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FLAVONOIDS OF RHEUM TATARICUM. V

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Continuing an investigation of the seeds and leaves of Rheum tataricum L. fil. [1], we have isolated the total flavonoids. Their separation from a concentrated methanolic extract was achieved on fine Kapron powder. After repeated chromatography of the individual fractions, we obtained quercetin with mp 313°-314° C, isoquercitrin with mp 240°-241° C, meratin with mp 182°-183° C, and rutin with mp 190°-190.5° C.

To determine the flavonoids in the raw material quantitatively [2], they were chromatographed in the ethyl acetate-formic acid-water (10:2:3) system. The spots were cut out and eluted with 1% aqueous ammonium chloride [3]. The optical densities of the eluates were measured with a SF-4A spectrophotometer at a wavelength of 415 m μ [4, 5]. The concentrations were calculated from calibration curves constructed for the pure flavonoids.

The seeds of Rheum tataricum contain 0.05% of quercetin, 0.066% of isoquercitrin, 0.044% of meratin, and 0.072% of rutin, and the leaves contain 0.15%, 0.30%, 0.22%, and 1.45%, respectively.

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FLAVONOLS OF HIBISCUS AND A HYBRID OF HIBISCUS WITH THE COTTON PLANT

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Continuing our investigation [1] of the flavonoids of the hybrid Hibiscus 3209 and 2332, we have isolated a second flavonol.

The products of acid and enzymatic hydrolysis and of peroxide oxidation were compared chromatographically on paper. It was found that the aglycone is identical with quercetin. The sugar was revealed by mixtures of diphenylamine

and urea and of diphenylamine and p-anisidine [2]. From the color of the spots on the chromatogram and from the Rf value [0.24, 1-butanol-acetic acid-water (10:3:7) system] it was established that the sugar is a biose in which the monoses are linked through the 1-2 hydroxyls. Subsequent acid hydrolysis of the biose obtained by oxidative degradation gave only the spot of glucose. The biose is apparently sophorose (1- β -D-glucosido-2- β -D-glucose).

The position of attachment of the sophorose at C-3 of the quercetin was determined by qualitative reactions: zinc dust and concentrated hydrochloric acid gave a pink coloration, zirconyl chloride with citric acid in methanol gave no coloration. Oxidative degradation with hydrogen peroxide selectively cleaves only C-3 glycosides [3]. The UV spectrum of the glycoside confirmed the position of sophorose.

Consequently, the flavonol that we isolated is quercetin 3-(1-\(\theta\)-D-glucosido-2-\(\theta\)-D-glucoside). It has been found previously in the flowers of Petunia hybrida [4], in the flowers of the cotton plant (G. barbadense) [5], and in the pollen of the alder (A. cordata Dest.) [6]. This is its first detection in the flowers of Hibiscus.

The flavonol hirsutrin has been isolated from the flowers of the hybrid of Hibiscus with the cotton plant [7].

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GALLOTECHINS OF THE ROOTS OF RHEUM MAXIMOVICZII

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In the present paper we give the results of the identification of four hydroxyflavanes from the roots of Rheum maximoviczii A. Los., which, on being freed from polymers on powder were desorbed by ethyl acetate [1, 2]. According to the results of two-dimensional paper chromatography, the ethyl acetate fraction contained gallic acid and eight flavane derivatives. This combination of substances was separated by partition chromatography on silica gel with ether as the mobile phase. The compounds investigated were contained in the following zones: R_1 0.17 and R_2 0.10 (-)-epigallocatechin, R_1 0.16 and R_2 0.13 (+)-gallocatechin, R_1 0.17 and R_2 0.15 (\pm)-gallocatechin, R_1 0.43 and R_2 0.16 a 4-hydroxyflavane. The final separation of these substances was effected by rechromatography on silica gel and recrystallization of the dry residues of the fractions from water.

The properties of the first three substances agreed with published data [3, 4]. The fourth compound had an absorption maximum in the UV spectrum at 278 m μ (log ϵ 3.93), gave a stable deep blue coloration with a 1% solution of ferric ammonium alum, a pink coloration with vanillin in HCl, and a yellow coloration with p-toluenesulfonic acid. The qualitative reactions, and also the formation of a phlobaphene and a golden yellow coloration when a solution was heated with 5% sulfuric acid shows that the 4-hydroxyflavane is a derivative of a hydroxy-3-flavonol with a pyrogallol ring. On being heated with 50% caustic potash (150° C), all four substances were cleaved giving phloroglucinol and gallic acid. On being kept with tallase in aqueous solution at 34° C for 10 min, only the fourth compound was hydrolyzed, forming gallic acid and (\pm)-gallocatechin.

The 4-hydroxyflavane forms slightly yellowish needles with mp $205^{\circ}-207^{\circ}$ C (decomp.). It is optically inactive in ethanol and acetone. It forms an octaacetyl derivative $C_{38}H_{34}O_{19}$ as colorless prisms with mp $163^{\circ}-165^{\circ}$ C, optically inactive in 1% ethanolic solution. When chromatographed on paper together with the catechins of tea it corresponds