

Research Article



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생산단계 잔류허용기준 설정을 위한 딸기 중 bistrifluron과 chlorantraniliprole의 잔류 특성 연구

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Residual Characteristics of Bistrifluron and Chlorantraniliprole in Strawberry (*Fragaria ananassa* Duch.) for Establishing Pre-Harvest Residue Limit

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Abstract

BACKGROUND: Pesticide residue analysis is essentially required for safety evaluation of agricultural products. Bistrifluron and chlorantraniliprole have been currently considered as potentials to deeply evaluate their residues in agricultural products because they are frequently found in strawberry. This work was performed to investigate the residual patterns of bistrifluron and chlorantraniliprole in strawberry after harvest.

METHODS AND RESULTS: Strawberry was treated with bistrifluron and chlorantraniliprole 0, 1, 2, 3, 5, 7 and 10 days before harvest under greenhouse conditions. The strawberry samples were subjected to solvent and solid phase extractions followed by LC-MS/MS analysis. There coverly percentages of bistrifluron and chlorantraniliprole for tified in the control samples ranged from approximately 82 to 103% with the method limit of 0.005 mg/kg. The

concentrations of bistrifluron and chlorantraniliprole in strawberry samples decreased significantly in 10 days after treatment, giving the safety levels of 0.04 to 0.06 mg/kg at 10 days after application, as considered maximum residue limit. The half-lives of bistrifluron and chlorantraniliprole based on first order kinetics were determined to 6.3 days and 6.4 days, respectively.

CONCLUSION: Bistrifluron and chlorantraniliprole are suggested to use in strawberry 10 days before harvest to reach residual safety levels.

Key words: Biological half-life, Bistrifluron, Chlorantraniliprole, Pre-harvest residue limit (PHRL), Strawberry

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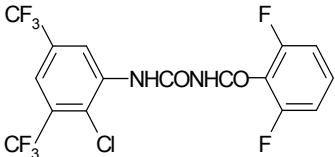
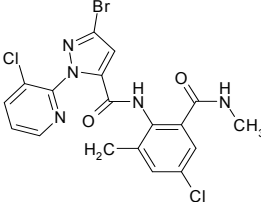
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Table 1. Physicochemical properties of bistrifluron and chlorantraniliprole

	Bistrifluron	Chlorantraniliprole
Structure		
IUPAC name	1-[2-chloro-3,5-bis(trifluoromethyl)phenyl]-3-(2,6-difluorobenzoyl)urea	3-Bromo-N-[4-chloro-2-methyl-6-(methylcarbamoyl)phenyl]-1-(3-chloropyridin-2-yl)-1H-pyrazole-5-carboxamide
Mol. wt.	446.7	483.15
V.P. (mPa)	2.7 10 ⁻³ mPa (25°C)	6.3 10 ⁻⁹ mPa (20°C) 2.1 10 ⁻⁸ mPa (25°C)
logP	5.74 (pH 7.8, 22°C)	2.76
Solubility in water	<0.03 mg/L (25°C)	0.9-1.0 mg/L (20°C)

(Hwang *et al.*, 2012).MRL
2013).(Kim *et al.*,PHRL
(Lee *et al.*, 2013).

vitamin

C

Choi *et al.*, 2013).(Nam *et al.*, 2012).

가

(Claeys *et al.*,

2008).

53

가 (MFDS, 2016).

가

가 bistrifluron chlorantraniliprole

bistrifluron chlorantraniliprole

재료 및 방법**시험농약**

bistrifluron (99.0%)

chlorantraniliprole (99.5%) Dr. Ehrenstorfer GmbH
(Germany)

bistrifluron 5% (: , ())

chlorantraniliprole 5% (: , ())

Table 1

시약, 재료 및 기구

bistrifluron chlorantraniliprole

acetonitrile dichloromethane Junsei
Chemical (Japan) GR , methanol

water Merck (Germany) GR

. Formic acid Sigma-Aldrich (USA)

sodium sulfate
anhydrous, sodium chloride Dae Jung (Korea)NH₂ SPE
cartridge (1 g) Phenomenex (USA)homogenizer (Nissei, Japan),
vacuum rotary evaporator

(Eyela, Japan)

분석기기

bistrifluron chlorantraniliprole

LC-MS/MS , HPLC
(Nanospace SI-2, Shiseido, Japan) (TSQ

Quantum ultra, Tehrmo scientific, USA)	acetone	1,000 mg/kg
Column bistrifluron Capcell Core-C ₁₈ (150×2.1 mm, 2.7 μm, Shiseido, Japan)	stock solution	
UK-C ₁₈ (100×2.0 mm, 3.0 μm, Imtakt, Japan)	0.05, 0.1, 0.2, 0.5, 1.0, 2.0 mg/kg working solution	
chlorantraniliprole	1 mL 가	(1 mL) blank
시험포장 및 농약살포	standard . Bistrifluron chlorantraniliprole	chromatogram
(:) ,	1.0 μL LC-MS/MS ,	peak matrix matched
(1)		
(2)		
2015 3 16 12		
1 40 m ² , 2 38.4 m ²	딸기 중 잔류농약 분석	bistrifluron chlorantraniliprole
3 1 m	가 20 g acetone 100 mL 가 homogenizer 3 , 10,000 rpm	acetone
, 1 2	50 mL, 100 mL 가 dichloromethane	
(KS-PK2000, , Korea)	50 mL, 50 mL 2 ,	
. Bistrifluron chlorantraniliprole	dichloromethane 5 mL .	
Table 2 .	SPE-NH ₂ cartridge (1 g) , dichloromethane	
시료채취	5 mL pre-washing SPE-NH ₂ cartridge (1 g)	
10 1 , 2	5 mL loading , (dichloromethane:methanol =95:5, v/v) 5 mL	
0 0, 1, 2, 3, 5, 7 10	acetone 2 mL	
. 2 kg	(0.2 μm membrane filter) , LC-MS/MS	
, 4	MS/MS	
-20°C	Table 3 .	
Bistrifluron 및 chlorantraniliprole 표준검량선 작성	딸기 중 회수율 분석	bistrifluron chlorantraniliprole
Bistrifluron (99.0%) 101.0 mg 100 mL		
chlorantraniliprole (99.5%) 100.5 mg 100 mL		

Table 2. Guidelines for the safe use of bistrifluron and chlorantraniliprole

Pesticide	Formulation	A.I. ^{a)} (%)	MRL ^{b)} (mg/kg)	Safe use guideline		
				PHI ^{c)} (day)	MNA ^{d)} (time)	Dilution
Bistrifluron	SC ^{e)}	5	0.5	2	2	2,000
Chlorantraniliprole	WG ^{f)}	5	1.0	2	2	2,000

^{a)}A.I.: Active ingredient, ^{b)}MRL: Maximum residue limit, established by MFDS, ^{c)}PHI: Pre-harvest interval, ^{d)}MNA: Maximum number of application, ^{e)}SC: Suspension concentrate, ^{f)}WG: Water dispersible granule

Table 3. Selected Reaction Monitoring (SRM) condition of bistrifluron and chlorantraniliprole

Compound	Precursor ion	product ion	CE	Q1 PW	Q3 PW	SRM mode
Bistrifluron	444.724	259.944	43	0.5	0.7	ESI-
		261.857	22	0.5	0.7	
		388.987	17	0.5	0.7	
Chlorantraniliprole	483.836	176.740	45	0.5	0.7	ESI+
		285.603	26	0.5	0.7	
		452.531	18	0.5	0.7	

Table 4. Linear equation of calibration curve for the quantification of the pesticide residues in strawberries

Pesticide	Linear equation	r ²
Bistrifluron	y=1678656.572x+182992.033	0.9958
Chlorantraniliprole	y=8585760.9956x-30434.9973	0.9937

Table 5. Recovery rate and MLOQ for bistrifluron and chlorantraniliprole in strawberries

Pesticide	Fortification level (mg/kg)	Recovery (%)				MLOQ (mg/kg)
		1	2	3	AVG±C.V.	
Bistrifluron	0.005	85.4	88.8	82.8	85.7±1.7	0.005
	0.05	98.5	103.9	95.9	99.5±4.3	
Chlorantraniliprole	0.005	88.0	100.2	89.4	92.5±7.2	0.005
	0.05	85.4	84.7	82.7	84.3±1.7	

bistrifluron chlorantraniliprole
 1 mL, 1 mg/kg 1 mL
 10 (0.05 mg/kg)
 30

20 g
 0.1 mg/kg
 (0.005 mg/kg),
 가 ,
 Table 4 .
 (r²)가 0.99

시험농약의 생물학적 반감기 및 생산단계 잔류허용기준
 (Pre-Harvest Residue Limit, PHRL) 산출
 (PHRL)
 first order kinetics
 , k
 (Hwang et al., 2014).

분석정량한계 및 회수율
 bistrifluron chlorantraniliprole
 0.005 mg/kg ,
 (0.005 mg/kg), 10 (0.05 mg/kg)
 가 3
 bistrifluron 82.8~103.9%, chlorantraniliprole
 82.7~100.2% , 10% (Coefficient of
 variation, C.V.) (Table 5).
 70~120%
 bistrifluron chlorantraniliprole
 (Lee, 2012).

결과 및 고찰

시험기간 중 환경조건과 딸기의 중량
 (1) (2)
 1 12.9~16.7°C,
 2 14.0~20.4°C ,
 51.0%~72.9%, 72.6%~83.4% . 1 2

bistrifluron chlorantraniliprole
 (Retention time, RT) 6.28 min., 3.94 min. .
딸기 생산단계 중 잔류량 변화에 따른 생물학적 반감기

bistrifluron
 26.21~32.02 g, 24.88~29.68 g ,
 chlorantraniliprole 24.40~31.05 g,
 24.89~30.14 g 1, 2
 가 .

bistrifluron 1 0.16 mg/kg,
 2 0.15 mg/kg , 10
 0.05 mg/kg 66.67%, 68.75%
 Chlorantraniliprole
 0.17 mg/kg , 10 1 0.04
 mg/kg, 2 0.06 mg/kg
 76.47%, 64.70% ,
 (bistrifluron: 0.5 mg/kg, chlorantraniliprole: 1.0
 mg/kg)

Bistrifluron 및 chlorantraniliprole 표준검량선 작성
 ,
 LC-MS/MS
 matrix effect
 matrix matched ,

Table 6. PHRL of bistrifluron and chlorantraniliprole in strawberries

Pesticides	PHRL (mg/kg)											
	Field	10 day	9 day	8 day	7 day	6 day	5 day	4 day	3 day	2 day	1 day	0 day
Bistrifluron	1	1.10	1.02	0.94	0.87	0.80	0.74	0.69	0.63	0.59	0.54	0.50
	2	1.23	1.13	1.03	0.94	0.86	0.78	0.72	0.66	0.60	0.55	0.50
Chlorantraniliprole	1	3.07	2.74	2.45	2.19	1.96	1.75	1.57	1.40	1.25	1.12	1.00
	2	2.29	2.10	1.94	1.78	1.64	1.51	1.39	1.28	1.18	1.09	1.00

bistrifluron 1 $y=0.1521e^{-0.1093x}$ ($r^2=0.9459$),
2 $y=0.1604e^{-0.1101x}$ ($r^2=0.9760$)

MRL

Chlorantraniliprole 1 $y=0.158e^{-0.1484x}$
($r^2=0.9570$), 2 $y=0.1649e^{-0.1076x}$ ($r^2=0.9610$)

요약

Kim (2007) 1 4.7, 2 6.4, bistrifluron (1), chlorantraniliprole (2),
2 0, 0, 1, 2, 3, 5, 7, 10
LC-MS/MS

Kim (2012) 가 가, bistrifluron 0.005 mg/kg, 82.8~103.9%,
chlorantraniliprole 82.7~100.2%,
5.4, 10% (Coefficient of variation, C.V.)

Lee (2009) 가, 25, bistrifluron 0.16 mg/kg, 0.17 mg/kg, MRL
(bistrifluron: 0.5 mg/kg, chlorantraniliprole: 1.0 mg/kg)
1.27, 가, 10, 1 0.05
mg/kg, 0.04 mg/kg, 2 0.05 mg/kg, 0.06
mg/kg, 66.67%, 76.49%

bistrifluron chlorantraniliprole

bistrifluron 6.3, chlorantraniliprole 4.7 (1) 6.4 (2)

가 bistrifluron chlorantraniliprole 10
1.10 mg/kg, 2.29 mg/kg

(Son *et al.*, 2009).

생산단계 잔류허용기준 설정

PHRL

MRL

bistrifluron chlorantraniliprole
Table 6 bistrifluron
MRL 0.5 mg/kg, chlorantraniliprole 1.0
mg/kg bistrifluron 10
1 1.10 mg/kg, 2 1.23 mg/kg
Chlorantraniliprole 10
1 3.07 mg/kg, 2 2.29 mg/kg
bistrifluron chlorantraniliprole
10 1.10 mg/kg, 2.29 mg/kg

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