PHENOLIC COMPOUNDS OF STACHYS PALUSTRIS

T. V. Zinchenko

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In the epigeal part of Stachys palustris L. (marsh betony) by paper chromatography we have established the presence of caffeic, 4-caffeylquinic, and chlorogenic acids. By two-dimensional chromatography [systems 1: BAW (4 : 1 : 3); and 2 : 15% CH_3COOH] we have detected no less than three substances of flavonoid nature in an aqueous ethanolic extract. Chromatography on a column of Kapron yielded substance A which, from its behavior on chromatograms and qualitative reactions [1], has been provisionally identified as a glycoside.

Glycoside A has mp 225–227° C (from ethanol), R_f 0.48 (1) and 0.4 (2); λ_{max} (in ethanol), mμ: 315, 305, 280, 225; IR spectrum, cm^{-1} [2, 3]: 3400 (OH), 2960, 2850 ($C—OCH_3$), 1727, 1745 (acyl substituent attached to the glycoside by an ester bond), and 1670, 1510 ($> C{=}O$). UV spectra with ionizing and complex-forming reagents, λ_{max}, mμ: ethanol + NaAc: 310, 305; ethanol + EtONa: 325, 250; ethanol + $Zr(NO_3)_2$: 325, 284.

In the product of the acid hydrolysis (4% HCl) of glycoside A the substances A-1, A-2, D-glucose, and glucuronic and aromatic acids were detected. The presence of the latter was also confirmed by alkaline hydrolysis (2% CH_3COONa). The order of attachment of the carbohydrate substituents was established by the stepwise acid hydrolysis (1% HCl) of substance A. Substance A-1 was isolated from the products of hydrolysis for 65 min, and the hydrolyzate contained D-glucose; after 135 min substance A-2 was obtained and D-glucose and glucuronic acid were detected in the hydrolyzate.

Substance A-1 formed yellow crystals, R_f 0.24 [2], λ_{max} (in ethanol), mμ: 315, 305, 280 mμ. From its behavior on chromatograms and qualitative reaction, this substance is a monoglycoside. Substance A-2 and glucuronic acid were found in the products of its acid hydrolysis. A spectroscopic analysis of substance A-1 in the UV region with ionizing and complex-forming reagents gave results identical with those for glycoside A.

Substance A-2 has mp 238–239° C (from aqueous ethanol), R_f 0.86 [benzene–ethyl acetate–acetic acid–formamide (24.5 : 73.5 : 2 : 1)], 0.82 (1), 0.095 (2); λ_{max} (in ethanol), mμ: 318, 305. When substance A-2 was subjected to acid hydrolysis, no cleavage was observed. In the cyanidin reaction, an orange pigment was formed which could be extracted with octanol; this characterizes substances A-2 as an aglycone [4]. The IR spectrum of A-2 has absorption bands at (cm^{-1}) 3400 (OH), 2860, 2930 ($C—OCH_3$), 1665, and 1610 ($> C{=}O$) and lacks the band of an ester bond. UV spectroscopy shows that the aglycone A-2 has free hydroxyl groups in the ortho position and position 5: λ_{max}, mμ: ethanol + NaAc + H_3BO_3 370, 300; ethanol + $Zr(NO_3)_2$: 350, 255. The very rapid decomposition of the aglycone with sodium acetate in an aqueous medium on heating, just as is the case with baicalein under these conditions, is apparently due to the presence of a 5, 6-dihydroxy grouping in their molecules.

By comparing the results of a spectral analysis of the glycosides A and A-1 and the aglycone A-2, it may be deduced that the carbohydrate substituents in these compounds are probably attached at position 5 [5] and the 7-hydroxy group may be methoxylated. The hypsochromic shift in the short-wave band of the UV spectrum on the addition of sodium ethoxide to glycoside A and A-1 and to the aglycone A-2 and also the benzoic acid found in the products of the alkaline degradation of all three compounds, show the absence of a hydroxy group in position 4'.

Thus, glucoside A, which we have called "palustrin," has been characterized provisionally as 5-(glucuronoglucosyl)-7-O-methylbaicalein, acylated with an aromatic acid, possibly in the carbohydrate moiety; the monoglycoside A-1, which we have called "palustrinoside," has been provisionally identified as the 5-glucuronoside of 7-methoxybaicalein, and its aglycone, A-2, as 7-O-methylbaicalein. These substances, which are new flavonoid compounds, have been isolated from marsh betony for the first time.

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Kiev Institute for Advanced Medical Training