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## THE QUERCIMERITRIN CONTENT OF SOME SPECIES OF CENTAUREA

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By the chromatography on Kapron of an ethanolic extract of the epigeal part of Centaurea cyanus L. (cornflower) prepared in the Kiev Botanical Gardens in 1965, we have isolated a flavonol glycoside with mp 247-249°C, mol. wt. 466.8.

The IR spectrum of the substance exhibited the following absorption bands: 3380, 3420, 1160, 1615, 1085, 1055, 1025, 940, 905, 885, 850, 800, 735, 705  $\text{cm}^{-1}$  (UR-10 spectrometer, tablets in KBr), which indicates the presence of hydroxy groups in ring A of the chromone nucleus and in the lateral phenyl radical, and the presence of a carbonyl group, a double bond, and a sugar in the pyranose form. In the UV:  $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$  375, 255;  $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$  372, 257;  $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{ONa}}$  361, 291 ( $\Delta\lambda + 3, + 34$ );  $\lambda_{\text{max}}^{\text{CH}_3\text{COONa}}$  370, 258 ( $\Delta\lambda + 1$ );  $\lambda_{\text{max}}^{\text{CH}_3\text{COONa}+\text{H}_3\text{BO}_3}$  395, 259 ( $\Delta\lambda + 23, + 2$ );  $\lambda_{\text{max}}^{\text{AlCl}_3}$  424, 364 ( $\Delta\lambda + 52$ ). Acid hydrolysis of the glycoside gave the aglycone with mp 309°C. The acetyl derivative had mp 192°C. By paper chromatography and its UV and IR spectra, the aglycone was identified as quercetin. Enzymatic hydrolysis with the enzyme from the fungus Aspergillus oryzae also gave quercetin, together with D-glucose.

On the basis of the above results, the glycoside was identified as 3, 5, 7, 3', 4'-pentahydroxyflavone 7- $\beta$ -D-glucopyranoside, which is known under the name of quercimeritrin (quercetin 7- $\beta$ -D-glucopyranoside). We have isolated the same glycoside from the flowers of C. cheiranthifolia Willd. collected in 1965 in the region of the Teberda reserve at a height of 3000 m. No quercimeritrin has been found in other species of centaury that we have investigated (C. ciscasicosa Sosn., C. nigrifimbria (C. Koch) Sosn., C. micranthos Gmel., C. rutenica Lam., C. solstitialis L., and C. sumensis Kalerh).

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## ANTHOCYANINS OF THE SEEDS OF RHEUM TATARICUM II

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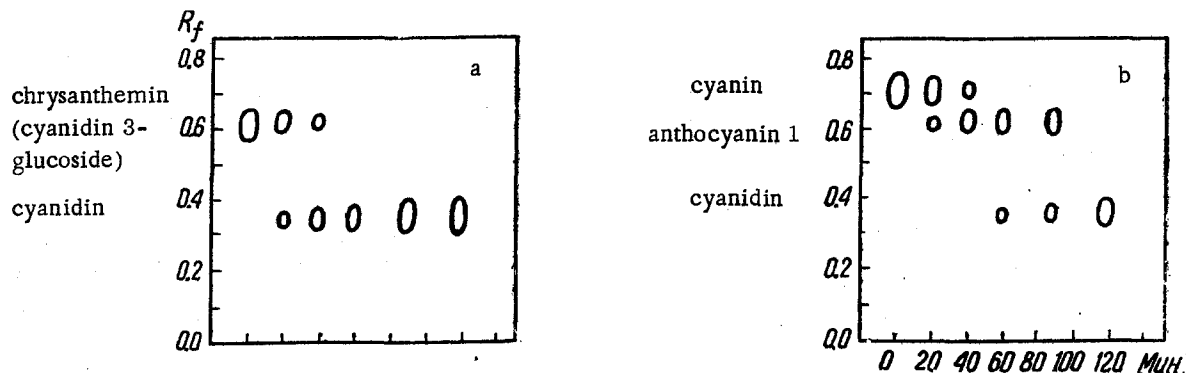
The anthocyanins of the rhubarbs of the family Polygonaceae Lind. have not been studied previously. The anthocyanins were extracted from the raw material with methanol containing 1% of hydrochloric acid. The resulting extract was chromatographed on a column of silica gel using the organic phase of the butan-1-ol-acetic acid - water (4:1:5) system as the mobile solvent and the aqueous phase as the stationary solvent.

The paper chromatography of the anthocyanin fraction in various systems of solvents showed the presence of two anthocyanins in the fraction. The combined anthocyanins were separated by preparative paper chromatography in the acetic acid-concentrated hydrochloric acid-water (5:1:5) system. The sharply separated zones were cut out and eluted with methanol containing 0.01% of hydrochloric acid. Hydrolysis of the anthocyanins under severe conditions showed that the two compounds were glycosides of the same aglycone cyanidin.

The ratio of the intensity of the light absorption of a solution at 440 m $\mu$  to the intensity at the corresponding maximum was twice as great for anthocyanin 1 as for anthocyanin 2, which indicates the diglucosidic structure of the latter [1].

	$\lambda$ , m $\mu$	$D$	$E_{440}/E_{max}$ , %
Anthocyanin 1 ( $6 \cdot 10^{-6}$ mole/l)	526	0.290	22
	440	0.065	
Anthocyanin 2 ( $4.6 \cdot 10^{-6}$ mole/l)	524	0.257	12
	440	0.031	

By paper chromatography in the systems butan-1-ol-hydrochloric acid-water (7:2:5); acetic acid-hydrochloric acid-water (3:1:8), (5:1:5), (30:3:10), and (15:3:82); butan-1-ol-acetic acid-water (4:1:5); and m-cresol-acetic acid-water (50:2:48), anthocyanin 1 was identified as cyanidin 3-monoglucoside (chrysanthemin) and anthocyanin 2 as cyanidin 3,5-diglucoside (cyanin).



One-dimensional ascending chromatograms of the products of the stepwise hydrolysis of anthocyanin 1 (a) and of anthocyanin 2 (b) in the glacial acetic acid-concentrated hydrochloric acid-water (5:1:5) system.

The stepwise hydrolysis [2] (figure) of anthocyanin 1 confirmed its identification as cyanidin 3-monoglucoside (chrysanthemin) and that of anthocyanin 2 as cyanidin 3,5-diglucoside (cyanin), since the stepwise hydrolysis of the latter at the stage of the formation of a monoglucoside a yellow spot with  $R_f$  0.74 appeared as well as the spot of cyanidin 3-monoglucoside. According to Willstätter [3], 5-monosides possess a yellow fluorescence.

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#### PRODUCTION OF AMINES OF LINOLOOL

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In order to obtain substances with gangliolytic activity, we have carried out the synthesis of an amine from linolool. It is known that only secondary amines possess appreciable activity [1, 2], while it is essential for high activity that one of the radicals connected to the nitrogen is a methyl or an ethyl group. Consequently, as the nitrile component of Ritter's amide condensation reaction [3] we used acetonitrile and made a detailed study of the behavior of linolool under the conditions of this reaction. It was found that the condensation of one mole linolool [1] in the presence of two moles of acetonitrile takes place with the highest yield at  $-5^\circ$  to  $10^\circ$  C. Under these conditions, the yield of 6-acetylamino-2,6-dimethylocta-2,7-diene (II) (mp  $120-121^\circ$  C) was 45%.

Reduction of the acetamide (II) with lithium aluminum hydride in absolute ether gave 6-ethylamino-2,6-dimethylocta-2,7-diene (III) and the corresponding hydrochloride with mp  $167-170^\circ$  C.