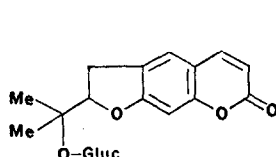
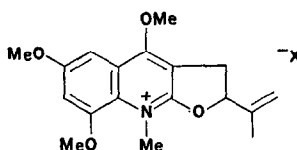


lassen sich für einige taxonomische Regelmäßigkeiten erkennen, denn ihr Vorkommen beschränkt sich auf bestimmte ssp. oder var.^{1,2}

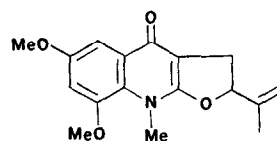
Wie kürzlich festgestellt werden konnte, ist eine dieser Komponenten ('royal blue fluorescent substance')¹ Nodakenin I.⁴ Als weitere für bestimmte Taxa spezifische Substanz ('light blue fluorescent substance')¹ konnte nun das quartäre Chinolin-Alkaloid II identifiziert werden.⁵ II läßt sich mit 70% igem wäßrigem Methanol aus der Rinde der Pflanzen gewinnen. Nach Entfernen des Methanols wird die wäßrige Lösung, um sie von den Cumarinen und tertiären Chinolonen zu befreien, mit Benzol extrahiert und das Alkaloid aus der wäßrigen Phase über Pikratfällung und Ionenaustausch gereinigt (Base Schmp. 191–194° (Bzl/MeOH); Hydrochlorid Schmp. 90–93° (H₂O)).



(I)



(II)



(III)

Das UV-Spektrum $\lambda_{\text{max}}^{\text{MeOH}}$ 347, 335, 301, 292, 283 (sh), 255, 214 nm; log ϵ : 3,67; 3,70; 3,94; 3,92; 4,76; 4,50 zeigt den für diesen Alkaloidtyp eigentümlichen Kurvenverlauf. Das KMR-Spektrum (TFE) entspricht weitgehend dem des Ptelefolons III⁶ mit Ausnahme der vier 3H-Singulets (4,45; 4,35; 4,0; 3,9; 1 $\times$ MeN–3 $\times$ MeO) und des Signals vom H5, das gegenüber III durch das fehlende peri-Carbonyl in das höhere Feld verschoben ist und als Doublett $\delta = 7,3$ ppm (J 2,5 Hz) erscheint. Im Massenspektrometer zerfällt II-Hydrochlorid nach *N*-Demethylierung und Ummethylierung (vgl. 7) zu III in der für dieses Alkaloid charakteristischen Weise.⁶

⁴ SZENDREI, K., NOVÁK, I., PETZ, M., REISCH, J., BAILEY, H. E. und BAILEY, V. L. (1973) *Lloydia* im Druck.

⁵ REISCH, J., NOVÁK, I., SZENDREI, K., PÁPAY, V. und MINKER, E. (1970) *Vortrag auf dem 1. Internationalen Kongreß für Pharmakognosie und Phytochemie* 21.–26 Juli 1970 München; (1970) *D. Apotheker Z.* **110**, 1109.

⁶ REISCH, J., SZENDREI, K., PÁPAY, V., NOVÁK, I. und MINKER, E. (1970) *Tetrahedron Letters* 3365.

⁷ REISCH, J., SZENDREI, K., MINKER, E. und NOVÁK, I., (1969) *Pharmazie* **24**, 699.

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SESAMIN FROM THE BARK OF TWO AFRICAN *ZANTHOXYLUM* SPECIES

FRANCIS FISH, PETER G. WATERMAN and NATHAN FINKELSTEIN*

Division of Pharmacognosy and Forensic Science, Department of Pharmaceutical Chemistry,
University of Strathclyde, Glasgow G1 1XW, Scotland

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Key Word Index—*Zanthoxylum chalybeum*; *Z. capense*; Rutaceae; sesamin; chemotaxonomy.

Plants. *Zanthoxylum chalybeum* Engl. (syn. *Fagara chalybea* Engl., *F. olitoria* Engl., *F. fischeri* Engl.) (Vouchers: FF 12, Herbarium of the Pharmaceutical Society, University

* Present address: Department of Pharmaceutical Sciences, Rhodes University, P.O. Box 94, Grahamstown, South Africa.

of Bradford, England and Gordon 183, Royal Botanic Garden, Edinburgh). *Zanthoxylum capense* Harv. (syn. *Fagara capensis* Thunb.) (Vouchers: FF 20, Herbarium of the Pharmaceutical Society, University of Bradford, England and Moll. and Müller 5705, Royal Botanic Garden, Edinburgh). *Sources*. *Z. chalybeum*—FF 12 from Kenya; Gordon 183 from Raffingora, Rhodesia. *Z. capense*—FF 20 from eastern Cape Province, South Africa; Moll. and Müller 5705 from Tongoland, South Africa. *Uses*. Both species have extensive ethnobotanical uses.¹⁻³ *Previous work*. *Z. chalybeum*—alkaloids,⁴⁻⁵ *Z. capense*—alkaloids.⁵⁻⁷

Present work. Ground root bark (400 g) of *Z. chalybeum* (FF 12) extracted with petrol. (40–60°) and concentrated gave white crystals (52 mg) m.p. 123–124° (from MeOH) (lit.⁸ m.p. 123–124°). The compound was identical with sesamin by UV, IR and MS (M^+ 354.1090, $C_{20}H_{18}O_6$ requires: 354.1103). PMR ($CDCl_3$) confirmed that the compound was the di-equatorial stereoisomer sesamin and not either asarinin or diasesamin.⁹ The optical rotation was found to be $[\alpha]_D^{24} + 53^\circ$ ($CHCl_3$) (lit.⁸ + 65°). A second sample of sesamin, similarly isolated from *Z. chalybeum* (Gordon 183), root and stem barks, was identical in all respects except that the optical rotation was found to be +61°. The petrol extract of ground stem bark of *Z. capense* (3000 g) (FF 20), on concentration gave crystals (47 mg) m.p. 120–122° (from MeOH) identical in all respects, including optical rotation (+65°), with published data for (+)-sesamin. The presence of sesamin in both root and stem barks of *Z. capense* (Moll. and Müller 5705) was established by TLC (3 systems). We were unable to detect the rarer isomers, asarinin and diasesamin, in either species.

The low optical rotation recorded for (+)-sesamin from *Z. chalybeum* may be attributed to its contamination with a small quantity of (–)-sesamin, a feature previously noted in two other African species, *Z. senegalense* DC (syn. *F. xanthoxyloides* Lam.) and *Z. viride* Waterm. (syn. *F. viridis* A. Chev.).⁸ The co-occurrence of sesamin in four of the seven African species investigated to date, and the presence of the structurally-similar liriore-sinol-*B* dimethyl ether in *Z. leprieurii* Guill. et Perr.,¹⁰ suggests that these compounds may have some chemotaxonomic value in the large genus *Zanthoxylum* L.

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¹ WATT, J. M. and BREYER-BRANDWIJK, M. G. (1962) *The Medicinal and Poisonous Plants of Southern and Eastern Africa*, 2nd Edn, pp. 918–920, Livingstone, Edinburgh.

² FINKELSTEIN, N. (1970) M.Sc. Thesis, University of Strathclyde.

³ WATERMAN, P. G. (1972) Ph.D. Thesis, University of Strathclyde.

⁴ FISH, F. and WATERMAN, P. G. (1972) *Phytochemistry* **11**, 1866.

⁵ FISH, F. and WATERMAN, P. G. (1972) *Phytochemistry* **11**, 3007.

⁶ CALDERWOOD, J. M., FISH, F. and FINKELSTEIN, N. (1970) *Phytochemistry* **9**, 675.

⁷ CALDERWOOD, J. M., FISH, F., FINKELSTEIN, N. and PARFITT, R. T. (1971) *Phytochemistry* **10**, 682.

⁸ CARNMALL, B., ERDTMAN, H. and PELCHOWICZ, Z. (1955) *Acta Chem. Scand.* **9**, 1111.

⁹ ATAL, C. K., DHAR, K. L. and PELTER, A. (1967) *J. Chem. Soc. C*, 2228.

¹⁰ FISH, F. and WATERMAN, P. G. (1972) *Phytochemistry* **11**, 1527.