FLAVONOIDS OF Stachys annua

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We have previously [1-4] reported the isolation of a number of flavonoid substances from Stachys annua L., the aglycones of which proved to be 4'-methoxyscutellarein and scutellarein.

As a result of a further study of the flavonoids of hedgenettle betony we have obtained another two substances, which we have called E and F.

Substance E ($C_{37}H_{38}O_{18}$, mp 117-119°C, $[\alpha]_D^{20}-50°$), which we have called acistachybioside is an acylated bioside. With tervalent iron, its alcoholic solutions form a green coloration rapidly changing to brown. A negative Bargellini reaction [5] shows the absence of three free vicinal hydroxyls in the molecule.

UV spectrum, nm: $\lambda_{\max}^{CH_3OH}$ 335, 202; $\lambda_{\max}^{+H_3BO_3+AcONa}$ 335, 202; $\lambda_{\max}^{+AcONa}$ 332, 202; $\lambda_{\max}^{+CH_3ONa}$ 310; $\lambda_{\max}^{+AlCl_3}$ 356, 287.

IR spectrum, cm^{-1}: 3420 (carbohydrate OH); 2940, 2850 (carbohydrate or methoxy CH); 1734 (ester C=O); 1669 (γ-pyrone C=O); 1620, 1520, 1510 (C=C of an aromatic system); 840 (para-substituted aromatic nucleus).

On acid hydrolysis with 5% sulfuric acid, acistachybioside underwent cleavage into D-glucose, D-mannose, p-coumaric acid, and an aglycone, $C_{16}H_{12}O_6$, with mp 290-292°C.

On the basis of qualitative reactions and UV and IR spectroscopy, and also from its conversion products, the aglycone of acistachybioside was identified as 4',5,6-trihydroxy-7-methoxyflavone (7-methoxyscutellarein). A similar aglycone has recently been isolated from Sorbaria stellipila, Sneid (Rosaceae) [6] and Galeopsis ladanum L. (Labiatae) [7].

Acistachybioside, like stachannoaciside [4], is hydrolyzed by the enzyme of the grape snail and by 2% sulfuric acid at 50°C for 48 h to stachybioside ($C_{28}H_{32}O_{16}$, mp 173-176°C, $[\alpha]_D -62°$) and p-coumaric acid.

The spectral analysis of acistachybioside and stachybioside in the UV region showed the presence of a free hydroxyl in position 5. The absence of bathochromic shifts of the long-wave band with sodium acetate and methoxide shows that the hydroxyls in positions 4' and 7 are substituted. Since the $-OCH_3$ group is located at C_7, the carbohydrate substituent is attached at $C_{4'}$.

The sequence of addition of the sugars was established by the stepwise hydrolysis of the glycoside with formic acid in cyclohexanol [2]. This gave 7-methoxyscutellarein 4'-O-β-D-glucoside and D-mannose. Consequently, the latter is in the terminal position.

The resistance of the glycoside to hydrolysis by rhamnodiastase, the enzyme of the grape snail [2], permits 1 → 6 and 1 → 4 bonds between the sugars to be excluded, and the degradation of both sugars in the initial glycoside and in its deacyl derivative on periodate oxidation shows the absence of a 1 → 3 bond [2]. The alkaline hydrolysis of stachybioside with 0.5% caustic potash solution did not lead to the splitting off of the biose, which is characteristic for phenolic biosides with a 1 → 2 link between the sugars.

The D-glucose and D-mannose were shown [2] to have β-glycosidic links and pyranose oxide rings.

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On the basis of the results of our investigation, the structure of acistachybioside can be represented as p-coumaroyl-7-methoxyscutellarein 4'-[O-β-D-mannopyranosyl-(1'' → 2'')-β-D-glucopyranoside], which is a new flavonoid compound.

The results obtained have permitted the sugar components of the glycoside investigated and of the stachannoaciside [4], stachannoside [2], and stachyflaside [3] studied previously to be identified.

Substance F is present in the plant in very small amount. On acid hydrolysis with 5% sulfuric acid it split into D-glucose, D-mannose, and an aglycone ($C_{15}H_{10}O_5$, mp 264-265°C), which was identified from its melting point, a mixed melting point with an authentic sample (kindly given to us by V. I. Litvinenko), and also by qualitative reactions as 5,6,7-trihydroxyflavone (baicalein).

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