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A NEOLIGNAN AND LIGNANS FROM *MAGNOLIA BIONDII*

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Key Word Index—*Magnolia biondii*; Magnoliaceae; 2.8′,9.*O*.7′-neolignan; 8.8′,7.*O*.9′-lignans; biondinin A; isomer of (−)fargesol.

Abstract—Two new compounds, *rel*-(7*S*,8*S*,8′*S*)-3,4,3′,4′-tetramethoxy-9,7′-dihydroxy-8.8′,7.*O*.9′-lignan and *rel*-(7*S*,8*S*,8′*S*)-3,4,3′,4′,7′-pentamethoxy-9-hydroxy-8.8,7.*O*.9′-lignan, together with six known 8.8′-linked lignans and one neolignan were isolated from the flower buds of *Magnolia biondii* (Magnoliaceae).

INTRODUCTION

Dried flower buds of *Magnolia biondii* (Magnoliaceae) are used for the treatment of nasal empyema and headache in China. The platelet-activating factor (PAF) receptor antagonistic activity on isolated platelet membranes of this plant led us to study intensively its chemical constituents [1–3]. We report here the isolation and more comprehensive structure determination of a neolignan and two new lignans.

RESULTS AND DISCUSSION

Nine compounds were isolated from the CH_2Cl_2 extract of the flower buds of *Magnolia biondii* by successive silica gel column chromatography, preparative TLC and HPLC. Compounds **1**–**3** had no PAF receptor antagonistic activity on isolated platelet membranes. The six known lignans fargesin (**4**), demethoxyaschantin (**5**), aschantin (**6**), pinoresinol dimethoxy ether (**7**), magnolin (**8**) and liroresinal-B dimethoxy ether (**9**), were identified by comparison of their spectral data with those described in the literature [4–7].

Compound **1**, biondinin A, had the molecular formula $C_{21}H_{26}O_6$ based on HREIMS and its structure was determined as described in ref. [3]. Based on biosynthetic arguments, its structure is proposed to be **1a**, rather than **1b**.

HREIMS indicated compound **2** had a molecular formula $C_{22}H_{28}O_7$. Compared to (−)fargesol [8], it had almost the same fragmentation pattern in the MS spectrum, and a similar ^{1}H NMR spectrum except that the peaks due to H-9 shifted upfield to δ3.43. A *trans*-orientation of H-7 and H-8 was proposed by the peaks for H-7 (δ4.53, *d*) [9]. A *cis*-orientation of H-8 and H-8′ was determined by $J_{8,8'} = 6.0$ Hz as Drieding model predicted. The configuration of **2** was further suggested by comparing the optical rotation of **2** ($[\alpha]_D = +80°$) with that of magnostellin A ($[\alpha]_D = +68°$) [6], and (−)fargesol ($[\alpha]_D = -354°$) [4]. The compound **2** should be a geometrical isomer of (−)fargesol.

Compound **3** had M^+ at *m/z* 418 for an empirical formula $C_{23}H_{30}O_7$ and $[\alpha]_D = +16°$. The ^{1}H NMR spectrum of **3** was very similar to that of **2**. The peak at δ3.21 (3H, *s*) was assigned to C-7′-OMe, which induced the upfield shift of H-7′ from δ4.68 (1H, *d*) in **2** to δ4.07 in **3**. The relative configuration of **3** was determined by comparing the chemical shift of H-9 with that of compound **2**. It shifted upfield from δ3.43 (2H, *d*) to δ3.30 and 3.34 (each 1H, *d*) because of the influence of the C-7′-OMe.

EXPERIMENTAL

General. ^{1}H NMR spectra were recorded at 500 or 400 MHz, and ^{13}C NMR at 125 MHz. EIMS and HREIMS were measured at 70 eV.

Plant material. Dried flower buds of *M. biondii* were collected in Henan province, China, in February 1984. The voucher specimens (No. 8902) have been deposited at Department of Botany, Beijing Medical University (Beijing, People's Republic of China).

Extraction and isolation. The CH_2Cl_2 extract of air-dried flower buds (1.5 kg) of *M. biondii* was concd (138 g), and then sepd into 4 frs by silica gel CC eluted with petrol (F_1), CH_2Cl_2 (F_2), EtOAc (F_3), and MeOH (F_4). F_3 was sepd by silica gel CC (Me_2CO–CH_2Cl_2 mixt.), and purefied by HPLC (MeOH–H_2O, 6:4) to give **1** (4.4 mg), **2** (5 mg), and **3** (7.8 mg). F_2 was sepd by silica gel CC (cyclohexane–EtOAc mixt.) and prep.TLC [$CHCl_3$–MeOH–H_2O (50:1:0.2) or *n*-hexane–EtOAc (3:1)] to give **4** (48 mg), **5** (150 mg), **6** (100 mg), **7** (62 mg), **8** (133 mg), **9** (31 mg).

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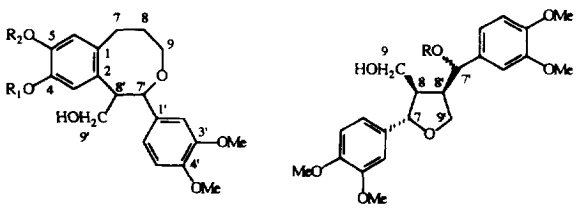

	R	R_1	R_2
1a		H	Me
1b		Me	H
2	H		
3	Me		

5,3′,4′-*Trimethoxy*-4,9′-*dihydroxy*-2,8′,9.O.7′-*neolignan* (**1**). Oil, $C_{21}H_{26}O_6$; HRMS *m/z*: 374.1700 (calcd: 374.1729); IR ν_{max}^{NaCl} cm^{-1}: 3397, 2939, 1605, 1516, 1497, 1462, 1328, 1141, 1026; UV λ_{max}^{MeOH} nm (log ε): 206.5 (4.48), 231.5 (3.95), 280.0 (3.50); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.89 (2H, *m*, 2 H-8), 2.68 (2H, *m*, 2 H-7), 3.61 (1H, *m*, H-8′), 3.70 (2H, *t*, *J* = 6.4 Hz, 2 H-9), 3.86 (3H, *s*, OMe), 3.87 (3H, *s*, OMe), 3.89 (3H, *s*, OMe), 3.91 (1H, *dd*, *J* = 11.0, 4.9 Hz, H-9′a), 3.98 (1H, *dd*, *J* = 11.0, 6.0 Hz, H-9′b), 5.57 (1H, *d*, *J* = 7.4 Hz, H-7′), 6.68 (2H, *s*, H-3, H-6), 6.83 (1H, *dd*, *J* = 6.9, 1.9 Hz, H-2), 6.95–6.96 (2H, *m*, H-2′, H-5′). ^{13}C NMR ($CDCl_3$) δ: 32.0 (C-8), 34.6 (C-7), 53.8 (C-8′), 56.0 (C-3′-OMe), 56.1 (C-5 – OMe), 62.3 (C-9′), 64.1 (C-9), 87.7 (C-7′), 109.6, 111.3, 112.8, 116.0, 118.7 (C-3, C-6, C-2′, C-5′, C-6′), 127.8, 133.9, 135.5 (C-1, C-2, C-1′), 144.3 146.7, 148.4, 149.1 (C-5, C-4, C-3′, C-4′); EIMS *m/z* (rel. int.): 374 $[M]^+$ (20), 356 $[M - H_2O]^+$ (48), 341 (40), 165 (61), 151 (100).

rel-[7S,8S,8′S]-3,4,3′,4′-*Tetramethoxy*-9,7′-*dihydroxy*-8.8′, 7.O.9′-*lignan* (**2**). Oil, $C_{22}H_{28}O_7$; $[\alpha]_D$ + 80° ($CHCl_3$, *c* 0.10); HREIMS *m/z*: 404.1825 (calcd: 404.1835); IR ν_{max}^{NaCl} cm^{-1}: 3432, 3061, 2940, 1594, 1516, 1463, 1235, 1026; UV λ_{max}^{MeOH} nm (log ε): 204.5 (4.04), 229.5 (3.94), 278.0 (3.64); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.03 (1H, *dt*, *J* = 7.9, 6.0 Hz, H-8), 2.63 (1H, *ddt*, *J* = 7.6, 6.0, 4.9 Hz, H-8′), 3.43 (2H, *d*, *J* = 6.0Hz, H-9), 3.85 (3H, *s*, OMe), 3.86 (6H, *s*, 2 OMe), 3.87 (3H, *s*, OMe), 4.04 (1H, *dd*, *J* = 9.2, 7.6 Hz, H-9′a), 4.24 (1H, *dd*, *J* = 9.2, 4.9 Hz, H-9′b), 4.53 (1H, *d*, *J* = 7.9 Hz, H-7), 4.68 (1H, *d*, *J* = 7.6 Hz, H-7′), 6.80–6.86 (5H, *m*, Ar-H), 6.90 (1H, *d*, *J* = 1.7 Hz, Ar-H). EIMS *m/z* (el. int.): 404 $[M]^+$ (3), 189 (56), 167 (90), 165 (53), 139 (100), 124 (30).

rel-[7S,8S,8′S]-3,4,3′,4′,7′-*Pentamethoxy*-9-*hydroxy*-8.8′, 7.O.9′-*lignan* (**3**). Oil, $[\alpha]_D$ + 16° ($CHCl_3$, *c* 0.10); IR ν_{max}^{NaCl} cm^{-1}: 3534, 2928, 2853, 1593, 1516, 1418, 1318, 1236, 1158, 1027; UV λ_{max}^{MeOH} nm (log ε): 206.0 (4.37), 228.0 (4.05), 277.5 (3.58); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.03 (1H, *m*, H-8), 2.63 (1H, *m*, H-8′), 3.21 (3H, *s* R-OMe), 3.30 (1H, *dd*, *J* = 11.0, 5.5 Hz, H-9a), 3.34 (1H, *dd*, *J* = 11.0, 5.5 Hz, H-9b), 3.86 (9H, *s*, 3Ar-OMe), 3.87 (3H, *s*, Ar-OMe), 4.05 (1H, obscured, H-9′a), 4.07 (1H, *d*, *J* = 7.9 Hz, *H*-7′), 4.16 (1H, *dd*, *J* = 9.1, 4.9 Hz, H-9′b), 4.51 (1H, *d*, *J* = 7.9 Hz, H-7), 6.79–6.83 (6H, *m*, Ar-H). EIMS *m/z* (rel. int.): 418 $[M]^+$ (4), 249 (10), 181 (100), 167 (15), 165 (30), 139 (15).

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REFERENCES

1. Han, G. Q., Pan, J. X., Li, C L. and Tu, F. (1991) *Int. J. Oriental Med.* **16**, 1.
2. Pan, J. X., Hensens, O., Zink, D., Chang, M. N. and Hwang, S. B. (1987) *Phytochemistry* **26**, 1377.
3. Ma, Y. L. and Han, G. Q. (1992) *Chinese Chem. Lett.* **3**(2), 121.
4. Kakisawa, T., Chen, Y. P. and Hsu, H. Y. (1972) *Phytochemistry* **11**, 2289.
5. Iida, T., Moro Y. and Ito, K. (1983) *Phytochemistry* **22**, 211.
6. Haensel, R. and Peter, A. (1969) *Arch. Pharmacol.* **302**, 940.
7. Greger, H. and Hofer, O. (1980) *Tetrahedron* **36**, 3551.
8. Huang, Y. L., Chen, C. C., Chen, Y. P., Hsu, H. Y. and Kou, Y. H. (1990) *Planta Med.* **56**, 237.
9. Tanaka, H., Nakamura, T., Ichino, K. and Ito, K. (1989) *Phytochemistry* **28**, 952.