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EBENACEAE

A NEW NAPHTHALDEHYDE FROM THE HEARTWOOD OF *DIOSPYROS MELANOXYLON*

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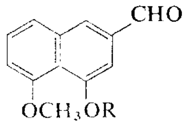
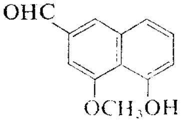
Abstract—A new compound isolated from the heartwood of *Diospyros melanoxylon* Roxb. has been shown to be 1-hydroxy-8-methoxy-3-naphthaldehyde.

SEVERAL naphthols and naphthaquinones were isolated and characterised earlier in this laboratory from the heartwood of *Diospyros melanoxylon* Roxb. (Ebenaceae).[1] Fraction 8 of the light petroleum extract (see Table 1)[1] has now been obtained as pale yellow crystals, m.p. 89–90° by vacuum sublimation. It analysed for $C_{12}H_{10}O_3$ (mol. wt., 202 by mass spectrum). Its u.v. spectrum resembles that of β-naphthaldehyde and its i.r. spectrum in KBr showed a hydroxyl peak at 3325 cm^{-1}. This is indicative of a perimethoxynaphthol; (such hydroxy groups give a broad i.r. band at *ca.* 3400 cm^{-1} in $CHCl_3$;[1,2] in KBr, a sharper peak at somewhat lower frequency is to be expected; thus 1-hydroxy-3-methyl-8-methoxynaphthalene which gives a broad band at 3400 cm^{-1} in $CHCl_3$,[1] gives a sharper peak at 3355 cm^{-1} in KBr). Peaks at 1685 cm^{-1} and at 2700 cm^{-1} show the presence of an aromatic aldehyde group.

Its NMR spectrum* suggests structure I or II: OCH_3 at 4·00; perimethoxynaphthol at 9·34 (D_2O exchangeable); CHO at 10·01; α-naphthalenic proton doublet at 7·69 *meta* coupled ($J = 1{\cdot}5$ c/s) with a β-proton doublet at 7·29; a shielded β-proton quartet at 6·86 forming part of an ABB′ or AB_2 system, the other two protons being spread over from 7·34 to 7·56.





(I) R = H
(III) R = $COCH_3$
(IV) R = H and CH_2OH instead of CHO

(II)

On acetylating the aldehyde, the two meta coupled protons shifted downfield to 7·51 and 8·15 from 7·29 and 7·69 respectively. The phenolic hydroxyl group must, therefore, be in the

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* Chemical shifts in δ = ppm in $CDCl_3$.

[1] G. S. SIDHU, A. V. B. SANKARAM and S. MAHMOOD ALI, *Indian J. Chem.* **6**, 681 (1968).

[2] A. G. BROWN, J. C. LOVIE and R. H. THOMSON, *J. Chem. Soc.* 2355 (1965).

same ring as the aldehyde group (Structure I). Further support for Structure I was provided by sodium borohydride reduction of acetate III to the known alcohol IV.[3,4]

It is interesting to note that this naphthaldehyde occurs with the corresponding methylnaphthalene in the same plant. Two similar naphthaldehydes have been isolated earlier from *Diospyros ebenum*[5] but the corresponding naphthalenes occur in *D. celebica.*[2]

EXPERIMENTAL

Isolation of 1-*Hydroxy*-8-*methoxy*-3-*naphthaldehyde* (I)

The traces of a brown impurity in fraction 8 (Table 1)[1] could not be removed by repeated column chromatography or recrystallisation. Vacuum sublimation of this compound at 80°/0·15 mm yielded a pale yellow crystalline solid m.p. 89–90° (0·002%). (Found: C, 71·4; H, 4·98; $C_{12}H_{10}O_3$ required: C, 71·28; H, 4·99%.) $\lambda_{max}^{Isooctane}$ 224·3, 259, 301·2, 317·5, 366·3, 384·6 (log ϵ 4·36, 4·65, 3·77, 3·77, 3·90, 3·94). Mass spectrum: m/e 204, 1·60%; 203, 13·1%; 202, 100% (M^+); 188, 3·9%; 187, 24·7%; 159, 17·8%; 158, 3·5%; 131, 8·9%; 115, 3·8%; 103, 2·2% and 102, 4·2%.

The acetate (III) was crystallised from ether and sublimed as white crystals m.p. 134–5°. (Found: C, 67·8; H, 4·85; $C_{14}H_{12}O_4$ required: C, 68·84; H, 4·95%.) $\lambda_{max}^{Isooctane}$ 216, 259, 285·7, 296·7, 311·5, 353·4, 371·7 (log ϵ 4·46, 4·78, 3·89, 3·89, 3·83, 3·89, 3·89), ν_{max}^{KBr} 2740, 1680 (aromatic aldehyde); 1740 (—$OCOCH_3$). NMR spectrum: 1—$OCOCH_3$, 2·35 (s); 2-H, 7·51 (d); 4-H, 8·15 (d) ($J_{2,4} = J_{4,2} = 1{\cdot}5$ c/s); 3-CHO, 10·09 (s); 5,6 and 7-H, 6·92–7·66 (m); 8-OCH_3, 3·91 (s).

1-*Hydroxy*-3-*hydroxymethyl*-8-*methoxynaphthalene* (IV)

10 mg of the acetate (III) reduced with 120 mg of $NaBH_4$ in methanol yielded IV; the crude product showed the following peaks in the NMR spectrum: 1-OH; 9·27 (s) (exchanged with D_2O); 3-$CH_2\underline{OH}$ 1·92 (broad, exchanged with D_2O); 3-$\underline{CH_2}OH$, 4·74 (singlet, broad), 8-OCH_3, 4·03 (s); five aromatic protons between 6·66–7·62 (m).

After further purification by column chromatography over silica gel and recrystallisation from ether a pale brown solid m.p. 131–2°, 3 mg, was obtained. ν_{max}^{KBr} 3350 (—OH, broad but sharpened at this frequency). Reported m.p. 135°.[4]

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Note Added in Proof—After submission of this paper, the naphthaldehyde corresponding to structure II has been isolated from Diospyros quiloensis by S. H. HARPER *et al., J. Chem. Soc.* (c), 626 (1970).

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[3] T. J. KING, private communication.

[4] B. O. HANDFORD and W. B. WHALLEY, *J. Chem. Soc.* 3896 (1963).

[5] A. G. BROWN and R. H. THOMSON, *J. Chem. Soc.* **4292** (1965).