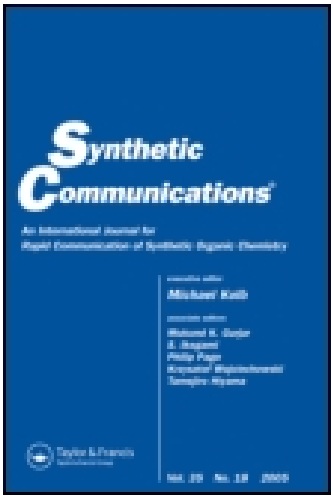

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A Facile Synthesis of 3,7-Diphenyl-4,6-Distyryl-2,8-Dioxo-2H,8H-Benzo[1,2-b:5,4-b′]dipyrans and Their Antifeedant Activity

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A FACILE SYNTHESIS OF 3,7-DIPHENYL-4,6-DISTYRYL-2,8-DIOXO-2H,8H-BENZO[1,2-b:5,4-b']DIPYRANS AND THEIR ANTIFEEDANT ACTIVITY

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Abstract : The synthesis, characterisation and antifeedant activity of some new dicoumarins prepared from 4,6-diacetyl resorcinol has been reported.

A number of diflavones[1] and diflavonols[2] derived from 4,6-diacetyl resorcinol (**I**) have been shown to exhibit significant antifeedant activity. Recently we have reported[3] the synthesis of 2,8-disubstituted-2,3,7,8-tetrahydro-4,6-dioxo-4H,6H-benzo-[1,2-b:5,4-b']dipyrans as potential antifeedants. Literature survey revealed that the synthesis and antifeedant activity of the title compounds have not been reported so far. Therefore in the present investigation the synthesis of some new 3,7-diphenyl-4,6-distyryl-2,8-dioxo-2H,8H-benzo[1,2-b:5,4-b']dipyrans have been taken up with a view to study the effect of dicoumarin moiety on their antifeedant activity.

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The required starting materials, the dichalcones (**2a-j**) were prepared by the condensation of 4,6-diacetyl resorcinol (**1**) with aromatic aldehydes in the presence of 60% aq. KOH and are characterised by comparison with authentic samples[2,4,5].

In the present investigation, an alternative and more facile approach involving modified Baker-Venkatraman transformation[6-8] has been explored. Thus, 4,6-dicinnamoyl resorcinol (**2a**, 0.01 mole) and phenyl acetyl chloride (0.02 moles) were dissolved in dry acetone and refluxed with anhydrous potassium carbonate for 10 hr. The acetone solution was filtered and the potassium carbonate was washed with acetone. The combined acetone solution on vaporation yielded a brown semi solid which was treated with ice-cold water. The solid that separated was crystallized from methanol as colourless needles in good yields (82.6%), m.p. 198°, $C_{40}H_{26}O_4$, M^+ 570.

The IR spectrum of the product showed absorption at 1718 cm^{-1} which is characteristic of carbonyl group of coumarins. The UV absorption data λ_{max}^{MeOH} nm (log ε) 341 (4.86) are in good agreement with those of 3-phenyl coumarins[9].

The PMR spectrum of **3a** exhibited two sharp singlets at δ 6.45 and δ 8.48 integrating for one proton which were assigned to H-10 and H-5 respectively. The spectrum also revealed two doublets at δ6.7 (J=16 Hz) and δ 7.62 (J=16 Hz) integrating for two protons each , which were assigned to α,α' and β, β' protons respectively. The aromatic region of spectrum showed a multiplet at δ 6.9-7.5 (20 H) for the protons of four phenyl

groups. The mass spectrum of **3a** showed molecular ion peak at 570 (10%). The prominent fragmentation ions at m/z 542 (12%) [M-CO], 514 (10%) [M-2CO], 105 (20%) [Ph-$\overset{+}{C}$O], 91 (100%) [Ph-$\overset{+}{C}H_2$] were highly diagnostic[10]. On the basis of the above analytical and spectral data compound **3a** has been characterized as 3,7-diphenyl-4,6-distyryl-2,8-dioxo-2H,8H-benzo[1,2-b:5,4-b'] dipyran (**3a**).

Following the above method several substituted 2,8-dioxo-2H,8H-benzo[1,2-b:5,4-b']dipyrans (**3b-j**) were synthesized and their analytical and spectral data are given in Table. This method is an one - step reaction, the conditions are mild, there was no significant substituent effect on the reaction, the yields are good to excellent and byproducts were not detected.

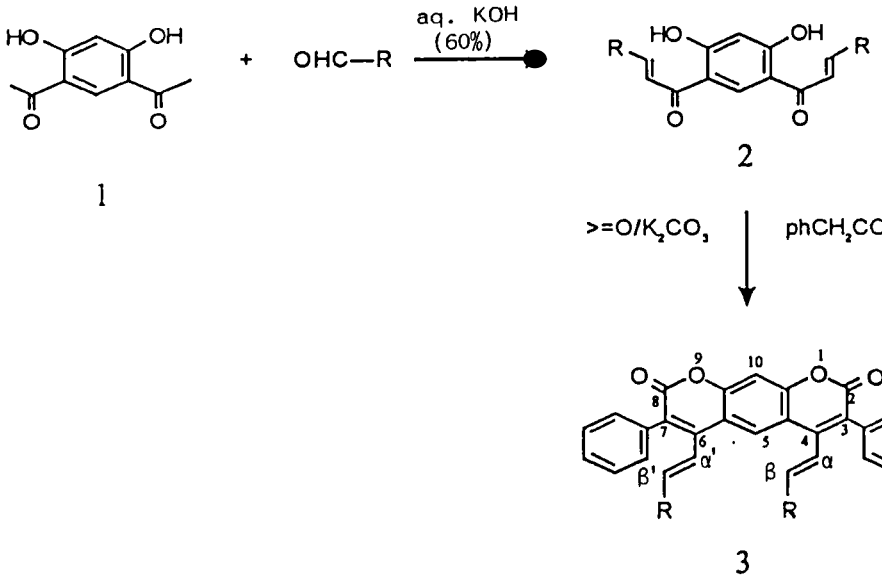
All the compounds (**3**) were tested for their antifeedant activity by the 'Non-choice test method' using 6 hr pre-starved fourth instar larvae of Spodoptera litura, and the results are shown in Table. Compounds **3e, 3g** and **3j** exhibited highest antifeedant activity.

EXPERIMENTAL

Dichalcones (2a-j) : General procedure

A mixture of **1** (0.01 mole) and appropriate aldehyde (0.02 mole) in ethanol (40 ml) and aq.KOH (60%, 10 ml) was kept at room temperature for 12 hr. The product obtained on dilution and acidification with dil. HCl was subjected to column chromatography over silica gel (200 mesh). Benzene : $CHCl_3$ (8:2 v/v) eluates on concentration afforded compound **2**.

SCHEME



1

R

a = Phenyl

b = 2-Chlorophenyl

c = 4-Chlorophenyl

d = 4-Methylphenyl

e = 4-Methoxyphenyl

f = 4-Hydroxyphenyl

g = 4-(N,N-Dimethyl)phenyl

h = 3,4-Methelenedioxyphenyl

i = 2-Furyl

j = 2-Thienyl

Synthesis of 3,7-diphenyl-4,6-distyryl-2,8-dioxo-2H,8H-benzo-[1,2-b:5,4-b']dipyrans (3a-j) : General procedure

A solution of dichalcone (**2**, 0.01 mole) and phenyl acetyl chloride (0.02 moles) in dry acetone (200 ml) was 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 products were crystallized from methanol to yield **3**.

TABLE

Compd	M.P. (°C)	M^+	IR (KBr) (>C=O Str.)	UV(MeOH) nm (log ε)	Yield (%)	Antifeedant activity (%)
3a	198	570	1718	341(4.86)	82.6	63.75
3b	216	638	1718	347(4.40)	80.2	84.16
3c	208	638	1728	324(4.12)	74.0	79.36
3d	172	598	1718	323(4.47)	77.5	72.98
3e	196	630	1718	306(4.25)	81.8	98.57
3f	192	602	1715	324(4.07)	72.0	83.01
3g	236	656	1716	321(3.92)	73.7	93.46
3h	175	658	1728	341(4.48)	71.0	62.25
3i	222	550	1718	323(4.82)	75.6	66.15
3j	186	582	1718	330(5.12)	80.9	100

All the compounds gave satisfactory elemental analysis.

NMR data of some of the title compounds are given below :

3a : ($CDCl_3$) : δ 6.45 (1H,s,H-10), 6.7 (2H,d,H-α, α'), 6.9-7.5 (20H,m,protons of four phenyl groups), 7.62 (2H,d,H-β, β'), 8.48 (1H,s,H-5).

3b : ($CDCl_3$) : δ 6.7 (1H,s,H-10), 6.8-7.6 (22H,m,H-α, α', β, β'-18 aromatic sprotons), 8.61 (1H,s,H-5).

3c : ($CDCl_3$) : δ 6.75 (3H,m,H-10, H-α, α'), 6.98 (4H,d,J=7 Hz, 2 x H-3' & 5'), 7.1 (4H,d,J=7 Hz, 2 x H-2' & 6'), 7.25 - 7.48 (10H,m,protons of phenyl groups), 7.3 (2H,d,H-β, β'), 8.48 (1H,s,H-5).

3d : ($CDCl_3$) : δ 2.38 (6H,s,2xCH_3), 6.78 (1H,s,H-10), 6.9 (2H, d,H-α, α'), 7.0-7.5 (18H,m,protons of phenyl groups), 7.8 (2H, d, H-β, β'), 8.48 (1H,s,H-5).

3e : ($CDCl_3$ + DMSO-d_6) : δ 3.65 (3H,s,OCH_3), 3.8 (3H,s,OCH_3), 6.4 (1H,s,H-10), 6.6 (2H,d,H-α, α'), 6.7-7.4 (18H,m,protons of phenyl groups), 7.6 (2H,d,H-β,β'), 8.55 (1H,s,H-5).

3f : ($CDCl_3$ + DMSO-d_6) : δ6.5 (1H,s,H-10), 6.9 (2H,d,H-α, α'), 7.0-7.6 (18H,m,protons of phenyl groups), 7.95 (2H,d,H-β, β'), 8.5 (1H,s,H-5), 13.5 (1H,s,-OH).

3h : ($CDCl_3$) : δ 6.05 (4H,s,2xO-CH_2-O), 6.31 (1H,s,H-10), 6.85 (2H,d,H-α, α'), 7.24 (2H,d,H-β, β'), 7.65-8.1 (16H,m,protons of C_3, C_4, & C_7 phenyl groups), 8.91 (1H,s,H-5).

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