SHORT COMMUNICATIONS

PROTON MAGNETIC RESONANCE STUDY OF 2-(*p*-METHOXYPHENYL)THIAZOLIDINE

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THE importance of penicillin lies in the thiazolidine part, which is a five-membered ring. Thiazolidine belongs to a group of heterocyclic compounds and is a saturated molecule with S and N atoms in 1 and 3 positions respectively in the five-membered ring. The presence of N–C–S linkages in the thiazolidine ring is postulated to account for the anti-fungal activity[1]. Thiazolidine derivatives have a variety of biological activities such as anti-radiation[2], anti-oxidant[3], pesticidal, bactericidal, fungicidal, insecticidal, tuberculostatic and anti-inflammatory activities. They are also important as hypoglycemic agents[4], effective hypertensive agents[5], and in the treatment of angina pectoris, arrhythmia and thrombosis[6]. The conformation of cysteamine and thiazolidine has been determined in aqueous solution using NMR spectroscopy[7].

The structural formula proposed for 2-(*p*-methoxyphenyl)thiazolidine (2pmpT) is shown in figure 1. The synthesis and characterization of this compound have been reported[8]. It was concluded from X-ray studies that 2pmpT is crystalline and belongs to the orthorhombic system, with space group $P2_12_12_1$. Its

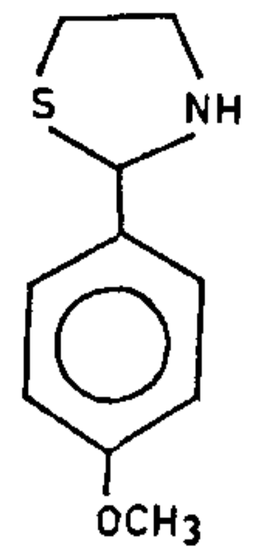

Figure 1. Proposed structure of 2-(*p*-methoxyphenyl)thiazolidine.

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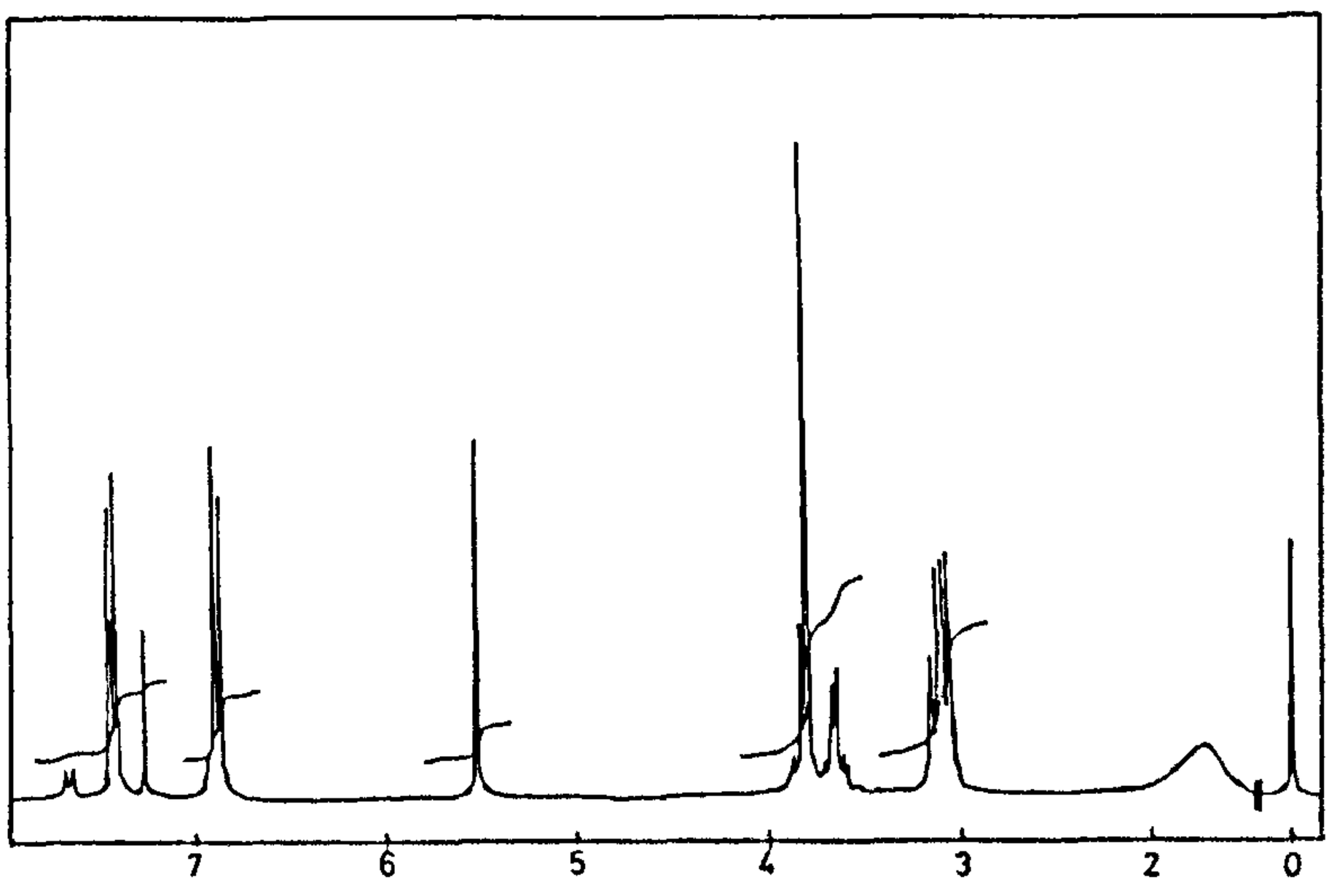

Figure 2. Proton magnetic resonance spectrum of 2pmpT.

density is 1.37 g cm^{-3}. The IR spectrum of the sample shows strong peaks corresponding to NH (3200 cm^{-1}), CS (1340 cm^{-1}), CN (1155 cm^{-1}), N–C–S (450 cm^{-1}), C_6H_4 (1590 cm^{-1}) and OCH_3 (2900 and 1460 cm^{-1}).

It is worth mentioning that NH is the only functional group in the IR spectrum and other groups come under the 'finger print region' (< 1600 cm^{-1}). In order to further establish the chemical groups of 2pmpT and thereby its proposed structure, a proton magnetic resonance (PMR) study was undertaken.

The PMR spectrum of 2pmpT in $CDCl_3$ was recorded on a Varian EM-390 spectrometer (figure 2). It is quite clear that the PMR spectrum exhibits a broad singlet at δ 1.8 due to NH, a complex 4 H multiplet around δ 3.00–3.25 due to hydrogens of the methylene groups, a sharp 3 H singlet at δ 3.82 due to methoxy group hydrogens, and 1 H singlet at δ 5.5 due to benzylic hydrogen. The aromatic hydrogens are indicated by the presence of two 2 H doublets of A_2B_2 pattern centred at δ 6.9 and 7.4 due to hydrogens in *meta* and *ortho* positions with methoxy group at *para* position.

The presence of CH_2 groups and NH supported by PMR peaks suggests the existence of thiazolidine ring while methoxy hydrogens and benzylic hydrogens revealed by δ 3.82 and 5.5 peaks support the existence of phenyl ring. The doublets at δ 6.9 and 7.4 confirm methoxy group in para position. Hence it is concluded that the PMR spectrum unambiguously supports the proposed structure of 2pmpT (figure 1). Crystal structure determination from X-ray diffraction studies is in progress and will be reported later.

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A FACILE SYNTHESIS OF 2,8-DISUBSTITUTED 4,6-DIOXO-4*H*, 6*H*-BENZO [1,2-*b*:5,4-*b*'] DIPYRANS AND THEIR ANTIFEEDANT ACTIVITY

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EARLIER[1] three title compounds were synthesized by heating an intimate mixture of 2,4-dihydroxy-5-acetylacetophenone, aromatic acid anhydride and sodium salt of the same acid at 180–185°C for 8 h. Because of the high temperature required in the above method, the yields are low and the reaction takes a long time for completion. Therefore the need for an alternative method for the synthesis of title compounds is imperative. Further it is reported in the literature that the linearly fused benzo-γ-dipyrones are more active than the angularly fused analogues in many physiological activities[2]. The antifeedant activity of the proposed compounds does not seem to have been studied so far. In the present investigation, an alternative and more facile approach has been explored to synthesize some new linearly fused benzo-γ-dipyrones, and their antifeedant activity has been studied.

2,4-Dihydroxy-5-acetylacetophenone (I)[3] was condensed with various aromatic aldehydes (benzaldehyde, *o*-chlorobenzaldehyde, 2,6-dichlorobenzaldehyde, *p*-methoxybenzaldehyde, *p*-methylbenzaldehyde, piperonal, furfural and thiophene-2-aldehyde) in the presence of 60% aq. KOH to yield the corresponding dichalcones (IIa–h), which gave deep red colouration with conc. H_2SO_4 and reddish-brown colouration with ethanolic $FeCl_3$. These dichalcones were characterized by comparison with authentic samples[4].

The dichalcones (II) were suspended in DMSO (30 ml) and a crystal of iodine was added. The mixture was refluxed for 10 min. Usual work-up of the reaction mixture gave the corresponding 2,8-disubstituted 4,6-dioxo-4*H*, 6*H*-benzo [1,2-*b*:5,4-*b*']-dipyrans (III) in better yields (80–85%). These compounds gave red colour in Shinoda test[5],