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Synthesis, Electronic Absorption, Fluorescence and Live Time Spectroscopic Study of Some New 3,7-Disubstituted Coumarin Derivatives as New Fluorescent Probes

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The synthesis of several novel 3-heterocyclic substituent-7-methoxycoumarin derivatives were carried out starting from 3-acetyl-7-hydroxy-2*H*-chromen-2-one (**3**), which reacted with DMF-DMA affords enaminone **4** which transformed into pyranone **8**, pyridine derivative **12a,b**, **23**, **24**, triaroylbenzene **22** and fuaranone **17** with treatment with hippuric acid (**5**), acetyl acetone (**12a**), ethyl acetoacetate (**12b**), acetic acid and ammonium acetate, 3-acetyl-7- hydroxy-2*H*-chromen-2-one (**3**), acetic acid and 1,4-naphthoquinone (**15**) respectively. The UV-visible, fluorescence and live time spectra for compounds were determined. Most of them displayed high fluorescence quantum yields ranging from 0.70 to 0.99 and life times in the nanosecond range, which can make these new 3-heterocyclic substituent-7-methoxycoumarin compounds very useful as new fluorescent probes.

Keywords: Fluorescence, Lifetimes, Coumarin, Enaminone, Pyridine, Fuaranone.

INTRODUCTION

Many coumarin derivatives have attracted considerable interest owing to their wide spectra of biological activities [1,2] such as antiproliferative and anticancer activities [3-8]. These coumarin derivatives find their application in pharmaceuticals, fragrances, agrochemicals and insecticides [9-11]. A literature survey revealed that a great deal of interest has been focused on the synthesis of functionalized coumarin derivatives due to their photochemical, photophysical properties [12], dispersed fluorescent and laser materials [13]. 7-Hydroxy-3-substituted heterocyclic coumarin derivatives among the efficient photostable laser materials, which is emitting in the blue-green region of the visible light. The lasing range produced by this coumarin derivatives were appreciably extended when the substituent is a heterocyclic moiety [14-16]. In the light of the above findings and in continuation of our efforts to synthesize new heterocyclic compounds and study its photophysical, photochemical characteristics, isomerization and tautomerism using absorption and emission spectra [13,17-25]. This work aims to synthesize a new 7-methoxycoumarin derivatives bearing different heterocyclic substituent moiety at the 3-position in which the six membered heteroaromatic ring are attached through a conjugated 3-aroyl ring or directly to the coumarin moiety, which expected to be used as new photostable laser materials and fluorescent probes. All compounds were studied from their UV-visible, emission and live time spectra.

EXPERIMENTAL

Melting points were measured on an Electrothermal IA 9000 series digital melting point apparatus. IR spectra were recorded in potassium bromide discs on PyeUnicam SP 3300 and Shimadzu FTIR 8101 PC infrared spectrophotometers. ^{1}H and ^{13}C NMR spectra were recorded on JEOL JNM-LA 500 FT NMR spectrometer at 300 MHz (^{1}H NMR) and run in deuterated chloroform ($CDCl_3$) or deuterated dimethyl sulfoxide (DMSO-d_6). Chemical shifts were related to that of the solvent. Mass spectra were recorded on a Shimadzu GCMS-QP1000 EX mass spectrometer at 70 eV. Elemental analyses were measured by using a German made Elementarvario LIII CHNS analyzer.

UV-visible spectra were recorded on Perkin-Elmer Lambda 5 spectrophotometer. Fluorescence spectra were measured on SPF-500 spectrofluorometer from SLM Instruments and all this spectra were corrected for the intensity of the lamp and the sensitivity of the photomultiplier tube.

The photochemical quantum yields (Φ) were determined using the next classical equation:

$$\Phi_x = (A_s \times F_x \times n_x^2 \times \Phi_s)/(A_x \times F_s \times n_s^2)$$

where A is the absorbance at the excitation wavelength, F is the area under the fluorescence curve and n is the refraction index. Subscripts s and x refer to the standard and unknown sample, respectively. The standard using is quinine sulphate dissolved in 1 N H_2SO_4 (Φ = 0.55) [16,26].

Live time spectra were determined with a mode-loked Nd:YAG laser (spectra-Physics model 3800) with a mode locker (spectra-Physics model 451) operating at 82 MHz repetition rate was used to pump a rhodamine 6G dye laser. Cavity dumping at 4 MHz was performed. The output pulses were frequency doubled (spectra-Physics model 390 frequency doubler). The $\lambda_{excit.}$ was 300 nm and the fluorescence decay signals of the probe molecule were collected at the λ_{max} of fluorescence. Lifetime spectra were determined using the Applied Photophysics photon-counting spectrometer (Model PS 60. Equipped with a XP 2020Q photomultiplier). The actual pulse width of the excitation pulse < 10 ps; however, due to the response time of the photon counting system it is broadened to 350 ps. Data were collected through a multichannel analyzer and then transferred to a computer for analysis.

3-Acetyl-7-hydroxy-2*H*-chromen-2-one (**3**) were prepared as previously described [26].

Synthesis of 3-[3-(dimethylamino)prop-2-enoyl]-7-methoxy-2*H*-chromen-2-one (4): A mixture of dimethyl formamide-dimethylacetal DMF-DMA (1.19 g, 10 mmol) and 3-acetyl-7- hydroxy-2*H*-chromen-2-one (**3**) (2.04 g, 10 mmol) was fused for 0.5 h at 120 °C. The formed solid after cooling was filtered off, washed with ethanol, dried and finally crystallized from ethanol to give pure product of compound 3-[3-(dimethylamino)prop-2-enoyl]-7-methoxy- 2*H*-chromen-2-one (**4**) as yellow solid.

Yield (75 %), m.p.: 220 °C (ethanol); IR (KBr, ν_{max}, cm^{-1}): 1712 (C=O); ^{1}H NMR (DMSO-d_6): δ 2.92 (s, 6H, $N(CH_3)_2$), 3.89 (s, 3H, OCH_3), 6.04 (d, *J* = 15 Hz, olefinic H), 6.96–7.83 (m, 4H, H Ar) and 8.53 (d, *J* = 15 Hz, olefinic H); MS *m/z* (EI): 273 (M^+). Anal. calcd. for $C_{15}H_{15}NO_4$ (273.28): C, 65.92; H, 5.53; N 5.13. Found: C, 65.84; H, 5.50; N 5.11 %.

Synthesis of *N*-[6-(7-methoxy-2-oxo-2*H*-chromen-3-yl)-2-oxo-2*H*-pyran-3-yl]benzamide (8): A mixture of compound **4** (2.73 g, 10 mmol) and hippuric acid (10 mmol) in acetic anhydride (50 mL) was refluxed for 3 h, The formed solid after cooling was filtered off, washed with ethanol, dried and finally crystallized from DMF To afford the corresponding *N*-[6-(7-methoxy-2-oxo-2*H*-chromen-3-yl)-2-oxo-2*H*-pyran-3-yl]benzamide (**8**). This compound was obtained as canary yellow solid.

Yield (75 %), m.p.: 292 °C; IR (KBr, ν_{max}, cm^{-1}): 3371 (NH), 1728 (CO), 1695 (CO) 1659 (amid CO); ^{1}H NMR (DMSO-d_6): δ 4.00 (s, 3H, OCH_3), 7.08-7.10 (m, 2H, H Ar), 7.59-7.70 (m, 6H, H Ar), 7.95 (d, *J* = 6Hz, 1H, pyran H-5), 8.28 (d, *J* = 6Hz, 1H, pyran H-4), 8.59 (s, 1H, coumarinyl H-4), 9.48 (s, 1H, NH); ^{13}C NMR: δ 55.80, 100.07, 105.88, 112.92, 113.34, 124.14, 124.09, 127.09, 127.22, 128.17, 130.57, 131.69, 134.21, 139.89, 148.41, 152.85, 155.20, 157.06, 163.53, 165.43; MS: *m/z* (EI) 389 (M^+). Anal. calcd. for $C_{22}H_{15}NO_6$ (389.35): C, 67.86; H, 3.88; N 3.60. Found: C, 67.72; H, 3.85; N 3.55 %.

Synthesis of 3-(6-methylpyridin-2-yl)-7-methoxy-2*H*-chromen-2-one derivatives (12a,b): A mixture of each compound **10a-b** (10 mmol), 3-[3-(dimethylamino)prop-2-enoyl]-7-methoxy-2*H*-chromen-2-one (**4**) (2.73 g, 10 mmol) and ammonium acetate (0.77 g, 10, mmol) in glacial acetic acid (30 mL) was refluxed for 2 h then left to cool to room temperature. The solid that separated was filtered off, washed with water and finally recrystallized from acetic acid to give the corresponding product, 3-(6-methylpyridin-2-yl)-7-methoxy-2*H*-chromen- 2-one derivatives **12a,b**.

3-(5-Acetyl-6-methylpyridin-2-yl)-7-methoxy-2*H*-chromen-2-one (12a): Yield (70 %); m.p.: 190 °C; IR (KBr, ν_{max}, cm^{-1}): 1720 (CO), 1674(CO), 1640 (CO); ^{1}H NMR (DMSO-d_6): δ 2.67 (s, 3H, CH_3), 2.78 (s, 3H, $COCH_3$), 3.96 (s, 3H, OCH_3), 7.07-7.98 (m, 3H, Ar-H), 8.3 (d, *J* = 7hz, 1H, pyridine H-4), 8.39 (d, *J* = 7 Hz, 1H, pyridine H-5), 8.99 (s, 1H, coumarinyl H-4); ^{13}C NMR: δ 29.37, 56.08, 59.08, 100.16, 112.64, 113.09, 119.86, 120.04, 130.92, 131.22, 138.32, 143.57, 152.14, 155.58, 159.36, 160.44, 163.57, 200.05; MS: *m/z* (EI) 309 (M^+). Anal. calcd. for $C_{18}H_{15}NO_4$ (309.31): C, 69.89; H, 4.89; N 4.53. Found: C, 69.79; H, 4.81; N, 4.53 %.

Ethyl 6-(7-methoxy-2-oxo-2*H*-chromen-3-yl)-2-methylnicotinate (12b): Yield (80 %); m.p.: 198 °C; IR (KBr, ν_{max}, cm^{-1}): 1721 (CO), 1672 (CO), 1645 (CO). ^{1}H NMR (DMSO-d_6): δ 1.42 (t, 3H, CH_3), 2.89 (s, 3H, CH_3), 3.9 (s, 3H, OCH_3), 4.40 (q, 2H, CH_2), 6.84-7.57 (m, 3H, Ar-H), 8.24 (d, *J* = 7 Hz, 1H, pyridine H-4), 8.34 (d, *J* = 7 Hz, 1H, pyridine H-5), 8.87 (s, 1H, coumarinyl H-4); ^{13}C NMR: δ 14.26, 25.08, 55.83, 61.14, 100.16, 113.19, 120.41, 124.33, 129.50, 130.17, 139.19, 143.71, 153.10, 156.06, 159.19, 160.37, 166.40; MS: *m/z* (EI) 339 (M^+). Anal. calcd. for $C_{19}H_{17}NO_5$ (339.34): C, 67.25; H, 5.05; N, 4.13. Found: C, 67.19; H, 5.01; N, 4.10 %.

3-[(5-Hydroxynaphtho[1,2-*b*]furan-3-yl)carbonyl]-7-methoxy-2*H*-chromen-2-one (17): To a stirred solution of 3-[3-(dimethylamino)prop-2-enoyl]-7-methoxy-2*H*-chromen-2-one (**4**) (2.73 g, 10 mmol) in glacial acetic acid (50 mL) 1,4-naphthoquinone (10 mmol) was added. Stirring was continued over night at room temperature. The reaction mixture was evaporated in vacuum and the formed solid products obtained were isolated by filtration and recrystallized from DMF to give 3-[(5-hydroxynaphtho[1,2-*b*]furan-3-yl)carbonyl]-7-methoxy-2*H*-chromen- 2-one (**17**) as yellow solid.

Yield (60 %); m.p.: 272 °C; IR (KBr, ν_{max}, cm^{-1}): 1720 (CO), 1640 (CO). ^{1}H NMR (DMSO-d_6): δ 3.96 (s, 3H, OCH_3), 7.1-8.34 (m, 7H, Ar-H), 8.57 (s, 1H, OH), 8.99 (s, 1H, coumarinyl H-4) and 10.4 (s, 1H, CHO); MS: *m/z* (EI) 386 (M^+). Anal. calcd. for $C_{23}H_{14}O_6$ (386.35): C, 71.50; H, 3.65 %. Found: C, 71.45; H 3.60 %.

3,3',3''-[Benzene-1,3,5-triyltri(carbonyl)]tris(7-methoxy-2*H*-chromen-2-one) (22): Compound 3-[3-(dimethylamino)-prop-2-enoyl]-7-methoxy-2*H*-chromen-2-one (**4**) (2.73 g, 10 mmol) was refluxed in glacial acetic acid (30 mL) for 2 h, then left to cool at room temperature. The precipitated material upon cooling was isolated by filtration and recrystallized from DMF to give 3,3',3''-[benzene-1,3,5-triyltri(carbonyl)]tris(7-methoxy-2*H*-chromen-2-one) (**22**) was obtained as canary yellow.

Yield (65 %); m.p.: 338 °C; IR (KBr, ν_{max}, cm^{-1}): 1720 (CO), 1659 (CO). ^{1}H NMR (DMSO-d_6): δ 3.96 (s, 9H, 3OCH_3),

7.10-8.01 (m, 9H, Ar-H), 8.55 (s, 3H, phenyl 2-H, 4H, 6-H), 8.58 (s, 3H, coumarinyl H-4); MS: *m/z* (EI) 684 (M^+). Anal. calcd. for $C_{39}H_{24}O_{12}$ (684.60): C, 68.42; H, 3.53. Found: C, 68.40; H, 3.50 %.

7-Methoxy-3-{5-[(7-methoxy-2-oxo-2*H*-chromen-3-yl)carbonyl]pyridin-2-yl}-2*H*-chromen-2-one (23): Compound 3-[3-(dimethylamino)prop-2-enoyl]-7-methoxy-2*H*-chromen-2-one (**4**) (2.73g, 10 mmol) and (0.77 g, 10 mmol) of ammonium acetate were refluxed in glacial acetic acid (30 mL) for 0.5 h, then left to cool at room temperature. The precipitated material upon cooling was isolated by filtration and recrystallized from DMF to afforded 7-methoxy-3-{5-[(7-methoxy-2-oxo-2*H*-chromen-3-yl)carbonyl]pyridin-2-yl}-2*H*-chromen-2-one (**23**) as yellow solid.

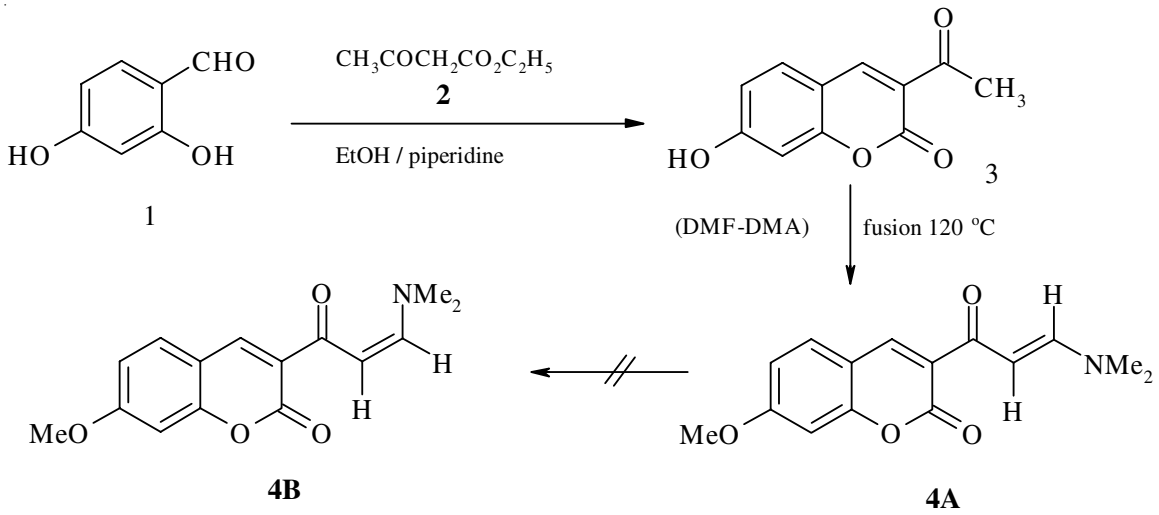
Yield: (65 %); m.p.: 260 °C; IR (KBr, ν_{max}, cm^{-1}): 1713 (CO), 1680 (CO); ^{1}H NMR (DMSO-d_6): δ 3.99 (s, 6H, $2OCH_3$), 7.08-7.94 (m, 6H, Ar-H), 8.35 (d, *J* = 8Hz 1H, pyridine H-3), 8.48 (d, *J* = 8hz,1H, pyridine H-4), 8.55 (s,1H, pyridine H-6), 9.029.13 (s, 2H, coumarinyl H-4); ^{13}C NMR: δ 55.77, 55.89, 100.44, 110.54, 111.38, 112.71, 112.84, 119.34, 121.90, 124.21, 129.32, 130.61, 131.15, 136.96, 143.72, 147.11, 148.12, 149.23, 154.95, 156.17, 156.58, 157.78, 159.40, 163.44, 164.64, 190.06; MS: *m/z* (EI) 455 (M^+). Anal. calcd. for $C_{26}H_{17}NO_7$ (455.43): C, 68.57; H, 3.76; N, 3.08. Found: C, 68.45; H, 3.75; N, 3.07 %.

7-Hydroxy-3-[6-(7-methoxy-2-oxo-2*H*-chromen-3-yl)pyridin-2-yl]-2*H*-chromen-2-one (24): A mixture of 3-[3-(dimethylamino)prop-2- enoyl]-7-methoxy-2*H*-chromen-2-one (**4**) (2.73 g, 10 mmol) and 3-acetyl-7-hydroxy-2*H*-chromen-2-one (**3**) (2.04 g, 10 mmol) in glacial acetic acid (30 mL) and (0.77 g, 10 mmol) of ammonium acetate, was refluxed for 1 h. The precipitated material was isolated by filtration and recrystallized from ethanol/DMF. To give 7-hydroxy-3-[6-(7-methoxy-2-oxo-2*H*-chromen-3-yl)pyridin-2-yl]-2*H*-chromen-2-one (**24**) as yellow crystals. Yield (65 %); m.p.: 292 °C; IR (KBr, ν_{max}, cm^{-1}): 1730 (CO), 1673 (CO); ^{1}H NMR (DMSO-d_6): δ 4.00 (s, 3H, OCH_3), 7.08-7.97 (m, 6H, Ar-H), 8.37 (d, *J* = 8 Hz, 1H, pyridine H-3), 8.47 (d, *J* = 8 Hz, 1H, pyridine H-4), 8.61 (d, *J* = 8 Hz, 1H, pyridine H-5), 10.73 (s, 1H, OH); MS: *m/z* (EI) 413 (M^+). Anal. calcd. for $C_{24}H_{15}NO_6$ (413.37): C, 69.73; H, 3.66; N, 3.39. Found: C, 69.70; H, 3.65; N 3.35 %.

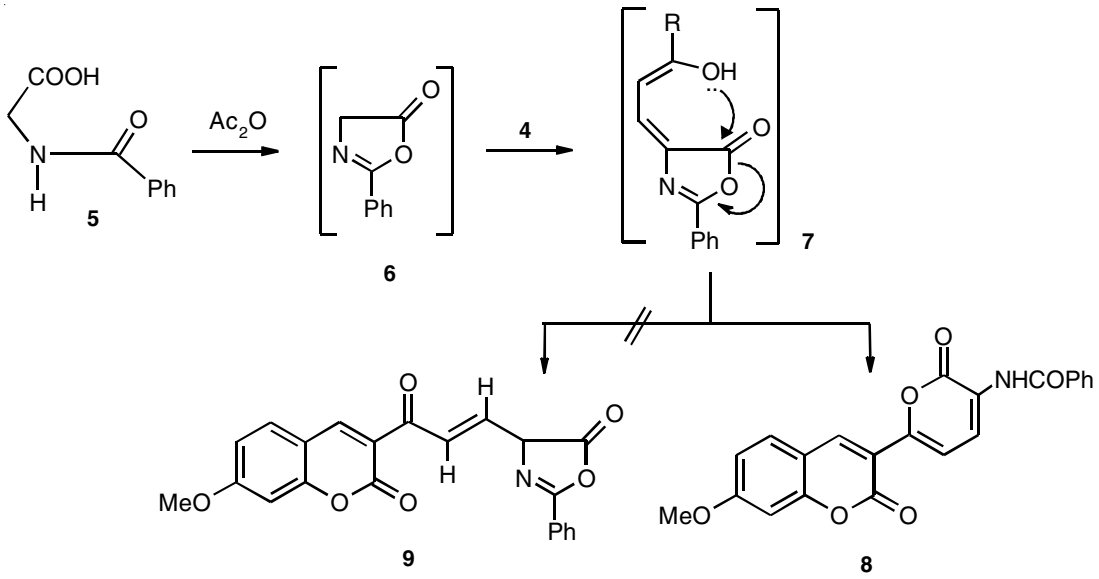
RESULTS AND DISCUSSION

In a previous work from our laboratory, we checked 3-substituted 7-hydroxycoumarins as efficient photo-stable laser dyes emitting in the blue-green region of the visible spectrum [13]. In continuation with this 3-acetyl-7-hydroxy-2*H*-chromen-2-one **(3)** was synthesized from the condensation of resorcinol aldehyde (**1**) with ethyl acetoacetate **2** [27]. This underwent several chemical transformations. Thus, fusion of **3** with dimethylformamide dimethylacetal (DMF DMA) at 120 °C afforded a product with a molecular formula $C_{15}H_{15}NO_4$. This was considered to be the enaminone **4** based on its ^{1}H NMR and mass spectra. For example ^{1}H NMR of the product **4** revealed the presence of three singlet signals at δ 2.92, 3.21 and 3.89 ppm corresponding to three methyl groups, two doublets at δ 6.04 and 8.53 ppm corresponding to two olefinic protons and a multiplet at δ 6.96-7.83 ppm corresponding to the aromatic protons. The mass spectrum of the same product further supports this. It showed a very intense molecular ion peak at *m/e* = 273 and also showed fragments at *m/e* 256 (M-CH_3) and at 203 (M-CH=CH-N(CH_3)$_2$). Two possible isomeric structures were expected for this compound **4**, either *trans* (*E*) isomer **4A** or *cis* (*Z*) isomer **4B** (**Scheme-I**). The ^{1}H NMR spectrum of **4** showed that the *trans* isomer is formed exclusively because the reactant olefinic protons have a *J* value of 15 Hz at δ = 6.05 and δ = 8.53 ppm (**Scheme-I**).

The reaction of enaminone **4** with hippuric acid (**5**) in refluxing acetic anhydride has afforded the pyranone **8** rather than its isomeric structure **9** based on ^{1}H NMR. Formation of **10** is assumed to proceed *via* initial addition of the active methylene moiety in the formed oxazolone **6** to the activated double bond in **4** followed by dimethylamine elimination to yield the another intermediate **7** which then rearranged to **8** under the same reaction conditions. The isomeric structure **9** was ruled out based on ^{1}H NMR and ^{13}C NMR spectral analyses. ^{1}H NMR revealed the presence of pyranone H-4 and H-5 as two doublets at δ = 7.95 and δ = 8.28 with *J* = 6 Hz. The high field doublet is assigned to H-4 and is shielded by the effect of electron donation by the benzoyl amino moiety. Coumarin H-4 appeared as a singlet at δ = 8.59 ppm, deshielding of this proton is attributed to van der Waal repulsion by H-5 and by oxygen lone pair in the most stable conformer **8** (**Scheme-II**).

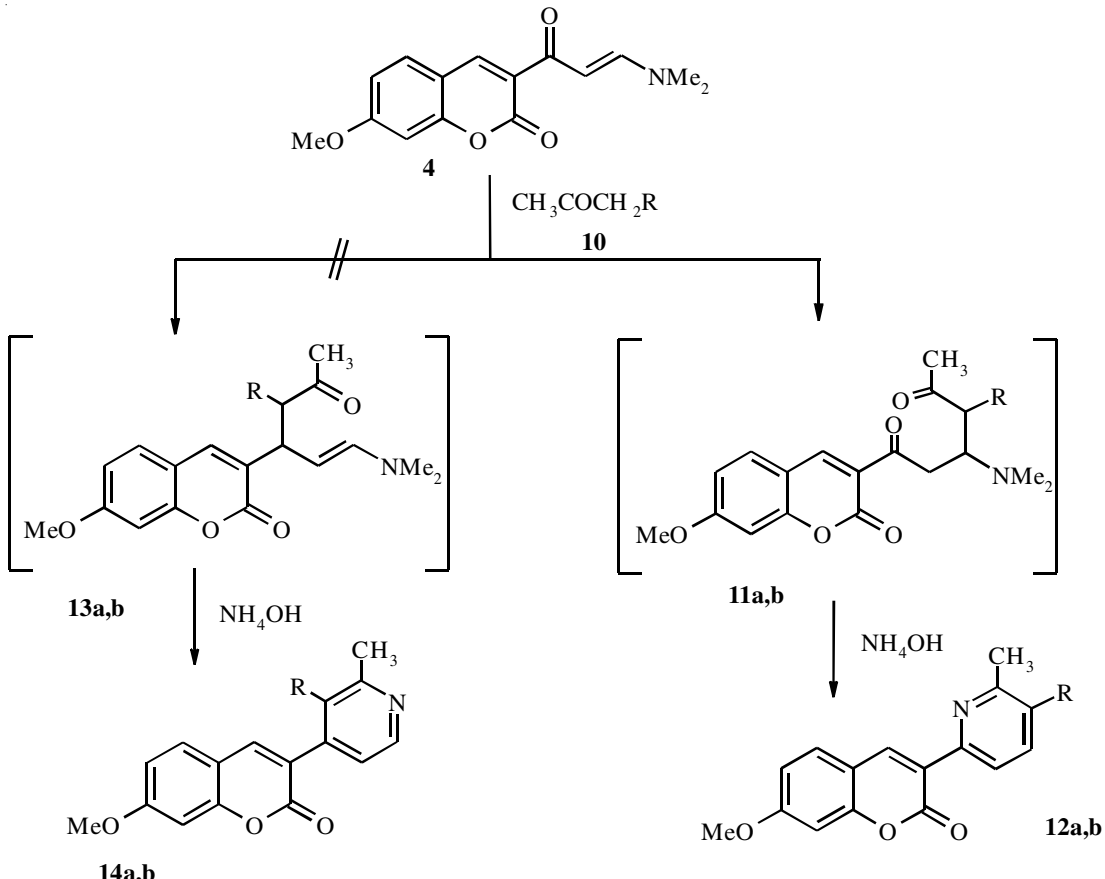


Scheme-I: Synthesis of enaminone derivative



Scheme-II: Synthesis of pyranone derivative

Furthermore the behaviour of enaminone **4** towards some active methylene reagents such as acetyl acetone, ethyl acetoacetate (**10a,b**) was also investigated. Thus, treatment of enaminone **4** with ethyl acetoacetate (**10b**) in refluxing acetic acid and in the presence of ammonium acetate afforded a product that can be formulated as pyridine derivative **12b** or its isomer **14**. Structure **12** was preferred as the reaction product based on ^{1}H NMR which revealed the presence of pyridine-H at $\delta = 8.24$ and 8.34 ppm with $J = 7$ Hz. If the reaction product is **14** one would expect a J value of 2-3 Hz. Formation of the reaction products **12a,b** from the reaction of enaminone **4** with acetyl acetone and ethyl acetoacetate respectively is believed to proceed *via* initial addition of the active methylene moiety in ethyl acetoacetate and acetyl acetone to the activated double bond in enaminone **4** yielding the Michael adduct that loses dimethylamine to give **11** which finally cyclizes into **12a,b** in the presence of ammonium acetate (**Scheme-III**).



10-14, a R = $COCH_3$, b R = $CO_2C_2H_5$

Scheme-III: Synthesis of pyridine derivatives

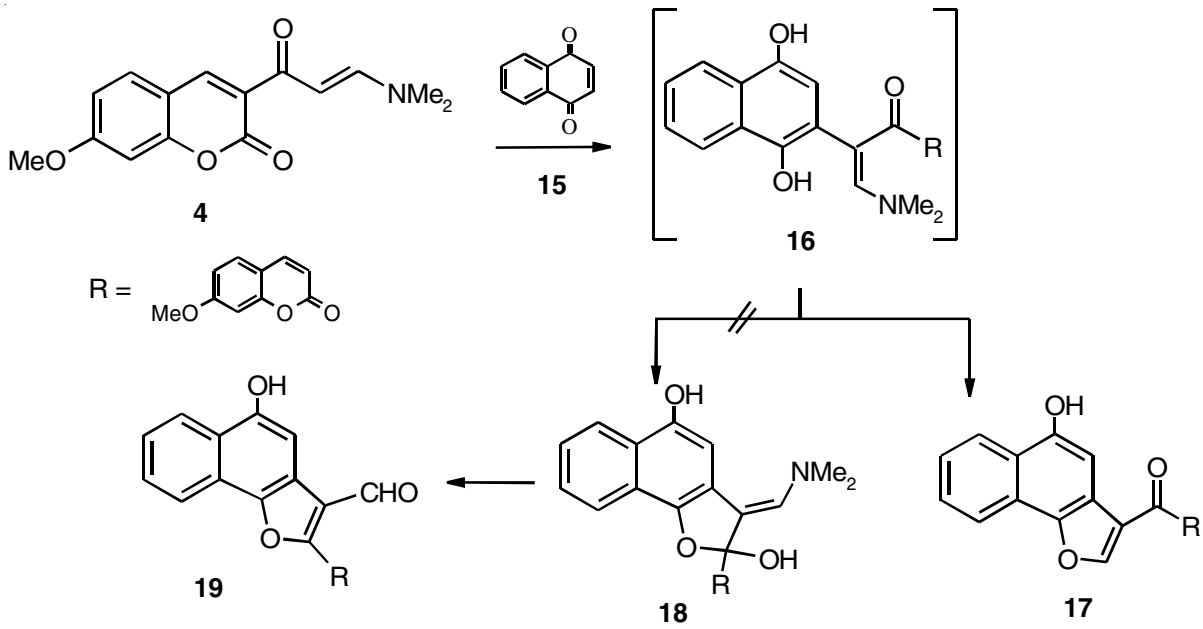
Compound **4** also reacted with 1,4-naphthoquinone (**15)** to yield the product that may be formulated as **17** or its isomer **19**. Structure **17** was established based on its ^{1}H NMR, which revealed the absence of the proton corresponding to the formyl group. Both **17** and **19** are assumed to proceed *via* intermediacy of **16,** which would then either cyclizes into **18** and then hydrolyze into **19** or alternatively cyclizes into **17** (**Scheme-IV**).

Similar to recently reported trimerization of enaminone [28] in refluxing acetic acid to yield triaroyl benzene, enaminone **4** trimerizes in refluxing acetic acid to give trimer product **22**. Formation of **22** is believed to occur *via* initial self condensation of enaminone **4** to give **20** that is further added to a third molecule of **4** followed by cyclization into the final isolable product. Also refluxing of enaminone **4** in acetic acid and ammonium acetate gives the pyridine derivative **23** *via* intermediacy of **20**. But refluxing the mixture of compounds **4** and **3** in acetic acid and ammonium acetate gives the pyridine derivative **24** (**Scheme-V**).

Electronic absorption spectra: The electronic absorption spectra of the newly synthesized dyes **4**, **8**, **12a,b**, **17**, **22**, **23** and **24** in dioxane, their concentration being in the 10^{-5} M showed two absorption maxima in the regions 440-345 and 300-250 nm. This like all the methoxy-substituted coumarins displayed an intense unresolved band, with a weak shoulder on its short-wavelength side [26]. All spectral characteristics are collected in Table-1. It was noted that the band maximum shifted to red when the 3-position of the coumarin moieties occupied by the hetero cyclic ring.

Excitation spectra: For fluorescence spectroscopy, the absorbance at the excitation wavelength was around 0.05, *i.e.* the dye concentration was in the 10^{-6} M range. For all the compounds, the excitation spectrum was similar to the absorption spectrum and did not vary with the emission wavelength. This indicates that the emitting species is the one responsible for the absorption spectrum. For new synthesized dye **8** the emission band maximum accompanied by slight red shift of the whole excitation spectrum when the emission was collected at high wavelengths (Fig. 1).

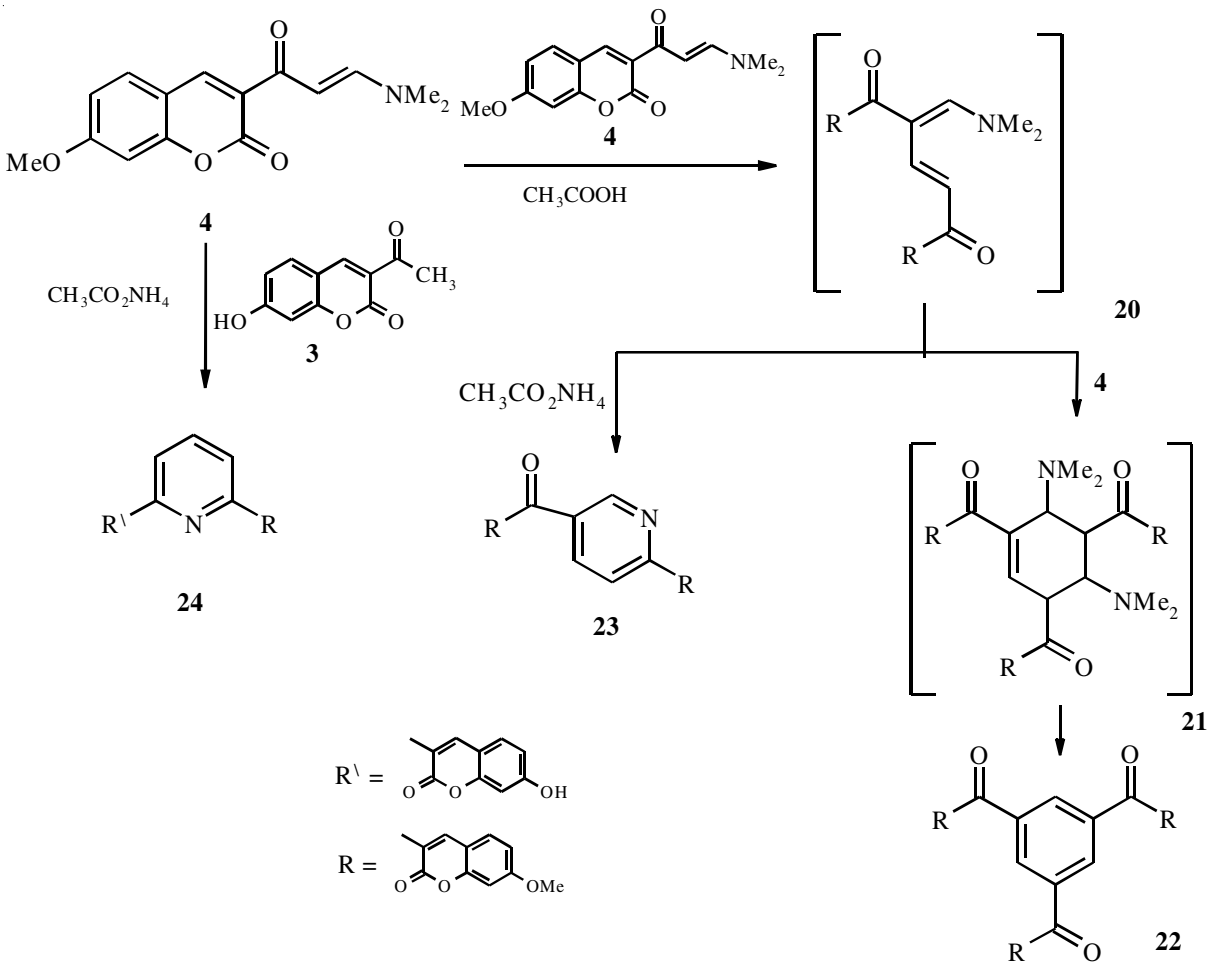
Fluorescence quantum yields and lifetimes: The fluorescence quantum yield (F_f) was determined by exciting at the absorption maximum for each compound (Table-1). The fluorescence quantum yield (F_f) was lowering than 0.1 for non-conjugated compounds **4**, **17**, **22** and **24**. However, the



Scheme-IV: Synthesis of fuaranone derivative

TABLE-1
SPECTRAL AND PHOTOPHYSICAL CHARACTERISTICS OF NEWLY SYNTHESIZED COMPOUNDS: MAXIMUM ABSORPTION WAVELENGTH (λ_{abs}), MOLAR EXTINCTION COEFFICIENT AT THE ABSORPTION MAXIMUM (Є), MAXIMUM EMISSION WAVELENGTH (λ_{em}, UNDER LINED IS THE PEAK OF MAJOR INTENSITY), FLUORESCENCE QUANTUM YIELD (Φ_f), WITH EXCITATION AT λ_{abs}), FLUORESCENCE LIFETIME (τ), RADIATIVE (K_r) AND NON-RADIATIVE (K_{nr}) DEACTIVATION CONSTANTS

Compound	λ_{abs} (nm)	Є (10^4 L mol^{-1} cm^{-1})	λ_{em} (nm)	Φ	τ (ns)	K_r (10^8 s^{-1})	K_{nr} (10^8 s^{-1})
17	250, 343	4.90, 2.80	408	0.01	1.12	0.09	8.84
12a	252, 366	1.85, 3.32	450	0.72	1.76	4.09	1.60
12b	258, 363	0.09, 3.14	440	0.96	2.50	3.83	0.172
22	252, 362	2.25, 5.13	440	0.006	1.20	0.01	8.28
23	249, 376	3.00, 5.43	436	0.20	1.45	1.38	5.52
4	300, 388	1.00, 3.24	460	0.001	0.95	0.01	10.52
8	250, 444, 419, 401	4.90, 2.25, 4.25, 4.22	530, 495, 456	0.71	1.77	4.01	1.64
24	256, 380	2.00, 3.62	450	0.09	0.97	0.93	9.38



Scheme-V: Synthesis of pyridine and triaroylbenzene derivatives

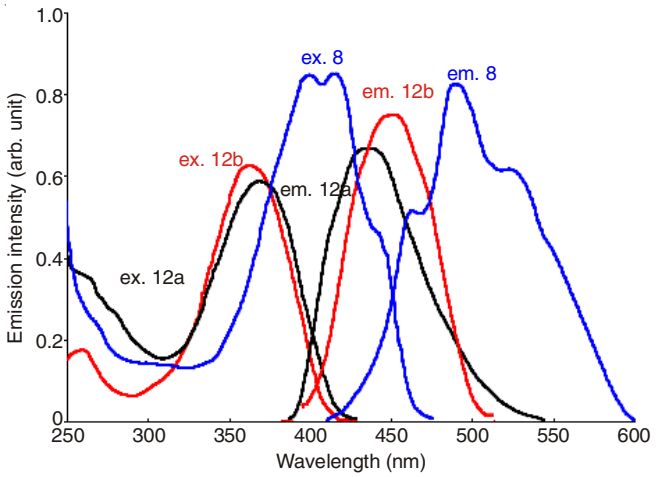


Fig. 1. Room temperature emission (em.) and excitation (ex.) spectra of 2×10^{-5} M of compounds **12a,b** and **8** in ethanol

fluorescence quantum yield (F_f) was drastically increased in conjugated compounds **8**, **12a,b** and **23** due to the presence of the heterocyclic ring substituent at position three in the coumarin moiety, since it was then between 0.2 and 0.96.

The fluorescence lifetimes were measured by exciting at 300 nm and collecting the signal at the maximum emission wavelength for each compound. Monoexponential decay was obtained in every case. A very low value (0.95 ns) was measured for compounds **4** and **24** and for all the other compounds, the fluorescence lifetimes ranged between 1.2 and 2.5 ns. The lifetime was increased in the presence of the heterocyclic ring at position three on the coumarin moieties.

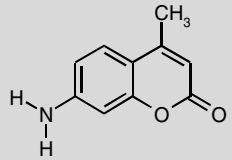
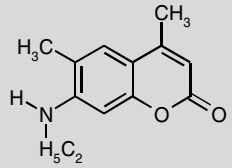
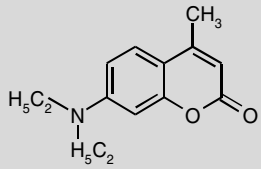
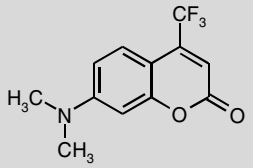
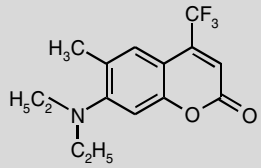
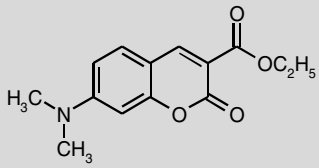
Deactivation constants: Determination of the fluorescence quantum yields and lifetimes gives access to the calculation of the radiative (K_r) and non-radiative (K_{nr}) deactivation constants, classically defined as $K_r = \Phi/t$ and $K_{nr} = (1-\Phi)/t$. The highest values of K_r were encountered for the compounds **12a,b** and **8**. Interestingly, a value lower by one order of magnitude was found for **17**. Regarding the K_{nr} constant, a very high value was found for compound **4** and to a lesser extent, for compounds **17** and **24** (Table-1).

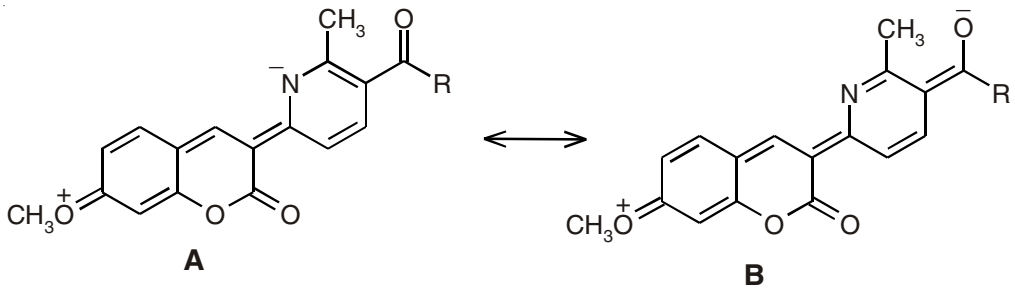
Photophysical properties of 3,7-disubstituted coumarin derivatives. Absorption, emission spectra, fluorescence quantum yields and decay times: Electronic absorption, excitation and emission spectra of the newly prepared 3,7-disubstituted coumarin derivatives with hetero aromatic substituent in position-3 have been measured. Most of the dyes possess high Φ_f values and one of the dyes ethyl 6-(7-methoxy-2-oxo-2*H*- chromen-3-yl)-2-methylnicotinate (**12b**) has a Φ_f value close to unity due to the large charge separation.

The quantum yield of fluorescence (Φ_f) is a measure of rate of non-radiative transitions competing with the emission of light. In efficient laser dyes it approaches to unity. The fluorescence quantum yields of the well known coumarin derivatives (such as simple 7-aminocoumarins lasing in the

blue are high in most organic solvents. While this is also true for coumarin **120** and coumarin **2** (Table-2) in aqueous media, the derivative with two alkyl groups at the nitrogen coumarin **1** (Table-2) has reduced fluorescence efficiency in organic solvents of high polarity [29]. This effect is even more pronounced in the corresponding dyes with electron withdrawing substituent in 3- or 4-position in coumarin moiety (Chart III) since the fluorescence quantum yield is rather low even in moderately polar solvents like methanol and ethanol. Accordingly coumarins **152**, **35** and **14** (Table-2) are poor laser dyes [30,31], it would be desirable to modify the molecular structure of such coumarins in such a way that they show high fluorescence efficiency even in polar solvents. The optical properties of coumarin derivatives in aqueous and alcoholic media are shown in Table-2. We have developed such dyes by introducing restricted rotation of hetero aromatic substitutions in the excited state and report here on their optical properties. The low florescence efficiency of coumarins **152**, **35**, **14** (Table-2) is explained in the same way as it was done for rhodamine dyes [32-34]. It is assumed that the π-electron density in the bond between the amino group and the benzene nucleus is reduced in the excited state and the ensuing mobility of the amino group is enhancing the probability for non-radiative transitions to the ground state. If this explanation is correct, structural rigidization by substituting the amino group by a methoxy group and inserting an aromatic moiety between the coumarin moiety and the electron withdrawing substituent at position three should prevent the lowering of the fluorescence efficiency in polar solvents. Applying the same principle, we have synthesized a series of new dyes. Absorption maximum, molar extinction coefficient, fluorescence maximum and quantum yield of fluorescence, all are measured at room temperature. The three new synthesized dyes **17**, **22** and **4** with methoxy groups at 7-positions have a low fluorescence quantum yield and consequently are poor laser dyes. This is due to the presence of carbonyl groups, which prevent the conjugation between the electron withdrawing group and the coumarin moiety at position three. The rigidization of the whole molecular structure through a restricted rotation of the heteroaromatic six-member ring at position three which is inserted between the coumarin moiety and the electron withdrawing group leads to the assumption that the emission will take place from forms **A** and **B** (**Scheme-VI**). If there is no possibility of rotation it implies that radiationless transitions

TABLE-2
COMPARISON OF OPTICAL PROPERTIES OF COUMARIN, DERIVATIVES [Ref. 35-37]

Molecular structure	Coumarin No.	λ_{abs} (nm)	ϵ_{max} (10^4 L mol^{-1} cm^{-1})	λ_{fl} (nm)	Φ_f
	**120**	354	1.85	430	0.75
	**2**	366	2.15	435	0.68
	**1**	373	2.35	445	0.50
	**152**	397	1.95	510	0.14
	**35**	402	2.12	510	0.08
	**14**	412	4.10	460	0.07



Scheme-VI: Resonance structure of 3-(6-methylpyridin-2-yl)-7-methoxy-2*H*-chromen-2-one derivatives

are reduced and the subsequent elongation of the conjugated system leads to a strong increase of the fluorescence quantum yield (Φ_f) and a considerable improvement of the laser performance of the new synthesized compound **23**. A Similar effect is observed in those derivatives that carry a carbethoxy pyridine group in the 3-position in the new synthesized coumarin derivative ethyl 6-(7-methoxy-2-oxo-2*H*-chromen-3-yl)-2-methylnicotinate (**12b**). This compound has a fluorescence quantum yield value (Φ_f) close to unity Table-1. This is due to the fact that the carbethoxy group is a stronger electron withdrawing group than the acetyl group in synthesized compound **12a**. So this dye (**12a**) has a fluorescence quantum yield (Φ_f) also high but less than dye **12b**. Also the two new synthesized coumarin dyes **8** and **24** carry other electron withdrawing substituent in position-3 and also have high fluorescence quantum yields (Φ_f). It can be seen in Table-1 that the newly synthesized dyes are potentially excellent laser dyes. For the new synthesized coumarin dye **8** plotting the emission and excitation intensities as a function of the wave numbers, from this figure and due to the Frank-Condone effect we obtain the required energy for 0-0, 0-1 and 0-2 transitions which are 2280, 2400, 2525 cm^{-1}, respectively. These results indicated that the difference in energy gaps between the S^0, S^1 and S^1, S^2 are the same, equal to 125 cm^{-1}, which lies in the range of vibration energy. The carbethoxy pyridine group in the position-3 leads to a broad fluorescence spectrum (Fig. 1), which should give rise to an exceptionally wide tuning range.

Conclusion

Several new 3,7-disubstituted coumarin derivatives with hetero aromatic substituent in position-3 were synthesized using simple methods *via* a versatile, readily accessible 3-acetyl-7- hydroxy-2*H*-chromen-2-one (**3**) are demonstrated. The structures of the newly synthesized compounds were established by spectral methods IR, ^1H NMR, ^{13}C NMR, mass spectra and elemental analysis. The excitation, emission spectra, photochemical quantum yield and live time of the newly prepared 3,7-disubstituted coumarin derivatives have been measured. Most of the dyes possess high Φ_f values so we can use these dyes as fluorescent probes and laser dyes.

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