

## SHORT COMMUNICATION

### FLUORESCENCE PROPERTIES OF 4-ACYL ISOCHROMAN-1,3-DIONES

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**ABSTRACT.** Fluorescence properties of 4-acylisochroman-1,3-diones are studied in this paper. Recently these properties had been recorded and the substituents effects were examined. In this paper are described the solvents effects on the intensity and wavelength of the fluorescence. Substituents effects are then confirmed.

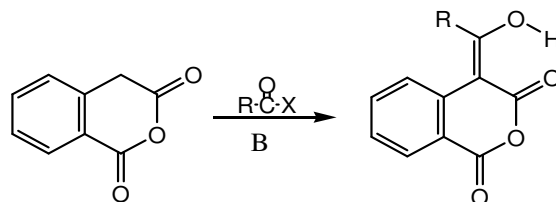
**KEY WORDS:** 4-Acyl isochroman-1,3-dione, Fluorescence, Solvents and substituents effects

## INTRODUCTION

Physical and chemical properties of 4-acylisochroman-1,3-diones are studied in our laboratory [1]. NMR spectra [2], crystallographic structure [3, 4] and fragmentation in mass spectrometry [5] were investigated. Furthermore, anti microbial activities of cytosporacin, a natural derivative of isochromandiones has been discovered and described recently [6]. In a previous paper, we revealed for the very first time, the fluorescence of these compounds and substituents effects on these properties [7]. In this paper, we describe solvents effects on the wavelength and the intensity of the fluorescence. The effects of the substituents on the fluorescence are also confirmed.

## EXPERIMENTAL

The compounds were synthesized by the following reaction and identified by spectroscopic methods [1-5, 7].



X = Cl or OCOR

B = pyridine or triethylamine

**1:** R = CH<sub>3</sub>; **2:** R = C<sub>2</sub>H<sub>5</sub>; **3:** R = C<sub>6</sub>H<sub>5</sub>; **4:** R = *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>; **5:** R = *p*-*t*-BuC<sub>6</sub>H<sub>4</sub>; **6:** R = *p*-ClC<sub>6</sub>H<sub>4</sub>; **7:** R = *p*-FC<sub>6</sub>H<sub>4</sub>; **8:** R = *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>; **9:** R = *p*-(CH<sub>3</sub>)<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>; **10:** R = *p*-CNC<sub>6</sub>H<sub>4</sub>

Scheme 1. Synthesis of 4-acylisochroman-1,3-diones.

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Fluorescence spectra were recorded on a KONTRON SFM 25 Spectrofluorometer (Zürich, Switzerland). The concentration was  $10^{-5}$  M for compound **9** and  $10^{-4}$  M for other compounds in dichloromethane ( $\epsilon = 8.9$ ) or ethyl acetate ( $\epsilon = 6.02$ ), ethanol ( $\epsilon = 24.6$ ), methanol ( $\epsilon = 32.7$ ), acetonitrile ( $\epsilon = 37.5$ ) and DMSO ( $\epsilon = 46.7$ ).

## RESULTS AND DISCUSSION

The effects of solvent are very different according to whether the substituent is aliphatic or aryl. The results are given in Table 1.

Table 1. Fluorescence wavelengths of compounds in different solvents: ( $\lambda_F$ ) in nm. ( $\epsilon$  = dielectric constants of the solvents).

Compound	1	2	3	4	5	6	7	8	9	10
CH <sub>2</sub> Cl <sub>2</sub> ( $\epsilon = 8.9$ )	425	398	-	390	420	426	415	-	-	-
C <sub>2</sub> H <sub>5</sub> OH ( $\epsilon = 24.6$ )	490	408	400	398	418	433	418	-	421	-
CH <sub>3</sub> OH ( $\epsilon = 32.7$ )	490	450	405	400	425	431	419	-	419	-
DMSO ( $\epsilon = 46.7$ )	495	489	410	400	428	438	422	-	434 and 508	-

### 1° Effect of solvent on the wavelength of fluorescence

The wavelength of fluorescence of every compound is very sensitive to the solvent polarity. This sensitivity is higher in the case of aliphatic substituents than the aryl substituents.

#### (a) Case of aliphatic R

In the case of aliphatic substituents (R = CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub>), a bathochromic effect is observed when the polarity of the solvent increase: in dichloromethane, wavelength of fluorescence is lower than 430 nm while it raises up higher than 480 nm, in a very polar solvent like DMSO. In the case of a methyl substituent, the wavelength of fluorescence is very greatly modified by the polarity of solvent: in dichloromethane it is obtained the fluorescence at 425 nm; the other solvents tested, which are more polar, cause a great bathochromic effect (Figure 1). When the substituent R is an ethyl group, a dispersion of wavelengths of fluorescence ( $\lambda_F$ ) is obtained. In this case, a gradual increasing of the polarity of solvent brings a gradual bathochromic effect. So, the wavelengths of fluorescence are 398 nm in dichloromethane, 408 nm in ethanol, 450 nm in methanol and 489 nm in DMSO (Figure 2).

#### (b) Case of aryl R

In this case, the wavelength of fluorescence was obtained between 390 and 440 nm. This range of wavelength is lower than aliphatic substituents one. When the aryl moiety is substituted in para position, its effect is weakly sensitive on the wavelength of fluorescence (Figure 3-8). In all the solvents used, most of the compounds exhibit one band of fluorescence, except compounds **8** (R = *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) and **10** (R = *p*-CNC<sub>6</sub>H<sub>4</sub>). These compounds exhibit no fluorescence. In the case of the compound **9**, when R = *p*-(dimethylamino) phenyl moiety, one band of fluorescence was observed in several solvents but, in DMSO, dual fluorescence is obtained. In the previous paper, this behaviour had been attributed to the effect of substituent [7], but the use of several solvents indicates that it must to be attributed to the effect of solvent. The first band was

obtained at 434 nm and the second at 508 nm. This range of difference of the two wavelengths is in accordance with the observed data in literature [8].

In both cases (R is an aliphatic or an aromatic moiety), the more polar the solvent, the higher the wavelength of fluorescence. This bathochromic effect is obtained with all the fluorescent compounds tested. So, for 4-acylated isochroman-1,3-diones, the wavelength of fluorescence is higher for aliphatic substituents than aryllic one. To obtain an energetic emission, it is recommended to choose an aryllic substituent R without a strongly withdrawing group on this moiety and to use a non-polar solvent.

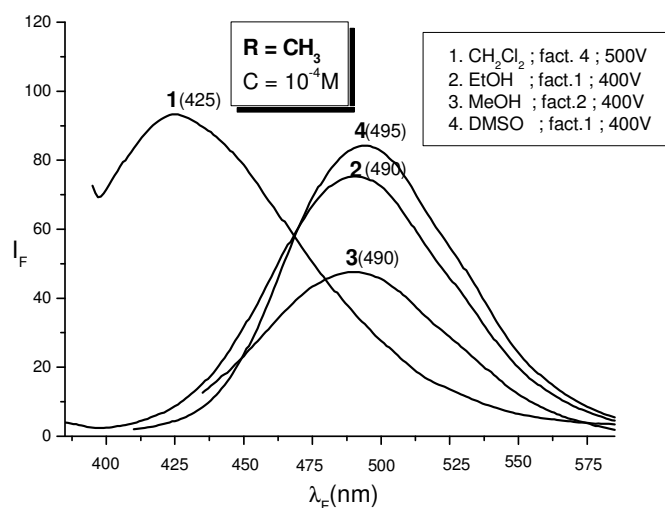


Figure 1. Effect of solvent on fluorescence of compound **1** ( ) maximum wavelength.

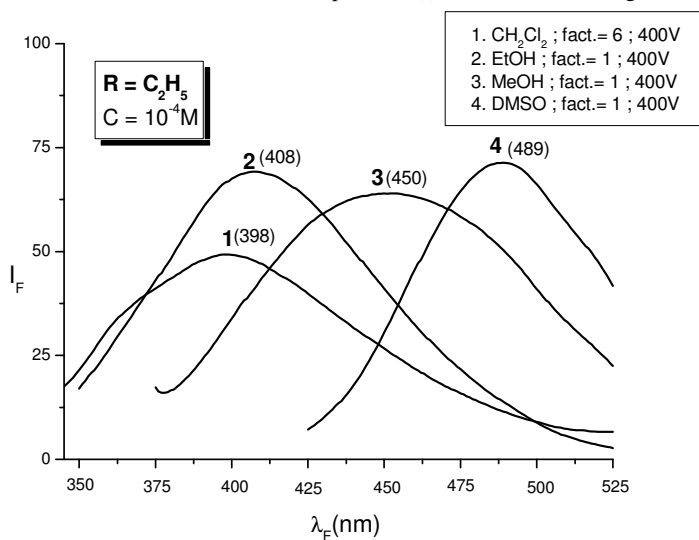


Figure 2. Effect of solvent on fluorescence of compound **2** ( ) maximum wavelength.

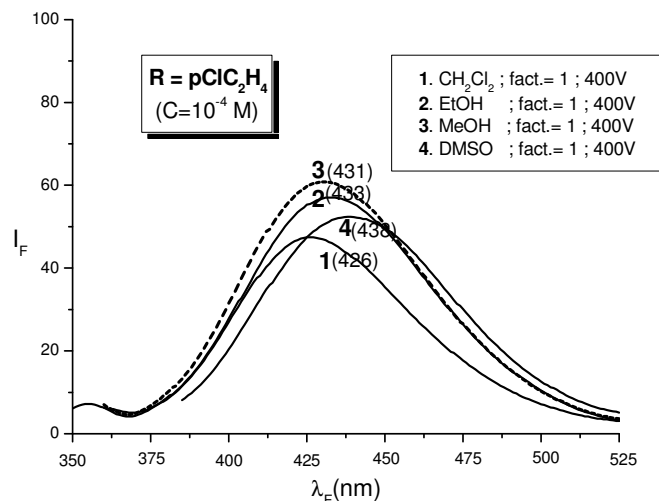


Figure 3. Effect of solvent on fluorescence of compound **6** ( ) maximum wavelength.

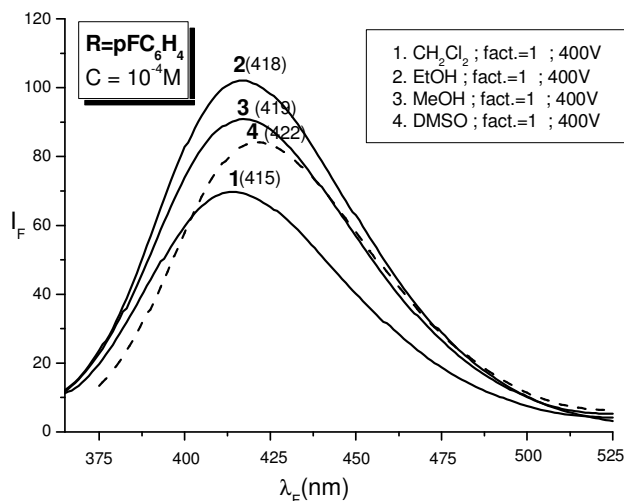


Figure 4. Effect of solvent on fluorescence of compound **7** ( ) maximum wavelength.

### 2° Effect of solvents on the intensity of fluorescence

No definite trend rule was obtained for the intensity of fluorescence. Only one certainly has been observed: The use of weak polar solvents leads to a decrease of the intensity of fluorescence of all the compounds tested. Thus, in the case of *p*-*t*-butylphenyl as substituent R, the intensity of fluorescence is strongly decreased in dichloromethane ( $\epsilon = 8.9$ ). The same result was observed in the case of R = phenyl, in ethyl acetate ( $\epsilon = 6.02$ ). On the other hand, when the substituent R is a strongly electron withdrawing substituent (for **8** when R = *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub> and **10** when R = *p*-CNC<sub>6</sub>H<sub>4</sub>), no fluorescence was obtained in any of the solvents tested. It is a

confirmation of the effect of strongly withdrawing substituents over the fluorescence properties of these compounds.

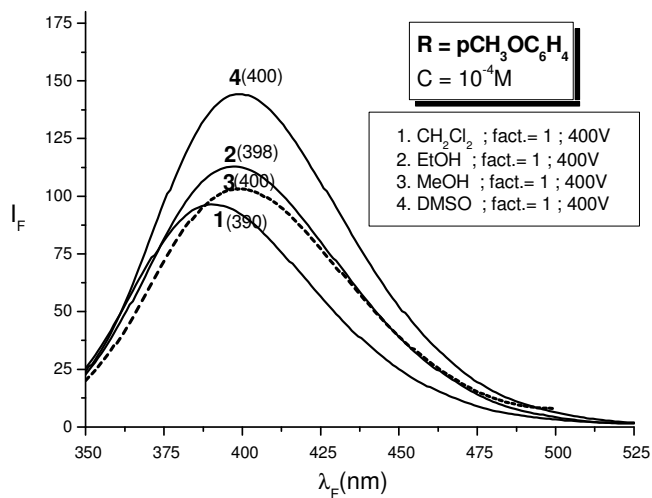


Figure 5. Effect of solvent on fluorescence of compound **4** ( ) maximum wavelength.

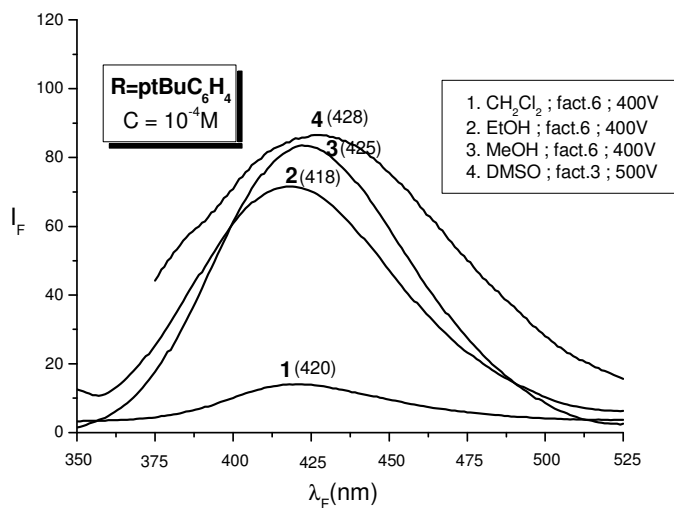


Figure 6. Effect of solvent on fluorescence of compound **5** ( ) maximum wavelength.

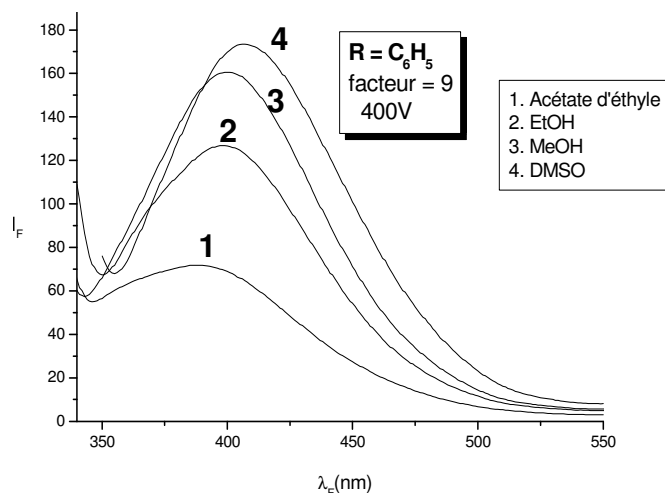


Figure 7. Effect of solvent on fluorescence of compound **3** ( ) maximum wavelength.

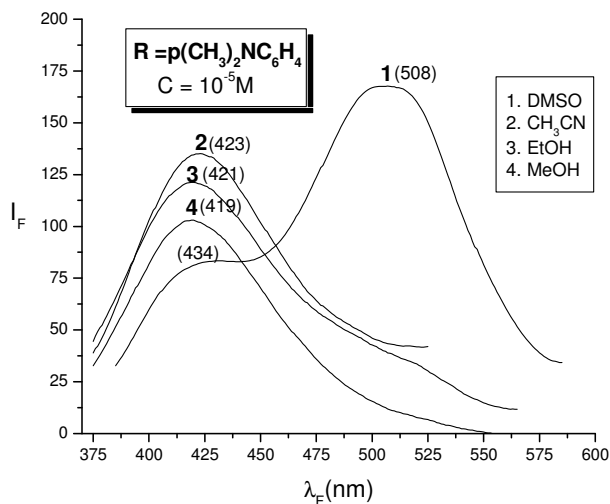


Figure 8. Effect of solvent on fluorescence of compound **9** ( ) maximum wavelength.

## CONCLUSIONS

All the compounds are fluorescent in all the solvents tested, except compounds **8** and **10**, respectively, when R = *p*-Nitrobenzoyle and R = *p*-Cyanobenzoyle, due to the strong withdrawing effect of these groups [7]. The compounds with an aromatic substituent R present more energetic fluorescence than the aliphatic substituted compounds. When R = *p*-(CH<sub>3</sub>)<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, dual fluorescence is observed in DMSO. No rule on the influence of the solvent on the intensity of fluorescence has emerged, but the use of weak polar solvents lead to a decrease of the intensity of fluorescence of all the compounds tested.

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