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COUMARINS FROM *Astragalus asper*

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We continued research on coumarins from the aerial part of *Astragalus asper*. The $CHCl_3$ fraction obtained by selective extraction of the total extract from *A. asper* Jacq. growing in the Caucasus foothills on Stavropol plateau [1] were placed on a silica-gel column (1:10 ratio) and eluted successively with hexane, hexane:$CHCl_3$ with increasing $CHCl_3$ content, and a gradient of $CHCl_3$:CH_3OH (9:1-6:4) [2].

Compounds **1-4** were obtained by elution with a gradient of hexane:$CHCl_3$ (4:6-2:8). Qualitative reactions, PC, and TLC identified the isolated compounds as α-pyrone-coumarin derivatives [2, 3]. Spots of **1** and **2** on the chromatograms gave blue fluorescence that intensified upon treatment with ethanolic KOH or ammonia vapor. This was consistent with a C7 hydroxyl in the coumarin ring [3].

The structures of the isolated compounds were established by comparison with standards and physicochemical constants from UV and IR spectroscopy using ionizing and complexing additives [SF-46 (USSR), UR-20 (Germany)]. Chromatography used BuOH:CH_3CO_2H:H_2O (1, 4:1:8) and $CHCl_3$ (2) (paper impregnated with formamide:acetone, 1:3).

Compound 1, $C_9H_6O_3$, white needle-like crystals, mp 231-233°C (MeOH), R_f 0.33 (system 1), 0.88 (system 2). UV spectrum (EtOH, λ_{max}, nm): 256, 325. Addition of sodium acetate produced a bathochromic shift of the long-wavelength band (240, 378 nm). IR spectrum (KBr, ν, cm^{-1}): 1616-1575 (–C=C–), 3300 (–OH), 1718 (>C=O). Based on these results and the lack of melting-point depression of a mixed sample with a standard, **1** was characterized as 7-hydroxy-coumarin, umbelliferone [2, 3].

Compound 2, $C_{10}H_8O_4$, white crystalline powder with a cream tint, mp 204-206°C (MeOH), R_f 0.56 (system 1), 0.38 (system 2). UV spectrum (λ_{max}, nm): 256, 300, 315, 340. Addition of sodium acetate produced a bathochromic shift of the long-wavelength band (240, 378 nm). IR spectrum (cm^{-1}): 1708 (>C=O), 3300-3350 (–OH), 2930, 2845 (–OCH_3).

Based on these results and comparison with a standard sample, **2** was characterized as 7-hydroxy-6-methoxycoumarin, scopoletin [3].

Compound 3, white needle-like crystals, mp 215-219°C (MeOH), soluble in water, methanol, ethanol. UV light produced a bright blue fluorescence that intensified after treatment with base. UV spectrum (EtOH, λ_{max}, nm): 250, 315. Acid hydrolysis formed an aglycon with mp 230-231°C that had the same mobility on paper chromatography as an authentic sample of umbelliferone. It was very soluble in ethanol, acetone, and diethylether and insoluble in water. UV spectrum (EtOH, λ_{max}, nm): 255, 324. The IR spectrum of the aglycon was completely identical to that of umbelliferone. Paper chromatography (*n*-BuOH:H_2O:Py, 6:4:3) of the carbohydrate part of the acid hydrolysate detected glucose upon detection by anilinium acid phthalate (100-105°C). Comparing our results with the literature led to the conclusion that **3** was umbelliferone 7-*O*-β-glucoside or skimmin [2].

Compound 4, white thin prismatic crystals, mp 212-215°C (MeOH), soluble in water, methanol, and ethanol. UV light produced bright blue fluorescence. UV spectrum (EtOH, λ_{max}, nm): 285, 310. Acid hydrolysis isolated an aglycon as white needle-like crystals, paper chromatography of which was the same as an authentic sample of scopoletin, mp 197-199°C, melting-point depression did not occur. UV spectrum (EtOH, λ_{max}, nm): 300, 345. The IR spectrum showed absorption bands characteristic of scopoletin. The sugar part of the hydrolysate contained glucose according to PC. Comparing our results with the literature found that **4** was scopoletin 7-*O*-β-glucoside or scopolin [2].

These coumarins were isolated for the first time from *A. asper* growing in the Caucasus foothills on Stavropol plateau.

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