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ANTHOCYANIN GLYCOSIDES OF THE FRUITS OF THE CULTIVATED BOG BILBERRY

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UDC 634.739.1:581.19(476)

In connection with the fall in the commercial stocks of the fruit of the wild bog bilberry Vaccinium uliginosum L. In the European part of the USSR, work on the plantation cultivation of high-quality characterized by a considerable productivity, a stable yield, and large size of the fruit rich in biologically active compounds is acquiring enormous importance [1]. An improved variety of bilberry has been isolated in the USA and Canada by the hybridization of, mainly, two tall species – V. corymbosum L. and V. australe Small. [2, 3].

The anthocyanin pigments of the fruits of the Rancocas and Gerbert [Herbert (?)] varieties grown at the trial and experimental base of the central botanical garden of the Academy of Sciences of the Belorussian SSR (mountain settlement of Gantsevichi, Brest province) have been investigated.

The dry comminuted fruit (10-15 g) was extracted with a 1% solution of HCl in 70% ethanol by steeping in the refrigerator at +4-5° for 30 h.

To find the qualitative composition of the anthocyanin aglycones of the bog bilberry, the extract of the fruit was subjected to acid hydrolysis. It was established that the aglycones of the anthocyanin glycoside consisted of delphinidin, petunidin, malvidin, cyanidin, and peonidin, which were identified by comparison with authentic samples using paper chromatography and also on the basis of the results of spectral analysis in the visible part of the spectrum [4].

The anthocyanin extracts obtained were subjected to ascending two-dimensional chromatography on Filtrak FN 7 paper (GDR) in the solvent systems: 1) butan-1-ol–CH_3COOH(glac.)–water (3:1:1) and 2) CH_3COOH(glac.)–HCl (conc.)–water (3:1:8).

It was established that the fruits of both varieties of bog billberry contained 16 anthocyanin glycosides, i.e., their qualitative compositions were identical eight glycosides (present in the fruit in the largest amount by visual estimation) were studied in detail. The spots of the glycosides on the chromatograms were cut out, and were repeatedly extracted with 90% ethanol containing 0.1% of HCl (conc.), and purified in system 2. The purifird anthocyanin glycosides were identified from the results of a study of their absorption spectra in 96% ethanol containing 0.01% HCl (conc.) and also after the acid hydrolysis followed by extraction with isoamyl alcohol of their aglycones, which were identified by paper chromatography with authentic samples in solvent system 3) CH_3COOH (glac.)–HCl(conc.)–water (30:3:10), while the sugar residues were identified in system 4) butan-1-ol–pyridine–water (6:4:3) [4].

It was shown that the anthocyanins of the fruits of the cultivated bog bilberry were represented by four aglycones – delphidinin, cyanidin, petunidin, and malvidin – combined with sugar residues of D-galactose, L-arabinose, and D-glucose [4].

Central Botanical Garden, Academy of Sciences of the Belorussian SSR, Minsk. Translated from Khimiya Prirodnykh Soedinenii, No. 4, p. 570, July-August, 1985. Original article submitted November 15, 1984.

0009-3130/85/2104-0537$09.50

On the basis of the results of spectral analysis, a study of the mobilities of the substance isolated, acid hydrolysis, and chromatographic comparison with authentic samples, the anthocyanins of the bog bilberry were characterized as delphindin 3-galactoside, delphindin 3-arabinoside, cyanidin 3-glucoside, cyanidin 3-galactoside, petunidin 3-galactoside, petunidin 3-arabinoside, malvidin 3-galactoside, and malvidin 3-arabinoside. These results agree with those reported from the USA [5, 6].

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FREE PHENOLIC CARBOXYLIC ACIDS OF Secale

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UDC 547.589+978

The wide distribution of phenolic carboxylic acids in the tissues of higher plants [1], the existence of growth-inhibiting activity in many of them [2], and their participation in the process of photosynthesis [3] and protective reactions against fungal and bacterial infections [4] prompt an investigation of these compounds in the organs of economically useful species.

The isolation and identification of the free phenolic carboxylic acids or rye was performed by the methods described in [2]. As the initial material we used the leaves of 20-day rye plants of the variety Khar'kovskaya 60 grown under artifical illumination.

In the ethereal fraction, on chromatographic separation by the two-dimensional ascending method on FN 12 paper in the solvents isopropanol–amonia–water (12:1:1) and 5% CH_3COOH, 13 components giving qualitative reactions for phenols were detected. On the basis of their combinations of properties they were divided into two groups.

One group of substances (eight compounds) had a light or deep blue fluorescence in UV light which was intensified in NH_3 vapor or on treatment with NaOH. The same components formed cis and trans isomers when they were chromatographed in weak acetic acid and in 20% KCl. The λ_{max} values in 96% ethanol of these compounds were in the 280-330 nm region. They were assigned to the hydroxycinnamic acids.

Another group of substances (five compounds) absorbed in the UV region, did not form cis and trans isomers, and had λ_{max} in the 250-280 nm region. They were assigned to the hydroxybenzoic acids.

A comparison of the solubilities, chromatographic mobilities, differential colorations with a stabilized diazonium salt, and the full UV spectra (96% ethanol) of the acids isolated with the analogous properties of markers permitted the main phenolic components of rye to be identified as p-coumaric acid (shoulder at 286 nm), ferulic acid (λ_{max} 320 nm), vanillic acid (λ_{max} 258, 286 nm), and p-hydroxybenzoic acid (λ_{max} 256 nm). Protocatechuic acid (λ_{max} 258,

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Translated from Khimiya Prirodnykh Soedinenii, No. 4, p. 571, July-August, 1985. Original article submitted January 29, 1985.

0009-3130/85/2104-0538$09.50