COUMARINS OF THE ROOTS OF Seseli coronatum

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UDC 547.9 : 582.89

From Seseli sessiliflorum Schrenk, which has been studied previously [1-4], sulfur-containing coumarins and chromone have been isolated. It appeared of interest to study the chemical composition of the species, taxonomically close to it, Seseli coronatum Ledeb., which is included in the same section Macrostylopodium Schischk.

The finely comminuted roots of S. Coronatum Ledeb. collected in the environs of the village of Priozerskii (East Kazakhstan oblast, Azisanskaya depression) were extracted successively with petroleum ether and with acetone. From the petroleum ether extract by chromatography on silica gel (L 40/100 μ) in the petroleum ether—ethyl acetate system with an increasing concentration gradient of the latter, we isolated a small amount of a mixture of psoralen and bergapten [δ, ppm: 4.20 s (CH_3O); 61.9 d (H_3); 8.04 d (H_4); 7.00 s (H_8); 6.91, d ($H_{4'}$); 7.50, d ($H_{5'}$)] in a ratio of 16 : 1, from which by rechromatography on silica gel in the same system we isolated psoralen with mp 164-166°C, identified with an authentic sample by means of its IR spectrum. The acetone extract on standing deposited a chromone $C_{19}H_{20}O_6S$ with mp 194-195°C, identical according to its IR spectrum with seselirin [1]. The chromatography of the petroleum ether and acetone extracts also yielded anomalin, $C_{24}H_{26}O_7$, with mp 174-175°C, seseliflorin, $C_{18}H_{18}O_5S$ with mp 143-144°C [3], and a substance $C_{23}H_{24}O_7S$ with mp 122-123°C, and the acetone extract gave, in addition, secorin, $C_{23}H_{20}O_6$ with mp 212-213°C [5].

The seselirin, anomalin, and seseliflorin were identical with the corresponding substances isolated from S. sessiliflorum according to their IR and NMR spectra and mixed melting points.

The compound $C_{23}H_{24}O_7S$, $[\alpha]^{20}_D$ −87.3° (c 0.97; ethanol) was, according to its IR spectrum (Fig. 1) and UV spectrum [λ^{EtOH}_{max}, nm 247, 257, 269, 320 infl (log ε 3.34, 3.43, 4.34, 4.11)], a coumarin derivative with an oxygen function in position 7. It follows from the NMR spectrum of the substance (Varian HA-100D, CCl_4, 0 — HMDS, 20°C) that it is based on a 7,8-disubstituted coumarin nucleus (H_3 — 6.12 ppm; H_1, d, J = 10 Hz; H_4 — 7.51 ppm, 1 H, d, J = 10 Hz; H_5 — 7.19 ppm, 1 H, d, J = 8.5 Hz; H_6 — 6.71 ppm, 1 H, d, J = 8.5 Hz) condensed with a 2',2'-dimethyl-3',4'-dihydropyran ring having two acyloxy groups in positions 3' and 4' [$(CH_3)_2{-}C{-}O$ — 1.39 and 1.41 ppm, s, 3 H each; $H_{3'}$ — 5.34 ppm, d, J = 5.0 Hz; $H_{4'}$ — 6.61 ppm, d, J = 5.0 Hz]. One of the acid residues is angeloyl (1.7-2.0 ppm, 6 H, m; 5.88 ppm, 1 H, m) and the other is a residue of

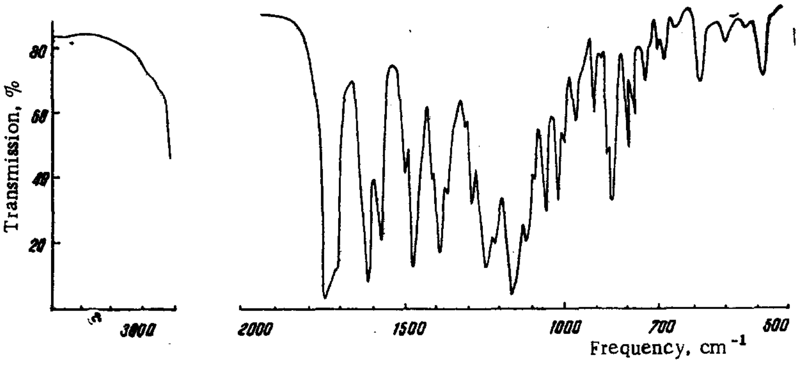
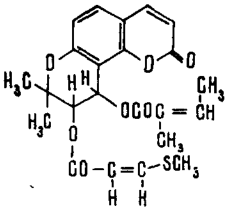


Fig. 1. IR spectrum of isofloroselin (mull in paraffin oil).

All-Union Scientific-Research Institute of Medicinal Plants. Translated from Khimiya Prirodnyk Soedinenii, No. 6, pp. 782-784, November-December, 1974. Original article submitted April 22, 1974.

cis-3-(methylthio)acrylic acid (CH_3-S – 2.34 ppm, s, 3 H; $-\underset{H}{C}=\underset{H}{C}-$ 7.26 and 5.70 ppm, d, 1 H each, J = 8.5 Hz) [4]. Thus, the substance has the structure (I) or a structure with the reversed position of the acyl residues in the 3' and 4' positions of the dihydropyran nucleus. However, the second variant is excluded since the latter corresponds to floroselin [2].



I

The substance differs from floroselin in its physicochemical constants, and in the NMR spectrum of a mixture with floroselin a separation of the signals from H_3', H_4', and from the α and β protons of the cis-3-(methylthio)acrylic acid residue is observed. Thus, the substance, which corresponds to the structure (I) is isomeric with floroselin and we have called it isofloroselin.

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