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SHORT COMMUNICATION

ALKALOIDS OF *HAPLOPHYLLUM SUAVEOLENS*: ISOLATION OF DICTAMNINE AND SKIMMIANINE

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Abstract—Two minor alkaloids, dictamnine (V), and skimmianine (VI), have been isolated from the aerial parts of *Haplophyllum suaveolens* (DC) G. Don. (Rutaceae). The chemotaxonomic interest of the occurrence of skimmianine in *Haplophyllum* species is discussed.

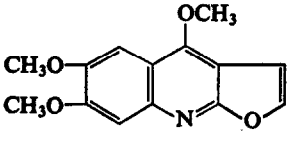
THE ISOLATION of three major alkaloids, kokusaginine (I), evoxine (II), and khaplofoline (III), from the aerial parts of the herbaceous plant *Haplophyllum suaveolens* (DC) G. Don. (Rutaceae), has been previously reported.[1] Recently, Uzbek workers found that evoxine (II), and *N*-methylkhaplofoline (IV) have a significant sedative action on the central nervous system.[2] At the same time, these workers reported analogous actions for many other alkaloids isolated from *Haplophyllum* species. It thus appeared of interest to us to isolate and identify the minor alkaloids from *H. suaveolens*.

Column chromatography of an ethanolic extract of this plant, led to the isolation of two other furoquinoline bases. One of these melts at 132–133° and is identical (u.v., i.r. spectra, R_f on TLC) with an authentic sample of dictamnine (V), isolated from roots of *Dictamnus albus* L.;[3] the other, which was purified as picrate (m.p. 194–195°), is identical in all respects with authentic skimmianine picrate from *D. albus*.[3] The free base (VI) melts at 175–176°.

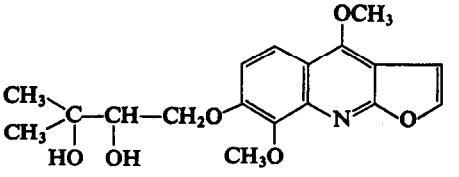
Both these alkaloids, dictamnine (V) and skimmianine (VI), were previously found in many other *Haplophyllum* species. Thus, dictamnine was isolated from *H. bungei*,[4] and *H. ramosissimum* Vved.,[5] and skimmianine from *H. bucharicum* Litv.,[6] *H. bungei*,[4] *H. dubium*, Eug. Kor.,[7] *H. foliosum* Vved.,[8] *H. pedicellatum* Bge.,[9] *H. perforatum* (M. B.) Kar. et Kir.,[9] *H. popovii*,[10] *H. ramosissimum* Vved.,[5] and *H. robustum* Bge.[11] Skimmianine thus seems to

[1] M. IONESCU, I. MESTER and M. VLASSA, *Rev. Roumaine Chim.* **13**, 1641 (1968).
[2] N. P. POLIEVTSEV and I. K. KAMILOV, *Farmakol. Alk.* (Tashkent:Nauka) *No.* 2, 14 (1965), cf. *Chem. Abs.* **66**, 74715w (1967); S. F. FAKHRUTDINOV and I. K. KAMILOV, *Farmakal. Alk.* (Tashkent:Nauka) *No.* 2, 96 (1965), cf. *Chem. Abs.* **66**, 64105h (1967).
[3] H. GERTIG and H. GRABARCZYK, *Acta Polon. Pharm.* **18**, 97 (1961).
[4] D. KURBANOV and S. YU. YUNUSOV, *Khim. Prir. Soed.* 289 (1967).
[5] D. KURBANOV, G. P. SIDYAKIN and S. YU. YUNUSOV, *Khim. Prir. Soed.* 67 (1967).
[6] S. M. SHARAFUTDINOVA and S. YU. YUNUSOV, *Khim. Prir. Soed.* 198 (1968).
[7] S. A. SULTANOV, V. I. PASTUKHOVA and S. YU. YUNUSOV, *Khim. Prir. Soed.* 355 (1967).
[8] M. ESKAIROV, G. P. SIDYAKIN and S. YU. YUNUSOV, *Dokl. Akad. Nauk Uzb. S.S.R. No.* 2, 21 (1957), cf. *Chem. Abs.* **52**, 2181d (1958).
[9] S. YUNUSOV and G. P. SIDYAKIN, *Zhur. obshchei Khim.* **22**, 1055 (1952).
[10] Z. SH. FAYZUTDINOVA, G. P. SIDYAKIN and S. YU. YUNUSOV, *Dokl. Akad. Nauk Uzb. S.S.R. No.* 1, 35 (1966), cf. *Chem. Abs.* **64**, 19700g (1966).
[11] I. M. FAKHRUTDINOVA, G. P. SIDYAKIN and S. YU. YUNUSOV, *Khim. Prir. Soed.* 107 (1965).

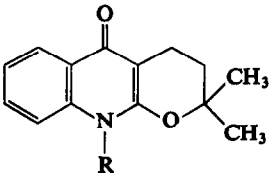
be a common feature of plants of this genus, having been found in ten of the eleven species studied. In the eleventh species, *H. tuberculatum*, it has not been deliberately sought for [12,13] and it may well be present here too.



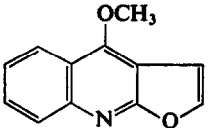
(I)



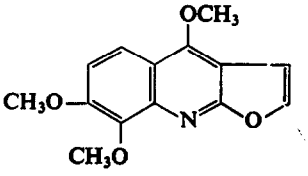
(II)



(III): R = H
(IV): R = CH_3



Dictamnine (V)



Skimmianine (VI)

EXPERIMENTAL

M.ps were determined on a Boetius apparatus. U.v. spectra were recorded in ethanolic solution and i.r. spectra in KBr pellets. TLC was performed on silica gel G (Merck), using benzene–ethanol (9:1) in an NH_3 atmosphere,[14] and the spots were detected in u.v. light and by means of Dragendorff's reagent.

Extraction of Alkaloids

The concentrated ethanolic extract of the powdered plant material (19 kg) was mixed with a double volume of 2 N HCl, filtered, the filtrate treated with conc. NH_4OH to pH 8–8·5, and extracted with CH_2Cl_2 to give the crude alkaloid mixture. A part (8 g) of this mixture was taken up in $CHCl_3$ and chromatographed on 800 g neutral alumina (Carlo Erba), to which 4%, w/w water was added; the alkaloids were eluted with $CHCl_3$, collecting fractions of 250 ml each. Fractions containing dictamnine and skimmianine were contaminated with kokusaginine, so they were further purified by preparative TLC.

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[12] D. LAVIE, N. DANIELI, R. WEITMAN and E. GLOTTER, *Tetrahedron* **24**, 3011 (1968).
[13] D. LAVIE, private communication (1969).
[14] G. SCHNEIDER, *Planta Med.* **13**, 425 (1965).