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ACETYLHAPLOPHYLLIDINE, A NEW ALKALOID FROM *Haplophyllum perforatum*

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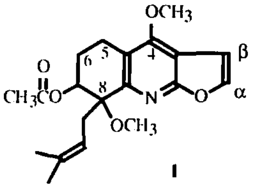
The plant *Haplophyllum perforatum* Kar. et Kir. (Rutaceae) is widely distributed throughout central Asia and is a rich source of quinolinic alkaloids, the composition of which varies greatly depending on the habitat [1]. More than 30 alkaloids have been isolated from it [2]. Many of these are produced only in certain localities.

Alkaloids of the above-ground part of *H. perforatum* collected during budding in the Kitabsk region of Kashkadar'insk district were studied. Haploperin (evoxine), skimmianine, and a small amount of compound 3 (0.22% of the total alkaloids), which was subsequently identified as haplophyllidine [4], were previously isolated from this material.

The ground dry material (800 g) was extracted with CH_3OH. The condensed extract was divided into basic, acidic, and neutral fractions according to the literature method [5]. Evoxine (0.4 g) precipitates from the basic fraction soluted in acid when the acidified solution is made alkaline with ammonia. Chromatography on a silica-gel column after removal of evoxine from the total alkaloids (0.46 g) gave compound **1** (0.08 g, mp 149-150°C, alcohol) and a mixture of crystals with an oil, from which treatment with acetone produced skimmianine (0.18 g). Chromatography of the remaining mother liquor produced haplophyllidine (0.07 g, mp 110-111°C, petroleum ether).

Column chromatography of the acidic fraction gave haplopine (0.06 g, mp 203-204°C, CH_3OH). Chromatography of the neutral fraction produced anhydroperforine (0.01 g, mp 143-144°C, ethanol) [6], flindersine (0.05 g, mp 185-186°C, dec., ethanol), and haplamine (0.07 g, mp 201-202°C, dec., ethanol) [5]. A total of 1.05 g of alkaloids (0.13% of the dry mass of the above-ground part) was obtained.

All known alkaloids were identified using authentic samples for direct comparison. Compound **1**, $C_{20}H_{25}NO_5$, is very soluble in $CHCl_3$, benzene, ether, and acetone and crystallizes from ethanol and methanol. Its UV spectrum exhibits maxima at 219 and 259 nm. A minimum at 234 nm is typical of 5,6,7,8-tetrahydrofuranoquinoline alkaloids [7]. The IR spectrum of **1** contains absorption bands of a furan ring (3155 and 3132 cm^{-1}) and an ester carbonyl (1741 cm^{-1}). The mass spectrum of **1** has peaks with *m/z* (%): 359 (M^+, 2), 327 (30), 312 (92), 290 (100), 270 (21), 268 (95), 248 (98), 233 (59), 188 (45), 173 (12), and 69 (8). The PMR spectrum ($CDCl_3$) shows signals for protons of a furan ring at 7.55 and 6.94 ppm (1H, d, J = 2.5 Hz, Hα and Hβ, respectively), of an isopentenyl substituent at 5.13 (1H, br. t, J = 5 Hz, –CH–), 3.40 (2H, dd, J = 18 and 5 Hz, $-CH_2-$), 1.66 and 1.54 (3H each, br. s, 2 × CH_3), methoxy groups at 4.24 and 3.08 ppm (3H each, s, 4-OCH_3, 8-OCH_3, respectively), an acetyl group at 1.90 (3H, s), and a proton geminal to an acetoxy group at 5.19 ppm (1H, q, J = 2.5 and 4.5 Hz). The methylene protons on C-5 and C-6 are observed as unresolved multiplets at 2.75-2.42 and 2.30-1.97 ppm. These data are similar to those of acetylhaplophyllidine [8]. Direct comparison of the isolated compound with an authentic sample obtained from haplophyllidine showed that they are identical.



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Thus, haplopine, flindersine, haplamine, anhydroperforine, and the new alkaloid acetylhaplophyllidine in addition to evoxine, skimmianine, and haplophyllidine are isolated from the above-ground part of *H. perforatum*.

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