4 -METHOXYSCUTELLAREIN FROM Stachys annua

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It is known that some species of the genus <u>Stachys</u> L. contain flavonoid compounds, but their aglycone composition has been studied comparatively little [1-2]. The aim of the present work was to investigate one of the main flavonoid aglycones of the epigeal part of <u>Stachys annua</u> L. (hedgenettle betony), family Labiatae L., collected in the environs of Khar'kov.

The raw material was extracted with ethanol until the cyanidin reaction was negative. The residue after the removal of the ethanol was purified with chloroform, evaporated to small bulk, deposited on a column of polyamide sorbent, and eluted with water and then with 25% ethanol. The ethanolic eluates, containing flavonoid substances, were evaporated to small bulk and allowed to crystallize. The resulting combined flavonoid glycosides were filtered off and hydrolyzed with 7% sulfuric acid for 2 h.

The mixture of aglycones was separated on a column of polyamide sorbent, being eluted with mixtures of chloroform and ethanol. This gave aglycone (I), $C_{16}H_{12}O_6$, mp 250-253°C, triacetate $C_{22}H_{18}O_9$, mp 209-211°C. Substance (I) formed a stable brown coloration with salts of tervalent iron and gave a positive Bargellini reaction [3].

The tetramethyl ether, C₁₉H₁₈O₆, mp 160-161°C, was identical with tetramethylscutellarein.

The IR spectrum of (I) exhibited absorption bands in the regions 3430 cm^{-1} (HO), 2860 cm^{-1} (OCH₃), and 840 cm^{-1} (para-substituted aromatic nucleus).

In order to determine the positions of the phenolic hydroxyls in the nucleus of I, UV spectra were recorded: $\lambda_{max}^{CH_3OH}$ 284, 302, 330*, 390*, nm, λ_{max}^{+AcONa} 295, 400* nm, $\lambda_{max}^{+CH_3ONa}$ 275, 365† nm, $\lambda_{max}^{+AlCl_a}$ 230, 327, 365* nm, $\lambda_{max}^{+H_3BO_4+AcONa}$ 292, 312*, 313* nm.

On the basis of the spectral results and color reactions, the aglycone was shown to contain HO groups in positions 5, 6, and 7.

To determine the position of the OCH₃ group, compound (I) was demethylated by the method of Arisawa et al. [4]. The resulting substance ($C_{15}H_{16}O_6$, mp 349-351°C) was identified by its physicochemical properties, IR and UV spectra, and the mixed melting point as scutellarein (4[•], 5, 6, 7-tetrahydroxyflavone), isolated previously from Sorbaria sorbifolia (L.), A. Br. [5].

To confirm the presence of a methoxy group in ring B, the initial substance I was subjected to alkaline degradation [3]. The reaction products were shown by paper chromatography to contain p-methoxybenzoic acid.

Thus, the structure of aglycone can be represented as 5,6,7-trihydroxy-4'-methoxyflavone (4'-meth-oxyscutellarein). The IR spectra were taken by I. P. Kovalev.

* Shoulder. †Weak maximum.

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