DEOXYMARRUBIALACTONE FROM *Chaiturus marrubiastrum*

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We have studied the isoprenoids of Chaiturus marrubiastrum Reichb. (synonym Leonurus marrubiastrum L.), from which the diterpenoids marrubiaside (a mono-D-glucoside of marrubiagenin) and marrubialactone have been isolated, their structures having been shown [1].

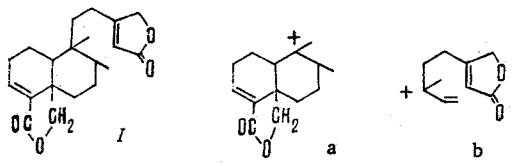
From an acetone extract of the epigeal part of this plant by chromatography on silica gel in chloroform, in addition to the substances described above, from the least polar fractions we isolated another new diterpenoid with a bitter taste having the composition $C_{20}H_{26}O_4$, mp 189-191°C (from ethanol), $[\alpha]_D$ −28.3° (c 3.5; chloroform), R_f 0.7 [Silufol; benzene–acetone (2:1)].

According to its spectral characteristics, this compound contains two α,β-unsaturated γ-lactone rings (1748, 1755, 1680 cm^{-1}) and differs from marrubialactone by the fact that it has no hydroxy groups. Its NMR spectra has the signals of two methyl groups (in place of the one in the spectrum of marrubialactone): the singlet of a tertiary methyl at 0.98 ppm and a doublet of a secondary methyl at 1.05 ppm. As in the spectrum of marrubialactone, in the 3.6-4.3 ppm region the signals of a AB system assigned to a C_{18}-methylene group, and also signals at 4.60 and 5.70 ppm belonging to two H_{16} allyl protons and a H_{14} vinyl proton. This has permitted the new diterpenoid to be assigned the structure of deoxymarrubialactone (I), as is confirmed by its mass-spectrometric fragmentation.

Thus, the mass spectrum of (I) has an intense peak with m/e 219 corresponding to the ion "a" (M−111) obtained by the splitting out of the side chain. This peak is also characteristic for the spectrum of olearin [2], which differs from marrubialactone by the position of the hydroxy group (at C_{12}), and in the spectrum of marrubiagenin it is represented by a peak with m/e 221. On the fragmentation of marrubialactone containing an OH group at C_{20}, instead of an ion of type "a," a dehydration ion is formed with m/e 217 (M−111−18).

The spectrum of deoxymarrubialactone also has peaks corresponding to the ions M−30 (300 m/e), M−97 (233 m/e), a peak of low intensity at M−18 (312 m/e), which are present in all the substances considered including marrubialactone acetate, and also a peak belonging to the ion "b" (165 m/e) obtained by the cleavage of the molecule at the C_9-C_{10} and C_7-C_8 bonds.

In addition to the substances described, β-sitosterol (0.05%) and phytol (0.04%) have been found in this plant.



I a b

LITERATURE CITED

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