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PHENOLCARBOXYLIC ACIDS FROM *Myosotis krylovii* AND *M. palustris*

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Species of the genus *Myosotis* L. are not used in official medicine. However, the decoction of the herb *M. imitata* Serg. is used internally in Yakutia folk medicine for tuberculosis. *M. arvensis* (L.) Hill is used for these same purposes in western European countries [1]. The aerial part of *M. arvensis* and *M. palustris* L. is used as a powder or juice for malignant tumors of the oral cavity and sex organs [2].

Phenolcarboxylic (polyphenolic) acids were first observed in species of the family Boraginaceae during a study of the medicinal action of the American species *Lithospermum ruderale* Dougl. ex Lehm. [3]. The observation of lithospermic, cinnamic, caffeic, chlorogenic, and *p*-coumaric acids and their derivatives is most often reported for representatives of the family Boraginaceae [4]. Phenolcarboxylic acids in species of the genus *Myosotis* have not been studied.

Phenolcarboxylic acids possess antimutagenic properties, strengthen the immune system, and are effective diuretics. Phenolcarboxylic acids are used in classical medicine as prophylactic agents against benign and malignant tumors and to treat diabetes, atherosclerosis, cataracts, and cardiovascular diseases [5, 6]. The medicinal properties of species of the genus *Myosotis*, especially antitumor, may be due to the presence in plants of these species of phenolcarboxylic acids.

We studied aqueous ethanol extracts of leaves of *M. palustris* L. and *M. krylovii* Serg. in order to determine the presence and qualitative composition of phenolcarboxylic acids in species of the genus *Myosotis*.

The samples of *M. palustris* (Altai mountains, Chistyi Lug, 200 m from the Altai Mountain Botanical Garden downstream of Sema, bottoms of a dried stream, green moss bog-bushy birch grove) and *M. krylovii* (Novosibirsk, Central Siberian Botanical Garden, SB, RAS, cultivated) were collected in 2000.

Phenolcarboxylic acids were identified by HPLC—MSD on an Agilent 1100 Series LC/MSD using a Zorbax Bonus-RP column (4.6 × 150 mm, 5 μm) with elution by HCOOH:MeOH (2%, linear gradient from 10 to 100% MeOH from 10 to 20 min) at flow rate 1 mL/min. The mass-selective detection was performed using a quadrupole analyzer (Model G1946C) with atmospheric pressure chemical ionization (APCI) and electrospray (ES) ionization. Negative and positive ions were scanned in the range *m*/*z* 140-700 with vaporizer temperature 450°C and N_2 vaporizer gas at 4 L/min for APCI; 10 L/min and 340°C, for ES.

We found caffeic and chlorogenic acids in extracts of *M. krylovii* and *M. palustris*.

The retention time and UV and mass spectra for peak A in the sample of *M. krylovii* were consistent with chlorogenic acid (RT 16.1, λ_{max} 246 and 326 nm, $[M - H]^+$ 353.1 *m*/*z*). Peak B gave the same negative ion and had a very similar UV spectrum (RT 15.9, λ_{max} 246 and 326 nm). Apparently this peak corresponded to an isomer of chlorogenic acid. The UV spectrum of the strongest peak C (RT 18.6, $[M - H]^+$ 359.1 *m*/*z*) was also similar to that of chlorogenic acid but had a molecular weight 6 Da higher. The retention time and UV and mass spectra for peak D corresponded to caffeic acid (RT 16.6, λ_{max} 244 and 324 nm, $[M - H]^+$ 179.1 *m*/*z*).

Peak A in the extract of *M. palustris* also corresponded to chlorogenic acid (RT 16.15, λ_{max} 246 and 326 nm, $[M - H]^+$ 353.1 *m*/*z*); peak B, to an isomer of chlorogenic acid (RT 15.9, λ_{max} 246 and 326 nm, $[M - H]^+$ 353.1 *m*/*z*); peak D, to caffeic acid (RT 16.6, λ_{max} 244 and 324 nm, $[M - H]^+$ 179.1 *m*/*z*).

The UV spectrum (λ_{max} 256, 310, 360) was obtained for peak E (RT 17.45). However, reliable mass spectral information corresponding to this peak could not be obtained either using chemical ionization (APCI) or electrospray ionization.

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Peak F had a UV spectrum typical of flavonoids (RT 18.65, λ_{max} 258 and 357 nm, $[M - H]^+$ 463.1 *m*/*z*), MW 464.1. This was probably a glycoside, the MW of the aglycon of which was 302.1. We made this conclusion after repetitive recording of the chromatograms with scanning of the positive ions. This peak did not give a pseudomolecular ion $[M + H]^+$ like most glycosides but did show clearly a fragment ion with *m*/*z* 303.1. This apparently corresponded to the aglycon. ES ionization of the solution showed a pseudomolecular ion $[M + H]^+$ at 465.1 and a fragment with 303.1 *m*/*z*.

Thus, we established for the first time the presence in the plant species *M. krylovii* and *M. palustris* of several phenolcarboxylic acids. Caffeic and chlorogenic acids were identified using existing pure compounds.

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