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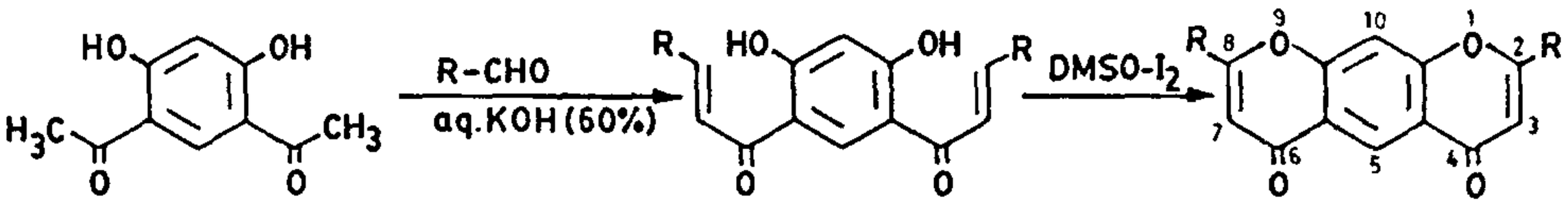
A FACILE SYNTHESIS OF 2,8-DISUBSTITUTED 4,6-DIOXO-4*H*, 6*H*-BENZO [1,2-*b*:5,4-*b*'] DIPYRANS AND THEIR ANTIFEEDANT ACTIVITY

S. PURUSHOTHAM REDDY, D. ASHOK and P. N. SARMA
Department of Chemistry, Osmania University, Hyderabad 500 007, India.

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],



I II III

R: a = Phenyl
b = 2-Chlorophenyl
c = 2,6-Dichlorophenyl
d = 4-Methoxyphenyl
e = 4-Methylphenyl
f = 3,4-Methylenedioxyphenyl
g = Furfuryl
h = 2-Thienyl

indicating their flavonoid nature. As a representative case, the spectral identification of 2,8-diphenyl-4,6-dioxo-4*H*, 6*H*-benzo[1,2-*b*:5,4-*b*']dipyran (IIIa) has been discussed. The IR spectrum of IIIa exhibited absorption at 1650 cm^{-1}, which is characteristic of carbonyl group of flavones[6]. The UV absorption data λ_{max}^{MeOH} (log ε), 208 (4.59), 265 (4.68) and 320 (4.54), are similar to those of flavones[7]. The ^1H NMR spectrum of IIIa revealed a singlet at δ 6.8 (2H) due to H-3 and H-7 protons. The spectrum also exhibited two sharp singlets at δ 7.26 and 9.08 each integrating for one proton, which were readily assigned to H-10 and H-5 respectively[4]. The aromatic region of the spectrum showed a multiplet between δ 7.51 and 7.97 integrating for ten protons, which was assigned to protons of C_2 and C_8 phenyl rings. The mass spectrum of IIIa showed molecular ion peak at 366 (100%). The prominent fragmentation ions were observed at *m/z* 338 (45%) [M-CO], 310 (8%) [M-2CO]. The ions at *m/z* 264 (28%) and 102 (24%) arise owing to RDA fission and are characteristic of flavonoids[8]. Further ions arising owing to RDA fission from *m/z* 338 were also observed at 236 (28%) and 102 (24%). The analytical and spectral data of all the compounds synthesized are given in table 1.

Table 1 *Analytical and spectral properties and antifeedant activity of 2,8-disubstituted 4,6-dioxo-4H,6H-benzo[1,2-b:5,4-b']dipyrans*

Compound	M.p. (°C)	Yield (%)	IR, $\nu_{max}^{CHCl_3}$ $>C=O$	UV, λ_{max}^{MeOH} (log ε)	Antifeedant activity (%)
IIIa	282 (lit.[1] 281)	85	1650	265 (4.68) 320 (4.54)	53.44
IIIb	235	83	1660*	260 (4.75) 324 (4.54)	65.39
IIIc	240	80	1660	260 (4.70) 324 (4.42)	67.24
IIId	205 (lit.[1] 192(d))	85	1661	265 (4.62) 328 (4.48)	86.00
IIIe	300	82	1650	265 (4.75) 325 (4.62)	83.08
IIIf	290	80	1655	268 (4.70) 328 (4.51)	56.05
IIIg	285	80	1652*	268 (4.70) 325 (4.51)	73.50
IIIh	280	82	1640	270 (4.72) 325 (4.55)	88.80

All the compounds gave satisfactory C and H analyses; *Recorded in KBr.

The method of synthesis used here is quicker, the conditions are mild, there was no significant substituent effect on the reaction, the yields are good to excellent, and by-products were not detected. The method appears to be of general applicability.

All the compounds synthesized have been tested for antifeedant activity following the 'non-choice test method'[9] using six-hour-prestarved fourth instar larvae of *Spodoptera litura*. The results are given in table 1. The present study reveals that 2,8-di(2-thienyl)-4,6-dioxo-4*H*, 6*H*-benzo[1,2-*b*:5,4-*b'*]dipyran (IIIh) has the highest antifeedant activity.

Dichalcones (IIa–h): General procedure

A mixture of I (0.01 mol) and the appropriate aldehyde (0.02 mol) in ethanol (40 ml) was kept at room temperature for 12 h with aq. KOH (60%, 10 ml). The product, obtained on dilution and acidification with dil. HCl, was subjected to column chromatography over silica gel (200-mesh). Benzene–chloroform (8:2, v/v) eluates, on concentration, afforded II.

2,8-Disubstituted 4,6-dioxo-4H,6H-benzo[1,2-b:5,4-b']dipyrans (IIIa–h): General procedure

Dichalcones (II) (0.01 mol) were suspended in dry dimethylsulphoxide (30 ml) and a crystal of iodine added. The mixture was refluxed for 10 min, cooled and diluted with cold water. The solid obtained was filtered, washed with 20% aq. $Na_2S_2O_3$, and recrystallized from alcohol.

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ESTERIFICATION WITH HYDROGEN FLUORIDE

TARIQ UMER QAZI
Welsh School of Pharmacy, University of Wales, Cardiff, UK.

LIQUID hydrogen fluoride is a very useful reagent with high solvent power, particularly for oxygen-containing substances and also for aromatic compounds. It has been extensively used for its dehydrating and condensing properties. Compared to concentrated sulphuric acid, it is less likely to permit secondary reactions such as enolization, sulphonation, polymerization and tarry residues. Askam and Qazi[1,2] reported cyclization in anhydrous fluoride with derivatives of diethyl phenylmalonate.

This communication reports the esterification reaction of various acids in the presence of anhydrous hydrogen fluoride. Fieser and Hershberg[3] synthesized ethyl acetate in the presence of hydrogen fluoride, but the yield was only 17.5%. It was concluded that the poor yield obtained was due to the fact that the equilibrium in hydrogen fluoride solution favoured the left hand side of the equation below.

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O.$$

Traces of water formed during the reaction and their presence in hydrogen fluoride were stated to contribute to easy hydrolysis of $CH_3COOC_2H_5$.

The following general method was used for the preparation of the various esters. A mixture of acid and alcohol in 1:3 molar ratio was dissolved in 4 m anhydrous hydrogen fluoride by gentle swirling. A clear solution resulted, which was allowed to stand at room temperature for 6 h in a screw-capped polythene bottle. (Hydrogen fluoride reacts with glass containers.)

After 6 h the water vapour was allowed to escape. Hydrogen fluoride solvent (2 m) was added and the mixture shaken further for a few minutes and allowed to stand a further 20 h. The excess hydrogen fluoride was then evaporated in a polythene beaker.