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Photodegradation of Bistrifluron in Aqueous Acetonitrile Solution by UV Irradiation

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Pesticides applied to agricultural fields are subjected to various decomposition pathways. Photolysis is one of the most important pathways of pesticide degradation in water or air, and on plant or soil surfaces (Burkhard and Guth 1979). Photolysis can be classified as direct or indirect photolysis (Davidson 1979). Chemicals with strong absorption in the near ultraviolet (UV) or visible (VIS) light range can be decomposed directly by sunlight; those with negligible light absorption can be broken down by sensitizing mechanisms. For example, chemically active oxygen species produced by various photosensitizers are involved in indirect photolysis (Gottfried et al. 1988). It has been suggested that investigation of their photochemical fate might contribute toward a better understanding of pesticide behavior in the environment (Klöpffer 1992). To date, the photoproducts of a number of pesticides have been studied using UV irradiation. These include dichlorprop (Meunier et al. 2002), fluchloralin (Saha and Bhattacharyya 2001), triasulfuron (Pusino et al. 1999), and tribenuron-methyl (Bhattacherjee and Dureja 1999). More information on the degradation time of a pesticide, and consequently, on its activity and environmental fate, can be obtained by studying the kinetics of both photolysis and hydrolysis reactions (Scheunert 1992).

Bistrifluron (*N*-(2,6-difluorobenzoyl)-*N*'-[2-chloro-bis(3,5-trifluoromethyl) phenyl]urea) is a new insecticide developed by Dongbu-Hannong Chemical Co (Korea). This benzoylphenylurea inhibits insect development and acts by interfering with the formation of the insect cuticle, probably through inhibition of *N*-acetylglucosamine incorporation into chitin. This inhibits the moulting process, leading to death (Song et al. 2000). The logP and vapor pressure are approximately 6.17 and 2.05×10^{-8} torr (25°C), respectively, it has a low acute toxicity of > 5,000 mg/kg (rat, dermal) and > 2,000 mg/kg (rat, oral) (Kim et al. 2002). Bistrifluron is only slightly soluble in water (0.03 mg/L at 25°C).

Benzoylphenylureas (BPUs), such as bistrifluron, diflubenzuron, chlorfluazuron, and flufenoxuron have been used in a range of insect control applications (Fischer and Hall 1992, Ishaaya 1990). Previous investigations have shown diflubenzuron to degrade more rapidly in filtered field water than in deionized water, since additional degradation pathways mediated by hydroxyl, carbonate and alkylperoxy radicals are also present (Mabury and Crosby 1996). These BPUs differ only in the substituents on the aniline portion of the molecule.

The physical properties of diflubenzuron should vary significantly from those of other BPUs, given the increase in molecular weight with the addition of chlorine and aromatic rings. For example, the increase in size resulted in lower water solubility

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and higher *K*ow (Marsella et al. 2000). Hexaflumuron is the most rapidly degraded by photodegradation in water, when compared with teflubenzuron and diflubenzuron (Marsella et al. 2000). However, there is no information in the literature on the photodegradation of bistrifluron. This paper reports the photochemical degradation of bistrifluron, the nature of its degradation products, and the degradation kinetics under UV light. Based on the results, a degradation pathway is proposed. The information provided by this study could aid in understanding the environmental fate and behavior of the insecticide bistrifluron.

MATERIALS AND METHODS

Technical grade bistrifluron (>97.0%) and its metabolites, 2,6-difluorobenzamide (DBA, 97.3%, **M1**), 2-chloro-bis(3,5-trifluoromethylphenyl)urea (CBU, 96.0%, **M3**), and 2-chloro-bis(3,5-trifluoromethyl)aniline (CBA, 93%, **M4**), were kindly provided by Dongbu-Hannong Chemical Co (Korea). These chemicals were used without further purification. All solvents (HPLC grade) were purchased from Duksan Co. (Korea) while acetic acid was purchased from Aldrich (USA). Silica gel 60 (40-63 μm) for column chromatography was obtained from Merck (Germany).

In order to obtain enough amounts of the photoproducts for structural analysis, bistrifluron (200 mg) dissolved in acetonitrile (400 mL), was diluted with distilled water (100 mL) and the solution was mixed thoroughly. The solution was irradiated under UV-B (312 nm, Spectroline EB-160C, USA) and UV-C (254 nm, Spectroline ENF-260C) lamps for 30 days. The UV-irradiated aqueous acetonitrile solutions of bistrifluron were concentrated under vacuum (≤40°C). The remaining aqueous portion was partitioned three times with dichloromethane (100 mL). The combined organic fractions were dried over anhydrous sodium sulfate and, after filtration, the filtrate was concentrated using a vacuum evaporator. The residue was again dissolved in acetone (1 mL) before loading on to a column (40 × 2.9 cm id) containing 10 g of activated silica gel. Elution was carried out with a step gradient of mixed acetone and hexane (5%, **F1**; 7.5%, **F2**; 10%, **F3**; 20%, **F4**, and 30%, **F5**). After the solvent had been removed *in vacuo*, the residue of each fraction was reconstituted with methanol (1 mL), and analyzed by HPLC and liquid chromatography/mass spectrometry (LC/MS).

The kinetics of the photodegradation of bistrifluron were investigated under UV-A (365 nm, Spectroline ENF-260C), -B, and –C lamps. Since bistrifluron is pooly soluble in water, a stock solution was prepared containing 1.12 mM bistrifluron in acetonitrile. This solution, maintained in the dark at 5°C, was stable for a long period. In the photolysis experiments, aliquots of the stock solution (1 mL) were diluted to 100 mL with a solvent mixture of acetonitrile and water (49/50, v/v). The final concentration of bistrifluron in the test solutions was 11.2 μM. The aqueous solution of bistrifluron was irradiated below 10 cm from light source. The temperature of the photolysis solution did not exceed 28°C. Dark control experiments were carried out under similar conditions, except the reaction vessel was covered with aluminum foil. At appropriate times, depending on the photolysis rate, aliquots (1 mL) were withdrawn in duplicate and analyzed by HPLC to monitor the rate of photolysis of bistrifluron.

HPLC analysis was conducted using a Hewlett Packard 1100 series HPLC (CA, USA) with an Eclipse XDB-C18 column (4.6 × 150 mm, 3.5 μm, HP, USA). The mobile phase consisted of water-acetonitrile containing 0.1% acetic acid, and the gradient was programmed linearly as follows: 40% acetonitrile at 0 min, 40% acetonitrile at 3 min, 70% acetonitrile at 15 min, 70% acetonitrile at 30 min, and 40%

acetonitrile at 31 min. The flow rate and detection wavelength were 0.7 mL/min and 210 or 254 nm, respectively. The photoproducts of bistrifluron were identified by co-chromatography with authentic reference standards using HPLC or LC/MS analysis. LC/MS was carried out by coupling the HP 1100 HPLC system to a Quattro LC triple quadrupole tandem mass spectrometer (Micromass, Manchester, UK) in electrospray ionization mode. The source temperature, desolvation temperature, cone voltage, and capillary voltage were kept at 120°C, 250°C, 25 V, and 3.0 kV, respectively. The nebulizer and desolvation gas was ultra-pure nitrogen set at 80 and 700 L/hr, respectively.

RESULTS AND DISCUSSION

The UV spectrum of bistrifluron is characterized by intense absorption at 210 nm and a band at 254 nm (Figure 1). The absorption is very weak at wavelengths longer than 310 nm. Therefore, UV-B and -C lamps were used to supply UV light in this study to produce sufficient amounts of the photoproducts for structural analysis.

HPLC analysis of the larger-scale samples showed the formation of several degradation products (Figure 2). The relative amounts of the different photoproducts are shown in Table 1 after 30 days irradiation. Silica gel column chromatography was performed to obtain enough material for LC/MS analysis because the proportions of **M2** and **M3** were very small. UV-B and –C irradiation produced the identical photoproducts. The major compounds of fractions **F1**, **F2**, **F3**, **F4**, and **F5** were **M3**, bistrifluron, **M3**, **M1**, and **M1**, respectively. **M2** was observed as a minor component in **F5**. The degradation products were identified by comparing the mass spectra or HPLC retention times with those of the pure standards (Table 2, Figure 3). **M1**, 2,6-difluorobenzamide (*m/z* 158 $[MH]^+$) was identified by matching the mass spectrum with that of a reference standard. The mass spectrum of **M3** showed a MH^+ peak m/z 307 and fragment ion peaks at *m/z* 287 and 264. It was identified as 2-chloro-bis(3,5-trifluoromethylphenyl)urea by comparison with a reference standard. **M4** was identified as 2-chloro-bis(3,5-trifluoromethyl)aniline (*m/z* 264 $[MH]^+$). The identification was confirmed by matching the spectrum with the mass spectrum of a reference standard. The minor photoproduct **M2** was tentatively identified as 2,6-difluorobenzoylurea (DBU) and its mass spectrum showed a molecular ion peak at *m/z* 201 ($[MH]^+$). To confirm the structure of the photoproducts identified in the LC/MS analysis (ESI^+ mode), LC/MS was also performed in electrospray (ESI) interface operating in negative mode. The peaks corresponding to $[M-H]^-$ of **M2**, **M3**, **M4**, and bistrifluron were observed at *m/z* 199, 305, 262, and 445, respectively. $[M+Cl]^-$ ions, a characteristic adduct ion in negative mode, were observed for each of the photoproducts.

The identification of these photoproducts suggests that the photoreaction of bistrifluron in aqueous acetonitrile solution includes cleavage of the urea bridge to give **M1** and **M4** as the major products. Ivie et al. (1980) previously observed photochemical cleavage of the urea bond for other benzoylphenylurea insecticides. **M3** is likely formed by cleavage of the amide bond of bistrifluron, and decarbonylation of **M3** may produce **M4**. **M3** was irradiated under UV-C to confirm the production of **M4** from **M3**. The conversion rate of **M3** to **M4** was very low (<3%) after 1 day of irradiation, suggesting that **M4** was principally produced by cleavage of the urea bond. Ivie et al. (1980) observed photoproducts analogous to **M1**, **M3**, and **M4** during the photolysis of diflubenzuron in water after heat treatment. A minor product, **M2**, may be formed by loss of the 2-chloro-bis(3,5-trifluoromethylphenyl) moiety. Although the conditions used in this work differ greatly from those in the practical use of bistrifluron, it is still feasible that the

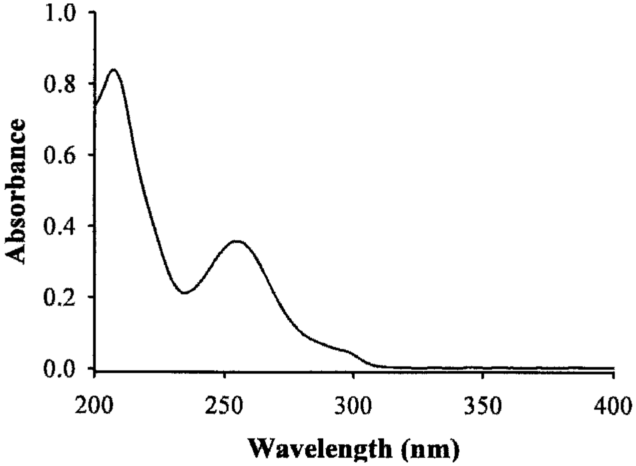

Figure 1. UV spectrum of bistrifluron in acetonitrile solution.

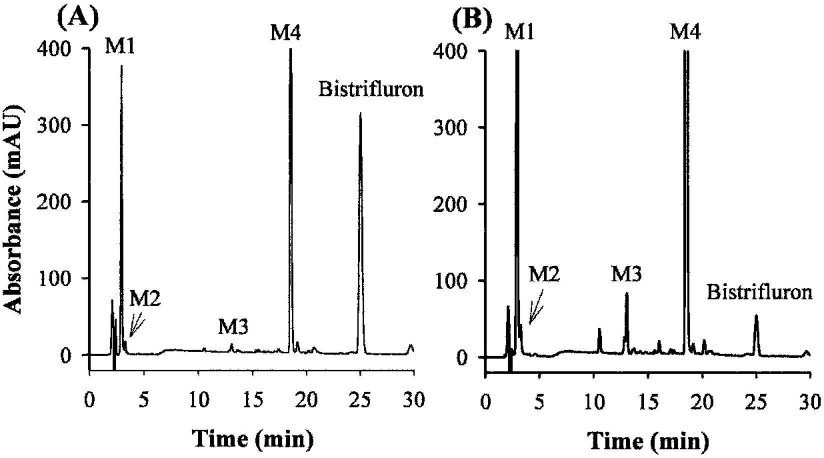

Figure 2. HPLC elution profile of an aqueous acetonitrile solution (concentration = 500 mg/L) of bistrifluron irradiated for 30 days at 312 nm (A) and 254 nm (B). **M1**, 2,6-difluorobenzamide; **M2**, 2,6-difluorobenzylurea; **M3**, 2-chloro -bis(3,5-trifluoromethylphenyl)urea; **M4**, 2-chloro-bis(3,5-trifluoro methyl) aniline.

degradation products reported here occur in or on soil, water, and plants that have been exposed to the material in field conditions.

Table 1. The relative amounts of the bistrifluron photoproducts.

Photoproducts	Relative amount (%)	
	UV-B (310 nm)	UV-C (254 nm)
DBA (M1)	16.7	30.5
DBU (M2)	1.1	1.1
CBU (M3)	0.6	1.9
CBA (M4)	40.7	61.1
Bistrifluron	34.8	2.4
Unidentified	6.1	3.0

Table 2. Mass fragmentation pattern (ESI$^+$ mode) and HPLC retention time of the photoproducts of bistrifluron.

Photoproducts	Retention time (min)	Mass found (*m/z*)	Structure
DBA (M1)	2.9	199	$[M+CH_3CN+H]^+$
		158	$[MH]^+$
		141	$[M-NH_2]^+$
		113	$[M-CONH_2]^+$
DBU (M2)	3.3	242	$[M+CH_3CN+H]^+$
		201	$[MH]^+$
		158	$[\mathbf{M1}+H]^+$
CBU (M3)	13.1	348	$[M+CH_3CN+H]^+$
		307	$[MH]^+$
		287	$[M-F]^+$
		264	$[\mathbf{M3}+H]^+$
CBA (M4)	18.5	305	$[M+CH_3CN+H]^+$
		264	$[MH]^+$
		244	$[M-F]^+$
Bistrifluron	25.0	488	$[M+CH_3CN+H]^+$
		447	$[MH]^+$
		427	$[M-F]^+$
		158	$[\mathbf{M1}+H]^+$

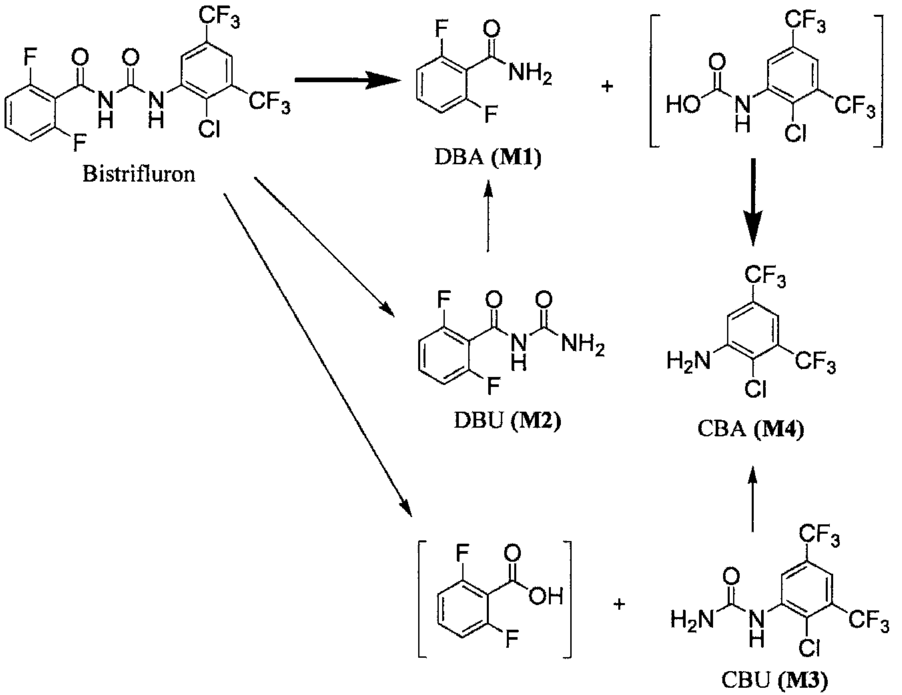

Figure 3. Degradation pathway of bistrifluron in aqueous acetonitrile solution.

The kinetics of UV photolysis of bistrifluron were also studied. **M1**, **M3**, and **M4** were the photodegradation products of bistrifluron (Figure 4). A maximum accumulation of **M1** and **M3** occurred at 72 and 12 hr after irradiation at 312 and 254 nm, respectively. **M2** was observed as minor product (< 5%) of bistrifluron. The rate of photodegradation of bistrifluron at different wavelengths followed pseudo-first-order kinetics with significantly different rate constants and high r^2 values (Table 3). The rate constant (k) was calculated by a regression analysis of the recovered bistrifluron concentration versus time. The half-life ($t_{1/2}$) was calculated using the equation $t_{1/2} = 0.693/k$ (Table 2). Degradation was found to be more extensive with UV-C irradiation than UV-B. No reaction occurred under UV-A irradiation and bistrifluron was recovered almost unchanged after 5 days. In general, negligible degradation of bistrifluron occurred in the dark controls. These results suggest that photochemical reactions are solely responsible for the disappearance of bistrifluron and the formation of its degradation products.

In conclusion, this study provides basic information about the photoreactivity, photoproducts, and photodegradation kinetics of bistrifluron under UV irradiation. The major processes in the photolysis of bistrifluron in aqueous acetonitrile solution are cleavage of the urea bridge and amide bond. The rate of photodegradation of bistrifluron in aqueous acetonitrile solution under UV-B and -C irradiation followed first-order kinetics. Therefore, photolysis could contribute to the detoxification of bistrifluron in aquatic environments.

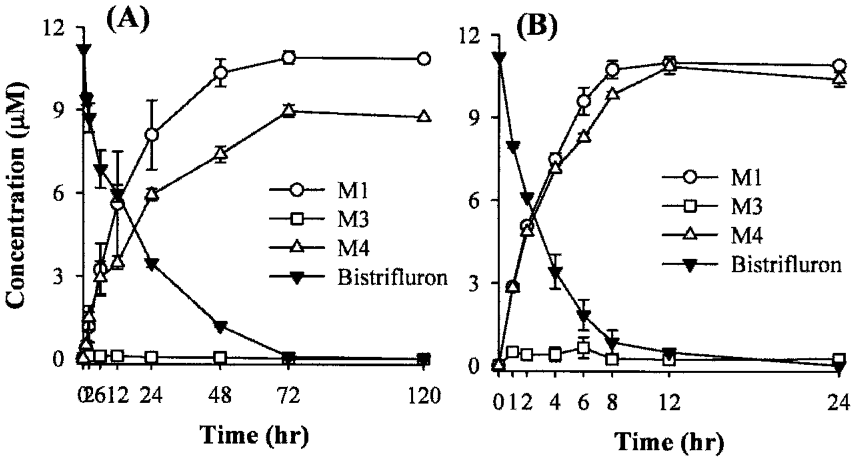

Figure 4. Kinetics of bistrifluron disappearance and formation of its photoproducts in aqueous acetonitrile solution (concentration = 11.2 μM) irradiated at 312 (A) and 254 nm (B). **M1**, 2,6-difluorobenzamide; **M2**, 2,6-difluorobenzylurea; **M3**, 2-chloro-bis(3,5-trifluoromethylphenyl)urea; **M4**, 2-chloro-bis(3,5-trifluoromethyl)aniline.

Table 3. Rate constants (*k*) and half-life ($t_{1/2}$) values for bistrifluron photodegradation at different wavelengths.

Wavelength (nm)	k (hr^{-1})	$t_{1/2}$ (hr)	r^2
UV-C (254)	0.272	2.5	0.980
UV-B (312)	0.062	11.2	0.952
UV-A (365*)	-	-	-

* No degradation was observed over the duration (5 days) of the experiments.

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