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TERPENOID COUMARINS OF *Ferula krylovii*

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From an acetone extract of the roots of *Ferula krylovii* Korov., by chromatography by alumina in the petroleum ether—acetate system with increasing concentrations of the latter we have isolated another three terpenoid coumarins, in addition to ferukrin [1]: kamolone [2, 3], M^+ 382, $C_{24}H_{30}O_4$, mp 188-189.5°C, $[\alpha]_D^{18}$ + 42° (c 1.0; chloroform); kamolol [2, 3], $C_{24}H_{32}O_4$, M^+ 384, mp 138-139.5°C, $[\alpha]_D^{16}$ −33° (c 1.0; chloroform); and a noncrystallizing terpenoid coumarin (I), $C_{24}H_{28}O_4$, M^+ 380, $[\alpha]_D^{16}$ +55° (c 1.0; ethanol). According to its UV spectrum [λ_{max}^{EtOH} 215, 242 sh., 252 sh., 326 nm (log ε 4.17, 3.44, 3.20, 4.13); λ_{min} 261 nm (log ε 2.84)]. The substance is a derivative of 7-hydroxycoumarin. In the carbonyl region of the UV spectrum there are the absorption bands of a saturated ketone of an α-pyrone ring (1710 and 1730 cm^{-1}); moreover, coumarin (I) gave a semicarbazone with mp 89-91°C. The NMR spectrum (Varian HA-100D, $CDCl_3$, TMS) contained, in addition to the signals of the umbelliferone part of the molecule, the signals of the following groups: $2CH_3{-}\overset{|}{\underset{|}{C}}{-}$, 1.0 ppm, s, 3 H, , and 1.14 ppm, s, 3 H; $CH_3{-}\overset{|}{C}{=}C$, 1.70 ppm, s, 3 H; $-CH_2OAr$, 4.53 ppm, d, J = 6 Hz, 2 H; $-\overset{|}{C}{=}\underline{C}\underline{H}{-}CH_2{-}OAr$, 5.39 ppm, t, J = 6 Hz, 1 H; $CH_2{=}\overset{|}{C}{-}$, 4.77 ppm, u.s., 1 H; and 4.98 ppm u.s, 1 H. The presence of a $CH_3{-}\overset{|}{C}{=}CH{-}CH_2{-}OAr$ grouping was shown by the double-resonance method.

These results permit us to put forward for this compound the structure of the ketone that should have been obtained by the oxidation of farnesiferol B [4]. However, the authors concerned did not isolate the ketone in the pure state, did not characterize it, and were unable to obtain farnesiferol B from it on reduction with $NaBH_4$. Compound (I) has also been obtained in admixture with an isomeric ketone by the oxidation of a mixture of farnesiferol B with kopetdaghin [5], but it was not isolated in the individual form. The reduction of (I) with $NaBH_4$ in methanol gave farnesiferol B, $C_{24}H_{30}O_5$, M^+ 382, mp 115-117°C with an NMR spectrum having signals corresponding to those given for this compound [5]. A report has recently appeared [7] on the isolation from *F. kopetdagensis* of the coumarin ferelone, which is apparently identical with (I).

The isolation and determination of the structure of ferukrin have been described elsewhere [1]: the main structural elements and stereochemistry of this compound were determined on the basis of NMR spectra. The orientation of the aryloxymethylene groups remain unproved, and the assumption of its equatorial orientation was based on a comparison of the nature of its signals in the PMR spectra of samarcandin, deacetylkellerin, and ferukrin. To confirm the correctness of this hypothesis, ferukrin was oxidized to the ketone (ferukrinone) $C_{24}H_{30}O_5$, mp 214-216°C. Dehydrodeacetylkellerin $C_{24}H_{30}O_5$, mp 214-216°C, obtained previously by the oxidation of deacetylkellerin, the stereochemistry of which has been established [6] should, if this hypothesis were correct, differ from it only by the orientation of the aryloxymethy-

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lene group. A comparison of these substances showed their complete identity (mixed melting point, IR and NMR spectra).

Thus, the aryloxymethylene group has the axial orientation and therefore structure (I) for ferukrin is correct [8].

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STRUCTURE OF THE NEW COUMARIN FESHURIN

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Continuing a study of the coumarins present in various representatives of the genus *Ferula* [1-3], from the roots of *Ferula schtschurowskiana* (Shurovskii's ferula), collected in the Kazakh SSR (Chimkent oblast) in the flowering stage, by chromatographing the neutral fraction of an ethanolic extract on a column of silica gel we have isolated gummosin [4] and a new terpenoid coumarin with the composition $C_{24}H_{32}O_5$ (I), M^+ 400, with mp 212-214°C $[\alpha]_D^{21}$ $-51°$ (c 0.51; pyridine), which we have called feshurin. Its UV spectrum has maxima at λ_{max} 220, 245, 254, 326 nm (log ε 4.10, 3.60, 3.51, 4.16), which are characteristic for umbelliferone drivatives. The IR spectrum of feshurin contains absorption bands at 3615-3580 cm^{-1} (hydroxy groups), 1720 cm^{-1} (α-pyrone carbonyl), and 1610, 1670, 1515 cm^{-1} (aromatic nucleus). The absence of absorption bands of keto and epoxy groups in the IR spectrum of (I) shows that the oxygen atoms present in the terpenoid moiety are included in hydroxy groups. The nature of the latter was determined by acetylation, oxidation, and dehydration reactions.

When (I) was oxidized with acetic anhydride in pyridine, an amorphous monoacetyl derivative with the composition $C_{26}H_{34}O_6$ (II) was obtained the IR spectrum of which contained, in addition to the absorption band of a hydroxy group, the maxima of an ester group at 1250 and 1735 cm^{-1}. The oxidation of feshurin with chromium trioxide in pyridine led to a monoketone with the composition $C_{24}H_{30}O_5$ (II), mp 195-196°C, identical with nevskone [5]. These facts permitted the conclusion that nevskin and feshurin are isomeric compounds.

To confirm the nature of the other hydroxy groups, we dehydrated feshurin with sulfuric acid in ethanol, which gave conferol (IV), with the composition $C_{24}H_{30}O_4$, mp 137-138°C. This was identified through its physicochemical constants and spectral (IR, PMR) characteristics [6].

The PMR spectrum of feshurin (JNM-4H-100/100 MHz, C_5D_5N, 0 — HMDS contains the signals at (ppm) 0.85, 1.13, 1.23, 1.28 (s, 3 H each), 3.51 (br. s, $\Sigma_{1/2}$ = 9 Hz, 1 H) 4.1 (q, $-\overset{|}{\underset{|}{C}}-CH_2-O$; 1 H: J_{gem} = 10.0, J_{vic} = 3.0 Hz), and 4.41 (q, 1 H, J_{gem}=10, J_{vic}=6 Hz). In addi-

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