

## A Revised Structure for Dehydrotectol and Tecomaquinone I

Rajinda N. Khanna and Pavan K. Sharma

Department of Chemistry, University of Delhi, Delhi 110007, India

Ronald H. Thomson\*

Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB9 2UE

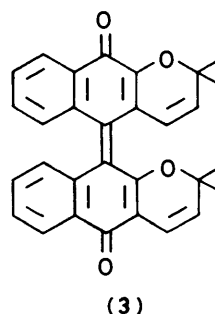
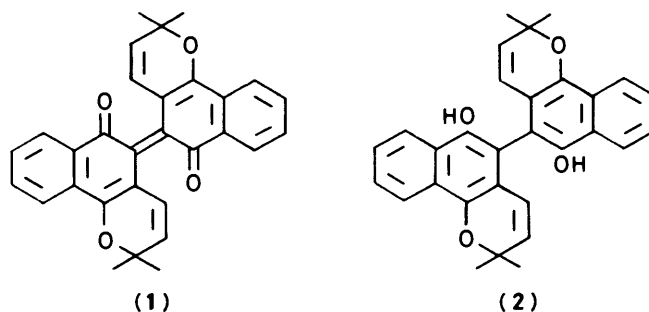
Tecomaquinone I and dehydrotectol are identical but the published structures are wrong. The revised structure is 3,10-dihydro-3,3-dimethyl-10-(2-methylprop-1-enyl)naphtho[2,3-*d*]pyrano[3',2':3,4]-naphthol[1,2-*b*]pyran-11,16-quinone (5).† Previous work is reinterpreted on this basis.

Natural green pigments, other than chlorophylls, are rare. Dehydrotectol [originally assigned structure (1)<sup>1</sup>], hitherto regarded as the first example of a natural extended *o*-quinone, is one of these which occurs in teak wood (*Tectona grandis*)<sup>2</sup> and various Bignoniaceae timbers.<sup>3</sup> The assigned structure of dehydrotectol rests mainly on that of tectol (2), a co-metabolite in teak. Tectol forms *inter alia* a diacetate and a tetrahydro derivative, and appropriate degradations yielded acetone and phthalic anhydride; the u.v. spectrum of tectol is very similar to that of lapachenol (the corresponding monomer).<sup>1</sup> Subsequently, the symmetrical structure (2) was fully supported<sup>4</sup> by the <sup>1</sup>H n.m.r. spectrum (see also Experimental section). As tectol could be oxidised to dehydrotectol with chloranil, and the product could then be reduced back to tectol with zinc and acetic acid, the structure of dehydrotectol was evidently (1), which was 'confirmed' by synthesis.<sup>1</sup>

Tecomaquinone I, previously thought to be [(3) or the *E* isomer] is another green pigment, found<sup>5</sup> in the heartwood of *Tabebuia pentaphylla* (Bignoniaceae). The structure was deduced from spectroscopic data, and the formation of a tetrahydro derivative and a leucodiacetate. However, structure (3) does not account for the colour and is biogenetically improbable. Since we had noted that dehydrotectol and tecomaquinone I are isomeric and both green it seemed likely that they are actually identical. Direct comparison has now shown that this is so, and further investigation revealed that both structures (1) and (3) are wrong although (2) for tectol is correct!

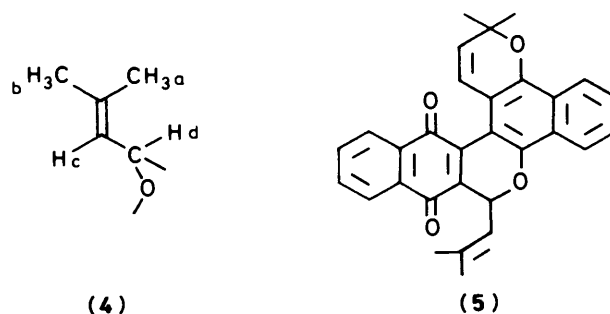
The <sup>1</sup>H n.m.r. spectrum (90 MHz in CDCl<sub>3</sub>) reported<sup>5</sup> for tecomaquinone I '3' includes three singlets for the methyl protons at δ 1.55 (3 H), 1.60 (6 H), and 2.00 (3 H), two vinyl doublets at δ 6.15 and 6.43 (each 1 H, *J* 12 Hz), and a 'mixed two-proton doublet around δ 5.50 (*J* 12 Hz)'. A similar spectrum (60 MHz in CDCl<sub>3</sub>), accepted<sup>6</sup> without comment for dehydrotectol, included methyl singlets at δ 1.52 (9 H) and 2.04 (3 H), vinyl doublets at δ 5.56, 6.17, and 6.44 (each 1 H, *J* 9.3 Hz), and a deformed doublet at δ 5.43 (1 H, *J* 9.3 Hz).

Re-examination of the <sup>1</sup>H n.m.r. spectrum at 360 MHz has now revealed, in the aliphatic region, two methyl singlets at δ 1.64 and 1.66, and three vinyl doublets centred at δ 5.58, 6.16, and 6.42, the former two coupled together (*J* 9.65 Hz). In addition there is a double multiplet centred at δ 5.45 (*J* 9.27, 1.33, and 1.28 Hz) coupled to the doublet at δ 6.42 and allylically coupled to two methyl doublets at δ 1.60 (*J* 1.28 Hz) and 2.05 (*J* 1.33 Hz). This indicates the presence of the side chain -CH<sub>d</sub>-CH=CMe<sub>2</sub>. From the <sup>13</sup>C n.m.r. spectrum there is only one sp<sup>3</sup> methine carbon in the molecule, which must be the carbon attached to H<sub>d</sub>. As this resonates at δ 67.79 it must also be attached to oxygen and hence the side



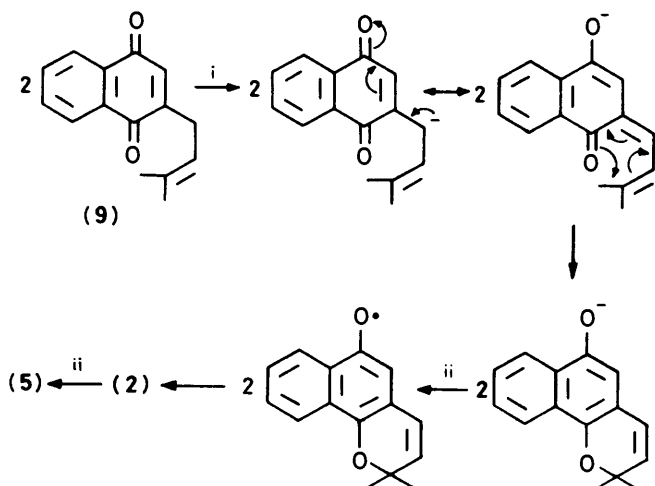
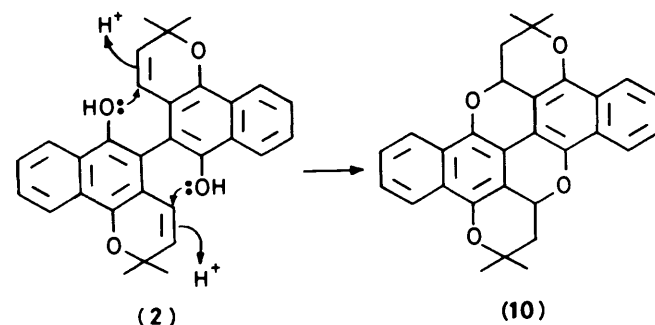
chain can be expanded to (4). The geometry was assigned from nuclear Overhauser effect difference spectra; irradiation of protons b at δ 2.05 enhanced the signal from H<sub>c</sub> by ca. 11%, while irradiation of protons a intensified the signal from H<sub>d</sub> by ca. 10%.

It follows from (4) that structures (1) and (3) are untenable. Reassessment of all the evidence now leads to structure (5) for dehydrotectol = tecomaquinone I, which is in full agreement with the n.m.r. data, accounts for the optical activity (measured on the leucodiacetate), and is biogenetically acceptable. In the mass spectrum the base peak at *m/z* 433 (*M*<sup>+</sup> - Me) signifies loss of a gem-methyl group, but fragmentation of the C<sub>4</sub> side

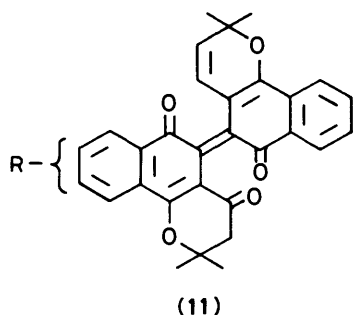


† 3,10-Dihydro-3,3-dimethyl-10-(2-methylprop-1-enyl)benzo[*h*]-naphtho[2,3-*c*]pyrano[3,2-*f*]chromene.



Scheme 3. Reagents: i, pyridine; ii, Cu<sup>II</sup>

Scheme 4.



metabolites of 'dehydrotectol' occurring in the aerial parts of *Putoria calabrica* (Rubiaceae) for which structures (11; R = H and OH) have been suggested.<sup>6</sup>

### Experimental

M.p.s. were determined on a Kofler block. The optical rotation was measured on a Perkin-Elmer 241 polarimeter. I.r. spectra were recorded with a Perkin-Elmer 197 spectrophotometer and u.v. spectra with a Perkin-Elmer 402 instrument. <sup>1</sup>H N.m.r. spectra were measured at 220 MHz on a Perkin-Elmer R34 spectrometer and at 360 MHz on a Bruker WH 360 spectrometer using tetramethylsilane as internal reference and <sup>13</sup>C spectra on a Bruker WH 360 instrument at 90 MHz. Mass spectra were obtained using an A.E.I. MS 30 mass spectrometer at 70 eV. Silica gel grade 62 (Grace) was used for dry column chromatography.

**Tecomaquinone I (5).**—Samples of tecomaquinone I and 'dehydrotectol' isolated from *T. grandis* and several Bignoniaceae spp. were identical (t.l.c., u.v., i.r., n.m.r., m.s.). The same

material was obtained when tectol (5 mg) and copper(II) acetate (20 mg) were stirred together in ether (3 ml) for 5 h. Dichloromethane (5 ml) was then added. After filtration and evaporation, the residue was purified by preparative t.l.c. (p.l.c.) on silica in chloroform, and crystallised from dichloromethane-methanol; m.p. 198–199 °C (3 mg);  $\delta_{\text{H}}$  as discussed above, with ArH multiplets centred at 8.15 (4 H), 7.72 (2 H), and 7.50 (2 H);  $\delta_{\text{C}}$  (90 MHz; CDCl<sub>3</sub>) 183.35(s), 182.09(s), 147.91(s), 143.45(s), 141.75(s), 136.48(s), 135.63(s), 133.39(d, 2 C), 133.11(s), 131.95(s), 127.91(d), 127.60(s), 126.58(d), 126.25(d), 125.81(d), 125.70(s), 125.09(d), 123.84(d), 129.00(d), 122.19(d), 117.60(d), 112.63(s), 111.23(s), 75.69(s), 67.79(d), 28.58(q), 25.85(q), 25.37(q), and 18.81(q);  $m/z$  450 (12%), 449 (18), 448.1724 (C<sub>30</sub>H<sub>24</sub>O<sub>4</sub> requires  $M$ , 448.1674; 45), 433.1460 (C<sub>29</sub>H<sub>21</sub>O<sub>4</sub> requires  $m/z$  433.1439; 100), 393.1173 (C<sub>26</sub>H<sub>17</sub>O<sub>4</sub> requires  $m/z$  393.1127; 10) and 210 (8).

**Leucodiacetate,**<sup>5</sup>  $[\alpha]_{\text{D}}^{20} + 5.4^\circ$  (c 0.24 in CHCl<sub>3</sub>);  $\delta_{\text{H}}$  8.88 (1 H, m, ArH), 8.17 (2 H, m, ArH), 7.70 (1 H, m, ArH), 7.54 (2 H, m, ArH), 7.46 (2 H, m, ArH), 6.59 (1 H, d,  $J$  9.76 Hz), 6.30 (1 H, d,  $J$  9.04 Hz), 5.64 (1 H, d,  $J$  9.76 Hz), 5.27 (1 H, dt,  $J$  9.04, and 1.26 Hz), 2.46 (3 H, s), 2.28 (3 H, s), 2.00 (3 H, d,  $J$  ~1 Hz), 1.67 (3 H, s), 1.56 (3 H, s), and 1.52 (3 H, d,  $J$  ~1 Hz);  $m/z$  534.2095 (C<sub>34</sub>H<sub>30</sub>O<sub>6</sub> requires  $M$ , 534.2042; 100%), 519 (44), 492 (42), 477 (51), 450 (83), 435 (81), 417 (17), 395 (8), 394 (21), 379 (15), 339 (21), and 211 (16).

**Tectol (2),**  $m/z$  450 ( $M^+$ , 72%), 435 (100), 379 (12), 339 (12), 211 (54), 210 (77), and 105 (9).

**Diacetate,**  $\delta_{\text{H}}$  (220 MHz) 8.27 (2 H, m, ArH), 7.68 (2 H, m, ArH), 7.50 (4 H, m, ArH), 5.95 (1 H, d,  $J$  10 Hz), 5.52 (1 H, d,  $J$  10 Hz), 1.98 (6 H, s, OAc), and 1.51 and 1.48 (each 6 H, s, Me);  $m/z$  534 ( $M^+$ , 18%), 492 (100), 478 (34), 450 (77), 435 (41), 211 (15), and 210 (27).

**2-(1-Bromoethyl)-3-chloro-1,4-naphthoquinone (8).**—A mixture of 2-chloro-3-ethyl-1,4-naphthoquinone (1.41 g), *N*-bromosuccinimide (1.21 g), and benzoyl peroxide (3 mg) in tetrachloromethane (33 ml) was boiled under reflux and irradiated with a 275 W tungsten lamp for 3 h. After filtration, the solution was evaporated and the residue was crystallised from methanol to give the required *quinone* (8) as yellow needles, m.p. 117–118 °C (1.25 g). The compound gradually loses HBr; a satisfactory C analysis could not be obtained (Found:  $M^+$ , 297.9374. C<sub>12</sub>H<sub>8</sub><sup>79</sup>Br<sup>35</sup>ClO<sub>2</sub> requires  $M$ , 297.9396);  $\nu_{\text{max}}$  (KBr) 1 686 and 1 668 cm<sup>-1</sup>;  $\delta_{\text{H}}$  (220 MHz) 8.14 (2 H, m, ArH), 7.77 (2 H, m, ArH), 5.66 (1 H, q,  $J$  6.50 Hz, CHMe), and 2.11 (3 H, d,  $J$  6.50 Hz);  $m/z$  298 ( $M^+$ , triplet, 4%), 219.0177 (C<sub>12</sub>H<sub>8</sub>ClO<sub>2</sub> requires  $m/z$  219.0213; 100), 183.0440 (C<sub>12</sub>H<sub>7</sub>O<sub>2</sub> requires  $m/z$ , 183.0446; 54), 155 (24), 129 (20), 127 (38), 76 (19), and 50 (18).

**14-Methoxy-6-methylindinaphtho[1,2-b:2',3'-d]pyran-7,12(6H)-quinone (7).**\*—A mixture of 2-(1-bromomethyl)-3-chloro-1,4-naphthoquinone (8) (0.90 g), and 4-methoxy-1-naphthol (0.525 g) in methanol (32 ml) containing pyridine (0.5 ml) was boiled under reflux for 1 h. Numerous compounds were formed. After removal of solvent the residue was passed down a column of dry silica in chloroform, and the least polar (blue) component was collected. After p.l.c. on silica, in benzene, to remove a second blue component (Russig's blue), the title compound (7) was crystallised from dichloromethane-methanol as short dark needles, m.p. 204–205 °C (14 mg) (Found: C, 76.3; H, 4.3%;  $M^+$ , 356.1112. C<sub>23</sub>H<sub>16</sub>O<sub>4</sub> requires C, 76.0; H, 4.3%;  $M$ , 356.1048);  $\lambda_{\text{max}}$  (MeOH) 249, 269sh, 301, and 574 nm (log  $\epsilon$  4.49, 4.40, 4.27, and 3.59);  $\nu_{\text{max}}$  (KBr) 1 667 and 1 644 cm<sup>-1</sup>;  $\delta_{\text{H}}$  8.16 (4 H, m, ArH), 7.75 (2 H, m, ArH), 7.97 (1 H, s, 13-H), 7.55 (2 H, m, ArH), 5.92 (1 H, q,  $J$  6.70 Hz), 4.07 (3 H, s,

\* 14-Methoxy-6-methylbenzo[*h*]naphtho[2,3-*c*]chromene-7,12(6H)-dione.

OMe), and 1.39 (3 H, d,  $J$  6.70 Hz);  $\delta_C$  184.72(s), 182.37(s), 149.83(s), 146.09(s), 136.06(s), 133.54(d), 133.62(d), 133.06(s), 132.73(s), 131.85(s), 128.06(s), 127.95(d), 126.63(d), 126.43(d), 125.94(s), 125.66(d), 122.79(d), 121.98(d), 112.03(s), 102.22(d), 68.04(d), 55.71(d), and 17.27(q);  $m/z$  356 (67%), 341 (100), and 298 (9).

*Compound (10)* (Supplied by Dr. Simatupang).— $\delta_H$  8.16 (4 H, m, ArH), 7.45 (4 H, m, ArH), 5.99 (2 H, dd,  $J$  10.90 and 6.50 Hz,  $2 \times$  CHO), 2.61 (2 H, dd,  $J$  12.70 and 6.50 Hz,  $2 \times$  CH of  $CH_2$ s), 2.42 (2 H, dd,  $J$  12.70 and 10.90 Hz,  $2 \times$   $CH_2$  of  $CH_2$ s), 1.67 (6 H, s, Me), and 1.45 (6 H, s, Me);  $\delta_C$  141.55(s), 139.34(s), 125.96(s and d), 125.54(s), 125.02(d), 122.32(d), 121.33(d), 109.80(s), 105.93(s), 76.81(s), 68.79(d), 38.86(t), 30.13(q), and 24.59(q);  $m/z$  450.1869 ( $C_{30}H_{26}O_4$  requires  $M$ , 450.1831; 85%), 394 (87), 338 (100), and 170 (18).

### Acknowledgements

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