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OCCURRENCE OF PONGAMOL AS THE ENOL STRUCTURE IN *TEPHROSIA PURPUREA*

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Key Word Index—*Tephrosia purpurae*; Leguminosae; β-hydroxychalcone; pongamol; X-ray analysis.

Abstract—Pongamol in its pure enol form has been found to occur in the whole plant of *Tephrosia purpurea* together with β-sitosterol, ursolic acid and spinasterol-α.

INTRODUCTION

Tephrosia purpurea is an important Indian medicinal plant. It is given as an anthelmintic to children; its root bark is given in cases of obstinate colic and its root is given in tympanites, dyspepsia and chronic diarrhoea [1]. The seed extract of this plant possesses insecticidal and repellent properties [2]. Although a number of rotenoids and flavanones have been isolated from *T. purpurea*, no flavone derivative has been reported in this species whereas a flavone glycoside, active against human epidermoid carcinoma of the nasopharynx in tissue culture (9 KB), has been isolated from the ethanolic extract of the aerial parts of *T. cqndida* [3]. In view of the variety of uses of *T. purpurea* and the cytotoxic activities of the *T. candida* flavone and other flavones [4–7], we have undertaken a study of the minor constituents of the whole plant of *T. purpurea*.

RESULTS AND DISCUSSION

β-Sitosterol, ursolic acid and sigmasterol-α were isolated from the petrol and benzene extracts of the whole plant by column chromatography. These compounds have not been reported previously from this species.

The ethanol extract of the plant on column chromatography yielded only one compound whose identification by spectroscopic and crystallographic methods is reported here. Its structure has been established unequivocally by a single crystal X-ray analysis as the β-hydroxybenzofuranchalcone (**1**).

The compound, mp 135–136°, analysed for $C_{18}H_{14}O_4$ (M^+ 294) and was recognised as a chalcone having a chelated hydroxy group from (i) a red colour with concentrated sulphuric acid, (ii) the appearance of a broad shallow band between 3400 and 2700 cm^{-1} and a band at 1595 cm^{-1} in its IR spectrum, and (iii) UV absorption maxima at 235 and 347 nm. The bathochromic shift of 19 nm in the UV maxima in the presence of both $AlCl_3$ and $AlCl_3$/HCl further supported the presence of a chelated hydroxy group. As no shift in λ_{max} was registered in the presence of sodium methoxide, it was concluded that no phenolic hydroxy group was present. The broad shallow band between 3400 and 2700 cm^{-1} in the IR spectrum and a singlet integrating for 1H at δ16.92 in the ^{1}H NMR spectrum was consistent with an enolic hydroxy group [8]. This was supported by a singlet at δ7.16 for 1H (H-11) in the 200 MHz ^{1}H NMR spectrum ($CDCl_3$) and two signals at δ97.97 (C-11) and δ184.32 (C-12) in the ^{13}C NMR spectrum. Its ^{1}H NMR, in addition, indicated the presence of one methoxy group (δ4.12, *s*, 3H), two *ortho*-coupled aromatic protons in the A-ring (δ7.28 and 7.85, each *d*, 1H, $J = 9$ Hz), an unsubstituted B-ring (δ7.48 and 7.94, each *m*, for 3H and 2H, respectively) and a furan ring fused to the A-ring (δ6.96 and 7.60, each *d*, 1H, $J = 2$ Hz). EIMS peaks were observed at *m/z* 105 and 77 for the B-ring fragments **a** and **b**, at *m/z* 175 for the A-ring fragment **c** and at *m/z* 276 $[M-H_2O]^+$.

The structure was firmly established as the β-hydroxybenzofuranchalcone (**1**) by an X-ray crystal structure analysis. This is the enol form of the compound Pongamol, first isolated from the seeds of *Pongamia glabra* [9] and designated as the β-diketo form (**2**) on the basis of chemical characterization. The same structure, based on spectroscopic evidence, was later attributed to a sample from *T. purpurea* [10].

This is the first benzofuranchalcone to be determined by X-ray methods, no such compound appearing in the Cambridge Crystallographic Database, and the first reported β-hydroxybenzofuranchalcone from any natural source. The molecule is shown in Fig. 1. Key molecular dimensions are: C-10–O-3 = 1.28, C-10–C-11 = 1.41, C-11–C-12 = 1.39, C-12–O-4 = 1.31 Å. While there is some evidence of delocalization over these atoms the tautomer was established by the location of atoms H-4 and H-11. The enol −OH is hydrogen bonded to the carbonyl oxygen (O-3–O-4 = 2.49, O-3–H-4 = 1.77 Å). The molecule consists of three planar groupings (Fig. 2), the mean plane of the benzofuran moiety (O-1, O-2, C-2–C-10) is twisted by 34.8° from the mean plane of the β-hydroxy chalcone (C-5–C-13, O-3, O-4) which is in turn twisted by 27.9° from the mean plane of the phenyl group (C-12–C-18). Full tables of refined atomic coordinates, tempera-

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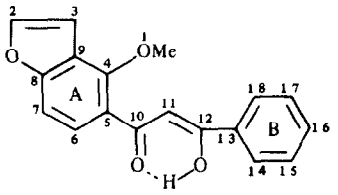
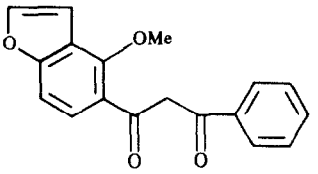


1



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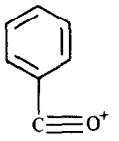
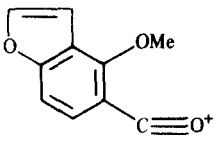


a *m/z* 105 (23.9 %)

b *m/z* 77 (27.7 %)



c 175 (36.1 %)

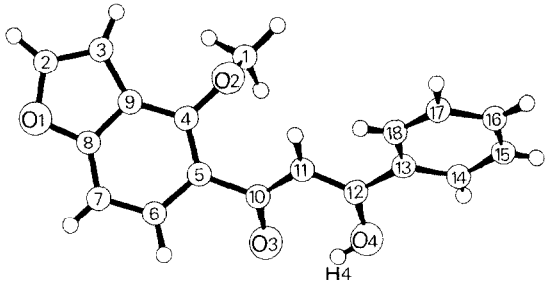


Fig. 1.

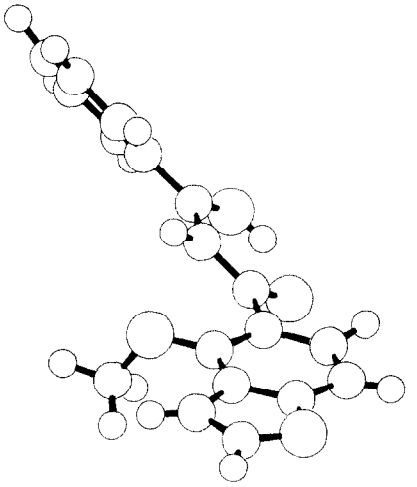


Fig. 2.

ture factors, bond lengths and angles have been deposited with the Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, U.K.

EXPERIMENTAL

Crystal data. $C_{18}H_{14}O_4$, $M_r = 294.3$, Monoclinic, Space group $P2_1/a$ (no. 14), $a = 13.613$ (14), $b = 9.740$ (10), $c = 10.933$ (11) Å, $\beta = 103.3$ (1)°, $U = 1410.9$ Å^3, $Z = 4$, $D_c = 1.39$ g/cm^3, $F(000) = 616$, λ (MoKα) = 0.71069 Å, μ (MoKα) = 0.6 cm^{-1}.

The lattice was characterized by oscillation and Weissenberg photographs taken with CuKα radiation ($\lambda = 1.5418$ Å). Diffraction data were recorded on a Stöe STADI-2 diffractometer, using the background –ω-scan–background mode with scan width 1.5°, scan speed 1.5 deg/min, $3 \leqslant \theta \leqslant 30°$, and MoK$\alpha$ radiation. 2010 unique data were corrected for Lorentz and polarization factors and used in the subsequent analysis. The structure was determined by the direct methods of SHELX [11] and refined by least squares, allowing anisotropic temperature factors for non-hydrogen atoms. All 14 hydrogens were located in a difference Fourier synthesis. The methyl hydrogens were included in the refinement at positions calculated from the geometry of the molecule. All other hydrogens were included at their located positions with individual isotropic temperature factors. In the final cycles only the 1520 data with $F > 6\sigma(F)$ were used and yielded a final R of 0.057.

Isolation procedure. Air-dried and powdered whole plant of *T. purpurea* (1 kg) was extracted with hot petrol, C_6H_6 and EtOH, in succession. The petrol and C_6H_6 extracts which were found to be similar were mixed and the residue obtained on removal of the solvent was column chromatographed over silica gel using C_6H_6–EtOAc with increasing polarity as eluants, when β-sitosterol, ursolic acid and spinasterol-α were obtained; they were identified from their spectral data and comparison with the corresponding authentic samples. The ethanolic extract was concd under red. pres. and macerated several times with dry Et_2O when a blackish-brown tarry mass was left behind. The Et_2O-soluble portion was freed from the solvents, dried and column chromatographed over silica gel using C_6H_6–EtOAc as the eluant.

Pongamol (**1**). C_6H_6–EtOAc (3:2) eluates of the column chromatogram of the Et_2O-soluble portion yielded **1** (100 mg), mp 135–136; IR ν_{max}^{KBr} cm^{-1}: 3400–2700 (*br*, shallow), 1595, 1450, 1370, 1290, 1210, 1130, 1060, 956, 795, 770, 740, and 690; UV λ_{max}^{MeOH} nm: 235, 347; $+AlCl_3$: 236, 284 (sh), 366; $+AlCl_3$/HCl: 236, 284 (sh), 366; +NaOAc: 238, 347; +NaOMe: 238, 342; $\delta_H(CDCl_3)$: 4.12 (3H, *s*, OMe), 6.96 (1H, *d*, $J = 2$ Hz, H-3), 7.16 (1H, *s*, H-11), 7.28 (1H, *d*, $J = 9$ Hz, H-7), 7.48 (3H, *m*, H-15, H-16 and H-17), 7.60 (1H, *d*, $J = 2$ Hz, H-2), 7.85 (1H, *d*, $J = 9$ Hz, H-6), 7.94 (2H, *m*, H-14 and H-18), 16.92 (1H, *s*, C-12 OH, exchangeable with D_2O); $\delta_C(CDCl_3)$: 61.76 (OMe), 97.97 (C-11), 105.25 (C-7), 107.09 (C-3), 119.6 (C-5), 122.18 (C-9), 126.59 (C-6), 127.16 (C-15 and C-17), 128.62 (C-14 and C-18), 132.08 (C-16), 135.70 (C-13), 144.85 (C-2), 152.78 (C-8), 158.78 (C-4), 184.32 (C-12), 186.14 (C-10); EIMS *m/z* (rel. int.): 294 $[M]^+$ (9.5), 276 $[M - H_2O]^+$ (2.8), 264 (16.6), 263 $[M - OMe]^+$ (100), 176 (4.3), 175 (36.1), 160 (10.0), 148 (6.9), 147 (4.2), 105 (23.9), 77 $[C_6H_5]^+$ (27.7); (Found: C, 73.91; H, 4.88. $C_{18}H_{14}O_4$ requires: C, 73.46; H, 4.76%).

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