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Oxidative coupling of methoxynaphthylenediols

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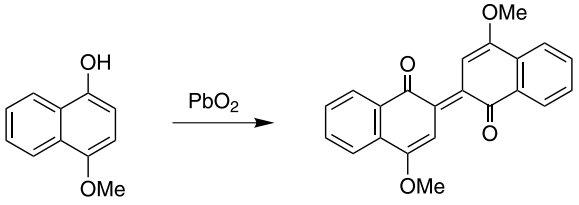
Abstract—The oxidative coupling of a mixture of 1-methoxy-7-methyl-4,5-naphthylenediol and 4-methoxy-7-methyl-1,5-naphthylenediol using lead(IV) oxide gives the symmetrical bisnaphthalene indigos diosindigo A and diosindigo B together with the corresponding unsymmetrical isomer. Oxidation of the first two by nitric acid gives the binaphthyldiquinones mamegakinone and biramentaceone, respectively; the third gives the unsymmetrical diquinone rotundiquinone. Similar oxidations of related naphthylenediols are described.

1. Introduction

The intensely coloured bisnaphthalene indigo 'Russig's Blue' **2**[1,2] is readily prepared by the lead(IV) oxide-induced oxidative coupling of 4-methoxy-l-naphthol **1**. Two symmetrically substituted derivatives of **2**, namely diosindigo A **13**[3] and diosindigo B **20**,[4] which occur naturally in woods of the *Diospyros* species, have been synthesised in a similar manner and converted by further oxidation into the corresponding orange-red binaphthyldiquinones mamegakinone **16** and biramentaceone **22**[3,5,6] which are found naturally in *Diospyros* and *Euclea* species.[7] We now describe the preparation of unsymmetrically substituted analogues of these quinones.



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2. Discussion

One of the starting materials required for the syntheses, the methoxynaphthylene diacetate **6**, was prepared by the sequence[8] shown in Scheme 1. The dihydrojuglone **3** formed the cyclic phenylboronate **4** which, on being treated with acetic anhydride and sodium acetate followed by water, produced a mixture of the diacetoxynaphthols **5** and **7**. Subsequent methylation with diazomethane gave a similar mixture of the methoxy diacetates **6** (~80%) and **8** (~20%), which we were unable to separate. However, as will be apparent later, the presence of the minor component had no discernible effect on the formation of the derived bisnaphthalene indigos. We have previously described the preparation of the diacetates of the other components required, the methoxynaphthylene diols **10**, **11**, and **18**.[8]

Of these starting materials the two methoxynaphthylene diacetates derived from juglone were the more accessible. The alkaline hydrolysis of a 1:1 mixture of **6** and the isomeric diacetate of **10** gave a mixture of the diols **10** and **17**. Treatment of this with lead(IV) oxide produced an intense blue mixture of the corresponding bisnaphthalene indigos which we separated by preparative TLC into the two symmetrically substituted quinones **12** (33%) (Scheme 2) and **19** (37%) (Scheme 3) and the unsymmetrical isomer **23** (17%) (Scheme 4). The first pair were identical with specimens prepared from the diols **10** and **17** separately. The poor solubility of the strongly hydrogen-bonded symmetrical quinone **12** prevented the measurement of its NMR signals and we characterised it as the leucoacetate **14**. The other symmetrical quinone **19** showed the expected NMR signals while the unsymmetrical quinone **23** gave a more complicated spectrum with the signals for the two types of hydroxy group, at δ 8.78 and 13.45, being particularly distinctive. An additional, yellow quinone isolated during the purification of the above blue compounds proved to be 5-methoxy-1,4-naphthoquinone **9**. This was derived from the minor contaminant **8** present in the methoxy diacetate **6**. The hydrolysis of **8** produced the 1,4-naphthylenediol which

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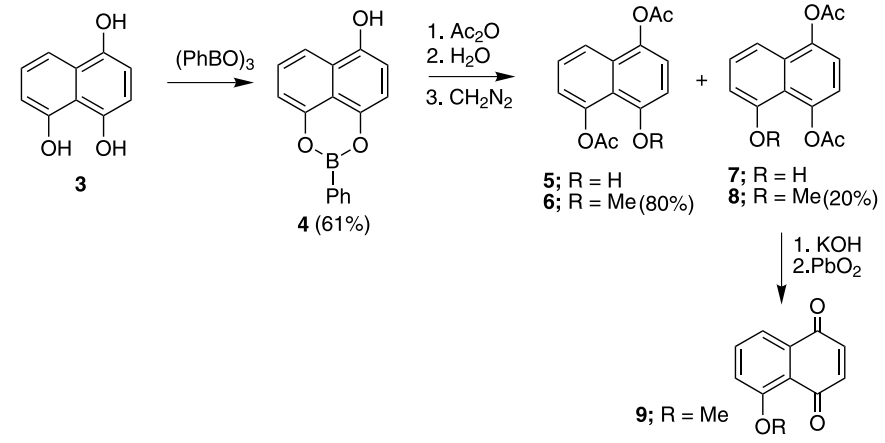
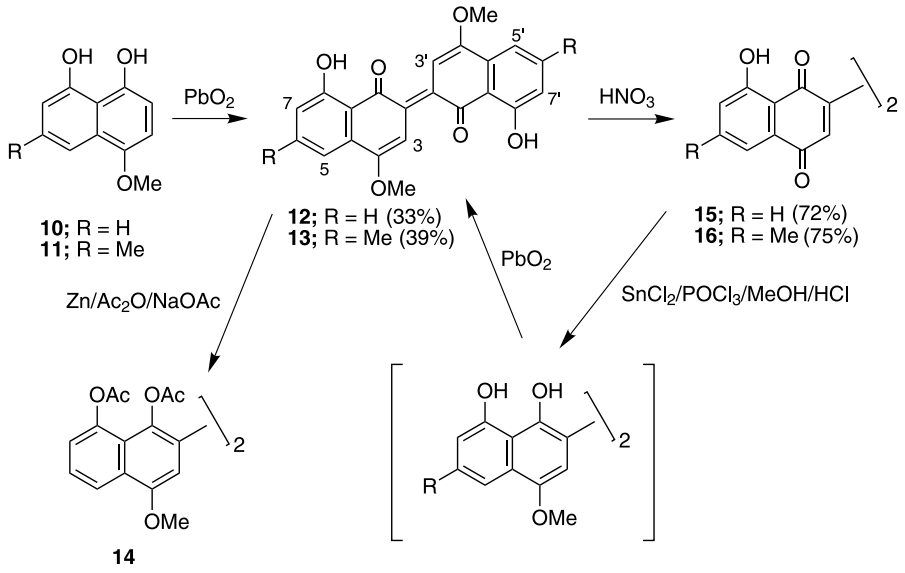
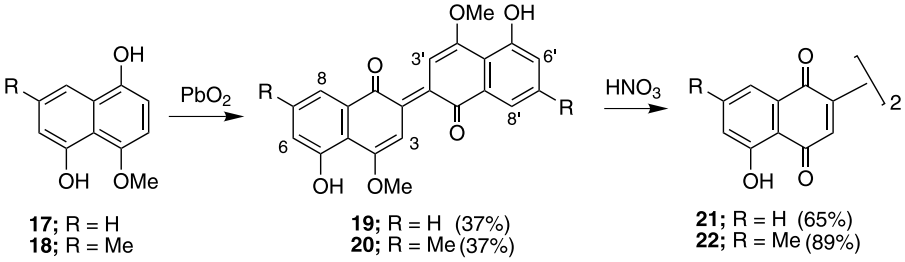


Scheme 1.



Scheme 2.

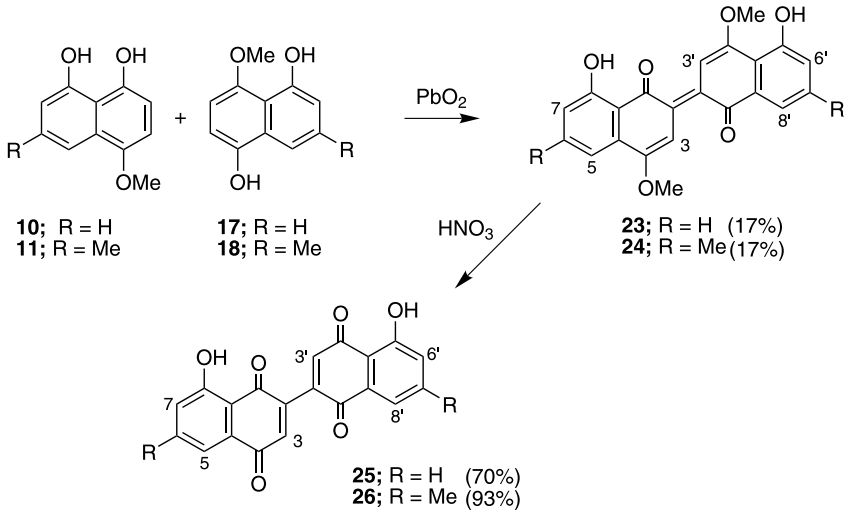


Scheme 3.

was oxidised immediately by lead(IV) oxide to the corresponding 1,4-naphthoquinone **9** (Scheme 1) and so did not participate in the phenolic coupling reactions.

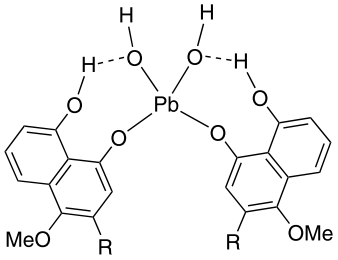
The application of the above hydrolysis with subsequent oxidation procedure to a mixture of the methyl-substituted methoxynaphthylene diacetates corresponding to the diols **11** and **18** gave the expected mixture of bisnaphthalene indigos (Schemes 2, 3 and 4) which we separated by preparative TLC into the symmetrical quinones diosindigo A **13** (39%) and diosindigo B **20** (37%). The structure of the third component, the unsymmetrical quinone **24** (17%), follows from its NMR signals which are similar to those[9] of diosindigo A plus those[4] of diosindigo B.

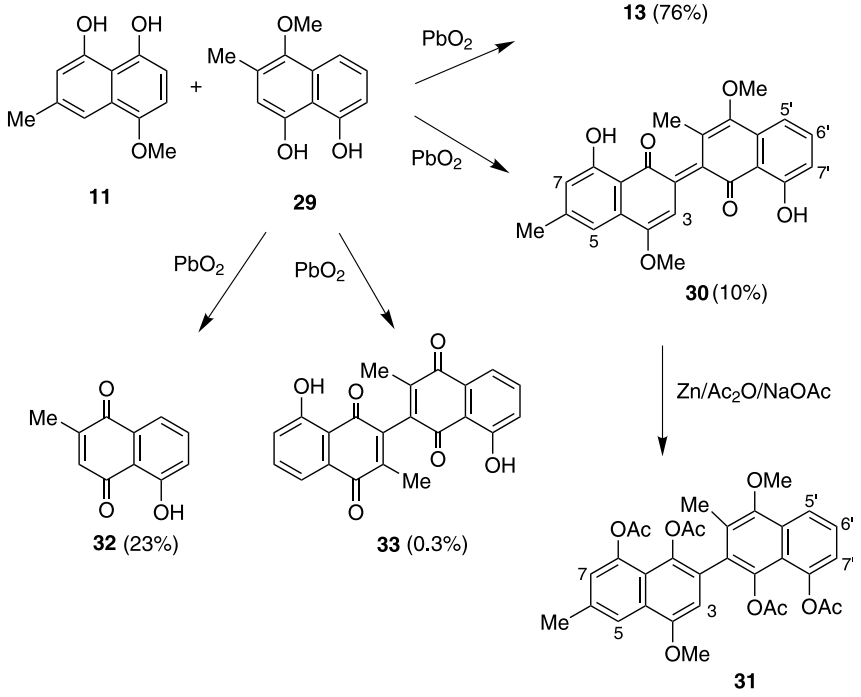
The oxidative coupling of two different phenols having similar reactivity would be expected to give the two symmetrical and the unsymmetrical products in the ratio



Scheme 4.

of 1:1:2. The much lower yields of the unsymmetrical bisnaphthalene indigos obtained in the present work indicate that the isomeric naphthols concerned react with lead(IV) oxide at differing rates. We attribute this to the difference in their hydroxylation patterns, the peri hydroxy groups of the 1,8-naphthylenediol systems in **10** and **11** providing stronger coordination to the metal than is possible with the 1,5-substituted isomers **17** and **18**. The rapid formation of a transient complex such as **27** between the diol **10** and lead(IV) oxide and the subsequent intramolecular coupling of its two naphthalene nuclei would effectively prevent much of the 1,8-dihydroxy compound **10** from coupling with the 1,5-dihydroxy isomer **17**. If four-fifths of the 1,8-isomer were removed from the reaction in this way the theoretical yields of each of the two symmetrical bisnaphthalene indigos would be 40% and that of the unsymmetrical quinone would be reduced to 20%. These values are in good agreement with those obtained experimentally and provide support for the above argument.





Scheme 5.

The bisnaphthalene indigos **12**, **19**, and **23** underwent oxidative demethylation readily on being treated with nitric acid, giving the corresponding binaphthyldiquinones **15**, **21** and **25**. The dimethyl analogues **13**, **24** and **20** behaved in a similar manner giving the naturally occurring diquinones[7] mamegakinone **16**, rotundiquinone **26**, and biramentaceone **22** (Schemes 2–4). Each of the unsymmetrical diquinones **25** and **26** showed two distinctive NMR signals for their hydroxy protons. In the mass spectrometer the molecular ions from the bijuglones **15**, **21** and **25** underwent cleavage of their quinone rings with the formation of characteristic[10] fragment radical-ions with *m*/*z* 120 ($C_7H_4O_2$) and 92 (C_6H_4O). The corresponding ions from their dimethyl counterparts **16**, **22**, and **26** had the expected *m*/*z* values of 134 and 106. We succeeded in reconverting the diquinone mamegakinone **16** into the monoquinone diosindigo A **13** by reductively methylating it using tin(II) chloride and phosphoryl(V) chloride in methanolic hydrochloric acid[8] and then oxidising the resulting binaphthyltetraol with lead(IV) oxide (Scheme 2).

All the above coupling reactions producing the bisnaphthalene indigos utilise methoxynaphthylenediols in which the aromatic ring with the hydroxy and methoxy groups carries no other substituents. We have noticed that the presence of a methyl group adjacent to the methoxy group has a deleterious effect on such reactions. Thus the oxidative coupling of the methoxynaphthylene diol **11** with the isomeric diol[8] **29** derived from plumbagin (Scheme 5) gave only two products, diosindigo A **13** (76%) and the cross-coupled bisnaphthalene indigo **30** (10%). The poor solubility of the latter prevented the measurement of its NMR spectrum and we characterised it as its leuco-acetate **31**. When we treated the methoxydiol **29** alone with lead(IV) oxide the products were plumbagin **32** (23%) and 3,3′-biplumbagin **33** (0.3%), both apparently resulting from heterolytic oxidative demethylation reactions. It appears that the presence of the two methyl groups in the postulated complex **28** largely inhibits the normal coupling reaction.

3. Experimental

3.1. General

Operations involving the formation of the free naphthols, particularly those in alkaline solution, were performed under nitrogen. IR spectra were measured for potassium bromide discs and UV–vis spectra were obtained for solutions in ethanol or, where indicated, in chloroform. ^{1}H NMR spectra were measured at 100 MHz for solutions in deuterochloroform or, where indicated, in perdeutero-acetone with tetramethylsilane as internal standard. Mass spectra were measured using EI at 70 eV. TLC was performed on silica gel (Merck GF_{254}). 'Light petroleum' refers to the fraction with bp 60–80 °C. The reaction products were colourless solids unless stated otherwise.

3.2. Oxidative coupling reactions

A mixture of the methoxynaphthylene diacetates (ca. 0.25 mmol) was boiled under reflux for 0.5 h with 3% methanolic potassium hydroxide (5 ml) under nitrogen. The mixture was added to 1 M sulphuric acid (10 ml) and shaken with chloroform (5×5 ml). The dried chloroform solution was warmed with lead(IV) oxide (500 mg, 2.42 mmol) for 5 min, filtered hot, and the deep blue filtrate was treated twice more with lead(IV) oxide (50 mg) in the same manner. The chloroform solution was then subjected to preparative TLC in order to separate the components of the mixture of bisnaphthalene indigos.

3.3. Oxidative demethylation reactions

A suspension of the bisnaphthalene indigo (10 mg) in 4 M nitric acid (1.5 ml) was heated on the steam-bath for 0.5 h and then poured into water (7 ml). The resulting solid was crystallised from light petroleum to give the substituted 2,2′-binaphthyl-1,4:1′,4′-diquinone (65–93%).

3.4. Reductive acetylation of quinones

A mixture of the quinone (4 mg), acetic anhydride (1 ml), zinc dust (50 mg) and anhydrous sodium acetate (50 mg) was boiled under reflux for 30–60 min and added to hot water. Extraction with chloroform gave the corresponding leucoacetate.

3.4.1. 1-Hydroxy-4,5-naphthylene phenylboronate 4. A mixture of 1,4,5-naphthalene triol[11] **3** (2 g, 11.36 mmol), phenylboronic anhydride (1.18 g, 11.36 mmol) and benzene (100 ml) was boiled under reflux using a Dean-Stark apparatus until the evolution of water was complete. Concentration of the solution gave a solid which crystallised from benzene to yield the phenylboronate **4** (1.8 g, 6.87 mmol, 61%) as needles, mp 200–202 °C (Found: M^+ 262.0798. C, 73.0; H, 4.0%. $C_{16}H_{11}{}^{11}BO_3$ requires *M* 262.0801. C, 73.3; H, 4.2%); *m*/*z* 262 (100%, M), 233 (19, M−CHO) and 131 (4, M^{2+}); ν_{max}/cm^{-1} 3210 (OH), 1638, 1618 and 1602 (aromatic C=C) and 1330 (B–O); λ_{max}/nm 319 (log ε 3.71), 334 (3.73) and 348 (3.73); δ_H [$(CD_3)_2CO$] 6.85 (2H, s, H-2 and -3), 6.99 (1H, dd, J=1.8 Hz, H-6), 7.20–7.63 (4H, m, H-7 and *m*- and *p*-H's of Ph), 7.75 (1H, dd, J=1.8 Hz, H-8) and 7.90–8.18 (2H, m, *o*-H's of Ph).

3.4.2. Reaction of 1-hydroxy-4,5-naphthylene phenylboronate 4 with acetic anhydride and sodium acetate. A mixture of the phenylboronate (410 mg, 1.57 mmol), acetic anhydride (5.4 g, 52.95 mmol) and anhydrous sodium acetate (80 mg, 0.98 mmol) was kept for 27 h at 20 °C, poured into water and extracted with chloroform. The chloroform solution, after being washed with aqueous sodium hydrogen carbonate and evaporated, afforded a solid which crystallised from benzene to give a mixture of 4,8-diacetoxy-1-naphthol **5** and 5,8-diacetoxy-1-naphthol **7** (110 mg, 0.43 mmol, 27%) as needles, mp 154–156 °C (Found: M^+, 260.0684. Calcd for $C_{14}H_{12}O_5$: *M*, 260.0684); *m*/*z* 260 (l.5%, M), 218 (5, M−CH_2CO), 176 (100, 218-CH_2CO) and 147 (3.5, 176-CHO); ν_{max}/cm^{-1} 3440 (OH) and 1750 (aryl acetate C=O); λ_{max}/nm 292infl (log ε 3.70), 303.5 (3.79), 317 (3.75) and 331 (3.67).

3.4.3. Methylation of the mixture of diacetoxynaphthols 5 and 7. A solution of diazomethane [from *N*-nitrosomethylurea (2 g, 19.4 mmol) in ether (30 ml)] was added to a solution of the mixture of diacetoxynaphthols (100 mg, 0.38 mmol) in

ether (20 ml) and the mixture was kept for four days at 20 °C. Evaporation of the solvent and crystallisation of the residue from light petroleum/chloroform gave a mixture of 4-methoxy-1,5-naphthylene diacetate **6** (80%) and 5-methoxy-l,4-naphthylene diacetate **8** (20%) (92 mg, 0.34 mmol, 88%) as needles, mp 107–112 °C (Found: M^+, 274.0840. Calcd for $C_{15}H_{14}O_5$: *M*, 274.0841); *m/z* 274 (26%, M), 232 (20, M−CH_2CO) and 190 (100, 232-CH_2CO); ν_{max}/cm^{-1} 1757 (aryl acetate C=O); λ_{max}/nm 298 (log ε 3.88), 312 (3.78) and 326.5 (3.64); δ_H 2.40 and 2.47 (each 3H, s, CH_3CO_2Ar), 3.98 (3H, s, CH_3OAr) and 6.75–7.85 (5H, m, ArH).

3.4.4. Oxidative coupling of 1-methoxynaphthylene-4,5-diol 10 with 4-methoxy-naphthylene-1,5-diol 17. A mixture of 4-methoxy-1,5-naphthylene diacetate **6** (27 mg, 0.10 mmol, containing 20% of 5-methoxy-1,4-naphthylene diacetate **8**) and 1-methoxy-4,5-naphthylene diacetate[8] (**10** diacetate) (22 mg, 0.085 mmol) was hydrolysed and oxidatively coupled as above. Preparative TLC afforded three blue products.

(a). The fastest-moving compound crystallised from chloroform to give 8,8′-dihydroxy-4,4′-dimethoxy-2,2′-binaphthyl-1,1′-quinone **12** as deep blue needles (10 mg, 0.027 mmol, 33%), mp > 350 °C (lit.,[6] (350 °C) (Found: M^+, 376.0947. C, 69.9; H, 4.0%. $C_{22}H_{16}O_6$ requires: *M* 376.0947. C, 70.2; H, 4.3%); *m/z* 376 (50%, M), 361 (32, M−Me), 346 (22, 361-Me), 345 (100, M−MeO) and 92 (30, C_6H_4O); ν_{max}/cm^{-1} 1578 (quinone C=O); λ_{max}/nm ($CHCl_3$) 285 (log ε 4.40), 326infl (4.02), 507 (3.57), 664infl (4.32) and 703 (4.40). This was identical with an authentic specimen prepared from 1-methoxy-4,5-naphthylene diacetate by the same procedure.

Reductive acetylation of the quinone **12** gave the corresponding leucotetra-acetate **14** which crystallised from ethanol in needles, mp 251.5–253.5 °C (Found: M^+, 546. C, 66.2; H, 5.0%. $C_{30}H_{26}O_{10}$ requires *M* 546. C, 65.9; H, 4.8%); *m/z* 546 (0.5%, M), 504 (10), 462 (13), 420 (1.5) and 378 (25) (each M−*n*CH_2CO), 444 (13, 462-H_2O), 402 (100, 420-H_2O), 387 (2, 402-Me), 360 (45, 378-H_2O), 346 (11, 402-2CO), 345 (11, 360-Me) and 331 (5, 346-Me); ν_{max}/cm^{-1} 1770 and 1758 (aryl acetate C=O) and 1598 (aromatic C=C); λ_{max}/nm 242 (log ε 4.72), 257infl (4.38), 262infl (4.32), 307 (4.03), 317 (4.02) and 330 (3.95); δ_H 2.00 (6H, s, CH_3CO_2Ar at C-1 and -1′), 2.35 (6H, s, CH_3CO_2Ar at C-8 and -8′), 3.98 (6H, s, CH_3O at C-4 and -4′), 6.75 (2H, s, H-3 and -3′), 7.18 (2H, dd, *J*=1.5, 8 Hz, H-7 and -7′), 7.52 (2H, dd, *J*=8, 8 Hz, H-6 and -6′) and 8.28 (2H, dd, *J*=1.5, 8 Hz, H-5 and -5′).

(b) The next blue product crystallised from light petroleum /chloroform to yield 5′,8-dihydroxy-4,4′-dimethoxy-2,2′-binaphthyl-1,1′-quinone **23** (5 mg, 0.013 mmol, 17%) as deep blue needles, mp 244–245 °C (decomp.) (Found: M^+, 376.0946. $C_{22}H_{16}O_6$ requires *M*, 376.0946); *m/z* 378 (19%, M+2H), 376 (84, M). 361 (45, M−Me), 345 (100, M−MeO); ν_{max}/cm^{-1} 3400 (hydrogen-bonded ArOH), 1595 and 1580 (quinone C=O); λ_{max}/nm ($CHCl_3$) 283 (log ε 4.36), 320infl (4.14), 514infl (3.69), 638infl (4.32) and 684 (4.41); δ_H 4.02 (3H, s, MeO at C-4), 4.15 (3H, s, hydrogen-bonded MeO at C-4′), 6.98–7.78 (6H, m, H-5, -6., -6′, -7, -7′ and -8′), 8.30 (1H, s, H-3), 8.49 (1H, s, H-3′), 8.78 (1H, s, OH at C-5′) and 13.45 (1H, s, OH at C-8).

(c) The slowest-moving blue product crystallised from chloroform to give 5,5′-dihydroxy-4,4′-dimethoxy-2,2′-binaphthyl-1,1′-quinone **19** (11 mg, 0.029 mmol, 37%) as deep blue needles, mp 259–260 °C (decomp.) (Found: M^+, 376.09433, $C_{22}H_{16}O_6$ requires *M*, 376.0946); *m/z* 378 (45%, M+2H), 376 (100, M), 361 (67, M−Me), 346 (20, 361-Me) and 345 (40, M−MeO); ν_{max}/cm^{-1} 3340 (ArOH), 1605 (quinone C=O) and 1588 (aromatic C=C); λ_{max}/nm ($CHCl_3$) 286 (log ε 4.18), 316infl (3.98) and 668 (4.28); δ_H 4.13 (6H, s, MeO at C-4 and -4′), ca. 7.11 (2H, m, H-6 and -6′), ca. 7.36 (2H, m, H-7 and -7′), ca. 7.76 (2H, m, H-8 and -8′), 8.40 (2H, s, H-3 and -3′) and 8.83 (2H, s, OH at C-5 and -5′). This was identical with an authentic specimen prepared from 4-methoxy-1,5-naphthylene diacetate by the same procedure.

The mother-liquor from the above crystallisations, on being subjected to TLC using chloroform, gave a solid which afforded 5-methoxy-1,4-naphthoquinone **9** (2.5 mg) as yellow needles, mp 184–185 °C (lit., [12] 186 °C) (Found: M^+, 188.0476. $C_{11}H_8O_3$ requires *M*, 188.0473); ν_{max}/cm^{-1} 1673 and 1666 (quinone C=O) and 1624 (aromatic C=C); λ_{max}/nm 245 (log ε 4.20), 328 (3.05) and 394 (3.58); δ_H 4.00 (3H, s, MeO at C-5), 6.67 (2H, s, H-2 and -3), ca. 7.32 (1H, m, H-6) and ca. 7.49 (2H, m, H-7 and -8). This was identical with an authentic specimen.[12]

3.4.5. Oxidative demethylation of the bisnaphthalene indigos 12, 19 and 23. (a) The oxidation product obtained from the symmetrical quinone **12** crystallised from light petroleum to give 8,8′-dihydroxy-2,2′-binaphthyl-1,4:1′,4′-diquinone **15** as red-brown needles (72%), mp 270–273 °C (decomp.) (Found: M^+, 346.0476. C, 69.1; H, 2.8%. $C_{20}H_{10}O_6$ requires *M* 346.0477. C, 69.4; H, 2.9%); *m/z* 346 (100%, M), 329 (17, M−OH), 290 (4, M−2CO), 289 (8, M−CO–CHO), 262 (5, 290-CO), 234 (3, 262-CO), 120 (10, $C_7H_4O_2$)- and 92 (21, C_6H_4O); ν_{max}/cm^{-1} 1670, 1650 and 1635 (quinone C=O) and 1608 (aromatic C=C); λ_{max}/nm 256infl (log ε 4.18), 274 (4.19), 434 (3.83) and 560infl (3.24); δ_H 7.06 (2H, s, H-3 and -3′), 7.33 (2H, dd, *J*=5, 5 Hz, H-6 and -6′), 7.70 (4H, dd, *J*=1, 5 Hz, H-5, -5′, -7 and -7′) and 11.73 (2H, s, OH at C-8 and -8′).

(b) The oxidation product from the unsymmetrical quinone **23** crystallised from light petroleum to give 5′,8-dihydroxy-2,2′-binaphthyl-1,4:1′,4′-diquinone **25** as red-brown needles (70%), mp 247–250 °C (decomp.) (Found: M^+, 346.0476. $C_{20}H_{10}O_6$ requires *M* 346.0477); *m/z* 348 (10%, M+2H), 346 (100, M), 329 (13, M−OH), 290 (6, M−2CO), 289 (10, M−CO–CHO), 262 (7, 290-CO), 120 (8, $C_7H_4O_2$) and 92 (16, C_6H_4O); ν_{max}/cm^{-1} 1670 and 1638 (quinone C=O) and 1600 (aromatic C=C); λ_{max}/nm 240infl (log ε 4.30), 266infl (4.27) and 434 (3.83); δ_H 7.02 and 7.05 (each 1H, s, H-3 and -3′), ca. 7.32 (2H, m, H-6′ and -7), ca. 7.69 (4H, m, H-5, -6, -7′ and -8′), 11.74 (1H, s, OH at C-8) and 11.84 (1H, s, OH at C-5′).

(c) The oxidation product from the symmetrical quinone **19** crystallised from light petroleum to give 5,5′-dihydroxy-2,2′-binaphthyl-1,4:1′,4′-diquinone **21** as yellow plates

(65%), mp 267–270 °C (decomp.) (Found: M^+, 346.0476. $C_{20}H_{10}O_6$ requires *M*, 346.0477); *m/z* 346 (100%, M), 329 (10, M−OH), 290 (3, M−2CO), 289 (8, M−CO–CHO), 262 (5, 290-CO), 234 (3, 262-CO), 120 (8, $C_7H_4O_2$) and 92 (22, C_6H_4O); ν_{max}/cm^{-1} 1638 and 1622 (quinone C=O) and 1602 (aromatic C=C); λ_{max}/nm 247 (log ε 4.31), 267infl (4.27) and 438 (3.94); δ_H 7.05 (2H, s, H-3 and -3′), 7.32 (2H, dd, *J*=5, 5 Hz, H-7 and -7′), 7.68 (4H, dd, *J*=1, 5 Hz, H-6, -6′, -8 and -8′) and 11.83 (2H, s, OH at C-5 and -5′).

3.4.6. Oxidative coupling of 1-methoxy-7-methyl-4,5-naphthylenediol 11 with 4-methoxy-7-methyl-1,5-naphthylenediol 18. A mixture of 1-methoxy-7-methyl-4,5-naphthylene diacetate[8] (**11** diacetate) (35 mg, 0.12 mmol) and 4-methoxy-7-methyl-1,5-naphthylene diacetate[8] (**18** diacetate) (35 mg, 0.12 mmol) was hydrolysed and oxidatively coupled as described above. Three blue products resulted.

(a) The fastest-moving compound crystallised from chloroform to yield 8,8′-dihydroxy-4,4′-dimethoxy-6.6′-dimethyl-2,2′-binaphthyl-1,1′-quinone (diosindigo A) **13** (19 mg, 0.047 mmol, 39%) as deep blue needles, mp 317 °C (decomp.) (lit.,[3] 317 °C decomp.) identical with an authentic specimen.

(b) The next product crystallised from light petroleum /chloroform to yield 5′, 8-dihydroxy-4,4′-dimethoxy-6,7′-dimethyl-2,2′-binaphthyl-1,1′-quinone **24** as deep blue needles (8 mg, 0.020 mmol, 17%), mp 257–258 °C (decomp.) (Found: M^+, 404.1260. $C_{24}H_{20}O_6$ requires *M* 404.1259); *m/z* 406 (16%, M+2H), 404 (67, M), 389 (56, M−Me) and 373 (100, M−MeO); ν_{max}/cm^{-1} 3400 (ArOH) and 1588 (hydrogen-bonded quinone C=O); λ_{max}/nm ($CHCl_3$) 292 (log ε 4.46), 322infl (4.23), 504infl (3.67), 665infl (4.50) and 694 (4.54); δ_H 2.38 (6H, s, Me at C-6 and -7′), 4.01 (3H, s, MeO at C-4), 4.13 (3H, s, MeO at C-4′), 6.80 (1H, br s, H-7), 6.94 (1H, br s, H-6′), 7.10 (1H, br s, H-5), 7.57 (1H, br s, H-8′), 8.26 (1H, s, H-3′), 8.47 (1H, s, H-3), 8.69 (1H, s, OH at C-5′) and 13.51 (1H, s, OH at C-8).

(c) The slowest-moving compound crystallised from chloroform to give 5,5′-dihydroxy- 4,4′-dimethoxy-7,7′-dimethyl-2,2′-binaphthyl-1,1′-quinone (diosindigo B) **20** (18 mg, 0.045 mmol, 37%) as deep blue needles, mp 275 °C (decomp.) identical with an authentic specimen.[8]

3.4.7. Oxidative demethylation of the methyl-substituted bisnaphthalene indigos 13, 20 and 24. (a) The oxidation product from diosindigo A **13** crystallised from light petroleum to give 8,8′-dihydroxy-6,6′-dimethyl- 2,2′-binaphthyl-1,4:1′,4′-diquinone **16** (mamegakinone) (75%) as orange-red needles, mp 254–256 °C (decomp.) (lit.,[13] 256 °C decomp.) (Found: M^+, 374.0793. $C_{22}H_{14}O_6$ requires *M*, 374.0790); *m/z* 374 (100%, M), 357 (20, M−OH), 318 (11, M−2CO), 317 (14, M−CO–CHO), 290 (13, 318-CO), 262 (6, 290-CO), 135 (5, $C_8H_7O_2$), 134 (13, $C_8H_6O_2$) and 106 (25, C_7H_6O); ν_{max}/cm^{-1} 1661, 1642 and 1627 (quinone C=O); λ_{max}/nm (EtOH +10% dioxan) 253 (log ε 4.27), 272infl (4.20) and 440 (3.85); δ_H 2.47 (6H, s, Me at C-6 and -6′), 6.98 (2H, s, H-3 and -3′), 7.13 (2H, br s, H-7 and -7′), 7.50 (2H, br s, H-5 and -5′) and 11.69 (2H, s, OH at C-8 and -8′). This was identical with an authentic specimen.[13]

(b) The oxidation product from the unsymmetrically substituted 5′,8-dihydroxy-4,4′-dimethoxy-6,7′-dimethyl-2,2′-binaphthyl-1,1′-quinone **24** crystallised from light petroleum giving 5′,8-dihydroxy-6,7′-dimethyl-2,2′-binaphthyl-1,4:1′,4′-diquinone **26** (rotundiquinone[14]) (93%) as orange-red needles, mp 239 °C (decomp.) (Found: M^+, 374.0789. $C_{22}H_{14}O_6$ requires *M*, 374.0790); *m/z* 374 (100%, M), 357 (21, M−OH), 318 (10, M−2CO), 317 (11, M−CO–CHO), 290 (13, 318-CO), 262 (3, 290-CO), 134 (6, $C_8H_6O_2$) and 106 (16, C_7H_6O); ν_{max}/cm^{-1} 1666 and 1643 (quinone C=O); λ_{max}/nm 253 (log ε 4.16), 274infl (4.09) and 438 (3.81); δ_H 2.46 (6H, s, Me at C-6 and -7′), 6.98 (1H, s, H-3), 7.03 (1H, s, H-3′), 7.13 and 7.15 (each 1H, br s, H-6′ and -7), 7.50 and 7.52 (each 1H, br s, H-5 and -8′), 11.70 (1H. s, OH at C-8) and 11.80 (1H, s, OH at C-5′).

(c) The oxidation product from diosindigo B **20** crystallised from light petroleum to give 5,5′-dihydroxy- 7,7′-dimethyl-2,2′-binaphthyl-1,4:1′,4′-diquinone **22** (biramentaceone) as orange-red needles (89%), mp 272 °C (decomp.) (Found: M^+, 374.0789. $C_{22}H_{14}O_6$ requires *M*, 374.0790); *m/z* 376 (10%, M+2H), 374 (100, M), 357 (28, M−OH), 346 (4, M−CO), 318 (10, 346-CO), 317 (14, 346-CHO), 303 (5, 318-Me), 290 (12, 318-CO), 262 (5, 290-CO), 187 (6, M^{2+}), 135 (6, $C_8H_7O_2$), 134 (10, $C_8H_6O_2$) and 106 (20, C_7H_6O); ν_{max}/cm^{-1} 1665 and 1645 (quinone C=O); λ_{max}/nm (EtOH +10% dioxan) 252 (log ε 4.26), 273infl (4.16) and 444 (3.90); δ_H 2.46 (6H, s, Me at C-7 and -7′), 7.01 (2H, s, H-3 and -3′), 7.13 (2H, br s, H-6 and -6′), 7.50 (2H, br s, H-8 and -8′) and 11.80 (2H, s, OH at C-5 and -5′). This was identical with an authentic specimen[15] of biramentaceone which had mp 272 °C (decomp.).

3.5. Conversion of mamegakinone 16 into diosindigo A 13

A mixture of mamegakinone **16** (5 mg, 0.013 mmol), tin(II) chloride dihydrate (5 mg, 0.022 mmol), phosphoryl(V) chloride (20 mg, 0.13 mmol), 4 M hydrochloric acid (2 ml) and methanol (10 ml) was boiled under reflux under nitrogen for 1 h, diluted with water, and extracted with chloroform. A mixture of the chloroform solution and lead(IV) oxide (200 mg, 0.97 mmol) was boiled under reflux for 0.5 h, filtered and evaporated. The resulting blue solid crystallised from chloroform to give diosindigo A **13** (5 mg, 0.012 mmol, 93%) identical with an authentic specimen.

3.5.1. Oxidative coupling of 1-methoxy-7-methyl-4,5-naphthylenediol 11 with 1-methoxy-2-methyl-4,5-naphthylenediol 29. A mixture of 1-methoxy-7-methyl-4,5-naphthylene diacetate (**11** diacetate)[8] (30 mg, 0.10 mmol) and 1-methoxy-2-methyl-4,5-naphthylene diacetate (**29** diacetate)[8] (30 mg, 0.10 mmol) was hydrolysed and oxidised as described above. TLC afforded two products the faster-moving of which crystallised from chloroform to give diosindigo A **13** (16 mg, 0.04 mmol, 76%) identical with an authentic specimen. The slower-moving product crystallised from light

petroleum/chloroform to give 8,8′-dihydroxy-4,4′-dimethoxy-3′,6-dimethyl-2,2′-binaphthyl-1,1′-quinone **30** (4 mg, 0.01 mmol, 10%) as deep blue needles, mp>360 °C (Found: $(M-Me)^+$, 389.1023. $C_{23}H_{17}O_6$ requires (M−Me), 389.1025); *m/z* 404 (6%, M), 389 (16, M−Me), 388 (45, 389-H), 375 (6, M−CHO), 374 (75, 389-Me), 373 (100, M−MeO), 360 (14, 388-CO), 359 (56, 388-CHO), 358 (18, 389-MeO), 357 (16, 388-MeO), 345 (11, 373-CO) and 343 (14, 374-MeO); ν_{max}/cm^{-1} 1580 and 1572 (hydrogen-bonded quinone C=O); λ_{max}/nm ($CHCl_3$) 291 (log ε 4.52), 337infl (4.23), 516infl (3.91) and 692 (4.49).

Reductive acetylation gave the corresponding leucotetra-acetate **31** which crystallised from ethanol as needles (Found: M^+, 574.1841. $C_{32}H_{30}O_{10}$ requires *M*, 574.1839); *m/z* 574 (2%, M), 532 (20, M−CH_2CO), 490 (22, 532-CH_2CO), 472 (5, 490-H_2O), 448 (3, 490-CH_2CO), 430 (100, 448-H_2O), 415 (7, 430-Me), 406 (35, 448-CH_2CO) and 388 (45, 406-H_2O); ν_{max}/cm^{-1} 1775 and 1765 (aryl acetate C=O) and 1610 (aromatic C=C); λ_{max}/nm 242 (log ε 4.84), 253infl (4.70), 282infl (4.35), 290infl (4.34), 313infl (4.21) and 328infl (4.07); δ_H 1.94 and 2.00 (each 3H, s, $MeCO_2Ar$ at C-1 and -1′), 2.34 (6H, s, $MeCO_2Ar$ at C-8 and -8′), 2.45 and 2.52 (each 3H, s, Me at C-3′ and -6), 3.93 and 3.95 (each 3H, s, MeO at C-4 and -4′), 6.66 (1H, s, H-3), 6.98–7.10 (2H, m, H-7 and -7′), 7.25–7.48 (1H, m, H-6′) and 7.98–8.14 (2H, m, H-5 and -5′).

3.5.2. Oxidative coupling of 1-methoxy-2-methyl-4,5-naphthylenediol 29. 1-Methoxy-2-methyl-4,5-naphthylene diacetate (**29** diacetate)[8] (0.5 g, 1.74 mmol) was hydrolysed and oxidised with lead(IV) oxide as described above. Separation of the products by TLC using chloroform on silica gel containing oxalic acid gave, as the major product, plumbagin **32** (73 mg, 0.39 mmol, 23%), identical with an authentic specimen.

The minor product crystallised from light petroleum to give 8,8′-dihydroxy-3,3′-dimethyl-2,2′-binaphthyl-1,4:1′,4′-diquinone **33** (3,3′-biplumbagin) (1 mg, 0.0027 mmol, 0.3%) as yellow needles, mp 214–216 °C (lit.,[16] 214–216 °C); *m/z* 374 (100%, M), 373 (9, M−H), 359 (92, M−Me), 357 (56, M−OH), 346 (7, M−CO), 345 (9, M−CHO), 331 (31, 359-CO), 330 (7, 345-Me), 329 (13, 357-CO), 317 (9, 346-CHO), 187 (7, M^{2+}), 149 (6, $C_8H_5O_3$), 121 (25, $C_7H_5O_2$), 120 (20, $C_7H_4O_2$) and 92 (33, C_6H_4O). This was identical (MS, UV and IR) with an authentic specimen.[16]

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