Journal of Photochemistry and Photobiology A: Chemistry 200 (2008) 282–286

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Photochemical and photophysical properties of lumazine in aqueous solutions

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ARTICLE INFO

Article history:
Received 7 May 2008
Received in revised form 15 July 2008
Accepted 6 August 2008
Available online 14 August 2008

Keywords:
Lumazine
Singlet oxygen
UV-A

ABSTRACT

Lumazine (pteridine-2,4(1*H*,3*H*)-dione, LU) was investigated for its efficiency of singlet oxygen ($^1O_2$) production and quenching in aqueous solution. The quantum yield of $^1O_2$ production (Φ_Δ) was determined by measurements of the $^1O_2$ luminescence in the near-infrared upon continuous excitation of the sensitizer. Values of Φ_Δ are sensitive to the pH and were found to be 0.44 ± 0.01 and 0.080 ± 0.004 in acidic and alkaline media, respectively. The photochemical stability of LU was investigated under different pH conditions, in the presence and in the absence of O_2. The photochemical consumption of LU in aqueous solution at room temperature under irradiation at 350 nm was followed by UV–vis spectrophotometry and HPLC. Values of the quantum yields of LU disappearance are low, indicating that LU is rather photostable under physiological conditions.

1. Introduction

Pteridines are heterocyclic compounds widespread in biological systems, participating in relevant biological functions. Pteridines contain the bicyclic pteridine ring system: a pyrimidine and a pyrazine, and include pterins and lumazines (Fig. 1). The chemical difference between the two groups of compounds lies in the pyrimidine ring.

The participation of pterins in different photobiological processes has been suggested or demonstrated in past decades, and interest in the photophysics and photochemistry of this group of compounds has subsequently increased. The photochemistry of the pterin (PT) moiety has recently been investigated [1]. PT is photostable in the absence of O_2, whereas excitation in air equilibrated solution leads to oxidation, yielding non-pterinic photoproducts (cleavage of PT moiety). The quantum yields of PT disappearance in the presence of O_2 are much lower than those corresponding to derivatives bearing oxidizable substituents [2]. Pterins, upon excitation with UV-A radiation, are able to generate reactive oxygen species (ROS), such as superoxide anion ($O_2^{\bullet -}$) and hydrogen peroxide (H_2O_2) [1,3–5]. In addition, most pterins are good sensitizers of singlet molecular oxygen ($O_2(^1\Delta_g)$, denoted throughout as $^1O_2$), under UV-A irradiation in aqueous solutions [2,6].

Lumazine derivatives are present in cells, since 6,7-dimethyl-8-ribityllumazine is the biosynthetic precursor of riboflavin (vitamin B2). Riboflavin is itself the precursor of flavin mononucleotide and flavin adenine dinucleotide, essential cofactors for a wide variety of redox enzymes [7]. Lumazines are also natural products from the metabolic degradation of pterins [8]. Lumazine (pteridine-2,4(1*H*,3*H*)-dione, LU) presents different acid–base equilibria in aqueous solutions. The only relevant equilibrium at physiological pH involves the neutral form and the monoanion (Fig. 2), with a pK_a value of 7.95 [9]. The absorption spectra of both acid–base forms, although quite different, have intense bands in the UV-A region (320–400 nm) (Fig. 2). Fluorescence properties of LU were described many years ago, and the fluorescence quantum yields depend on the pH, being 0.24 ± 0.02 at pH 10, and lower in acidic media (<0.08) [10]. Lumazines have been of interest recently for their fluorescent properties and their potential use as reporter groups in DNA probes [11].

In spite of the biological importance of lumazine derivatives, little is known about the photochemistry of these compounds [12]. In the present work, we have investigated the photochemistry of LU under UV-A irradiation in both acidic and alkaline aqueous solutions. The quantum yields of LU disappearance are reported. The capability of LU to produce reactive oxygen species was studied. In particular, as previously reported for PT and its derivatives [6], LU may act as a singlet oxygen ($^1O_2$) sensitizer by energy transfer from its triplet excited state to dissolved molecular oxygen (reactions (1) and (2), Sens = LU).

$$^1\text{Sens} \xrightarrow{h\vartheta} {}^1\text{Sens}^* \rightarrow {}^3\text{Sens}^* \quad (1)$$

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doi:10.1016/j.jphotochem.2008.08.003

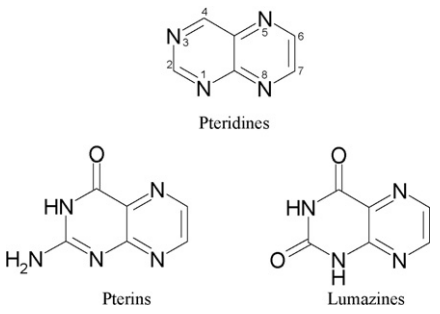

Fig. 1. Chemical structures of natural pteridines.

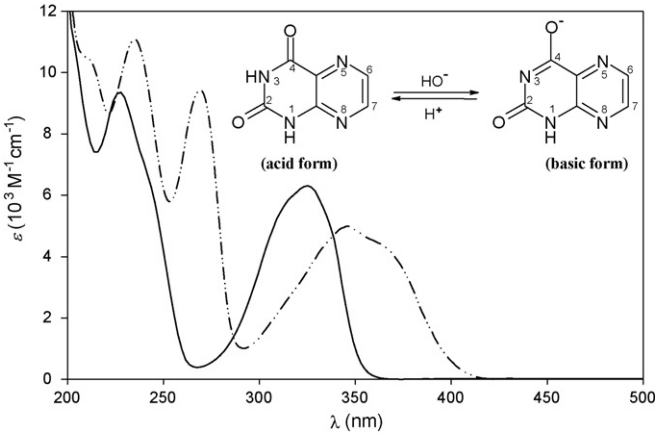

Fig. 2. Molecular structure of LU, and the corresponding absorption spectra in air-equilibrated aqueous solutions; solid line: acid form of LU (pH 5.5); dashed-dotted line: basic form of LU (pH 10.5).

$$^3\text{Sens}^* + {}^1\text{O}_2 \rightarrow {}^1\text{Sens} + {}^1\text{O}_2 \quad (2)$$

Singlet oxygen is one of the main activated species responsible for the damaging effects of light on biological systems (photodynamic effects) [13], and it has been shown that photosensitization is primarily responsible for the production of $^1O_2$ in vivo [14]. This activated metastable species has been attracting interest for several decades in both practical and fundamental aspects [13,15]. We have determined the quantum yield of $^1O_2$ production (Φ_Δ) by LU. Moreover, this compound may be oxidized by $^1O_2$ and physically quench this species (reactions (3) and (4), Q = LU).

$$\text{Q} + {}^1\text{O}_2 \xrightarrow{k_r} \text{QO}_2 \quad (3)$$

$$\text{Q} + {}^1\text{O}_2 \xrightarrow{k_q} \text{Q} + {}^3\text{O}_2 \quad (4)$$

The rate constant of $^1O_2$ total quenching ($k_t = k_r + k_q$) by LU was determined and the role of $^1O_2$ on the mechanism of the photooxidation of LU was analyzed. The results obtained in this study are compared with previous studies reported for pterins.

2. Experimental

2.1. Chemicals

Lumazine (pteridine-2,4(1*H*,3*H*)-dione, LU) was purchased from Schircks Laboratories (Switzerland) (purity > 97.5%) and used without further purification. Other chemicals from Sigma–Aldrich were used as received. The pH of the aqueous solutions was adjusted, by adding drops of HCl and NaOH solutions from a micropipette. The concentration of the acid and the base used for this purpose ranged from 0.1 M to 2 M. The ionic strength was approximately 10^{-3} M in all the experiments.

In singlet oxygen ($^1O_2$) experiments, D_2O (Euriso-top, Groupe CEA, Saclay, France, minimum isotopic purity of 99.9%), solutions of DCl (Aldrich, 99.5% D) and NaOD (CEA) in D_2O were employed.

2.2. Photolysis experiments

2.2.1. UV irradiation

The continuous irradiation of 3 cm^3 LU solutions (100–400 μM) were carried out in quartz cells (1 cm optical path length) at room temperature. Rayonet RPR lamps emitting at 350 (±10) nm (Southern N.E. Ultraviolet Co.) were employed for the irradiation. Photolysis experiments were performed in the presence and in the absence of air. Deaerated solutions were obtained by bubbling with argon for 20 min.

2.2.2. UV–vis spectrophotometric analysis

UV–vis spectra were registered on a Cary 3 (Varian) spectrophotometer, using a program for smoothing and averaging signals. Absorption spectra of the solutions were recorded at regular intervals of irradiation time in the cells used for the irradiations (Section 2.2.1).

2.2.3. High-performance liquid chromatography (HPLC)

A high-performance liquid chromatograph Prominence from Shimadzu (solvent delivery module LC-20AT, on-line degasser DGU-20A5 and UV–vis photodiode array detector SPD-M20A, autosampler SIL-20AHT) was employed for monitoring the reaction. A Pinnacle-II C18 column (250 mm × 4.6 mm, 5 μm; Restek) was used for product separation. An aqueous solution of potassium phosphate (20 mM, pH 5.5) containing 3% of acetronitrile was used as eluent.

2.2.4. Quantum yield determinations

The quantum yields of LU disappearance (Φ_{-LU}) were determined in experiments performed in 1 cm × 1 cm quartz cells (3 cm^3 of solution) under different conditions. The evolution of the concentrations of LU during the irradiation time was followed by HPLC. The incident photon flux ($q_{p,0}$) at the wavelength of excitation (350 nm) was determined by actinometry using Aberchrome 540 as an actinometer [16,17] ($q_{p,0} = 1.3\ (\pm 0.1) \times 10^{-6}$ Einstein s^{-1} at 350 nm). Aberchrome 540 is the anhydride form of the (*E*)-α-(2,5-dimethyl-3-furylethylidene)(isopropylidene)succinic acid which under irradiation in the spectral range 316–366 nm leads to a cyclized form [16]. Values of $q_{p,a}$ (photon flux absorbed by the reactant) were calculated from $q_{p,0}$ using the Beer–Lambert law

$$q_{p,a} = q_{p,0}(1 - 10^{-A}) \quad (5)$$

where *A* is the absorbance of the reactant (LU) at the excitation wavelength.

2.3. Singlet oxygen ($^1O_2$) studies

Singlet oxygen relaxes to its triplet ground state by both radiationless and radiative pathways (reactions (6) and (7), respectively). In most solvents, the rate constant of the former process is much larger than that of the latter ($k_d \gg k_e$), and the $^1O_2$ lifetime (τ_Δ) in a given solvent is given by $1/k_d$

$$^1\text{O}_2 \xrightarrow{k_d} {}^3\text{O}_2 \quad (6)$$

$$^1\text{O}_2 \xrightarrow{k_e} {}^1\text{O}_2 + h\vartheta' \quad (7)$$

If a substance in solution (which may be the sensitizer itself) is able to quench or trap $^1O_2$, chemical reaction (reaction (3)) and physical quenching (reaction (4)) must be considered.

2.3.1. Determination of quantum yields of $^1O_2$ production

The quantum yields of $^1O_2$ production (Φ_Δ) were determined by direct analysis of the weak $^1O_2$ near-infrared luminescence at 1270 nm (reaction (7)) [18–20], produced during continuous irradiation of LU in aqueous solution.

The main features of the method and the equipment have already been described in detail [21–23]. Briefly, the sample solution in a quartz cuvette was irradiated with a xenon/mercury arc through a water filter, focusing optics and a monochromator (6 nm bandwidth). The $^1O_2$ luminescence was collected with a mirror, chopped and, after passing through focusing lens, a cut-off filter (1000 nm) and an interference filter (1271 nm), was detected at 90° with respect to the incident beam using a cooled NIR photomultiplier (Hamamatsu).

For determining Φ_Δ, the intensities of the $^1O_2$ luminescence signals were measured in 1 cm × 1 cm quartz cells (3 cm^3 of solution) alternating between the sensitizer under study (S_e^S) and the reference sensitizer (S_e^R) (3 min irradiation time for each sample). The absorbances at the wavelength of irradiation were the same for the reference sensitizer (R) and the sample solution (S). Under these conditions, the ratio of the luminescence signals, S_e^S/S_e^R is given by the following equation:

$$\frac{S_e^S}{S_e^R} = \frac{q_{p,0}^S}{q_{p,0}^R}\frac{\Phi_\Delta^S}{\Phi_\Delta^R}\frac{k_d}{k_d + k_t^S[\text{Sens}]} \quad (8)$$

where $q_{p,0}^S/q_{p,0}^R$ is the ratio of the incident photon fluxes at the wavelength of excitation of the sensitizer investigated and of the reference. If k_d (the non-radiative rate constant of $^1O_2$ deactivation by the solvent) and k_t^S (the rate constant of $^1O_2$ total quenching by the sensitizer itself) are known in the solvent used, Φ_Δ may be calculated from Eq. (8) by measuring S_e^S and S_e^R, as well as the corresponding incident photon fluxes. The latter were calculated from the incident radiant powers (P_0, W) measured with a thermopile ($q_{p,0}^S/q_{p,0}^R = (P_0^S\lambda_{ex}^S)/(P_0^R\lambda_{ex}^R)$, where λ_{ex}^S and λ_{ex}^R are the wavelengths of excitation of sensitizer under study and reference, respectively). Eq. (8) is valid if $^1O_2$ quenching by the reference sensitizer itself is negligible compared to quenching by the solvent ($k_t^R[R] \ll k_d$), which is the case for the reference sensitizers used in this work. Because of the short lifetime of $^1O_2$ (τ_Δ) in H_2O (3.1–3.8 μs), D_2O, where τ_Δ is much longer (62 μs) was used as solvent in all experiments [24,25]. Measurements with LU were carried out at an excitation wavelength (λ_{ex}) of 310 nm in acidic media and 367 nm in alkaline media. Rose bengal (RB) in D_2O (λ_{ex} = 547 nm, $\Phi_\Delta^R = 0.75$ [26,27]) and 1*H*-phenalen-1-one (PHE) in D_2O (λ_{ex} = 367 nm, $\Phi_\Delta^R = 0.98$ [28]) were used as reference sensitizers.

2.3.2. Determination of rate constants of $^1O_2$ total quenching by lumazine

The rate constant of $^1O_2$ total quenching (k_t) by LU was determined by Stern–Volmer analysis of the $^1O_2$ luminescence quenching. The main features of the method was described elsewhere [6,29]. $^1O_2$ was generated by photosensitization, using RB as a sensitizer. Groups of experiments were carried out irradiating solutions of LU and RB at 547 nm, where the investigated compound does not absorb. The RB concentration was kept constant, whereas the LU concentration was varied within a series of experiments. Under our experimental conditions [6], a linear relationship between the ratio of the luminescence intensities in the absence (S_e^0) and in the presence (S_e) of quencher (Q = LU) and the quencher concentration was observed in the following equation:

$$\frac{S_e^0}{S_e} = 1 + k_t\,\tau_\Delta[Q] \quad (9)$$

where τ_Δ is the $^1O_2$ lifetime in the solvent used (D_2O) in the absence of Q. Therefore, knowing τ_Δ, k_t can be calculated from the slope of the Stern–Volmer plot.

3. Discussion

3.1. Photolysis of lumazine

Taking into account the acid–base equilibria of LU and to avoid interferences between the neutral and the monoanionic forms, we performed our experiments in the pH ranges 5.0–5.5, where LU is present at more than 99% in its neutral form, and 10.2–10.7, where LU is present at more than 99% in its monoanionic form (Fig. 2).

Air-equilibrated and O_2-free aqueous solutions of LU were irradiated at 350 nm under both pH conditions. Only slight spectral changes were registered even after several hours of irradiation, suggesting that LU is rather photostable. HPLC measurements of the concentration of LU during irradiation were in agreement with the spectral analysis. The quantum yields of LU consumption (Φ_{-LU}) were calculated from the values of the initial rate of LU consumption (r_{-LU}) determined by HPLC and the initial absorbed photon flux ($q_{p,a}$) determined by actinometry (Section 2). Corresponding values are listed in Table 1. Note that the calculated rates and quantum yields have rather large errors due to the very limited consumption of the reactant. The values of Φ_{-LU} are similar under all conditions investigated and are in the range of 2×10^{-4} to 3.5×10^{-4}. These low values confirm that LU is rather stable under UV-A irradiation. The Φ_{-LU} values obtained in anaerobic conditions are slightly higher than those obtained in air-equilibrated solutions and the pH has practically no effect.

The quantum yields of consumption of LU in air-equilibrated solution are lower than those reported for the related compound pterin [1] (PT, Fig. 1) (Table 1), thus indicating that LU is more pho-

Table 1
Quantum yields of consumption (Φ_{-LU}), quantum yields of $^1O_2$ production (Φ_Δ) and rate constant of $^1O_2$ total quenching (k_t [$M^{-1}\,s^{-1}$]) measured for lumazine

	Lumazine		Pterin[a]	
	pH 5.5	pH 10.5	pH 5.5	pH 10.5
$\Phi_{-LU/PT}$ (air)	$(2 \pm 1) \times 10^{-4}$	$(2.7 \pm 0.7) \times 10^{-4}$	$(0.82 \pm 0.06) \times 10^{-3}$	$(1.2 \pm 0.2) \times 10^{-3}$
$\Phi_{-LU/PT}$ (Ar)	$(3.0 \pm 0.7) \times 10^{-4}$	$(3.5 \pm 0.6) \times 10^{-4}$	0	0
Φ_Δ (air)	0.44 ± 0.01	0.080 ± 0.004	0.18 ± 0.02	0.30 ± 0.02
Φ_Δ (O_2)	0.44 ± 0.01	0.077 ± 0.004	–	–
k_t	–	$(7.2 \pm 0.7) \times 10^5$	–	$(2.9 \pm 0.3) \times 10^6$

All the values correspond to experiments performed in aqueous solutions under UV-A irradiation.
[a] Values for pterin are given for comparison. Data from Refs. [1,6].

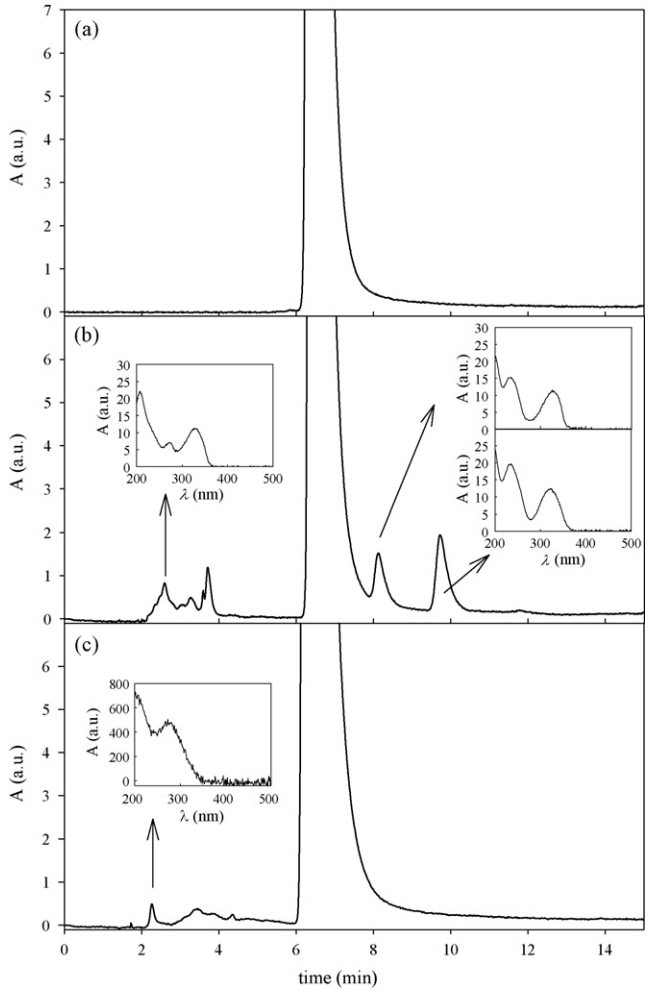

Fig. 3. Chromatograms obtained in HPLC analysis: (a) non-irradiated solution; (b) solution irradiated 240 min in argon atmosphere; (c) solution irradiated 240 min in air atmosphere. $[LU]_0 = 400\ \mu M$, pH 5.5, $\lambda_{an} = 230$ nm.

tostable than PT. In addition, the photolysis of PT has been reported to be an O_2-dependent process, PT being photostable in anaerobic conditions [1]. Therefore, the photochemistry of PT and LU appears to be quite different.

Under both pH conditions, HPLC analysis of irradiated air-equilibrated solutions of LU showed the presence of several photoproducts (Fig. 3). These results suggest that the photolysis of LU proceeds through different pathways. Spectra of the photoproducts were recorded using the DAD detector of the HPLC equipment (Section 2). Such analyses, especially those carried out for long irradiation times ($t_i > 4$ h), where conversion of the reactant was significant, suggested that most photoproducts detected are non-pteridinic compounds; i.e. the characteristic absorption bands of lumazines in the UV-A region were lost (Fig. 3c). In addition, a photoproduct, with a spectrum compatible with a pteridinic structure, was also detected but only in alkaline media.

Many photoproducts were also detected by HPLC analysis under anaerobic conditions (Fig. 3b). However, in both acidic and alkaline media, the comparison between the chromatograms and spectra corresponding to different peaks reveals that the photoproducts are different (Fig. 3). Moreover, in anaerobic conditions, several pteridinic derivatives were detected. These results show that the photolysis mechanisms are O_2-dependent.

3.2. Rate constants of $^1O_2$ total quenching (k_t) and quantum yields of $^1O_2$ production (Φ_Δ) by lumazine

The values of the rate constants of $^1O_2$ total quenching ($k_t = k_r + k_q$) by LU were determined as indicated in Section 2. The Stern–Volmer plot of the quenching of the near-infrared $^1O_2$ luminescence (Eq. (9)) was linear within the range of concentrations used (Fig. 4). The value of k_t ($7.2 \pm (0.7) \times 10^5\ M^{-1}\ s^{-1}$) was calculated from the slope of this plot, taking a value of 62 μs for the $^1O_2$ lifetime (τ_Δ) in D_2O. This value is of the same order of magnitude as other k_t values previously determined for related heterocyclic compounds, e.g. some pterin derivatives [2] and adenine nucleotides [30].

The values of the quantum yields of $^1O_2$ production (Φ_Δ) by LU were determined in air-equilibrated and O_2 saturated D_2O solutions, by monitoring the near-infrared $^1O_2$ luminescence (*vide supra*). LU was excited at 367 nm in alkaline media and 310 nm in acidic media. LU has a relatively high fluorescence quantum yield (Φ_F) [10]. Therefore, control experiments in argon-saturated solutions were carried out in order to check possible tailing of the fluorescence emission of LU in the near-infrared. No luminescence at 1270 nm could be detected under those conditions, independently of the pD.

The experiments were performed in the pD ranges of 5.0–6.0 and 10.0–11.0. (1*H*-phenalen-1-one ($\lambda_{ex} = 367$ nm) and rose bengal ($\lambda_{ex} = 547$ nm) were used as reference sensitizers in experiments performed in acidic and alkaline media, respectively. Significant $^1O_2$ emission was detected for LU, in both media. The values of Φ_Δ in alkaline media for LU were calculated using Eq. (8) (Section 2.3.1). Under the experimental conditions used in this work, k_d (reaction (4)) was much larger than the product k_t^S [Sens] ($k_d/(k_t^S$ [Sens]) > 10). A value of 0.080 ± 0.004 was obtained for Φ_Δ in air-equilibrated solutions at pD 10.5.

k_t^S was not measured in acidic medium, therefore the quantum yield of $^1O_2$ production (0.44 ± 0.01) determined for the acid form (pD 5.5) is an apparent value (Φ_Δ^{app}), not corrected for the quenching by the sensitizer itself. However, it may be assumed that the k_t^S value either do not change drastically at lower pH, or might be even be lower in acidic than in alkaline media (*vide supra*), as observed for other compounds [31,32]. Therefore, the reported Φ_Δ^{app} value may be considered as the Φ_Δ value.

It is worth mentioning that values of Φ_Δ did not increase when the solutions were saturated with oxygen (0.077 ± 0.004 and

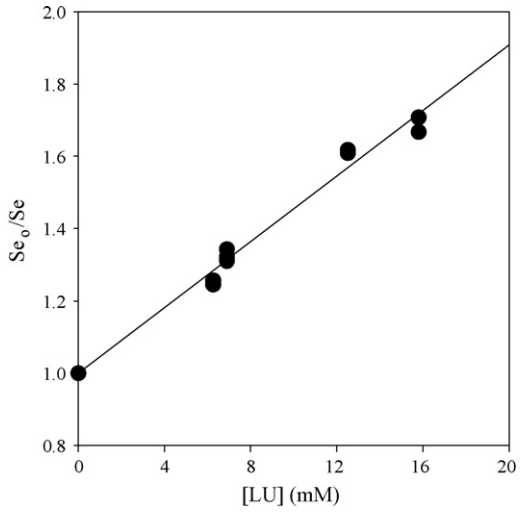

Fig. 4. Stern–Volmer plot of the quenching of the $^1O_2$ near-infrared luminescence by lumazine in D_2O (rose bengal was used as a sensitizer, $\lambda_{ex} = 547$ nm).

0.44 ± 0.01 for alkaline and acid forms, respectively). It is therefore probable that all excited triplet states were quenched by oxygen already under air equilibrated conditions.

In contrast to results obtained in this work for LU, pterin derivatives have higher Φ_Δ values in alkaline than in acidic media [6] (Table 1). This behavior may be correlated with the emission properties of lumazines and pterins: whereas fluorescence quantum yields of acidic forms (neutral forms) of pterins ($\Phi_F = 0.33 \pm 0.01$ for PT) are higher than those corresponding to the basic forms (monoanions) ($\Phi_F = 0.27 \pm 0.01$ for PT), LU presents the opposite behavior [10]. In the case of LU, a more efficient intersystem crossing may be assumed for the neutral form, leading to a relatively high Φ_Δ (0.44) and a low Φ_F (<0.08) in acidic medium.

4. Conclusions

In this work we have studied lumazine (pteridine-2,4(1*H*,3*H*)dione, LU) as a singlet oxygen ($^1O_2$) photosensitizer under UV-A irradiation in aqueous solution at different pH. The neutral form of LU (Fig. 2), the predominant acid–base form at physiological pH, has a high quantum yield of $^1O_2$ production ($\Phi_\Delta = 0.44$). On the other hand, the monoanionic form (Fig. 2) is a much less efficient $^1O_2$ sensitizer ($\Phi_\Delta = 0.08$). The value of the rate constant of $^1O_2$ total quenching by LU ($k_t = 7.2(\pm 0.7) \times 10^5\ M^{-1}\ s^{-1}$) shows that the studied compound is a poor $^1O_2$ quencher, which means that, in aqueous media, $^1O_2$ produced photochemically by LU is not quenched significantly by LU itself. Quantum yields of LU consumption obtained when solutions were exposed to UV-A radiation were very low, thus indicating that the compound is relatively photostable. In conclusion, LU efficiently generates $^1O_2$ under UV-A irradiation at physiological pH, is a poor $^1O_2$ quencher (low k_t) and does not undergo photolysis under UV-A irradiation. These facts make this natural compound an efficient $^1O_2$ photosensitizer.

Acknowledgements

The present work was partially supported by Agencia de Promoción Científica y Tecnológica (ANPCyT Grant N° PICT 33919), Consejo Nacional de Investigaciones Cientificas y Técnicas (CONICET-PIP 6301/05), and Universidad Nacional de La Plata (UNLP). C.L. and A.H.T. thank the Deustche Akademische Austauschdienst (DAAD) for research fellowships. A.H.T. and C.L. are research members of CONICET. M.P.D. thanks the ANPCyT for a graduate research fellowship.

References

[1] F.M. Cabrerizo, M.L. Dántola, A.H. Thomas, C. Lorente, A.M. Braun, E. Oliveros, A.L. Capparelli, Photooxidation of pterin in aqueous solutions: biological and biomedical implications, Chem. Biodiv. 1 (2004) 1800–1811.
[2] C. Lorente, A.H. Thomas, Photophysics and photochemistry of pterins in aqueous solution, Acc. Chem. Res. 39 (2006) 395–402.
[3] G. Petroselli, J.M. Bartsch, A.H. Thomas, Photoinduced generation of H_2O_2 and O_2^- by 6-formylpterin in aqueous solutions, Pteridines 17 (2006) 82–89.
[4] A.H. Thomas, R. Cabrerizo, M. Vignoni, R. Erra-Balsells, F.M. Cabrerizo, A.L. Capparelli, Photoinduced formation of reactive oxygen species from the acid form of 6-(hydroxymethyl)pterin in aqueous solution, Helv. Chim. Acta 89 (2006) 1090–1104.
[5] F.M. Cabrerizo, A.H. Thomas, C. Lorente, M.L. Dántola, G. Petroselli, R. Erra-Balsells, A.L. Capparelli, Generation of reactive oxygen species during the photolysis of 6-(hydroxymethyl)pterin in alkaline aqueous solutions, Helv. Chim. Acta 87 (2004) 349–365.
[6] A.H. Thomas, C. Lorente, A.L. Capparelli, C.G. Martínez, A.M. Braun, E. Oliveros, Singlet oxygen ($^1\Delta_g$) production by pterin derivatives in aqueous solutions, Photochem. Photobiol. Sci. 2 (2003) 245–250.
[7] K. Kis, K. Kugelbrey, A. Bacher, Biosynthesis of riboflavin the reaction catalyzed by 6,7-dimethyl-8-ribityllumazine synthase can proceed without enzymatic catalysis under physiological conditions, J. Org. Chem. 66 (2001) 2555–2559.
[8] H. Rembold, W.L. Gyure, Biochemistry of the pteridines, Angew. Chem. Int. Ed. Engl. 11 (1972) 1061–1072.
[9] W. Pfleiderer, I. Pteridine, Über 2,4-dioxotetrahydropteridine, Chem. Ber. 90 (1957) 2582–2587.
[10] R. Klein, I. Tatischeff, Tautomerims and fluorescence of lumazine, Potochem. Photobiol. 45 (1987) 55–65.
[11] W. Bannwarth, F. Müller, Energy transfer from a lumazine (=pteridine-2,4(1*H*,3*H*)-dione) chromophore to bathophenanthroline-ruthenium(II) complexes during hybridization processes of DNA, Helv. Chem. Acta 74 (1991) 2000–2008.
[12] A. Momzikoff, R. Santus, Photochimie des ptéridines en zone euphotique: premières données, Océanis Hors-Série V (1979–1980) 505–511.
[13] A.A. Frimer, Singlet Oxygen, vols. I–IV, CRC Press, Boca Raton, 1985.
[14] M. Tarr, D.P. Valenzeno, Singlet oxygen: the relevance of extracellular production mechanisms to oxidative stress in vivo, Photochem. Photobiol. Sci. 2 (2003) 355–361.
[15] A.M. Braun, M.-T. Maurette, E. Oliveros, Photochemical Technology, Wiley, Chichester, 1991, pp. 445–499, and references cited therein (translated by D. Ollis, N. Serpone).
[16] A.M. Braun, M.-T. Maurette, E. Oliveros, Photochemical Technology, Wiley, Chichester, 1991, pp. 85–88 (translated by D. Ollis N. Serpone).
[17] H.J. Kuhn, S.E. Braslavsky, R. Schmidt, IUPAC technical report on chemical actinometry, Pure Appl. Chem. 76 (2004) 2105–2146.
[18] A.A. Krasnovsky Jr., Photosensitized luminescence of singlet oxygen in aqueous solutions, Biophysics 24 (1979) 769–771.
[19] A.U. Kahn, Direct spectroscopic observation of 1.27 mm and 1.58 mm emission of singlet ($^1\Delta_g$) molecular oxygen in chemically generated and dye-photosensitized liquid solutions at room temperature, Chem. Phys. Lett. 72 (1980) 112–114.
[20] P. Murasecco-Suardi, E. Oliveros, A.M. Braun, H.-J. Hansen, Singlet-oxygen quenching by carotenoids: steady-state luminescence experiments, Helv. Chim. Acta 71 (1988) 1005–1010.
[21] T. Aminian-Shagafi, G. Nasini, T. Caronna, A.M. Braun, E. Oliveros, Quantum yields of singlet-oxygen production by some natural quinoid fungal metabolites and derivatives, Helv. Chim. Acta 75 (1992) 531–538.
[22] A.M. Braun, E. Oliveros, Applications of singlet oxygen reactions: mechanistic and kinetic investigation, Pure Appl. Chem. 62 (1990) 1467–1476.
[23] E. Oliveros, P. Suardi-Murasecco, T. Aminian-Shagafi, A.M. Braun, H.J. Hansen, 1*H*-Phenalen-1-one: photophysical properties and singlet oxygen production, Helv. Chim. Acta 74 (1991) 79–90.
[24] C. Schweitzer, R. Schmidt, Physical mechanisms of generation and deactivation of singlet oxygen, Chem. Rev. 103 (2003) 1685–1757.
[25] L.A. Martínez, C.G. Martínez, B.B. Klopotek, J. Lang, A. Neuner, A.M. Braun, E. Oliveros, Nonradiative and radiative deactivation of singlet molecular oxygen in micellar media and microemulsions, J. Photochem. Photobiol. B 58 (2000) 94–107, and references cited therein.
[26] P. Murasecco-Suardi, E. Gassmann, A.M. Braun, E. Oliveros, Determination of the quantum yield of intersystem crossing of rose bengal, Helv. Chim. Acta 70 (1987) 1760–1773.
[27] D.C. Neckers, Rose bengal, J. Photochem. Photobiol. A: Chem. 47 (1989) 1–29.
[28] R. Schmidt, C. Tanielian, R. Dunsbach, C. Wolff, Phenalenone, A universal reference compound for the determination of quantum yields of singlet oxygen $O_2(^1\Delta_g)$ sensitization, J. Photochem. Photobiol. A: Chem. 79 (1994) 11–17.
[29] C. Tournaire, S. Croux, M.-T. Maurette, I. Beck, M. Hocquaux, A.M. Braun, E. Oliveros, Antioxidant activity of flavonoids: eficiency of singlet oxygen ($^1\Delta_g$) quenching, J. Photochem. Photobiol. B: Biol. 19 (1993) 205–215.
[30] G. Petroselli, R. Erra-Balsells, F.M. Cabrerizo, C. Lorente, A.L. Capparelli, A.M. Braun, E. Oliveros, A.H. Thomas, Photosensitization of 2'-deoxyadenosine-5'-monophosphate by pterin, Org. Biomol. Chem. 5 (2007) 2792–2799.
[31] N.A. García, Singlet molecular oxygen-mediated photodegradation of aquatic phenolic pollutants. A kinetic and mechanistic overview, J. Photochem. Photobiol. B: Biol. 22 (1994) 185–196.
[32] M. Luiz, A.T. Soltermann, A. Biasutti, N.A. García, A kinetic study on the singlet molecular oxygen [$O_2(^1\Delta_g)$] generation and quenching by dihydroxynaphtalenes, Can. J. Chem. 74 (1995) 49–54.