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).

FLAVONOIDS OF TURKMENIAN SPECIES OF THE GENUS *Achillea*

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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 isoscopoletin. 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, $\lambda_{max}^{C_2H_5OH}$, 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 neilreihii* [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*.

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0009-3130/87/2302-0255$12.50

LITERATURE CITED

1. V. V. Shmatova, A. I. Derkach, M. O. Karryev, and N. F. Komissarenko, Khim. Prir. Soedin., 561 (1985).
2. M. D. Alaniya, N. F. Komissarenko, and E. P. Kemertelidze, Khim. Prir. Soedin., 351 (1975).
3. F. Geissman, J. Org. Chem., 21, 1395 (1956).
4. I. P. Kovalev and V. I. Litvinenko, Khim. Prir. Soedin., 233 (1965).
5. G. S. Zurabishvili, Khim. Prir. Soedin., 253 (1974).

FLAVONOIDS OF *Astragalus adsurgens*

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We have studied the flavonoids of the epigeal part of *Astragalus adsurgens* Pall., family Fabaceae, growing in the Tuva ASSSR. The dried and comminuted herbage was extracted with 80% ethanol, and the extract was evaporated to an aqueous residue, which was treated successively with chloroform and ethyl acetate. The ethyl acetate fraction and the aqueous residue after evaporation were separated on columns of polyamide sorbent at a ratio of the mixture of substances being separated to sorbent of 1:30 [1]. The columns were washed with water and with aqueous ethanol (from 5 to 30% of ethanol). As a result, the ethyl acetate extract yielded two (I and II) and the aqueous extract yielded three (III-V) flavonoid glycosides.

Substance (I) — $C_{22}H_{22}O_{12}$, mp 192-198°C, $[\alpha]_D^{21}$ — 56° (DMFA). On hydrolysis with grape-snail enzyme [3], it split into the aglycon isorhamnetin [4] and D-glucose. The β-configuration of the glycosidic bond of the carbohydrate component and its position at C_3 of the aglycon were established by UV spectroscopy with diagnostic reagents [5] and by a comparison of the molecular rotation of the substance with those of phenyl O-α- and -β-D-glucopyranosides [6]. Substance (I) was identical with the isorhamnetin 3-O-β-D-glucopyranoside isolated previously from sea buckthorn [7].

Substance (II) — $C_{21}H_{20}O_{19}$, mp 192-194°C, $[\alpha]_D^{20}$ — 30° (ethanol). On hydrolysis with 3% sulfuric acid it split into the aglycon kaempferol and D-galactose. Its further study was carried out in a similar manner to that of substance (I). It was found that compound (II) was kaempferol 3-O-β-D-galactopyranoside (trifolin), which has been obtained previously from *Astragalus galegiformis*.

Substance (III) — $C_{33}H_{40}O_{19}$, mp 187-189°C, $[\alpha]_D^{21}$ — 83.5° (ethanol—DMFA (8:2). Enzymatic hydrolysis with rhamnodiastase [7] split the glycoside into kaempferol 7-O-α-L-rhamnoside [$C_{22}H_{20}O_{10}$, mp 227-229°C, $[\alpha]_D^{20}$ — 128° (ethanol)] and robinobiose. UV spectroscopy with diagnostic additives showed that the robinobiose was attached at the C_3 position of the kaempferol. A comparison of the cleavage products, UV spectra, and physicochemical properties of substance (III) and robinin showed their identity was established [8].

Substance (IV) — $C_{28}H_{32}O_{16}$, mp 220-223°C, $[\alpha]_D^{20}$ — 104° (ethanol). On hydrolysis with 3% sulfuric acid, it split into the aglycon isorhamnetin and two sugars: D-glucose and L-rhamnose. However, on enzymatic hydrolysis with rhamnodiastase only D-glucose was split off and not rutinose, as is observed for rutinosides [7]. The substance formed as the result of enzymatic hydrolysis [$C_{22}H_{22}O_{11}$, mp 118-119°C, $[\alpha]_D^{21}$ — 122° (ethanol)] was identical with isorhamnetin 7-O-α-L-rhamnopyranoside [7]. A comparison of the properties of compound (IV) with an authentic sample of isorhamnetin 3-O-β-D-glucopyranoside 7-O-α-L-rhamnopyranoside showed their identity [7].

Substance (V) — $C_{27}H_{30}O_{15}$, mp 204-208°C, $[\alpha]_D^{20}$ — 24° (ethanol) was split by rhamnodiastase into kaempferol and rutinose. The position of attachment of the biose to the aglycon determined by UV spectroscopy with diagnostic additives was C_3. A comparison of the properties of substance (V) with an authentic sample of kaempferol 3-O-rutinoside [8] showed their identity.

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