COMPONENTS OF *Haplophyllum bucharicum*

E. F. Nesmelova, I. A. Bessonova, and
S. Yu. Yunusov

UDC 547.944/945

Continuing a study of alkaloids of the genus *Haplophyllum* [1], we have investigated the epigeal part of *H. bucharicum* Litv. collected by S. A. Khamidkhodzhaev in the environs of the village of Derbent in the Baisun region of Sukhandar' province in the budding–incipient flowering stage on May 17, 1980. The plants from this growth site have not been studied previously [2].

A methanolic extract obtained from the dry comminuted epigeal part (4300 g) was separated into basic, acidic, and neutral fractions. By chromatography of the neutral fraction on a column of alumina, by rechromatography of the individual fractions on a column of silica gel and crystallization, five substances were isolated: (I) – mp 76°C (benzene–ethyl acetate); (II) – mp 134–135°C (acetone); (III) – mp 176–177°C (methanol); (IV) – mp 113–114°C (acetone); and (V) – mp 150–151°C (methanol).

On the basis of features of its IR, PMR, and mass spectra, substance (I) was identified as n-triacantonol [3]. A comparison of the mass spectrum of (II) with that published by Razakov et al. [4] showed that compound (II) was β-sitosterol (M^+ 414) containing as impurities very small amounts of sigmasterol (M^+ 412), campesterol (M^+ 400), and cholesterol (M^+ 386).

Substances (III) and (V) were identified as the alkaloids skimmianine and bucharaine, respectively, which have been isolated previously from this plant obtained from a different growth site [5].

Substance (IV) contains a nitrogen atom. Its UV spectrum in ethanol (λ_{max} 277, 272, 282, 313, 324, 338 nm; log ε 4.10, 3.50, 3.41, 3.35, 3.46, 3.35) is characteristic for 4-alkoxy-2-quinolones [6] and, like the latter, did not change on acidification. The IR spectrum of (IV) contains absorption bands at 3300 and 1650 cm^{-1} (NH–CO). Mass spectrum, m/z (%) 297 (M^+, 6), 229 (M – 68, 25), 228 (M – 69, 100), 214 (18), 212 (27), 200 (16), 186 (26), 174 (24), 69 (36). The NMR spectrum of (IV) ($CDCl_3$) shows signals at (ppm) 7.65 (quadruplet, 1 H), 7.45–7.08 (multiplet, 3 H) – the aromatic protons H_5 and $H_{6,7,8}$, respectively; 5.51 and 5.25 (triplets, 1 H each, J = 7.5 Hz); 4.44 and 3.37 (doublet, 2 H each, J = 7.5 Hz); and 1.82, 1.75, 1.61 (singlets, 3 H, 3 H, and 6 H, respectively) – two isopentyl groups, one of which is attached to the 2-quinolone nucleus directly and the other through an oxygen atom. These facts give grounds for suggesting that (IV) is 3-dimethylallyl-4-dimethylallyloxy-2-quinoline, which has been isolated previously from *Haplophyllum tuberculatum* [7]. A chemical confirmation of this was the conversion of (IV) on boiling with 85% formic acid into haplofoline and dihydroflindersine [7]. This is the first time that the alkaloid (IV) has been detected in Central Asian species of plants of the genus *Haplophyllum*.

LITERATURE CITED

1. V. I. Akhmedzhanova and I. A. Bessonova, Khim. Prir. Soedin., 613 (1981).
2. S. Yu. Yunusov, Alkaloids [in Russian], Tashkent (1981), p. 247.
3. R. T. Holman, Prog. Chem. Fats Other Lipids, No. 15, 219 (1978); S. R. Ries, V. Wert, C. C. Sweeley, and R. A. Leavitt, Science, No. 195, 1339 (1977).
4. R. Razakov, A. K. Kasimov, Kh. I. Aslanov, and A. S. Sadykov, Khim. Prir. Soedin., 81 (1981).

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 4, p. 532, July-August, 1982. Original article submitted April 6, 1982.

0009-3130/82/1804-0507$07.50

5. S. M. Sharafutdinova and A. S. Sadykov, Khim. Prir. Soedin., 198 (1968).
6. I. A. Bessanova and S. Yu. Yunusov, Khim. Prir. Soedin., 303 (1977).
7. D. Lavie, N. Danieli, R. Weitman, and E. Glotter, Tetrahedron, 24, 3011 (1968).

BUCHAPINE — A NEW ALKALOID FROM *Haplophyllum bucharicum*

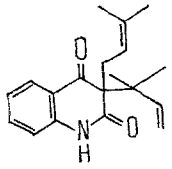
E. F. Nesmelova, I. A. Bessonova, and
S. Yu. Yunusov

UDC 547.944/945

Continuing a study of the chemical composition of the epigeal part of *Haplophyllum bucharicum* Litv. [1], from the neutral fraction of the methanolic extract, by chromatography on columns of alumina and silica gel, we have obtained a new alkaloid (I) with mp 134-135°C (hexane) and have called it buchapine. Buchapine has the composition $C_{19}H_{23}NO_2$, identical with that of 3-dimethylallyl-4-dimethylallyloxy-2-quinoline (II) [2].

The mass spectrum of (I) — m/z (%) 297 (M^+ 10), 229 (M — 68, 34), 228 (M — 69, 100), 214 (20), 212 (24), 200 (16), 186 (38), 174 (24), 69 (20) — almost coincides with that of (II): There are only slight differences in the intensities of some peaks. These results, and also the presence in the IR spectrum of buchapine of absorption bands at 1692 cm^{-1} together with the band of an amide carbonyl group at 1660 cm^{-1} have permitted the suggestion that it is based on a 1,2,3,4-tetrahydroquinoline-2,4-dione nucleus with two prenyl substituents in position 3. This conclusion is in harmony with the UV spectrum of (I).

UV spectrum of buchapine: λ_{max} (nm) 234, 238 (shoulder), 242 infl., 244 infl., 258 shoulder, 324, 329 shoulder, 325 infl. (log ε 4.44, 4.41, 4.32, 3.72, 3.60, 3.41, 3.50, 3.40) differs from those of the 4-alkoxy-2-quinolone alkaloids, in particular (II) [2], by the absence of maxima in the 260—290 nm region characteristic for this group of substances [3], but it is close to those of 3,3-diprenyl-1,2,3,4-tetrahydroquinoline-2,4-dione compounds [4]. The structure of buchapine follows from its PMR spectrum ($CDCl_3$, δ scale), which contains signals at 7.74 and 7.5—6.82 ppm (doublet, 1 H, J = 8.5 Hz, and multiplet, 3 H) relating to the H-5 and H-6,7,8 aromatic protons, and also at 5.76 and 4.81 ppm (A_2B system, 1 H and 2 H respectively: $-CH=CH_2$), 4,65 and 2.77 ppm (triplet, 1 H; doublet, 2 H, J = 7.5 Hz, $=CH-CH_2$), and 1.88, 1.40, and 1.09 ppm (singlets, 3 H, 3 H, and 6 H, respectively), belonging to the protons of two prenyl substituents one of which has the structure $-C(CH_3)_2-CH=CH_2$ and the other $-CH_2-CH=C(CH_3)_2$. Consequently, buchapine has the structure of 3-(α,α-dimethylallyl)-3(γ,γ-dimethylallyl)-1,2,3,4-tetrahydroquinoline-2,4-dione.



I

Buchapine is the only alkaloid of the 1,2,3,4-tetrahydroquinoline-2,4-dione type with phenyl substituents of different structures in position 3.

LITERATURE CITED

1. E. F. Nesmelova, I. A. Bessonova, and S. Yu. Yunusov, Khim. Prir. Soedin., 532 (1982) [preceding paper in this issue].
2. D. Lavie, N. Danieli, R. Weitman, and E. Glotter, Tetrahedron, 24, 3011 (1968).

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 532-533, July-August, 1982. Original article submitted April 27, 1982.

 0009-3130/82/1804-0508$07.50