

Research Article



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## 수박 중 Pyridalyl 및 Fluopicolide의 잔류 특성 및 생물학적 반감기 산출

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### Residue Patterns and Biological Half-lives of Pyridalyl and Fluopicolide in Watermelon

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Received: 10 February 2017 / Revised: 1 March 2017 / Accepted: 24 March 2017

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#### Abstract

**BACKGROUND:** The present study was carried out to identify the residue patterns of insecticide pyridalyl and fungicide fluopicolide in watermelon and calculate the biological half-lives for establishing the pre-harvest residue limits (PHRLs).

**METHODS AND RESULTS:** The watermelon samples for residue analysis were harvested 7 times during 0~10 days (Field 1) and 0~20 days (Field 2) after treatment of pesticides on watermelon in two different fields at the recommended dose, respectively. The residue analysis was conducted with HPLC/UVD. The method limit of quantitation (MLOQ) were set at 0.05 and 0.02 mg/kg, respectively, and overall mean recoveries were 81.2~90.5% for pyridalyl and fluopicolide. The residues in sample were stable for 43~47 days. The initial residue amount in field 1 and 2 were 0.12~0.16 mg/kg for pyridalyl and 0.23~0.24 mg/kg for fluopicolide, which were below maximum residue limit (MRL). The biological half-lives in field 1 and 2 were 26.9 and 17.9 days for pyridalyl and 16.6 and 94.2

days for fluopicolide, respectively.

**CONCLUSION:** The PHRL for watermelon were estimated as 0.21 and 1.03 mg/kg for pyridalyl and fopicolide at 10 days before harvesting. The residue patterns of pyridalyl and fluopicolide were characterized by a very slow decrease of residue levels in watermelon.

**Key words:** Biological half-life, Fluopicolide, Pyridalyl, Residue pattern, Watermelon

#### 서론

가 (Park *et al.*, 2009).

가  
(Maximum Residue Limit, MRL)  
(RDA, 2016; MFDS, 2016).

(Pre-Harvest Residue Limit, PHRL)  
(MFDS, 2016).

(Biological half-life)

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Table 1. Chemical structures and physico-chemical properties of pyridalyl and fluopicolide

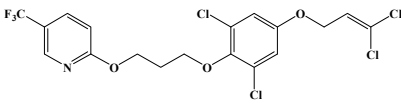
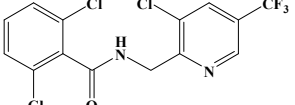
Pesticides	Pyridalyl	Fluopicolide
Chemical structure		
Mol. wt.	491.1	383.6
V.p. (mPa)	$6.24 \times 10^{-5}$ mPa (20°C)	$3.03 \times 10^{-4}$ mPa (20°C)
logP	8.1	3.26 (pH 7.8, 22°C)
Solubility in water	0.15 ppb (20°C)	2.8 mg/L (pH 7, 20°C)

Table 2. Safe use guidelines for pyridalyl and fluopicolide on watermelon

Pesticides	Formulation	a.i. <sup>a)</sup> (%)	Safe use guidelines			MRL <sup>d)</sup> (mg/kg)
			PHI <sup>b)</sup> (days)	MAF <sup>c)</sup> (time)	Dilution	
Pyridalyl	EW <sup>e)</sup>	10	7	3	1,000	0.2
<b>Fluopicolide</b> +propamocarb hydrochloride	SC <sup>f)</sup>	55 (5+50)	14	3	1,000	1.0

<sup>a)</sup>Active ingredient, <sup>b)</sup>Pre-harvest interval, <sup>c)</sup>Maximum application frequency, <sup>d)</sup>Maximum residue limit, <sup>e)</sup>Emulsion in water, <sup>f)</sup>Suspension concentrate

10 (Hwang *et al.*, 2012; Kim *et al.*, 2014). (Augsburg, Germany)

(*Citrullus vulgaris* Schrad.) Table 1

가 acetone, *n*-hexane HPLC (J.T. Baker, Center Valley, USA), sodium sulfate

가 (Lee, 1983; Park and Kang, 2006; MAFRA, 2002). citrullin arginine anhydrouse sodium chloride Jusei chemical (Tokyo, Japan) Florisil cartridge (1 g, 6 mL) Waters (Milford, USA), Florisil (0.15~0.25 mm) Merck (Darmstadt, Germany)

가 (Lee, 1983; Lee, 1994). 가 EYELA (Tokyo, Japan) N-1000 LapTecho (Seoul, Korea) LT-24

(Hong *et al.*, 2008). 가 시험작물 및 포장시험

(Hwang *et al.*, 2012; Lee *et al.*, 2013; Kim *et al.*, 2014), ( 1 ) ( 2 ) ( ) ( )

pyridalyl 1 ( ) 2 ( )

fluopicolide )

재료 및 방법

1 9.6~12.0 m×2.7 m, 2 13.5~14.4 m×2.5 m 3

시험농약 및 시약 (MSB20Li, Maruyama, Tokyo, Japan) 2.1 kgf/cm<sup>2</sup> 1 Table

) fluopicolide+propamocarb hydrochloride 55(5+50)% ( ) 2 (0 )

(99.0%) fluopicolide (98.5%) Dr. Ehrenstorfer , 1, 2, 3, 5, 7, 10 5

Table 3. HPLC conditions for residue analysis of pesticides in watermelon

Instrument	Agilent 1100 series (USA)
Column	Pyridalyl - Phenomenex Gemini-NX (150×4.6 mm, 3 μm, Torrance, USA) Fluopicolide - Phenomenex Luna C18(250×4.6 mm, 5 μm, Torrance, USA)
Column Temp.	25°C
Mobile phase	Pyridalyl-acetonitrile:water=85:15 (v/v) Fluopicolide-acetonitrile:water=65:35 (v/v)
Flow rate	Pyridalyl-0.8 mL/min Fluopicolide-1.0 mL/min
Detection	Pyridalyl 222 nm, Fluopicolide 220 nm
Injection volume	20 μL

2 14 20 가  
Fluopicolide 25 g  
( ) 4 methanol 100 mL 가 15000 rpm 2  
(4°C ) methanol 40 mL  
(RDA, 2016). 1000 mL  
300 mL, 50 mL 가  
-20°C dichloromethane/*n*-hexane (20/80, v/v) 100 mL 1  
sodium sulfate anhydrous  
*n*-hexane 10 mL  
표준용액 조제 및 표준검량선 작성  
pyridalyl (99.0%) 10.101 mg fluopicolide 25 g  
(98.5%) 10.152 mg acetonitrile 100 mL sodium sulfate anhydrous 2 g  
100 mg/kg stock solution mL 가 3 mL/min Ethyl  
Stock solution acetonitrile mL acetate/*n*-hexane (7/93, v/v) 100 mL ethyl  
pyridalyl 0.25, 0.5, 1.0, 2.0, 5.0 mg/kg acetate/*n*-hexane (7/93, v/v) 100 mL ,  
working solution fluopicolide 0.05, 0.1, 0.5, 1, 2, acetonitrile 10 mL , HPLC-  
5 mg/kg working solution 20 μL DAD Pyridalyl  
HPLC-DAD chromatogram peak fluopicolide Table 3  
Stock solution  
4°C

#### 분석정량한계, 회수율 및 저장안정성 시험

#### 수박 중 잔류농약 분석

Pyridalyl 20 g  
acetone 100 mL 가 200 rpm 30 (Method limit of quantitation, MLOQ)  
, acetone 50 mL (Lee *et al.*, 2009).  
, 500 mL  
90 mL 10 mL 가 pyridalyl 0.2 mg/kg (4 MLOQ MRL) 0.5  
*n*-hexane 70 mL 2 sodium mg/kg (10 MLOQ) , fluopicolide  
sulfate anhydrous 0.2 mg/kg (10 MLOQ) 1.0 mg/kg (50 MLOQ  
*n*-hexane 4 mL . SPE-florisil (1 g, MRL)  
6 mL) *n*-hexane 5 mL 4 mL  
*n*-hexane 6 mL acetone/  
*n*-hexane (5/95, v/v) 14 mL , pyridalyl 0.5 mg/kg (10 MLOQ), fluopicolide 1.0 mg/  
acetonitrile 4 mL HPLC-DAD kg (50 MLOQ MRL)  
3

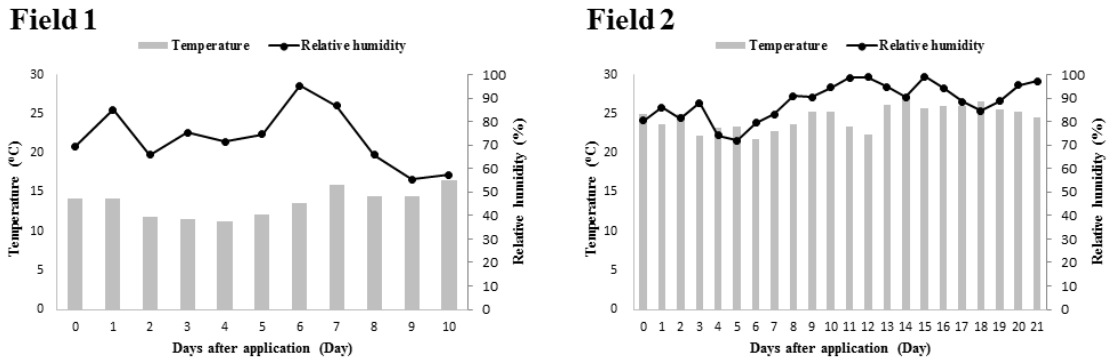


Fig. 1. Temperature and relative humidity during experimental period on field 1 and 2.

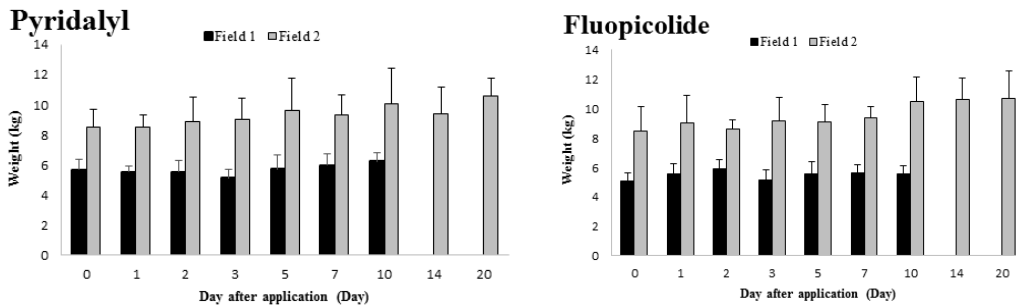


Fig. 2. Weight change of watermelon during experimental period in field 1 and 2.

시험농약의 생물학적 반감기 및 생산단계 잔류허용기준 산출

pyridalyl      fluopicolide

$$C_t = C_0 \times e^{-kt} \quad (C_t, C_0, k, t)$$

(Chang *et al.*, 2011).

$$PHRLs = MRL \times e^{kt}$$

(MFDS, 2016).

**결과 및 고찰**

기상조건 및 수박의 증체율

1      2      11~  
17°C, 21.8~27.4°C      66~95%, 71.8~  
99.1% (Fig. 1).      1      2  
10°C,      15%가

가  
1      5~6 kg  
2      8~11 kg  
가

분석정량한계, 회수율 및 저장안정성

pyridalyl      fluopicolide  
,      (R<sup>2</sup>)가      0.999

HPLC-DAD      pyridalyl      fluopicolide  
10.5 min, 8.0 min

Fig. 3

pyridalyl      fluopicolide  
5.0 ng, 1.0 ng      (MLOQ)  
0.05 mg/kg, 0.02 mg/kg  
, pyridalyl 85.0~97.0%,  
fluopicolide 76.6~98.5%  
70~120% (Table 4).  
pyridalyl 85.2~87.2%, fluopicolide  
70.0~80.0%      43, 47  
(Table 5).

수박 중 시험농약의 잔류량 변화

1      0      pyridalyl  
1      0.16 mg/kg,      2      0.12 mg/kg  
, fluopicolide      1      0.23 mg/kg,      2  
0.23 mg/kg

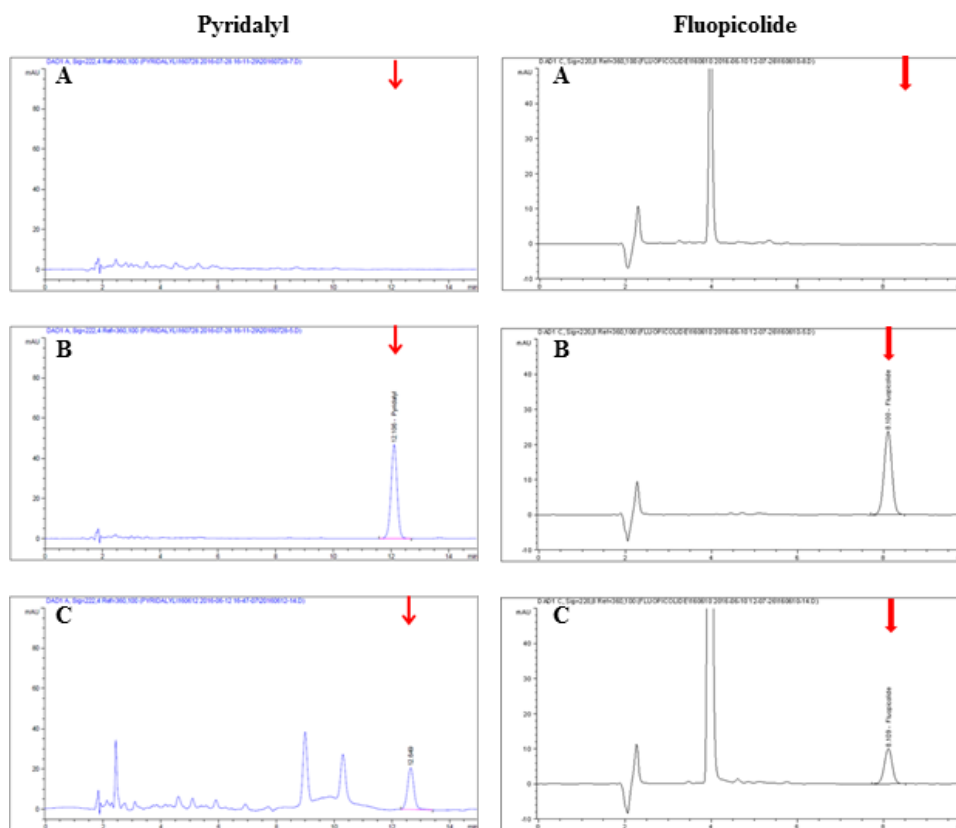


Fig. 3. HPLC chromatograms of pyridalyl and fluopicolide. (A) control, (B) standard solution at 5 ppm, (C) fortified at 0.5 and 1.0 mg/kg.

Table 4. Recovery for pyridalyl and fluopicolide in watermelon

Pesticides	Fortification (mg/kg)	Recovery <sup>a)</sup> (%)	MLOQ <sup>b)</sup> (mg/kg)
Pyridalyl	0.2	90.5±6.7	0.05
	0.5	90.0±5.2	
Fluopicolide	0.2	88.1±10.3	0.02
	1.0	81.2±4.9	

<sup>a)</sup>Mean±C.V. (coefficient of variation), n=3, <sup>b)</sup>Method limit of quantitation

Table 5. Storage stability of pyridalyl and fluopicolide in watermelon

Pesticides	Fortification (mg/kg)	Storage period (days)	Recovery <sup>a)</sup> (%)
Pyridalyl	0.5	43	86.5±1.3
Fluopicolide	1.0	47	73.8±7.3

<sup>a)</sup>Mean±C.V. (coefficient of variation), n=3

MRL (pyridalyl 0.2 mg/kg, fluopicolide 1.0 mg/kg; (Lee *et al.*, 2009).  
 Table 2) , 가 1 10 pyridalyl 27%,  
 1 5 fluopicolide 39% 0.05, 0.09 mg/  
 kg  
 (Fig. 4). , 2  
 20  
 (Wang and Liu, 2007), 20  
 가 pyridalyl 0.07 mg/kg, fluopicolide 0.04 mg/kg



가	pyridalyl	fluopicolide	
MRL	가		
MRL			
가			
<b>요 약</b>			
	pyridalyl	fluopicolide	
			1
10	2	20	
	HPLC/UVD		
		0.05 mg/kg, 0.02 mg/kg	
		81.2~90.5%	
43~47			pyridalyl
0.12~0.16 mg/kg,		0.23~0.24 mg/kg	
	pyridalyl		1 26.9
	2	17.9	fluopicolide
	1	16.6	2 94.2
pyridalyl	fluopicolide	10	
	0.21 mg/kg,	1.03 mg/kg	

### Acknowledgment

This research was supported by a grant from Ministry of Food and Drug Safety in 2016.

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