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CHEMICAL CONSTITUENTS FROM *Daphne pedunculata*

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The genus *Daphne* (Thymelaeaceae), including 44 species, is widely distributed in the southwest and northwest regions of China. Different classes of natural products have been isolated from these species, including coumarins, flavonoids, and diterpenoids. Some species are widely used for treating wound, bruises, and faucitis in folk medicine. It is reported that coumarins of genus *Daphne* are the most important constituents for their antiinflammation and antitumor activities [1]. The species of *Daphne pedunculata* H. F. Zhou ex C. Y. Chang is an aiophyllus arbuscular plant, and no phytochemical investigation has been reported on this plant yet. Herein, we present the study results on the chemical composition of this plant.

The leaves and stems of *D. pedunculata* were collected in Anning, Yunnan Province, China, in May 2006. The plant material was authenticated by Prof. Hanchen Zheng, Department of Pharmacognosy, Second Military Medical University. A voucher specimen (collection No. 0603) is deposited at the Herbarium of the School of Pharmacy, Shanghai Jiao Tong University, Shanghai, China.

Air-dried aerial parts of *D. pedunculata* (11.5 kg) were extracted with 70% ethanol (50 L × 3) at room temperature. The ethanol extract was dissolved in 2 L of H_2O to form a suspension and extracted successively with petroleum ether, $CHCl_3$, EtOAc, and *n*-BuOH. The $CHCl_3$ and EtOAc soluble fractions (100.0 g and 120.0 g, respectively) were subjected to a series of chromatographic techniques, such as silica gel column (200–300 mesh), Sephadex LH-20, and PTLC, yielding compounds **1**–**16**. The compounds were identified using mass and NMR spectral data, and all these data were in good agreement with the literature [2–15]. All those compounds were isolated from *D. pedunculata* for the first time.

Umbelliferone (1) (7-Hydroxycoumarin), $C_9H_6O_3$, yellow amorphous powder, mp 225–227°C; ESI-MS *m/z*: 163 $[M+H]^+$, 185 $[M+Na]^+$. The ^1H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6) data as described in [2].

Herniarin (2) (7-Methoxycoumarin), $C_{10}H_8O_3$, white amorphous powder, mp 117–118°C; ESI-MS *m/z*: 177 $[M+H]^+$. The ^1H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6) data as described in [3].

Hydrangetin (3) (7-Methoxy-8-hydroxycoumarin), $C_{10}H_8O_4$, white amorphous powder, mp 172–173°C; ESI-MS *m/z*: 215 $[M+Na]^+$. The ^1H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6) data as described in [4].

Daphnin (4) (Daphnetin-7-*O*-*β*-D-glucoside), $C_{15}H_{16}O_9$, white amorphous powder, mp 223–224°C; ESI-MS *m/z*: 363 $[M+Na]^+$. The ^1H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6) data as described in [5].

Daphkoreanin (5) (Daphnetin-8-*O*-*β*-D-glucoside), $C_{15}H_{16}O_9$, white amorphous powder, mp 223–224°C; ESI-MS *m/z*: 363 $[M+Na]^+$. The ^1H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6) data as described in [5].

Daphnorin (6) (Daphnoretin-7-*O*-*β*-D-glucoside), $C_{25}H_{22}O_{12}$, white amorphous powder, mp 202–204°C; ESI-MS *m/z*: 537 $[M+Na]^+$; ^1H NMR (500 MHz, pyridine-d_5, δ, ppm, J/Hz): 3.78 (3H, s, 6-OCH_3), 4.21–4.91 (6H, m, Glc-H-2–6), 5.83 (1H, d, J = 7.0, Glc-H-1), 6.36 (1H, d, J = 9.0, H-3′), 7.14 (1H, dd, J = 8.0, 2.0, H-6′), 7.15 (1H, s, H-8), 7.18 (1H, d, J = 2.0, H-8′), 7.49 (1H, d, J = 8.0, H-5′), 7.58 (1H, s, H-5), 7.68 (1H, d, J = 9.0, H-4′), 7.74 (1H, s, H-4); ^{13}C NMR (125 MHz, pyridine-d_5, δ): 56.0 (6-OCH_3), 70.8 (Glc-C-5), 74.4 (Glc-C-3), 78.2 (Glc-C-4), 78.8 (Glc-C-6), 101.7 (C-8′), 104.0 (Glc-C-2), 104.5 (C-8), 106.4 (Glc-C-1), 109.3 (C-5), 112.3 (C-10), 113.6 (C-6′), 114.4 (C-3′), 114.8 (C-10′), 129.6 (C-5′), 129.6 (C-4), 137.7 (C-3), 143.1 (C-4′), 147.3 (C-6), 147.4 (C-7), 150.2 (C-9), 155.6 (C-9′), 157.0 (C-7′), 159.9 (C-2), 160.0 (C-2′) [6].

Apigenin (7) (4′,5,7-Trihydroxyflavone), $C_{15}H_{10}O_5$, white amorphous powder, mp 352–354°C; ESI-MS *m/z*: 271 $[M+H]^+$. The ^1H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6) data as described in [7].

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Luteolin (8) (3′,4′,5,7-Tetrahydroxyflavone), $C_{15}H_{10}O_6$, yellow amorphous powder, mp 328–330°C; ESI-MS *m/z*: 287 $[M+H]^+$. The ^1H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6) data as described in [8].

Luteolin-7,3′-dimethylether-5-*O*-β-D-glucoside (9), $C_{23}H_{24}O_{11}$, yellow amorphous powder, mp 264–266°C; ESI-MS *m/z*: 499 $[M+Na]^+$. The ^1H NMR (500 MHz, DMSO-d_6, δ, ppm, J/Hz): 3.15–3.74 (6H, m, Glc-H-2–6), 3.87 (6H, s, 7,3′-OCH_3), 4.74 (1H, d, J = 7.0, Glc-H-1), 6.83 (1H, s, H-3), 6.87 (1H, d, J = 2.0, H-6), 6.91 (1H, d, J = 8.0, H-5′), 7.11 (1H, d, J = 2.0, H-8), 7.57 (1H, s, H-2′), 7.61 (1H, d, J = 8.0, H-6′), 9.91 (1H, s, 4′-OH); ^{13}C NMR (125 MHz, DMSO-d_6, δ): 55.9 (3′-OCH_3), 56.0 (7-OCH_3), 60.9 (Glc-C-6), 69.9 (Glc-C-4), 73.5 (Glc-C-2), 75.7 (Glc-C-3), 77.6 (Glc-C-5), 96.6 (C-8), 103.5 (C-6), 104.2 (Glc-C-1), 106.1 (C-3), 109.2 (C-10), 110.0 (C-2′), 115.7 (C-5′), 120.0 (C-6′), 121.4 (C-1′), 147.9 (C-3′), 150.3 (C-4′), 158.1 (C-5), 158.4 (C-9), 161.2 (C-2), 163.4 (C-7), 176.9 (C-4) [9].

Yuanhuanin (10) (Luteolin-7-methylether-5-*O*-β-D-glucoside), $C_{22}H_{22}O_{11}$, yellow amorphous powder, mp 266–268°C; ESI-MS *m/z*: 485 $[M+Na]^+$. The ^1H NMR (500 MHz, DMSO-d_6, δ, ppm, J/Hz): 3.13–3.74 (6H, m, Glc-H-2–6), 3.91 (3H, s, 7-OCH_3), 4.74 (1H, d, J = 7.0, Glc-H-1), 6.61 (1H, s, H-3), 6.87 (1H, d, J = 8.0, H-5′), 6.91 (1H, d, J = 3.0, H-6), 7.04 (1H, d, J = 3.0, H-8), 7.37 (1H, s, H-2′), 7.39 (1H, d, J = 8.0, H-6′), 9.30 (1H, s, 3′-OH), 9.88 (1H, s, 4′-OH); ^{13}C NMR (125 MHz, DMSO-d_6, δ): 56.0 (7-OCH_3), 60.9 (Glc-C-6), 69.9 (Glc-C-4), 73.6 (Glc-C-2), 75.7 (Glc-C-3), 77.6 (Glc-C-5), 96.6 (C-8), 103.5 (C-6), 103.8 (Glc-C-1), 105.9 (C-3), 109.2 (C-10), 113.0 (C-2′), 115.9 (C-5′), 118.6 (C-6′), 121.4 (C-1′), 145.7 (C-3′), 149.3 (C-4′), 158.1 (C-5), 158.4 (C-9), 161.6 (C-2), 163.4 (C-7), 176.9 (C-4) [9].

Glucogenkwanin (11) (Genkwanin-5-*O*-β-D-glucoside), $C_{22}H_{22}O_{10}$, yellow amorphous powder, mp 273–274°C; ESI-MS *m/z*: 469 $[M+Na]^+$. The ^1H NMR (500 MHz, DMSO-d_6, δ, ppm, J/Hz): 3.13–3.74 (6H, m, Glc-H-2–6), 3.87 (3H, s, 7-OCH_3), 4.74 (1H, d, J = 7.0, Glc-H-1), 6.72 (1H, s, H-3), 6.93 (1H, d, J = 3.0, H-6), 6.96 (2H, m, H-3′, 5′), 7.08 (1H, d, J = 3.0, H-8), 7.96 (2H, m, H-2′, 6′), 10.30 (1H, s, 4′-OH); ^{13}C NMR (125 MHz, DMSO-d_6, δ): 56.0 (7-OCH_3), 60.9 (Glc-C-6), 69.9 (Glc-C-4), 73.6 (Glc-C-2), 75.7 (Glc-C-3), 77.6 (Glc-C-5), 96.6 (C-8), 103.5 (C-6), 103.8 (Glc-C-1), 105.9 (C-3), 109.2 (C-10), 113.0 (C-2′), 115.9 (C-5′), 118.6 (C-6′), 121.4 (C-1′), 145.7 (C-3′), 149.3(C-4′), 158.1 (C-5), 158.4 (C-9), 161.6 (C-2), 163.4 (C-7), 176.9 (C-4) [10].

Yuankanin (12), $C_{27}H_{30}O_{14}$, white amorphous powder, mp 185–188°C; ESI-MS *m/z*: 601 $[M+Na]^+$. The ^1H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6) data as described in [11].

Horsfieldin (13), $C_{20}H_{20}O_6$, white amorphous powder, mp 164–165°C; EI-MS *m/z*: 356 $[M]^+$. The ^1H NMR (500 MHz, $CDCl_3$, δ, ppm, J/Hz): 3.07 (1H, m, H-8′), 3.33 (2H, m, H-9), 3.86 (2H, m, H-9′), 3.94 (3H, s, 4′-OCH_3), 4.15 (1H, d, J = 9.0, H-8), 4.49 (1H, d, J = 6.0, H-7), 4.86 (1H, d, J = 6.0, H-7′), 5.97 (2H, s, OCH_2O), 6.77 (1H, d, J = 8.0, H-5), 6.78 (1H, d, J = 8.0, 2.0, H-6), 6.86 (1H, dd, J = 8.0, 2.0, H-6′), 6.89 (1H, d, J = 2.0, H-2), 6.90 (1H, d, J = 8.0, H-5′), 6.99 (1H, d, J = 2.0, H-2′); ^{13}C NMR (125 MHz, $CDCl_3$, δ): 52.2 (C-8′), 54.6 (C-8), 56.0 (4′-OCH_3), 69.8 (C-9), 71.7 (C-9′), 82.1 (C-7′), 85.9 (C-7), 101.1 (OCH_2O), 106.5 (C-2′), 108.2 (C-5′), 108.6 (C-2), 114.3(C-5), 119.0 (C-6′), 119.5 (C-6), 132.3 (C-1), 135.2 (C-1′), 145.6 (C-3), 146.4 (C-4), 147.2 (C-4′), 148.0 (C-3′) [12].

Daphnenone (14) (1-(4-Hydroxyphenyl)-5-phenyl-2-penten-1-one), $C_{17}H_{16}O_2$, white amorphous powder, mp 151–153°C; EI-MS *m/z*: 252 $[M]^+$. The ^1H NMR (500 MHz, CD_3OD, δ, ppm, J/Hz): 1.83 (2H, m, H-4), 2.71 (2H, m, H-5), 3.08 (2H, m, H-2), 4.17 (1H, m, H-3), 6.82 (2H, d, J = 7.0, H-3′, 5′), 7.14 (1H, m, H-4″), 7.18 (4H, m, H-2″, 3″, 5″, 6″), 7.86 (2H, d, J = 7.0, H-2′, 6′), 10.29 (1H, s, 4′-OH); ^{13}C NMR (125 MHz, CD_3OD, δ): 32.9 (C-5), 40.3 (C-4), 46.6 (C-2), 68.9 (C-3), 116.2 (C-3′, 5′), 126.7 (C-4″), 129.4 (C-2″, 3″, 5″, 6″), 130.4 (C-1′), 132.0 (C-2′, 6′), 143.4 (C-1″), 163.9 (C-4′), 200.0 (C-1) [13].

***p*-Hydroxybenzoic acid (15),** $C_7H_6O_3$, white needles, mp 103–104°C; ESI-MS *m/z*: 139 $[M+H]^+$. The ^1H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6) data as described in [14].

***n*-Octacosanol (16)**, $C_{28}H_{58}O$, white amorphous powder, mp 81–83°C; EI-MS *m/z*: 420 $[M]^+$. The ^1H NMR (500 MHz, DMSO-d_6) data as described in [15].

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