COUMARINS OF Ferula tuberifera

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We have investigated for the first time the coumarin composition of the roots of Ferula tuberifera Korov., collected in the Kugitang range (Turkmen SSR). In a methanolic extract compounds were found with R_f values 0.63, 0.42, 0.36, and 0.17 (TLC, Silufol, benzene–methanol (95:5)). By chromatography on a column of silica gel followed by crystallization we isolated chromatographically individual crystalline fractions with R_f 0.42 and 0.63 (mp 119 and 157°C, respectively). Yields on the weight of the dry raw material 0.22 and 0.07%.

A consideration of the NMR spectrum showed that each of the fractions consisted of two terpenoid coumarins, in ratios of 7:1 (R_f 0.42) and 4:1 (R_f 0.63). We have succeeded in separating these compounds.

Compound (1) (R_f 0.42), with the composition $C_{24}H_{30}O_4$ (M^+ 382), mp 140°C, $[\alpha]_D^{20}$ −83.72° (c 1.0; ethanol) was isolated by sevenfold fractional crystallization from ethyl acetate–diethyl ether–petroleum ether (1:1:7). On the basis of its UV, IR, and mass spectra and the absence of a depression of the melting point, it was identified as conferol [1] (a sample and the spectra of conferol were kindly given to us by V. V. Vandyshev and M. E. Perel'son).

Compound (2) (R_f 0.42), with the composition $C_{24}H_{30}O_4$ (M^+ 382), mp 186°C, $[\alpha]_D^{20}$ −42.95° (c 0.43; chloroform) was obtained from the mother liquors from (1) by 11-fold fractional crystallization from CCl_4–hexane (7:1).

On the basis of the melting point, the $[\alpha]_D$ values, and the UV, IR, NMR, and mass spectra, this compound was identified as badrakhemin [2, 3].

The composition of the mixtures in the separation of these substances was followed by means of the NMR spectrum (Varian, HA-100D, $CDCl_3$, 0 – HMDS) from the signals at 5.48 ppm (cyclic olefinic proton of conferol) and at 4.46 and 4.83 ppm (protons of the exocyclic methylene group of badrakhemin).

Compounds (3) and (4) (R_f 0.63) consisted of the acetates of compounds (1) and (2), having in their NMR spectra the signals of two acetoxy groups (1.94 and 1.97 ppm) and of a proton geminal to an acetoxy group at 4.57 ppm (triplet, $\Sigma J = 5.7$ Hz).

Acetylation of the crystalline fraction with R_f 0.42 gave us a compound with R_f 0.63.

The UV, IR, NMR, and mass spectra of the acetates synthesized were identical with the acetates of the natural mixture. Fractional crystallization of the natural mixture of acetates with R_f 0.63 from CCl_4–hexane (1:1) yielded compounds (3) and (4). Compound (3) had the composition $C_{26}H_{32}O_5$ (M^+ 424), mp 160°C, $[\alpha]_D^{20}$ −42.39° (c 0.9; chloroform) – conferol acetate [1].

Compound (4) had the composition $C_{26}H_{32}O_5$ (M^+ 424), mp 172.5°C, $[\alpha]_D^{20}$ −22.28° (c 0.16; chloroform) – badrakhemin acetate [2]. Componds (3) and (4) were identified by their melting points, $[\alpha]_D$ values, and UV, IR, NMR, and mass spectra.

Thus, we have isolated four terpenoid coumarins: conferol, badrakhemin, conferol acetate, and badrakhemin acetate. This is the first time that conferol acetate and badrakhemin acetate have been found in plants.

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