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## KAEMPFEROL GLYCOSIDES OF THE LEAVES

### OF *Laurocerasus officinalis*

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Continuing a chemical study of the flavonoid compounds of *Laurocerasus officinalis* Roem. (*Prunus laurocerasus*; common laurel cherry) [1, 2], we have isolated two kaempferol glycosides from the leaves of this plant.

To isolate the glycosides, an aqueous ethanolic extract was evaporated in vacuum and the aqueous residue was washed with chloroform and chromatographed on a column of polyamide. Elution was carried out with distilled water and with aqueous ethanol of various concentrations. The individual glycosides were obtained by the rechromatography of the fractions obtained on a polyamide column (elution with isopropanol).

Glycoside (I) formed pale yellow acicular crystals with mp 168-170°C,  $[\alpha]_D^{20} - 85^\circ$  (c 0.2; CH<sub>3</sub>OH). UV spectrum,  $\lambda_{\max}$ , nm, (C<sub>2</sub>H<sub>5</sub>OH): 267, 351; + CH<sub>3</sub>COONa: 273, 361; + NaOH: 276, 402; + AlCl<sub>3</sub>: 276, 396.

Glycoside (II) formed yellow acicular crystals with mp 172-174°C,  $[\alpha]_D^{20} - 103.2^\circ$  (c 0.2; CH<sub>3</sub>OH). UV spectrum,  $\lambda_{\max}$ , nm (C<sub>2</sub>H<sub>5</sub>OH): 268, 350; + CH<sub>3</sub>COONa: 276, 360; + NaOH: 276, 404; + AlCl<sub>3</sub>: 276, 396.

R<sub>f</sub> values of glycosides (I) and (II) (ascending method): 0.77, 0.76 (water-saturated phenol); 0.49, 0.52 (butan-1-ol-acetic acid-water (4:1:5)); 0.68, 0.64 (15% acetic acid); 0.80, 0.85 (ethyl acetate-formic acid-water (10:2:3)), respectively.

The spectral characteristics of glycosides (I) and (II) and of their aglycones in the UV region and qualitative reactions showed that the carbohydrate moieties were present in the C-3 positions [3, 4].

In a study of the products of acid hydrolysis of compound (I) (2 N HCl), kaempferol, D-galactose, and D-glucose were detected, and in the case of (II) kaempferol, D-galactose, and D-xylose. The percentage amounts of the aglycones (40 and 43.6%), and also the ratio of the intensities of absorption of the maxima of bands I in the UV region of the spectra of the glycosides and their aglycones (38 and 40%) showed that the glycosides under investigation were biosides [5].

When (I) and (II) were subjected to stepwise acid hydrolysis [6], monosides were formed which were identified in each case as kaempferol 3-β-D-galactoside (trifolin). The order of the bonds between the sugars was established by oxidative degradation with hydrogen peroxide and by enzymatic hydrolysis with rhamnodistase [7]. The sizes of the oxide rings of the sugars and the forms of the bonds were determined by IR spectroscopy and polarimetric analysis [8].

According to the results obtained, glycoside (I) is kaempferol 3-O-(6-O-β-D-glucofuranosyl-β-D-galactopyranoside) and glycoside (II) is kaempferol 3-O-(6-O-α-D-xylofuranosyl-β-D-galactopyranoside).

This is the first time that kaempferol glycosides with such combinations of sugars have been isolated.

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## PHENOLIC ACIDS OF *Amelanchier sanguinea*

## AND *A. oligocarpa*

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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%  $\text{CH}_3\text{COOH}$  (1) and butan-1-ol- $\text{CH}_3\text{COOH}-\text{H}_2\text{O}$  (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:  $\lambda_{\text{max}}$  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:  $\lambda_{\text{max}}$  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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