

FLAVONOIDS OF SOME SPECIES OF *Salvia*

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We have investigated the flavonoid composition of three species of sage: *Salvia seravschanica* Regel et Schmalh., *S. kopetdaghensis* Kudr., and *S. deserta* Schang. From these species we have isolated nine substances of flavonoid nature. The aglycones apigenin (I) (*S. kopetdaghensis*) and luteolin (II) (*S. seravschanica* and *S. kopetdaghensis*) were identified from their UV and NMR spectra and by comparison with authentic samples. The other seven substances consisted of flavone glycosides.

Substance (III), mp 202-207°C, $[\alpha]_D^{27} - 60.6^\circ$ (c 0.33; pyridine), $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$ 251, 268, 346 nm ($\log \epsilon$ 4.28; 4.25; 4.35), was isolated from *S. seravschanica* and *S. deserta*. The NMR spectrum of the trimethylsilyl ether had the signals of the following protons: H-2',6', m, 7.24 ppm (2H); H-5', d, 6.76, J=8 Hz (1H); H-8, d, 6.56, J=2.5 Hz (1H); H-3, s, 6.27 (1H); H-6, d, 6.21, J=2.5 (1H); d, 4.85, J=7 Hz (1H) assigned to the proton of the anomeric center of the carbohydrate component; OCH₃, s, 3.83 (3H); and the protons of the carbohydrate moiety at 3.2-4.0 ppm (6H). The hydrolysis of compound (III) gave an aglycone with M⁺ 300 and glucose. The NMR spectrum showed 3',4'-substitution. In the mass spectrum of the aglycone, a fragment with m/e 148 showed the presence of a methoxy group in ring B [1]. This fragment must belong to diosmetin or chrysoeriol. However, the aglycone differed considerably in chromatographic behavior from diosmetin. A bathochromic shift of 56 nm with a rise in the intensity of the long-wave maximum in the aglycone and the glycoside in the presence of sodium methoxide showed the presence of a free OH group in position 4'. As the facts presented show, the aglycone is 4',5,7-trihydroxy-3'-methoxyflavone, and (III) has the structure of chrysoeriol 7-O-β-D-glucoside. Substance (III) was chromatographically identical with ther mopso-side [2].

Substance (IV), mp 198-202°C, $[\alpha]_D^{27} - 72.5^\circ$ (c 0.29; pyridine), from *S. seravschanica* and *S. kopetdaghensis*, $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$ 249, 270, 337 nm. NMR spectrum: H-2',6', m, 7.24 ppm (2H); H-5', d, 6.77, J=8 Hz (1H); H-8, d, 6.41, J=2.5 Hz (1H); H-3, s, 6.45 (1H); H-6, d, 6.24, J=2.5 Hz (1H); d, 4.99, J=7 Hz (1H) - the signal of the anomeric center of the carbohydrate component; OCH₃, s, 3.82 (3H); m, 3.35-4.0 ppm (4H) - the signals of the protons of the carbohydrate moiety. The aglycone of substance (IV) was identified as chrysoeriol. The nature of the signals of the protons in the 3.35-4.0-ppm region differed substantially from that of the signals of compound (III) and was similar to that of the signals of glucuronides of luteolin, apigenin, and scutellarein, which have been isolated previously by one of the authors [3]. The results of hydrolysis with β-glucuronidase confirmed that (IV) contained a glucuronic acid residue attached in position 7 (UV spectrum). Consequently, (IV) has the structure of chrysoeriol 7-O-β-D-glucuronide.

Substance (V), C₂₁H₂₀O₁₀ · 1.5 H₂O, mp 179-182°C (from *S. seravschanica* and *S. kopetdaghensis*) was identified on the basis of its hydrolysis product and the results of UV, mass, and NMR spectroscopy as apigenin 7-O-β-D-glucoside (cosmosiin), and substance (VI), C₂₁H₂₀O₁₁, mp 252-254°C, $[\alpha]_D^{20} - 40.5$ (DMFA), isolated from all the species of sage investigated, was identified as luteolin 7-O-β-D-glucoside (cynaroside).

Substance (VII) was isolated in very small amounts from *S. seravschanica* by preparative separation on paper. IR spectroscopy showed the presence of free hydroxy groups at positions 3', 4', and 5 in its molecule. The IR spectrum had a broad band at 1605 cm⁻¹, which is characteristic for glucuronides in the salt form. The acid hydrolysis of (VII) led to luteolin and glucuronic acid, which was identified chromatograph-

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ically. The glucuronic acid is attached to the aglycone in position 7 (UV spectrum). Thus, substance (VII) is luteolin 7-O- β -D-glucuronide, as was confirmed by a chromatographic comparison with a sample isolated previously from Phlomis tuberosa [3].

Substance (VIII), $C_{20}H_{18}O_9 \cdot 1.5 H_2O$, mp 226-228°C, is, according to its UV and NMR spectra, a glycoside of apigenin, and substance (IX), $C_{21}H_{20}O_{10}$, mp 280-282°C, is a glycoside of chrysoeriol. Compounds (VIII) and (IX) were distinguished from the related glucosides by greater mobility in TLC on Silufol [chloroform-methanol (9:1) and (8:2)]. In the products of hydrolysis by the enzyme glucodelemarin we found apigenin, chrysoeriol, and a common sugar - xylose. The values of the coupling constants of the anomeric proton of the xylose, $J = 6$ Hz, and the features of the UV spectra permit us to propose for (VIII) the structure of apigenin 7-O- β -D-xyloside and for (IX) that of chrysoeriol 7-O- β -D-xyloside.

This is the first time that all these flavonoids, with the exception of (II), (V), and (VI), have been found in sages.

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