



# Unravelling the reactivity of bifenazate in water and on vegetables: Kinetics and byproducts

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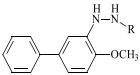





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## HIGHLIGHTS

- Bifenazate undergoes degradation in the dark and under simulated solar light.
- Rates and byproducts are affected by the medium and oxygen.
- Autoxidation takes place in oxygenated water and methanol.
- The reactivity on green pepper is affected by the water contained in the vegetable.
- Using wax or solvent is not adequate to mimic reactions on vegetables.

## GRAPHICAL ABSTRACT

 <b>Bifenazate</b>	 <b>Wax</b>	 <b>Green Pepper</b>	 <b>Water</b>
 	-	<b>Bif-diazene P1</b>	<b>Bif-diazene P1</b>
	<b>Bif-diazene + Adducts</b>	<b>Bif-diazene P2+ Adducts</b>	<b>Bif-diazene P2</b>

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## ABSTRACT

In this study, we aimed to better understand the transformation mechanisms of bifenazate, a biphenyl hydrazine derivative insecticide poorly studied up to now. For this, we compared its reactivity in the dark and under simulated solar light irradiation in different media (water, non-aqueous polar solvent, surface of apolar wax films, skin of vegetable). In air-saturated pH = 5.7 water, bifenazate underwent both autoxidation in the dark ( $t_{1/2} = 34$  h) and photolysis ( $t_{1/2} = 17$  h). In an aprotic polar solvent such as acetonitrile, bifenazate was stable in the dark but was quickly photodegraded in the presence of oxygen ( $t_{1/2} = 2$  h). The phototransformation of bifenazate was due to the oxidation of excited states by oxygen and to the cleavage of the N—N bond, while the autoxidation in water started by the initial oxidation of the molecule by oxygen and involved the superoxide anion as chain carrier. On paraffinic wax film, photodegradation ( $t_{1/2} = 365$  h) and dark autoxidation ( $t_{1/2} = 1600$  h) were very slow. On green pepper skin, bifenazate disappeared both in the dark ( $t_{1/2} = 34$  h) and through photolysis ( $t_{1/2} = 23$  h) at rates close to those measured in water. This shows that on green pepper skin, bifenazate is affected by water contained in the vegetable and possibly released by transpiration. Bifenazate diazene was the major degradation product in all studied conditions. Minor byproducts were detected too. They depended on the experimental conditions showing that degradation pathways are governed by the nature and properties of the medium. In particular, on green pepper one found byproducts generated in acetonitrile and on wax by photolysis and in water by autoxidation. This finding highlights the need for a better model than wax to mimic photolysis on plant surfaces.

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## 1. Introduction

Pesticides are widely used to protect crops from harmful organisms such as weeds, plants pathogens or pests. However the use of pesticides can also be associated with risks to the environment and human health mainly by the exposure of farmers or contamination of food, and water (Damalas and Eleftherohorinos, 2011; Rodriguez-Cabo et al., 2018; Villaverde et al., 2018). After application on target areas, pesticides are dissipated or degraded by different natural processes. In some cases, photolysis can be a major destructive degradation pathway of pesticides (Katagi, 2004), leading to the formation of various photoproducts. Being destructive, photolysis can decrease pesticides amounts applied on crops and thus affect the treatments effectiveness (Leach et al., 2017). Therefore, increasing the amount of pesticides applied or shortening intervals between sprays become necessary, resulting in higher exposure and potential health risks.

The photolysis of pesticides is the subject of an intense research (Reddy and Kim, 2015; Burrows et al., 2002; Remucal, 2014). Through these studies it has been demonstrated that in many cases, photoproducts can have higher toxicity than the parent pesticide. This is the case of sulcotrione (a triketonic herbicide) and some other organophosphorus pesticides (Goujon et al., 2014). Most of the photodegradation studies were performed in liquid matrices, especially water (Burrows et al., 2002). Fewer studies focused on the photodegradation of pesticides on plants (Lavieille et al., 2010; Sleiman et al., 2017) or on supports mimicking the surface of leaves (Monadjemi et al., 2011). However, it has been demonstrated that the nature of the photoproducts formed or the kinetics of the reaction are affected by the medium in which the pesticide is photodegraded (Sanz-Asensio et al., 1999; Schwack et al., 1995; Cooke et al., 2017). Thus, to get a better insight into the fate of pesticides in the different environmental compartments, it is necessary to investigate their photodegradation both in solution and in solid matrices.

This study focused on unveiling the mechanism of photodegradation of the commonly used insecticide bifentazate (isopropyl 2-(4-methoxybiphenyl-3-yl)hydrazino-formate) (BIF, Fig. 1). This pesticide is used for the control of phytophagous mites on various types of crops such as apples, peaches, pears, plums, grapes, cotton, hops and strawberries (Maienfisch et al., 2012), on many fruiting vegetables (tomatoes, peppers, aubergines, cucumbers, courgettes, melons, watermelons) and on flowering and ornamental plants (EFSA, 2017). Its fate in the environment was poorly investigated to our knowledge. Some studies concerned the uptake and the dissipation of BIF in tomatoes and kidney beans and tea (Satheshkumar et al., 2014; Abd El-Zaher et al., 2011). Report of FAO (The Food and Agriculture Organization of the United Nations) described the degradation of BIF in water in the dark and upon exposure to simulated solar light (FAO, 2006; FAO, 2008). BIF was reported to be unstable in aqueous solutions, especially in basic medium. The time necessary to achieve 50% of degradation

(DT<sub>50</sub>) was comprised between 1.6 h at pH 9 and 9.1 d at pH 4. Under light exposure, BIF readily disappeared, the DT<sub>50</sub> being comprised between 0.72 and 0.8 d at pH 5 (FAO, 2006A). BIF-diazene (Fig. 1) was the main primary byproduct formed in the dark and under irradiation (EFSA, 2017; FAO, 2006; FAO, 2008). Like BIF, BIF-diazene was very unstable in aqueous basic medium with a DT<sub>50</sub> of 0.28 h at pH 9 but more stable at pH 4 with a DT<sub>50</sub> of 58 h (FAO, 2006; FAO, 2008). BIF-diazene also underwent fast photolysis with a DT<sub>50</sub> of 1.5 d under solar light (FAO, 2006; FAO, 2008). Along with BIF-diazene, hydroxylated BIF-diazene, 3,4-dihydroxybiphenyl, 3-hydroxy-4-methoxybiphenyl and 3-amino-4-methoxybiphenyl were found as minor photoproducts. Degradation in the dark yielded the same products except the hydroxylated BIF-diazene.

Our objective in this work was to better understand the degradation reactions of this pesticide under relevant environmental conditions. We investigated the fate of BIF in different media: in water and acetonitrile, chosen as a polar non-aqueous solvent, on solid supports such as paraffin wax films that mimic the plant leaves surface and on the skin of a vegetable, the green pepper. In these different conditions, we studied the reactivity of bifentazate in the dark and under simulated solar light exposure from kinetic and analytical points of views. Studies on transient species were also performed to understand the reaction mechanisms.

## 2. Materials and methods

### 2.1. Chemicals

BIF (Pestanal) was purchased from Sigma Aldrich. Paraffin wax was supplied from Acros Organics. Water was purified using a reverse osmosis RIOS 5 and Synergy (Millipore) device (resistivity 18 MΩ·cm, DOC <0.1 mg·L<sup>-1</sup>). The other solvents or reactants were of the highest grade available. Organic green peppers were purchased from a supermarket in Clermont-Ferrand, France.

### 2.2. Analyses

UV–vis spectra were recorded using a Varian Cary 3 spectrophotometer in a 1-cm quartz cell. Fluorescence spectra were recorded on Perkin-Elmer LS55 apparatus. Analysis of the irradiated solutions were performed using liquid chromatography (Shimadzu NEXERA XR HPLC) coupled to a photodiode array detector. The analytical column used was a Macherey Nagel EC100/2 NUCLEODUR Polartec column (100 mm × 2.1 mm, 1.8 μm particle size). A mixture of water (solvent A) and acetonitrile (ACN, solvent B) was used as a mobile phase at a flow rate of 0.25 mL·min<sup>-1</sup>. The elution was performed using the following gradient: 15% B for 1 min, linear increase of B to 55% in 5 min, 55% of B for 5 min and increase of B to 100% in 10 min. The identification of degradation products was performed using High resolution mass spectrometry (HRMS)

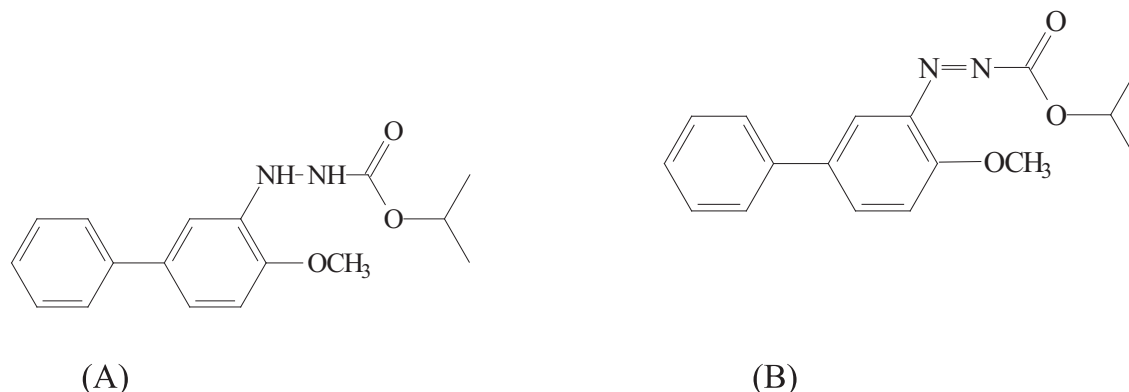


Fig. 1. Chemical structure of A) BIF and B) BIF-diazene.

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