

FLAVONE GLYCOSIDES OF GERANIUM COLLINUM. III

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Continuing a study of the leaves of Geranium collinum Steph. (upland geranium) [1], by the chromatography of an aqueous extract of an ethereal solution on Kapron with elution by water and then with methanol, we isolated a product with mp 178–180° C and isoquercitrin. The acid hydrolysis of the product gave quercetin and arabinose in a molar ratio of 1:1. The UV spectrum with ionizing and complex-forming additives showed that the substituent occupied position 3 of the quercetin molecule. The low melting point [2] showed that the product was a mixture of isomers of quercetin 3-arabinoside. By extracting its aqueous solution with ether, we isolated successively quercetin 3- α -L-arabofuranoside with mp 217–219° C; $[\alpha]_D^{25}$ –133°, and quercetin 3-(α -L-arabopyranoside) with mp 237–239° C [3].

The isoquercitrin with mp 238–240° C; $[\alpha]_D^{25}$ –73°, was identified on the basis of acid and enzymatic hydrolysis, the UV spectrum with ionizing and complex-forming additives, the IR spectrum, and the specific rotation [4].

When an extract of the leaves after its treatment with ethyl acetate was chromatographed on Kapron with elution by water, we isolated rutin with mp 190–192° C, which was identified from the results of acid hydrolysis, the UV spectra with additives, and the absence of a depression of the melting point of a mixture with an authentic sample of rutin.

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ISOQUERCITRIN — A NEW FLAVONE GLYCOSIDE OF SOLIDAGO CANADENSIS

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By chromatographing on polyamide an extract from the epigeal part of Solidago canadensis L., family Compositae (Canada goldenrod), we have isolated an individual substance (I). The positive cyanidin reaction showed the flavonoid nature of the substance isolated.

From the products of the acid hydrolysis of substance (I) we obtained an aglycone [substance (II)] and a sugar component. By paper chromatography in the butanol–acetic acid–water (4:1:2) system, the sugar component of substance (I) was identified as glucose.

In the IR spectrum of substance (II) (table) with sodium acetate, bathochromic shifts of band (I) (by 15 m μ) and of band (II) (by 20 m μ) were observed, showing the presence of free hydroxy groups in positions 4' and 7. The bathochromic shift of band (I) by 15 m μ in the UV spectrum of substance (II) with boric acid and sodium acetate permits the assumption of the presence of hydroxy groups in positions 3' and 4'. Phloroglucinol and 3,4-dihydroxybenzoic acid were identified in the products of the alkaline decomposition of substance (II).

On the basis of the results obtained and its physicochemical properties, substance (II) was identified as 3,5,7,3',4'-pentahydroxyflavone (quercetin). A mixture of substance (II) and quercetin gave no depression of the melting point.

The UV spectra of substance (I) with all the ionizing and complex-forming additives, with the exception of sodium methoxide, did not differ from the UV spectrum of substance (II) with the same additive. When sodium methoxide was

added, two absorption bands appeared in the UV spectrum of substance (I) in contrast to the UV spectrum of substance (II). This fact shows that the sugar component is attached at position 3 of quercetin.

Main Physicochemical Properties of Substances (I) and (II)

Sub- stance	Elemen- tary com- position	Mp, °C	[α] _D ²⁰ (in metha- nol), deg	UV spectra				
				λ _{max} (initial)	ditto + so- dium ace- tate	ditto + so- dium meth- oxide	ditto + bo- ric acid + sodium acetate	ditto + alu- minum chloride
(I)	C ₂₁ H ₂₀ O ₁₂	220—225	— 16	355 300* 267**	380	408 325*	375 295**	435 335* 300**
(II)	C ₁₅ H ₁₀ O ₇	311—314	0	256 370 300* 272** 254	273 385 322 274	271 332 285** 245	260 385 305* 257	274 457 385* 300** 271

*Weak absorption band

**Shoulder

A comparison of the molecular rotations of substance (I) and phenyl β-D-glucopyranoside showed that substance (I) is glycosidated β-D-glucopyranose and is 5,7,3',4'-tetrahydroxyflavone 3-(β-D-glucopyranoside) (isoquercitrin).

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THE PHENOLIC COMPOUNDS OF HEDYSARUM KOMAROVII

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From 176.0 g of the herb *Hedysarum Komarovii* B. Fedtsch collected on Shikotan Island, we obtained an ethanolic extract the evaporation of which gave a crystalline substance A (yield 1.3%). After recrystallization from ethanol, substance A was identified as a substance of a xanthone nature—mangiferin (hedysaride), which is the 2-C glucoside of 1,3,6,7-tetrahydroxyxanthone [1]. From the ethanolic extract after the separation of substance A, by chromatography on a column of polyamide sorbent, we isolated two flavonoid glycosides—substances B and C.

Substance B was identified as hyperoside on the basis of the products of acid and enzymatic hydrolysis, IR and UV spectra with the addition of ionizing and complex-forming agents, and by a direct comparison with an authentic sample.

Substance C was identified as polystachoside (quercetin 3-β-L-arabofuranoside) on the basis of the hydrolysis products, the results of UV and IR spectroscopy, and a comparison of the molecular rotation of glycoside C and the corresponding phenyl glycosides [2].

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