

4-Hydroxycoumarins as New Fluorescent Compounds: Synthesis and Characterization

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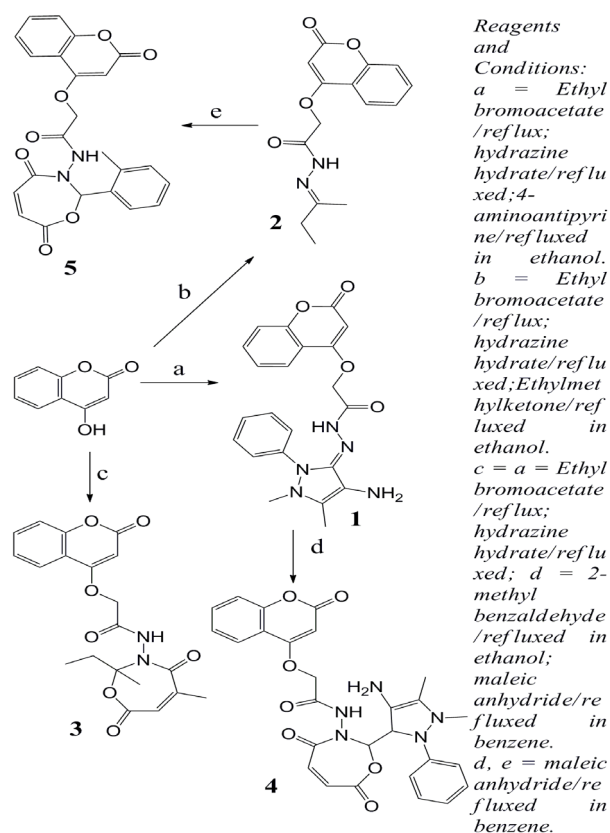
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Abstract New 4-hydroxycoumarins compounds were designed, synthesized and characterized as fluorescent compounds. Absorption and fluorescence spectra of these derivatives have been investigated in alcoholic media. The substituting groups with varying electron donating ability exhibits fluorescence at a longer wavelength i.e. 420-460 nm in ethanol in compound (1-5). Compounds 1-5 exhibited high quantum yield in ethanol. The fluorescence intensities of compounds 2 and 5 were extremely strong. Compounds 2 and 5 exhibited high fluorescent quantum yields in solution compared to compounds 1,3,4.

Keywords Fluorescence, 4-hydroxy-coumarin, Emission, Synthesis

1. Introduction

Fluorescent compounds play an important role in solid state lighting, solar energy conversion and as biomarkers in the life sciences [1-6]. As an important group of organic heterocycles, coumarin derivatives have been found to possess versatile pharmacological/biological activities, which can display anticancer [7, 8], anti-HIV [9], antiviral [10], antimicrobial [11], anti-inflammatory [12, 13], and antioxidant [14] activities, 4-Hydroxycoumarin and its derivatives have been effectively used as anticoagulants for the treatment of disorders in which there is excessive or undesirable clotting, such as thrombophlebitis [15], pulmonary embolism [16], and certain cardiac conditions [17]. Moreover, their unique photochemical and photophysical properties make them useful in a variety of optical application such as in optical brighteners, laser dyes, nonlinear optical chromophores, solar collector systems and organic lightemitting diodes (LED). Coumarin fluorescent probes or labels have extensive and diverse applications, as they exhibit extended spectral range and high emission quantum yields [18]. Coumarin-based fluorescent chemodosimeter with salicylaldehyde functionality were used as a binding site for selective detection of cyanide anions over other anions in water at biological pH [19], Shihai Zhou et al., [20] have studied 3-(2-benzothiazolyl) coumarins for their fluorescent properties in which the coumarin acts as a donor while the benzothiazole moiety



Scheme 1. Reaction sequences of the synthesized compounds

acts an acceptor. P Moeckli et al., [21] introduced some new red fluorescent coumarin molecules by keeping electron donating group on 7th position of the coumarin ring and withdrawing group on 3-position. The oxygen

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atom at the 3-carbonyl group act as a hydrogen bond acceptor and electron donating group on 7th position enhance the fluorescence emission [22] Chiyomi Murata et al., [23] examined coumarin derivatives with both electron donating groups at the 6- and 7-positions and an electron-withdrawing group at the 3-position, which develop intense fluorescence.

In this work, we present simple novel fluorescent coumarins synthesis and characterization by the means of NMR, FT-IR techniques in addition of CHN analysis. We utilize the unique advantage of simple coumarins as eco-friendly fluorescent compounds. Moreover, the approach of synthesized these fluorescent compounds are demonstrated in scheme 1.

2. Experimental Section

2.1. Chemistry

All synthesized compounds were published by the Al-Amiry et al. [24].

2.2. Fluorescence

The fluorescence spectra were recorded on F-8500 spectrofluorometer ethanol at a concentration of 1 mg mL^{-1} . The fluorescence spectra were recorded using excitation into the maximum of the longest wavelength absorption band program. The fluorescence of the solution was measured in a 1 cm^3 cuvette in the right angle arrangement. The quantum yield of the coumarin derivatives were determined using Rhodamine B as the standard in the respective medium. The fluorescence spectra were taken by the excitation into the maximum of the longest wavelength absorption band.

Calculation of the quantum yield

$$\Phi_x = \Phi_s [A_s/A_x] [R_s/R_x] [D/D_s]$$

Φ = Fluorescence quantum yield

Subscripts x and s denotes test and standard respectively

R = refractive index of the solvent

D = area under the corrected, extrapolated emission spectra [25, 26].

3. Result and Discussion

3.1. Fluorescence Properties

The studies of fluorescence were performed in ethanol at a concentration of $1.0 \times 10^{-5} \text{ mol/L}$, and fluorescence spectra were obtained at their respective maximum excitation wavelength. Coumarin derivatives substituted an electron-donating group were known to exhibit strong fluorescence. The fluorescence quantum yields (Table 1) of compounds (1-5) were determined via comparison method. The electron donating substituent i.e., (N-NH) group 1-5 exhibited longer emission wavelength ranging from 393 to 472 nm [27], where benzocoumarin part served as strong

donor [28-31] to constitute a strong push-pull system to exhibit high fluorescent intensities.

Table 1. Electronic absorption (UV λ_{Max}), emission (Em λ_{Max}) and Stoke shifts of compounds (1-5)

No.	λ_{Max} (nm)	Excitation (nm)	Emission (nm)	Stoke shifts (nm)
1	237, 263	329	443	114
2	241, 293	321	395	74
3	256, 266	326	401	75
4	273, 301	311	472	161
5	270, 289	324	393	69

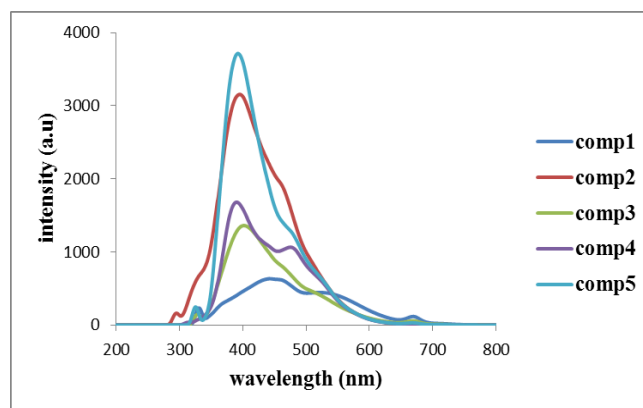


Figure 1. Excitation spectra of compounds (1-5)

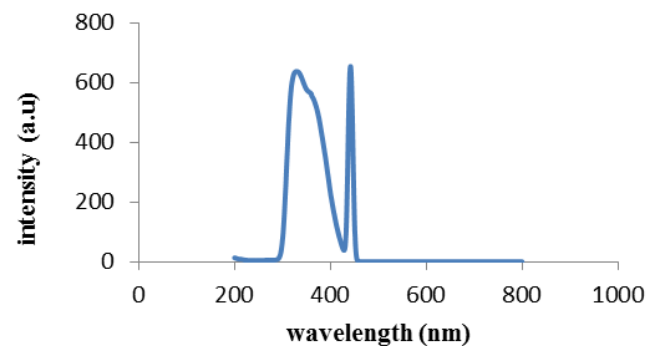


Figure 2. Fluorescence emission of compound (1)

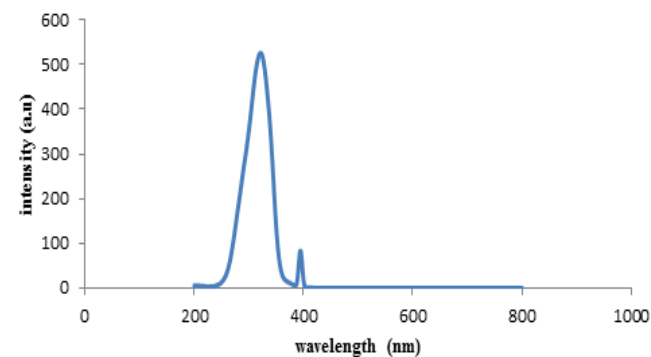


Figure 3. Fluorescence emission of compound (2)

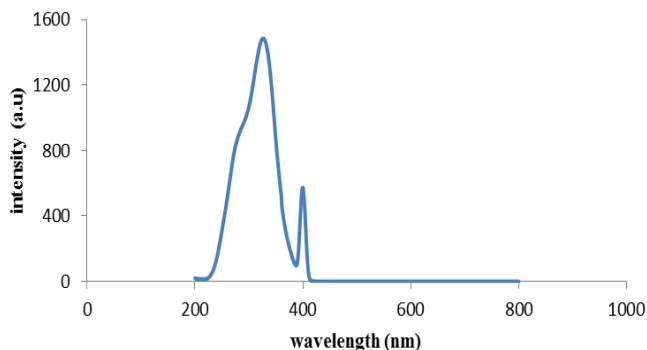


Figure 4. Fluorescence emission of compound (3)

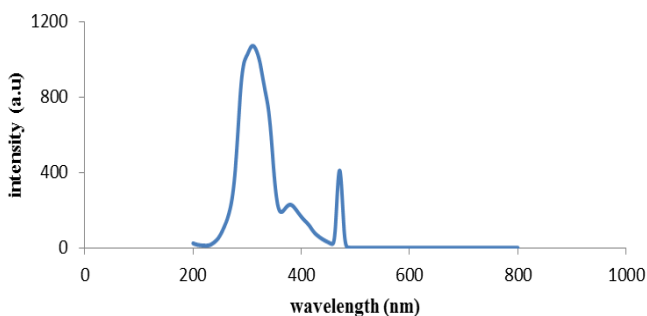


Figure 5. Fluorescence emission of compound (4)

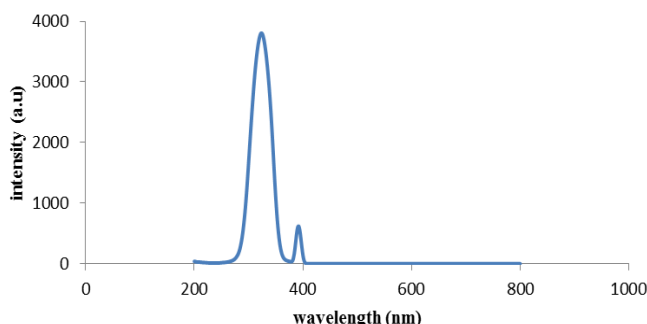


Figure 6. Fluorescence emission of compound (5)

4. Conclusions

A series of new cyclic compounds based 4-hydroxycoumarin were successfully synthesized and structures were confirmed by spectral analysis performed by IR, NMR and elemental analysis. The fluorescence properties of all the synthesized compounds were studied in ethanol. The results obtained were interesting that the compounds (1-5) shows fluorescent in ethanol with high quantum yield and show high activity.

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REFERENCES

- [1] Geddes, C. D. et al., Metal-Enhanced Fluorescence (MEF) Due to Silver Colloids on a Planar Surface: Potential Applications of Indocyanine Green to in Vivo Imaging, *J. Phys.Chem. A*. 107, 3443–3449 (2003).
- [2] Noginov, M. A. et al., Demonstration of a spaser-based nanolaser, *Nature*. 460, 1110–1112(2009).
- [3] Seidel, J., Grafstroem, S., Eng, L. Stimulated emission of surface plasmons at the interface, *Phys. Rev. Lett.* 94, 177401 (2005).
- [4] Oulton, R.F., Surface plasmon lasers: sources of nanoscopic light, *Materials Today* 15, 26–34 (2012).
- [5] Aslan, K., Leonenko, Z., Lakowicz, J. R., Geddes, C. D. Annealed silver-island films for applications in metal-enhanced fluorescence: interpretation in terms of radiating plasmons, *J. Fluoresc.* 15, 643–654 (2005), and references therein.
- [6] Aslan, K., Gryczynski, I., Malicka, J., Lakowicz, J.R. Geddes, C.D., Metal-Enhanced Fluorescence: An Emerging Trend in Biotechnology, *Curr. Opin. Biotechnol.* 16, 55–62 (2005)
- [7] Riveiro M. E., Moglioni A., Vazquez R., Gomez N., Facorro G., *Bioorg. Med. Chem.*, 2008, 16, 2665 .
- [8] Riveiro M. E., Vazquez R., Moglioni A., Gomez N., Baldi A., *Biochem. Pharmacol.*, 2008, 75, 725.
- [9] Spino C., Dodier M., Sotheeswaran S., *Bioorg. Med. Chem. Lett.*, 1998, 8, 3475
- [10] Jih R. H., Raghunath S., Shih C. H., Yung H. C., Asish R. D., *Antiviral Research*, 2008, 77, 157.
- [11] Samir B., Ramy R., Hassan A. E., Ahmed A. F., *Eur. J. Med. Chem.*
- [12] Christos A. K., Dimitra H. L., *Bioorg. Med. Chem. Lett.*, 2004, 14, 611
- [13] Manjunath G., Manohar D., Kulkatni V., Shobha R., *Eur. J. Med. Chem.*, 2003, 38, 297.
- [14] Rene T., Francesca F., Brenda M., Francisco U., *Phytochemistry*, 2006, 67, 984.
- [15] Shapiro, S.; Sherwin, B. Thromboembolization. II. The use of dicumarol (3,3'-methylenebis (4hydroxycoumarin) in embolization. Report of five cases. *N. Y. State J. Med.* 1943, 43, 45–52.
- [16] Butsch, W.L.; Stewart, J.D. Administration of dicoumarin compound for prophylaxis of postoperative thrombosis and embolism. *Arch. Surg.* 1942, 45, 551–553.
- [17] Hintz K.K; Ren J. Tetramethylpyrazine elicits disparate responses in cardiac contraction and intracellular Ca (2+) transients in isolated adult rat ventricular myocytes. *Vascul. Pharmacol.* 2003, 40, 213–217.
- [18] Ivana, K.; Andrea, J.; Pavol, K. Synthesis of coumarin or ferrocene labeled nucleosides via Staudinger ligation. *Beilstein J, Org. Chem.* 2006, 2, No. 23.
- [19] Lee, K. S.; Kim, H. J.; Kim, G. H.; Shin, I.; Hong, J. I. Fluorescent chemodosimeter for selective detection of cyanide in water. *Org. Lett.* 2008, 10(1),49-51.

- [20] Zhou, S. H.; Jia, J. H.; Gao, J. R.; Han, L.; Li, Y. J.; Sheng, W. J.. The one-pot synthesis and fluorimetric study of 3-(2-benzothiazolyl)coumarins. *Dyes and Pigments*. 2010, 86, 123-128.
- [21] Moeckli, P. Preparation of some new red fluorescent 4-cyanocoumarin dyes. *Dyes and Pigments*. 1980, 1, 3-15.
- [22] Kuo, P. Y.; and Yang, D. Y. Design of a coumarin-based triketone as a fluorescent protecting group for primary amines. *J. Org. Chem*. 2008, 73, 6455-6458.
- [23] Murata, C.; Masuda, T.; Kamochi, Y.; Todoroki, K.; Yoshida, H.; Nohta, H.; Yamaguchi, M.; Takadate, A. Improvement of fluorescence characteristics of coumarins; syntheses and fluorescence properties of 6-methoxycoumarin and benzocoumarin derivatives as novel fluorophores emitting in the longer wavelength region and their application to analytical reagents, *Chem.Pharm. Bull*. 2005, 53(7), 750758.
- [24] Al-Majedy, Y., Kadhum, A. H., Al-Amiery, A. A. and Mohamad, A. ynthesis and Characterization of Some New 4-Hydroxycoumarin Derivatives. *Molecules* 2014, 19, 11791-11799.
- [25] Sadashiva, B. K.; Prasad, V. Mesomorphic properties of 1-(4 dodecylbiphenyl-4-yl)-3-(2 or 3 alkoxyphenyl) propane-1,3 diones: The influence of alkoxy substituent position. *J, Chem, Soc. Perkin Trans*, 1996, 2, 755-759.
- [26] Radhika, S.; Srinivasa, H. T.; Sadashiva, B. K. Anticlinic smetic c phase in new and novel five-ring hockey stick-shaped compounds. *Liq. Cryst*. 2011, 38, 785-792 and references cited therein.
- [27] Magde D. R., Rojas G. E., Seybold P. G., *Photochem. Photobiol.*, 1999, 70, 737.
- [28] Rajesha.; Naik, H. S. B.; Kumar, H. N. H.; Hosamani, K. M.; Mahadevan, K. M. Studies on the synthesis and fluorescent properties of long-chained 2-(5-alkyl-1, 3,4-oxadiazol-2-yl)-3Hbenzo[f]chromen-3-ones. *Arkivoc*. 2009, (ii), 11-19.
- [29] Rajesha, G.; Kumar, H. C. K.; Naik, H. S. B.; Mahadevan, K. M. Synthesis of new benzocoumaryl oxadiazolyls as strong blue-green fluorescent brighteners. *S. Afr. J. Chem*. 2011, 64, 88-94.
- [30] Rajesha, Kiran K.H.C.; Bhojya, N. H. S.; Mahadevan, K. M. Synthesis and fluorescence study of 2-[5-(2-arylethenyl)-1, 3, 4-oxadiazol-2-yl]-3H-benzo[f]chromen-3-ones. *Org. Chem. Indian J*. 2012, 8(1), 34-40.
- [31] Harishkumar, H. N.; Mahadevan K. M.; Masagalli, J.N. Facile synthesis of 2-(1,3benzoxazol/benzothiazol-2-yl)-3H-benzo[f]chromen-3-one as blue fluorescent brighteners. *S. Afr. J. Chem*, 2012, 65, 5-9.