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SCIENCE DIRECT®
Food Control 17 (2006) 1012–1017
FOOD CONTROL
www.elsevier.com/locate/foodcont

The dissipation rates of cyprodinil, fludioxonil, procymidone and vinclozoline during storage of grape juice

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Received 10 April 2005; received in revised form 25 July 2005; accepted 29 July 2005

Abstract

The disappearance of the fungicides cyprodinil, fludioxonil, procymidone and vinclozoline, which are widely used to control grey mold in vineyards, from commercially sterilized white grape juice was studied. Fungicide losses from white grape juice stored at 40 °C were monitored for about 2 months in order to simulate in a fast way the shelf-life of the product at room temperature (about 1 year). The fungicides were determined by using a simple method based on a liquid–liquid extraction (LLE) and gas chromatographic separation, followed by mass spectrometric detection (GC–MSD). Fortified white grape juice subsamples were taken three times a week from the oven and the degradation of the fungicides monitored for 56 days. The half-lives at 40 °C for vinclozoline and procymidone were found to be 11 and 20 days, respectively. Those for the more recently introduced fungicides fludioxonil and cyprodinil were somewhat longer (33 and 44 days, respectively). Based on the first-order rate constants obtained, the fungicides dissipated in the following sequence: vinclozoline ($0.062\ d^{-1}$) > procymidone ($0.035\ d^{-1}$) > fludioxonil ($0.021\ d^{-1}$) > cyprodinil ($0.016\ d^{-1}$).

Keywords: Fungicides; Cyprodinil; Fludioxonil; Procymidone; Vinclozoline; White grape juice; Dissipation

1. Introduction

Grey mold (*Botrytis cinerea*) is a widespread fungus that infects vineyards (López, López, & Riba, 1989) and is fought by using various fungicides including procymidone and vinclozoline (Sala et al., 1996), or the more recent cyprodinil and fludioxonil to effectively prevent resistance phenomena (Cabras et al., 1997). Procymidone and cyprodinil are systemic fungicides of the dicarboximide and anilinopyrimidine family, respectively. Vinclozoline and fludioxonil are non-systemic fungicides with contact action that belong to the dicarboximide and phenylpyrrole family, respectively. All four are extensively applied to various fruits. In previous work, the authors found them at levels between 0.2 and 3.0 mg/kg in white grapes (Rial-Otero, Cancho-Grande, & Simal-Gándara, 2003).

Although correct usage of fungicides avoids health and environmental problems of public concern, failing to adhere to safety recommendations can lead to undesirably high residues remaining on grapes after harvest. Fungicide residues on grapes can pass to juice (Cabras & Angioni, 2000; Cabras, Angioni, Garau, & Minelli, 1997; Cabras, Angioni, Garau, Pirisi, & Brandolini, 1998a; Cabras et al., 1998b) and may pose risks to consumers' health with the reduction in safety and quality of the resulting juice (Cantagrel, Vidal, Lurton, Desache, & Estreguil, 1993). Consumers' concern about fungicide usage and the presence of fungicide residues in food has led to increasingly strict regulations on fungicide application to grapes. The 76/895/EEC and 90/

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doi:10.1016/j.foodcont.2005.07.009

642/EEC European Directives, and their subsequent modifications, have established maximum residue limits (MRLs) for the fungicides procymidone and vinclozoline in grapes (5 mg/kg). The limits for cyprodinil and fludioxonil in Spanish legislation (the Real Decreto 280/1994 regulation and its modifications) are 2 and 1 mg/kg, respectively. Several methods have been proposed for the determination of fungicide residues in grapes and other processing products (Bernal, del Nozal, Jiménez, & Rivera, 1997; Jiménez, Bernal, del Nozal, Toribio, & Mayorga, 2001; Matisová, Kakalíková, Lesko, & de Zeeuw, 1996; Simal-Gándara, Paseiro, González, & Romero, 1993; Vitali, Guidotti, Giovinazzo, & Cedrone, 1998).

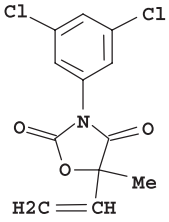
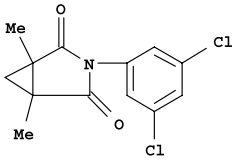
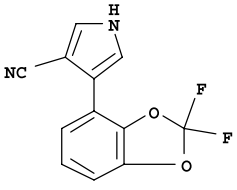
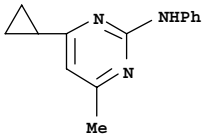
Fruit is often treated close to harvest to ensure that the produce reaches consumers in a good condition. Because fruit juice is more concentrated than natural fruit, it can contain greater amounts of residual fungicides (Cabras & Angioni, 2000). The presence of fungicide residues in bottled pure fruit juices can thus be a major source of human exposure. In addition, children drink proportionally more fruit juice than do adults. No information about the persistence of these fungicides in fruit juices is available. The purpose of this work was to examine losses of the selected fungicides as a result of chemical processes (reactions with sugars and acids mainly) in white grape juice. The tests were conducted at 40 °C in order to accelerate degradation reactions and shorten shelf-life (about 1 year at room temperature).

2. Material and methods

2.1. Chemicals and small apparatus

Cyprodinil [121552-61-2], fludioxonil [131341-86-1], procymidone [32809-16-8] and vinclozoline [50471-44-8] (all > 99% pure; Table 1) were obtained from Riedel-de-Haën. Lindane (97%), which was used as internal standard, was purchased from Aldrich (Steinheim, Germany). A stock standard solution (ca. 1000 mg/L) of

Table 1
Characteristics of the studied fungicides

Chemical family	Fungicide	Structure	K_{ow}[a]	ADI[b] (mg/kg bw/day)	Oral LD_{50}[b] (rats; mg/kg)
Dicarboximide	Vinclozolin		3.1	0.07	10,000
	Procymidone		3.1	0.05	6800
Phenylpyrrole	Fludioxonil		4.1	0.05	>5000
Anilinopyrimidine	Cyprodinil		4.0	0.04	2800

[a] From SciFinder Scholar (2004 version, by American Chemical Society).
[b] From The Pesticide Manual (2000 version, by The British Crop Protection Council, Surrey, UK).