FLAVONOIDS OF Vicia variabilis

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The fresh inflorescences (0.5 kg) of Vicia variabilis Freyn et Sint. (family Fabiaceae) [1], collected in the environs of Kislovodsk (village of Padkumok, slopes of the Dzhinal'skii range, May, 1971), were exhaustively extracted with methanol in an apparatus of a Soxhlet type. On standing in the cold, the methanolic extract deposited a precipitate of substance A. The crystallization of the precipitate from aqueous ethanol gave colorless prisms readily soluble in water and insoluble in organic solvents; decomp. temperature 127-260°C, R_f 0.06 in BAW (4:1:5) and 0.48 in $CH_3OH-0.5$ N NH_3 (7:3) according to Anderson [2]. From its physicochemical properties and its IR spectrum, substance A was assigned to the inositol phosphatides [3-5].

After the separation of the precipitate of substance A, the filtrate was concentrated under vacuum to $^1/_4$ of the initial volume, and an equal amount of water was added; after some time a white curd-like precipitate of substance B, sparingly soluble in alcohol, deposited.

After crystallization from methanol and dimethyl formamide – methanol (1:1) substance B formed pale-yellow crystals with mp 275-276°C, almost insoluble in many organic solvents, R_f 0.57 in BAW (4:1:5), 0.19 in 2% CH_3COOH, and 0.66 in $HCOOH-EtOAc-H_2O$ (10:2:3). $\lambda_{max}^{CH_3OH}$ 345, 251 nm. The following sugars were found in the products of acid hydrolysis: L-rhamnose, D-glucose, and rutinose (1% H_2SO_4, 0.5 h on the water bath). The aglycone had mp 258-259°C (ethanol), and its acetate mp 197-198°C (50% C_2H_5OH); R_f 0.70 in $CHCl_3-AcOH-H_2O$ (13:1:6). Demethylation by the Deloffe – Herrero method $[HI + P + (CH_3CO)_2O]$ gave 3',4',5,7-tetrahydroxyflavone (luteolin). The facts given, and also the results of alkaline degradation, mixed melting points, and UV and IR spectroscopy permit the aglycone of substance B to be identified as 3',5,7-trihydroxy-4'-methoxyflavone (diosmetin) and the glycoside itself as diosmetin 7-O-rutinoside (diosmin) [6].

After the separation of the diosmin, the residue was treated successively with $CHCl_3$ and ethyl acetate. The ethyl acetate extract yielded a mixture of flavonoids. The crystallization of this mixture from acetone, ethanol, and aqueous ethanol led to substance C (yield 1.9%).

Substance C gave crystals in the form of yellow needles with mp 171-173°C, $[\alpha]_D^{20}-175°$ (1 = 0.2 dm, c 0.0202; C_2H_5OH), R_f 0.52 in 15% CH_3COOH and 0.80 in BAW (4:1:5). UV spectrum: $\lambda_{max}^{C_2H_5OH}$ 347, 265 nm; $\lambda_{max}^{AlCl_3}$ 395,342 shoulder, 301 shoulder, 275 nm; $\lambda_{max}^{AlCl_3+HCl}$ 393, 342 (?), 300 shoulder, 273 nm. Acetyl derivative amorphous [6]. Acid hydrolysis with 6% H_2SO_4 gave the aglycone (yield 64%) with mp 273-274°C (from CH_3OH-H_2O); mp of its acetyl derivative 170-172°C (C_2H_5OH); and L-rhamnose. On the basis of the investigations performed, and also alkaline degradation, a mixed melting point, and IR spectroscopy, the flavonol glyoside isolated, C, was identified as kaempferol 3-O-α-L-rhamnopyranoside (afzelin), a sample of which was kindly given to us by Prof. R. Pohl (Freiburg, GFR) [7].

Afzelin is present only in the inflorescences of the plant, while we found diosmin in the leaves as well. This is the first time that flavonoid substances have been isolated from plants of the genus Vicia.

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