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Photodegradation of the Acaricide Abamectin: A Kinetic Study

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The acaricide abamectin is a mixture of two colorless homologues in a molar ratio of at least 4:1 with the same structure of macrocyclic lactone. The kinetics of its degradation under direct (254 nm) and dye-sensitized (>400 nm) photoirradiation in methanol solution has been studied by UV−vis spectrophotometry, potentiometric detection of dissolved oxygen, stationary fluorescence, laser flash photolysis, and time-resolved detection of singlet molecular oxygen ($O_2(^1\Delta_g)$) phosphorescence. The results indicate that the degradation is very efficient under direct irradiation with UV light (254 nm), with a quantum yield of 0.23. On the contrary, under visible-light irradiation, using the natural pigment riboflavin or the synthetic dye rose bengal as sensitizers, the degradation is very inefficient and proceeds through a $O_2(^1\Delta_g)$-mediated mechanism, with a bimolecular rate constant for the overall $O_2(^1\Delta_g)$ quenching (the sum of physical and chemical quenching) of 5.5×10^5 M^{-1} s^{-1}. This value is similar to those reported for the rate constants of the reactions of $O_2(^1\Delta_g)$ with isolated double bonds or conjugated dienes and points to similar processes in the case of abamectin.

KEYWORDS: Abamectin; direct photolysis; photodegradation; photooxidation; photosensitization; singlet molecular oxygen

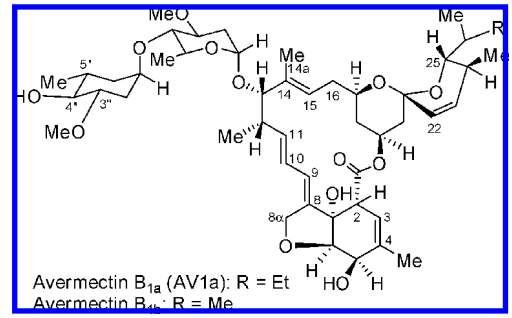
INTRODUCTION

The acaricide abamectin (ABA), also called avermectin B_1, is a mixture of two colorless homologues with the same structure of macrocyclic lactone: avermectin B_{1a} (AV1a) and avermectin B_{1b}, in a molar ratio of at least 4:1 (**Chart 1**) (*1*). ABA is produced by the soil actinomycete *Streptomyces avermitilis* and is widely employed in veterinary medicine (*2*) and agriculture (*3*), in spite of its extremely low acceptable daily intake (ADI) value (0−1 μg per kg of body weight (*4*)), its detrimental impact in the environment (*5*), and its observed teratogenic effects in mouse reproduction (*6*). ABA acts by stimulating the release of γ-aminobarbituric acid thus causing paralysis (*7*). It is used to control motile stages of mites and some other insects on fruits.

A number of reports have been published about its persistence in nature. Thus, some degradation studies using a nondiscriminated combination of bio- and photoprocesses indicate a persistence of 2−4 weeks (*3, 8, 9*), either dispersed in the soil or deposited in the field from sheep feces. Emamectin benzoate, a semisynthetic derivative of the second generation of avermectin pesticides with the structure of 4″-(*epi*-methylamino)-4″-deoxy-AV1a, has shown half-lives in the range of 1−22 days when photodegraded in water under natural sunlight irradiation (*10*).

The degradation products of AV1a under different conditions have also been studied. In soils and under laboratory environmental conditions, the major product was an equilibrium mixture of 8α-CHOH-AV1a and the corresponding ring-opened aldehyde (*11*). On the other hand, in an effort directed to know the structures of the formed products under conditions that mimic natural layers of these pesticides on leaves, the thin-film UV photodegradations of AV1a and of its derivative with the former 4″-substituent have been studied (*12, 13*). In the case of AV1a, products from the oxygenation of 8α-CH_2 to 8α-CHOH—the

Chart 1. Chemical Structures of the Two Components of Abamectin: Avermectin B_{1a} (≥80%) and Avermectin B_{1b} (≤20%)



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same product detected in soils—and 8α-C=O, from the demethylation of 3″-CHOMe to 3″-CHOH, and from isomerizations of the (8*E*)- and (10*E*)-double bonds to the corresponding (8*Z*)- and (10*Z*)-isomers, were found, and their appearance was explained through radical-forming reactions and intermediate hydroperoxides; in addition, the appearance of the main products, with 14-OH or 15-OH and the 14,15 double bond shifted to positions 15,16 and 14,14a, respectively, was explained as the results of ene reactions with singlet molecular oxygen ($O_2(^1\Delta_g)$) that generate the corresponding allylic hydroperoxides, although the source of $O_2(^1\Delta_g)$ could not be clarified (*12*). In the case of the former methylamino-AV1a derivative, the observed photoproducts were somewhat different because the most sensitive group to changes under irradiation was the 4″-NHMe group, and the corresponding derivatives with 4″-NMeCHO, 4″-NHCHO, and 4″-NH_2, as well as the (8*Z*)-isomers of the two latter compounds, were identified in the mixture of products; in addition, the (8*Z*)-isomer of the irradiated compound, the product from the 3,4-double-bond shift to position 2,3, and a 4″-OH-5″-demethyl-ABA, were also detected. As in the case of AV1a, some of these changes were explained through the participation of $O_2(^1\Delta_g)$ of unknown origin (*13*). However, the kinetic aspects of all these photodegradations remain unknown.

In natural environments, pesticides and their degradation products appear finally as solutions or suspensions in surface waters. Consequently, the photochemical pathways of their degradation in aerated solution and under sunlight irradiation, i.e., mimicking the natural photochemical decay of all these substances, is a topic of growing interest. When the pesticide absorbs UV light, it can be degraded by direct photolysis through bond scissions or oxidations that take place in its electronically excited states. When the pesticide does not absorb any wavelength of the sunlight, its degradation can also be carried out through reactive oxygen species (ROS), such as ($O_2(^1\Delta_g)$), superoxide radical anion ($O_2^{\bullet-}$), and hydroxy radical ($OH^{\bullet}$), if a visible-light absorbing compound (sensitizer), able to generate ROS, is present in the medium (*14*).

The aim of the present work was to study the kinetics of the photodegradation of ABA in solution, especially under irradiation conditions similar to those frequently found in nature. The results could be of help for the design of programmed decays of ABA and for the knowledge of its natural fate in aqueous environments, crucial information for its use in crop protection and other practical applications.

MATERIALS AND METHODS

Materials. Abamectin, a ca. 4:1 mixture of avermectin B_{1a} and avermectin B_{1b} (*1*), was kindly provided by Chemiplant S. A. (Argentina). It was purified by recrystallization from acetone. A pondered molecular weight of 870.5 g mol^{-1} was employed in the calculations of molar concentrations so that the determined rate constant and quantum yield values should be taken as apparent values of this particular mixture, and not of the pure compounds. Riboflavin (Rf), rose bengal (RB), and monodeuterated methanol (MeOD, 99.5% deuterium content) were from Sigma. Methanol (MeOH, HPLC quality) was from Sintorgan (Argentina). Potassium iodate, potassium iodide, and potassium borate were from Aldrich. Although ABA is slightly soluble in water (*1*), MeOH solutions were employed in the present work in order to prepare enough concentrated solutions for their study with the available techniques.

Methods. The stationary fluorescence of air-equilibrated solutions of Rf at 25 ± 1 °C was registered in an RF 5301-PC Shimadzu spectrofluorimeter. Excitation and emission wavelengths were 445 and 515 nm, respectively. Ground-state absorption spectra were recorded in a Hewlett-Packard 8452A diode array spectrophotometer. Nitrogen-saturated aqueous solutions of Rf, 0.02 mM, were photolyzed using a flash photolysis apparatus. A nanosecond Nd:YAG laser system (Spectron) at 355 nm was the excitation source, employing a 150 W xenon lamp as analyzing light. The detection system comprised a Photon Technology International (PTI) monochromator and a red-extended photomultiplier (Hamamatsu R666). The signal, acquired and averaged by a digital oscilloscope (Hewlett-Packard 54504A), was transferred to a PC via a Hewlett-Packard interface bus, where it was analyzed and stored. Stationary aerobic photolysis of methanol solutions containing ABA and Rf (both 0.05 mM) or ABA (0.05 mM) plus RB (A_{530} = 0.5) were carried out in a PTI unit provided with a high-pass monochromator and a 150 W Xe lamp, irradiating with 440 ± 10 nm, or in a homemade photolyzer for nonmonochromatic irradiation provided with a 150 W quartz—halogen lamp. In this case, a cutoff filter at 400 nm ensured that the light was absorbed only by the sensitizer.

Irradiation at 254 nm of ABA solutions ($A_{254} > 2$) in MeOH, and of the actinometer potassium iodide (0.6 M) plus potassium iodate (0.1 M) in buffered (pH = 9.25) aqueous solution, was achieved with an Osram germicide lamp (15 W) in a magnetically stirred 1 × 1 cm^2 fluorescence quartz cuvette. The actinometry was performed following described methodology (*15*). The progress of the respective reactions was evaluated by the absorbance decay of the irradiated mixture at 245 nm, for the ABA disappearance, and by the absorbance increase at 352 nm, for the appearance of the species triiodide in the actinometer solution, both as a function or the irradiation time. Rates of oxygen consumption in MeOH by ABA, sensitizing with Rf or RB, were determined with the specific oxygen electrode Orion 97-08.

The laser-kinetic spectrophotometer for time-resolved phosphorescence detection (TRPD) of $O_2(^1\Delta_g)$ has been previously described (*16*). MeOD was employed, instead of MeOH, in order to enlarge the lifetime of $O_2(^1\Delta_g)$ (*17*), according to the temporal window of our equipment (*16*). RB solutions with absorbance at the excitation wavelength (532 nm) of ca. 0.3 were employed. The decay kinetics was first order in all cases.

RESULTS

Direct Photolysis of Abamectin. Photoirradiation with monochromatic light of 254 nm of air-equilibrated solutions of ABA, ca. 0.03 mM, in MeOH produces the spectral changes shown in **Figure 1**. The quantum yield for the photodegradation of ABA under these conditions was high, $\Phi_r = 0.23 \pm 0.02$, indicating that direct photolysis is a very efficient method for the degradation of the acaricide. Φ_r was graphically obtained from the respective rates of ABA and actinometer photolysis (**Figure 1**, inset **A**) employing the iodate—iodide actinometer (*15*). The rates of ABA photoconsumption were practically the same, within experimental error, when the photolysis was carried out in N_2-equilibrated conditions (**Figure 1**, inset **B**).

Riboflavin-Sensitized Photoirradiation of Abamectin. The spectral evolution during the irradiation with visible light (cutoff at 400 nm) of a solution of ABA, 0.03 mM, plus Rf, 0.04 mM, in MeOH, corrected by subtracting the spectrum of nonirradiated Rf, 0.04 mM, in the same solvent, is shown in **Figure 2**. The sensitizer is decomposed, as shown in **Figure 2**, inset **C**, upon photoirradiation of a methanolic solution of Rf. This fact can be appreciated by the changes in the negative region of the visible spectral range and by the absorbance increase in the region of 245 nm, where ABA also absorbs. This behavior of Rf precludes the use of absorbance changes for the direct evaluation of ABA disappearance. In **Figure 2**, inset **A**, the rates of spectral changes at 245 nm during the irradiation of a solution of Rf, 0.04 mM, in MeOH, in the absence and in the presence of ABA, 0.03 mM, are shown. Although both rates narrowly differ, the disparity is quite reproducible. Taking into account that only the sensitizer absorbs the exciting light, the decrease in the rate of Rf decomposition in the presence of ABA

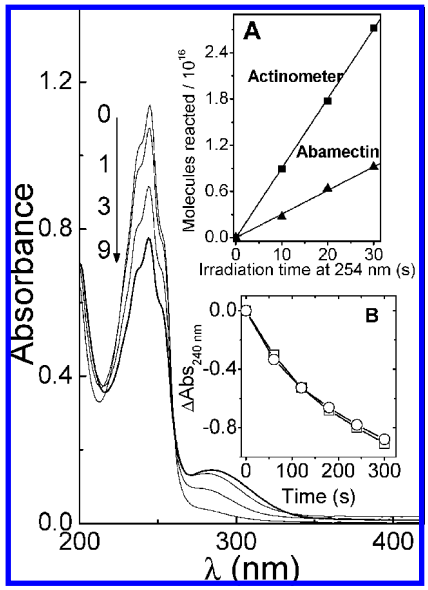

Figure 1. Spectral evolution of abamectin, 0.03 mM, upon direct (254 nm) photoirradiation in MeOH. Inserted numbers indicate minutes of irradiation. Inset **A**: plot of molecules of actinometer and abamectin reacted as a function of irradiation time with 254 nm light, employed for the determination of the quantum yield of the direct photodegradation of the pesticide. Inset **B**: absorbance decrease at 245 nm of abamectin, 0.04 mM, in MeOH in N_2-saturated and in air-saturated MeOH solutions, as a function of the irradiation time with 254 nm light.

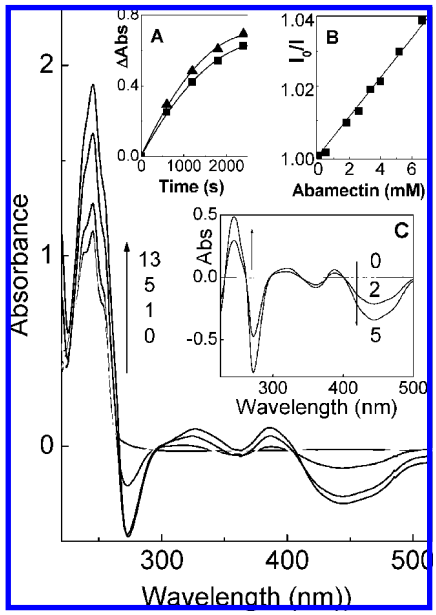

Figure 2. Spectral evolution of a mixture of abamectin, 0.03 mM, and riboflavin, 0.04 mM, in MeOH vs riboflavin, 0.04 mM, in the same solvent upon photoirradiation with visible light (cutoff at 400 nm). Inset **A**: absorbance increase at 245 nm of the process in the main figure in the absence (▲) and in the presence (■) of abamectin, 0.03 mM. Inset **B**: Stern−Volmer plot for the stationary quenching of the fluorescence of riboflavin, 0.06 mM, by abamectin, in MeOH. Inset **C**: spectral evolution of riboflavin, 0.05 mM, in MeOH vs riboflavin, 0.05 mM, in the same solvent, upon photoirradiation with visible light (cutoff at 400 nm). Numbers in the spectra indicate minutes of irradiation. The experimental conditions in the runs in the main figure and in inset **C** are not exactly the same and, hence, should not be quantitatively compared.

could be due to (a) quenching of Rf excited states by ABA (the photodegradation of Rf under visible-light irradiation

Scheme 1. Main Possible Processes in the Dye-Sensitized Photodegradation of Abamectin (ABA)[a]

$$^3S^* + O_2(^3\Sigma_g^-) \xrightarrow{k_{ET}} S + O_2(^1\Delta_g) \quad (1)$$

$$^3S^* + O_2(^3\Sigma_g^-) \xrightarrow{k_{eT}} S^{\bullet+} + O_2^{\bullet-} \quad (2)$$

$$^3S^* + eD \longrightarrow S^{\bullet-} + eD^{\bullet+} \quad (3)$$

$$S^{\bullet-} + O_2(^3\Sigma_g^-) \longrightarrow S + O_2^{\bullet-} \quad (4)$$

$$O_2(^1\Delta_g) + ABA \xrightarrow{k_r} \text{products} \quad (5)$$

$$O_2(^1\Delta_g) + Q \xrightarrow{k_q} O_2(^3\Sigma_g^-) + Q \quad (6)$$

$$O_2(^1\Delta_g) + S \longrightarrow \text{products} \quad (7)$$

$$O_2^{\bullet-} + ABA \longrightarrow \text{products} \quad (8)$$

[a] S, sensitizer (riboflavin, Rf, or rose bengal, RB); eD, electron-donating compound; Q, physical quencher.

proceeds mainly through the triplet state, ^{3}Rf*) (*18*) and/or (b) decrease in the absorbance of the spectral component of ABA at 245 nm, due to photoreaction, producing a delay in the observed rate of overall (Rf + ABA) absorbance increase at this wavelength.

Rf presents an intense fluorescence emission band centered at 515 nm, with a reported fluorescence quantum yield of 0.25 (*18*). **Figure 2**, inset **B**, shows the Stern−Volmer plot for the quenching of the stationary emission of Rf in MeOH. As can be seen, the quenching by ABA up to 0.05 mM, a concentration higher than that employed in the photolysis experiments, is negligible. In parallel experiments, the addition of ABA (up to 0.1 mM) to a N_2-saturated solution of Rf, 0.01 mM, in MeOH did not affect the ^{3}Rf* lifetime of 15 μs observed in the absence of ABA, a value in agreement with literature data (*18*). Besides, the transient absorption spectrum of the solution taken at 0.1 μs after the laser pulse, that is accepted as corresponding to the neutral ^{3}Rf* species (*19*), does not change in the presence of ABA.

In synthesis, the results on the potential quenching of Rf singlet and triplet excited states by ABA, obtained by means of stationary fluorescence and laser flash photolysis, indicate absence of interaction between ABA and the excited states of Rf, at least within the tested concentration range of ABA, 0.05−0.10 mM, values higher than those employed in the experiments shown in **Figure 1**.

It is known that Rf in MeOH produces $O_2(^1\Delta_g)$ (process 1, **Scheme 1**, with S = Rf) and $O_2^{\bullet-}$ (process 2), with quantum yields of 0.48 and 0.009, respectively (*20*). In principle, the very low quantum yield for the $O_2^{\bullet-}$ generation discards the participation of this radical anion in the photodegradation of ABA (process 8). Hence, the remaining possibility is $O_2(^1\Delta_g)$-mediated reactions (process 5).

Oxygen consumption was observed in the visible-light photoirradiation of solutions of Rf, 0.05 mM, plus ABA, 0.1 mM, in MeOH−H_2O 3:1 v/v. The photolysis was accompanied by a fading of the sensitizer, as directly observed by the marked bleaching of the solution, pointing again to the chemical involvement of Rf in the photooxygenation process. It is well-known that Rf is involved in redox processes in nature through different mechanisms, including its own $O_2(^1\Delta_g)$-mediated photooxidation (process 7, **Scheme 1**, with S = Rf), and a rate

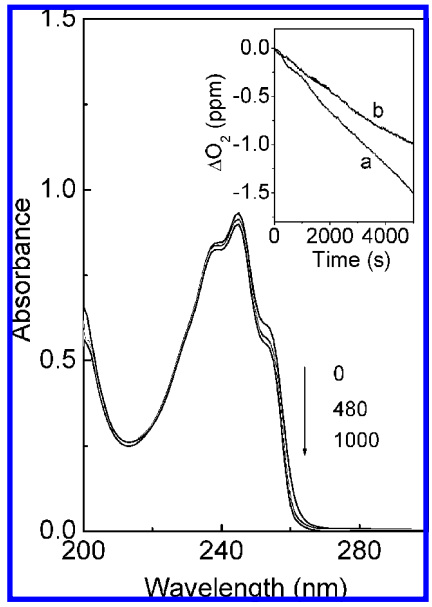

Figure 3. Spectral evolution of abamectin, 0.025 mM, in MeOH in the presence of rose bengal (A_{560} = 0.46), taken vs rose bengal (A_{560} = 0.46) in the same solvent. Numbers in the spectra indicate seconds. Inset: oxygen uptake of a solution of abamectin, 1 mM, in MeOH in the absence (**a**) and in the presence (**b**) of sodium azide, 0.1 mM.

constant k_t (the sum of $k_r + k_q$, processes 5 and 6, respectively, with Q = Rf) of 6×10^7 M^{-1} s^{-1} has been reported for the overall quenching process in MeOH (*20*).

Rose Bengal-Sensitized Photoirradiation of Abamectin. The possible participation of $O_2(^1\Delta_g)$ in the photodegradation of ABA was evaluated employing RB, a well-known and almost exclusive $O_2(^1\Delta_g)$ generator, with a quantum yield in MeOH of 0.81 (*21*). The spectral changes of a MeOH solution of ABA, 0.025 mM, plus RB (A_{560} = 0.46) upon visible-light photoirradiation are shown in **Figure 3**. The rate of oxygen consumption of a MeOH solution containing ABA, 1 mM, and RB (A_{560} = 0.46) as a photosensitizer was lower in the presence of sodium azide (NaN_3), 0.1 mM, than in the absence of the salt. NaN_3 is a well-known physical quencher of $O_2(^1\Delta_g)$, with a reported rate constant value, k_q, of 2.3×10^8 M^{-1} s^{-1} in MeOH (*17*), and this quencher has been repeatedly used to confirm/discard the involvement of $O_2(^1\Delta_g)$ in a given photooxidative process.

By means of time-resolved quenching of $O_2(^1\Delta_g)$ phosphorescence, an overall quenching constant value, k_t, of $5.5 \pm 0.2 \times 10^5$ M^{-1} s^{-1} was obtained for ABA in MeOD, with RB as a sensitizer (**Figure 4**). This experiment unambiguously demonstrates interaction between $O_2(^1\Delta_g)$ and ABA. The decay kinetics of $O_2(^1\Delta_g)$ phosphorescence in the same solvent was first order, and the observed $O_2(^1\Delta_g)$ lifetime in the absence of ABA, ca. 33 μs, was in excellent agreement with literature data (*17*).

DISCUSSION

The results shown indicate that ABA undergoes photodegradation with high quantum yield (Φ_r = 0.23, see above) when irradiated with 254 nm light, i.e., with an energetic input of ca. 470 kJ einstein^{-1}, a value strong enough as to break down C−H and C−C bonds. A simple oxygen-mediated oxidative process can be discarded due to the lack of influence of the concentration of dissolved oxygen on the reaction rate. This kind of energetically expensive treatment for the ABA degradation through direct photoirradiation could be of interest in case of deposits of the pesticide for which a rapid degradation is needed.

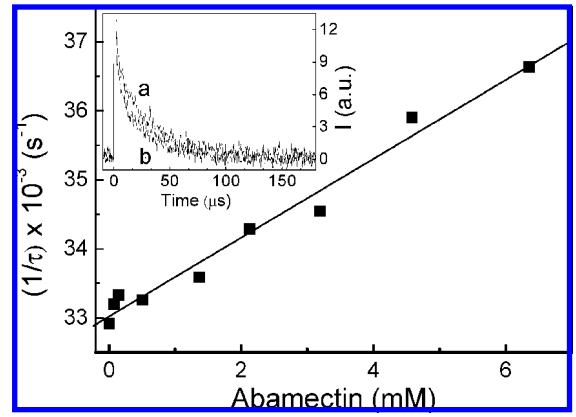

Figure 4. Stern−Volmer plot for the quenching of $O_2(^1\Delta_g)$ phosphorescence by abamectin in MeOD. Inset: decay of the $O_2(^1\Delta_g)$-phosphorescence signal in the absence of abamectin (**a**), and in the presence of abamectin, 3.37 mM (**b**).

Since ABA only absorbs light with wavelengths lower than the so-called UV−B range of solar irradiation, it is clear that natural light does not produce any chemical transformations in the molecule of this pesticide. As said above, photodegradation of these compounds can be carried out through photosensitized processes, i.e., the irradiation of the pesticide solution in the presence of a photosensitizer, using light of wavelengths longer than those absorbed by the pesticide. In particular, Rf, a well-known pigment present in waters of rivers, lakes, and seas (*22*), has been postulated as a possible sensitizer for the natural photooxidative degradation of some pesticides and related contaminants (*23*). The disappearance of the shoulder at 233 nm in the ABA spectrum upon Rf-sensitized photoirradiation, observed in **Figure 2**, is consistent with former results from Crouch et al. (*12*) in the photoirradiation of AV1a.

Under visible-light irradiation, Rf produces $O_2(^1\Delta_g)$ and $O_2^{\bullet-}$ (processes 1 and 2, **Scheme 1**). In the presence of electron-donating species (eD), $O_2^{\bullet-}$ can also appear through processes 3 and 4, with S = Rf (*24, 25*). Evidently, the two avermectins hardly act as electron-donating agents, as suggested by the high oxidation potential that corresponds to their structures (*26*). Through process 7, Rf competes with ABA for the reaction with $O_2(^1\Delta_g)$. The rather low k_t value obtained for the quenching of $O_2(^1\Delta_g)$ with ABA ($5.5 \pm 0.2 \times 10^5$ M^{-1} s^{-1}) is similar to those generally reported for the k_r values of the reactions of $O_2(^1\Delta_g)$ with isolated double bonds to form allylic hydroperoxides, the so-called Schenck ene reaction (*27*), or with conjugated dienes yielding unsaturated endoperoxides (*28*), as in the cases of 2,5-dimethyl-2,4-hexadiene (configuration unknown), with $k_r = 2 \times 10^6$ M^{-1} s^{-1} in MeOH (*29*), or *trans*,*trans*-2,4-hexadiene, with $k_r = 1.1 \times 10^5$ M^{-1} s^{-1} in chloroform (*30*). Accordingly, in the case of ABA, the probable targets for $O_2(^1\Delta_g)$ addition, with subsequent ABA degradation, could be the three isolated double bonds at positions 3, 14, and 22, as well as the conjugated diene group at positions 8−11 (**Chart 1**). The involvement of $O_2(^1\Delta_g)$ of unknown origin has been formerly proposed for the formation of the degradation products found in the UV irradiation of the pesticides AV1a (*12*) and 4″-(*epi*-methylamino)-4″-deoxy-AV1a (*13*). The present results unambiguously demonstrate, through TRPD experiments, the participation of $O_2(^1\Delta_g)$ as the main responsible species of ABA degradation under sensitizing conditions in the presence of a visible-light absorbing compound, i.e., a dye. Nevertheless, in a contaminated medium and in the presence of other efficient to moderated competitors for the reaction with $O_2(^1\Delta_g)$, ABA

possesses limited possibilities of photosensitized degradation induced by environmental light.

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