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CLAISEN REARRANGEMENTS—X[1]

SYNTHESIS OF THE COUMARINS, HORTIOLONE AND HORTINONE

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Abstract—The linear furanocoumarin, hortiolone **1** from *Hortia arborea* has been synthesised in five steps from 7-hydroxy-5-prenyloxycoumarin in 76% overall yield. The spectroscopic evidence for the co-occurring hortinone has been reassessed and the revised angular furanocoumarin structure **9** confirmed by synthesis.

Recent studies[2,3] of the root constituents of *Hortia arborea* have revealed the presence of nine coumarins, two of which, hortiolone and hortinone possess the 2-isopropenylfuran moiety found in only three other coumarins, oroselone **3**,[4,5] arnocoumarin **10**[6] and arnottianin **11**.[6] Hortiolone **1** was shown to be a linear furanocoumarin since acetylation resulted in marked diamagnetic shifts for H-4 and the furan ring proton. The remaining substituent, a 1,1-dimethylallyl group, consequently had to be placed at C-8.[3] Two Claisen rearrangement methods were considered for introduction of the 1,1-dimethylallyl substituent in a synthesis of hortiolone; *para*-rearrangement of a 1,1-dimethylallyl ether[1] or *ortho*-rearrangement of a 3,3-dimethylallyl ether.[7] The directness of the former method, developed for the synthesis of furopinnarin **13**, was likely to be offset by difficulties in preparing the requisite ether efficiently.[1] On the other hand, prenyl ethers are easily obtained but the phenolic O atom of the *ortho*-rearrangement product would have to be incorporated into either the furan ring or the lactone ring of hortiolone. Consideration was therefore given to synthesis of the prenyl ether **5**, *ortho* rearrangment to **4** followed by base-induced lactone-ring isomerisation[8] of this 5-hydroxycoumarin to give hortiolone (Scheme).

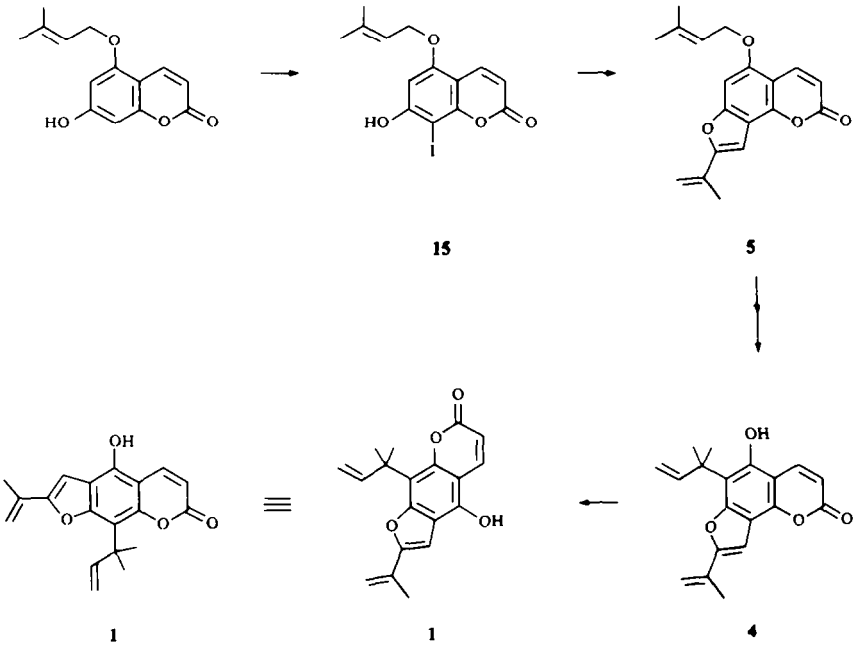
Alkylation of 5,7-diacetoxycoumarin proceeds slightly faster at the 5-position leading, after hydrolysis, to a predominance of the 5-alkoxy-7-hydroxycoumarin.[9,10] 7-Hydroxy-5-prenyloxycoumarin,[10] like 7-hydroxy-coumarin, underwent regiospecific iodination at C-8,[11] with iodine and mercury-(II) oxide.[12] Coupling the iodocoumarin **15** (89%) with the copper(I) acetylide from 2-methylbut-1-en-3-yne[13] in dry pyridine at 80° under argon afforded the isopropenylfuranocoumarin **5** (92%). That the product was the required angular furanocoumarin and not the alternative linear isomer followed from the absence of long-range coupling in its ^{1}H NMR spectrum which would have been discernible between H-8 and H-4 for the latter compound.[8,14]

o-(1,1-Dimethylallyl)phenols, the products of normal Claisen rearrangement of prenyl aryl ethers, are transformed thermally via two 1,5-H shifts into *o*-(1,2-dimethylallyl)phenols.[14] Consequently thermal rearrangements of such ethers have been carried out in the presence of butyric anhydride to trap the first-formed phenol as its butyrate.[7,15] However when **5** was heated in butyric anhydride and diethylaniline at 190° only the "abnormal" product **6** was obtained. In an endeavour to prevent incursion of the second rearrangement, the pyrolysis of **5** was repeated in butyric anhydride at 195° in the presence of a stronger base, sodium butyrate. The desired "normal" rearrangement product **4** was now trapped cleanly as its butyrate **7** (95%) but freeing the latter from traces of butyric anhydride proved difficult. This problem was circumvented by performing the rearrangement of **5** in refluxing acetic anhydride containing sodium acetate, the crystalline acetate **8** being produced quantitatively. Our reaction conditions are more convenient than those employed recently[16] for such rearrangements since sealed reaction vessels are not required, hence the progress of the reaction can be monitored by TLC.

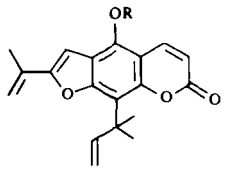
Hydrolysis of **8** with 1.5 equivalents of NaOH in methanol at room temperature for 1 hr afforded the desired phenol **4** (95%). When the hydrolysis was repeated using 3 equivalents of base, hydrolysis to **4** was complete in 20 min. However, prolonged exposure to base resulted in the anticipated lactone-ring opening and alternative ring closure, isomerisation to hortiolone **1** being virtually quantitative after 5 hr.

The possibility that hortiolone may be an artefact should be considered since 30% KOH was used to separate the *H.arborea* coumarins from other root constituents.[3] It is conceivable that the natural product may be the alkali-sensitive angular furanocoumarin **4**. With this in mind it was of interest to examine the evidence for the co-occurring hortinone for which the linear furanocoumarin structure **12** had been proposed.[3]

The UV spectrum of hortinone was found to be similar to those of hortiolone **1** and bergapten **15**,[17] both 5-oxygenated linear furanocoumarins. It should be noted however that it is also similar to that of the 5-methoxy angular furanocoumarin, isobergapten **17**.[18] In the ^{1}H NMR spectrum of hortinone, the single benzenoid proton and the furan ring proton resonate as a two-proton singlet at δ 6.75. Significantly, the benzenoid (H-8) proton is bergapten appears at δ 7.12 whereas H-6 in isobergapten is found at δ 6.86.[18] The Italian workers concluded[3] that hortinone was the linear furanocoumarin **12** from the shifts, relative to H-3, induced by Pr(fod)$_3$.[19] In particular, the δ 6.75 proton which experienced the larger shift (0.23) was assigned to the benzenoid ring and placed at C-8. The smaller shift, ascribed to the furan-ring proton, was not given but has now been found to be 0.16.

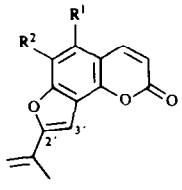


Scheme 1.



1: R = H

2: R = Me



3: $R^1 = R^2 = H$

4: $R^1 = OH$, $R^2 = CMe_2CH=CH_2$

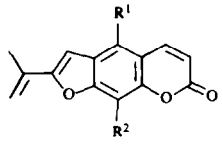
5: $R^1 = OCH_2CH=CMe_2$, $R^2 = H$

6: $R^1 = OCOPr$, $R^2 = CHMeCMe=CH_2$

7: $R^1 = OCOPr$, $R^2 = CMe_2CH=CH_2$

8: $R^1 = OAc$, $R^2 = CMe_2CH=CH_2$

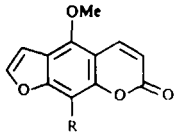
9: $R^1 = OMe$, $R^2 = H$



10: $R^1 = R^2 = H$

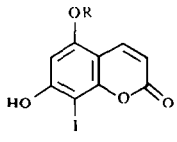
11: $R^1 = H$, $R^2 = OMe$

12: $R^1 = OMe$, $R^2 = H$



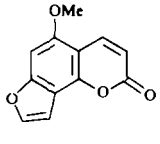
13: R = $CMe_2CH=CH_2$

14: R = H



15: R = $CH_2CH=CMe_2$

16: R = Me



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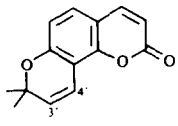

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We conclude that hortinone should be reformulated as the angular furanocoumarin **9** with the shifts of 0.23 and 0.16 assigned to the proton on the furan ring and H-6 on the benzenoid ring, respectively. The former value is identical with those found for the furan-ring proton in the angular furanocoumarin, oroselone **3** and the benzylic proton in the angular pyranocoumarin, seselin **18**[19] (Table 1). Conversely, the shifts of H-6 for oroselone, seselin, and citropten(5,7-dimethoxycoumarin) are 0.12, 0.13, and 0.16, respectively whereas H-8 is 0.28 for citropten and 0.29 for bergapten.

Synthetic confirmation of the revised structure **9** for hortinone was readily accomplished. 7-Hydroxy-5-methoxycoumarin[9] underwent regiospecific monoiodination[20] to **16** with iodine in the presence of mercury(II) oxide[12] (87%) or morpholine (66%).[21] The 8-

Table 1. ^{1}H NMR Lanthanide-induced shifts relative to H-3 = 1.00

Substrate		Proton at position						Isopropenyl group			1,1-Dimethylallyl group			
		4	5	6	8	2'	3'	CH_3	$=CH_2$		CH_3	=CH	$=CH_2$	
Bergapten	14	0.32	0.12[a]		0.29	0.09	0.11	-	-	-	-	-	-	-
Citropten[19]		0.31	0.09[a]	0.16	0.28	-	-	-	-	-	-	-	-	-
Seselin[19]	18	0.30	0.20	0.13	-	0.04[b]	0.23[b]	-	-	-	-	-	-	-
Oroselone	3	0.32	0.17	0.12	-	-	0.23	0.04	0.06	0.03	-	-	-	-
Methylhortiolone	2	0.31	0.12[a]	-	-	-	0.13	0.05	0.07	0.05	0.27	0.31	0.19	0.26
Hortinone	9	0.33	0.14[a]	0.16	-	-	0.23	0.04	0.07	0.04	-	-	-	-

[a] OCH_3

[b] for seselin the 3' and 4' positions on the pyran ring correspond to the 2' and 3' furan positions.

iodocoumarin was coupled with copper(I) isopropenyl-acetylide in hot pyridine to give the angular furanocoumarin **9** which was found to be identical with a sample of natural hortinone. Examination of the ^{1}H NMR spectrum of hortinone reveals no broadening of the H-4 doublet which would result from further coupling to H-8 if hortinone possessed the linear furanocoumarin structure **12**.

EXPERIMENTAL

M.ps were determined with a Kofler hot stage apparatus. Microanalyses were performed by Mrs. W. Harkness and her staff. IR spectra were recorded on a Perkin–Elmer 225 spectrophotometer by Mrs. F. Lawrie and her staff. ^{1}H NMR spectra of soln in $CDCl_3$ (unless otherwise stated) with TMS as internal standard were recorded on a Perkin–Elmer R32 90 MHz spectrometer. Mass spectra were recorded by Mr. A. Ritchie and his staff on an AEI-GEC MS 12 mass spectrometer. Light petroleum refers to the fraction of b.p. 40–60°.

7-Hydroxy-8-iodo-5-(3-methylbut-2-enyl)oxycoumarin **15**

Yellow mercuric oxide (1.16 g, 5.37 mmole) and I_2 (1.36 g, 5.37 mmole) were added alternatively portionwise with stirring over 15 min to a soln of 7-hydroxy-5-(3-methylbut-2-enyl)oxycoumarin[10] (1.32 g, 5.37 mmole) in $CHCl_3$ (60 ml) and acetone (10 ml). Stirring was continued for 30 min, the mixture filtered through celite and the filtrate evaporated under reduced pressure. The residue was extracted with EtOAc, washed with aqueous sodium thiosulphate, brine, dried and evaporated to give *7-hydroxy-8-iodo-5-(3-methylbut-2-enyl)oxycoumarin* **15** (1.78 g, 89%) tan-yellow needles, m.p. 163–165° (dec.) (from EtOAc) (Found: C, 45.15; H, 3.25. $C_{14}H_{13}IO_4$ requires: C, 45.1; H, 3.5%); ν_{max}(KBr) 3325, 1700, 1600 and 1570 cm^{-1}; mass spectral peaks at *m/z* 372 (M^+, 11%), 305 (20), 304 (100), 280 (50), 279 (15) and 247 (10); NMR signals (DMSO-d_6) at δ 1.74 (6H, bs), 4.61 (2H, bd, J = 6.5 Hz), 5.46 (1H, bt, J = 6.5 Hz), 6.12 (1H, d, J = 9.5 Hz), 6.53 (1H, s) and 7.89 (1H, d, J = 9.5 Hz).

5-(3-Methylbut-2-enyl)oxyoroselone **5**

A soln of copper(I) isopropenyl-acetylide (216 mg, 1.68 mmole) in dry pyridine (10 ml) was added to a soln of **15** (564 mg, 1.53 mmole) in dry pyridine (10 ml) and the mixture heated under argon for 12 hr with stirring (oil bath 85 ± 2°). The cooled mixture was poured into ice, extracted with EtOAc, washed with a saturated soln of Cu_2SO_4, water, brine, dried and evaporated. The residue was chromatographed on silica gel, elution with EtOAc-light petroleum (1:9) afforded *5-(3-methyl-but-2-enyl)oxyoroselone* **5** (434 mg, 92%) tan-yellow plates, m.p. 144–146° (from EtOAc–hexane) (Found: C, 73.75; H, 5.75. $C_{19}H_{18}O_4$ requires C, 73.55; H, 5.85%); ν_{max} ($CHCl_3$) 1735, 1625, 1610 and 1560 cm^{-1}; mass spectral peaks at *m/z* 310 (M^+, 34%), 243 (62), 242 (100) and 214 (52); NMR signals at δ 1.78 (3H, s), 1.82 (3H, s), 2.11 (3H bs), 4.64 (2H, bd, J = 7 Hz), 5.17 (1H, bs), 5.53 (1H, bt, J = 7 Hz), 5.73 (1H, bs), 6.25 (1H, d, J = 9.5 Hz), 6.84 (2H, bs) and 8.13 (1H, d, J = 9.5 Hz).

Abnormal Claisen rearrangement of **5**

A mixture of **5** (78 mg), diethylaniline (5 ml) and butyric anhydride (0.2 ml) was stirred at 175 ± 5° for 2 hr. The cooled mixture was diluted with water (30 ml), stirred for 2 hr and extracted with EtOAc. The extract was washed with dil HCl, saturated $NaHCO_3$, brine, dried and evaporated. The crude product was purified by preparative TLC on Kieselgel GF_{254} (Merck); elution with EtOAc–light petroleum (1:3) to give the *butyrate* **6** (48 mg, 50%) as a colourless oil; ν_{max} (CCl_4) 1760, 1750 and 1630 cm^{-1}; mass spectral peaks at *m/z* 380 (M^+, 84%; $C_{23}H_{24}O_5$ requires M^+ 380), 310 (100), 290 (98) and 267 (26); NMR signals at δ 1.05 (3H, t, J = 7.5 Hz), 1.51 (3H, d, J = 7 Hz), 1.60 (3H, s), 1.77 (2H, m, J = 7.5 Hz), 2.13 (3H, bs), 2.59 (2H, t, J = 7.5 Hz), 4.22 (1H, q, J = 7 Hz), 5.00 (2H, bs), 5.27 (1H, bs), 5.80 (1H, bs), 6.35 (1H, d, J = 9.5 Hz), 6.95 (1H, s) and 7.60 (1H, d, J = 9.5 Hz).

Normal Claisen rearrangement of **5**

(i) *In butyric anhydride.* A mixture of **5** (139 mg), sodium butyrate (48 mg) and butyric anhydride (0.5 ml) was heated with stirring under argon for 1 hr (oil bath 190°). The cooled mixture was diluted with dil HCl, extracted with EtOAc and the extract washed with dil HCl, saturated $NaHCO_3$, brine, dried and evaporated. Complete removal of unreacted butyric anhydride proved difficult. The crude product was purified by silica gel chromatography to give the butyrate **7** (160 mg, 95%) as a colourless powder, m.p. 129–131° (from EtOAc-hexane); ν_{max} ($CHCl_3$) 1770, 1750 and 1620 cm^{-1}; NMR signals at δ 1.05 (3H, t, J = 7.5 Hz), 1.77 (2H, m, J = 7.5 Hz), 1.77 (6H, s), 2.13 (3H, bs), 2.58 (2H, t, J = 7.5 Hz), 4.98 (1H, d, J = 10 Hz), 5.08 (1H, d, J = 18 Hz), 5.27 (1H, bs), 5.78 (1H, bs), 6.27 (1H, dd, J = 18 and 10 Hz), 6.32 (1H, d, J = 9.5 Hz), 6.94 (1H, s) and 7.48 (1H, d, J = 9.5 Hz). When the reaction was performed under N_2 the yield was only 56 mg (33%).

(ii) *In acetic anhydride.* A mixture of **5** (200 mg), NaOAc (80 mg) and Ac_2O (2.5 ml) was refluxed under argon for 2 hr (oil bath 160°). The cooled mixture was filtered, the solid washed with EtOAc and the filtrate evaporated. The residue was extrac-

ted with EtOAc, washed with dil HCl, saturated $NaHCO_3$, brine, dried and evaporated to give 5-*acetoxy*-6-(1,1-*dimethylallyl*)*oroselone* **8** (225 mg, 100%) needles, m.p. 149–152° (from EtOAc) (Found: M^+ 352.1317. $C_{21}H_{20}O_5$ requires: M^+ 352.1310); ν_{max} ($CHCl_3$) 1765, 1730, 1620, 1570 and 1560 cm^{-1}; mass spectral peaks at *m/z* 352 (32%) 311 (21) , 310 (100), 295 (87), 267 (44) and 115 (22); NMR signals at δ 1.70 (6H, s), 2.16 (3H, bs), 2.33 (3H, s), 5.04 (1H, d, *J* = 10 Hz), 5.10 (1H, d, *J* = 18 Hz), 5.30 (1H, bs), 5.81 (1H, bs), 6.30 (1H, dd, *J* = 18 and 10 Hz), 6.36 (1H, d, *J* = 9.5 Hz), 6.97 (1H, s) and 7.54 (1H, d, *J* = 9.5 Hz).

5-*Hydroxy*-6-(1,1-*dimethylallyl*)*oroselone* **4**

A suspension of the acetate **8** (170 mg, 0.48 mmole) in MeOH (25 ml) and 1% NaOH/MeOH (3 ml, 0.75 mmole) was stirred at room temp and monitored by TLC. After 1 hr the concentration of the less polar product was maximal. The mixture was neutralised with dil HCl, the MeOH evaporated under reduced pressure and the residue partitioned between EtOAc and brine. The organic layer was washed with brine, dried and evaporated. The residue was chromatographed rapidly on silica gel; extended contact resulted in degradation. Elution with EtOAc–light petroleum (1:9) afforded 5-*hydroxy*-6-(1,1-*dimethylallyl*)*oroselone* **4** (140 mg, 95%), yellow needles, m.p. 160–164° (from MeOH) (Found: M^+ 310.1229. $C_{19}H_{18}O_4$ requires M^+ 310.1233); ν_{max} ($CHCl_3$) 3430, 1725, 1620 and 1560 cm^{-1}; mass spectral peaks at *m/z* 310 (100%), 295 (96), 267 (56), 239 (30) and 115 (27); NMR signals at δ 1.72 (6H, s), 2.12 (3H, bs), 5.16 (1H, bs), 5.44 (1H, d, *J* = 10 Hz), 5.50 (1H, d, *J* = 18.5 Hz), 5.66 (1H, bs), 6.25 (1H, d, *J* = 9.5 Hz), 6.43 (1H, dd, *J* = 18.5 and 10 Hz), 6.84 (1H, s), 6.84 (1H, s, OH), and 8.06 (1H, d, *J* = 9.5 Hz).

Hortiolone **1**

A suspension of the acetate **8** (360 mg, 1.02 mmole) in MeOH (25 ml) and 2% NaOH/MeOH (6 ml, 3.0 mmole) was stirred at room temp and monitored by TLC. After 20 min, a soln was obtained and maximal transformation to the less polar product achieved. Stirring was continued for 5 hr until TLC indicated virtually complete transformation to a more polar product. The soln was neutralised with dil HCl and worked up as above to give **1** (309 mg, 98%) tan-yellow plates, m.p. and mixed m.p. 220–223° (lit.[2] 226–227°) (from MeOH) identical (TLC, IR, mass spectrum and NMR) with an authentic sample. Treatment of hortiolone with ethereal diazomethane gave **2** needles m.p. 156–158° (lit.[3] 156–158°) (from ether) having identical NMR signals to those quoted.[3]

7-*Hydroxy*-8-*iodo*-5-*methoxycoumarin* **16**

(i) Yellow mercuric oxide (130 mg, 0.6 mmole) and I_2 (152 mg, 0.6 mmole) were alternatively added portionwise with stirring over 15 min to a soln of 7-hydroxy-5-methoxy-coumarin (115 mg, 0.6 mmole) in $CHCl_3$ (20 ml) and acetone (10 ml). Stirring was continued for 30 min. Work up as for **15** gave **16** (161 mg, 87%) tan yellow needles, m.p. 208–210° (lit.[20] 235–237°) (from EtOH) (Found: C, 37.6; H, 1.85. Calc for $C_{10}H_7IO_4$: C, 37.75; H, 2.2%); ν_{max} (KBr) 3300, 1700, 1590 and 1550 cm^{-1}; NMR signals (DMSO-d_6) at δ 3.87 (3H, s), 6.11 (1H, d, *J* = 9.5 Hz), 6.53 (1H, s) and 7.89 (1H, d, *J* = 9.5 Hz).

(ii) Morpholine (0.26 ml, 3 mmole) was added with stirring to an ice-salt cooled soln of 7-hydroxy-5-methoxycoumarin (192 mg, 1 mmole) and I_2 (385 mg, 1.5 mmole) in dry EtOH (10 ml). After 15 min, the mixture was allowed to warm to room temp and stirred for 24 hr. The solvent was removed under reduced pressure, the residue extracted with EtOAc, washed with dil sodium thiosulphate, brine, dried and evaporated. The solid was crystallised from EtOH to give **16** (210 mg, 66%).

Hortinone **9**

Copper(I) isopropenylacetylide (71 mg, 0.55 mmole) in dry pyridine (10 ml) was added with stirring to a soln of **16** (159 mg, 0.5 mmole) in dry pyridine (10 ml) under argon. The mixture was stirred and heated (oil bath 85 ± 2°) for 8 hr. Work up as for **5** gave **9** (119 mg, 95%), tan yellow needles, m.p. 155–157° (lit.[3] 136–138°) (from ether) (Found: M^+ 256.0730. Calc for $C_{15}H_{12}O_4$: M^+ 256.0736) ν_{max} ($CHCl_3$) 1730, 1610 and 1480 cm^{-1}; NMR signals at δ 2.09 (3H, bs), 3.91 (3H, s), 5.15 (1H, bs), 5.70 (1H, bs), 6.22 (1H, d, *J* = 9.5 Hz), 6.75 (2H, s) and 8.01 (1H, d, *J* = 9.5 Hz); mass spectral peaks at *m/z* 256 (100%), 241 (43), 213 (21), 185 (18) and 128 (9), identical (TLC, mass spectrum and NMR) with an authentic sample of hortinone. We obtained a tiny sample (~0.5 mg) of natural hortinone from Professor Delle Monache. Our synthetic hortinone, m.p. 155–157°, was identical (TLC and MS) with this sample and its NMR spectrum was identical with a copy sent to us. The literature m.p. of hortinone is given as 136–138° in Ref. 3, but we recorded the m.p. of two crystals from the sample sent to us as 147–152° and 145-149°. It is our opinion that natural hortinone is slightly impure and that the literature m.p. of 136–138° is clearly incorrect.

Lanthanide-induced shifts (LIS) experiments. The normal ^1H NMR spectrum of each coumarin (20–40 mg) in $CDCl_3$ (0.3 ml) was recorded. A soln of $Pr(fod)_3$ in $CDCl_3$ (25–50 μl, ~0.30 M) was added, the soln shaken and the spectrum re-run. This was repeated four times. All spectra were recorded at 35°. In each case, the shifts of all the protons were measured relative to TMS and LIS was $\delta_{H[Pr(fod)_3]} - \delta_{H(untreated)}$. The LIS for each proton was always divided by LIS of the proton attached to C-3 and average values obtained for each substrate.

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