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Absorption–Emission Spectra Studies of 3-Hetarylcoumarins†

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SUMMARY

The synthesis of several coumarins substituted with a five-membered heterocyclic ring at the 3-position have been synthesised. The hetaryl rings substituted at the 3-position are the furyl, oxazolyl and the oxadiazolyl systems. The 3-furylcoumarins were prepared by reacting salicylaldehyde derivatives with a furylacetonitrile derivative. The oxazolyl and the oxadiazolyl derivatives were synthesised from coumarin-3-carboxylic acid derivatives by the usual routes. The absorption characteristics of these compounds have been recorded.

1. INTRODUCTION

Several coumarin derivatives with a hetaryl ring at the 3-position have been patented in recent years for use as optical brighteners for textile fibres. However, little information is available concerning the relationship between the nature of the hetaryl ring and the absorption and emission characteristics of derived coumarins.

In the present paper, we describe the synthesis of some coumarins with three types of five-membered hetaryl rings at the 3-position. Accordingly, we have chosen the furyl, the oxazolyl and the oxadiazolyl coumarins for

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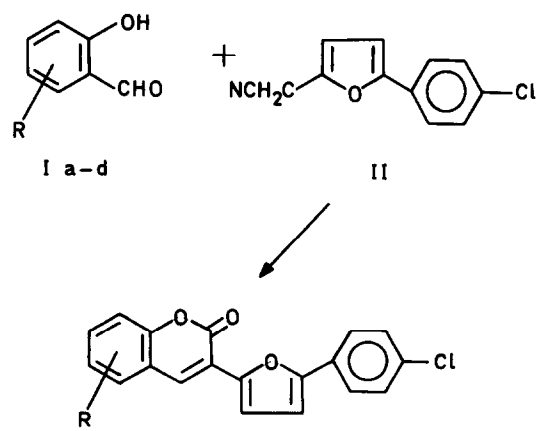
our studies in order to determine the effect of additional nitrogen atoms in the five-membered ring.

2. RESULTS

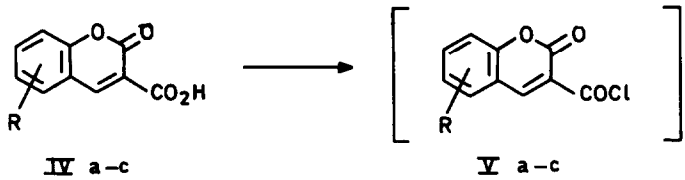
3-(2-Furyl)coumarins (**III**) were synthesised (Scheme 1) by the reaction of the appropriate salicylaldehyde derivatives with 5-(*p*-chlorophenyl)furyl-2-acetonitrile (**II**). The furylacetonitrile (**II**) used in the above was synthesised from 5-(*p*-chlorophenyl)furfuraldehyde by a standard synthetic sequence. The coumarins thus obtained were characterised by elemental analysis and infra-red spectrum. Yields and melting points are shown in Table 1.

3-(2-Oxazolyl)coumarins were synthesised (Scheme 2) by the procedure reported by Davidson.[1] The coumarin-3-carboxylic acid chloride derivatives **V** were then condensed with the benzoin derivatives **VI–VIII** to give the corresponding desyl esters **IX–XI** which were subsequently cyclised by ammonium acetate in acetic acid to the desired oxazolyl coumarins (**XII–XIV**). Yields and melting points of the desyl esters and oxazolylcoumarins are given in Table 3 and 4 respectively.

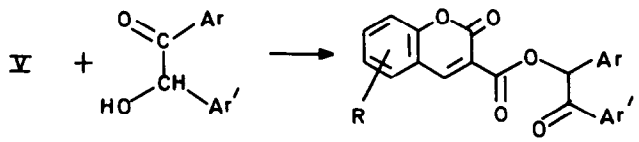
In the literature[2,3] the synthesis of oxadiazolylcoumarins has been



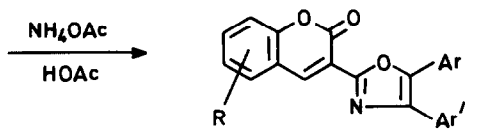
Scheme 1



IV a–c V a–c



VI – VIII IX a–c
X a–c
XI a



XII a–c
XIII a–c
XIV a

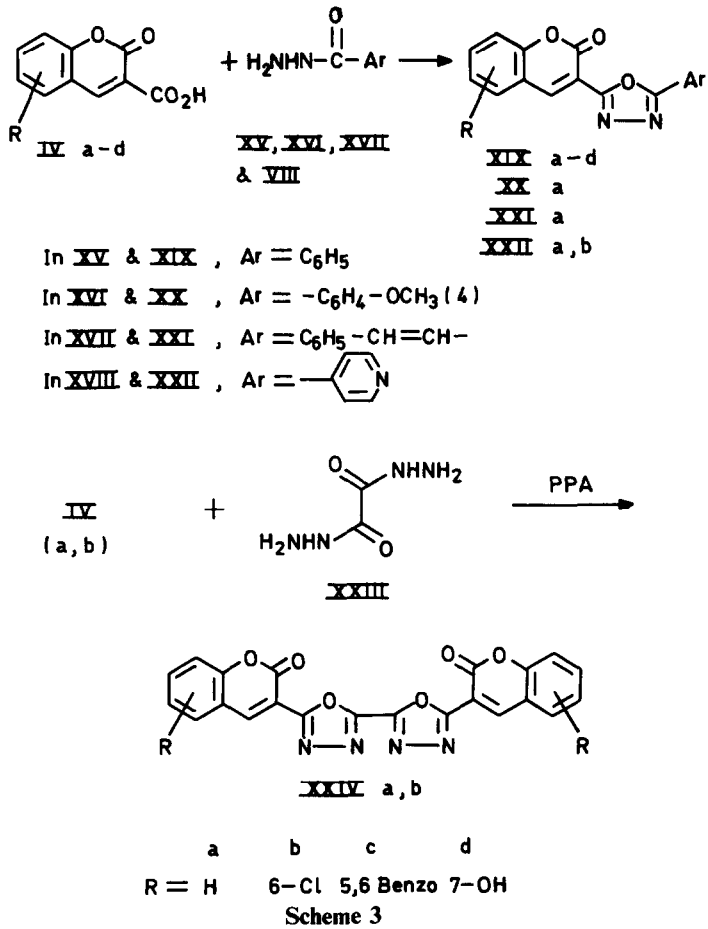
In VI, IX & XII Ar = Ph ; Ar′ = Ph
In VII, X & XIII Ar = Ph ; Ar′ = Ph–NMe_2 (4)
In VIII, XI & XIV Ar = Ph ; Ar′ = Ph–OMe (4)

	a	b	c
R ⇒	H	6–Cl	5,6 Benzo

Scheme 2

effected by a three-step sequence, viz. (a) synthesis of the acid hydrazide, (b) conversion of the acid hydrazide to the diacylhydrazide, (c) cyclisation to the oxadiazole. We found it to be more convenient to synthesise the 3-(2-oxadiazolyl)coumarins by the reaction of coumarin-3-carboxylic acid derivatives with acylhydrazides directly in polyphosphoric acid, under which conditions the desired oxadiazolylcoumarins were obtained in high yields (Scheme 3). Of particular interest in this series were the compounds derived from cinnamic acidhydrazide and oxalic acidhydrazide. Yields and melting points of the compounds thus synthesised are given in Table 6.

The absorption and emission data of the different hetaryl coumarins



Scheme 3

are set out in Tables 2, 5 and 7. The furyl derivatives **III** absorb in the 390 nm region, shifted bathochromically to 412 nm in the case of the derivative **IIIc** containing an additional fused phenyl ring. Introduction of additional hetero nitrogen atoms into the 3-hetaryl residue results in hypsochromic shifts in the absorption maxima, which follow the general order

$$\text{oxadiazolyl} < \text{oxazolyl} < \text{furyl}$$

The fluorescence emission spectra follow a similar order and whilst the furyl and oxazolyl derivatives had a greenish-blue fluorescence, the more acceptable blue to bluish-violet fluorescence required for optical whitening agents was only observed with the oxadiazolyl derivatives.

3. EXPERIMENTAL

All melting points are uncorrected. The UV and visible spectra were recorded on Beckman DK-2 and Unicam SP 8000 spectrophotometers. The IR spectra were recorded on Perkin-Elmer Models 397 and 21 spectrophotometers, and fluoroescence spectra on an Aminco Bawman spectrophotofluorimeter.

Synthesis of 3-[2-(5-*p*-chlorophenyl)furyl]coumarins

5-Chlorosalicylaldehyde,[4] 2-hydroxynaphthaldehyde[5] and resorcylaldehyde[6] were prepared by reported procedures. 5-(*p*-Chlorophenyl)-2-furylacetonitrile (**II**) (m.p. 72–4 °C, AcOH) was prepared from 5-(*p*-chlorophenyl)-2-furfuraldehyde[7] according to a procedure reported for the preparation of 2-furylacetonitrile[8–11] and was characterised by elemental analysis and IR spectrum (—C≡N peak at 2250 cm^{-1}).

An equimolar mixture of salicylaldehyde derivatives (**Ia–d**) and **II** (0·01 mol) was heated in the presence of piperidine (2 ml) in an oil-bath at 140–150 °C for 2 h. After cooling, the solid mass was treated with 1:1 HCl (20 ml) and left overnight. The insoluble solid was dissolved in warm alkali and reprecipitated by dilute acid. The yields, melting points, crystallisation solvents and molecular formulae of the various 3-furylcoumarins are given in Table 1. The absorption–emission data and evaluation data on polyester are given in Table 2.

Synthesis of 3-(2-oxazolyl)coumarin derivatives

p-Dimethylaminobenzoin[12] and *p*-methoxybenzoin[13] were prepared by the known procedures. Coumarin-3-carboxylic acid,[14] 6-chlorocoumarin-3-carboxylic acid (m.p. 199–200 °C, EtOH), 5,6-benzocoumarin-3-carboxylic acid[15] and 7-hydroxycoumarin-3-carboxylic acid[16] were prepared by the alkaline hydrolysis of the corresponding esters.

General method for the synthesis of 3-oxazolylcoumarins
This involves two steps:

(a) *Preparation of desyl esters:* The mixture of coumarin-3-carboxylic acid chloride (from 0·01 mol acid and $SOCl_2$), benzoin derivative (0·01 mol), benzene (20 ml) and pyridine (4 ml) was refluxed for 4–5 h followed by removal of solvent to yield **IX**, **X** and **XI** after

TABLE 1
Physical Data of the 3-Furylcoumarins

Compound	*Yield* (%)	*M.p.* (°C)	*Recrystallisation solvent*	*Mol. formula*[a]
IIIa	80	218	C_6H_6: EtOH (9:1)	$C_{19}H_{11}ClO_3$
IIIb	70	232	C_6H_6: EtOH (9:1)	$C_{19}H_{10}Cl_2O_3$
IIIc	50	257	C_6H_6	$C_{23}H_{13}ClO_3$
IIId	40	280	C_6H_6	$C_{19}H_{11}ClO_3$

[a] Satisfactory elemental analyses were obtained.

TABLE 2
Absorption–Emission Data and Dyeing Evaluation on Polyester of 3-Furylcoumarins

Compound	λ^A_{max} (*nm*)	*log E*	λ^F_{max} (*nm*)	*Pick-up*[a]	*Lightfastness*	*Sublimation fastness*
Standard (Uvitex ERN)	376	4·41	438	4	—	—
IIIA	388	4·53	480	1	1–2	3–4
IIIb	390	4·26	490	1	1–2	3–4
IIIc	412	4·63	500	4	1–2	3–4
IIId	394	4·35	496	—	—	—

[a] Pick-up values: 5, 2 × standard depth; 4, 1 × standard depth; 3, 0·5 × standard depth; 2, 0·33 × standard depth, 1, 0·16 × standard depth.

TABLE 3
Physical Data for the Various Desyl Esters

Compound	*Yield* (%)	*M.p.*[a] (°C)	*Mol. formula*[b]
IXa	83	128	$C_{24}H_{16}O_5$
IXb	80	143	$C_{24}H_{15}ClO_5$
IXc	77	162	$C_{28}H_{18}O_5$
Xa	85	135	$C_{26}H_{21}NO_5$
Xb	81	180	$C_{26}H_{20}ClNO_5$
Xc	80	210	$C_{25}H_{18}O_6$
XIa	70	120	$C_{25}H_{18}O_6$

[a] All compounds were crystallised from EtOH.
[b] Satisfactory elemental analyses were obtained.

TABLE 4
Physical Data for the Various Oxazole Derivatives

Compound	*Yield* (%)	*M.p.* (°C)	*Recrystallisation solvent*	*Mol. formula*[a]
XIIa	60	200	EtOH	$C_{24}H_{18}NO_3$
XIIb	56	194	EtOH	$C_{24}H_{14}ClNO_3$
XIIc	50	237	EtOH	$C_{28}H_{17}NO_3$
XIIIa	62	218	EtOH	$C_{26}H_{20}N_2O_3$
XIIIb	60	205	C_6H_6	$C_{26}H_{19}ClN_2O_3$
XIIIc	60	195	EtOH:C_6H_6 (1:1)	$C_{30}H_{22}N_2O_3$
XIVa	40	190	EtOH	$C_{25}H_{10}NO_4$

[a] Satisfactory elemental analyses were obtained.

adding to water. The yields, melting points, crystallisation solvents and molecular formulae of the desyl esters are given in Table 3.

(b) *Cyclisation of the desyl esters:* A mixture of the crude desyl ester (0·05 mol), ammonium acetate (2 mol), and glacial HOAc (20 ml) was refluxed for 2 h, cooled and added to ice-water to yield the 3-(oxazolyl)coumarin.

TABLE 5
Absorption–Emission Data and Dyeing Evaluation on Polyester for Oxazole Derivatives

Compound	λ^A_{max} (*nm*)	*log E*	λ^F_{max} (*nm*)	*Pick-up*[a]	*Lightfastness*	*Sublimation fastness*
XIIa	374	4·18	510	1	1–2	4–5
XIIb	380	4·18	518	1	3	4–5
XIIc	358	4·31	440	0		Yellowish[b]
XIIIa	412 315	4·40	480	1	2	4–5
XIIIb	408 325	4·40	518	2	2	4–5
XIIIc	410 300	4·30	—	2	2	4–5
XIVa	395	3·87	516	2	2	4–5

[a] Pick-up values: see footnote, Table 2.
[b] Compound **XIIc** readily underwent yellowing on heat treatment.

The yields, melting points, crystallisation solvents and molecular formulae of the various 3-oxazolyl coumarins thus obtained are shown in Table 4. Absorption–emission and evaluation data on polyester are given in Table 5.

Synthesis of 3-(oxadiazolyl)coumarins

Benzhydrazide, *p*-anisic acid hydrazide, cinnamic acid hydrazide and oxalic acid hydrazide were prepared by reported procedures. Commercially available isonicotinic acid hydrazide, m.p. 162–3 °C was used directly.

General procedure for the preparation of 3-oxadiazolylcoumarins
An equimolar mixture of coumarin-3-carboxylic acid (**IVa–d**, 2 g) and the appropriate acid hydrazide (in case of bishydrazides, two moles of carboxylic acid derivative were used) was added to polyphosphoric acid (from 14 g P_2O_5 and 7 g H_3PO_4) at 120 °C under stirring. The reaction mixture was further maintained at 180–5 °C for 30 min and after the usual work-up yielded the various oxadiazoles. The yields, melting points, crystallisation solvents and molecular formulae of various oxadiazolyl coumarins are given in Table 6. The absorption–emission and evaluation data on polyester are listed in Table 7.

TABLE 6
Physical Data of the Various Oxadiazole Derivatives

Compound	*Yield* (%)	*M.p.* (°C)	*Recrystallisation solvent*	*Mol. formula*[a]
XIXa	92	220	EtOH	$C_{17}H_{10}N_2O_3$
XIXb	89	256	EtOH	$C_{17}H_{19}ClN_2O_3$
XIXc	20	204	C_6H_6	$C_{21}H_{12}N_2O_3$
XIXd	75	280	C_6H_6	$C_{17}H_{10}N_2O_4$
XXa	85	280	EtOH	$C_{18}H_{12}N_2O_4$
XXIa	75	280	EtOH	$C_{19}H_{12}N_2O_3$
XXIIa	90	260	EtOH	$C_{16}H_9N_3O_3$
XXIIb	86	280	EtOH	$C_{16}H_{10}N_4O_6$
XXIVa	75	280	DMF:MeOH (1:1)	$C_{22}H_{10}N_4O_6$
XXIVb	72	280	DMF:MeOH	$C_{22}H_8Cl_2N_4O_6$

[a] Satisfactory elemental analyses were obtained.

TABLE 7
Absorption–Emission Data and Dyeing Evaluation on Polyester of Oxadiazole Derivatives

Compound	λ^{A}_{max} (*nm*)	*log E*	λ^{F}_{max} (*nm*)	*Grade*[a]
XIXa	358	4·31	434	1–2
XIXb	362	4·25	438	1–2
XIXc	393	4·46	458	0 (Yellowish)
XIXd	384	4·12	440	0 (Yellowish)
XXa	360	4·35	432	1–2
XXIa	364	4·27	432	1–2
XXIIa	342	4·3	432	1
XXIIb	352	4·23	434	1
XXIVa	359	4·51	438	1–2
XXIVb	364	4·44	436	1–2

[a] The grading shown refers to the whitening effect produced on polyester fibre with respect to Uvitex ERN (grade 3) as reference.

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