Ebenaceae Extractives. Part 9.[1] New Naphthoquinones and Binaphthylquinones from Macassar Ebony

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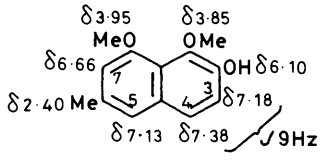
In addition to macassar II (**1**) and its methyl ether, macassar III, the heartwood of *Diospyros celebica* contains diomelquinone A (**2**), the *o*-naphthoquinone (**3**), celebaquinone (**8**), isocelebaquinone (**21**), and diosindigo B (**10**) and its dihydro-derivative (**13**). These extractives appear to be related biogenetically to the dihydric methoxynaphthols (**15**) and (**27**). Two other products, diosindigos B_1 (**17**) and B_2 (**18**), which contain ethoxy groups, are artefacts formed during the extraction procedure.

Macassar ebony, the heartwood of *Diospyros celebica* Bakh, was shown in 1965[2] to contain the dimethoxynaphthol (**1**) ('macassar II') and its methyl ether ('macassar III'). The isolation procedure, involving extraction with heptane and subsequent partition of the extract between ether and aqueous sodium hydroxide, was appropriate for such compounds but would furnish neither the more highly polar components of the wood nor those, such as quinones, which are vulnerable to aerial oxidation under alkaline conditions. We thought it likely that *D. celebica*, as with so many other members of this genus, would contain quinonoid compounds and have now examined both the light petroleum- and the chloroform-soluble components of the wood, separating the individual compounds by chromatography.

The light petroleum extract afforded, as before,[2] macassar II, macassar III, and betulinic acid but, in addition, we obtained from it a yellow quinone, $C_{12}H_{10}O_4$, a red quinone, $C_{12}H_{10}O_3$, and a green quinone, $C_{23}H_{18}O_6$, for which we propose the name 'celebaquinone'. The first of the quinones shows spectroscopic properties which are in full agreement with structure (**2**). For example, the n.m.r. spectrum shows the presence of three *C*-methyl protons allylically coupled to an olefinic proton, two *o*-coupled aromatic protons, one of which is deshielded by an adjacent *peri* carbonyl group, three methoxy protons, and one unchelated hydroxy proton. Structure (**2**) had already been assigned to diomelquinone A, a naphthoquinone from *D. melanoxylon*,[3] and our product proved to be identical with an authentic sample of this. The m.p. and spectral data previously recorded[3] for diomelquinone A differ significantly from the values we have obtained. The red quinone, $C_{12}H_{10}O_3$, shows u.v.-visible light absorption resembling closely that[2] of 8-methoxy-1,2-naphthoquinone, and n.m.r. signals which indicate the presence of three arylmethyl protons, three methoxy protons, two *m*-coupled aryl protons, and two vicinal



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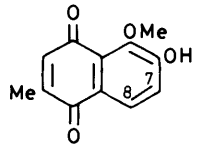

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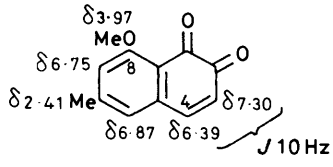

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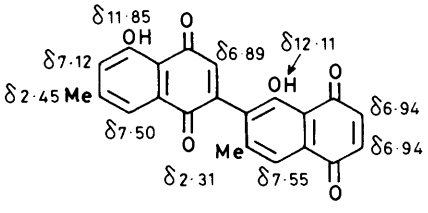

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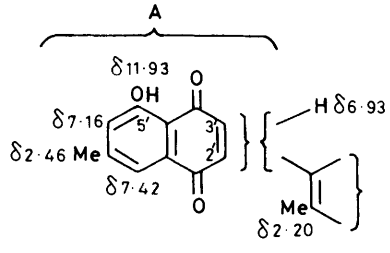

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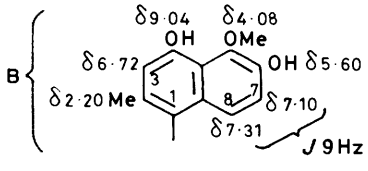

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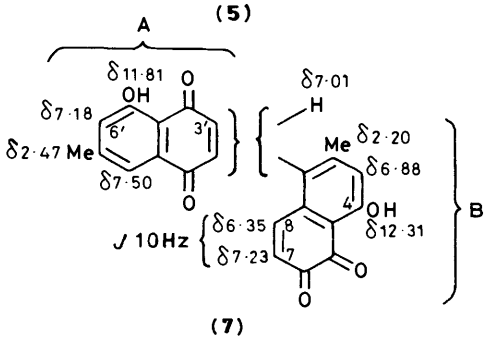
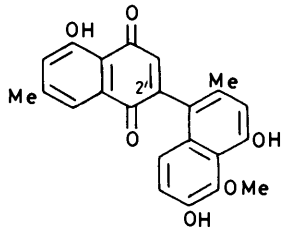


(**7**)

olefinic protons. The compound is therefore the *o*-naphthoquinone (**3**), identical with a synthetic specimen.[2] It has not previously been obtained from a natural source and is only the second *o*-naphthoquinone to be isolated from a member of the Ebenaceae, the first being the isomeric 8-methoxy-3-methyl-1,2-naphthoquinone.[4]

The green celebaquinone, $C_{23}H_{18}O_6$, underwent reductive acetylation to give a leucopenta-acetate $C_{23}H_{15}O(OAc)_5$, the formula of which establishes that celebaquinone itself is a trihydroxymonoquinone. The presence of a binaphthyl system in both compounds follows from the resemblance of the u.v. absorption of the leucopenta-acetate to those of methoxy-substituted 1,1′- and 1,2′-binaphthyl.[5,6] The mass spectrum of celebaquinone includes ions having *m/z* 163, 135, 134, and 106, such as are also observed in the fragmentation of diospyrin (**4**), suggesting[7] that celebaquinone is a substituted 7-methyljuglone containing the part-structure (**5**); the abundant $(M - Me)^+$ ion confirms[7] that a methyl group is located *ortho* to the internuclear link. The n.m.r. signals for the protons of the 7-methyljuglone group [(**5**); unit A] in celebaquinone are in good agreement with those[7] for the corresponding protons of diosyprin (**4**). The substituents on the other nucleus (unit B) must be, in addition to the methyl group, one methoxy and two hydroxy groups. The locations of these, and the position of the internuclear link, are also indicated by the n.m.r. data. The hydroxy proton signals at δ 9.04 and 5.60 are typical of those obtained from *peri*-methoxynaphthols and *o*-methoxynaphthols respectively,[2] while the signals from the three aryl protons resemble closely those from the protons at C-3, -4, and -7 of macassar II (**1**). Accordingly, unit B must have the structure (**6**), being linked to unit A *via* C-1. The *o*-methoxynaphthol system in (**6**) would be expected to undergo oxidative demethylation, and indeed treatment of celebaquinone with nitric acid or with sodium periodate[2] gave a red diquinone, $C_{22}H_{14}O_6$, which has spectroscopic properties characteristic of an *o*-quinone. Like the 1,2-naphthoquinone (**3**) it gives an abundant $(M + 2H)^{+\bullet}$ ion while the $(M - CO)^{+\bullet}$ ion is the base peak. Its proton n.m.r. signals establish that it has the structure (**7**) which contains both 1,2- and 1,4-quinone systems. Thus the *o*-quinonoid ring proton signals resemble closely those from the 1,2-naphthoquinone (**3**). Of the two hydroxy-proton signals, that at δ 12.31 can be attributed to the *peri*-hydroxy proton of unit B; we think it significant that the corresponding hydroxy-protons in neodiospyrin and 8′-hydroxyisodiospyrin, which have somewhat similar structural features, give signals at δ 12.28 and 12.27, respectively.[8] The remaining signals assigned in (**7**) are similar to those from celebaquinone itself and confirm that the oxidation has not affected the rest of the molecule. The position of attachment of unit B to unit A in celebaquinone follows from the chemical shift of the C-5′ hydroxy proton in the part-structure (**5**). An aryl substituent at C-2′ of the 7′-methyljuglone system would be expected[8] to give a shift of δ 11.89 while a similar substituent at C-3′ would produce a hydroxy-proton shift of δ 11.70. The value observed for celebaquinone, namely δ 11.93, indicates that the link between the two units involves C-2′ and consequently that celebaquinone has structure (**8**).

From the blue chloroform extract we isolated more macassar II and macassar III, a mixture of three blue quinones, a polyhydric phenol $C_{24}H_{22}O_6$, a second green quinone $C_{23}H_{18}O_6$ for which we propose the name 'isocelebaquinone', and a carboxylic acid, $C_{13}H_{14}O_5$, the last of which will be the subject of a later paper. The separation of the mixture of blue quinones by t.l.c. required many repetitions but finally gave the three pure components. These show u.v. and visible light



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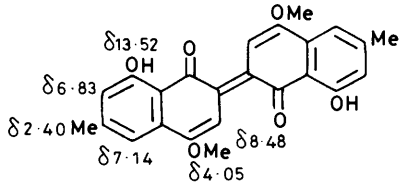

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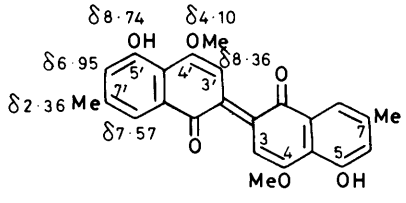

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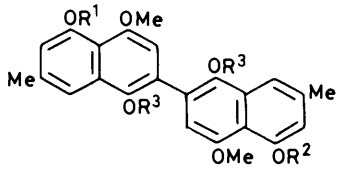
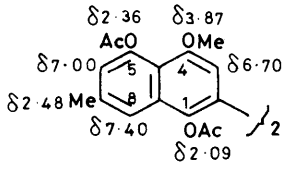


(**11**) $R^1 = R^2 = H$; $R^3 = Ac$
(**12**) $R^1 = H$, $R^2 = R^3 = Ac$
(**13**) $R^1 = R^2 = R^3 = H$



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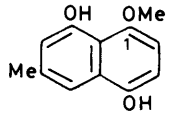

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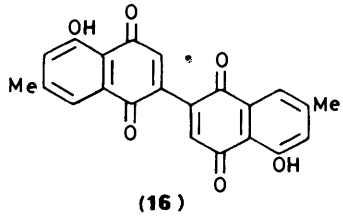
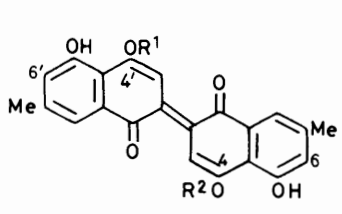


(**16**)

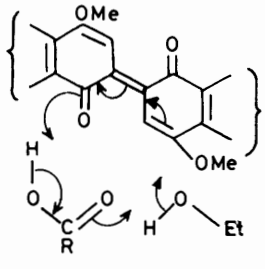
absorption similar to that[9] displayed by diosindigo A (**9**) and are therefore bisnaphthaleneindigos; we refer to them as diosindigos B, B_1, and B_2. Diosindigo B, $C_{24}H_{20}O_6$, the major component, is isomeric with diosindigo A and we formulate it as (**10**). Like diosindigo A it contains two hydroxy groups and a quinone system as shown by the formation of a diacetate, a dihydroxy leucodiacetate (**11**), a hydroxy leucotriacetate (**12**), and a leucotetra-acetate (**14**). The simplicity of the n.m.r. spectrum of diosindigo B, and its general resemblance to that[10] of diosindigo A (**9**), implies that the former compound has a symmetrical structure and contains the same substituents as does diosindigo A, namely two hydroxy, two methoxy, and two methyl groups. That the hydroxy groups are *peri* to the methoxy groups follows from the chemical shifts of the hydroxy protons of diosindigo B (δ 8.74) and of the corresponding dihydroxy leucodiacetate (**11**) (δ 9.23), which are typical[2] of 8-methoxy-1-naphthols. The shift of the methoxy proton signals by *ca.* 0.13 p.p.m. to higher field which accompanies the acetylation of both diosindigo B and its dihydroxy leucodiacetate provides further indication that the methoxy groups are hydrogen-bonded to the hydroxy groups. Of the possible arrangements incorporating the above substituents, only structure (**10**) meets the biogenetic requirement that compounds of this type should in principle[11] be derivable from 3-methylnaphthalene-1,8-diol, and accounts satisfactorily for all the spectral properties (see Experimental section) of diosindigo B. We confirmed that this structure is correct by synthesising the quinone from the diol (**15**) by oxidation with lead(IV) oxide.[12] Since the completion of this work,[12,13] the isolation of both diosindigo B and diosindigo A from *Diospyros melanoxylon* has been reported.[14]

Diosindigos B_1 and B_2 resemble diosindigo B closely in their chemical and spectroscopic properties. Thus, diosindigo B_2 on reductive acetylation also gave a leucotetra-acetate, while oxidation by nitric acid (as[12] with diosindigo B) produced biramentaceone (**16**). The molecular formulae of diosindigo B_1 ($C_{25}H_{22}O_6$) and of diosindigo B_2 ($C_{26}H_{24}O_6$) differ from that of diosindigo B by CH_2 and C_2H_4, respectively. Their n.m.r. spectra show that these extra atoms are present in the alkoxy groups, diosindigo B_1 containing one methoxy and one ethoxy group, and diosindigo B_2 having two ethoxy groups; we formulate them as (**17**) and (**18**), respectively. While diosindigos B and B_2 are poorly soluble in chloroform, diosindigo B_1 dissolves more readily, presumably because of its unsymmetrical structure. Because they contain ethoxy groups, diosindigos B_1 and B_2 cannot themselves be natural products but are artefacts formed during the extraction procedure. The chloroform used contained a little (2%) ethanol which must be the source of the ethoxy groups because when methylene chloride was used for the extraction only diosindigo B was obtained from *D. celebica*. Diosindigo B was unaffected when boiled with chloroform in the presence of the silica gel which was used for t.l.c. and decomposed when treated in chloroform with mineral acids, but readily gave diosindigos B_1 and B_2 when kept in chloroform at room temperature for several hours with some of the previously extracted wood. We suspected that an acidic constituent of the wood was involved and found that benzoic acid also brought about the transetherification reaction. The efficacy of a carboxylic acid in catalysing the reaction suggests that a hydrogen-bonded quinone–carboxylic acid–ethanol complex is formed which undergoes the bond rearrangements shown in structure (**19**). Loss of the elements of methanol from the resulting adduct would give diosindigo B_1 and repetition of the process would give diosindigo B_2.

The mass spectrum of diosindigo B, like those of diosindigos B_1 and B_2, shows an intense $(M + 2H)^{+\cdot}$ ion in addition to the molecular ion and in this respect differs markedly from the mass spectrum of diosindigo A[9] which under the same conditions shows only the usual insignificant isotopic $(M + 2)^{+\cdot}$ ion. We suggest that this difference in behaviour is linked to the ease of disproportionation of the two compounds in the mass spectrometer source. Diosindigo B would be expected to give rise to a dihydro-derivative readily because the accompanying dehydro-compound would be the relatively stable, fully conjugated diquinone (**20**). In contrast, no structure of comparable stability can be written for the dehydro-compound derived from diosindigo A.



(**17**) R^1 = Me; R^2 = Et
(**18**) R^1 = R^2 = Et



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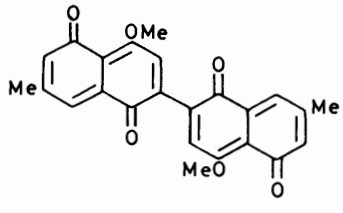

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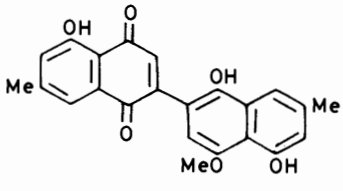

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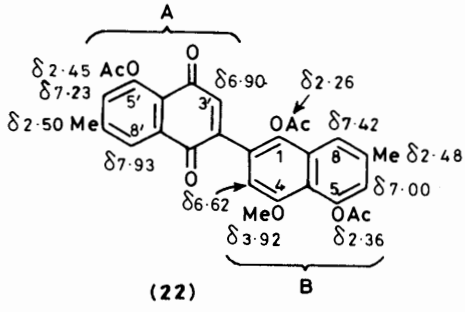

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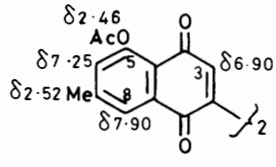


(**23**)

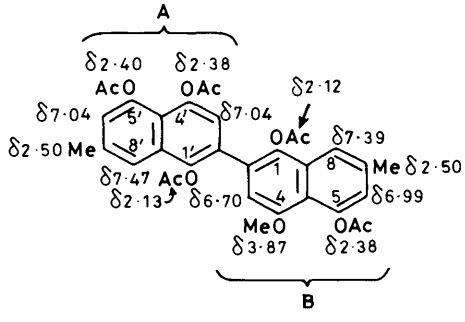
The phenol $C_{24}H_{22}O_6$ contains two methoxy groups and underwent oxidative demethylation on treatment with nitric acid to give biramentaceone (**16**). Acetylation of the phenol gave a tetra-acetate which was identical with the leucotetra-acetate derived from diosindigo B and it follows that the phenol $C_{24}H_{22}O_6$ is dihydrodiosindigo B (**13**). While the crystalline

dihydro compound is relatively unreactive it does undergo aerial oxidation rapidly when adsorbed on silica gel with the formation of diosindigo B. We therefore considered the possibility that diosindigo B might itself be an artefact produced during the isolation procedure either from the dihydro compound or from the closely related naphthol (**15**). When air was bubbled through chloroform solutions of the two compounds diosindigo B was indeed obtained quantitatively but when the two compounds were subjected to the conditions which had been used during the isolation procedure they were recovered largely unchanged and only a trace of diosindigo B was produced. Finally, when the powdered *D. celebica* wood was treated with cold chloroform under an atmosphere of nitrogen the deep blue colour of diosindigo B appeared immediately. We conclude that diosindigo B exists as such in the wood.

Many of the features of the second green quinone, isocelebaquinone ($C_{23}H_{18}O_6$) which we formulate as (**21**), resemble those of celebaquinone (**8**). Thus it forms a triacetate and a leucopenta-acetate showing that it also is a trihydroxyquinone. However the oxidative demethylation of isocelebaquinone with nitric acid gave biramentaceone (**16**), establishing that the carbon skeleton and the positions of the oxygen functions differ from those in celebaquinone and are the same as in diosindigo B. The mass spectrum of isocelebaquinone shows significant fragment ions with *m/z* 135 and 106 suggesting that a 7-methyljuglone unit is present and this is supported by the carbonyl bands in the i.r. spectrum at 1 665 and 1 633 cm^{-1} which resemble closely those shown by biramentaceone[15] at 1 662 and 1 639 cm^{-1}; the hydroxy band at 3 385 cm^{-1} is typical[2] of a *peri*-methoxynaphthol. Because of the low solubility of isocelebaquinone it was not possible to obtain a satisfactory n.m.r. spectrum but the more soluble triacetate gave the signals shown in structure (**22**). The assignments follow from the close resemblance of the signals of (a) the unit A protons to those[16] shown by biramentaceone diacetate (**23**), and (b) the unit B protons to those shown by diosindigo B leucotetra-acetate (**14**). Isocelebaquinone leucopenta-acetate gives the n.m.r. signals shown in structure (**24**). The resemblance of the unit B signals to those of diosindigo B leucotetra-acetate (**14**) is even closer, while the unit A signals, with the exception of those from the C-1′ acetoxy protons, are in excellent agreement with those from the corresponding protons of the triacetoxynaphthalene (**25**).[17] The C-1′ acetoxy group is adjacent to the internuclear linkage and its protons are shielded to some extent by the aromatic system of unit B; the C-1 acetoxy protons are affected in the same way. As expected, the protons of the corresponding acetoxy group at C-1′ of celebaquinone leucopenta-acetate (**26**), which give a signal at δ 1.85 are more highly shielded because of the more effective overlap of this acetoxy group with the aromatic system of unit B in this isomer.

Both celebaquinone (**8**) and isocelebaquinone (**21**) give yellow solutions in organic solvents. Their green colours in the crystalline state probably result from charge-transfer interactions of the quinhydrone type. They resemble the *Diospyros ebenum* extractive ebenone[18] in containing both substituted naphthyl and naphthoquinonyl units. Celebaquinone appears to be unique among *Diospyros* extractives in having different patterns of oxygenation in its two component units.

Each of the naphthalenes and naphthoquinones isolated from macassar ebony contains a *peri*-methoxy group. Apart from the *o*-naphthoquinone (**3**), they appear to originate from the dihydric 1-methoxynaphthols (**15**) and (**27**), or their equivalents, by the normal biogenetic processes of methylation, hydroxylation, dehydrogenation, and oxidative coupling. The exception, the *ortho*-quinone (**3**), has a methoxy group at C-8 but we suggest that it likewise results from the 1-methoxynaphthol (**27**), dehydrogenation in this case being accompanied by migration of the methyl group as in structure (**29**). It seems likely that the dihydric methoxynaphthols (**15**) and (**27**) result from the hydroxylation of the methoxynaphthol (**28**), which is known to occur in *Diospyros melanoxylon* and is thought[4] to be the precursor of the other naphthalene and naphthoquinone derivatives present in that species and in *D. chloroxylon*.



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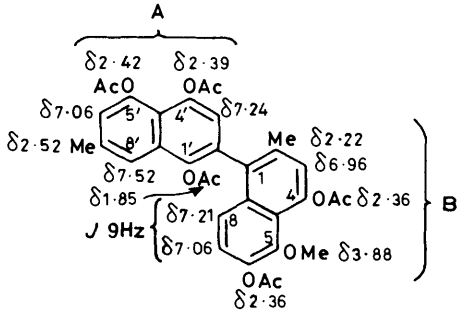

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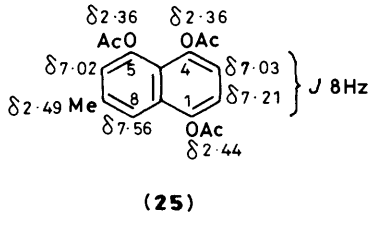

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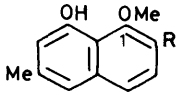
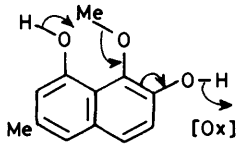


(**27**) R = OH
(**28**) R = H



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Experimental

General instructions are given in Parts 4[9] and 5.[7] Mass spectra were obtained using an A.E.I. MS-30 spectrometer at 70 eV.

Extraction of D. celebica *Bakh Heartwood* (*Macassar Ebony*).—The finely ground wood (1.4 kg) was extracted (Soxhlet) for 72 h periods first with light petroleum (4 l) and then with chloroform (4 l). Concentration of the pale-green light petroleum solution to 2 l resulted in the separation, overnight, of a green solid (420 mg) which crystallised from ethanol to give betulinic acid (250 mg). Further concentration of the extract (to 250 ml) and addition of chloroform (10 ml) afforded a yellow-brown solid (21.5 g) which was separated by column chromatography on acid-washed silica gel into (a) macassar III (9.3 g; eluted by benzene) which crystallised from light petroleum–chloroform as needles, m.p. 69—70 °C (lit.,[2] 70 °C); δ 2.45 (3 H, s, MeAr), 3.88, 3.93, and 3.95 (each 3 H, s, MeOAr), 6.67 and 7.13 (each 1 H, br s, 7- and 5-H), and 7.20 and 7.43 (2 H, ABq, *J* 9 Hz, 3- and 4-H), and (b) macassar II (**1**) [9.9 g; eluted by benzene–chloroform (9:1)] which crystallised from light petroleum–chloroform as prisms, m.p. 106 °C (lit.,[2] 107—107.5 °C); $\nu_{max.}$ 3 350 cm^{-1} (OH); $\lambda_{max.}$(MeOH) 247.5 (log ε 4.32), 287 (4.00), 298 (3.98), 336 (3.69), and 348 nm (3.75); $\lambda_{infl.}$ 278 nm (log ε 3.84); δ 2.40 (3 H, s, MeAr), 3.85 and 3.95 (each 3 H, s, MeOAr), 6.10 (1 H, s, HO), 6.66 and 7.13 (each 1 H, br s, 7- and 5-H), and 7.18 and 7.38 (2 H, ABq, *J* 9 Hz, 3- and 4-H). Finally the concentrated extract was evaporated and the resulting oil (2.8 g) was separated by t.l.c. on silica gel [chloroform–methanol (19:1)] into bands (i)—(vi) (in order of decreasing R_F). Bands (i)—(iii) yielded more macassar III (0.9 g), macassar II (1.19 g), and betulinic acid (126 mg), respectively.

Celebaquinone (4,5′,6-*Trihydroxy*-5-*methoxy*-2,7′-*dimethyl*-1,2′-*binaphthyl*-1′,4′-*quinone*) (**8**).—The dark oily solid from band (iv), after repeated t.l.c. on silica gel [benzene–ethyl acetate (9:1)], gave *celebaquinone* which crystallised from chloroform–light petroleum as green needles (30 mg), m.p. 201 °C (decomp.) (Found: *M*, 390.1103. $C_{23}H_{18}O_6$ requires *M*, 390.1103); $\nu_{max.}$ 3 342 (OH), 1 665, and 1 640 cm^{-1} (quinone C=O); $\lambda_{max.}$(MeOH) 232 (log ε 4.72), 294 (3.92), 304 (3.91), 335 (3.80), 348 (3.87), and 426 nm (3.60); $\lambda_{infl.}$ 240 (log ε 4.66) and 545 nm (2.86); δ[$(CD_3)_2CO$] 2.20 and 2.46 (each 3 H, s, 2- and 7′-Me), 4.08 (3 H, s, MeOAr), 6.72 and 6.93 (each 1 H, s, 3- and 3′-H), 7.10 and 7.31 (2 H, ABq, *J* 9 Hz, 7- and 8-H), and 7.16 and 7.42 (each 1 H, br s, 6′- and 8′-H); δ($CDCl_3$) 5.60, 9.04, and 11.93 (each 1 H, s, 6-, 4-, and 5′-OH); *m/z* 390 [100%, $(M)^{+\bullet}$], 375 [89%, $(M - Me)^+$], 347 (20%, 375 − CO), 163 (2%), 135 (5), 134 (5), and 106 (5).

Reductive acetylation for 1 h as described below for diosindigo B gave the corresponding *leucopenta-acetate* (**26**) as needles (from ethanol), m.p. 145 °C (Found: $M - CH_2CO$, 560.1678. $C_{31}H_{28}O_{10}$ requires *M*, 560.1682); $\nu_{max.}$ 1 770 cm^{-1} (aryl acetate C=O); $\lambda_{max.}$(MeOH) 230 (log ε 4.90), 292 (4.12), and 330 nm (3.64); $\lambda_{infl.}$ 315 nm (log ε 3.78); δ 1.85, 2.36, 2.36, 2.39, and 2.42 (each 3 H, s, $MeCO_2$ at C-1′, -4, -6, -4′, and -5′), 2.22 and 2.52 (each 3 H, s, 2- and 7′-Me), 3.88 (3 H, s, MeOAr), 6.96, 7.06br, 7.24, and 7.52br (each 1 H, s, 3-, 6′-, 3′-, and 8′-H), and 7.06 and 7.21 (2 H, ABq, *J* 9 Hz, 7- and 8-H); *m/z* 602 [1%, $(M)^{+\bullet}$], 560 (28%), 518 (35), 476 (56), 434 (100), and 392 (63) [each $(M - nCH_2CO)^{+\bullet}$].

4,5′-*Dihydroxy*-2,7′-*dimethyl*-1,2′-*binaphthyl*-1′,4′:5,6-*di-quinone* (**7**).—(*a*). A suspension of celebaquinone (10 mg) in 4M-nitric acid (3 ml) was heated on a steam-bath for 5 min and poured into water (20 ml). The resulting solid crystallised from light petroleum–chloroform to give the *diquinone* (8 mg) as red needles, m.p. 220—222 °C [Found: (*M* + 2 H), 376.0943. $C_{22}H_{16}O_6$ requires *M*, 376.0947]; $\nu_{max.}$ 1 680, 1 641, and 1 632 cm^{-1} (quinone and H-bonded quinone C=O); $\lambda_{max.}$(EtOH) 252.5 (log ε 4.30) and 445 nm (3.77); $\lambda_{infl.}$ 580 nm (log ε 3.08); δ 2.20 and 2.47 (each 3 H, s, 2- and 7′-Me), 6.35 and 7.23 (2 H, ABq, *J* 10 Hz, 8- and 7-H), 6.88 and 7.01 (each 1 H, s, 3- and 3′-H), 7.18 and 7.50 (each 1 H, br s, 6′- and 8′-H), and 11.81 and 12.31 (each 1 H, s, 5′- and 4-OH); *m/z* 376 [50%, $(M + 2H)^{+\bullet}$], 374 [27%, $(M)^{+\bullet}$], 359 [32%, $(M - Me)^+$], 358 [40%, $(M + 2H - H_2O)^{+\bullet}$], 346 [100%, $(M - CO)^{+\bullet}$], 163 (9%), 135 (20), 134 (11), and 106 (22).

(*b*). A mixture of celebaquinone (3 mg) in acetone (1 ml) and sodium periodate (15 mg) in water (1.5 ml) was kept overnight and then evaporated. Extraction with methylene chloride yielded the diquinone (2 mg).

6-*Hydroxy*-5-*methoxy*-2-*methyl*-1,4-*naphthoquinone* (**2**).—Band (v) gave a solid which sublimed at 130 °C/5 × 10^{-2} mmHg and then crystallised from light petroleum–chloroform to give the quinone as yellow needles (7 mg), m.p. 139—140 °C (lit.,[3,4] 152—153 °C) (Found: *M*, 218.0578. Calc. for $C_{12}H_{10}O_4$: *M*, 218.0579); $\nu_{max.}$ 3 330 (OH), 1 665 and 1 651 cm^{-1} (quinone C=O); $\lambda_{max.}$(MeOH) 262 (log ε 4.18) and 399 nm (3.38); $\lambda_{infl.}$ 530 nm (log ε 2.59); δ 2.15 (3 H, d, *J* 2 Hz, *Me*CR=CH–), 3.96 (3 H, s, MeOAr), 6.59 (1 H, br s, OH), 6.73 (1 H, m, MeCR=C*H*–), and 7.26 and 7.90 (2 H, ABq, *J* 8 Hz, 7- and 8-H); *m/z* 218 [100%, $(M)^{+\bullet}$], 200 [20%, $(M - H_2O)^{+\bullet}$], 172 (45%, 200 − CO), and 171 (35%, 172 − H). This was identical with an authentic specimen of diomelquinone A (supplied by Dr. G. S. Sidhu), which had m.p. 140—141 °C.

8-*Methoxy*-6-*methyl*-1,2-*naphthoquinone* (**3**).—Band (vi) afforded a solid which, after repeated t.l.c. [chloroform–methanol (93:7)], crystallised from light petroleum–chloroform to give the quinone as red cubes (37 mg), m.p. 164—165 °C (lit.,[2] 165 °C) (Found: *M*, 202.0628. Calc. for $C_{12}H_{10}O_3$: *M*, 202.0630); $\nu_{max.}$ 1 686 and 1 665 cm^{-1} (quinone C=O); $\lambda_{max.}$(MeOH) 245 (log ε 4.21), and 416 nm (3.79); δ 2.41 (3 H, s, MeAr), 3.97 (3 H, s, MeOAr), 6.39 and 7.30 (2 H, ABq, *J* 10 Hz, 4- and 3-H), and 6.75 and 6.87 (each 1 H, br s, 7- and 5-H); *m/z* 204 [15%, $(M + 2H)^{+\bullet}$], 202 [16, $(M)^{+\bullet}$], 174 [100, $(M - CO)^{+\bullet}$], 146 (25, 174 − CO), 145 (71, 146 − H), 144 (22, 174 − CH_2O), 131 (28, 146 − Me), 116 (56, 144 − CO), and 115 (94, 145 − CH_2O).

Examination of the Chloroform Extract.—Concentration of the extract (to 200 ml) and addition of methylene chloride (50 ml) resulted in the separation, overnight, of a blue crystalline solid (fraction 1; 259 mg). Further concentration (to 50 ml) and addition of methylene chloride (100 ml) gave a green solid (fraction 2; 40 mg); evaporation of all the solvent followed by addition of methylene chloride (100 ml) and light petroleum (10 ml) gave a colourless solid (fraction 3; 30 mg). Finally, evaporation of the solution afforded an oil (10 g) which was chromatographed on a column of acid-washed silica gel. Elution with benzene followed by benzene–chloroform (9:1) and benzene–chloroform (1:2) gave, respectively, macassar III (140 mg), macassar II (103 mg), and a solid (66 mg) identical with, and added to, fraction 3. Finally, elution with chloroform–methanol (97:3) afforded a brown gum which on trituration with benzene and crystallisation from chloroform–light petroleum gave an *acid*, $C_{13}H_{14}O_5$, as needles (833 mg), m.p. 140—141 °C.

Diosindigo B_2 (4,4′-*Diethoxy*-5,5′-*dihydroxy*-7,7′-*dimethyl*-2,2′-*binaphthyl*-1,1′-*quinone*) (**18**).—Fraction 1 was separated by repeated t.l.c. (chloroform) into blue bands (i)—(iii) (in order of decreasing R_F). Band (i) afforded a solid which crystallised from chloroform to give *diosindigo* B_2 as deep blue needles (59 mg), m.p. 275 °C (decomp.) [Found: (*M* + 2H), 434.1725. $C_{26}H_{26}O_6$ requires *M*, 434.1729]; $\nu_{max.}$ 3 406 (OH), 1 640, and 1 605 cm^{-1} (quinone C=O); $\lambda_{max.}$($CHCl_3$) 297 (log ε 4.48) and 698 nm (4.55); $\lambda_{infl.}$ 326 (log ε 4.30) and 671 nm (4.53); δ 1.56 (6 H, t, *J* 7 Hz, 4- and 4′-*Me*CH_2O), 2.35 (6 H, s, 7- and 7′-Me), 4.36 (4 H, q, *J* 7

Hz, 4- and 4′-MeCH_2O), 6.92br, 7.55br, and 8.31 (each 2 H, s, 6- and 6′-H, 8- and 8′-H, and 3- and 3′-H), and 8.92 (2 H, s, 5- and 5′-OH); *m/z* 434 [100%, $(M + 2H)^{+\cdot}$], 432 [10, $(M)^{+\cdot}$], 403 [16, $(M - Et)^+$], 402 (18, 403 − H), 387 [11, $(M - EtO)^+$], 375 (28, 403 − CO), 374 (28, 375 − H), and 359 (89, 387 − CO).

Reductive acetylation gave the corresponding *leucotetra-acetate* which crystallised from ethanol as needles, m.p. 215—216 °C [Found: ($M - CH_2CO$), 560.2044. $C_{32}H_{32}O_9$ requires *M*, 560.2046]; $\nu_{max.}$ 1 769 cm^{-1} (aryl acetate C=O); $\lambda_{max.}$(EtOH) 258 (log ε 4.40), 307 (4.10), and 335 nm (4.01); $\lambda_{infl.}$ 320 nm (log ε 4.06); δ 1.48 (6 H, t, *J* 7 Hz, 4- and 4′-*Me*CH_2O), 2.10 and 2.38 (each 6 H, s, 1-, and 5- and 5′-MeCO_2), 2.48 (6 H, s, 7- and 7′-Me), 4.08 (4 H, q, *J* 7 Hz, 4- and 4′-Me*C*H_2O), 6.68, 6.97br, and 7.39br (each 2 H, s, 3- and 3′-, 6- and 6′-, and 8- and 8′-H); *m/z* 602 [0.5%, $(M)^{+\cdot}$], 560 (47), 518 (100), 476 (35), and 434 (11) [each $(M - nCH_2CO)^{+\cdot}$].

Oxidation of Diosindigo B_2.—A suspension of diosindigo B_2 (10 mg) in 4M-nitric acid (3 ml) was heated on a steam-bath for 30 min and poured into hot water (20 ml). The resulting solid crystallised from light petroleum–chloroform to give birament-aceone (7 mg) as orange-red needles, m.p. 272 °C (decomp.) [lit.,[15] 235 °C (decomp.)]. An authentic specimen[15] had m.p. 272 °C (decomp.).

Diosindigo B_1 (4-*Ethoxy*-5,5′-*dihydroxy*-4′-*methoxy*-7,7′-*dimethyl*-2,2′-*binaphthyl*-1,1′-*quinone* (**17**).—Band (ii) afforded a solid which, after crystallisation from light petroleum–chloroform, gave *diosindigo* B_1 as deep blue needles (47 mg), m.p. 265 °C (decomp.) (Found: *M*, 418.1413. $C_{25}H_{22}O_6$ requires *M*, 418.1416); $\nu_{max.}$ 3 380 (OH), 1 633, and 1 605 cm^{-1} (quinone C=O); $\lambda_{max.}$($CHCl_3$) 296 (log ε 4.20) and 703 nm (4.29); $\lambda_{infl.}$ 330 (log ε 3.98) and 675 nm (4.24); δ 1.54 (3 H, t, *J* 7 Hz, 4-*Me*CH_2O), 2.33 (6 H, s, 7- and 7′-Me), 4.06 (3 H, s, 4′-MeO), 4.34 (2 H, q, *J* 7 Hz, 4-Me*C*H_2O), 6.92, 7.54, and 8.32 (each 2 H, br s, 6- and 6′-, 8- and 8′-H, and 3- and 3′-H), and 8.71 and 8.90 (each 1 H, s, 5′- and 5-OH); *m/z* 420 [40%, $(M + 2H)^{+\cdot}$], 418 [56, $(M)^{+\cdot}$], 403 [11, $(M - Me)^+$], 402 (18, 420 − H_2O), and 389 [100, $(M - Et)^+$].

Diosindigo B [*5,5′-Dihydroxy*-4,4′-*dimethoxy*-7,7′-*dimethyl*-2,2′-*binaphthyl*-1,1′-*quinone*) (**10**).—Band (iii), on similar treatment, yielded *diosindigo B* as deep blue needles (130 mg), m.p. 275 °C (decomp.) (Found: *M*, 404.1259. $C_{24}H_{20}O_6$ requires *M*, 404.1260); $\nu_{max.}$ 3 375 (OH), 1 634, and 1 612 cm^{-1} (quinone C=O); $\lambda_{max.}$($CHCl_3$) 296 (log ε 4.47) and 698 nm (4.55); $\lambda_{infl.}$ 330 (log ε 4.27) and 678 nm (4.53); δ 2.36 (6 H, s, 7- and 7′-Me), 4.10 (6 H, s, 4-and 4′-MeO), 6.95br, 7.57br, and 8.36 (each 2 H, s, 6- and 6′-H, 8- and 8′-H-, 3- and 3′-H), and 8.74 (2 H, s, 5- and 5′-OH); *m/z* 406 [77%, $(M + 2H)^{+\cdot}$], 404 [79, $(M)^{+\cdot}$], 389 [100, $(M - Me)^+$ and 406 − OH], 388 (40, 406 − H_2O), 374 (50, 389 − Me), 373 [75, $(M - MeO)^+$], and 359 (45, 374 − Me). When in contact with silica gel which had been washed with aqueous hydrochloric or oxalic acid, diosindigo B, like its homologues B_1 and B_2, rapidly decomposed to give yellow products.

Treatment of diosindigo B (7 mg) with acetic anhydride (2 ml) and pyridine (1 drop) at room temperature for 12 h yielded the corresponding *diacetate* (8 mg) which crystallised from chloroform as blue needles (8 mg), m.p. 272 °C (decomp.) (Found: *M*, 488.1470. $C_{28}H_{24}O_8$ requires *M*, 488.1471); $\nu_{max.}$ 1 750 (aryl acetate C=O), 1 628, and 1 600 cm^{-1} (quinone C=O); $\lambda_{max.}$($CHCl_3$) 292 (log ε 4.31) and 676 (4.28); $\lambda_{infl.}$ 325 nm (log ε 4.12); δ 2.31 (6 H, s, 5- and 5′-MeCO_2), 2.42 (6 H, s, 7- and 7′-Me), 3.98 (6 H, s, 4- and 4′-MeO), 7.04br, 7.92br, and 8.32 (each 2 H, s, 6- and 6′-H, 8- and 8′-H, and 3- and 3′-H); *m/z* 488 [100%, $(M)^{+\cdot}$], 446 [7, $(M - CH_2CO)^{+\cdot}$], 404 (6, 446 − CH_2CO), 389 (67, 404 − Me), and 373 (28, 404 − MeO).

Reductive Acetylation of Diosindigo B.—A mixture of diosindigo B (18 mg), zinc dust (30 mg), anhydrous sodium acetate (50 mg), and acetic anhydride (1.5 ml) was boiled under reflux for 30 min and then poured into hot water. Extraction with chloroform gave a solid which was separated by t.l.c. into bands (i)—(iii) (in order of decreasing R_F). Band (i) afforded 5,5′-*dihydroxy*-4,4′-*dimethoxy*-7,7′-*dimethyl*-2,2′-*binaphthyl*-1,1′-*diyl diacetate* (**11**) which crystallised from ethanol as needles (5 mg), m.p. 241 °C (Found: *M*, 490.1624. $C_{28}H_{26}O_8$ requires *M*, 490.1628); $\nu_{max.}$ 3 400 (OH) and 1 770 cm^{-1} (aryl acetate C=O); $\lambda_{max.}$(EtOH) 248 (log ε 4.25), 313 (3.68), 328 (3.69), and 342 nm (3.74); $\lambda_{infl.}$ 261 (log ε 4.07), 283 (3.58), and 298 nm (3.59); δ 2.10 (6 H, s, 1- and 1′-MeCO_2), 2.44 (6 H, s, 7- and 7′-Me), 4.01 (6 H, s, 4- and 4′-MeO), 6.65, 6.81br, and 7.00 br (each 2 H, s, 3- and 3′-H, 6- and 6′-H, and 8- and 8′-H), and 9.23 (2 H, s, 5- and 5′-OH); *m/z* 490 [6%, $(M)^{+\cdot}$], 448 [45, $(M - CH_2CO)^{+\cdot}$], and 406 (100, 448 − CH_2CO).

Band (ii) gave 5-*hydroxy*-4,4′-*dimethoxy*-7,7′-*dimethyl*-2,2′-*binaphthyl*-1,1′,5′-*triyl triacetate* (**12**) which crystallised from ethanol as needles (6 mg), m.p. 228 °C (Found: *M*, 532.1732. $C_{30}H_{28}O_9$ requires *M*, 532.1733); $\nu_{max.}$ 3 400 (OH), and 1 770 cm^{-1} (aryl acetate C=O); $\lambda_{max.}$(EtOH) 248 (log ε 4.34), and 308 nm (3.70); $\lambda_{infl.}$ 262 (log ε 4.16), 282 (3.70), 324 (3.67), and 337 nm (3.64); δ 2.11, 2.11, and 2.37 (each 3 H, s, 1-, 1′-, and 5′-MeCO_2), 2.44 and 2.49 (each 3 H, s, 7- and 7′-Me), 3.88 and 4.02 (each 3 H, s, 4′- and 4-MeO), 6.65, 6.71, 6.81br, 7.00br, 7.00br, and 7.40br (each 1 H, s, 3-, 3′-, 6-, 8-, 6′- and 8′-H), and 9.24 (1 H, s, 5-OH); *m/z* 532 [3.5%, $(M)^{+\cdot}$], 490 (50), 448 (100), and 406 (45) [each $(M - nCH_2CO)^{+\cdot}$].

Band (iii) afforded 4,4′-*dimethoxy*-7,7′-*dimethyl*-2,2′-*binaphthyl*-1,1′,5,5′-*tetrayl tetra-acetate* (*diosindigo B leucotetra-acetate*) (**14**) which crystallised from ethanol as needles (9 mg), m.p. 182 °C (Found: $M - CH_2CO$, 532.1733. $C_{30}H_{28}O_9$ requires *M*, 532.1733); $\nu_{max.}$ 1 757 cm^{-1} (aryl acetate C=O); $\lambda_{max.}$(EtOH) 248 (log ε 4.70), 305 (4.11), and 335 nm (3.96); $\lambda_{infl.}$ 262 (log ε 4.49), 295 (4.11), 3.18 (4.03), and 360 nm (2.94); δ 2.09 and 2.36 (each 6 H, s, 1- and 1′-, and 5- and 5′-MeCO_2), 2.48 (6 H, s, 7-and 7′-Me), 3.87 (6 H, s, 4- and 4′-MeO), and 6.70, 7.00br, and 7.40 br (each 2 H, s, 3- and 3′-, 6- and 6′-, and 8- and 8′-H); *m/z* 574 [0.5%, $(M)^{+\cdot}$], 532 (40), 490 (100), 448 (45), and 406 (14) [each $(M - nCH_2CO)^{+\cdot}$].

When a similar reaction mixture was boiled for 1 h the leucotetra-acetate was the sole product.

Isocelebaquinone (1,5,5′-*Trihydroxy*-4-*methoxy*-7,7′-*dimethyl*-2,2′-*binaphthyl*-1′,4′-*quinone* (**21**).—Fraction 2 of the chloroform extract, after repeated t.l.c. (chloroform) and crystallisation from chloroform, gave *isocelebaquinone*, as green needles (30 mg), m.p. 244 °C (decomp.) (Found: *M*, 390.1104. $C_{23}H_{18}O_6$ requires *M*, 390.1103); $\nu_{max.}$ 3 385 (OH), 1 665 and 1 633 cm^{-1} (quinone C=O); $\lambda_{max.}$($CHCl_3$) 342 (log ε 4.07), 454 (3.72), and 645 nm (3.30); $\lambda_{infl.}$ 327 nm (log ε 4.05); *m/z* 390 [100%, $(M)^{+\cdot}$], 375 [50, $(M - Me)^+$], 359 [7, $(M - MeO)^+$], 135 (10), and 106 (7).

Acetylation, as for diosindigo B, gave the corresponding *triacetate* (**22**) which crystallised from chloroform as yellow needles (12 mg), m.p. 178 °C (Found: *M*, 516.1417. $C_{29}H_{24}O_9$ requires *M*, 516.1420); $\nu_{max.}$ 1 770 (aryl acetate C=O), and 1 660 cm^{-1} (quinone C=O); $\lambda_{max.}$(EtOH) 248 (log ε 4.59) and 304 nm (4.03); $\lambda_{infl.}$ 258 (log ε 4.48), 331 (3.82), 357 (3.62), and 430 nm (3.10); δ 2.26, 2.36, and 2.45 (each 3 H, s, 1-, 5-, and 5′-MeCO_2), 2.48 and 2.50 (each 3 H, s, 7- and 7′-Me), 3.92 (3 H, s, 4-MeO), 6.62, 6.90, 7.00br, 7.23br, 7.42br, and 7.93br (each 1 H, s, 3-, 3′-, 6-, 6′-, 8- and 8′-H); *m/z* 516 [2%, $(M)^{+\cdot}$], 474 (45), 432 (75), 390 (100) [each ($M - nCH_2CO$)], and 375 (28, 390 − Me).

Reductive acetylation of isocelebaquinone gave the corresponding *leucopenta-acetate* (**24**) which crystallised from ethanol as needles, m.p. 162 °C (Found: *M*, 602.1790. $C_{33}H_{30}O_{11}$

requires M, 602.1788); $\nu_{max.}$ 1 766 cm^{-1} (aryl acetate C=O); $\lambda_{max.}$(EtOH) 251 nm (log ε 4.63); $\lambda_{infl.}$ 279 (log ε 4.08), 291 (4.05), 302 (3.98), and 332 nm (3.68); δ 2.12, 2.13, 2.38, 2.38, 2.40 (each 3 H, s, 1-, 1′-, 4′-, 5-, and 5′-$MeCO_2$), 2.50 (6 H, s, 7- and 7′-Me), 3.87 (3 H, s, 4-MeO), and 6.70, 6.99br, 7.04, 7.04br, 7.39br, and 7.47br (each 1 H, s, 3-, 6-, 3′-, 6′-, 8-, and 8′-H); m/z 602 [0.3%, $(M)^{+\bullet}$], 560 (89), 518 (100), 476 (60), 434 (89), and 392 (89) [each $(M - n CH_2CO)^{+\bullet}$].

Oxidation of isocelebaquinone (10 mg) as described above for diosindigo B_2 gave biramentaceone (7 mg), m.p. 272 °C (decomp.).

Dihydrodiosindigo B (*4,4′-Dimethoxy-7,7′-dimethyl-2,2′-binaphthyl-1,1′,5,5′-tetraol*) (**13**).—Fraction 3 of the chloroform extract, after column chromatography on acid-washed silica gel [benzene–chloroform 1:2)], gave *dihydrodiosindigo B* which crystallised from chloroform as needles (25 mg), m.p. 266—272 °C (decomp.) (Found: M, 406.1416. $C_{24}H_{22}O_6$ requires M, 406.1416); $\nu_{max.}$ 3 390 and 3 300 cm^{-1} (OH); $\lambda_{max.}$($CHCl_3$) 321 (log ε 4.05) and 353 nm (4.22); $\lambda_{infl.}$ 265 (log ε 4.43), and 340 nm (4.10); δ ($CDCl_3$ + CF_3CO_2D) 2.50 (6 H, s, 7- and 7′-Me), 4.06 (6 H, s, 4- and 4′-MeO), and 6.64, 6.89br, and 7.18br (each 2 H, s, 3-, 3′-, 6-, and 6′-, 8- and 8′-H); m/z 406 [100%, $(M)^{+\bullet}$], 391 [8, $(M - Me)^+$], 374 (18, 391 − OH), and 3.59 (56, 374 − Me). When adsorbed on silica gel it underwent rapid aerial oxidation giving diosindigo B; on oxidation as described for diosindigo B_2 it (10 mg) gave biramentaceone (7 mg).

Treatment of dihydrodiosindigo B (10 mg) with acetic anhydride (1.5 ml) and concentrated sulphuric acid (1 drop) for 12 h at 20 °C gave the corresponding tetra-acetate (12 mg) which crystallised from ethanol as needles, m.p. 182 °C, and was identical with the leucotetra-acetate of diosindigo B.

Acknowledgements

We thank Dr. G. S. Sidhu and Professor R. H. Thomson for specimens and the University of Aberdeen for a research studentship.

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Received 31*st July* 1985; *Paper* 5/1326