p_H-Dependent Fluorescence Spectra of 3-Substituted Umbelliferones [1]

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Fluorescence data of 3-ethoxycarbonyl-, 3-acetyl-, 3-phephyl-, 4-methyl-3-phenyl-, 3-(2-benzothiazolyl)- and 3-cyano-substituted 7-hydroxycoumarines are reported as a function of acidity (p_H 0–9). Unlike umbelliferone or its 4-methyl derivative they do not exhibit significant photoautomerism in acidified solutions, but with the exception of the benzothiazolyl derivative. This behaviour can be interpreted in terms of a) steric hindrance by the substituent and b) enhanced charge delocalisation in the first excited singlet state, leading to lower basicities at the ring carbonyl oxygen.

Coumarines such as umbelliferone (7-hydroxycoumarine) or its 4-methyl derivative (4-MU) can be used in widely tunable dye lasers [2–5] due to a variety of fluorescence bands in acidified alcoholic solutions. Emission has been shown to occur from neutral, anionic, protonated and phototautomeric (exciplex) forms [6–12], the nature of the latter, however, still being investigated [13].

The enhanced fluorescence intensity of umbelliferones having an electron withdrawing substituent in 3-position [14] as well as their low lasing threshold[15] made it interesting to study their emission p_H-dependence with regard to a possible phototautomerism in the first excited singlet state. Spectra of some of the compounds have been reported in water solutions "under optimal conditions of p_H and wavelength" [16], but not in a neutral or acidic milieu.

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Experimental

Compounds **1** [17], **2** [18], **3** [19], **4** [20], **5** [21] in Table 1 have been synthesized according to literature known procedures. **6**, which could not be prepared by the reported method [18] (*trans*-ethyl-*α*-cyano-2,4-dihydroxycinnamate of mp. 166° being isolated instead), was obtained by applying a related condensation [22]: 2,4-

Table 1. Absorption and emission data of some 3-substituted umbelliferones (in nm).

Nr.	7-hydroxy-coumarin		benzene	meth-anol	DMSO	water p_H 9	water p_H 4			water 0.1 *N* HCl		
						anion	anion	neutral	others	anion	neutral	others
1	3-ethoxy-carbonyl	$\lambda_{max(ab)}$	343, 360 [a]	352, 370 [a]	350, 370 [a]	402	—	351, 365 [a]	—	—	351, 365 [a]	—
		$\lambda_{max(fl)}$	406	409	414	446	445	—	—	444	412	—
		λ_{exc}	360	360	360	406	—	361	—	—	366	—
2	3-acetyl	$\lambda_{max(ab)}$	356	363	364	413	—	360	—	—	361	—
		$\lambda_{max(fl)}$	430	423	424	459	458	420 [a]	490 (?)	454	427	—
		λ_{exc}	368	370	370	420	—	370	—	—	370	—
3	3-phenyl	$\lambda_{max(ab)}$	336	342	346	383	—	338	—	—	337	—
		$\lambda_{max(fl)}$	422, 445 [b]	430	434	462	472	428 [b]	—	465	433	—
		λ_{exc}	348	350	360	386	—	340	—	—	342	—
4	4-methyl-3-phenyl	$\lambda_{max(ab)}$	—	330	326	367	—	327	—	—	327	—
		$\lambda_{max(fl)}$	—	414 [c]	423 [c]	462	458	—	478	452	432	480
		λ_{exc}	—	338	334	372	—	338	—	—	338	—
5	3-(2-benzo-thiazolyl)	$\lambda_{max(ab)}$	391, 378, 415	385, 391, 415	393, 417	439	—	373 [c]	—	—	380, 432	—
		$\lambda_{max(fl)}$	438 [a], 462, 485 [a]	465, 450 [a], 486 [b]	474, 453 [a]	490	485	455 [a]	—	—	466	508
		λ_{exc}	394	398	406	445	—	386	—	—	418	—
6	3-cyano	$\lambda_{max(ab)}$	350, 366 [a]	355, 370 [a]	358, 370 [a]	408	—, —	355, 367 [a]	—, —	—	355, 367	—
		$\lambda_{max(fl)}$	405	411	418	453	453	—	485 [b]	452	420 [a]	485 [b]
		λ_{exc}	350	365	369	410	—	365	—	—	365	—

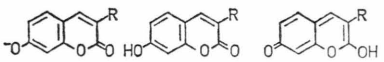
[a] shoulder [b] inflexion [c] broad

Dihydroxybenzaldehyde (2.8 g), malononitrile (1.3 g) and one drop of piperidine were dissolved in absolute ethanol (10 ml). After standing for two days, the precipitate was collected and recrystallized from 95% ethanol (with a few drops of concentrated hydrochloric acid) and then from absolute ethanol. The compound formed faintly yellowish crystals of mp. 261°. Analysis: Found C 64.3, H 2.6, N 7.5. $C_{10}H_5NO_3$ (87.5) requires C 64.2, H 2.7 and N 7.5%.

All compounds were carefully purified by repeated crystallisation from different solvents. Benzene, methanol and dimethylsulfoxide were of spectrograde purity (UVASOL®, Merk), buffers (phosphate and citrate) and 0.1 N HCl were commercially available products (Merck).

Results

Absorption and fluorescence maxima in benzene, methanol, DMSO and aqueous solutions of different p_H are compiled in Table 1. The spectra in organic solvents have been run in order to find the location of the neutral molecule emission hand, since in water solution several fluorescent species (e. g. anion A, neutral molecule N, tautomer T and protonated forms P_1 and P_2) may be present simultaneously.



A N T

P_1 P_2

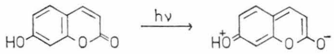
Solvatochromism is observed in the absorption and more distinct in the fluorescence spectra, indicating a highly dipolar excited state.

In aqueous solution of p_H 9 both absorption and emission occur from the excited anion (Table 1). All the compounds in alkaline solution exhibit shoulderless emission bands and a very strong fluorescence intensity. With increasing acidity (at p_H 6 – 5) the anion absorption bands diappear (p_K 6.5 – 7), whereas the location of the fluorescence maxima remains unchanged, albeit at reduced intensity (photodissociation). In the p_H 4 region, however, new emission bands begin to arise as shoulders or inflexions.

As the emission maxima of the neutral forms are known from the methanol spectra, their assignement (Table 1) can readily be made. Additional new bands at p_H 4, referred under "others", are tentatively assigned to phototautomeric and not to protonated species, since protonation is not expected to take place in the coumarin series at this relatively low acidity.

In 0.1 N HCl solution the anion emission band in some cases is still present as a shoulder (**2**, **3**, **4**) or as a well defined band (**1**). And with the exception of **5** the longwave emission band is a very weak one. One of the requirements of broadband tunable dye lasers, namely continuous emission over a wide range, is best fulfilled with 0.1 N HCl solutions of **4**, and with p_H 2 – 3 aqueous alcoholic solutions of compound **5**.

The limited ability of 3-substituted umbelliferones to form longwave emitting phototautomers can be explained by steric and electronic reasons. Bulky substituents in 3-position (in particular phenyl) prevent the attack of a proton to the lactone carbonyl oxygen during the lifetime of the excited state, which is usually in the order of some nanoseconds [6, 9]. Furthermore electron withdrawing substituents are able to reduce the excited state basicity of the ring carbonyl oxygen. Following electronic excitation of umbelliferone or 4-MU, negative charge is transferred to the carbonyl oxygen exclusively ($S_0 \rightarrow S_1$), leading to a drastically enhanced basicity there. This state is best represented by formula S_1.

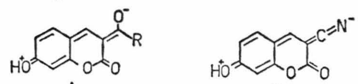


S_0 S_1

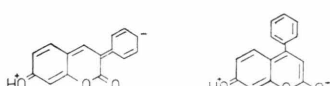
With an electron attracting substituent in position 3 charge transfer is not only to be expected towards the lactone carbonyl oxygen, but also towards the substituent (S_1 formulae **A**, **B** or **C**). In other words, excited state basicity is delocalized over several atoms [23]. In the case of the relatively electron rich benzothiazolyl substituent with practically no electronegative properties, in 0.1 N HCl solution the long wave emission band of the phototautomer (508 nm) is very strong for this reason.

Another consequence follows from the above considerations: The substituents in Table 1 should not affect a possible phototautomerism when attached to the lactone ring in 4-position, since no resonance structures like **A**, **B** or **C** can be formulated for the S_1 state in this case (**D**).

Indeed 4-phenyl-7-hydroxycoumarin in aqueous solution at no p_H fluoresces from its neutral form [24].



A B



C D

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