A COUMARIN FROM THE ROOTS OF Ferula nevskii

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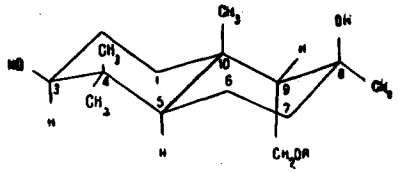
After the isolation of samarcandin [1, 2] from the neutral fraction of the resin from the roots of Ferula nevskii Korov., elution of the column was continued with chloroform. This gave a coumarin with the composition $C_{24}H_{32}O_5$, mp 193-194°C (chloroform), $[\alpha]_D^{26}-79°$ (pyridine), which we have called nevskin. Yield 1%. Its IR spectrum (mull in paraffin oil) has absorption bands at (cm^{-1}) 3424 (OH), 1703 (α-pyrone CO), 1615, 1560, and 1513 (C=C of an aromatic system). From a comparison of the mass spectra of samarcandin and nevskin taken under the same conditions (MKh-1306 spectrometer, introduction into the ion source, E 50 eV, 180°C) it can be seen that they differ only in the relative intensities of a number of peaks. Such a difference in mass spectra is characteristic for stereoisomers [3]. Thus, while in the mass spectrum of samarcandin the relative intensities of the ions with m/e 400 (M+), 382 ($M-H_2O$)+, 221 ($M-H_2O-RO$)+, 220 ($M-H_2O-ROH$)+ and 203 ($M-H_2O-RO-H_2O$)+ (R here and below represents an umbelliferone residue) are 5, 3, 30, 36, and 49%, respectively, the intensities of the same peaks in nevskin are 16, 1, 6, 4, and 18%. The signals of the geminal protons at the acetate groups in the NMR spectra (JMN-4H-100/100 MHz instrument in $CDCl_3$) of the monoacetates of samarcandin (δ 4.67 ppm) and of nevskin (δ 4.53 ppm) – its acetate was amorphous but chromatographically pure – appear, respectively, in the form of a singlet (half-width of the line ~5 Hz) and a triplet ($\Sigma J_{H-3} \approx 17$ Hz). These facts show that in samarcandin and nevskin monoacetates the acetate groups have the axial and equatorial orientations, respectively [4]. The identity of the chemical shifts of the protons of the methyl group at C_8 (δ 1.26 ± 0.01 ppm) in the acetates of samarcandin and nevskin is due to the fact that the methyl group in each of these compounds probably occupies the equatorial position. In view of this, a similar influence on the chemical shift of the protons of the methyl group at C_8 of axial and equatorial substituents at C_9 may be expected. Substantial differences in the positions of the signals of the protons of the angular methyl group are observed on passing from samarcandin acetate (δ 0.98 ppm) to nevskin acetate (δ 1.13 ppm). The upfield shift of the signals of the protons of the angular methyl group in samarcandin is apparently due to the screening action of the substituent at C_9. Consequently, the substituent at C_9 in samarcandin, as in badrakemin [5, 6] occupies the equatorial position, and in nevskin the axial position; i.e., the substituent at C_9 and the angular methyl group are in the cis position in samarcandin and in the trans position in nevskin. Nevskin is represented by structure (I)



I

The IR spectra were taken on a UR-10 spectrophotometer, the NMR spectra on a JNM-4H-100 MHz spectrometer (TMS, 0 ppm, δ), the mass spectra on an MKh-1306 instrument, and the specific rotations on a Cary-60 recording spectropolarimeter.

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