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## NAPHTHOQUINONES OF *EUCLEA* AND *DIOSPYROS* SPECIES

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**Key Word Index**—*Diospyros*; *Euclea*; Ebenaceae; naphthoquinones; 7-methyl-juglone; diospyrin; isodiospyrin; mamegakinone; bisisodiospyrin; 2,2'-binaphthyl-1,1'-quinone.

The naphthoquinone producing family Ebenaceae is represented in southern Africa by several species of the genera *Euclea* and *Diospyros*.<sup>1</sup> Our interest in the naphthoquinones of natural origin, has lead to a phytochemical survey of several of these species. This report deals with the results which we obtained with five new species, with larger samples of three species which we have previously reported on,<sup>2</sup> and two species (*E. natalensis* and *E. divinorum*) of which only the stem bark has been the subject of investigation.<sup>3</sup>

It should be noted that when a preliminary TLC-check of concentrated chloroform extracts was made, only the major naphthoquinones (one to four) could be observed (visual detection, colour change with OH<sup>-</sup>), whilst PLC of these same extracts revealed a much more complex naphthoquinone composition (six or more). Stem extracts of three *Euclea* species and the extracts of green fruit, however, do not show any trace of naphthoquinone constituents, not even with PLC. The compounds given in Table 1 are the major naphthoquinones.

Since photochemical modification of certain naphthoquinones have been noted<sup>4</sup> the present investigation was carried out in semi-darkness to minimize the possibility of artefact formation.

### EXPERIMENTAL

CHCl<sub>3</sub> extracts of the dried plant material were concentrated *in vacuo* and subjected to PLC on silicagel with CHCl<sub>3</sub> as mobile phase. The blue and orange/red zones (colour change with OH<sup>-</sup> to blue/purple) were separately extracted and purified by PLC on silicagel with CHCl<sub>3</sub> and/or CHCl<sub>3</sub>:cyclohexane (7:3). The concentration of a few naphthoquinones was too small (due to limited plant material) to risk a further loss by purification and could only be identified by co-TLC with authentic reference substances. Purified compounds were initially identified by co-TLC with reference substances, identification was confirmed with UV and NMR spectroscopy (CDCl<sub>3</sub>, 60 MHz; in the case of small amounts and/or poor solubility, 100 MHz with Fourier transform was used).

NMR spectrum of the blue coloured bn-quinone:  $\delta$  (CDCl<sub>3</sub> + TMS, 100 MHz with Fourier transform): 2.40 (s; 6 + 6' Me), 4.05 (s; 4 + 4' OMe), 6.83 (s, br; 7 + 7' H), 7.14 (s, br; 5 + 5' H), 8.48 (s; 3 + 3' H), 13.52 (s; 8 + 8' OH).

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<sup>1</sup> DEWINTER, B. (1963) *Flora of Southern Africa* (DYER, R. A., CODD, L. E. and RYCROFT, H. B., eds.), Vol. 26, pp. 54-99, Government Printer, Pretoria, South Africa.

<sup>2</sup> VAN DER VIJVER, L. M. and GERRITSMAN, K. W. (1973) *Phytochemistry* **12**, 230.

<sup>3</sup> TANNOCK, J. (1973) *Phytochemistry* **12**, 2066.

<sup>4</sup> WERBIN, H. and STROM, E. T. (1968) *J. Am. Chem. Soc.* **90**, 7296.

TABLE 1. NAPHTHOQUINONES FROM EBENACEAE

Plant	Root	Stem	Fruit
<i>D. natalensis</i> (Harv.) Brenan subsp. <i>natalensis</i> F. White (specimen 6406/1a) S1*	bn-quinone† 7-Me-juglone†‡ diospyrin	bn-quinone‡ 7-Me-juglone‡ diospyrin	
<i>D. inhacaensis</i> F. White (specimen 6406/2) S1	diospyrin isodiospyrin	7-Me-juglone diospyrin isodiospyrin	
<i>D. rotundifolia</i> Hiern (specimen 6406/6) S1	7-Me-juglone	7-Me-juglone diospyrin	
<i>D. austro-africana</i> DeWinter var. <i>rubriflora</i> (DeWinter) DeWinter (specimen 6406/8d) S2	bn-quinone 7-Me-juglone diospyrin isodiospyrin	diospyrin	ripe fruit: isodiospyrin bisodiospyrin
<i>D. lycioides</i> Desf. subsp. <i>lycioides</i> DeWinter (specimen 6406/15a) S3	isodiospyrin	isodiospyrin	ripe fruit: isodiospyrin bisodiospyrin
<i>D. lycioides</i> Desf. subsp. <i>guerkei</i> (Kuntze) DeWinter (specimen 6406/15c) S1	bn-quinone diospyrin isodiospyrin	diospyrin isodiospyrin	green fruit: no naphthoquinones
<i>E. natalensis</i> A. DC. (specimen 6404/8) S1	bn-quinone‡ 7-Me-juglone mamegakinone diospyrin	7-Me-juglone‡ diospyrin§	
<i>E. crispa</i> (Thunb.) Guerin var. <i>crispa</i> DeWinter (specimen 6404/9a) S3	bn-quinone 7-Me-juglone diospyrin isodiospyrin	no naphtho- quinones	ripe fruit: diospyrin
<i>E. divinorum</i> Hiern (specimen 6404/11) S4	7-Me-juglone mamegakinone diospyrin isodiospyrin	no naphtho- quinones	green fruit: no naphthoquinones
<i>E. schimperi</i> (A. DC.) Dandy var. <i>daphnoides</i> (Hiern) DeWinter (specimen 6404/14b) S4	7-Me-juglone mamegakinone diospyrin isodiospyrin	no naphtho- quinones	ripening fruit: traces of naphthoquinones

Identification of plant material by the National Herbarium, Pretoria, South Africa. Voucher specimens are deposited in the herbarium of the Pharmacy Laboratory, University, Potchefstroom, South Africa.

\* Source of plant material. S1, coastal region, north-eastern Natal; S2, mountain slopes of the Drakensberg, Natal; S3, Potchefstroom district, Transvaal; S4, Empangeni district, Natal.

† bn-Quinone: 8,8'-dihydroxy-4,4'-dimethoxy-6,6'-dimethyl-2,2'-binaphthyl-1,1'-quinone, 7-Me-juglone: 7-methyl-juglone.

‡ Due to limited material, the partially purified substance was identified only by co-TLC with authentic reference samples.

§ Tannock,<sup>3</sup> found euclein to be present in stem bark extracts of this tree, but according to Prof. A. Correia Alves, euclein is identical to diospyrin (private communication).