STRUCTURE AND CONFIGURATION OF THE COUMARINS MOGOLTADONE AND MOGOLTADIN

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From the roots of Ferula mogoltavica Eug. Kor. collected in the Mogoltau mountains, Leninabad oblast, we have isolated two new terpenoid coumarins, which have been called mogoltadone and mogoltadin.

Mogoltadone (I) has the composition $C_{24}H_{28}O_4$, M^+ 380, mp 131-132°C, $[\alpha]_D^{21}$ −41.7° (c 1.1; chloroform). The IR spectrum of the substance shows maxima at 219, 243, 253, and 325 nm (log ε 4.27, 3.60, 3.38, 4.32) which are characteristic for a 7-hydroxycoumarin, and the IR spectrum (Fig. 1) has absorption bands at (cm^{-1}) 1735 (carbonyl of a pyrone ring), 1690 (carbonyl in a six-membered ring), 1620, and 1520 and an inflection at 1580 (aromatic nucleus).

The presence of a carbonyl group is confirmed by the preparation of a 2,4-dinitrophenylhydrazone (2,4-DNPH) with mp 137-139°C. The mass spectrum of (I) has peaks with m/e 380 $(M)^+$, 219 $(M-ArO)^+$, 218 $(M-ArOH)^+$, 201 $(M-ArO-H_2O)^+$, and 162 $(ArOH)^+$, characteristic of the terpenoid coumarins of the iresane group [1] and showing that mogoltadone is an ether of 7-hydroxycoumarin and a sesquiterpene hydroxy ketone with the composition $C_{15}H_{24}O_2$. With this composition, one double bond (exocyclic methylene, as shown by the NMR spectrum), and a carbonyl group, this terpenoid residue must have a bicyclic structure.

The nature of the NMR spectrum and also biogenetic considerations permit the conclusion that it (and, equally, mogoltadin) belongs to the terpenoid coumarins of the iresane series.

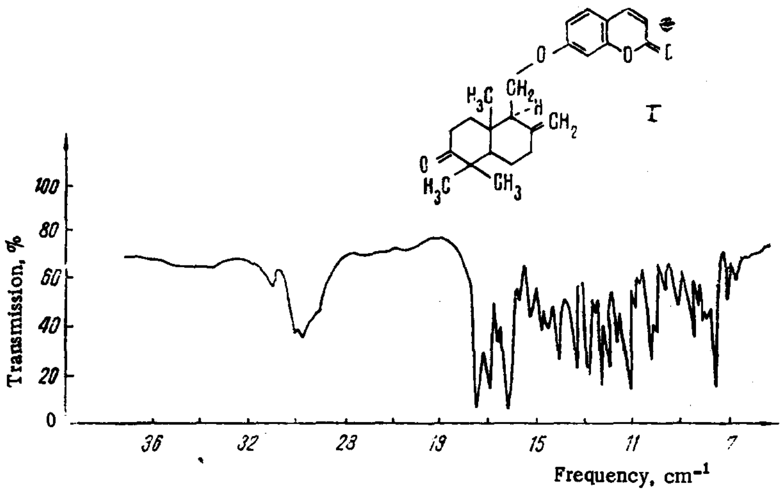

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Fig. 1. IR spectrum of mogoltadone.

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We have obtained substances of this structure by the reduction of the ketone gummosin with sodium tetrahydroborate. A mixture of these substances showed no depression of the melting point.

EXPERIMENTAL

The UV spectra were taken on a Hitachi spectrophotometer, the IR spectra (KBr) on a UR-10 spectrometer, the mass spectra on an MKh-1303 spectrometer at an ionizing voltage of 40 V, and the NMR spectra on a JNM-4H-100/100 MHz instrument.

Isolation of Mogoltadone. The comminuted roots of Ferula mogoltavica (1 kg) were extracted three times with methanol. The methanolic extract was concentrated, diluted with water (1 : 2), and treated with ether. Elimination of the solvent gave 62 g of a light-brown viscous mass.

This fraction (30 g) was separated on a column of type KSK silica gel (d = 5, h = 50 cm). Elution was performed with petroleum ether–ethyl acetate (3 : 1), 50-ml fractions being collected. Fractions 22-28 yielded, when the eluent was driven off, a substance with mp 131-132°C (from ether), R_f 0.27, in the form of colorless crystals readily soluble in chloroform and sparingly soluble in ethanol and ether. The 2,4-DNPH of mogoltadone was obtained in the usual way, and formed orange-red crystals with mp 137-139°C.

Isolation of Mogoltadin. Fractions 57-64 yielded mogoltadin with mp 158-159°C (from ether), R_f 0.17, readily soluble in chloroform, sparingly soluble in ethanol and ether. Mogoltadin acetate was obtained by heating the substance with acetic anhydride in the presence of pyridine at 80°C for 2 h, and formed colorless crystals with mp 149-150°C (from ether).

CONCLUSIONS

Two new terpenoid coumarins – mogoltadone and mogoltadin – have been isolated from the roots of Ferula mogoltavica. Mogoltadone has the composition $C_{24}H_{28}O_4$, $[\alpha]_D^{21}$ −41.7° (c 1.1; chloroform). On the basis of spectral characteristics, it has been shown that it is the ether of umbelliferone and 3-oxo-4,4,10-trimethyl-8-vinyldecalin-9-ylmethanol with the trans linkage of rings A and B and the equatorial orientation of the substituent at C_9. Mogoltadin has the composition $C_{24}H_{30}O_4$, $[\alpha]_D^{21}$ −55° (c 1.0; ethanol) and is the ether of umbelliferone and 3-hydroxy-4,4,10-trimethyl-8-vinyldecalin-9-ylmethanol with the trans linkage of rings A and B and the diequatorial arrangement of the substituents at C_3 and C_9.

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