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Environmental Analysis

SEPARATION AND IDENTIFICATION OF PHOTOLYSIS PRODUCTS OF CLOTHIANIDIN BY ULTRA-PERFORMANCE LIQUID TANDEM MASS SPECTROMETRY

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Photolysis of clothianidin by Xenon lamp was investigated by Ultra-Performance Liquid Chromatography Electrospray Ionization tandem mass spectrometry (UPLC-ESI/MS/MS). Quantitative study on the photodegradation of clothianidin found that the photodegradation obeyed first order kinetics ($C = 9.9917e - 0.187t$, $R^2 = 0.994$). The half-life was about 3.6 hours. Qualitative study on photolysis products of clothianidin were taken by checking all total ion spectra of different sample time. A total of eight products was found in this study. The structure of each product was determined by the total ion spectrometry spectrum and daughter-scan spectrum. The mechanism of photodegradation of this pesticide included radical denitration, nucleophilic substitution, and rearrangement, ring-open, and ring-close. Through the analysis of the change of every product and the mass information, the photolysis pathway was drawn. From this study, products of V, VI, and VII seemed more stable than clothianidin.

Keywords: Clothianidin; Degradation pathway; Photodegradation; Ultra-performance liquid tandem mass spectrometry

INTRODUCTION

Photodegradation is one of important elimination progresses of pesticides, which influences pesticides residue, efficacy, toxicity, and the environment. The photodegradation information of pesticides is required for registration in many countries, as it is related to safety evaluations of pesticides in the ecological environment (Lu et al. 2010). In all aspects of photolysis study, photodegradation in water is considered the most important for pesticides because it was the basis for UV

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irradiation method development, which is currently one of the most efficient methods for remediation of contaminated water (Burrows et al. 2002). Though, many of pesticides, such as etridiazole (C. Liu et al. 2009), bromoxynil, and triflurali (Chelme-Ayala, El-Din, and Smith 2010), atrazine (Baranda, Barranco, and de Maranon 2012), imidacloprid (Moza 1998), EPTC (Abu-Qane and Duncan 2002), and thiacloprid (Abramovic, Banic, and Sojic 2010) have already been studied on the photodegradation in water. However, more pesticides need to be studied.

Neonicotinoids were the newest of the five major classes of insecticides and made up approximately one-fourth of the world insecticide market (Jeschke et al. 2011; Tomizawa and Casida 2011). Clothianidin, (E)-1-(2-chloro-1,3-thiazol-5-ylmethyl)-3-methyl-2-nitroguanidine, was a novel of important neonicotinoids. The structure and absorption spectra of clothianidin is shown in Fig. 1. Due to affectivity and low toxicity (Uneme 2011), clothianidin had been registered as an insecticide in many countries. Although clothianidin is on the market, there is not enough information about the photodegradation of this compound. Recently, research about clothianidin has focused more attention on the residues in food (Dimuccio et al. 2006; Eiki 2007; S. Liu et al. 2010; Xiao et al. 2011) rather than the behavior on environmental. Considering the environmental relevance and importance of the photodegradation of pesticides, we thought this compound was worthy of study.

Liquid Chromatography coupled with Tandem Mass Spectrometry (LC-MS/MS) had become the technique of choice in the degradation product studies due to its selectivity, sensitivity, and speed of analysis (Z.-Y. Liu et al. 2011). Moreover, mass spectrometry provided a rapid and convenient method for structural elucidation on the basis of tandem mass spectrometry (Li et al. 2009). Thus, many

Figure 1. The structure and absorption spectra of clothianidin.

scholars applied this new technique to identification of photolysis products of pesticide (Dearth, Korniski, and Gerlock 1995; Ding, Jacobs, and Lavine 2011; Gu et al. 2003; Guzsany et al. 2010; Lovdahl et al. 2000). In this study, the aim was to investigate the photolysis of clothianidin. To achieve this goal, we took advantage of UPLC-ESI/MS/MS to quantitatively determine the photodegradation of clothianidin and identify the structure of photolysis products in the process. Moreover, we wanted to find out the mechanistic pathway for clothianidin photodegradation.

MATERIALS AND METHODS

Chemicals and Solutions

Clothianidin with 99.6.0% analytical purity was obtained from Dikma (Beijing, China). Methanol and acetonitrile were of HPLC grade and were purchased from Merck (Rahway, NJ, USA). Formic acid was purchased from Tedia (Dayton, OH). Milli-Q quality water (Millipore, Bedford, MA) was used during the whole analysis. Sodium chloride and sodium hydroxide were obtained from the Beijing Chemical Factory Co (Beijing, China). Bond Elut Plexa cartridges (3 mL/60 mg) were purchased from (Agilent, USA).

Individual stock solutions of clothianidin dissolved in methanol were established at a concentration of 1,000 mg/L. Working solutions were diluted to 10 mg/L with Milli-Q quality water before use. The initial pH of working solution was 7.05. All stock solutions were stored in a refrigerator at 4°C.

Photolysis of Clothianidin

Photolysis experiments were carried out in a Xutepmt (Hangzhou, China) photolysis reactor equipped with xenon lamp. The UV spectra of this xenon lamp used in this study were mainly in the range of 190nm–800 nm, which is close to the sunlight spectrum. Clothianidin strongly absorbs UV irradiation over a wide range of wavelengths, from 200 to 340 nm (Fig. 1), with the maximum absorption band at 266.9 nm. Hence, this lamp met the requirement. The light intensity was approximately 4000 lx in the process of the experiment, measured by a TES 1330 digital lux meter (Taipei, China). Twelve quartz test tubes were placed in a circular rotary device around the lamp. The lamp was placed at central part of the reactor, which was cooled by air circulation to avoid uncontrolled heating of the irradiated solutions and to maintain a constant temperature of $25 \pm 2^\circ\text{C}$. Twelve quartz tubes of the photo reactor were filled with 30 mL of working solutions and irradiated by the xenon lamp for 2 days. Control samples consisted of clothianidin solutions filled in quartz tubes wrapped in aluminum foil and protected from light exposure.

Analysis and Identification

The UPLC-MS/MS system was a Waters Acquity Ultra-Performance liquid chromatography coupled with EX Premier (Waters, Milford, MA). The system was controlled by MassLynx 4.1 software (Micromass, Manchester, UK). UPLC mobile phase A was water with 0.1% formic acid, and mobile phase B was methanol with 0.1% formic acid. The UPLC column was an Acquity UPLC BEH C18 100 mm

2.1 mm, 1.7 μ m column (Waters, USA). The gradient profile consisted of 0–3 min, 90%–60%A; 3–4 min, 60%–40%A; 4–8 min, 40%–10%A. Flow rate was 0.2 mL/min. Column oven temperature was set at 35°C, and auto sampler temperature was set at 20°C. Injection volume was 5 μ L, and the total run-time was eight minutes. The nitrogen gas was set to 600 L/h at a temperature of 350°C; the cone gas (nitrogen) was set to 50 L/h, and the source temperature to 120°C.

For the degradation study of clothianidin, the UPLC-MS/MS instrument was operated in multiple reactions monitoring (MRM) mode. The cone voltage was 25 V, the collision energies of daughter 168.91, 131.91, and 110.2 were 14 eV, 18 eV, and 28 eV, respectively. The ion pair 250.072 > 168.91 was used for quantitative analysis. For identification of the structure of photolysis products of clothianidin, the UPLC-MS/MS instrument was operated in full-scan and daughter-scan mode. Mass range was from m/z = 50 to 450. The daughter-scan model was used to analyze the structure of the parent ion.

Sample Pretreatment

For analysis study, water samples collected from test tubes were filtrated via a 0.22- μ m microporous film and injected into the UPLC-MS/MS system.

For identification of the structure of photolysis products, samples from the photodegradation progress were pretreated by Bond Elut Plexa cartridge. The Plexa cartridge was first conditioned with 3 mL of methanol and 3 mL of water. Then, 10 mL of sample was loaded onto the cartridge, washed with 3 mL of water, and then centrifuged to dry. Finally, the cartridge was eluted with 10 mL of methanol. The eluant was collected and evaporated to dryness by an R-215 rotatory evaporator (Buchi, Switzerland), and then dissolved in 1 mL of methanol/water solution (methanol: water = 1:1, v/v). The solution was filtrated via a 0.22- μ m microporous film and injected into the UPLC-MS/MS system. For this pretreatment, the recovery of clothianidin was above 90%.

RESULTS AND DISCUSSION

Optimization of Separate Conditions

We used UPLC to improve separation methods with low solvent usage, and selected a 100 mm long column filled with 1.7- μ m particle sizes of BEH C18. It is a well-known fact that the smaller is the size of the particle the better is the efficiency and sensitivity obtained. In order to achieve good separation of the photodegradation products, methanol and acetonitrile mobile phases were compared in the test. The results showed that methanol contented 0.1% (v/v) of formic acid provided better ionization conditions. Furthermore, 0.1% (v/v) of formic acid in water system gave better ionization efficiency.

Degradation of Clothianidin

Quantitative analysis showed a high degree of linearity ($r > 0.9983$) over the range 0.01 mg/L–10 mg/L. The recoveries were 89%–99%. The relative standard

deviation of this method was 3.3% to 9.1%. Two mL aliquots of the photolysis solution were collected periodically from test tubes via syringe for UPLC-MS/MS analysis at 0, 1, 2, 3, 5, 7, 10, 12, 16, 20, 24, 32, and 40 h. Degradation of clothianidin was not observed in the control samples. Approximately 90% of clothianidin in the solution decomposed (Table 1) after twelve hours. The kinetics of photolysis was determined to be first-order ($C = 9.9917e - 0.187^t$, $R^2 = 0.994$) with a half-life of 3.7 hours.

Identification the Photolysis Products

Ten mL aliquots of the photolysis solution were collected periodically from test tubes for identification the photolysis products at 0, 1, 2, 3, 5, 7, 10, 12, 16, 20, 24, 32, and 40 hours. By analyzing the reaction solution with UPLC-MS/MS full-scan mode, several pertinent peaks were tentatively identified as presented in Fig. 2. Figure 2(A) shows a total ion spectrum of clothianidin solution prior to photolysis. The sole peak in the chromatogram at 3.41 min was clothianidin. An ESI mass spectrum of the solution showed the clothianidin molecular ion plus proton $[M+H]^+$ peak at $m/z = 250.67$, as well as the $[M+Na]^+$ peaks at $m/z = 272.58$. The daughter-scan model was used to analyze the structure of parent ion. The daughters of clothianidin were $m/z = 169.59$, $m/z = 132.55$, $m/z = 113.63$, as seen in the mass spectra in Figure 3. The daughter of $m/z = 169.59$ was clothianidin loss of Cl and NO_2 . The daughter of $m/z = 132.55$ was obtained by clothianidin loss of $C_2H_5N_4O_2$ ($m/z = 117$). The daughter of $m/z = 113.63$ came from $m/z = 169.59$ loss of $C_2H_2N_2$.

As time elapsed, clothianidin decomposed and different compounds were formed. A total of eight fragments were found in the clothianidin solution by UPLC-MS/MS in scan mode. The total ion-scan spectrum is shown in Fig. 2, where the fragments were numbered from I to VIII, while the pesticide was labeled by name. Figure 2(A–F) show the irradiated progress, where several ions appeared in the irradiated clothianidin solution at different irradiated times and were absent at the beginning. The products $[M+H]^+$ and major fragment are listed by retention time in Table 2.

The retention time of peak I ($m/z = 192.55$) was 0.65 min, as shown in Fig. 4 (a), which implied the polarity of peak I was strong. According to the fragment ions $m/z = 178.67$, $m/z = 160.58$, $m/z = 142.63$, and $m/z = 85.68$. The loss between Peak I

Table 1. Residues and degradation rate of clothianidin in water at different photolysis time

Sample time (h)	Residues in water (mg/L)	RSD (%)	Degradation (%)
0	9.82	2.4	0
1	8.53	1.7	13
2	6.67	2.4	32
3	5.42	3.1	45
5	4.03	2.2	59
7	2.82	4.1	71
10	1.69	6.4	83
12	0.95	5.2	90

Figure 2. Total ion-scan spectrum of clothianidin solution at 0, 1, 2, 5, 12, and 40 hours.

($m/z = 192.55$) and fragments were 13.88, 18.09, 17.95, and 56.95, which should be CH_2 , H_2O , H_2O , CH_2COO^- . Therefore, the structure of peak I should contain at least two oxygen atoms. The fragment $m/z = 85.68$ was the 4,5-dihydrothiazole structure.

Figure 3. Total ion-scan spectrum and daughter-scan spectrum of clothianidin.

Table 2. The m/z values and fragments of major photolysis products of clothianidin

Peak number	Retention time (min)	Products(m/z)	Major fragment ions(m/z)
I	0.66	192.55	178.67, 160.58, 142.63, 114.64, 85.68
II	0.80	169.65	113.64
III	1.55	221.61	132.57 ^a , 134.57, 113.62, 165.60, 185.62, 89.63
IV	1.77	205.62 ^a	132.56 ^a , 134.57, 113.62, 169.68, 149.61, 81.74
V	2.21	135.77	157.75, 117.80, 89.84, 73.88
VI	2.87	206.61 ^a	175.52 ^a , 177.57, 132.56, 113.61, 86.71
clothianidin	3.45	250.67 ^a	272.58 ^a , 169.59, 132.55, ^a 134.56, 113.63
VII	3.80	183.62	159.59, 127.61, 99.61
VIII	4.33	229.87	207.82, 167.81, 131.83, 109.83, 73.89

^aPresence of a chlorine.

Thus, structure of peak I should be I in Fig. 4(a). We noticed that the peak of product was reduced by time. We thought that this phenomenon might be due to the photodegradation of product I. The same situation also occurred in product II and product III.

The m/z of peak II was 169.65 and was same as the one fragment ion of clothianidin. The major fragment ions of $m/z = 169.65$ was $m/z = 113.64$, which was the same as another fragment ion of clothianidin. Thus, we inferred that the structure of peak II (m/z) was the same as the fragment ion of clothianidin in Fig. 4(b).

The difference of mass between clothianidin and peak III ($m/z = 221.6$) was approximately 28, which implied that there was a loss of ethyl group (28.0307), N_2 (28.0055), CH_2N (28.0181), or CO (27.9943). According to the structure of clothianidin, CH_2N (28.0181) was possible. As a result, the structure of peak III should be in Fig. 4(c)

Figure 4. Spectrum and structure of major photolysis products.

According to Fig. 2, peak III was formed earlier than peak IV. And, peak IV ($m/z = 205.61$) had same fragment of 132.56, 134.57, 113.62, and 169.68; thus, this fragment should come from peak III by loss of NH_2 [Fig. 4(d)].

The fragments of peak V were $m/z = 157.8$ and $m/z = 135.84$; there was $m/z = 22$ between them. Therefore, $m/z = 157.8$ ought to be the $[\text{M} + \text{Na}^+]$ form of peak V, while $m/z = 135.77$ was the $[\text{M} + \text{H}^+]$ form. We determined $m/z = 117.8$, $m/z = 89.84$, and $m/z = 73.88$ by checking the daughter-scan of $m/z = 135.77$. The $m/z = 135.77$ was formed by $m/z = 118$ an added $-\text{OH}$ ($m/z = 17$), which meant that clothianidin broken down at the bond of (CH_2-NH) ; the left side added an $-\text{OH}$ forming peak V [Fig. 4(e)].

Peak VI ($m/z = 206.61$) had almost the same m/z as peak IV, though the main fragments of them were different. Peak VI's main fragments were $m/z = 175.52$, $m/z = 132.56$, $m/z = 113.61$, and $m/z = 86.71$. The $m/z = 175.54$ and peak VI ($m/z = 206.61$) contained chlorine. From the value of m/z , we inferred that $m/z = 175.54$ came from peak VI ($m/z = 206.61$) by loss of O_2 . With the other main fragments, the structure is drawn in Fig. 4(f).

Clothianidin loss of NO_2 and Cl atom was $m/z = 185$. Peak VII was $m/z = 183.62$. There was an $m/z = 2$ loss between them. Therefore, peak VII must be a cyclic structure. Fortunately, we obtained the structure by several debates and a referenced daughter-scan of $m/z = 183.62$. We thought the structure was similar to the structure in Fig. 4(g). The mechanism of the formation of product VII was similar to Fig. 5. First, product VI reacted by nucleophilic substitution. The chlorine atom was substituted for hydroxyl. Then, two steps of rearrangement reacted. The ring opened. Finally, product VII was formed by another rearrangement and ring closing.

According to the chlorine isotope rule, there appeared to be no chlorine in the structure of peak VII. The m/z of peak VIII was 229.74, which was $m/z = 15$ weightier than clothianidin without the chlorine atom. This meant that peak VIII ($m/z = 229.74$) formed clothianidin by adding a methyl while losing a chlorine atom [Fig. 4(h)].

We estimated the change in the amount by analysis of the area of every product. Along with the radiation time increase, product II and III were found in the first hour; the concentration reached maximum after 12 hours and then began to decrease. While, products of V, VI, and VII continued to increase over the period of radiation time, the amount of products of I, IV, and VIII gradually stabilized after reaching a certain concentration.

Figure 5. The mechanism of the formation of product VII.

Figure 6. The photolysis path way of clothianidin.

According to all the aforementioned information, the photolysis pathway was drawn as shown in Fig. 6.

CONCLUSION

Clothianidin was highly photolabile in solution. The kinetics of photolysis was determined to be first-order ($C = 9.9917e^{-0.187t}$, $R^2 = 0.994$) with a half-life of 3.7 hours. Additionally, the present findings showed that clothianidin degraded by photo reactions could be complex. From the UPLC-MS/MS study on the photolysis, eight products were identified. The mechanism of photodegradation of this pesticide included radical denitration, nucleophilic substitution, and rearrangement, ring-open, and ring-close. Through the analysis of the change of every product and the mass information, the photolysis pathway was drawn. From this study, products of V, VI, and VII seemed more stable than clothianidin. These compounds could be more toxic than clothianidin itself and pose a danger to man. Thus, the toxicity of these products requires further study.

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