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NEW FLAVONOIDS FROM THE LEAVES OF CRATAEGUS CURVISEPALA LINDM. (FAMILY ROSACEAE)

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By chromatography on polyamide columns of the total flavonoids isolated previously from the leaves of Crataegus curvisepala Lindm. (campylocalycate hawthorn) [1], two new flavonoids have been isolated: flavonoid (I) and flavonoid (II).

Flavonoid (I), $C_{15}H_{10}O_7$, mp 311-313°, formed a compound of the composition $C_{25}H_{20}O_{12}$, mp 199-201° on acetylation. On investigating the UV spectra of flavonoid (I) with the addition of sodium acetate, a bathochromic shift of 33 mμ was found in the short-wave region, which is apparently due to the presence of a strongly ionized hydroxyl group in position 7. A bathochromic shift of 19 mμ in the long-wave region of the UV spectrum of flavonoid (I) on the addition of sodium acetate and boric acid indicates the presence of hydroxyl groups in the 3'-, and 4'-positions [2].

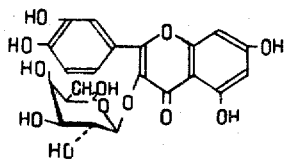
The formation of phloroglucinol in the alkaline decomposition of flavonoid (I), and also the results of UV spectroscopy and the absence of a depression of the melting point of a mixture of flavonoid (I) and quercetin, indicates that flavonoid (I) is identical with quercetin (3, 5, 7, 3', 4'-pentahydroxyflavone).

Flavonoid (II), $C_{21}H_{20}O_{12}$, mp 238-239°, is a flavone glycoside. Hydrolysis with 2% hydrochloric acid of flavonoid (II) gave an aglycone of composition $C_{15}H_{10}O_7$ and mp 311-313°. Acetylation of the aglycone of flavonoid (II) gave a compound $C_{25}H_{20}O_{12}$ with mp 199-201°, the physicochemical properties of which did not differ from the acetylated derivative of quercetin. The methyl derivative of the aglycone of flavonoid (II), $C_{20}H_{20}O_7$, mp 152-154°, was identical with the methyl derivative of quercetin.

Among the products of the alkaline decomposition of the aglycone of flavonoid (II), paper chromatography showed the presence of phloroglucinol and 3, 4-dihydroxybenzoic acid, showing the presence in the aglycone of hydroxyl groups at the 5-, 7-, 3'-, and 4'-positions.

UV spectroscopy of the aglycone of flavonoid (II) with various additives (sodium acetate, sodium acetate + boric acid) confirmed the assumption that the aglycone of flavonoid (II) contains hydroxyl groups in the 5-, 7-, 3'-, and 4'-positions. A positive zirconium test [3] showed the presence in the aglycone of flavonoid (II) of a hydroxyl group in position 3. Thus, the aglycone of flavonoid (II) has the structure of quercetin.

Chromatography of the products of the acid hydrolysis of flavonoid (II) in the butanol-acetic acid-water (4: 1: 5) system showed the presence of galactose. A mixture of the phenylosazone of the sugar of flavonoid (II) and galactose gave no depression of the melting point (182-185°). The addition of zinc and hydrochloric acid to a solution of the aglycone of flavonoid (II) led to a characteristic red coloration. The positive zinc/hydrochloric acid reaction shows that the sugar is present in the 3- position of flavonoid (II) [4].



The conformation of the galactose was established by Reeves' method [5]. The negative value of the difference between the molecular rotation of the cuprammonium complex of flavonoid (II) and the pure flavonoid (II) showed that the sugar of flavonoid (II) is in the C1 form. The rapid enzymatic hydrolysis of flavonoid (II) with rhamnodiastase, which is specific for a β- linkage, confirms the assumption that flavonoid (II) is glycosidated in the 3- position with β-D-galactose. Consequently, flavonoid (II) is 5, 7, 3', 4'-tetrahydroxyflavone-(3)-β-D-galactoside (hyperoside; cf. formula).

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ISOLATION OF SHIKONIN FROM MACROTOMIA UGAMENSIS M. POP.

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Macrotomia ugamensis (family Boraginaceae) is a perennial herbaceous plant which is distributed in Central Asia on stony slopes and crags in the alpine zone of the Tien-Shan.

The plants were collected in the Aksu-Dzhebagly reserve in August 1963 by M. I. Vlasov and K. I. Boryaev, staff members of All-Union Research Institute for Medicinal and Aromatic Plants. Qualitative reactions and paper chromatography have shown that the roots of Macrotomia ugamensis contain a pigment similar in properties to alkannin or shikonin [1, 2].

Using Brockmann's method [3], we obtained a dark red crystalline substance (yield 0.67%).

Found: C 66.96, 67.20; H 5.74, 5.90; H (act.) 1.22, 1.11; OCH_3 0%. Calculated for $C_{16}H_{16}O_5$: C 66.66; H 5.56%; H (act.) 1.04.

Mp 146.5-147.5° (from benzene), a mixture with the shikonin found in the roots of Lithospermum erythrorhizon Sieb. et Zucc.* gave no depression of the melting point. The IR and UV spectra of the substance that we isolated and those of shikonin were identical. We were unable to determine the angle of rotation accurately because the solution was very strongly colored. However, it was ascertained that a 0.01% solution of the substance in benzene has a dextrorotation. Thus, the substance of composition $C_{16}H_{16}O_5$ obtained from the roots of Macrotomia ugamensis is shikonin.

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*Lithospermum erythrorhizon Sieb. et Zucc. has small roots in comparison with Macrotomia ugamensis M. Pop. and is very rarely found in the Soviet Union.