A Revised Structure for Dehydrotectol and Tecomaquinone I

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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)¹], hitherto regarded as the first example of a natural extended o-quinone, is one of these which occurs in teak wood (*Tectona grandis*)² and various Bignoniaceae timbers.³ 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).¹ Subsequently, the symmetrical structure (2) was fully supported⁴ by the ¹H 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.1

Tecomaquinone I, previously thought to be [(3) or the *E* isomer] is another green pigment, found ⁵ 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 ¹H n.m.r. spectrum (90 MHz in CDCl₃) reported ⁵ 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 CDCl₃), accepted ⁶ 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 ¹H 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_d-CH=CMe₂. From the ¹³C n.m.r. spectrum there is only one sp³ methine carbon in the molecule, which must be the carbon attached to H_d. As this resonates at δ 67.79 it must also be attached to oxygen and hence the side

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



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_e by *ca*. 11%, while irradiation of protons a intensified the signal from H_d 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^+ – Me) signifies loss of a gem-methyl group, but fragmentation of the C₄ side



chain gives an ion at m/z 393 ($M^+ - C_4H_7$) of much lower intensity (10%). There are no other peaks in the spectrum m/z>120 and >10% intensity (cf. ref. 5). Analogous ¹H n.m.r. and mass spectra were obtained for the leucodiacetate of tecomaquinone I.

An initial objection to the extended *p*-quinone structure (3) was the colour of tecomaquinone I. It forms green solutions in chloroform (λ_{max} . 618 nm) and blue solutions in methanol $(\lambda_{max}, 590 \text{ nm})$ while the tetrahydro derivative (6) gives blue solutions in chloroform (λ_{max} , 608 nm) and violet solutions in methanol (λ_{max} . 580 nm).* These colours evidently arise from charge transfer. The molecule (5) [also (6)] comprises a donor 'half' and an acceptor 'half'. When suitably stacked above each other (the donor 'half' of one molecule above the acceptor 'half' of another, and vice versa) conditions for charge transfer will exist and may be influenced by solvent. Support for this view was obtained from the quinone (7), which was obtained by condensation of the quinone (8) with 4-methoxy-1-naphthol. Like compound (6), the model compound (7) gives coloured solutions: blue in chloroform (λ_{max} , 600 nm) and violet in methanol (λ_{max} . 574 nm).



We now suggest that compound (5) should be referred to as tecomaquinone I and not as dehydrotectol. Although the latter name has priority it has become chemically misleading.

Some of the earlier results now require re-interpretation.

(a) Oxidation¹ of tectol (2) with chloranil gives compound (5). This has been confirmed. In principle it could proceed by either a free radical or an ionic mechanism.⁷ The latter is shown in Scheme 1 but a radical mechanism could be written. It is significant that tetrahydrotectol, which could not undergo the oxidative rearrangement shown in Scheme 1, was not affected by chloranil but gave a blue colour with silver(1) oxide, suggesting formation of the corresponding extended o-quinone.

(b) Reduction¹ of compound (5) with zinc and acetic acid gives tectol (2). See Scheme 2; this is essentially Scheme 1 reversed. Interestingly, Sandermann and Simatupang¹ reported that reductive acetylation of 'dehydrotectol' gave tectol diacetate whereas Rohatgi *et al.*⁵ found that reductive acetylation of tecomaquinone I, under somewhat different conditions, gave the leucodiacetate. Sandermann and Simatupang¹ refluxed 'dehydrotectol' (5) with acetic anhydride (no doubt containing some acetic acid) and a large excess of zinc, followed by addition of pyridine and further warming to complete the acetylation.



Scheme 1.

On repeating the experiment we found that tectol diacetate was the main product, several others were formed (t.l.c.), but tecomaquinone I leucodiacetate could not be detected. Under these conditions the reaction follows Scheme 2 with final acetylation. The excess of zinc would promote reductive cleavage of the benzylic ether bond thus preventing formation of the leucodiacetate of compound (5). Rohatgi *et al.*⁵ used less zinc and carried out the reductive acetylation in the presence of a basic catalyst (sodium acetate). On repeating this experiment we again observed that several products were formed; the leucodiacetate was predominant and tectol diacetate was a minor product. Under these conditions most of the quinol (Scheme 2) is rapidly trapped as the diacetate before it can rearrange to tectol (2).



Scheme 2. Reagents: i, Zn-HOAc

(c) 'Synthesis of dehydrotectol.' In this reaction ¹ deoxylapachol (9) was oxidised with copper(II) acetate in the presence of pyridine. By analogy with previous work ⁸ it was assumed that the reaction proceeded essentially as in Scheme 3 to form 'dehydrotectol' (2) which was then oxidised further to yield the green pigment, regarded then as (1). As tectol can be oxidised by copper(II) acetate to form the same green pigment, the final stages in Scheme 3 are therefore analogous to Scheme 1 (radical or ionic) the end product being compound (5).

Another reaction of tectol (2) observed by Sandermann and Simatupang¹ is a rearrangement effected by treatment with hydrogen chloride in chloroform solution. Structure (10) was suggested for the product, which could be formed as indicated (Scheme 4). The symmetrical structure is fully confirmed by its ¹H and ¹³C n.m.r. spectra (see Experimental section).

Finally, in the light of this work, the structures of two other natural pigments require reconsideration. These are co-

^{*} Not published in ref. 5.



Scheme 3. Reagents: i, pyridine; ii, Cu"



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.⁶

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. ¹H 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 ¹³C spectra on a Bruker WH 360 instrument at 90 MHz. Mass spectra were obtained using an A.E.I. MS 30 mass spectrometer at 70eV. 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 dichloromethanemethanol; m.p. 198—199 °C (3 mg); $\delta_{\rm H}$ as discussed above, with ArH multiplets centred at 8.15 (4 H), 7.72 (2 H), and 7.50 (2 H); δ_{c} (90 MHz; CDCl₃) 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 (C₃₀H₂₄O₄ requires M, 448.1674; 45), 433.1460 $(C_{29}H_{21}O_4 \text{ requires } m/z \text{ 433.1439; 100}), 393.1173 (C_{26}H_{17}O_4)$ requires m/z 393.1127; 10) and 210 (8).

Leucodiacetate, ${}^{5} [x]_{20}^{20} + 5.4^{\circ}$ (c 0.24 in CHCl₃); $\delta_{\rm H}$ 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 (C₃₄H₃₀O₆ 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, $\delta_{\rm H}$ (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. C₁₂H₈⁷⁹Br³⁵ClO₂ requires M, 297.9396); v_{max}(KBr) 1 686 and 1 668 cm⁻¹; $\delta_{\rm H}$ (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 (C₁₂H₈ClO₂ requires m/z 219.0213; 100), 183.0440 (C₁₂H₇O₂ requires m/z, 183.0446; 54), 155 (24), 129 (20), 127 (38), 76 (19), and 50 (18).

14-Methoxy-6-methyldinaphtho[1,2-b:2',3'-d]pyran-

7,12(6H)-quinone (7).*—A mixture of 2-(1-bromomethyl)-3chloro-1,4-naphthoquinone (8) (0.90 g), and 4-methoxy-1naphthol (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_{2.3}H₁₆O₄ requires C, 76.0; H, 4.3%; M, 356.1048); $\lambda_{max.}$ (MeOH) 249, 269sh, 301, and 574 nm (log ε 4.49, 4.40, 4.27, and 3.59); $v_{max.}$ (KBr) 1 667 and 1 644 cm⁻¹; $\delta_{\rm H}$ 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); δ_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).— $\delta_{\rm H}$ 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 × CHO), 2.61 (2 H, dd, J 12.70 and 6.50 Hz, 2 × CH of CH₂s), 2.42 (2 H, dd, J 12.70 and 10.90 Hz, 2 × CH₂ of CH₂s), 1.67 (6 H, s, Me), and 1.45 (6 H, s, Me); $\delta_{\rm C}$ 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 (C₃₀H₂₆O₄ requires *M*, 450.1831; 85%), 394 (87), 338 (100), and 170 (18).

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