

COMPONENTS OF *Haplophyllum bucharicum*

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Haplophyllum bucharicum Litv. (*H. nigripes* Nevski, Rutaceae) is a bushy perennial common in Kashkadar'inskii and Surkhandar'inskii districts [1]. The aerial part of the plant from two sites, near Dekhkanabad in Kashkadar'inskii district [2] and Derbent in Baisunskii region of Surkhandar'inskii district [3] has been previously studied. A total of 13 quinoline alkaloids were isolated from this plant [4]. The main component in both instances was bucharaine, the content of which was >90% of the alkaloids. The plant is atypical because it produces quinoline alkaloids with a terpene fragment (bucharaine, bucharidine, bucharaminol) [5] that are unique to this species within not only the genus but also the family.

Chromatographic investigation on Silufol UV-254 plates of the total alkaloids and the acidic and neutral fractions remaining after separation of bucharaine and other alkaloids and neutral compounds [3] revealed several spots belonging to components that previously had not been isolated from this plant.

Acid-insoluble mother liquors remaining after isolation and purification of bucharaine were dried (8.5 g) and treated with NaOH solution (4%). The alkali-soluble portion developed a precipitate (2.38 g) upon acidification by glacial $\text{CH}_3\text{CO}_2\text{H}$ that was crystallized from ethylacetate after treatment with hot CHCl_3 . Yield 1.5 g of diphyllin, mp 285-286 °C [6]. The solid was washed with hot CH_3OH and crystallized from $\text{CH}_3\text{CO}_2\text{H}$ (60%). Yield 0.23 g of **1**. Bucharaine (3.8 g) was isolated from the alkali-insoluble part (5.1 g). The CHCl_3 -soluble fraction was chromatographed on a silica-gel column. Skimmianine (0.3 g) and three minor compounds **2-4** were isolated.

Compound 1, $\text{C}_9\text{H}_7\text{O}_2\text{N}$, mp 353-354 °C (decom.). PMR (400 MHz, DMSO, δ , ppm, J , Hz): 5.69 (1H, s, H-3), 7.05 and 7.40 (1H each, t, $J = 8$, H-6, H-7), 7.21 and 7.75 (1H each, dd, $J = 8.0$: 2.0, H-8, H-5), 11.09 (2H, br. s, NH, OH).

Compound 2, $\text{C}_{10}\text{H}_9\text{O}_2\text{N}$, mp 254-256 °C (decom.) (acetone).

PMR (100 MHz, CDCl_3): 3.91 (3H, s, OCH_3), 5.95 (1H, s, H-3), 7.00-7.55 (3H, m, H-6, H-7, H-8), 7.85 (1H, dd, $J = 8.0$: 2.5, H-5), 11.95 (1H, br. s, NH).

Compound 3, $\text{C}_{21}\text{H}_{16}\text{O}_6$, mp 231-232 °C (MeOH), M 364.

PMR (100 MHz, CDCl_3): 3.75, 4.00 (3H each, s, $2 \times \text{OCH}_3$), 5.36 (2H, s, Ar- CH_2 -O), 6.01, 6.03 (1H each, d, $J = 1.2$, O- CH_2 -O), 6.76 (1H, dd, $J = 8.0$: 1.5, H-6'), 6.82 (1H, s, H-2'), 6.96 (1H, dd, $J = 8.0$: 1.0, H-5'), 7.07, 7.15 (1H each, s, H-5, H-8), 7.63 (1H, s, H-4).

Compound 4, $\text{C}_{23}\text{H}_{18}\text{O}_8$, mp 231-232 °C ($\text{C}_2\text{H}_5\text{OH}$), M 422.

PMR (100 MHz, CDCl_3): 2.46 (3H, s, OAc), 3.75, 4.00 (3H each, s, $2 \times \text{OCH}_3$), 5.19 (2H, s, Ar- CH_2 -O), 6.01, 6.04 (1H each, d, $J = 1.2$, O- CH_2 -O), 6.76 (1H, dd, $J = 8.0$: 1.5, H-6'), 6.81 (1H, s, H-3'), 6.95 (1H, dd, $J = 8.0$: 1.5, H-5'), 7.06, 7.12 (1H each, s, H-5, H-8).

Comparison of the compositions, melting points, and PMR spectra of **1-4** with known quinoline alkaloids and aryl-naphthalide ligands identified **1-4** as 4-hydroxyquinolin-2-one, 4-methoxyquinolin-2-one [7], justicidin B [8], and acetyldiphyllin [9], respectively. Compounds **1-4** were first isolated from *H. bucharicum*.

It was previously established using labeled compounds that the biosynthetic pathway from anthranilic acid to quinoline alkaloids passes through 4-hydroxyquinolin-2-one as an intermediate [10]. However, the last was not isolated from the plant. From this viewpoint, the preparation of 4-hydroxyquinolin-2-one from *H. bucharicum* is an important confirmation of its involvement in the biosynthesis of quinoline alkaloids, in particular, bucharaine, from which bucharamine and bucharidine are formed by Claisen rearrangement [5].

Roots of *H. bucharicum* growing near Derbent of Surkhandar'inskii district contain 0.13% of a mixture of alkaloids, from which known furanoquinolines (skimmianine, dictamnine, γ -fagarine, robustine, haplopine) and pyranoquinolin-2-ones

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(flindersine, haplamine) were isolated [4].

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