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PHENOLIC ACIDS OF *Amelanchier sanguinea* AND *A. oligocarpa*

N. V. Sergeeva, D. K. Shapiro
V. A. Bandyukova, L. V. Anikhimovskaya,
and T. I. Narikhnaya

UDC 581.19 + 634.17

The freshly gathered fruit of *Amelanchier sanguinea* DC (round-leaf serviceberry) and *A. oligocarpa* Roem. (*A. bartramiana*; bartram serviceberry), family Rosaceae, cultivated in the Central Botanical Garden of the Academy of Sciences of the Belorussian SSR, was extracted with 96% ethanol three times in the cold and then with the same solvent and equal number of times with heating on the boiling water bath.

The combined extracts were concentrated in vacuum to the consistency of a syrup and the residue was treated successively with n-hexane and ethyl acetate. The ethyl acetate extracts were combined and were dried with anhydrous sodium sulfate, the solvent was driven off, and the residue was treated with water and filtered.

It was established by two-dimensional chromatography on paper (Leningrad "M" ["slow"], No. 3) in the 2% CH_3COOH (1) and butan-1-ol – CH_3COOH – H_2O (4 : 1 : 5) (2) systems that the fruit of the round-leaf serviceberry contained no less than eight, and the fruit of the bartram serviceberry no less than four, substances possessing blue and violet fluorescences in UV light and having an acidic nature, as was shown by spraying the chromatograms with a 0.1% ethanolic solution of Bromthymol Blue.

The acids were separated by preparative paper chromatography in system 1, each zone being eluted with 96% ethanol and rechromatographed in system 2. The eluates were studied by chromatography in the presence of markers with the subsequent treatment of the chromatograms with chromogenic reagents [2] and by UV spectroscopy [3], and they were also subjected to acid hydrolysis (2N HCl with heating on the water bath for 30 min). As a result, it was established that three of the substances of the round-leaf serviceberry did not undergo hydrolysis and corresponded in their R_f values, color reactions, and UV spectra to caffeic, ferulic, and p-coumaric acids.

Substance 4 with R_f 0.62 (system 1) and 0.38 (system 2) had a blue fluorescence in UV light which was intensified in ammonia vapor; with diazotized sulfanilic acid it formed a violet dye. On acid hydrolysis it gave ferulic and quinic acids. UV spectrum: λ_{max} 318, 290 sh., 245 nm. It was identified as 3-feruloylquinic acid.

Substance 5 with R_f 0.65 (system 1) and 0.43 (system 2) also had a blue fluorescence in UV light which was intensified in ammonia vapor and its reaction with diazotized sulfanilic acid was positive. The hydrolyzate after hydrolysis with 2 N HCl was found to contain p-coumaric and quinic acids. UV spectrum: λ_{max} 305 nm. This substance is 3-p-coumaroylquinic acid.

Substance 6 was identified as chlorogenic acid in the same way. Substances 7 and 8 have not been identified.

Chlorogenic and caffeic acids have been identified in the fruit of the bartram serviceberry.

The total amount of phenolic acids in the round-leaf serviceberry was 242.5 mg/100 g of the crude weight of the fruit, and in the bartram serviceberry 138 mg per 100 g of crude weight. Quantitative determination was

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Pyatigorsk Pharmaceutical Institute. Central Botanical Gardens, Academy of Sciences of the Belorussian SSR, Minsk.

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carried out as described by Mzhavanade et al. [4].

We are the first to have established the composition of the phenolic acids of the round-leaf and bartram serviceberries.

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IRIDOIDS OF *Stachys inflata* AND *S. iberica*

N. F. Komissarenko, A. I. Derkach, I. P. Sheremet, and D. A. Pakaln

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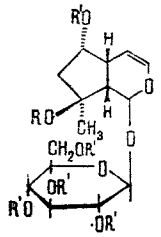
As has been established previously [1], plants of the genus *Stachys* contain iridoid compounds. Continuing investigations in this direction, we have studied the iridoids of the epigeal part of two species: *Stachys inflata* Benth. and *Stachys iberica* Bieb. From *S. iberica* we isolated four substances of iridoid nature with R_f 0.41, 0.45, 0.51, and 0.61, and from *S. inflata* two substances with R_f 0.45 and 0.61 in the butan-1-ol–acetic acid–water (4:1:2) system. The substances with R_f 0.41 and 0.51 were identified as harpagide and harpagide acetate, which have been obtained previously from *S. atherocalyx* [1]. The substances with R_f 0.45 and 0.61 are new compounds for the genus *Stachys*. When chromatograms were treated with Stahl's reagent [2] it appeared in the form of blue spots.

The iridoids were isolated from the raw material by the method described previously [1]



I. R = R′ = H
II. R = Ac; R′ = H
III. R = H; R′ = Ac
IV. R = R′ = Ac

Ajugol (I) forms a white amorphous powder with R_f 0.45, empirical formula $C_{15}H_{23}O_9$, $[\alpha]_D^{20}$ −165°C (c 0.1; methanol). On hydrolysis with the enzymes of the grape snail, it split into D-glucose and an aglycone, the transformation products of which colored the solution blue with the subsequent deposition of a dark precipitate.

Acetylation of the substance under investigation with acetic anhydride in pyridine at 18-22°C led to the formation of ajugol pentaacetate (III), $C_{25}H_{34}O_{14}$, mp 127-128°C, $[\alpha]_D^{20}$ −163° (c 0.1; methanol), and acetylation at 50°C led to the formation of ajugol hexaacetate (IV) $C_{27}H_{37}O_{15}$, mp 172-173°C, $[\alpha]_D^{20}$ −120° (c 0.1; methanol).

From the physicochemical properties of the initial substance and its acylation products, and R_f values, the compound under investigation (I) was identified as ajugol [3], which has been isolated from *Ajuga reptans*.

Ajugoside (II), a substance with R_f 0.61, was isolated in the form of a white amorphous powder with the empirical formula $C_{17}H_{26}O_{10}$, mp 173-176°C, $[\alpha]_D^{20}$ −110° (c 0.1; methanol). Saponification with a 5% solution of alkali formed a substance identical with ajugol (I). On acetylation under the usual conditions, ajugoside was converted into ajugol hexaacetate (IV), which shows the presence of an acetyl residue in the initial substance.

On analyzing the properties of known iridoids, we came to the conclusion that the iridoid isolated was iden-

Kharkov Scientific-Research Institute of Pharmaceutical Chemistry. Ukraine Zonal Experimental Station for Medicinal Plants, All-Union Scientific-Research Institute of Medicinal Plants, Lubny.

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