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FLAVONOIDS OF CERTAIN SPECIES OF *Hypericum* L.

E. Yu. Makovetskaya

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Representative samples of ten species of the herb genus *Hypericum* L. belonging to the most typical section were investigated. These are *H. attenuatum* Choisy, *H. erectum* Thunb. ex Murray, *H. graveolens* Buckley, *H. kamtschaticum* Ledeb., *H. mitchellianum* Rydb., *H. perforatum* L., *H. pseudomaculatum* Bush., *H. pseudopetiolatum* R. Keller, *H. punctatum* Lam., and *H. undulatum* Schousb. ex Willd. The species were grown on test plots of the CBG of the NAS of Ukraine. Samples were collected during full flowering in the second year of growth (1997).

Flavonoids were isolated from the herb by treatment with $CHCl_3$ to remove pigments, lipids, and resinous substances. The lipophilic fraction was filtered off. The herb was dried and extracted with 70% ethanol. Flavonoids were isolated from the dried aqueous ethanol extract by ethylacetate. The ethylacetate was removed. The total flavonoids (10 g) were placed on a column (60×2.8 cm) filled with Woelm polyamide sorbent. The column was eluted with $CHCl_3$ and a $CHCl_3$–CH_3OH mixture with an increasing methanol gradient. The eluates were monitored by TLC on Silufol UV-254 plates using ethylacetate-toluene-85% formic acid (25:25:3) and $CHCl_3$–CH_3OH (7:3) and by paper chromatography (PC) on FN-12 paper using butan-1-ol-CH_3COOH-water (4:1:2.2). Fractions purified of accompanying substances (anthraquinones, coumarins, phenolic acids) were combined and separated into pure components by two-dimensional PC using butan-1-ol-CH_3COOH-water (4:1:2.2) (first direction) and water (second direction).

A mixture of flavonoid-like substances was isolated. The four principal components (**1-4**) were identified. One of these was the aglycone (**1**). Three compounds acted like glycosides (**2-4**).

The compounds obtained were identified by PC and TLC using the chromatographic procedures described above. Melting points were determined. Electronic spectra were recorded (Specord M-80).

Compounds **2-4**, which acted like glycosides, were analyzed by acid hydrolysis (2% H_2SO_4, 40 min). The hydrolysis products of **2**, **3**, and **4** contained the aglycone, identified as 3,5,7,3′,4′-pentahydroxyflavone (quercetin) by physicochemical data, UV spectroscopy with complexing and ionizing additives, and comparison with an authentic sample. The hydrolysates were compared with standard sugars using PC. The sugar component of **2** is *D*-galactose; of **3**, *L*-rhamnose; of **4**, *L*-rhamnose and *D*-glucose.

Data for the isolated compounds are given below.

Compound **1**: $C_{15}H_{10}O_7$, mp 318-320°C, λ_{max} (C_2H_5OH) 370, 270 nm. Identified as 3,5,7,3′,4′-pentahydroxyflavone, quercetin, by comparison with an authentic sample.

Compound **2**: $C_{21}H_{20}O_{12}$, mp 238-240°C, λ_{max} (C_2H_5OH) 361, 258 nm. Identified as 5,7,3′,4′-tetrahydroxy-3-O-β-*D*-galactopyranoside, hyperoside, by comparison with an authentic sample.

Compound **3**: $C_{21}H_{20}O_{11}$, mp 185-187°C, λ_{max} (C_2H_5OH) 356, 257 nm. Identified as 5,7,3′,4′-tetrahydroxy-3-O-α-*L*-rhamnoside, quercitrin, by comparison with an authentic sample.

Compound **4**: $C_{27}H_{29}O_{16}$, mp 188-190°C, λ_{max} (C_2H_5OH) 360, 258 nm. Identified as 5,7,3′,4′-tetrahydroxy-3-O-α-*L*-rhamno-1,6-α-*D*-glucoside, rutin, by comparison with an authentic sample.

Quercetin, hyperoside, and rutin were observed chromatographically and preparatively in all 10 studied species of *Hypericum* L. Quercitrin was found in 8 species (in all except *H. pseudomaclatum* and *H. pseudopetiolatum*).

The results confirm literature data about the flavonoid composition of *Hypericum* sp. [1-4], which suggest the presence of hyperoside and rutin in most previously studied species of *Hypericum*. Quercetin and quercitrin are not signature compounds of the genus although they occur in several species [4-7].

N. N. Grishko Central Botanical Garden (CBG), National Academy of Sciences (NAS) of Ukraine, Kiev, Ukraine, fax (044) 277 85 30. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 671-673, September-October, 1999. Original article submitted May 18, 1999.

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Quercitrin was isolated for the first time from seven of the species mentioned above. The yields were 21.8 g of quercitrin from 1 kg of *H. attenuatum*; 14.5 g, from 1 kg of *H. erectum*; 16.0 g, *H. graveolens*; 25.1 g, *H. kamtschaticum*; 18.1 g, *H. mitchellianum*; 15.3 g, *H. perforatum*; 23.7 g, *H. punctatum*; 14.6 g, *H. undulatum*.

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