FLAVONOIDS OF THE ROOTS OF Scutellaria altissima

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The present paper reports the isolation and the determination of the structure of flavonoids from the roots of Scutellaria altissima L. (tall skullcap), family Labiatae. Previously, only an investigation of the flavonoids of the epigeal part has been reported, in which scutellarin was isolated for the first time. In the extracts from the roots we detected three glycosides and four aglycones by chromatography.

By fractional extraction and column chromatography on polyamide solvent we separated the glycosides and the aglycones. Baicalein and baicalin, wogonin and wogonoside, oroxylin and oroxyloside, and a new compound which we have called altisin (I) were isolated in the individual state. Substance (I) was obtained from the aglycone fraction by chromatography on polyamide (eluent: petroleum ether); composition $C_{19}H_{18}O_7$, mp 165-167°C (from 70% ethanol), λ_{max} (nm) in methanol 265, 290 (sh.), 345 (sh.); with sodium acetate no changes were observed; with alkali — 385 nm; with zirconyl chloride — 405 nm. After demethylation with pyridinium chloride (180-200°C, 1 h) we obtained demethoxyaltisin (II) with the composition $C_{15}H_{10}O_7$, amorphous, λ_{max} (nm) in methanol 270, 290 (sh.), and 350 (sh.), with sodium acetate and alkali it was destroyed, with zirconyl chloride — 415 nm.

To show the structure of (I), together with the UV spectra we used NMR spectroscopy. The substance was dissolved in CCl_4—$CDCl_3$ (3:1), and the spectrum was recorded on an R-20A instrument with a working frequency of 60 MHz. Tetramethylsilane was used as internal standard.

Analysis of the spectrum showed that compound (I) contains one hydroxy group at C_5 (12.52 ppm, s, 1H). The protons of ring B form two groups of signals: a one-proton quartet (doublet of doublets) at δ 7.29 ppm, ($J_1 = J_2 = 8.5$ Hz) due to the proton at $C_{4'}$ and a two-proton doublet at 6.55 ppm, J = 8.5 Hz, due to the protons at $C_{3'}$ and $C_{5'}$. This distribution of the lines of the signal is characteristic for 2',6'-distributed flavones, i.e., when the three aromatic protons are adjacent to one another while two of them, being in the ortho positions to the third, are equivalent and differ considerably from it in chemical shift [2]. The marked upfield shift of the signals of the protons at $C_{3'}$, and $C_{5'}$ is due to their presence in the ortho and para positions to the methoxy groups, which are electron-donating substituents. The spectrum also contains two one-proton singlets of aromatic protons at 6.26 and 6.12 ppm. The singlet nature of these signals shows that the A-ring contains only one aromatic proton, at C_8 or C_6. The first signal can be assigned to the proton at C_3 and the upfield displacement of the second signal is characteristic of a C_6 proton in 5,7-substituted flavones [2].

Four methoxy groups were detected in (I) — at C_7 (3.88 ppm, 3H), and $C_{2'}$ and $C_{6'}$ (3.79 ppm, 6H), and at C_8 (3.74 ppm, 3H). The results of a comparison of the magnitudes of the bathochromic shifts of the complexes of (I) and (II) with zirconyl chloride [60 nm for (I) and 65 nm for (II)] with the shift of a 6-hydroxy-substituted flavone (baicalin with $\Delta\lambda$ = 30-40 nm) shows that there is no substituent reducing the bathochromy at C_6 in (I) and (II) [3].

On the basis of the investigation performed, altisin can be characterized as 5-hydroxy-2',6',7,8-tetramethoxyflavone. This new compound belongs to the fairly rare group of 2',6'-

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disubstituted flavones of the type of zapotin [4].

LITERATURE CITED

1. Molish and H. G. Goldschmidt, Monatsh. Chem., 22, 679 (1901).
2. T. J. Mabry, K. R. Markham, and M. B. Thomas, The Systematic Identification of Flavonoids, Springer, New York (1970).
3. V. I. Litvinenko, in: Phenolic Compounds and Their Physiological Properties [in Russian], Alma-Ata (1973), p. 104.
4. Z. Tarkas, A. Gottsegen, and M. Nagradi, Tetrahedron Lett., No. 37, 3993 (1968).