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SHORT COMMUNICATION

OCCURRENCE AND DISTRIBUTION OF 7-METHYLJUGLONE AND PLUMBAGIN IN THE DROSERACEAE

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Abstract—7-Methyljuglone has been isolated and identified from different *Drosera* species. The distribution of 7-methyljuglone and plumbagin in twenty-two species of three families has been recorded. The chemical data support the taxonomic assumption that Byblidaceae and Roridulaceae are not related to Droseraceae.

THE DROSERACEAE are known to contain naphthoquinones.[1] Our interest in the biogenesis of these compounds has led us to investigate the distribution of plumbagin (5-hydroxy-2-methyl-1,4-naphthoquinone), the major quinone reported to occur in aerial parts of the genus *Drosera*. Furthermore, it was of interest from a chemosystematic[2] point of view to study the distribution of this compound in the closely related genera[3] *Aldrovanda*, *Dionaea* and *Drosophyllum*, and in the families Byblidaceae and Roridulaceae suspected to be related to Droseraceae.

Extraction of fresh leaves with ether and subsequent TLC of the extracts revealed predominantly two major naphthoquinones. One was identified as plumbagin by co-chromatography with an authentic sample, u.v. spectrum and chemical degradation to 3-hydroxyphthalic acid.[4] The second quinone was present in relative large amounts in several species (0·7 per cent dry weight in *Drosera capensis*) and was isolated by separation of the extracts on thin-layer plates, elution and sublimation. By mass spectrometry, NMR and i.r. spectroscopy the substance was identified as 7-methyljuglone (5-hydroxy-7-methyl-1,4-naphthoquinone). The identity was furthermore confirmed by co-chromatography with an authentic sample and by chemical degradation to 3-hydroxy-5-methylphthalic acid. Recently the occurrence of traces of this quinone in *D. intermedia* was suggested.[5] The distribution of the two *major* quinones is shown in the table.

All species so far investigated of the family Droseraceae contain either one or other of these quinones. Only *Byblis and Roridula* (the only known genera, each with two species) do not contain any of these naphthoquinones; thus the chemical data confirm the taxonomic

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[2] H. MERXMÜLLER, *Ber. Deut. Botan. Ges.* **80**, 608 (1967).
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[4] E. LEISTNER and M. H. ZENK, *Z. Naturforschg.* **23b**, 259 (1968).
[5] G. BENDZ and G. LINDBERG, *Acta Chem. Scand.* **22**, 2722 (1968).

view,[7] that both families are not related to the Droseraceae. The co-occurrence of plumbagin and 7-methyljuglone in *D. capensis* and *D. cistiflora*, which has previously also been reported for *Diospyros ebenum*,[6] may be of biogenetic importance.

TABLE 1. DISTRIBUTION OF PLUMBAGIN AND 7-METHYLJUGLONE IN DROSERACEAE AND RELATED TAXA

Species	Plumbagin	7-Methyljuglone
Drosera aliciae Hamet.	−	+
D. auriculata Planch.	+	−
D. binata Labill.	+	−
D. burkeana Planch.	−	+
D. capensis L.	(+)	+
D. cistiflora L.	(+)	+
D. cunaeifolia L. fil.	−	+
D. dichotoma Smith	+	−
D. hamiltonii C. Andrews	−	+
D. indica L.	+	−
D. longifolia L.	+	−
D. lunata D. C.	+	−
D. madagascariensis D. C.	−	+
D. spathulata Labill.	−	+
D. tracii Macfarlane	−	+
D. trinervia Spreng.	−	+
D. whitakeri Planch.	+	−
Aldrovanda vesiculosa L.	+	−
Byblis gigantea Lindl.	−	−
Dionaea muscipula Ell.	+	−
Drosophyllum lusitanicum Link.	+	−
Roridula gorgonias Planch.	−	−

EXPERIMENTAL

Fresh leaves of the species investigated were cut and extracted with ether for 24 hr. The extracts were taken to dryness and the residue dissolved in methanol and subjected to preparative TLC. Silica gel GF plates were developed in benzene:petrol ether (30–50°) (2:1) and the quinones (plumbagin, R_f 0·4; 7-methyljuglone, R_f 0·3) eluted with CH_2Cl_2. The eluate was concentrated and the residue sublimed *in vacuo*. Both quinones were chromatographically pure as checked by chromatography in five solvent systems. 7-Methyljuglone had m.p. 85° after sublimation, considerably different from that reported in the literature (125–126).[6] Oxidations (H_2O_2/OH^-) of the quinones were conducted as described.[4] 7-Methyljuglone: u.v.-spectrum in methanol: max_1=252 nm; max_2=425 nm. Infra-red (in KBr): 3010 (w), 2910 (w), 1667 (m), 1630 (ss), 1600 (sh), 1588 cm^{-1} (m). NMR[8] (in $CDCl_3$; 60 MHz; δ_{TMS}=0·00 ppm): δ=2·47 (s, CH_3); 7·00 (s, H-2, H-3); 7·18 (broad s, H-6); 7·51 (broad s, H-8); 12·00 ppm (s, OH). MS[9] (70 eV): *m/e* 188 (M^+); prominent fragment ions at *m/e* 173 (M-CH_3); 160 (M-CO); 134 (M-CO-C_2H_2); 132 (160-CO); 131, 106, 77. Voucher specimens of all plants have been deposited in the Ruhr University herbariun.

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[7] A. ENGLER, *Syllabus der Pflanzenfamilien*, Vol. II (1964).
[8] Compare R. E. MOORE and P. SCHEUER, *J. Org. Chem.* **31**, 3272 (1966).
[9] Compare J. H. BOWIE, D. W. CAMERON and D. H. WILLIAMS, *J. Am. Chem. Soc.* **87**, 5094 (1964).