

Studying the essential oil of *Artemesia heptapotamica* Poljak [1], we have turned our attention to the fact that the herbage contains a considerable amount of nonpolar flavonoids and we have made these the object of our investigations.

The raw material (epigeal part), which was collected in August, 1983, in the Syugatin-skaya valley, Trans-Ili Ala-Tau, was extracted with chloroform, and the extract was chromatographed on KSK silica gel with elution by hexane and chloroform.

The rechromatography of the chloroform fraction with elution of the column by chloroform yielded two crystalline substances giving the cyanidin reaction which, according to Bryant's test, were aglycons [2].

Flavonoid (I) was a yellow crystalline substance with the composition $C_{18}H_{16}O_7$ (found: C 62.73; H 4.76; O 32.51%; M^+ 344; calculated: C 62.79; H 4.65; O 32.55%), mp 228–230°C (from ethanol), M^+ 344 (100%, mass spectrum), yield 0.08%. Readily soluble in chloroform, ethyl acetate, and DMSO, sparingly in ethanol, and insoluble in water.

UV spectrum, $\lambda_{\text{max}}^{\text{ethanol}}$, nm: 254 sh., 278, 342 ($\lg \epsilon$ 3.15; 3.23; 3.38); + CH_3ONa $\Delta\lambda$ 35 nm (–OH at C-4'); + $\text{ZrO}(\text{NO}_3)_2$ $\Delta\lambda$ 23 nm (–OH at C-5) [3]. IR spectrum, $\nu_{\text{max}}^{\text{KBr}}$, cm^{-1} : 1665 ($>\text{C}=\text{O}$ γ -pyrone, 1625, 1520, 1460 (aromatic nucleus); 2850–2870 (– OCH_3); 3300–3380 (–OH). PMR spectrum (in $\text{DMSO}-d_6$, δ , ppm): d 7.03 (1 H, $J = 8$ Hz) and d 7.59 (1 H, $J = 8$ Hz), br.s 7.48 (1 H) – the H-5', H-6', and H-2' protons; s 6.57 and br.s 6.88 (1 H each) – H-6 and H-8 of ring A; s 3.72, s 3.8, s 3.82 (3 H each) – 3- OCH_3 groups in an aromatic nucleus; 10.0–10.7 – –OH at C-4'; s 12.98 – –OH at C-5. Mass spectrum, m/z (%): M^+ 344 (100), 166 (11.2), 147 (5.8).

On the basis of the facts given, substance (I) has the structure of 4',5-dihydroxy-3,3',7-trimethoxyflavone, i.e., quercetin 3,3',7-trimethylether [4–6].

Flavonoid (II) was a yellow crystalline substance with the composition $C_{18}H_{14}O_7$ (found: C 61.83; H 4.30; O 33.87%; M^+ 330; calculated: C 61.81; H 4.24; O 33.94%), mp 223–225°C (from ethanol), M^+ 330 (100%, mass spectrum), yield 0.07%. Readily soluble in ethyl acetate, DMSO, and DMFA, sparingly in ethanol, and insoluble in water.

UV spectrum, $\lambda_{\text{max}}^{\text{ethanol}}$, nm: 254 sh, 275, 350 ($\lg \epsilon$ 3.24; 3.29; 3.50), + CH_3ONa $\Delta\lambda$ 65 nm (–OH at C-4'); + $\text{ZrO}(\text{NO}_3)_2$ $\Delta\lambda$ 23 nm (–OH at C-5); + CH_3COONa $\Delta\lambda$ 35 nm (–OH at C-7) [3]. IR spectrum, $\nu_{\text{max}}^{\text{KBr}}$, cm^{-1} : 1660 ($>\text{C}=\text{O}$ of a γ -pyrone); 1625, 1580, 1520 (aromatic nucleus); 3400–3500 (–OH). PMR spectrum (in $\text{DMSO}-d_6$, δ , ppm): broadened signal (singlet and doublet) 7.48 (2 H) – the H-2' and H-6' protons; d 6.9 ($J = 8.5$ Hz, 1 H) – H-5'; s 6.55 and s 6.75 (1 H each) – H-6 and H-8; s 3.72 and s 3.85 (3 H each) – two – OCH_3 groups in an aromatic nucleus; broadened signal at 10.0–11.0 and 12.00 – three –OH groups. Mass spectrum, m/z (%): M^+ 330 (100), 152 (17.7), 147 (8.5). The acetate of flavonoid (II) had mp 213–215°C and its PMR spectrum contained three singlets at 2.39, 2.28, and 2.3 ppm (3 H each) due to three acetoxy groups.

Thus, substance (II) had the structure of 4',5,7-trihydroxy-3,3'-dimethoxyflavone, or quercetin 3,3'-dimethyl ether [7, 8].

This is the first time that these flavonoids have been detected in plants of the genus *Artemesia* L.

LITERATURE CITED

1. M. I. Goryaev, F. S. Sharipova, L. A. El'chibekova, and E. S. Nodel'ko, Khim. Prir. Soedin., 572 (1980).

Institute of Chemical Sciences, SSR Academy of Sciences of the Kazakh. Alma-Ata. Translated from Khimiya Prirodnikh Soedinenii, No. 2, pp. 300–301, March–April, 1987. Original article submitted March 3, 1986; revision submitted November 11, 1986.

2. L. K. Klyshev, V. A. Bandyukova, and L. S. Alyukina, Plant Flavonoids [in Russian], Alma-Ata (1978).
3. T. J. Mabry, K. R. Markham, and M. B. Thomas, The Systematic Identification of Flavonoids, Springer, New York (1970).
4. Flavonoids and Bioflavonoids: Current Research Trends. Proceedings of the Fifth Hungarian Bioflavonoid Symposium, Matrafured, Budapest (1977), p. 285.
5. J. B. Harborne, C. A. Williams, and K. L. Wilson, Phytochemistry, 21, No. 10, 2490, 1982.
6. E. Wollenweber, J. Schober, W. D. Clark, and G. Latshievic, Phytochemistry, 24, No. 9, 2129 (1985).
7. E. Ayanoglu, A. Ululelen, W. D. Clark, G. K. Brown, B. B. Kerr, and T. J. Mabry, Phytochemistry, 20, No. 7, 1715 (1981).
8. E. Wollenweber and K. Egger, Tetrahedron Lett., 19, 1601 (1970).

FLAVONIDS OF TURKMENIAN SPECIES OF THE GENUS *Achillea*

V. V. Shmatova, M. O. Karreyev,
and N. F. Komissarenko

UDC 547.972

We have previously [1] reported on the isolation from the chloroform fraction of the epigeal part of *Achillea biebersteinii* Afan. and *Achillea krasheninnicovii* of hydroxycoumarins — umbelliferone, scopoletin, and isoscapoletin. Continuing a study of these species, in the following ethyl acetate fraction we have detected flavonoid substances and have separated them on a column of polyamide sorbent. The column was eluted with water and then with mixtures of water and ethanol with the concentration of the latter being increased to 40%.

As a result, three substances were isolated.

Substance (I) had the composition $C_{21}H_{20}O_{11}$, $[\alpha]_D^{20}$, mp 241–243°C; UV spectrum, $\lambda_{C_2H_5OH}^{max}$, nm: 257, 372.

When substance (I) was hydrolyzed with grape-snail enzyme [2], it split to give an aglycon with mp 309–311°C, which was identified by its R_f value, IR spectrum, and a mixed melting point as quercetin.

The sugar component was identified by paper chromatography as D-glucose. The position of attachment of the sugar component to the aglycon was determined with the aid of UV spectroscopy with ionizing and complex-forming reagents [3].

The β -configuration of the glycosidic bond in the substance (I) under investigation was established by the method of comparing molecular rotations [4].

On the basis of what has been said, substance (I) was 3,3',4',5-tetrahydroxyflavone 7-O- β -D-glucopyranoside, or quercimeritrin. This substance has been obtained previously from *Achillea neilreichii* [5].

In addition to quercimeritrin, two aglycons were isolated, one of which fluoresced yellow in UV light while the other absorbed.

Substance (II), with the composition $C_{15}H_{10}O_7$, mp 309–311°C, was identified as quercetin.

Substance (III) with the composition $C_{15}H_{10}O_6$, mp 330–331°C, had, according to UV spectroscopy with diagnostic additives, free OH groups in positions 3', 4', 5, and 7 and corresponded to luteolin. A comparison in various systems confirmed this suggestion.

Thus, quercimeritrin, quercetin, and luteolin have been obtained for the first time from the epigeal parts of *A. biebersteinii* and *A. krasheninnicovii*.

Institute of Botany, Academy of Sciences of the Turkmen SSR, Ashkhabad. All-Union Scientific-Research Institute of Drug Chemistry and Technology, Kharkov. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 301–302, March–April, 1987. Original article submitted May 26, 1986; revision submitted November 10, 1986.