Chemistry of Natural Compounds, Vol. 46, No. 3, 2010

PHENOLIC COMPOUNDS FROM THE AERIAL PART OF *Scutellaria orientalis*

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UDC 547.972

The tincture of aerial part of the perennial plant *Scutellaria orientalis* L. (Lamiaceae) exhibits experimental hypotensive and sedative properties whereas the plaster is used for tumors [1].

Previous investigations [2, 3] have found different flavonoid compositions for the plant, which prompted a study of *S. orientalis* L. growing near the village Baberd (Artashat Region, Armenia).

Air-dried aerial part of the plant (580 g) that was collected during budding–flowering was soaked on a water bath (15 min). The aqueous tincture was extracted with $CHCl_3$. The solvent was vacuum distilled. The residue (2.4 g) was loaded on silica gel KSK (120/160 mesh) and L (40/100 mesh) columns with elution by $CHCl_3$:MeOH (0→4%). Column chromatography produced the flavones (IR spectrum, orange cyanidin reaction) wogonin (**1**), chrysin (**2**), a mixture of 2- and 2′-methoxychrysin (**3**), baicalein (**4**), and apigenin (**5**).

Wogonin (5,7-dihydroxy-8-methoxyflavone) (1), yellow needle-like crystals (~84 mg), $C_{16}H_{12}O_5$, mp 201–203°C ($CHCl_3$:MeOH). UV spectrum [MeOH, λ_{max} ratio of intensities (r.i.), nm]: 248sh (0.41), 276 (1.00), 316 (0.37), 354sh (0.14) with diagnostic additives (d.a.) agreed with the literature [4]. Mass spectrum (EI, 70 eV, *m*/*z*, I_{rel}, %): 284 (89) $[M]^+$, 269 (100) $[M - CH_3]^+$, 182 (16) $[A_1]^+$, 181 (18) $[A_1 - H]^+$, 105 (6) $[B_2]^+$, 102 (12) $[B_1]^+$.

PMR spectrum (300 MHz, DMSO-d_6, CCl_4, 1:3, δ, ppm): 3.88 (3H, s, MeO-8), 6.25 (1H, s, H-6), 6.77 (1H, s, H-3), 7.55 (3H, m, H-3′, H-4′, H-5′), 8.01 (2H, m, H-2′, H-6′), 10.31 (1H, br., HO-7), 12.31 (1H, s, HO-5). ^{13}C NMR spectrum (75 MHz): 60.4 (MeO-8), 99.0 (C-6), 103.6 (C-10), 104.8 (C-3), 125.7 (C-2′, C-6′), 128.5 (C-3′, C-5′), 130.9 (C-2′), 131.0 (C-4′), 131.1 (C-8), 149.2 (C-9), 156.4 (C-5), 157.1 (C-7), 162.4 (C-2), 181.4 (C-4).

Chrysin (5,7-dihydroxyflavone) (2), light-yellow fine crystalline compound (~176 mg), $C_{15}H_{10}O_4$, mp 283–284°C ($CHCl_3$:MeOH). UV spectrum [MeOH, λ_{max} (r.i.), nm]: 247sh (0.54), 269 (1.00), 317 (0.47), with d.a. agreed with the literature [4]. Mass spectrum (*m*/*z*, I_{rel}, %): 254 (100) $[M]^+$, 226 (16), 153 (4) $[A_1 + H]^+$, 152 (20) $[A_1]^+$, 105 (5) $[B_2]^+$, 102 (7) $[B_1]^+$. PMR spectrum (300 MHz, DMSO-d_6, CCl_4, 1:3, δ, ppm, J/Hz): 6.16 (1H, d, J = 2.0, H-6), 6.38 (1H, d, J = 2.0, H-8), 6.73 (1H, s, H-3), 7.49-7.54 (3H, m, H-3′, H-4′, H-5′), 7.94-7.98 (2H, m, H-2′, H-6′), 10.43 (1H, br., HO-7), 12.62 (1H, s, HO-5). ^{13}C NMR spectrum (75 MHz): 93.5 (C-8), 98.9 (C-6), 103.9 (C-10), 105.1 (C-3), 125.9 (C-2′, C-6′), 128.5 (C-3′, C-5′), 131.02 (C-4′), 131.03 (C-1′), 157.3 (C-9), 161.7 (C-5), 162.6 (C-2), 164.3 (C-7), 181.4 (C-4).

Mixture of 2- and 2′-methoxychrysin (5,7-dihydroxy-2′-methoxyflavone) (3). Mass spectrum of **2** and **3** mixture (**3** ions given) (*m*/*z*, I_{rel}, %): 284 (37) $[M]^+$, 153 (19) $[A_1 + H]^+$, 152 (22) $[A_1]^+$, 135 (7) $[B_2]^+$, 121 (9), 118 (8) $[B_1 - CH_2]^+$, 117 (6) $[B_1 - CH_3]$+, 107 (5) $[B_2 - CO]^+$, $C_{16}H_{12}O_5$. PMR spectrum (300 MHz, DMSO-d_6, CCl_4, 1:3, δ, ppm, J/Hz) of **2** and **3** mixture (data for **3** given, ~37% of the mixture): 3.98 (3H, s, MeO-2′), 6.14 (1H, d, J = 2.1, H-6), 6.31 (1H, d, J = 2.1, H-8), 6.78 (1H, s, H-3), 7.08 (1H, td, J_1 = 7.5, J_2 = 1.1, H-5′), 7.12 (1H, dd, J_1 = 8.5, J_2 = 0.7, H-3′), 7.47 (1H, ddd, J_1 = 8.5, J_2 = 7.5, J_3 = 1.8, H-4′), 7.82 (1H, dd, J_1 = 7.8, J_2 = 1.8, H-6′), 10.36 (1H, m, HO-7), 12.67 (1H, s, HO-5).

Baicalein (5,6,7-trihydroxyflavone) (4), dark-green clusters (~20 mg), $C_{15}H_{10}O_5$, mp 265–266°C ($CHCl_3$:MeOH). Positive Barghellina test for three vicinal hydroxyls. UV spectrum [MeOH, λ_{max} (r.i.), nm]: 246 (0.80), 282 (1.00), 325 (0.86), with d.a. agreed with the literature [4, 5]. Mass spectrum (*m*/*z*, I_{rel}, %): 270 (100) $[M]^+$, 269 (11) $[M - H]^+$, 242 (6) $[M - CO]^+$, 241 (8) $[M - COH]^+$, 169 (5) $[A_1 + H]^+$, 168 (25) $[A_1]^+$, 112 (12) 105 (9) $[B_2]^+$, 102 (11) $[B_1]^+$. PMR spectrum (300 MHz, DMSO-d_6, CCl_4, 1:3, δ, ppm): 6.55 (1H, s, H-8), 6.70 (1H, s, H-3), 7.19-7.54 (3H, m, H-3′, H-4′, H-5′), 7.96 (2H, m, H-2′, H-6′), 8.49 (1H, br., HO-6), 9.95 (1H, br., HO-7), 12.52 (1H, s, HO-5).

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 0009-3130/10/4603-0466

Apigenin (5,7,4′-trihydroxyflavone) (5), colorless finely crystalline compound (~10 mg), $C_{15}H_{10}O_5$, mp 345–347°C (MeOH), mixed mp of **5** with an authentic sample of apigenin was not depressed.

Rechromatography of the nonpolar fraction by column chromatography over silica gel L (40/100 mesh) with elution by $CHCl_3$:MeOH (1%) isolated a fraction containing a mixture of vanillin (4-hydroxy-3-methoxybenzaldehyde) (**6**) (30%) and acetovanillone (4-hydroxy-3-methoxyacetophenone) (**7**), the structures of which were established based on spectroscopic data of the native products and products of chemical transformations of the mixture (oximes and acetates).

The studies confirmed that plants of the genus *Scutellaria* are polymorphic. The aerial part of *S. orientalis* L. growing near Baberd (Armenia) has a different flavonoid composition than that in the literature [2, 3]. Column chromatography and TLC (Silufol UV-254, $CHCl_3$:MeOH, 19:1) both indicated that the main compound in the $CHCl_3$ residue of *S. orientalis* (Baberd) was chrysin (**2**), which did not occur in the subterrean part of the plant [2] and which was not the main constituent of the aerial and subterrean parts of the plant [3]. The contents of **1** and **4** were quantitatively much lower than chrysin (**2**) in *S. orientalis* (Baberd). Furthermore, no mention of **3**, **6**, and **7** were made previously [2, 3]. These data suggest a different chemotaxonomy for *S. orientalis* growing near Baberd (Armenia).

The variety of surface flavonoids produced by the plant, including the methoxylated ones, agreed with the hypothesis [6] about an increased content of methoxylated flavonoids due to the increased intensity of UV radiation that produced low-wavelength shifts, one of the protective mechanisms of the plant to the destructive action of UV-B radiation (280–315 nm [7]). The isolation from the plant of baicalein, apigenin, wogonin, and chrysin, which have UV absorption bands at 282, 302, 316, and 317 nm, respectively, also agrees with this hypothesis.

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