THE STRUCTURE OF MOGOLTAVIN, A COUMARIN FROM THE ROOTS OF Peucedanum mogoltavicum

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We have previously reported the structure of mogoltin [1] – one of the three new coumarins isolated from the roots of the epidemic species Peucedanum mogoltavicum Korov. The present paper gives the results of a study of the second component – mogoltavin – and the determination of its structure. Mogoltavin, $C_{26}H_{32}O_6$ (corrected on the basis of the mass spectrum) is an optically active coumarin with mp 196-197°C, $[\alpha]^{30}_{D}$ $-108°$ (c 2.65; chloroform; l 2.0), R_f 0.56. As we have shown [2], it is an ether of umbelliferone and a sesquiterpene alcohol with the composition $C_{17}H_{28}O_4$. The lactone contains a free hydroxy group, which is confirmed by IR absorption bands at 3440 cm^{-1} (inflection) and 3525 cm^{-1} (Fig. 1) and by the formation of an acetate with mp 195°C (from methanol). These facts enable us to give its developed formula in the form $C_{17}H_{26}O_2(OH)-O-C_9H_5O_2$.

The NMR spectrum of mogoltavin, with respect to the chemical shifts of the signals and their intensities and spreadings, is similar to that of the coumarin mogoltin [2]. The only difference is the presence in it of a singlet at 2.08 ppm (3 H) corresponding to the methyl of an acetyl group, and the absence of the signal of the proton of one of the hydroxyls at 5.47 ppm. This unambiguously shows that mogoltavin is a monoacetate of mogoltin. This is also confirmed by the mass spectrum of mogoltavin, in which, in addition to the peak of the molecular ion M^+ 440, there is a peak with m/e 397 corresponding to the fragment remaining after the ejection of a CH_3CO group; the remaining parts of the spectra of the substances compared are identical. The saponification of mogoltavin with caustic alkali gave mogoltin, identified by a mixed melting point and by its IR spectrum; mogoltin diacetate and mogoltavin acetate are also identical. The position of the acetyl group in the mogoltin molecule was deduced on the basis of a comparison of the NMR spectra of the coumarins under investigation and, in particular, the paramagnetic shift on the signal of one of the methine protons (doublet at 4.52 ppm) connected with the electron-accepting influence of the acetyl group. As shown in our preceding paper, this doublet corresponds to the proton in position 6. Consequently, mogoltavin has been assigned the structure shown in Fig. 1.

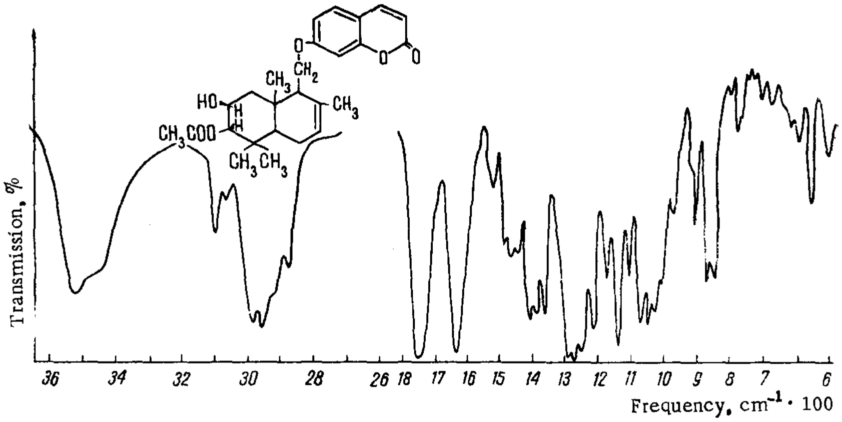

Fig. 1. IR spectrum of mogoltavin (KBr).

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EXPERIMENTAL

The NMR spectrum was taken on a JNM-4-H-100/100 spectrometer at 100 MHz ($CDCl_3$), and the chemical shifts are given in the δ scale from the signal of HMDS taken as 0; the IR spectrum was taken on a UR-20 spectrometer (KBr) and the mass spectrum on an MKh-1303 instrument. The purity of the substances was checked by paper chromatography in the n-hexane–benzene–methanol (5 : 4 : 1) system, the spots being revealed with diazotized sulfanilamide.

Hydrolysis of Mogoltavin. A solution of 0.14 g of the substance in 5 ml of methanol was treated with 1 ml of 10% caustic soda solution and heated in the water bath for 20 min. The liquid was diluted with 20 ml of water, the methanol was distilled off, and the residue was washed with ether (2 × 25 ml). The alkaline solution was acidified and treated with ether (2 × 25 ml). The extract was washed with 10% sodium carbonate solution and dried, and the solvent was distilled off. The residue consisted of mogoltin, with mp 183-184°C (from methanol).

Mogoltin diacetate was obtained by heating a solution of the substance in pyridine with acetic anhydride for 6 h. Colorless acicular crystals deposited with mp 195-196°C (from methanol).

SUMMARY

On the basis of NMR and mass spectra, hydrolysis products, and acetylation, it has been established that the coumarin mogoltavin is the ether of umbelliferone and 6-acetoxy-7-hydroxy-2,5,5,8a-tetramethyl-Δ^2-octahydro-1-naphthylmethanol (the natural 6-O-acetate of mogoltin).

LITERATURE CITED

1. G. K. Nikonov, Khim. Prirodn. Soedin., 7, 572 (1971).
2. G. K. Nikonov and V. B. Kuvaev, Zh. Obshch. Khim., 34, No. 3, 1020 (1964).