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Full Paper

Quinquangulin and Rubrofusarin: A Spectroscopy Study

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Abstract: In this work, excitation and emission spectra were evaluated in order to elucidate the properties of quinguangulin and rubrofusarin in water/ethanol mixture. The study demonstrates that the maximum excitation wavelength can be significantly modulated changing the proportion of organic solvent in the water/organic solvent system. Quinquangulin presented the higher wavelength of maximum excitation in an ethanol-water mixture containing 70% of water. Probably, the organization between ethanol and water molecules in this condition favors the formation of strong polar interactions with the π^* orbitals of naphthopyrones. It is interesting to register that the additional methyl group in quinquangulin seems to develop a decisive function related to the ability to formation of hydrogen bonds, altering significantly the mechanism of solute-solvent interaction. This work, which involves both theoretical and experimental analyses, demonstrates the relevance of the studies focused on solvent mixtures as well as emphasizes the potential of quinguangulin and rubrofusarin as photosensitizers.

Keywords: density functional theory; fluorescence spectroscopy; photosensitizer; quinguangulin; solvatochromism; rubrofusarin

1. INTRODUCTION

Quinquangulin (2,9-dimethyl-5,6-dihydroxy-8-methoxy-naphtho-γ-pyrone) and rubrofusarin (2-methyl-5,6-dihydroxy-8-methoxy-naphtho-γ-pyrone) (Figure 1) are well-known naphthopyrones employed for several pharmacological purposes, such as treatment of mycobacterial infection [1, 2]. Both are benzenoid compounds characterized by the presence of two condensed benzene rings in the molecular structure (Figure 1), and a relatively intense absorption band near 340 nm. These organic

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compounds have interesting biochemical action, such as ability to modify the regulatory properties of the enzyme present in Calmodulin protein (CaM) [1, 2].

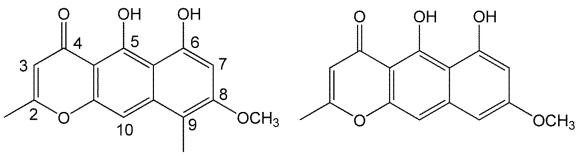

Figure 1. Molecular structures of quinquangulin and rubrofusarin.

While rubrofusarin is insoluble in water, quinquangulin is soluble in this solvent. Both compounds are soluble in organic solvents as for example ethanol and dimethyl sulfoxide, and present chelation behavior for metal ions. They complexes with six-membered rings by coordination to the carbonyl and phenolate ion in C(4) and C(5), or in C5 and C6 [3, 4]. These compounds can be obtained from roots and seed of plants, mainly from Peru. Rubrofusarin was firstly isolated from the seeds of the leguminosae, *Cassia tora L*, by Rangaswami [3] and it also can be obtained as a metabolic product of the fungus *Fusarium culmorum*. Species as *Senna*, for example, are known in several countries for its therapeutic properties and its significant quantities of naphthopyrones [5]. Both compounds (quinquangulin and rubrofusarin) have demonstrated important biochemical properties, such as the potential to modify the properties of calmodulin-regulated enzymes which acts as intracellular receptor for Ca^{2+} [6]. In addition, studies have identified significant cytotoxic action against colon cancer cells [7]. In this context, it is interesting to register the relevance of the physico-chemical properties of rubrofusarin and quinquangulin. In fact, these properties has been emphasized in studies on the influence of the physiological environment on the photophysical behavior of compounds with potential for in biological applications and as fluorescent probes [8-12].

In the present study, we focused on the photophysical behavior of rubrofusarin and quinquangulin, evaluating relevant physical-chemical, spectroscopic and solvatochromic properties, in order to evaluate the potential of these compounds as matrixes for the design of new phototherapeutic agents (PA).

2. MATERIAL AND METHODS

Solutions containing rubrofusarin or quinquangulin in 2 mL of different water/ethanol, varying the water content from 0 to 100%. The mixtures were prepared with ultrapure water and organic solvents of spectroscopic grade. Excitation and emission spectra were done using a Jobin-Yvon Spex FloroMax-2 spectrofluorimeter and an Ocean Optics USB 4000 setup configured for absorption and emission measurements. Emission spectra were obtained considering the lowest energy maximum intensity obtained from the excitation spectra of the samples. All measurements were done using front-face geometry. All measurements were done at 298 K.

Aiming to obtain a more reliable description of the systems under study, the ground state structure of both compounds surrounded by four explicit solvent molecules was optimized in a continuous dielectric corresponding to ethanol generated using the integral equation formalism variant (IEFPCM) [13, 14]. The density functional theory (DFT) level with B3LYP hybrid functional [15] was employed in all optimizations, being the 6-31G(d,p) atomic basis set applied in the calculations. The energy of the first ten singlet and triplet excited states were calculated using the time-dependent approach of DFT (TD-DFT), making possible the description of the excitation spectrum of the species as well as the energy diagram of the first non-relaxed states. Using the configuration interaction single (CIS) approach [16], the structure of the first three singlet and triplet excited states were optimized. The energy of these relaxed states was calculated by TD-DFT in order to enable comparison between the energy diagram for the non-relaxed and relaxed excited states in ethanol.

The orbitals involved in the electronic transitions were identified by analysis of the molecular orbitals. Furthermore, it was possible to estimate the behavior of each transition as well as the effect of solvent on these transitions. All calculations were done using the Gaussian 09 computational package [17]. The molecular orbitals and excitation spectra were described using GaussView 5.0.8.

3. RESULTS AND DISCUSSION

The experimental spectral properties of the compounds are reported in Table 1. In all spectra (Figure 2), is remarkable that depending on the solvent has different emission wavelength for the low energy $\pi \rightarrow \pi^*$ electronic transition (between 512-517

nm). Considering that the unique structural difference between these organic compounds consists in a presence of an additional methyl group in quinquangulin (Figure 1), were observed a small batocromic shift (~ 2 nm) caused by this group. We observed a shift to longer wavelengths in solvent with higher polarity (water). A small shift in about 5 nm and 7 nm, for the quinquangulin and rubrofusarin, respectively, are observed with the increase of proportion the water. In the case of mixtures water/ethanol, the increases the proportion of organic solvent reduces both the dielectric constant and the polarity of the system, thus generating spectral bands for blue shifted compared to the data obtained in water (higher polarity). The shift in the fluorescence peaks towards longer wavelengths could be due to markedly different excited state charge distribution of the solute than that in ground state. This would leads to a stronger interaction with polar solvents in the excited state [18].

Table 1. Photophysical characteristics and solvent polarity function of quinquangulin (A) and rubrofusarin (B) in water/ethanol mixture.

% water	$\Delta f(\varepsilon.n)$	A			B		
		ν_{Abs} (cm^{-1})	ν_F (cm^{-1})	$\Delta\nu$ (cm^{-1})	ν_{Abs} (cm^{-1})	ν_F (cm^{-1})	$\Delta\nu$ (cm^{-1})
0	0.29009	28653	19531	9122	28818	19479	9339
10	0.29471	28571	19493	9078	28736	19493	9242
20	0.29866	28490	19479	9010	28736	19479	9257
30	0.30135	28490	19458	9033	28736	19479	9257
40	0.30341	28409	19436	8974	28571	19458	9114
50	0.30505	28409	19417	8992	28571	19494	9078
60	0.30638	28409	19417	8992	28409	19455	8954
70	0.30748	28329	19380	8949	28329	19417	8911
80	0.31004	28409	19417	8992	28249	19417	8831
90	0.31387	28329	19342	8986	28249	19417	8831
100	0.3207	28249	19342	8906	28249	19417	8831

ν_{Abs} = maximum wavenumbers of excitation; ν_F = maximum wavenumbers of fluorescence; $\Delta\nu$ = Stokes shift; $\Delta f(\varepsilon,n)$: solvent polarity function, calculated taking dielectric constants and refractive indices of pure solvents from literature.

Figure 2 presents the fluorescence spectra of quinquangulin (a) e rubrofusarin (b) obtained using different ethanol-water ratios. For these compounds, it is possible to observe a peculiar spectral behavior dependent on the percentage of water. The intensity is decreased still with 10% of water probably due the formation of hydrogen bonding with water and the ease of intramolecular proton transfer in water [19, 20]. This specific interactions due higher water concentrations induce an efficient vibronic coupling with the excited states of compounds, reducing the fluorescence quantum yield and increasing the rate of internal conversion [8]. Above this proportion, there is an expressive increment, due the polarity of the mixtures. This effect increases the energy of activation associated to the conversion of the planar excited electronic state to an intramolecular charge transfer, favoring the quantum yield of fluorescence [19].

Excitation wavelength of quinquangulin (Figure 3A) presents a quadratic ratio of increase in the range between 10 and 60% of water, probably related to the formation of intermolecular hydrogen bonds between quinquangulin and the solvents. These strong polar interactions must stabilize the solute in the solvent mixture, causing a small but perceptible decrease in the excitation energy. It should be emphasized that this compound is soluble in water, which ultimately favors the effect observed. Above 60% of water saturation should occur, and the excitation wavelength remains practically constant. This suggests that, at this point, the organization between ethanol and water is well defined, implying in a saturation of intermolecular hydrogen bonds capable to reduce the excitation gap.

The increase of the excitation wavelength with the amount of water is observed in Figure 3B for rubrofusarin. This trend presents a different regimen, approximately linear, probably related to its low solubility in water. This suggests that the photophysical behavior of these compounds should present subtle differences, what is corroborated by the analysis of excited electronic states and molecular orbitals.

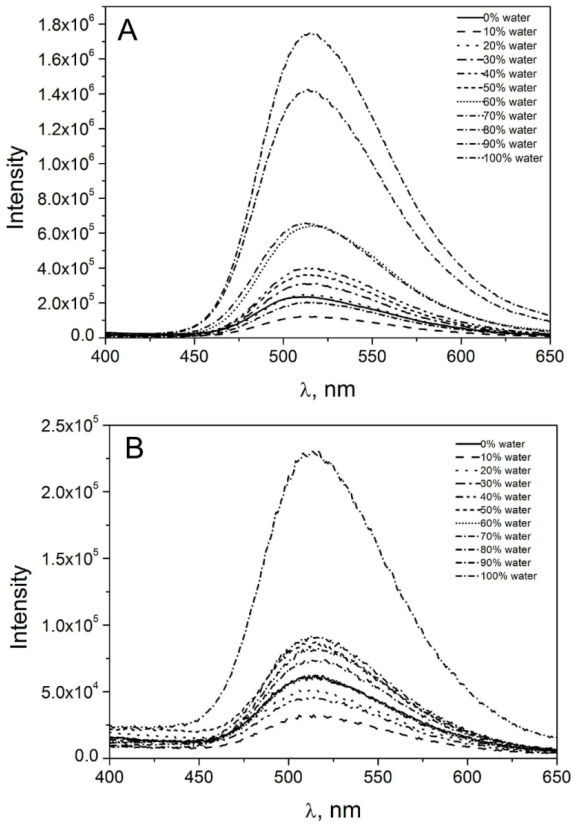

Figure 2. Emission spectra of Quinquangulin (A) and rubrofusarin (B) in water/ethanol mixtures. (λ_{exc} = 350 nm).

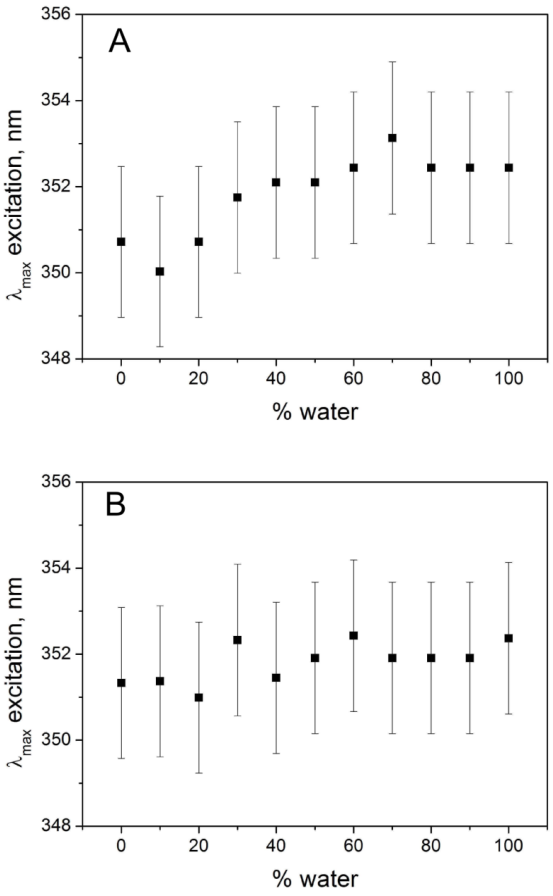

Figure 3. Changes in the maximum excitation wavelength as function of the water percentage of quinquangulin (A) and rubrofusarin (B) in water/ethanol mixture.

The spectral shifts (measured in fluorescence and absorption) caused by the solvent effects are used to estimate the ground- and excited-state dipole moments [21, 22]. There are a linear correlation between the Stokes shifts, $\Delta\nu$, and a solvent polarity function, Δf [21]. The solvent sensitivity of the Stokes' shift is commonly explained by the following Lippert-Mataga equation which is based on the Onsager's reaction field theory [23, 24]:

$$\nu_a - \nu_f = \frac{2(\mu_e - \mu_g)^2}{4\pi\varepsilon_0 hca_0^3}\Delta f(\varepsilon, n) + C \qquad \text{Eq. 1}$$

where ν_a *and* ν_f are the wavenumbers of absorption and fluorescence transition, respectively, h is the Planck's constant, c the speed of light, μ_e and μ_g are the excited state and ground state dipole moments of a solute molecule, a_0 is the cavity. Where Δf can be calculated by [19, 25]:

$$\Delta f(\varepsilon, n) = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \qquad \text{Eq. 2}$$

The ε and n of the pure solvents and mixed solvents were taken from the literature [26-29].

It can be seen that the increasing participation of the organic compound results in a decrease of the intensity the fluorescence together with a slight blue shift in the emission maximum. It can be seen that this maximum and Stokes decreases constantly as the inorganic component is increased, ie, in solvents with low polarity were found lower values of $\Delta\nu$. This indicates greater changes between interactions with less polar solvents relative to those more polar [21].

Figure 4 show the variation of Stokes shift ($\Delta\nu$) with solvent polarity function $\Delta f(\varepsilon,n)$. Dipole–dipole interaction between the solute and solvent is responsible for the large solvent-dependent fluorescence shift proven by linearity of plots [30]. The increase in the Stokes shift with increasing solvent polarity, indicates that there is an increase in the dipole moment on excitation [21]. We observed a decrease in the Stokes shift with increasing polarity. This evaluation indicated that the moment of dipole of the compounds in the excited electronic state is less than in the fundamental electronic state [19].

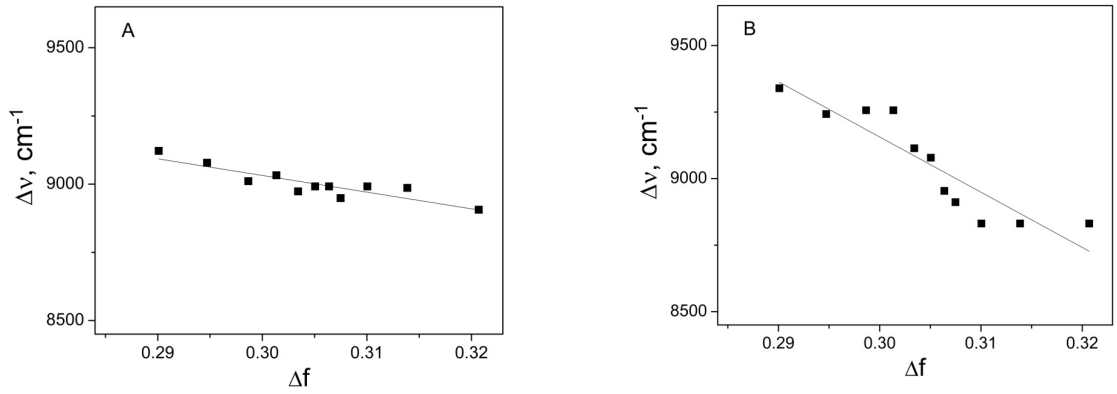

Figure 4. Variation of the Stokes shift as function of the solvent system of quinquangulin (A) and rubrofusarin (B) in water/ethanol mixture.

For both compounds, the possible occurrence of intermolecular hydrogen bonds should affect the energetics and symmetry of the π,π* transition responsible by the transition related to the excitation maximum, as is suggest the theoretical simulations. A theoretical exercise applying a time-dependent self-consistent field (TD-SCF) approach based on a TD-DFT methodology to rubrofusarin in ethanol suggests that S_1 is related to a weak π,π* electronic transition involving exclusively HOMO and LUMO orbitals (Figure 5), with an oscillator strength of 0.1043 (Figure 6), corresponding to a molar absorptivity of approximately 6,000 mol L^{-1} cm^{-1}. The theoretical excitation maximum was estimated as being approximately 379 nm higher the experimental data.

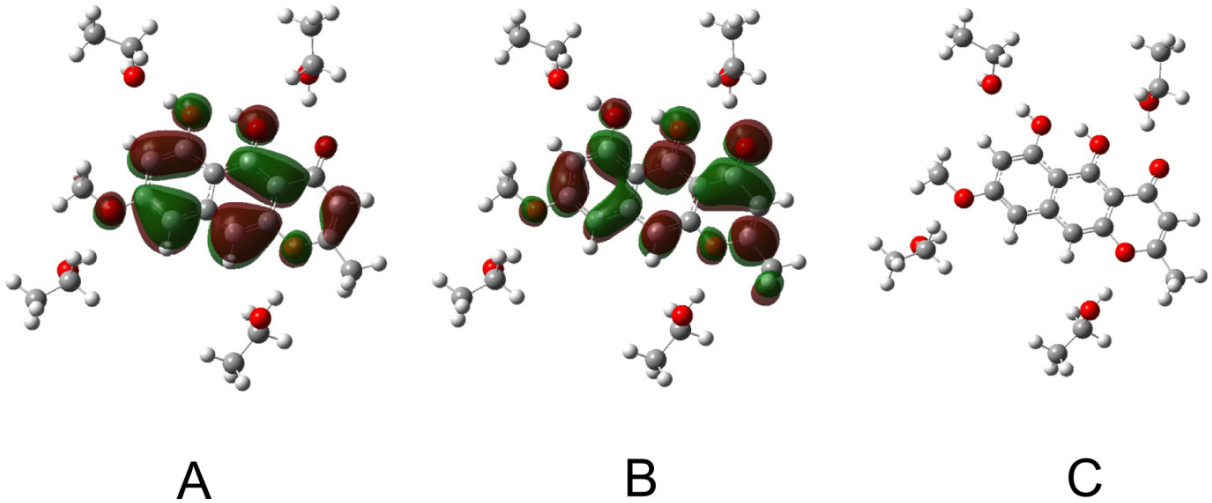

Figure 5. A) Rubrofusarin MO#123-HOMO; B) Rubrofusarin #MO124-LUMO; C) Rubrofusarin surrounded by four molecules of ethanol in a continuous dielectric (characteristics of the ethanol) generated by IEFPC model.

For quinquangulin in ethanol, the theoretical data suggests that S_1 is also related to a weak π,π* electronic transition involving exclusively HOMO and LUMO (Figure 7) orbitals, with an oscillator strength of 0.0963 (Figure 6), corresponding to a molar absorptivity of about 6,000 mol L^{-1} cm^{-1}. The theoretical excitation maximum was estimated as being approximately 386 nm higher the experimental data.

These results are very interesting in respect to solvatochromic behavior of these chemical systems considering solvent mixtures involving different proportions of water and ethanol. The arrangement between ethanol and water should propitiate a condition of more effective interaction with the naphthopyrone compounds, when compared to pure

aqueous solutions. Considering that the unique structural difference between these organic compounds consists in a presence of an additional methyl group in quinquangulin (Figure 1), it is possible to infer that this radical affect significantly the polarity of all compound, modifying the potential to form hydrogen bonds of the respective naphthopyrone. Quantum-mechanical calculations show that the presence of the methyl group is sufficient to change the structure of electronically excited states, especially for relaxed states in the solvent (Figure 8).

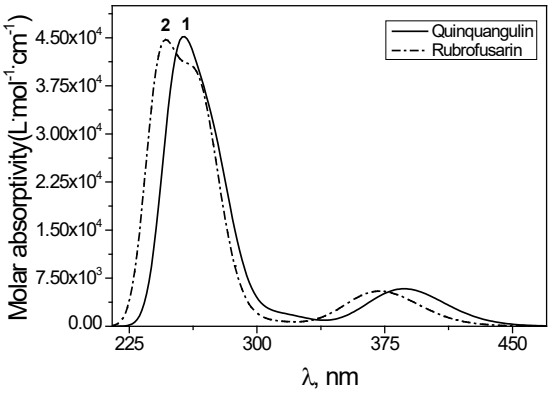

Figure 6. UV-VIS Spectrum simulated for rubrofusarin in ethanol. S_0,S_1 is a HOMO→LUMO π,π* transition (f=0.1043). For quinquangulin, in ethanol. S_0,S_1 is a HOMO→LUMO π,π* transition (f=0.0963).

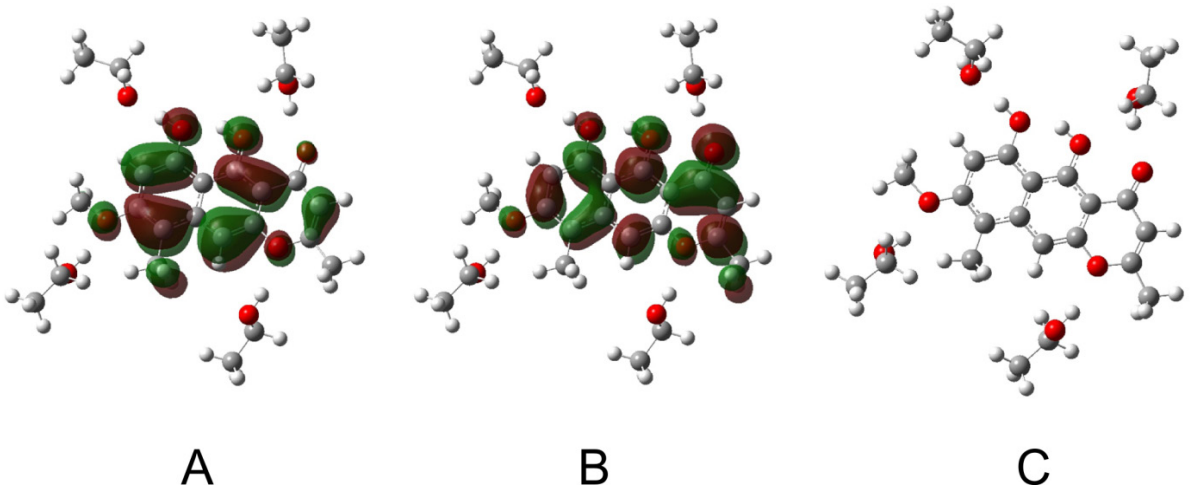

Figure 7. A) Quinquangulin MO#127-HOMO; B) Quinquangulin MO#128-LUMO - C- Quinquangulin surrounded by four molecules ethanol in a continuous dielectric (characteristics of the ethanol) generated by IEFPC model.

Relaxed states in the solvent (geometry of the states optimized with CIS). Diagram of states to the rubrofusarin in ethanol: (C) Non-relaxed states in the solvent; (D) Relaxed states in the solvent (geometry of the states optimized with CIS)

For relaxed states of rubrofusarin, theoretical simulation suggests an efficient intersystem crossing (ISC) between S_1 and T_3, since that these states are adjacent and present different orbital symmetries (El Sayed's Rule). As can be seen from Figures 8C and D this is only possible because of the occurrence of inversion between triplet states due to the relaxation of the excited states in the solvent. It should be noted that the significant energy gap predicted to occur between S_1 and T_3 is sufficiently high to minimize or derail the reversion of the S → T conversion, warranting an efficient population of the triplet state [8]. Furthermore, it is known that the presence of carbonyl groups in conjugate aromatic structures tends to favor kST [19].

The increase in the energy gap between S_2 and S_1 due to solvent relaxation, observed for rubrofusarin, minimizes the influence of S_2 (n,π*) on S_1 (π,π*), favoring the population of T_1 for rubrofusarin (Figures 8C and D) due to the occurrence of favorable conditions for intersystem crossing between S_1 and T_3 and the significant increase in energy between S_1 and the adjacent triplet state ($\Delta E(S_1,T_3)$ = 57.65 kJ mol^{-1}). In view of this, Φ_{ISC} can present a significant value.

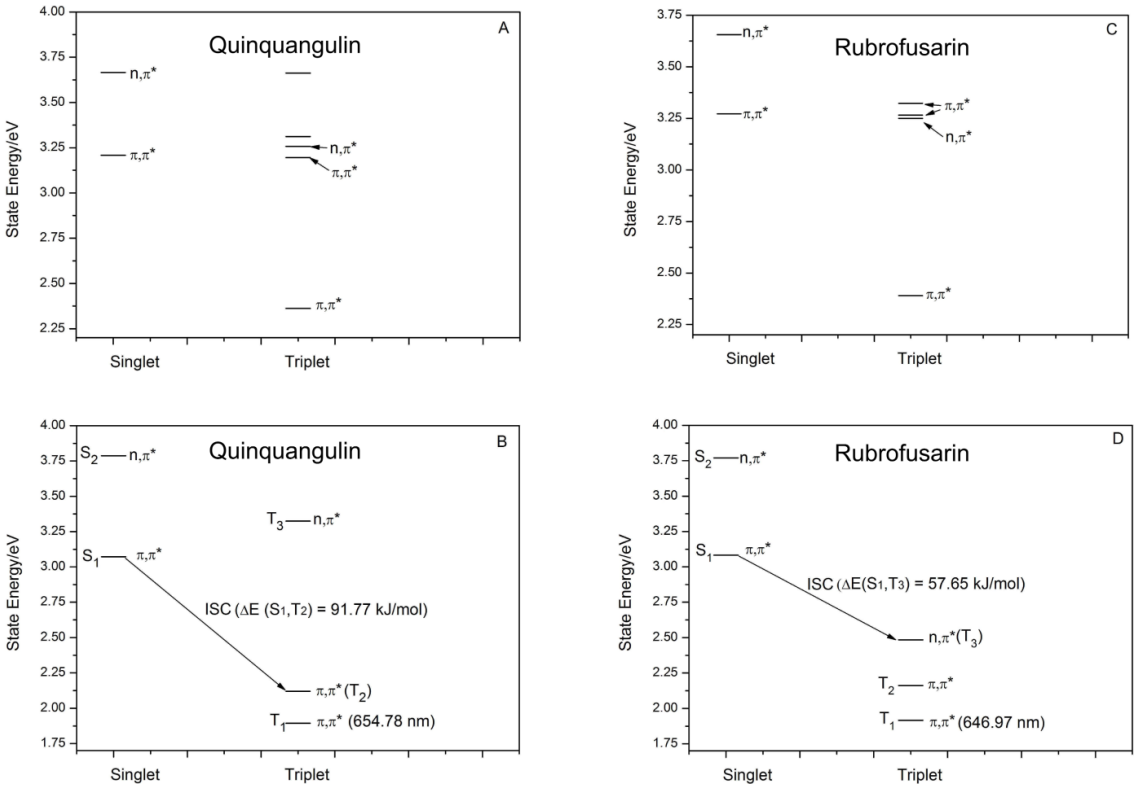

Figure 8. States diagram to the quinquangulin in ethanol: (A) Non-relaxed states in the solvent; (B)

A similar effect is expected for quinquangulin (Figures 8A and B). However, an opposite effect is expected, since that S_1 and T_2, the adjacent triplet state, are both of the same orbital symmetry. On the other hand, the largest energy difference between these states ($\Delta E(S_1,T_2)$ = 91.77 kJ mol^{-1}) and the presence of carbonyl groups in the conjugate aromatic structure [8, 19] can favor to a limited extent the occurrence of intersystem crossing between these species.

The energy associated to the relaxed T_1 state (182.7 kJ mol^{-1} to the quinquangulin and 184.9 kJ mol^{-1} to the rubrofusarin) is enough to sensitize the generation of singlet oxygen ($^1O_2$). Therefore, it is possible that both compounds can act as photosensitizer in singlet oxygen ($^1O_2$) generation for photodynamic therapy (PDT) application, being this more feasible for rubrofusarin. The data of the two compounds are in accordance to the quantum chemical calculations. Therefore, for the most important transition, the HOMO → LUMO is located approximately in 379 and 386 nm for rubrofusarin and quinquangulin, respectively. The fluorescence emission spectra of the rubrofusarin and quinquangulin are similar. However, they have different fluorescence quantum yields (ϕ_F). For quinquangulin ϕ_F is probably larger than rubrofusarin. Therefore, the larger fluorescence quantum yield of quinquangulin can be ascribed to the presence of the methyl group.

The difference in dipole moment of the two molecules in ethanol was calculated based on our data, and then the charge injection process of the electron density of the methyl group to the π dye ring should be attenuated and thus lessening TICT process. The dipole moments of rubrofusarin and quinquangulin were computed by DFT method and the values found were 9.397 and 9.908 D, respectively. This fact in part reflects the inductive effect of the methyl group in the aromatic ring of the compound. This behavior is ascribed to a better redistribution of charges around the molecules. The values of the dipole moment indicate that the charge density distribution around molecules is nonuniform with negative zones of the potential centered at oxygen atoms present in molecules in the neighborhood of the carbon atoms. The positive zones are located around the carbons atoms opposite to the methyl group in quiquangulin molecule. Therefore, in the rubrofusarin molecule the charge distribution is more uniform.

4. CONCLUSION

Napthtophyrones absorb light in the visible

region which can be a useful characteristic for a coadjuvant compound in therapies like PDT. Moreover, this class of organic compounds is significantly soluble in several solvent systems (for example, ethanol), which favor the elaboration of several systems of drug delivery. In this way, the present data are important pre-requisites to apply quinquangulin and rubrofusarin as a potential drug, mainly as photosensitizers, as well as to explain the mechanisms of action of these compounds. Present results demonstrate that the organization between ethanol and water molecules affects significantly excitation and emission spectra of quinquangulin and rubrofusarin. It is important to register that the additional methyl group in quinquangulin seems to develop a decisive function related to the ability to formation of hydrogen bonds, altering significantly the mechanism of solute-solvent interaction. Furthermore, the ethanol, due to its amphipatic character, can develop actions as base of Lewis and/or acid of Lewis, depending of the chemical neighborhood. This fact reinforces the relevance of tests involving mixtures of solvents, since the "biological" solvent, water, inhibits the quantum yield of the naphthopyrones, which would preclude the potential of application of these compounds, like, for example, as photosensitizers in photodynamic therapy. In this way, mixtures of solvents could to promote an optimum condition in order to obtain a maximum quantum yield with a minimum toxicity. It is interesting to register that the fluorescence quantum yield of these naphthopyrones obtained in water is very low, being significant in several pure organic solvents. This fact reinforces the relevance of tests involving solvent mixtures, since the "biological" solvent, water, inhibits the quantum yield of the naphthopyrones, which would preclude the potential of application of these compounds, for example, as photosensitizers in PDT. In this way, mixtures of solvents could to promote an optimum condition in order to obtain a maximum quantum yield with a minimum toxicity.

In summary, quinquangulin and rubrofusarin present representatively different spectroscopic behaviors with the different relation water/ethanol. This fact demonstrated the great physico-chemical influence of the methyl group on the molecular structure and makes quinquangulin a more apolar molecule than rubrofusarin. In this way, the optimization of the solvent-system to each naphtopyrone should be evaluated independently in order to obtain suitable results to therapeutic applications, as the case of the photosensitizers (PS) in photodynamic therapy (PDT).

5. ACKNOWLEDMENTS

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