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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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PHYTOCHEMICAL INVESTIGATION OF <u>Paliurus spina-christi</u>

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We have previously reported a chemical study of the neutral lipids of <u>Paliurus spina-christi</u> Mill. (Christ's thorn) [1]. The interesting biological activity of an extract of the plant impelled us to study it phytochemically.

In the fruit of Christ's thorn we detected flavonoids, the total amount of which, determined photocolorimetrically, was 2.5% [2]. On separating the combined flavonoids on a column of polyamide sorbent [3] we isolated three individual compounds.

Substance (I) — light yellow crystals with the compositions $C_{27}H_{30}O_{16}$, mp 190-192°C, $[\alpha]_D^{20}$ −11.4° (c 0.5; methanol). Acid hydrolysis led to an aglycon in the form of yellow acicular crystals with the composition $C_{15}H_{10}O_7$ (M^+ 302), mp 315-316°C, identical with quercetin. D-Glucose and L-rhamnose were found in the carbohydrate fraction of the hydrolysate.

Substance (II) — dark yellow acicular crystals with the composition $C_{21}H_{20}O_{12}$, mp 216-217°C, $[\alpha]_D^{20}$ −55.2° (c 0.1; dimethylformamide). On acid hyrolysis, this substance was split into D-glucose and quercetin.

Substance (III) — yellow acicular crystals with the composition $C_{21}H_{20}O_{12}$, mp 235-237°C, $[\alpha]_D^{20}$ −60.0°. Acid hydrolysis gave the aglycon quercetin, and D-galactose was shown to be present in the carbohydrate fraction.

On the basis of their physicochemical constants and spectral characteristics, substance (I) was characterized as rutin, (II) as isoquercitrin (quercetin 3-O-β-D-glucoside), and (III) as hyperoside (quercetin 3-O-β-D-galactoside) [4, 5].

The presence of epigallocatechin, gallocatechin, and catechin in the leaves, fruit, and flowers of Christ's thorn has been established previously [6], and coumarins [7] and traces of steroid compounds [8] have been detected.

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