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Some aspects of the **ANALYSIS OF RESIDUES OF DICARBOXIMIDE FUNGICIDES IN FOOD**

Prepared for publication by

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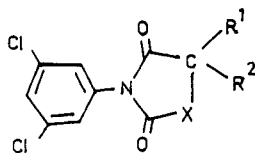
Some aspects of the analysis of residues of dicarboximide fungicides in food

Abstract

The commercially important members of the group - iprodione, procymidone and vinclozolin - are considered. The metabolism in plants, the residue levels in field treated crops, and the analytical methods for determining the residues of these compounds are summarized. The data indicate that the residues of parent compounds are present in food at such concentrations which enable their determination with several multiresidue procedures. Since the total residues deriving from approved, registered use of the compounds are toxicologically acceptable, the MRLs should be expressed and the residues analysed as the parent compounds alone to simplify the analysis of a great number of samples in the regulatory laboratories.

INTRODUCTION

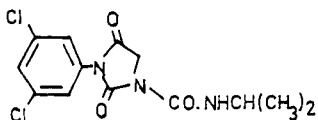
The term dicarboximide fungicide has been applied to anti-fungal compounds of the general formula:



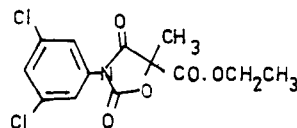
with R^1 and/or $R^2 = H$ or various hydrocarbon groups, $X = O, N - R$ or Cl .

The common names, chemical structures and molecular mass (Mm) of the compounds are:

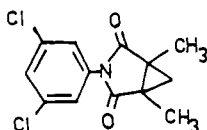
Iprodione
 $C_{13}H_{13}Cl_2N_3O_3$
 Mm.: 330.16



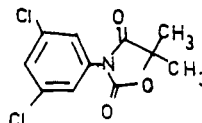
Chlozolinate
 $C_{13}H_{11}Cl_2NO_5$
 Mm.: 332.1



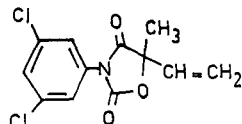
Procymidone
 $C_{13}H_{11}Cl_2NO_2$
 Mm.: 284.13



Dichlozoline
 $C_{11}H_9Cl_2NO_3$
 Mm.: 274.11



Vinclozolin
 $C_{12}H_9Cl_2NO_3$
 Mm.: 286.1



Currently the commercially important members of the group are iprodione, procymidone and vinclozolin which are considered further in this paper.

Vinclozolin is a non-systemic contact fungicide, whereas procymidone has been reported to be moderately systemic. In the case of iprodione, root uptake has been shown to occur from soil by several plants.

These products are mainly used against Botrytis, Sclerotinia, and Monilia spp. at a rate of 0.5 - 1.5 kg active ingredient/ha as a foliar treatment. In addition, the pesticides may be applied post harvest and for seed dressing.

Residues in crops receiving foliar treatments consist of the intact parent compound and some metabolites in widely varying proportions. The unique feature of this group of compounds is that all metabolites identified contain the 3,5-dichloroaniline moiety except the 3-isopropylhydantoin identified from iprodione. There is no evidence of significant impurities in the technical products or formulations carrying through to be residues in crops.

Maximum Residue Limits [MRL: the maximum concentration of a pesticide residue which is legally permitted in or on a food commodity (1)] have been set for these pesticides in many crops and countries. The FAO/WHO Panel of Experts on Pesticide Residues also made recommendations for MRLs for international use (3-5).

Limits for iprodione and procymidone are generally expressed in terms of the parent compounds, although the tolerance for iprodione in the USA includes the parent compound, its isomer, and a metabolite indicated as I₂ on Figure 1. The MRLs of vinclozolin are expressed either as parent compound alone or as the combined residue of parent compound and metabolites containing the 3,5-dichloroaniline moiety.

Derivatized 3,5-dichloroaniline can be determined with suitable sensitivity in various matrices after alkaline hydrolysis and derivatization, generally with chloroacetyl chloride. The combined residues of active ingredient and metabolites are determined. However, the method is not selective and cannot distinguish members of the group from each other and it includes any 3,5-dichloroaniline, which may have come from other sources.

Alternatively, these fungicides can be satisfactorily determined as the parent compounds using several well established multi-residue procedures. These enable analysts to screen for the presence of these pesticides and for many others within the same process.

Knowledge of the identity of individual dicarboximids is important in screening because the MRLs, established for these compounds in the same crop, differ in certain cases. Table 1 illustrates the wide variation of MRLs.

The objectives of this paper are to present the data available on residues of iprodione, procymidone and vinclozolin so as to recommend a uniform approach in setting and enforcing MRLs.

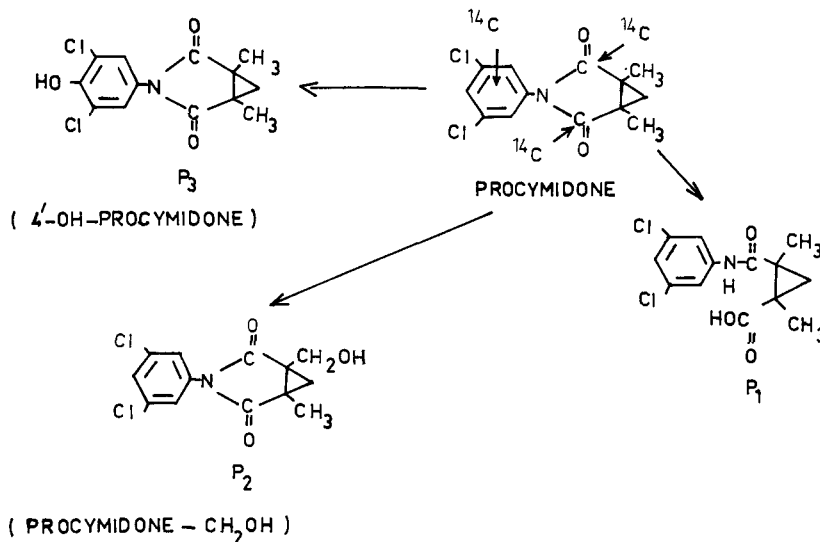


Fig. 1. Metabolic pathways of procymidone.
(The trivial names given to metabolites by the manufacturer are given in brackets.)

METABOLISM IN PLANTS

The metabolic fate of the compounds was studied with ¹⁴C-phenyl ring labelling in iprodione and vinclozolin and with ¹⁴C labelling in the carbonyl group of procymidone. The plants received foliar treatment. In addition, the uptake by roots was also studied.

The metabolic pathways of procymidone, iprodione and vinclozolin are shown in Figures 1-3 respectively. Details of the relevant experiments are summarized in Table 2.

The main degradation route for all compounds was cleavage of the cyclic imide linkage. Pathways differed as various side-chain modification also occurred. All major metabolites contained the intact 3,5-dichloroaniline moiety. The metabolites are mostly present in conjugated or bound form.

The half lives of initial residue deposits were reported to be about 20 days for procymidone on bean leaves (2) and 9 to 16 days, and 5 days, for vinclozolin on peaches and lettuces, respectively (6).

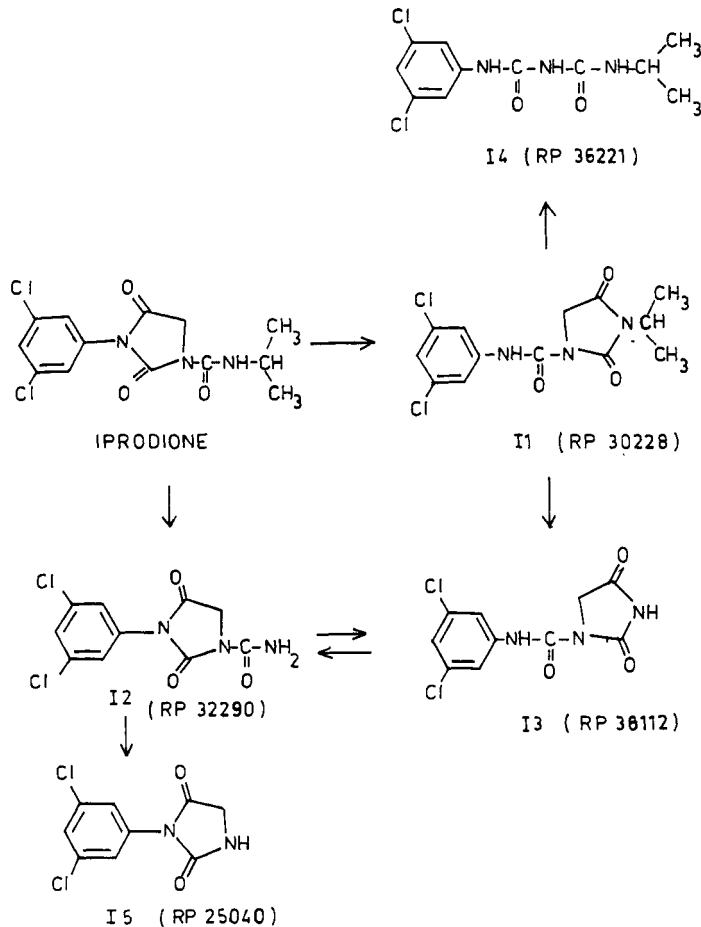


Fig. 2. Metabolic pathways of iprodione in plants.
 (The code numbers given to metabolites by the manufacturer are given in brackets.)

The ratio of parent compounds in the total residue decreased after application. Up to 10 days following a single treatment, the parent compounds were the main components of the total residue of each pesticide. Thereafter polar metabolites began to occur in widely varying proportions. Vinclozolin was converted to polar metabolites to the greatest extent. This resulted in a relatively low level of parent compound in treated crops harvested 4 to 7 weeks after application.

The fate of procymidone was investigated in bean and cucumber. In both cases, the parent compound amounted to over 90% of total residue recovered from various crops 3 to 4 weeks after treatment, and only 0.6 to 1 % were attributable to the sum of P₁ and P₂, the major metabolites. Residues of 3,5-dichloroaniline in cucumber and soybean were below the limit of determination (0.01 mg/kg) (7).

The fate of iprodione has been studied in a number of crops. Generally the parent compound is the major component of the total residue. A relative increase in the proportion of metabolites and bound residues was observed in certain crops or crop fractions. Results of field experiments, summarized in Table 3, show the sum of metabolites I₁ and I₂ may amount to about one half of the total residue in leafy vegetables and rice, while in other crops the parent compound was the major component of the residue.

The analysis of individual results revealed that:

i) if the parent compound occurred in high concentration the amount of metabolites was relatively negligible in that sample. This can be seen by comparing the maximum values of parent compound and the sum of residues measured;

ii) in other samples, taken from the same type of crops, the sum of parent, I₁ and I₂ was always lower than the total residue found in samples containing the parent compound at high concentration.

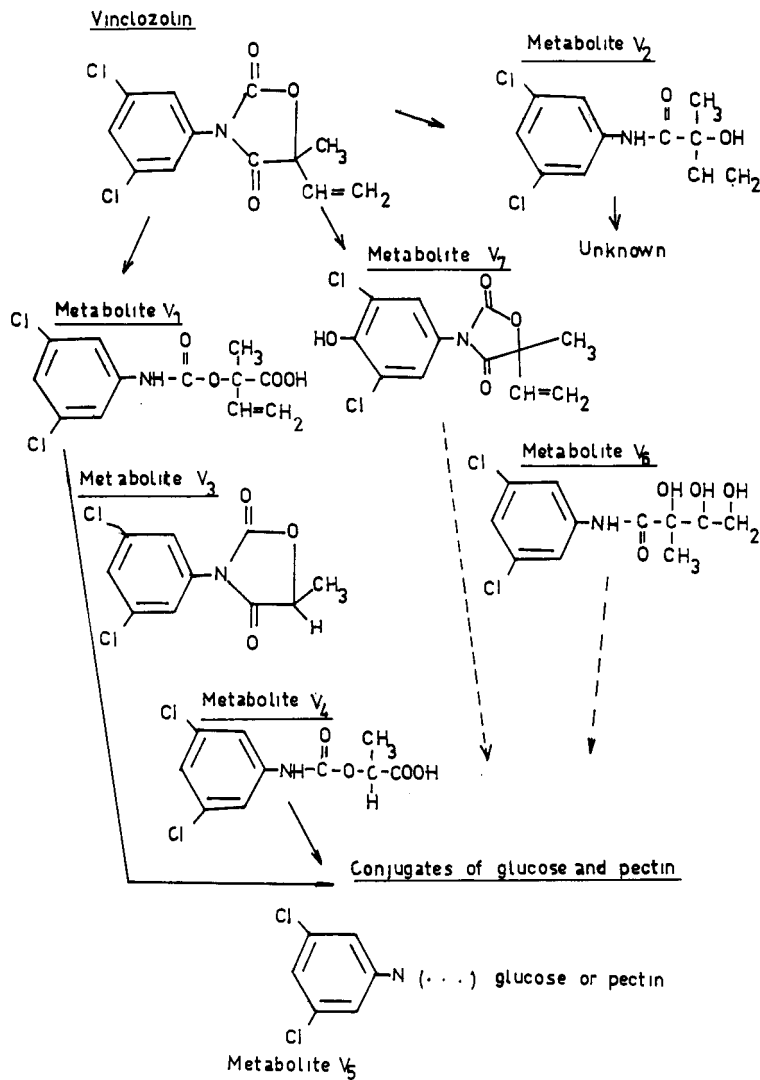


Fig. 3. Tentative metabolic pathways of vinclozolin in plants.

The residue uptake from treated soils showed that iprodione residues entering wheat and strawberry plants via root absorption are mostly bound residues and metabolites with little parent compound. Foliar spray reaching the soil at the time of application may be one of the sources of variation of metabolite concentration in plants, even if root uptake is a minor route of absorption compared with foliar uptake from the recommended use.

DECLINE OF RESIDUES AFTER APPLICATION

The results of supervised trials are summarized in Table 4 to 11, based on unpublished reports provided by the companies. The iprodione and procymidone residues were measured as intact parent compound, while the residues of vinclozolin, with one exception, were determined as the sum of parent compound and its metabolites in the form of 3,5-dichloroaniline derivative.

The residues remain mainly on the plant surface and very little, if any, penetration occurs into the inner layers. Consequently the residue levels are greatly influenced by external factors.

The residue ranges on crops receiving similar dosages were of approximately the same magnitude. The rate of decrease of residue concentrations did not show significant differences.

The results suggest that dilution caused by weight increase of crops accounts for a considerable part of the reduction of residue levels in some cases.

RESIDUE LEVELS IN MARKETED CROPS

A summary of market surveys carried out in Denmark (10), Sweden (11) and United Kingdom (12) is given in Table 12. Analysis of samples were carried out with methods measuring the parent compounds alone.

The spread and frequency of residues are in line with results obtained for other compounds detected in commodities moving in commerce (13). The picture obtained may be considered representative of dicarboximide residues, especially of those of vinclozolin, which was screened in a large number of samples.

METHODS OF RESIDUE ANALYSIS

The manufacturing companies developed specific methods for the determination of parent compounds and metabolites in samples derived from supervised trials.

In plant materials, iprodione is determined as the parent compound alone (14) or as the parent, I₁ and I₂ individually, after separation on a Florisil column (15). The parent compound is measured in samples treated with procymidone (16). The analytical method developed for vinclozolin determines the parent compound together with all metabolites containing the 3,5-dichloroaniline moiety (17). The method is based on direct alkaline hydrolysis of samples to yield 3,5-dichloroaniline, which is reacted with chloroacetyl chloride to form N-(3,5-dichlorophenyl)-chloroacetamide. The latter is determined by GLC with an electron capture detector (3).

In addition to the unpublished methods of the manufacturers, there are several multi-residue procedures and individual methods which can be used for the determination of the parent compounds. The multi-residue procedures can only be used for the determination of the parent compounds.

Acetone is by far the most widely used solvent for the extraction of fruits, vegetables and foliage of high water content (18 - 24). Other solvents, such as petroleum ether (25, 26), acetonitrile (27) and benzene (26) or solvent mixtures: cyclohexane/benzene 8+2 (28), dichloromethane/acetone 9+1 (29) are reported by one or two authors. Methanol is also an efficient extraction solvent and has given high recoveries of vinclozolin and iprodione from fruits (30). Although iprodione has been reported to rearrange in alcoholic solvents (31) no losses were found with methanol extraction of acidic fruits where partitioning took place within an hour of extraction (30). Dry samples (cereal grains, rice) are extracted with dichloromethane (19, 21) or the lower layer obtained from the mixture of 92:7:1 of dichloromethane, methanol and concentrated hydrochloric acid. Samples with high vegetable oil content (rape seed, sunflower seed) are extracted with acetone containing 0.5 mol/l sulphuric acid for removing vinclozolin and its metabolites (32), or with acetonitrile* for the three compounds. Must and wine samples are extracted with light petroleum ether (33).

The extracts can be purified on silica gel/active carbon (18), on a mixture of active carbon/magnesium oxide/celite 1+2+4 (34), on neutral alumina (34) and on Florisil (23, 32) columns.

Efficient clean up was achieved by passing through the extracts of apples and pears on Sep Pack Florisil (22) or Sep Pack C₁₈ cartridges (22, 27) and carbon/cellulose (30). Gel permeation chromatography on Bio Beads SX-3 was successfully applied to a wide variety of samples followed by an additional clean up on silica (21, 24), Florisil (34) or silver loaded alumina (24) columns.

The concentrated, cleaned extracts are mostly analysed by gas liquid chromatograph using ⁶³Ni ECD (14-16, 18, 22-25, 27, 32, 35, 36), ⁶³Ni ECD and NPTID (21, 29, 37) or Hall ECD (20). The compounds may be eluted on liquid phases from nonpolar (OV-1, SE-30, OV-101), through medium polarities (OV-17, OV-1701, OV-22) to high polarities (OV-225, DEGS, QF-1).

Packed columns with 2-3% liquid phase on Chromosorb WHP or equivalent supports (14, 15, 18, 21, 23, 29, 35-37) as well as wall coated capillary columns (22, 24, 25, 27) and bound phase fused silica columns (38) are used. Iprodione, procymidone and vinclozolin are well separated. Figures 4 and 5 show their chromatograms on SE-30 and OV-22 columns respectively.

Limits of determinations reported are in the same range for both packed and capillary columns.

* The findings of the authors (unpublished).

Typical values (mg/kg) for fruits and vegetables are:

iprodione: 0.02-0.05
procymidone: 0.01-0.02
vinclozolin: 0.005-0.01

The HPLC technique is also used for analysing fruit samples. The main advantage of the methods is that little or no clean up of extracts is necessary before determination. The extracts are dried in a rotary evaporator under vacuum before being taken up in the eluent mixture. The pesticides are eluted with water/acetonitrile 50+50 or 45+55 mixtures on reverse phase columns [Merck Hybar RP8 and LiChrosorb RP18] and detected with UV detectors at 210-221 nm (28, 33). The limit of determination is between 0.02-0.05 mg/kg for the three compounds depending on the sample. It is essential to have good clean up of certain substrates (such as strawberry, red pepper and lettuce)when using UV detectors.

Recoveries of the compounds are over 80% in most of the cases for all methods discussed.

Confirmation of the identity of the residues is mostly carried out with GC-MS applying electron impact ionization (38-40) or by positive or negative chemical ionization (40, 42). In the absence of GC-MS, additional chromatographic methods, including two dimensional capillary GC (43), may be used for confirmation.

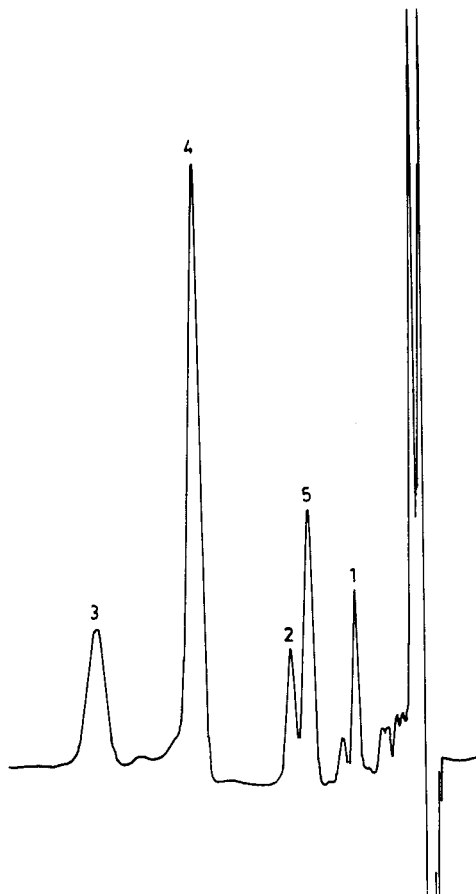


Fig. 4. Chromatogram of an apple extract fortified at 0.2 mg/kg level (26) Chromatographic conditions: packing: 3% SE-30 on Supelcoport 100-120 mesh in 50cm x 2mm Pyrex column; detector: NPTID; temperature: 180° for 1 min, 5°C/min, 200°C for 4 min; Compounds: vinclozolin (1), procymidone (2), iprodione (3), triazophos (4), unknown (5)

DISCUSSION

The active ingredients of dicarboximide fungicides can be determined with several widely used multi-residue procedures. The typical limit of determination (mg/kg) is five or more times lower than the lowest MRL. Studies on the plant metabolism of the active ingredients revealed that the parent compounds amount to over 70% of the residues in plants within three weeks period after application, with the exception of vinclozolin in strawberries and lettuce. Although the proportion of vinclozolin is low in the latter cases, it was present in quantifiable concentration 23 days after application.

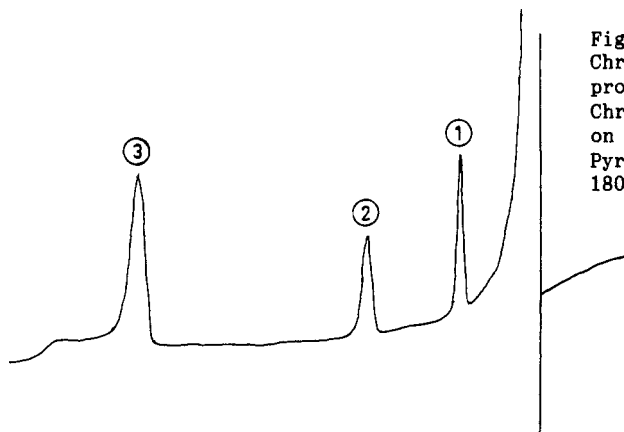


Fig. 5.
Chromatogram of 1 ng of vinclozolin (1),
procymidone (2) and iprodione (3)
Chromatographic conditions: packing: 3% OV-22
on Supelcoport 100-120 mesh in 50cm x 2mm
Pyrex column; detector: NPTID; Temperature:
180°C for 1 min, 5°C/min, 220°C for 4 min.

Since the dicarboximide fungicides are active against the same fungus diseases, they can be used alternately to protect the crops. Residues of more than one active ingredient may therefore be present in the harvested crops. Within the group, the MRLs for some commodities vary up to five-fold. Consequently the identity of the parent compound must be determined in each suspect sample otherwise the residue results cannot be interpreted.

The analytical method based on the analysis of 3,5-dichloroaniline, the common moiety of the active ingredients and all of the metabolites of the group, cannot distinguish the origin of the residues. It also includes any occasional dichloroaniline contamination of the commodity, derived from other sources, with the pesticide residues. Consequently this indirect method cannot be used alone for analysis of food commodities of unknown origin for the enforcement of MRL.

If the MRL is expressed as a combined total residue its enforcement always requires additional analysis which is time consuming and expensive, and inevitably reduces the number of lots which can be controlled by the laboratory.

RECOMMENDATION

Since the total residues deriving from approved, registered use of the compounds are toxicologically acceptable, the MRLs should be expressed and the residues analysed as the parent compounds alone. This will simplify the control of compliance with registered use patterns.

The redefinition of residue included in the MRL requires reconsideration (decrease) of some limits for vinclozolin which are based on 21 days or longer preharvest intervals.

The limited information available to the authors on the concentrations of parent vinclozolin on treated crops does not allow estimation of the new limits. However, it is considered that sufficient data conforming to the redefined residue is available in the files of national registration authorities in countries where the parent compound alone is used for MRL. Therefore further review of that data base is recommended.

TABLES

Abbreviations used in the tables:

Countries:

AUS: Australia,
B: Belgium,
BR: Brasil,
CH: Switzerland,
CND: Canada,
D: Federal Republic of Germany,
DK: Denmark,
F: France,
H: Hungary,
I: Italy,
J: Japan,
NL: The Netherlands,
NZ: New Zealand,
UK: United Kingdom,
USA: United States of America.

Pesticides:

I: Iprodione,
P: Procymidone,
V: Vinclozolin.

Miscellaneous:

a.i.: active ingredient,
B: bound residues,
h: harvest,
NC: not characterized,
ND: not detected.

TABLE 1. Example for MRLs¹ and preharvest intervals recommended by JMPR, and registered in various countries

Crop	Com- pound	JMPR	AUS	B	BR	CH	D	F	H	I	J	NL	NZ
Apples	I	10 (10-14)	3 ²					10 (15)	3 (10)				
	P	5 (7)											
	V	1 (14-21)	2										
Cherries	I		10					10	5 (10)			5 (7)	10 (1)
	P	5 (3)	10 (1)						3 (14)				3 (1)
	V	3 (14-21)	10	0.5	10		0.5	10	3 (14)	1.5			3
Currants	I	5 (7)					7 (7)		3 (14)			15	10 (1)
	P	10 (7)							3 (14)				
	V	5 (7)										5	
Grapes	I	10 (14-21)	20 (7)			7	5 (28)	10 (15)	5 (7)				10 (1)
	P	5 (21)						5	3 (14)				5 (1)
	V	5 (7-14)	2		5		5	10	3 (14)	1.5			2
Peaches	I	10 (10-14)	10 (1)					10 (15)	5 (10)				10 (1)
	P	10 (7)	10 (1)								3 (14)		3 (1)
	V	2	10	0.5	0.5			10	3 (14)	1.5			3
Raspberries	I	5 (10-21)	2 (14)					7 (7)	3 (14)			5 (7)	10 (1)
	P	5 (7)							3 (14)				
	V	5 (10-21)							3 (14)			5	
Strawberries	I	10 (14)					10 (10)	7 (2)	3 (14)			10 (14)	
	P	10 (7)							3 (14)		3 (3)	3 (14)	0.5 (1)
	V	10 (4-7)		5	0.5		8	15	3 (14)	1.5		10	5
Lettuce	I	10 (14-28)	5 (7)			6	10 (14)	10 (21)				5 (28)	
	P	5 (21)						5			2 (7)	1 (14)	1 (3)
	V	5 (14-28)	12	5			5	5	5 (21)	1.5	5	2	
Cucumber	I	5 (3-6)					5	5 (3)					
	P	2 (21)									2 (1)		
	V	1 (3)		1								1	
Tomatoes	I	5 (3-7)	2 (7)			6 (3)		5					5 (3)
	P	5 (3)									2 (3)	1 (3)	1 (3)
	V	3 (3)		3					3 (14)	1.5		1	5
		JMPR	AUS	B	BR	CH	D	F	H	I	J	NL	NZ

Notes: 1. The maximum residue limits (MRLs) are either expressed as parent compound alone, or as the total residue expressed as parent compound. The pre-harvest intervals are given in brackets

2. Post-harvest treatment.

TABLE 2. Proportion of parent compound and metabolites in plants after foliar treatment

Plant	Compound	Dosage a. i.	Sampling at ¹ .	Total Residue	Distribution of residues (%) Parent compound	Metabolites	Reference	
Beans	P	250 µg/leaf	30	40.2% ²	92	P ₁ + P ₂ =1	2	
Cucumber	P	250 µg/leaf	23	64 % ²	97	P ₁ + P ₂ + P ₃ =0.6	2	
Grape	V	0.75 kg/ha 1.0 kg/ha	21	1.18 mg/kg	85	SP=7 VP=2.5	3, 6	
			30	0.45 mg/kg	55	SP=29 VP=7		
Lettuce	I	0.75 kg/ha	0	64 mg/kg	98	I ₁ =0.3 B=0.1	8	
			25	6.3 mg/kg	91	I ₁ =2.9 B=1.9		
			12	0.7 mg/kg	13	SP=57 VP=29		3, 6
21	0.24 mg/kg	3	SP=64 VP=33					
Peach	I	1.12 kg/ha twice 1.12 kg/ha 3 times	64	0.03 mg/kg	70	B =6	9	
			8(h)	1.9 mg/kg	94	I ₁ =0.8 I ₂ =0.5 B=0.4		
			14	2.85 mg/kg	85	V ₁ =0.6 V ₂ =0.4 VP=0.7		3, 6
			21	1.36 mg/kg	80	V ₁ =14.3 V ₂ =3.3 VP=18.3		
28	1.89 mg/kg	72	V ₁ =12.2 V ₂ =4.6 VP=23.6					
Peanut	I	1.12 kg/ha twice	10(h)				9	
			-hay	43 mg/kg	54	I ₁ =15 I ₂ =8.8 I ₃ =3.1 I ₅ =5.4 B=5.8		
			-meat	0.05-11 mg/kg	NC	B =12		
			-hulls	0.13 mg/kg	43	I ₁ <3 I ₂ =3.5 I ₅ =5.9 B=12		
Rice	I	1.12 kg/ha twice	40(h)				9	
			-head/ -stalks	9.9 mg/kg	56	I ₁ =19 I ₂ +I ₃ =1.7 I ₄ =0.33 I ₅ =6.2 B=6		
			-brown	0.78 mg/kg	37	I ₁ =21 I ₂ +I ₃ +I ₄ =5 I ₅ =3.7 B=21		
			-polished	0.26 mg/kg	36	I ₁ =21 I ₂ +I ₃ +I ₄ =5.6; I ₅ =5.1 B=26		
Strawberry	I	1 kg/ha	14	59 mg/kg	75	I ₁ =8.3 I ₂ =2.7 B=0.9	8	
			32	62 mg/kg	61	I ₁ =16 I ₂ =4.5 B=8.7		
			32	0.84 mg/kg	56	I ₁ =3.6 I ₂ =ND B=4.8		
Strawberry	V	0.5 kg/ha	6	3.3 mg/kg	79	SP=16 VP=27	3, 6	
			10	1.95 mg/kg	63	SP=23 VP=7		
			17	1.34 mg/kg	59	SP=29 VP=5		
			23	0.46 mg/kg	46	SP=37 VP=11		
Wheat	I	1 kg/ha	15	5.2 mg/kg	82	I ₁ =2.7 I ₂ =3.8 B=1.9	9	
			96(h)	25 mg/kg	25	I ₁ =33 I ₂ =1.2 B=28		
			96(h)	1.35 mg/kg	NC	NC B=60		

Notes: 1. days after last application

2. Percentage of applied radioactivity recovered from the treated leaves

SP: slightly polar compounds containing V_s moiety;VP: very polar compounds containing V_s moiety

TABLE 3. Summary of results of supervised field trials carried out with iprodione in the United States of America

Crop	No. of trials	No. of applications	Dosage kg ai/ha per treatment	Sampling at days after last treatment	Maximum residue ranges from each test			Sum of residues ² mg/kg
					Parent mg/kg	Metabolites in % of parent.		
					I ₁	I ₂		
Strawberries	12	6-9	1.12	0	0.67-9.87	1.1-6.2	1.9-11.4	10.4
Escarole	7	3	1.12	14-15	0.17-21.62	nd ³ -5.3	nd-57.4	22.4
Endive	5	3	1.12	14-15	nd-12.36	nd-96.3	nd-10.7	12.72
Romaine salad	6	3	1.12	14	0.07-20.02	nd-71.4	nd-16	20.5
Bibb salad	5	3	1.12	14	0.87-13.71	1.4-6.9	2-10.3	14.18
Celery stalks	2	11	1.12	0	8.71-14.39	1.5-1.7	nd-0.9	14.44
	4	13	1.12	0	6.18-48.37	1.4-1.9	nd-0.5	49.14
	4	13	2.24	0	7.54-68.94	1.2-2.6	nd-0.9	70.97
Grapes	5	6-7	1.12	0	2.69-20.6	nd-1.4	nd-7.8	20.75
Carrot roots	9	8	1.12	0	0.49-3.13	nd-3.6	nd	3.18
	9	8	2.24	0	0.77-7.22	nd-18.2	nd-3.3	7.39
Succulent beans	5	2	1.12	14	0.58-1.28	nd	nd	1.28
Rice	14	2	0.56	32-36	0.74-7.26	5.0-41.9	1.9-12.2	8.45
Rice bran	1	2	0.56	35	5.22	16.1	4.8	6.31
	1	2	1.12	35	5.75	28.3	5.2	7.68
Rice straw	2	2	0.56	32	25.38-26.68	26.1-26.3	0.3-0.31	32.7
Rice	8	2	0.56	42-58	0.5-2.5	nd-118	nd-24	3.12
Rice polished	1	2	0.56	35	0.14	50	nd	0.21
	1	2	1.12	35	0.42	38.1	nd	0.58
Rice hulls	1	2	0.56	35	8.95	9.7	11.6	10.87
	1	2	1.12	35	17.6	8.1	6.9	20.24
	1	2	0.56	35	5.22	16.1	4.8	6.31
	1	2	1.12	35	5.75	28.3	5.2	7.68
Peanut hay	3	3	1.12	0	28.3-146.7	0.3-3.5	1-1.9	148.5
	4	3	1.12	3-4	15.6-56.7	0.7-1.3	0.3-3	58.8
	4	3	1.12	9-11	25.6-89.7	1.6-9.5	2.9-7.2	104.6
Peanut hull	3	3	1.12	0	0.57-5.23	nd-8.2	nd-24.6	5.66
	4	3	1.12	3-4	0.39-5.25	15.4-26.3	4.2-15.4	6.85
	4	3	1.12	9-11	0.26-1.13	nd-169	nd-20.3	1.46
Peanut meat	11	3	1.12	0-11	nd	nd	nd	
	1	3	1.12	4	0.21	52.4	nd	0.32
	1	3	2.24	4	0.27	66.7	nd	0.45

- Notes: 1. The metabolite concentration is compared to that of parent in the same test.
 2. The sum of residues is given for that sample in which the maximum of parent was detected.
 3. nd indicates residues below 0.05 mg/kg, the limit of determination.

TABLE 4. Decay of residues in cucumber grown in greenhouse

Compound	Country	Year	Application No.	Rate kg ai/ha	Residues (mg/kg) (days) after application	Residues (mg/kg) at intervals			
						0	1	2/3	4/5
Vinclozolin	NL	1982	2	0.25	0.35	0.28			0.18
			2	0.75	1.08	0.98			0.64
Iprodione	DK	1980	1	0.5	0.68			0.2	0.27
			1	0.75	0.5	0.51	0.44	0.22	
Vinclozolin	NL	1985	3	1.25		0.39			
			3	1.25		0.32			
Procymidone	J	1976	3	1.25	0.35	0.11			0.09
			3	1.25	1.25	0.67			0.28
			6	1.25	0.33	0.16			0.11
			6	1.25	1.18	0.87			0.33

TABLE 5. Decay of residues in lettuce grown in greenhouse

Com- pound	Coun- try	Year	Application		Residues (mg/kg) at intervals										Note	
			No.	Rate kg ai/ha	0	1	3/4	7/8	14	20/21	28	34/42	61/66			
P	UK	1979	4	0.25						0.76						
I	UK	1974	4	0.56	19	16	18	14								1
			4	0.56	59	40	41	21								
P	F	1977-78	3	500 ppm				29	16	9.5	3.4					1
			3	500 ppm								1.7				
			3	750 ppm				48	18	12	3.4					
			3	1000 ppm				77	45	17	14					
V	B	1979	1	0.3						0.46						2
			1	0.3						0.57						
			1	0.5						0.59						
			1	0.5						0.67						
	D	1981	1	1.0						10.6						2
I	D	1979	1	1.0	70			30	23	10	3.2					
V	NL	1981	1	1.0											0.14	
		1978	1	1.5									0.12			3
		1981	1	1.67									0.16			4
I	D	1978	1	1.5	79					8.4	3.2	0.9				
			1	1.5	122					25	6.4	<0.1				

Notes: 1. Lettuces were not trimmed before analysis.
 2. Average of 3 trials.
 3. Average of 4 trials. Residues ranged from 0.05 to 0.4 mg/ha
 4. Average of 4 trials.

TABLE 6. Decay of residues in lettuce grown in outdoor

Com- pound	Coun- try	Year	Application		Residues (mg/kg) at intervals										Note	
			No.	Rate kg ai/ha	0	1	3/4	7/8	14	20/22	28	34/35	45	56		
I	D	1979	1	1.0	70			30	23	10	3.2					
V	D	1978	1	1.0						0.18	0.25	0.1				
		1978	1	1.0						2.2	1.5	0.3				
		1979	1	1.5						0.07		0.08	0.07	0.06		
		1979	1	1.5								0.24	0.27	<0.05		
I	D	1978	1	1.5	79			84	3.2	0.9						
		1978	1	1.5	122			25	6.4	<0.1						
P	NL	1978	1	2.0												0.06 ¹
	D	1978	3	0.255	5.3		2.5	1.1	0.2	0.1	0.1					
			3	0.255	3.2		2.3	1.1	0.6	0.1	0.1					
	NL	1978	1	3.0												0.09 ¹
V	F	1977	3	0.5	19.3			2.3	0.4	0.18	0.08					
	UK	1978	3	0.5		22		12.4	5.6	2.2	2.0					
		1978	3	0.5		10.9		0.7	0.16							
P	J	1977	3	0.75-1			0.02	0.01	LD	LD						
		1976	3	1.1			1.3	0.8	0.16	0.44						
		1977	6	0.75-1			0.3	0.02	0.01	0.01						
		1976	6	1.1			1.1	0.9	0.4	0.3						

Notes: 1. Average of 16 samples derived from two trials 88 days after application.
 2. LD denotes residues below the limit of determination.

TABLE 7. Decay of residues in tomatoes

Compound	Country	Year	Application No.	Rate kg ai/ha	Residues (mg/kg) at intervals (days) after application							Note	
					0	1	3	5	7	9	14		21
Procimidone (greenhouse application)	UK	1976-77	5	0.2-0.25		0.76	0.59		0.39		0.72		
			5	0.35		0.77	0.66		0.51		0.5		
			5	0.5		1.1	0.32		0.57		0.63		
			J	1976	3	1.25		0.35	0.11		0.09		
			3		1.25		1.25	0.67		0.28			
	6	1.25			0.33	0.16		0.11					
	I	1977	6	1.25		1.18	0.87		0.33				
	4		1.5			0.83		0.48		0.62	0.18		
	Vinclozolin (greenhouse application)	D	1977	3	0.45	2.1		2.4	1.8	0.8		0.9	0.4
				3	0.45	1.6		1.2	0.3	1.4		0.4	0.3
3				0.75	5.1		2.3	0.9	1.2		0.5	1.0	
3				0.75	2.9		3.6	1.8	1.1		1.0	0.6	
3				0.75	4.7		2.1	0.4	3.4		1.2	0.5	
J		1977	4	0.45			0.35		0.49				
3			0.84		0.6	0.4		0.3					
3			0.84		2.0	1.8		1.8					
				3	1.25		0.6	0.6					
				3	1.25		2.8	2.8					
				5	1.25		3.5	2.2					
outdoors		D	1978	5	1		1.5	0.56	1.2	0.7			
		4		0.5-1	0.55		0.39	0.4	0.46				
	5	0.5-1		0.7		0.74	0.59	0.29					
Procymidone (outdoors)	NZ	1978	3	0.5	0.12		0.11			0.12	0.04		
	F	1979	3	0.75	2.7		1.7		1.5	1.4	0.74		
	NZ	1978	3	1.0	0.22		0.14			0.29	0.16		

Notes: 1. Average of three trials
2. Average of two trials.

TABLE 8. Decay of residues in strawberries

Compound	Country	Year	Application No.	Rate kg ai/ha	Residues (mg/kg) at intervals (days) after application							Note
					0/1	3	4/5	7/8	10	14/16	21/22	
I	D	1974	3	0.94		2.7			1.1		0.38	
			3	1.25		3.6			2.0		0.67	
P	F	1978/80	3	0.5	2.1			1.5		0.68	0.49	
			1-4	0.75	5.0	3.6		1.9		1.5	1.8	
	NL	1978	5	1.5		2.7	1.2		0.6			
			5	1.5		3.1	2.9		2.1			
	D	1978	3	0.75	1.1	0.9	0.9		0.7	0.6		
			3	0.95	1.8	1.4	1.1		1.0	0.9		
V	NL	1977	3	0.25	0.2	0.2		0.1	0.8	0.3		
			5	0.25	0.6	0.6		0.4	0.8	0.3		
			3	0.5	1.3	1.1		0.6	1.3	0.9		
			5	0.5	1.1	1.1		0.2		0.7		
	UK	1977	3	0.5	2.1	1.0		0.8	0.6	0.6		
			4	0.5	8.0	4.6		2.9	1.8	1.3	1.1	
			3	0.75	1.6	0.9		0.5	0.5	0.4		
			4	0.75	2.6	2.2		3.2	3.3	1.9	1.0	
	D	1976	3	0.5				1.4		0.6	0.5	
			4	0.5		3.2	2.9					
			4	0.75		2.5		1.1				
			3	0.5	4.0	4.4		3.0	2.1	1.9	1.2	
D	1976	3	0.75	10.2	6.9		4.2	4.2	2.9	1.6		
		3	1.0	15.3	11.5		5.1	4.5	3.8	2.1		

Notes: 1. Maximum residues detected in five experiments.
2. Maximum residues detected in eight experiments.

TABLE 9. Decay of residues in grapes

Com- pound	Coun- try	Year	Application No.	Rate kg ai/ha	Residues (mg/kg) at intervals (days) after application							Note
					0	7/9	13/16	20/22	27/28	31/35	42	
I	D	1974	4	0.5					2.1		1.9	1.3 ¹
	D	1974	5	0.4		2.7				3.4		0.55 ¹
	F	1974	4	0.75	8.4	6.4	4.8	4.2				
	CND	1979	1	1	2.5	1.2	1.0					
P	NZ	1979	1	0.7		1.7	1.0	1.6				
	F	1977-80	3-4	0.75	4.9	4.7	4.8	3.5	1.0			2
	NZ	1978	5	0.75	0.62	0.49	0.44					
	I	1976	4	0.85					1.94			3
	F	1977-80	3	1.0	6.4	3.1	2.2		2.8			
	NZ	1979	1	1.05		4.3	2.7	2.5				
	I	1976	4	1.275					4.12			
	D	1977	5	1.25	11.2		8.4	2.1	9.3			
			5	1.25			9.3	1.0	6.6	5.1		
			5	1.25	7.2		5.7	5.9	5.2	2.4		
			4	1.25	8.0		5.6	4.2	3.7	0.6		
		4	1.25	4.2		3.7		3.2	2.9	1.8		
		4	1.25	5.0		3.7	2.4	2.0	1.9			
V	NZ	1982	1	0.75	5.1	2.2	1.8	1.7	1.4			
			1	1.5	5.8	2.9	2.8	1.9	1.3			
			4	0.75	4.6	3.7	3.9	2.2				
	F	1984	4	0.75				4.8	4.15			
			4	0.75	5.2		3.7	3.0	2.3	1.8		
			2	1	4.7		3.6	2.7	2.5	2.5		
	D	1980	5	0.75	0.71		0.58	0.74	0.53	0.52		
			4	1.25	2.62		4.36	1.28	0.84	1.36	0.97	
			5	1.25	4.7	4.2	3.3	2.55	3.5	2.3		
	AUS	1979	5	1.0	2.35	2.3	3.3					

Notes: 1. Residues detected 71 - 84 days after last application.

2. Maximum residues detected in five experiments.

3. Maximum residues detected in two experiments.

TABLE 10. Decay of residues in cherries

Com- pound	Coun- try	Year	Application No.	Rate kg ai/ha	Residues (mg/kg) at intervals (days) after application						Note	
					0/1	3	5/6	7/8	13/14	21		28
I	CND	1978	6	0.7	4.0		2.5	2.6				
P	J	1977	1	3.5				1.88	0.96	1.7		1
			3	3.5				3.76	2.39	1.75		1
V	D	1978	3	0.75	1.3		0.76		0.42	0.38	0.4	
			3	0.75			0.85		0.68	0.61	0.4	
			3	0.75	2.27		0.67		0.61	0.55	0.3	
			3	0.75	1.99		0.52		0.48	0.33	0.43	
			3	0.75	3.48		2.35		1.7	0.94	0.56	
	AUS	1980	1	0.5%	3.1	2.85	1.5			1.96	0.5	2
USA	1979	3	0.84	0.87	0.78	0.68		0.63				

Notes:

1. Maximum residues detected in two experiments.

2. Maximum residues detected in four experiments. Samples were also taken 35 and 42 days after last application, their residue contents were 0.42 and 0.39 respectively.

TABLE 11. Decay of residues in peaches

Com- pound	Coun- try	Year	Application No.	Rate kg ai/ha	Residues (mg/kg) at intervals (days) after application						Note	
					0/1	3	4/5	7/9	12/15	21/23		40
I	CND	1978	3	0.7	2.4	2.3	2.3	2.45				
			3	0.75	3.8			1.4	0.8	0.36		
			4	0.75	2.2			1.8	0.72	0.65		
P	NZ	1978/80	2	0.2	0.4		0.6	0.37	0.27			1
			2	0.4	1.7		1.1	1.3	1.1			
			2	0.6	2.4		1.1	1.2	0.33			
			7	0.75	0.66			0.53	0.38			
			6	1.5	0.32		0.43	0.42	0.67			
V	I	1981	2	1	0.41		0.37	0.26	0.27			
			AUS	1980	1	0.25%	1.0	0.9		0.8		
	1	0.375%	4.0		3.5		2.1					
	1	0.5%	3.5		1.2		1.2					
	1	0.75%	4.1		5.1		1.35					
		NZ	1980	2	0.75	10.5	6.0		4.1			
	USA			1982	1	1.0	0.96				1.03	
		1978	3		1.1	4.3	3.5		2.6			
		1982	2		1.0	9.4		1.54		1.36	0.2	1
			2		1.0	0.98				1.9		1

Note: 1. The parent compound alone was determined with HPLC.

TABLE 12. Residue¹ levels detected in market surveys

Crop	Iprodione		Procymidone		Vinclozolin	
	No. of samples analysed	Residues (mg/kg) detected ²	No. of samples analysed	Residues (mg/kg) detected	No. of samples analysed	Residues (mg/kg) detected
Apple	1291	2-5(1); 5-10(1)			1320	0,4-1(3)
Cabbage					168	0,4-1(2)
Celery					20	0,4-1(1)
Cucumber			45	0.09-0.52(5)	40	<0.05
Grapes			61	0.06-0.66(4)	40	<0.05
Lettuce	165	0.25, 1.16			495	0.4-1(3); 1-2(2)
Kiwi fruit					39	5-10(1)
Peach					33	0.04-0.53(6)
Pear					937	0.02-1.42(6); 0.4-1(4),0.2,0.3
Pepper			141	0.12-0.53(3)	408	0.03-1.0(10)
Raspberries	26	0.1-0.4(4)			10	0.7; 1.0; 3.3
Strawberries	236	0.1;0.2;2-5(4)	129	0,37;0.76	368	0,1-0,2(4); 0,4-1(13); 1-2(2)
Tomatoes	467	0,2-0.4(4);0.4-1(5)	141	0.03	153	0.01-0.57(50)

Notes: 1. All residues were measured as parent compounds.

2. Number of samples falling in residue ranges is given in brackets.

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