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W. Harvey Newsome<sup>a</sup>; Peter Collins<sup>a</sup>

<sup>a</sup> Food Research Division, Bureau of Chemical Safety, Foods Directorate, Health and Welfare Canada, Ottawa, Ontario, Canada

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# DETERMINATION OF IPRODIONE, VINCLOZOLIN, AND PROCYMIDONE AS THE HEPTAFLUOROBUTYRAMIDES OF 3,5-DICHLOROANILINE

W. HARVEY NEWSOME and PETER COLLINS

*Food Research Division, Bureau of Chemical Safety, Foods Directorate, Health and  
Welfare Canada, Ottawa, Ontario, Canada K1A 0L2*

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A method was developed for the determination of three fungicides in foods based on alkaline degradation to 3,5-dichloroaniline, isolation of the latter by steam distillation and measurement of the heptafluorobutyrate by gas chromatography. Recoveries averaged 91% from several commodities spiked at from 10-80 ppb. The minimum detectable limit of 2.6 ppb was attainable in grape, with similar limits found in strawberry, tomato and beans. The method was capable of determining degradation products formed as a result of cooking.

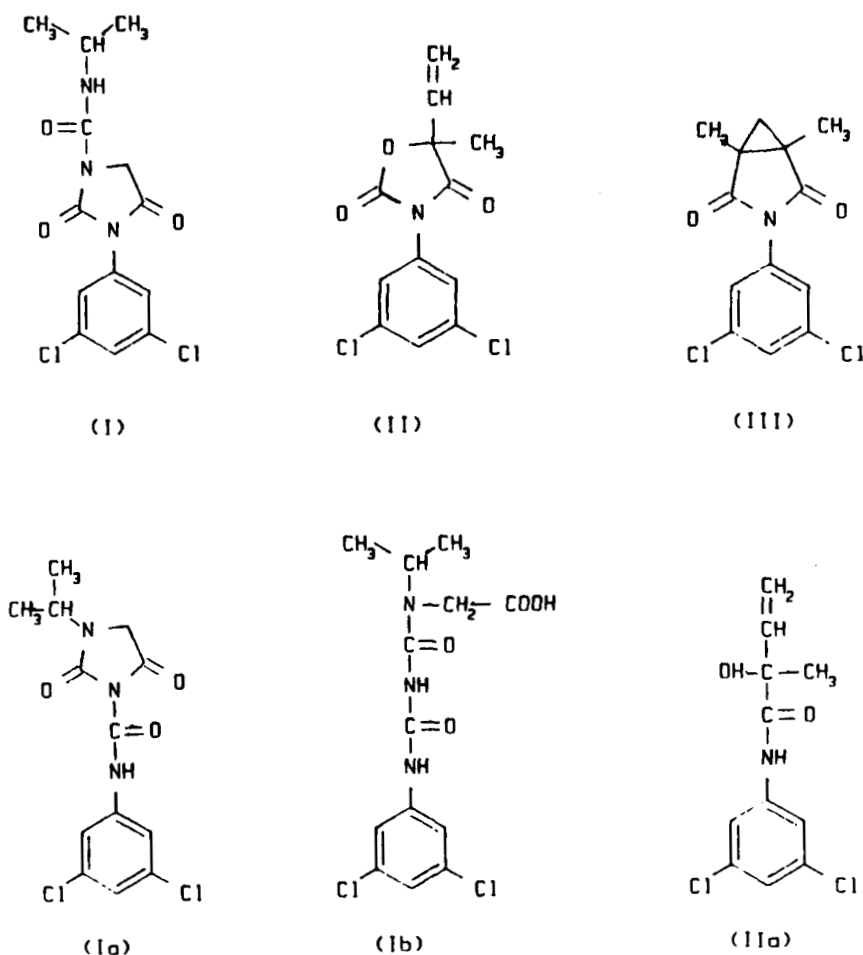
KEY WORDS: Iprodione, vinclozolin, procymidone, foods.

## INTRODUCTION

Iprodione [3-(3,5-dichlorophenyl)-N-isopropyl-2,4-dioxoimidazolidine-1-carboxamide] (I) is a contact fungicide registered in Canada on a variety of crops with maximum residue limits ranging from 0.3 ppm on beans to 10 ppm on tomatoes. The analogous 3,5-dichloroaniline-containing fungicides vinclozolin [3-(3,5-dichlorophenyl)-5-methyl-5-vinylloxazolidine-2,4-dione] (II) and procymidone [N-(3,5-dichlorophenyl)-1,2-dimethylcyclopropane-1,2-dicarboxamide] (III) are used in other countries, primarily on grapes.<sup>1</sup> The structures of these and other relevant components are shown in Figure 1.

Iprodione has been found<sup>2</sup> to rearrange on dissolution in ethanol to a less fungitoxic isomer [3-isopropyl-N-(3,5-dichlorophenyl)-2,4-dioxo-1-imidazolidine-carboxamide] (Ia). In addition, the parent compound was found to undergo ring opening to form the open-chain carboxylic acid 3-isopropyl carbamoyl-5-(3,5-dichlorophenyl)hydantoic acid<sup>3</sup> (Ib). Cabras *et al.*<sup>4</sup> studied the stability of iprodione, vinclozolin, and procymidone in wine and observed that while iprodione appeared unchanged over a period of 92 days, vinclozolin and procymidone degraded, with half-lives of 37 and 56 days, respectively, at pH 4.0. The degradation product of vinclozolin was identified as 3,5-dichloro-2-methylbut-3-enalide (IIa), resulting from opening of the oxazolidine ring, while procymidone yielded 3,5-dichloroaniline which was then converted to unidentified products.<sup>5</sup>

Both gas chromatographic<sup>6,7</sup> and reversed-phase liquid chromatographic<sup>1</sup> methods have been developed which are suitable for the determination of the



**Figure 1** Structures of iprodione (I), vinclozolin (II), procymidone (III), 3-isopropyl-N-(3,5-dichlorophenyl)-2,4-dioxo-1-imidazolidinecarboxamide (Ia), 3-isopropyl carbamoyl-5-(3,5-dichlorophenyl)hydantoic acid (Ib), and 3,5-dichlorophenyl-2-methylbut-3-enalide (IIa).

parent fungicides in foods, but are incapable of determining the open-chain or other di-chloroaniline-containing degradation products. Since residues of these fungicides or their degradation products may occur in imported foods on which there is no approved residue limit in Canada, it was necessary to develop a method capable of determining them at levels less than 100 ppb to permit regulation under the Food and Drugs Act and Regulations.

## EXPERIMENTAL

### Materials

Heptafluorobutyric anhydride, reagent grade was obtained from the Pierce Chemi-

cal Co. (Rockford, IL, USA) and 3,5-dichloroaniline, 98%, from Aldrich Chemical Co. (Milwaukee, WI, USA).

Heptafluorobutyramido-3,5-dichloroaniline was prepared by slowly adding a solution of 3,5-dichloroaniline (160 mg; 1 mmol) in toluene (5 ml) to a stirred solution of heptafluorobutyric anhydride (820 mg; 2 mmol) in toluene (5 ml). The reaction mixture was refluxed for 30 min, cooled, and the solvent evaporated to 1–2 ml on a rotary evaporator. Hexane was added and the resulting crystals filtered. They were recrystallized from hot hexane to obtain white crystals, mp. 122–123 °C. A standard for GC was prepared by weighing 10 mg of crystals in a 50 ml volumetric flask and making to the mark with hexane. Sub-dilutions were prepared to give 4 ng ml<sup>-1</sup> concentrations.

Iprodione reference standard, 97.3%, its isomer, 3-isopropyl-N-(3,5-dichlorophenyl)-2,4-dioxo-1-imidazolidine-carboxamide (Ia; metabolite A), and a potential metabolite (3-(3,5-dichloro-phenyl)-2,4-dioxo-1-imidazolidinecarboxamide (metabolite B) were gifts from May & Baker (Dagenham, England).

Vinclozolin reference standard, 99.5% was obtained from Sumitomo Chemical Co. (Hyogo, Japan) and procymidone reference standard, 100% from BASF (Birkenweg 2, Federal Republic of Germany).

All fungicide standards were dissolved in methanol and diluted to give solutions containing 2–16 µg ml<sup>-1</sup>. For recovery studies, aliquots of 25 µL were used to spike samples immediately prior to analysis. Silicic acid used for column chromatographic clean-up was Woelm, 100–200 µm (ICN Nutritional Biochemicals, Cleveland, OH, USA).

### *Apparatus*

Hydrolyses were conducted in 30 ml glass vials (Hypo-Vial, Pierce Chemical Co.) sealed with PTFE coated septa. The steam distillation was performed using a Garman steam distillation apparatus (1000 mL, No. JD-3210, SGA Scientific, Bloomfield, NJ, USA).

Gas chromatography was carried out on a Varian 3700 fitted with a J&W on-column injector (J&W Scientific, Rancho Cordova, CA, USA) and <sup>63</sup>Ni electron-capture detector. The column was a 30 m × 0.25 mm i.d. J&W DB-5 with a 0.25 µm film thickness. The initial column temperature was 100 °C and after a 2 min post injection delay was programmed at 10 °C min<sup>-1</sup> to 200 °C. The detector temperature was maintained at 300 °C.

Column chromatography was conducted using 20 cm × 6 mm i.d. glass columns fitted with 50 ml reservoirs (Chromaflex K 420100, Kontes, Vineland, NJ, USA). The columns were packed with 2 g of silicic acid in hexane.

### *Procedure*

Commodities to be analyzed were homogenized in a Waring blender and sub-samples of 5.0 g weighed into 30 ml vials. 12.5% NaOH (20 ml) was added, the vial

sealed, and the sample hydrolyzed by heating at 115 °C for 4 h. After cooling, the vial content was transferred to the sample cup of the steam distillation apparatus, the vial rinsed with 1 N H<sub>2</sub>SO<sub>4</sub> (5 ml), and distillation carried out until 15 ml of distillate had been collected in a 125 ml separatory funnel containing 1 N H<sub>2</sub>SO<sub>4</sub> (5 ml). The distillate was rendered alkaline with 50% NaOH (1 ml) and extracted with toluene (2 ml). The toluene layer was recovered, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and an aliquot (1.0 ml) taken for derivatization.

The heptafluorobutyrate was prepared by adding heptafluorobutyric anhydride (20 μl) to the dried extract in a 15 ml centrifuge tube fitted with an air condenser and heating in a tube heater (Kontes K-720002 or equivalent) at 100 °C for 30 min. After cooling the reaction solution was diluted with hexane (1 ml) and chromatographed on a silicic acid column. After addition of the sample, the column was washed first with 10% toluene in hexane (15 ml), and the washings discarded. The derivative was then recovered by elution with 40% toluene in hexane (15 ml) and an aliquot (1 μl) of this eluate analyzed by gas chromatography.

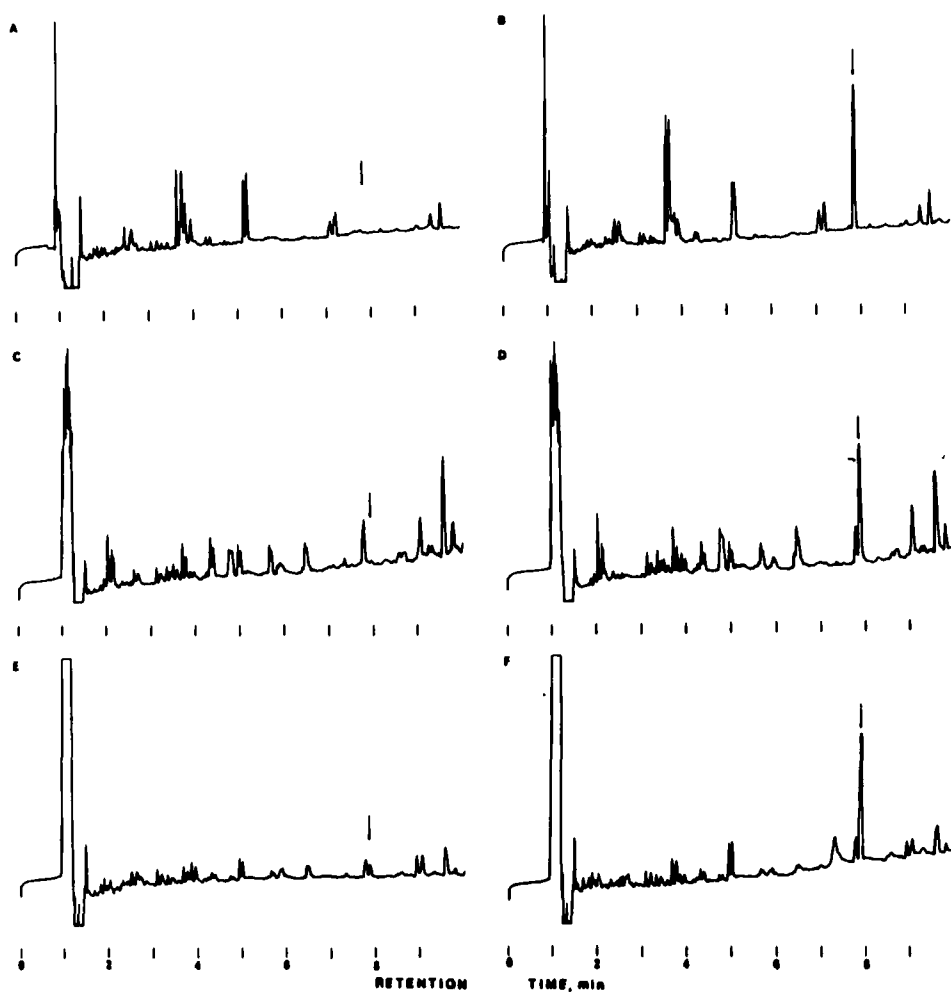
For the determination of the effect of cooking on the fate of these dichloroaniline-containing fungicides, 5 g samples of grape homogenate were placed in ampules, spiked with 0.5 ppm of the respective fungicide, sealed, and heated at 105 °C for 30 min. These, and duplicate samples which had not been heated, were analyzed for the parent compounds by gas chromatography with N-P detection after extraction and clean-up on Florisil by the method described previously.<sup>8</sup> Replicate ampules were also analyzed by hydrolysis to dichloroaniline according to the present method.

## RESULTS AND DISCUSSION

Hydrolysis and subsequent steam distillation to effect clean-up of the resulting aniline has been used to determine residues of several urea herbicides,<sup>9,10</sup> the herbicide alachlor,<sup>11</sup> and the insecticides chlorphenamide<sup>12</sup> and amitraz.<sup>13</sup> Iprodione was found resistant to hydrolysis with refluxing 6 N HCl, and required a 2 h period in 10% NaOH for complete release of the dichloroaniline moiety. Vinclozolin was also quantitatively hydrolyzed in 2 h, but procymidone yielded approx. 45% of the expected dichloroaniline and required a 4 h heating in alkali to produce quantitative results. As shown in Figure 2, steam distillation produces a chromatogram free of interferences and permits a minimum detection limit, defined as three standard deviations above background,<sup>14</sup> of 2.6 ppb in grape. Similar detection limits were attainable with the other commodities tested.

Recoveries of the three fungicides from grape spiked at from 10 to 80 ppb were similar and exceeded 80% (Table 1). Iprodione and vinclozolin were recovered in satisfactory yield from all commodities examined. In a replication study, the mean recovery of iprodione from 6 samples of grape spiked at 40 ppb was 90.5% with a CV of 2.3%.

The recoveries of all three fungicides from uncooked grape were similar, whether measured as the parent compound or as dichloroaniline after hydrolysis (Table 2). As shown by the data in Table 2, conversion to other compounds did occur upon



**Figure 2** Gas chromatograms of (A) tomato, (C) strawberry, and (E) grape blanks and of (B) tomato, (D) strawberry, and (F) grape spiked with 20 ppb of iprodione. Arrows indicate the retention time of the heptafluorobutyramide of 3,5-dichloroaniline. Each injection represents the equivalent of 189  $\mu\text{g}$  of sample.

**Table 1** Recovery<sup>a</sup> of iprodione, vinclozolin, and procymidone from various commodities as heptafluorobutyramido-3,5-dichloroaniline

Commodity	Compound	Amount added (ppb)			
		10	20	40	80
Grape	Iprodione	105	95	94	90
	Vinclozolin	98	91	99	88
	Procymidone	86	92	83	80
Strawberry	Iprodione	89	99	89	83
	Vinclozolin	95	86	94	87
	Iprodione	92	98	87	91
Tomato	Metabolite A	—	—	—	81
	Metabolite B	—	—	—	84
	Iprodione	105	94	96	92

<sup>a</sup>Values are the means of duplicate determinations.

**Table 2** Effect of cooking on the recovery of iprodione, vinclozoline, and procymidone from grape

Compound	Percentage recovery <sup>a</sup>			
	Uncooked		Cooked	
	As parent	As DCA	As parent	As DCA
Iprodione	82	102	58	100
Vinclozolin	93	94	79	86
Procymidone	83	82	62	80

<sup>a</sup>Values are the means of duplicate experiments.

cooking iprodione or procymidone, but the hydrolytic method was capable of accounting for all residues formed. Vinclozolin was unexpectedly stable, in contrast to the findings of degradation studies in wine.<sup>4</sup>

### References

1. P. Cabras, P. Diana, M. Meloni, F. M. Pirisi and R. Pirisi, *J. Chromatog.* **256**, 176 (1983).
2. B. K. Cooke, R. S. T. Loeffler and A. C. Pappas, *Pestic. Sci.* **10**, 393 (1979).
3. O. Belafdal, M. Bergon and J. P. Calmon, *Pestic. Sci.* **17**, 335 (1986).
4. P. Cabras, M. Meloni, F. M. Pirisi and R. Pirisi, *Pestic. Sci.* **15**, 247 (1984).
5. F. M. Pirisi, M. Meloni, P. Cabras, M. R. Bionducci and A. Serra, *Pestic. Sci.* **17**, 109 (1986).
6. L. Lacroix, M. Laurent and M. Buys, in: *Analytical Methods for Pesticides and Plant Growth Regulators*, G. Zweig and J. Sherma, eds. (Academic Press, New York, 1980), Vol. 11, pp. 247.
7. E. Lemperle, N. Emmanouilidis and N. E. Kerner, *Deut. Lebensm. Rundschau.* **78**, 6 (1982).
8. W. H. Newsome, in: *Pesticide Science and Biotechnology*, R. Greenhalgh and T. R. Robert, eds. (Blackwell, Oxford, 1987), pp. 349.
9. I. Baunok and H. Geissbuehler, *Bull. Environ. Contam. Toxicol.* **3**, 7 (1968).
10. D. J. Caverly and R. C. Denney, *Analyst* **103**, 368 (1978).
11. W. H. Newsome, P. Collins and D. Lewis, *J. Assoc. Off. Anal. Chem.* **69**, 591 (1986).
12. H. Geissbuehler, K. Kossmann, I. Baunok and V. F. Boyd, *J. Agric. Food Chem.* **19**, 365 (1971).
13. W. B. Crummett *et al.*, *Anal. Chem.* **52**, 2242 (1980).