

Constituents of *Gnetum montanum*

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Abstract

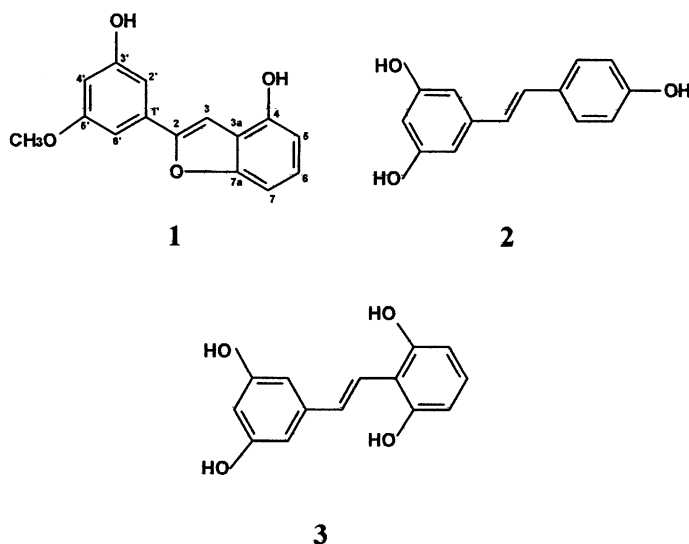
A new stilbene, gnetifolin M (**1**), was isolated from the lianas of *Gnetum montanum*, together with seven known compounds, resveratrol (**2**), gnetol (**3**), 4',5,7-trihydroxy-3'-methoxyflavone, β -sitosterol, daucosterol, ursolic acid, and tetracosanoic acid. The structure of **1** was determined to be 2-(5'-methoxy-3'-hydroxyphenyl)-4-hydroxybenzofuran on the basis of spectroscopic evidence. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: *Gnetum montanum*; Stilbenes; Sterols; Flavonoids; Triterpenoids; Aliphatics

1. Introduction

Gnetum montanum Markgraf (Gnetaceae) has been used as a folk medicine in China for treatment of rheumatism, arthritis and bronchitis [1]. In previous papers [2,3], stilbenes and dimeric stilbenes obtained from this genus were reported. In pursuing Mao Lin's studies on bioactive constituents from the *Gnetum* genus, we report here the isolation from the lianas of *G. montanum* collected from the southern part of Yunnan province, China, of a new compound, named gnetifolin M (**1**), along with seven known compounds, resveratrol (**2**) [4], gnetol (**3**) [5], 4',5,7-trihydroxy-3'-methoxyflavone, β -sitosterol, daucosterol, ursolic acid, and tetracosanoic acid. No dimeric stilbene was obtained in our reinvestigation of the plant.

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2. Experimental

2.1. Plant material

G. montanum lianas were collected in the Wenshan of Yunnan province, in July 2000, and authenticated by Professor Xi-Wen Li at Kunming Institute of Botany, Academia Sinica, Kunming, Yunnan, PR China, where a voucher specimen was deposited.

2.2. Extraction and isolation

The air-dried and powdered plant (2.3 kg) was extracted with EtOH (7 l \times 3) at room temperature for 10 h each time. The EtOH extract was evaporated in vacuo. The residue was suspended in water, and then extracted with petrol and EtOAc, respectively. The EtOAc layer was concentrated in vacuo to give a dark brown residue (70 g) that was chromatographed on Si-gel column (200–300 mesh, 500 g) and eluted with CHCl₃ containing increasing amounts of MeOH (CHCl₃–MeOH 99.5:0.5–90:10). Fractions 1–8 (obtained with CHCl₃–MeOH 99:1) were further purified by recrystallization to yield β -sitosterol (2.8 g), tetracosanoic acid (165 mg), ursolic acid (102 mg), and daucosterol (1.0 g). Fractions 9–20 (obtained with CHCl₃–MeOH 98:2) were further purified on Si-gel column to afford 4',5,7-trihydroxy-3'-methoxyflavone (31 mg), compounds **1** (39 mg), **2** (80 mg), and **3** (48 mg). In the experiment, the fractions were combined by monitoring with TLC.

Gnetifolin M (**1**). C₁₅H₁₂O₄, yellow crystals; mp 140–142 °C; IR bands (KBr): 3282, 1605, 1491, 1462, 1443 and 1156 cm⁻¹; ¹H-NMR (500 MHz, CD₃COCD₃): δ

8.94 (1H, *s*, OH-4), 8.66 (1H, *s*, OH-3'), 7.27 (1H, *s*, H-3), 7.12 (1H, *t*, *J* 8.0 Hz, H-6), 7.04 (1H, *d*, *J* 8.0 Hz, H-7), 7.00 (1H, *t*, *J* 2.0 Hz, H-2'), 6.98 (1H, *t*, *J* 2.0 Hz, H-6'), 6.68 (1H, *d*, *J* 8.0 Hz, H-5), 6.44 (1H, *t*, *J* 2.0 Hz, H-4'), 3.83 (3H, *s*, OCH₃); ¹³C-NMR (125 MHz, CD₃COCD₃): 162.4 (C-5'), 159.9 (C-3'), 157.3 (C-7a), 155.0 (C-2), 152.1 (C-4), 133.2 (C-1'), 126.3 (C-3), 119.5 (C-3a), 108.9 (C-5), 105.2 (C-2'), 103.6 (C-6), 102.7 (C-4'), 102.4 (C-6'), 100.1 (C-7), 55.7 (OCH₃); EI-MS (70 eV): *m/z* (rel. int.%) 256 [M]⁺ (100), 242 (3), 227 (4), 213 (11), 197 (2), 184 (2), 168 (2), 155 (3), 139 (5), 128 (10).

3. Results and discussion

Gnetifolin M (**1**) was obtained as yellow crystals, having the molecular formula C₁₅H₁₂O₄ (by EIMS and NMR). The IR spectrum showed hydroxyl groups (3282 cm⁻¹), aromatic groups (1605, 1491 cm⁻¹). The ¹H-NMR spectrum of **1** indicated one benzofuranic proton at δ 7.27 (1H, *s*), three aromatic protons with *meta* coupling (*t*, *J* 2.0 Hz) at δ 7.00, 6.98, 6.44, three aromatic protons with *ortho* coupling at δ 7.12 (1H, *t*, *J* 8.0 Hz), δ 7.04 (1H, *d*, *J* 8.0 Hz), δ 6.68 (1H, *d*, *J* 8.0 Hz), two hydroxyl groups at δ 8.94 (1H, *s*) and δ 8.66 (1H, *s*), one methoxyl group at δ 3.83 (3H, *s*). The ¹³C-NMR spectrum of **1** showed signals of one methoxyl carbon at δ 55.7, twelve aromatic carbons and two benzofuranic carbons at δ 162.4–100.1. In the HMBC experiment, the correlations between the methoxyl group (δ_H 3.83) and C-5' (δ_C 162.4) suggested the methoxyl group was attached to C-5', which was further confirmed by the correlations among the protons at δ 3.83 (OCH₃), δ 6.98 (H-6') and δ 6.44 (H-4') in the NOESY experiment. Therefore, compound **1** was assigned to the structure of 2-(5'-methoxy-3'-hydroxyphenyl)-4-hydroxybenzofuran.

The NMR spectra of compounds **2** and **3** suggested typical structures of stilbene, which had two *trans* olefinic protons (*J* 16.3 and 16.6 Hz). As the spectral data of **2** and **3** were in good agreement with those published in the literature, the compounds **2** and **3** were elucidated as resveratrol and gnetol, respectively. The other five known compounds were also identified by detailed analysis of their NMR and EIMS spectra as well as comparison with the published data.

References

- [1] Jiangsu New Medicinal College. Zhongcaoyao dacidian. Shanghai People's Press, 1985, p. 990.
- [2] Huang KS, Wang YH, Li RL, Lin M. J Nat Prod 2000;63:86.
- [3] Lins AP, Ribeiro MN, Gottlieb OR, Gottlieb HE. J Nat Prod 1982;45:755.
- [4] Li JB, Lin M, Li SZ. Acta Pharma Sin 1991;26:437.
- [5] Lin M, Li JB, Li SZ, Yu DQ, Liang XT. Phytochemistry 1992;31:633.