symmetrical A_2X_2 pattern (δ 7.18, δ 6.91) and the AMX spin system (δ 6.51, δ 6.85, δ 6.76) as well as an olefinic proton at δ 7.54 (H-3) and a hemiacetalic proton at δ 5.89 (H-1) in the ^{1}H-nmr spectrum of **4** clearly suggested that it was an analogue of **1**. While no methyl doublet was observed, signals at δ 4.24 and δ 4.10 were attributable to a hydroxymethyl group. An additional olefinic proton (H-8) exhibited a triplet at δ 6.10 in **4** instead of a quartet as in **1**. The ^{13}C-nmr data of **4** were superimposable with those of **1** except for the signals of C-10 (59.3 t) and C-8 (129.6 d), indicating that C-10 was hydroxylated in compound **4**. Upon acetylation, **2** provided a hexaacetate **5**, which showed five aliphatic acetyl singlets and one aromatic acetyl singlet in the ^{1}H-nmr spectrum. Moreover, the C-10 methylene protons were downshifted from δ 4.24 and δ 4.10 to δ 4.79 and δ 4.70, respectively. Other correlations of **5** match very closely those of **2**. Comparison of specific rotation and

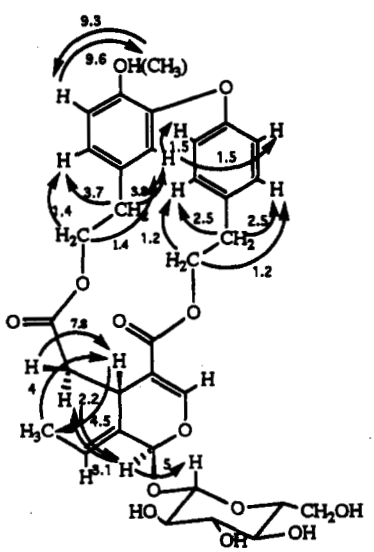


FIGURE 2. NOe studies of uhdoside A [**1**] and uhdoside A monomethylate [**3**].

TABLE 2. ^{13}C-nmr Spectral Data[a] (75 MHz) for Compounds **1** and **4**.

Carbon	Compound	
	1	**4**
C-1	95.1 d	94.5 d
C-3	155.3 d	155.2 d
C-4	109.6 s	109.5 s
C-5	31.3 d	31.8 d
C-6	40.8 t	40.6 t
C-7	172.6 s	172.5 s
C-8	125.1 d	129.6 d
C-9	129.9 s	130.3 s
C-10	13.7 q	59.3 t
C-11	167.9 s	167.7 s
C-1′	66.3 t	66.4 t
C-2′	34.7 t	34.6 t
C-3′	132.3 s	132.2 s
C-4′	119.9 d	120.1 d
C-5′	146.9 s	146.7 s
C-6′	147.5 s	147.7 s
C-7′	117.7 d	117.7 d
C-8′	124.9 d	125.0 d
C-1″	65.9 t	66.1 t
C-2″	35.8 t	35.7 t
C-3″	135.4 s	135.2 s
C-4″,-8″	131.5 d	131.4 d
C-5″,-7″	120.9 d	120.6 d
C-6″	157.3 s	157.5 s
C-1‴	100.9 d	100.9 d
C-2‴	74.7 d	74.7 d
C-3‴	77.8 d	77.9 d
C-4‴	71.4 d	71.4 d
C-5‴	78.2 d	78.3 d
C-6‴	62.6 t	62.7 t

[a]Multiplicities determined by DEPT; measured in CD_3OD.

coupling constants of **4** with those of **1** indicated identical stereochemistry for **1** and **4**. In conclusion, uhdosides A and B are similar in structure to jasminin from the genus *Jasminum* (10).

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Specific rotations were recorded on a Perkin-Elmer 141 polarimeter. The ir and uv spectra were measured on a Perkin-Elmer 1600 FTIR and Perkin -Elmer Lambda UV/VIS spectrophotometers, respectively. Eims were recorded on a Hewlett Packard 5890 GC/MS, and high resolution mass data were provided by the Midwest Center for Mass Spectrometry. The ^{1}H- and ^{13}C-nmr spectra were recorded on either Bruker 300MHz or Varian 500 MHz instruments. 2D experiments, COSY, NOESY, HETCOR, and COLOC, were performed by standard Bruker pulse sequences. The HMBC data were recorded on a Varian 500 MHz spectrometer optimized at 8 Hz.

EXTRACTION AND ISOLATION.—The plant material was collected in February 1989, in the Taipei Botanical Garden, Taipei, Taiwan. A voucher specimen was kept in the School of Pharmacy, National Taiwan University. Fresh leaves (1 kg) of *F. uhdei* were ground and extracted with EtOH. The combined EtOH extracts were concentrated to a green tar. After diluting with H_2O (200 ml), the resulting suspension was passed through a charcoal column (120 g) and washed, successively, with H_2O (1 liter), 5% EtOH (1 liter), 10% EtOH (1 liter), and EtOH (2 liters). The EtOH fraction was collected and reduced under vacuum to a secoiridoid-containing residue (35 g). Part of this residue (30 g) was applied on a LH-20 column (250 g) and eluted with MeOH to give a residue (15 g), which was flash chromatographed on a Si gel column (120

g) and eluted with the lower layer of the mixture $CHCl_3$/MeOH/H_2O by increasing polarity to give four fractions: A (1.34 g), B (1.02 g), C (3 g), and D (2.5 g). Uhdoside A [**1**] and verbascoside were obtained directly from fractions A and D, respectively, without further purification. Fraction C was rechromatographed on a LH-20 column and eluted with MeOH to give a residue (125 mg), which was purified by preparative tlc [Si gel, 1 mm thickness, lower layer of $CHCl_3$-MeOH-H_2O (65:35:10)] to furnish uhdoside B [**4**] (35 mg).

Uhdoside A [**1**].—Isolated as colorless crystals: $[\alpha]^{25}D$ −72° (*c*=1, MeOH); ir ν max (KBr) cm^{-1} 3400, 2920, 1707, 1618, 1565, 1508, 1415, 1290, 1225, 1162, 1075; uv λ max (MeOH) nm (log ε) 208 (4.49), 230 (4.25, sh), 273 (3.51), 282 (3.45, sh); ^1H nmr see Table 1; HMBC data (500 MHz, CD_3OD) [C-1, H-1‴], [C-3, H-1], [C-4, H-3], [C-5, H-6, H-8, H-3], [C-7, H-1′], [C-8, H-1, H-10], [C-9, H-6, H-10], [C-10, H-8], [C-11, H-3, H-1′], [C-3′, H-2′, H-4′, H-7′, H-8′], [C-4′, H-2′, H-8′], [C-5′, H-4′, H-7′], [C-6′, H-4′, H-8′], [C-8′, H-2′], [C-2″, H-4″, H-8″], [C-3″, H-1″, H-5″, H-7 ″], [C-6″, H-4″, H-5″, H-7″, H-8″], [C-1‴, H-1]; hr fabms $[M+Na]^+$ 651.2054 ($C_{32}H_{36}O_{13}$+Na calcd 651.2053); eims *m/z* (rel. int.) $[M-Glc]^+$ 466 (0.9), $[M-glc-H_2O]^+$ 448 (4.5), 389 (5.3), $[C_{16}H_{18}O_4]^+$ 274 (2.4), 256 (28), 239 (39), 238 (100), 225 (28), 107 (19).

Uhdoside A pentaacetate [**2**].—Acetylation [Ac_2O-pyridine (2:1); room temperature] of **1** (40 mg) gave, after workup and chromatography [preparative tlc; Si gel, 1 mm, toluene-EtOAc (4:1)], **2** (34 mg) as a solid: $[\alpha]^{25}D$ −78° (*c*=0.22, $CHCl_3$); ^1H nmr δ (500 MHz, $CDCl_3$) 5.65 (1H, br s, H-1), 7.53 (1H, s, H-3), 3.76 (1H, dd, overlap H-5), 2.39 (1H, dd, *J*=15.6, 3.7 Hz, H-6α), 2.09 (1H, dd, overlap, H-6β), 5.97 (1H, q, *J*=6.7 Hz, H-8), 1.67 (3H, d, *J*=6.7 Hz, H-10), 4.28 (1H, m, H_a-1′), 4.00 (1H, m, H_b-1′), 2.80 (1H, br t, *J*=5.2 Hz, H-2′), 2.77 (1H, br t, *J*=5.5 Hz, H-2′), 6.53 (1H, d, *J*=1.6 Hz, H-4′), 7.03 (1H, d, *J*=8.1 Hz, H-7′), 6.83 (1H, dd, *J*=8.1, 1.6 Hz, H-8′), 4.35 (1H, m, H_a-1″), 4.64 (1H, m, H-1_b″), 3.07 (1H, m, H_a-2″), 2.89 (1H, m, H_b-2″), 7.16 (2H, d, *J*=8.4, Hz, H-4″, -8″), 7.00 (2H, d, *J*=8.4, H-5″ -7″), 5.02 (1H, d, *J*=7.9 Hz, H-1‴), 2.02, 2.03×2, 2.04 (12H, s, OAc), 2.31 (3H, s, OAc); ^{13}C nmr δ (75 MHz, $CDCl_3$) 93.58 (d, C-1), 153.66 (d, C-3), 108, 59 (s, C-4), 29.58 (d, C-5), 39.15 (t, C-6), 174.80 (s, C-7), 125.20 (d, C-8), 127.32 (s, C-9), 13.55 (q, C-10), 166.20 (s, C-11), 64.43 (t, C-1′), 33.81 (t, C-2′), 139.26 (s, C-3′), 118.34 (d, C-4′), 150.10 (s, C-5′), 134.60 (s, C-6′), 123.05 (d, C-7′), 122.98 (d, C-8′), 64.90 (t, C-1″), 34.52 (t, C-2″), 137.78 (s, C-3″), 130.34×2 (d, C-4″,-8″), 120.76×2 (d, C-5″,-7″), 154.83 (s, C-6″), 96.99 (d, C-1‴), 70.61 (d, C-2‴), 72.44 (d, C-3‴), 68.20 (d, C-4‴), 72.11 (d, C-5‴), 61.70 (t, C-6‴), 20.58×5(q, Ac), 169.11, 169.34, 170.09, 170.53×2(s, Ac); eims *m/z* (rel. int.) $[M-glc(Ac)_4-H_2O]^+$ 491 (2.1), $[491-Ac]^+$ 449 (6.1), $[glc(Ac)_4]^+$ 331 (38), 238 (20), 239 (25), 169 (100).

Uhdoside A monomethylate [**3**].—Uhdoside A [**1**] (5 mg) was treated with an excess of CH_2N_2 and allowed to react overnight at 0–5°. The reaction mixture was reduced under vacuum and purified by preparative tlc (Si gel, 0.25 mm) to give **3** (3 mg): ^1H nmr see Table 1; eims *m/z* (rel. int.) $[M-162]^+$ 480 (5.1), 288 (7.6), 270 (16), 252 (100); nOe difference data (%) 6′-OMe to H-7′ (9.3), H-7′ to 6′-OMe (9.6).

Alkaline hydrolysis of uhdoside A [**1**].—Hydrolysis (0.5M NaOH, 10 ml; room temperature) of **1** (100 mg) provided, after workup as described in previous papers (2,3), compound **6** and a secoiridoid glucoside. The latter was further methylated with CH_2N_2/Et_2O to give **7**, identical (^1H nmr, [α], ir, and tlc) with oleoside 7,11-dimethyl ester (3). Compound **6**: uv λ max (MeOH) nm (log ε) 275 (3.54), 282 (3.48, sh); ^1H nmr δ (CD_3OD, 300 MHz) 3.64 (2H, t, *J*=7.0 Hz, H-1′), 2.67 (2H, t, *J*=7.0 Hz, H-2′), 6.73 (1H, d, *J*=1.8 Hz, H-4′), 6.84 (1H, d, *J*=8.0 Hz, H-7′), 6.87 (1H, dd, *J*=8.0, 1.8 Hz, H-8′), 3.73 (2H, t, *J*=7.0 Hz, H-1″), 2.78 (2H, t, *J*=7.0 Hz, H-2″), 7.17 (2H, d, *J*=8.5 Hz, H-4″, 8″), 6.85 (2H, d, *J*=8.5 Hz, H-5″, 7″).

Uhdoside B [**4**].—Isolated as a white powder: $[\alpha]^{25}D$ −80° (*c*=0.28, MeOH) ir ν max (neat) cm^{-1} 3404, 2916, 1706, 1622, 1508, 1294, 1222, 1166, 1074; uv λ max (MeOH) nm (log ε) 210 (4.50), 2.73 (3.62), 281 (3.50, sh); ^1H nmr see Table 1; ^{13}C nmr see Table 2; fabms $[C_{32}H_{36}O_{14}+Na]^+$ 667, $[C_{32}H_{36}O_{14}+1]^+$ 645; eims *m/z* (rel. int.) $[M-glc-H_2O]^+$ 464 (0.2), 420 (9.0), $[C_{16}H_{18}O_4]^+$ 274 (43), 257 (20), 256 (18), 243 (96), 238 (9.1), 225 (62), 165 (28), 107 (75).

Uhdoside B hexaacetate [**5**].—Acetylation [Ac_2O-pyridine (2:1); room temperature] of **2** (12 mg) gave, after workup and chromatography [preparative tlc; Si gel, 1 mm, toluene-EtOAc (4:1)], **5** (10 mg) as a solid: $[\alpha]^{25}D$ −57° (*c*=0.26, $CHCl_3$); ^1H nmr δ (300 MHz, $CDCl_3$) 5.66 (1H, br s, H-1), 7.53 (1H, s, H-3), 3.78 (1H, dd, *J*=10.5, 3.6 Hz, H-5), 2.39 (1H, dd, *J*=16.2, 3.6 Hz, H-6α), 2.10 (1H, dd, overlap, H-6β), 5.97 (1H, q, *J*=6.3 Hz, H-8), 4.78 (1H, d, *J*=13.5, 7.2 Hz, H-10), 4.70 (1H, d, *J*=13.5, 4.8 Hz, H-10), 4.29 (1H, m, H-1′), 3.97 (1H, m, H-1′), 2.81 (2H, br t, *J*=5.1 Hz, H_a-2′, H_b-2′), 6.51 (1H, d, *J*=1.8 Hz, H-4′), 7.03 (1H, d, *J*=8.2 Hz, H-7′), 6.84 (1H, dd, *J*=8.2, 1.8 Hz, H-8′), 4.33 (1H, m, H_a-1″), 4.68 (1H, m, H_b-1″), 3.08 (1H, m, H_a-2″), 2.89 (1H, m, H_b-2″), 7.15 (2H, d, *J*=8.4, Hz, H-4″, -8″), 6.99 (2H, d, *J*=8.4, H-5″ -7″), 5.02 (2H, d, *J*=7.8 Hz, H-1‴), 2.02, 2.03, 2.04×2, 2.06 (15H, s, OAc), 2.31 (3H, s, OAc); ^{13}C nmr δ (75 MHz, $CDCl_3$) 92.59 (d, C-1), 153.57 (d, C-3), 108.27 (s, C-4), 30.42 (d, C-5), 39.10 (t, C-6), 174.20 (s, C-7), 124.70 (d, C-8), 130.28 (s, C-9), 60.83 (t, C-10), 165.82 (s, C-11), 64.62 (t, C-

1′), 33.85 (t, C-2′), 139.36 (s, C-3′), 118.33 (d, C-4′), 150.07 (s, C-5′), 134.47 (s, C-6′), 123.13 (d, C-7′), 123.06 (d, C-8′), 65.14 (t, C-1″), 34.42 (t, C-2″), 137.74 (s, C-3″), 130.33×2 (d, C-4″,-8″), 120.71×2 (d, C-5″,-7″), 154.94 (s, C-6″), 96.94 (d, C-1‴), 70.64 (d, C-2‴), 72.42 (d, C-3‴), 68.13 (d, C-4‴), 72.24 (d, C-5‴), 61.64 (t, C-6‴), 20.55, 20.61×2, 20.87×3 (q, Ac), 170.68, 170.53, 170.24, 170.12, 169.35, 169.14 (s, Ac); eims *m/z* (rel. int.) $[M-1]^+$ 897 (0.1), $[M-Ac-1]^+$ 855 (0.1), $[M-HOAc]^+$ 838 (0.04), 549 (1.1), $[M-glc(Ac)_4-H_2O]^+$ 507 (4.8), $[glc(Ac)_4]^+$ 331 (19), 271 (6.3), 238 (8.8), 211 (5.4), 169 (100).

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