FLAVONOIDS OF THE EPIGEAL PART OF Betonica officinalis

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From the epigeal part of common betony we have isolated three flavonoids (I-III) by chromatography on polyamide and by preparative TLC on silica gel. The Molisch reaction [1] and Bryant's cyanidin reaction [2] characterized substances (I) and (II) as aglycons, and (III) as a glycoside. From the nature of their UV spectra, all the substances isolated were flavones [3, 4].

Substance (I) – $C_{15}H_{10}O_5$, yellow crystals, mp 342-345°C (decomp.). The bathochromism of the first band of the UV spectrum under the influence of chromogenic reagents indicated the presence of free hydroxy groups in the 4', 5, and 7 positions. Substance (I) gave no depression of the melting point with an authentic sample of apigenin, which shows their identity.

Substance (II) – $C_{18}H_{16}O_7$, yellow crystals, mp 218-220°C (ethanol), insoluble in water, soluble in alcohol, chloroform, and ether. On chromatograms it appeared in the form of a dark spot yellowing in the presence of alkali. The nature of its UV spectrum showed the presence of the chromophore of 3',4',5,5',7-pentahydroxyflavone [4]: λ_{max} 204, 271 (sh), 310 (sh), 331 nm. The bathochromism of the first band in the presence of alkali was 37 nm, and in the presence of $AlCl_3$ and of $AlCl_3$ + HCl it was 52 nm (hydroxy groups in positions 4! and 5, respectively); there was no ortho-dihydroxy grouping in the molecule. The products of the alkaline degradation of substance (II) could not be identified. The IR spectrum showed the presence of methoxy groups (2930, 2860, 1470, and 1430 cm^{-1}).

The demethylation of compound (II) followed by alkaline degradation led to the appearance of phloroglucinol and gallic acid. This means that the initial product was a methoxylated 3',4',5,5',7-pentahydroxyflavone.

PMR spectrum of (II) (60 MHz, deuteropyridine, δ scale from the signal of HMDS, ppm): singlets at 3.68 (6 H), and 3.78 (three aromatic OCH_3 groups); doublets at 6.72 and 6.95 (J = 2 and 5 Hz) corresponded to H-6 and H-8; a singlet at 7.12 (2 H) to H-2' and H-6' protons, and a singlet at 6.72 to a H-3 proton. Thus, the three methoxy groups may be located at the 3'-, 5'-, and 7-carbon atoms. Consequently, substance (II) was 4',5'-dihydroxy-3', 5',7-trimethyoxyflavone (7-methoxytricin), which is a new compound not previously described in the literature.

Substance (III) – $C_{21}H_{20}O_{11}$, yellow-brown crystals mp 214°C, sparingly soluble in water, soluble in alcohols, insoluble in ether and chloroform. The nature of its UV spectrum corresponded to a 4',5,6,7-tetrahydroxyflacone chromophore: λ_{max} 209, 272, 333 nm. There were bathochromic shifts of the first band amounting to 42 nm in the presence of alkali, to 55 nm in the presence of $AlCl_3$ and $AlCl_3$ + HCl, and to 7 nm in the presence of H_3BO_3 (hydroxy groups in the 4' and 5 positions and the presence of an ortho-dihydroxy grouping in the molecule). Acid hydrolysis gave a mixture of two aglycons, which was caused by the rearrangement of 5,6,7-trihydroxyflavone into 5,7,8-trihydroxyflavone [5] and D-glucose. Similar results were obtained on enzymatic hydrolysis with emulsin.

The UV spectra of the aglycons obtained coincided with the initial ones, while the bathochromism of the first band in the prsence of sodium acetate by 7 nm (followed by the degradation of the aglycon) indicated the presence of a free hydroxy group in position 7 formed as the result of hydrolysis. The β-configuration of the glycosidic bond was shown by enzymatic hydrolysis. Thus, substance (III) was scutellarein 7-glucoside (4',5,6,7-tetrahydroxyflavone 7-O-β-D-glucopyranoside).

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ROBININ AND KAEMPFEREOL FROM Vinca erecta

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In a study of the alkaloid composition of the epigeal part of the plant Vinca erecta Regel et Schmalh. introduced into the valley of the R. Pskem (Tashkent province), we have isolated, in addition to alkaloids, two new substances with mp 198-199°C (from water) (I) and 276-278°C (from acetone) (II, M^+ 286).

The UV spectra of the substances [$\lambda_{max}^{ethanol}$ 268, 356 (log ε 4.30; 4.21) (I); 266, 370 (log ε 3.99; 4.16) (II)] and their changes on alkalinization were typical for flavonols, which was confirmed by their IR spectra in which there were absorption bands of hydroxy groups at 3400 cm^{-1} (I) and 3330 cm^{-1} (II) and of carbonyl groups at 1660 cm^{-1} (I) and 1610 cm^{-1} (II) [1]. The PMR spectrum of (I) indicated the presence of sugar residues in its molecule.

When (I) was hydrolyzed with 5% sulfuric acid, an aglycon was obtained which proved to be identical with (II). L-Rhamnose and D-galactose were found in the carbohydrate part of the hydrolysate by the GLC method in a quantitative ratio of 2:1. The acetylation of (I) with acetic anhydride in pyridine gave an acetyl derivative the NMR spectrum of which showed the signals of 11 acetoxy groups, which agreed with the results of hydrolysis.

The presence of the peaks of ions with m/z 273 and 111 in the mass spectrum of the acetyl derivative showed that the terminal sugar residue was L-rhamnose in the pyranose form [2].

The structure of the aglycon followed from a consideration of its NMR spectrum which clearly showed the signals of two meta-protons at δ 6.05 ppm (d, 1 H, J = 3 Hz) and 6.25 ppm (d, 1 H, J = 3 Hz) and the protons of a para-substituted benzene ring at δ 6.77 ppm (d, 2 H, J = 9 Hz) and 7.95 ppm (d, H, J = 9 Hz).

From its melting point and spectral characteristics, (II) was identified as kaempferol (3,4',5,7-tetrahydroxyflavone) [3]. Thus, (I) was a kaempferol trioside, and from its properties it was identical with robinin (kaempferol 7-O-α-L-rhamnopyranoside 3-O-β-robinobioside) [4], as was confirmed by a direct comparison with a sample of robinin (TLC, mixed melting point, IR spectra).

This is the first time that robinin and kaempferol have been detetced in the plant Vinca erecta.

The Khar'kov Scientific-Research Institute of Pharmaceutical Chemistry recommends robinin as highly effective agent for the treatment of diseases of the kidneys [5].

The epigeal part of the plant V. erecta contains 0.5% of robinin on the weight of the raw material and can serve as a source of its preparation.

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