FLAVONOIDS FROM *Rhododendron decorum*

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Rhododendron decorum Fr., a well-known poisonous plant, is widely distributed in the southwestern region of China. *R. decocum* is an evergreen shrub or tree.The dried roots and leaves of this plant have been used as Chinese folk medicine for relieving pain, clearing heat and removing dampness, traumatic injury, invigorating blood, and resolving blood-stasis [1]. Previous studies reported that four grayanane diterpenoids, grayanotoxins I, IV, VIII, and XXI, were isolated from the leaves of this plant [2, 3]. In continuation of the search for biologically active constituents, nine flavonoids were firstly isolated from this plant.

The aerial parts of *R. decorum* were collected in HeQing, Yunnan Province, People's Republic of China, in May, 2006 and was authenticated by Prof. Lishan Xie, Kunming Botanic Garden, Chinese Academy of Sciences. The air-dried and powdered aerial parts of *R. decorum* (10 kg) were extracted with 95% EtOH (3×50 L) three times at room temperature. The extract was evaporated under vacuum to afford a residue extract (1.5 kg), which was partitioned with petroleum ether, $CHCl_3$, EtOAc, and *n*-BuOH successfully. The EtOAc extract (250 g) was chromatographed on the series of chromatographs, such as silica gel column, Sephadex LH-20, and prep. HPLC to afford nine flavonoids **1–9**.

Quercetin (1): $C_{15}H_{10}O_7$, yellow needles, mp 313°C; ESI-MS *m/z* 301.1 $[M–H]^-$. Identification of compound **1** was performed by ^{1}H NMR data with those reported in the [4].

Myricetin (2): $C_{15}H_{10}O_8$, yellow crystal, mp 326°C; ESI-MS *m/z* 317.0 $[M–H]^-$. Identification of compound **2** was performed by ^{1}H NMR data with those reported in the [5].

Dihydromyricetin (3): yellow amorphous powder, mp 245–247°C; ESI-MS *m/z* 319.1 $[M–H]^-$; ^{1}H NMR (500 MHz, CD_3OD, δ, J/Hz): 4.47 (1H, d, J = 11.5, H-3), 4.84 (1H, d, J = 11.5, H-2), 5.89 (1H, d, J = 2.0, H-6), 5.92 (1H, d, J = 2.0, H-8), 6.54 (2H, s, H-2′, 6′); ^{13}C NMR (125 MHz, CD_3OD, δ): 73.6 (C-3), 85.2 (C-2), 96.3 (C-8), 97.3 (C-6), 101.8 (C-10), 108.1 (C-2′, 6′), 129.1 (C-1′), 134.9 (C-4′), 146.8 (C-3′, 5′), 164.4 (C-9), 165.2 (C-5), 168.6 (C-7), 198.2 (C-4) [6].

Dihydroquercetin (4): yellow amorphous powder, mp 210–212°C; ESI-MS *m/z* 303.1 $[M–H]^-$; ^{1}H NMR (500 MHz, CD_3OD, δ, J/Hz): 4.50 (1H, d, J = 11.0, H-3), 4.90 (1H, d, J = 11.0, H-2), 5.89 (1H, d, J = 2.0, H-6), 5.92 (1H, d, J = 2.0, H-8), 6.80 (1H, d, J = 8.0, H-5′), 6.85 (1H, dd, J = 8.0, 2.0, H-6′), 6.96 (1H, d, J = 2.0, H-2′); ^{13}C NMR (125 MHz, CD_3OD, δ): 73.7 (C-3), 85.1 (C-2), 96.3 (C-8), 97.3 (C-6), 101.8 (C-10), 115.9 (C-5′), 116.1 (C-2′), 120.9 (C-6′), 129.9 (C-1′), 146.3 (C-3′), 147.2 (C-4′), 164.5 (C-9), 165.3 (C-5), 168.7 (C-7), 198.4 (C-4) [7].

Dihydrokaempferol (5): white needles, mp 204–207°C; ESI-MS *m/z* 287.1 $[M–H]^-$; ^{1}H NMR (500 MHz, CD_3OD, δ, J/Hz): 4.54 (1H, d, J =12.0, H-3), 4.98 (1H, d, J = 12.0, H-2), 5.88 (1H, d, J = 2.0, H-6), 5.93 (1H, d, J = 2.0, H-8), 6.83 (2H, d, J = 8.0, H-3′, 5′), 7.35 (2H, d, J = 8.0, H-2′, 6′); ^{13}C NMR (125 MHz, CD_3OD, δ): 73.7 (C-3), 85.0 (C-2), 96.3 (C-8), 97.3 (C-6), 101.9 (C-10), 116.2 (C-3′, 5′), 129.3 (C-1′), 130.4 (C-2′, 6′), 159.2 (C-4′), 164.6 (C-9), 165.3 (C-5), 168.7 (C-7), 198.5 (C-4) [8].

(+)-Catechin (6): white needles, mp 175–176°C; $[\alpha]_D^{20}$ +15.0° (*c* 0.13, MeOH); ESI-MS *m/z* 289.1 $[M–H]^-$. Identification of compound **6** was performed by ^{1}H NMR data with those reported in the [9].

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(–)-Epicatechin (7): white needles, mp 249–251°C; $[\alpha]_D^{20}$ –60.2° (*c* 0.23, MeOH); ESI-MS *m/z* 289.1 $[M–H]^-$. Identification of compound **7** was performed by ^{1}H NMR data with those reported in the [10].

Quercetin-3-*O*-β-D-glucopyranoside (8): yellow powder, mp 236–238°C; ESI-MS *m/z* 463.1 $[M–H]^-$; ^{1}H NMR (500 MHz, DMSO-d_6, δ, J/Hz): 3.05–3.90 (6H, m, Glu-H), 5.15 (1H, d, J = 7.0, Glu-H-1), 6.18 (1H, d, J = 2.0, H-6), 6.35 (1H, d, J = 2.0, H-8), 6.85 (1H, d, J = 8.0, H-5′), 7.55 (1H, d, J = 2.0, H-2′), 7.60 (1H, dd, J = 8.0, 2.0 Hz, H-6′); ^{13}C NMR (125 MHz, DMSO-d_6, δ): 61.6 (Glu-C-6), 70.0 (Glu-C-4), 74.1 (Glu-C-2), 76.6 (Glu-C-3), 77.6 (Glu-C-5), 93.9 (C-8), 98.9 (C-6), 101.2 (Glu-C-1), 104.3 (C-10), 115.2 (C-2′), 116.4 (C-5′), 121.1 (C-1′), 121.9 (C-6′), 133.7 (C-3), 144.9 (C-3′), 148.5 (C-4′), 156.7 (C-2), 156.8 (C-9), 161.2 (C-5), 164.2 (C-7), 177.7 (C-4) [11].

Quercetin-3-*O*-β-D-galactopyranoside (9): yellow powder, mp 246–248°C; ESI-MS *m/z* 463.1$[M–H]^-$; ^{1}H NMR (500 MHz, DMSO-d_6, δ, J/Hz): 3.29–3.64 (6H, m, Gal-H), 5.37 (1H, d, J = 7.7, Gal-H-1), 6.20 (1H, d, J = 2.1, H-6), 6.40 (1H, d, J = 2.1, H-8), 6.81 (1H, d, J = 8.0, H-5′), 7.51 (1H, d, J = 2.2, H-2′), 7.66 (1H, dd, J = 8.0, 2.1 Hz, H-6′); ^{13}C NMR (125 MHz, DMSO-d_6, δ): 60.1 (Gal-C-6), 67.9 (Gal-C-4), 71.2 (Gal-C-2), 73.2 (Gal-C-3), 75.8 (Gal-C-5), 93.5 (C-8), 98.7 (C-6), 101.8 (Gal-C-1), 103.9 (C-10), 115.2 (C-2′), 115.9 (C-5′), 121.1 (C-1′), 133.5 (C-3), 144.8 (C-3′), 148.5 (C-4′), 156.3 (C-2), 161.2 (C-5), 164.1 (C-7), 177.5 (C-4) [11].

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