CRATESIDE – A NEW FLAVONOL GLYCOSIDE FROM *Crataegus monogyna* AND *C. pentagyna*

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The present paper gives the results of a chemical study of a new flavonol glycoside isolated from the leaves of Crateagus monogyna L. with a yield of 0.002% and previously called substance B [1, 2]. We have isolated a flavonoid with similar properties from the leaves and flowers of C. pentagyna W. et K. with yields of 0.005 and 0.1%, respectively (with respect to the dry raw material). The leaves of C. monogyna were collected in the environs of Sofia and the leaves and flowers of C. pentagyna in the environs of Burgas (People's Republic of Bulgaria) during the flowering period (May, 1970).

Flavonoid B, with the composition $C_{20}H_{18}O_{11}$, was shown to be a flavonol monoglycoside by means of qualitative color reactions, the results of chemical and spectroscopic investigations, and the molecular weight determined spectroscopically, and also by oxidation with sodium metaperiodate. The products of its hydrolysis with 5% sulfuric acid were found to contain D-glucose and L-arabinose in approximately equal amounts, in addition to the aglycone. This shows that the substance is not an individual compound but is an isomorphous mixture of two monoglycosides – a glucoside and an arabinoside – of similar structure.

To separate this mixture we used selective enzymatic cleavage with a stereospecific enzyme – rhamnodiastase – since the isomorphic mixture isolated underwent practically no separation when it was chromatographed on polyamide, cellulose, and other adsorbents or in preparative chromatographic separation on paper in various systems of solvents. From the products of enzymatic cleavage of the mixture that had been freed from the aglycone by extraction with ether a new flavonoid, crateside, was isolated (the physicochemical properties of a mixture of the flavones crateside and the aglycone are given in Table 1).

Crateside has the composition $C_{20}H_{18}O_{11}$ [UV spectrum: λ_{max}^{init} 253, 268 (shoulder), 364 nm], and according to the bathochromic shifts shown contains free phenolic hydroxyls at C_3, C_5, C_7, and C_4'.

From the products of the acid hydrolysis of the flavonoid were isolated the aglycone and L-arabinose (mp 155-158°C), identified by its physicochemical properties, its R_f value, and the properties of the phenylosazone (mp 162-165°C). The aglycone of crateside, with the composition $C_{15}H_{10}O_7$ [UV spectrum: λ_{max}^{init} 254, 272 (shoulder), 378 nm] was identified by qualitative color reactions, physicochemical properties, and also the properties of the acetyl and methyl derivatives as 3,3',4',5,7-pentahydroxyflavone (quercetin).

The UV spectrum of the flavonoid showed no bathochromic shifts with boric acid and sodium acetate, unlike the aglycone of this substance, which is possible only if the sugar component is attached in the 3' position.

On the basis of a comparison of the molecular rotations of crateside and the corresponding phenyl arabinosides it was established that the arabinose in the flavonoid is present in the β-L-furanose form. Consequently, the flavonoid is 3,3',4',5,7-pentahydroxyflavone 3'-β-L-arabofuranoside.

EXPERIMENTAL

Isolation of Crateside. With heating, 0.5 g of the mixture of flavonoids was dissolved in 250 ml of 20% ethanol and, after cooling, 0.5 g of the enzyme rhamnodiastase was added and the mixture was left in

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TABLE 1

Properties of the substance	Mixture of flavonoids	Crateside	Quercetin
Mp, °C	211-213	220-223	311-313
R_f value in the ethyl acetate–formic acid–water (10:2:3) system	0.35	0.33	0.75
Color in UV light	Yellow		
Reaction with ferric chloride (color of the reaction products)	Brownish green		Dirty green

the thermostat at 40°C. After five days, it was evaporated to dryness and extracted with 95% ethanol (3 × 100 ml) and the extract was evaporated to 5-6 ml and then 30 ml of diethyl ether and 45 ml of distilled water were added and the mixture was shaken for 5 min. The lower layer was shaken out twice more with 20 ml of diethyl ether each time. The aqueous layer, after standing in an open vessel for two days, deposited acicular crystals. After recrystallization from aqueous acetone and drying over P_2O_5, the crystals had mp 220-223°C.

Isolation of Quercetin. A mixture of 50 mg of crateside and 5 ml of 5% sulfuric acid was heated in the boiling water bath for 1.5 h. Then it was left for crystallization. Acicular crystals with mp 311-313°C deposited.

Acetylation of Crateside. A solution of 0.1 g of the substance in 2 ml of pyridine was treated with 1 ml of acetic anhydride. On the following day, the mixture was poured into 50 ml of cold water, and the precipitate that deposited was washed with water and recrystallized from strong ethanol. This gave an acetate with mp 122-125°C.

Acetylation. The quercetin was acetylated by the usual method in acetic anhydride with the addition of a few drops of sulfuric acid. The melting point after recrystallization from strong ethanol was 202-204°C.

Methylation. Quercetin was methylated in the usual way with dimethyl sulfate in acetone with the addition of potassium carbonate for 16 h. The melting point of the methyl derivative was 152-154°C (high).

Quantitative Periodate Oxidation of Crateside. A solution of 3 mg of the substance in 4 ml of 50% ethanol was treated with 6 mg of sodium metaperiodate. Then 0.1 g of potassium iodide was dissolved in 0.5 ml of the reaction mixture after it had been diluted with 5 ml of water, and three drops of a starch solution was added. The iodine liberated was titrated with a 0.01 N solution of sodium thiosulfate. In 4 h, crateside absorbed 2 moles of sodium metaperiodate.

SUMMARY

From the leaves of Crataegus monogyna L., and also from the leaves and flowers of C. pentagyna W. et K. we have isolated a new natural flavonoid and have called it crateside. It has been established by a chemical and spectroscopic investigation that crateside is quercetin 3'-β-L-arabofuranoside.

LITERATURE CITED

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