

Effects of ZnO Nanoparticle on Photo-Protection and Insecticidal Synergism of Rotenone

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Abstract

Rotenone has an effective insecticidal activity. However, the photodegradation of rotenone under sunlight or UV (ultraviolet light) leads to negative effects on its insecticidal activity and persistence. This study examined the photo-protection of rotenone when exposed to UV combined with various nanoparticles. The remaining concentration of rotenone was analyzed by LC-MS/MS (liquid chromatography-triple quadrupole tandem mass spectrometry) at particular intervals. It indicated that various nanoparticles had different effects and combination with ZnO nanoparticle provided remarkable degree of photo-protection of rotenone in UV radiation. In comparison with ZnO, SiO₂ nanoparticle provided moderate degree of photo-protection of rotenone in UV radiation. In addition, TiO₂, Fe₂O₃ and CuO nanoparticle exerted catalytic degradation effects on rotenone to a certain degree. The combination of rotenone and ZnO nanoparticle(4:1) increased the efficiency of mortality to the highest compared with the same concentration of sole rotenone or ZnO nanoparticle treatment alone and their co-toxicity coefficient was 128.63. ZnO nanoparticle has good UV photo-protective properties and insecticidal synergism on rotenone. The application of this proposed method can provide significant and practical guidance for improving the photostability and insecticidal activity of rotenone as well as other biopesticides.

Keywords: ZnO nanoparticle, photo-protection, insecticidal synergism, rotenone

1. Introduction

Protection against ultraviolet (UV) radiation is the major function of sunscreen lotions and UV-protective coatings for vehicles, homes, equipment and clothing. Sunscreen formulations have been optimized to become protective over a broader spectrum of UV radiation and maintain greater photostability. They are composed of organic and inorganic components that act as chemical and physical UV protectors, respectively. Some of the organic components are limited by their spectrum of protection and photostability. Studies using solid lipid nanoparticles, recently explored organic molecules and inorganic components attempt to further optimize UV protection (Morabito et al., 2011). Inorganic pigments with a high refractive index, such as titanium dioxide and zinc oxide (ZnO), also block UV light. Nanoparticle grades of these materials are often incorporated into sunscreen formulations by virtue of their small particle size, because they are more effective than the bulk pigments in absorbing and scattering UV light, which usually play a role of physical sunscreen in absorbing, reflecting and scattering UV radiation (Dunford et al., 1997; Westerdahl et al., 2000; Popov et al., 2005; Jaroenworoluck et al., 2006; Nohynek et al., 2008; Morabito et al., 2011). ZnO is a mineral and prepared in particles that have a typical size ranging from 20 to 80 nm and it can be considered a better sunscreen ingredient than TiO₂ depending on the formulation requirements, because ZnO is more transparent and covers a broader UVA spectrum (Pinnell et al., 2000; Cross et al., 2007; Chen et al., 2010).

Biopesticides are becoming increasingly important as pest management tools in various cropping systems in the tropics essentially to remedy problems associated with the indiscriminate use of 'hard' and non-environmental friendly inorganic pesticide. In these past few decades, many biopesticidal products, both microbial-based and plant-based botanicals have been studied for their use against insect pests. So rotenone-based botanical

insecticide has received increasing attention (Xu & Huang, 2001; Xu, 2001; Huang et al., 2002; Xu et al., 2003; Tan & Song, 2006). Rotenone is one of several isoflavonoids produced in the roots or rhizomes of the tropical legumes *Derris* and *Tephrosia* which is a broad-spectrum, botanical insecticide for controlling aphids, trips and suckers with some acaricidal properties (Nawrot et al., 1989; Chiu & Huang, 1998; Xu & Huang, 2001; Xu et al., 2003; Murray, 2006; Qin et al., 2014). Rotenone's photosensitivity was widely studied for its use as insecticide because it limited the duration of its efficiency. It has been reported that rotenone was degraded in at least 20 compounds and its bioactivity is diminishing under field conditions, resulting in inadequate persistence in the environment and unsatisfactory field performance (Xu, 2001; Lei et al., 2004; Qin et al., 2014).

In this investigation, attempts to protect rotenone composition from the damaging UV radiation and maintain its photo-protection yielded success. Photo-protection can be achieved by various nanoparticles, such as ZnO, TiO₂, SiO₂, Fe₂O₃, and CuO nanoparticle. According to literature investigation, this is the first time to analyze the effects of ZnO nanoparticle on photo-protection and insecticidal synergism of rotenone. We undertook this study to determine whether combined with selected could prevent the light-induced degradation of rotenone under controlled conditions. Experiments were carried out to demonstrate how the ability of these effective nanoparticles can protect rotenone against photodegradation.

2. Materials and Experiments

2.1 Equipments and Materials

2.1.1 Equipments

The instruments namely BS210S electronic balance, 365 nm UV lamp and UV-A irradiation photometer were obtained from Sartorius company of Germany, Phillips, Netherlands, Beijing Normal University Company, China, respectively. Agilent 1200 Series HPLC system equipped with an Agilent 6460 Triple Quadrupole LC/MS system was made by Agilent Co. (USA), HPLC analysis was performed with an Agilent 1200 HPLC system equipped with a binary pump, auto plate-sampler, column oven and diode-array detector.

2.1.2 Materials

Rotenone (96.15%) was purchased from Aldrich, USA. ZnO (30 nm), TiO₂ (30 nm), SiO₂ (30 nm), Fe₂O₃ (30 nm) and CuO nanoparticle (30 nm) were purchased from Shenzhen Jingcai Chemical Co., Ltd, China and all the nanoparticle were analytical grade reagents. Ethanol and acetonitrile were obtained from DIKMA Technology Inc. USA.

2.1.3 Tested Insects

Pieris rapae Linne: lepidoptera, plutellidae. the pupae of *Pieris rapae* were collected from Yangzhou University Experimentation Farm, Yangzhou, China. The next generation were reared with cabbage seedlings in an environmental chamber with the temperature held at 26±1 °C under a photoperiod of light:dark = 14:10 h.

2.2 Experiments Method

2.2.1 Degradation of Rotenone on the Surface of Glass Slides

The method of degradation of rotenone on the surface of glass slides was referenced by the related literature (Chen et al., 2009). Solutions of rotenone (5.0 µg mL⁻¹) were prepared along with nanoparticles in mol ratio of 4:1 (rotenone:nanoparticle) and 1:0 (no nanoparticle) in ethanol. The irradiation wavelength was 365 nm and the irradiation intensity was 4120 µW cm⁻². The remaining concentration of rotenone was then analyzed using LC-MS/MS (liquid chromatography-triple quadrupole tandem mass spectrometry). The irradiation experiment was repeated three times. Control samples collected at the same time intervals and analyzed similarly.

2.2.2 Degradation of Rotenone on Cabbage Leaf Surface

The method of degradation of rotenone on cabbage leaf surface was referenced by the related literature (Chen et al., 2009). The irradiation wavelength was 365 nm and the irradiation intensity was 2530 µW cm⁻². Samples were collected at 0, 12, 24, 36, 48 and 60 h intervals. The remaining concentration of rotenone was then analyzed using LC-MS/MS. The experiment was repeated three times. Control samples collected at the same time intervals were extracted and analyzed similarly.

2.2.3 Determinations of Rotenone by LC-MS/MS

Separation was conducted on Agilent Eclipse Plus chromatographic columns C₁₈ (4.6 mm × 150 mm (i.d.), 5 µm) at 20 °C, with mobile solvents consisting of acetonitrile/water = 70:30 (V:V), isocratic at 1 mL min⁻¹. Aliquots of 5 µL were injected directly to the LC-MS/MS system to test rotenone and quantify with external standard peak area.

Mass spectra were recorded on an Agilent 6460 triple quadrupole (QQQ) mass spectrometer equipped with an ESI source. System control and data acquisition were controlled by Agilent Mass Hunter software. Detailed MS conditions were: cluster voltage: 100 V; gas temperature: 300 °C, gas flow 10 L min⁻¹, nebulizer pressure: 15 psi, sheath gas temperature: 250 °C; sheath gas flow: 7 L min⁻¹, capillary voltage: 4 kv, nozzle voltage: 500 V. ESI was operated in the positive ion mode in the MRM (multiple reaction monitoring).

2.2.4 Statistical Analysis

The dissipation curves of rotenone were analyzed using nonlinear regression with Microsoft Excel software. The degradation kinetics followed first-order kinetics, $C_t = C_0 e^{-kt}$, where C_t is chemical concentration (mg kg⁻¹) at time t (hours), C_0 is initial concentration (mg kg⁻¹), and k is the first-order rate constant (hours⁻¹) independent of C and C_0 . The correlation coefficient (r) is used to represent the congruence between the data and the first-order dynamic equation. The dissipation of those compounds has been generally expressed in terms of $T_{1/2}$, that is, the time after which 50% of the pesticide has been depleted, which can be calculated using Hoskins formula ($T_{1/2} = (\ln 2)/k$).

2.2.5 Biological Assays

A five-point standard curve was prepared for rotenone and ZnO nanoparticle. The calibration curves were created by plotting the concentration of each compound against the inhibition rates of *Pieris rapae* 3rd instar larvae. Simple linear regression analysis was performed to calculate the slope and intercept. The correlation coefficient (r) for each compound was also determined. A standard curve was drawn according to the concentration of each compound as the X-axis, and the inhibition rates of the *Pieris rapae* 3rd instar larvae as the Y-axis.

Leaf-dip experiments were conducted as described previously (Chen et al., 2007; Hitchner et al., 2012). In order to study the synergic effects, combinations were made as rotenone, ZnO nanoparticle, rotenone+ZnO nanoparticle. The test solution was made by dissolving or suspending the compound in a small amount of ethanol, then adding a few drops of Tween 80, and finally adding enough water to give a concentration of rotenone solution (200, 100, 50, 25 and 12.5 mg mL⁻¹), ZnO nanoparticle solution (1200, 600, 300, 150 and 75 mg mL⁻¹), rotenone+ZnO nanoparticle solution (150, 75, 37.5, 18.75 and 9.375 mg mL⁻¹). The concentration of ethanol was less than 5.0% and that of the surfactant was no more than 2%. Cabbage leaves were dipped into the prepared solutions for 5 s, and then dried for 30-40 min at room temperature. As a control, a solution of ethanol-water with surfactant only was used. The treated leaves were placed in the beakers and 10 3rd-instar larvae of *Pieris rapae* were introduced into each beaker (3rd instar larvae starved for 4 h before feeding on treated leaf). The mortality was determined by counting dead larvae in the treated beakers 48 h after treatment. All the bioassay was repeated three times and the parallel treatments were incubated. All data were analyzed by Duncan multiple comparison.

3. Results

3.1 LC-MS/MS Optimal Detection Condition of Rotenone Standard

It indicated that mobile solvents system consisting of acetonitrile/water = 70:30 (V:V) and LC-MS/MS separation affects of rotenone culminated in the highest sensitivity under mobile solvents system in the MRM positive mode (Figures 1-2). Chromatographic separation of rotenone was achieved with isocratic elution in the reverse phase mode, giving retention times for rotenone of 4.72 min. Parent compound of rotenone was subjected to collision-induced dissociation in the MRM positive mode. The observed mass transitions and collision energy used for quantitation of rotenone were summarized in Table 1. As shown in Table 1, a product ion scan of the rotenone gave unique mass fragments. For rotenone, intense fragmentation ions were observed at m/z 213, 241, and 192. Selected reaction monitoring of the precursor-product ion transition was m/z 395/213 for rotenone for the quantitative ion transition. The second and third transitions were used for confirmatory purposes for samples. For the LC-MS/MS, quantitation of rotenone was used with quantitative determination of peak areas obtained from the MRM of rotenone.

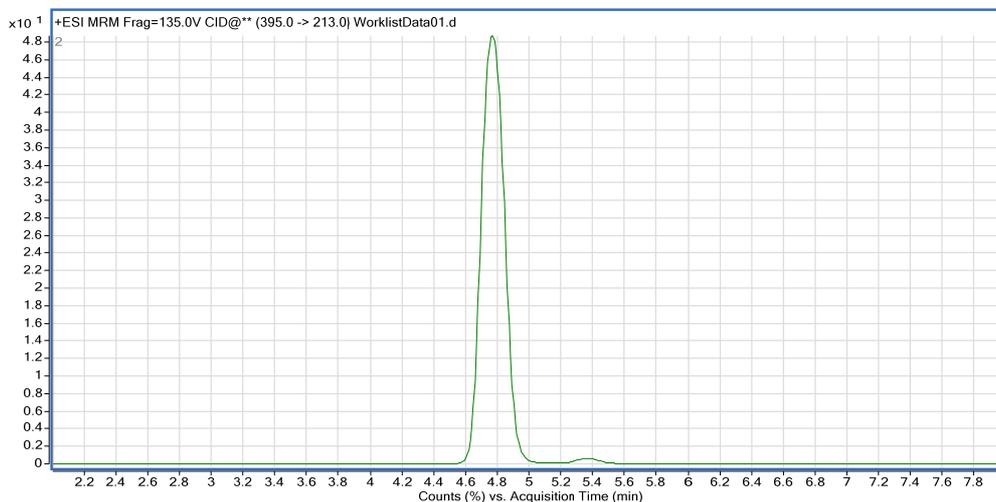


Figure 1. Selected ionization chromatography of rotenone by MRM mode (m/z 395/213)

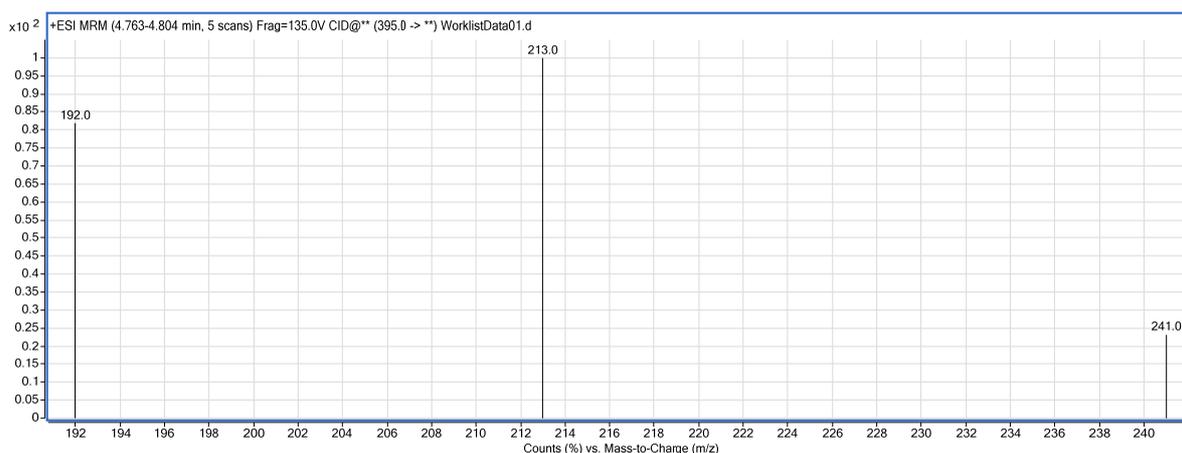


Figure 2. Mass spectroscopy figure of rotenone

Table 1. The LC-MS/MS parameters for rotenone

Ion transition	Collision energy (eV)	Note
395/213	22	Quantitative ion transition
395/241	20	Qualitative ion transition
395/192	24	Qualitative ion transition

3.2 Degradation of Rotenone on the Surface of Glass Slides

The mean recoveries and relative standard deviations at 3 fortification levels from 3 replicates of rotenone on the glass ranged from 84.93 % to 93.41% (Table 2).

Table 2. Recoveries and relative standard deviation of rotenone on the glass

Fortification levels (mg kg^{-1})	Average recoveries (%)	Relative Standard deviation	Coefficient of variance (%)
5.0	93.41	0.1380	2.95
0.5	86.21	0.0146	3.38
0.1	84.93	0.0028	3.25

Note. The remaining amount was the average of three replicates.

Combinated with various nanoparticles such as ZnO and SiO₂ nanoparticle, the rate of degradation of rotenone was found to be lower than in comparison to that rotenone alone. The percentage of remaining rotenone recovered at different intervals of time for different treatments (ethanolic solutions of rotenone with and without nanoparticles) from different slides exposed to UV light conditions were shown in Tables 3 and 4 respectively. Various nanoparticles had different effects and the addition of ZnO nanoparticle enhanced the photo-protection of rotenone in UV radiation to the remarkable degree. While in terms of SiO₂ nanoparticle, the degree decreased to moderate. And as for TiO₂, Fe₂O₃ and CuO nanoparticle, they exerted catalytic degradation effects on rotenone to a certain degree.

Table 3. Degradation rate of rotenone combinated with various nanoparticles (rotenone/nanoparticle = 4/1) (24 h)

Treatments	Initial concentration ($\mu\text{g mL}^{-1}$)	Residual concentration ($\mu\text{g mL}^{-1}$)	Degradation rate (%)
Rotenone	5.00	1.7316 \pm 0.0021c	65.37
Rotenone+ZnO	5.00	2.3842 \pm 0.0019a	52.32
Rotenone+SiO ₂	5.00	2.0608 \pm 0.0017a	58.78
Rotenone+TiO ₂	5.00	1.2907 \pm 0.0024f	74.19
Rotenone+Fe ₂ O ₃	5.00	1.3709 \pm 0.0014e	72.58
Rotenone+CuO	5.00	1.4651 \pm 0.0031d	70.70

Note. All the experiments were repeated thrice as average \pm standard error of average.

Table 4. Degradation rate of rotenone combinated with various nanoparticles (rotenone/nanoparticle = 4/1) (48 h)

Treatments	Initial concentration ($\mu\text{g mL}^{-1}$)	Residual concentration ($\mu\text{g mL}^{-1}$)	Degradation rate (%)
Rotenone	5.00	1.0946 \pm 0.0027c	78.11
Rotenone+ZnO	5.00	1.7617 \pm 0.0015a	64.77
Rotenone+SiO ₂	5.00	1.5459 \pm 0.0013b	69.08
Rotenone+TiO ₂	5.00	0.8540 \pm 0.0028f	82.92
Rotenone+Fe ₂ O ₃	5.00	0.9638 \pm 0.0019e	80.72
Rotenone+CuO	5.00	1.0026 \pm 0.0020d	79.95

Note. All the experiments were repeated thrice as average \pm standard error of average.

Half-life values for rotenone combinated with ZnO nanoparticle under UV radiation were found to be higher than those of rotenone alone. The half-life value for rotenone combinated with ZnO nanoparticle was 29.98 h. The half-life values for rotenone combinated with ZnO nanoparticle increased at approximately 1.45 fold as compared with rotenone alone. The rate constant values and values of dissipation half-life of rotenone combinated with ZnO nanoparticle were listed in Table 5.

Table 5. Degradation kinetic of rotenone with ZnO nanoparticle on the glass

Treatments	Degradation kinetic equation	Related coefficient	Velocity constant	T _{1/2} (h)
Rotenone	$C_t = 5.1466e^{-0.0336t}$	0.9882	0.0243	20.63
Rotenone+ZnO	$C_t = 5.0876e^{-0.0232t}$	0.9849	0.0175	29.88

3.3 Degradation Kinetic of Rotenone with ZnO Nanoparticle on Cabbage Leaf

The mean recoveries and relative standard deviations at 3 fortification levels from 3 replicates of rotenone on cabbage leaf ranged from 82.24 % to 88.80% (Table 6).

Table 6. Recoveries and relative standard deviation of rotenone on cabbage leaf

Fortification levels(mg kg ⁻¹)	Average recoveries (%)	Standard deviation	Coefficient of variance (%)
5.0	88.80	0.1066	2.40
0.5	85.93	0.0146	3.39
0.1	82.24	0.0030	3.69

Note. The remaining amount was the average of three replicates.

The rate of degradation of rotenone alone or rotenone with ZnO nanoparticle as thin film on cabbage leaf under sunlight was investigated. The half life of degradation of rotenone on leaf surface was 48.47 h while half-life of rotenone with ZnO nanoparticle was 68.62 h (Table 7). ZnO nanoparticle is a novel nanomaterial which has good UV photo-protective properties on rotenone.

Table 7. Degradation kinetic of rotenone with ZnO nanoparticle on the cabbage leaf

Treatments	Degradation kinetic equation	Related coefficient	Velocity constant	T _{1/2} (h)
Rotenone	$C_t = 5.20270e^{-0.0143t}$	0.9847	0.0143	48.47
Rotenone+ZnO	$C_t = 5.3106e^{-0.0101t}$	0.9816	0.0101	68.62

3.4 Insecticidal Activities of Rotenone and ZnO Nanoparticle against *Pieris Rapae* 3rd Instar Larvae

The LC₅₀ value of the *Pieris rapae* 3rd instar larvae exposed to rotenone+ZnO nanoparticle was 49.52 µg mL⁻¹ at 48 h. The LC₅₀ value of the *Pieris rapae* 3rd instar larvae exposed to rotenone and ZnO nanoparticle was 52.46 µg mL⁻¹ at 48 h. The LC₅₀ value of the *Pieris rapae* 3rd instar larvae exposed to ZnO nanoparticle was 444.60 µg mL⁻¹ at 48 h (Table 8). The combination of rotenone and ZnO nanoparticle (4:1) increased the efficiency of mortality to the highest compared with the same concentration of sole rotenone or ZnO nanoparticle treatment alone and their co-toxicity coefficient was 128.63. ZnO nanoparticle has insecticidal synergism on rotenone against *Pieris rapae*.

Table 8. Insecticidal activities of rotenone and ZnO nanoparticle against *Pieris rapae* 3rd instar larvae (48 h)

Treatments	Toxicity regression equation	LC ₅₀ (µg mL ⁻¹)	95% Confidence interval	Correlation coefficient (r)
Rotenone	$y = 1.8678 + 1.8212x$	52.46	39.63~69.45	0.9812
ZnO	$y = -0.0029 + 1.8893x$	444.60	328.84~601.12	0.9855
Rotenone+ZnO (4:1)	$y = 1.2256 + 2.2094x$	49.52	38.22~64.16	0.9880

4. Conclusion

The data presented in this study suggested that the combination of ZnO nanoparticle could provide better photo-protection for rotenone molecule. ZnO nanoparticle possess good UV photo-protective properties and has insecticidal synergism on rotenone against *Pieris rapae*.

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