FLAVONOIDS OF THE EPIGEAL PART OF Glycyrrhiza uralensis

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Plants of the genus *Glycyrrhiza* L. (fam. Fabaceae) are a rich source of flavonoids, coumarins, terpenoids, and tanning substances, some of which are used in folk medicine for the treatment of pneumonias, bronchitises, bronchial asthmas, pulmonary tuberculosis, whooping cough, peptic ulcer, diseases of the kidneys and the gall bladder, anemia, and sugar diabetes [1]. In the present communication we give the results of a study of the flavonoids of the epigeal part of *Glycyrrhiza uralensis* Fisch. gathered in May, 1987 in the Tashkentskii oblast (village of Kibrai). The raw material was exhaustively extracted with ethanol. The alcoholic extract was concentrated in vacuum, diluted with water, and extracted successively with chloroform and ethyl acetate. Chromatography of the ethyl acetate fraction on silica gel in a chloroform – petroleum ether gradient system and in chloroform led to the isolation of compounds (1)-(3). To identify them we used UV, PMR, and mass spectra and also the results of chemical transformations and direct comparison with authentic specimens.

Glabranin (1) [5,7-dihydroxy-8-(γ , γ -dimethylallyl)flavanone] — C₂₀H₂₀O₄, mp 168-169°C (methanol), λ_{max} 297, 344 nm, characteristic for flavanone derivatives [2]. The mass spectrum showed peaks of ions with m/z 324 (M⁺), 309, 281, 269, 256, 220, 219, 205, 192, 179, 177, 165, 149, 104.

The PMR spectrum (CDCl₃) contained signals of protons at (ppm) 1.65 [6H, br.s, $=C(CH_3)_2$], 2.68 (1H, dd, J = 5.3 and 17.5 Hz, equatorial proton, H-3), 2.93 (1H, dd, J = 10.5 and 17.5 Hz, axial proton, H-3'), 3.24 (2H, d, J = 6.5 Hz, Ar-CH₂), 5.18 (1H, m, =CH), 5.35 (1H, dd, J = 10.5 and 5.3 Hz, H-2), 5.95 (1H, s, H-6), and 7.33 (5H, br.s, $-_6H_5$).

The acetylation of glabranin with acetic anhydride in the presence of pyridine gave the diacetate, with mp 85-86°C, M^+ 408 [3].

Pinocembrin (2) (2S-5,7-dihydroxyflavanone) – $C_{15}H_{12}O_4$, (M⁺ 256), mp 195-196°C, λ_{max} 292, 326 nm, characteristic for flavanone derivatives.

The flavanone nature of substance (2) was confirmed by its PMR spectrum, which contained the characteristic H-2 signal in the form of a doublet of doublets with the SSCCs 4.5 and 12.0 Hz at 5.31 ppm, the signals of protons at C-3 in the form of a doublet of doublets, each with SSCCs of 12.0 and 16.5 Hz for the axial proton at 3.02 ppm and 4.5 and 16.5 Hz for the equatorial proton at 2.63 ppm. The spectrum also showed the signals of the protons of a monosubstituted ring (7.05-7.48 ppm, 5H, m), H-6 (6.17 ppm, 1H, d, 2.0 Hz), and H-8 (6.26 ppm, 1H, d, 2.0 Hz).

Acetylation of pinocembrin with acetic anhydride in the presence of pyridine gave the diacetate, with mp 119-120°C, M^+ 340 [3].

Galangin (3) (3,5,7-trihydroxyflavone) — $C_{15}H_{10}O_5$ (M⁺ 270), mp 217-219°C (methanol), ν_{max} 268, 362 nm; +CH₃COONa 276, 385 nm; +AlCl₃ 272, 410 nm; +AlCl₃/HCl 273, 412 nm; +CH₃ONa 279, 414 nm.

In the PMR spectrum (Py-d₅), signals were observed from protons at (ppm) 6.52 (1H, d, J = 2.2 Hz, H-6), 6.62 (1H, d, J = 2.2 Hz, H-8), 7.13-7.15 (3H, m, H-3',4',5'), and 8.15-8.50 (2H, m, H-2',6') [2].

Pinocembrin possesses pronounced biological activity [4]. It was present at a level of 0.63% in the epigeal part of *Glycyrrhiza uralensis*, and this plant can be used as an additional source of it.

This is the first time that flavonoids (1)-(3) have been isolated from G. uralensis.

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