42. Quantum Yields of Singlet-Oxygen Production by Some Natural Quinoid Fungal Metabolites and Derivatives

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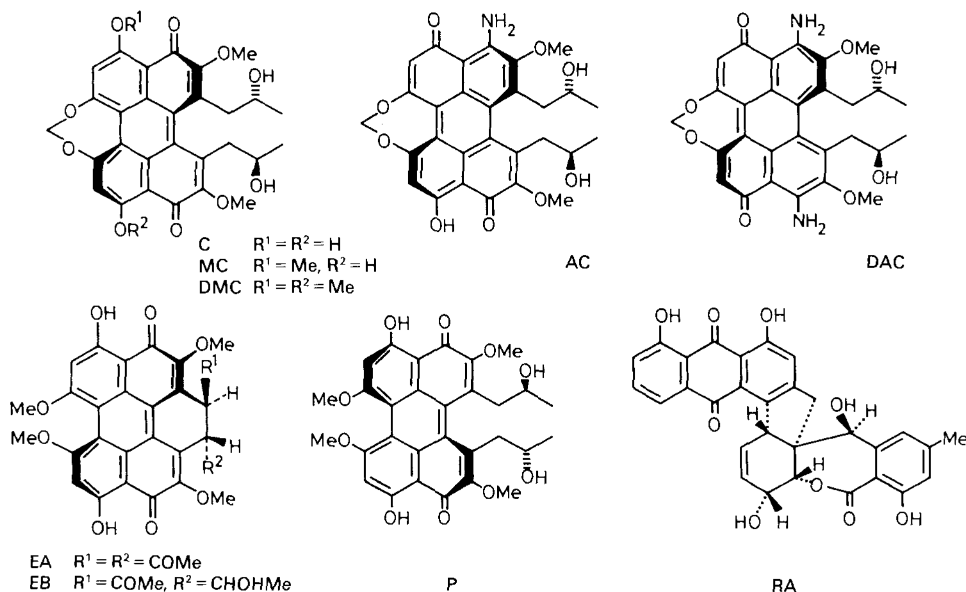
Perylene quinone compounds of natural and synthetic origin have been investigated for their quantum efficiency of singlet-oxygen production (Φ_Δ). The results may be interpreted by a qualitative relation between Φ_Δ and the planarity of the sensitizer molecules, highest values (0.8–0.9) being observed where planarity is favoring tautomeric structures. On the other hand, derivatives exhibiting non-planar quinoid structures show lower Φ_Δ, and methylated derivatives react photochemically.

Introduction. – In the presence of a dye (sensitizer) and molecular oxygen, singlet oxygen $O_2(^1\Delta_g)$ (denoted below $^1O_2$) is one of the main activated species responsible for the damaging effects of light on biological systems (photodynamic effect) [1–3]. Potential applications of $^1O_2$-mediated toxicity in cancer therapy [3] have stimulated the search for efficient, stable, specific, and biologically compatible $^1O_2$ sensitizers [4] [5].



Some fungal strains of the genus *Cercospora*, *Elsinoë*, and *Cladosporium*, produce red perylene quinone pigments, a class of compounds of chemical and biological interest: in addition to their particular stereochemical problems (*i.e.* axial chirality combined with asymmetric C-atoms) [6], these metabolites cause necrotic diseases [7], mainly as a result of their photodynamic activity [6]. Cercosporin, for example, is an efficient $^1O_2$ sensitizer [8] [9], and this property may be one of the reasons of its function as a toxin of the phytopathogenic strains of *Cercospora* spp. In [10], a scale of photodynamic efficiency of some quinoid fungal metabolites was established, based on the production of hydroperoxides, when these compounds were irradiated in the presence of methyl oleate, used as a $^1O_2$ acceptor.

In this paper, we report the quantum yields of $^1O_2$ production (Φ_Δ) by nine natural quinoid fungal metabolites and derivatives: cercosporin (C), methylcercosporin (MC), dimethylcercosporin (DMC), aminocercosporin (AC), diaminocercosporin (DAC), elsinochromes A (EA) and B (EB), phleichrome (P), and rubellin A (RA). The structures of these compounds are represented above (for each structure, only one of possible tautomeric forms has been given).

Method of Analysis. – The quantum yields of $^1O_2$ production (Φ_Δ) have been determined by direct analysis of the near-IR luminescence of $^1O_2$ produced by energy transfer from the triplet state of the sensitizer to molecular oxygen (*Eqn. 1*). In solution and in the absence of a (physical) quencher or (chemical) acceptor, $^1O_2$ is deactivated by collision with solvent molecules (*Eqn. 2*), by luminescence (*Eqn. 3*) and, eventually, by physical quenching by the sensitizer itself (*Eqn. 4*). Depending on its structure, the sensitizer might also be oxidized by $^1O_2$.

$$^3\mathrm{Sens}^* + {}^3O_2 \xrightarrow{k_{et}} {}^1O_2 + \mathrm{Sens} \quad (1)$$

$$^1O_2 \xrightarrow{k_d} {}^3O_2 \quad (2)$$

$$^1O_2 \xrightarrow{k_e} {}^3O_2 + h\nu'' \quad (3)$$

$$^1O_2 + \mathrm{Sens} \xrightarrow{k_q^{Sens}} {}^3O_2 + \mathrm{Sens} \quad (4)$$

The rate constant of $^1O_2$ luminescence (k_e) is much smaller than the rate constant of $^1O_2$ deactivation by the solvent (k_d) [11] [12]. However, it has been shown that this weak monomolecular luminescence can be monitored in the near-IR at 1270 nm [13] [14]. Measurements carried out under monochromatic continuous irradiation of the sensitizer [15–17] allow the determination of quantum yields of $^1O_2$ production (Φ_Δ) [18].

The quantum yield of $^1O_2$ luminescence (Φ_e) is related to Φ_Δ by *Eqn. 5*.

$$\Phi_e = \Phi_\Delta \frac{k_e}{k_d + k_q^{Sens}\,[\mathrm{Sens}]} \quad (5)$$

Φ_e is independent of the sensitizer concentration, if the quenching of $^1O_2$ by the sensitizer is negligible compared to the deactivation by the solvent, *i.e.* if $k_q^{Sens}\,[\mathrm{Sens}] \ll k_d$ (*Eqns. 2* and *4*).

Φ_e is also given by *Eqn. 6*.

$$\Phi_e = \frac{P_e}{P_a} = \frac{S_e C}{P_a} \tag{6}$$

where P_a photonic flux absorbed by the sensitizer,
P_e photonic flux emitted by $^1O_2$ at the wavelength of analysis (1270 nm),
S_e intensity of the measured luminescence signal [mV],
C equipment specific proportionality factor (a constant, if the absorbances of the different solutions investigated are identical at the excitation wavelength(s) [17]).

For determining Φ_Δ, the luminescence signals of a solution containing the sensitizer under investigation (S_e) and of a solution containing a reference sensitizer (S_e^R) in the same solvent are alternatively measured, using identical absorbances at the wavelength(s) of excitation. The ratio of the luminescence signals, S_e/S_e^R (denoted S), is obtained by combining *Eqns. 5* and *6*. If a reference sensitizer is chosen so that its physical quenching of $^1O_2$ is negligible compared to $^1O_2$ quenching by the solvent (as it is the case for rose bengal [19], and if the wavelength of excitation is the same for both sensitizers, S is given by *Eqn. 7*.

$$S = \frac{S_e}{S_e^R} = \frac{\Phi_\Delta}{\Phi_\Delta^R} \frac{k_d}{k_d + k_q^{Sens}[Sens]} \tag{7}$$

If k_d in the solvent used is known, Φ_Δ and k_q^{Sens} can be estimated by measuring the luminescence signals at two different absorbances (see *Results*). If the ratio S remains constant, then $k_q^{Sens}[Sens] \ll k_d$ for the sensitizer investigated under the corresponding experimental conditions, and S is equal to the ratio of the quantum yields of $^1O_2$ production ($\Phi_\Delta/\Phi_\Delta^R$).

If sensitizer and reference are excited at different wavelengths, the ratio of the luminescence signals depends also on the ratio of the incident photonic fluxes (P_0/P_0^R) (*Eqn. 8*).

$$S = \frac{S_e}{S_e^R} = \frac{P_0}{P_0^R} \frac{\Phi_\Delta}{\Phi_\Delta^R} \frac{k_d}{k_d + k_q^{Sens}[Sens]} \tag{8}$$

Results. – The $^1O_2$ luminescence signals produced by rose bengal, as a reference sensitizer, and by the nine quinoid fungal toxins and derivatives were measured at 1270 nm using CD_3OD as a solvent. The excitation wavelength was 547 nm and/or 436 nm, depending on the absorption spectra of the compounds. Experiments were carried out at absorbances of *ca.* 1.48 and 0.67 at the excitation wavelengths. The luminescence signals were stable under irradiation, except for MC and DMC for which decreasing signals were observed. This result indicates that MC and DMC undergo a photochemical reaction leading to the formation of products which have lower efficiencies of $^1O_2$ sensitization than MC and DMC. The signal decrease was faster for DMC. Chemical reaction was confirmed by changes observed in the absorption spectra. In fact, it has been shown recently that photodemethylation occurs [20]. For MC and DMC, calculations were made in using the values of the luminescence signals at the very beginning of irradiation. Spectral characteristics of the nine sensitizers investigated and average values of Φ_Δ^{app} (*Eqn. 9*) are given in *Table 1*.

Table 1. *Spectral Characteristics and Average Values of Φ_Δ^{app} of the Nine Sensitizers Investigated* (R = rose bengal)

Sensitizer	λ_{ex} [nm]	$\varepsilon(\lambda_{ex})$ [$l \cdot mol^{-1} \cdot s^{-1}$]	[Sens] [$mol \cdot l^{-1}$]	Φ_Δ^{app} [a])
Cercosporin (C)	547	5140 ± 100	2.90×10^{-4}	0.66
			1.28×10^{-4}	0.73
Methylcercosporin (MC)	547	6920 ± 150	9.80×10^{-5}	0.57
	436	18150 ± 250	8.14×10^{-5}	0.61
			3.70×10^{-5}	0.66
Dimethylcercosporin (DMC)	547	5300 ± 100	2.77×10^{-4}	0.30
			1.28×10^{-4}	0.39
	436	21300 ± 250	3.10×10^{-5}	0.60
Aminocercosporin (AC)	547	5180 ± 100	2.87×10^{-4}	0.79
			1.31×10^{-4}	0.78
Diaminocercosporin (DAC)	547	3390 ± 100	4.39×10^{-4}	0.50
			1.99×10^{-4}	0.59
Elsinochrome A (EA)	436	13470 ± 200	1.10×10^{-4}	0.83
			5.04×10^{-5}	0.89
Elsinochrome B (EB)	547	8500 ± 150	1.75×10^{-4}	0.73
			7.89×10^{-5}	0.79
	436	18750 ± 250	7.90×10^{-5}	0.81
			3.60×10^{-5}	0.87
Phleichrome (P)	547	9170 ± 150	1.62×10^{-4}	0.69
			7.32×10^{-5}	0.75
Rubellin A (RA)	436	12550 ± 200	1.18×10^{-4}	0.74
			5.33×10^{-5}	0.75

[a]) *Eqn. 9* (see text for the definition of S and P); standard deviation: ±3% at 547 nm and ±6% at 436 nm (standard deviation is higher at 436 nm due to the errors on the determination of P).

$$\Phi_\Delta^{app} = \Phi_\Delta^{R} S P = \Phi_\Delta \frac{k_d}{k_d + k_q^{Sens}\,[\text{Sens}]} \tag{9}$$

where Φ_Δ^{app} apparent Φ_Δ, which has not been corrected for a potential $^1O_2$ quenching by the sensitizer,

P = P_0^R/P_0, P being equal to 1, if reference and sensitizer are excited at the same wavelength.

If $^1O_2$ quenching by the sensitizer is significant compared to the quenching by the solvent, then Φ_Δ^{app} should increase with decreasing concentration of the sensitizer (*Eqn. 9*).

The value of k_q^{Sens} can be estimated using *Eqn. 10* (or *Eqn. 11*), obtained by combining *Eqn. 7* (or *Eqn. 8*), for two different absorbances of sensitizer and reference solutions. The $^1O_2$ lifetime ($\tau_\Delta = 1/k_d$) in CD_3OD was determined on a time-resolved luminescence detection apparatus [21] to be 236 ± 5 µs.

$$k_q^{Sens} \doteq \frac{k_d\,(S_2 - S_1)}{S_1\,[\text{Sens}]_1 - S_2\,[\text{Sens}]_2} \tag{10}$$

$$k_q^{Sens} = \frac{k_d\,(S_2 P_2 - S_1 P_1)}{S_1 P_1\,[\text{Sens}]_1 - S_2 P_2\,[\text{Sens}]_2} \tag{11}$$

For the majority of the compounds investigated, the variation of S ($= S_e/S_e^R$), and, therefore, of Φ_Δ^{app}, between concentrations 1 and 2 of the sensitizer (*Eqns. 10* and *11*), does not exceed 10%, and, hence, only upper limit values of k_q^{Sens} can be estimated. These values have been calculated by using experimental values of S for the two different

sensitizer concentrations (*i.e.* for DAC, *Table 1*), or by considering that k_q^{Sens}[Sens] is, at the most, equal to 10% of k_d, when S_1 and S_2 values may be considered equal within experimental error (*i.e.* for AC, *Table 1*).

Φ_Δ have been calculated using *Eqn. 7* (or *Eqn. 8*), the quantum yield of $^1O_2$ production by rose bengal (Φ_Δ^R) in CD_3OD being 0.76 [22–24]. The corresponding results (k_q^{Sens} and Φ_Δ) for the nine sensitizers investigated are given in *Table 2*. In the case of MC and DMC, the rate constants indicated are, in fact, the overall rate constants of $^1O_2$ quenching by the sensitizer (k_t^{Sens}), *i.e.* they include the contribution of the chemical reaction to the quenching process.

Table 2. *Quantum Yields of $^1O_2$ Production, Φ_Δ, and Upper Limits of the Rate Constants of $^1O_2$ Quenching, k_q^{Sens}, by the Nine Sensitizers Investigated*

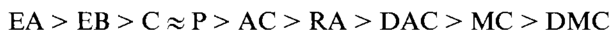
Sensitizer	λ [nm]	Φ_Δ [a])	k_q^{Sens} [$l \cdot mol^{-1} \cdot s^{-1}$]	Hydroperoxide formation [%] [10] [c])
C	547	0.81	$3.5 \cdot 10^6$	80
MC	547	0.69	$\leq 10^7$ [b])	
	436	0.71		
DMC	547	0.51	$1.1 \cdot 10^7$ [b])	35
	436	0.66		
AC	547	0.79	$\leq 3 \cdot 10^6$	
DAC	547	0.69	$3.6 \cdot 10^6$	
EA	436	0.94	$\leq 5 \cdot 10^6$	85
EB	547	0.85	$\leq 5.5 \cdot 10^6$	75
	436	0.91		
P	547	0.81	$\leq 6 \cdot 10^6$	75
RA	436	0.76	$\leq 8 \cdot 10^6$	50

[a]) Calculated using *Eqn. 7* (λ_{ex} = 547 nm) or *Eqn. 8* (λ_{ex} = 436 nm); standard deviation: ±6% at 547 nm and ±10% at 436 nm.

[b]) Overall rate constant of $^1O_2$ quenching (see text).

[c]) Percentage of methyl oleate hydroperoxide formation (detected and quantified by HPLC followed by photodensitometry), in MeCN under polychromatic irradiation of the sensitizer (λ > 300 nm).

Table 2 shows that the elsinochromes EA and EB are the most efficient $^1O_2$ sensitizers of the series investigated, where Φ_Δ vary from 0.94 to 0.51 in the following order:



$$EA > EB > C \approx P > AC > RA > DAC > MC > DMC$$

A variation of Φ_Δ, greater than the limits of error, is indicating their dependence on the wavelength of excitation, an increase being observed at 436 nm compared to 547 nm.

The upper limits of the rate constants of $^1O_2$ quenching are lower than $8 \cdot 10^6$ $l \cdot mol^{-1} \cdot s^{-1}$, except for MC and DMC which undergo a photochemical reaction [20] and have also the lowest Φ_Δ of the series. All the other compounds investigated are good $^1O_2$ sensitizers with Φ_Δ in the range of 0.70 to 0.94. It should be noted that EA, EB, C, and P, which are particularly efficient $^1O_2$ sensitizers with $\Phi_\Delta \geq 0.8$, are all natural quinoid fungal toxins.

A relative scale of photodynamic efficiency has been previously obtained for six sensitizers of this series, by determining the percentage of hydroperoxidation of methyl oleate by $^1O_2$, after a given irradiation time [10]. The agreement with the present results is

rather good (*Table 2*), considering the differences in experimental conditions (solvent, irradiation time, spectral domain of irradiation).

Discussion. – The value of Φ_Δ of a $^1O_2$ sensitizer is a function of its quantum yield of intersystem crossing, Φ_{ISC}, which in turn depends on the sensitizer structure. All the compounds investigated, with the exception of RA, have the same perylene-quinoid molecular structure, the only apparent differences being due to small changes in the substituents. These sensitizers present interesting problems related to the chirality of the extended quinoid system. In previous investigations, we were able to determine their stereochemical features by collecting data from a series of physico-chemical measurements (CD, NMR, X-ray analysis, ...) [6].

An important result is that, in the case of both C and P, the perylene-quinoid system is not planar, and CD measurements indicate that the degree of distortion should be the same, although axial and chain chiralities are opposite. *Table 2* shows that the same value of Φ_Δ (0.81) is obtained for both compounds.

The situation is different in the case of EA: CD measurements show a lower overall intensity of the spectrum compared with that of C and P, and this finding is consistent with a lower degree of skewedness; X-ray analysis confirms this conclusion [25]. Possibly, the additional cycle forces EA into a more planar conformation than found in C and P, leading to a stronger interaction between OH and C=O groups and, hence, favoring different tautomeric structures. This hypothesis is supported by the fact that two different dimethoxy derivatives are isolated upon methylation of EA. The more planar structure in EA leads to an increase of Φ_Δ compared to C and P (*Table 2*), and the same arguments may apply to EB, the Φ_Δ of which is only slightly lower than that of EA.

In MC and DMC, the quinoid structures are favored, rendering a potential tautomerism improbable. In DAC, the stable form is the structure given in *Formulae* above. This absence of tautomerism seems to decrease Φ_Δ below values of 0.7. On the other hand, DAC and DMC are more efficient $^1O_2$ quenchers than the corresponding monosubstituted compounds.

Other results previously reported are in agreement with our findings: noranhydrocercosporin, for which a planar structure has been proposed [26], has a quantum yield of $^1O_2$ production of 0.73, while the complete blocking of the OH groups of cercosporin (as in hexaacetylcercosporin) leads to a Φ_Δ as low as 0.16 [9].

In summary, *Table 2* shows that EA and EB, exhibiting a more planar structure, are also the best $^1O_2$ sensitizers of the series investigated, while an efficiency decrease is observed for more skewed and tautomerically blocked systems. These differences in molecular structures may influence the electronic configuration of the triplet state which is known to lead to less efficient $^1O_2$ sensitizers at higher contributions of the n,π^*-configuration [18]. This latter situation, where the quinoid structure is favored, is encountered in MC and DMC, both being photochemically reactive.

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Experimental. – *Chemicals.* Rose bengal, purchased from *Fluka*, was used as a reference sensitizer. Fungal toxins and derivatives were obtained from agar cultures of suitable fungal strains or by chemical synthesis, and were of chromatographic purity (*Table 3*).

Table 3. *Fungal Toxins and Derivatives*

Compound	Source	Ref.
Cercosporin (C)	*Cercospora kikuchii*	[26]
Methylcercosporin (MC)	chemical synthesis	[26]
Dimethylcercosporin (DMC)	chemical synthesis	[26]
Aminocercosporin (AC)	chemical synthesis	[27]
Diaminocercosporin (DAC)	chemical synthesis	[27]
Elsinochrome A (EA)	*Elsinoë annonae*	[28]
Elsinochrome B (EB)	*Elsinoë annonae*	[28]
Phleichrome (P)	*Cladosporium phlei*	[29]
Rubellin A (RA)	*Mycosphaerella rubella*	[30]

Preparation of AC and DAC. Cercosporin (C, 100 mg) was dissolved in MeOH (10 cm^3), and the soln. was saturated with ammonia; after 2 weeks at r.t., the dark green soln. was evaporated and the residue chromatographed on a silica-gel column with 2% $KHPO_4$ added using CH_2Cl_2/MeOH 10:1. Two main products were obtained: aminocercosporin (AC, 30 mg) and diaminocercosporin (DAC, 20 mg).

Preparation of MC and DMC. To 15 cm^3 of a dry acetone soln. containing 200 mg of cercosporin, 200 mg of Ag_2O and 1.5 cm^3 of MeI were added. The mixture was stirred for 5 h at r.t. in the dark; after the filtration of Ag_2O, the soln. was chromatographed by PLC using CH_2Cl_2/MeOH 15:1. Two main products were eluted: methylcercosporin (MC, 50 mg) and dimethylcercosporin (DMC, 100 mg).

Absorption Spectra. Ground-state absorption spectra were recorded on a *Jarco UVIDEC 510* or a *Shimadzu UV-260* spectrophotometer in EtOH or MeOH. The molar absorption coefficients at the excitation wavelengths (547 nm and/or 436 nm) are given in *Table 1*. No aggregation effects were observed in the range of sensitizer concentrations used in this work ($3 \cdot 10^{-5}$ mol·l^{-1} to $4.5 \cdot 10^{-4}$ mol·l^{-1}).

$^1O_2$ Luminescence Measurements. The sensitizers were dissolved in CD_3OD (> 99.5%; *Glaser*; absorbances of *ca.* 1.48 and 0.67 at the excitation wavelength(s), corresponding concentrations are given in *Table 1*). A deuterated solvent was chosen, as more intense luminescence signals are obtained due to a longer $^1O_2$ lifetime, thus improving the sensitivity of the method. Equivalent 1 × 1 cm fluorescence cells were used for the experiments. For each experiment, series of independent measurements alternating between reference and sample (adjusted to the same absorbances) were carried out. The results are the average of at least two series of measurements with a limit of error less than 3%. The steady-state near-IR luminescence apparatus used has already been described in detail [18]. Note that the sample solns. were irradiated with a Xe/Hg lamp (*Osram, Müller*, 1 kW), through a monochromator (*ISA Jobin-Yvon*, 6-nm band width). Irradiation time for each sample was *ca.* 3 min. The incident radiant powers (F_0, mW) at 436 nm and 547 nm were measured without cell using a thermopile (*Laser Instrumentation*, model *154*) before and after each series of experiments. The ratio of the incident photonic fluxes at the two different wavelengths of excitation (P_0^R/P_0) is equal to the product (F_0^R/F_0) ($\lambda_{ex}^R/\lambda_{ex}$). Values of F_0^{547} and F_0^{436} varied from 2.3 to 2.8 mW and from 3.0 to 3.6 mW, respectively.

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