https://doi.org/10.15255/KUI.2023.018
KUI-1/2024
Original scientific paper
Received April 18, 2023
Accepted June 23, 2023

Substituent and Solvent Effects on the Spectral Properties of 3-Substituted Derivatives of 4-Hydroxycoumarin

E. Bečić,* *M. Dedić*, *B. Imamović*, *S. Špirtović-Halilović*, and *E. Omeragić*

University of Sarajevo, Faculty of Pharmacy, Zmaja od Bosne 8, 71 000 Sarajevo, Bosnia and Herzegovina

Abstract

Solvent and substitution effects on the UV/Vis spectroscopic and fluorescence behaviour of seven synthesized 3-substituted 4-hydroxycoumarin derivatives were tested. The tested compounds were dissolved in ethyl acetate, acetonitrile, and dimethyl sulfoxide. Absorption and emission spectra were recorded in the range of 200–800 nm. All tested 4-hydroxycoumarin derivatives showed good absorption in a wide range of 200–550 nm, depending on the properties of the substituents on the benzene ring of the cinnamoyl moiety and the type of solvent. In comparison to the unsubstituted analogue, compounds with an electron-donating group exhibited bathochromically shifted UV/Vis absorption and emission spectra. The highest fluorescence quantum yield was observed for compounds with dimethylamino and acetamido groups as substituents at the benzene ring. Considering that both substitution and solvent affect the absorption and emission spectra of the tested compounds, it can be concluded that judiciously selecting these parameters can improve their absorption and fluorescence properties, making them suitable for various analytical uses.

Keywords

Coumarin derivatives, spectral properties, fluorescence, substitution

1 Introduction

Many natural and synthetic coumarins and hydroxycoumarins are biologically active compounds with various chemical, biological, and pharmacological effects.[1–10] In addition to pharmacological and biological effects, coumarin derivatives are often used as fluorescent probes, laser dyes, fluorescent markers, *etc.*, because they have a wide range of polarity, pH, viscosity, and other sensitivities.[11–16] Coumarin derivatives fluorescence is relatively photostable, and their excitation and emission maxima are suitable to use for measurements in cellular components, tissues, and biological fluids.[17] The importance of coumarin compounds as fluorescent agents is derived from their stability and relatively easy synthesis.[18]

Many coumarin derivatives show a characteristic fluorescence in basic and neutral solutions and in concentrated sulphuric acid, especially in the UV region. This property is particularly pronounced in 7-hydroxycoumarin derivatives, and is associated with a change in its polarisation in alkaline solution and in sulphuric acid.[19] The fluorescence intensity is significantly influenced by the position of substitution as well as the properties of the substituent itself. The double bond on the pyrone ring absorbs light with a wavelength greater than 300 nm, so it can be concluded that complete aromatisation and delocalisation of the double bond at the 3,4-position of the lactone ring do not occur.[20] Three major tautomeric forms of 3-substituted-4-hydroxy coumarin can be formed.[21] The occurrence of tautomerism for 4-, 5-, and 7-hydroxycoumarins was also observed.[22,23] The introduction of electron acceptor groups in position 3 on the coumarin ring (carbonyl, cyano group) leads to the transfer of electrons in the pyrone ring, which causes fluorescence even in neutral solutions. If these groups are in position 4, no fluorescence occurs.[24] The oxygen atom at the 3-carbonyl group acts as a hydrogen bond acceptor and donating group and at the 7-position enhances the fluorescence emission.[25,26] *Murata et al.*, examined coumarin derivatives with both donating groups at the 6- and 7-positions and an electron-withdrawing group at the 3-position, which develop intense fluorescence.[27] Previous investigations of the fluorescent properties of coumarin derivatives showed that the position of the absorption and emission spectra depend on the position and type of substituents introduced, and the intensity of the emission depends on the pH.[28] The introduction of donating groups at the 6- and 7-positions along with a withdrawing group at the 3-position, leads to the development of intense fluorescence.[27]

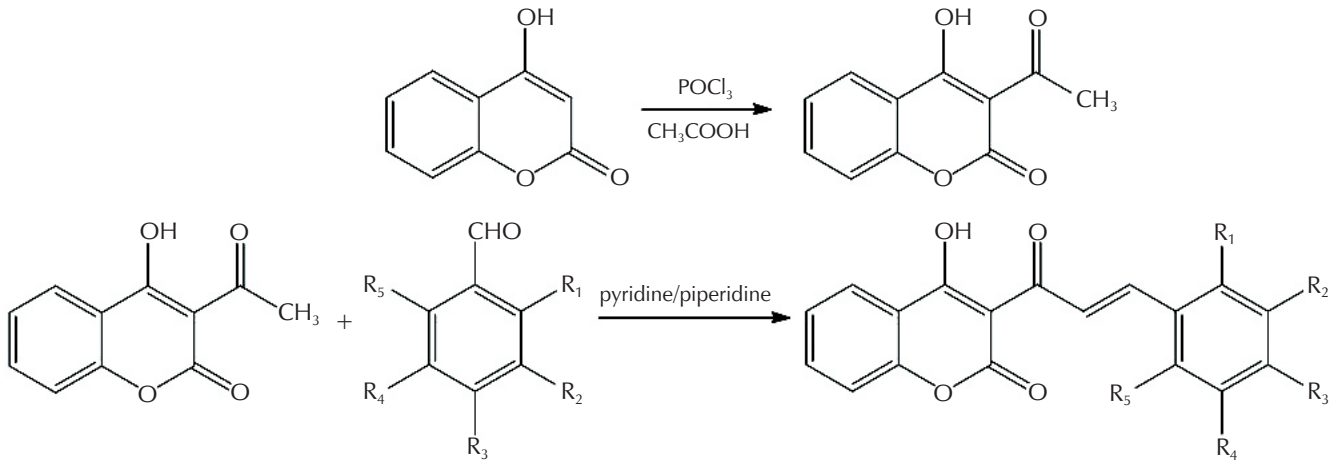
In this study, 4-hydroxycoumarin derivatives, (**1-7**), containing a chalcone moiety with electron-withdrawing or electron-donating substituents were spectroscopically investigated.

2 Experimental

2.1 Material and methods

The compounds investigated in this study were synthesized according to the procedure described by *Zavrsnik et al.*[29] using chemicals of analytical grade. Briefly, the first step was the acylation of 4-hydroxycoumarin with acetic acid and phosphorous oxychloride. By reaction with 3-acetyl-4-hydroxycoumarin, and with appropriate aromatic aldehydes with pyridine and piperidine as catalysts, seven 4-hydroxycoumarin derivatives were prepared with a phenyl-prop-2-enoyl moiety at position 3.

* Corresponding author: Assoc. Prof. Ervina Bečić
Email: ervina.becic@ffsa.unsa.ba



Scheme 1 – Synthesis of 4-hydroxycoumarin derivatives (**1-7**)

Table 1 – Chemical names of synthesized compounds

No	Chemical name	R_1	R_2	R_3
1.	3-cinnamoyl-4-hydroxy-2*H*-chromen-2-one	H	H	H
2.	3-(3-chloro-cinnamoyl)-4-hydroxy-2*H*-chromen-2-one	H	Cl	H
3.	3-(4-acetamido-cinnamoyl)-4-hydroxy-2*H*-chromen-2-one	H	H	$NHCOCH_3$
4.	3-(2-methoxy-cinnamoyl)-4-hydroxy-2*H*-chromen-2-one	OCH_3	H	H
5.	3-(4-dimethylamino-cinnamoyl)-4-hydroxy-2*H*-chromen-2-one	H	H	$N(CH_3)_2$
6.	3-(4-hydroxy-cinnamoyl)-4-hydroxy-2*H*-chromen-2-one	H	H	OH
7.	3-(2-nitro-cinnamoyl)-4-hydroxy-2*H*-chromen-2-one	NO_2	H	H

The synthesis procedure is shown in Scheme 1. All the tested compounds, except compound 5, were obtained as yellow crystals. Compound 5 was obtained as a red crystal. Analytical data of synthesized compounds (IR and NMR) were presented in our previous paper.[30]

Chemical names of synthesized compounds are presented in Table 1.

After optimisation of measurement methods, the tested compounds were dissolved in ethyl acetate (ETAC), acetonitrile (ACN), and dimethyl sulfoxide (DMSO), with their concentrations in the 10^{-6} M range for UV/Vis and 10^{-7} M for fluorescence measurements. The UV/Vis absorption spectra were recorded on a Shimadzu 1601 UV/Vis spectrophotometer in the range of 200–800 nm, using a 1 cm quartz cuvette. Fluorescence was measured on a Shimadzu RF-5301PC spectrofluorophotometer with Panorama fluorescence 1.1 software in a 1 cm cuvette in the right-angle arrangement. Excitation and emission slits were both 5 nm. Fluorescence spectra were taken at excitation into the maximum of the longest wavelength absorption band of each tested compound. The temperature of the samples was controlled using a circulating water bath during the absorption and fluorescence spectra measurements; therefore, the ambient temperature was used.

Molar extinction coefficients (ε) were determined by linear least squares fitting of Beer's Law plots of absorbance versus concentration. Fluorescence quantum yields (Φ) were determined using the Eq. (1).

$$\Phi_x = (A_s F_x n_x^2 \Phi_s) / (A_x F_s n_s^2) \quad (1)$$

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 sample of unknown quantum yield, respectively.[31]

The relative fluorescence quantum yield was determined using quinine sulphate in 0.1 M (Φ = 0.58) as a standard for compounds 1, 2, 3, 4, 6, and 7. The standard for compound 5 was Rhodamine B in water (Φ = 31).[31]

3 Results and discussion

3.1 Influence of the substituent and solvent properties on UV/Vis absorption

Numerous studies of the spectroscopic properties of a large number of substituted coumarin derivatives have shown two absorption maxima. One from the coumarin ring around 250–280 nm, and other at a longer wavelength originating from the substituent.[32] Considering the type of substituents on cinnamoyl moiety, the tested compounds were divided into two groups: compounds with

withdrawing substituents, such as chlorine and nitro group at the benzene ring, and compounds with electron-donating substituents acetamido, metoxy, dimethylamino, and hidroxy. In order to measure the effects of substituent and solvent, changes in the absorption properties of these compounds were observed in comparison to compound 1, the benzene ring of which was not substituted. The absorption spectra of compound 1 in ACN and DMSO, showed two bands with maxima between 260 and 280 nm and 350 and 370 nm, while in ETAC, compound 1 had only one maximum at about 370 nm (Fig. 1).

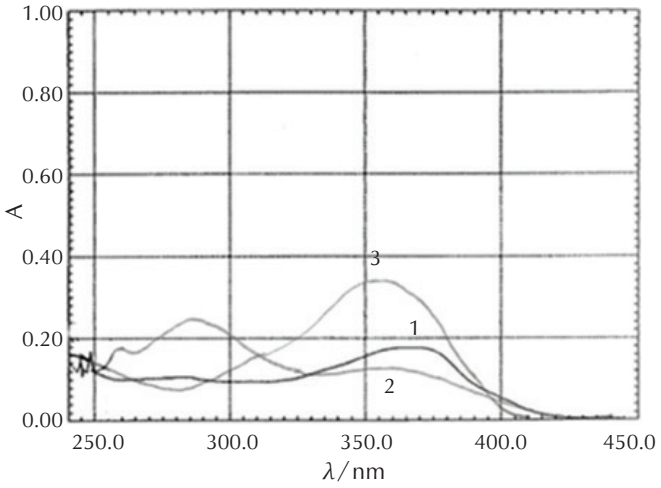


Fig. 1 – Absorption spectra of compound 1 in ETAC (1), ACN (2), and DMSO (3)

It was expected that the maximum at longer wavelength depended on the substitution on the benzene ring of the cinnamoyl moiety; therefore, the focus was on the changes in the position of the maximum at longer wavelength.

Comparing the absorption maxima of compound 1 and compound 2 with electron-withdrawing substituent chlorine, the difference in absorption maxima in all solvents was ± 3 nm. Substitution with nitro group caused a hypsochromic shift of the absorption maximum in ETAC ($\Delta\lambda$ = 9 nm), while in DMSO, the absorption maximum was shifted bathochromically ($\Delta\lambda$ = 8 nm). In ACN there were no changes in the position of the absorption maxima. Due to the presence of electron-donating substituents, longer absorptions were shifted bathochromically in all solvents in comparison with compound 1. This shift was largest for compound 5, with $\Delta\lambda$ = 123 nm in ETAC, $\Delta\lambda$ = 144 nm in ACN, and $\Delta\lambda$ = 167 nm in DMSO (Fig. 2).

3.2 Fluorescence properties

Studies on the fluorescence properties of synthesized derivatives showed changes in fluorescence properties.[34,35] It is also known that the substitution of a coumarin moiety with a benzene ring in the 3-position enhances the emission yield.[32] For fluorescence spectroscopy of tested compounds, the excitation spectra were similar to the absorption spectra, and emission occurred at the maximum absorption. Our results showed that the fluorescence of the tested compounds depended on the solvent properties and the substituents on the benzene ring. Table 2 summarizes the spectral data based on absorption and emission for the parent compound 1 and all the tested compounds. It can be seen that compound 1 exhibited zero fluorescence in all solvents.

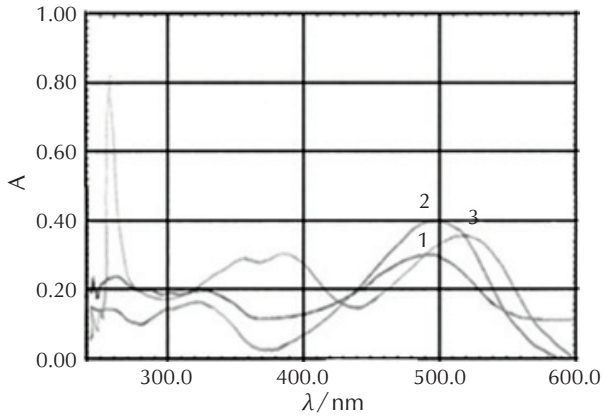


Fig. 2 – Absorption spectra of compound 5 in ETAC (1), ACN (2), and DMSO (3)

Compounds with chlorine and nitro groups had no fluorescence in ETAC and DMSO, as could be expected, since they are known as fluorescence quenchers.[36] In the presence of nitro group, the absence of fluorescence can be explained by the $S_1 \rightarrow S_0$ internal conversion as a result of the strong influence of nitro group as the electron-withdrawing group.[31]

However, in ACN, the compound with the nitro group showed fluorescence, which can be explained by the influence of solvents.

In polar solvents, the n → π* transition shifts towards higher energies and π → π* towards lower energies, which can result in the appearance of or increase in the intensity of emission.[31] The appearance of fluorescence could be caused by donor-acceptor crossings between the compound and the triple bond in ACN.

Electron-donating substituents, such as acetamido (compound 3), methoxy (compound 4), dimethylamino (compound 5), and hydroxy (compound 6) lead to the appearance of fluorescence in all solvents. The presence of free electrons on the electron-donor substituents should not affect the π → π* transition, which is responsible for the emissions of the tested compounds. However, based on the results, it is possible to conclude that the emission was caused by interaction with aromatic ring π-electrons. This intramolecular charge transfer requires that the substituent be planar in relation to the aromatic ring. If they are not planar, the number of conjugations is reduced, which causes a reduction in emission intensity.[35,36] Departure from coplanarity with the aromatic ring is also pronounced with alkoxy groups. Alkoxy groups exhibit significant deviation from planarity with the aromatic ring, which was the case with compound 4 with a methoxy group.[31]

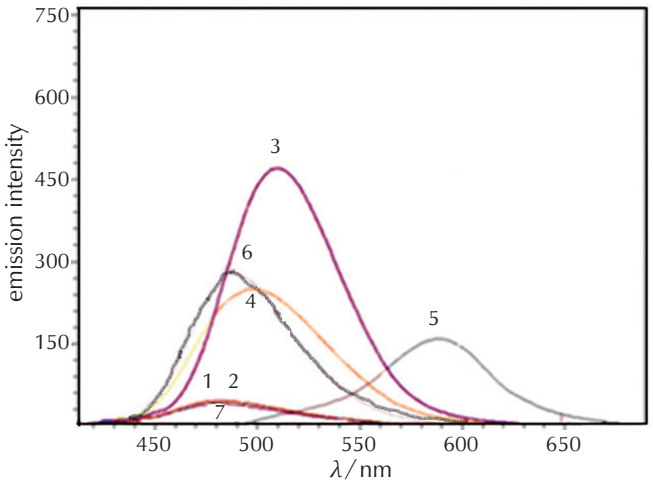


Fig. 3 – Emission spectra of compounds (1-7) in ACN

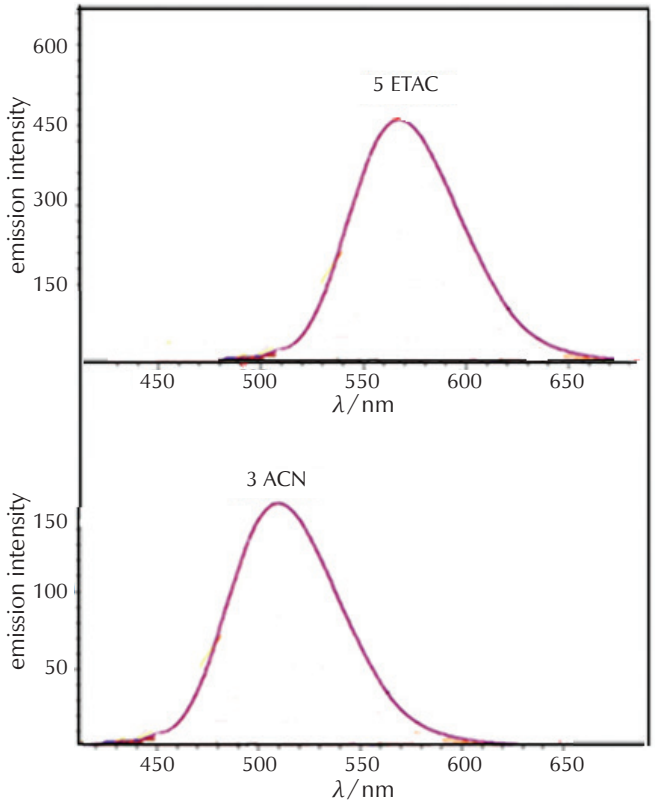


Fig. 4 – Emission spectra of compound 5 in ETAC and compound 3 in ACN

The results obtained for compound 4, which had a methoxy group as a substituent, showed that compound 4 had a lower fluorescence quantum yield than compounds 5 and 6, which were substituted with dimethylamino and hydroxy groups, respectively (Table 2).

In ACN, the fluorescence of all tested compounds was observed, which could be explained by donor-acceptor transitions between compounds and the triple bond in ACN (Fig. 3).

As seen from Fig. 4, compound 5 with a dimethylamino group in ETAC and compound 3 with an acetamido group in ACN had the highest fluorescence quantum yield. The fluorescence quantum yield of compound 5 was three times higher in ETAC than in ACN (Table 2).

Table 2 – Summary of the UV/Vis and fluorescence spectral data

	Ethyl acetate (ETAC)					Acetonitrile (ACN)					Dimethyl sulfoxide (DMSO)				
Comp.[a]	λ_A[b] / nm	log ε[c]	λ_F[d] / nm	SS[f] / cm^{-1}	Φr[e]	λ_A[b] / nm	log ε[c]	λ_F[d] / nm	SS[f] / cm^{-1}	Φr[e]	λ_Ab / nm	log ε[c]	λ_F[d] / nm	SS[f] / cm^{-1}	Φr[e]
1.	369.5	4.33	--	--	--	358.0 235.0	4.59	485.0	7314.40	0.015	353.0 286.0	4.53	--	--	--
2.	365.5 260.5	4.35	--	--	--	356.0 246.0	4.52	486.0	7513.75	0.016	352.0 284.0	4.33	--	--	--
3.	*	*	*	*	*	397.0 251.5	4.17	514.0 -	5733.66	0.40	330.0 249.0	4.67	527.0	11327.7	0.05
4.	388.0 260.0	4.46	483.0 --	5069.26	0.23	385.5 252.0	4.46	501.0 -	5980.60	0.22	352.0 285.0	4.22	513.0	8915.92	0.03
5.	492.5 315.5 260.0	4.59	571.0 -- --	2812.07	0.41	500.0 323.0 262.0	4.65	590.0 536.0 -	3050.85	0.16	521.0 387.0 356.0	4.75	582.0	2011.72	0.09
6.	403.0 250.0	4.65	483.0	4109.96	0.27	385.0 249.0	4.27	483 --	5270.09	0.26	359.0 307.0	4.65	518.0	8550.14	0.02
7.	360.5 266.5	4.63	--	--	--	359.0	4.57	489	7405.26	0.015	361.0 285.0	4.23	--	--	--

* not soluble; **--** no fluorescence; [a] Structure of the compounds according to Fig. 1; [b] Maximum of the longest absorption band; [c] Log of decadic extinction coefficient ($dm^3\,mol^{-1}\,cm^{-1}$); [d] Maximum of the emission band; [e] Relative quantum yield to quinine sulphate (Φ = 0.58) for compounds 1, 2, 3, 4, 6, and 7 and compound 5 to Rhodamine B in water (Φ = 31); [f] Stokes shift (cm^{-1}).

4 Conclusion

The present study indicates that the UV/Vis and fluorescence properties of synthesized derivatives **(1-7)** are dependent on the properties of the substituents attached to the cinnamoyl and solvent properties.

As shown in the present paper, by judiciously choosing the substituent on the phenyl ring of cinnamoyl moiety of 4-hydroxycoumarin derivatives, it is possible to obtain a sufficient bathochromic shift of the UV/Vis band and fluorescence transition to render these compounds useful for analytical applications.

List of abbreviations

ACN – acetonitrile
DMSO – dimethyl sulfoxide
ETAC – ethyl-acetate
IR – infrared
NMR – nuclear magnetic resonance
UV/Vis – ultraviolet/visible

References
Literatura

1. *A. Stefanachi, F. Leonetti, L. Pisani, M. Catto, A. Carotti,* Coumarin: A natural, privileged and versatile scaffold for bioactive compounds, Molecules **23** (2) (2018) 250, doi: https://doi.org/10.3390/molecules23020250.
2. *Y. K. Al-Majedy, A. A. H Kadhum, A. A. Al-Amiery, A. B Mohamad*, Coumarins: The antimicrobial agents, Sys. Rev. Pharm. **8** (2017) 62–70, doi: https://doi.org/10.5530/srp.2017.1.11.
3. *G. Kirsch, A. B. Abdelwahab, P. Chaimbault,* Natural and Synthetic Coumarins with Effects on Inflammation, Molecules **21** (2016) 1322, doi: https://doi.org/10.3390/molecules21101322.
4. *X. F. Song, J. Fan, L. Liu, X. F. Liu, F. Gao,* Coumarin derivatives with anticancer activities: An update, Arch. Pharm. **353** (2020) e2000025, doi: https://doi.org/10.1002/ardp.202000025.
5. *Y. Yamaguchi, N. Nishizono, T. Yoshimura, K. Wada, D. Kobayashi,* Evaluation of synthesized coumarin derivatives on aromatase inhibitory activity, Bioorg. Med. Chem. Lett. **27** (2017) 2645–2649, doi: https://doi.org/10.1016/j.bmcl.2017.01.062.
6. *N. Cui, DD. Lin, Y. Shen, J. G. Shi, B. Wang, M. Z. Zhao, L. Zheng, H. Chen, J. H. Shi,* Triphenylethylene-Coumarin Hybrid TCH-5c Suppresses Tumorigenic Progression in Breast Cancer Mainly Through the Inhibition of Angiogenesis, Anticancer-Agents Med. Chem. **19** (10) (2019) 1253–1261, doi: https://doi.org/10.2174/1871520619666190404155230.
7. *Y. K. Al-Majedy, A. A. H. Kadhum, A. A. Al-Amiery, A. B. Mohamad,* Coumarins: The Antimicrobial agents, Sys. Rev. Pharm. **8** (2017) 62–70, doi: https://doi.org/10.5530/srp.2017.1.11.
8. *J. J. Zhu, J. G Jiang,* Pharmacological and Nutritional Effects of Natural Coumarins and Their Structure-Activity Relationships, Mol. Nutr. Food Res. **62** (14) (2018) e1701073, doi: https://doi.org/10.1002/mnfr.201701073.
9. *M. Khoobi, A. Foroumadi, S. Emami, M. Safavi, G. Dehghan, B. H. Alizadeh, A. Ramazani, S. K. Ardestani, A. Shafie,* Coumarin-based bioactive compounds: facile synthesis and biological evaluation of coumarin-fused 1,4-thiazepines, Chem. Biol. Drug Des. **78** (4) (2011) 580–586, doi: https://doi.org/10.1111/j.1747-0285.2011.01175.x.
10. *C. Zaragozá, F. Zaragozá, I. Gayo-Abeleira, L. Villaescusa,* Antiplatelet Activity of Coumarins: *In Vitro* Assays on COX-1, Molecules **26** (10) (2021) 3036, doi: https://doi.org/10.3390/molecules26103036.
11. *V. F. Traven, L. I. Vorobjeva, T. A. Chibisova, E. A. Carberry, N. J. Beyer,* Electronic absorption spectra and structure of hydroxycoumarin derivatives and their ionized forms, Can. J. Chem. **75** (1997) 365–376, doi: https://doi.org/10.1139/v97-042.
12. *X. Sun, T. Liu, J. Sun, X. Wang,* Synthesis and application of coumarin fluorescence probes, RSC Adv. **10** (2020) 10826–10847, doi: https://doi.org/10.1039/C9RA10290F.
13. *M. Kaholek, P. Hrdlovič, J. Bartos,* Singlet probes based on coumarin derivatives substituted at position 3; spectral properties in solution and polymer matrices, Polymer **41** (2000) 991–1001, doi: https://doi.org/10.1016/S0032-3861(99)00241-4.
14. *X. Y. Sun, T. Liu, J. Sun, X. J. Wan*, Synthesis and application of coumarin fluorescence probes, RSC Adv. **10** (2020) 10826–10847, doi: https://doi.org/10.1039/C9RA10290F.
15. *H. Raunio, O. Pentikaeinen, R. O. Juvonen,* Coumarin-based profluorescent and fluorescent substrates for determining xenobiotic metabolizing enzyme activities *in vitro*, Int. J. Mol. Sci. **21** (2020) 4708, doi: https://doi.org/10.3390/ijms21134708.
16. *B. D. Wagner,* The Use of Coumarins as Environmentally-Sensitive Fluorescent Probes of Heterogeneous Inclusion Systems, Molecules **14** (1) (2009) 210–237, doi: https://doi.org/10.3390/molecules14010210.
17. *R. O. Juvonen, M. Ahinko, J. Huuskonen, H. Raunio, O. Pentikäinen,* Development of new Coumarin-based profluorescent substrates for human cytochrome P450 enzymes, Xenobiotica **49** (9) (2019) 1015–1024, doi: https://doi.org/10.1080/00498254.2018.1530399.
18. *M. M. Abdou, R. A. El-Saeed, S. Bondock,* Recent advances in 4-hydroxycoumarin chemistry. Part 1: Synthesis and reactions, Arab. J. Chem. **12 (**1) (2019) 88–121, doi: https://doi.org/10.1016/j.arabjc.2015.06.012.
19. *W. R. Sherman, E. Robins,* Fluorescence of substituted 7-hydroxycoumarins, Anal. Chem. **40** (4) (1968) 803–805, doi: https://doi.org/10.1021/ac60260a045.
20. *K. V. Sashidhara, A. Kumar, M. Kumar, J. Sarkar, S. Sinha,* Synthesis and *in vitro* evaluation of novel coumarin-chalcone hybrids as potential anticancer agents, Bioorg. Med. Chem. Lett. **20** (2010) 7205–7211, doi: https://doi.org/10.1016/j.bmcl.2010.10.116.
21. *W. R. Porter, W. F. Trager,* 4-Hydroxycoumarin/2-Hydroxychromone Tautomerism: Infrared Spectra of 3-Substituted-2-13C-4-hydroxycoumarins, J. Heterocyclic Chem. **19** (1982) 475–480, doi: https://doi.org/10.1002/jhet.5570190305.
22. *C. C. S. Sousa, M. F. Victor, M. M. Morais, R. A. Matos*, Energetics of the isomers: 3- and 4-hydroxycoumarin, J. Chem. Thermodyn. **42** (11) (2010) 1372–1378, doi: https://doi.org/10.1016/j.jct.2010.06.003.
23. *C. B. Aguirre Pranzoni, G. I. Furque, C. E. Ardanaz, A. Pacciaroni, V. Sosa, C. E. Tonn, M. Kurina-Sanz,* Biotransformation of dihydrocoumarin by *Aspergillus niger* ATCC 11394,

Arkivoc **7** (2011) 170–181, doi: https://doi.org/10.3998/ark.5550190.0012.715.

24. *A. K. Satpati, S. Senthilkumar, M. Kumbhakar, S. Nath, D. K. Maity, H. Pal,* Investigations of the solvent polarity effect on the photophysical properties of coumarin-7 dye, Photochem. Photobiol. **81** (2005) 270–278, doi: https://doi.org/10.1111/j.1751-1097.2005.tb00184.
25. *H .E. Katerinopoulos*. The coumarin moiety as chromophore of fluorescent ion indicators in biological systems, Curr. Pharm. Des. **10** (30) (2004) 3835–3852, doi:_https://doi.org/10.2174/1381612043382666.
26. *W. R. Sherman, E. Robins*, Fluorescence of substituted 7-hydroxycoumarins, Anal. Chem. **40** (4) (1968) 803–805, doi: https://doi.org/10.1021/ac60260a045.
27. C. *Murata, T. Masuda, Y. Kamochi, K. Todoroki, H. Yoshida, H. Nohta, M. Yamaguchi, A. Takadate*, 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. **53** (7) (2005) 750–758, doi: https://doi.org/10.1248/cpb.53.750.
28. *V. K. Sharma, P. D Saharo, N. Sharma, R. C. Rastogi, S. K. Ghoshal, D. Mohan*, Influence of solvent and substituent on excited state characteristics of laser grade coumarin dyes, Spectrochim. Acta A Mol. Biomol. Spectrosc. **59** (6) (2003) 1161–1170, doi: https://doi.org/10.1016/s1386-1425(02)00296-2.
29. *D. Završnik, S. Špirtović-Halilović, Dž. Softić,* Synthesis, structure and antibacterial activity of 3-substituted derivatives of 4-hydroxycoumarin, Period. Biol. **113** (1) (2011) 93–97.
30. *E. Bečić, M. Šober, B. Imamović, D. Završnik, S. Špirtović-Halilović,* UV/VIS absorption and fluorescence spectroscopic study of some 3-substituted derivatives of 4-hydroxycoumarin, Pigment Resin Technol. **40** (5) (2011) 292–297, doi: https://doi.org/10.1108/03699421111176199._
31. *B. Valeur,* Molecular Fluorescence: Principles and Application. Vol. 3, Wiley-Verlag Chemie GmbH, Weinheim, Germany, 2001.
32. *H. Ammar, S. Abid, S. Fery-Forgues,* Synthesis and spectroscopic study of new biscoumarin dyes based on 7-(4-methylcoumarinyl) diesters, Dyes Pigm. **78** (2008) 1–7, doi: https://doi.org/10.1016/j.dyepig.2007.09.008.
33. *J. D. Hepworth, Ch. D. Gabbut, B. M. Heron,* Pyrans and their Benzo Derivatives: Structure, in: A. R. Katritzky, W. Rees, E. F. V. Scriven (Eds.), Comprehensive in heterocyclic chemistry, 2nd Ed., Pergamon Press, Elsevier Science, Ltd., Tarrytown, NY, USA, 1996, pp. 301–350, doi: https://doi.org/10.1016/b978-008096518-5.00110-6.
34. *J. Donovalová, M. Cigáň, H. Stankovičová, J. Gašpar, M. Danko, A. Gáplovský, P. Hrdlovič,* Spectral Properties of Substituted Coumarins in Solution and Polymer Matrices, Molecules. **17** (2012) 3259–3276, doi: https://doi.org/10.3390/molecules17033259.
35. *R. Choorikkat, K. K. Vijayan, V. K. Praveen, N. S. Saleesh Kumar*, Photophysical investigation of 3-substituted 4-alkyl and/or 7-acetoxy coumarin derivatives-A study of the effect of substituents on fluorescence, Spectrochim. Acta A Mol. Biomol. Spectrosc. **75** (5) (2010) 1610–1616, doi: https://doi.org/10.1016/j.saa.2010.02.027.
36. *J. R. Lakowicz,* Quenching of Fluorescence, in: J. R. Lakowicz (Ed.), Principles of Fluorescence Spectroscopy, Springer, New York, USA, 1999, pp. 237–265, doi: https://doi.org/10.1007/978-1-4757-3061-6.

SAŽETAK

Utjecaj supstituenta i otapala na spektralna svojstva 3-supstituiranih derivata 4-hidroksikumarina

Ervina Bečić, Mirza Dedić, Belma Imamović, Selma Špirtović-Halilović* i *Elma Omeragić*

Istraživan je učinak otapala i supstitucije na apsorpciju i emisiju zračenja novosintetiziranih 3-supstituiranih derivata 4-hidroksikumarina (**1-7**). Ispitivani spojevi otopljeni su u etil-acetatu, acetonitrilu i dimetil-sulfoksidu. Apsorpcijski i emisijski spektri snimljeni u području od 200 do 800 nm. Ispitani derivati 4-hidroksikumarina pokazali su dobru apsorpciju u širokom rasponu od 200 do 550 nm, ovisno o vezanim supstituentima na benzenovom prstenu cinamoilnog dijela molekule i vrsti otapala. U usporedbi s nesupstituiranim analogom, spojevi elektron- donirajućim supstituentima pokazali su batokromno pomaknute apsorpcijske i emisijske spektre. Najveći kvantni prinos fluorescencije zabilježen je za derivate s dimetilamino i acetamidnom skupinom. S obzirom na to da i supstituent i otapalo utječu na apsorpcijska i emisijska svojstva ispitivanih spojeva, može se zaključiti da se njihovim odabirom mogu poboljšati apsorpcijska i fluorescencijska svojstva, što ih može učiniti prikladnima za različite analitičke primjene.

Ključne riječi
Derivati kumarina, spektralna svojstva, fluorescencija, supstitucija

Univerzitet u Sarajevu, Farmaceutski fakultet,
Zmaja od Bosne 8, 71 000 Sarajevo,
Bosna i Hercegovina

Izvorni znanstveni rad
Prispjelo 18. travnja 2023.
Prihvaćeno 23. lipnja 2023.