COMPONENTS OF *Helichrysum arenarium*

K. A. Eshbakova[1*] and H. A. Aisa[2]

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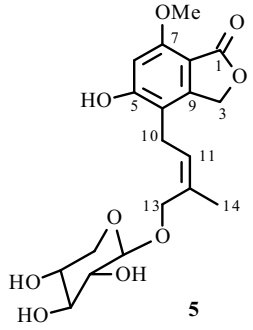
Helichrysum arenarium L. (Compositae) is a perennial herbaceous plant of height 15–40 cm that flowers in June-August. It is broadly distributed in Europe, western Siberia, and central Asia. It grows in sandy soils, more rarely in open rocky places, and is found in dry pine forests [1].

H. arenarium has been used since antiquity in folk and modern medicine and exhibits various properties. The extract increases blood pressure and possesses hepatoprotective, hypolipidemic, hepatotropic, antioxidant, and antiviral properties. Galenic preparations (decoction, dry extract, granules) are included in the domestic pharmacopoeia (8th through 10th editions) and those of several countries and are used as a cholegogic agent for gallstone disease, cholecystitis, hepatitis, and bile duct dyskinesia; for thermal and chemical burns of eyes, erosions, and corneal ulcers of various etiology; and as a regenerative and antibiotic agent. The preparations in medical practice are used as anti-inflammatory, antibacterial, spasmolytic, tonic, and exchange-normalizing compounds [2].

Organic acids, essential oils, carotinoids, steroids, tanning agents, quinones [3], coumarins [4], heterocyclic O-containing and aromatic compounds [5], and flavonoids [5–11] have been isolated from the plant.

We investigated the aerial part of *H. arenarium* collected in Xinjiang AR PRC during flowering within the framework of the "Project on high-technology hypoglycemic capsules of the Department of Science and Technology, Xinjiang Uygur AR, China." Ground air-dried raw material (5 kg) was exhaustively extracted with EtOH (70%) at room temperature. The combined extract was evaporated in vacuo. The condensed residue was first treated with petroleum ether and then separated successively into 30%, 50%, and 70% alcohol fractions.

The petroleum ether fractions were chromatographed over a column of silica gel (1:25 ratio) with elution by hexane and hexane:EtOAc with increasing EtOAc concentration. Chromatographic separation with elution by hexane:EtOAc (9:1, 7:1, 4:1) isolated compounds **1**–**3**. Chromatography of the 30% fraction over silica gel with gradient elution by $CHCl_3$ and $CHCl_3$:CH_3OH isolated compounds **4**–**6**.



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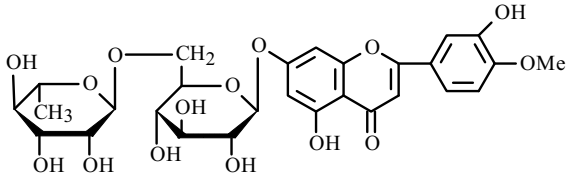

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We used UV, IR, PMR, ^{13}C NMR, HMBC, HMQC, COSY, NOESY, and mass spectra to identify the isolated compounds. The results were compared with the literature and directly with authentic samples.

***β*-Sitosterol (1)**, $C_{29}H_{50}O$, mp 131–132°C, identified directly with an authentic sample [12].

Oleanolic acid (2), $C_{30}H_{48}O_3$, mp 301–302°C, identified using spectral data as oleanolic acid [12].

***β*-Sitosterol *β*-D-glucopyranoside (3)**, $C_{35}H_{60}O_6$, mp 276–278°C, identified using spectral data as *β*-sitosterol *β*-D-glucopyranoside [13].

1) S. Yu. Yunusov Institute of the Chemistry of Plant Substances, Academy of Sciences of the Republic of Uzbekistan, Tashkent, fax: (99871) 120 64 75, e-mail: e_komila@yahoo.com; 2) Xinjiang Technical Institute of Physics and Chemistry, Academy of Sciences, Urumchi, 830011, P. R. China, e-mail: haji@ms.hjb.ac.cn. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 774–775, November–December, 2009. Original article submitted May 18, 2009.

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Naringenin (4), $C_{15}H_{12}O_5$, mp 251–252°C. UV spectrum (MeOH, λ_{max}, nm): 230, 290, 334. PMR spectrum (600 MHz, DMSO-d_6, δ, ppm, J/Hz): 7.32 (2H, dd, J = 2.8, 8.8, H-2′,6′), 6.91 (2H, dd, J = 2.8, 8.8, H-3′,5′), 6.04 (1H, d, J = 2.4, H-8), 6.01 (1H, d, J = 2.4, H-6), 5.34 (1H, dd, J = 3.5, 12.0, H-2), 3.11 (1H, dd, J = 12.0, 15.0, H-3α), 2.78 (1H, dd, J = 2.8, 16.8, H-3β), 12.07 (1H, s, OH-5).

^{13}C NMR spectrum (150 MHz, DMSO-d_6, δ, ppm): 79.7 (C-2), 43.3 (C-3), 197.2 (C-4), 164.7 (C-5), 96.5 (C-6), 167.5 (C-7), 95.6 (C-8), 164.3 (C-9), 102.8 (C-10), 130.7 (C-1′), 128.7 (C-2′), 116.2 (C-3′), 158.5 (C-4′), 158.5 (C-5′), 128.8 (C-6′) [11, 14, 15].

Helichrysumphthalide (5), $C_{19}H_{24}O_9$, mp 185–186°C. IR spectrum (KBr, ν_{max}, cm^{-1}): 3390, 2626, 1701, 1651, 1545. UV spectrum (MeOH, λ_{max}, nm): 226 (4.20), 259 (4.02), 296 (3.74). Mass spectrum (*m*/*z*): 419.4, 414.4, 397.4, 265.3, 247.3, 229.3, 189.3. PMR spectrum (600 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.70 (3H, s, H-14), 3.19 (2H, d, J = 8.4, H-10), 4.27 (2H, s, H-13), 5.16 (2H, s, H-3), 5.32 (1H, t, J = 2.4, H-11), 6.50 (1H, s, H-6); OMe 3.79 (3H, s), 4.11 (1H, d, J = 7.8, H-1′), 2.97 (1H, t, J = 8.4, H-2′), 3.09 (1H, t, J = 8.7, H-3′), 3.29 (1H, m, H-4′), 3.03 (1H, t, J = 10.8, H-5b′), 3.71 (1H, dd, J = 11.4, 5.4, H-5a′).

^{13}C NMR spectrum (150 MHz, DMSO-d_6, δ, ppm): 168.2 (C-1), 67.4 (C-3), 112.6 (C-4), 162.0 (C-5), 98.7 (C-6), 157.4 (C-7), 103.3 (C-8), 149.9 (C-9), 22.5 (C-10), 125.6 (C-11), 132.0 (C-12), 66.1 (C-13), 21.3 (C-14), 102.4 (C-1′), 73.2 (C-2′), 76.6 (C-3′), 69.6 (C-4′), 65.7 (C-5′), 55.3 (OMe) [16].

Diosmin (6), $C_{28}H_{32}O_{15}$, mp 301–302°C. PMR spectrum (600 MHz, DMSO-d_6, δ, ppm, J/Hz): 7.57 (1H, d, J = 7.8, H-6′), 7.45 (1H, s, H-2′), 7.14 (1H, d, J = 9, H-5′), 6.83 (1H, d, J = 3.0, H-3), 6.77 (1H, d, J = 2.4, H-8), 6.46 (1H, d, J = 1.8, H-6), 5.07 (1H, d, J = 7.8, H-1″), 4.54 (1H, s, H-1‴), 3.15-3.77 (sugar protons), 1.07 (3H, d, J = 5.4, H-6‴), 3.87 (3H, s, OMe), 9.45 (1H, s, OH-3′), 12.93 (1H, s, OH-5).

^{13}C NMR spectrum (150 MHz, DMSO-d_6, δ, ppm): 164.2 (C-2), 100.5 (C-3), 181.95 (C-4), 146.8 (C-5), 99.9 (C-6), 162.9 (C-7), 94.8 (C-8), 156.4 (C-9), 105.4 (C-10), 122.9 (C-1′), 113.1 (C-6′), 151.3 (C-3′), 161.2 (C-4′), 118.9 (C-2′), 112.2 (C-5′), 99.6 (Glc-1), 73.0 (Glc-2), 76.2 (Glc-3), 70.7 (Glc-4), 75.6 (Glc-5), 60.7 (Glc-6), 100.5 (Rha-1), 70.3 (Rha-2), 69.5 (Rha-3), 72.0 (Rha-4), 68.3 (Rha-5), 17.8 (Rha-6), 55.0 (OMe) [17, 18].

Oleanolic acid, β-sitosterol β-D-glucopyranoside, and diosmin were isolated for the first time from *H. arenarium*.

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