ACACETIN AND ITS GLYCOSIDES IN PLANTS OF THE GENUS Linaria

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From the methanolic mother solution obtained in the crystallization of acetylpectolinarin and pectolinarin [1] from Linaria kurdica by repeated chromatography on columns of polyamide we have isolated, in addition to pectolinarigenin and linaroside [2] three other minor components. A chloroform eluate contained the flavone aglycone (I), $C_{16}H_{12}O_5$, mp 258-260°C, mol. wt. 284 (mass spectrometry), NMR spectrum: doublet at 7.69 ppm, J = 8 Hz, 2 H (H-2', 6'); doublet at 6.84 ppm, J = 8 Hz; 2 H (H-3', 5'); doublet at 6.41 ppm, J = 2.5 Hz, 1 H (H-6); singlet at 6.37 ppm, 1 H (H-3); doublet at 6.07 ppm, J = 2.5 Hz, 1 H (H-8); and singlet at 3.77 ppm, 3 H (CH_3O group) [3].

The substituents in positions 5 and 7 are free hydroxy groups (UV spectroscopy). A methoxy group is present in position 4' (the mass spectrum has a fragment with m/e 132). These facts show that (I) is acacetin.

A mixture of acacetin with linaroside and then a mixture with a flavone glycoside (II) were eluted by a 5% solution of methanol in chloroform; mp of (II) 237-240°C (decomp.), $[\alpha]_D^{20}$ −63.0° (pyridine). The acid hydrolysis of (II) formed acacetin and glucose. The carbohydrate component was present in position 7 (UV spectroscopy). The value of the coupling constant of the anomeric proton of the glucose in the NMR spectrum of the trimethylsilyl derivative of (II) (6 Hz) is characteristic for the β configuration of the glycosidic bond. The results of the gas–liquid chromatography of the completely methylated carbohydrate component of (II) [4] showed that the glucose is present in the compound in the pyranose form. Consequently, (II) is acacetin 7-O-β-D-glucopyranoside.

On desorption with 50% methanol in chloroform, a flavone glycoside (III), $C_{28}H_{32}O_{14} \cdot H_2O$ with mp 260°C (decomp.), $[\alpha]_D^{20}$ −90.1° (pyridine) was eluted. Acacetin, glucose, and rhamnose were found in the products of the acid hydrolysis of (III). The results of UV and NMR spectroscopy permit the assumption that (III) is acacetin 7-O-rutinoside (linarin). The results of a comparison with an authentic sample confirmed the identity of these compounds.

We have found the same substances in L. kokanica and L. sessilis.

LITERATURE CITED

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