



Short Communication

Synthesis and fluorescence properties of 3-coumarinyl carboxylates

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Abstract

3-Coumarinyl Carboxylates were synthesized from 3-hydroxycoumarin by O-acylation with acid chlorides or acid anhydrides in the presence of an appropriated base. The fluorescence spectra of these compounds were recorded in acetonitrile. Except the compounds 2g With R=(CH₃)₂N as substituent which exhibits an unstructured broad spectrum at a long wavelength ($\lambda_{em}=488nm$; $\Delta\lambda=177nm$), all compounds emit in the same chromatic range ($300nm < \lambda_{em} < 400nm$). This compounds exhibited high fluorescent intensities that vary according to the electronic nature of the different substitutes.

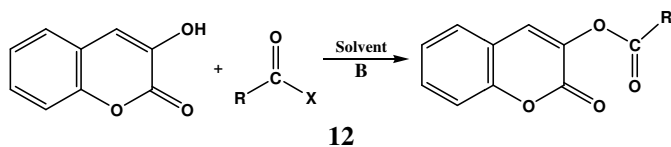
Keywords: 3-Coumarinyl carboxylates, 3-hydroxycoumarin, fluorescence spectra, acetonitrile.

Introduction

Coumarins are important compounds exhibiting several physical and biological properties. It is known that coumarins are natural occurring compounds and have been investigated for their synthetic routes¹⁻⁵, and their physical, chemical and biologic properties⁶⁻¹³. To our knowledge, 3-coumarinyle carboxylates are the little less known derivatives (Scheme-1). So, the title compounds were synthesized according to a described convenient method, from 3-hydroxycoumarin and acid chloride or acid anhydride in the presence of a base¹⁴⁻¹⁶. Their fluorescence spectra were recorded in acetonitrile, to observe the effect of substitute on fluorescence. In this present study, we investigate the florochromic character of these compounds in correlation with the electronic effect of the different substituents R. In another study, we will discuss the effects of solvent on the behavior of fluorescence emission spectra.

Materials and methods

Preparation of 3-coumarinyl carboxylates: 3-Coumarinyl Carboxylates were synthesized from 3-hydroxycoumarin by O-acylation with acid chlorides or acid anhydrides in the presence of an appropriated base as shown below (Scheme-1). They have been identified by IR, ESI-MS; EIMS and ¹H and ¹³CNMR spectra¹⁷⁻²⁰.



R = alkyl: solvent = Diethylether and B = Pyridine.

R = aryl: solvent Tetrahydrofuran and B = Triethylamine.

Scheme-1: Formation of 3-coumarinyl carboxylate.

2a: R=CH₃; 2b: R=C₂H₅; 2c: R=C₆H₅; 2d: R=p-ClC₆H₄;
2e: R=p-CNC₆H₄; 2f: R=p-MeOC₆H₄; 2g: R=p(CH₃)₂NC₆H₄.

The fluorescence spectra: The fluorescence spectra were recorded in acetonitrile (analytical grade) at room temperature, on a KONTRON SFM-25 spectrofluorometer, at a concentration of 10⁻⁵ mole/l.

Table-1: Fluorescence and excitation wave length(nm) of compounds 2 in acetonitrile.

Compounds	Acetonitrile		
	Excitation	Emission	Stoke shifts
	λ_{ex} (nm)	λ_{em} (nm)	$\Delta\lambda$ (nm)
2a : R=CH ₃	331	384	53
2b : R= C ₂ H ₅	332	387	55
2c : R= C ₆ H ₄	335	387	52
2d : R=pClC ₆ H ₄	319	386	67
2e : R = pCNC ₆ H ₄	325	388	63
2f : R=pMeOC ₆ H ₄	339	384	45
2g: R=pN(CH ₃) ₂ C ₆ H ₄	311	488	177

Results and discussion

Compounds with R aliphatic (R= CH₃; C₂H₅): Concerning the evolution of parameters of fluorescence, the wave length and the intensity, these parameters are dependent on the polarity of the solvent and substituent used.

The very first remark is that all the compounds are fluorescent in acetonitrile. Regarding the effect of substituent R, when the substituent R is aliphatic (CH₃ and C₂H₅) the fluorescence emission wavelength seems varied depending on the length of the carbon chain. By passing from the spectrum of 2a (R=CH₃) to the spectrum of 2b (R=C₂H₅) in the same solvent, there is a slight increase in the wave length $\lambda_{em}(C_2H_5) - \lambda_{em}(CH_3) = 3nm$. The increase in the size of the molecule (lengthening of the hydrocarbon chain) generates a bathochromic. However, at the level of the fluorescence intensities, the difference is not sensitive (Figure-1, Figure-2).

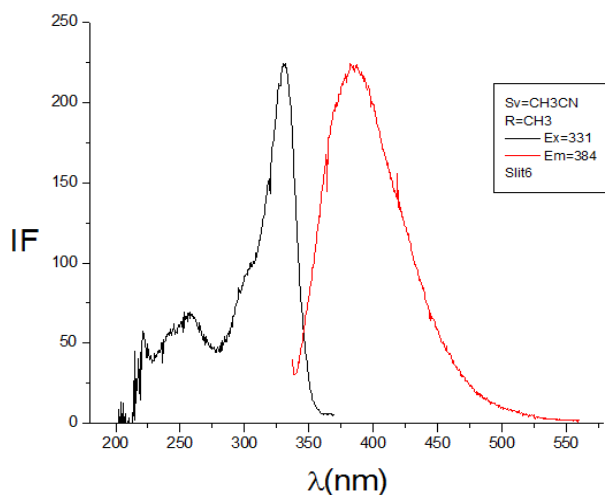


Figure-1: Fluorescence spectrum of 2a.

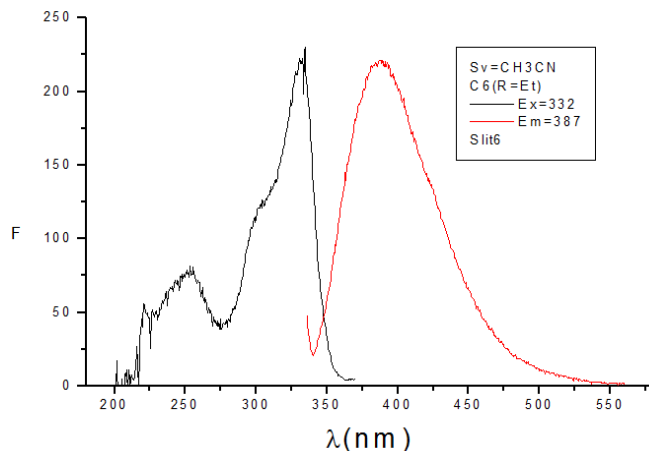


Figure-2: Fluorescence spectrum of 2b.

Compounds with R aromatic (R=C₆H₅; R=p-ClC₆H₄): Compounds 2c (R=C₆H₄), 2d (R=p-ClC₆H₄) all have an

aromatic R. Compared to the preceding compounds whose R residues were aliphatic, large values are observed at the level of the fluorescence intensities. The substitution of an aliphatic group by an aromatic group results in an increase in the intensity of the fluorescence. The presence of the aryl group therefore enhances the fluorescence (Figure-3, Figure-4).

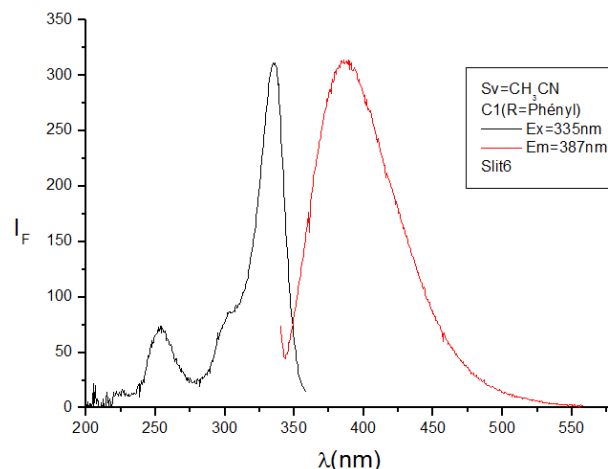


Figure-3: Fluorescence spectrum of 2c.

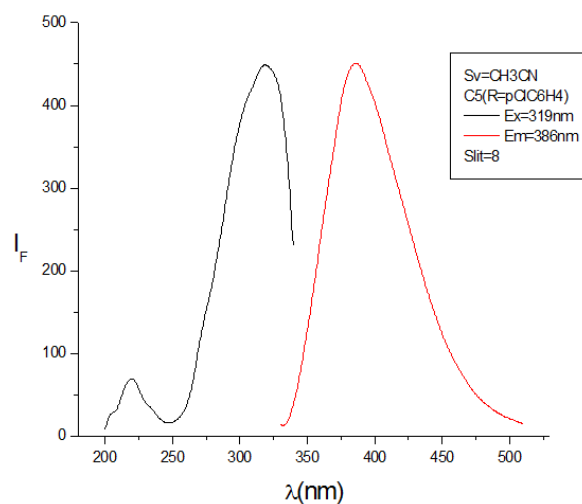


Figure-4: Fluorescence spectrum of 2d.

Compounds with R aromatic (R=p-CNC₆H₄; R=p-MeOC₆H₄; R=p-(CH₃)₂NC₆H₄): The compounds 2f (R=p-OMe) 2g (R=(CH₃)₂N) substituted an electron-donating group were known to exhibit strong fluorescence^{21,22}. The structure of these compounds is particularly interesting (Scheme-2). On these molecules, the electron-donating group is conjugated with an electron-withdrawing group, the carbonyl group (C=O). As a result, there is a photo induced charge transfer with a dipole moment growth. This explains the shift of the spectrum towards long wavelengths when the electron-donating character becomes strong²³. By passing from compound 2f to compound 2g under the same conditions, there is a shift towards long wavelengths and an increase in fluorescent intensities (Figure-5, Figure-6).

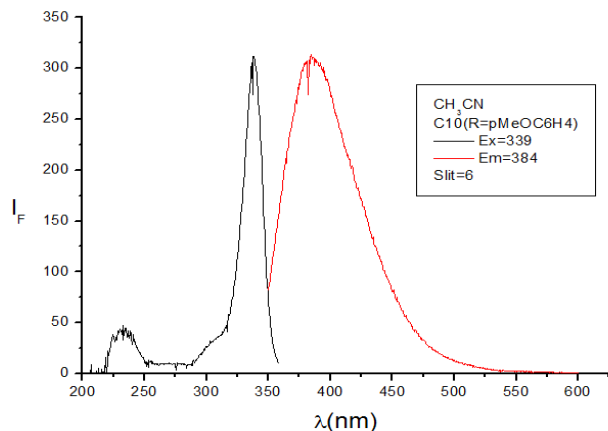


Figure-5: Fluorescence spectrum of 2f.

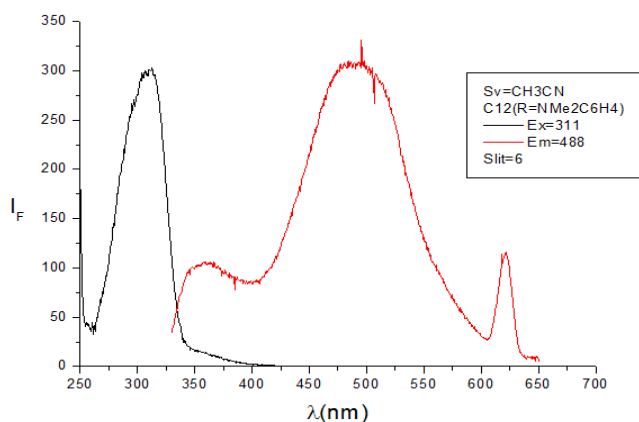


Figure-6: Fluorescence spectrum of 2g.

The greater the mesomer or mesomer donor (+M) effect of the substituent R, the greater the maximum of the fluorescence band shifts towards the low energy transitions. On the other hand, the electro-attractant substituents in general, because of the attracting inductive effect (-I) that they exert on the rest of the structure, move these bands towards the transitions of greater energies with weak I_F . For the case of the compound 2e (R = CNC_6H_4), on remark that the intensity of the fluorescence is weak $I_F > 140$; and $\lambda_{em}=388nm$ (Figure-7). The same results have been obtained by Cissé and et al. for 4,7-disubstituted coumarins²¹ and by A. Djandé and et al. for 4-acyl isochroman-1, 3-diones²².

Other parameters can influence the behavior of the spectra. For reasons of steric hindrance, the groups $R=N(CH_3)_2$, $R=Ome$ can be twisted out of the plane of the aromatic ring. Under these conditions, the steric arrangement lowered the degree of the conjugation of the π electrons. This generally leads to broad and unstructured spectra²³. This is the case of compound 2g (Figure-6) which emits particularly in green blue (488nm). By analyzing the Stokes shifts, we note that the values are the highest in the case of this compound ($\Delta\lambda=177nm$). The non-coplanarity found here is an explanation, since the extent of the Stokes shift gives an indication of the difference in geometry between the excited

state and the ground state²². Organic compounds with this behavior present a great interest in tissular and cellular investigations where the local concentrations of dyes are difficult to control^{25,26}.

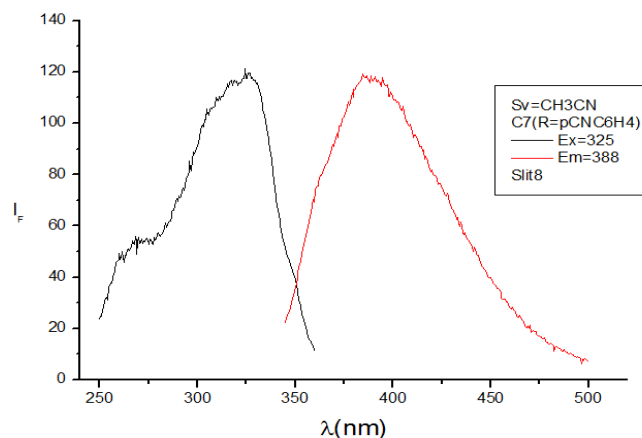


Figure-7: Fluorescence spectrum of 2e.

Conclusion

In this study, we have discussed the synthesis and the fluorochrome character and R substitution effects of 3-coumarinyl carboxylates qualitatively. The series of new cyclic compound were successfully synthesized and structures were confirmed by spectral analysis performed by IR, MS and NMR. The fluorescence spectra analyzes show that these compounds are all fluorescent with a fluorescence intensity that varies according to the structure of the molecule. Except compound 2g which is distinguished by emitting in blue-green ($\lambda=488nm$) with broad unstructured spectrum, all fluorescent compounds with a wavelength ranging from 300nm to 400nm. On electronic contributions, there is a strong mesomeric effect related to the presence of π bonds.

Acknowledgements

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References

1. Perkin W.H. (1868). VI.—On the artificial production of coumarin and formation of its homologues. *Journal of the chemical society*, 21, 53-63.
2. Trivedi K. and Sethan S. (1960). 3-Hydroxycoumarins. *The Journal of Organic Chemistry*, 25(10), 1817-1819.
3. Kalinin A.V., da Silva A.J., Lopes C.C., Lopes R.S. and Snieckus V. (1998). Directed ortho metalation-cross coupling links. Carbamoyl rendition of the baker-venkataraman rearrangement. Regiospecific route to substituted 4-hydroxycoumarins. *Tetrahedron letters*, 39(28), 4995-4998.

4. Potdar M.K., Mohile S.S. and Salunkhe M.M. (2001). Coumarin syntheses via Pechmann condensation in Lewis acidic chloroaluminate ionic liquid. *Tetrahedron Letters*, 42(52), 9285-9287.
5. Ferguson J., Zeng F. and Alper H. (2012). Synthesis of coumarins via Pd-catalyzed oxidative cyclocarbonylation of 2-vinylphenols. *Organic Letters*, 14(21), 5602-5605.
6. Shilling W.H., Crampton R.F. and Longland R.C. (1969). Metabolism of coumarin in man. *Nature*, 221, 664-665.
7. Goodwin R.H. and Taves C. (1950). The effect of coumarin derivatives on the growth of Avena roots. *American Journal of Botany*, 37(3), 224-231.
8. Rodighiero G. and Antonello C. (1958). Synthesis of some derivatives of 3-aminocoumarin and first report on their antibacterial properties. *Bollettino chimico farmaceutico*, 97(10), 592-601.
9. Bailly F., Maurin C., Teissier E., Vezin H. and Cotelte P. (2004). Antioxidant properties of 3-hydroxycoumarin derivatives. *Bioorganic & medicinal chemistry*, 12(21), 5611-5618.
10. Rattanapan J., Sichaem J. and Tip-pyang S. (2012). Chemical constituents and antioxidant activity from the stems of Alyxia reinwardtii. *Records of Natural Products*, 6(2), 288-291.
11. Issa Y.M., Omar M.M., Sabrah B.A. and Mohamed S.K. (1992). Complexes of cerium (III), thorium (IV) and dioxouranium (II) with 8-(aryloxy)-7-hydroxy-4 methylcoumarin dyes. *Journal of the Indian Chemical Society*, 69(4), 186-189.
12. Zhao Y., Zheng Q., Dakin K., Xu K., Martinez M.L. and Li W.H. (2004). New caged coumarin fluorophores with extraordinary uncaging cross sections suitable for biological imaging applications. *Journal of the American Chemical Society*, 126(14), 4653-4663.
13. Hassan Ewais A., Abdulla Asiri M., Iqbal M.I. Ismail, Salem A. Hameed and Ahmed Abdel-Khalek A. (2012). Kinetics and Mechanism of the ring opening of 3-carboethoxy coumarin by sodiumhydroxide and hydrazine. *Research journal of Chemical Sciences*, 2(12), 57-64.
14. Saba Adama (1996). Thèse Unique, Recherche dans la série des sels de benzopyrylium: Synthèse et étude de la structure des sels de 2-benzopyrylium. UFR-SEA, Université de Ouagadougou.
15. Djandé A., Sessouna B., Cissé L., Kaboré L., Tine A and Saba A. (2011). AM1 and ESI/MS study of the fragmentation of 4-Acyl Isochroman-1, 3-diones: Correlation between electronic charges of Atoms and fragmentations processes. *Research journal of Chemical Sciences*, 1(3), 606.
16. Abou A., Djandé A., Kakou-Yao R., Saba A. and Tenon A. J. (2013). 2-Oxo-2H-chromen-4-yl 4-methylbenzoate. *Acta Cryst.*, E69, o1081-o1082.
17. Jules Yoda (2015). Thèse unique (spécialité Chimie Organique): synthèse et étude des propriétés physico-chimiques des carboxylates de 3-coumarinyle. UFR-SEA Université de Ouagadougou.
18. Yoda J., Chiavassa T. and Saba A. (2014). Fragmentations processes of 3-coumarinyl carboxylates in ESI/MS and their Correlation with the Electronic charges of their atoms. *Research journal of chemical sciences*, 4(4), 12-16.
19. Ziki E., Yoda J., Djandé A., Saba A. and Kakou-Yao R. (2016). Crystal structure of 2-oxo-2H-chromen-3-yl propanoate. *Acta Crystallographica Section E: Crystallographic Communications*, 72(11), 1562-1564.
20. Yoda J., Djandé A., Kaboré L., House P., Traoré H. and Saba A. (2016). EIMS and AM1 study of the fragmentations of 3-coumarinyl Carboxylates: Interpretation from electronic charges of atoms. *J. Soc. Ouest-Afr. Chim*, 41, 51-58.
21. Lamine CISSE, Thèse d'Etat (2012). Études des caractéristiques spectrales de dérivés de Coumarines ; Synthèse et caractérisation: corrélations entre processus de fragmentation et charges des atomes. Effets du milieu et de la structure sur les spectres UV d'absorption et de fluorescence; Calcul des moments dipolaires au 1^{er} état excité singulet. Université Cheikh Anta DIOP de Dakar.
22. Djandé A., Cisse L., Kaboré L., Saba A., Tine A. and Aycard J.P. (2008). Synthesis and fluorescence properties of 4-acylisochroman-1, 3-diones. *Heterocyclic communications*, 14(4), 237-244.
23. Bernard Valeur (2004). Invitation à la fluorescence moléculaire. *De Boeck et Larcier*. s. a. 1^e édition.
24. Srividya N., Ramamurthy P. and Ramakrishnan V.T. (1997). Solvent effects on the absorption and fluorescence spectra of some acridinedione dyes: determination of ground and excited state dipole moments. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 53(11), 1743-1753.
25. Le Gourierec D., Ormson S.M. and Brown R.G. (1994). Excited-state intramolecular proton transfer. Part 2: ESIPT to oxygen. *Progr. React. Kinet.*, 19, 211-275.
26. Klymchenko A.S., Ozturk T., Pivovarenko V.G. and Demchenko A.P. (2001). Synthesis and spectroscopic properties of benzo- and naphthofuryl-3-hydroxychromones. *Canadian Journal of Chemistry*, 79(4), 358-363.