FLAVONOIDS OF *Hypericum rumeliacum*

G. Kitanov

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The flavonoid composition of *Hypericum rumeliacum* Boiss., endemic to the Balkan peninsula, has been little studied. Its chromatography has shown qualitatively the presence in the epigeal part of this species of hypericin [1], 0.05% of an essential oil including α-pinene, β-pinene, n-nonane, and n-undecane [2], the polyphenolic compounds leucocyanidin, leucodelphinidin, myricetin, and quercetin [3], and the xanthone C-glycoside mangiferin [4].

In an ethyl acetate extract from the epigeal part of the plant collected in the People's Republic of Bulgaria in the flowering period we have detected 17 polyphenolic compounds. Nine of them have been assigned to the flavonoids, three of these being aglycones. The isolation and identification of these aglycones is discussed in the present paper.

To isolate the total flavonoids, 0.5 kg of raw material was exhaustively extracted with 70% ethanol. The alcohol wa distilled off in vacuum and the residue was purified with chloroform in order to eliminate ballast substances. The aqueous residue was hydrolyzed with 6% HCl with heating in the boiling water bath for 3 h. Under these conditions all the glycosides underwent complete hydrolysis. The hydrolysate was cooled, the aglycones were extracted repeatedly with diethyl ether, the extracts were dried with anhydrous sodium sulfate, and the ether was distilled off to dryness.

The mixture of aglycones was purified and separated on a column of polyamide sorbent, and also by preparative paper chromatography. Three substances were isolated.

Substance (I) had R_f values of 0.05, 0.55, 0.65, and 0.87, respectively, in solvent systems 1) 15% CH_3COOH, 2) 60% CH_3COOH, 3) acetic acid—hydrochloric acid—water (30:3:10), and 4) butan-1-ol—acetic acid—water (40:10:22); λ_{max} (methanol) 267, 367 nm. UV spectra in the presence of complex-forming and ionizing reagents showed the presence of free hydroxy groups in the 3,4',5, and 7 positions.

Substance (II) had mp 308-310°C; R_f 0.43 (system 2): 0.76 (system 4); λ_{max} (methanol), nm; 258, 375 (log ε 4.25, 4.28), $E_{1\%}^{1\%}{}_{cm}$ = 663. The features of the UV spectra show the presence of free hydroxyls in the 3, 3', 4', 5, and 7 positions.

Substance (III) had mp 218-222°C (decomp.), R_f 0.28 (system 2), 0.57 (system 4), λ_{max} (methanol), nm; 254, 378 (log ε 4.26, 4.30). A positive Bargellini reaction [5] showed the presence of three free hydroxyls in the vicinal position in the molecule of (III). Their location in ring B was confirmed by UV spectra and alkaline cleavage. In the presence of sodium ethanolate a bathochromic shift of the absorption maxima was observed in the UV spectra of substance (I), a hypsochromic shift in the case of substance (II), and rapid decomposition in the case of substance (III).

On the basis of their physical constants, chemical transformations, UV and IR spectra, chromatographic behavior, color reactions with diagnostic reagents, and comparison with authentic samples, the compounds isolated were identified as kaempferol (I), quercetin (II), and myricetin (III).

As a result of the investigation of the individual glycosides, two of them were assigned to derivatives of myricetin on the basis of chromatographic behavior and qualitative characteristics. This is the first time that myricetin glycosides have been detected in species of the genus *Hypericum*.

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FLAVONOIDS OF *Astragalus flexus*

P. Khozhambergenova and K. F. Blinova

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We have previously isolated quercetin and kaemferol from the epigeal part of *Astragalus flexus* Fisch. (flexile milkvetch) [1]. In a further separation of the total flavonoids on a column of polyamide sorbent, we have isolated another three substances.

Substance (I) with the composition $C_{16}H_{12}O_7$ [mp 303-305°C (from 40% ethanol), melting point of the acetate 202-204°C, λ_{max} (ethanol) 370, 255 nm] was assigned to the aglycones [2]. Qualitative reactions and IR and UV spectroscopy showed the presence of free hydroxy groups in positions 3, 4', 5, and 7, and of a methoxy group in position 3'. The results obtained enable substance (I) to be characterized as 3,4',5,7-tetrahydroxy-3'-methoxyflavone (isorhamnetin).

Substance (II) had the composition $C_{21}H_{20}O_{11}$, mp 179-180°C (from 40% ethanol), λ_{max} (ethanol) 357, 255 nm. The acid hydrolysis of (II) gave an aglycone, which was identified as kaempferol, and glucose, which was identified by paper chromatography. A study of the UV spectra of the aglycone and of the glycoside showed that the glycoside had free hydroxy groups in positions 4', 5, and 7 and the sugar component in position 3. On the basis of the results obtained, it may be concluded that substance (II) has the structure of kaempferol 3-O-β-D-glucopyranoside and is identical with astragalin [3].

Substance (III) had the composition $C_{22}H_{22}O_{12}$, mp 171-173°C (from 40% ethanol), λ_{max} (ethanol) 355, 257 nm. Acid hydrolysis gave the aglycone, identical with isorhamnatin (yield 49.7%) and glucose, which was identified by paper chromatography. Qualitative reactions and UV spectroscopy with diagnostic additives enabled the substance under investigation to be characterized as isorhamnatin 3-O-β-D-glucopyranoside [4]. This is the first time that any of these compounds have been isolated from *Astragalus flexus*.

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