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New Chromophore Systems from Coumarin-Oxazol-5-one Combination

Derya Topkaya¹ · Serap Alp¹

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Abstract Coumarin-oxazol-5-one (COX), 3a-d, were synthesized with 7-methoxy-2-oxo-2H-chromene-4-carbaldehyde and benzoylglycine derivatives. The characterizations of the COX derivatives by ¹H NMR, FT-IR and elemental analysis were achieved. To obtain the photophysical data of the synthesized COX derivatives were used spectrophotometric and spectrofluorimetric methods. Evaluation of the absorption and emission properties of the structures was carried out in six different solvents. Maximum absorption and emission wavelengths (λ ; nm), molar extinction coefficients (ε ; cm⁻¹ M⁻¹), Stoke's shifts ($\Delta\lambda_{ST}$; nm) and quantum yields (ϕ_F), of the COX derivatives were declared.

Keywords Coumarin · Oxazol-5-one · Chromophore

Introduction

Coumarin derivatives have an important position in synthetic organic chemistry and naturally occurring products, they have been extensively investigated for different studies [1–5]. Because of their high thermal stability, superior optical properties and photostability, they have many optical applications in laser dyes [6], polymers science [7, 8], optical recording and solar energy collectors [9–11]. Furthermore, coumarins are used as non-linear optical chromophores and as a probe to study solvation dynamic in homogeneous solutions as well as arranged media [12–14].

Another feature of the coumarin derivatives is that photophysical and spectroscopic properties can be easily changed by the connection of different substituent to the coumarin ring and this position giving them more flexibility to fit well in various applications. For example, coumarins substituted at position 7 with an electron-donating group are exhibited strong fluorescence [15]. In the previous studies have been reported that the photophysical properties like maximum wavelength, quantum yield, lifetime, polarization, and excited-state dipole moment of these compounds not only depend on the position of substituent group in the molecule but also vary with surrounding media [16–21].

Coumarin derivatives are well known as having high levels of biological activity besides the photophysical properties. For example, polycyclic coumarin derivatives like calanolides which obtained from Callophyllum plant have anti-HIV (NNRTI) properties [22]. Coumarins are found at the structure of some antibiotics such as novobiocin, clorobiocin and coumermycin A_1 and these antibiotics are strong catalytic inhibitor of the DNA [23]. In many studies it has been reported that 7-hydroxycoumarin derivatives show anti-tumor activity in the human tumor cell [24].

Coumarins can be synthesized by various methods including the Perkin [25], Pechmann [26], Knoevenagel [27], Reformatsky [28] and Wittig [29] reactions. Among these, the Pechmann reaction has been the most widely used method since it proceeds from very simple starting materials and gives good yields of variously substituted coumarins. Substituted phenols are condensed with β -keto esters in the presence of an acid to afford coumarins. Various acids have been used to carry out this reaction [30–32].

The other part of the synthesized target molecule consists of oxazol-5-one derivatives. Oxazol-5-ones exhibit a wide spectrum of pharmacological activities including anticancer, antimicrobial, antifungal, sedative, etc. [33]. Oxazol-5-ones that are internal anhydrides of N-acyl amino acids make an important class of five-membered heterocycles. These are

Serap Alp serap.alp@deu.edu.tr

¹ Department of Chemistry, Faculty of Sciences, Dokuz Eylul University, Tinaztepe Campus, 35160, Buca, Izmir, Turkey

highly versatile intermediates used for the synthesis of several organic molecules, including amino acids, peptides, antimicrobial or antitumor compounds [34].

Recently, oxazol-5-one derivatives containing N-phenylaza-15-crown-5 moiety [35] or carbazole structures [36] have been synthesized and evaluations of the spectroscopic properties of these derivatives have been carried out in different solvents.

In this study, coumarin-oxazol-5-one (COX) derivatives were synthesized to combine the advantages of coumarin and oxazol-5-one heterocyclics. For this purpose, four pushpull substituted COX derivatives were obtained and the basic photophysical properties were exhibited.

Experimental

Reagents and Apparatus

All solvents used in this study were analytical grade and have been purchased from Merck, Fluka, and Riedel. All melting points were measured in sealed tubes using an electrothermal digital melting points apparatus and are uncorrected. Infrared spectra were recorded on a Perkin ELMER FTIR infrared spectrometer (spectrum BX-II). ¹H-NMR spectra were obtained on a high resolution fourier transform Bruker WH-400 NMR spectrometer with CDCl₃ as an internal standard. Analytical and preparative thin layer chromatography (TLC) was carried out using silica gel &0 HF_254 (Merk). Column chromatography was carried out by using 70–230 mesh silica gels (0.063–0.2 mm, Merk). UV/visible absorption spectra were recorded with Schimadzu UV-1601 spectrophotometer. All fluorescence measurements were undertaken by using Varian-Carry Eclipse spectrofluorimeter.

Synthesis

The synthetic route of the target compounds is presented in Fig. 1.

Synthesis of 7-methoxy-4-methyl-2H-chromen-2-one (1)

3-methoxyphenol (12.4 g, 0.1 mol) was dissolved in 15 mL of 75% concentrated H_2SO_4 , then solution was heated to 75 °C and ethyl acetoacetate (13.4 g, 0.1 mol) was added dropwise. After 40 min, the reaction solution was poured into 100 g ice. The precipitate was collected, washed with water and recrystallized with ethanol [18].

Yield %85, mp 156-158 °C,

FT-IR (KBr) (cm⁻¹): 3065, 3022 (=CH), 2949 (-CH), 1725 (-O-C = O), 1608(-C = C-),

¹H NMR (CDCl₃) (ppm); 2.40 (s, 3H, Me); 3.78 (s, 3H, -OMe); 6.13 (s, 1H, H₃); 6.76–7.51 (m, 3H, H₅, H₆, H₈);

Synthesis of of

7-methoxy-2-oxo-2H-chromene-4-carbaldehyde (2)

7-methoxycoumarin (1.9 g 0.01 mol) was dissolved in 50 mL dimethylbenzene during heating. Following this, selenious acid (1.93 g, 0.015 mol) was added. The reaction solution was refluxed for 20 h. After the work up and purification processes, the yellow crystal product was obtained [4].

Yield %78 mp 128-130 °C.

FT-IR (KBr) (cm⁻¹): 3057–2985 (=CH), 2960, 2744 (-CH), 1724, (-O-C = O), 1704(-HC = O) 1613 (-C = C-) cm⁻¹.

¹H NMR (CDCl₃, 400 MHz) δ(ppm); 3.97 (s, 3H, -OMe); 6.50 (s, 1H, H₃); 6.97–7.95 (d,1H, H₈); 6.97–7.95 (d,1H, H₆); 7.01(s,1H, H₈); 7.98(s,1H, H₅); 10,61(s,1H, H-C = O). Anal. calcd. for C₁₁H₈O₄: C, 64.65; H, 3.91. Found: C, 64.49; H, 3.89.

General Synthesis of coumarin-oxazol-5-one (COX) Derivatives (3a-d)

A solution of 4-formyl-7-methoxy coumarin 2 (1 g; 4.88 mmol), 4-methylbenzoyl glycine (1.16 g; 4.88 mmol), acetic anhydride (1.84 mL; 9.76 mmol) and sodium acetate (0.66 g; 4.88 mmol) was heated until the mixture just liquefied, and then heating was continued for 4 h. After completion of the reaction (determined by thin layer chromatography), ethanol (20 mL) was added and the mixture was kept at room temperature for 18 h. The solid product thus obtained was purified by washing cold ethanol, hot water and then a small amount of hexane. The solid was recrystallized from hot ethanol to afford pure crystals of 3c [34]. The other coumarin-oxazol-5-ones were prepared the same procedure using appropriate glycine derivatives 3a, 3b and 3d.

Structural Analysis of 4-[(7-methoxy-2-oxo-2H-chromen-4-yl)methylene] -2-phenyl-1,3-oxazol-5(4H)-one (3a)

Yield: 70%. M.p. 245–248 °C.

FT-IR (KBr) (cm⁻¹): 3088–3010 (=CH), 2944 (-CH), 1732 (-O-C = O, -coumarin-), 1801 (-O-C = O, -oxazol-5-one-), 1623 (-C = N-),

¹H NMR (CDCl₃) (ppm); 3.91 (s, 3H, -OCH₃), 6.95–6.89 (m, 2H, H₆", H₈"); 7.60–7.55 (m, 3H, H₃", H₅", H₃"); 7.68–7.69, (t,1H, H₄"); 7.72–7.70 (d,1H, H₅"); 8.23–821 (d, 2H, H₂", H₆"). Anal. calcd. for $C_{20}H_{13}NO_5$: C, 69.10; H, 3.74; N, 4.03 Found: C, 68.86; H, 3.46, N, 3.85.

Structural Analysis of 4-[(7-methoxy-2-oxo-2H-chromen-4-yl)methylene]-2-(1-naphthyl)-1,3-oxazol-5(4H)-one(3b)

Yield: 65%. M.p. 224-228 °C.

FT-IR (KBr) (cm⁻¹): 3092-3014 (=CH), 2935 (-CH), 1717 (-O-C = O, -coumarin-), 1797 (-O-C = O, -oxazol-5-one-), 1615 (-C = N-),

Fig. 1 Synthetic route of COX derivatives. i) Ethyl acetoacetate, 12 M H₂SO₄, 80 °C, 6 h; ii) H₂SeO₃, 1,4-dioxan, 24 h reflux, iii) NaOAc, Ac₂O, ArCONHCH₂COOH, 80 °C, 3 h



H₃C





Fig. 2 Schematic structures of COX (3a-d) derivatives. (3a) (4Z)-4-[(7-methoxy-2-oxo-2Hchromen-4-yl)methylene]-2-phenyl-1,3-oxazol-5(4H)-one. (3b) (4Z)-4-[(7-methoxy-2-oxo-2H-chromen-4-yl)methylene]-2-(1-naphthyl)-1,3-oxazol-5(4H)one. (3c) (4Z)-4-[(7-methoxy-2oxo-2H-chromen-4yl)methylene]-2-(4-nitrophenyl)-1,3-oxazol-5(4H)-one. (3d) (4Z)-4-[(7-methoxy-2-oxo-2H-chromen-4-yl)methylene]-2-(4methylphenyl)-1,3-oxazol-5(4H)one

¹H NMR (CDCl₃) (ppm); 3.91 (s, 3H, -OCH₃), 6. 96–6.89 (m, 2H, H₆", H₈"); 7.42 (s, 1H, H_f) 7.56–7.65 (m, 3H, H₅", H₆", H₃"); 7.73–7.79, (m,2H, H₃", H₅"]); 7.95–7.97 (d,1H, H₇"); 8.15–8.17 (d, 1H, H₄"); 8.46–8.48, (d, 1 H, H₂"), 9.37–9.39 (d, 1H, H₈").

Anal. calcd. for $C_{25}H_{15}NO_5$: C, 75.49; H, 3.77; N, 3.52 Found: C, 75.27; H, 3.56, N, 3.59.

Structural Analysis of 4-[(7-methoxy-2-oxo-2Hchromen-4-yl)methylene]-2-(4-nitrophenyl)-1,3-oxazol-5(4H)-one (3c)

Yield: 53%. M.p. 263-264 °C.

FT-IR (KBr) (cm⁻¹): 3092–2969 (=CH), 2841(-CH), 1707 (-O-C = O, -coumarin-), 1799 (-O-C = O, -oxazol-5-one-), 1612 (-C = N-), 1557 (-NO₂) cm⁻¹.

¹H NMR (CDCl₃) (ppm); 3.87 (s, 3H, -OCH₃), 6.68 (s, 1H, H_{3"}); 6. 90–6.87 (s, H_{6"}); 6.99, (s,1H, H₈"), 7.42 (s, 1H, H_f),

7.72–7.70, (d, 1H, H_{5"}); 8.16–8.18 (d, 2H, H_{2'}, H_{6'}); 8.29–8.27 (d, 2H, H_{3'}, H_{5'}).

Anal. calcd. for $C_{20}H_{12}N_2O_7$: C, 61.17; H, 3.05; N, 7.13 Found: C, 60.57; H, 3.05; N, 6.92.

Structural Analysis of 4-[(7-methoxy-2-oxo-2Hchromen-4-yl)methylene]-2-(4-methylphenyl)-1,3oxazol-5(4H)-one (3d)

Yield: 45%. M.p. 239-242 °C.

FT-IR (KBr) (cm⁻¹): 3080–3010 (=CH), 2981(-CH), 1712 (-O-C = O, -coumarin-), 1800 (-O-C = O, -oxazol-5-one -), 1613 (-C = N-),

¹H NMR (CDCl₃) (ppm); 3.91 (s, 3H, -OCH₃), 6.94– 6.90 (m, 2H, H_{6"}, H_{8"}); 7.36–7.39 (m, 3H, H₃', H_{3"}, H₆'); 7.67 (s, 1H, H_f); 7.72–7.70 (d, 1H, H₅"); 8.10– 8.12 (d, 2H, H₂', H₆').



Fig. 3 ¹H NMR spectrum of 3d

Table 1 Spectral data obtainedfrom absorption and emissionspectra for compouns 3a-3d

		λ^{ab}_{max} (nm)	$\overset{\epsilon_{max}}{(M^{-1} \text{ cm}^{-1})}$	λ^{emis}_{max} (nm)	λ^{exc}_{max} (nm)	$\Delta\lambda$ (nm)	$\phi_{\rm f}$
3a	Toluene	365	10,900	540	362	175	
	Xylene	368	10,400	537	361	179	
	Dichloromethane	366	44,347	555	361	189	0,19
	Tetrahydrofuran	365	27,200	560	365	195	0,17
	Chloroform	377	2990	530	377	153	
	Acetonitrile	357	7800	577	365	220	0,13
3b	Toluene	402	10,000	545	405	143	
	Xylene	401	34,170	545	410	144	
	Dichloromethane	400	15,384	577	400	177	0,67
	Tetrahydrofuran	393	14,800	592	391	199	0,39
	Chloroform	408	17,400	570	415	162	
	Acetonitrile	391	22,000	570	520	179	0,22
3c	Toluene	358	31,800	564	361	203	
	Xylene	357	12,300	565	361	204	
	Dichloromethane	356	11,671	583	361	222	0,06
	Tetrahydrofuran	371	15,000	597	355	242	0,07
	Chloroform	360	14,000	566	300	206	
	Acetonitrile	352	15,000	570	360	218	0,05
3d	Toluene	358	31,800	564	361	203	
	Xylene	357	12,300	565	361	204	
	Dichloromethane	373	12,044	550	370	180	0,32
	Tetrahydrofuran	371	22,000	555	361	194	0,20
	Chloroform	377	20,000	541	377	164	
	Acetonitrile	365	30,000	570	365	144	0,12

Anal. calcd. for $C_{21}H_{15}NO_5$: C, 69.73; H, 4.05; N, 3.875 Found: C, 70.23; H, 3.93; N, 4.03.

Results and Discussion

Figure 2 shows schematic structures of the newly synthesized four COX derivatives according to synthetic route at Fig. 1.



Firstly, 3-methoxy phenol was condensed with β -keto ester in the presence of an acid to prepared 7-methoxy-2-oxo-2Hchromene-2-one by Pechmann reaction [18]. After that, methyl group at four position of the coumarin ring in this derivative was oxidized to aldehyde with selenious acide [37]. Oxazolone derivatives were performed by condensation reaction of several benzoylglycine derivatives with this aldehyde group on the coumarin ring [34]. The structural analysis of the





Fig. 5 Emission and excitation spectra of compounds 3a-d measured in dichloromethane

synthesized derivatives was done by elemental analysis, FT-IR and ¹H-NMR spectroscopic techniques. The ¹H–NMR spectrum of 3d derivative was given as an example in Fig. 3. Absorption and emission spectroscopic studies of all COX derivatives were performed in the solvents of toluene, xylene, dichloromethane, tetrahydrofuran, chloroform and acetonitrile (Table 1, Figs. 4 and 5).

Although COX derivatives have two different chromophore parts, which are coumarin and oxazol-5-one ring, the



Fig. 7 The photostability test result of 3a-d in dichloromethane after 1 h of monitoring

recorded absorption spectra of the COX derivatives demonstrated only one absorption band over 300 nm (See Fig. 4). The molecules excited around maximum absorption wavelengths, the recorded fluorescence emission spectra were again demonstrated only one emission band (See Fig. 5) as shown in Table 1. This can be attributed that the new chromophore system formed by integration of two different chromophores (coumarin and oxazole-5-one). Other evidence can be found with evaluation of IR spectra. The infrared spectra of these derivatives support where the most delocalization part occurred in new COX compounds. The wavenumber values



Fig. 6 The infrared spectra of 3a-3b derivatives and the wavenumber values of carbonyl stretching vibration bands

of carbonyl stretching vibration bands given in Fig. 6 are used for explaining this concept. From the analysis of these bands, it can be concluded that, while the carbonyl group of oxazol-5-one is not influenced with the exchange of aryl groups, the carbonyl group of coumarin is influenced. As a result, the electronic delocalization of COX derivatives have changed and a new chromophore system has occurred. The new chromophore systems have shown with bold black parts on molecule structures in Fig. 2.

To determine the photophysical parameters UV-vis absorption and emission spectra of COX derivatives were measured and given in Table 1. Evaluation of the absorption and emission properties of the structures was carried out in six solvents having different polarity.

Molar extinction coefficients and Stokes' shift values of each derivative in all solvents were calculate to be in the range of $1.0 \times 10^{4-4}$.5 $\times 10^{4}$ cm⁻¹ M⁻¹ and 143–242 nm respectively.

Quantum yield values were also calculate only in three solvents, acetonitrile, tetrahydrofuran and dichloromethane. 8-hydroxypyrene-1,3,6-trisulfonic acid trisodium salt (HPTS) was used as reference quantum yield standard at $\lambda_{ex} = 400$ nm and the quantum yields (Φ_F) of synthesized COX derivatives were determined by the formula [38]:

$$\Phi = \Phi_{\text{std}} x \left(F A_{\text{std}} \eta^2 \right) / \left(F_{\text{std}} A \eta_{\text{std}}^2 \right)$$

where *F* and *F*_{std} are the areas under the fluorescence emission curves of the samples and the standard. *A* and *A*_{std} are the respective absorbance of the samples and standard at the excitation wavelength and η and η_{std} the refractive indexes of solvents used for the samples and standard. 3b derivative in dichloromethane exhibited the highest quantum yield values of 0.67. This can be explaining by the reduced charge transfer efficiency of the molecules to the solvent in the excited state due to the steric effects of naphthalene.

The photostabilities of 3a-3d derivatives were tested in all solvents. Using the xenon arc lamp, photostability tests of COX derivatives were carried out with a steady state spectro-fluorimeter in the mode of "Time Based Measurements". All of the derivatives were excited at around 370 nm and the data were acquired at their maximum emission wavelengths during one hour of monitoring. During the monitoring, no decreases were determined any COX derivatives in all solvents. As a result, the photostabilities of COX derivatives in all solvents can be saying as excellent. The acquired data of 3a-3d in dichloromethane were shown as an example in Fig. 7.

Conclusions

In this study, new coumarin-oxazol-5-one derivatives (3a-3d) are successfully synthesized. The derivatives were prepared

by substituting at the 2- position of the oxazol-5-one ring in order to form a set of push-pull effect. After the structural characterization by ¹H NMR, FT-IR, elemental analysis, the photophysical properties of the new compounds were studied by UV–vis and emission spectroscopy. As it was expected, the characteristic absorption and emission bands of the two different heterocyclic coumarin and oxazolone chromophore systems at the new synthesized molecules were not observed. Surprisingly, a single new absorption and emission bands in different wavelengths were detected. This can be attributed to the formation of a new chromophore system with high molar extinction coefficients the Coumarin-oxazol-5-one derivatives. By evaluation of the carbonyl stretching bands extracted from the FT-IR Spectra, forming of the new chromophore were also proved.

Emission quantum yields were obtained for all derivatives in several solvents. Among them, 3b derivative in dichloromethane exhibited the highest quantum yield value of 0.67. This favourable value can be defined with the effect of naphthalene having condensed π electron system.

Consequently, because of the chemical and biological activities of the coumarin and oxazol-5-one cores, all COX compounds are promising for future works.

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