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FLAVONOIDS OF *Calluna vulgaris*

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We have previously reported the isolation from Scotch heather and identification of quercetin and hyperoside [1]. Continuing an investigation of the flavonoids of this plant, we have isolated another two substances.

Substance (I) — mp 245-248°C, λ_{max}, 245, 298, 370 nm (+NaOAc 250, 330, 370 nm; +$AlCl_3$ 264, 340, 380 nm; +$AlCl_3$ + HCl 319, 372 nm; +NaOAc + H_3BO_3 249, 309, 380 nm; +NaOMe 252, 300, 380 nm). The intense absorption maximum at 298 nm is characteristic for substances of flavanonol nature, as was confirmed by the NMR spectrum.

The NMR spectrum of the substance had the following signals: d, 7.04 ppm, 2H, J = 8 Hz (H-2', 6'); d 6.50 ppm, 2H, J = 8 Hz (H-3', 5'); d, 4.66 ppm, 1H, J = 11 Hz (H-2); and m, 4.00 ppm, 1H (H-3). On silylation, the substance isomerized, as was shown at the signals of the H-6 and H-8 protons.

Judging from the experimental results, the substance isolated has the structure of 3,4',5,7,8-pentahydroxyflavanone or 3,4',5,6,7-pentahydroxyflavanone. On the basis of biogenetic considerations, we tend to consider that it has the structure of 3,4',5,7,8-pentahydroxyflavanone, since from the plant under investigation we have previously isolated a substance based on 3,4',5,7,8-pentahydroxyflavone (herbacetin) [2]. This was confirmed by the oxidation of (I) by atmospheric oxygen to herbacetin, which was identified by paper chromatography (in the presence of an authentic sample of herbacetin) and by UV spectroscopy.

Thus, it may be concluded that the compound isolated has the structure of 4',5,7,8-tetrahydroxyflavanonol (dihydroherbacetin) and is a new natural substance.

Substance (II) — mp 278-282°C, $[\alpha]_D^{20}$ − 40° (c 0.13; methanol), λ_{max} 273, 329, 376 nm. Substance (II), like (I) has, according to NMR spectroscopy, substituents in positions 3,4', 5,7, and 8, but it is a flavonol derivative, as is confirmed by the nature of the UV spectrum with intense both short-wave and long-wave maxima at 273 and 376 nm). The acid hydrolysis of (II) gave an aglycone which, from its melting point and UV and NMR spectroscopic characteristics was identified as herbacetin [2], and D-glucose.

The NMR spectrum of substance (II) has, in addition to the signals characteristic for herbacetin, a doublet at 4.68 ppm, 1H, J = 6 Hz, which is characteristic for the proton of the glycosidic center of β-glucose. The other glucose protons give a signal in the 3.4-3.9 ppm region. The UV-spectroscopic characteristics show that the hydroxy groups in positions 3,4',5, and 7 are free, and the glucose can be present only in position 8. Judging from the specific rotation, the glucose has a pyranose ring.

On the basis of what has been said above, it may be concluded that substance (II) has the structure of 8-β-D-glucopyranosyloxy-3,4',5,7-tetrahydroxyflavone (herbacetin 8-glucoside).

Herbacetin 8-glucoside has not previously been isolated from plants.

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FLAVONOIDS FROM *Hieracium pilosella*

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In the flowers of *Hieracium pilosella* L. (mouse-ear hawkweed) collected in the flowering phase in the Belorussian SSR we have detected by paper chromatography no less than 12 substances of flavonoid nature.

From an ethanolic extract of the flowers of this plant, by column chromatography on a polyamide sorbent we have isolated five substances of flavonoid nature (I-V). Substances (I) and (II) have been identified with the previously isolated luteolin [1] and luteolin 7-glycoside [2]. Substances (III) and (IV) have been identified on the basis of UV, IR, and NMR spectra, melting points, and elementary analyses as apigenin [3] and isorhamnetin [4, 5], respectively.

Substance (V) with the composition $C_{15}H_{10}O_7$ appears in UV light in the form of a bright brown spot, which shows its flavone or 3-substituted flavone structure. The UV spectrum of the substance has absorption maxima at 252 sh., 266, and 377 nm. The long-wave maximum is characteristic for a flavonol, but this does not agree with its NMR spectrum. The NMR spectrum of the TMS ether of the substance (Fig. 1) had the following signals: doublet at 6.12 ppm, 1H, J = 2.5 Hz (H-6); doublet at 6.26 ppm, 1H, J = 2.5 Hz (H-8). These signals show the

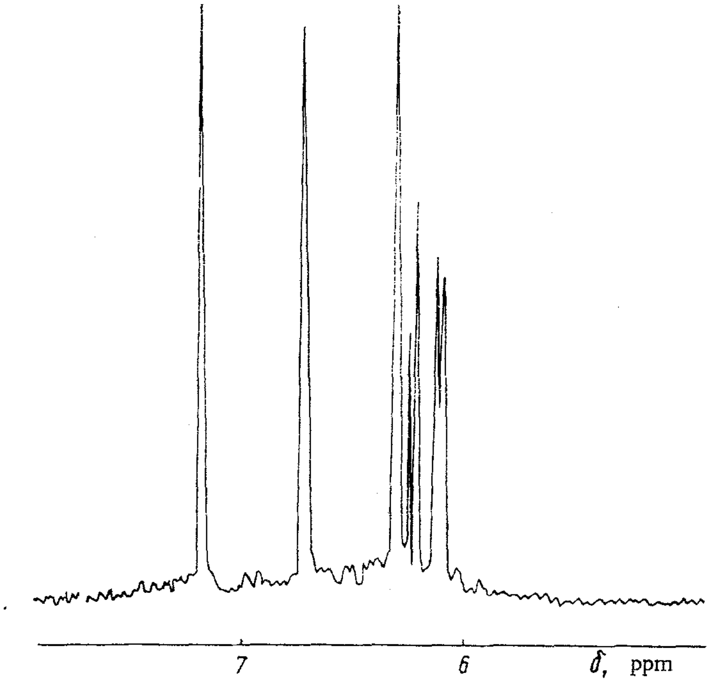

Fig. 1. NMR spectrum of 3',4',5,6',7-pentahydroxyflavone.

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