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FLAVONOIDS OF Teucrium hircanicum

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Continuing an investigation of the epigeal part of <u>Teucrium hircanicum</u> L., family Lamiaceae [1, 2], from the ethyl acetate-soluble fraction of a methanolic extract previously treated with benzene and chloroform, by column chromatography on polyamide, we have isolated three substances of flavone nature (qualitative reactions, UV spectra) [3, 4].

Substance (I) $-C_{16}H_{12}O_7$ - light yellow acicular crystals with mp 300-302°C (methanol), M⁺ 316, R_f 0.71 (Silufol UV-254; ethyl acetate-methanol-water (7:2:1) - system 1); 0.15 (chloroform-methanol (19:1) - system 2). IR spectrum: v_{max}^{KBr} , cm⁻¹: 3500-3400 (OH), 1660 (C=0 of a γ -pyrone); 1620, 1570 (C=C of a γ -pyrone); 1605, 1510 (Ar); 2860, 1470 (OCH₃). UV spectrum, $\lambda_{CH_3OH}^{CH_3OH}$, nm: 235 sh, 249 sh, 256 sh, 286, 347. According to its UV spectra max with ionizing and complex-forming reagents [5], substance (I) contained free hydroxy groups

in positions 5, 6, 3', and 4'. The Bargellini [6] and gossypetone [7] reactions were negative.

The acetylation of (I) with acetic anhydride in pyridine led to a tetraacetyl derivative with the composition $C_{24}H_{20}O_{11}$, M⁺ 484, mp 236-239°C, R_f 0.79 (system 1), 0.50 (system 2). The mass spectrum of (I) and its tetraacetate had the peak of an ion with m/z 181, the formation of which for a 6-hydroxyflavone confirmed the presence of a hydroxy group at C-5 and showed a CH₃O-7 group in the absence of a substituent at C-8 [8].

PMR spectrum of the tetraacetate (Varian T-60, TMS, CD_2Cl_2 , δ , ppm): 7.66 dd, $J_5'_{,6}' = 9$ Hz, $J_2'_{,6}' = 2$ Hz (H-6'); 7.63 d, $J_2'_{,6}' = 2$ Hz (H-2'); 7.25 d, $J_5'_{,6}' = 9$ Hz (H-5'); 6.90 s (H-8); 6.47 s (H-3), 3.83 s (3H, OCH₃); 2.28 s (3H, CH₃COO); 2.23 s (9H, CH₃COO).

The facts given above permitted the assumption for substance (I) of the structure of 3',4',5,6-tetrahydroxy-7-methoxyflavone, which is known as pedalitin (pedalin) [4, 9-12], for which spasmolytic activity [13] and an inhibiting action on bovine pancreatic ribonuclease I [14] have been described.

Substance (II) $-C_{21}H_{20}O_{11}$ - colorless crystals with mp 234-236°C (methanol), Rf 0.58 (system 1). UV spectrum, λCH_3OH , nm: 255, 266 sh, 352. Its peracetate had mp 235-237°C, max Rf 0.41 (benzene-methanol (6:1)).

On the basis of qualitative reactions, the results of UV spectroscopy with additives, the mass spectra of the flavonoid and of its peracetate, and also TLC and a mixed melting point with an authentic sample, substance (II) was identified as luteolin 7-0- β -D-glucopy-ranoside [4].

Substance (III) - a minor component of the ethyl acetate fraction - consisted of a colorless crystalline substance with mp 262-264°C (methanol), R_f 0.69 (system 1). UV spectrum, λCH_3OH , nm: 270, 328. Its peracetate had mp 118-121°C, R_f 0.86 (system 1); 0.44 (system 2). The nature of the mass and PMR spectra of the peracetate showed the glycosidic nature of substance (III).

By rechromatography on a column of silica gel of the ethyl acetate fraction that had been passed through a polyamide column, we isolated and identified luteolin (TLC and melting point in comparison with an authentic sample).

This is the first time that pedalitin and luteolin 7-O- β -D-glucopyranoside have been detected in the genus <u>Teucrium</u>.

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FLAVONOIDS OF Astragalus virgatus

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Continuing the search for biologically active substances in plants of the genus Astragalus, we have studied the flavonoid composition of the epigeal part of <u>Astragalus</u> virgatus Pall., collected on the territory of the Northern Caucasus in the flowering period.

The air-dry comminuted herbage was extracted with 70% ethanol in an apparatus of the Soxhlet type. The ethanol was distilled off, and the aqueous residue was purified with chloroform, after which the flavonoids were extracted with ethyl acetate. The ethyl acetate was distilled of and the residue was chromatographed on a column of polyamide sorbent. Seven individual flavonoids (1-7) were isolated.

Substance 1 - $C_{21}H_{20}O_{12}$, mp 238-241°C, $[\alpha]_D^{20}$ -69.2° (c 0.1; methanol); λ_{max} , nm: 363, 255 - quercetain 3-O- β -D-glucopyranoside, or isoquercitrin.

Substance $2 - C_{21}H_{20}O_{11}$, mp 178-180°C, $[\alpha]_D^{20} - 69^\circ$ (c 0.48; methanol); λ_{max} , nm: 357, 265 - kaempferol 3-O- β -D-glucopyranoside, or astragalin.

Substance 3 - $C_{22}H_{22}O_{12}$, mp 172-174°C, $[\alpha]_D^{20}$ -30° (c 0.4; methanol); λ_{max} , nm: 357, 256 - isorhamnetin 3-O- β -D-glucopyranoside.

Substance 4 - $C_{21}H_{20}O_{11}$, mp 269-271°C, $[\alpha]_D^{20}$ -48.2° (c 0.1; ethanol); λ_{max} , nm: 365, 224 - kaempferol 7-O- β -D-glucopyranoside, or populnin.

Substance 5 - $C_{28}H_{32}O_{16}$, mp 183-185°C, $[\alpha]_D^{2^{\circ}}$ -38.2° (c 0.5; formamide); λ_{max} , nm: 358, 255 - isorhamnetin 3-O-[O- β -L-rhamnopyranosyl-(1 \rightarrow 6)- β -D-glucopyranoside], or narcissin.

Substance 6 - $C_{15}H_{10}O_6$, mp 277-279°C; λ_{max} , nm: 370, 265 - kaempferol.

Substance 7 - $C_{15}H_{10}O_7$, mp 310-312°C; λ_{max} , nm: 370, 265, 256 - quercetin.

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