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Photochemical transformation of azoxystrobin in aqueous solutions

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Abstract

The photochemical behaviour of azoxystrobin fungicide (AZX) in water was studied under laboratory conditions. Photodegradation was initiated using a solar simulator (xenon arc lamp) or a jacketed Pyrex reaction cell equipped with a 125 W, high-pressure mercury lamp. HPLC/MS analysis (APCI and ESI in positive and negative modes) was used to identify AZX photoproducts. The calculated polychromatic quantum efficiencies (ϕ) of AZX at pH 4.5, 7 and 9 were 5.42×10^{-3}, 3.47×10^{-3} and 3.06×10^{-3} (degraded molecules per absorbed photon), respectively. The relatively narrow range of values indicates the stability of AZX with respect to photodegradation in the studied pH range. Results from the HPLC/MS analysis suggest that the phototransformation of AZX proceeds via multiple, parallel reaction pathways including: (1) photo-isomerization ($E \rightarrow Z$), (2) photo-hydrolysis of the methyl ester and of the nitrile group, (3) cleavage of the acrylate double bond, (4) photohydrolytic ether cleavage between the aromatic ring giving phenol, and (5) oxidative cleavage of the acrylate double bond.

Keywords: Fungicide; Strobilurins; Azoxystrobin; Photodegradation; HPLC–MS analysis

1. Introduction

Strobilurin fungicides constitute a relatively new fungicide class developed from natural fungicidal derivatives such as strobilurin A, oudemansin A or myxothiazol A (Sauter et al., 1999; Bartlett et al., 2002). These compounds operate by binding at the ubiquinol-oxidation centre (Qo-site) of the bc1-enzyme complex (complex III) (Bartlett et al., 2002) of a fungi where electron transfer can take place. These well-known strobilurins have either an (*E*)-methyl methoxyiminoacetate moiety or isosteric (*E*)-methyl β-methoxyacrylate group which acts as a common pharmacophoric sub-structure. It has been shown that (*E*)-configured compounds exhibit a higher biological activity than that of the corresponding (*Z*)-stereoisomers (Sauter et al., 1999).

The great impact of the strobilurin fungicides on agriculture is reflected by the widespread use of azoxystrobin (AZX), a chemical which has been approved for use on more than 80 different crops representing over 400 crop/disease systems (Bartlett et al., 2002). In recent years, much research has dealt with the behaviour of this xenobiotic in grapes, a crop of special importance in Mediterranean countries (Cabras and Angioni, 2000; Schira et al., 2002; Abreu et al., 2005; Lentza-Rizos et al., 2006). In particular, the influence of various processes on their degradation during their journey from vine to wine has been monitored in the end product (Cabras et al., 1998, 1999; Cabras and Angioni, 2000). In addition to appearing in wines, these pesticides also find their way into the environment where their behavior and ultimate fate has yet to be studied in depth. Joseph (1999) studied the abiotic degradation of AZX in three different soils. He reported that in the dark

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and under aerobic conditions, the half-life ($t_{1/2}$) of AZX was typically in the range of eight to twelve weeks and that the major metabolite formed upon degradation resulted from the hydrolysis of the ester moiety. In sterile soil there was no significant degradation. Joseph (1999) also showed that photolytic degradation is important and that a much shorter half-life of 14 d is obtained for these species under field conditions.

The aim of this work is to study the photochemical behavior of the pure, synthetic (*E*)-compounds in order to identify the largest number of photoproducts and to try to elucidate the more complete pathway for AZX photodecomposition.

2. Materials and methods

2.1. Chemicals and reagents

AZX (Methyl (*E*)-2-{2-[6-(2-cyanophenoxy)pyrimidin-4-yloxy]-phenyl}-3-methoxyacrylate) with a purity >99.6% (w/w) was used for the photodegradation experiments and were obtained from FLUKA-RIEDEL DE HAËN (SIGMA–ALDRICH CHIMIE). Standards of 2-hydroxy-benzonitrile and pirimidine-4,6-diol (purity >98% and 99% respectively) used for product identification were obtained from the same company. Acetonitrile used for HPLC analysis (HPLC grade) was purchased from Fisher Scientific and methanol for making solutions of AZX from Merck. Ultra pure water for making AZX solutions was purified with a MILLIPORE-MILLI Q system.

Working solutions were prepared by dissolving AZX in water/methanol (99:1) (v/v). Methanol was added to aid in dissolution of AZX as its solubility is only 6 mg l^{-1} in water compared to a much larger solubility of 20 g l^{-1} in methanol at 20 °C. Solutions were buffered by adding KH_2PO_4 (50 mM) and adjusted to various pH values using NaOH. AZX is known to be stable with respect to hydrolysis between 25 and 50 °C and pH values ranging from 5 to 9 (Tomlin, 2000; European Commission, 1997). Nevertheless, to test for the effects of hydrolysis, experiments identical to those testing photodegradation were also carried out in the dark. All concentrations used were in accordance with the European Chemical Industry & Toxicological Centre (E.C.E.T.O.C) recommendations suggesting that, for measurements of quantum efficiency, pesticide concentrations range between 10^{-4} and 10^{-5} M and that solutions contain a maximum of 1% co-solvent (ECETOC, 1984; Lemaire et al., 1985).

2.2. Photodegradation equipment

Two borosilicate (Pyrex) reactors were used during irradiation of AZX solutions at wavelengths >290 nm. The first reactor is a solar light simulator (Suntest CPS+, HERAEUS), equipped with a 1.5 kW xenon arc lamp. The second reactor, used to accelerate the rate of photochemical degradation, was a 50 ml cylindrical vessel equipped with a high-pressure mercury UV lamp (PHILIPS HPK 125 W). Experiments in both vessels were carried out at 19 ± 1 °C.

2.3. Spectrometer apparatus

The UV–visible absorption spectra were recorded using a double beam Uvikon 930 spectrophotometer (KONTRON INSTRUMENTS).

2.4. Kinetics experiments

Fifty millilitres aliquots of 19.8 μM AZX in water/methanol (99:1 v/v) adjusted to different pH values were irradiated for 221 h in both reactors. Samples from the solution were taken at regular time intervals for HPLC–DAD analysis without pre-concentration. The same procedure for hydrolysis experiments was carried out, but samples were kept in the dark.

2.5. Quantum efficiencies

Polychromatic quantum efficiency (ϕ) values were calculated using custom application software (Vulliet et al., 2002; Boudina et al., 2003). This software determines the number of absorbed photons from the pesticide absorption spectrum, the emission spectrum of the light source and the actinometric result. The kinetic measurements on the photodegradation reaction (<10% of degradation) gave the number of photodegraded molecules during the same time. Incident photonic flux was measured by chemical actinometry using uranyl oxalate purchased from Fluka. Two values were established: quantum efficiency (ϕ_{Hg}) using a high-pressure mercury lamp and quantum efficiency (ϕ_{Xe}) using a xenon lamp to forecast the AZX persistence under sunlight irradiation.

2.6. HPLC–DAD conditions

HPLC analyses were conducted using a SHIMADZU VP series chromatograph, equipped with a photodiode array detector (DAD). A Kromasil C_{18} (5 μm, 150 × 4 mm) with a pore size 100 Å, and a pre-column eluted with a gradient of acetonitrile (A) and water (B) was used for the analyses. The pH during analysis was maintained at 2.8 using phosphoric acid. The following gradient was used: from 60% (B) at t = 0–25% (B) at 12 min, with this value maintained until 13 min. The flow rate was set to 1 ml min^{-1} with an injection volume of 20 μl.

2.7. Solid-phase extraction

As the resulting photoproducts formed had very low concentrations, a pre-concentration step was required prior to HPLC–MS analysis. For pre-concentration, each sample was first extracted on solid-phase extraction (SPE) cartridges ISOLUTE ENV$^+$ (INTERNATIONAL SORBENT TECHNOLOGY) packed with 25 mg of highly-linked