We have also determined the amounts of the aglycones in the various organs in the nodding dragonhead by a chromatographic-spectrophotometric method after enzymatic hydrolysis. The leaves contained the maximum amount of aglycones — 0.156% of apigenin and 0.273% of luteolin. The flowers and the stems contained small amounts of the aglycones — 0.117 and 0.097% of apigenin and 0.118 and 0.116% of luteolin, respectively. Thus, luteolin predominated in the leaves and stems while luteoline and apigenin were present in approximately equal amounts in the flowers.

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C-GLYCOFLAVONOIDS FROM *Hypericum hirsutum*

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We have previously reported the isolation of six polyphenolic compounds from the epigeal part of *Hypericum hirsutum* L. (hairy St. John's wort). Of the compounds isolated (V) and (VI) have, on the basis of their isomerization on acid hydrolysis, been assigned to the C-glycosides [1].

To isolate the C-glycoflavonoids, 1.5 kg of raw material was extracted with ethanol. The total material obtained was separated on polyamide, and also by preparative paper chromatography. In this way we isolated substance (II), identified previously as quercetin [1], and substances (V), (VI), (VII), and (VIII).

Substance (V) had mp 262-263°C (20% ethanol), R_f 0.16 and 0.42 (here and below, respectively, systems 1) 15% acetic acid and 2) butan-1-ol—acetic acid—water (40:10:22)), and on the basis of the Shinoda [2] and Bryant [3] tests and its UV spectrum it was assigned to the flavone glycosides UV spectum: $\lambda_{max}^{CH_3OH}$ 258, 267 sh., 351 nm (log ε 4.28, 4.27, 4.34). The UV spectra with ionizing and complex-forming additives showed the presence of free hydroxy groups in the 3', 4', 5, and 7 positions, and the value of $[E_{1cm}^{1\%}]$ = 486 characterized (V) as a monoside [4]. Acid hydrolysis with 10% and 20% H_2SO_4 led to its isomerization with the appearance of a new substance having R_f 0.32 (system 1) and 0.56 (system 2). This fact shows that the sugar is located at C_8 [5], and this was confirmed by the PMR spectrum. On acid hydrolysis according to Kiliani [6] and decomposition with HI in liquid phenol, luteolin and glucose were isolated and identified.

IR spectrum of (V) (cm^{-1}): 3520-3350 (OH); 1663 (C=O); 1618, 1520 (C=C); 1090, 1050, 1020 (pyranose form of a sugar) [4].

NMR spectrum in DMSO (ppm): 7.52 (m, H-2',6'); 6.90 (d, 8.5 Hz, H-5'); 6.68 (s, H-3); 6.28 (s, H-6); 4.73 (d, 10 Hz, H-1"); the signal of the anomeric proton (d, 4.73; 10 Hz) showed the β configuration of the glycosidic bond [5, 7, 8].

The octaacetate of (V) had mp 200-202°C, R_f 0.21 (TLC, silica gel, benzene—acetone (3:1)). Its PMR spectrum in $CDCl_3$ (ppm): 6.84 (d, 7 Hz, H-5'); 6.66 (s, H-3); 6.61 (s, H-6); 5.45 (m, H-1"); 2.45 (s, C_5—OAc); 2.39, 2.37, 2.35 — overlapping singlets (C_7, C_3', C_4'—OAc); 2.10 (s, 4"—OAc); 2.04 (s, 3"—OAc); 1.93 (s, 6"—OAc) 1.75 (1.70) (d, 2"-OAc).

A comparison of the physical constants, R_f values, features of the UV, IR, and PMR spectra, and chemical transformations has enabled (V) to be identified as luteolin 8-C-β-D-glucopyranoside (orientin).

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Substance (VI) had mp 229-230°C (20% ethanol), R_f 0.32 (system 1), 0.56 (system 2). The UV and IR spectra of (VI) were similar to those of (V), $[E^{1\%}_{1cm}]$ = 344. On acid hydrolysis with 10% H_2SO_4, the substance underwent isomerization with the formation of orientin. On the basis of the mutual transformations of (V) and (VI) on acid hydrolysis and the results of the spectral investigations, substance (VI) was identified as the orientin isomer homoorientin (luteolin 6-C-β-D-glucopyranoside).

Substance (VII), mp 318-321°C, R_f 0.04 (system 1), 0.83 (system 2), 0.50 (60% acetic acid), $[E^{1\%}_{1cm}]$ = 772, was assigned to the aglycones. Analysis of its UV spectrum showed the presence of free hydroxy groups in positions 3', 4', 5, and 7. On comparing the physical constants, R_f values, and UV and IR spectra of (VII) with those of an authentic sample of luteolin they were found to be completely identical. As a result, substance (VII) has been identified as 3',4',5,7-tetrahydroxyflavone (luteolin).

Substance (VIII) was detected in minor amounts; λ_{max} (methanol) 253, 376 nm. In the presence of sodium methanolate it rapidly decomposed, which is characteristic for flavonoids with free vicinal hydroxyls in ring B and a free C_3-OH group [5]. A positive Bargellini test also showed vicinal substitution in the (VIII) molecule [9]. On the basis of these results, a chromatographic comparison with an authentic sample, and the effects of diagnostic reagents, substance (III) was identified tentatively as 3',3,4',5,5',7-hexahydroxyflavone (myricetin).

We are the first to have isolated the four phenolic compounds identified from representatives of the genus *Hypericum*. The presence of flavones in St. John's wort has been reported only by Lebreton and Bouchez, who detected luteolin chromatographically in hairy St. John's wort [10]. In an investigation of 17 other species of *Hypericum* growing on the territory of Bulgaria, no C-glycoflavonoids were detected in any of them. Since until now it has been considered that only flavonols accumulate in *Hypericum* species, the isolation of flavones and their C-glycosides will force us to change our ideas on the flavonoid complex of species of this genus.

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