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NAPHTHOQUINONES FROM *ZEYHERA TUBERCULOSA**

MARIA DE L. DUARTE WEINBERG, OTTO R. GOTTLIEB†
and GEOVANE G. DE OLIVEIRA

Instituto de Ciências Exatas, Universidade Federal de Minas Gerais, Belo Horizonte; †Instituto de Química,
Universidade de São Paulo, Brasil

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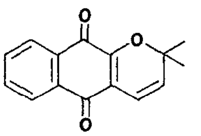
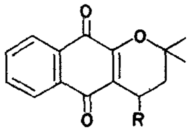
Key Word Index—*Zeyhera tuberculosa*; Bignoniaceae; lapachol; α-lapachone; dehydro-α-lapachone; 4-hydroxy-α-lapachone; zeyherol.

A report that the extracts of *Zeyhera tuberculosa* (Vell.) Bur., an arborescent Bignoniaceae species, appear to have anti-tumour properties, stimulated the examination of a leaf extract and led to the isolation of 5,6,7-trimethoxyflavone and 5,6,7,8-tetramethoxyflavone [2]. The present report concerns the examination of a trunk wood extract which led to the isolation of sitosterol, β-amyrin, lapachol, dehydro-α-lapachone (**1**), α-lapachone (**2a**), 4-hydroxy-α-lapachone (**2b**) and zeyherol [1].



(**1**)



(**2a**) R = H
(**2b**) R = OH
(**2c**) R = OAc

The structure of 4-hydroxy-α-lapachone (**2b**), $C_{15}H_{14}O_4$, a derivative of α-lapachone (**2a**), $C_{15}H_{14}O_3$, resulted upon comparison of the PMR spectra of both compounds. The triplet (τ7·37) due to the benzylic methylenes of **2a** was replaced by a triplet (τ 5·13) due to an oxymethine proton in the spectrum of **2b**. The secondary nature of the carbinol function was confirmed by the strong paramagnetic shift (1·18 ppm) of this signal upon acetylation. In accordance with expectation **2b** was easily transformed into **1** by treatment with acid.

EXPERIMENTAL

Isolation of the constituents of Zeyhera tuberculosa. Plant material was collected at Cipó Ridge, Minas Gerais State, and identified by the botanist J. L. Pedersoli. A ground trunk wood sample (8 kg) was extracted successively with C_6H_6 and EtOH. The C_6H_6-extract (28 g) was chromatographed on silica (500 g) yielding the following useful fractions with the indicated eluants: A_1–A_6 (C_6H_6) and A_7 (C_6H_6–$CHCl_3$, 1:1). A_1 was recrystallized from EtOH giving lapachol (2·16 g). A_2 was recrystallized from EtOH giving **1** (191 mg). A_3 was recrystallized from EtOH giving β-amyrin (154 mg). A_4 was recrystallized from EtOH giving **2a** (413 mg). A_5 was recrystallized from EtOH giving sitosterol (1·85 g). A_6 was purified by passage through Sephadex LH 20 (MeOH) giving **2b** (1·12 g). A_7 was purified by passage through Sephadex LH 20 (MeOH) giving zeyherol (84 mg).

Lapachol. Yellow crystals, mp and mmp with an authentic sample 138–140° (lit. [3] mp 140°).

Dehydro-α-lapachone (**1**). Red crystals, mp, UV, IR and PMR identical to data given in lit. [3].

α-Lapachone (**2a**). Yellow crystals, mp, UV, IR identical to data given in lit. [3]. PMR ($CDCl_3$ τ): 1·81–2·45 (*m*, C_6H_4), 7·39 (*t*, *J* 6·5 Hz, CH_2), 8·20 (*t*, *J* 6·5 Hz, CH_2), 8·58 [*s*, $C(Me)_2$]. MS (*m/e*): 242 (98%) M, 228 (19), 227 (100), 214 (21), 199 (19), 196 (9), 181 (12), 171 (6), 160 (7), 159 (58), 158 (17).

4-*Hydroxy-α-lapachone* (**2b**). Yellow oil (M found 258·0898. $C_{15}H_{14}O_4$ requires 258·0892). ν_{max}^{film} (cm^{-1}): 3500, 2990, 1685, 1645, 1615, 1600, 1580, 1335, 1305, 1270, 1200, 1130, 1045, 990, 955, 840, 740. λ_{max}^{EtOH} (nm): 245, 250, 280, 330 (ε 41 200, 43 000, 29 900, 5200); $\lambda_{max}^{EtOH+NaOH}$ (nm): 250, 274 (ε 23 200, 39 700). PMR ($CDCl_3$, τ): 1·98–2·50 (*m*, C_6H_4), 5·13 (*t*, *J* 6·0 Hz, C$\underline{H}$OH), 6·28–6·55 (broad *s*, OH), 8·00 (*d*, *J* 6·0 Hz, CH_2), 8·52 (*s*, Me), 8·62 (*s*, Me). MS (*m/e*): 258 (9%) M, 243 (3), 203 (27), 202 (11), 176 (26), 146 (36), 105 (28), 98 (33), 83 (100). *Acetate* (**2c**). Yellow crystals, mp 118–120° (EtOH). ν_{max}^{KBr} (cm^{-1}): 1740, 1680, 1650, 1615, 1600, 1250, 940, 725. λ_{max}^{EtOH} (nm): 223 inf., 245, 251, 283 (ε 22 800, 36 900, 38 700, 27 300). PMR ($CDCl_3$, τ): 1·90–2·47 (*m*, C_6H_4), 3·95 (*t*, *J* 5·0 Hz, CHOAc), 7·90 (*d*, *J* 5·0 Hz, CH_2), 7·97 (*s*, COMe), 8·50 (*s*, Me), 8.54 (*s*, Me). *Dehydro-derivative.* A solution of **2b** (80 mg) in dry C_6H_6 (100 ml) and *p*-toluenesulphonic acid (0·1 g) was heated under reflux (30 min). The mixture was cooled to room temp., washed with aq. 10% $NaHCO_3$, dried with Na_2SO_4 and evaporated under red pres. The residue was recrystallized from EtOH giving **1** (30 mg; 40%).

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