Chemistry of Natural Compounds, Vol. 48, No. 4, September, 2012 [Russian original No. 4, July–August, 2012]

CHEMICAL CONSTITUENTS OF *Ziziphora clinopodioides*[a]

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UDC 547.972

Ziziphora clinopodioides Lam. (Labiatae), distributed mainly in Xinjiang of China, Central Asia, and Mongolia [1], is widely used as an Uighur folk medicine for the treatment of hypertension, coronary artery disease, and other cardiovascular diseases [2–4]. It has been reported that the total flavonoids of *Z. clinopodioides* showed significantly antimyocardial ischemic and antioxidant activities [5, 6]. In our research on the chemical constituents from *Z. clinopodioides*, five compounds were isolated, and their structures were identified as picein (**1**), linarin (**2**), 5,7,2′-trihydroxyflavone-2′-*O*-*β*-D-glucopyranoside (**3**), apigenin (**4**), and daucosterol (**5**).

Z. clinopodioides was collected from Xinjiang Province in July 2008 and authenticated by Prof. Guanmian Shen of the Xinjiang Institute of Ecology and Geography, Chinese Academy of Sciences. The air-dried *Z. clinopodioides* (7 kg) was extracted with 70% ethanol at room temperature. The extract was suspended in water and successively partitioned with CH_2Cl_2, *n*-butanol, and water. The *n*-butanol extract (239 g) was chromatographed on silica gel column eluted with $CHCl_3$–MeOH and $CHCl_3$–MeOH–H_2O to give 15 fractions. Compounds **1** (14.0 mg), **2** (11.0 mg), **3** (3.8 mg), **4** (15.0 mg), and **5** (7.0 mg) were isolated from fraction 12. All the compounds were identified by a combination of spectroscopic methods (MS, ^{1}H NMR, ^{13}C NMR). The spectroscopic data of all the compounds were in good agreement with the literature data.

Picein (1). $C_{14}H_{18}O_7$, mp 194°C. ^{1}H NMR spectrum (600 MHz, CD_3OD, δ, ppm, J/Hz): 7.93 (2H, d, J = 8.4, H-4, H-8), 7.12 (2H, d, J = 8.4, H-5, H-7), 4.98 (1H, d, J = 6.0, H-1′), 3.86 (1H, dd, J = 12.0, 1.5, H-6′), 3.65 (1H, dd, J = 11.4, 5.7, H-6′), 3.27–3.46 (4H, m, H-2′, H-3′, H-4′, H-5′), 2.52 (3H, s, H-1). ^{13}C NMR spectrum (150 MHz, CD_3OD, δ): 199.5 (C-2), 163.2 (C-6), 132.7 (C-3), 131.8 (C-4, C-8), 117.4 (C-5, C-7), 101.7 (C-1′), 78.4 (C-5′), 78.1 (C-3′), 74.9 (C-2′), 71.4 (C-4′), 62.6 (C-6′), 26.6 (C-1) [7].

Linarin (2). $C_{28}H_{32}O_{14}$. ESI-MS *m/z* 591 $[M + H]^-$. ^{1}H NMR spectrum (600 MHz, DMSO-d_6, δ, ppm, J/Hz): 12.89 (1H, s, OH-5), 8.05 (2H, d, J = 8.4, H-2′, H-6′), 7.15 (2H, d, J = 8.4, H-3′, H-5′), 6.93 (1H, s, H-3), 6.79 (1H, d, J = 2.0, H-8), 6.45 (1H, d, J = 1.6, H-6), 5.06 (1H, d, J = 7.2, Glc-1), 4.55 (1H, s, Rha-1), 3.86 (3H, s, MeO-4′), 1.08 (3H, d, J = 6.0, Rha-6′) [8].

5,7,2′-Trihydroxyflavone 2′-*O*-*β*-D-Glucopyranoside (3). ^{1}H NMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 12.90 (1H, s, OH-5), 10.87 (1H, s, OH-7), 7.87 (1H, d, J = 8.0, H-6′), 7.55 (1H, dd, J = 8.0, 8.0, H-4′), 7.35 (1H, d, J = 8.0, H-3′), 7.21 (1H, dd, J = 8.0, 8.0, H-5′), 7.01 (1H, s, H-3), 6.47 (1H, d, J = 2.0, H-8), 6.21 (1H, d, J = 2.0, H-6), 5.08 (1H, d, J = 5.6, H-1″), 3.16–3.71 (5H, m, proton of sugar). ^{13}C NMR spectrum (100 MHz, DMSO-d_6, δ): 161.4 (C-2), 110.3 (C-3), 181.9 (C-4), 157.6 (C-5), 98.8 (C-6), 164.3 (C-7), 93.9 (C-8), 161.4 (C-9), 103.8 (C-10), 120.2 (C-1′), 155.4 (C-2′), 115.4 (C-3′), 132.9 (C-4′), 121.9 (C-5′), 129.1 (C-6′), 100.1 (C-1″), 73.3 (C-2″), 76.7 (C-3″), 69.5 (C-4″), 77.2 (C-5″), 60.6 (C-6″) [9].

Apigenin (4). ^{1}H NMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 12.97 (1H, s, OH-5), 10.83 (1H, s, OH-7), 10.36 (1H, s, H-4′), 7.92 (2H, d, J = 8.8, H-2′, H-6′), 6.92 (2H, d, J = 8.8, H-3′, H-5′), 6.79 (1H, s, H-3), 6.48 (1H, d, J = 2.0, H-8), 6.19 (1H, d, J = 2.0, H-6). ^{13}C NMR spectrum (100 MHz, DMSO-d_6, δ): 163.7 (C-2), 102.8 (C-3), 181.7 (C-4), 161.1 (C-5), 98.8 (C-6), 164.1 (C-7), 93.9 (C-8), 157.3 (C-9), 103.7 (C-10), 121.1 (C-1′), 128.5 (C-2′, C-6′), 115.9 (C-3′, C-5′), 161.4 (C-4′) [10].

Compounds **1** and **3** were isolated from the genus *Ziziphora* for the first time.

[a]Materials presented at the 9th International Symposium on the Chemistry of Natural Compounds (SCNC, People′s Republic of China, Urumqi, Oct. 16–19, 2011).

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ACKNOWLEDGMENT

This work was supported by the China National Science Fund for Distinguished Young Scholars (No. 30925045) National Natural Science Foundation of China (81102891) and the CAS/SAFEA International Partnership Program for Creative Research Teams (2008-18).

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