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Two New Arylnaphthalene Lignan Glycosides from *Mananthes patentiflora*

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Abstract: Two new diphyllin glycosides, mananthoside A (**1**) and B (**2**), together with six known compounds, were isolated from the ethanolic extract of the whole plants of *Mananthes patentiflora*. Their structures were determined on the basis of chemical and spectral evidences.

Keywords: *Mananthes patentiflora*, arylnaphthalene lignans, mananthoside A, mananthoside B.

The genus *Mananthes* (Acanthaceae) comprises about 5 species mainly distributed in south Asia and two of them occur in China. *Mananthes patentiflora (*Hemsl.*)* Bremek is a herb native to Yunnan, Hunan and Guangdong Provinces of China. No phytochemical investigation has been reported on this plant. In this study, it was revealed that the ethanolic extract of the whole plants showed moderate cytotoxic activity against human N-04 and Bre-04 carcinoma cell lines. Phytochemical investigation led to the isolation of two new arylnaphthalene lignan glycosides mananthoside A (**1**) and mananthoside B (**2**) (**Figure 1**), together with six known arylnaphthalene lignans diphyllin[1], justicidin A[1, 2], helioxanthin[3], 5-methoxyjusticidin A[4], tuberculatin[5] and cleistanthin B[6] from the whole plants and their structures were elucidated by spectral analysis. Mananthoside A (**1**) demonstrated cytotoxicity against human N-04 and Bre-04 cells with corresponding GI_{50} values 0.21 and 12.27 μg/mL. The GI_{50} values of mananthoside B (**2**) to N-04 and Bre-04 cells are 13.48 and 29.72 μg/mL, respectively.

Mananthoside A (**1**) was obtained as white amorphous powder and its molecular formula was assigned as $C_{27}H_{26}O_{11}$ from the ion peak in positive HRFABMS at *m/z* 527.1601 $[M+H]^+$. The EIMS spectrum of **1** showed a significant peak at *m/z* 380 $[M-146]^+$, which was due to the loss of a hexose, corresponding to an aglycone with a formula $C_{21}H_{16}O_7$ (HREIMS *m/z*: 380.0882). The compound showed blue fluorescence under UV light and gave positive Molisch and Dragendorff tests. The UV spectrum was typical for an arylnaphthalene system. The IR absorption band at 1746 cm^{-1}, the ^1H NMR signals at δ 5.43, 5.50 (each 1H, d, J =15.2 Hz) and ^{13}C NMR signal at δ 170.6 suggested the presence of γ-lactone unit. The deshielded doublet signals at δ 5.43 and

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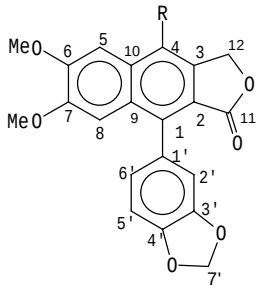
5.50 assigned to $-CH_2-$ in lactone suggested that **7** could be a glycoside of 1-aryl-3-hydroxymethylnaphthalene-2-carboxylic acid lactone.

The ^{1}H NMR signal at δ 3.79 (s, 3H) could be assigned to 7-OMe due to the shielding effect of 1-phenyl ring, whereas the signal at δ 4.04 (s, 3H) could be assigned to 6-OMe. The ^{1}H NMR signals at δ 6.03 (s, 1H) and 6.06 (s, 1H) and IR absorption band at 930 cm^{-1} revealed the presence of a methylenedioxy group, which could be located to 3′, 4′ considering the five ^{1}H NMR signals at δ 7.96 (s, 1H, H-5), 7.12 (s, 1H, H-8), 6.84 (d, 1H, *J*=1.6 Hz), 6.94 (d, 1H, *J*=8.0 Hz), 6.80 (dd, 1H, *J*=1.6, 8.0 Hz) for aromatic protons.

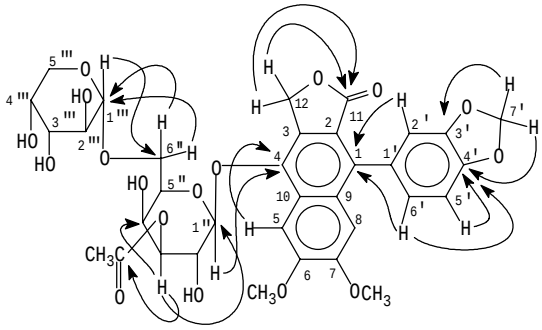
Acid hydrolysis of **7** yielded diphyllin, which was identified by co-TLC with an authentic sample, and L-rhamnose identified by direct PC comparison with an authentic sugar. The ^{13}C NMR signals at δ 101.1, 71.4, 72.4, 74.4, 71.2 and 16.1 and ^{1}H NMR signal at δ 4.80 (d, 1H, *J*=2.0 Hz) in this compound suggested the presence of α-L-rhamnopyranosyl group. The ^{13}C and ^{1}H NMR data of the aglycone moiety of **7** were quite similar to those of diphyllin. Therefore, the structure of **7** could be elucidated as diphyllin 4-O-α-L-rhamnopyranoside.

Figure 1 Structures of Compounds **1**- **2**



1 R=O-L-rhamnopyranosyl
2 R=O-[L-arabinopyranosyl (1→6)]-3-O-acetyl-D-galatopyranosyl

Figure 2 Important HMBC Correlation in **2**



Mananthoside B (**2**) was isolated as white crystallic solid. The peak at *m/z* 717.2112 $[M+H]^+$ in its HRFABMS (positive) suggested the molecular formula $C_{34}H_{36}O_{17}$. The compound gave positive Molisch and Dragendorff tests and showed the resemble UV spectrum to those of diphyllin and **1**. Acid hydrolysis of **2** afforded diphyllin identified by co-TLC with authentic sample, and D-arabinose identified by direct PC comparison with the authentic sample. Further base hydrolysis of the hydrolysate gave D-galactose determined by co-PC comparison with the authentic sample. The anomeric protons appearing at δ 4.92 (d, 1H, *J*=7.8 Hz, H-1″) and 4.16 (d, 1H, *J*=8.1 Hz, H-1‴), and their corresponding carbons resonating at δ 105.9 (C-1″) and 104.0 (C-1‴) from HMQC experiment suggested the presence of β-D-galactopyranosyl and α-D-arabinopyranosyl groups. The IR absorption band at 1712 cm^{-1}, the ^{13}C NMR signals at δ 171.1 and 21.8 as well as ^{1}H NMR signal at δ 2.36 (s, 3H) revealed the presence of *O*-acetyl group.

The ion peak at *m/z* 739 $[M+Na]^+$, 717 $[M+H]^+$, 585 $[M+H-ara]^+$ and 381

$[M+H-ara-gal\ (acetyl)]^+$ in its FABMS (positive) suggested the sugar linkage ara-gal (acetyl)-. The HMBC correlation H-1‴/ C-6″ and H-6″/ C-1‴ indicated the linkage ara (1→6) gal. The *O*-acetyl group could be located to C-3″ upon the HMBC correlation H-3″/ $CH_3\underline{C}O$ and C-1″. The evidence mentioned above suggested the presence of [α -D-arabinopyranosyl (1→6)]-3-*O*-acetyl-β-D-galactopyranosyl moiety. The location of sugar moiety was succeeded by the HMBC correlation H-1″ and H-5 / C-4.

Except for the signals for the sugar moiety, the ^1H and ^{13}C NMR spectra of **2** were quite similar to those of diphyllin. Therefore, the structure of **2** could be elucidated as diphyllin 4-*O*- [α-D-arabinopyranosyl (1→6)]-3-*O*-acetyl-β-D-galactopyranoside.

Mananthoside A (**1**). White amorphous powder, mp 216-218°C. UV λ_{max} (MeOH) (log ε): 260.7 (4.75) nm. IR ν (KBr) cm^{-1}: 3421, 2935, 1746, 1623, 1508, 1481, 1435, 1339, 1168, 1038 and 930. HRFABMS (positive) *m/z*: 527.1601 $[M+H]^+$ (calcd.: 527.1553 for $C_{27}H_{27}O_{11}$); FABMS (positive) *m/z* (%): 527 $[M+H]^+$ (95), 549 $[M+Na]^+$ (100), 565 $[M+K]^+$ (81), 381$[M+H-146]^+$ (9). HREIMS *m/z*: 380.0883 $[M-146]^+$ (calcd.: 380.0896 for $C_{21}H_{16}O_7$). ^1H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) data: see **Table 1**.

Table 1 NMR Data of Mananthoside A (**1**) and B (**2**)

No.	**1**			2		HMBC
	δ_C	δ_H	J_{Hz}	δ_C	δ_H J_{Hz}	(H to C)
1	136.6 s			135.8 s		
2	119.2 s			120.0 s		
3	130.9 s			130.5 s		
4	147.6 s			145.5 s		
5	101.3 d	7.94 s		102.6 d	8.22 s	4, 6, 7, 10
6	152.2 s			152.3 s		
6-OMe	55.9 q	4.04, s		56.7 q	3.92, s	
7	150.8 s			150.8		
7-OMe	55.3 q	3.80, s		56.1 q	3.68, s	
8	106.7 d	7.12 s		106.3 d	7.01 s	1, 6, 7
9	128.4 s			129.2 s		
10	129.6 s			130.9 s		
11	170.2 s			171.0 s		
12	67.2 t	5.43, d, 15.2		68.1 t	5.63, d, 14.7	2, 3, 4, 11
		5.50, d, 15.2			5.52, d, 14.7	
1′	127.3 s			131.6 s		
2′	110.7 d	6.84, d, 1.6		111.9 d	6.94, d, 1.4	1
3′	147.6 s			147.7 s		
4′	147.8 s			147.8 s		
5′	108.0 d	6.94, d, 8.0		108.8 d	7.06, d, 8.0	1′, 3′, 4′
6′	123.6 d	6.81, dd, 8.0, 1.6		124.6 d	6.82, dd, 8.0, 1.4	1, 4′
7′	101.2 t	6.06 and 6.03, each s		102.0 t	6.14, s	3′, 4′
1″	101.1 d	4.80, d, 2.0		105.9 d	4.92, d, 7.8	3″, 4
2″	71.4 d			71.0 d	3.32, m	4″
3″	72.4 d			74.0 d	3.82, m	1″, $CH_3\underline{C}O$
4″	74.4 d			68.8 d	4.03, m	6″
5″	71.2 d			76.6 d	4.74, m	3″
6″	16.1 q	1.37, d, 6.0		68.2 t	3.94, m	1‴
					3.73, m	
1‴				104.0 d	4.16, d, 8.1	6″
2‴				71.8 d		
3‴				73.2 d		
4‴				69.1 d		
5‴				65.8 t	3.64, m	3‴, 4‴
					3.36, m	
$CH_3\underline{C}O$				171.1 s		
$\underline{C}H_3CO$				21.8 q	2.16, s	$CH_3\underline{C}O$

Mananthoside B (**2**). White crystalline solid, mp 177-179°C. UV λ_{max} (MeOH) (log ε): 209.7 (4.82), 260.7 (4.85) nm. IR ν (KBr) cm^{-1}: 3441, 2922, 1756, 1712, 1622,1507, 1479, 1435, 1349, 1168, 1039 and 927. HRFABMS (positive) *m/z*: 717.2112 $[M+H]^+$ ($C_{34}H_{37}O_{17}$, calcd.: 717.2031); FABMS (positive) *m/z* (%): 717 $[M+H]^+$ (8), 739 $[M+Na]^+$ (100), 585 $[M+H-132]^+$ (49) and 381 $[M+H-132-204]^+$ (37). ^1H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6) data: see **Table 1**.

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