



Photochemical transformation of the plant activator Acibenzolar-S-methyl in solution



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ABSTRACT

Acibenzolar-S-methyl (BTH) is used to protect plants from pathogens by triggering Systemic Acquired Resistance. While this compound absorbs solar light strongly, little is known on its ability to undergo photodegradation and on the generated photoproducts. In the present work, we studied the photolysis of BTH dissolved in solvents of different polarities: *n*-heptane to mimic the hydrophobic surface of leaves and more polar solvents to simulate polar environmental compartments. We found that BTH is easily photodegraded in simulated solar light. The quantum yield of photolysis at 313 nm ranges from 0.048 to 0.092 depending on the solvent. LC-ESI-HRMS analyses in negative and positive modes revealed the presence of numerous photoproducts arising from two initial reaction pathways. As confirmed by DFT calculations, the main pathway involves the S–N bond cleavage followed by N₂ loss. The scission of the thioester bond with the generation of acyl and SCH₃ radicals also takes place. Based on these findings, it can be predicted that BTH should undergo fast photodegradation once released in the environment and lead to numerous new compounds.

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1. Introduction

Plant diseases account for a considerable proportion of crop loss worldwide. Technological advances in biochemical and molecular biological tools have improved our understanding of plant-pathogen interactions [1–4]. Exogenous applications of several biotic or abiotic compounds can trigger systemic acquired resistance (SAR)-like responses that mimic pathogen-induced resistance in plants. This new generation of plant protection products, are termed activators or synthetic elicitors [5,6]. These compounds may serve as promising alternatives to conventional biocidal pesticides, and they may also help to reduce the environmental load of potentially toxic chemicals, leading to a more sustainable crop protection. The market for biological crop protection products grows by 15% per year. The market is of €100 millions per year in France (5% of agrochemical market) and €550 millions per year in Europe.

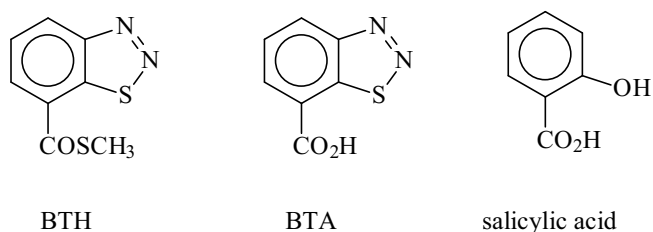
One of the most frequently used elicitors is benzo-(1,2,3)-thiadiazole-7-carbothioic acid S-methyl ester (BTH) or acibenzolar S-methyl, commercialized by Syngenta [7] (Scheme 1). BTH is a structural analog of salicylic acid that is naturally produced by plants (Scheme 1). The product is registered in the United States as Actigard[®] 50WG, in Europe as Bion[®], and in other parts of the world as Blockade[®] and Boost[®] to control downy mildew on leafy vegetables and to manage a range of fungal, bacterial, and viral diseases of crops by activating the SAR in several plant species such as tomato, cucumber, broccoli, tobacco, melon, apple and pear trees [8–16].

To our knowledge very few data are reported in the literature on the fate of BTH in the environment. It is mentioned in the draft assessment report that BTH is rapidly photodegraded in water at pH 5 (DT₅₀ < 1d, quantum yield of photolysis between 0.021 and 0.036) into numerous products (all <10%), mostly volatiles, including CO₂. BTH undergoes hydrolysis in soil into 1,2,3-benzothiadiazole-7-carboxylic acid (BTA, Scheme 1) and it is biograded into BTA hydroxylated derivatives [17].

The objective of this work was to evaluate the photoreactivity of BTH in solvents of different polarity and to get further information

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Scheme 1. Chemical structure of BTH, BTA and salicylic acid.

on the photoproducts. *n*-Heptane was selected as an apolar solvent because it offers BTH a medium polarity close to the one of surface leaves on which BTH is sprayed in agricultural conditions and exposed to solar. Polar solvents such as acetonitrile, methanol and water were also chosen because BTH is expected to reach more polar environmental compartments, in particular surface waters, through wash-off. The kinetics of BTH photolysis was investigated in the different solvents and the product studies in acetonitrile due to the satisfactorily solubility of both BTH and its photoproducts in this solvent.

2. Experimental section

2.1. Chemicals

BTH (Pestanal, 99.9%) and BTA (Pestanal, 99.6%) were purchased from Sigma-Aldrich. Methanol (99%, HPLC grade), acetonitrile (99%, HPLC grade), *n*-heptane (99%, HPLC grade) were provided by Riedel de Haën (Saint-Quentin Fallavier, France). Water was purified using a Millipore Milli-Q system (Millipore α Q, resistivity $18 \text{ M}\Omega \text{ cm}^{-1}$, $\text{DOC} < 0.1 \text{ mg L}^{-1}$). All other chemicals were of the highest grade available.

2.2. Irradiations

For decay kinetics and quantum yield measurements and monitoring of spectral changes upon irradiation, air-saturated solutions of BTH (2×10^{-5} to $4 \times 10^{-5} \text{ M}$) were irradiated at 313 nm in parallel beam in a quartz cuvette using a mercury arc lamp (200 W) equipped with a Lot-Oriel monochromator. The photon fluence rate was measured using a radiometer QE65000 from Ocean Optics; it was comprised between 2 and 4×10^{14} photons $\text{cm}^{-2} \text{ s}^{-1}$ at 313 nm. The quantum yields of photolysis, Φ , were calculated using Eq. (1):

$$\Phi = \frac{r_{\text{BTH}}}{I_0(1 - 10^{-A})} \quad (1)$$

where r_{BTH} is the initial rate of BTH consumption, I_0 is the photon fluence rate, A is the absorbance of BTH at 313 nm, and l is the cell pathlength. Measurements were made when the conversion extent of BTH reached 10–15%. For photoproducts characterization, air-saturated solutions of BTH ($2.0 \times 10^{-4} \text{ M}$) in acetonitrile were irradiated in a solar simulator (CPS Atlas) set at an irradiance of 550 W m^{-2} within the wavelength range 295–800 nm. BTH solutions were irradiated until a conversion extent of 50% and analyzed by liquid chromatography-mass spectrometry for photoproducts identification.

2.3. Analyses

UV-vis spectra were recorded using a Cary 3 (Varian) spectrophotometer. The monitoring of BTH concentration was performed using an Alliance Waters separation module 2695 equipped with a photodiode array detector (Waters model 2998).

The column was a reversed phase column, model Kinetex™ C₁₈, $100 \times 2.1 \text{ mm}$, with a particle size of $2.6 \mu\text{m}$, and a size pore of 100 \AA . The eluent was a mixture containing water with formic acid 0.1% (v/v) and acetonitrile (30–70, v/v). The flow rate was set at 0.2 mL min^{-1} . High resolution mass spectrometry (HRMS) was performed on an Orbitrap Q-Exactive (ThermoScientific) coupled to an ultra-high performance liquid chromatography (UHPLC) instrument Ultimate 3000 RSLC (ThermoScientific). Analyses were made simultaneously in negative (ESI⁻) and positive (ESI⁺) electrospray modes. The column was a Kinetec EVO C18 ($100 \times 2.1 \text{ mm}$), particle size of $1.7 \mu\text{m}$ (Phenomenex). The binary solvent system used was composed of acetonitrile and acidified water by formic acid. The gradient elution started with 5% of acetonitrile and reached 95% after 9 min. The flow was set at 0.45 mL min^{-1} .

3. Results and discussion

3.1. Photolysis quantum yield

In *n*-heptane, methanol, acetonitrile and water, BTH shows three absorption bands at 252–256 nm ($\epsilon = 12500\text{--}19800 \text{ M}^{-1} \text{ cm}^{-1}$), 289 nm ($\epsilon = 4700\text{--}7000 \text{ M}^{-1} \text{ cm}^{-1}$) and 324–327 nm ($\epsilon = 6500\text{--}10200 \text{ M}^{-1} \text{ cm}^{-1}$) (Fig. 1, Table 1). Due to this latter band, there is a good spectral overlap with sunlight making BTH photolysis likely in the different environmental compartments (surface waters, soils and leaves surface). Decay kinetics were measured at 313 nm because this radiation is absorbed by BTH and contained in the solar radiations reaching the earth surface. The kinetics of BTH photolysis in air-saturated *n*-heptane, methanol, acetonitrile and neutral water are shown in Fig. 2. The plots of $\ln(c_0/c)$ against the irradiation time, where c_0 and c are the concentrations of BTH at initial time and in the course of the irradiation, respectively, are all linear indicating that decays follow apparent first order kinetics. This is explained by the moderate absorption of the solutions at the excitation wavelength (< 0.2). Quantum yields measured using Eq. (1) are gathered in Table 1. They are comprised between 0.048 and 0.092, showing that BTH photodegradability is rather efficient whatever the solvent used. The lowest quantum yield of photolysis is obtained in water.

3.2. Photoproducts identification

In a first step, we monitored the spectral changes induced by an extended irradiation of BTH. Typical data obtained when BTH is dissolved in acetonitrile are shown in Fig. 3. While the absorbances at 250 and 329 nm regularly decrease as the irradiation time

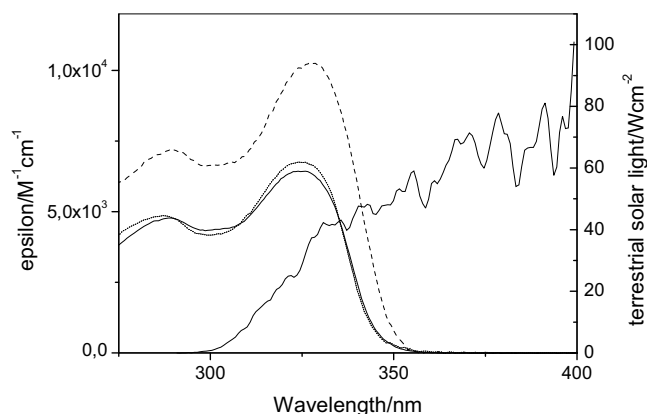


Fig. 1. UV spectrum of BTH in *n*-heptane (short dot), acetonitrile (solid) and water (dash) and spectral distribution of terrestrial sunlight.

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