COUMARIN COMPOSITION OF THE ROOTS, STEMS, AND FRUIT OF Prangos lophoptera

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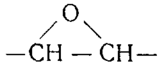
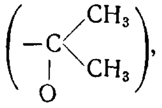
In studying the chemical composition of the roots, stems, and fruit of Prangos lophoptera Boiss, collected in May, 1972, in the environs of the village of Arafsa (Dzhul'fa region, Nakhichevan ASSR), we found in it a number of compounds (I-XIV) of coumarin nature.

The identification of compounds (I-XII) with ostole, suberosin, suberenol, imperatorin, isoimperatorin, oxypeucedanin hydrate, (−)-heraclenin, (+)-heraclenol, gosferol, pranchimgin, and umbelliferone, respectively, was made on the basis of their physicochemical properties, their R_f values, and their IR and NMR spectra.

Substance (XIII) with the composition $C_{16}H_{14}O_5$, mp 72-73.5°C, and (XIV) with the composition $C_{15}H_{16}O_5$, mp 183-184°C, M^+ 276 (mass spectroscopically) proved to be new; we have called them isogosferol and lophopterol, respectively. On the basis of its chemical and spectral characteristics, (XIII) was assigned to the 8-monosubstituted furocoumarins, and (XIV) to the 6,7-disubstituted coumarins. The present paper gives the results of a study of the structure of (XIV). Substance (XIV) contains one methoxy group and a fragment consisting of $C_5H_9O_2$ and containing one hydroxy group. The presence of the latter is confirmed by the formation of a monoacetyl derivative (XV), $C_{17}H_{18}O_6$, with mp 127-129°C the IR spectrum of which lacks the absorption band of a hydroxy group.

In the NMR spectrum of (XIV) (Figure 1a), in the region of aromatic protons there are two doublets with chemical shifts of 6.27 and 7.66 ppm (J = 10 Hz) and two singlets at 7.66 and 6.83 ppm (1 H each). The first signals are due to the protons at C_3 and C_4 and the second to the protons at C_5 and C_8 of a coumarin nucleus. Consequently, (XIV) is a 6,7-disubstituted coumarin. In the region of aliphatic protons there are also two doublets at 2.90 and 4.85 ppm (1 H each) (J = 8 Hz) probably due to the presence in the side chain of (XIV) of a  $-\overset{}{CH}-O-CH-$ grouping. A three-proton singlet at 3.89 ppm corresponds to a methoxy group bound to an aromatic ring in position 7. A one-proton singlet at 2.32 ppm relates to the proton of a hydroxy group. The signals of two methyl groups attached to a quaternary carbon atom with a hydroxy group appear at 1.28 and 1.41 ppm (3 H each), each of these signals being split additionally into two components with a separation from one another of 2 Hz, which is characteristic for nonequivalent methyl groups. Furthermore, the additional splitting of the signals of the methyls is apparently also due to their interaction with the proton of the hydroxy group. This is confirmed by the NMR spectrum of lophopterol acetate (Fig. 1b) in which four three-proton singlets are observed at 1.26; 1.38  $\left(-\underset{O}{C}(CH_3)_2\right)$, 2.09 ($COCH_3$) and 3.90 ppm ($OCH_3$).

As was to be expected, the signals from the methine proton adjacent to the acetyl group have undergone a strong paramagnetic shift and appear at 5.98 ppm (doublet, 1 H, J = 8 Hz). The signal from the second methine proton, attached to the aromatic ring, has remained unchanged (3.10 ppm, doublet, J = 8 Hz). The signals that appear in the weak field at 6.26 and 7.62 ppm (doublets, 1 H each, J = 10 Hz) and 7.46 and 6.82 ppm (singlets, 1 H each) correspond to the aromatic protons in positions 3, 4, 5, and 8 of the coumarin nucleus.

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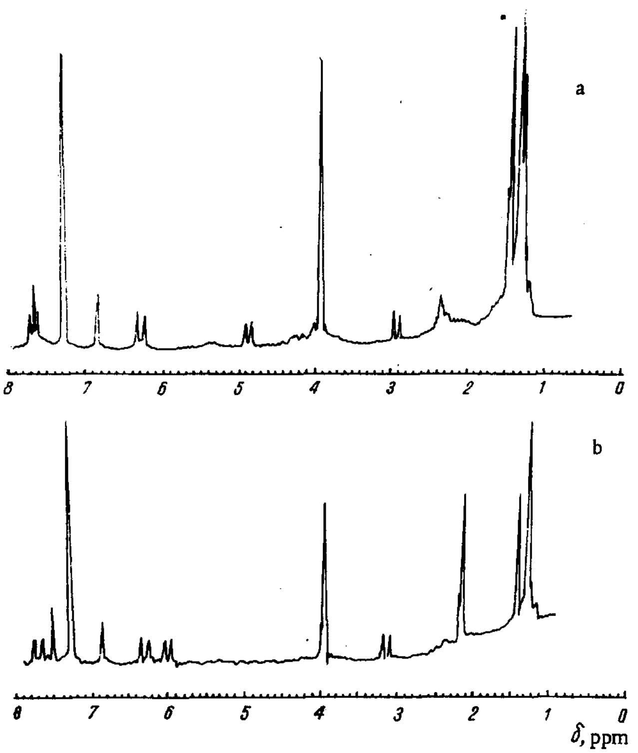
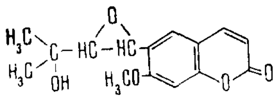


Fig. 1. NMR spectra of lophopterol (a) and of lophopterol monoacetate (b).

On the basis of the facts given above and the results of a comparison of the NMR spectra of suberenol [1] and lophopterol we have come to the conclusion that for the latter it is possible to propose as the most probable structure 6-(3'-hydroxy-1',2'-epoxyisopentyl)-7-methoxycoumarin (XIV).



XIV

EXPERIMENTAL

The IR spectra were taken on a UR-20 instrument (in paraffin oil), the NMR spectra on a Varian HA-100D spectrometer (in $CDCl_3$ with HMDS as internal standard), and the mass spectrum on a LKB-9000 instrument. The melting points were determined on a Kofler block. The compositions of the fractions and the purities of the substances were checked by thin-layer chromatography on alumina (activity grade IV) in the benzene, chloroform, and ethyl acetate–benzene (1 : 1) systems.

Isolation of the Coumarins. The dried and comminuted roots (500 g), the stems (52 g), and the fruit (25 g) of Prangos lophoptera Boiss, were extracted three times with chloroform. The chloroform extracts were evaporated to eliminate the solvent under vacuum. This gave 47.2 g of residue from the roots, 7 g from the stems, and 5 g from the fruit. The residues were dissolved in small amounts of chloroform and were chromatographed on columns (1-3) filled with alumina (activity grade IV, 200, 100, and 50 g, respectively) using as eluents petroleum ether, benzene, benzene–chloroform (4 : 1 and 2 : 1) and chloroform. The volume of each fraction was 50 ml. Fractions having similar compositions were combined and the concentrated eluate was rechromatographed under the conditions described above. Twelve individual substances were obtained from the roots (I with mp 79-81°C; II with mp 86-87°C; IV with mp 98-99°C; V with mp 104-106°C; VI with mp 141-142°C; VII with mp 132-134°C; VIII with mp 103.5-104.5°C; IX with mp 120-122°C; X with mp 135-137°C; XI with mp 136-138°C; XII with mp 231-232°C; and XIII with mp 72-73.5°C); ten from the fruit (I, II, III with mp 172-174°C, V-VIII, XI, XII, and XIV with mp 183-184°C); and thirteen from the stems (I-IX, XI-XIV).

Isolation of (XIII) and (XIV). When the benzene fractions from column 1 were concentrated and the residue was recrystallized from ethanol, colorless crystals of (XIII) (0.17 g) were obtained, while the fractions obtained by the elution of columns 2 and 3 with benzene–chloroform (4 : 1) yielded (XIV) (0.087 g).

Acetylation of (XIV). Compound (XIV) (0.050 g) was acetylated with acetic anhydride (2 ml) inpyridine (1 ml) for 1 h. The reaction mixture was worked up in the usual way, giving 0.073 g of (XV) with mp 127-129°C (from petroleum ether).

SUMMARY

The coumarin composition of the roots, stems, and fruit of *Prangos lophoptera* has been studied; in addition to known coumarin derivatives two new compounds have been isolated and have been called *isogosferol* (XIII) and *lophopterol* (XIV).

On the basis of a study of the IR, mass, and NMR spectra, and chemical properties of the latter, the most probable structure of 6-(3'-hydroxy-1',2'-ethoxyisopentyl)-7-methoxycoumarin has been proposed for it.

LITERATURE CITED

1. G. B. Guise, E. Ritchie, R. G. Senior, and W. C. Taylor, Austr. J. Chem., 20, 2429 (1967).