FLAVONOIDS FROM RHIZOMES OF *Veratrum dahuricum*

Jian Tang,[1] Hui-Liang Li[2], Yong-Li Li[2], and Wei-Dong Zhang[1,2*] UDC 547.972

Previous studies on chemical constituents mainly focused on steroidal alkaloids of *Veratrum* plants. To date, the isolation of 3,5-dihydroxy-7-methoxyflavone and 3,5,7-trihydroxyflavone from *Veratrum lobelianum* Bernh. [1] and apigenin-7-*O*-glucoside, luteolin-7-*O*-glucoside, and chrysoeriol-7-*O*-glucoside from *Veratrum grandiflorum* has been reported [2]. Herein, we report ten flavonoids isolated from *Veratrum dahuricum* for the first time.

The alcoholic extracts of rhizomes of *Veratrum dahuricum* were concentrated *in vacuo* to an aqueous residue, which was successively partitioned with petroleum ether, chloroform, ethyl acetate, and *n*-butanol. The chloroform extract (125 g) was subjected to silica gel column chromatography, eluting with the chloroform and the gradient $CHCl_3/CH_3OH$, and the fractions obtained were submitted to column chromatography over Sephadex LH-20 to afford compounds **1** (40 mg), **2** (8 mg), **3** (12 mg), **4** (9 mg), **5** (8 mg). The ethyl acetate extract was purified repeatedly over silica gel and ODS column chromatography to give **6** (15 mg), **7** (7 mg). Compounds **8** (9 mg), **9** (6.5 mg), and **10** (9 mg) were obtained from *n*-butanol extract by polyamide and ODS column chromatography.

On the basis of UV, PMR (600 MHz), ^{13}C NMR (150 MHz), NOESY, ^{1}H–^{13}C HMBC, HMQC, and mass spectra of ten flavonoids, these compounds were determined as eupatilin (**1**) [3], pectolinarigenin (**2**) [4], acacetin (**3**) [4], 5-hydroxy-4′,7-dimethoxyflavone (**4**) [5], 7,3′,4′-trimethylluteolin (**5**) [6], 3-methoxyl isorhamnetin (**6**) [7], quercetin-7-rhamnoside (**7**) [8], isoquercitrin (**8**) [9], acacetin-7-glucoside (**9**) [10], and quercetin-3-sophoroside (baimaside, **10**) [9].

Eupatilin (1): $C_{18}H_{16}O_7$, yellow needles (acetone), mp 235 – 237°C. UV (MeOH, λ_{max}, nm): 275, 339. IR (KBr, ν, cm^{-1}): 3002, 1655, 1618, 1562, 1577, 1465, 1380, 1265, 816. ESIMS: 343 $[M-H]^-$, 328 $[M-H-Me]^-$, 313 $[M-H-2Me]^-$, 298 $[M-H-Me]^-$. PMR (600 MHz, $CDCl_3$, δ, ppm, J/Hz): 6.63 (1H, s, H-3), 6.47 (1H, s, H-8), 7.35 (1H, d, J = 1.8, H-2′), 6.90 (1H, d, J = 7.8, H-5′), 7.33 (1H, dd, J = 8.4, 1.8, H-6′), 3.85 (3H, s, 6-OCH_3), 3.89 (3H, s, 3′-OCH_3), 4.21 (3H, s, 4′-OH_3). ^{13}C NMR (150 MHz, $CDCl_3$, δ, ppm): 163.3 (C-2), 107.1 (C-3), 180.7 (C-4), 150.7 (C-5), 134.3 (C-6), 157.5 (C-7), 93.4 (C-8), 147.3 (C-9), 112.0 (C-10), 126.0 (C-1′), 112.9 (C-2′), 146.3 (C-3′), 146.6 (C-4′), 114.9 (C-5′), 124.9 (C-6′), 62.6 (OCH_3), 61.9 (OCH_3), and 55.9 (OCH_3).

5-Hydroxy-4′,7-dimethoxyflavone (4): $C_{17}H_{14}O_5$, yellow needles (methanol), mp 172–175°C. UV (MeOH, λ_{max}, nm): 270, 328. IR (KBr, ν, cm^{-1}): 3089, 2950, 2847, 1670, 1606, 1511, 1446, 1385, 1338, 1274, 833. ESIMS: 299 $[M+H]^+$, 297 $[M-H]^-$, 595 $[2M-H]^-$, 284 $[M+H-Me]^+$. PMR (600 MHz, DMSO-d_6, δ, ppm, J/Hz): 6.63 (1H, s, H-3), 6.32 (1H, d, J = 1.8, H-6), 6.66 (1H, d, J = 1.8, H-8), 7.77 (2H, d, J = 8.4, 1.8, H-2′,6′), 6.86 (1H, d, J = 9, H-3′, 5′), 3.90 (3H, s, 7-OCH_3), 3.88 (3H, s, 4′-OCH_3), 12.45 (1H, s, 5-OH). ^{13}C NMR (150 MHz, DMSO-d_6, δ, ppm): 167.8 (C-2), 104.3 (C-3), 178.7 (C-4), 159.1 (C-5), 94.2 (C-6), 168.5 (C-7), 89.7 (C-8), 145.5 (C-9), 110.3 (C-10), 122.9 (C-1′), 132.9 (C-2′,6′), 115.9 (C-3′, 5′), 158.7 (C-4′), 56.3 (7-OCH_3), 56.0 (4′-OCH_3).

7,3′,4′-Trimethylluteolin (5): $C_{18}H_{16}O_6$, yellow crystals (methanol), mp 167 – 169°C. UV (MeOH, λ_{max}, nm): 210, 244, 340. IR (KBr, ν, cm^{-1}): 3045~2900, 2835, 1660, 1625, 1505, 1446, 810. ESIMS: 329 $[M+H]^+$, 327 $[M-H]^-$, 314 $[M+H-Me]^+$. PMR (600 MHz, DMSO-d_6, δ, ppm, J/Hz): 6.64 (1H, s, H-3), 6.32 (1H, d, J = 1.8, H-6), 6.68 (1H, d, J = 1.8, H-8), 7.51 (1H, d, J = 1.8, H-2′), 6.87 (1H, d, J = 7.8, H-5′), 7.42 (1H, dd, 8.4, 1.8, H-6′), 3.91 (3H, s, 7-OCH_3), 3.88 (3H, s, 3′-OCH_3), 3.77 (3H, s, 4′-OCH_3), 12.60 (1H, s, 5-OH). ^{13}C NMR (150 MHz, DMSO-d_6, δ, ppm): 163.8 (C-2), 104.3 (C-3), 181.7 (C-4), 162.1 (C-5), 98.0 (C-6), 165.5 (C-7), 92.4 (C-8), 150.5 (C-9), 105.3 (C-10), 123.9 (C-1′), 108.0 (C-2′), 149.1 (C-3′), 152.3 (C-4′), 111.2 (C-5′), 121.0 (C-6′), 55.4 (7-OCH_3), 56.5 (3′-OCH_3), 56.0 (4′-OCH_3).

1) School of Pharmacy, Shanghai Jiao Tong University, Shanghai 200240, P. R. China; 2) Department of Phytochemistry, School of Pharmacy, Second Military Medical University, Shanghai 200433, P. R. China; tel: +86 21 25070386; fax: +86 21 25070386, wdzhangy@hotmail.com. Published in Khimiya Prirodnykh Soedinenii, No. 6, pp. 577-578, November-December, 2007. Original article submitted September 6, 2006.

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Acacetin-7-glucoside (9): $C_{22}H_{22}O_{10}$, yellow crystals (methanol), mp 260–263°C. UV (MeOH, λ_{max}, nm): 268, 325. IR (KBr, ν, cm^{-1}): 3428, 3102, 1657, 1610, 1579, 1498, 1092, 980, 830, 772. ESIMS: 469 [M+Na]+, 915 $[2M+Na]^+$, 445 $[M-H]^-$, 891 $[2M-H]^-$, 283 $[M-H-Glc]^-$, 283 $[M-H-Glc]^-$, 307 $[M+Na-Glc]^+$. PMR (600 MHz, DMSO-d_6, δ, ppm, J/Hz): 6.95 (1H, s, H-3), 6.28 (1H, d, J = 1.8, H-6), 6.70 (1H, d, J = 2.4, H-8), 7.92 (2H, d, J = 8.4, H-2′, 6′), 7.01 (2H, d, J = 9, H-3′, 5′), 3.90 (3H, s, 4′-OCH_3), 5.12 (1H, d, J = 7.2, Glc-1), 3.30–3.75 (6H, Glc), 12.86 (1H, s, 5-OH). ^{13}C NMR (150 MHz, acetone-d_6, δ, ppm): 164.5 (C-2), 104.1 (C-3), 182.1 (C-4), 161.6 (C-5), 98.6 (C-6), 165.6 (C-7), 92.3 (C-8), 150.8 (C-9), 106.2 (C-10), 124.0 (C-1′), 130.7 (C-2′, 6′), 116.1 (C-3′,5′), 158.4 (C-4′), 56.2 (4′-OCH_3), 100.3 (Glc-1), 73.8 (Glc-2), 76.6 (Glc-3), 70.0 (Glc-4), 77.3 (Glc-5), 60.8 (Glc-6).

Quercetin-3-sophoroside (baimaside, 10): $C_{27}H_{30}O_{17}$, yellow needles (methanol), mp 203–205°C. UV (MeOH, λ_{max}, nm): 255, 354. IR (KBr, ν, cm^{-1}): 3432, 1665, 1598, 1560, 1491, 1359, 1270, 1079, 982, 834. ESIMS: 469 $[M+Na]^+$, 915 $[2M+Na]^+$, 445 $[M-H]^-$, 891 $[2M-H]^-$, 283 $[M-H-Glc]^-$, 307 $[M-Na-Glc]^+$. PMR (600 MHz, DMSO-d_6, δ, ppm, J/Hz): 6.20 (1H, d, J = 1.8, H-6), 6.40 (1H, d, J = 1.8, H-8), 7.56 (1H, s, H-2′), 7.61 (1H, d, J = 8.4, H-6′), 6.84 (1H, d, J = 9, H-5′), 5.48 (1H, d, J = 7.2, Glc), 4.58 (1H, d, J = 7.2, Glc-1′), 12.26 (1H, s, 5-OH), 10.02 (1H, s, OH), 9.32 – 9.45 (2H, OH). ^{13}C NMR (150 MHz, DMSO-d_6, δ, ppm): 156.0 (C-2), 132.3 (C-3), 178.0 (C-4), 161.3 (C-5), 98.6 (C-6), 163.4 (C-7), 93.6 (C-8), 156.1 (C-9), 103.7 (C-10), 121.1 (C-1′), 115.7 (C-2′), 144.3 (C-3′), 148.2 (C-4′), 116.0 (C-5′), 121.4 (C-6′), 98.6 (Glc-1), 82.4 (Glc-2), 76.6 (Glc-3), 69.9 (Glc-4), 76.4 (Glc-5), 60.9 (Glc-6), 102.9 (Glc-1′), 74.4 (Glc-2′), 77.1 (Glc-3′), 69.9 (Glc-4′), 77.0 (Glc-5′), 60.8 (Glc-6′).

All compounds were isolated from *Veratrum dahuricum* for the first time.

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