Chemistry of Natural Compounds, Vol. 50, No. 3, July, 2014 [Russian original No. 3, May–June, 2014]

FLAVONOIDS FROM *Camelina sylvestris* SEEDS

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Seeds of *Camelina sylvestris* L. (Brassicaceae) contain about 30–40% fatty oil that is used for food and commercial purposes [1]. We studied earlier the fatty-acid composition of fatty oil from *C. sylvestris* seeds [2]. However, other compounds, in particular flavonoids, the content of which according to our data was ~0.3% [3], are also interesting for comprehensive use of this plant raw material.

Herein we present results for the flavonoid composition of *C. sylvestris* seeds cultivated in Samara Region.

We studied *C. sylvestris* seeds that were cultivated at Samara Tulaikov Agricultural Research Institute, RAAS (Bezenchuk, Samara Region).

Air-dried *C. sylvestris* seeds (150 g) were collected in July 2013 and were extracted by EtOH (70%) first at room temperature twice for 24 h and then with heating on a boiling-water bath for 30 min. The combined aqueous EtOH extract was evaporated *in vacuo* to 50 mL, mixed with silica gel L 40/100 (30 g), and dried. The dried powder (dry extract + silica gel) was placed on a layer of silica gel that was formed as a suspension in $CHCl_3$ and eluted with $CHCl_3$ and $CHCl_3$–EtOH (97:3, 95:5, 93:7, 90:10, 85:15, 80:20, 70:30, 60:40, and 50:50). Separation of the compounds was monitored using TLC on Sorbfil PTSKh-AF-A-UF plates.

Fractions dominated by **1** were combined. The resulting precipitate was separated and recrystallized from EtOH to afford **1** in 0.05% yield (of air-dried raw material mass). Fractions containing **2** were rechromatographed over Woelm polyamide with elution by H_2O and aqueous EtOH (20, 40, 70, and 96%) to afford **2** (40% EtOH eluent) that was additionally purified by recrystallization from aqueous EtOH.

The PMR spectrum of **1** exhibited resonances for five aromatic protons (H-2′, H-6′, H-5′, H-8, and H-6). The observation of a 3H singlet at 3.83 ppm was indicative of a methoxy in **1** that was assigned to the C-3′ position of flavonoid ring B based on mass spectra (peak for an ion with *m*/*z* 151 corresponded to a fragment of ring B) and also UV spectra [4].

The PMR spectrum of **2** showed two 2H doublets at 7.96 (H-2′, 6′) and 6.87 (H-3′, 5′) and resonances for ring A aromatic protons (H-8 and H-6).

Acid hydrolysis of **1** (2% HCl at 100°C) cleaved glucose, rhamnose, and the aglycon, which was identified as 3,5,7,4′-tetrahydroxy-3′-methoxyflavone (isorhamnetin) based on mass spectra ($[M]^+$ 316, 100%) and UV spectra [4]. Acid hydrolysis of **2** (2% HCl at 100°C) cleaved glucose, rhamnose, and the aglycon, which was identified as 3,5,7,4′-tetrahydroxyflavone (kaempferol) based on mass spectra ($[M]^+$ 286, 100%) and UV spectra [4]. UV spectra indicated that the 3-OH of both flavonoids was glycosylated. The long-wavelength band of the aglycons of **1** and **2** experienced a bathochromic shift (+Δ57 nm) in the presence of $AlCl_3$ [4].

The combined spectral data identified **1** and **2** as narcissin (3,5,7,4′-tetrahydroxy-3′-methoxyflavone 3-*O*-rutinoside) and nicotiflorin (3,5,7,4′-tetrahydroxyflavone 3-*O*-rutinoside), respectively [5, 6].

Thus, narcissin and nicotiflorin were isolated and characterized by PMR and UV spectroscopy and mass spectrometry for the first time from *C. sylvestris* seeds as a result of the study of the flavonoid composition.

PMR spectra were obtained on a Bruker AM 300 instrument (300 MHz). Mass spectra were taken on a Kratos MS-30 mass spectrometer. UV spectra were recorded on a Specord 40 spectrophotometer (Analytik Jena).

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0009-3130/14/5003-0539

3,5,7,4′-Tetrahydroxy-3′-methoxyflavone 3-*O*-rutinoside (1). Yellow crystals from EtOH, $C_{28}H_{32}O_{16}$, mp 173–175°C (aqueous EtOH). Mass spectrum (70 eV, 200°C, *m/z*, %): M^+ aglycon 316 (100), 301 (70, 153 (10), 151 (9). UV spectrum (λ_{max}, nm): 257, 268 sh, 358; + NaOAc 261, 274 sh, 371; + NaOAc + H_3BO_3 261, 274 sh, 372; +$AlCl_3$ 268, 276 sh, 403. ^{1}H NMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 12.53 (1H, s, 5-OH), 7.83 (1H, d, J = 2.0, H-2′), 7.50 (1H, dd, J = 2.0, 8.5, H-6′), 6.87 (1H, d, J = 8.5, H-5′), 6.36 (1H, d, J = 2.0, H-8), 6.14 (1H, d, J = 2.0, H-6), 5.40 (d, J = 7.0, H-1″ Glc), 4.41 (d, J = 2, H-1‴ Rha), 3.83 (3H, s, CH_3O), 3.1–3.8 (10H sugars, m), 0.99 (d, J = 6.0, CH_3 Rha).

3,5,7,4′-Tetrahydroxyflavone 3-*O*-rutinoside (2). Light-yellow crystals, $C_{27}H_{30}O_{15}$, mp 182–186°C (aqueous EtOH). Mass spectrum (70 eV, 200°C, *m/z*, %): M^+ aglycon 286 (100), 153 (25), 121 (20). UV spectrum (λ_{max}, nm): 269, 355; +NaOAc 272, 304, 365; +$AlCl_3$, 274, 304, 345, 394; +$AlCl_3$ + HCl 275, 304, 345, 394; + NaOMe 275, 326, 400. ^{1}H NMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 12.58 (1H, s, 5-OH), 7.96 (2H, d, J = 9, H-2′, 6′), 6.87 (2H, d, J = 9, H-3′, 5′), 6.33 (1H, d, J = 2.0, H-8), 6.15 (1H, d, J = 2.0, H-6), 5.38 (d, J = 7.0, H-1″ Glc), 4.35 (d, J = 2, H-1‴ Rha), 3.0–4.0 (10H sugars, m), 0.99 (d, J = 6.0, CH_3 Rha).

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