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FLAVONOIDS OF THALICTRUM FOETIDUM

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Thalictrum foetidum L. (fetid meadowrue), family Ranunculacease, is a perennial herbaceous plant growing in the high pastures and valleys of Kirghizia. In addition to alkaloids [1-3], flavonoid compounds have been found in the plant by qualitative reactions. The total content of flavonoids in the epigeal part of the fetid meadowrue is 1.5%.

The qualitative composition of the total flavonoids was determined by one- and two-dimensional paper chromatography. Two flavonoid substances were detected, one of which was identified as rutin [4].

The chromatography on Kapron of the total flavonoid substances yielded the second glycoside in the crystalline state. In the 15% acetic acid system, the glycoside studied had R_f 0.55, and in the benzene—ethyl acetate—acetic acid (24.5 : 73.5: 2) system R_f 0.1.

On the basis of qualitative reactions, spectroscopic characteristics in the UV region with the use of ionizing and complex-forming reagents [5,6], and an analysis of the products of the acid hydrolysis and of the alkaline cleavage of the aglycone, the substance under investigation may be regarded as a flavonoid glycoside with free hydroxy groups in positions 5, 3', and 4' (table).

Acid hydrolysis of the glycoside led to the isolation of rhamnetin and D-glucose. The results of enzymatic hydrolysis with emulsin, the rate of acid hydrolysis, and the IR spectrum show the presence in the substance of a β sugar bond with the aglycone in position 3.

The positive azo coupling reactions of the glycoside, the aglycone, and its acetyl derivative and the presence of phloroglucinol in the products of alkaline cleavage show that there must be a donor substituent—a hydroxyl or alkoxyl group—in position 7. But no bathochromism in the UV spectrum with sodium acetate was observed either for the glycoside or for the aglycone. All this permits the assumption that the group mentioned is not free. In order to free it, we dealkylated the aglycone and isolated the product, which was identified as quercetin. A comparision of the properties of the aglycone and the acetate with the properties given for rhamnetin [7] shows their complete identity.

Thus, the glycoside obtained from the herb fetid meadowrue can be characterized as rhamnetin 3-β-D-glucopyranoside.

Of rhamnetin glycosides, only the 3-trioside xanthorhamnin, isolated from purging buckthorn, was known previously [7]. Consequently, the rhamnetin 3-glycoside from fetid meadowrue is a new compound; it is appropriate to call it glucorhamnin.

Comparative Characteristics of the Glycoside T-2 and Its Derivatives

Solutions and reagents	Absorption bands	Glycoside T-2		Aglycone		Product of dealkylation of the aglycone	
		λ	Δ λ	λ	Δ λ	λ	Δ λ
Ethanolic solution	I	360,300	—	372	—	370	—
	II	265,257	—	265,255	—	266,256	—
Ethanolic solution + sodium acetate	I	360,390	0	377	5	380	10
	II	265,257	0	265,255	0	270	4
Ethanolic solution + sodium methoxide	I	400	40	345	—27	300	—70
	II	270	5	285,240	20	270	4
Ethanolic solution + boric acid and sodium acetate	I	385	25	390	18	395	25
	II	267	2	260	— 5	270	4
Ethanolic solution + zirconyl nitrate	I	410	50	470	98	455	85
	II	270	5	280	15	272	6
Ethanolic solution + zirconyl nitrate + citric acid	I	360	0	425	53	420	50
	II	270	5	280	15	470	4

Experimental

The chromatograms were made on "S" paper of the Volodarskii Leningrad mill. The UV spectra were taken on an SF-4A spectrophotometer. The optical rotation was measured on an SPU-E spectropolarimeter.

Isolation of the flavonoids. One hundred grams of the herb T. foetidum was extracted with methanol until the flavonoids (with metallic zinc and magnesium in conc HCl) was negative. The extract was evaporated in vacuum, diluted with water, and purified with chloroform. The flavonoids were extracted from the aqueous solution with ethyl acetate. A precipitate deposited from the concentrated ethyl acetate extracts. It amounted to 1.05%.

Glucorhamnin. The combined flavonoids were deposited on a column of polyamide and were eluted with mixtures of water and ethanol with gradually increasing ethanol contents. The fraction obtained by elution with 40–60% ethanol contained the glucorhamnin which, on concentration, deposited in the form of bright yellow acicular crystals with mp 220–223° C, $[\alpha]_D$ −67.0° (c 0.3; dimethylformamide).

Acid hydrolysis. The glycoside (0.05 g) was dissolved in 10 ml of 50% methanol containing 10% of HCl solution, and the mixture was hydrolyzed for 1 hr. After dilution with water (1 : 1), the aglycone precipitated. After recrystallization from ethanol yellow needles with mp 296–298° C were obtained. Yield 0.0325 g (65% of the weight of the glycosides). The carbohydrate component was identified as D-glucose.

Enzymatic hydrolysis. The glycoside (0.01 g) was dissolved in 20 ml of hot water and, after cooling, 2 ml of a colloidal solution of emulsin (0.01 g in 10 ml of water) was added and the mixture was left at 36° C for 24 hr. The hydrolysis products were diluted with 96% ethanol (1 : 1) and heated to the boil to denature the enzyme proteins. Rhamnetin and D-glucose were isolated from the hydrolysis products.

Acetate of the aglycone. One drop of conc H_2SO_4 was added to a solution of 0.1 g of the aglycone of the glycoside glucorhamnin in 5 ml of acetic anhydride; after 10–15 min 50 ml of cold distilled water was added. The acetate of the aglycone had mp 190–192° C.

Alkaline degradation of the aglycone. 0.5 g of caustic potash was fused in a porcelain crucible with a few drops of distilled water and then 0.05 g of the aglycone of the glycoside was added and the mixture was heated for 2–3 min. After cooling, the alkaline melt was neutralized with H_2SO_4 and extracted with diethyl ether. The ethereal extracts were evaporated to dryness. Phloroglucinol and protocatechuic acid were found in the reaction products by paper chromatography.

Demethylation of the aglycone. A mixture of 20 mg of the aglycone, 0.4 ml of hydriodic acid (sp. gr. 17), and 0.32 ml of liquid phenol was heated at a gentle boil for 8 hr. After cooling, the dark brown liquid was poured into 6 ml of a saturated solution of sodium hyposulfite. A precipitate deposited. Its recrystallization from dilute ethanol gave quercetin with mp 312–314° C.

Conclusions

Two fluavonoid glucosides have been isolated from the herb Thalictrum foetidum L.: rutin and a new flavonoid glucorhamnin with an aglycone rarely found in nature. Glucorhamnin has been characterized as rhamentin 3-β-D-glucopyranoside.

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