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ALKALOIDS OF Haplophyllum foliosum.

III. STRUCTURE OF FOLIDINE

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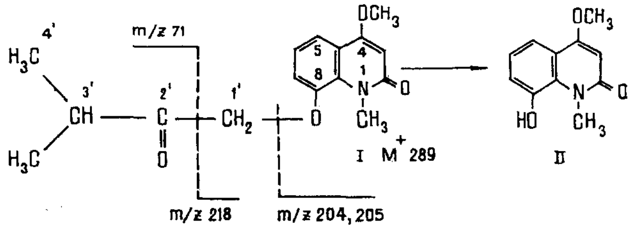
The new alkaloid folidine with mp 148-149°C (acetone–petroleum ether) has been isolated from the epigeal part of the plant Haplophyllum foliosum Vved., and on the basis of spectral characteristics and passage to the known alkaloid folifidine (8-hydroxy-4-methoxy-1-methyl-2-quinoline) its structure has been established as 4-methoxy-1-methyl-8-(2'-oxo-3'-methylbutoxy)-2-quinolone.

Continuing an investigation of the alkaloid composition of the epigeal part of the plant Haplophyllum foliosum Vved. [1], from the graveoline mother liquor we have isolated a new base with mp 148-149°C (acetone–petroleum ether) which we have called folidine (I). The substance is readily soluble in ether, chloroform, acetone, and ethanol, sparingly soluble in petroleum ether and benzene, and insoluble in water and alkalis.

The IR spectrum of (I) has absorption bands at 1730 cm^{-1} (CO) and 1640 cm^{-1} (amide carbonyl group of a 2-quinolone [2, 3]). The UV spectrum of folidine – λ_{max} 233, 249, 273, 286, 325 nm (log ε 3.42, 3.32, 2.89, 2.84, 2.60) – is typical for 4,8-dialkoxy-substituted derivatives of 2-quinolone alkaloids [3, 4].

The fact that (I) belonged to this group of substances was confirmed by its NMR spectrum which exhibited the signals of the protons of a 2-quinolone nucleus at (δ, ppm) 7.72 (q, 1 H, J_{ortho} = 7.5 Hz, J_{meta} = 3 Hz; H_5); 7.45-6.85 (m, 2 H; $H_{6,7}$); 6.08 (s, 1 H; H_3); of a methoxy and an N-methyl group at 3.94 and 3.9 (s, 3 H each) and of an isoprenoid substituent at 4.78 (s, 2 H; CH_2O); 2.80 (q, 1 H, J = 7.5 Hz, $C\underline{H}-(CH_3)_2$; 1.14 (d, 6 H, J = 7.5 Hz; $CH-(C\underline{H}_3)_2$). The absence of coupling between the protons of the methine and O-methylene groups indicated that the carbonyl group belonging to (I) shown above was located between them, i.e., the isoprenoid substituent had the structure $O-CH_2-CO-CH(CH_3)_2$. This was confirmed by the mass spectrum of (I), which contained the peak of the molecular ion with m/z 289 (89%) and the peaks of ions with m/z (62%), 205 (59%), 204 (100%), and 71 (26%) (scheme)



When compound (I) was fused with alkali, the known alkaloid folifidine (II) was obtained [5]. The passage to folifidine confirmed the structure of the heterocyclic skeleton of (I) and showed that the isoprenoid substituent in the folidine molecule was located at C_8.

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Thus, folidine has the structure of 4-methoxy-N-methyl-8-(3'-methyl-2'-oxobutoxy)-2-quinolone.

EXPERIMENTAL

The UV spectrum was taken on an EPS-3T spectrophotometer (Hitachi) (in ethanol), IR spectra on a UR-20 instrument (KBr), the PMR spectrum on a JNM-C-60/60 MHz spectrometer ($CDCl_3$), and the mass spectrum on a MKh-1303 instrument. For TLC (silica gel 5/40 μ) the solvent system toluene–ethyl acetate–formic acid (5:4:1) was used.

For the isolation of the mixture of alkaloids from the raw material and its separation, see [1].

Folidine (I). The mother liquor from graveoline (0.5 g) was treated with acetone and graveoline (0.3 g), mp 188-189°C (ethanol), was separated off. The residue after the evaporation of the acetone was treated wth ether. The concentrated ethereal solution was treated with petroleum ether until a turbidity appeared and was left to crystallize in the cold. This gave folidine (0.05 g) with mp 148-149°C (acetone–petroleum ether).

Fusion of Folidine with Alkali. A mixture of folidine (0.03 g), caustic soda (0.1 g), and water (1 drop) was heated at 160-180°C for 3 minutes and was then cooled and dissolved in water (3 ml). The aqueous solution was washed with ether and was then saturated with ammonium chloride and extracted with chloroform. The residue after the chloroform had been distilled off was crystallized from ethanol. This gave 0.01 g of (II) with mp 226-227°C, ν_{max} 2900-2500 cm^{-1} (OH), 1650 cm^{-1} (NCO), identical according to TLC, IR spectrum, and a mixed melting point with an authentic sample of folifidine which had been isolated previously from *H. foliosum* [5].

SUMMARY

The new alkaloid folidine has been isolated from the epigeal part of the plant *Haplophyllum foliosum*, and on the basis of spectral characteristics and a passage to the known alkaloid folifidine its structure has been established as 4-methoxy-N-methyl-8-(3'-methyl-2'-oxobutoxy)-2-quinolone.

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