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NEW TERPENOID COUMARINS OF *Ferula kopetdaghensis*

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By the chromatographic separation on a column of silica gel of a methanolic extract of the roots of *Ferula kopetdaghensis* Eug. Kor. we have isolated two new coumarins: $C_{26}H_{32}O_5$, M^+ 424. n_D^{20} 1.5607. $[\alpha]_D^{18}$ + 29.8° (c 0.67; $CHCl_3$), R_f 0.85 (I) (0.0083% of the weight of the dry plant) and $C_{24}H_{28}O_4$, M^+ 380, n_D^{20} 1.5837, $[\alpha]_D^{20}$ + 47° (c 0.84; $CHCl_3$), R_f 0.73 (II) (0.0061%) in the chloroform–ethyl acetate (3:1) system on Silufol, which we have called, respectively, fekolin and fekolone. Both compounds are umbelliferone derivatives (characteristic UV spectra). The IR spectrum of (I) shows absorption bands at 1738 cm^{-1} (C=O of an α-pyrone), 1730 cm^{-1} (C=O of an ester group), and 1617 and 1560 cm^{-1} (aromatic ring).

The PMR spectrum of fekolin (JNM-4H-100/100 MHz, $CDCl_3$, 0 — HMDS), δ, ppm: 0.84, s (2 $C\underline{H}_3{-}C{-}$); 1.67 and 1.73, singlets ($2C\underline{H}_3{-}C{=}CH$); 1.99, s ($CH_3{-}COO^-$); 4.56, d, J = 6.0 Hz ($Ar{-}O{-}C\underline{H}_2{-}CH$); 4.61, m, ΣJ = 15 Hz ($\underline{H}{-}C{-}OAc$); 5.19, m, $W_{1/2}$ = 10 Hz and 5.41, t, J = 6.0 Hz ($2\underline{H}{-}C{=}C{-}CH_3$); 6.18, d, J = 9.5 Hz ($C_3{-}H$); 6.79, m ($C_6{-}H$, $C_8{-}H$); 7.35, d, J = 9.0 Hz ($C_5{-}H$); 7.6 d, J = 9.5 Hz ($C_4{-}H$).

The results obtained enabled us to assign fekolin to the acylated terpenoid coumarins. In fact, the alkaline hydrolysis of (I) gave a substance $C_{24}H_{30}O_4$, M^+ 382, mp 124-125°C, $[\alpha]_D^{20}$ +31° (c 1.0; $CHCl_3$) which was identified as kopetdaghin [1]. Consequently, fekolin is the natural acetate of kopetdaghin.

In the IR spectrum of fekolone (II), in addition to other absorption bands there is a band at 1710 cm^{-1} (ketone C=O). The presence of a carbonyl group was established by the pre aration of a 2,4-dinitrophenylhydrazine with mp 89-90°C.

From the composition of fekolone and its spectral characteristics, it may be assumed th the terpenoid part of (II) has a monocyclic nature. This was confirmed by the preparation of 1,2,3,4-tetramethylbenzene on the dehydrogenation of fekolone with selenium.

The PMR spectrum of fekolone resembled the spectrum of farnesiferol B [2] but differed by the absence of the signal of the hemihydroxylic proton and by a shift of the signals of the methyl groups, on the basis of which it may be considered that (II) is the ketone of farnesiferol B. This was confirmed by the preparation of farnesiferol B by the reduction of fekolone with sodium tetrahydroborate. Furthermore, a mixture of the 2,4-dinitrophenylhydrazone of (II) and of the ketone of farnesiferol B gave no depression of the melting point.

Thus, fekolone is the natural ketone corresponding to farnesiferol B.

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