TRICIN APIOSIDE FROM Salsola collina

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Continuing a study of the flavonoid compounds of Salsola collina Pall. [1], we have isolated a new tricin derivative from the n-butanol-soluble fraction of an aqueous ethanolic extract.

Isolation was achieved by repeated column chromatography on polyamide and silica gel, using the chloroform–methanol (0 → 50) solvent system. Final purification was performed by preparative chromatography on Silufol plates in the chloroform–methanol (87:13) system followed by passage through Molselect G-15 in the methanol–water (1:1) system. The result was the isolation of ~17 mg of compound (I) with mp 166-168°C.

The molecular mass of (I) – 463 $(M + H)^+$, determined with the aid of FAB mass spectrometry, in combination with other spectral characteristics, corresponded to the empirical formula $C_{22}H_{22}O_{11}$. The FAB mass spectrum contained, in addition to the quasi-molecular ion, an ion with m/z 331 $(M + H -$ a pentose$)^+$, which corresponds to the molecular mass of tricin.

In the ^1H NMR spectrum of (I) taken in DMSO-d_6 there were the signals of protons at (ppm) 6.22 (1H, d, 2 Hz, H-6); 6.58 (1H, d, 2 Hz, H-8); 7.06 (1H, s, H-3); 7.32 (2H, s, H-2', H-6'); 3.90 (6H, s, OCH_3-3',5'); 12.86 (1H, s, 5-OH), confirming the tricin structure [1] and also a one-proton doublet at 5.58 ppm with J = 1.5 Hz (H-1") and a multiplet at 3.5-4.1 ppm belonging to the protons of a carbohydrate.

The presence of free hydroxy groups in positions 5 and 7 of the molecule was established by the method of UV spectroscopy with ionizing and complex-forming reagents [2]: λ_{max} (MeOH) 272 (lg ε 4.06); 310 sh., 328 (lg ε 4.08); +NaOMe 277, 300 sh., 367; +$AlCl_3$ 281, 300, 346, 384; +HCl + $AlCl_3$ 280, 300, 343, 382; +NaOAc 280, 300, 359; NaOAc + H_3BO_3 272.315 sh., 330 nm.

The carbohydrate substituent was found to be apiose, as followed from the ^{13}C NMR spectrum (Table 1), the assignment of the CSs in which was based on a comparison of literature figures for tricin [1], tricetin [3], and apiosides [4, 5].

On the basis of the facts given above, we have established for the compound isolated the structure of tricin 4'-O-β-D-apiofuranoside (4'-β-D-apiofuranosyloxy-5,7-dihydroxy-3',5'-dimethoxyflavone).

TABLE 1. ^{13}C NMR Spectrum (DMSO-d_6, δ, ppm, TMS – 0)

Atom	δ, ppm	Atom	δ, ppm	Atom	δ, ppm
C-2	162,83	C-9	157,69	C-6′	104,05
C-3	103,40	C-10	105,09	C-1″	109,25
C-4	181,69	C-1′	126 68	C-2″	76,73
C-5	161,53	C-2′	104,(5	C-3″	79,59
C-6	99,36	C-3′	153,73	C-4″	75,43
C-7	162,83	C-4′	136,24	C-5″	64.12
C-8	94,88	C-5′	153,73	$OCH_3 \times 2$	56,44

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We have found no information on the isolation on (I) in the literature.

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METHOD FOR THE QUANTITATIVE DETERMINATION OF THE ISOFLAVONES AND POLYHYDROXYSTILBENES OF Maackia amurensis

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Isoflavones (retusin, genistein, and formononetin) and polyhydroxystilbenes (resveratrol, piceatannol) from the heartwood of Maackia amurensis Rupr. et Maxim., family Fabaceae, [1] exhibit a specific physiological activity [2]. In view of this, we have developed a method for the quantitative determination of these groups of compounds which consists in the chromatographic separation of accompanying substances on a silica gel column and the spectrophotometry of the eluate at two wavelengths close to the isobestic points of the isoflavones and the polyhydroxystilbenes. We used stilbene as the comparison substance. Coefficients eliminating the mutual influence of the groups of compounds concerned on the results of their determination have been introduced into the formulas for calculation. A comparison of the results obtained by HPLC [3] and by the proposed method has shown that the latter permits the determination of the actual amounts of the desired components on the wood.

Procedure. Air dry sawdust (≤ 1 mm; 5 g) is steeped in 50 ml of ethanol at room temperature in a dark place. The extract is filtered, and 5 ml of the filtrate is evaporated to dryness. The residue is dissolved in ethanol (1 ml) and the solution is added to 1.5 g of silica gel L (Czechoslovakia), 60-100 mesh, impregnated with a solution of acetic acid (100 g of silica gel + 30 ml of a 3:7 solution of acetic acid in water). After the complete volatilization of the solvent, the silica gel with the sample is transferred to a column (1.5 × 7 cm) of the same silica gel (2.5 g) equilibrated with benzene. The isoflavones and the polyhydroxystilbenes are eluted with benzene–acetone (3:1) at the rate of 1-1.5 ml/min, 30 ml of the eluate is collected in a 50 ml measuring flask, the volume is made up to the mark with acetone (solution A), and 1 ml of solution A is transferred to a 25 ml measuring flask. The solvent is driven off with a stream of air, and the residue is dissolved in ethanol up to the mark (solution B). The optical densities of solution B at the wavelengths 272 and 320 nm – D_1 and D_2, respectively – are measured in a cell (l = 10 mm) during the first 10 min after its preparation, against ethanol. The optical densities of a solution of stilbene at the wavelengths 272 and 320 nm – D_3 and D_4, respectively – are measured under similar conditions. The total amount of isoflavones (X) and the total amount of polyhydroxystilbenes (Y) in percentages on the absolutely dry wood are calculated from the formulas:

$$X = \frac{m \cdot (D_1 - 0{,}283 \cdot D_2)\, 1250}{m_1 \cdot D_3 \cdot 0{,}936\,(100 - W)}, \qquad Y = \frac{m \cdot (D_2 - 0{,}226 \cdot D_1)\, 1250}{m_1 \cdot D_4 \cdot 0{,}936 \cdot (100 - W)},$$

where m is the weight of the stilbene, g; m_1 is the weight of the wood, g; 0.266, 0.283, and 0.936 are coefficients taking into account the mutual influence of the isoflavones and the polyhydroxystilbenes on the results of their determination; and W is the loss in weight on drying, %.

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