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Three new lignan glycosides, mananthosides I–K (**1**–**3**), were isolated from the ethanolic extract of the aerial part of *Mananthes patentiflora*. The structure elucidation of these compounds was mainly established on the basis of 1D NMR, 2D NMR and HR-MS spectroscopic analysis.

Keywords: *Mananthes patentiflora*; lignan glycosides; mananthoside I; mananthoside J; mananthoside K; Acanthaceae

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1. Introduction

Mananthes patentiflora (Hemsl.) Bremek is a herb of the genus *Mananthes* in the Acanthaceae family, distributed in southern China. Previously phytochemical studies on this plant have afforded lignans.[1,2] In the search for cytotoxic constituents from this plant,[1,3] three new lignan glycosides, mananthosides I (**1**), J (**2**), and K (**3**) were isolated from the aerial part of the plant. Their structures were elucidated by spectral analysis.

2. Results and discussion

Compound **1** was a white amorphous solid. The molecular formula was determined as $C_{32}H_{34}O_{16}$ from negative HRESI-MS $[M - H]^-$ at *m/z* 673.1779. The UV spectrum was typical for arylnaphthalene.[4] The IR spectrum showed hydroxyl (3423 cm^{-1}), γ-lactone (1752 cm^{-1}) and aromatic (1624 cm^{-1}) absorption bands.[5,6] The ^{1}H NMR spectrum of **1** exhibited the presence of five aromatic protons, two singlets at δ 8.94 (1H, s) and 7.34 (1H, s), and three ABX system protons at δ 7.03 (1H, d, $J = 7.6$ Hz), 7.14 (1H, d, $J = 7.6$ Hz), and 7.12 (1H, s). Two γ-lactone methylene protons at δ 6.22 (1H, d, $J = 14.5$ Hz) and 5.73 (1H, d, $J = 14.5$ Hz) were non-equivalent, similar to those of arabelline.[7] The ^{1}H NMR and ^{13}C NMR spectral data (see Table 1), and an ion peak at *m/z* 379 in the negative FAB-MS (corresponded to molecular formula $C_{21}H_{15}O_7$ of the diphyllin moiety) suggested the presence of diphyllin unit in **1**.[1] In addition, the ^{1}H NMR spectrum also exhibited a series of signals between δ 3.59–5.36 characteristic of sugar moieties. The presence of two anomeric protons (at δ 5.35, 1H, d, $J = 7.6$ Hz and δ 4.77, 1H, d, $J = 6.7$ Hz) revealed that the molecule contained two sugar units. By means of HSQC, HMBC, and ^{1}H-^{1}H COSY, the ^{13}C NMR signals at δ 106.7, 72.7, 75.2, 70.1, 75.6 and 69.6 belonged to galactopyranose moiety.[1,8] The other sugar unit was indicated as arabinopyranose moiety (^{13}C NMR signals at δ 105.3, 72.2, 74.3, 69.3, and 66.8).[1] The configurations of galactose and arabinose were determined as β and α, based on coupling constants of anomeric protons, 7.6 and 6.7 Hz, respectively.[1,8] The galactose moiety was directly linked to C-4 of diphyllin by the correlation between H-1″ (δ 5.35, 1H, d, $J = 7.6$ Hz) and C-4 (δ 146.2) in HMBC spectrum. The downfield shift of C-6″ suggested that the arabinose was linked at C-6″ of the galactose, which was confirmed by the HMBC correlation between H-1‴ (δ 4.77, 1H, d, $J = 6.7$ Hz) and C-6″ (δ 69.6). Therefore, compound **1,** named mananthoside I, could be elucidated as 4-[α-arabinopyranosyl-(1 → 6)-β-galactopyranosyl]-*O*-diphyllin (Figure 1).

Compound **2** was a white amorphous solid. The molecular formula was determined as $C_{45}H_{54}O_{26}$ from negative HRESI-MS $[M - H]^-$ at *m/z* 1009.2852. The UV and IR absorption bands were similar to those of **1**. The ^{1}H NMR and ^{13}C NMR spectral data (see Table 1), and an ion peak at *m/z* 379 in the negative FAB-MS suggested the presence of diphyllin unit in **2**.[1] The carbon signals at δ 175.1 and 22.4, and the proton signals at δ 2.14 (3H, s) suggested the presence of an AcO group. In addition, the ^{1}H NMR spectrum also exhibited a series of signals between δ 3.28–4.77 characteristic of sugar moieties. The presence of four anomeric protons at δ 4.77 (1H, d, $J = 7.5$ Hz), 4.73 (1 H, d, $J = 7.0$ Hz), 4.21 (1H, d, $J = 5.5$ Hz) and 4.41 (1H, d, $J = 7.0$ Hz) in **2** indicated that the molecule contained four sugar units. By means of HSQC, HMBC, and ^{1}H-^{1}H COSY, the sugar units were deduced as galactose (δ 106.4, 72.7, 82.3, 73.1,

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Table 1. ^{1}H NMR and ^{13}C NMR spectral data of compounds **1** and **2**.

No.	**1**		**2**	
	^{1}H NMR	^{13}C NMR	^{1}H NMR	^{13}C NMR
1		136.1		137.5
2		120.2		120.1
3		132.2		132.0 (131.8)[a]
4		146.2		146.1
5	8.94 s	102.9	7.75 s (7.70 s)[a]	103.2
6		152.7		153.0
7		151.0		151.3
8	7.34 s	107.6	6.45 d (5.5) (6.42 d (5.0))[a]	107.0
9		128.4		129.1
10		131.1		131.4
11		170.3		173.6
12	6.22 d (14.5)	68.3	5.60 d (14.5)	70.5
	5.73 d (14.5)		5.31 d (14.5)	
1′		131.1		129.7 (129.6)[a]
2′	7.12 s	111.8 (111.6)[a]	6.37 s	112.4 (112.1)[a]
3′		147.9		149.0
4′		147.9		149.0
5′	7.14 d (7.6)	108.5	6.74 d (7.3)	109.9 (110.0)[a]
6′	7.03 d (7.6)	124.6 (124.4)[a]	6.32 d (7.3)	125.5
7′	6.02 s, 5.93 s	101.7	5.77 s, 5.75 s	103.2
6-OMe	4.12 s	56.3	3.85 s	57.7
7-OMe	3.67 s	55.5	3.30 s	56.8
1″	5.35 d (7.6)	106.7	4.77 d (7.5)	106.4
2″	4.89 t (8.6)	72.7	4.21[b]	72.7
3″	4.18[b]	75.2	4.11[b]	82.3
4″	4.45 s	70.1	5.63[b]	73.1
5″	4.18[b]	75.6	3.67[b]	74.4
6″	4.75[b], 4.35 d (9.8)	69.6	3.94[b], 3.89[b]	70.3
4″-CO$\overline{C}H_3$			2.14 s	22.4
4″-$\underline{C}OCH_3$				175.1
1‴	4.77 d (6.7)	105.3	4.73 d (7.0)	105.7
2‴	4.38[b]	72.2	3.42[b]	75.7
3‴	4.14[b]	74.3	3.56[b]	77.6
4‴	4.28[b]	69.3	3.52[b]	71.4
5‴	4.26 d (12.0), 3.71 d (12.0)	66.8	3.58[b]	77.0
6‴			3.89[b], 3.57 d (11.5)	68.1
1⁗			4.21 d (5.5)	105.0
2⁗			3.56[b]	72.5
3⁗			3.42[b]	74.9
4⁗			3.67[b]	70.0
5⁗			3.78 d (12.0), 3.39 d (12.0)	67.8
1⁗′			4.41 d (7.0)	105.9
2⁗′			3.64[b]	72.7
3⁗′			3.50[b]	74.3
4⁗′			3.67[b]	70.2
5⁗′			3.87[b], 3.78 d (12.5)	68.0

[a] Signal splitting due to atropisomerism (slow rotation about the glycosidic linkage to the aglycone).
[b] Overlapping signals.

74.4, and 70.3),[1,8] glucose (δ 105.7, 75.7, 77.6, 71.4, 77.0 and 68.1),[9] arabinose (δ 105.0, 72.5, 74.9, 70.0, and 67.8), and arabinose (δ 105.9, 72.7, 74.3, 70.2, and 68.0).[1] Based on coupling constants of anomeric protons of galactose (7.5 Hz), glucose (7.0 Hz), arabinose (5.5 Hz) and arabinose (7.0 Hz), the anomeric configurations of galactose, glucose, arabinose, and arabinose were determined as β, β, α, and α, respectively. The galactose moiety was directly linked to C-4 of diphyllin by HMBC correlation between H-1″ (δ 4.77, 1H, d, $J = 7.5$ Hz) and C-4 (δ 146.1). The HMBC correlation between H-1‴ (δ 4.73, 1H, d, $J = 7.0$ Hz) and C-3″ (δ 82.3) indicated that glucose moiety was linked to the C-3″ position of galactose. One arabinose was linked to C-6″ of galactose by HMBC correlation between H-1⁗ (δ 4.21, 1H, d, $J = 5.5$ Hz) and C-6″ (δ 70.3). The other arabinose was linked to C-6‴ of glucose by HMBC correlation between H-1⁗′ (δ 4.41, 1H, d, $J = 7.0$ Hz)

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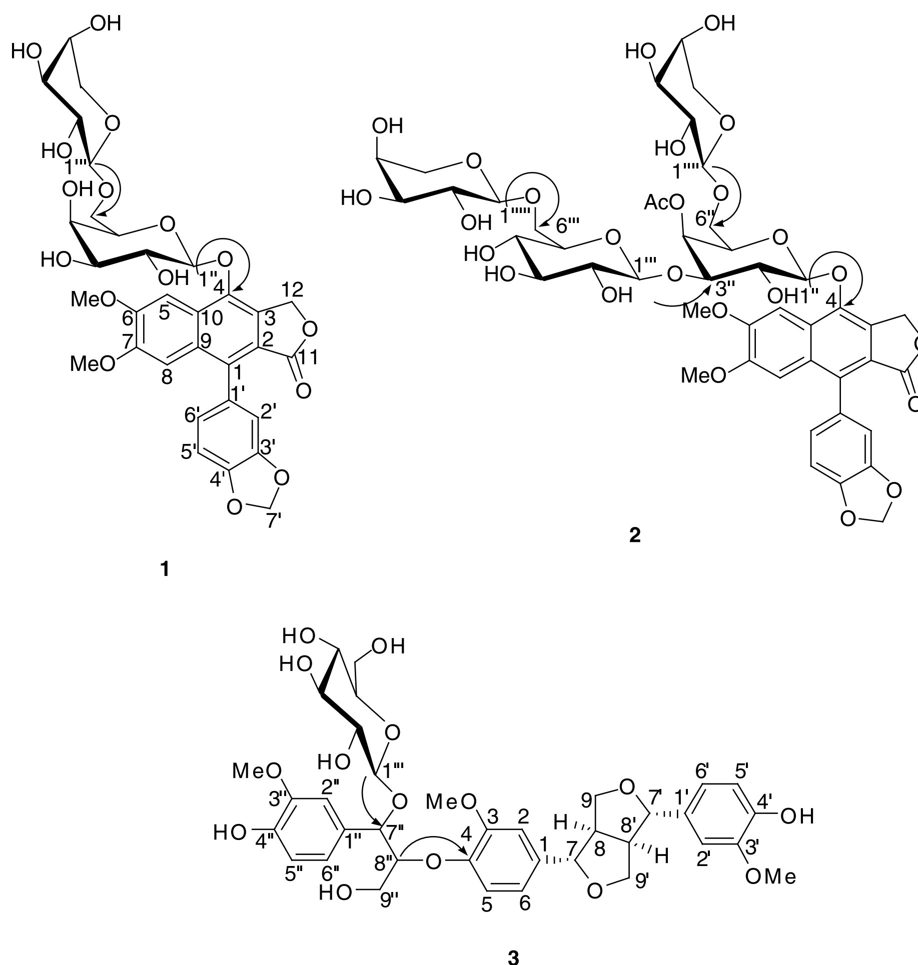

Figure 1. Structures and key HMBC correlations of **1**–**3**.

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and C-6‴ (δ 68.1), the HMBC correlation between H-4″ (δ 5.63, 1H) and the carbon signal at δ 175.1 revealed that the AcO group located at C-4″ of the galactose. Therefore, compound **2,** named mananthoside J, could be elucidated as 4-{α-arabinopyranosyl-(1 → 6)-[α-arabinopyranosyl-(1 → 6)-β-glucopyranosyl-(1 → 3)]-4-*O*-acetyl-β-galactopyranosyl}-*O*-diphyllin (Figure 1).

Compound **3** was a white amorphous solid. The molecular formula was determined as $C_{36}H_{44}O_{15}$ from negative HRESI-MS $[M - H]^-$ at *m/z* 715.2605. The ^{1}H NMR and ^{13}C NMR spectral data were similar to those of dracunculifoside R.[10] Thus, compound **3** was deduced to be a sesquilignan glycoside consisting of pinoresinol, β-glucopyranose, 3-(4-hydroxy-3-methoxyphenyl)-propan-1,2,3-triol. Based on similar chemical shifts and coupling constants of H-7 (δ 4.72, 1H, d, $J = 3.8$ Hz) and H-8 (δ 3.12, 1H, brs), H-7′ (δ 4.70, 1H, d, $J = 4.1$ Hz) and H-8′ (δ 3.12, 1H, brs) to those of dracunculifoside R, the relative configuration of C-7, C-8, C-7′ and C-8′ of **3** was proposed to be the same as those of dracunculifoside R with H-7, H-8, H-7′, H-8′ as β, α, β, and α, respectively.[10] In the HMBC experiment, the correlation between H-8″ (δ 4.40, 1H, d, $J = 4.3$ Hz) of 3-(4-hydroxy-3- methoxyphenyl)-propan-1,2,3-triol and C-4 (δ 149.2) of pinoresinol indicated that C-8″ linked to C-4 via an oxygen atom, the correlation between H-1‴ (δ 4.17, 1H, d, $J = 7.3$ Hz) of glucose and C-7″ (δ 77.9) of 3-(4-hydroxy-3-methoxyphenyl)-propan-1,2,3-triol indicated that glucose was linked to C-7″. The coupling constant of H-7″ (d, $J = 4.3$ Hz) indicated that the relative configuration of C-7″ and C-8″was *erythro orientated*.[10] Therefore, compound **3,** named mananthoside K, could be elucidated as 4-{2-[3-(4-hydroxy-3-methoxyphenyl)-3-*O*-β-glucopyranosyl-propan-1-ol]}-*O*-pinoresinol (Figure 1).

3. Experimental

3.1 General experimental procedures

Optical rotations were measured on a Horiba SEPA-300 spectropolarimeter. The UV spectra were measured on a Shimadzu double beam 210A spectrophotometer. IR spectra were measured on a FTS-135 infrared

spectrophotometer. 1D NMR spectra were recorded on a Brucker AM-400 spectrometer; 2D NMR spectra were recorded on a Brucker DRX-500 spectrometer using TMS as the internal standard. FAB-MS (negative) and HRESI-MS (negative) were determined on a VG Autospec-3000 spectrometer. Silica gel (300–400 mesh) for column chromatography and silica GF254 for TLC were made by the Qingdao Marine Chemical Factory of China. C_{18} reversed-phase silica gel (60 μm, Merck, Darmstadt, Germany) and sephadex LH-20 (Amershan Biosciences, Sweden) were employed for column chromatography.

3.2 Plant material

The aerial part of *Mananthes patentiflora* (Hemsl.) Bremek was collected in *Xishuangbanna*, Yunnan, China, in August 2004. A voucher specimen of the plant (BN0408133) was identified by Professor Deding Tao, and has been deposited in the herbarium of Kunming Institute of Botany.

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3.3 Extraction and isolation

The ethanolic extract of the air-dried aerial part of *Mananthes patentiflora* (6.9 kg) was suspended in H_2O (2.5 L) and then extracted successively with EtOAc and *n*-BuOH. The EtOAc solution was evaporated and the residue (200 g) was purified by CC (silica gel, 2 kg, petroleum ether/EtOAc and EtOAc/MeOH of increasing polarity) to give 11 fraction*s* (Fr. 1–11). Fraction 9 (15.2 g) was chromatographed on silica gel (200–300 mesh, 320 g) and eluted with $CHCl_3$/MeOH (10:0.5 → 0:10). Based on the differences in composition exhibited by TLC, 17 fractions (Fr. 9A–9Q) were obtained. Fraction 9K (925 mg) was repeated by CC to give compound **3** (7 mg). The *n*-BuOH solution was evaporated and the residue (7.0 g) was purified by CC (D101, eluted with H_2O and acetone successively) to give two fractions. Fraction 2 (1.8 g) was repeatedly chromatographed by CC (silica gel, $CHCl_3$/MeOH 8:2; RP-18, MeOH/H_2O 6:4) to give **1** (30 mg) and **2** (42 mg).

3.3.1 Mananthoside I (*1*)

$C_{32}H_{34}O_{16}$, white amorphous solid (MeOH). $[\alpha]_D^{25}$ −12.4 (*c* 0.38, MeOH). UV λ_{max} (nm) (log ε): 202 (4.52), 225 (4.36), 262 (4.58), 309 (3.89), 350 (3.54). IR ν_{max} (KBr) (cm^{-1}): 3423, 2925, 1752, 1624, 1508, 1481, 1435, 1341, 1264, 1231, 1169, 1072, 1039, 1008. ^1H NMR (C_5D_5N, 500 MHz) spectral data: see Table 1. ^{13}C NMR (C_5D_5N, 125 MHz) spectral data: see Table 1. FAB-MS (negative) *m/z*: 674 $[M]^-$ (31), 379 (100). Negative HRESI-MS *m/z*: 673.1779 $[M-H]^-$ (calcd for $C_{32}H_{33}O_{16}$, 673.1768).

3.3.2 Mananthoside J (*2*)

$C_{45}H_{54}O_{26}$, white amorphous solid (MeOH). $[\alpha]_D^{25}$ + 7.9 (*c* 0.82, H_2O). UV λ_{max} (nm) (log ε): 199 (4.58), 225 (4.28), 261 (4.61), 314 (3.95), 390 (2.54). IR ν_{max} (KBr) (cm^{-1}): 3424, 2921, 1742, 1624, 1508, 1481, 1436, 1344, 1263, 1230, 1169, 1074, 1006. ^1H NMR (CD_3OD, 500 MHz) spectral data: see Table 1. ^{13}C NMR (CD_3OD, 125 MHz) spectral data: see Table 1. FAB-MS (negative) *m/z*: 1010 $[M]^-$ (15), 379 (100). Negative HRESI-MS *m/z*: 1009.2852 $[M-H]^-$ (calcd for $C_{45}H_{53}O_{26}$, 1009.2825).

3.3.3 Mananthoside K (*3*)

$C_{36}H_{44}O_{15}$, white amorphous solid (MeOH). $[\alpha]_D^{25}$ + 2.0 (*c* 0.34, MeOH). UV λ_{max} (nm) (log ε): 205 (4.70), 230 (4.30), 280 (3.89), 333 (2.81), 352 (2.66), 360 (2.77). IR ν_{max} (KBr) (cm^{-1}): 3424, 2934, 2877, 1607, 1515, 1463, 1453, 1430, 1369, 1273, 1231, 1158, 1127, 1076, 1032. ^1H NMR (CD_3OD, 400 MHz) δ (ppm): 6.97 (H-2, s), 6.87 (H-5, d, $J = 8.3$ Hz), 6.81 (H-6, d, $J = 8.3$ Hz), 4.72 (H-7, d, $J = 3.8$ Hz), 3.12 (H-8, brs), 4.22 (H-9, d, $J = 6.6$ Hz), 3.85 (H-9, overlap), 3.84 (3-OMe, overlap), 6.94 (H-2′, s), 6.76 (H-5′, d, $J = 8.5$ Hz), 6.81 (H-6′, d, $J = 8.5$ Hz), 4.70 (H-7′, d, $J = 4.1$ Hz), 3.12 (H-8′, brs), 4.22 (H-9′, d, $J = 6.6$ Hz), 3.85 (H-9′, overlap), 3.85 (3′-OMe, overlap), 7.13 (H-2″, s), 6.74 (H-5″, d, $J = 8.3$ Hz), 6.87 (H-6″, d, $J = 8.3$ Hz), 5.19 (H-7″, d, $J = 4.3$ Hz), 4.40 (H-8″, d, $J = 4.3$ Hz), 3.88 (H-9″, dd, $J = 11.6$, 6.0 Hz), 3.56 (H-9″, dd, $J = 11.6$, 6.0 Hz), 3.79 (3″-OMe, overlap), 4.17 (H-1‴, d, $J = 7.3$ Hz), 3.31 (H-2‴, overlap), 3.28 (H-3‴, overlap), 3.31 (H-4‴, overlap), 3.12 (H-5‴, brs), 3.88 (H-6‴, dd, $J = 12.0$, 6.0 Hz), 3.68 (H-6‴, dd, $J = 12.0$, 6.0 Hz). ^{13}C NMR (CD_3OD, 100 MHz) δ (ppm): 136.6 (C-1), 111.3 (C-2), 151.6 (C-3), 149.2 (C-4), 118.3 (C-5), 119.7 (C-6), 87.2 (C-7), 55.5 (C-8), 72.7 (C-9), 56.5 (3-OMe), 133.9 (C-1′), 111.0 (C-2′), 149.2 (C-3′), 147.4 (C-4′), 116.1 (C-5′), 120.1 (C-6′), 87.5 (C-7′), 55.3 (C-8′), 72.7 (C-9′), 56.4 (3′-OMe), 130.2 (C-1″), 112.7 (C-2″), 149.0 (C-3″), 147.4 (C-4″), 115.7 (C-5″), 121.8 (C-6″), 77.9 (C-7″), 85.9 (C-8″), 62.0 (C-9″), 56.3 (3″-OMe), 101.1 (C-1‴), 75.2 (C-2‴), 77.8 (C-3‴), 71.9 (C-4‴), 77.9 (C-5‴), 62.8 (C-6‴). FAB-MS (negative) *m/z*: 715 $[M-H]^-$ (51), 513 (22), 469 (26), 425 (21), 357 (25), 325 (100). Negative HRESI-MS *m/z*: 715.2605 $[M-H]^-$ (calcd for $C_{36}H_{43}O_{15}$, 715.2601).

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