

Research Article



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## 시설 내 오이(*Cucumis sativus* L.) 재배 중 Penthiopyrad 및 Pyriofenone의 잔류특성과 생산단계 잔류허용기준 설정

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### Establishment of Pre-Harvest Residue Limits and Residue Characteristics of Penthiopyrad and Pyriofenone in Cucumber (*Cucumis sativus* L.) Under Greenhouse Condition

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#### Abstract

**BACKGROUND:** Greenhouse crops are one of agricultural products consumed largely in Korea. Cucumber is a typical example as main vegetables of greenhouse crops. Thus, pesticide residue analysis is an important requirement to guarantee pesticide safety of cucumber. This work was aim to investigate the residues of penthiopyrad and pyriofenone in cucumber after harvest.

**METHODS AND RESULTS:** Cucumber was subjected to treat with penthiopyrad and pyriofenone at a level of recommended dose 0, 1, 2, 3, 5, 7 and 10 days before harvest under greenhouse conditions. The samples were extracted with organic solvent by using a homogenizer and purified on solid phase cartridge column followed by LC-MS/MS analysis. The recovery levels of penthiopyrad and pyriofenone ranged from approximately 81 to 93% with the method limit of 0.005 mg/kg and coefficient of variation less than 10%. Penthiopyrad and pyriofenone were detected at a

level less than maximum residue limit in cucumber at 10 days before. The half-lives of penthiopyrad and pyriofenone were determined to 2.4 ~ 2.6 days.

**CONCLUSION:** Penthiopyrad and pyriofenone are suggested to use in cucumber 10 days before harvest to reach their levels less than maximum residue limit.

**Key words:** Biological half-life, Cucumber, Penthiopyrad, Pyriofenone, Pre-harvest residue limits (PHRLs)

#### 서론

2015 가 271,040 ton 가 85% (240,212 ton) (MAFRA, 2016).

가 가 가 가 가 (Lee *et al.*, 2005).

가 , 가 , , , 가 가 가 가 가 (Lee

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**Table 1. Safe use guidelines for penthiopyrad and pyriofenone in *Cucumis sativus* L**

Pesticides	Formulation	A.I <sup>a)</sup> (%)	Dilution	Safe use guidelines		MRL <sup>d)</sup> (mg/kg)
				PHI <sup>b)</sup> (day)	MNA <sup>c)</sup> (time)	
Penthiopyrad	EC <sup>e)</sup>	20	4,000	2	3	0.5
Pyriofenone	SC <sup>f)</sup>	10	2,000	2	3	0.7

<sup>a)</sup>A.I.: Active ingredient, <sup>b)</sup>PHI: Pre-harvest interval, <sup>c)</sup>MNA: Maximum number of application, <sup>d)</sup>MRL: Maximum residue limit, MFDS, <sup>e)</sup>EC: Emulsifiable concentrate, <sup>f)</sup>SC: Suspension concentrate

*et al.*, 2009; Nam *et al.*, 2010).

penthiopyrad pyriofenone 64  
가  
가 10 (Lee *et al.*,  
2005).  
(Kim and park,  
2002).  
penthiopyrad pyriofenone  
가  
(KCPA,  
2015).  
(Maximum Residue Limit, MRL) 0.5 mg/kg, 0.7  
mg/kg

(Pre-Harvest Residue Limit, PHRL)

가  
가 (Park. *et al.*,  
2011; Ha *et al.*, 2012; MAFRA, 2016).

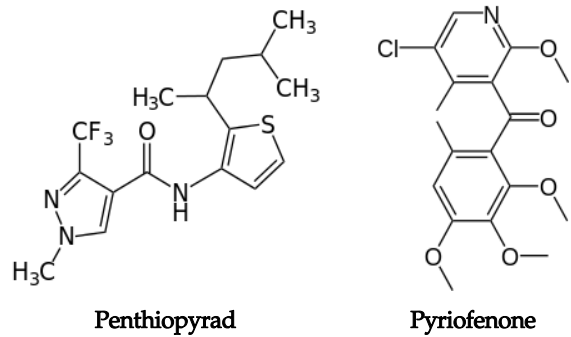
pyriofenone penthiopyrad

가

**재료 및 방법**

**시험농약 및 시험포장**

20% penthiopyrad  
( : , ( )) 10% pyriofenone  
( : , ( ))  
가 1 ( 1) 21  
( 2)  
50 m



**Fig. 1. Chemical structure of penthiopyrad and pyriofenone.**

3  
1 m  
2016 4 2  
4 15 14

(Table 1, KCPA, 2015).

**시약, 재료 및 기구**

penthiopyrad pyriofenone  
Dr. Ehrenstorfer GmbH (Germany)  
98.2%, 97.33%

Fig. 1 (Turner, 2015).

Junsei Chemical (Japan) acetonitrile  
dichloromethane , methanol water  
Merck (Germany) GR . Sodium  
sulfate anhydrous, sodium chloride DAE JUNG  
(Korea) , NH2 solid  
phase extraction (SPE) cartridge (1 g) Phenomenex  
(USA) . Homogenizer vacuum  
rotary evaporator Nissei EYELA  
HPLC, DIONEX  
UltiMate 3000 (Thermo Scientific, USA)  
TSQ Quantum Max (Thermo Science, USA)

**시료채취 및 잔류분석**

2 0 0, 1, 2, 3, 5, 7, 10  
2 kg

**Table 2. Analytical conditions for the determination of penthiopyrad and pyriofenone in *Cucumis sativus* L**

HPLC	DIONEX UltiMate 3000 (Thermo Scientific, USA)																					
Detector	TSQ Quantum Access Max (Thermo science, USA)																					
Column	Shiseido Capcell Core-C <sub>18</sub> (2.7 μm, 2.1 mm I.D.×150 mm)																					
Oven temp.	40°C																					
Flow rate	0.3 mL/min.																					
Injection vol.	1.0 uL																					
	0.1% formic acid+0.5 mM ammonium formate in Water:0.1% formic acid in Acetonitrile=A:B																					
	<table border="1"> <thead> <tr> <th>Time (min.)</th> <th>A (%)</th> <th>B (%)</th> </tr> </thead> <tbody> <tr> <td>0.0</td> <td>95</td> <td>5</td> </tr> <tr> <td>2.0</td> <td>95</td> <td>5</td> </tr> <tr> <td>3.0</td> <td>10</td> <td>90</td> </tr> <tr> <td>6.0</td> <td>10</td> <td>90</td> </tr> <tr> <td>6.5</td> <td>95</td> <td>5</td> </tr> <tr> <td>10.0</td> <td>95</td> <td>5</td> </tr> </tbody> </table>	Time (min.)	A (%)	B (%)	0.0	95	5	2.0	95	5	3.0	10	90	6.0	10	90	6.5	95	5	10.0	95	5
Time (min.)	A (%)	B (%)																				
0.0	95	5																				
2.0	95	5																				
3.0	10	90																				
6.0	10	90																				
6.5	95	5																				
10.0	95	5																				
Ion source	ESI +																					
Spray voltage	3,500 V																					
temperature	Vaporizer: 350°C, Capillary: 320°C																					
gas pressure (N <sub>2</sub> )	Ion sweep: 1.0 unit, Sheath: 35.0 unit, Aux: 10.0 unit																					

**Table 3. Selected Reaction Monitoring (SRM) condition of penthiopyrad and pyriofenone**

Compound	Precursor ion	Product ion	CE	Q1 PW	Q3 PW	Retention time
Penthiopyrad	360.158	177.068	30	0.7	0.7	7.77 min.
		256.061	19	0.7	0.7	
		276.067	13	0.7	0.7	
Pyriofenone	366.100	166.110	35	0.7	0.7	8.17 min.
		184.060	23	0.7	0.7	
		209.120	23	0.7	0.7	

가 , cartridge . Dichloromethane 5 mL  
 -20°C pre-washing cartridge  
 Penthiopyrad pyriofenone loading , (dichloromethane:methanol=95:5, v/v)  
 5 mL , penthiopyrad pyriofenone  
 acetonitrile 20 g . acetonitrile 2 mL  
 acetonitrile 100 mL 가 , homogenizer 3 , (0.2 μm membrane filter) ,  
 (10,000 rpm) . , acetonitrile . LC-MS/MS chromatography peak  
 100 mL 50 mL (Table 2, 3).  
 가 separatory funnel dichloromethane 50,  
 50 mL 2 . 분석법 검증  
 anhydrous sodium sulfate , .  
 dichloromethane 5 mL . Penthiopyrad (Method Limit of Quantification,  
 pyriofenone SPE , NH<sub>2</sub> 1 g MLOQ) 10 (0.05 mg/kg), 50 (0.25 mg/kg)

**Table 4. Linear equation of calibration curve for the quantification of the pesticide residues in *Cucumis sativus* L.**

Pesticide	Linear equation	R <sup>2</sup>
Penthiopyrad	y=23,312,661.04x+51,749,80821	0.9987
Pyriofenone	y=43,761,803.01x+237,167.5128	0.9997

**Table 5. Recovery rate and MLOQ for penthiopyrad and pyriofenone in *Cucumis sativus* L**

Pesticide	Fortification level (mg/kg)	Recovery (%)				MLOQ <sup>a)</sup> (mg/kg)
		1	2	3	AVG±C.V. <sup>b)</sup>	
Penthiopyrad	0.05	92.8	94.9	95.4	94.3±1.5	0.005
	0.25	94.9	93.1	93.2	93.7±1.1	
Pyriofenone	0.05	87.3	89.8	83.4	86.8±3.8	0.005
	0.25	81.2	82.7	81.0	81.7±1.1	

<sup>a)</sup>Method of Limit of Quantification, <sup>b)</sup>Coefficient of variation

pyriofenone 20 g penthiopyrad  
 1 mg/kg, 5 mg/kg 1  
 mL 가 3 , 30  
 시설 내 기상조건 및 중량  
 1, 2  
 19.8~26.9°C, 17.6~24.8°C  
 63.8%~88.1%, 46.5%~88.6%  
 1, 2 179.1~234.2  
 g, 165.0~209.7 g

**결과 및 고찰**

**표준검량선 작성**

pyriofenone (98.2%)  
 1,000 mg/kg stock solution  
 (Minimum Detectable Amount, MDA)  
 mg/kg 2.0 mg/kg  
 matrix  
 matched (R<sup>2</sup>) 0.99  
 (Table 4).

**분석정량한계 및 회수율**

pyriofenone (Lee *et al.*, 2009).  
 penthiopyrad 0.005 mg/kg  
 0.5 mg/kg, 0.7 mg/kg  
 (10 MLOQ, 50 MLOQ) 3  
 70~120%  
 x100) 10%  
 pyriofenone 7.77 min., 8.17 min.

(Lee *et al.*, 2009).

**잔류특성과 생물학적 반감기**

pyriofenone penthiopyrad  
 Penthiopyrad 1 2  
 0.122 mg/kg, 0.117 mg/kg  
 pyriofenone 1 0.091 mg/kg, 2  
 0.107 mg/kg

(Kanazawa, 1992). Moon (2016)

(Kim *et al.*, 2003; Lee *et al.*, 2004).  
 가 가 가 가 가 가  
 가 (Moon *et al.*, 2016).



(Park *et al.*, 2005).  
 penthiopyrad pyriofenone  
 $y=0.1433e^{-0.266x}$  ( $R^2=0.9461$ ),  $y=0.1535e^{-0.274x}$  ( $R^2=0.9379$ )  
 $y=0.0999e^{-0.277x}$  ( $R^2=0.9543$ ),  $y=0.1245e^{-0.287x}$  ( $R^2=0.9184$ )  
 PHRL  
 10  
 3.44 mg/kg, 4.63 mg/kg  
 penthiopyrad  
 pyriofenone MRL 0.5 mg/kg, 0.7 mg/kg  
 (Fig. 3).

**요약**

penthiopyrad pyriofenone  
 가  
 Penthiopyrad  
 1 1 2  
 2 0 0, 1, 2, 3, 5,  
 7, 10  
 acetonitrile, dichloromethane, SPE NH<sub>2</sub> cartridge  
 LC-MS/MS  
 0.005 mg/kg 10, 50  
 penthiopyrad  
 pyriofenone 92.8~95.4%, 81.0~89.8%  
 10%  
 1, 2  
 penthiopyrad 2.6 2.5, pyriofenone  
 2.5 2.4 Penthiopyrad  
 pyriofenone 10  
 3.44 mg/kg, 4.63 mg/kg  
 MRL (Penthiopyrad: 0.5 mg/kg,  
 Pyriofenone: 0.7 mg/kg)  
 penthiopyrad pyriofenone  
 가

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