A New Lignan and Four New Lignan Glycosides from *Mananthes patentiflora*

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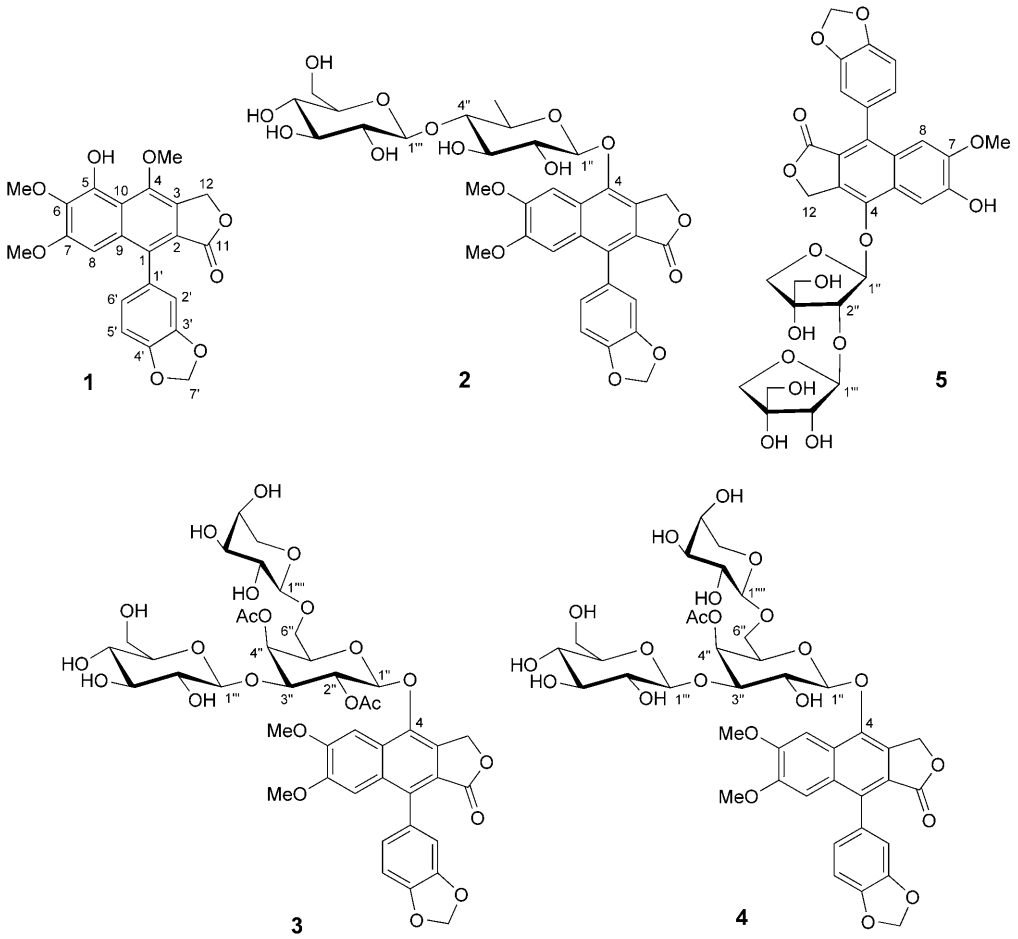
A new lignan, 5-hydroxyjusticidin A (=9-(1,3-benzodioxol-5-yl)-5-hydroxy-4,6,7-trimethoxynaphtho[2,3-*c*]furan-1(3*H*)-one; **1**), and four new diphyllin-type lignan glycosides, mananthosides C–F (**2**–**5**), containing glucosyl (Glc), arabinosyl (Ara), galactosyl (Gal), and/or apiosyl residues, have been isolated from *Mananthes patentiflora*, together with five known compounds. Their structures and configurations were elucidated by in-depth 1D- and 2D-NMR experiments, as well as MS analysis.

Introduction. – *Mananthes patentiflora* (HEMSL.) BREMEK. is a Chinese herb from which several lignans have been isolated [1]. In the search for cytotoxic constituents from this plant [1–3], a new arylnaphthalene lignan named 5-hydroxyljusticidin A (**1**), and four new lignan glycosides, mananthosides C–F (**2**–**5**), were isolated from the aerial parts of the plant, together with the five known compounds justicidin A [4][5], mananthoside A [1], mananthoside B [1], arabelline [6], and tuberculatin [7][8].

Results and Discussion. – Compound **1** was obtained as a yellow, amorphous powder, with the molecular formula $C_{22}H_{18}O_8$, as determined by positive-ion HR-ESI-MS (*m/z* 433.0907 ($[M+Na]^+$; calc. 433.0899)). The UV spectrum was typical for an arylnaphthalene system; and IR bands at 1764 and 934 cm^{-1} suggested the presence of a γ-lactone and a OCH_2O group, respectively [9]. In the ^{1}H-NMR spectrum of **1** (*Table 1*), there were four aromatic H-atoms: one signal appeared at δ(H) 6.67 (*s*, H–C(8))[1]), together with an *ABX* system characteristic of a 1,3,4-trisubstituted aromatic unit (δ(H) 6.95 (*d*, J=7.8, 1 H); 6.66 (*dd*, J=7.8, 1.5, 1 H); 6.77 (*d*, J=1.5, 1 H)).

In the HMBC spectrum (*Fig. 1*), correlations between CH_2(7′) at δ(H) 6.08/6.07 (2*s*) and C(3′) and C(4′) at δ(C) 148.4, and 148.2, resp., confirmed the presence of an OCH_2O moiety. The HMBC correlation between CH_2(12) at δ(H) 5.64 (*s*) and C(11) at δ(C) 169.2 confirmed the presence of a γ-lactone. In fact, both the ^{1}H- and the ^{13}C-NMR spectra of **1** (*Tables 1* and *2*, resp.) were very similar to those of justicidin A [4][5]. However, the lack of a signal at *ca.* δ(H) 7.5 (H–C(5)) suggested that C(5) was substituted in **1**. This was confirmed by a ROESY correlation between the 5-OH group at δ(H) 9.46 (*s*) and the 4-MeO moiety at δ(H) 4.28 (*s*).

[1]) Arbitrary atom numbering. For sytematic nams, see *Exper. Part.*



From the above data, in combination with further results from HSQC, HMBC, ^{1}H,^{1}H-COSY, and ROESY spectra, the structure of **1** was deduced as 5-hydroxyjusticidin A.

The molecular formula of compound **2** was determined as $C_{33}H_{36}O_{16}$ by negative-ion HR-ESI-MS (*m/z* 687.1911 ([*M* – H]$^-$; calc. 687.1925)). The UV spectrum was typical for an arylnaphthalene [9], and the IR spectrum showed OH (3426), γ-lactone (1747), and aromatic absorption bands (1623 cm^{-1}) [10][11]. The ^{1}H-NMR spectrum of **2** (*Table 1*) indicated five aromatic H-atoms[2]), two resonances at δ(H) 8.12 and 7.05, and an *ABX* system characteristic of a 1,3,4-trisubstituted unit (δ(H) 6.95 (*d*, *J* = 7.8); 6.77 (*dd*, *J* = 7.8, 1.5); 6.78 (*d*, *J* = 1.5)). Two γ-lactone CH_2 H-atoms at δ(H) 5.58, 5.45 (2*d*, *J* = 15.1 each) were non-equivalent, similar to those of arabelline [6].

[2]) Some ^{1}H-NMR signals of **2**–**5** were split due to atropisomerism.

Table 1. *^{1}H-NMR Data of* **1**–**5**. At 400 MHz and 25° in (D_6)acetone (for **1**) or in CD_3OD (for **2**–**5**); δ in ppm, J in Hz. Arbitrary atom numbering.

	1	**2**	**3**	**4**	**5**
H–C(5)		8.12/8.11 (*s*)[a])	7.55 (*s*)	8.14 (*s*)	7.68 (*s*)
H–C(8)	6.67 (*s*)	7.05 (*s*)	7.00/6.98 (*s*)[a])	7.00/6.97 (*s*)[a])	7.00/6.99 (*s*)[a])
CH_2(12)	5.64 (*s*)	5.58 (*d*, *J* = 15.1), 5.45 (*d*, *J* = 15.1)	5.72 (*d*, *J* = 15.1), 5.45 (*d*, *J* = 15.1)	5.74 (*d*, *J* = 15.4), 5.45 (*d*, *J* = 15.4)	5.49 (*d*, *J* = 14.8), 5.43 (*d*, *J* = 14.8)
H–C(2′)	6.77 (*d*, *J* = 1.5)	6.78 (*d*, *J* = 1.5)	6.75/6.74 (*d*, *J* = 1.5)[a])	6.80/6.71 (*s*)[a])	6.72 (*s*)
H–C(5′)	6.95 (*d*, *J* = 7.8)	6.95 (*d*, *J* = 7.8)	6.94/6.93 (*d*, *J* = 7.8)[a])	6.93 (*d*, *J* = 7.8)	6.92/6.90 (*d*, *J* = 7.5)[a])
H–C(6′)	6.66 (*dd*, *J* = 7.8, 1.5)	6.77 (*dd*, *J* = 7.8, 1.5)	6.74/6.72 (*dd*, *J* ≈ 7.7, 1.5)[a])	6.75 (*d*, *J* = 7.8)	6.69 (*d*, *J* = 7.5)
CH_2(7′)	6.08, 6.07 (2*s*)	6.05, 6.04 (2*s*)	6.04, 6.02 (2*s*)	6.04, 6.03 (2*s*)	6.04, 6.02 (2*s*)
4-MeO	4.28 (*s*)				
6-MeO	3.85 (*s*)	4.01 (*s*)	4.02 (*s*)	3.97 (*s*)	
7-MeO	3.69 (*s*)	3.72 (*s*)	3.69 (*s*)	3.69/3.67 (*s*)[a])	3.61 (*s*)
H–C(1″)		4.82 (*d*, *J* = 7.9)	5.33 (*d*, *J* = 5.0)	4.86 (*d*, *J* = 7.7)	5.61 (*d*, *J* = 2.4)
H–C(2″)		3.69 (*m*)	5.59 (*m*)	4.10 (*m*)	4.55 (*d*, *J* = 2.4)
H–C(3″)		3.57 (*m*)	4.21 (*m*)	3.89 (*m*)	
H–C(4″) or CH_2(4″)		3.33 (*m*)	5.61 (*m*)	5.52 (*m*)	4.28 (*d*, *J* = 12.0), 3.90 (*d*, *J* = 12.0)
H–C(5″)		3.47 (*m*)	4.19 (*m*)	3.94 (*m*)	3.77 (*s*)
H–C(6″) or CH_2(6″)		1.41 (*d*, *J* = 6.0)	3.87 (*dd*, *J* = 12.0, 2.3), 3.69 (*m*)	3.83 (*d*, *J* = 9.9), 3.66 (*dd*, *J* = 9.9, 2.8)	
2″-AcO			2.11 (*s*)		
4″-AcO			2.20 (*s*)	2.19 (*s*)	
H–C(1‴)		4.41 (*d*, *J* = 7.9)	4.42 (*d*, *J* = 7.8)	4.55 (*d*, *J* = 7.2)	5.30 (*d*, *J* = 3.6)
H–C(2‴)		3.22 (*m*)	3.12 (*m*)	3.23 (*m*)	4.10 (*d*, *J* = 3.6)
H–C(3‴)		3.36 (*m*)	3.30 (*m*)	3.37 (*m*)	
H–C(4‴) or CH_2(4‴)		3.29 (*m*)	3.23 (*m*)	3.25 (*m*)	4.15 (*d*, *J* = 12.0), 3.93 (*d*, *J* = 12.0)
H–C(5‴)		3.38 (*m*)	3.27 (*m*)	3.28 (*m*)	3.61 (*s*)
CH_2(6‴)		3.92 (*dd*, *J* = 11.9, 1.8), 3.67 (*d*, *J* = 11.9)	3.87 (*dd*, *J* = 12.0, 2.3), 3.63 (*dd*, *J* = 12.0, 6.0)	3.85 (*d*, *J* = 12.0), 3.61 (*dd*, *J* = 12.0, 5.5)	
H–C(1⁗)			4.19 (*d*, *J* = 6.9)	4.17 (*d*, *J* = 6.6)	
H–C(2⁗)			3.53 (*m*)	3.46 (*m*)	
H–C(3⁗)			3.41 (*m*)	3.42 (*m*)	
H–C(4⁗)			3.76 (*m*)	3.76 (*s*)	
CH_2(5⁗)			3.82 (*dd*, *J* = 12.4, 3.0), 3.47 (*d*, *J* = 12.4)	3.75 (*d*, *J* = 12.0), 3.43 (*d*, *J* = 12.0)	

[a]) Signal splitting due to atropisomerism (slow rotation about the glycosidic linkage to the aglycone). The aromatic H-atoms are, thus, exposed to two different environments, and the sugar H-atoms may either lie above or below the plane of the naphthalide ring system [6].

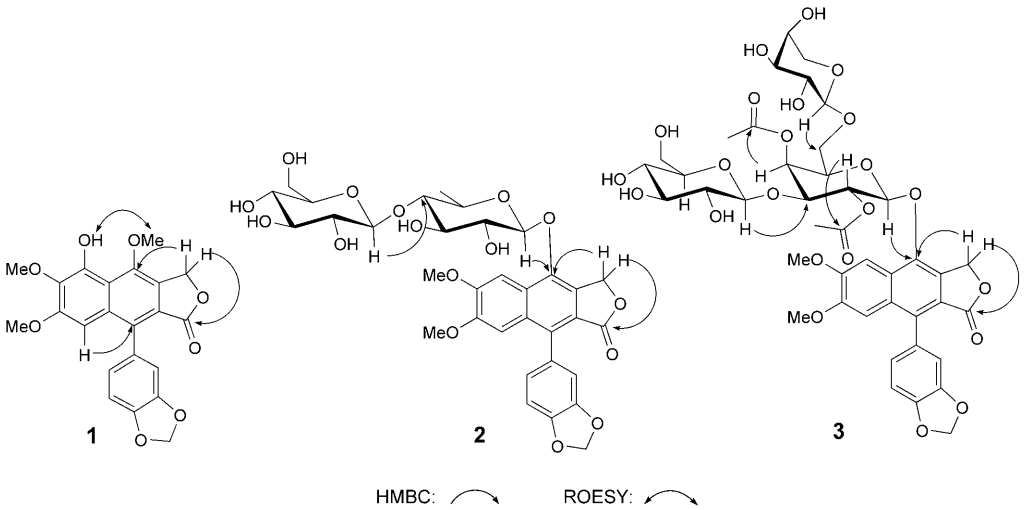


Fig. 1. *Key HMBC and ROESY correlations for* **1**–**3**

The ^{1}H- and ^{13}C-NMR data of **2** (*Tables 1* and *2*, resp.), and a FAB-MS signal at *m/z* 379 ($C_{21}H_{15}O_7$) suggested the presence of a diphyllin[3]) unit [1][7].

The ^{1}H-NMR spectrum of **2** also exhibited a series of sugar signals at δ(H) 3.20–3.93, with two anomeric H-atoms at δ(H) 4.82, 4.41 (2*d*, J=7.9 each). By means of HSQC, HMBC, and ^{1}H,^{1}H-COSY experiments, the signals at δ(C) 106.4, 75.4, 76.3, 86.4, 72.5, and 18.2 could be assigned to a 6-deoxyglucosyl moiety [12]. The second sugar unit was found to be a glucosyl (Glc) group, with signals at δ(C) 105.1, 75.1, 78.0, 71.5, 78.2, and 62.6 [13]. The 6-deoxyglucosyl moiety was linked to C(4) of the diphyllin, as inferred from an HMBC correlation between H–C(1″) at δ(H) 4.82 (*d*, J=7.9) and C(4) at δ(C) 146.4 (*Fig. 1*). The downfield shift of C(4″) suggested that the Glc residue was at C(4″) of the 6-deoxyglucose, which was supported by HMBC correlations between H–C(1‴) at δ(H) 4.41 (*d*, J=7.9) and C(4″) at δ(C) 86.4. Comparison of the ^{13}C-NMR data of the two sugar moieties with literature values revealed that they were both present in their pyranoside forms [12][13]. Their configurations at the anomeric centers were determined as β, based on coupling constants of 7.9 Hz each for H–C(1″) and H–C(1‴) [12][13].

From the above data, in combination with further results from HSQC, HMBC, and ^{1}H,^{1}H-COSY experiments, the structure of **2** was assigned as 4-*O*-(6-deoxy-4-*O*-β-D-glucopyranosyl-β-D-glucopyranosyl)diphyllin, and named *mananthoside C*.

The molecular formula of compound **3** was $C_{42}H_{48}O_{23}$, based on negative-ion HR-ESI-MS (*m/z* 919.2514 ([$M-H$]$^-$; calc. 919.2508)). The ^{1}H- and ^{13}C-NMR spectra of **3** (*Tables 1* and *2*) were similar to those of **2**, except for the sugar resonances.

The aglycone of **3** also corresponded to diphyllin [1][7]. Anomeric resonances at δ(H) 5.33 (*d*, J=5.0), 4.42 (*d*, J=7.8), and 4.19 (*d*, J=6.9), resp., suggested that **3** contained three sugar units. The ^{13}C-NMR signals at δ(C) 101.8, 72.3, 79.1, 72.3, 75.3, and 69.2 indicated a galactosyl (Gal) group [1][14], and those at δ(C) 106.2, 74.8, 78.1, 71.4, 78.0, 63.0, and at δ(C) 105.1, 72.4, 74.3, 69.5, 66.8,

[3]) Diphyllin = 9-(1,3-benzodioxol-5-yl)-4-hydroxy-6,7-dimethoxynaphtho[2,3-*c*]furan-1(3*H*)-one.

Table 2. *^{13}C-NMR Data of* **1**–**5**. At 125 MHz and 25° in (D_6)acetone (for **1**) or in CD_3OD (for **2**–**5**); δ in ppm. Arbitrary atom numbering.

	1	**2**	**3**	**4**	**5**
C(1)	135.4 (*s*)	137.7 (*s*)	136.6 (*s*)	137.6 (*s*)	137.1 (*s*)
C(2)	121.7 (*s*)	120.0 (*s*)	120.5 (*s*)	120.2 (*s*)	119.2 (*s*)
C(3)	125.2 (*s*)	132.2 (*s*)	127.1 (*s*)	132.3 (*s*)	129.7 (*s*)
C(4)	150.2 (*s*)	146.4 (*s*)	145.9 (*s*)	146.2 (*s*)	145.7 (*s*)
C(5)	147.8 (*s*)	102.8 (*d*)	101.9 (*d*)	102.9 (*d*)	105.9 (*d*)
C(6)	137.6 (*s*)	153.4 (*s*)	153.4 (*s*)	153.3 (*s*)	150.9 (*s*)
C(7)	154.7 (*s*)	151.8 (*s*)	151.8 (*s*)	151.7 (*s*)	150.9 (*s*)
C(8)	99.5 (*d*)	107.1 (*d*)	107.0 (*d*)	107.0 (*d*)	106.9 (*d*)
C(9)	133.7 (*s*)	128.9 (*s*)	127.1 (*s*)	128.9 (*s*)	131.4 (*s*)
C(10)	116.8 (*s*)	132.0 (*s*)	131.6 (*s*)	131.8 (*s*)	129.0 (*s*)
C(11)	169.2 (*s*)	172.1 (*s*)	172.1 (*s*)	172.4 (*s*)	172.2 (*s*)
C(12)	67.2 (*t*)	69.1 (*t*)	69.2 (*t*)	69.5 (*t*)	68.8 (*t*)
C(1′)	129.8 (*s*)	130.0 (*s*)	130.0 (*s*)	130.0 (*s*)	130.2 (*s*)
C(2′)	111.5 (*d*)	111.8 (*d*)	111.8 (*d*)	112.0/111.7 (*d*)[a])	111.8 (*d*)
C(3′)	148.4 (*s*)	149.0 (*s*)	148.9 (*s*)	148.9 (*s*)	148.9 (*s*)
C(4′)	148.2 (*s*)	149.0 (*s*)	148.9 (*s*)	148.9 (*s*)	148.9 (*s*)
C(5′)	108.7 (*d*)	109.0 (*d*)	109.0 (*d*)	109.0/108.9 (*d*)[a])	108.9 (*d*)
C(6′)	124.4 (*d*)	124.7 (*d*)	124.8 (*d*)	124.9/124.8 (*d*)[a])	124.7 (*d*)
C(7′)	102.1 (*t*)	102.6 (*t*)	102.6 (*t*)	102.6 (*t*)	102.5 (*t*)
4-MeO	61.5 (*q*)				
6-MeO	60.5 (*q*)	56.8 (*q*)	56.8 (*q*)	56.7 (*q*)	
7-MeO	55.8 (*q*)	56.1 (*q*)	56.0 (*q*)	56.0 (*q*)	56.0 (*q*)
C(1″)		106.4 (*d*)	101.8 (*d*)	106.5 (*d*)	111.3 (*d*)
C(2″)		75.4 (*d*)	72.3 (*d*)	72.0 (*d*)	85.3 (*d*)
C(3″)		76.3 (*d*)	79.1 (*d*)	82.4 (*d*)	81.1 (*s*)
C(4″)		86.4 (*d*)	72.3 (*d*)	72.3 (*d*)	75.9 (*t*)
C(5″)		72.5 (*d*)	75.3 (*d*)	74.6 (*d*)	65.0 (*t*)
C(6″)		18.2 (*q*)	69.2 (*t*)	69.5 (*t*)	
2″-AcO			21.4 (*q*)		
			172.1 (*s*)		
4″-AcO			20.9 (*q*)	21.0 (*q*)	
			172.6 (*s*)	173.0 (*s*)	
C(1‴)		105.1 (*d*)	106.2 (*d*)	105.8 (*d*)	111.6 (*d*)
C(2‴)		75.1 (*d*)	74.8 (*d*)	75.5 (*d*)	78.2 (*d*)
C(3‴)		78.0 (*d*)	78.1 (*d*)	77.8 (*d*)	80.5 (*s*)
C(4‴)		71.5 (*d*)	71.4 (*d*)	71.5 (*d*)	75.3 (*t*)
C(5‴)		78.2 (*d*)	78.0 (*d*)	78.1 (*d*)	65.2 (*t*)
C(6‴)		62.6 (*t*)	63.0 (*t*)	62.9 (*t*)	
C(1⁗)			105.1 (*d*)	104.9 (*d*)	
C(2⁗)			72.4 (*d*)	72.1 (*d*)	
C(3⁗)			74.3 (*d*)	74.1 (*d*)	
C(4⁗)			69.5 (*d*)	69.3 (*d*)	
C(5⁗)			66.8 (*t*)	66.5 (*t*)	

[a]) Signal splitting due to atropisomerism at 25°.

resp., were assigned to glucosyl (Glc) and arabinosyl (Ara) moieties [1][13]. The signals at δ(C) 172.1, 172.6, 21.4, and 20.9 suggested the presence of two AcO groups, which could be located at C(2″) and C(4″) of the Gal residue by HMBC correlations between H–C(2″) at δ(H) 5.59 (*m*) and δ(C) 172.1, and between H–C(4″) at δ(H) 5.61 (*m*) and δ(C) 172.6, respectively. Further HMBC correlations between H–C(1″) at δ(H) 5.33 (*d*, $J=5$) and C(4) at δ(C) 145.9 indicated that the Gal unit was linked to the 4-O-atom of diphyllin. Interglycosidic linkages of the (1 → 3) and (1 → 6) types were confirmed by HMBC correlations between H–C(1‴) at δ(H) 4.42 (*d*, $J=7.8$) of the Glc unit and C(3″) of Gal at δ(C) 79.1, and between H–C(1⁗) at δ(H) 4.19 (*d*, $J=6.9$) of the Ara unit and C(6″) of Gal at δ(C) 69.2. The coupling constants of the anomeric resonances, 5.0, 7.8, and 6.9 for H–C(1″), H–C(1‴), and H–C(1⁗), respectively, indicated the configurations of the Gal, Glc, and Ara residues as β, β, and α, respectively [1][13][14].

From the above data, compound **3** was identified as 4-*O*-{α-L-arabinopyranosyl-(1 → 6)-[β-D-glucopyranosyl-(1 → 3)]-2,4-di-*O*-acetyl-β-D-galactopyranosyl}diphyllin, and named *mananthoside D*.

The molecular formula of compound **4** was deduced as $C_{40}H_{46}O_{22}$, based on negative-ion HR-ESI-MS (*m/z* 877.2411 ($[M-H]^-$; calc. 877.2402). There were only minor differences between the spectroscopic data of **3** and **4**, the aglycone of **4** also being diphyllin.

By means of HSQC, HMBC (*Fig. 2*), and ^{1}H,^{1}H-COSY experiments, a Gal (δ(C) 106.5, 72.0, 82.4, 72.3, 74.6, 69.5), a Glc (δ(C) 105.8, 75.5, 77.8, 71.5, 78.1, 62.9), and an Ara moiety (δ(C) 104.9, 72.1, 74.1, 69.3, 66.5) were identified. The HMBC correlation between H–C(1″) at δ(H) 4.86 (*d*, $J=7.7$) and C(4) at δ(C) 146.2 revealed that Gal was linked at C(4) of the diphyllin aglycone. According to ^{13}C-NMR and HMBC data, there was only one AcO group at C(4″), as inferred from the correlation between H–C(4″) at δ(H) 5.52 (*m*) and δ(C) 173.0.

From the above data, compound **4** was identified as the mono-acetyl congener of **3**, and named *mananthoside E*.

From negative-ion HR-ESI-MS (*m/z* 629.1489 ($[M-H]^-$; calc. 629.1506)), the molecular formula of compound **5** was assigned as $C_{30}H_{30}O_{15}$. The UV and IR data

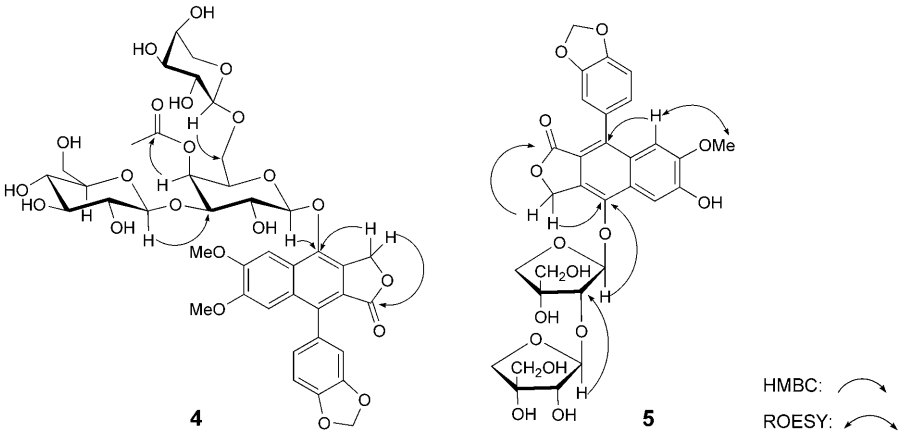


Fig. 2. *Key HMBC and ROESY correlations for* **4** *and* **5**

revealed the presence of an arylnaphthalene unit [9–11]. Compound **5** had to be similar to **4** by comparison of the ^{1}H- and ^{13}C-NMR data. However, there was only one MeO group in **5**.

The ROESY correlation between δ(H) 3.61 (*s*, MeO) and H–C(8) at δ(H) 7.00 (*s*) revealed that the MeO group was at C(7). The sugar moieties were identified as two apiofuranoses (=3-*C*-(hydroxymethyl)-β-D-erythrofuranoses), with resonances at δ(C) 111.3, 85.3, 81.1, 75.9, 65.0, and at 111.6, 78.2, 80.5, 75.3, 65.2, respectively [7][8]. The sugar moiety was linked at C(4) of diphyllin, based on HMBC correlations (*Fig. 2*) between H–C(1″) at δ(H) 5.61 (*d*, J=2.4) and C(4) at δ(C) 145.7. The downfield shift of C(2″) at δ(C) 85.3 suggested that the second apiose was linked at C(2″) [7], which was supported by the HMBC correlation between H–C(1‴) at δ(H) 5.30 (*d*, J=3.6) with C(2″) at δ(C) 85.3. The coupling constants of the anomeric H-atoms were 2.4 and 3.6 Hz, in accord with β-configuration [7][8].

From the above data, compound **5** was deduced as 4-*O*-{2-*O*-[3-*C*-(hydroxymethyl)-β-D-erythrofuranosyl]-3-*C*-(hydroxymethyl)-β-D-erythrofuranosyl}-6-*O*-demethyldiphyllin, and named *mananthoside F.*

Experimental Part

General. Column chromatography (CC): C_{18} reverse-phase silica gel (60 μm; *Merck*) and *Sephadex LH-20* (*Amershan Biosciences*). Melting points (m.p.): *Yuhua 104* melting-point apparatus; uncorrected. UV Spectra: *Shimadzu 210A* double-beam spectrophotometer; λ_{max} (log ε) in nm. Optical rotations: *Horiba SEPA-300* spectropolarimeter. IR Spectra: *Bio-Rad FTS-135* spectrophotometer, KBr pellets, in cm^{-1}. 1D- and 2D-NMR Spectra: *Bruker AM-400* and *DRX-500* spectrometers, resp.; δ in ppm, J in Hz. EI-MS, FAB-MS (neg.), and HR-ESI-MS: *VG Autospec-3000* spectrometer; in *m*/*z*.

Plant Material. The aerial parts of *Mananthes patentiflora* (HEMSL.) BREMEK. were collected in the *Xishuangbanna* district, Yunnan province, P. R. China, in August, 2004. The plant was identified by Prof. *Deding Tao*, and a voucher specimen (BN0408133) was deposited at the herbarium of the Kunming Institute of Botany, Yunnan, P. R. China

Extraction and Isolation. The EtOH extract of the air-dried aerial parts of *M. patentiflora* (6.9 kg) was suspended in H_2O (2.5 l), and extracted successively with AcOEt and BuOH. The AcOEt soln. was evaporated, and the residue (200 g) was purified by CC (2 kg SiO_2; petroleum ether/AcOEt mixtures of increasing polarity): eleven fractions (*Fr. 1–11*). *Fr. 5* (12 g) was subjected to repeated CC (SiO_2; petroleum ether/AcOEt 7:3) to afford **1** (15 mg) and justicidin A (1.39 g) [4][5]. *Fr.* 9 (15.2 g) was also purified by repeated CC (SiO_2; $CHCl_3$/MeOH 9:1) to provide **2** (7 mg), **5** (18 mg), mananthoside A (8 mg) [1], mananthoside B (10 mg) [1], and arabelline (15 mg) [6]. The above BuOH extract was evaporated, and the residue (7.0 g) was purified by CC (*D101*; H_2O/acetone): two fractions (*Fr. A* and *B*). *Fr. B* (1.8 g) was purified by repeated CC (1. SiO_2, $CHCl_3$/MeOH 8:2; 2. *RP-18*, MeOH/H_2O 6:4) to afford **3** (6 mg), **4** (13 mg), and tuberculatin (41 mg) [7][8]. The known compounds were identified by spectroscopic methods and by comparison with literature data.

5-Hydroxyjusticidin A (= *9-(1,3-Benzodioxol-5-yl)-5-hydroxy-4,6,7-trimethoxynaphtho[2,3-*c*]furan-1(3*H*)-one*; **1**). Yellow, amorphous powder. M.p. 211–213°. UV (MeOH): 203 (4.66), 268 (4.53), 310 (3.69), 370 (3.58). IR (KBr): 3346, 3281, 2925, 2854, 1764, 1633, 1594, 1504, 1477, 1458, 1439, 1391, 1365, 1263, 1250, 1205, 1154, 1107, 1056, 1033, 1001, 977, 934. ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. EI-MS: 410 (100, M^+), 365 (38), 335 (11), 305 (10), 190 (14). HR-ESI-MS (pos.): 433.0907 ([M+Na]$^+$, $C_{22}H_{18}NaO_8^+$; calc. 433.0899).

Mananthoside C (=*9-(1,3-Benzodioxol-5-yl)-4-[(6-deoxy-4-*O*-β-D-glucopyranosyl-β-D-glucopyranosyl)oxy]-6,7-dimethoxynaphtho[2,3-*c*]furan-1(3*H*)-one*; **2**). Colorless, amorphous powder. M.p. 181–183°. UV (MeOH): 205 (4.53), 261 (4.50), 290 (3.86), 314 (3.84), 384 (2.62). $[\alpha]_D^{26}$ = –13.7 (c=0.3, MeOH). IR (KBr): 3426, 2923, 1747, 1623, 1508, 1481, 1435, 1386, 1342, 1264, 1230, 1168, 1070, 1036, 770. ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. FAB-MS (neg.): 779 (4, [M+Gly–H]$^-$), 687 (23, [M–H]$^-$), 379 (100). HR-ESI-MS (neg.): 687.1911 ([M–H]$^-$, $C_{33}H_{35}O_{16}^-$; calc. 687.1925).

Mananthoside D (=*4-({α-*L*-Arabinopyranosyl-(1 → 6)-[β-*D*-glucopyranosyl-(1 → 3)]-2,4-di-*O*-acetyl-α-*D*-galactopyranosyl}oxy)-9-(1,3-benzodioxol-5-yl)-6,7-dimethoxynaphtho[2,3-*c*]furan-1(3*H*)-one*; **3**). Colorless, amorphous powder. M.p. 185–187°. UV (MeOH): 195 (4.41), 205 (4.42), 224 (4.40), 261 (4.63), 294 (3.98), 315 (3.99), 346 (3.66). $[\alpha]_D^{26} = -6.63$ ($c = 0.4$, MeOH). IR (KBr): 3440, 2924, 1744, 1624, 1507, 1480, 1435, 1371, 1349, 1263, 1229, 1169, 1073, 1037, 770. ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. FAB-MS (neg.): 920 (25, M^-), 379 (100). HR-ESI-MS (neg.): 919.2514 ($[M-H]^-$, $C_{42}H_{47}O_{23}^-$; calc. 919.2508).

Mananthoside E (=*4-({α-*L*-Arabinopyranosyl-(1 → 6)-[β-*D*-glucopyranosyl-(1 → 3)]-4-*O*-acetyl-α-*D*-galactopyranosyl}oxy)-9-(1,3-benzodioxol-5-yl)-6,7-dimethoxynaphtho[2,3-*c*]furan-1(3*H*)-one*; **4**). Colorless, amorphous powder. M.p. 186–187°. UV (MeOH): 205 (4.69), 261 (4.72), 315 (4.05). $[\alpha]_D^{26} = -2.72$ ($c = 0.5$, MeOH). IR (KBr): 3431, 2921, 1741, 1624, 1508, 1481, 1436, 1386, 1344, 1263, 1230, 1169, 1074, 1036, 770. ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. FAB-MS (neg.): 877 (31, $[M-H]^-$), 379 (100). HR-ESI-MS (neg.): 877.2411 ($[M-H]^-$, $C_{40}H_{45}O_{22}^-$; calc. 877.2402).

Mananthoside F (=*6-Hydroxy-4-({2-O-[3-C-(hydroxymethyl)-β-*D*-erythrofuranosyl]-3-C-(hydroxymethyl)-β-*D*-erythrofuranosyl}oxy)-7-methoxynaphtho[2,3-*c*]furan-1(3*H*)-one*; **5**). Colorless, amorphous powder. M.p. 158–160°. UV (MeOH): 203 (4.75), 224 (4.49), 263 (4.67), 290 (3.96), 323 (4.03). $[\alpha]_D^{24} = -111.1$ ($c = 0.74$, MeOH). IR (KBr): 3424, 2925, 2890, 1744, 1625, 1509, 1494, 1455, 1439, 1390, 1342, 1269, 1228, 1207, 1169, 1124, 1106, 1065, 1035, 1003, 960, 930. ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. FAB-MS (neg.): 629 (100, $[M-H]^-$), 364 (11). HR-ESI-MS (neg.): 629.1489 ($[M-H]^-$, $C_{30}H_{29}O_{15}^-$; calc. 629.1506).

REFERENCES

[1] B. Chen, Y. Liu, C. Feng, B. G. Li, G. L. Zhang, *Chin. Chem. Lett*. **2002**, *13*, 959.
[2] J. Asano, K. Chiba, M. Tada, T. Yoshii, *Phytochemistry* **1996**, *42*, 713.
[3] S. H. Day, Y. C. Lin, M. L. Tsai, L. T. Tsao, H. H. Ko, M. I. Chung, J. C. Lee, J. P. Wang, S. J. Won, C. N. Lin, *J. Nat. Prod.* **2002**, *65*, 379.
[4] N. Fukmiya, K. H. Lee, *J. Nat. Prod.* **1986**, *49*, 348.
[5] T. R. Govindachari, S. S. Sathe, N. Viswanathan, B. R. Pai, M. Srinivasan, *Tetrahedron Lett.* **1969**, *25*, 2815.
[6] Y. A. Abed, S. Sabri, M. A. Zarga, Z. Shah, Atta-ur-Rahman, *J. Nat. Prod.* **1990**, *53*, 1152.
[7] G. S. Nukul, M. H. Zarga, S. S. Sabri, D. M. Al-Eisawi, *J. Nat. Prod.* **1987**, *50*, 748.
[8] G. M. Sheriha, K. M. A. Amer, *Phytochemistry* **1984**, *23*, 151.
[9] A. C. Siani, M. D. G. B. Zoghbi, E. L. A. Wolter, I. Vencato, *J. Nat. Prod.* **1998**, *61*, 796.
[10] G. V. Subbaraju, D. Rajasekhar, J. Kavitha, J. I. Jimenez, *Ind. J. Chem., Sect. B* **2001**, *40*, 313.
[11] S. H. Day, N. Y. Chiu, L. T. Tsao, J. P. Wang, Y. C. Lin, *J. Nat. Prod.* **2000**, *63*, 1560.
[12] M. Mori, S. Tejima, T. Niwa, *Chem. Pharm. Bull.* **1986**, *34*, 4037.
[13] N. Li, A. Q. Jia, Y. Q. Liu, J. Zhou, *Acta Bot. Yunnan.* **2003**, *25*, 241.
[14] L. Y. Zhou, Y. Hua, W. Ni, C. X. Chen, *Acta Bot. Yunnan.* **2004**, *26*, 349.

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