

COUMARINS FROM THE BARK OF *Daphne marginata*

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The genus *Daphne* (Thymelaeaceae), including 44 species, is widely distributed in the southwest and northwest regions of China [1]. The roots or barks of most plants of this genus have been used to treat wound, bruises, and faucitis as a folk medicine in China [2]. *Daphne marginata* is an ornamental plant whose growth is restricted to the South of China. The barks of *D. marginata* were collected in Dayu (Jiangxi province, China) in March 2005, and were authenticated by Prof. Tan Ceming, Jiangxi Plantation Research Institute, China. A voucher specimen is deposited in the Department of Pharmacognosy, Second Military Medical University.

The air dried barks (7.5 kg) of *D. marginata* were extracted with 75% ethanol at room temperature. The EtOH extract was partitioned with petroleum ether, CHCl₃, EtOAc, and *n*-BuOH. Part of the EtOAc extract (50 g) was subjected to column chromatography on silica gel with gradient elution by CHCl₃–MeOH (100:1–1:1) to afford **1–9**.

The compounds were identified using UV, IR, mass, and NMR spectra, and all these data were in good agreement with the literature data [3–10]. All those compounds were isolated from *D. marginata* for the first time. The ¹³C NMR data of compounds **1**, **3**, **4**, **8**, **9** are reported in this paper for the first time.

Umbelliferone (1) (7-hydroxycoumarin), C₉H₆O₃, 162 [M]⁺, mp 226–228°C, UV (λ_{max}, MeOH, nm): 325. IR (KBr, cm⁻¹): 3100, 1660, 1585, 1500, 1110, 820, 740. ¹³C NMR (125 MHz, DMSO-d₆, δ, ppm): 102.1 (C-8), 111.2 (C-10), 111.3 (C-3), 113.1 (C-6), 129.6 (C-5), 144.4 (C-4), 155.5 (C-9), 160.4 (C-2), 161.2 (C-7) [3].

Herniarin (2) (7-methoxycoumarin), C₁₀H₈O₃, 176 [M]⁺, mp 117–118°C, UV (λ_{max}, MeOH, nm): 247, 320 [4].

Daphnetin (3) (7, 8-dihydroxycoumarin), C₉H₆O₄, 178 [M]⁺, mp 225–227°C, UV (λ_{max}, MeOH, nm): 261, 325. IR (KBr, cm⁻¹): 3500, 3050, 1680, 1570, 1490, 1320, 1290, 1000, 810. ¹³C NMR (125 MHz, DMSO-d₆, δ, ppm): 111.1 (C-3), 112.0 (C-10), 112.4 (C-6), 118.8 (C-5), 132.1 (C-8), 143.7 (C-9), 145.0 (C-4), 149.7 (C-7), 160.3 (C-2) [5].

Hydrangetin (4) (7-hydroxy-8-methoxycoumarin), C₁₀H₈O₄, 192 [M]⁺, mp 157–158°C, UV (λ_{max}, MeOH, nm): 247, 256, 320. IR (KBr, cm⁻¹): 3320, 1680, 1588, 1500, 835. ¹³C NMR (125 MHz, DMSO-d₆, δ, ppm): 56.6 (-OCH₃), 111.5 (C-3), 112.3 (C-10), 112.7 (C-6), 118.7 (C-5), 142.5 (C-9), 144.8 (C-4), 149.7 (C-7), 152.1 (C-8), 160.8 (C-2) [6].

Daphnoretin (5) (6-methoxy-7-hydroxy-3,7'-bicycoumarin), C₁₉H₁₂O₇, 352 [M]⁺, mp 244–245°C, UV (λ_{max}, MeOH, nm): 222, 265, 324, 345. IR (KBr, cm⁻¹): 3400, 1680, 1590, 1480, 1250, 820. [3, 5].

Daphneticin (6) (6-demethoxy-5''-methoxycycloleomiscosin B), C₂₀H₁₈O₈, 386 [M]⁺, mp 235–238°C, UV (λ_{max}, MeOH, nm): 242, 260, 317. IR (KBr, cm⁻¹): 3480, 3210, 1735, 1610, 1575, 1450, 1340, 1270, 835. [7].

Skimmin (7) (umbelliferone-7-*O*-β-D-glucoside), C₁₅H₁₆O₈, 324 [M]⁺, mp 219–221°C. Acid hydrolysis of **7** produced umbelliferone and *D*-glucose. IR (KBr, cm⁻¹): 3420, 2910, 2850, 1720, 1700, 1620, 1500, 1400, 1350, 1280, 1240, 1200, 1170, 1120, 1080, 1020, 840. [8].

Daphnin (8) (daphnetin-7-*O*-β-D-glucoside), C₁₅H₁₆O₉, 340 [M]⁺, mp 223–224°C, UV (λ_{max}, MeOH, nm): 258, 311. IR (KBr, cm⁻¹): 3400, 2890, 1705, 1620, 1570, 1495, 1465. Acid hydrolysis of **8** produced daphnetin and *D*-glucose.

¹³C NMR (125 MHz, DMSO-d₆, δ, ppm): 60.7 (glu:C-6), 69.7 (glu:C-4), 73.2 (glu:C-2), 75.7 (glu:C-3), 77.3 (glu:C-5), 101.8 (glu:C-1), 112.1 (C-6), 113.4 (C-3), 114.4 (C-10), 118.2 (C-5), 133.9 (C-8), 142.6 (C-9), 144.6 (C-4), 148.1 (C-7), 160.0 (C-2) [3, 9].

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Daphkoreanin (9) (daphnetin-8-*O*- β -D-glucoside), C₁₅H₁₆O₉, 340 [M]⁺, mp 223–225°C, UV (λ_{max} , MeOH, nm): 256 (sh), 326. IR (KBr, cm⁻¹): 3400, 2900, 1710, 1620, 1570, 1490, 1460. Acid hydrolysis of **9** produced daphnetin and D-glucose. ¹³C NMR (125 MHz, DMSO-d₆, δ , ppm): 60.8 (glu:C-6), 69.7 (glu:C-4), 73.9 (glu:C-2), 76.2 (glu:C-3), 77.3 (glu:C-5), 103.8 (glu: C-1), 111.7 (C-6), 112.0 (C-10), 113.4 (C-3), 124.0 (C-5), 131.0 (C-8), 144.7 (C-4), 147.7 (C-9), 153.2 (C-7), 159.9 (C-2) [9,10].

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