

Fig. 1. NMR spectrum of feshurin (C₅D₅N).

tion, the signals from five protons of a coumarin nucleus appeared in the 6.17-7.51 region (Fig. 1).

On the basis of the facts given above, it may be concluded that feshurin is an isomer of nevskin at the C_6 :-OH. Structure (I) is suggested for it.

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FLAVONOIDS OF Bidens cernua

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We have previously [1] isolated the chalcone butein and the aurones sulphuretin (I) and maritimetin (II) from the flowering herb *Bidens cernua* L. (nodding beggar-ticks) collected in the water meadows in the environs of the town of Miknov, Khmelnitskaya oblast. Continuing a study of the flavonoids of this plant, by preparative chromatography on columns of Kapron we have isolated another five compounds (substances III-VII).

Substance (III) with mp 165-167°C (ethanol) and substance (IV) with mp 236-239°C (ethanol) were identified on the basis of their chemical properties and UV, IR, and PMR spectra as butin 7-0- β -D-glucopyranoside ((R-2)isocoreopsin), and isookanin 7-0- β -D-glucopyranoside ((R-2)flavanomarein) obtained from *Bidens tripartita* L. [2-4].

Substance (V) had mp 179-181°C (aqueous ethanol). $[\alpha]_D^{2^\circ}$ -118.6° (c 0.87; methanol), λ_{max} 259, 268*, [†] 358 nm (in methanol). On hydrolysis (1% H₂SO₄, 40 min) an aglycone (mp 309-310°C) and rhamnose were formed. The PMR spectrum of the glycoside (DMSO, δ scale) showed the signals of the protons of hydroxy groups at C₅ (12.63 ppm, singlet), C₇ (10.8 ppm), C₄ (9.63 ppm), and C₅ (9.28 ppm) and also those of the aromatic protons H-2 (7.29 ppm, doublet,

†Footnote omitted as in Russian original - Publisher.

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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 CH₃ 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 3-0- α -L-rhamno-pyranoside (quercitrin).

Substance (VI), with mp $185-200^{\circ}\text{C}$ (aqueous ethanol), λ_{max} 328, 398 nm, $[\alpha]_{D}^{2\circ}$ -63.8° (c 0.65; methanol) and substance (VII) with mp $256-272^{\circ}\text{C}$ (aqueous ethanol), λ_{max} 280, 325*, †410 nm, $[\alpha]_{D}^{2\circ}$ -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 H₂SO₄, and did not give colored products in the cyanidin and tetrahydroborate reactions. The hydrolysis of substance (VI) with 2% H₂SO₄ 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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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: $\lambda_{\rm max}$ (ethano1), 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-trihydroxy-flavone (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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