## ANTHOCYANINS OF Malva silvestris

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An investigation of extracts of the flowers of the high mallow <u>M</u>. <u>silvestris</u> L. (family Malvaceae) has shown the presence of three anthocyanin glycosides.

The extraction, preparation, and isolation of the individual anthocyanins of the high mallow were performed by a method described previously [1], giving three crystalline substances of anthocyanin nature with mp 174-176°C, 182-183°C, and 162-163°C.

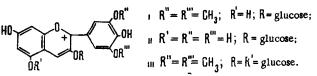
Anthocyanin (I) consisted of fine violet crystals with mp 174-176°C and the  $R_f$  values 0.36 in system 1 [butan-1-ol-acetic acid-water (6:1:2)] and \* in system 2 [water-acetic acid-concentrated hydrochloric acid (82:15:3)];  $\lambda_{max}$  534 nm (0.01% HCl in methanol); on the addition of a 5% solution of aluminum tri-chloride in ethanol no shift was observed.

The acid hydrolysis of the substance led to the formation of glucose and an aglycone which appeared on chromatograms at the level of an authentic sample of malvidin. Its IR and UV spectra were also identical with those of malvidin. On enzymatic hydrolysis of the substance with  $\beta$ -glucosidase (24 h, 36°C, pH 6.0), again, glucose was formed.

Anthocyanin (II) formed fine dark violet crystals with mp 182-183°C, readily soluble in ethanol and moderately soluble in water, with R<sub>f</sub> values in systems 1 and 2, respectively, 0.16 and 0.26;  $\lambda_{max}$  535 nm and with the addition of AlCl<sub>3</sub> 571 nm; readily hydrolyzed under mild conditions forming the aglycone delphinidin and glucose.

Anthocyanin (III) consisted of a dark violet microcrystalline powder with a golden tinge having mp 162-163°C, readily soluble in water and ethanol, and having  $R_f$  values 0.29 and 0.57 in systems 1 and 2, respectively;  $\lambda_{max}$  533 nm, no shift was observed on the addition of AlCl<sub>3</sub>. Its acid hydrolysis led to the formation of glucose and the aglycone malvidin.

On the basis of a study of the products of acid and enzymatic hydrolyses and the oxidative degradation with hydrogen peroxide of the glycosides themselves, and also of a study of the alkaline cleavage of their aglycones and the results of UV and IR spectroscopy, anthocyanin (I) was identified as malvidin  $3-\beta$ -D-glucopyranoside, anthocyanin (II) as delphinidin  $3-\beta$ -D-glucopyranoside (myrtillin), and anthocyanin (III) as malvidin  $3-\beta$ -D-glucopyranoside  $-5-\beta$ -D-glucopyranoside (malvin):



Malvin has been isolated from this plant previously by Willstätter et al., [2], but this is the first time that the other anthocyanin glucosides have been isolated from the flowers of <u>M</u>. silvestris L.

## LITERATURE CITED

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- 2. R. Willstätter and W. Mieg, Ann., 408, 122 (1915).

\*R<sub>f</sub> value for system 2 not given in Russian original - Consultants Bureau.

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