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## EBENACEAE

# IDENTIFICATION OF METHYLNAPHTHAZARIN IN *DIOSPYROS* SPECIES

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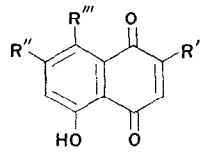
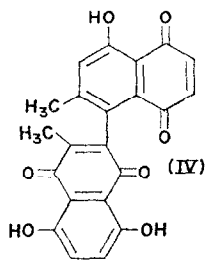
**Key Word Index**—*Diospyros lycioides*; *D. heterotricha*; Ebenaceae; methylnaphthazarin.

Naphthoquinone pigments occur frequently in species of *Diospyros* and the list of such compounds isolated includes several monomers, a number of dimers, a trimer, and a tetramer.[1] Until recently all the dimers described were derivatives of 7-methyljuglone (I) or 2-methyljuglone (II), but recently a team of Japanese researchers identified a new dimer, which they designated 8′-hydroxyisodiospyrin (IV).[2] This substance is the first example of a dimer derived from 7-methyljuglone and methylnaphthazarin (III) and it was also identified by us in the root bark of *Diospyros lycioides* subsp. *sericea* and *D. heterotricha*, as will be described in a subsequent publication. Although 7-methyljuglone has been isolated from several species of *Diospyros*, methylnaphthazarin has not hitherto been identified in plants belonging to this genus. However, we have now isolated a quinone pigment from the root bark of *D. lycioides* subsp. *sericea* (Bernh *ex* Krauss) de Winter and *D. heterotricha* (B. L. Burtt) F. White which proved to be identical with methylnaphthazarin.



(I) $R' = H, R'' = CH_3, R''' = H$
(II) $R' = CH_3, R'' = H, R''' = H$
(III) $R' = CH_3, R'' = H, R''' = OH$



(IV)

Methylnaphthazarin was isolated by chloroform extraction and was purified by TLC and column chromatography (silicic acid). Crystallization from benzene afforded red crystals, m.p. 178–180°; $\lambda_{max}$ (MeOH) 274, 482, 510, 546 nm; $\lambda_{max}$ (MeOH/$OH^-$) 298, 578, 616 nm; $\nu_{max}$ (KBr) 1610, 1580, 1452, 1405, 1370, 1310, 1265, 1240 sh, 1210, 1170, 1030, 1130, 1010, 940, 910, 905, 870, 850, 820, 790, 750 $cm^{-1}$; $\tau$ ($CDCl_3$) 7·76 (III, $CH_3$), 3·11 (III, 3H), 2·82 (III, 6H and 7H); MS (intensities as indicated) *m/e* 204 (100), 203 (8), 189 (15), 176 (8), 148 (7), 147 (13), 108 (15), 102 (6), 91 (8), 69 (6), 65 (7), 58 (15), 57 (6), 55 (8), 53 (12), 52 (8) and 51 (10). Found: C, 64·51; H, 4·45%; M, 204. $C_{11}H_8O_4$ requires: C, 64·70;

[1] R. H. THOMSON, *Naturally Occurring Quinones*, Academic Press, London (1971).
[2] K. YOSHIHIRA, M. TEZUKA, C. TAKAHASHI and S. NATORI, *Chem. Pharm. Bull.* **19**, 851 (1971).

H, 3·94%; M, 204. All these characteristics agree very well with those of a sample of methylnaphthazarin previously isolated by us from *Euclea lanceolata*[3] and they prove that both substances are the same compound.

The plants of *D. lycioides* were collected near Sá da Bandeira, Angola and herbarium specimens are in the Institute for Scientific Research, Luanda: *D. heterotricha* was collected in Salazar, Angola and specimens are in the University of Coimbra.

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[3] A. CORREIA ALVES, A. CRUZ COSTA and M. A. FERREIRA, *Garcia Orta Lisbon* **17**, 299 (1969).

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## GERANIACEAE

# STEROLS AND TRITERPENES OF *PELARGONIUM HORTORUM*

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**Key Word Index**—*Pelargonium hortorum*; Geraniaceae; sterols; triterpenes; sitosterol; β-amyrin.

*Plant. Pelargonium hortorum. Previous work.* An unidentified sterol, m.p. 136–137°[1] and monoterpene biosynthesis.[2]

*Present work.* In conjunction with investigations on the translocation of sterols and triterpenes in plants it was necessary to identify the principal nonsaponifiable constituents of the geranium. This plant is particularly adaptable for laboratory experiments throughout the year, being readily accessible in greenhouse culture. The completely dried flowering plants (385 g) were extracted exhaustively with hot EtOH. The extract was distilled to dryness. A neutral fraction (5 g) was obtained by mild treatment with KOH followed by extraction with $Et_2O$. The neutral fraction was chromatographed on alumina and separated into hydrocarbons, steryl and triterpene esters, free triterpenes and free sterols. Of the material eluted the esterified sterols (80 mg) accounted for 9% while the free sterols (785 mg) accounted for 91%. The ester fraction was saponified in 15% KOH (benzene–$H_2O$–EtOH

[1] F. ESTERNER and K. H. LISHEN, *Arch. Pharm.* **295**, 823 (1962).
[2] A. N. CAMPBELL, *Diss. Abs.* **22**, 4170 (1960).