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INVESTIGATION OF THE FLAVONOID COMPOSITION OF *Scutellaria adenostegia*

I. I. Chemesova, M. Iinuma, and A. L. Budantsev

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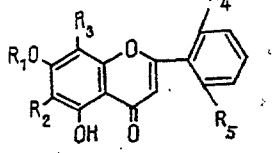
The flavonoid composition of Scutellaria adenostegia Briq. (family Lamiaceae) has been studied. The material for investigation was collected under the natural conditions for the growth of the plant in the Tien-Shan (Talassian range, valley of the R. Itagar, 1.5 km above its mouth, 2000 m above sea level, roots, one-year shoots), and in the Pamir-Alai (Peter I range, environs of the village of Dzhelandy, 2100 m above sea level, roots, epigeal part).

The samples under investigation were subjected to extraction with aqueous ethanol (70%), and then, with the aid of chloroform and ethyl acetate, the extracted substances were separated into fractions containing components of similar polarity. The fractions so obtained were chromatographed on columns with various adsorbents (polyamide and silica gels L 100/160 and L 140/100 [sic]), using the eluents chloroform and ethanol and mixtures of them (ethanol–chloroform (1:100), (1:10), and (2:10)).

As a result of the separation of the chloroform fraction of the extracts of the roots, substances (I), (II), and (III) and a pale yellow crystalline precipitate that gave a single dark spot on chromatographs in various systems but was, according to its mass spectrum [m/z (%) 254 (M^+, 100%, 264 (M^+, 100%)], a mixture of two compounds difficult to separate by the usual chromatographic method were obtained. The acetylated mixture (Ac_2O + pyridine) was separated preparatively (PTLC): solvent: n-hexane–ethyl acetate (3:1), and the acetates (IV) and (VI) were obtained. The chromatographic separation of the ethyl acetate fraction of the extract of the roots led to the isolation of compound (VII), and that of the chloroform fraction from one-year shoots led to substances (IV) and (V). All the compounds were shown to be flavonoids by their IR spectra.



I. $R_1=R_3=R_4=R_5=H$; $R_2=OH$
II. $R_1=CH_3$; $R_2=R_3=CCH_3$; $R_4=R_5=OH$
III. $R_1=CH_3$; $R_2=H$; $R_3=OCH_3$; $R_4=R_5=OH$
IV. $R_1=R_2=R_3=R_4=R_5=H$
VI. $R_1=R_2=R_3=R_5=H$; $R_4=OCH_3$

Flavonoids (I) (mp 266°C, $C_{15}H_{10}O_5$), (II)* (mp 242°C, $C_{18}H_{16}O_8$), (IV) (mp 279°C, $C_{15}H_{10}O_4$), and (V) (mp 347°C, $C_{15}H_{10}O_5$) were identified on the basis of a comparison of their spectral characteristics and physical constants as bacalein, 2', 5,6'-trihydroxy-6,7,8-trimethoxyflavone, chrysin, and apigenin, respectively [1-3].

* Flavonoid (II) gave no depression of the melting point in admixture with a sample of 2',5,6'-trihydroxy-6,7,8-trimethoxyflavone kindly provided by Dr. T. Tomimori (Japan).

V. L. Komarov Botanical Institute, Russian Academy of Sciences, St. Petersburg. Pharmaceutical Institute, Gifu, Japan. Translated from Khimiya Prirodnykh Soedeninii, No. 1, pp. 157-159, January-February, 1993. Original article submitted November 26, 1991.

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Flavonoid (III), mp 291°C (chloroform–ethanol), $C_{17}H_{14}O_7$. UV spectrum: $\lambda_{max}^{C_2H_5OH}$ nm: 265(313), 342 (log ε 3.31; 2.86). The presence of NaOAc in a solution of (III) did not cause a bathochromic shift of the absorption maximum, which permitted the assumption that there was no free hydroxyl in position 7. NaOEt caused a shift by 31 nm, thanks to which it was possible, on the one hand, to assume that there were substituents in positions 2' and 6' of ring B [4] and, on the other hand, to confirm the absence of free hydroxy groups, except for position 5, in ring A. PMR (100 MHz, DMSO, δ, ppm): 3.70 m 3.94 (3H, s, OCH_3-8 m 3H, s, OCH_3-7); 6.25 (s, H-3); 6.45 (2H, d, J = 8 Hz, H-3', H-5'); 6.60 (s, H-6); 7.12 (t, J = 8 Hz, H-4'), 9.96 s, 2'-OH, 6'-OH); 12.75 (s, 5-OH). The presumed structure of 2',5',6'-trihydroxy-7,8-dimethoxyflavone was confirmed by the ^{13}C NMR spectrum (25.15 MHz, DMSO): 162.82 (C-2); 111.88 (C-3), 182.29 (C-4), 146.0 (C-5), 128.47 (C-8), 158.37 (C-7), 95.98 (C-6), 149.91 (C-9), 104.15 (C-10), 108.28 (C-1'), 156.9 (C-2' and C-6'), 106.71 (C-3' and C-5'), 132.2 (C-4'), 61.13 (OCH_3-8), 56.58 (OCH_3-7), and the substance agreed in its physical and spectral parameters with viscidulin, which has been isolated from S. baicalensis [5].

Flavonoid (VI), mp 288°C, $C_{16}H_{12}O_5$. Mass spectrum of the diacetate, m/z (%): 368 (0.5), 326 (50), 284 (100), 254 (25). PMR spectrum of the diacetate of (VI) (399.65 MHz, $CDCl_3$): 7.83 (dd, J = 8 Hz, J = 2 Hz, H-6'); 7.47 (ddd J = 8 Hz, J = 7 Hz, J = 2 Hz, H-4'); 7.30 (d, J = 2 Hz, H-8); 7.09 (dd, J = 8 Hz, J = 7 Hz, H-5'); 7.02 (br.d, J = 8 Hz, H-3'); 6.99 (s, H-3); 6.83 (d, J = 2 Hz, H-6); 3.91 (3H, s, 2'-OCH_3); 2.43 (3H, s, $OCOCH_3$); 2.34 (3H, s, $OCOCH_3$). The suppression of spin-spin coupling by irradiation with a radiofrequency signal of the resonance frequency corresponding to an OCH_3 group caused a sharp change in the intensities of the signals of protons 3 and 3' in the spectrum (Overhauser effect), which showed the presence of an OCH_3 group in position 2'. Flavonoid (VI) was identified as 2'-methoxychrysin.

Flavonoid (VII) was determined from its IR spectrum as a glycoside, and its structure is being studied.

Thus, for the first time, the flavonoids chrysin, 2'-methoxychrysin, bacalein, 2',5,6'-trihydroxy-6,7,8-trimethoxyflavone, and 2',5,6'-trihydroxy-7,8-dimethoxyflavone have been isolated from the roots of Scutellari adenostegia, and chrysin and apigenin from its one-year shoots.

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