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2,4,2'-TRIHYDROXY-4'-METHOXYBENZIL FROM ZOLLERNIA PARAENSIS*

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Abstract—A new phenolic compound, isolated from the wood of Zollernia paraensis, has been shown to be 2,4,2'trihydroxy-4'-methoxybenzil by spectral data and synthesis

INTRODUCTION

In previous papers [1, 2], we reported the isolation of ten flavonoids from a benzene extract of *Zollernia paraensis* Hub Further studies of the more polar fraction led to the isolation of a new compound, 2,4,2'-trihydroxy-4'methoxybenzil (1) Benzils have not been isolated so far from natural sources, but have been obtained only as degradation products of lignins [3, 4]

RESULTS AND DISCUSSION

The ¹H NMR spectrum of 1, $C_{15}H_{12}O_6$ (M⁺ at m/z 288), showed signals for a methoxy group ($\delta 3$ 90), six aromatic protons ($\delta 6$ 50–7 50) of two 1,2,4-trisubstituted rings and one or two chelated hydroxyl groups (br, $\delta 11$ 0–11 50) Methylation of 1 with methyl iodide gave the trimethyl ether 2, $C_{18}H_{18}O_6$ (M⁺ at m/z 330), the ¹H NMR spectrum of which showed a new methoxyl group coincident with the methoxyl group of 1 ($\delta 3$ 85), while the other two methoxy groups resonated upfield ($\delta 3$ 55)

*Part 3 of the series "Flavonoids and Isoflavonoids from Zollernia paraensis" For part 2 see ref [2] A preliminary communication of this work was presented at the 2nd International Conference on Chemistry and Biotechnology of Biologically Active Natural Products, Budapest, 1983 The fragmentation pattern of 1 in the mass spectrum showed two major ions at m/z 151 (a, 100%) and 137 (b, 90%), which were both shifted to m/z 165 (c, 100%) in the mass spectrum of the methyl derivative 2 Consideration of the ¹H NMR spectra and the typical MS fragmentation of benzils [5] suggested for the three ions the structures **a**-c, and consequently structure 1 for the natural product

A benzil structure was confirmed by oxidative cleavage of 2 with alkaline hydrogen peroxide to give 2,4-dimethoxybenzoic acid Direct synthesis of compound 1 by oxidation of the corresponding benzylated chalcone by TTN in perchloric acid [6] was unsuccessful, as was the attempted synthesis of the trimethyl ether of 1 via benzoin [7] Conversely compound 2 was synthesized by reaction



of *m*-dimethoxybenzene with oxalyl chloride in ethylene chloride [8], and it was found to be identical (spectral data and mmp) with the trimethylderivative of 1

Finally, synthetic 2,4,2',4'-tetramethoxybenzil was treated with aluminium chloride [8] to give two products 2,2'-dihydroxy-4,4'-dimethoxybenzil (3) and 2,4,2'-trihydroxy-4'-methoxybenzil (1) identical with the natural product

EXPERIMENTAL

Mps uncorr, ¹H NMR 60 MHz, TMS as int standard, MS 70 eV (direct inlet), TLC and CC Kieselgel 60 (Merck), elemental analyses were in agreement with the molecular formulae

Plant material Z paraensis Hub was collected in Pacatuba, Cearà State, Brazil and was identified by Dr J Matos A voucher sample (ZP 1981) is in the Herbarium of Centre Chimica Recettori del CNR

2,4,2'-Trihydroxy-4'-methoxybenzil (1) Mp 166-168° (C₆H₆), UV λ_{max}^{MeOH} nm 326, 285, 229, $\lambda_{max}^{AlCl_3}$ nm 365 sh, 307, 227, λ_{max}^{NaOAc} nm 346, 285, 225, ¹H NMR (Me₂CO-d₆) δ 3 90 (3H, s, OMe), 6 30-6 65 (4H, m, H-3, H-3', H-5, H-5'), 7 37 (1H, d, J = 9 0 Hz, H-6 or H-6'), 7 40 (1H, d, J = 9 0 Hz, H-6' or H-6), 11 0-11 5 (2H, s (br), 2OH), ¹H NMR (C₅D₅N) δ 3 70 (3H, s, OMe), 6 40-6 80 (4H, m, H-3, H-3', H-5, H-5'), 7 80 (2H, d, J = 9 0 Hz, H-6, H-6'), EIMS m/z (rel int) 288 [M]⁺ (10), 151 (100), 137 (90), 109 (20), 108 (10), IR $\nu_{max}^{CHCl_3}$ cm⁻¹ 3200, 2960, 1700, 1620, 1500, 1450, 1360, 1320, 1230, 1120, 1020, 800

2,4,2',4'-Tetramethoxybenzil (2) By methylation with MeI Mp 128–130° (EtOH), ¹H NMR (CDCl₃) δ 3 55 (6H, s, 2OMe), 3 85 (6H, s, 2OMe), 6 35–6 75 (4H, m, H-3, H-3', H-5, H-5'), 8 0 (2H, d, J = 9 0 Hz, H-6, H-6'), EIMS m/z (rel int) 330 [M]⁺ (30), 165 (100), 150 (50), 135 (50), 122 (50), 107 (40), 92 (40)

2,4,2'-Triacetoxy-4'-methoxybenzil (4) Vitreous solid, ¹H NMR (CDCl₃) δ 2 00 (3H, s, OAc), 2 03 (3H, s, OAc), 2 40 (3H, s, OAc), 3 97 (3H, s, OMe), 6 8–7 2 (4H, m, H-3, H-3', H-5, H-5'), 8 07 (1H, d, J = 9 0 Hz, H-6 or H-6'), 8 13 (1H, d, J = 9 0 Hz, H-6' or H-6)

Oxidative cleavage of 2,4,2',4'-tetramethoxybenzil (2) To a soln of 2 (20 mg) in MeOH (5 ml) and 0 5 M NaOH (5 ml), H_2O_2 10 %

(5 ml) was added dropwise under stirring for 20 hr at room temp The reaction mixture was acidified and extracted with CHCl₃ After purification by silica gel CC, the residue gave 2,4-dimethoxybenzoic acid (9 mg), mp 107–109° (H₂O)

Synthesis of 2,4,2',4'-tetramethoxybenzil A mixture of mdumethoxybenzene (035 ml) and oxalyl chloride (013g) in $C_2H_4Cl_2$ (3 ml) was treated with AlCl₃ and worked up as in ref [7] The crude product crystallized from EtOH gave 016 g of 2,4,2',4'tetramethoxybenzil identical with 2 (spectral data and mmp)

Demethylation of 2,4,2',4'-tetramethoxybenzil To synthetic 2, 4,2',4'-tetramethoxybenzil (66 mg) in $C_2H_4Cl_2$ (15 ml), AlCl₃ (106 mg) was added The mixture was heated on a steam bath for 2 hr, after cooling dil HCl was added and the organic layer was extracted with 10% NaOH Acidification of the alkaline phase and extraction with EtOAc yielded two products which were separated on a silica gel column using CHCl₃ The former (31 mg) was 2,2'-hydroxy-4,4'-methoxybenzil (3) ($C_{16}H_{14}O_6$), mp 135–137° (EtOH); ¹H NMR (CDCl₃) $\delta 3$ 85 (6H, s, 2 × OMe), 6 30–6 50 (4H, m, H-3, H-3', H-5, H-5'), 7 40 (2H, d, J = 9 0 Hz, H-6, H-6'), 11 80 (2H, s, 2 × OH), and the latter (26 mg) was 2,4,2'trihydroxy-4'-methoxybenzil identical with natural compound 1 (mmp and spectral data)

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