

ANTHOCYANS OF *Adelia neo-mexicana* FRUIT

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Anthocyanins and other polyphenols possess antiradiation, anti-inflammatory, and capillary strengthening activities [1]. Anthocyanins have been reported in fruits and flowers of various plants of Azerbaidzhan flora [2-6]. We continued the study of the qualitative composition and quantitative content of anthocyanins of adelia fruit (*Adelia neo-mexicana* Ktze), a decorative and consistently abundantly fruiting plant that was introduced into the Botanical Garden of the National Academy of Sciences of Azerbaidzhan.

Anthocyanins were isolated from fresh fruit by grinding and extracting at room temperature with MeOH containing HCl (1%). The powdery total anthocyanins were obtained by column chromatography [7]. Paper chromatography (PC) of the total anthocyanins using various solvent systems showed the presence of three anthocyanins. The total anthocyanins were separated by preparative column chromatography using cellulose hydrochloride powder. Two fractions were obtained. Two-dimensional PC (first, *n*-butanol—acetic acid—water, 4:1:2; second, water—acetic acid—conc. HCl, 82:15:3) found that the first fraction contains one; the second, two anthocyanins. Preparative PC isolated three pure anthocyanins that were arbitrarily called **1**, **2**, and **3**. Hydrolysis of the isolated anthocyanins under harsh conditions determined that **1** and **2** were cyanidin derivatives; **3**, delphinidin. The identities of cyanidin and delphinidin were found by comparing UV spectra and chromatograms with authentic samples.

Anthocyan glycosides were identified by studying of absorption spectra (270-600 nm) in MeOH and with added AlCl₃, of products of acid hydrolysis and oxidation by H₂O₂, and comparison of chromatograms with those of authentic samples [2-6, 8, 10].

Acid-hydrolysis products of **1** and **2** contained cyanidin and glucose. Therefore, **1** and **2** were cyanidin glycosides. Stepwise hydrolysis of anthocyan **2** formed first anthocyan **1** and then the aglycon cyanidin [8, 9]. This means that anthocyan **2** is a diglycoside. This was confirmed by the E₄₄₀/E_{max} ratio. For anthocyan **2**, it was one half of that for anthocyan **1** [8, 11]. The detection of glucose after oxidation of anthocyan **1** and **2** by H₂O₂ confirmed that it was bound to C-3 in anthocyan **1** whereas the two glucoses in anthocyan **2** were bound to C-3 and C-5 of the aglycon [8-12].

Anthocyan **3** had λ_{max} 543 nm in the UV spectrum. Adding AlCl₃ (5%) in EtOH produced a bathochromic shift by 25 nm. This is consistent with the presence of free hydroxyls at the 3'- and 4'-positions of the anthocyan. Stepwise hydrolysis formed first a delphinidin monoglycoside and rhamnose and then delphinidin and glucose. Oxidation of the anthocyan by H₂O₂ [8, 11] indicated that the sugar was bound to C-3 and was a bioside.

Thus, anthocyan **1** was identified as cyanidin-3-O-β-D-glucopyranoside; **2**, cyanidin-3-O-β-D-glucopyranosyl-5-O-β-D-glucoside; **3**, delphinidin-3-O-β-D-glucopyranosyl-6-α-L-rhamnopyranoside. All anthocyanins in *A. neo-mexicana* fruit were detected for the first time. Photoelectrocolorimetry established that the amount of anthocyanins in the fruit was highest during botanical ripening (2.44% of raw mass) and remained unchanged for 1.5-2 months.

Owing to the high anthocyan content in adelia fruit, it can be considered a promising plant for producing food dyes and biologically active anthocyan preparations.

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