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FLAVONOIDS OF ARTEMISIA TRANSILIENSIS

II. A New Flavonoid Glycoside Transilin

T. K. Chumbalov, O. V. Fadeeva, and I. S. Chanysheva

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Continuing a study of the flavonoid composition of Artemisia transiliensis Poljak, we have isolated a new flavonoid and have called it transilin. With Mg and HCl the flavonoid forms a crimson pigment insoluble in octanol. Consequently, the flavonoid is a glycoside.

On acid hydrolysis, transilin was split into glucose and an aglycone. On a chromatogram, the aglycone was revealed in UV light in the form of a dark spot. An alkaline solution of the aglycone is stable with respect to atmospheric oxygen and on acidification it is extracted by ether.

The qualitative reaction with zirconyl chloride in the presence of citric acid was negative [1]. All this shows substitution of the OH group in position 3. Elementary analysis showed the presence of one methoxyl group in the glycoside. The positive reaction with ammoniacal solution of $AgNO_3$ shows that the molecule of the flavonoid contains ortho dihydroxy groups in the B ring [2].

Alkaline fusion gave protocatechuic acid and phloroglucinol, which were identified by paper chromatography with standard substances.

To determine the free hydroxy groups and the position of the carbohydrate substituent in the glycoside more accurately, a spectral study in the UV region using ionizing and complex-forming reagents was carried out [3].

As can be seen from the table, free hydroxy groups were found in the 5, 3', and 4' positions of the glycoside and in the 7, 5, 3', and 4' positions of the aglycone. Consequently, position 3 of the aglycone is substituted and the carbohydrate substituent is located at position 7.

In a spectral study, the IR region of the spectrum of the glycoside was found to contain, in addition to bands at 3380 cm^{-1} (—OH) and 1670 cm^{-1} (C = 0), bands at 2940 and 2860 cm^{-1}, which are characteristic for the $-OCH_3$ group. The qualitative reactions, elementary analysis, and UV spectra with additives show that the $-OCH_3$ group is present in position 3.

The identity of the aglycone as 3-O-methylquercetin was confirmed by the preparation of an acetyl derivative, the melting point of which corresponded to that given in the literature [4, 5]. The dementhylation of the aglycone [6] gave quercetin, which was identified by paper chromatography with an authentic sample. The reduction with Mg and HCl of the demethylated aglycone gave cyanidin.

The configuration of the glycosidic bond and the size of the oxide ring in the glycoside were determined by comparing the molecular rotation of the substance with the corresponding phenyl glycosides [7].

The results of the comparison show the presence of β-glycosidic linkage and the pyranose form of the D-glucose. The IR spectra confirm these conclusions [8].

Solutions and reagents	Absorption bands	Glycoside		Aglycone	
		λ_{max}	$\Delta\lambda$	λ_{max}	$\Delta\lambda$
		mn			
$2 \cdot 10^{-5}$ M in absolute ethanol	I	360	—	360	—
	II	257	—	258	—
$2 \cdot 10^{-5}$ M in absolute ethanol + sodium acetate	I	358	—2	369	9
	II	257	0	264	6
$2 \cdot 10^{-5}$ M in absolute ethanol + sodium ethoxide	I	405	45	410	55
	II	270	13	272	14
$2 \cdot 10^{-5}$ M in absolute ethanol + boric acid + sodium acetate	I	390	30	382	22
	II	266	9	266	8
$2 \cdot 10^{-5}$ M in absolute ethanol + zirconyl chloride	I	398	38	410	50
	II	262	5	270	13
$2 \cdot 10^{-5}$ M in absolute ethanol + zirconyl chloride and citric acid	I	358	—2	359	—1
	II	257	0	257	—1

Thus, the results obtained permit transilin to be characterized as 3-O-methylquercetin 7-β-D-glucopyranoside. The amount of transilin was determined directly on paper by the spectrophotometric method and was found to be 0.2% of the weight of the absolutely dry raw material.

Experimental

Isolation of transilin. The air-dry herb Artemisia transiliensis was treated with petroleum ether to eliminate the essential oils. The defatted raw material was extracted with 80% methanol. The alcoholic extract was evaporated and the aqueous residue was subsequently treated with petroleum ether, diethyl ether, ethyl acetate, and butanol. The ethyl acetate extract was evaporated to dryness and the residue was dissolved in a small amount of methanol and transferred to a Kapron column. The flavonoids were eluted with methanol; their separation was checked by paper chromatography in the systems: 1) butanol–acetic acid–water (4 : 1 : 5); 2) 15% acetic acid; and 3) 2% acetic acid. The first eluates, which contained a glycoside with R_f 0.49 (1), 0.5 (2), and 0.12 (3), were evaporated to small bulk. Pale yellow crystals separated out in the form of needles which after recrystallization from 80% methanol, had mp 244–245° C, $[\alpha]_D^{20}$ −72.7° (c 0.5; methanol).

Found, %: C 55.1; H 4.43; OCH_3 6.45. Calculated for $C_{22}H_{22}O_{12}$, %: C 55.23; H 4.6; OCH_3 6.48.

Acid hydrolysis of transilin. A mixture of 0.15 g of transilin and 3 ml of 5% H_2SO_4 solution was heated in the water bath for 4 hr. The completeness of the hydrolysis was confirmed by paper chromatography in the above-mentioned solvent systems. After hydrolysis, one spot was found with R_f 0.87 (1), 0.19 (2), and 0.0 (3). The precipitate that had deposited was filtered off, washed with water, and dried. After recrystallization from dilute ethanol the aglycone had mp 259–260° C.

Found, %: C 61.1; H 4.0; OCH_3 10.5. Calculated for $C_{16}H_{12}O_7$, %: C 60.7; H 3.8; OCH_3 9.8.

The hydrolysate was found to contain glucose, which was identified by paper chromatography with an authentic sample.

Acetyl derivative of the aglycone. A mixture of 0.05 g of the aglycone, 0.1 g of calcined solium acetate, and 3 ml of acetic anhydride was heated in the water bath for 1.5 hr. The mixture was poured into ice water and was left in the refrigerator for 2 days. After crystallization from ethanol, the substance was obtained in the form of white needles with mp 179–180° C.

Demethylation. A mixture of 0.05 g of the aglycone and 30 ml of pyridine saturated with gaseous HCl was heated in an atmosphere of nitrogen on a sand bath at 120° C for 4 hr. The mixture was diluted with distilled water. The yellow precipitate obtained was identified by paper chromatography with a reference sample of quercetin in the above solvent systems. The anthocyanidin obtained from the precipitate was identified as cyanidin.

Alkaline cleavage. A mixture of 0.1 g of the substance and 4 ml of 50% KOH was heated on the sand bath at 170° C for 20 min. The mixture was cooled, acidified with H_2SO_4, and extracted with ether. The ethereal extract was found by paper chromatography with standard samples to contain protocatechuic acid and phloroglucinol.

Conclusions

From Artemisia transiliensis we have isolated a new glycoside and have called it transilin. On the basis of spectral and chemical investigations the structure of 3-O-methylquercetin 7-β-D-glucopyranoside has been proposed for it.

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Kirov Kazakh State University