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 $R=(\text{CH}_3)_2N$ as substituent which exhibits an unstructured broad spectrum at a long wavelength ($\lambda_{em}=488\text{nm}$; $\Delta\lambda=177\text{nm}$), all compounds emit in the same chromatic range (300nm < $\lambda_{em}$ < 400nm). This compounds exhibited high fluorescence 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-coumarinyl 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 $^1$H and $^{13}$CNMR spectra17-20.

![Scheme-1: Formation of 3-coumarinyl carboxylate.](image)

2a: $R=\text{CH}_3$; 2b: $R=\text{C}_2\text{H}_5$; 2c: $R=\text{C}_6\text{H}_5$; 2d: $R=p-\text{ClC}_6\text{H}_4$; 2e: $R=p-\text{NCOC}_6\text{H}_4$; 2f: $R=p-\text{MeOC}_6\text{H}_4$; 2g: $R=(\text{CH}_3)_2\text{NC}_6\text{H}_4$.

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$^{-3}$mole/l.

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

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Excitation</th>
<th>Emission</th>
<th>Stoke shifts</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a : $R=\text{CH}_3$</td>
<td>331</td>
<td>384</td>
<td>53</td>
</tr>
<tr>
<td>2b : $R=\text{C}_2\text{H}_5$</td>
<td>332</td>
<td>387</td>
<td>55</td>
</tr>
<tr>
<td>2c : $R=\text{C}_6\text{H}_5$</td>
<td>335</td>
<td>387</td>
<td>52</td>
</tr>
<tr>
<td>2d : $R=p\text{ClC}_6\text{H}_4$</td>
<td>319</td>
<td>386</td>
<td>67</td>
</tr>
<tr>
<td>2e : $R=p\text{NCOC}_6\text{H}_4$</td>
<td>325</td>
<td>388</td>
<td>63</td>
</tr>
<tr>
<td>2f : $R=p\text{MeOC}_6\text{H}_4$</td>
<td>339</td>
<td>384</td>
<td>45</td>
</tr>
<tr>
<td>2g : $R=(\text{CH}_3)_2\text{C}_6\text{H}_4$</td>
<td>311</td>
<td>488</td>
<td>177</td>
</tr>
</tbody>
</table>
Results and discussion

Compounds with R aliphatic (R= CH$_3$; C$_2$H$_5$): 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 (CH$_3$ and C$_2$H$_5$) the fluorescence emission wavelength seems varied depending on the length of the carbon chain. By passing from the spectrum of 2a (R=CH$_3$) to the spectrum of 2b (R=C$_2$H$_5$) in the same solvent, there is a slight increase in the wave length $\lambda_{em}(C_2H_5)-\lambda_{em}(CH_3) = 3$nm. 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).

Compounds with R aromatic (R=C$_6$H$_5$; R= p-ClC$_6$H$_4$): Compounds 2c (R=C$_6$H$_5$), 2d (R=p-ClC$_6$H$_4$) 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).

Compounds with R aromatic (R=p-CNC$_6$H$_4$; R=p-MeOC$_6$H$_4$; R=p(CH$_3$)$_2$NC$_6$H$_4$): The compounds 2f (R=p-OMe) 2g (R=(CH$_3$)$_2$N) 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 strong$^{23}$. 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).
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$_6$H$_4$), on remark that the intensity of the fluorescence is weak $I_F > 140$; and $\lambda_{em}=388$nm (Figure-7). The same results have been obtained by Cissé and et al. for 4,7-disubstituted coumarins$^{21}$ and by A. Djandé and et al. for 4-acyl isochroman-1, 3-diones$^{22}$.

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 $\pi$ electrons. This generally leads to broad and unstructured spectra$^{23}$. This is the case of compound 2g (Figure-6) which emits particularly in green blue ($\lambda=488$nm). By analyzing the Stokes shifts, we note that the values are the highest in the case of this compound ($\Delta\lambda=177$nm). The non-coplanite 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 state$^{22}$. Organic compounds with this behavior present a great interest in tissular and cellular investigations where the local concentrations of dyes are difficult to control$^{25,26}$.

**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 ($\lambda=488$nm) 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 $\pi$ bonds.

**Acknowledgements**

We are grateful to Pr Alphonse TINE from University of Cheikh Anta DIOP, Dakar (Sénégal) for recording fluorescence spectra.

**References**


