J = 2.5 Hz), H-6' (7.23 ppm, quartet, J = 7.0 Hz and 2.5 Hz), H-5' (6.84 ppm doublet, J = 7.0 Hz), H-6 (6.38 ppm, doublet, J = 2.0 Hz), and H-8 (6.19 ppm, doublet, J = 2.0 Hz). In addition a doublet of the anomeric proton of rhamnose (5.24 ppm, J = 1.0 Hz) and a doublet of the rhamnose CH_3 group (1.81 ppm, J = 5.0 Hz) were found. The rhamnose protons gave a complex unresolved signal in the 5.0-2.8 ppm region. On the basis of these facts and an analysis of UV and IR spectra, substance (V) has been characterized as quercetin 3-O-α-L-rhamnopyranoside (quercitrin).

Substance (VI), with mp 185-200°C (aqueous ethanol), λ_{max} 328, 398 nm, $[\alpha]_D^{22°}$ −63.8° (c 0.65; methanol) and substance (VII) with mp 256-272°C (aqueous ethanol), λ_{max} 280, 325*, †410 nm, $[\alpha]_D^{22°}$ −82.5° (c 0.95; methanol) had very similar properties. They possessed a bright greenish-yellow fluorescence in UV light, were colored crimson under the action of alkali and of concentrated H_2SO_4, and did not give colored products in the cyanidin and tetrahydroborate reactions. The hydrolysis of substance (VI) with 2% H_2SO_4 led to the formation of glucose and (I) and the cleavage of (VII) under similar conditions gave the same sugar and (II). A study of the UV spectra with diagnostic additives and also of the IR and PMR spectra enabled substance (VI) to be characterized as sulphuretin 6-O-β-D-glucopyranoside (sulphurein), and substance (VII) as maritimetin 6-O-β-D-glucopyranoside (maritimein). The structures of both these aurone glycosides were confirmed by their synthesis from (III) and (IV), respectively.

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†Footnote omitted as in Russian original — Publisher.

FLAVONOID AGLYCONES OF *Dracocephalum nutans*

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Two aglycones of flavonoid nature have been isolated by the chromatography on a polyamide sorbent of an ethanolic extract of the herb *Dracocephalum nutans* L. (nodding dragonhead).

Aglycone (1), mp above 340°C, R_f 0.61 (60% acetic acid). UV spectrum: λ_{max} (ethanol), 333, 268 nm.

Aglycone (2), mp 330-332°C, R_f 0.46 (60% acetic acid). UV spectrum: λ_{max} (ethanol), 355, 268, 255 nm. On the basis of spectral analysis in the UV region with complex-forming and ionizing additives, and IR spectroscopy, aglycone (1) was identified as 4',5,7-trihydroxyflavone (apigenin), and aglycone (2) as 3',4',5,7-tetrahydroxyflavone (luteolin) [1-3].

In order to determine the composition of the aglycones of the flavonoids of the nodding dragonhead, we subjected an extract containing the total flavonoids to hydrolysis with the enzyme preparation "Pektavomarin." The completeness of hydrolysis was checked by paper chromatography. It was achieved after 72 h. The total aglycones after enzymatic hydrolysis consisted of two substances, which were isolated by preparative chromatography on polyamide and were identified as apigenin and luteolin. This permitted the conclusion that all the flavonoids of this plant are derivatives of luteolin and apigenin.

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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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