792. Ebenaceae *Extractives. Part II.*[1] *Naphthaldehydes from* Diospyros ebenum *Koen*

By A. G. Brown and R. H. Thomson

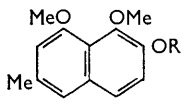
The two β-naphthaldehydes (II; R = H and Me) have been isolated from the heartwood of *Diospyros ebenum*. Betulinic acid is also present.

The ebony which comprises the dense, black heartwood of *Diospyros ebenum* has not been examined previously although 2-methyljuglone has been found in the bark and is also present, together with 7-methyljuglone, in the leaves and fruit.[2]

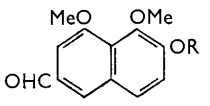
Extraction of the heartwood yielded a complex mixture from which betulinic acid was obtained by sublimation, whilst thin-layer chromatography led to the isolation of two pale yellow, crystalline solids, $C_{13}H_{12}O_4$, m. p. 165°, and $C_{14}H_{14}O_4$, m. p. 125°. Chemical tests and infrared and nuclear magnetic resonance (n.m.r.) data showed that both compounds were aromatic aldehydes and, from their ultraviolet absorption, they were apparently naphthalene derivatives. Moreover, the infrared spectrum of the compound $C_{14}H_{14}O_4$, which has three *O*-methyl groups, showed a very close resemblance, in the 1100—680-cm.$^{-1}$

[1] Part I, *J.*, 1965, 2355.
[2] R. G. Cooke and H. Dowd, *Austral. J. Sci. Res.*, 1952, **5***A*, 760.

region, to that of macassar III (I; R = Me) isolated from the heartwood of *D. celebica*.[1] This suggests that the compound, m. p. 125°, is the trimethoxynaphthaldehyde (II; R = Me) which is consistent with its n.m.r. spectrum and was established, later, by synthesis (see below). The compound, m. p. 165°, contains two *O*-methyl groups, it forms a deep yellow solution in aqueous sodium hydroxide, and on methylation gives the aldehyde (II; R = Me), m. p. 125°. It is therefore a hydroxydimethoxynaphthaldehyde, and since the hydroxyl stretching frequency lies at 3510 cm.$^{-1}$ (in $CHCl_3$) and the hydroxyl proton resonance appears at τ 3·38 (in $CDCl_3$) it is clearly an *ortho*-methoxynaphthol and not a *peri*-methoxynaphthol (see Part I [1]). The phenolic aldehyde is therefore (II; R = H), the two aldehydes (II; R = H and Me) from *D. ebenum* bearing the same relationship to each other as macassar II and III (I; R = H and Me) from *D. celebica*.[1]



(I)



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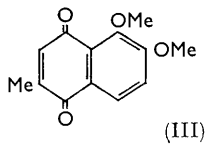
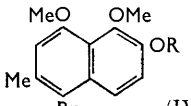
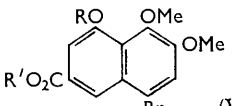


(III)



(IV)



(V)

Synthesis.—Two unsuccessful attempts were made to convert macassar III (I; R = Me) into the aldehyde (II; R = Me). Direct oxidation of a methyl side-chain to an aromatic aldehyde has been effected with persulphate in the presence of silver ions [3] but in our case the product was a yellow dimethoxymethylnaphthaquinone, $C_{13}H_{12}O_4$. (It was obtained in much better yield in the absence of silver ions.) Comparison of the light absorption of the new quinone ($\lambda_{max.}$ 262, 393 mμ, log ε 4·2, 3·48) with that of 5,7-dimethoxy-2-methyl-1,4-naphthaquinone ($\lambda_{max.}$ 270, 408 mμ, log ε 4·25, 3·6) [4] suggests that it has structure (III). This was confirmed by the n.m.r. spectrum which revealed the presence of two *ortho*-coupled protons at τ 2·73 and 2·09 (J = 9 c./sec.).

A proposed synthesis of the aldehyde (II; R = Me) *via* side-chain bromination of macassar III (I; R = Me) with *N*-bromosuccinimide failed at the outset as the bromine atom entered a nuclear position. This was evident from the n.m.r. spectrum which showed that only three aromatic protons were present, two of them occupying *ortho*-positions. Bromination had therefore occurred *ortho* to the methyl group, most probably at C-5 (IV). The same compound was obtained by treatment of macassar II (I; R = H) with bromine, followed by methylation.

The trimethoxynaphthaldehyde (II; R = Me) was finally synthesised as follows: Stobbe condensation of 6-bromoveratraldehyde with diethyl succinate, followed by cyclisation with acetic anhydride–sodium acetate, gave the bromo-diester (V; R = Ac, R′ = Et). Hydrogenolysis over Raney nickel, hydrolysis, and methylation then led to methyl 4,5,6-trimethoxy-2-naphthoate which was reduced to the alcohol (I; R = Me, CH_2OH in place of Me) with lithium aluminium hydride. Oxidation of this alcohol [also obtained by treatment of the bromotrimethoxy-ester (V; R = R′ = Me) with lithium aluminium hydride] with activated manganese dioxide gave 4,5,6-trimethoxy-2-naphthaldehyde (II; R = Me) identical with the alkali-insoluble aldehyde extracted from *D. ebenum*.

Experimental

N.m.r. spectra were measured in $CDCl_3$ on a Varian A60 spectrometer using $SiMe_4$ as internal standard.

[3] R. G. R. Bacon and J. R. Doggart, *J.*, 1960, 1335.
[4] H. Schmid and M. Burger, *Helv. Chim. Acta*, 1952, **35**, 928.

Extraction of Diospyros ebenum *Heartwood.*—Ebony shavings (150 g.) were exhaustively extracted (Soxhlet) with n-heptane (1·5 l.); the pale yellow solution was filtered and evaporated to dryness leaving a yellow solid (0·65 g.). Subsequent extraction with ether (1·5 l.) gave a further 0·14 g. of chomatographically identical material. A sample (50 mg.), when heated *in vacuo*, gave a yellow oil at 130°/0·05 mm. and a solid, m. p. 312—315°, which sublimed at 200°/0·05 mm. and was identical (mixed m. p., i.r.) with betulinic acid. The main bulk of the extract was chromatographed in chloroform on layers of Silica Gel G (Merck) (eighty-seven 8 × 8 in. plates) when ten bands developed. Two principal bands (R_F 0·44 and 0·60), which fluoresced yellow in ultraviolet light, were removed mechanically and extracted, separately, with hot methanol, filtered, and taken to dryness. The residue from band 7 (R_F 0·60) was refluxed with n-heptane, cooled, filtered, and evaporated leaving a pale yellow solid (90 mg.) which crystallised from n-heptane to give 4,5,6-*trimethoxy*-2-*naphthaldehyde* as pale yellow plates, m. p. 125°; $\nu_{max.}$ (KBr) 1685 cm.$^{-1}$; $\lambda_{max.}$ (EtOH) 262, 330, 367 mμ (log ε 4·33, 3·77, 3·88); the n.m.r. spectrum showed singlet peaks (3 protons) at τ = 6·08, 5·98, 5·94 (OCH_3), doublets (2 protons) at 2·74, 2·19 (J = 1·5 c./sec.) (*m*-ArH) and 2·60, 2·30 (J = 11 c./sec.) (*o*-ArH) and a singlet (one proton) at 0·02 (CHO) (Found: C, 68·3; H, 5·8; OMe, 37·4. $C_{14}H_{14}O_4$ requires C, 68·3; H, 5·75; OMe, 37·8%). The compound gave positive tests with Brady's and Tollens's reagents. By a similar procedure band 6 (R_F 0·44) yielded a solid (150 mg.) which crystallised from n-heptane to give 6-*hydroxy*-4,5-*dimethoxy*-2-*naphthaldehyde* as pale yellow needles, m. p. 165°, $\nu_{max.}$ (KBr) 3425, 1680 cm.$^{-1}$, $\nu_{max.}$ ($CHCl_3$) 3510 cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 255, 261, 330, 365 mμ (log ε 4·21, 4·23, 3·76, 3·85) (Found: C, 67·0; H, 5·5; OMe, 26·2. $C_{13}H_{12}O_4$ requires C, 67·25; H, 5·25; OMe, 26·7%). It gave positive reactions with Brady's and Tollens's reagents and formed a deep yellow fluorescent solution in aqueous sodium hydroxide. The hydroxyaldehyde (27 mg.) was boiled for 3 hr. with dimethyl sulphate (1 ml.) and anhydrous potassium carbonate (3 g.) in acetone (35 ml.). Working up in the usual way gave the methyl ether as yellow plates. m. p. 124° (from n-heptane), identical (mixed m. p., i.r., R_F) with the trimethoxyaldehyde isolated from band 7.

5,6-*Dimethoxy*-2-*methyl*-1,4-*naphthaquinone* (III).—(*a*) Macassar III (0·46 g.) and potassium persulphate (1·08 g.) were added to 0·01M-silver nitrate solution (20 ml.) at 60—65° and stirred vigorously at 60° for 5 hr. After 30 min. the solution was orange. On cooling, brown polymeric material was filtered off, and the filtrate was extracted with chloroform, dried ($MgSO_4$), and evaporated. The residual orange-brown solid was chromatographed on silica gel. Elution of a yellow band with chloroform gave solid material (0·27 g.) which crystallised from methanol to give 5,6-*dimethoxy*-2-*methyl*-1,4-*naphthaquinone* as yellow needles, m. p. 190° (62·5%), $\nu_{max.}$ (Nujol) 1675, 1655 cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 262, 393 mμ (log ε 4·20, 3·48); the n.m.r. spectrum showed a doublet (3 protons) at τ 7·88 (J = 1·5 c./sec.) (quinone-CH_3), singlets (3 protons) at 6·09, 6·03 (OCH_3), a quadruplet (1 proton) at 3·30 (C=CH), and doublets (2 protons) at 2·73, 2·09 (J = 9 c./sec.) (*o*-ArH) (Found: C, 66·9; H, 5·2; OMe, 26·2. $C_{13}H_{12}O_4$ requires C, 67·25; H, 5·15; OMe, 26·7%). Thin-layer chromatography of the crude product showed the absence of trimethoxynaphthaldehyde.

(*b*) In a similar experiment, omitting the silver nitrate, the yield of quinone was 86%.

1-*Bromo*-4,5,6-*trimethoxy*-2-*methylnaphthalene* (IV; R = Me).—(*a*) Bromine (0·36 g.) in acetic acid (2·5 ml.) was added slowly to a stirred solution of macassar II (0·436 g.) in the same solvent (4 ml.). After 5 min. the solution was poured into water to precipitate the *bromonaphthol* which was collected, dried, and crystallised from light petroleum (b. p. 80—100°) as needles, m. p. 126° (Found: C, 52·4; H, 4·2; Br, 27·3; OMe, 20·6. $C_{13}H_{13}BrO_3$ requires C, 52·8; H, 4·35; Br, 26·9; OMe, 20·9%). Methylation with dimethyl sulphate–potassium carbonate–acetone gave the *methyl ether*, needles, m. p. 87° (from aqueous methanol); the n.m.r. spectrum showed singlet peaks at τ = 7·43 (3 protons) (aryl-CH_3), 6·13 (3 protons) (OCH_3), 6·06 (6 protons) (OCH_3), 3·33 (one proton) (ArH), and doublets (2 protons) at 2·70, 1·97 (J = 10 c./sec.) (*o*-ArH) (Found: C, 54·0; H, 4·6; Br, 24·4; OMe, 31·0. $C_{14}H_{15}BrO_3$ requires C, 54·0; H, 4·8; Br, 25·7; OMe, 29·9%).

(*b*) Macassar III (116 mg.) and *N*-bromosuccinimide (79 mg.) were refluxed in carbon tetrachloride (35 ml.) with a trace of benzoyl peroxide for 4 hr. Working up gave an oil (150 mg.) which solidified. It crystallised from aqueous methanol to give needles, m. p. 85—87° identical with the product obtained as described in (*a*).

Ethyl 4-*Acetoxy*-8-*bromo*-5,6-*dimethoxy*-2-*naphthoate* (V; R = Ac, R′ = Et).—6-Bromoveratraldehyde (24·5 g.) and anhydrous diethyl succinate (20·5 g.) in anhydrous t-butyl alcohol

(150 ml.) were added to a solution of potassium t-butoxide (from 4·3 g. potassium in 120 ml. t-butyl alcohol). The yellow-orange solution was refluxed for ¾ hr., cooled, diluted with water, acidified, and extracted with ether. The ether solution was exhaustively extracted with aqueous sodium hydrogen carbonate; the alkaline solution was acidified and the precipitate taken into ether, dried (Na_2SO_4), and evaporated leaving an orange-yellow solid (34·25 g.). This was refluxed with acetic anhydride (100 ml.) and anhydrous sodium acetate (11 g.) for 5 hr., cooled, poured into water, and left overnight. The gummy mass was extracted with large volumes of ether, dried ($MgSO_4$), and evaporated. The residue was refluxed with light petroleum (b. p. 60—80°) for 4 hr., filtered, and taken to dryness, leaving *ethyl 4-acetoxy-8-bromo-5,6-dimethoxy-2-naphthoate* which crystallised from aqueous ethanol as pale yellow needles, m. p. 134° (10·35 g., 27·3%), $\nu_{max.}$ (Nujol) 1775, 1725 cm.$^{-1}$ (Found: C, 51·3; H, 4·6; Br, 20·9. $C_{17}H_{17}BrO_6$ requires C, 51·4; H, 4·3; Br, 20·15%).

Methyl 8-Bromo-4,5,6-trimethoxy-2-naphthoate (V; R = R′ = Me).—The above diester (0·5 g.) was refluxed in ethanol (120 ml.) containing potassium hydroxide (3 g.) for several hours, and poured into ice-cold 2N-hydrochloric acid to precipitate *8-bromo-4-hydroxy-5,6-dimethoxy-2-naphthoic acid*. It crystallised from methanol as needles, m. p. 304—306° (87%), $\nu_{max.}$ (Nujol) 3300, 1690 cm.$^{-1}$ $\lambda_{max.}$ (EtOH) 252, 332, 345, 355 mμ (log ε 4·44, 3·82, 3·85, 3·84) (Found: C, 47·3; H, 3·6; Br, 24·2. $C_{13}H_{11}BrO_5$ requires C, 47·7; H, 3·35; Br, 24·5%). Methylation with dimethyl sulphate–potassium carbonate–acetone gave *methyl 8-bromo-4,5,6-trimethoxy-2-naphthoate*, needles, m. p. 132—133° (from aqueous methanol) (80%), $\nu_{max.}$ (Nujol) 1720 cm.$^{-1}$ (Found: C, 50·7; H, 4·4; Br, 22·4; OMe, 34·6. $C_{15}H_{15}BrO_5$ requires C, 50·7; H, 4·2; Br, 22·55; OMe, 34·9%).

Methyl 4,5,6-Trimethoxy-2-naphthoate.—A solution of ethyl 4-acetoxy-8-bromo-5,6-dimethoxy-2-naphthoate (0·5 g.) in ethanol (120 ml.) containing 2N-sodium hydroxide (2 ml.) was shaken with Raney nickel (0·2 g.) and hydrogen until 1 mol. was absorbed (¾ hr.). The filtered solution was refluxed with potassium hydroxide (3 g.) for several hours and poured into an excess of 2N-hydrochloric acid to precipitate *4-hydroxy-5,6-dimethoxy-2-naphthoic acid* which crystallised from methanol in needles, m. p. 275—277° (87%), $\nu_{max.}$ (Nujol) 3350, 1680 cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 252, 325, 340, 355 mμ (log ε 4·42, 3·74, 3·74, 3·73) (Found: C, 62·4; H, 4·8; OMe, 25·6. $C_{13}H_{12}O_5$ requires C, 62·9; H, 4·85; OMe, 25·05%). Methylation, as above, gave *methyl 4,5,6-trimethoxy-2-naphthoate*, needles, m. p. 118—120° (from aqueous methanol) (88%), $\nu_{max.}$ 1710 cm.$^{-1}$ (Found: C, 65·2; H, 5·8; OMe, 44·9. $C_{15}H_{16}O_5$ requires C, 65·2, H, 5·8; OMe, 44·9%).

4,5,6-Trimethoxy-2-naphthaldehyde (II; R = Me).—Methyl 8-bromo-4,5,6-trimethoxy-2-naphthoate (0·32 g.) (or methyl 4,5,6-trimethoxy-2-naphthoate) was extracted (Soxhlet) during 7 hr. with boiling ether (300 ml.) containing lithium aluminium hydride (2 g.). After cooling, the excess of reagent was destroyed by careful addition of ethyl acetate (10 ml.) and the mixture poured on to ice and 2N-sulphuric acid, and the ether layer separated. The aqueous phase was extracted with ether and the combined extracts were dried ($MgSO_4$) and evaporated. The residual 2-hydroxymethyl-4,5,6-trimethoxynaphthalene distilled at 150—160° (bath)/0·05 mm. as a pale yellow oil, $\nu_{max.}$ (film) 3400 cm.$^{-1}$. This alcohol (200 mg.) was shaken in carbon tetrachloride (25 ml.) with activated manganese dioxide [5] (2 g.) for 6 hr. Filtration and removal of the solvent left a yellow gum which solidified. It crystallised from n-heptane to give 4,5,6-trimethoxy-2-naphthaldehyde as pale yellow feathery plates, m. p. 123—124° (130 mg.) identical (mixed m. p., u.v., i.r., R_F) with the trimethoxynaphthaldehyde isolated from *D. ebenum* (Found: C, 68·5; H, 5·7; OMe, 38·2. Calc. for $C_{14}H_{14}O_4$: C, 68·3; H, 5·75; OMe, 37·8%).

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THE UNIVERSITY, OLD ABERDEEN, SCOTLAND. [*Received, February 24th*, 1965.]

[5] J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J.*, 1952, 1094.