

spectrum ( $D_2O$ ,  $\delta$ -values, extern standard TMS) 7.80 (*d*,  $J$  1.0 Hz, H-3), 6.12 (*m*, H-7), 5.51 (*d*,  $J$  7.0 Hz, H-1), 5.18 (*d*,  $J$  8.0 Hz, anom H), 4.53 (*br s*, 2H, H-10), and 4.00 ppm (*s*, 3H,  $OCH_3$ ) *Penta-acetate* ( $Ac_2O$  in pyridine), m.p. 133–133.5°,  $[\alpha]_D^{21} + 6.2^\circ$  (*c* 2, MeOH) [lit. values <sup>4</sup> m.p. 133.5–134°,  $[\alpha]_D + 16.6^\circ$  MeOH] <sup>1</sup>H NMR data ( $CDCl_3$ ,  $\delta$ -values) 7.45 (*d*,  $J$  1.0 Hz, H-3), 5.85 (*m*, H-7), 4.75 (*br s*, 2H, H-10), 3.75 (*s*, 3H,  $OCH_3$ ), 3.16 (*m*, H-5), and 2.0–2.15 ppm (15H, OAc)

On repeated chromatography on columns of silica gel [solvents, BuOH–MeOH– $H_2O$ , 7:1:3, and EtOAc–PrOH– $H_2O$ , 5:3:2] fraction *B* yielded, apart from geniposide (230 mg), another component (blue with  $SbCl_5$ ) which, after acetylation and preparative TLC (Bz–EtOAc–MeOH, 3:1:1), afforded monotropein penta-acetate (32 mg), m.p. 168–170°,  $[\alpha]_D^{21} - 92^\circ$  (*c* 0.8, EtOH) [lit. values m.p. 173–174.5°, <sup>5</sup> 165.9–167.7°  $[\alpha]_D^{18} - 82.5^\circ$  (*c* 0.8, EtOH), <sup>5</sup>  $[\alpha]_D^{23} - 94.25^\circ$  (*c* 1.08, EtOH)<sup>6</sup>], exhibiting an <sup>1</sup>H NMR spectrum identical with that recorded <sup>6</sup>

Though new to Cornaceae, monotropein has been previously encountered in a number of families, geniposide solely within Rubiaceae. Their joint appearance in *Cornus suecica*, however, seems unprecedented.

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<sup>4</sup> INOUE, H., ARAI, T. and MIYOSHI, Y. (1964) *Chem. Pharm. Bull.* **12**, 888.

<sup>5</sup> STICHER, O. (1971) *Pharm. Acta Helv.* **46**, 121.

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Phytochemistry, 1973, Vol. 12, pp. 2066 to 2067. Pergamon Press. Printed in England.

## NAPHTHAQUINONES FROM *DIOSPYROS* AND *EUCLEA* SPECIES

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**Key Word Index**—*Diospyros*, *Euclea*, Ebenaceae, naphthaquinones, euclein, isodiospyrin, 7-methyljuglone

Nineteen species of the Ebenaceae are known to occur in Rhodesia,<sup>1</sup> some of which have previously been examined, and the presence of naphthaldehydes,<sup>2</sup> and mono- and binaphthaquinones<sup>3,5</sup> reported. Our interest in chemical plant taxonomy has led to a study of the hexane extracts of the stems of a further seven locally occurring species.

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<sup>1</sup> ANON. (1893/1966) *Index Kewensis*, Oxford University Press, Oxford, WHITE, F., personal communication.

<sup>2</sup> HARPER, S. H., KEMP, A. D. and TANNOCK, J. (1970) *J. Chem. Soc. C*, 626.

<sup>3</sup> FERREIRA, M. A., COSTA, A. C. and ALVES, CORREIA, A. (1972) *Plant Med. Phytother.* **6**, 32.

<sup>4</sup> VAN DER VUUR, L. M. and GERRITSMAN, K. W. (1973) *Phytochemistry* **12**, 230.

<sup>5</sup> TEZUKA, M., TAKAHASHI, C., KUROYANAGI, M., SATAKE, M., YOSHIHARA, K. and NATORI, S. (1973), *Phytochemistry* **12**, 175, and references therein.

*Plant Diospyros kirkii* Hiern (voucher No Orpen 6/73\*) *Source* Hartley district  
*Present work Stem* Hexane extract contained no naphthalene or naphthaquinone derivatives

*Plant Diospyros mespiliformis* Hochst ex A DC (voucher No Orpen 3/73) *Source* Hartley district Umfuli river *Uses* Edible fruit, heavy fine-grained timber *Previous work* On bark <sup>6</sup> *Present work Stem* Hexane extract contains no naphthalene or naphthaquinone derivatives

*Plant Diospyros natalensis* subsp *nummularia* (Brenan) F White (voucher No Orpen 2/73) *Source* Hartley district, Umfuli river, *Present work Stem* Hexane extract contains no naphthalene or naphthaquinone derivatives

*Plant Diospyros senensis* Klotzsch (voucher No Guy 2093) *Source* Mana pools district  
*Present work Stem* Hexane extract contains no naphthalene or naphthaquinone derivatives

*Plant Diospyros whyteana* (Hiern) F White (voucher No Orpen 7/73) *Source* Hartley district *Present work Stem* Hexane extract contains isodiospyrin and 7-methyljuglone

*Plant Euclea divinorum* Hiern (voucher No Orpen 5/73) *Source* Marandellas district  
*Uses* Edible fruit *Present work Stem* Hexane extract contains no naphthalene or naphthaquinone derivatives

*Plant Euclea natalensis* A DC (voucher No Orpen 4/73) *Source* Hartley district *Uses* Root Toothache and headache remedy *Present work† Stem* Hexane extract contains euclein,<sup>7</sup> isodiospyrin, and 7-methyljuglone

Previous work on *Euclea* species<sup>4</sup> had revealed the presence of naphthaquinones only in the roots and fruit, and not in the stem extracts The results above, and those of Alves *et al* show that this is not true for the genus as a whole

#### EXPERIMENTAL

The Dried stems were stripped of their bark, chipped and milled (Wyllie mill, 60 mesh) The hexane extracts (soxhlet) were concentrated *in vacuo*, and were examined by preparative TLC on kieselgel GF<sub>254</sub> nach Stahl (Merk) with CHCl<sub>3</sub> All bands were examined by NMR and those showing naphthaquinonoid character were further purified by crystallization from aq MeOH and light petrol (140–160°) All species examined contained triterpenes and fatty material which were not further examined Euclein, isodiospyrin and 7-methyljuglone were identical in all respects (m p, m m p IR, UV, NMR, and TLC) with authentic samples

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\* Voucher specimens are deposited at the Government Herbarium, Salisbury, Rhodesia, and specimens will also be at The Royal Botanic Gardens, Kew, England, Centro Botanico, Lisbon, Portugal, and The Botanical Institute, Pretoria, South Africa

† After the isolation of these compounds the author was informed by Professor A Correia Alves that his group has also worked on this tree, with similar results

<sup>6</sup> FALLAS, A L and THOMSON, R H (1968) *J Chem Soc C*, 2279

<sup>7</sup> FERREIRA, M A, COSTA, A C, ALVES, CORREIA, A and LOBES, M H (1973) *Phytochemistry* 12, 433