COUMARINS OF *Ferula malacophyla*

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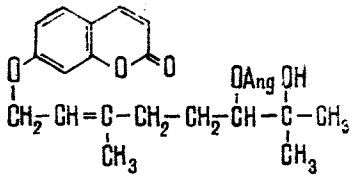
From the neutral fraction of an ethanolic extract of the roots of *Ferula malacophyla* M. Pim. et J. Baran [1] collected in the Alimtau region (Chimkent oblast. KazSSR) in the fruit-bearing phase (July, 1977), by column chromatography on silica gel, we have isolated, in addition to the previously-known auraptene [2] and diversin [3, 4], a new liquid compound (I) with the composition $C_{24}H_{30}O_6$, M^+ 414, n_D^{20} 1.5656, $[\alpha]_D^{20}$ +9° (c 2.88; chloroform), R_f 0.27 (TLC on Silufol: chloroform–ethyl acetate (3:1) system).

The UV spectrum [$\lambda_{max}^{C_2H_5OH}$ 218, 244, 254, 326 nm (log ε 4.37, 3.83, 3.67, 4.12)] shows that the molecule of (I) contains a 7-hydroxycoumarin chromophore, while in the IR spectrum there are absorption bands at 3490 cm^{-1} (OH group), 1740 and 1722 cm^{-1} (C=O of an α-pyrone and of an ester group), and 1615, 1560, and 1515 cm^{-1} (aromatic nucleus).

The PMR spectrum of (I) (JNM-4H-100/100 MHz, $CDCl_3$, 0 — HMDS) contains signals at (ppm) 1.26 (s, 6 H, methyls in a $H_3C-\underset{\underset{OH}{|}}{\overset{\overset{C}{|}}{C}}-CH_3$ grouping), 1.75 (s, 3 H methyl group at a double bond), 1.90-1.98 (6 H, methyl groups in an angeloyl residue), 4.56 (d, 2 H, J = 6 Hz, methylene protons in a $Ar-O-CH_2-CH$ grouping), 5.42 (t, 1 H, J = 6 Hz, olefinic protons in a $Ar-O-\underline{CH_2}-\underline{CH}=C$ fragment), 4.88 (q, 1 H, J_1 = 9 Hz, J_2 = 4 Hz, hemiacyl proton), and 6.03 ppm (oc, 1 H, $J_1 = J_2 = J_3$ = 7 Hz, J_4 = 2 Hz, olefinic protons in an angeloyl residue). At 6.16-7.59 ppm are the signals of the protons of the umbelliferone moiety of the molecule.

The composition and spectra characteristics permitted us to assume that the compound under investigation was an acylated coumarin the terpenoid part of which consisted of an aliphatic monoterpene.

When (I) was saponified with caustic alkali, angelic acid was obtained, with mp 44-45°C, together with the coumarin marmin, $C_{19}H_{24}O_5$, M^+ 332, mp 124-125°C, $[\alpha]_D^{20}$ + 28° (c 1.0; ethanol) [5, 6]. Consequently the coumarin isolated is marmin monoangelate. The position of the angeloyl residue was deduced from the following facts. The signal in the PMR spectrum at 4.88 ppm (q, 1 H, J_1 = 9 Hz, J_2 = 4 Hz) due to the hemiacyl proton, undergoes a diamagnetic shift and appears at 3.30 ppm in the de-angelate. These facts permit the conclusion that the coumarin studied is an ester of angelic acid and marmin at the secondary hydroxy group and has the structure (I).



I

It must be mentioned that sesquiterpene lactones have been isolated previously from the roots of *Ferula malacophyla* collected in the environs of Lake Ashikul (Karatau range) [7]. Such a considerable qualitative change in chemical composition is apparently due to differences in the vegetation period and growth site of the plant.

LITERATURE CITED

1. M. G. Pimenov and Yu. V. Baranova, Byull. Gl. Bot. Sada, No. 106, 43 (1977).

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 226-227, March-April, 1979. Original article submitted November 29, 1978.

 0009-3130/79/1502-0194$07.50

2. V. N. Borisov, A. I. Ban'kovskii, V. I. Sheichenko, and V. S. Kabanov, Khim. Prir. Soedin., 659 (1974).
3. N. P. Kir'yalov, Khim. Prir. Soedin., 51 (1969).
4. V. Kiseleva, G. K. Nikonov, and M. O. Karryev, Khim. Prir. Soedin., 344 (1975).
5. J. Fischer, H. E. Nordby, A. C. Waiss, and W. L. Stanley, Tetrahedron, 23, 2523 (1967).
6. A. Chatterjee, C. P. Dutta, S. Bhattacharrya, H. Audier, and B. C. Das, Tetrahedron Lett., No. 5, 471 (1967).
7. V. Yu. Bagirov, V. I. Sheichenko, R. Yu. Gasanova, and M. Pimenov, Khim Prir. Soedin., 445 (1978).

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: $2CH_3-\overset{|}{C}-$, 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; $-\overset{|}{C}=CH-CH_2-OAr$, 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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