THE STRUCTURE OF MOGOLTAVININ – A COUMARIN FROM THE ROOTS OF Peucedanum mogoltavicum

G. K. Nikonov UDC 547.587.51: 547.913: 668.5

As reported previously [1] we have isolated three coumarins from the roots of Peucedanum mogoltavicum Korov. and we have proposed structures for two of them [2, 3]. The present paper gives the results of the determination of the structure of the third component – mogoltavinin.

Mogoltavinin is an individual coumarin with the composition $C_{29}H_{36}O_6$, mp 180-182°C (from methanol), $[\alpha]_D^{33}$ −119.2° (c 1.30; chloroform). Under the action of a mixture of acetic and sulfuric acids, it is cleaved into umbelliferone and a terpenoid alcohol and is consequently an ether of these two components. The mass spectrum of the coumarin shows the peak of the molecular ion with M^+ 480. Intense peaks with m/e 162 and 163 are due, as has been shown by P. I. Zakharov et al. for the case of kamolone and kamolol [4], to the molecular and protonated ions of umbelliferone, and the fragment with m/e 318 to the terpenoid part of the mogoltavinin molecule. In addition, an intense peak is observed with m/e 381 corresponding to the fragments formed in the detachment from the molecule of an acid residue with m/e 99 $[M^+-CH_3-CH(CH_3)COO]$. Peaks of moderate intensity with m/e 175 and 176 are apparently due to α-cleavage in relation to the oxygen atom of the ester bond with and without the transfer of hydrogen from the terpenoid part of the molecule to the coumarin moiety. These results show that mogoltavinin is an ether of umbelliferone and a terpenoid alcohol with the composition $C_{20}H_{32}O_4$ which includes an acid residue of five carbon atoms.

The IR spectrum of mogoltavinin (Fig. 1) shows a broad absorption band at 1710-1730 cm^{-1} (α-pyrone carbonyl) and bands at (cm^{-1}) 1620, 1560, 1465 (aromatic nucleus), 1365, 1390 (gem-dimethyl group), 2850-2860 (C-methyl group), and 3530-3580 (secondary hydroxyl). The presence of one hydroxy group was shown by the direct determination of mobile hydrogen and the preparation of an acetate $C_{31}H_{38}O_7$ with mp 158-159°C (methanol).

The NMR spectrum of the coumarin (Fig. 2) is extremely close to that of mogoltavin. It has the signals of the protons of the umbelliferone residue – doublets at 7.60 and 6.18 ppm, J = 10 Hz, and at 7.28 and 6.75 ppm, J = 80 Hz, and also a singlet at 6.74 ppm corresponding to the H-4, H-3, H-5, H-6, and H-8 protons. In addition to this, signals are found of protons which correspond by their chemical shifts and spin–spin coupling constants to the structural elements of the terpenoid moiety of mogoltavin and mogoltin: six-proton and three-proton singlets at 0.95 and 0.87 ppm (methyl groups on quaternary carbon atoms), a broadened singlet

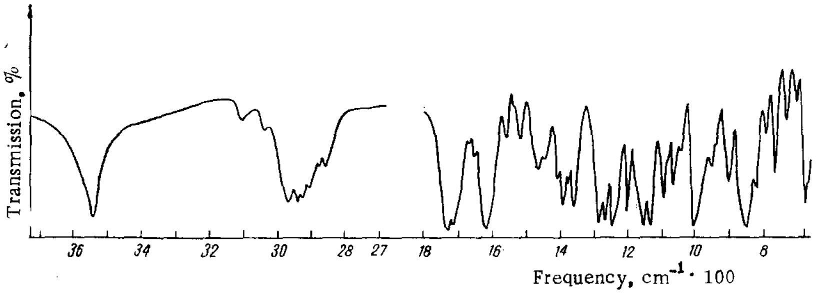

Fig. 1. IR spectrum of mogoltavinin (KBr).

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 54-57, January-February, 1972. Original article submitted October 18, 1971.

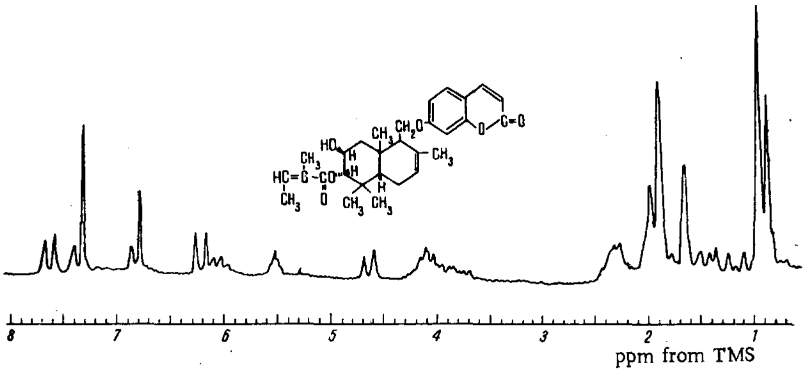

Fig. 2. NMR spectrum of mogoltavinin ($CDCl_3$).

at 1.65 ppm (methyl group on a double bond), a multiplet at 5.52 ppm (olefinic proton), and a multiplet at 3.8-4.3 ppm (3 H; protons of Ar$-$OCH$_2$ and H$-$C$-$OH groupings). The spectrum of mogoltavinin differs only by the fact that it contains, in place of the signal of the methyl of an acetyl group (singlet at 2.09 in mogoltavin), two three-proton singlets at 1.90 and 1.99 ppm due to the presence of the methyl groups of angelic acid in the α and β positions and a multiplet with a center at 6.06 ppm corresponding to its olefinic proton. What has been said above permits the assumption that mogoltavinin is based on mogoltin acylated at one of the hydroxyls by angelic acid. The broad carbonyl band in the IR spectrum of the lactone, and also a fragment with m/e 381 in the mass spectrum support this hypothesis.

To prove its structure, mogoltavinin was saponified with caustic alkali. This gave a hydroxylactone with mp 179-181°C showing no depression of the melting point in admixture with mogoltin. Their IR spectra were also identical. In addition to mogoltin, saponification gave an acid identified by its IR spectrum as angelic acid.

The position of the angeloyl residue follows from a consideration of the signals of the methine protons on the second and third carbon atoms of the terpenoid moiety. In comparison with mogoltin, a paramagnetic shift is observed here for the signal of the C-6 proton of the decalin nucleus (doublet at 4.62 ppm, $J = 11$ Hz, in mogoltavinin and at 3.27 ppm in mogoltin). Thus, the angelic acid residue is located in the equatorial position at C-6. Consequently, mogoltavinin is the ether of umbelliferone and of 6-angeloyloxy-7-hydroxy,2,5,5,8a-tetramethyl-Δ^2-octahydro-1-naphthylmethanol.

EXPERIMENTAL

The NMR spectrum was taken on a JNM-4H-100/100 MHz spectrometer ($CDCl_3$, chemical shifts given in the δ scale from the signal of HMDS, taken as 0); the IR spectrum was recorded on a UR-20 spectrometer (KBr); and the mass spectrum on a MKh-1303 instrument.

Hydrolysis of Mogoltavinin. A. Isolation of Mogoltin. To 0.14 g of the substance in 3 ml of methanol was added 1 ml of a 10% solution of KOH, and the mixture was heated in the water bath for 20 min. Then the liquid was diluted with water, and the unchanged part of the starting material was extracted with ether. The alkaline solution was acidified and treated with ether (2 × 20 ml), and the ethereal extract was washed with 5% sodium carbonate solution and dried, and the solvent was distilled off. The residue consisted of mogoltin with mp 179-181°C (from methanol).

B. Isolation of Angelic Acid. To 1.00 g of mogoltavinin in 10 ml of ethanol was added 10 ml of a 10% solution of KOH in the same solvent, and the mixture was heated in the water bath for 30 min. The liquid was diluted with 20 ml of water, the ethanol was distilled off, and the residue was treated with ether (2 × 30 ml). The ethereal extracts were combined and were shaken with 5% sodium carbonate solution. The alkaline solution was acidified with 20% sulfuric acid and 20 ml was distilled off with heating on a sand bath. The distillate was treated with ether, the extract was distilled, and the residue was sublimed in vacuum with heating on the water bath. This gave colorless crystals gradually deliquescing in the air, readily soluble in water, and having a characteristic odor. The IR spectra of the substance isolated and of angelic acid were identical.

SUMMARY

On the basis of its NMR, IR, and mass spectra and the products of alkaline hydrolysis it has been established that the coumarin mogoltavinin is the ether of 7-hydroxycoumarin and 6-angeloyloxy-7-hydroxy-2,5,5,8a-tetramethyl-Δ^2-octahydro-1-naphthylmethanol.

LITERATURE CITED

1. G. K. Nikonov and V. B. Kuvaev, Zh. Obshch. Khim., 34, No. 3, 1020 (1964).
2. G. K. Nikonov, Khim. Prirodn. Soedin., 7, 572 (1971).
3. G. K. Nikonov, Khim. Prirodn. Soedin., 8, 54 (1972) [in this issue].
4. P. I. Zakharov, V. S. Kabanov, M. E. Perel'son, A. I. Ban'kovskii, and N. E. Ermatov, Khim. Prirodn. Soedin., 6, 296 (1970).