FLAVONOIDS OF *Naumburgia thyrsiflora*

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Loosestrife is a common, although infrequently found, plant of marshes and swampy shores of water bodies usually growing directly in the water. In the world flora and in the flora of the Soviet Union there is a single species — *Naumburgia thyrsiflora* (L.) Rchb. (*Lysimachia thyrsiflora*) (water loosestrife), family *Primulaceae* [1]. In a preliminary study of this loosestrife we have previously detected saponins and flavonoids [2] and have established the structure of saponins [3, 4].

The aim of the present work was to study the flavonoid composition of *N. thyrsiflora*. We studied the air-dry raw material (the whole plant) collected in 1980–1981 in the territory of Vitebsk province in the flowering phase. The comminuted raw material was repeatedly extracted with 80% aqueous ethanol at the boil, and the extracts were combined and evaporated. The aqueous residue was treated successively with dichloroethane, diethyl ether, ethyl acetate, and n-butanol. The ethereal fraction was separated by chromatography on a column of polyamide sorbent using mixtures of ethanol and chloroform as eluents. A mixture containing 2% of ethanol eluted substance (I), and mixtures containing 10-15% ethanol eluted substance (II). The ethyl acetate fraction evaporated to small bulk deposited a crystalline yellow precipitate consisting of a mixture of substances. By chromatographic separation on a polyamide column, mixtures of ethanol and chloroform eluted substances (III) and (IV). All the substances isolated were subjected to purification by rechomatography on polyamide columns.

On the basis of the results of paper chromatography and also the cyanidin reaction [5], the isolated substances were assigned to the flavonoids. Bryant's test [6] revealed that substances (I) and (II) were flavonoid aglycones and (III) and (IV) were glycosides.

The hydrolysis of substance (III) with 3% sulfuric acid gave an aglycone identical with substance (I), and substance (IV) under the same conditions gave an aglycone identical with substance (II). The carbohydrate moieties in both flavonoid glycosides were represented by D-glucose.

The structure of the substances isolated have been established on the basis of their physicochemical constants and the results of UV and PMR spectroscopy, and also those of acid hydrolysis.

Substance (I), $C_{16}H_{12}O_7$, mp 304–307°C, M^+ 316, λ_{max} (CH_3OH), 255, 268, sh., 370 nm is 3,4',5,7-tetrahydroxy-3'-methoxyflavone (isorhamnetin) [7].

Substance (II), $C_{15}H_{10}O_7$, mp 308–310°C, M^+ 302, λ_{max} (CH_3OH), 258, 268, sh., 372 nm, is 3,3',4',5,7-pentahydroxyflavone (quercetin) [7].

Substance (III), $C_{22}H_{22}O_{12}$, mp 243–246°C, (C_2H_5OH), λ_{max} 358, 257 nm; $[\alpha]_D^{20}$ − 60° (c 0.5; ethanol) is isorhamnetin 3-O-β-D-glucopyranoside [8].

Substance (IV), $C_{21}H_{20}O_{12}$, mp 228°–230°C (ethanol), λ_{max} 362, 255, (265) nm; $[\alpha]_D^{20}$ −69° (c 0.106; methanol) is quercetin 3-O-β-D-glucopyranoside [6].

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PHENOLIC COMPOUNDS OF *Artemisia sieversiana*

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We have studied the phenolic composition of the epigeal part of *Artemisia sieversiana* Willd. taken from four different sites of the Mongolian People's Republic at different phases of development of the plants (budding, flowering, fruit-bearing). The materials were collected in 1972–1974 by the resource-prospecting section of the Soviet-Mongolian Complex Biological Expedition.

A preliminary study by two-dimensional paper chromatography [with the systems BAW (6:1:2) and 15% CH_3COOH] established the identity of the compositions of the specimens studied.

The air-dry raw material was treated in the following way: extraction with 96% ethanol, extraction of the total flavonoids from the concentrated ethanolic extract with hot water, and treatment of the aqueous fraction successively with chloroform and ethyl acetate.

Chromatography of the chloroform extract on a column of silica gel (L 100/160 μm, Lachema) led to the isolation of substance (I) (yield 0.012% on the weight of the air-dry raw material) with the composition $C_{20}H_{20}O_8$, mp 160°C (ethanol), M^+ 388, λ_{max}^{MeOH} 260, 277, 349 nm. Features of the UV spectra with ionizing and complex-forming additives showed the presence of an OH group at C_5.

IR spectrum (cm^{-1}): 1640, 1590, 1510, 1160, 1100, 1070, 1030. PMR spectrum ($CDCl_3$, δ, ppm): 7.74 (d, 1 H, J = 2 Hz, C_2,—H), 7.67 (dd, 1 H, J_1 = 2 Hz, J_2 = 9 Hz, C_6,—H); 7.01 (d, 1 H, J = 9 Hz, C_5,—H); 6.45 (s, 1 H, C_8—H); 3.97 (s, 9 H, $C_{3'}$,$_{4'}$,$_{7}$—OCH_3); 3.93 (s, 3 H, C_3—OCH_3); 3.87 (s, 3 H, C_6—OCH_3). The PMR spectrum was identical with that of artemisetin [1]. The mass spectrum of (I) showed a strong peak with m/z 373^+ $(M-15)^+$, which gives grounds for assuming the presence of an OCH_3 group at C_6 [2]. On the basis of the facts given above and a comparison of them with those given in the literature [3], substance (I) was identified as artemisetin.

It must be mentioned that artemisetin had accumulated in more considerable amounts in the specimen collected during the flowering-fruit bearing phase.

The chromatography of the ethyl acetate extract on polyamide (with elution by $CHCl_3$) gave substance (II) (yield 0.01%), composition $C_{19}H_{18}O_8$, mp 181°C, M^+ 374, λ_{max}^{MeOH} 262, 275, 357 nm. Features of the UV spectra with additives permit the assumption of the presence of OH group at C_5 and $C_{4'}$.

IR spectrum (cm^{-1}): 3320, 1660, 1590, 1570, 1520, 1170, 1140, 1100, 1080, 1040, 1010. PMR spectrum ($CDCl_3$, δ, ppm): 7.74 (d, 1 H, J = 2 Hz, C_2,—H); 7.64 (dd, 1 H, J_1 = 2 Hz, J_2 = 9 Hz, C_6,—H); 7.05 (d, 1 H, J = 9 Hz, C_5,—H); 6.5 (s, 1 H, C_8—H); 3.99 (s, 3 H,

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