CHRYSANTHEMIN AND CYANIN IN SPECIES OF THE GENUS *Rhaponticum*

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Triterpene glycosides and phenolic compounds have been isolated from *Rhaponticum carthamoides* (Willd) Iljin previously [1-2].

We have investigated the anthocyanin pigments of the flowers of four species of the genu *Rhaponticum* (Asteraceae): *Rhaponticum carthamoides* (Willd) Iljin, *Rh. scariosum* Lam., *Rh. pulchrum* Fisch. et May., and *Rh. lyratum* Winkl. ex Iljin, which were collected in the systematics sections of the Central Botanical Garden of the Academy of Sciences of the Belorussian SSR in the flowering period (May-June, 1977).

The extraction of the anthocyanin glycosides, purification, chromatographic separation, spectral analysis, and acid hyrolysis were performed as described in the literature [3, 4]. To determine the qualitative composition of the aglycones, a purified extract of the plants under investigation was subjected to acid hydrolysis. It was found that the aglycones of the anthocyanin glycosides were cyanidin and pelargonidin, these being identified by their chromatographic behavior with markers, and also on the basis of the results of spectral analysis in the visible region of the spectrum and qualitative reactions [3, 5].

By using ascending two-dimensional chromatography on Filtrak FN-12 paper in system 1) butan-1-ol—acetic acid—water (3:1:1) and 2) 10% acetic acid, it was established that the species mentioned above contain, respectively, 9, 5, 5, and 5 anthocyanin glycosides. The two main (with respect to their amounts in all the species) glycosides were subjected to detailed study, being denoted provisionally as anthocyanins 1 and 2. The spots of the glycosides on the chromatograms were cut out, repeatedly extracted with methanol containing 0.01% of hydrochloric acid, and purified in systems 2 and 3) acetic acid—concentrated hydrochloric acid—water (15:3:82).

The anthocyanin glycosides were identified from the results of a study of their absorption spectra in the 270-600-nm region in methanol with and without the addition of $AlCl_3$, from the products of hydrolysis and of oxidation with H_2O_2, and by their chromatographic behavior with markers [3, 6, 7].

After acid hydrolysis and the extraction of the aglycones with isoamyl alcohol for both anthocyanin 1 and anthocyanin 2 we identified cyanidin, and glucose was found in the hydrolysates. Consequently, anthocyanins 1 and 2 are cyanidin glucosides. The stepwise hydrolysis of anthocyanin 2, the products of which were chromatographed in system 3, 4) acetic acid—concentrated hydrochloric acid—water (30:3:10), and 5) butan-1-ol—2 N hydrochloric acid (1:1) led to the formation first of anthocyanin 1, i.e., cyanidin monoglucoside (chrysanthemin) and after hydrolysis for 60-90 min, to the aglycone cyanidin, which means that anthocyanin 2 is a diglucoside. This was confirmed by the E_{440}/E_{max} ratio for anthocyanin 2. The detection of glucose on the oxidation of anthocyanin 1 and 2 with H_2O_2 confirmed that in anthocyanin 1 it was attached to C_3 and in anthocyanin 2 the two molecules of glucose are attached to the aglycone in positions 3 and 5, respectively [3, 6-8]. The chromatography of anthocyanin 1 with chrysanthemin and of anthocyanin 2 with cyanin confirmed their respective identities. Thus, in the species *Rhaponticum carthamoides*, *Rh. scariosum*, *Rh. pulchrum*, and *Rh. lyratum*, 9, 5, 5, and 5, respectively, anthocyanin glycosides have been detected, the main ones in terms of amount being cyanidin 3-glucoside (chrysanthemin) and cyanidin 3,5-diglucoside (cyanin). This is the first time that these glycosides have been identified in the species mentioned, and they may be of interest for chemotaxonomy.

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INFLUENCE OF TRACE ELEMENTS ON THE ACCUMULATION OF ANTHOCYANINS IN THE FRUIT OF *Aronia melanocarpe*

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It has been established that in addition to vitamins, catechins, and flavonoids, the active substances of the fruit of *Aronia melanocarpa* Elliot. (black chokeberry) are anthocyanins — substances possessing a high biological activity [1].

The aim of our work was to study the accumulation of anthocyanins in the ripe fruit of the black chokeberry under the influence of trace elements and to investigate their qualitative composition.

Foliar feeding was carried out with 0.03% solutions of: H_3BO_3; $ZnSO_4 \cdot 7H_2O$; $CoSO_4 \cdot 7H_2O$; $CuSO_4 \cdot 5H_2O$; $(NH_4)_2MoO_4$; $FeSO_4 \cdot 7H_2O$; and $MnSO_4 \cdot nH_2O$ by a method described previously [2] in the "Kiritsy" sovkhoz [communal farm] in the Spassk region of the Ryazan oblast and at the young naturalists's mountain station.

The anthocyanin substances were isolated from the crude ripe fruit with 1% HCl in methanol (1:99) [3]. The extract was evaporated in vacuum and was studied by partition paper chromatography (Leningrad type "M" ["slow"] paper) in the n-butanol—acetic acid—water (4:1:5) system. In all variants of the experiment three anthocyanin substances were detected, having R_f 0.35, 0.44, and 0.67 and with the respective UV spectra: $\lambda_{max}^{CH_3OH + 1\% HCl}$ 531, 535, and 537 nm [4]. After the hydrolysis of these substances with 2 N HCl for 30 min [5] and rechromatography of the hydrolysis products isolated by isoamyl alcohol, the three anthocyanin substances formed one and the same aglycone, which was identified as cyanidin, having R_f 0.62. UV spectra: $\lambda_{max}^{C_2H_5OH}$ 545 nm and $\lambda_{max}^{CH_3OH + 1\% HCl}$ 542 nm [3, 4].

The amounts of the anthocyanins in the ripe fruit of the 1973-1976 harvests were determined as cyanidin by the photocolorimetric method [6]. The results of the analysis (in % of the dry matter) were treated by the statistics of variations [7].

It was established that Co, Zn, B, Mn, Mo, Cu, and B + Zn increase the accumulation of anthocyanins by 7, 9, 11, 12, 13, 19, and 20%, respectively.

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