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ZEYHEROL, A DILIGNOL FROM *ZEYHERA DIGITALIS**

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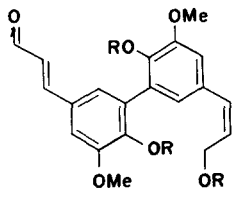
Key Word Index—*Zeyhera digitalis*; Bignoniaceae; lapachol; zeyherol; dilignol.

Abstract—The stem wood of *Zeyhera digitalis* (Bignoniaceae) contains, besides D-glucose, vanillic acid, veratric acid and lapachol, a natural dilignol type compound for which the structure of 2,2′-dihydroxy-3,3′-dimethoxy-5-(ω-oxo-*E*-propenyl)-5′-(ω-hydroxy-*Z*-propenyl)-biphenyl is proposed.

The shrub *Zeyhera digitalis* (Vell.) Hoehne has a flexible stem which contains, besides lapachol [1], a typical constituent of other Bignoniaceae, up to 1% D-glucose and three compounds whose biosynthesis may be connected with its incipient lignification: vanillic acid, veratric acid and the dilignol **1a**, named zeyherol.



(**1a**) R = H
(**1b**) R = Ac

The compound, $C_{20}H_{20}O_6$, was recognised as a biphenyl derivative upon inspection of its UV spectrum. This, and other structural assignments based on spectroscopical data, were confirmed through oxidation of zeyherol triacetate (**1b**) to di-*O*-acetyldehydrodivanillic acid [2]. The structures of the side chains were based on NMR spectral evidence which demonstrated the association of a *trans*-olefin (J_{vic} 15 Hz) with the formyl group and of a *cis*-olefin (J_{vic} 8 Hz) with the hydroxymethylene group.

EXPERIMENTAL

Isolation of the constituents of Zeyhera digitalis. Plant material was collected near Lagoa Santa, Minas Gerais, and identified by J. L. Pedersoli. Powdered stem wood (4·5 kg) was extracted successively with C_6H_6 and with EtOH. The C_6H_6-extract (11 g) was chromatographed on Si gel (220 g), yielding the following fractions with the indicated eluants: A_1, A_2 (C_6H_6) and A_3 ($CHCl_3$–MeOH, 95:5). A_1 was recrystallized from EtOH giving lapachol (97 mg). A_2 was recrystallized from EtOH giving sitosterol (133 mg). A_3 was purified by passage through Sephadex LH 20 (MeOH). The intermediate fractions gave, by PLC, zeyherol (166 mg). The EtOH extract (110 g) was chromatographed on Si gel (470 g) yielding the following fractions with the indicated eluants: B_1 (C_6H_6), B_2 ($CHCl_3$), B_3, B_4 ($CHCl_3$–MeOH, 99:1) and B_5 ($CHCl_3$–MeOH, 9:1). B_1 was recrystallized from EtOH giving sitosterol (177 mg). B_2 was purified by passage through Sephadex LH 20 (MeOH). Crystallization of the intermediate fractions from Et_2O gave veratric acid (62 mg). B_3 was purified by passage through Sephadex LH 20 (MeOH). The intermediate fractions gave, after extraction with aq. 10% Na_2CO_3, vanillic acid (105 mg). B_4 was purified by passage through Sephadex LH 20 (MeOH) giving zeyherol (211 mg). B_5 (90 g) was recrystallized from H_2O giving D-glucose (36 g).

Lapachol, veratric acid, vanillic acid and D-*glucose* (phenylhydrazone mp 122–124°) were identified by direct comparison with authentic samples.

Zeyherol (**1a**). Yellow oil (M^+ found: 356·1248; $C_{20}H_{20}O_6$ requires: 356·1260). IR: ν_{max}^{film} (cm^{-1}): 3400, 1670, 1620, 1580, 1520, 1480, 1220, 1140. UV: λ_{max}^{EtOH} nm (log ε): 230, 286, 344 (4·49, 4·07, 4·43); UV: $\lambda_{max}^{EtOH+NaOH}$ nm (log ε): 250, 298, 352 (4·50, 4·23, 4·52). MS (*m/e*): 356 (77%) M^+, 340 (24), 339 (100), 328 (9), 327 (39), 326 (9), 324 (35), 312 (8), 307 (11), 306 (17), 295 (10), 165 (12), 151 (12), 137 (29). PMR [$(CD_3)_2CO$, 220 MHz, τ]: 0·42 (*d*, *J* 10·0 Hz, CHO), 2·46 (*d*, *J* 15·0 Hz,

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CH=CHCHO), 2·72 (*s*, H-4), 2·75 (*s*, H-6), 3·00 (*s*, H-4'), 3·13–3·25 (*m*, CH=CHCH$_2$), 3·21 (*s*, H-6'), 3·38 (*dd*, *J* 15·0, 10·0 Hz, CH=CHCHO), 4·37 (*d*, *J* 8·0 Hz, CH=CHCH$_2$), 6·12 (*s*, OMe-3), 6·21 (*s*, OMe-3'), 6·18–6·25 (*m*, CH$_2$). *Triacetate* (**1b**). Yellow oil. IR: ν_{max}^{film} (cm^{-1}): 1765, 1740, 1670, 1600, 1510, 1470, 1375. PMR [(CD$_3$)$_2$CO, 220 MHz, τ]: 0·42 (*d*, *J* 10·0 Hz, CHO), 2·44 (*d*, *J* 15·0 Hz, CH=CHCHO), 2·68 (*s*, H-4, H-6), 2·81 (*s*, H-4'), 2·95–3·10 (*m*, H-6', CH=CHCH$_2$), 3·35 (*dd*, *J* 15·0, 10·0 Hz, CH=CHCHO), 4·33 (*d*, *J* 9·0 Hz, CH=CHCH$_2$), 5·55–5·68 (*m*, CH$_2$), 6·11 (*s*, OMe-3), 6·24 (*s*, OMe-3'), 7·81 (*s*, 2COMe), one COMe peak covered by solvent peak.

Oxidation of zeyherol triacetate (**1b**, 12 mg) with excess $KMnO_4$ in Me_2CO at *ca* 50° and work up of the reaction mixture in the usual way gave *di-O-acetyldehydrodivanillic acid* (4 mg), compared with a synthetic sample, prepared according to Elbs and Lerch [2]. IR: ν_{max}^{KBr} (cm^{-1}): 3480, 1760, 1687, 1595, 1205, 1172, 902. UV: λ_{max}^{EtOH} nm (log ϵ): 219, 297 (4·47, 3·71). PMR (TFA, τ): 2·15 (*d*, *J* 2·0 Hz, H-6, H-6'), 2·22 (*d*, *J* 2·0 Hz, H-4, H-4'), 6·03 (*s*, 2OMe), 7·77 (*s*, 2COMe). MS (*m/e*): 418 (2%) M$^+$, 376 (11) M$^+$-CH$_2$CO, 334 (64) M$^+$-2CH$_2$CO, 316 (50), 274 (10), 270 (13), 242 (10), 239 (10), 43 (100).

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