FLAVONOL AGLYCONS OF SOME TRANSBAIKALIAN SPECIES OF THE GENUS *Oxytropis*

E. I. Sakanyan and K. F. Blinova

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Representatives of the genus *Oxytropis* DC. have been studied previously for the presence of various groups of biologically active compounds, including flavonoids. This led to the isolation of individual flavonoid compounds from several species widely used in traditional Tibetan and folk medicine [1]. Of these species, we have studied *Oxytropis sylvatica* (Pall.) DC, and *O. oxyphylla* (Pall.) DC., which are used in Tibetan medicine for the treatment of such serious diseases as plague, measles, anthrax, meningitis, influenza of epidemic nature, and others, and the species *O. turczaninovii* Jurtzev, which is systematically close to them. They are all widely represented in the flora of Cisbaikalia [Pribaikal'e] and Transbaikalia.

By paper chromatography, in the epigeal parts of all the species we detected free flavonol aglycons. Five were detected in *O. oxyphylla*, two in *O. sylvatica*, and one in *O. turczaninovii*. To isolate and separate the free aglycons, aqueous ethanolic extracts of the epigeal parts of the plants were treated successively with chloroform and ethyl acetate. Individual compounds were isolated from the chloroform and ethyl acetate fractions with the aid of absorption column chromatography on a polyamide sorbent and also by preparative paper chromatography followed by fractional crystallization from 96% ethanol.

Five aglycons (I-V) were isolated from *O. oxyphylla*. They were identified by using various methods of physicochemical analysis (melting points of the substances and of their acetates, of the products of alkaline degradation, paper chromatography in various systems with markers, mixed melting points, and UV spectroscopy).

Substance (I), mp 275-277°C, $\lambda_{max}^{C_2H_5OH}$, 370, 265 nm, was determined as 3,4',5,7-tetrahydroxyflavone, or kaempferol.

Substance (II), mp 305-306°C, $\lambda_{max}^{C_2H_5OH}$, 371, 255 nm, was identified as 3,4',5,7-tetrahydroxy-3'-methoxyflavone, or isorhamnetin.

Substance (III), mp 297-298°C, $\lambda_{max}^{C_2H_5OH}$, 375, 257 nm, was identified as 3,3',4',5-tetrahydroxy-7-methoxyflavone, or rhamnetin.

Substance (IV), mp 310-311° $\lambda_{max}^{C_2H_5OH}$, 374, 255 nm, was 3,3',4',5,7-pentahydroxyflavone, or quercetin.

Substance (V), mp 214-217°C, $\lambda_{max}^{C_2H_5OH}$, 374, 254 nm, was determined as 3,4',5-trihydroxy-3',7-dimethoxyflavone, or rhamnazin.

Rhamnetin and rhamnazin have been isolated from *O. oxyphylla* previously [2], but this is the first time that the other aglycons have been isolated from this species.

Two flavonol aglycons were isolated from *O. sylvatica*. Substance (I), with mp 276-277°C, $\lambda_{max}^{C_2H_5OH}$, 370, 266 nm, was similar in its physicochemical characteristics to substance (I) from *O. oxyphylla* and was identified as kaempferol. Substance (II) with mp 216-218°C $\lambda_{max}^{C_2H_5OH}$, 374, 255 nm, was similar to substance (V) from *O. oxyphylla* and was identified as rhamnazin.

From *O. turczaninovii* an aglycon with mp 275-277°C, $\lambda_{max}^{C_2H_5OH}$, 370, 267 nm, was isolated and was identified as kaempferol.

Thus, from the epigeal parts of plants of all three species free flavonol aglycons have been isolated, this being the first time that aglycons have been isolated from *O. sylvatica* and *O. turczaninovii* and the first time that the three aglycons have been isolated from *O. oxyphylla*.

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FASTIGENIN, HARPAGIDE, AND 8-O-ACETYLHARPAGIDE FROM *Teucrium orientale*

G. B. Oganesyan, A. M. Galstyan,
and V. A. Mnatsakanyan

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We have investigated the epigeal part of *Teucrium orientale* L., family *Lamiaceae* (oriental germander) collected in the budding-flowering phase in the region of Lake Sevan, Armenian SSR.

An aqueous methanolic (80% MeOH) extract was dried in vacuum, diluted with water (1:1), and filtered, and the filtrate was extracted successively with benzene, chloroform, and ethyl acetate.

By the chromatographic elimination of pigments [1] of the benzene extract on a silica gel column with chloroform, a light yellow crystalline substance (I) was isolated with the composition $C_{18}H_{16}O_7$, M^+ 344, mp 194-196°C (methanol). On the basis of its UV and IR spectra (3400 (OH), 1670 (C=O of a γ-pyrone), 1620, 1570 (C=C of a γ-pyrone), 1595, 1500 cm^{-1} (benzene ring) and the cyanidin reaction [2], substance (I) was assigned to the flavones. According to the results of UV spectroscopy with various additives [3], there were free hydroxy groups in positions 4' and 5: $\lambda_{max}^{CH_2OH}$, 275, 340 nm (log ε 4.07; 4.18); CH_3COONa; 274, 338 nm; $CH_3COONa + H_3BO_3$; 275, 343 nm; $AlCl_3$: 263, 286, 370 nm; $AlCl_3 + HCl$: 263, 293, 368 nm; CH_3ONa 272, 300 sh, 328 sh., 378 nm; $ZrOCl_2$ 294, 371 nm; $ZrOCl_2$ + citric acid; 273 sh., 344 nm.

When the flavone was acetylated with acetic anhydride in pyridine, a diacetate was formed $C_{22}H_{20}O_9$, M^+ 428 (28%), mp 164-166°C (methanol).

According to its IR spectrum (2850, 1740 cm^{-1}) and PMR spectrum, the flavone contained three methoxy groups in positions 3',6, and 7, which was confirmed on the basis of SSCCs ($CDCl_3$, HMDS, Varian T-60): 7.47 d, J = 2 Hz (H-2'); 7.40 dd, J_1 = 2 Hz, J_2 = 9 Hz (H-6'); 6.92 d, J = 9 Hz (H-5'); 6.37 s, (H-8), 6.35 s, (H-3); 3.98 s, 6H (2 OCH_3); 3.90 s, 3H (OCH_3), and also from the results of mass spectrometric fragmentation of the substances: formation of ions with m/z 181 (24%) and m/z 149 (27%) [4].

On the basis of the result obtained, the structure of 4',5-dihydroxy-3',,6,7-trimethoxyflavone, known in the literature as fastigenin [5], was established for substance (I). This is the first time that fastigenin has been detected in plants of the genus *Teucrium*.

By column chromatogrrphy on silica gel in the chloroform—methanol, (7%) solvent system, from the resins obtained from both the chloroformic and the ethyl acetate extracts we isolated a colorless crystalline substance (II) with the composition $C_{17}H_{26}O_{11}$, mp 154-155°C (methanol), $[\alpha]_D^{17.4}$ −104.1° (s 1.58; methanol), R_f 0.38 (ethyl acetate—methanol—water (7:2:1), spots detected with benzidine, the vanillin reagent and Ehrlich's reagent) and substance (III), composition $[\alpha]_D^{20.8}$ −163.7 ± 0.28° (s 3.54; methanol), R_f 0.27. No substances gave a positive color reaction for iridoids [6].

The IR, PMR, and mass spectra of compounds (II) and (III) agreed well with those for the natural glycosides 8-O-acetylharpagide [7] and harpagide [8], respectively.

The identity of substances (II) and (III) as 8-O-acetylharpagide and harpagide was confirmed by the preparation from each substance on acetylation of a separable mixture of harpagide hexa- and heptaacetates, and also by the formation of harpagide on the alkaline saponification of substance (II) [8].

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