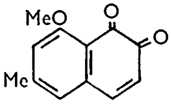
432. Ebenaceae *Extractives. Part I. Naphthalene Derivatives from Macassar Ebony* (Diospyros celebica *Bakh*)

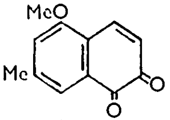
By A. G. Brown, J. C. Lovie, and R. H. Thomson

Macassar II, the principal aromatic extractive from the heartwood of *Diospyros celebica* Bakh, is the naphthol (IV). Macassar III is its methyl ether. Betulin is also present in the heartwood and betulinic acid in the sapwood.

Many *Ebenaceae* heartwoods are dark brown or black, especially *Diospyros* spp., some of which are of commercial value. Although several investigations of *Diospyros* have been reported little attention has been paid to the heartwoods (ebony) and the nature of the pigments is unknown.

Macassar ebony, the heartwood of *D. celebica* Bakh, was briefly examined by Sandermann and Dietrichs[1] during a study of the termite resistance of various timbers. Paper chromatography of a light petroleum extract revealed the presence of several compounds, three of which showed a blue fluorescence in ultraviolet light in the presence of ammonia; they were named macassar I, II, and III, in order of increasing R_F value. Only macassar II was isolated. We now report on the structure of macassar II and III.


(I)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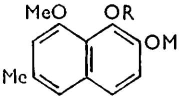
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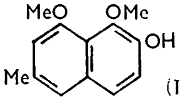
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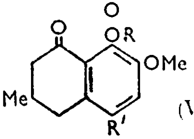
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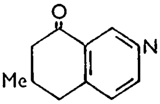
(VI)

The isolation procedure of Sandermann and Dietrichs[1] was modified by dividing the light petroleum extract into acidic and neutral fractions. The former yielded macassar II, and the latter macassar III and betulin. None of the macassar group could be detected in the sapwood but betulinic acid was isolated.

Macassar II has the molecular formula $C_{13}H_{14}O_3$[1] containing one *C*-Me and two *O*-Me-groups. It gives a blue fluorescent solution in aqueous sodium hydroxide, and form a picrate,[1] a monoacetate, a monobenzoate, and a monomethyl ether by treatment with dimethyl sulphate and potassium carbonate. The methyl ether is identical with macassar III. From these data, and the ultraviolet absorption (Table 1), macassar II appears to be a dimethoxymethylnaphthol. Oxidation of macassar II with alkaline hydrogen peroxide yielded 3-methoxy-5-methylphthalic anhydride which established the substitution pattern in one ring, whilst treatment with sodium metaperiodate (and several other oxidising agents) afforded a monomethoxymethyl-β-naphthaquinone whose light absorption was nearly identical with that of 8-methoxy-1,2-naphthaquinone. The oxidation product is evidently the quinone (I) and was found to be different from the alternative (II), obtained by synthesis. The formation of the *o*-quinone (I) indicates[2] the presence of a methoxyl group *ortho* to the phenolic group in macassar II, and therefore macassar III, its methyl ether, must be (III; R = Me). This is supported by its nuclear magnetic resonance (n.m.r.) spectrum and was confirmed by synthesis (see below).

It follows that macassar II is either the naphthol (II; R = H) or the isomer (IV). Its failure to react with diazomethane in ether[1] parallels the known behaviour of 8-methoxy-1-naphthol although 1-methoxy-2-naphthol and 2-methoxy-1-naphthol react sluggishly under these conditions. However both the two latter compounds, *and* macassar II, can

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[1] W. Sandermann and H. H. Dietrichs, *Holz als Roh- und Werkstoff*, 1957, **15**, 281.

[2] E. Adler and R. Magnusson, *Acta Chem. Scand.*, 1959, **13**, 505.

be methylated with diazomethane in ether–methanol whereas 8-methoxy-1-naphthol and the naphthol (III; R = H), obtained later by synthesis, are still inert under these conditions. This behaviour indicates that macassar II has structure (IV) which agrees with its ready solubility in cold aqueous alkali (the naphthol (III; R = H) is cryptophenolic). These properties, which reflect the greater strength of the intramolecular hydrogen bond in *peri*-methoxynaphthols (6-membered ring) as compared to *o*-methoxynaphthols (5-membered ring), are in complete accord with their infrared and nuclear magnetic resonance spectra which show decisively that macassar II has the structure (IV). The resonance frequency of the hydroxyl proton in α- and β-naphthol, which lies near τ 5, is shifted to near τ 4 in *o*-methoxynaphthols, and further down field to near τ 1 in *peri*-methoxynaphthols (Table 2), and, in agreement, the hydroxyl stretching frequency in the *o*-methoxynaphthols ($\nu_{max.}$ 3509—3520 cm.$^{-1}$) is displaced to 3400 cm.$^{-1}$ in the *peri*-methoxynaphthols (Table 1). These data show that macassar II is an *o*-methoxynaphthol, *i.e.*, (IV), and it is clear (Table 1 and 2) that the synthetic isomer (III; R = H) behaves as a *peri*-methoxynaphthol, its hydroxyl group being hydrogen bonded to the 8- in preference to the 2-methoxyl group. Structure (IV) is also supported by the fact that oxidation of macassar II with a dozen reagents yielded the *o*-quinone (I) and in no case could we detect either a *p*-quinone or a dimer.

TABLE 1

Absorption spectra of methoxynaphthols

Compound	$\lambda_{max.}$ (mμ) (EtOH)	$\nu_{max.}$ OH (cm.$^{-1}$) (in $CHCl_3$)
2-Methoxy-1-naphthol	237, 292, 302, 330 (log ε 4·53, 3·54, 3·54, 3·35)	3540
1-Methoxy-2-naphthol	230, 280, 291, 333 (log ε 4·49, 3·52, 3·47, 3·33)	3536
8-Methoxy-1-naphthol [a]	298, 315·5, 330 (log ε 3·86, 3·82, 3·83)	3400 [b]
Macassar II (IV)	230, 235, 285, 297, 335, 347 (log ε 4·59, 4·54, 3·74, 3·71, 3·46, 3·51)	3520
Naphthol (III; R = H)	235, 291, 305, 340 (log ε 4·23, 3·32, 3·32, 3·29)	3400 [b]

[a] D. C. Allport and J. D. Bu'Lock, *J.*, 1960, 654. [b] Broad.

TABLE 2

Magnetic resonance absorptions of hydroxylic protons (in $CDCl_3$)

Compound	τ	Compound	τ
1-Naphthol	4·85 [a]	3-Methoxy-2-naphthol	4·10
2-Naphthol	5·50 [a]	Macassar II	3·80
2-Methoxy-1-naphthol	3·93	8-Methoxy-1-naphthol	0·72
1-Methoxy-2-naphthol	3·93	Naphthol (III; R = H)	0·78

[a] Broad.

Macassar II and all the β-naphthols in Table 2 gave a green colour in the modified[3] Gibbs' test but, unlike the blue solutions obtained with the isomer (III; R = H) and the other α-naphthols, there was no absorption in the region 575—675 mμ characteristic of indophenols. This agrees with the observations of King *et al.*[3] on anomalous Gibbs' colorations.

The *o*-quinone (I) was obtained by oxidation of *both* isomers (III; R = H) and (IV) with Fremy's salt, and the *o*-quinone (II) was prepared by a similar oxidation of 5-methoxy-7-methyl-1-naphthol. These are exceptions to the general rule that a phenol with a free *para*-position yields the corresponding *p*-quinone on treatment with Fremy's salt although 1,5-dihydroxynaphthalene gives a mixture of 5-hydroxy-1,2- and 1,4-naphthaquinones.[4] 2-Methoxy- and 8-methoxy-1-naphthol behaved normally and formed the corresponding *p*-quinones whilst 1-methoxy-2-naphthol gave 1,2-naphthaquinone.

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[3] F. E. King, T. J. King, and L. C. Manning, *J.*, 1957, 563.

[4] H.-J. Teuber and N. Götz, *Chem. Ber.*, 1954, **87**, 1236.

Synthesis.—The tetralone (V; R = Me, R′ = H) was obtained from γ-(3,4-dimethoxyphenyl)-β-methylbutyric acid by chlorination at position 6, followed by cyclisation to the chlorotetralone (V; R = Me, R′ = Cl) and subsequent hydrogenolysis. Dehydrogenation with sulphur then gave the corresponding naphthol, the methyl ether of which was identical with macassar III in all respects.

Macassar II was synthesised starting from 3-methyl-1-tetralone. Nitration gave the nitrotetralone (VI) which was converted, by standard procedures, into 8-methoxy-6-methyl-2-naphthol and then oxidised with Fremy's salt to the *o*-quinone (I). Reduction to the quinol and partial methylation with methyl sulphate and potassium carbonate gave two dimethoxynaphthols and the isomer (IV), soluble in cold aqueous sodium hydroxide, was identical with macassar II. The other compound (III; R = H) did not dissolve in cold aqueous alkali. Attempts to synthesise the latter by dehydrogenation of the tetralones (V; R = H, R′ = H or Cl) and their derivatives were unsuccessful.

EXPERIMENTAL

Extraction of Diospyros celebica.—(i) *Heartwood.* The procedure of Sandermann and Dietrichs [1] was modified as follows. Shavings (100 g.) were exhaustively extracted (Soxhlet) with n-heptane, the solution was filtered and the solvent removed leaving a dark brown oil (2·4 g.) which solidified overnight. This, in ether, was shaken with 2N-sodium hydroxide (3 × 200 ml.) and the aqueous phase was acidified with dilute hydrochloric acid and extracted with ether. When dried ($MgSO_4$) and evaporated, there remained a brown viscous oil (1·7 g.) which solidified. The solid sublimed at 105—110°/0·05 mm. yielding macassar II as almost colourless prisms, m. p. 105—106°, raised to 107—107·5° (lit.,[1] 105—105·5°) after sublimation at 80°/2 × 10^{-4} mm. (Found: C, 71·3; H, 6·6; OMe, 28·1; CMe, 6·5. $C_{13}H_{14}O_3$ requires C, 71·5; H, 6·5; OMe, 28·4; CMe, 6·9%). The picrate formed dark red needles, m. p. 131—132° (from methanol) (lit.,[1] 129—130°). The *acetate* crystallised from light petroleum (b. p. 40—60°) in prisms, m. p. 60° (Found: C, 69·5; H, 6·0; OMe, 23·8. $C_{15}H_{16}O_4$ requires C, 69·2; H, 6·2; OMe, 23·8%) and the *benzoate* separated from aqueous methanol in prisms, m. p. 121° (Found: C, 74·3; H, 5·7; OMe, 19·0. $C_{20}H_{18}O_4$ requires C, 74·5; H, 5·65; OMe, 19·3%).

The ether solution containing the alkali-insoluble fraction was filtered, dried ($MgSO_4$), and evaporated, leaving a gum. Trituration with a little ether and filtration, gave a solid (0·18 g.) which crystallised from ethanol in needles, m. p. 255—258°, identical (mixed m. p., i.r.) with authentic betulin. More betulin was precipitated by addition of benzene to the ether filtrate, and the solution was then applied to layers of Silica Gel G (Merck) (thirteen 8 in. × 8 in. plates) and developed with n-heptane saturated with methanol. A band showing strong blue fluorescence in ultraviolet light was separated mechanically and extracted with hot methanol. Evaporation left a pale yellow oil (0·15 g.) which solidified. Crystallisation from aqueous ethanol afforded *macassar* III as needles, m. p. 70° (Found: C, 72·3; H, 7·0; OMe, 41·5. $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·9; OMe, 40·1%). The *picrate* formed dark red-brown needles, m. p. 125° (from ethanol) (Found: C, 51·7; H, 4·2; N, 8·9; OMe, 19·5. $C_{20}H_{19}N_3O_{10}$ requires C, 52·0; H, 4·2; N, 9·1; OMe, 20·1%). Methylation of macassar II with dimethyl sulphate–acetone–potassium carbonate in the usual way gave macassar III, m. p. and mixed m. p. 70°.

(ii) *Sapwood.* Shavings (100 g.) were exhaustively extracted with ether (1·5 l.) and the filtered solution was taken to dryness leaving a pale yellow-green residue (1·65 g.). Trituration with light petroleum (b. p. 40—60°) gave a solid which was sublimed at 210—215°/0·01 mm. and then repeatedly crystallised from ethanol forming needles, m. p. 312—315° (324 mg.) identical (mixed m. p., i.r.) with authentic betulinic acid.

Oxidation of Macassar II.—(ii) *With hydrogen peroxide.* To macassar II (1·5 g.) in 2N-sodium hydroxide (100 ml.) was added hydrogen peroxide (30 ml.; 100 vol.). The solution was heated on the steam-bath for 15 min., cooled, acidified, and extracted with ether. Evaporation of the dried ($MgSO_4$) extract left a pale yellow solid which was refluxed with acetic anhydride (15 ml.) for 30 min. and again evaporated. Sublimation of the residue at 100—110°/12 mm. gave 3-methoxy-5-methylphthalic anhydride (0·68 g.) as needles, m. p. 166—167°, identical (mixed m. p., i.r.) with authentic material (Found: C, 62·5; H, 4·4; OMe, 16·4. Calc. for $C_{10}H_8O_4$: C, 62·5; H, 4·2; OMe, 16·1%). Hydrolysis of the anhydride gave the acid, m. p. 200° (lit.,[5] 200—202°).

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[5] A. J. Birch and P. Hextal, *Austral. J. Chem.*, 1955, **8**, 96.

(ii) *With sodium metaperiodate.* To a solution of macassar II (0·21 g.) in the minimum of acetone, sodium metaperiodate (1 g.) in water (15 ml.) was added, with shaking, giving a deep red solution from which 8-*methoxy*-6-*methyl*-1,2-*naphthaquinone* (I) separated overnight. It formed orange needles, m. p. 165° from light petroleum (b. p. 100—120°) 0·16 g. (80%); $\nu_{max.}$ (in KBr) 1681, 1659 cm.$^{-1}$; $\lambda_{max.}$ (in EtOH) 218, 244, 420 mμ (log ε 4·44, 4·27, 3·87) (Found: C, 71·4; H, 5·0; OMe, 14·9. $C_{12}H_{10}O_3$ requires C, 71·3; H, 5·0; OMe, 15·3%). The *quinoxaline* separated from aqueous alcohol in golden yellow needles, m. p. 167—168° (Found: C, 78·6; H, 5·1; N, 9·9; OMe, 11·3. $C_{18}H_{14}N_2O$ requires C, 78·8; H, 5·1; N, 10·2; OMe, 11·3%). Reductive acetylation of the quinone gave 1,2-*diacetoxy*-8-*methoxy*-6-*methylnaphthalene* as needles, m. p. 130° from light petroleum (b. p. 80—100°) (Found: C, 66·7; H, 5·7; OMe, 10·7. $C_{16}H_{16}O_5$ requires C, 66·7; H, 5·3; OMe, 10·75%).

(iii) *With Fremy's salt.* The reagent (4 g.) in water (600 ml.) and M/6 potassium dihydrogen phosphate (150 ml.) was added to a solution of macassar II (1 g.) in acetone (50 ml.). After 24 hr. the quinone (II) was collected as orange needles, m. p. 165—166° (0·80 g., 88·0%).

(iv) *With other oxidising agents.* The same quinone (I) was obtained by oxidation of macassar II with ferricyanide, ferric chloride, potassium persulphate, lead tetra-acetate, manganese dioxide, silver oxide, lead dioxide, chromium trioxide, chloranil, and with oxygen and the laccase from *Polyporus versicolor.*[6]

Oxidation of Other Methoxynaphthols.—(i) 8-*Methoxy*-1-*naphthol.* [*Acetate*, needles, m. p. 81—82°, from light petroleum (b. p. 60—80°) (Found: C, 71·9; H, 5·6; Ac, 19·9. $C_{13}H_{12}O_3$ requires C, 71·9; H, 5·6; Ac, 20·3%).] Fremy's salt (1 g.) in water (70 ml.) and M/6-potassium dihydrogen phosphate (17 ml.) were added to a solution of 8-methoxy-1-naphthol (0·29 g.) in acetone (40 ml.). After 1½ hr. the dark orange solution was diluted with water (150 ml.) and extracted with chloroform. After evaporation of the solvent and crystallisation of the residue from methanol 8-methoxy-1,4-naphthaquinone was obtained as orange-brown needles, m. p. 185—186° (0·27 g., 84·4%) identical (mixed m. p., i.r.) with authentic material.

(ii) 2-*Methoxy*-1-*naphthol.*[7] The naphthol (0·3 g.) in acetone (30 ml.) was oxidised in the usual way with Fremy's salt. On being kept overnight 2-methoxy-1,4-naphthaquinone (0·25 g.) separated and a further 70 mg. were obtained by chloroform extraction. After crystallisation from ethanol it had m. p. and mixed m. p. with an authentic sample, 180—181°. 1,2-Naphthaquinone could not be detected by thin-layer chromatography.

(iii) 1-*Methoxy*-2-*naphthol.* The naphthol (100 mg.) was oxidised with Fremy's salt as before. Extraction with chloroform next day afforded 1,2-naphthaquinone, m. p. 132° (80 mg.) identified by its infrared spectrum.

(iv) 2,8-*Dimethoxy*-6-*methyl*-1-*naphthol* (III; R = H). The naphthol (135 mg.) in acetone (5 ml.) was oxidised in the usual way with Fremy's salt (0·4 g.). The orange-brown solution was kept at room temperature for 20 hr., extracted with chloroform, dried and evaporated, leaving a red oil which solidified. Crystallisation from benzene–heptane and then light petroleum (b. p. 100—120°) gave 8-methoxy-6-methyl-1,2-naphthaquinone as orange-red needles, m. p. and mixed m. p., 163—164° (92%).

Methylation of Methoxynaphthols with Diazomethane.—(i) *Macassar* II. The naphthol (100 mg.) in methanol (2 ml.) was treated with diazomethane (from 5 g. *N*-methylnitrosourea) in ether (120 ml.) and kept at room temperature for 4 days. Removal of the ether left an oil which distilled at 85—95° (bath)/0·05 mm. yielding a solid distillate which crystallised from aqueous ethanol as prisms, m. p. and mixed m. p. with macassar III, 68—69° (0·1 g., 95·0%). The naphthol (III; R = H) completely failed to react under these conditions.

(ii) 1-*Methoxy*-2-*naphthol and* 2-*methoxy*-1-*naphthol.* Treatment of either naphthol with diazomethane, as above, gave 1,2-dimethoxynaphthalene and no starting material could be detected by thin-layer chromatography. In the absence of methanol, methylation was still incomplete after 4 days.

5-*Chloro*-7,8-*dimethoxy*-3-*methyl*-1-*tetralone* (V; R = Me, R′ = Cl).—To a vigorously stirred solution of β-methyl-γ-(3,4-dimethoxyphenyl)butyric acid (3·95 g.) in acetic acid (10 ml.) at 10°, chlorine (1·4 g.) in acetic acid (15 ml.) was added, dropwise, during 1½ hr. After stirring 1 hr. further, the solution was boiled for a few minutes, cooled, diluted with ice–water and

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[6] G. Benfield, S. M. Bocks, K. Bromley, and B. R. Brown, *Phytochemistry*, 1964, **3**, 79; B. R. Brown and A. R. Todd, *J.*, 1963, 5564.

[7] H. S. Chang and J. T. Edward, *Canad. J. Chem.*, 1963, **41**, 1233.

extracted with ether. Removal of solvents *in vacuo* from the dried (Na_2SO_4) extract left the chloro-acid which was distilled, the fraction b. p. 130—140°/0·05 mm. being collected as a golden viscous oil (4·25 g.). It was then dissolved in sodium-dried benzene (40 ml.) and treated with phosphorus pentachloride (7 g.). The mixture was kept at 40—50° for 2 hr., then cooled to 0° and stannic chloride (7 ml.) was added, with shaking. After being kept at 0° for 36 hr., it was poured on to hydrochloric acid, ice, and ether, and worked up in the usual way to give a brown viscous oil (2·63 g.) which solidified. Crystallisation from light petroleum (b. p. 60—80°) gave 5-*chloro*-7,8-*dimethoxy*-3-*methyl*-1-*tetralone* as prisms, m. p. 85—86° (73%), $\nu_{max.}$ (Nujol) 1690 cm.$^{-1}$ (Found: C, 61·1; H, 5·7; Cl, 13·6; OMe, 24·6. $C_{13}H_{15}ClO_3$ requires C, 61·3; H, 5·9; Cl, 13·55; OMe, 24·35%). The 2,4-*dinitrophenylhydrazone* crystallised from ethyl acetate in golden yellow needles, m. p. 221° (Found: C, 52·3; H, 4·5; N, 12·9. $C_{19}H_{18}ClN_4O_6$ requires C, 52·45; H, 4·35; N, 12·9%).

5-*Chloro*-8-*hydroxy*-7-*methoxy*-3-*methyl*-1-*tetralone* (V; R = H, R′ = Cl).—The above tetralone (0·5 g.) in acetic acid (5 ml.) was refluxed with concentrated hydrochloric acid (20 ml.) for 2 hr., cooled, and poured into water. The *product* crystallised from light petroleum (b. p. 60—80°) in yellow needles, m. p. 107°, $\nu_{max.}$ 1645 cm.$^{-1}$ (Found: C, 59·7; H, 5·2; Cl, 14·9. $C_{12}H_{13}ClO_3$ requires C, 59·85; H, 5·4; Cl, 14·7%). It gave a dark green colour with ferric chloride. The *benzyl ether* was obtained by refluxing the hydroxyketone (0·6 g.) in acetone (120 ml.) with benzyl chloride (2 ml.), potassium iodide (0·2 g.), and potassium carbonate (8 g.) for 27 hr., and had m. p. 124° (needles from light petroleum, b. p. 60—80°), $\nu_{max.}$ 1690 cm.$^{-1}$ (Found: C, 69·1; H, 5·6; Cl, 11·1; OMe, 9·7. $C_{19}H_{19}ClO_3$ requires C, 69·0; H, 5·75; Cl, 10·75; OMe, 9·35%). Two drops of concentrated sulphuric acid were added to the hydroxyketone (0·54 g.) in acetic anhydride (5·5 ml.). After 20 min. the yellow solution was poured into water to precipitate 1,8-*diacetoxy*-5-*chloro*-3,4-*dihydro*-7-*methoxy*-3-*methylnaphthalene* which formed needles, m. p. 133°, from light petroleum (b. p. 60—80°); $\nu_{max.}$ (Nujol) 1750 (CO) and 1680 (C:C) cm.$^{-1}$; $\lambda_{max.}$ (EtOH) 224, 253, 323 mμ (log ε 4·14, 3·56, 3·22) (Found: C, 59·5; H, 5·4; Cl, 11·2; OAc, 25·9. $C_{16}H_{17}ClO_5$ requires C, 59·15; H, 5·2; Cl, 10·9; OAc, 26·5%).

7,8-*Dimethoxy*-3-*methyl*-1-*tetralone* (V; R = Me, R′ = H).—To a solution of 5-chloro-7,8-dimethoxy-3-methyl-1-tetralone (1·5 g.) in ethanol (200 ml.), 2% palladised strontium carbonate (5 g.) and 10% ethanolic potassium hydroxide (4 ml.) were added and the mixture was shaken with hydrogen until 1 mol. was absorbed. After removal of catalyst and solvent, the residue was treated with water (150 ml.) and extracted with ether. The ether was evaporated to give an orange oil (1·1 g.) which distilled at 110—120°/0·8 mm. and then solidified as pale yellow needles, m. p. 64—65°, from aqueous methanol (0·8 g., 62·0%), $\nu_{max.}$ 1680 cm.$^{-1}$ (Found: C, 70·7; H, 7·2; OMe, 28·1. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·25; OMe, 28·5%). The 2,4-*dinitrophenylhydrazone* formed orange-red plates, m. p. 245° (decomp.), from ethyl acetate (Found: C, 56·9; H, 5·0; N, 14·3. $C_{19}H_{19}N_4O_6$ requires C, 57·0; H, 5·0; N, 14·0%).

8-*Hydroxy*-7-*methoxy*-3-*methyl*-1-*tetralone* (V; R = R′ = H).—Partial demethylation of 7,8-dimethoxy-3-methyl-1-tetralone with hydrochloric acid in acetic acid, as above, gave the *product* as an oil which crystallised from light petroleum (b. p. 60—80°) in prisms, m. p. 62°, $\nu_{max.}$ 1640 cm.$^{-1}$ (Found: C, 69·8; H, 6·8; OMe, 15·3. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·8; OMe, 15·05%). Treatment with cold acetic anhydride containing sulphuric acid, as before, gave 1,8-*diacetoxy*-3,4-*dihydro*-7-*methoxy*-3-*methylnaphthalene*, m. p. 120° (needles from light petroleum); $\nu_{max.}$ (Nujol) 1755 (acetate CO) and 1675 (C:C) cm.$^{-1}$; $\lambda_{max.}$ (EtOH) 223·5, 252, 323 mμ (log ε 4·30, 3·89, 3·08) (Found: C, 66·0; H, 6·3; OAc, 31·1. $C_{16}H_{18}O_5$ requires C, 66·2; H, 6·25; OAc, 29·6%).

1,2,8-*Trimethoxy*-6-*methylnaphthalene* (III; R = Me).—7,8-Dimethoxy-3-methyl-1-tetralone (0·68 g.) was heated with sulphur (0·1 g.) at 260—265° until the evolution of hydrogen sulphide ceased (*ca.* 1·5 hr.). The residue distilled at 240—250° (bath)/0·5 mm. to give a pale yellow oil (100 mg.); $\nu_{max.}$ (film) 3400 (OH) cm.$^{-1}$; $\lambda_{max.}$ (EtOH) 233, 296, 307, 327, and 335 mμ, soluble in aqueous sodium hydroxide. This was refluxed in acetone (30 ml.) with dimethyl sulphate (2 ml.) and anhydrous potassium carbonate (5 g.). After 7½ hr. further additions of dimethyl sulphate (2 ml.) and anhydrous potassium carbonate (5 g.) were made and refluxing continued until a Gibbs test was negative (10½ hr.). Working up gave 1,2,8-*trimethoxy*-6-*methylnaphthalene* which crystallised from aqueous ethanol as needles, m. p. 68—69°, identical (mixed m. p., u.v., i.r., R_F) with macassar III (Found: C, 72·2; H, 7·1; OMe, 39·9. $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·9; OMe, 40·1%).

3-*Methyl*-7-*nitro*-1-*tetralone* (VI).—3-Methyl-1-tetralone (8·9 g.) was stirred into concentrated sulphuric acid (30 ml.) at 0°. A cooled mixture of concentrated nitric acid (8 ml.) and concentrated sulphuric acid (12 ml.) was added, dropwise, to the stirred solution at or below 0°. After stirring 10 min. further the mixture was poured on to ice. The precipitated *nitro-tetralone* crystallised from light petroleum (b. p. 60—80°) in pale yellow needles, m. p. 103° (10·7 g., 94%) (Found: C, 64·5; H, 5·5; N, 7·0. $C_{11}H_{11}NO_3$ requires C, 64·35; H, 5·4; N, 6·8%). The 2,4-*dinitrophenylhydrazone* formed orange needles, m. p. 247—248° from ethyl acetate (Found: C, 52·9; H, 4·2; N, 18·8. $C_{17}H_{15}N_5O_6$ requires C, 53·0; H, 3·9; N, 18·4%).

1-*Methoxy*-3-*methyl*-7-*nitronaphthalene*.—To a solution of 3-methyl-7-nitro-1-tetralone (1·03 g.) in carbon tetrachloride (40 ml.) was added N-bromosuccinimide (0·9 g.) and a trace of benzoyl peroxide. After refluxing for 2 hr. the mixture was cooled, filtered and evaporated, leaving an orange oil. This was dissolved in acetic acid (10 ml.) containing anhydrous sodium acetate (1 g.), refluxed for 30 min. and poured into water to precipitate 3-*methyl*-7-*nitro*-1-*naphthol* which crystallised from benzene–n-heptane (1 : 1) as orange needles, m. p. 200—202° (0·81 g., 80%) (Found: C, 64·7; H, 4·8; N, 6·9. $C_{11}H_9NO_3$ requires C, 65·0; H, 4·5; N, 6·9%). Methylation with dimethyl sulphate–potassium carbonate in acetone afforded the *methyl ether* as yellow needles, m. p. 134—135° from light petroleum (b. p. 60—80°) (Found: C, 66·6; H, 5·3; N, 6·2; OMe, 14·1. $C_{12}H_{11}NO_3$ requires C, 66·35; H, 5·1; N, 6·45; OMe, 14·3%).

8-*Methoxy*-6-*methyl*-1,2-*naphthaquinone* (I).—1-Methoxy-3-methyl-7-nitronaphthalene (2·08 g.) was hydrogenated in ethyl acetate (80 ml.) over Adams catalyst. Removal of the catalyst and solvent left the naphthylamine as a brown oil (1·9 g.). The *acetyl derivative* crystallised from n-heptane in prisms, m. p. 185° (Found: C, 73·0; H, 6·7; N, 6·3. $C_{14}H_{15}NO_2$ requires C, 73·35; H, 6·6; N, 6·1%). The amine in water (20 ml.) and concentrated sulphuric acid (2 ml.) was treated slowly, at 0°, with sodium nitrite (1 g.) in water (5 ml.). The resulting orange solution was shaken for 15 min., poured into a boiling solution of copper sulphate (3·5 g.) in water (100 ml.), boiled for 5 min., cooled and extracted with ether. The extract was shaken with 2N-sodium hydroxide, the aqueous phase was acidified with hydrochloric acid and the naphthol taken into ether and dried ($MgSO_4$). Distillation gave an orange oil (0·28 g.), b. p. 125—135° (bath)/0·05 mm.; $\lambda_{max.}$ (EtOH) 254, 320, 327 mμ. This (0·22 g.) in acetone (10 ml.) was treated with a solution of Fremy's salt (1 g.) in water (50 ml.) and M/6-potassium dihydrogen phosphate (15 ml.). After 1½ hr. the solution was diluted with water, extracted with chloroform, dried, and evaporated leaving an orange oil (30 mg.) which crystallised from light petroleum (b. p. 100—120°) to give orange-red needles of 8-methoxy-6-methyl-1,2-naphthaquinone, m. p. 163—164°, identical (mixed m. p., i.r.) with the quinone obtained by oxidation of macassar II.

Methylation of 1,2-*dihydroxy*-8-*methoxy*-6-*methylnaphthalene*.—Hydrogenation of the above quinone in ethyl acetate over Adams catalyst gave 1,2-*dihydroxy*-8-*methoxy*-6-*methylnaphthalene* which sublimed at 80°/10^{-4} mm. in needles, m. p. 148—149°, $\nu_{max.}$ (Nujol) 3450, 3320 (OH) cm.$^{-1}$ (Found: C, 70·4; H, 6·1; OMe, 15·2. $C_{12}H_{12}O_3$ requires C, 70·6; H, 5·9; OMe, 15·2%). The *o*-quinol (0·75 g.) in acetone (200 ml.) was refluxed for 18 hr. with dimethyl sulphate (0·5 g.) and anhydrous potassium carbonate, cooled, diluted with water (500 ml.), and extracted with ether (3 × 100 ml.). The extract was shaken with 2N-sodium hydroxide (3 × 100 ml.), then dried and evaporated, leaving a brown oil. This, in ether, was transferred to a column of silicic acid and eluted with ether–benzene (1 : 1) as an oil (120 mg.) which solidified. Crystallisation from light petroleum (b. p. 60—80°) followed by sublimation at 90—95°/0·05 mm. gave 2,8-*dimethoxy*-6-*methyl*-1-*naphthol* as needles, m. p. 90—91°, $\lambda_{max.}$ (EtOH) 235, 291, 305, 340 mμ (log ε 4·23, 3·32, 3·32, 3·29) (Found: C, 71·4; H, 6·6; OMe, 29·6. $C_{13}H_{14}O_3$ requires C, 71·5; H, 6·5; OMe, 28·4%). This naphthol is insoluble in cold, but soluble in hot, 2N-aqueous sodium hydroxide. The isomer soluble in cold alkali was isolated by acidification of the above alkaline extract, taken into ether and chromatographed in the same way on silicic acid. The residual red-brown oil (25 mg.) solidified when kept, and was sublimed at 100—105°/0·05 mm. and again at 57—60°/10^{-4} mm. yielding 1,8-*dimethoxy*-6-*methyl*-2-*naphthol* as needles, m. p. 106—107°, identical (mixed m. p., u.v., i.r., R_F) with macassar II (Found: C, 71·6; H, 6·5; OMe, 27·1. $C_{13}H_{14}O_3$ requires C, 71·3; H, 6·5; OMe, 28·4%).

8-*Methoxy*-1,2-*naphthaquinone*.—Sulphanilic acid (0·98 g.) in aqueous sodium carbonate (12 ml., 2·5%) was diazotised in the usual way and added to an ice-cold solution of 8-methoxy-2-naphthol [8] (0·98 g.) in 2N-sodium hydroxide (6 ml.). The azo-solution was then reduced to the amino-naphthol and oxidised by standard procedures.[9] The resulting *quinone* was isolated

[8] A. J. Shand and R. H. Thomson, *Tetrahedron*, 1963, **19**, 1919.

[9] *Org. Synth.* Coll., Vol. II, 430.

by extraction into chloroform followed by evaporation, and crystallised from benzene–light petroleum (b. p. 100—120°) in orange-red needles, m. p. 153—154° (0·2 g., 21%); $\lambda_{max.}$ (EtOH) 216, 242, 422 mμ (log ε 4·34, 4·22, 3·82); $\nu_{max.}$ (KBr) 1681sh, 1653 cm.$^{-1}$ (Found: C, 70·0; H, 4·3; OMe, 16·1. $C_{11}H_8O_3$ requires C, 70·2; H, 4·3; OMe, 16·5%). The *quinoxaline* separated from aqueous ethanol as golden needles, m. p. 141—142° (Found: C, 78·2; H, 4·6; N, 10·9; OMe, 11·9. $C_{17}H_{12}N_2O$ requires C, 78·5; H, 4·6; N, 10·75; OMe, 11·9%).

5-*Methoxy*-7-*methyl*-1,2-*naphthaquinone* (II).—5-Methoxy-7-methyl-1-tetralone [10] (1 g.) was heated with sulphur (0·2 g.) at 260° for *ca.* 1 hr. Distillation at 220—230° (bath)/2 mm. gave an oil which was dissolved in methanol and diluted with water to give 5-*methoxy*-7-*methyl*-1-*naphthol* as needles, m. p. 56—58° (40%) (Found: C, 76·8; H, 6·1; OMe, 16·0. $C_{12}H_{12}O_2$ requires C, 76·6; H, 6·4; OMe, 16·5%). To a solution of the naphthol (0·15 g.) in acetone (30 ml.) was added a mixture of Fremy's salt (0·6 g.) in water (100 ml.) and M/6-potassium dihydrogen phosphate (20 ml.). The solution changed immediately from purple to red and 5-*methoxy*-7-*methyl*-1,2-*naphthaquinone* slowly separated. It crystallised from light petroleum (b. p. 100—120°) in fine red needles, m. p. 207—208° (decomp.) (95%); $\lambda_{max.}$ (EtOH) 216, 262, 376, 472 mμ (log ε 4·32, 4·26, 3·24, 3·64); $\nu_{max.}$ (KBr) 1695, 1653 cm.$^{-1}$ (Found: C, 70·9; H, 5·1; OMe, 16·0. $C_{12}H_{10}O_3$ requires C, 71·3; H, 5·0; OMe, 15·3%). The *quinoxaline* formed orange needles, m. p. 199—200° (from ethanol) (Found: C, 78·6; H, 5·2; N, 9·9; OMe, 11·5. $C_{18}H_{14}N_2O$ requires C, 78·8; H, 5·1; N, 10·2; OMe, 11·3%).

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THE UNIVERSITY, OLD ABERDEEN, SCOTLAND.

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[10] R. G. Cooke and H. Dowd, *Austral. J. Chem.*, 1953, **6**, 53.