

Dipterocarpol (IIIa) and 28-hydroxy- β -amyron (IIId). The oily fractions 14–18 (0.7 g) were a mixture (TLC) of two substances. Their acetylation (acetic anhydride–pyridine at R_f) and chromatography (silica-gel; hexane–Et₂O, 9:1) of the crude product gave a ketoacetate (400 mg) and a ketoalcohol (230 mg). The latter was shown to be dipterocarpol (IIIa) m.p. 135–136°, $[\alpha]_D^{25} +67^\circ$ (c 1.1) whose reduction by NaBH₄ gave dammarenediol (IIIb) m.p. 142–144° compared with an authentic sample. The oily ketoacetate, hydrolysed with methanolic KOH (10%), gave 28-hydroxy- β -amyron (IIId) m.p. 189–192° (from MeOH): $[\alpha]_D^{25} +85^\circ$ (c 1); MW 440 (MS); ν_{\max} 3600, 1710 cm⁻¹. (Found: C, 81.78; H, 10.79. C₃₀H₄₈O₂ requires: C, 81.76; H, 10.98%; δ 5.15 (1H, m , =C=CH–), 3.35 (2H, q , J 11 Hz, =C–CH₂OH). The NaBH₄ reduction of (IIId) gave erythrodiol (IIb) m.p. 229–234°. Furthermore, (IIId) was prepared by refluxing oleanonic aldehyde (IIa) in isopropanolic KOH (10%) for 2 hr. After additional 8 hr only erythrodiol (IIb) from (IIa) is obtained.

26-Hydroxy-tirucallone (Ic). Fractions 19–21 (0.4 g), after chromatography (alumina; hexane–Et₂O 17:3), gave 300 mg of oily 26-hydroxy-tirucallone (Ic) $[\alpha]_D^{25} +14^\circ$ (c 1); MW 440 (MS); ν_{\max} 1710, 3600 cm⁻¹. (Found: C, 81.82; H, 10.85. C₃₀H₄₈O₂ requires: C, 81.76; H, 10.98%; δ 4.08 (2H, s , =C–CH₂OH). LiAlH₄ reduction of (Ic) afforded isomasticadienediol (Id) m.p. and m.m.p. 152–154°.

Dammarenediol (IIIb) and erythrodiol (IIb). Fractions 22–26 (1.2 g) were a mixture (TLC) of two substances. After acetylation (acetic anhydride–pyridine at R_f), chromatography (silica-gel; C₆H₆–Et₂O, 4:1) of the crude product gave both oily monoacetate (480 mg) and diacetate (630 mg). The former, after hydrolysis by methanolic KOH (10%), gave dammarenediol (IIIb) m.p. 142–144°, $[\alpha]_D^{25} +27^\circ$ (c 1.4) compared with authentic material. The diacetate, hydrolysed in the same way, gave erythrodiol (IIb) m.p. 230–235°, $[\alpha]_D^{25} +79^\circ$ (c 1).

Isomasticadienediol (Id). Fractions 27–32 (0.9 g) gave, after recrystallization from hexane–Et₂O (7:3), isomasticadienediol (Id) m.p. 152–154°, $[\alpha]_D^{25} -7^\circ$; MW 442 (MS); ν_{\max} 3600 cm⁻¹. (Found: C, 81.34; H, 11.38. C₃₀H₅₀O₂ requires: C, 81.39; H, 11.38%; δ 5.22 (1H, m , =C=CH–), 4.08 (2H, s , =C–CH₂OH) identical with a synthetic sample obtained by LiAlH₄ reduction of methyl isomasticadienonate (Ie).

Oleanonic acid (IIe) and oleanolic acid (IIIf). Acidic extract¹ (10 g) was adsorbed on silica-gel (300 g; HCl washed). Elution with C₆H₆–Et₂O (19:1) gave 580 mg of crude oleanonic acid (IIe) converted by CH₂N₂ into the corresponding methylester m.p. 181–182°, $[\alpha]_D^{25} +76^\circ$ (c 1) compared with an authentic sample. The subsequent elution with C₆H₆–Et₂O (4:1) then afforded 200 mg of crude oleanolic acid (IIIf) which, treated with CH₂N₂, gave the corresponding methylester m.p. 195–197°, $[\alpha]_D^{25} +82^\circ$ (c 1.3) also compared with an authentic sample.

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QUINONES AND OTHER CONSTITUENTS FROM *TABEBUIA ROSEA*

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Key Word Index—*Tabebuia rosea*; Bignoniaceae; quinones; lapachol; dehydrotectol; dehydro- α -lapachone and isolapachone.

Plant. *Tabebuia rosea* DC. Voucher specimen No. 11334 deposited in the R.U.B.L. Herbarium. **Previous work.** No work has been reported on this species. On sister species^{1,2} *T. flavescens*,^{3,4} *T. ipe*,⁴ *T. avellanadae*,^{5–8} *T. chrysantha* Nichols⁹ and *T. doennell* Smittii.⁹

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Present work. The finely grounded heartwood (2 kg) was exhaustively extracted with hot light petrol. (60–80°). The extract was concentrated to dryness, taken in Et₂O, extracted with 2 N Na₂CO₃ and acidified with 2 N HCl.

Acidic component. The acidic fraction was chromatographed over silica gel. C₆H₆ (100%) gave compound I, fine yellow needles, m.p. 139–140° (50% C₆H₆ and light petrol.). (Found: C, 74.34; H, 5.71. Calc. for C₁₅H₁₄O₃: C, 74.38; H, 5.78 %); ν_{\max} (Nujol) 3350, 1660, 1630, 1580 cm⁻¹. These data indicated that compound I was lapachol and this was confirmed by comparison with an authentic specimen (co-TLC, IR and m.m.p.).

Neutral components. The neutral fraction was chromatographed over deactivated alumina and afforded compounds II, III, IV, V and VI.

Compound II. From light petrol.–C₆H₆ (9:1), first crop blue green crystals, m.p. 194–195° (MeOH). (Found: C, 80.00; H, 5.88. Calc. for C₃₀H₂₄O₄: C, 80.35; H, 5.35 %); ν_{\max} (Nujol) 1645 (C=O) cm⁻¹; λ_{\max} (EtOH) 271, 340 nm (log ϵ 4.53, 3.09). From the above data, compound II appeared to be dehydrotectol and this was confirmed (co-TLC, IR and m.m.p.).

Compound III. From light petrol.–C₆H₆ (9:1), second crop orange needles, m.p. 143–144° (50% benzene and light petrol.); C₁₅H₁₂O₃; ν_{\max} (Nujol) 1680, 1640, 1580, 1560 cm⁻¹; M⁺ 240; NMR (CDCl₃): δ 1.54 (6H, s) indicated two methyl groups, 5.76 (1H, d) and 6.73 (1H, d, $J_{11,12}$ 9 Hz) correspond to H-11 and H-12 which are olefinic protons, 7.72 (2H, m) assigned to H-6 and H-7, 8.13 (2H, m) assigned to H-5, H-8 aromatic protons respectively. These data suggested that compound III was dehydro- α -lapachone (co-TLC, IR and m.m.p.).

Compound IV. From light petrol.–C₆H₆ (1:1), golden yellow leaflets m.p., 108–109° (100% light petrol.). (Found: C, 74.99; H, 5.03. Calc. for C₁₅H₁₂O₃: C, 75.00; H, 5.00 %); ν_{\max} (Nujol) 1667, 1637, 1621, 1587, 1562 cm⁻¹. λ_{\max} (EtOH) 253, 295, 342 nm (log ϵ 4.45, 3.86, 3.18); M⁺ 240; NMR (CDCl₃): δ 1.80 (3H, s) indicated Me–C=, 3.07 (1H, q) and 3.23 (1H, q) assigned to ring methylene protons, 5.08 (2H, d) correspond to vinyl protons, 5.40 (1H, t) assigned to tertiary proton and 7.60 (2H, m) of H-6 and H-7, 7.93 (2H, m) of H-5 and H-8 aromatic protons. From the above data compound IV was dehydro-*iso*- α -lapachone (co-TLC, IR and m.m.p.).

Compound V. From C₆H₆–light petrol. (9:1), fine colourless needles, m.p. 94–95° (MeOH). (Found: C, 82.81; H, 11.46. Calc. for C₂₉H₄₈O: C, 84.40; H, 11.11 %); ν_{\max} (Nujol) 1666 (C=O) cm⁻¹; M⁺ 412. These data suggested that compound V was sitostenone.

Compound VI. From C₆H₆ (100%), colourless flakes, m.p. 136–137° (MeOH); C₂₉H₅₀O; ν_{\max} (Nujol) 3400 (OH) cm⁻¹. From the above data compound VI was sitosterol.

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