### **PROPICONAZOLE (160)**

## **EXPLANATION**

Propiconazole was evaluated in 1987 and 1991. The 1991 JMPR required information on GAP and residue data from applications of the parent compound to barley and rice as a result of reconsidering the general limit for cereals (based on data submitted to the 1987 JMPR) as requested by the CCPR (ALINORM 91/24, para. 222; 91/24A, para. 202). In addition, residue data on melons, peppers and tomatoes from trials carried out according to GAP were considered desirable.

Current information on GAP has been submitted for barley, cucurbits, grapes, melons, peppers, rice, sugar beet, tomatoes and wheat. The manufacturer does not recommend the use of propiconazole on melons or tomatoes.

Additional residue data on barley and rice, as well as on grapes, cucumbers and peppers, were provided by the manufacturer.

### **USE PATTERN**

Propiconazole is used on barley in most of the cereal-producing countries. Detailed information on GAP is given in Table 1 where those countries are listed for which residue data from supervised trials are available. As the national recommendations are rather uniform, these countries represent well the major barley-producing areas of the world.

Propiconazole is used on rice in Columbia, Italy, Malaysia and the USA. It is applied in the USA before the boot splits and the head emerges and in Malaysia at booting to heading, which corresponds to 35-40 days and a minimum of 40 days respectively.

The use of propiconazole on peppers is recommended only in Italy.

## **RESIDUES RESULTING FROM SUPERVISED TRIALS**

Supervised field trials conducted in various countries were reported to the Meeting. In these trials residues of the parent propiconazole, and in some cases total residues of compounds containing the common moiety dichlorobenzoic acid (DCBA), were determined.

<u>Grapes</u>. Seven supervised field trials were conducted in Spain, applying propiconazole 3 or 4 times at rates between 0.0094 and 0.08 kg ai/ha. Samples taken 32 to 80 days after the last application did not contain detectable residues (<0.02 mg/kg). As the samples were taken at much longer intervals than the registered PHI (15 days) the results do not affect the present MRL.

<u>Peppers</u>. The residues of propiconazole in peppers were measured in one Italian and three Spanish trials. The fungicide was applied as a liquid formulation. The spraying was repeated 2-5 times at 2-

week intervals. The application rate ranged from 25 to 48 g ai/ha. The residues of propiconazole in the fruits were <0.02-0.27 mg/kg after a pre-harvest interval of 13-23 days (Table 2).

<u>Other vegetables</u>. In two trials on artichokes in Spain propiconazole was applied at rates of 0.04 and 0.052 kg ai/ha. Samples taken 11 days after application contained residues of 0.13 and 0.06 mg/kg respectively. In a single trial on cucumbers propiconazole was applied at a rate of 0.075 kg ai/ha. Residues 4-11 days after application were below the limit of determination (<0.02 mg/kg).

Crop	Country		PHI, days			
		Form. & g ai/l	No.	g ai/hl	kg ai/ha	_
Barley	Bolivia	EC 250	1-2		0.125	30
	Brazil	EC 250	2-3		0.125	37
	Canada	EC 250	2		0.125	45
	Denmark	EC 500	1-4		0.125	30
		EC 450	1-4		0.125	30
		EC 250	1-2		0.125	30
	France	EC 125	1-2		0.125	
		EC 500	1-2		0.125	
		EC 475	1-2		0.125	
		SC 275	1-2		0.125	
		SC 325	1-2		0.125	
		SC 412	1-2		0.125	
		SC 387.5	1-2		0.125	
	Germany	EC 250	2-3		0.125	35
	South Africa	EC 250	1-2		0.125	40
	Spain	EC 100	1-2	3-5	0.125	15
	Switzerland	WP 450	1	25-40	0.125	
	UK	EC 250	2-4		0.125	35
		EC 450	1		0.125	35
		EC 475	2-3		0.125	35
		EC 500	2-3		0.125	35
	USA	EC 430	1		0.125	
Cucurbits	Spain	EC 100	3-4	3-5	0.015-0.025	15
Grapes	Spain	EC 100	3-5	3-5	0.045-0.075	15
Peppers	Italy	EC 100	1-2	2-5	0.02-0.05	28
		EC 250	1-2	2-5	0.02-0.05	28
Rice	Bolivia	EC 250	1		0.187	30
		EC 250	1-2		0.125	
	Columbia	EC 250	1-2		0.125	
	Italy	EC 100	Max $2^1$		0.1-0.15	36
	Italy	EC 250	Max $2^1$		0.1-0.15	
	Malaysia	EC	2		0.200	
	USA	EC 430	1		0.316	
		EC 430	2		0.190	
Sugar beet	Italy	EC 100	2-4		0.2-0.25	21
		EC 250	2-4		0.2-0.25	21

Table 1. National use patterns of propiconazole.

1044

Crop	Country		Application				
		Form. & g ai/l	orm. & g ai/l No. g ai/hl kg ai/ha				
	Spain	EC 100	1-3	3-5	0.075-0.125	15	
Wheat	Spain	EC 100	1	3-5	0.125	15	

<sup>1</sup> At 30-day intervals

<u>Sugar beet</u>. Seven trials conducted in Denmark, Germany and Italy, which had already been evaluated by the 1987 JMPR, were re-submitted by Spain. Propiconazole was applied at 0.19 and 0.25 kg ai/ha. Samples were taken during the period 0 to 42 days after application. Propiconazole residues were <0.02 mg/kg in beet roots regardless of the PHI. Residues in three leaf samples were 0.08, 0.33 and 0.34 mg/kg 14 days after application.

<u>Barley</u>. Twenty new trials were carried out in Canada (5 trials), France (9) and Germany (6). Propiconazole was applied either alone in a gel, wettable powder or liquid formulation, or in a mixture with other fungicides as liquid formulations. One or two sprays were made at a rate of 125 g ai/ha. Grain was sampled at harvest. The pre-harvest interval ranged from 34 to 75 days, depending on the growth stage at the last treatment, the variety and the weather conditions.

No residues of the parent compound were detectable (<0.02 mg/kg) after a pre-harvest interval of 48 days or longer. They were at or about the limit of determination (0.02-0.03 mg/kg) after a PHI of 5 weeks. Total residues calculated as the parent compound but determined as DCBA decreased from 0.07-0.12 mg/kg after 5 weeks to <0.04-0.1 mg/kg after 7 and 9 weeks (Table 3).

In barley forage both propiconazole and the total residue containing the dichlorophenyl moiety were determined. The results, given in Table 4, indicate that the parent compound was below the limit of determination (<0.04 mg/kg) and DCBA amounted to 0.2 mg/kg which is equivalent to 0.36 mg/kg expressed as propiconazole.

<u>Wheat</u>. Four supervised trials were reported from Canada in which the parent compound as well as DCBA residues were measured in forage and grain. The residues found are shown in Table 4. They indicate that the parent compound amounted to 12-14.5% of total residue expressed as parent.

<u>Rice</u>. Ten new trials were carried out in Italy (4) and the USA (6). Propiconazole was applied once or twice in liquid formulations at rates ranging from 125 to 250 g ai/ha.

No propiconazole (<0.02 mg/kg) or total (<0.05 mg/kg) residues were detectable in the ears after a pre-harvest interval of 7 weeks or longer. After shorter PHIs only total residues were measurable 0.07-0.43 and <0.05-0.15 mg/kg after 5 and 6 weeks respectively (Table 5).

### **FATE OF RESIDUES**

The proportion of the parent compound in the total residue was determined with radiolabelled propiconazole in peanuts grown in a greenhouse (Madrid and Cassidy, 1980) and in grapes (Blattmann, 1980). These trials were reported in the 1987 Evaluations, so only the proportions of the parent compound in the total residues are shown in Table 6.

## METHODS OF RESIDUE ANALYSIS

In addition to the methods described in the 1987 Evaluations the following methods were used for determining propiconazole residues in samples from supervised trials.

The parent propiconazole residues are extracted by shaking with an 8 + 2 mixture of methanol and water. The extract is diluted with water and the compound re-extracted into hexane/*tert*-butyl methyl ether. After evaporation the residue is dissolved in hexane and cleaned up on an alumina column. The final determination is by gas chromatography with NP detection. The lower practical limit of determination is 0.02 mg/kg in grain and 0.04 mg/kg in straw. Recovery values in plant material fortified at concentrations from 0.04 to 0.8 mg/kg ranged from 76 to 105% (Forrer, 1991).

In another method wheat samples (grain, straw) are extracted with methanol. After filtration and water/methylene chloride partition, clean-up is on an alumina column. Quantification is by GLC with an NP detector. Limits of determination are 0.02 mg/kg for grain and 0.04 mg/kg for straw (Ciba France, 1990).

An improved version of an earlier method (AG-454A) has been developed. It determines propiconazole and all metabolites containing the 2,4-dichlorophenyl moiety. The methyl ester of 2,4-dichlorobenzoic acid (DBCA) is determined by capillary gas chromatography with electron-capture detection. The limit of determination is 0.05 mg/kg expressed as propiconazole. The average recovery was  $88.2 \pm 15.0\%$  at over a fortification range of 0.05-2.0 mg/kg (Manuli and Toth, 1989).

Country	Application		Residue, mg/kg, at in	Ref.	
	No.	g ai/ha	13-14	23	
Italy	2	25		0.13	27
Spain	3	28	0.05		28
	5	40	0.27		29
	3	48	<0.02		30

Table 2. Residues of propiconazole from supervised trials on peppers, 1981. All EC 100 formulation.

Table 3. Residues of propiconazole following supervised trials in Barley treated with 125 g ai/ha.

Country, Year	Applicat	cation Residue, mg/kg, at interval, days			Ref.		
	Form	No.	34-37	48-53	59-66	71-75	
Canada 1990	WP 41	1			< 0.02		19
	WP 41	2		<0.02-0.03			16
	EC 250	1			< 0.02		18
	EC 250	2		< 0.02			15
France, 1989	GEL 62	2			< 0.02		9
France, 1991	EC 625	2		< 0.02			10
	EW 625	2		< 0.02			10
France, 1988	EC 500	1			< 0.02		5

Country, Year	Applica	tion		Residue, mg/kg, at interval, days			
	Form	No.	34-37	48-53	59-66	71-75	
France, 1986	EC 500	1			< 0.02		4
	EC 500	1				< 0.02	3
	SC 275	2				< 0.02	6
France, 1989	SC 275	2			< 0.02		7
	SC 275	2			< 0.02		8
Germany, 1986	EC 420	2		<0.04*			11
	EC 420	2	0.07*				11
	EC 420	2	0.12*				12
	EC 420	2			0.05*		13
	EC 420	2		0.05*			14
Germany, 1987	EC 420	2		0.10*			15

\* Total residues based on dichlorobenzoic acid (DCBA)

Table 4. Residues of propiconazole in wheat and barley forage and grain treated with Tilt EC 250 at 125 g ai/ha in Canada.

Crop	Plant part	Days after last of 1-2 applicns.	Residue, mg/kg		% of parent in total residue	Ref.
			Propiconazole	Total based on DCBA		
Wheat	Forage	3 7 14 28	1.24 0.9 0.27 0.11	1.18 1.12 0.87 0.76	approx 100 80 28 14.5	33
Wheat	Forage	4 8 21 28	1.46 0.84 0.05 <0.04	2.1 1.68 0.37 0.24	70 50 13.5 <12	32
Wheat	Grain	52	<0.02*	<0.03	<32	35
Wheat	Grain	52	<0.02*	0.036	<28	34
Barley	Forage	3 7 14 28	1.12 0.41 0.11 <0.04	1.46 1.14 0.75 0.36	77 36 15 <8	36

\* Two applications 23 days apart

Table 5. Residues of propiconazole from supervised trials on rice

Country, Year	Application			Residue, mg/kg, at PHI, days			Ref.
	Form	No.	g ai/ha	34-35	41-43	≥50	
Italy, 1991	EC 250	1	125			< 0.021	21
	EC 250	1	125			< 0.021	20
	EC 250	2	125			< 0.02	22
	EC 250	2	125			< 0.02 <sup>2</sup>	23

1047

Country, Year	Application			Resid	Ref.		
	Form	No.	g ai/ha	34-35	41-43	≥50	
USA, 1989	EC 420	1	250			< 0.05*	24
	EC 420	2	187		0.09-0.15*		24
	EC 420	1	250	0.35-0.43*			26
	EC 420	2	187	0.08-0.10*			26
	EC 420	1	187		<0.05*		25
	EC 420	2	187	0.07-0.10*			25

<sup>1</sup> Samples were taken 78-83 days after application
<sup>2</sup> Samples were taken 62 days after application
<sup>3</sup> Samples were taken 27-28 days after application
\* Total residues based on dichlorobenzoic acid (DCBA)

## Table 6. Proportion of parent propiconazole in peanuts and grapes.

Plant (age in days)	No. of sprays	Interval after last application, days	% of parent in total residue
Peanut (35)	1	0 35 49	89 8 11
Peanut (84)	2	0 35	57 8
Peanut (119)	3	0 14	45 17
Grape, fruit	4	30	21
Grape, fruit leaves	4	63	23 18

# NATIONAL MAXIMUM RESIDUE LIMITS

The reported MRLs expressed as propiconazole are summarized below.

Table 7. National MRLs expressed as propiconazole.

Сгор	Country	MRL, mg/kg	Remarks
Barley	Brazil	0.02	
	France	0.05	cereals
	Germany	0.1	cereals
	Italy	0.05	
	South Africa	0.05	
	Spain	0.2	cereals
	Switzerland	0.02	cereals
	USA	0.1	based on DCBA
Cucurbits	Italy	0.05	melon

1048

Сгор	Country	MRL, mg/kg	Remarks
	Spain	0.2	
Grapes	Australia	1	
	Italy	0.5	
	South Africa	0.2	
Peppers	Italy	0.1	
Rice	Italy	0.05	
	USA	0.1	based on DCBA
Sugar beet	Italy	0.05	

### APPRAISAL

Propiconazole was evaluated in 1987 and 1991. The 1991 JMPR required information on GAP and residue data from applications of the parent compound to barley and rice. In addition, residue data on melons, peppers and tomatoes from trials carried out according to GAP were considered desirable.

Current use patterns have been submitted for barley, cucurbits, grapes, peppers, rice, sugar beet and wheat. The manufacturer does not recommend use on melons or peppers.

New residue trials were carried out in countries where propiconazole is registered or which have similar climatic conditions to countries where the compound is in use. The application rates and the number of the sprays applied accorded well with the corresponding GAP.

The results of new supervised trials were considered together with those evaluated by previous Meetings.

The Meeting estimated the proportion of parent propiconazole in the total residue containing the dichlorophenyl moiety from the results of field trials and plant metabolism studies reported in the 1987 Evaluations. In supervised trials reported from Canada the parent compound amounted to 12-14.5% and 28-32% of the total residue expressed as the parent in wheat forage and grain respectively. In barley forage the parent compound amounted to about 8% of the total residue after 28 days. The proportion of the parent compound was 8-17% in peanut plants 14-49 days after application, and 21-23% in grapes after 30-63 days. The results indicate that the parent compound is present in the total residue in varying proportions depending on the number of applications and the time after application.

The residues of parent propiconazole in barley were at or about the limit of determination (0.02-0.03 mg/kg) after a PHI of 5 weeks in supervised trials from Canada (4 trials, 1990), France (9 trials, 1986-1991) and Germany (6 trials, 1986-87). No residues were detectable (<0.02 mg/kg) after pre-harvest intervals of 48 days and longer. Total residues based on the determination of dichlorobenzoic acid (DCBA) were between 0.07 and 0.12 mg/kg after 5 weeks, and decreased to 0.05 mg/kg after 7 and 9 weeks. In view of the rapid decline of residues in cereals and the average proportion of 30% of the parent compound in the total residue in wheat grain, the Meeting concluded that the one high value (0.11 mg/kg) from a GAP application rate reported in the 1987 Evaluations from a UK trial on barley could be disregarded. The residues expressed as the parent compound should not exceed 0.05 mg/kg in barley 35-40 days after application at the recommended rate of 0.125 kg ai/ha. The Meeting estimated a maximum residue level of 0.05 mg/kg.

In rice the compound is usually used about 36-40 days before harvest. No propiconazole (<0.02 mg/kg) or total (<0.05 mg/kg) residues were detectable in the ears after a pre-harvest interval of 7 weeks or longer. After shorter PHIs only total residues were measurable: 0.07-0.43 and <0.05-0.15 mg/kg after 5 and 6 weeks respectively.<sup>1</sup>

The Meeting also considered the parent residues (0.08, 0.14, 0.15 and 0.19 mg/kg) detected 5 weeks after the last application of 0.1 or 0.2 kg ai/ha in Indonesian rice trials (1987 Evaluations, p. 132). The results suggested a maximum residue level of 0.2 mg parent compound/kg in rice from applications in conformity with Malaysian use patterns. The results were supplemented by the total residues ranging from <0.05 to 0.4 mg/kg found in trials according to US GAP, when the parent residue was calculated from the total residues by applying a factor of 0.3. However, the Meeting concluded that the data were not sufficient to estimate a maximum residue level for a major commodity such as rice.

The residues of propiconazole in peppers were <0.02-0.27 mg/kg after a pre-harvest interval of 13-23 days. Since the compound is registered for peppers in only one country and no residues were available at the registered PHI, no maximum residue level could be estimated.

The residues in sugar beet leaves were recorded in the 1987 Evaluations were reconsidered. Residues in three leaf samples were 0.08, 0.33 and 0.34 mg/kg 14 days after application. As the trial conditions were in agreement with the current use patterns, the Meeting concluded that they supported a limit of 0.5 mg/kg for sugar beet leaves or tops.

Animal transfer studies, reported in the 1987 Evaluations, at feeding levels of 15-100 ppm for cows and 4.5 ppm for goats resulted in undetectable parent residues in milk and tissues (<0.05 mg/kg). After feeding cows for 14 days at 15 ppm the total residues were undetectable in milk and 0.63 mg/kg in kidney. Taking into account the average daily feed consumption of cows (15 kg dry weight) and goats (3 kg dry weight), a maximum of approximately 20% of beet tops in their feed and a conversion factor of 6.25 for wet/dry beet leaves or tops, the maximum daily beet top consumption is about 19 kg for cows and 3.8 kg for goats. Consequently the maximum residues (since the proposed MRL is 0.5 mg/kg) which might be consumed daily by cows and goats would be 9.5 mg and 1.9 mg respectively. Since the feeding studies were with higher residue levels, the proposed 0.5 mg/kg MRL for beat leaves and tops would not result in detectable residues in milk or meat.

Since there was no information on relevant GAP for artichokes and the data are insufficient for both cucumbers and artichokes, maximum residue levels cannot be estimated for these crops.

Analytical methods for determining the parent propiconazole and the total residues based on DCBA have been updated. They are suitable for regulatory purposes.

<sup>&</sup>lt;sup>1</sup>Shown incorrectly as 0.35-0.40, 0.07-0.10 and <0.05-0.15 mg/kg after 4, 5 and 6 weeks respectively in the report of the Meeting (p. 163)

## RECOMMENDATIONS

On the basis of data on residues from supervised trials the Meeting concluded that the residue levels listed below are suitable for establishing maximum residue limits.

Definition of the residue: propiconazole.

Commodity	Recommended	Recommended MRL (mg/kg)	
	New	Previous	
GC 0640 Barley	$0.05^{1}$	0.2 T	35
AV 0596 Sugar beet leaves or tops	0.5	0.1	14

<sup>1</sup> The limit is no longer temporary.

#### REFERENCES

1. Australia 1993. Information on compounds being on the priority list.

2. Blattmann P. 1980. Metabolism of CGA 64250 in grapevine Project Report 42/80, Ciba-Geigy Basle, November 14, 1980.

3. Ciba-Geigy Ltd, 1986, Barley France. Unpublished Report No. RR29/86.

4. Ciba-Geigy Ltd, 1986, Barley France. Unpublished Report No. RR31/86.

5. Ciba-Geigy Ltd, 1988, Barley France. Unpublished Report No. RR39/88.

6. Ciba-Geigy Ltd, 1989, Barley France. Unpublished Report No. RR32/89.

7. Ciba-Geigy Ltd, 1989, Barley France. Unpublished Report No. RR33/89.

8. Ciba-Geigy Ltd, 1989, Barley France. Unpublished Report No. RR34/89.

9. Ciba-Geigy Ltd, 1989, Barley France. Unpublished Report No. RR85/89.

10. Ciba-Geigy Ltd, 1991, Barley France. Unpublished Report No. RR028F/91.

11. Ciba-Geigy Ltd, 1986, Barley Germany. Unpublished Report Nos. RR2441/86, RR2442/86.

12. Ciba-Geigy Ltd, 1986, Barley Germany. Unpublished Report No. RR2443/86.

13. Ciba-Geigy Ltd, 1986, Barley Germany. Unpublished Report No. RR2444/86.

14. Ciba-Geigy Ltd, 1986, Barley Germany. Unpublished Report No. RR2445/86.

15. Ciba-Geigy Ltd, 1987, Barley Germany. Unpublished Report No. RR2223/87.

16. Ciba-Geigy Ltd, 1990, Barley Canada. Unpublished Report No. RR2097/90.

17. Ciba-Geigy Ltd, 1990, Barley Canada. Unpublished Report No. RR2099/90.

- 18. Ciba-Geigy Ltd, 1990, Barley Canada. Unpublished Report No. RR2100/90.
- 19. Ciba-Geigy Ltd, 1990, Barley Canada. Unpublished Report No. RR2102/90.
- 20. Ciba-Geigy Ltd, 1991, Rice Italy. Unpublished Report No. RR2077/91.
- 21. Ciba-Geigy Ltd, 1991, Rice Italy. Unpublished Report No. RR2078/91.
- 22. Ciba-Geigy Ltd, 1991, Rice Italy. Unpublished Report No. RR2083/91.
- 23. Ciba-Geigy Ltd, 1991, Rice Italy. Unpublished Report No. RR2084/91.
- 24. Ciba-Geigy Ltd, 1989, Rice USA Unpublished Report No. RRMW-FR-707-89.
- 25. Ciba-Geigy Ltd, 1989, Rice USA Unpublished Report No. RRMW-FR-708-89.
- 26. Ciba-Geigy Ltd, 1989, Rice USA Unpublished Report No. RRMW-FR-709-89.
- 27. Ciba-Geigy Ltd, 1981, Peppers Italy. Unpublished Report No. RR2222/81.
- 28. Ciba-Geigy Ltd, 1981, Peppers Spain. Unpublished Report No. RR2003/81.
- 29. Ciba-Geigy Ltd, 1981, Peppers Spain. Unpublished Report No. RR2004/81.
- 30. Ciba-Geigy Ltd, 1981, Peppers Spain. Unpublished Report No. RR2315/81.

31. Ciba France, 1990, Determination de CGA 64250 dans les endives, fraises, grains, pailles, Unpublished Report No. RES 13/90.

- 32. Ciba-Geigy Ltd, 1991, Wheat Canada, Unpublished Report No. RR2049/91.
- 33. Ciba-Geigy Ltd, 1991, Wheat Canada, Unpublished Report No. RR2050/91.
- 34. Ciba-Geigy Ltd, 1991, Wheat Canada, Unpublished Report No. RR2059/91.
- 35. Ciba-Geigy Ltd, 1991, Wheat Canada, Unpublished Report No. RR2060/91.
- 36. Ciba-Geigy Ltd, 1991, Barley Canada, Unpublished Report No. RR2051/91.

37. Blattman, P. 1980, Metabolism of CGA 64250 in grapevine. PR. 42/80, Ciba-Geigy, Basle..

38. Forrer, K. 1991. Propiconazole (CGA 64250), Gas chromatographic determination of residues of parent compound; plant material and soil Analytical Method REM 130.02, Ciba-Geigy Basle, Switzerland.

39. Madrid, S.O. and Cassidy, J.E. 1980. The uptake, distribution and characterization of triazole- and phenyl <sup>14</sup>C-CGA-64250 and their metabolites in greenhouse-grown peanuts Report ABR-80006, Ciba-Geigy Corp., USA.

40. Manule, P.J. and Toth, J. 1989. Determination of total residues of propiconazole in crops as 2,4-dichlorobenzoic acid by capillary gas chromatography Analytical Method AG-454B, Ciba-Geigy.

41. Spain 1993. Information on compounds being on the priority list.