

Research Article



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노지재배 복숭아 중 Bistrifluron과 Cyenopyrafen의 생산단계 잔류특성에 따른 감소추이

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¹ , ²

Residue Dissipation Behavior of Bistrifluron and Cyenopyrafen in Peach for the Cultivation Periods under Field Conditions

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Abstract

BACKGROUND: This study was performed to calculate the biological half-lives and regression coefficient of bistrifluron and cyenopyrafen dissipation in peach and to estimate the Pre-Harvest Residue Limits (PHRLs).

METHODS AND RESULTS: The bistrifluron and cyenopyrafen were prepared on the basis of good agricultural practice for peach and treated with a single application. Peaches were harvested at 0, 1, 3, 5, 7, 10 and 14 days after application, prepared for analysis, and analyzed by HPLC-DAD. The limits of quantitation (LOQ) of bistrifluron and cyenopyrafen were 0.02 mg/kg and 0.04 mg/kg, respectively. The recoveries of bistrifluron and cyenopyrafen were 99.5~108.7% and 88.4~98.9% at two different concentration levels. The biological half-lives of field I (Sejong) and field II (Pyeongtaek) were 6.1 and 7.0 days for bistrifluron, and 6.3 and 7.0 days for cyenopyrafen, respectively. The 95% confidence intervals of dissipation rate constants of bistrifluron in peach were 0.0805~0.1457 and 0.0577~0.1417 for field I and field II, respectively, and those of

cyenopyrafen were 0.0911~0.1278 and 0.0576~0.1417, respectively.

CONCLUSION: Residue dissipation of bistrifluron and cyenopyrafen in peach were similar to that of correction to sample weight difference during the harvest periods. This study suggests that residue dissipation rate would be helpful to set the PHRLs that protect public health.

Key words: Bistrifluron, Cyenopyrafen, Dissipation, Pre-harvest residue limit, Peach

서론

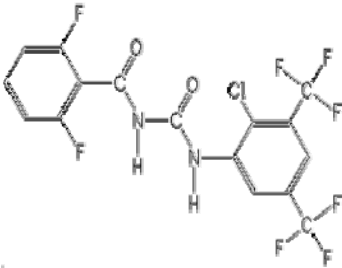
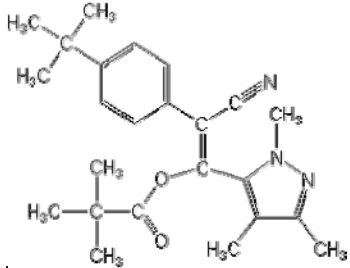
1 , (Kim, 2007; Woo *et al.*, 2010).

35%가 , 가 (Kim and Kim, 2001; Kim and Kim, 2011).

2016 166,473 ha
2.2% 가 , 1,165 ha
237,711 7.5% 13.0% 가

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Table 1. Chemical structures and physico-chemical properties of bistrifluron and cyenopyrafen (Turner J. A., 2015)

Pesticide	Bistrifluron	Cyenopyrafen
Chemical structure		
Vapor pressure (mPa)	0.0027 (25°C)	5.2E-4 (25°C)
log Kow	5.74	5.6
Water solubility (mg/l, 20-25°C)	<0.03	0.3
Organic solubility (g/l, 20-25°C)	Soluble in dichloromethane (64.0), hexane (3.5), methanol (33.0)	-

(KOSTAT, 2016a; 2016b).

가 , 가 5~10 가 (Jeon *et al.*, 2000; Woo and Park, 2001; Kim *et al.*, 2002; Ha *et al.*, 2012).

bistrifluron (97.6%, Sigma-Aldrich, USA) cyenopyrafen (97.3%, Sigma-Aldrich, USA) acetone, acetonitrile, dichloromethane, *n*-hexane ethyl acetate Merck(Germany), Sodium sulfate sodium chloride Junsei chemical(guaranteed reagent grade, Japan), Solide phase extraction cartridge(florisil, 1 g, 6 cc) Agilent Technologies(USA)

포장시험

가 42 km 가 2 (I, :) (II, :) 1 , 3 1 (KCPA, 2014) (YAMATO, DY-435Y) I(2015 07 28) II(2015 07 (Table 2). 0, 1, 3, 5, 7, 10 14 1 kg (5 cyenopyrafen) polyethylene bag , ice box 24

재료 및 방법

시험약제 및 시약 bistrifluron 10% (, 주) , cyenopyrafen 25% (, 주)

시료 조제

가 deepfreezer (-70°C) 48 , homogenizer 가 (-15°C)

Table 2. Good agricultural practice and maximum residue limit of bistrifluron and cyenopyrafen on peach in Korea

Pesticide	Formulation		Application			PHI ^{b)} (days)	MRL ^{c)} (mg/kg)
	Type	%AI ^{a)}	Spray concentration (kg ai/hl)	Max. No.	Interval (days)		
Bistrifluron +Flubendiamide	EC ^{d)}	10+13	0.0025	3	10	14	1.0
Cyenopyrafen	EC	25	0.0125	3	-	14	0.5

a) Active ingredient

b) Pre-harvest interval

c) Maximum residue limit

d) Emulsifiable concentrate

Table 3. Instrumental conditions for the analysis of bistrifluron and cyenopyrafen in peach

Pesticide	Bistrifluron	Cyenopyrafen			
Instrument	Agilnet 1260 Infinity Series HPLC				
Column	Phenomenex Luna 5 μ C18 (250 \times 4.60 mm)				
Detector	Diode Array Detector (DAD)				
Flow rate	1.0 mL/min				
Mobile phase	Acetonitrile/Water (75/25, v/v), Isocratic	Acetonitrile/Water (80/20, v/v), Gradient			
		Time(min)	Acetonitrile	Water	Flow
		13	80	20	1.0
		15	100	0	2.0
		39	100	0	2.0
41	80	20	1.0		
Wavelength	250 nm	294 nm			
Injection volume	30 μ L	40 μ L			

분석법 정량한계

(Limit of Quantification, LOQ)

, Signal to noise ratio
(S/N)가 10 ,(Park *et al.*, 2017). Bistrifluron cyenopyrafen
HPLC Table 3 .**직선성**Bistrifluron (97.6%) 10.25 mg acetone 10
mL 1,000 mg/L ,acetonitrile 0.05, 0.1, 0.2, 0.5, 1.0, 2.0
5.0 mg/L ,Cyenopyrafen (97.3%) 5.14 g acetone 10
mL 500 mg/L ,acetonitrile 0.1, 0.5, 1.0, 2.0 5.0 mg/L
bistrifluroncyenopyrafen chromatogram peak
area(r²) .**회수율 시험 및 잔류분석**

Bistrifluron 10 g

(0.02 mg/kg) 10 (0.2 mg/kg) ,

cyenopyrafen (Maximum

Residue Limit, MRL) (0.5 mg/kg)

(2.0 mg/kg)

3 . 10 g acetone 100 mL

가 250 rpm 20

. 1,000 mL

300 mL 100 mL 가 bistrifluron

dichloromethane 100 mL 50 mL 2 ,

cyenopyrafen dichloromethane 100 mL 1

. sodium sulfate

, 40 $^{\circ}$ C rotary vacuum evaporator (V-700,
BUCHI, Switzerland) .*n*-hexane 4 mL . *n*-Hexane 4 mL

florisil SPE cartridge (1 g, 6 cc) 2

mL , bistrifluron *n*-hexane/ethyl acetate (85/
15, v/v) 10 mL , cyenopyrafen *n*-hexane 10mL *n*-hexane/ethyl acetate (95/5, v/v) 2 mL

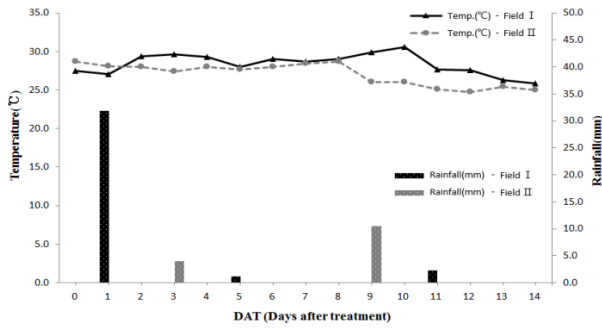


Fig. 1. Climatic conditions in residue field trials for peach.

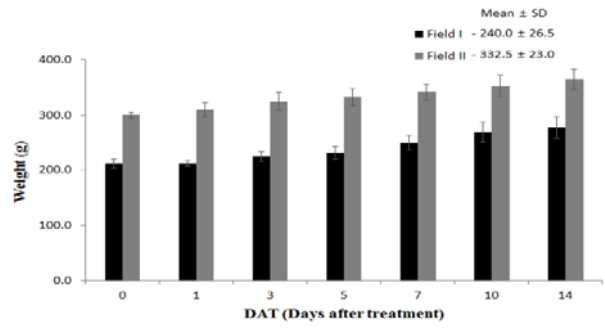


Fig. 2. Changes of peach weight at sample harvest intervals.

n-hexane/ethyl acetate (95/5, v/v) 5 mL *n*-hexane/ethyl acetate (90/10, v/v) 8 mL N₂ gas acetonitrile 2 mL HPLC-DAD (Agilnet 1260 Infinity Series, Agilent Technologies, USA) (Table 3). (-20°C)

3 10 g bistrifluron cyenopyrafen 1.0 mg/kg, bistrifluron 83, cyenopyrafen

25

Bistrifluron cyenopyrafen

복숭아 시료의 개체 중량 차이에 의한 희석 영향 산출

cyenopyrafen (Lee *et al.*, 2013).

$$\text{(mg/kg)} = \frac{\text{(kg)}}{\text{(kg)} \times \text{(mg/kg)}} \times \text{(kg)}$$

생물학적 반감기 산출 및 생산단계 잔류허용기준(안) bistrifluron cyenopyrafen

, *F* *t*

, 95% (MFDS, 2014).

결과 및 고찰

포장시험

28.4°C 27.0°C, 1.0 mm I II
 3 2 (Fig. 1, KMA, 2015). I
 1

(RDA, 2011).

26.5 g 332.5±23.0 g I II 240.0±
 가 , I II
 30.6% 21.6% (Fig. 2).

Table 4. Limit of quantification and recoveries of bistrifluron and cyenopyrafen in peach

Pesticide	Fortification level (mg/kg)	Recovery (%)				CV ^{b)}	LOQ ^{c)} (mg/kg)
		Replicate			Mean±SD ^{a)}		
		1	2	3			
Bistrifluron	0.02	99.5	108.7	101.8	103.3±4.8	4.7	0.02
	0.2	100.3	101.2	102.1	101.2±0.9	0.9	
Cyenopyrafen	0.5	90.2	91.6	88.4	90.1±1.6	1.8	0.04
	2.0	95.4	98.9	97.8	97.7±1.2	1.3	

a) Standard deviation
 b) Coefficient of variation
 c) Limit of quantification

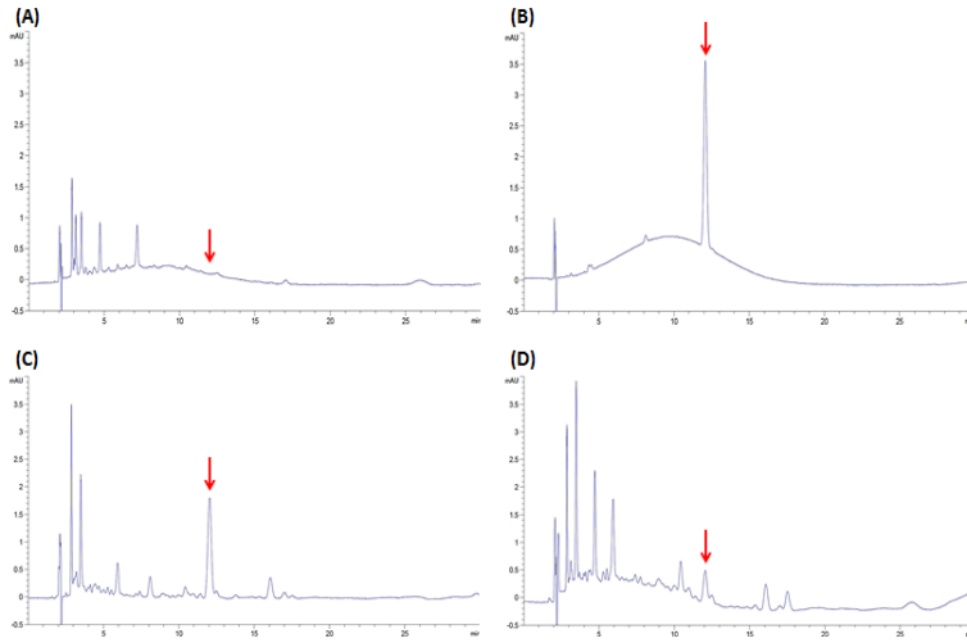


Fig. 3. Representative chromatograms of bistrifluron by HPLC-DAD analysis (A; blank peach, B; standard 1.0 mg/kg, C; recovery 2.0 mg/kg, D; sample 0 day (Field II)).

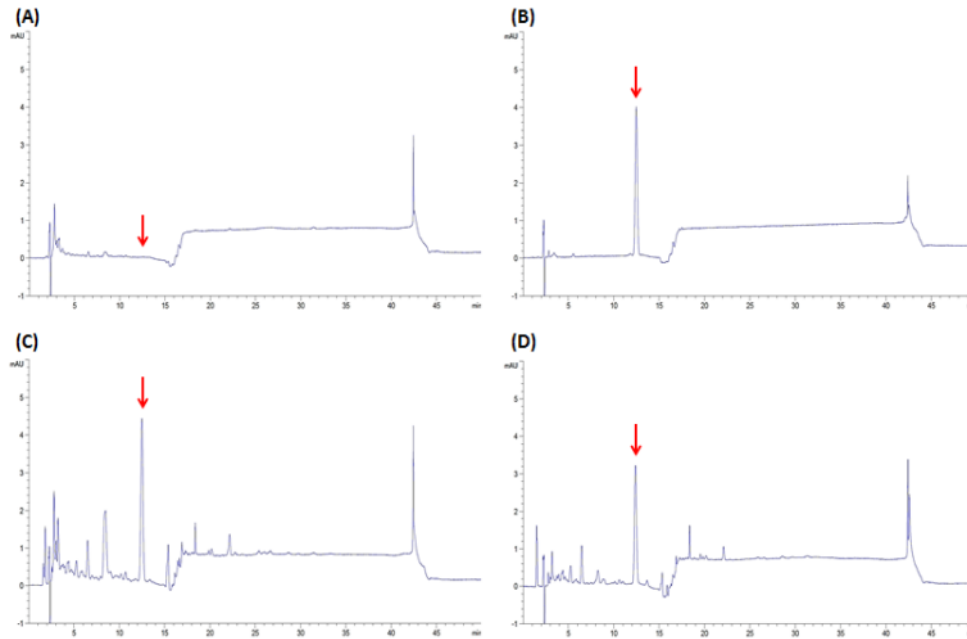


Fig. 4. Representative chromatograms of cyenopyrafen by HPLC-DAD analysis (A; blank peach, B; standard 1.0 mg/kg, C; recovery 0.5 mg/kg, D; sample 3 day (Field II)).

분석법 검증

Bistrifluron cyenopyrafen
 0.02 mg/kg 0.04 mg/kg
 7 (0.05 ~ 5.0 mg/L) 5
 (0.1 ~ 5.0 mg/L)
 $y=1.44338x-0.60804$ ($r^2=0.999$) $y=1.64724x-1.00638$ ($r^2=$

0.999) . Bistrifluron cyenopyrafen
 99.5~108.7% 88.4~98.9%, (%
 coefficient of variation) 0.9~4.7% 1.3~1.8% .
 70~110% 20% (Table 4,
 MFDS, 2014). Bistrifluron cyenopyrafen HPLC-

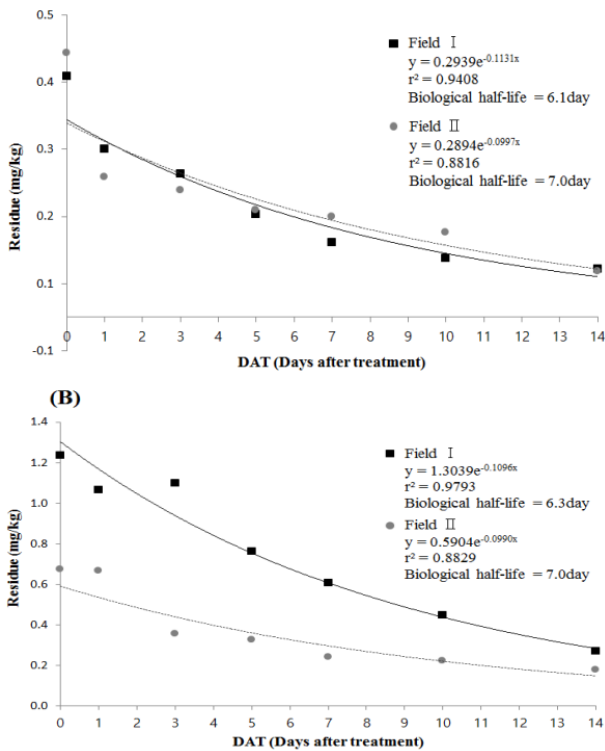


Fig. 5. Dissipation curves and half-lives of bistrifluron (A) and cyenopyrafen (B) in peach.

DAD peak (Fig. 3, 4).

일자별 잔류량 변화

	Bistrifluron	cyenopyrafen	
Fig. 5			0
bistrifluron	I	II	0.36 mg/kg
0.39 mg/kg		cyenopyrafen	1.24 mg/kg
0.67 mg/kg		Cyenopyrafen	I II 0

1.24 g	0.77 g	2	가
Bistrifluron		I	II
0		1.0 mg/kg	
cyenopyrafen	I	10	II
3		0.5 mg/kg	
(MFDS, 2017a).			

bistrifluron	I	0.097~0.36 mg/kg	
II	0.079~0.39 mg/kg	cyenopyrafen	
I	0.34~1.24 mg/kg	II	0.22~0.67 mg/kg
mg/kg		bistrifluron	cyenopyrafen
I	II		

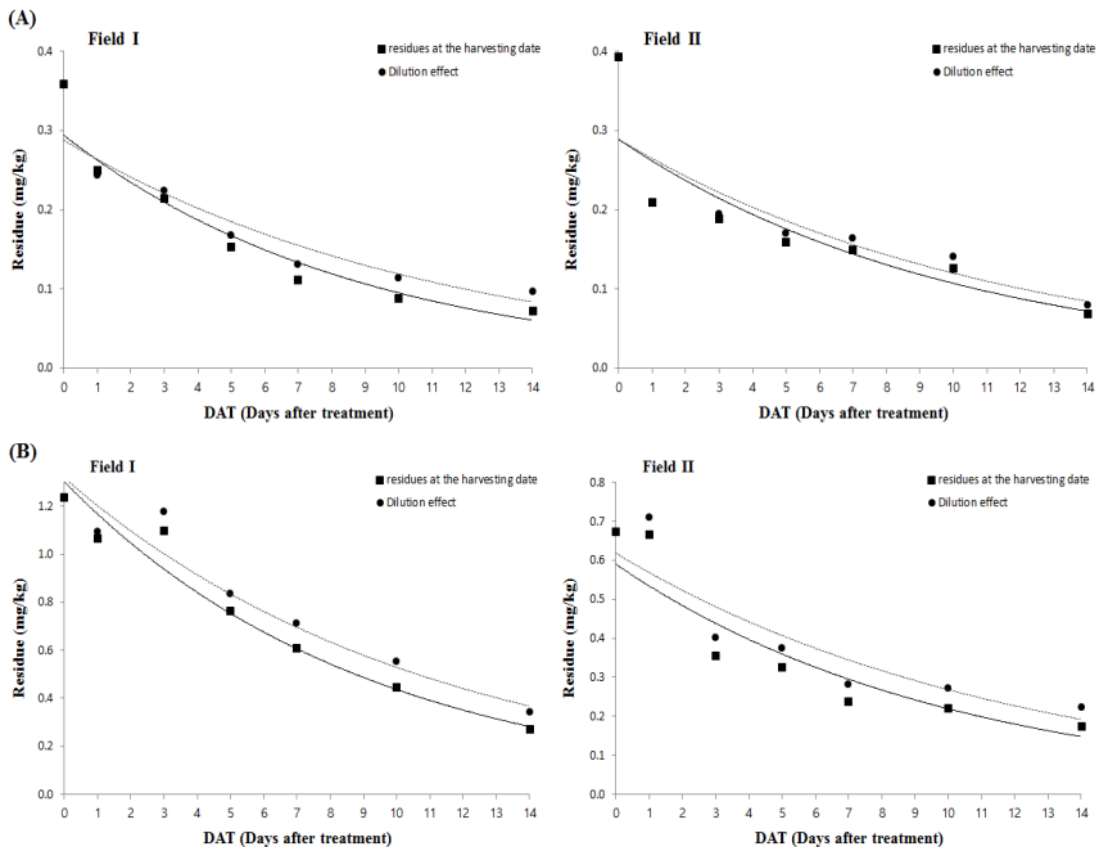


Fig. 6. Dissipation curves of bistrifluron (A) and cyenopyrafen (B) for dilution effects by increasing peach weights.

Table 5. Regression analysis for the dissipation of bistrifluron and cyenopyrafen on peach

Pesticide	Bistrifluron		Cyenopyrafen	
	Field I	Field II	Field I	Field II
Dissipation regression equation ^{a)}	$y=0.2939e^{-0.1131x}$ ($r^2=0.9408$)	$y=0.2894e^{-0.0997x}$ ($r^2=0.8816$)	$y=1.3039e^{-0.1095x}$ ($r^2=0.9793$)	$y=0.5904e^{-0.0990x}$ ($r^2=0.8829$)
Dissipation rate constant ^{b)}	0.0805 ~ 0.1457	0.0577 ~ 0.1417	0.0911 ~ 0.1278	0.0576 ~ 0.1417
Lower limit of dissipation rate constant	0.0805	0.0577	0.0911	0.0576

^{a)} Significant at $p < 0.05$ by the F -test

^{b)} Significant at $p < 0.05$ by the t -test

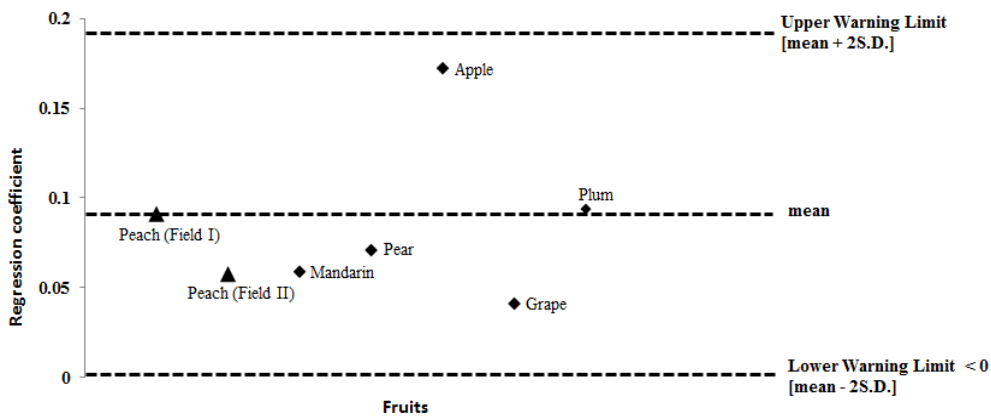


Fig. 7. Dissipation rate constants evaluation of cyenopyrafen on peach with fruits proposed by MFDS.

가 (Fig. 6). 95% bistrifluron I II 0.0805
 ~0.1457 0.0577~0.1417 , cyenopyrafen
 , 10 16 0.0911~0.1278 0.0576~0.1417 . 95%
 가 ,
 가 (Lee *et al.*, 2008). 0.0805 0.0577 , cyenopyrafen II
 15 29.6% 가 0.0576 (Table 5). 0.0911
 가
 가
 (Kim *et al.*, 2009).
 I II 0 14 가 bistrifluron
 21.6~30.6% 가 0.0400 0.0316,
 cyenopyrafen , , , , 0.0589,
 0.0709, 0.1723, 0.0411 0.0934 (MFDS, 2017b).
 Cyenopyrafen 5
 생물학적 반감기 및 감소상수 ±2SD(standard deviation) 0.0362~0.187
 bistrifluron I II (Fig. 7, Moser H. and J. Römbke, 2009; Lee *et al.*,
 6.1 7.0 cyenopyrafen 6.3 2015; Park *et al.*, 2017). Bistrifluron
 7.0 (Fig. 5). 가 2
 bistrifluron cyenopyrafen 1
 F- t-

Note

The authors declare no conflict of interest.

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