ALKALOIDS OF Haplophyllum acutifolium

D. M. Gulyamova, I. A. Bessonova,
and S. Yu. Yunusov

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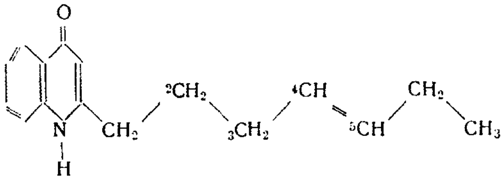
We have investigated the epigeal part of the plant Haplophyllum acutifolium (family Rutaceae) collected in the fruit-bearing period in the Kora-Kol region near Palvan-Zau, Turkmen SSR.

Chloroform extraction (of 9 kg of the raw material) gave the combined alkaloids (0.066%), and these were chromatographed on alumina. The ethereal eluates yielded an alkaloid with mp 176°C identified as skimmianine; the chloroformic eluates yielded a base with mp 122-123°C (from acetone) in the form of colorless prisms with mol. wt. 241 (mass spectrometry). The base had no methoxy group or N-methyl group. The IR spectrum exhibited bands at 1510, 1560, 1597, and 1635 cm^{-1} of approximately equal intensities, which is characteristic for 4-quinolone derivatives [1]. The UV spectra of the substance showed its similarity to the 4-quinolones substituted in position 2 [2], especially to 2-n-propyl-4-quinolone [3] and to 2-n-tridecyl-4-quinolone [4].

Solvent	λ_{max}, nm (log ε)	λ_{min}, nm (log ε)
Ethanol	214 (4.45); 35 (4.61); 305 inflection (3.92); 318 (4.04); 330 (3.97)	221 (4.34); 261 (3.12); 325 (3.93)
Ethanol + H^+	332 (4.70); 302 (3.88)	217 (4.50); 263 (2.61)
Ethanol + OH^-	246 (4.71); 315 (4.42)	235 (4.63); 265 (3.22)

The NMR spectrum (solution of the substance in $CDCl_3$) showed the signals of four adjacent aromatic protons at 1.76 ppm (H) and 2.73 ppm (3H) and of the C-3 proton at 3.79 ppm (H), showing the absence of substituents in the benzene ring and at C-3 of the 4-quinolone nucleus. The spectrum also had a three-proton triplet at 9.2 ppm (terminal methyl group), a weakly resolved six-proton signal in the 7.9-8.6 ppm region (methylene groups), and two two-proton signals at 7.38 and 4.88 ppm (methylene group attached to a ring, and equivalent olefinic protons).

On bombardment with electrons, the base decomposed into ions with m/e 173 (24%), 172 (46%), 159 (100%), 130 (11%), the formation of which agrees with a 2-n-heptenyl-4-quinolone structure of the alkaloid [4]. The presence of an NH group was shown by the deuteration of the substance. In the spectrum of the deutero analog the M^+ peaks and those of the ions with m/e 173, 172, 159, and 130 had shifted by one unit. The facts given above make it possible to suggest provisionally that the double bond is located in the C_4-C_5 position of the side chain.



2-n-Heptenyl-4-quinolone is a new base. This is the first time that alkaloids of this type have been found in representatives of the genus Haplophyllum.

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