LITERATURE CITED

1. S. I. Sagitov, Uzb. Biol. Zh., No. 3, 27 (1962).
2. V. A. Kompantsev, Abstracts of Lectures at the First Scientific Conference of Young Scientists [in Russian], Pyatigorsk (1973), p. 28.
3. V. A. Kompantsev and V. I. Glyzin, Khim. Prirodn. Soedin., 553 (1973).
4. V. A. Kompantsev and A. L. Shinkarenko, Khim. Prirodn. Soedin., 370 (1970).

A FLAVONOID FROM *Achillea cartilaginea*

G. G. Zapesochnaya and A. I. Ben'kovskii

UDC 547.972

Among the flavone glycosides that we have isolated from the flower heads of *Achillea cartilaginea* [1], compound (VIII) with mp 221-224°C, $[\alpha]_D^{20}$ 138.6° (c 0.66; formamide) was erroneously identified as apigenin 7-O-β-D-glucopyranoside.

Acetylation of the glycoside gave, instead of the expected hexaacetate, a pentaacetate with the composition $C_{33}H_{32}O_{16}$, mp 200-203°C. Careful investigation of the products of acid hydrolysis (20% H_2SO_4, 6 h at 100°C) showed the presence of apigenin and glucuronic acid. The presence of a band at 1745 cm^{-1} in the IR spectrum of compound (VIII) and of three aliphatic acetoxy groups in the pentaacetate (NMR, Fig. 1) also confirms the presence of a uronic acid residue. Furthermore, in the NMR spectrum of the acetate there is the doublet (4.22 ppm, J = 9 Hz) of a proton at C-5" of a D-glucuronide and the signals of an ethoxycarbonyl group (triplet, 3 H at 1.2 ppm, and quartet, 2 H at 4.15 ppm).

Consequently, the carbohydrate moiety of compound (VIII) is ethyl D-glucuronate, the position of attachment of which at the 7-OH group of apigenin was shown previously from UV spectra.

In the NMR spectrum of the TMS ether of the glycoside, the two-proton quartet corresponding to the $-CH_2O$ group in the $-COOCH_2CH_3$ fragment fuses with the signals of the four protons of the glucuronic acid, forming a multiplet in the 3.5-4.15 ppm region with an intensity of 6 H. The signal of the anomeric proton (4.92 ppm, J = 6.5 Hz) corresponds to a β-bound D-glucopyranosiduronate. Thus, compound (VIII) has the structure of ethyl (apigenin 7-O-β-D-glucopyranosid)uronate.

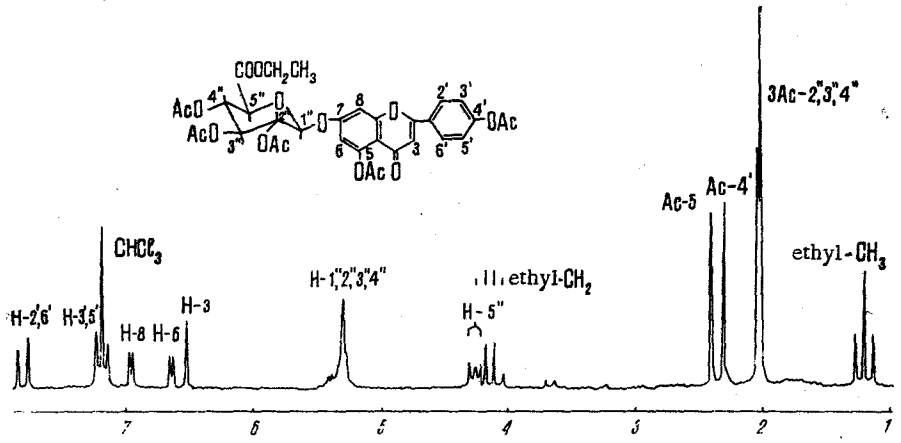

Fig. 1. NMR spectrum of the pentaacetate of ethyl (apigenin 7-glucosid)uronate in $CDCl_3$ (100 MHz, internal standard DMS).

All-Union Scientific-Research Institute of Medicinal Plants, Moscow. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 814-815, November-December, 1976. Original article submitted July 30, 1976.

The elementary analysis corresponds to the calculated figures for both the composition given previously, $C_{21}H_{20}O_{10}$, and also the new one, $C_{23}H_{22}O_{11}$.

The isolation of methyl (apigenin 7-galactosid)uronate has been reported by Ahmed et al. [2], and these authors considered the substance to be native and not a consequence of extraction with methanol. We do not exclude the possibility that the plant contains free apigenin 7-glucosiduronic acid which is converted into the ethyl ester during extraction with ethanol on heating.

LITERATURE CITED

1. I. D. Neshta, G. G. Zapesochnaya, N. A. Kaloshina, and A. I. Ban'kovskii, Khim. Prirodn. Soedin., 796 (1973).
2. Z. F. Ahmed, H. Rimpler, et al., Phytochem., 9, 1595 (1970).

FLAVONOIDS OF *Atraphaxis muschketovii*

T. K. Chumbalov and V. B. Omurkamzinova

UDC 547.972

We have previously [1-3] reported an investigation of the flavonoid composition of the leaves of two species of Atraphaxis of the 14 found in the territory of Kazakhstan — *Atraphaxis pyrifolia* and *Atraphaxis frutescens*, belonging to the subgenus Tragopyrun. *Atraphaxis muschketovii* Krassn., which is widely distributed in the mountains of the Trans-Ili Ala-Tau belongs to the same subgenus. A bioecological investigation of some species of the family Polygonaceae has shown that this species is characterized by a high flavonoid content in the leaves. The flavonoid complex was isolated and separated in the same way as the flavonoids of *Atraphaxis pyrifolia*, the total flavonoids being obtained by extracting the leaves with acetone. The extract was evaporated and the residue was treated with a small amount of hot water and was extracted successively with benzene, ether, and ethyl acetate. From the ethyl acetate extract by chromatography on silica gel (with elution by chloroform–methanol in various proportions) followed by purification on polyamide, two flavonoid glycosides were isolated: I) with mp 158-160°C, $[\alpha]_D^{25}$ −118.1° (c 0.4; methanol; R_f 0.80 [I–BAW (4:1:5)] and 0.78 (II–15% CH_3COOH), and (II) with mp 183-185°C, $[\alpha]_D^{25}$ −110.5° (c 0.29; methanol), R_f 0.58 (I) and 0.63 (II).

On the basis of the results of physicochemical analysis (qualitative reactions, acid and alkaline hydrolysis, alkaline cleavage, acylation, and methylation, and IR, UV, and NMR spectroscopy) and a comparison with the glycosides that we isolated previously from the leaves of *Atraphaxis pyrifolia* [5], glycoside (I) was identified as 8-acetoxy-3,3',4',5-tetrahydroxy-7-methoxyflavone 3-O-α-L-rhamnopyranoside, and (II) as 3,3',4',5,8-pentahydroxy-7-methoxyflavone 3-O-α-L-rhamnopyranoside. Quantitative determinations of these flavonoids were performed by the spectrophotometric method after the chromatogram had been treated with a 1% ethanolic solution of $AlCl_3$. Found: glycoside (I) — 0.32%; (II) — 0.19% (calculated on the absolutely dry raw material). In the ethereal extract, after isolation by the bicarbonate method, by paper chromatography [6] and a comparison with markers we identified p-hydroxybenzoic, protocatechuic, and caffeic acids. It follows from a comparison of the chemical compositions of the three species of *Atraphaxis* mentioned that *Atraphaxis pyrifolia* and *Atraphaxis muschketovii* have the same composition and differ considerably from *Atraphaxis frutescens*, the polyphenol complex of which shows the quercetin and kaempferol glucosides that are characteristic for the Polygonaceae family.

S. M. Kirov Kazakh State University, Alma-Ata.

Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 815-816, November-December, 1976. Original article submitted August 16, 1976.