STU FCHPT
SLOVENSKÁ TECHNICKÁ UNIVERZITA V BRATISLAVE
FAKULTA CHEMICKEJ A POTRAVINÁRSKEJ TECHNOLÓGIE

seminár

Príspevky mladých inovátorov k rozvoju analytickej chémie

SEMMLAD 2023

SPEKTRUM STU

2023

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ISBN 978-80-227-5300-5

Publikáciu vydala Slovenská technická univerzita v Bratislave vo Vydavateľstve SPEKTRUM STU, 2023, 1. vydanie

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Kontrola kvality a bezpečnosti výrobkov

1.17

Determination of transformation products of difenoconazole in tomato by LC-Q-Orbitrap-MS and a non-target approach: laboratory trials

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Introduction

Difenoconazole, a broad-spectrum systemic triazole fungicide, was approved as an active substance in Spain and Slovakia, and therefore, it is routinely monitored in commercialised agricultural products. Nonetheless, the monitorisation of its transformation products (TPs) currently remains largely disregarded, despite this likeliness of such TPs to be present in foodstuff treated with difenoconazole plant protection products (PPPs). Hence, identifying possible TPs emerging from its dissipation, as well as monitoring them is a key task, either those previously addressed in literature, or those not listed, using a non-targeted approach (suspect screening and unknown analysis).

Experimental methods

To this purpose, laboratory trials were carried out in tomato samples hoping to monitor the degradation of difenoconazole into TPs. Ceremonia 25 EC® was diluted and applied to tomato samples at different concentrations. Moreover, laboratory trials were performed at single and twofold dose, for 30 days at room temperature. A solid-liquid extraction method (SLE) was applied, with acetonitrile (MeCN) as extracting solvent (5 g tomato per 5 mL MeCN). Data acquisition was carried out by ultra-high performance liquid chromatography coupled to Q-Orbitrap high resolution mass spectrometry (LC-Q-Orbitrap-MS), in Full Scan MS and data independent acquisition (DIA) modes. Data processing was performed by a non-target approach combining suspect screening, through a home-made database from literature review, and unknown analysis, through MassChemSite, which predicts possible TPs generated from a arent compound.

Results and discussion

In all, 3 TPs of difenoconazole were tentatively identified and semiquantified by an analytical standard of difenoconazole, due to their structural similitude. Tentatively identified TPs were hydroxy-difenoconazole, CGA-205374, and CGA-205375 (also known as difenoconazole-alcohol). As it can be observed in Tab. 1, hydroxy-difenoconazole was only detectable from the 12th day after PPP application and remained detectable until the end of the study, in which it reached a concentration of 5 µg/kg after 30 days. On the other hand, CGA-

205374 appeared 2 hours after Ceremonia was applied and remained detectable for up to 21 days but was not detected after 30 days. Finally, CGA-205375 (difenoconazole-alcohol), was not detected until the second day, but its presence persisted throughout the entire trial period, when a concentration of 3 µg/kg was reached after 30 days.

Tab 1. Identification and semi-quantification of difenoconazole TPs in tomato.

TP	2 h	8 h	Day 1	Day 2	Day 5	Day 12	Day 15	Day 21	Day 30
Hydroxy-difenoconazole	ND	ND	ND	ND	ND	<LOQ	<LOQ	<LOQ	**5 µg/kg[1]**
CGA-205374	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	ND
CGA-205375	ND	ND	ND	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	**3 µg/kg[1]**

Abbreviations: ND: not detected; < LOQ: Detected, but its concentration is lower than the limit of quantification. [1] Concentration values for double dose trials

Conclusions

To summarise, the present study delivers an interesting insight into the identification of 3 TPs of difenoconazole, a highly common fungicide applied worldwide, in tomatoes, which will definitely help expand the knowledge in terms of food safety. This study also hopes to put the likely presence of TPs in vegetables treated with difenoconazole PPPs on the spotlight, as it serves as an evidence that TPs can be detected in vegetables.

Keywords: difenoconazole, plant protection products, tomato, high resolution mass spectrometry, transformation products

Acknowledgement

Authors gratefully acknowledge the Spanish Ministry of Economy and Competitiveness and FEDER-EU (project ref. PID2019-106201RB-I00) for financial support. RLR acknowledges to the Andalusian Ministry of Economic Transformation, Industry, Knowledge and Universities for financial support (Ayudas para Captación, Incorporación y Movilidad de Capital Humano de I+D+I, PAIDI 2020). AJMR acknowledges the Ministry of Universities for financial support (FPU, ref. FPU19/04260).

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Publikáciu vydala Slovenská technická univerzita v Bratislave vo Vydavateľstve SPEKTRUM STU, 2023, 1. vydanie

elektronická forma vydania

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Hroboňová Katarína
Hrouzková Svetlana
Špánik Ivan

Recenzenti zborníka:
Ing. Michal Kirchner, PhD.
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