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Synthesis of Some New Coumarins as Potential Laser Dyes in the Blue–Green Region. Part 2: Synthesis of 1,1,7,7-Tetramethyl-2,3,6,7-Tetrahydro-1H,5H,11H-[1]-Benzopyrano[6,7,8-*i*,*j*]Quinolizine-10-Phenyl-11-Ones

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ABSTRACT

The title compounds have been synthesized by two different routes starting from 1,1,7,7-tetraalkyl-8-hydroxyjulolidine. In the first method this compound was condensed with phenyl and substituted phenyl acetic acids in the presence of PPA using a modified Nencki's reaction to give the corresponding phenolic esters, which on formylation with $POCl_3$–dimethylformamide yielded the respective coumarins, through the intermediate aromatic aldehydes formed in situ, *in an overall yield of 52%. In the second method, the hydroxyjulolidine was condensed with α-formylphenylacetic esters by refluxing with $ZnCl_2$ in ethanol to yield the same coumarins, but in lower yield (24%). The new coumarins were found to be good laser dyes in the blue–green region*

1 INTRODUCTION

Coumarins in general are good laser dyes in the blue–green region.[1] The presence of a hydroxy or amino group at the 7-position has been found to be necessary for the merocyanine chromophore to exhibit lasing action.[2] Replacement of the two amino hydrogens by various alkyl groups has been reported to increase their lasing efficiency.[3] Introduction of a phenyl group at the 3-position has also been found to increase the

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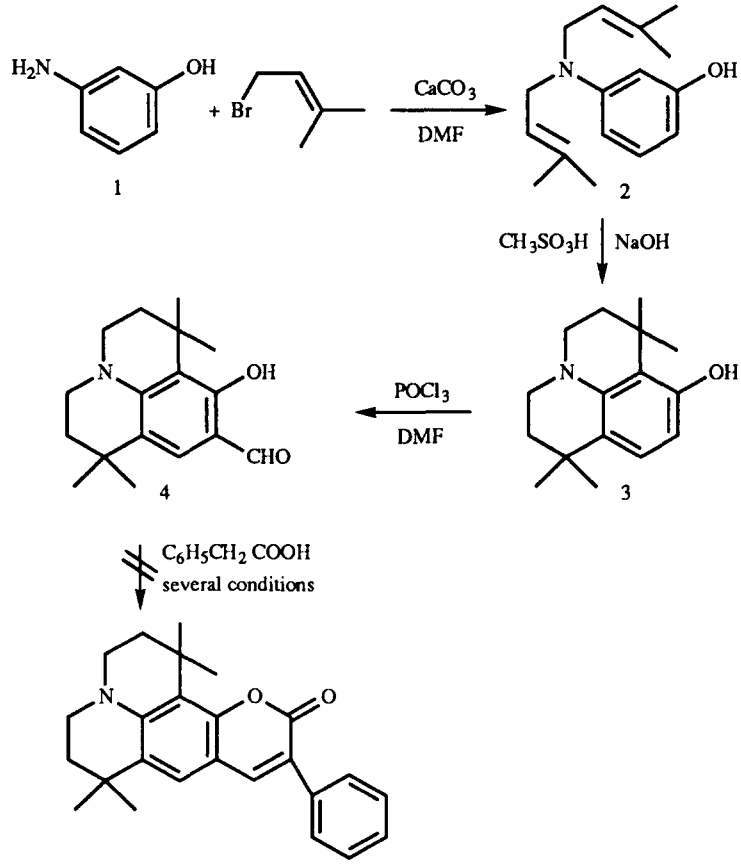
lasing efficiency and a number of 7-*N*,*N*-diallylamino-3-phenylcoumarins have been synthesized and their lasing action reported.[4]

Annulation of the *N*-alkyl groups, restricting the C—N rotation, has been found to improve the lasing efficiency of coumarin dyes[5] by reducing the non-radiative decay. Some coumarins have been synthesized starting from 8-hydroxyjulolidine and their lasing action studied.[6,7] A few coumarin derivatives starting from 1,1,7,7-tetraalkyl-8-hydroxyjulolidine with different substituents at position 3 or 4 have also been prepared[8] and their lasing action studied.[9] This substitution at the 1,1,7,7-position of julolidine removes sites of potential photo-oxidation, an effect that could play a role in the improved lasing efficiency and photostability for this class of dyes.[10] We describe here the synthesis and characterization of some tetraalkyl coumarin derivatives containing a phenyl or substituted phenyl group at the 3-position, and study their lasing action. Absorption and emission data will be reported later.



Scheme 1

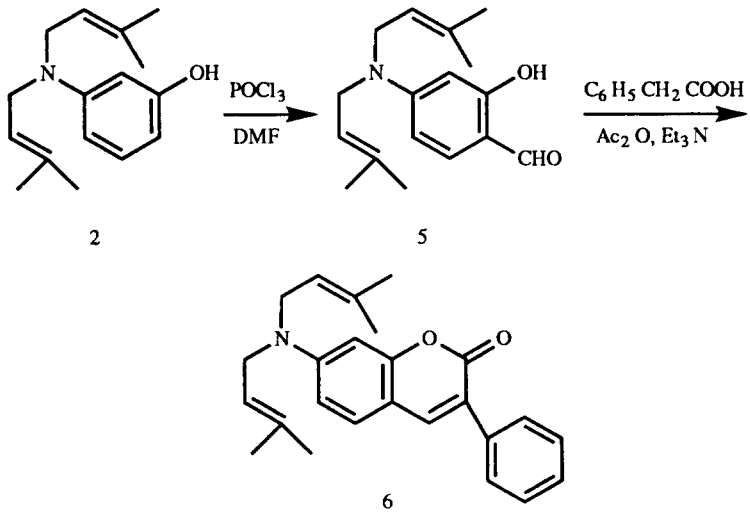
2 RESULTS AND DISCUSSION

The initially attempted synthesis of the compounds used 3-amino-phenol as starting material (**1**) (Scheme 1). This was prenylated with prenyl bromide at 85°C in DMF in the presence of $CaCO_3$ to furnish 3-*N*,*N*-diprenylaminophenyl (**2**) in a yield of 44%.[8] Subsequent heating with methane sulfonic acid at 100°C gave 8-hydroxy-1,1,7,7-tetramethyljulolidine (**3**) in a yield of 50%.[8] This was then formylated with phosphorus oxychloride in dimethylformamide under Vilsmeier–Haack conditions to give 9-formyl-8-hydroxy-1,1,7,7-tetramethyljulolidine in 80% yield.[8] The next stage involved condensation of this *o*-hydroxyaldehyde with phenyl-acetic acid or its derivatives under various conditions reported in the literature. Surprisingly, none of the procedures listed below gave the desired product from the condensation of **4** with phenylacetic acid:

1. heating in pyridine in the presence of piperidine at 160° for 40 h;[11]
2. heating in the presence of sodium acetate in methanol for 20 h;[12]
3. heating with sodium phenylacetate and acetic anhydride at 160°C for 40h;[11]
4. refluxing with benzyl cyanide in ethanol in the presence of piperidine;[11]
5. heating with phenylacetic anhydride in the presence of sodium phenylacetate and acetic anhydride at 180°C for 20 h;[13]
6. refluxing with methylphenylacetate in ethanol in the presence of piperidine;[11]
7. refluxing with phenylacetyl chloride in acetone in the presence of potassium carbonate;[14]
8. refluxing with *N*,*N*-diethylphenylacetamide in the presence of phosphorus oxychloride in chloroform.[15]
9. condensation of the aldehyde under phase transfer conditions using phenylacetyl chloride, TBA HSO_4, dichloromethane, 20% aq. K_2CO_3[16] and phenylacetic anhydride, BTEA, benzene and K_2CO_3[17].

The highly unreactive nature of the aldehyde group in this julolidine derivative might be explained in terms of the decreased positive charge on the aldehyde carbonyl carbon due to the electron donating mesomeric influence of the lone pair electrons of the nitrogen at the *para* position.

In an alternative approach (Scheme 2), an attempt was made to synthesize the α-pyrone ring in the first instance, and defer the annulation of the *N*-prenyl groups to the final step, on the basis that the mesomeric influence of the freely rotating *N*,*N*-diprenyl group may be comparably



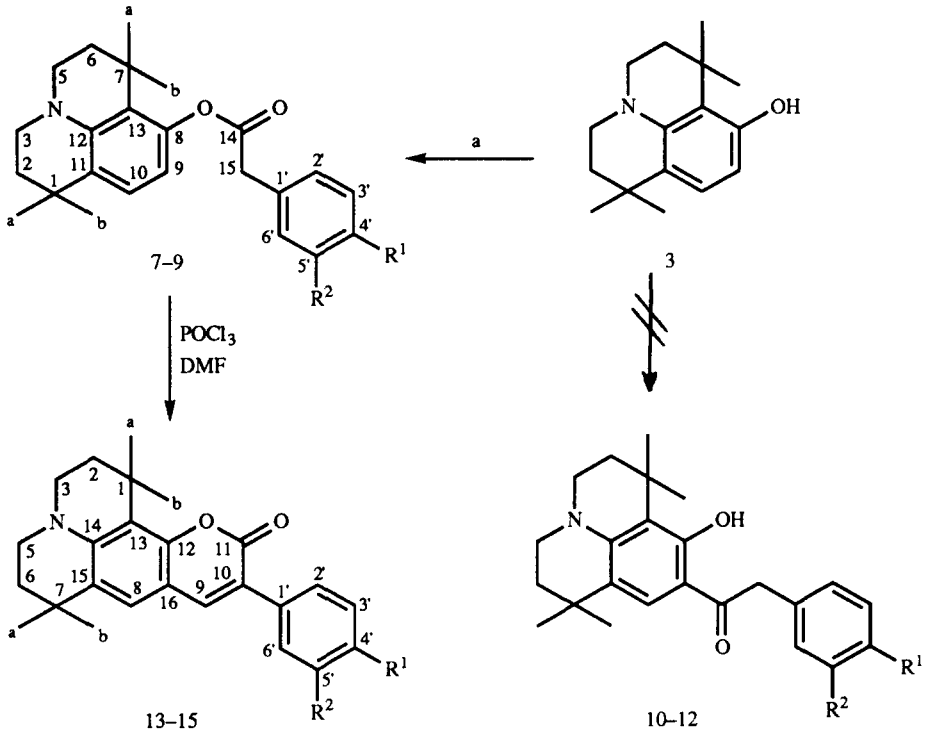
2 5 6

Scheme 2

smaller. 3-Bisprenylaminophenol was formylated with $POCl_3$ in dimethylformamide to give the corresponding aldehyde (**5**) but in very poor yield (5%).[8] Compound **5** was then condensed with phenylacetic acid in the presence of acetic anhydride and triethylamine,[18] to give 7-*N*,*N*-diprenylamino-3-phenylcoumarin (**6**) in 40% yield.

This new coumarin was fluorescent in organic solvents; the coumarin carbonyl was observed at 1710 cm^{-1} in the IR spectrum[19] and the H-4 proton as a singlet at δ 7·7 in the ^1H NMR spectrum.[20] Although this method of synthesis demonstrated increased reactivity of the aldehyde group and yielded the coumarin derivative in moderate yield (40%), the very poor yield (5%) in the earlier formylation step discouraged the adoption of this method for the general synthesis of the desired coumarins.

In a further attempt, esterification of tetralkyl-*o*-hydroxyjulolidine (**3**) was attempted using phenylacetyl chloride, in the presence of pyridine,[21] in the presence of NaH in DMF[22] and in the presence of K_2CO_3 in acetone,[23] but all these methods failed to yield the ester, as did esterification with phenylacetic anhydride or phenylacetyl chloride in the presence of boron trifluoride etherate, indicating some steric crowding factors at the alkyl groups. A modified Nencki's reaction using phenylacetic acid and polyphosphoric acid as a Lewis acid on phenolic compounds has recently been reported to give the deoxybenzoins in very good yields (over 80%).[24] Extending this reaction to 8-hydroxyjulolidine (**3**), condensation with phenylacetic acid in the presence of PPA at 45°C (Scheme 3) resulted in a product in 80% yield. The product exhibited carbonyl absorption at



Compounds	R^1	R^2	
7, 10, 13	H	H	a (i) $C_6H_5CH_2COOH$, PPA
8, 11, 14	MeO	H	(ii) 4-MeO $C_6H_4CH_2COOH$, PPA
9, 12, 15	MeO	MeO	(iii) 3,4-$(MeO)_2C_6H_3CH_2COOH$, PPA

Scheme 3

1740 cm^{-1} suggesting an ester nature rather than an aromatic ketone. The ^1H NMR spectrum showed a pair of *ortho* coupled aromatic protons at δ 6·2 and 7·0 (J = 9 Hz) as in 8-hydroxyjulolidine, indicating no further substitution in the aromatic ring and that the product was a phenolic ester. This was supported by the presence of ester carbonyl carbon at δ 170·029 in the ^{13}C NMR spectrum.[25]

In view of this result other ester derivatives were similarly prepared, giving yields of 74% and 68% respectively, with 4-methoxyphenylacetic acid and 3,4-dimethoxyphenylacetic acid. The structures of all three new esters were characterized by their IR (Table 1), ^1H NMR (Table 2), ^{13}C NMR (Table 3) and mass spectral data.

The phenylacetate of 8-hydroxyjulolidine (**7**) was then formylated by

TABLE 1
Physical and Analytical Data of Esters **7–9**

Compound	*M.p.*	*Yield (%)*	R_f[a]	*UV* (λ_{max}^{EtOH}, *nm*)	*IR* ($\nu_{max}^{CHCl_3}$, cm^{-1})
1,1,7,7-Tetramethyljulolidine-8-phenylacetate (**7**)	139°	80	0·70	311·5, 270·1, 229, 215	3520, 1740, 1600, 1360, 1320
1,1,7,7-Tetramethyljulolidine-8-(4'-methoxyphenyl)-acetate (**8**)	128°	74	0·57	317·2, 273·1, 236·6, 215·4	3760, 3440, 1760, 1600, 1385
1,1,7,7-Tetramethyljulolidine-8-(3',4'-dimethoxy-phenyl)acetate (**8**)	142°	68	0·33	316·7, 273·9, 235·5	3680, 3010, 1750, 1600, 1380

[a] Ratio EtOAc : C_6H_{14} = 1 : 9.

heating with phosphorus oxychloride in DMF at 75°C and underwent cyclisation *in situ* to give a product which was found to be the desired coumarin drivative. It was characterized by its colour reaction, a coumarin carbonyl absorption at 1710 cm^{-1} in its IR spectrum,[19] a typical H-4 proton signal as a singlet at δ 7·8 in its ^{1}H NMR spectrum,[20] and the diagnostic carbon signals, carbonyl carbon at δ 161—139 and the olefinic

TABLE 2
^{1}H NMR Data of Esters **7–9**[a]

Proton no.	*Chemical shifts*		
	7	***8***	***9***
1 a,b and 7 a,b	1·2 (s)	1·2 (s)	1·2 (s)
2 and 6	1·7 (d/d, J = 12 & 7 Hz)	1·7 (d/d, J = 12 & 7 Hz)	1·7 (d/d, J = 12 & 7 Hz)
3 and 5	3·1 (d/d, J = 12 & 7 Hz)	3·1 (d/d, J = 12 & 7 Hz)	3·1 (d/d, J = 12 & 7 Hz)
9	6·2 (d, J = 9 Hz)	6·2 (d, J = 9 Hz)	6·2 (d, J = 9 Hz)
10	7·0 (d, J = 9 Hz)	6·9 (d, J = 9 Hz)	6·95 (d, J = 9 Hz)
11	3·9 (2)	3·8 (s)	3·75 (s)
Aromatic protons	7·4 (br s, 5H)	—	6·9 (m 3H)
3' and 5'	—	6·95 (d, J = 9 Hz)	—
2' and 6'	—	7·3 (d, J = 9 Hz)	—
OMe	—	3·8 (s, 3H)	3·85 (s, 3H)
OMe	—	—	3·85 (s, 3H)

[a] δ $CDCl_3$, TMS.

TABLE 3
^{13}C NMR Data of Esters **7–9** and **3**[a]

Carbon no.	*Chemical shifts*			
	7	*8*	*9*	*3*
1 ab	31·774	31·740	31·774	32·192
1	32·401	32·307	32·401	32·341
2	40·158	40·094	40·158	40·635
3	47·461	47·404	47·461	47·676
5	46·901	46·837	46·871	47·318
6	37·058	36·991	37·055	37·473
7	32·102	32·039	32·102	32·341
7 ab	29·626	29·592	29·656	29·179
8	148·339	148·276	149·115	153·153
9	110·926	110·922	110·926	105·228
10	121·726	121·555	121·816	124·829
11	124·680	124·617	124·680	124·084
12	143·178	143·084	143·118	143·566
13	121·428	121·394	121·398	116·684
14	170·029	170·264	170·268	
15	42·276	41·288	41·769	
1'	133·362	125·392	125·874	
2'	128·612	130·494	112·836	
3'	129·394	114·025	148·339	
4'	129·543	158·807	148·399	
5'	128·612	114·025	111·463	
6'	129·394	128·256	128·350	
OMe	—	55·161	55·941	
OMe	—	—	55·881	

[a] δ $CDCl_3$, TMS.

carbons at δ 141·328 and 109·738 in its ^{13}C NMR spectrum[26,27] (Tables 4–6). The structure of the coumarin formed could thus be established as 1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1H,5H,11H-[1]-benzopyrano[6,7,8-*i,j*]-quinolizine-10-phenyl-11-one (**13**).

The above condensation was repeated with 4-methoxyphenylacetic ester (**8**) and 3,4-dimethoxyphenylacetic ester (**9**) and the products isolated after 7 h were found to be the corresponding coumarins (**14** and **15**), characterization for which are shown in Tables 4–6.

The mass spectral fragmentations of the three coumarins supported their structures. All three compounds exhibited prominent molecular ions, together with a number of ions of low intensity due to extensive fragmentation. The usual ions formed by successive loss of alkyl groups preceded the fragmentation of the α-pyrone system, showing that the

TABLE 4
Physical and Analytical Data of Coumarins **13–15**

Compound	*M.p.*	*Yield (%)*	*Molecular formula*	*UV (λ_{max}^{EtOH}, nm)*	*IR ($\nu_{max}^{CHCl_3}$, cm^{-1})*
1,1,7,7-Tetramethyl-2,3,6,7-tetrahydro-1H, 5H,11H-[1]-benzopyrano-[6,7,8-*i,j*]-quinolizine-10-phenyl-11-one (**13**)	198°	65	$C_{25}H_{27}NO_2$	420·8, 339·7, 285, 224	2900, 1710, 1600, 1380
1,1,7,7-Tetramethyl-2,3,6,7-tetrahydro-1H, 5H,11H-[1]-benzopyrano-[6,7,8-*i,j*]-quinolizine-10-(4'-methoxyphenyl)-11-one (**14**)	162°	66	$C_{26}H_{29}NO_3$	424·9, 291·5, 225·8	2880, 1710, 1600, 1380
1,1,7,7-Tetramethyl-2,3,6,7-tetrahydro-1H, 5H,11H-[1]-benzopyrano-[6,7,8-*i,j*]-quinolizine-10-(3',4'-dimethoxyphenyl)-11-one (**15**)	175°	64	$C_{27}H_{31}NO_4$	426·2, 282·5, 222·4	2940, 1720, 1610, 1385

TABLE 5
^{1}H NMR Data of Coumarins **13–15**[a]

Proton no.	*Chemical shifts*		
	13	***14***	***15***
1 a,b	1·3 (s)	1·3 (s)	1·3 (s)
2 and 6	1·8 (d/d, J = 12 & 7 Hz)	1·8 (d/, J = 12 & 7 Hz)	1·8 (d/, J = 12 & 7 Hz)
3 and 5	3·3 (d/d, J = 12 & 7 Hz)	3·25 (d/d, J = 12 & 7 Hz)	3·35 (d/d, J = 12 & 7 Hz)
7 a,b	1·6 (s)	1·6 (s)	1·6 (s)
8	7·15 (s)	7·1 (s)	7·15 (s)
9	7·8 (s)	7·65 (s)	7·65 (s)
Aromatic protons	7·5 (m, 5H)	—	7·3 (m 3H)
3' and 5'	—	6·9 (d, J = 9 Hz)	—
2' and 6'	—	7·6 (d, J = 9 Hz)	—
OMe	—	3·85 (s, 3H)	3·9 (s, 3H)
OMe	—	—	3·9 (s, 3H)

[a] δ $CDCl_3$, TMS.

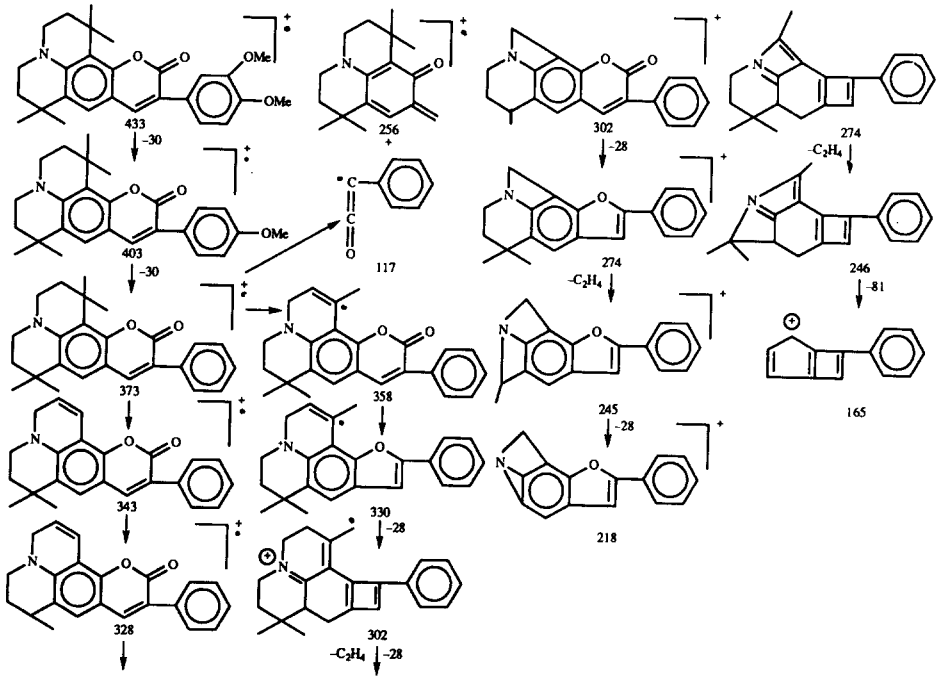


Fig. 1. Typical fragmentation pattern.

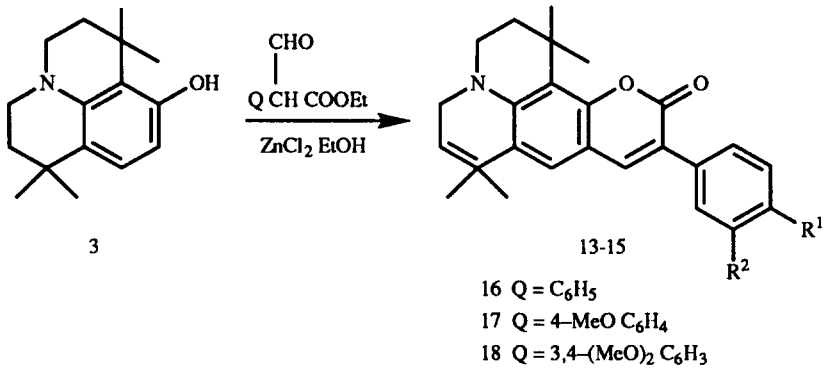
TABLE 6
^{13}C NMR Data of Coumarins **13–15**[a]

Carbon no.	*Chemical shifts*			
	13	***14***	***15***	***3***
1 a,b	29·000	29·000	29·626	29·179
1	32·162	32·102	32·192	32·341
2	35·862	35·862	35·921	37·473
3	46·841	46·741	46·871	47·318
5	47·259	47·169	47·228	47·676
6	39·472	39·472	39·531	40·635
7	32·222	32·162	32·520	32·341
7 a,b	30·730	30·760	30·790	32·192
8	127·365	128·201	128·499	124·829
9	141·328	140·135	140·373	
10	109·738	109·793	109·822	
11	161·139	161·228	161·347	
12	152·457	152·153	152·218	153·153
13	114·924	114·505	114·954	116·684
14	145·207	144·908	145·028	143·566
15	123·487	123·808	123·785	124·084
16	119·578	119·191	119·220	105·228
1'	136·018	128·380	137·501	
2'	128·171	129·213	113·492	
3'	128·171	113·641	148·697	
4'	128·171	159·080	148·697	
5'	128·111	113·641	113·492	
6'	128·111	129·213	128·287	
OMe	—	55·165	56·149	
OMe	—	—	55·941	

[a] δ $CDCl_3$, TMS.

energy is localized on the nitrogen rather than on the oxygen of the pyrone unit. The loss of one or both of the methoxyls as formalin units was also evident and all three coumarins gave a common ion at *m/z* 165. A typical fragmentation of one derivative is shown in Fig. 1.

The coumarins **13–15** were also obtained by a different approach, as shown in Scheme 4, by condensing 8-hydroxyjulolidine (**3**) with pre-formylated phenylacetic esters (**16–18**) in an overall yield of 24%, as a result of poor yield (less than 40%) at the formylation step. While this method involved the formylation of an active methylene group, the earlier method involved formylation at the more reactive position *ortho* to a phenolic group and subsequent cyclisation in situ to give the coumarins **13–15** in higher yields (52%).



Scheme 4

3 EXPERIMENTAL

3.1 General

Melting points were determined on a VEB Analitica Dreader HMK hot plate, and are uncorrected. IR spectra were recorded on a Perkin-Elmer 841 IR spectrophotometer in $CHCl_3$. ^1H NMR spectra were recorded either on a Perkin-Elmer R-32 (90 MHz) or a JEOL-JNM EX-90 (90 MHz) NMR spectrophotometer using $CDCl_3$ as solvent and TMS as internal standard. ^{13}C NMR spectra were recorded on a JEOL-JNM EX-90 (25 MHz) spectrophotometer. Mass spectra were run on a JEOL JMS-300 mass spectrometer, and purity of the compounds was assessed using a Schimadzu-6A HPLC instrument with a shim-pack CLC-ODS (0·15 × 6·0∅) column with 1 : 1 acetonitrile : methanol as the mobile phase and a flow rate of 1 ml min^{-1} using a UV detector.

3.2 Synthesis of compounds 2–4 and 16–18

Compounds **2–4**[8] and ethyl α-formylphenylacetates (**16–18**)[28] were prepared using procedures described in the literature; relevant characterization data are given below for compounds **2–4.**

*3.2.1 3-[*N,N-*Bis(3-methyl-2-buten-1-yl)]aminophenol (3-*N,N-*diprenylaminophenol) (2)*

Crystallized from ethyl acetate as light brown crystals (44%), m.p. 168°C. R_f = 0·5 (1 : 4 EtOAc : C_6H_{14}). ^1H NMR 1·6 (br s, 12H, 4 × —CH_3), 3·7 (br s, 4H, 2 × —NCH_2—), 5·1 (br s, 2H, 2 × =CH), 6·1 (br s, 3H, C_2—H, C_4—H and C_6—H), 6·85 (t, 1H, C_5—H, J = 6 Hz) nm. IR 3600, 3010, 1600, 1460 cm^{-1}.

3.2.2 8-Hydroxy-1,1,7,7-tetramethyljulolidine (3)
Crystallized from ethyl acetate–hexane as colourless solid (50%), m.p. 158°C. R_f = 0·8 (1 : 9 EtOAc : C_6H_{14}). ^{1}H NMR 1·25 (s, 6H, 2 × —CH_3), 1·4 (s, 6H, 2 × —CH_3), 1·8 (d/d, 4H, 2 × —CH_2—, J = 12 and 7 Hz), 3 (d/d, 4H, 2 × —NCH_2, J = 12 and 7 Hz), 6 (d, 1H, C_9—H, J = 8 Hz), 6·9 (d, 1H, C_{10}—H, J = 8 Hz), nm. IR 3600, 1600, 1385 cm^{-1}.

3.2.3 9-Formyl-8-hydroxy-1,1,7,7-tetramethyljulolidine (4)
Crystallized from EtOAc–hexane as pale blue solid (80%), m.p. 75°C. R_f = 0·9 (1 : 9 EtOAc : C_6H_{14}). ^{1}H NMR 1·3 (s, 6H, 2 × —CH_3), 1·5 (s, 6H, 2 × —CH_3), 1·75 (br s, 4H, 2 × —CH_2), 3·3 (d/d, 4H, 2 × —NCH_2, J = 12 and 7 Hz), 7·1 (s, 1H, C_{10}—H), 9·4 (s, 1H, —CHO), 12·0 (s, 1H, —OH) nm. IR 3077, 2825, 1660, 1600, 1380 cm^{-1}.

3.3 4-*N*,*N*-Diprenylamino-2-hydroxybenzaldehyde (5)

Phosphorus oxychloride (3·5 ml, 37·5 mmol) was added to *N*,*N*-dimethylformamide (10 ml) cooled in an ice bath. The pale yellow solution was stirred at room temperature for 1 h, 3-*N*,*N*-diprenylaminophenol (**2**, 5·8 g, 23·5 mmol) added and the mixture heated at 65°C for 1 h. The mixture was cooled, poured into water and extracted with chloroform (5 × 20 ml). After drying ($MgSO_4$) and evaporating the solvent, the residual dark green mass was purified by column chromatography on silica gel using 0·5% ethyl acetate–hexane as eluant to yield 4-*N*,*N*-diprenylamino-2-hydroxybenzaldehyde (**5**) as an oil (0·32 g, 5%). R_f = 0·9 (1 : 9 EtOAc : C_6H_{14}). ^{1}H NMR 1·7 (br s, 12H, 4 × —CH_3), 3·85 (br s, 4H, 2 × —$NC\underline{H}_2$), 5·1 (br s, 2H, 2 × =C<u>H</u>), 5·9 (s, 1H, C_3—H), 6·15 (dd, 1H, C_5—H, J = 9 and 1 Hz), 7·05 (d, C_6—H, J = 9 Hz), 9·4 (s, 1H, —CHO), 11·2 (s, 1H, OH) nm. IR 3100, 2810, 1660, 1600, 1530, 1440 cm^{-1}.

3.4 7-*N*,*N*-Diprenylamino-3-phenylcoumarin (6)

A mixture of 4-*N*,*N*-diprenylamino-2-hydroxybenzaldehyde (**5**, 0·32 g, 0·001 mol), phenylacetic acid (0·1496 g, 0·001 mol) acetic anhydride (2 ml) and triethylamine (0·75 ml) was heated at 160°C for 24 h. The reaction mixture was cooled, poured onto crushed ice and extracted with chloroform (10 × 15 ml). The chloroform extracted was washed with water, dried ($MgSO_4$), and the solvent distilled off. The resulting mixture was purified by column chromatography over silica gel, using 1% EtOAc–hexane as eluant, to yield 7-*N*,*N*-diprenylamino-3-phenylcoumarin (0·117 g, 40%), which was crystallized from chloroform–hexane, m.p. 75°C. R_f = 0·6 (1 : 9 EtOAc : C_6H_{14}). ^{1}H NMR 1·8 (s, 12H, 4 × —CH_3), 3·95 (m, 4H,

2 × —NCH_2), 5·25 (m, 2H, 2 × =CH), 6·6 (s, 1H, C_8—H), 6·7 (d, 1H, C_5—H, J = 9 Hz), 7·3 (s, 1H, C_6—H), 7·4 (br, s, 5H, 5Ar.—H), 7·7 (s, 1H, C_4—H) nm. IR 2900, 1710, 1610, 1520, 1400, 1370, 1200 cm^{-1}. HPLC (R_t) 5·387, percentage purity 93·6%, mobile phase acetonitrile, flow rate 1 ml/min^{-1}, detector UV (406 nm).

3.5 Condensation of 8-hydroxy-1,1,7,7-tetramethyljulolidine with (un)substituted phenylacetic acids–general procedure for esterification

A mixture of 8-hydroxy-1,1,7,7-tetramethyljulolidine (0·5 mmol), (un)-substituted phenylacetic acid (0·5 mmol) and polyphosphoric acid (PPA, 14 ml) was stirred at 45°C for 20 h. The resulting dark mass was poured into ice cold water (100 ml) and stirred well to yield a light brown precipitate which was filtered, purified by column chromatography and crystallized from chloroform–hexane as a colourless solid.

Using this process, 8-hydroxy-1,1,7,7-tetramethyljulolidine was condensed with phenylacetic acid, 4-methoxyphenylacetic acid and 3,4-dimethoxyphenylacetic acid to yield the respective phenylacetates **7–9** in 80–68% yield.

3.5.1 1,1,7,7-Tetramethyljulolidine-8-phenylacetate (7)
Crystallized from chloroform–hexane as colourless needles (80%), m.p. 139°C. R_f = 0·7 (1 : 9 EtOAc : C_6H_{14}). MS *m/z* (rel. int.) 363 (100), 348 (31), 273 (18), 214 (88), 160 (51), 77 (20).

3.5.2 1,1,7,7-Tetramethyljulolidine-8-(4'-methoxyphenyl)acetate (8)
Crystallized from chloroform–hexane as colourless needles (74%), m.p. 128°C. R_f = 0·57 (1 : 9 EtOAc : C_6H_{14}). MS *m/z* (rel. int.) 393 (100), 363 (68), 245 (83), 214 (44), 174 (24), 77 (10).

3.5.3 1,1,7,7-Tetramethyljulolidine-8-(3',4'-dimethoxyphenyl)acetate (9)
Crystallized from chloroform–hexane as colourless needles (68%), m.p. 142°C. R_f = 0·33 (1 : 9 EtOAc : C_6H_{14}). MS *m/z* (rel. int.) 423 (100), 393 (4), 363 (49), 245 (58), 214 (29), 174 (28), 151 (25), 146 (40), 77 (50).

3.6 Formation of coumarins (13–15) from esters (7–9)–general procedure

Vilsmeier–Haack reagent was prepared by the dropwise addition of phosphorus oxychloride (0·015 mol) to DMF (0·02 mol) cooled to 0·5°C and maintained at 0–5°C during the addition. The reagent was stirred at room temperature for 1 h and then the ester (0·005 mol) was added over 15 min. The mixture was then stirred at 75°C for 7 h and the resulting dark

greenish red mass poured into ice cold water. The solid was filtered, purified by column chromatography and the resulting coumarins crystallized from $CHCl_3$–hexane (64–66% yields). These were further purified by HPLC, on a shim-pack CLC-ODS column with 1 : 1 acetonitrile : methanol as the mobile phase with a flow rate of 1 ml min^{-1} using a UV detector.

The coumarins **13–15** were prepared from the esters **7–9** by this method.

*3.6.1 1,1,7,7-Tetramethyl-2,3,6,7-tetrahydro-1H,5H,11H-[1]-benzopyrano[6,7,8-i,j]quinolizine-10-phenyl-11-one (**13**)*
Crystallized from chloroform–hexane as bright yellow needles (65%), m.p. 198°C. R_f = 0·6 (1 : 9 EtOAc : C_6H_{14}). MS *m/z* (rel. int.) 373 (100), 358 (93), 343 (50), 328 (15), 302 (28), 274 (20), 165 (40). HPLC (R_t) 4·921, percentage purity 100%.

*3.6.2 1,1,7,7-Tetramethyl-2,3,6,7-tetrahydro-1H,5H,11H-[1]-benzopyranol[6,7,8-i,j]quinolizine-10-(4'-methoxyphenyl)-11-one (**14**)*
Crystallized from chloroform–hexane as yellow crystals (66%), m.p. 162°C. R_f = 0·51 (1 : 9 EtOAc : C_6H_{14}). MS *m/z* (rel. int.) 403 (100), 373 (46), 343 (46), 343 (54), 313 (50), 302 (27), 274 (24), 246 (20), 165 (23). HPLC (R_t) 4·976, percentage purity 99·7%.

*3.6.3 1,1,7,7-Tetramethyl-2,3,6,7-tetrahydro-1H,5H,11H-[1]-benzopyranol[6,7,8-i,j]quinolizine-10-(3',4'-dimethoxyphenyl)-11-one (**15**)*
Crystallized from chloroform–hexane as dark yellow needles (64%), m.p. 175°C. R_f = 0·30 (1 : 9 EtOAc : C_6H_{14}). MS *m/z* (rel. int.) 433 (100), 403 (41), 373 (30), 343 (22), 330 (18), 328 (11), 302 (20), 274 (15), 246 (18), 165 (17). HPLC (R_t) 4·536, percentage purity 98·06%.

3.7 Formation of coumarins (13–15) from 8-hydroxy-1,1,7,7-tetramethyljulolidine (3)–general procedure

A mixture of 8-hydroxy-1,1,7,7-tetramethyljulolidine (1·225 g, 0·005 mol) ethyl α-formyl (un)substituted phenylacetate (0·0055 mol), freshly fused anhydrous zinc chloride (0·0275 mol) and absolute ethanol (10 ml) was refluxed for 14 h, allowed to cool and poured into dilute HCl (75 ml). The resulting oil was extracted with chloroform, dried ($MgSO_4$) and purified by column chromatography over silica gel. The solid was collected and crystallized from chloroform–hexane and its purity checked on HPLC.

Following this procedure the above three coumarins, **13**, **14**, **15**, were prepared in 60%, 61% and 63% yield from ethyl α-formylphenylacetate (**16**, 40%), ethyl α-formyl 4-methoxyphenylacetate (**17**, 41%) and ethyl α-formyl-3,4-dimethoxyphenylacetate (**18**, 36%) respectively.

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