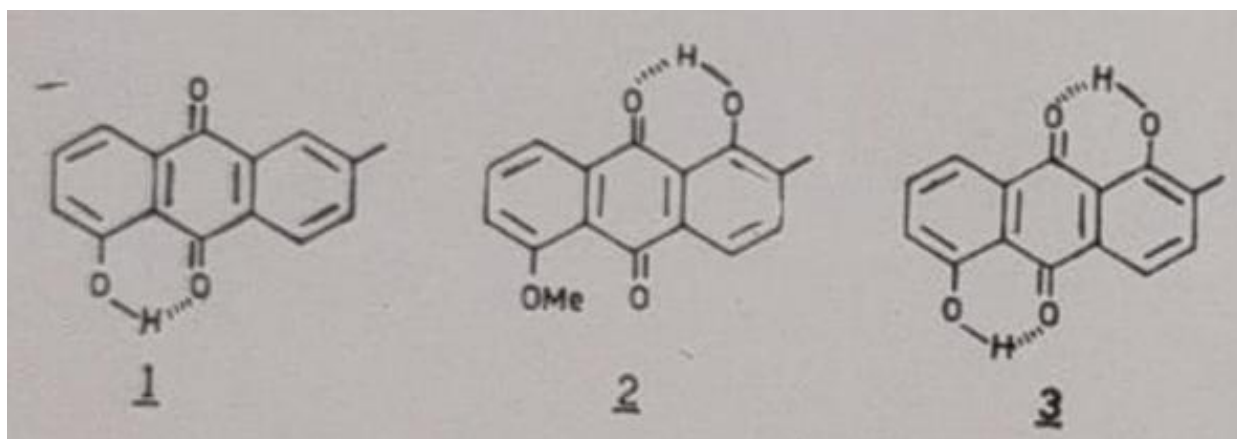


Further Studies on Anthraquinone Derivatives from *Tectona grandis*

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TECTONA grandis Linn. f. (Verbenaceae) popularly known as 'teak' or 'sagwan', occurs in all tropical and subtropical regions. Earlier work on this plant led to the isolation of a number of compounds ¹. We reinvestigated a Sawai Madhopur collection of teakwood and reported a new 1,4-anthraquinone derivative and three 9,10 -anthraquinone derivatives (**1** – **3**) as minor constituents along with the previously reported compounds. The present report deals with the isolation and characterisation of these rare and minor 9,10 -anthraquinone derivatives (**1** – **3**).



EXPERIMENTAL

The air-dried powdered heartwood shavings of *T. grandis* (5 kg) were extracted with petrol (b.p. 60 – 80°) on a steam-bath (3 × 12 h) and the extracts were concentrated under reduced pressure. The reddish brown semi-solid mass was taken up in ether and fractionated into acidic and neutral parts by extracting with 2N Na₂CO₃ solution. The Na₂CO₃- soluble part on neutralisation with 6 N HCl furnished lapachol (20 mg) as bright yellow crystals, m.p. 139 – 40°. The Na₂CO₃- insoluble part (neutral fraction) was column chromatographed over deactivated neutral alumina and afforded tectoquinone as brown needles (500 mg), m.p. 174 – 76° from the petrol, tecomaquinone-I as green blue needles (50 mg), m.p. 198 – 99° from the petrol-benzene (1:1), dehydro- α -lapachone as red needles (45 mg), m.p. 143 – 44° from benzene, and 9,10 -dimethoxy-2-methyl-1,4-anthraquinone as yellow crystals (12mg) from the C₆H₆-EtOAc (9:1) eluates. The C₆H₆-EtOAc (3:1) fraction afforded a mixture of three anthraquinone derivatives (70 mg) which on repeated prep-tlc gave **1**(20mg), **2**(20mg) and **3**(15mg). The molecular formulae of the quinones (**1** – **3**) could be established as C₁₅H₁₀O₃ (238.0632), C₁₆H₁₂O₄ (268.0734) and C₁₅H₁₀O₄ (254.0577). The presence of hydrogen bonded OH groups, unchelated and chelated C = O groups was ascertained by the appearance of broad bands at 3350 and sharp bands at 1670 and 1640 – 1630 cm⁻¹ respectively. The presence of chelated hydroxyls was also confirmed by the appearance of sharp singlets in down-field region (δ 12.12 – 13.30ppm) in the ¹H nmr spectra. The sequence of the protons was established by spin-decoupling experiments.

5-Hydroxy-2-methyl-9,10-anthraquinone (**1**): - It gave yellow crystals (20mg), m.p. 146 – 47° (lit. ²147°); $\nu_{\max}$ (CCl₄) 3350(OH), 1670 (unchelated C = O), 1640 (chelated C = O), 1580 and 1560 cm⁻¹ (C = C); δ (400MHz; CDCl₃) 8.12 (br s, H – 1), 8.21 (d, *J* 8 Hz, H – 4), 7.85 (dd, *J* 8, 1.5 Hz, H – 8), 7.63 (dd, *J* 8, 1.5 Hz, H – 6), 7.32 (dd, *J* 8, 1.5 Hz, H – 3), 7.69 (t, *J* 8 Hz, H – 7), 12.64 (s, OH) and 2.55 (s, CH₃); *m/z* (rel. int.) 238.0632 [*M*⁺](C₁₅H₁₀O₃), (100), 223 [*M* – Me]⁺ (6), 210 [*M* – Co]⁺ (8), 195 [223 – CO]⁺ (4), 182 [210 – CO]⁺ (12) and 181 [210 – CHO]⁺ (14).

1-Hydroxy-5-methoxy-2-methyl-9,10-anthraquinone (**2**): It gave yellow crystals (20mg), m.p. 183 – 84° (lit. ⁴ 189 – 91°); $\nu_{\max}$ (CCl₄) 3350(OH), 1670, 1630 (C = O), 1590 and 1560 cm⁻¹ (C = C); δ (400MHz; CDCl₃) 7.98 (d, *J* 8 Hz, H – 8), 7.71 (d, *J* 8 Hz, H – 4), 7.76 (t, *J* 8 Hz, H – 7), 7.51 (d, *J* 8 Hz, H – 3), 7.38 (d, *J* 8 Hz, H – 6), 4.09 (s, OCH₃), 2.38 (s, CH₃), 13.30 (s, OH); *m/z* rel. int.) 268.0734 [*M*⁺](C₁₆H₁₂O₄) (100), 253 [*M* – Me]⁺ (8), 240 [*M* – Co]⁺ (4), 239 [*M* – CHO]⁺ (18), 237 [*M* – OMe]⁺ (4), 222 [237 – Me]⁺ (26) and 149 (38).

1,5-Dihydroxy-2-methyl-9,10-anthraquinone (3) It gave yellow crystals (15 mg), m.p. 195 – 96° (lit. ³196 – 97°); $\nu_{\max}(\text{CCl}_4)$ 3350(OH), 1625 (chelated C = O), 1610, 1580 and 1560 cm^{-1} ; $\delta(400\text{MHz}; \text{CDCl}_3)$ 7.86(dd, J 8, 1 Hz, H – 8), 7.79(d, J 8 Hz, H-4), 7.70 (t, J 8 Hz, H – 7). 7.58 (d, J 8 Hz, H – 3), 7.30 (dd, J 8, 1 Hz, H – 6), 2.39 (s, CH_3), 12.12(s , OH), 12.42(s, OH); m/z (rel. int.) 254.0577[M^+]($\text{C}_{15}\text{H}_{10}\text{O}_4$)(100), 239[$M - \text{Me}$]⁺(20), 237[$M - \text{OH}$]⁺ (18), 226[$M - \text{Co}$]⁺(4), 209[237 – Co]⁺(4) and 149 (70).

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