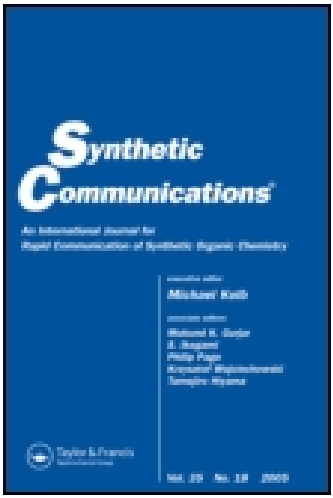

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

A Facile Synthesis of 3,7-Diphenyl-4,8-distyryl-2,6-dioxo-2H,6H-benzo[1,2-b:3,4-b′] Dipyrans and Their Antifeedant Activity.

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Published online: 22 Aug 2006.

To cite this article: P. Sampath Rao , K. Vishnu Vardhan Reddy & K. Venkat Reddy (1997) A Facile Synthesis of 3,7-Diphenyl-4,8-distyryl-2,6-dioxo-2H,6H-benzo[1,2-b:3,4-b′] Dipyrans and Their Antifeedant Activity., Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 27:19, 3361-3369, DOI: 10.1080/00397919708005636

To link to this article: http://dx.doi.org/10.1080/00397919708005636

SYNTHETIC COMMUNICATIONS, 27(19), 3361-3369 (1997)

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

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

Since the first report of the formation of 4,6-diacetyl resorcinol as a major product along with its isomer 2,4-diacetyl resorcinol in a single pot acetylation of resorcinol with $ZnCl_2$ and acetic anhydride[1], this method has been adopted[2-9] to prepare 4,6-diacetyl resorcinol and utilise it in the synthesis of 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 2,4-diacetyl resorcinol has been utilised recently to obtain few angular benzo-γ-dipyrones[10]. Literature survey revealed that synthesis and antifeedant activity of the title compounds have not been reported so for. Therefore in the present investigation the synthesis of some new 3,7-diphenyl-4,8-distyryl-2,6-

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dioxo-2H,6H-benzo[1,2-b:3,4-b'] dipyrans have been taken up with a view to study the effect of angular dicoumarin moiety on their antifeedant activity.

The required starting materials, the dichalcones **(2a-i)** were prepared by the condensation of 2,4-diacetyl resorcinol **(1)** with aromatic aldehydes in the presence of 90% aq KOH and are characterised by comparison with authentic samples[11].

In the present investigation an alternative and more facile approach involving modified Baker Vankatraman transformation[12-14] has been explored. Thus 2,4-dicinnamoyl resorcinol (**2a**, 0.01 mole) and phenyl acetyl chloride (0.02 moles) were dissolved in dry acetone and refluxed with anhydrous K_2CO_3 for 12 hrs. Work up of the reaction mixture followed by column chromatography yielded compound **3a**. Compound **3a** was crystallised from methanol as colourless needles, mp 228°C, $C_{40}H_{26}O_4$, M^+ 570.

The IR spectrum of the product **(3a)** showed absorption at 1710cm^{-1} which is characteristic of corbonyl group of coumarins[15]. The UV absorption data λ_{max}^{MeOH}nm (log ε) : 305 (4.25) are in good agreement with those of 3-phenyl coumarins[16].

The PMR spectrum of **3a** exhibited two AB doublets at δ7.4 (1H, J=9.8 Hz) and 7.88 (1H, J=9.8 Hz) assignable to H-10 and H-9 respectively. The spectrum also revealed two doublets at δ6.68 (J=14 Hz) and δ7.6 (J=14 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 δ6.7 - 7.38 (20H) for the protons of four phenyl groups. The mass spectrum of **3a** showed molecular ion peak at

570 (14%). The prominent fragmentation ions at m/z 542 (15%) (M-CO), 514 (12%) (M-2CO), 105 (40%) (Ph-CO), 91 (100%) (Ph-CH_2) were highly diagnostic[17]. On the basis of the above analytical and spectral data, compound **3a** has been characterised as 3,7-diphenyl-4,8-distyryl-2,6-dioxo-2H,6H-benzo [1,2-b:3,4-b'] dipyran **(3a)**.

Following the above method several substituted 3,7-diphenyl-4,8-distyryl-2,6-dioxo-2H,6H-benzo [1,2-b:3,4-b'] dipyrans **(3a-i)** were synthesised and their analytical and spectral data are given in table. This method is one step reaction. 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.

All the compounds **(3a-i)** were tested for their antifeedant activity by the "Non choice test method"[18] using 6 hours pre-starved fourth instar larvae of spodaptera litura and the results are shown in table. The compound **3e**, **3g,** and **3i** exhibited highest antifeedant activity.

EXPERIMENTAL

Melting points were determined on a polmon melting point apparatus and are uncorrected. Mass spectra were recorded on VG Micromass 7070H spectrometer. ^{1}H-NMR spectra were recorded on a Gemini 200 MHz spectrometer using TMS as an internal standard. IR spectra were recorded on Nicolet 740 FT-IR spectrometer. UV spectra were recorded on a Perkin-Elmer Lambda-15 spectrometer. Column chromatography was carried out using some silica gel. All solvents were dried prior to use.

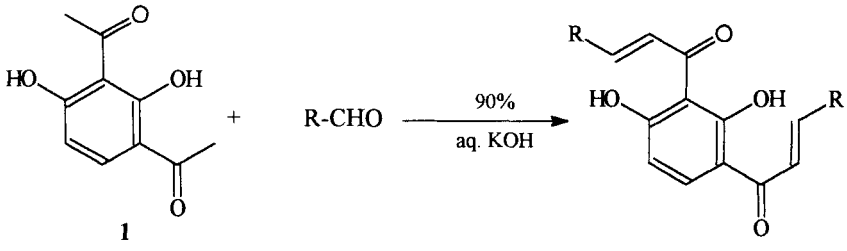
TABLE

Analytical and spectral data of title compounds **(3 a-i)**

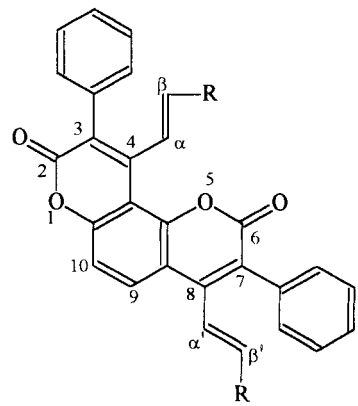
Compd.	Molecular formula	M.P (°C)	M$^+$	IR KBr (>C=O str)	UV(MeOH) nm (log ε)	yield (%)	Antifeedant activity (%)
3a	$C_{40}H_{26}O_4$	228	570	1710	305 (4.25)	80.5	74.31
3b	$C_{42}H_{30}O_6$	178	630	1718	345 (4.78)	77.6	85.68
3c	$C_{40}H_{24}O_4Cl_2$	186	638	1718	320 (4.43)	88.0	83.07
3d	$C_{42}H_{30}O_4$	205	598	1714	325 (4.07)	86.7	72.05
3e	$C_{40}H_{24}O_4Cl_2$	210	638	1718	324 (4.15)	73.5	93.85
3f	$C_{40}H_{26}O_6$	185	602	1720	306 (4.22)	72.0	65.35
3g	$C_{36}H_{22}O_6$	225	550	1720	325 (4.80)	87.5	95.05
3h	$C_{44}H_{34}O_8$	218	690	1718	340 (4.65)	85.0	82.00
3i	$C_{36}H_{22}O_4S_2$	214	582	1720	320 (4.70)	90.0	100.00

All the compounds gave satisfactory elemental analysis.

SCHEME



R = a = Phenyl
b = 4-Methoxyphenyl
c = 2-Chlorophenyl
d = 4-Methylphenyl
e = 4-Chlorophenyl
f = 4-Hydroxyphenyl
g = 2-Furyl
h = 3,4-Dimethoxyphenyl
i = 2-Thienyl



3a-i

Dichalcones (2a-i): General Procedure.

A mixture of **1** (0.01 mole) and appropriate aldehyde (0.02 mole) in ethanol (40ml) and aq KOH (90%, 15ml) was kept at room temperature for 32hrs. The product obtained on dilution and acidification with dil Hcl was subjected to column chromatography over silica gel (200 mesh) Benzene: Chloroform (6:4 v/v) eluates on concentration afforded compound **2**.

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

A solution of dichalcones (**2**, 0.01 mole) and phenyl acetyl chloride (0.02 moles) in dry acetone (200 ml) was refluxed with anhydrous K_2CO_3 (6g) for 12 hrs on a steam bath, the acetone solution was filtered, the K_2CO_3 residue washed with acetone. The combined acetone solution was evoporated and cold water was added to the residue. The separated product was filtered, washed with 2% aq sodium bicorbonate and water. The crude product was subjected to column chromatography over silica gel (200 mesh) Benzene : Chloroform (8:2 v/v), crystallised from methanol to yield **3**.

NMR data of some of the title compounds:

3a : ($CDCl_3$): δ7.4 (1H,d, J=9.8 Hz, H-10), 7.88(1H,d, J=9.8 Hz, H-9), 6.68(2H,d, J=14 Hz, H-α,α'), 7.6 (2H,d, J=14 Hz, H-β,β') and 6.7-7.38 (20 H,m, protons of four phenyl groups)

3b : ($CDCl_3$) δ 3.82 (6H, s, 2 X OCH_3), 7.32 (1H, d, J=8.1 Hz, H-10), 7.78 (1H, d, J = 8.1 Hz H-9) 6.59 (2H, d, H-α,α'), 7.63 (2H, d, H-β,β') 6.72-7.5 (18H, m, protons of phenyl groups).

3c : ($CDCl_3$) δ 7.2 (1H, d, J=9.8 Hz, H-10), 7.83 (1H, d, J=9.8, Hz, H-9) 6.7-7.18 (20H, m, H-α,α', -18 aromatic protons), 7.48 (2H, d, H-β,β')

3d : ($CDCl_3$): δ2.55 (6H, s, 2 X CH_3), 7.53 (1H, d, H-10), 6.88 (2H, d, H-α,α') 7.1-7.5(18H, m, protons of phenyl groups), 7.9 (2H, d, H-β,β'), 7.98 (1H, d, H-9).

3e : ($CDCl_3$): δ 6.72 (2H, d, H-α,α'), 7.3(1H, d, J=7.5 Hz, H-10), 7.35 (2H, d, H-β,β') 7.92 (1H, d, J=7.5 Hz, H-9), δ6.8-7.28 (18H, m, aromatic protons).

3f : ($CDCl_3$) δ 7.30 (1H, d, J=7.5 Hz, H-10), 6.9 (2H, d, H-α,α'), 7.0-7.78 (20H, m, protons of phenyl groups, and β, β' protons) 8.1 (1H, d, J=7.5 Hz, H-9) 12.8 (2H, s, 2 X -OH).

Acknowledgements:

The authors are thankful to Dr (Mrs) Amarjit Kaur and S. Sambamurthy, Department of Zoology, Nizam College, Osmania University, for screening antifeedant activity.

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(Received in the UK 28th January 1997)