TERPENOID COUMARINS FROM *Ferula teterrima*

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Ferula teterrima Kar. et Kor (Umbelliferae) is an endemic monocarpic plant occurring in the Pribalkhash and the Ala-Kul' depression (Eastern Kazakhstan). In E. P. Korovin's system, this species is included in the miscellaneous section Neonartex Korov. However, in a combination of morphological and chemical characteristics, *F. teterrima* is close to the taxons *F. persica* Willd., *F. microloba* Boiss, and *F. mogoltavica* Lipsky et Korov which E. P. Korov combined into the subgenus Merwia.

We have studied chemically the roots of *F. teterrima* collected in the Balkhash – Ala-Kul' depression close to the western end of Lake Sassyk Kul'. From an acetone extract of the roots by chromatography on alumina in the petroleum – ethyl acetate system using gradient elution we isolated four terpenoid coumarins forming derivatives of umbelliferone (I-IV). The PMR spectrum (Varian HA-100D, $CDCl_3$, 20°C, 0 – TMS, δ) of substance (I), $C_{26}H_{32}O_5$, mp 173-174°C (from methanol), $[\alpha]^{20}_{D}-37.8°$ (chloroform), R_f 0.54 [Silufol, petroleum ether – ethyl acetate (1 : 1)], contained, in addition to the signals of a coumarin nucleus, broadened signals at 4.56 and 4.93 ppm, $W_{1/2}=5$ Hz due to a exocyclic methylene group in the 2' position of a decalin ring; the signals of three methyl groups attached to quaternary carbon atoms in positions 5' and 9' (0.94, 0.91, and 0.89) and of the methyl of an acetoxy group (2.09 ppm) at $C_{6'}$; an unresolved signal of a proton geminal to an acetoxy group at 4.72 ppm, $W_{1/2}=7$ Hz; and a multiplet with its center at 4.19 ppm relating to a methylene group in position 1'. On the basis of the features of its PMR spectrum and a comparison of the IR spectra of (I) and an authentic sample, the substance was identified as badrakemin acetate [1, 2].

The PMR spectrum of substance (II), $C_{24}H_{30}O_4$, mp 195-196°C (from methanol), $[\alpha]^{20}_{D}-53.6°$ (chloroform), R_f 0.32, is similar to the spectrum of (I) but it lacks the signal of the acetoxy group and the signal of the proton at $C_{6'}$ is shifted downfield (3.47 ppm, $W_{1/2}=7$ Hz). These facts, and also the absence of a depression of the melting point of a mixed sample and the identity of their IR spectra enables substance (II) to be identified as badrakemin [1-3].

Substance (III), $C_{24}H_{28}O_4$, mp 184-186°C (from methanol), $[\alpha]^{20}_{D}-39.8°$ (chloroform), R_f 0.41 is badrakemon, according to its PMR spectrum [6.24, d, 1H, J = 9.5 Hz (H_3); 7.63, d, 1H, J = 9.5 Hz (H_4); 7.37, d, 1H, J = 9.0 Hz (H_5); 6.83, q, 1H, $J_1=9$ Hz, $J_2=2.5$ Hz (H_6); 6.81, d, 1H, J = 2.5 Hz (H_8); 4.97, s, 1H, and 4.61, s, 1H, $W_{1/2}=5$ Hz ($C_{2'}=CH_2$); 4.23, d, 2H ($C_{1'}-CH_2$); 2.90-1.90, m, and 1.80-1.56, m ($-CH_2-$and $-CH-$groups of a decalin ring); 1.12, s, 3H, and 1.04, s, 3H [$C_{5'}(CH_3)_2$]; and 1.05, s, 3H ($-C_{9'}-CH_3$)]. The oxidation of badrakemin with chromic anhydride and a comparison of the badrakemone obtained in this way [1, 4] with substance (III) showed their complete identity.

Substance (IV), $C_{26}H_{34}O_6$, mp 153-154°C (from methanol), $[\alpha]^{20}_{D}+32.8°$ (ethanol), R_f 0.22 is – according to its PMR spectrum, which contains the signals of a methylene group at C_1, (4.39, q and 4.18, q), of four methyl groups at $C_{2'}$, $C_{5'}$, and $C_{9'}$ (1.25, 0.88, 0.96, and 0.88, all s), of an acetoxy group at $C_{6'}$ (2.07 s), and of a proton geminal to it (4.67, u.s., $W_{1/2}=6$ Hz) – samarcandin acetate [5], as was confirmed by the identity of the spectra of samarcandin acetate and of (IV), and also by the absence of a depression in a mixed melting point test.

In addition to the substances mentioned, conferone was detected in the fractions containing badrakemin by means of the PMR spectrum (signals of an olefinic proton in position 3' of the decalin ring at 5.56 ppm, $W_{1/2}=10$ Hz, methyl group on a double bond in position 2' at 1.68 ppm, u.s., $W_{1/2}=5$ Hz) [6].

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CIRCULAR DICHROISM OF FARNESIFEROL A AND SOME OF ITS ANALOGS

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In the proof of the structure of farnesiferol A and its analogs, the determination of the orientation of the substituents at C_9 proved to be the most complex problem [1-6]. Recently, from the shift of the Cotton effect (CE) in the 300 nm region it has been possible to determine the orientation of substituents at C_9 in such diterpenoids as giberellinic acid, cafestol, and kaurene, but no unambiguous results were obtained for derivatives of eperuic acid and, in particular, farnesiferol A [7]. We have considered the interconnection between the nature of the circular dichroism (CD) curves and the stereochemistry at C_9 in farnesiferol A (I), gummosin (II), mogoltadone (III), colladonin (IV), badrakemin (V), and the ketone of badrakemin (VI). In addition to Cotton effects in the 320 and 230 nm regions connected with transitions in the coumarin nucleus, all the compounds considered have a Ce at 200 nm caused by a $\pi \rightarrow \pi^*$ transition in the exomethylene bond. We directed our attention precisely to this CE, since the asymmetric center of interest to us is adjacent to this chromophoric group. As can be seen from the results obtained (Table 1), the orientation of the substituents affects the amplitude of the CE in the 200 nm region. In the case of axial orientation of the C_9-CH_2-R group (I-III), the intensity of the CE is several times greater than for the equatorial orientation (IV-VI). This increase in intensity can probably be explained by the fact that in the axial orientation the aromatic nucleus and the exomethylene group prove to be close to one another in space and partial overlapping of their π orbitals becomes possible.

The CD spectra were recorded ona JASCO-J-20 spectropolarimeter at a concentration of the solution of 0.5 mg/ml with cell thicknesses of 0.05 and 0.01 cm. The solvent was methanol.

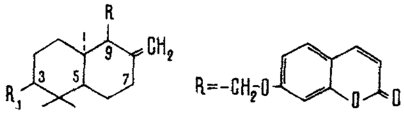

TABLE 1

Substance	R-axial			Substance	R equatorial		
	R_1	λ_{max}, nm	$\Delta\varepsilon$		R_1	λ_{max}, nm	$\Delta\varepsilon$
I	α-OH	203	−16,1	IV	α-OH	204	−2,3
II	β-OH	202	−19,3	V	β-OH	205	−5,6
III	-O	202	−18,4	VI	-O	200	−4,7

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