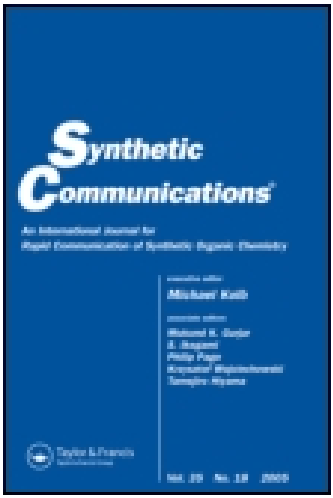

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A Facile Synthesis of 3,7-Disubstituted-4,8-dimethyl-2,6-dioxo-2H,6H-benzo[1,2-b:3,4-b′]dipyrans and Their Antifeedant Activity

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SYNTHETIC COMMUNICATIONS, 26(18), 3373-3381 (1996)

A FACILE SYNTHESIS OF 3,7-DISUBSTITUTED-4,8-DIMETHYL-2,6-DIOXO-2H,6H-BENZO[1,2-b:3,4-b']DIPYRANS AND THEIR ANTI-FEEDANT ACTIVITY

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ABSTRACT : The synthesis, characterisation and antifeedant activity of some new dicoumarins prepared from 2,4-diacetyl resorcinol has been reported.

Since the first report of the formation of 4,6-diacetyl resorcinol (**1**) as a major product along with its isomer 2,4-diacetyl resorcinol (**2**) in a single pot acetylation of resorcinol with zinc chloride and acetic anhydride[1], this method has been adopted by us[2-6] and others[7-9], to prepare 4,6-diacetyl resorcinol (**1**) and utilise it in the synthesis of a large number of α and γ-benzopyrones. In contrast to the extensive work reported on 4,6-diacetyl resorcinol the work on the isomeric 2,4-diacetyl resorcinol is scanty, probably because of its low yield (5%). It may be mentioned here that

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2,4-diacetyl resorcinol has been utilized recently to obtain few angular benzo-γ-dipyrones[10]. Therefore in the present investigation the synthesis of some new angularly fused benzo-α-dipyrones from 2,4-diacetyl resorcinol has been taken up with a view to test their antifeedant activity.

In the present investigation, an alternative and more facile approach involving modified Baker Venkatraman transformation[11-13] has been explored. Thus 2,4-diacetyl resorcinol (**2**, 0.01 mole) and phenyl acetyl chloride (0.04 moles) were dissolved in dry acetone and refluxed with anhydrous potassium carbonate for 10 hr. Work-up of the reaction mixture followed by column chromatography yielded two compounds viz. compound A and B.

Compound-A was recrystallized from ethanol as colourless needles, Mp 269°C, $C_{26}H_{18}O_4$, M^+ 394. The IR spectrum of the product showed adsorption at 1710 cm^{-1} which is characteristic of carbonyl group of coumarins[14]. The UV absorption data λ_{max}^{MeOH} nm (log ε) : 302 (4.19) are in good agreement with those of 3-phenyl coumarins[15].

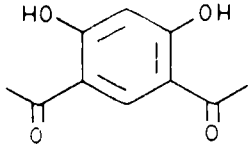
The PMR spectrum of the compound exhibited two singlets at δ 2.4 (3H) and 2.75 (3H) due to protons of allylic methyl groups situated at C-4 and C-8 positions respectively. The spectrum also revealed two AB doublets at δ 7.3 (1H, J=9.8 Hz) and 7.85 (1H, J=9.8 Hz) assignable to H-10 and H-9 respectively. The aromatic region of the spectrum showed a multiplet between

δ 7.3-7.6 (10H) for C-3 and C-7 phenyl ring protons. The mass spectrum of **3a** showed molecular ion peak at 394 (100%). The prominent fragmentation ions at m/z 366 (49%) [M-CO], 338 (17%) [M-2CO], 337 (50%) [M-2CO-H$^{\cdot}$], 105 (35%) [$Ph\text{-}\overset{+}{C}O$] were highly diagnostic[16]. On the basis of the above analytical and spectral data, compound-A has been characterized as 4,8-dimethyl -3,7-diphenyl-2,6-dioxo-2H,6H-benzo[1,2-B:3,4-b']dipyran (**3a**). Compound-B, Mp 142°, analysed for $C_{18}H_{14}O_4$ (M^+ 294) was readily recognised as a monocoumarin (3-phenyl-4-methyl-5-hydroxy-6-acetyl coumarin) based on analytical and spectral data.

Following the above method several substituted 2,6-dioxo-2H,6H-benzo[1,2-b:3,4-b']dipyrans (**3**) were synthesised and their analytical spectral data are given in Table. In all these reactions their corresponding mono coumarins (**4b-f**) were also isolated and were characterized with the help of spectral data. All the mono coumarins gave blue colour in Gibbs test[17] indicating the presence of a free position para to phenolic hydroxyl group.

All the compounds (**3,4**) were tested for their antifeedant activity by the "Non-choice test method"[18] using 6 hr pre-starved fourth in star larvae of Spodoptera litura, and the results are shown in Table. Compounds **3c, 3f** and **4f** exhibited highest antifeedant activity.

SCHEME



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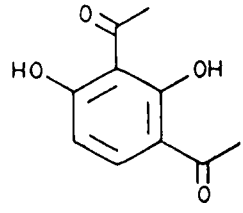

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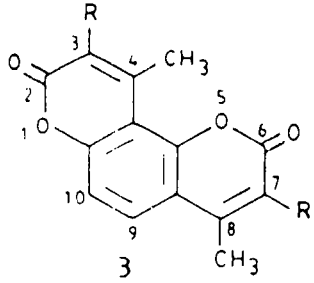

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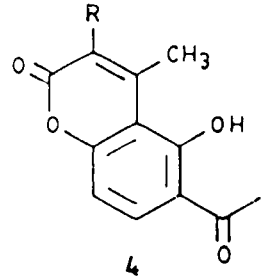

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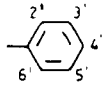
3a R = 

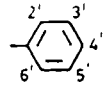
b R = 4-Methoxy phenyl

c R = 3,4-Dimethoxy phenyl

d R = 2-Chloro phenyl

e R = 4-Chloro phenyl

f R = 2-Thienyl

4a R = 

b R = 4-Methoxy phenyl

c R = 3,4-Dimethoxy phenyl

d R = 2-Chloro phenyl

e R = 4-Chloro phenyl

f R = 2-Thienyl

EXPERIMENTAL

Synthesis of 3,7-disubstituted-4,8-dimethyl-2,6-dioxo-2H,6H-benzo [1,2-b:3,4-b']dipyrans (3a-f). General Procedure

A solution of 2,4-diacetyl resorcinol (**2**, 0.01 mole) and phenyl acetyl chlorides (0.04 moles) in dry acetone (200 ml) was

TABLE

Compd.	Mp (°C)	M^+	IR(KBr) (>C=O str)	UV (MeOH) nm (log ε)	Yield (%)	Antifeedant activity(%)
3a	269	394	1710	302 (4.19)	47.2	79.57
3b	230	454	1700	314 (4.31)	42.0	32.10
3c	226	514	1715	322 (4.19)	37.4	98.57
3d	238	462	1712	302 (4.06)	46.8	67.15
3e	218	462	1705	307 (4.05)	48.0	48.25
3f	263	406	1712	314 (4.11)	40.6	100
4a	142	294	1710	273 (4.78)	32.9	62.90
4b	85	-	1690	300 (4.41)	38.5	25.08
4c	240	354	1710	280 (4.82)	43.0	84.16
4d	224	328	1705	279 (4.49)	31.2	53.00
4e	164	328	1712	273 (4.83)	30.0	89.05
4f	192	300	1712	280 (4.75)	39.7	100

All the compounds gave satisfactory elemental analysis.

refluxed with anhydrous potassium carbonate (5 g) for 10 hr on a steam bath. The acetone solution was filtered, the potassium carbonate residue washed with acetone. The combined acetone solution was evaporated and cold water was added to the residue. The separated product was filtered, washed successively with 2% aqueous sodium bicarbonate and water. The crude product was found to be a mixture containing two compounds. Hence it was subjected to column chromatography

over silica gel (200 mesh). Benzene : chloroform (1:1 v/v) elutions on concentration afforded the mono coumarins (**4a-f**) and the chloroform : methanol (8:2 v/v) elutions yielded dicoumarins (**3a-f**).

NMR DATA

3a : ($CDCl_3$) δ 2.4 (3H,s,CH_3), 2.75 (3H,s,-CH_3), 7.3 (1H,d, J=9.8 Hz, H-10), 7.3-7.6 (10H,m,protons of phenyl gps), 7.85 (1H,d,J=9.8 Hz, H-9).

3b : ($CDCl_3$) δ 2.35 (3H,s,CH_3), 2.74 (3H,s,-CH_3), 3.86 (6H,s, 2xOCH_3), 6.98 (4H,d,J=8.0 Hz, 2xH-3' & 5'), 7.25 (4H,d, J=8.0 Hz, 2xH-2' & 6), 7.31 (1H,d,J=8.0 Hz, H-10), 7.79 (1H,d,J=8.0 Hz, H-9).

3f : ($CDCl_3$) δ 2.57 (3H,s,CH_3), 2.90 (3H,s,CH_3), 7.35 (1H,d,J= 7.5 Hz, H-10), 7.83 (1H,d,J=7.5 Hz, H-9), 7.1-7.55 (7H,m, 2xH-3', 4', 5' & 8).

4a : ($CDCl_3$) δ 2.55 (3H,s,CH_3), 2.7 (3H,s,-$COCH_3$), 6.90 (1H,d, J=8.0 Hz, H-8), 7.25 (2H,m,H-2' & 6'), 7.4 (3H,m,H-3', 4' & 5'), 7.89 (1H,d,J=8.0 Hz, H-7), 14.30 (1H,s,-OH).

4b : ($CDCl_3$) δ 2.55 (3H,s,CH_3), 2.7 (3H,s,-$COCH_3$), 3.85 (3H,s, OCH_3), 6.8 (2H,d,J=8.0 Hz, H-3' & 5'), 7.0 (2H,d,J=8.0Hz, H-2' & 6'), 7.2 (1H,d,J=8.0 Hz, H-8), 7.75 (1H,d,J=8.0Hz, H-7), 14.3 (1H,s,-OH).

4c : ($CDCl_3$) δ 2.55 (3H,s,CH_3), 2.7 (3H,s,-$COCH_3$), 3.95 (3H,s, one OCH_3), 3.98 (3H,s,one -OCH_3), 6.95 (4H,m,H-2',5',6'& 8), 7.95 (1H,d,J=8.0 Hz,H-7), 14.3 (1H,s,-OH).

4d : ($CDCl_3$) δ 2.55 (3H,s,CH_3), 2.7 (3H,s,-$COCH_3$), 6.85 (2H,d, J=8.0 Hz, H-3' & 5'), 7.22 (2H,d,J=8.0 Hz, H-2' & 6'), 7.35 (1H,d,J=8.0 Hz, H-8), 7.8 (1H,d,J=8.0 Hz, H-7), 14.3 (1H,s,-OH).

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