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SHORT COMMUNICATION

NAPHTHOIC ACID DERIVATIVES FROM *DIOSPYROS EBENUM*[1]

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Abstract—6-Hydroxy-4,5-dimethoxy-2-naphthoic acid and its methyl ester have been isolated from *Diospyros ebenum Koen.*

From the heartwood of the valued timber ebony, *Diospyros ebenum* Koen (Ebenaceae), Brown and Thomson[2] isolated and characterized 4,5,6-trimethoxy-2-naphthaldehyde and 6-hydroxy-4,5-dimethoxy-2-naphthaldehyde. We have now isolated the acid and methyl ester corresponding to the latter aldehyde from the heartwood of this tree growing in South India.

Extraction by cold percolation of the powdered heartwood (4·0 kg) with petrol. ether (60–80°) and recrystallization of the product from methanol yielded an ester "A" as yellow needles, m.p. 107–108° (2·4 g). Subsequent extraction of the heartwood powder with cold ethanol and concentration of the extract yielded a crystalline residue (32 g) which, after repeated crystallization from benzene–methanol, yielded light-brown needles of an acid "B", m.p. 264–266° (2·4 g). Ester A, $C_{14}H_{14}O_5$[3] (M^+, 262); ν_{max} 3450, 1705, 1282, 1248, 1190, 813, 769, 700 cm^{-1}, formed an acetate, $C_{16}H_{16}O_6$, m.p. 131–132°, a methyl ether, $C_{15}H_{16}O_5$, m.p. 116–118°, and yielded acid B on hydrolysis with ethanolic KOH. Acid B, $C_{13}H_{12}O_5$ (M^+, 248); λ_{max} 242, 246·5, 252, 258, 262·5, 319, 332 and 347·5 nm (ϵ, 33240, 35770, 33000, 29620, 24440, 9150, 8750 and 7810 respectively); ν_{max} 1681 cm^{-1}, formed an acetate, $C_{15}H_{14}O_6$, m.p. 234–236°, a methyl ether methyl ester identical to the methyl ether of A and a methyl ether ethyl ester, m.p. 76–78°.

A consideration of the NMR spectra[4] of A, its acetate, its methyl ether and the methyl ether ethyl ester of B indicated that A had one acetylatable OH and three OCH_3 groups, one of which was an ester OCH_3. The four aromatic protons in the molecule gave rise to two pairs of doublets. One pair centred at τ 2·30 and τ 2·68 (J, 9·0 cps) indicated *ortho* coupling and the other pair centred at τ 1·8 and τ 2·52 (J, 1·6 cps) indicated *meta* coupling. Oxidation of A (1·2 g) with conc. HNO_3 at room temperature for 30 min yielded 6-methoxytrimellitic acid,[5]

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[1] Communication No. 1306 from the Central Drug Research Institute.

[2] A. G. Brown and R. H. Thomson, *J. Chem. Soc.* 4292 (1965).

[3] C and H analysis given in Table 1. U.v. and i.r. spectra determined in EtOH and KBr respectively. Uncorrected capillary m.p.s reported.

[4] 60 Mcs spectra in $CDCl_3$ with TMS as internal standard.

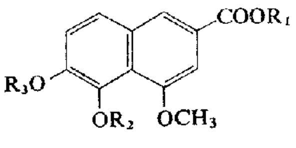
[5] T. Posternak, *Helv. Chim. Acta* **23**, 1046 (1940).

$C_{10}H_8O_7$ (M^+, 240), m.p. 248–250° (0·7 g), which formed a trimethyl ester, m.p. 152–154°, whose NMR spectrum only had signals for four OCH_3 and two *meta*-coupled aromatic protons (doublets centred at τ 1·75 and τ 2·22, J, 1·5 cps).

TABLE 1. ANALYTICAL DATA

Compound	Analysis
1. Ester A (methyl 6-hydroxy-4,5-dihydroxy-2-naphthoate)	Found: C, 64·39; H, 5·68. $C_{14}H_{14}O_5$ required: C, 64·11; H, 5·34%.
2. A acetate (methyl 6-acetoxy-4,5-dimethoxy-2-naphthoate)	Found: C, 63·68; H, 5·58. $C_{16}H_{16}O_6$ required: C, 63·16; H, 5·26%.
3. A methyl ether (methyl 4,5,6-trimethoxy-2-naphthoate)	Found: C, 65·43; H, 6·02. Calc. for $C_{15}H_{16}O_5$: C, 65·23; H, 5·80%.
4. Hydrolysis product of A methyl ether (4,5,6-trimethoxy-2-naphthoic acid)	Found: C, 64·38; H, 5·62. Calc. for $C_{14}H_{14}O_5$: C, 64·11; H, 5·34%.
5. Acid B (6-hydroxy-4,5-dimethoxy-2-naphthoic acid)	Found: C, 62·96; H, 5·21. $C_{13}H_{12}O_5$ required: C, 62·89; H, 4·84%.
6. B acetate (6-acetoxy-4,5-dimethoxy-2-naphthoic acid)	Found: C, 62·12; H, 4·94. $C_{15}H_{14}O_6$ required: C, 62·07; H, 4·83%.
7. B methyl ether ethyl ester (ethyl 4,5,6-trimethoxy-2-naphthoate)	Found: C, 65·96; H, 6·04. $C_{16}H_{18}O_5$ required: C, 66·20; H, 6·21%.
8. Oxidation product of B (6-methoxytrimellitic acid)	Found: C, 49·86; H, 3·62. Calc. for $C_{10}H_8O_7$: C, 50·00; H, 3·33%.

On the basis of the data outlined, A and B can be assigned structures I (R_1 = Me) and I (R_1 = H) respectively with either R_2 or $R_3 = CH_3$. In confirmation, the methyl ether of A was identified as methyl 4,5,6-trimethoxy-2-naphthoate[2] by comparison with an authentic sample. The location of the remaining hydroxyl and methoxyl functions at positions 6 and 5 respectively follows from a consideration of the NMR spectra. Thomson and his co-workers[6] have shown that whereas the hydroxyl proton signal in 1-methoxy-2-naphthols is located around τ 4·0, it is shifted downfield to the τ 0·75 region in the spectra of 8-methoxy-1-naphthols, possibly on account of hydrogen bonding with the *peri* methoxyl oxygen atom. In the spectrum of ester A the hydroxyl proton gives rise to a singlet at τ 3·48; a signal not seen in the spectra of the acetate and methyl ether. Ester A is, therefore, methyl 6-hydroxy-4,5-dimethoxy-2-naphthoate (I, $R_1 = R_2 = CH_3$; R_3 = H) and acid B, 6-hydroxy-4,5-dimethoxy-2-naphthoic acid (I, $R_2 = CH_3$; $R_1 = R_3$ = H).



(I)

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