LITERATURE CITED

1. V. L. Shelyuto, L. P. Smirnova, V. I. Glyzin, and L. I. Anufrieva, Khim. Prirodn. Soedin., 652 (1975).
2. Z. P. Pakudina and A. S. Adykova, The Distribution in Plants and Physicochemical Properties of Flavonols, Flavones, and Their Glycosides [in Russian], Tashkent (1970), p. 19.

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

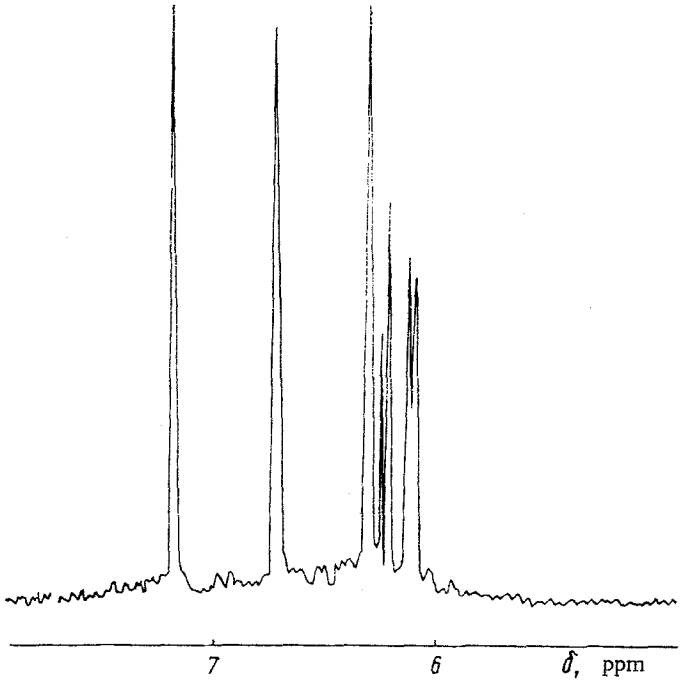

Fig. 1. NMR spectrum of 3',4',5,6',7-pentahydroxyflavone.

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presence of substituents in positions 5 and 7 of ring A. Apart from these signals, in the weak-field region the spectrum of the substance differs from those of many known flavonoids having substituents in positions 4'; 3',4'; or 3',4',5' [6]. In addition to the doublets mentioned, the spectrum contained three signals of one proton unit each at 6.32, 6.72, and 7.16 ppm. Two of them must be assigned to ring B, i.e., 7.16 ppm (H-2'), 6.72 ppm (H-5'), and 6.32 ppm (H-3). Hence it follows that the substituents in ring B of the compound isolated may be present in positions 3',4',6'. With a different arrangement of the substituents the signals of 2' and 5' protons would not appear in the form of a singlet.

The results of UV spectroscopy confirm the presence of hydroxy groups in positions 3', 4',5,7.

The substituents in position 3' 4', 5,6',7 are hydroxy groups, as is shown by the results of UV spectroscopy, the absence of the signals of protons of other substituents in the NMR spectrum, and the mass-spectral results.

The mass spectrum of substance (V) has the molecular peak M 302^+ (94%) corresponding to the number of substituents in the molecule and, in addition, the peaks of fragments of ring A with m/e 151 (16%) and a strong peak with m/e 153 (100%) corresponding to a fragment of ring B with the heteroatom. The peak with m/e 150 (30%) also corresponds to ring B with three hydroxy groups. Thus, the substance isolated has the structure of 3',4',5,6',7-pentahydroxyflavone, which has not been described in the literature, and we have called it hieracin.

LITERATURE CITED

1. N. A. Kaloshina, Abstracts of lectures at the IInd Congress of Pharmacists of the Belorussian SSR [in Russian], Minsk (1970), p. 70.
2. M. Haag-Berrurier and P. Duquénois, Compt. Rend., 257, No. 21, 3239 (1963).
3. V. L. Shelyuto, V. I. Glyzin, A. I. Ban'kovskii, and N. T. Bubon, Khim. Prirodn. Soedin., 371 (1971).
4. S. A. Medvedeva and N. A. Tyukavkina, Khim. Prirodn. Soedin., 676 (1972).
5. T. A. Geissman, The Chemistry of Flavonoid Compounds, Pergamon, New York (1962), p. 424.
6. T. J. Mabry, K. R. Markham, M. B. Thomas, The Systematic Identification of Flavonoids, Springer, New York (1970), p. 254.

FLAVONOIDS OF *Galinsoga parviflora*

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We have studied the chemical composition of the epigeal part of *Galinsoga parviflora* Cav., collected in the flowering period in the region of Pyatigorsk. In the leaves we have found saponins of the triterpene series, polyphenolc compounds, tanning substances, and inulin. The amount of "crude" saponins was 1.59% (on the air-dry weight of raw material), of tanning substances 2.4% (by a standard method [1]), and of flavonoids 2.4% [2]. To isolate the inulin, the raw material was extracted with water and the inulin was precipitated with ethanol; its amount was 10.7% (mean of three determinations).

By paper chromatography, no less than five substances of flavonoid nature were detected in the ethanolic extracts. Acid hydrolysis showed the presence of three aglycones, two of which were identified as apigenin and luteolin. To isolate the glycosides, 1 kg of air-dry leaves was exhaustively extracted with 70% ethanol on the boiling water bath, the ethanolic extracts were concentrated, and the residue was freed from lipophilic impurities and treated with boiling water. The aqueous solution obtained was washed with chloroform, and the flavonoids were extracted with ethyl acetate.

After the elimination of the ethyl acetate, the residue was dissolved in ethanol and the flavonoids were separated on a column of polyamide sorbent using increasing concentrations of

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