STRUCTURE OF MOGOLTONE, A NEW ELEMANONE FROM Ferula mogoltavica AND F. samarcandica

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From a methanolic extract of the roots of Ferula mogoltavica Lipsky and F. samarcandica Eug. Kor., collected in the Chashma region (Leninabad oblast) and the gorge of the R. Angren (Tashkent oblast), respectively, we have isolated a new substance with the composition $C_{15}H_{24}O_2$, mp 95-96°C, $[\alpha]_D^{23}+166°$ (c 1.1; chloroform) which we have called mogoltone.

The substance is neutral in nature and is readily soluble in ether, chloroform, carbon tetrachloride, and ethanol, sparingly soluble in petroleum ether, and insoluble in water.

The UV spectrum of mogoltone has a maximum at 310 nm (log ε 3.15), which is characteristic for a carbonyl group in a six-membered ring, and the IR spectrum (Fig. 1) shows absorption bands at (cm^{-1}) 3400-3500 (hydroxy group), 3085, 1645 (exocyclic methylene group), and 1710 (ketone carbonyl). In the ORD curve there is a maximum at 315 nm with a positive Cotton effect which is characteristic for a carbonyl group in a six-membered ring [1].

The mass spectrum of the substance shows peaks of ions with m/e 236 $(M)^+$, 221 $(M-CH_3)^+$, 218 $(M-H_2O)^+$, 208 $(M-CO)^+$. In the NMR spectrum of mogoltone (Fig. 2), δ scale, solution of the substance in CCl_4) there are the signals of methyl groups: doublet at 0.84 ppm, J = 6 Hz (6H, $-CH{<}^{CH_3}_{CH_3}$); singlets at 0.97 (3H, , $\rangle\!\!-CH_3$) and 1.68 ppm (3H, $=\underset{|}{C}-CH_3$). In addition, in the 255 ppm region there is a broadened singlet (1H), due to a hydroxy group, and a singlet at 3.58 ppm (1H) relating to the methine proton in a $\underset{|}{C}=\underset{|}{C}-\underset{|}{CH}-\underset{|}{C}=O$ grouping. In the 4.58 and 4.9 ppm regions there are one-proton singlets of the protons of a vinyl group, and in the 4.56-5.94 ppm range there is a multiplet with a total intensity of three proton units due to the $-CH=CH_2$ grouping. This assignment was confirmed by a calculation of the relative intensities and the spin-spin splitting constants of the signals of the grouping mentioned, which belong to an AB_2 three-spin system [1]. A six-proton doublet at 0.84 ppm (J = 6 Hz) corresponds to two secondary geminal methyl groups, a singlet at 0.97 ppm to an angular methyl group, and a singlet at 1.68 ppm to a methyl group on a double bond.

The composition is $C_{15}H_{24}O_2$, and the presence of two exocyclic methylene groups and of four methyl groups permits the assumption that mogoltone has the elemane skeleton, which agrees well with its spectral characteristics.

According to the UV and IR spectra and the ORD curve, the keto group is present in a six-membered ring. As mentioned above, in the NMR spectrum of mogoltone there is a one-proton singlet at 3.85 ppm the paramagnetic shift of which is due partly to the electron-accepting influence of the carbonyl group. The nature of this signal shows that the proton concerned is located between two quaternary carbon atoms, i.e., in the C_5 position, and the carbonyl group is located at C_6, of the elemane skeleton.

The reduction of mogoltone with sodium borohydride gave us a diol, mogoltol, $C_{15}H_{26}O_2$ with mp 61-63°C. In the NMR spectrum of this compound, the signal of the proton under discussion had shifted upfield by 90 Hz and appeared in the form of a doublet at 2.1 ppm (J = 2 Hz) because of interaction with a methine

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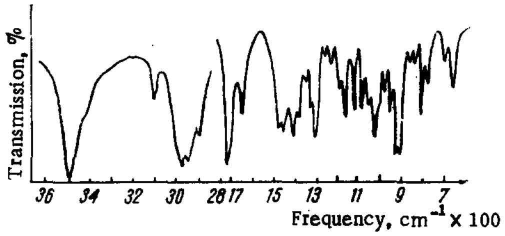

Fig. 1. IR spectrum (KBr) of mogoltone.

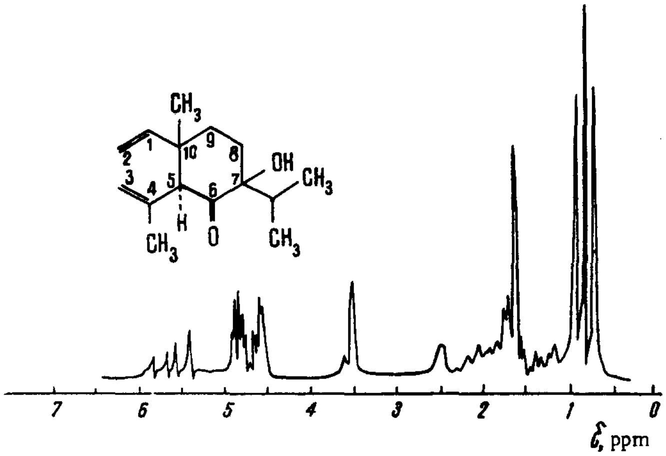

Fig. 2. NMR spectrum of mogoltone.

proton present in the geminal position to a hydroxy group. The methine proton at C_6 in the NMR spectrum of mogoltol appeared at 3.15 ppm (J = 2 Hz).

The hydroxy group in the mogoltone molecule is tertiary: it was not acetylated on treatment with acetic anhydride in pyridine, but in the presence of sodium acetate it gave an acetate with M^+ 278, R_f 0.7. Thus, this group can only be located at C_7 of the elemane nucleus. This position is confirmed by the results of the oxidation of mogoltone by periodic acid (with a consumption of one mole of the acid).

It is known that when a hydroxy group is vicinal to a carbonyl group in a six-membered ring the maximum in the UV spectrum and in the ORD curve changes according to the orientation of the hydroxyl. Thus, if the latter is present in the axial position, the maximum undergoes a bathochromic shift by 12-23 nm, and if it is in the equatorial position there is a hypsochromic shift by 9-13 nm. In the UV spectrum (310 nm) and in the ORD curve (315 nm) of mogoltone the maximum appears in the longer-wave region (bathochromic shift) as compared with the maximum of six-membered cyclic ketones having no hydroxy group adjacent to the carbonyl (290 nm) [2]. This shows that the hydroxy group at C_7 has the axial orientation. The spin–spin splitting constant of the proton at C_5 (J = 2 Hz) in the NMR spectrum of mogoltone corresponds to its equatorial orientation. All that has been said permits mogoltone to be assigned the most probable structure and orientation shown in Fig. 2.

EXPERIMENTAL

The UV spectra were taken on a Hitachi spectrophotometer, the IR spectra (in KBr) on a UR-10 spectrophotometer, the mass spectra on an MKh-1303 mass spectrometer at an ionizing voltage of 40 eV, and the NMR spectra on a JEOL 60 HL instrument. Chromatography was performed in a thin fixed layer of KSK silica gel, and the spots were revealed with sulfuric acid containing 1% of vanillin. The results of elementary analysis corresponded to the calculated figures.

Isolation of Mogoltone. A methanolic extract (20 g) of the roots of Ferula mogoltavica was separated on a column 30 cm high and 6 cm in diameter filled with type KSK silica gel (particle size 0.25 mm). On elution with a mixture of ethyl acetate and petroleum ether (1 : 3), fractions 8-13 yielded a crystalline substance with mp 95-96°C (from ether), R_f 0.24. By the same method, a substance with mp 95-96°C was obtained from Ferula samarcandica and was identical according to its IR spectrum and specific rotation, and a mixed melting point, with mogoltone.

Mogoltol. A solution of 0.1 g of mogoltone in 30 ml of 80% methanol was treated with 0.4 g of sodium tetrahydroborate, and the mixture was left for 6 h. After it had been diluted with water (1 : 2), the mogoltol was extracted with ether. Colorless crystals with mp 61-63°C (from ether).

SUMMARY

From the roots of *Ferula mogoltavica* Lipsky and *F. samarcandica* Eug. Kor. has been isolated a new elemanone $C_{15}H_{24}O_2$ with mp 95-96°C, $[\alpha]_D^{23}$ +166°, which has been called mogoltone. On the basis of the UV, IR, and NMR spectra, its ORD curve, and its reduction products, the most probable structure and configuration of mogoltone are considered to be 7-hydroxy-7-isopropylelemam-6-one with the C_7-OH in the axial position and the C_5-H in the equatorial position.

LITERATURE CITED

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2. C. Djerassi, Optical Rotatory Dispersion, McGraw-Hill, New York (1960).