Dissipation of Propiconazole and Tebuconazole in Peppermint Crops (*Mentha piperita* (Labiatae)) and Their Residues in Distilled Oils

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The broad-spectrum, systemic fungicides propiconazole (**1**) and tebuconazole (**2**) are used to control rust in peppermint (*Mentha piperita* L.). An analytical method, using gas chromatography combined with detection by high-resolution mass spectrometry, was developed to allow for the simultaneous monitoring of both pesticides in peppermint leaves and oil. Field trials were established to determine the rate of dissipation of tebuconazole and propiconazole in peppermint crops. Three applications of each fungicide were trialed at two rates (125 and 250 g of active ingredient (ai)/ha). At harvest, 64 days after the final application, propiconazole was detected at levels of 0.06 mg/kg and 0.09 mg/kg of dry weight, and tebuconazole was detected at 0.26 and 0.80 mg/kg dry weight, in identical trials. Rates of dissipation of propiconazole and tebuconazole were lower at a second trial site, where three applications of 125 g/ha ai for each fungicide resulted in residue levels of 0.21 mg/kg for both pesticides, detected 89 days after the last application. Propiconazole and tebuconazole were detected in the distilled oil at levels between 0.02 and 0.05 mg/kg and between 0.011 and 0.041 mg/kg, respectively. Propiconazole had a higher tendency to co-distill with the peppermint oil, with 0.7% of that present in the vegetative material ending up in the oil, compared to 0.09% of tebuconazole.

INTRODUCTION

Peppermint oil, distilled from the herb of the genus *Mentha*, is used in the food, confectionary, and cosmetic industries. Rust presents serious problems in commercial peppermint crops. The broad-spectrum, systemic fungicides "Tilt" (propiconazole, **1**) and "Folicur" (tebuconazole, **2**) are applied in spring before the dispersal and multiplication of the fungi urediospores.
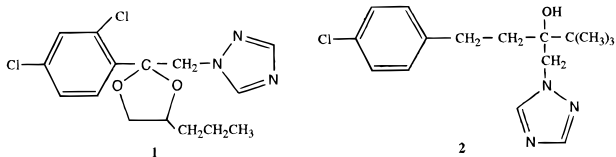
Typical of the triazole fungicides, both inhibit the biosynthesis of ergosterol. Temporary permits are issued by the National Registration Authority (NRA) for the use of the fungicides in Australia. To obtain registration, the number of days between application and harvest, required for residues to dissipate to an acceptable level, must be established to determine withholding periods prior to harvest. Quality control also requires that an acceptable maximum residue level (MRL) for the active ingredients (ai) be established for the distilled oil product, based on analytical detection limits and the anticipated average daily intake (ADI) of the essential oil.

Propiconazole and tebuconazole are used in a wide range of crops, including cereals, vegetables, nuts, and grapes, to control fungi such as powdery mildew, leaf spot, rust, and root rot. Analytical methods developed for propiconazole in water, soil, and fresh plant material (Büttler, 1983) detected residues on the order of 0.02–0.09 mg/kg in soil and grapes, respectively. Residue levels up to 0.70 mg/L of propiconazole in wine, 0.01 mg/L in must (Lopez et al., 1989), and 0.13 mg/kg in cucumbers (Lee et al., 1995) have been reported. The residue behavior of propiconazole in crops of wheat and vegetables has been investigated (Bai et al., 1995; Siebers et al., 1991; Singh et al., 1994). Propiconazole did not appreciably dissipate in boronia crops over the period of active growth and was detected in the matrix of boronia concrete at levels of 9.2 ppm (Groenewoud et al., 1995). Bioassays, based on inhibition of the spores of fungi on thin layer chromatographic (TLC) plates, have been used for the semiquantitative analysis of fungicides in crops (Balinova et al., 1995).

Residues of tebuconazole in plant material and soil were determined by gas chromatography (GC) using a thermionic nitrogen/phosphorus detector (TID) or mass selective detector (MSD) (Allmendinger, 1991). GC with detection using TID and MS was also used to establish that a decay rate of $t_{1/2}$ of 8 days for tebuconazole in grapes resulted in residue levels ranging from <0.05 to 0.22 mg/kg in the must and wine (Cabras et al., 1997a,b). In the present study, the method of Groene-

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woud et al. (1995), using gas chromatography/mass spectrometry (GCMS) with high-resolution selected ion monitoring (HRSIM), was modified to quantify both propiconazole and tebuconazole in peppermint leaf material and oil. No cleanup procedures were required. Detection limits were 8 and 20 μg/kg respectively for propiconazole and tebuconazole, relative to plant dry weight, and 20 and 50 μg/kg respectively in the distilled oil.

Although the persistence of residues of organophosphorus insecticides and fungicides in peppermint has been studied (Bélanger, 1989; Kiiegemagi et al., 1973; Inman et al., 1983), the fates of propiconazole and tebuconazole, applied to peppermint, have not been determined. Chlorinated pesticides have been reported to persist in the vegetative material of peppermint and have co-distilled with the oil during steam distillation (Gould, 1960; Starr et al., 1963; Ballee et al., 1970).

The level of residues in the peppermint oil is related to the propensity of the chemical to be carried across during steam distillation. Since peppermint yields approximately 0.3% (w/w) of oil from fresh leaves, there is a potential for a 300-fold increase in pesticide concentration in the oil if all of the pesticide residues were to co-distill with the peppermint oil. However, previous studies have found that, for some chlorinated pesticides, the amount of pesticide distilling with the oil is only slightly related to that present on the hay (Gould, 1960).

Experiments were conducted to determine the rates of dissipation of propiconazole and tebuconazole during the growth of the peppermint crops and to analyze for residues in the distilled oils.

EXPERIMENTAL PROCEDURES

Field Design and Treatments. Field trials were designed to meet the specifications set by the NRA for residue trials (National Registration Authority, Crop Residue Trials, 1995). The data generated are to be presented to that body to support the extension of the registration of Tilt and Folicur for usage in peppermint crops.

Two commercial peppermint crops in Tasmania were selected. The plot size for each treatment was 36 m². Each plot was separated by a 1 m buffer zone. At site 1, three replicates of each application rate of 500 and 1000 mL/ha of the commercial product, "Tilt EC 250" (propiconazole, 250 g/L) and "Folicur 250 EW" (tebuconazole, 250 g/L) were applied in a randomized block layout. At site 2, rates of 500 mL/ha for both Folicur and Tilt were applied on each of three replicates for each treatment. To ensure no reinfection with rust spores occurred, all areas of the commercial peppermint farms required the application of systemic fungicides. Therefore at each site, control plots for propiconazole were sprayed with the 500 mL/ha Folicur, while plots treated with 500 mL of Tilt provided controls for tebuconazole. Pesticide applications were repeated a further 2 times at approximately 2 week intervals. The equivalent of 92 mL/ha of "Topwet" (commercial product of "Schering"), a nonionic surfactant, was added to each formulation. Pesticides were applied with a Buchmester backpack attached to a Matabi 1.4 m boon with a four nozzle cone spray.

Samples were collected by harvesting a 1 m quadrat, randomly selected, from each plot. Sampling occurred immediately before and 2 h after each application and then at 1, 4, 14, 33, and 64 days after the last application. Samples were weighed before subsampling. The remaining material was reweighed before and after a drying period of 72 h at 35 °C and at constant humidity. At final harvest, the peppermint collected from each quadrat was steam distilled in acid washed, glass apparatus to produce the peppermint essential oil. The

Table 1. Recoveries of Fungicides in Peppermint Leaves

fungicide	fortification level, mg/kg	% recovery ± SD ($n = 4$)
propiconazole	0.2	87.5 ± 9
	4	83.6 ± 3
	20	87.1 ± 3
	100	83.8 ± 3
tebuconazole	0.2	85.1 ± 2
	4	88.6 ± 0.7
	20	82.1 ± 5
	100	76.1 ± 0.6

distillation was carried out for 1 h in a liquid/liquid, light over heavy extractor, with an Allihn sidearm condensor. The mean wet weight of leaf distilled from site 1 was 1.2 kg, yielding 0.21% (SD ±0.02) oil. A mean of 0.78 kg of leaf distilled from site 2 produced a 0.30% (SD ±0.03) oil yield.

Chemicals. Analytical grade propiconazole (99%) was supplied by Ciba-Geigy, Victoria (Australia). Tebuconazole (99.6%) was obtained from Bayer. *n*-Octadecane (99%) was purchased from Sigma Chemical Co. (St. Louis, MO). Methanol was from Mallinckrodt and of ChromAR HPLC grade.

Standard Solution Preparation. A 11.3 mg sample of propiconazole and a 10.6 mg sample of tebuconazole were dissolved in methanol and made up to 100 mL. This resulted in a 100 μg/mL stock solution from which 10, 1, and 0.1 μg/mL working standard solutions were prepared by volumetric serial dilution.

Extraction Procedure. A 5 g sample of the vegetative material from field samples was homogenized with 3×10 s bursts of an ultraturrax and extracted in 25 mL of methanol. The samples were sonicated for 15 min and then placed on a shaker bath for 45 min at 150 cpm. A 1 mL aliquot of the extracts was transferred, quantitatively, to GC vials and spiked with 25 μL of a 222 μg/mL solution of octadecane. One plant sample was subsampled 5 times to obtain a measure of variability within samples.

At harvest, and after the vegetative material had been subsampled, the remaining leaves were steam distilled in a glass distillation apparatus, previously washed in chromic acid. Approximately 20 mg of each oil was dissolved in 1 mL of methanol and spiked with 25 μL of a 222 μg/mL solution of octadecane before analysis.

Calibration Curves. The standard solutions were used to fortify 1 mL extracts of peppermint leaf, which had not been treated with the target pesticide, to establish standard curves. A 25 μL aliquot of a 222 μg/mL solution of octadecane was added as an internal standard. Samples were analyzed over 7 separate analyses days. The concentrations for the calibration curves ranged from the equivalent of 0.2−200 mg/kg for the analyses of samples collected within 32 days after the first application of pesticides down to 0.008−4 mg/kg for the analyses of samples collected close to the harvest date. Samples which had levels of residues above the upper range were diluted with methanol and reanalyzed.

Recoveries in Fortified Samples. Samples of peppermint leaf, known to be free of the target analyte, were spiked with 0.2, 4, 20, and 110 mg/kg dry weight of the respective pesticide. Recoveries are listed in Table 1. Concentration levels of the fungicides did not substantially affect their corresponding recoveries in the assayed concentration range.

On each day of analyses five samples of peppermint leaf, known to be free of propiconazole and tebuconazole, were spiked with 1.413 and 1.056 μg of standards of each active ingredient, respectively. Extractions were performed as described for field samples. These recoveries were used to account for any factors specific to each day of analyses, such as variation in the relative volume subsampled due to sampling technique and water content in the peppermint leaf. The mean recovery rates were between 67 and 107% for propiconazole and between 62 and 95% for tebuconazole. Standard deviations (SD) from the mean recovery did not exceed 3% on any 1 day of the analyses.

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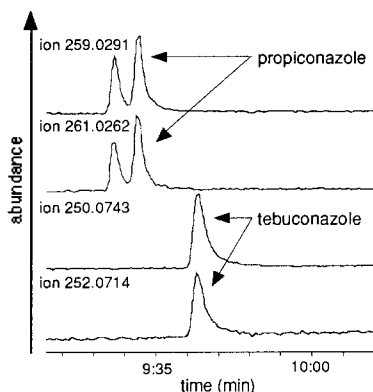
Figure 1. GCMS HR SIM chromatogram of fragment ions of propiconazole and tebuconazole.

Apparatus and Chromatography. Samples were analyzed on a HP 5890 gas chromatograph directly coupled to a Kratos Concept ISQ mass spectrometer. The GC was equipped with a BP1 fused silica capillary column (25 m, 0.22 mm i.d., 0.25 μm film thickness).

GCMS Analysis by HRSIM. The mass spectrum of propiconazole (**1**) has been previously reported (Groenewoud et al., 1995). The mass spectrum of tebuconazole (**2**) gave the following m/z (rel intens): 307 [M$^+$] (23), 252 (33) 250 (100), 163 (10), 127 (10), 125 (30), 83 (33), 70 (29), 57 (11).

Splitless injections of 1 L each of samples were analyzed using a carrier gas flow program of 30 psi/min from 25 to 40 psi and were held for 0.1 min, then at 30 psi/min to 25 psi, then at 1 psi/min to 35 psi. The GC injection temperature was 260 °C, and the oven temperature was programmed from 60 to 290 °C at 20 °C/min. The ions of highest abundance were not necessarily selected for monitoring because matrix components, with equivalent m/z, sometimes have the same retention time as the target molecular fragment. Ions monitored by SIM were m/z 259.0291 ($C_{12}H_{13}Cl_2O_2$), and 261.0262 for propiconazole, m/z 250.0743 ($C_{12}H_{13}ClN_3O$) and 252.0714 for tebuconazole, and m/z 254.2973 ($C_{18}H_{38}$) for the C_{18} internal standard. A dwell time of 300 ms/ion and a 50 ppm voltage sweep were employed for all ions. Resolution was 10 000 (10% valley definition), and the ion at m/z 242.9856 from perfluorokerosene was used as the lock mass for both analytes and the internal standard. Electron ionization was undertaken at a source temperature of 210 °C and an electron energy of 70 eV, with an accelerating voltage of 5.3 kV. The two diastereomers of propiconazole, the mass spectra of which are essentially indistinguishable, were both monitored, and their areas were summed for quantification calculations. A representative chromatogram, at the 0.5 mg/kg level, is presented in Figure 1.

RESULTS AND DISCUSSION

The standard curves of {peak area propiconazole (m/z 259):peak area C_{18}(m/z 254)} vs the concentration of propiconazole (μg/mL) and {peak area tebuconazole (m/z 250):peak area C_{18}(m/z 254)} vs the concentration of tebuconazole (μg/mL) were reestablished on each of the 7 days of the analyses and gave a mean correlation coefficient of 0.991 (SD ±0.012) and 0.992 (SD ±0.014) for propiconazole and tebuconazole, respectively. The range of concentrations under which calibration curves were obtained did not affect their corresponding correlation coefficient.

Tables 2 and 3 list the amount of propiconazole and tebuconazole residues, respectively, detected in the peppermint leaves, at specified days after the first treatment, for sites 1 and 2. All results have been corrected for percentage recoveries.
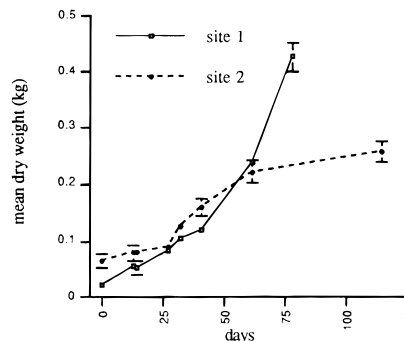
Figure 2. Dry weights of 1 m^2 quadrats of peppermint collected over 16 weeks, from time of first application, at sites 1 and 2.
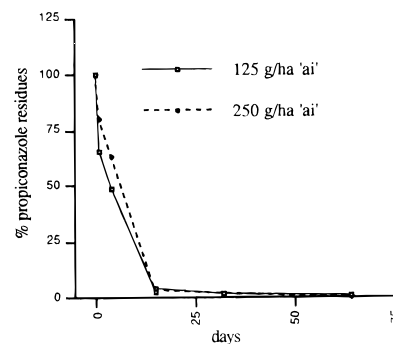
Figure 3. Percentage of propiconzole remaining after final applications.

To account for the dilution of pesticides by plant growth, all the 1 m^2 samples were weighed on the day of collection. The growth rate at sites 1 and 2 were markedly different, as illustrated in Figure 2.

Correction factors were calculated from the results illustrated in Figure 2 and were applied to adjust the residue concentrations listed in Tables 2 and 3, thereby eliminating the effects of growth dilution on residual pesticide concentration. The residues determined at each sampling time, corrected for growth dilution, can then be expressed as a percent relative to the amount detected at the time of the most recent application.

$$\% \text{ pesticide remaining} = \frac{\text{mg/kg of ai at specific time}}{\text{mg/kg at time of most recent application}} \times 100$$

The percentages of propiconazole remaining at various samping times at site 1 are plotted in Figure 3. Two distinct rates of decrease in propiconazole are evident over the course of the experiment, both of which can best be described by linear relationships between the percent of pesticide remaining and time

$$\% \text{ pesticide residue remaining} = (\text{rate of disappearance}) \times \text{days} + C$$

where C is a constant.

Propiconazole concentration decreases most rapidly over the first 2 weeks after application, as described by the slope of the graph illustrated in Figure 3, between 0 and 15 days. After 15 days, and up until harvest, the rate decreases by a factor of approximately 100. Table 4 lists the slopes for the two distinct sections, within each graph, of the percentage of propiconazole and tebucoanzole residues remaining at sites 1 and 2 over time.

Table 2. Residues of Propiconazole (mg/kg) in Peppermint at Sites 1 and 2

| | | | residues of propiconazole detected (mg/kg dry weight) | | | |
| | | | site 1 | | site 2 | |
events	n	days	125 g ai/ha mean ± SE	250 g ai/ha mean ± SE	days	125 g ai/ha mean ± SE
application 1	3	0	51 ± 10	62 ± 21	0	48 ± 8
	3	17	0.45 ± 0.02	0.51 ± 0.06	14	1.9 ± 0.5
application 2	3	17	83 ± 17	168 ± 12	14	56 ± 5
	3	32	1.6 ± 0.2	3.9 ± 0.5	24	1.9 ± 0.5
application 3	3	32	52 ± 4	90 ± 6	24	41 ± 8
	3	33	37 ± 5	79 ± 4	25	33 ± 5
	3	36	22 ± 2	49 ± 6	28	23.1 ± 0.6
	3	45	1.31 ± 0.04	2.1 ± 0.5	38	1.9 ± 0.2
	3	64	0.31 ± 0.06	0.6 ± 0.1	47	0.7 ± 0.3
	3	96	0.06 ± 0.02	0.09 ± 0.07	113	0.2 ± 0.1

Table 3. Residues of Tebuconazole (mg/kg) in Peppermint at Sites 1 and 2

| | | | residues of tebuconazole detected (mg/kg dry weight) | | | |
| | | | site 1 | | site 2 | |
events	n	days	125 g ai/ha mean ± SE	250 g ai/ha mean ± SE	days	125 g ai/ha mean ± SE
application 1	3	0	54 ± 16	55 ± 14	0	31 ± 4
	3	17	1.9 ± 0.5	4 ± 2	14	3 ± 1
application 2	3	17	a	268 ± 69	14	43 ± 17
	3	32	1.21 ± 0.06	11 ± 4	24	2.4 ± 0.3
application 3	3	32	38 ± 4	142 ± 42	24	30 ± 10
	3	33	17 ± 3	65 ± 4	25	27 ± 3
	3	36	28 ± 10	45 ± 9	28	21 ± 6
	3	45	4 ± 1	4.9 ± 0.4	38	1.71 ± 0.06
	3	64	0.26 ± 0.04	1.3 ± 0.3	47	1.5 ± 0.2
	3	96	0.26 ± 0.09	0.8 ± 0.2	113	0.2 ± 0.1

[a] Samples lost during storage.

Table 4. Rates of Decrease in Propiconazole and Tebuconazole Residues Remaining over Time As Described by the Slopes of the Graph of Percent Residue Remaining vs Days

| | residues detected (mg/kg) | | | | | |
| | 0−15 days | | | 15 days to harvest | | |
rate applied (g of ai)	slope	constant	r^2 value	slope	constant	r^2 value
			Propiconazole			
site 1, 125 g ai/ha	−6.04	90.02	0.918	−0.058	4.17	0.895
site 1, 250 g ai/ha	−6.28	95.48	0.992	−0.056	4.06	0.973
site 2, 125 g ai/ha	−6.66	96.97	0.992	−0.067	6.77	0.756
			Tebuconazole			
site 1, 125 g ai/ha	−6.06	102.48	0.989	−0.20	14.84	0.45
site 1, 250 g ai/ha	−5.90	85.24	0.743	−0.03	4.88	0.36
site 2, 125 g ai/ha	−6.44	100.82	0.990	−0.11	11.60	0.95

Over the first 2 weeks the linear relationship between the percent of tebuconazole remaining and the time after the last application is well-supported by the low r^2 values associated with the model. However, at site 1 the second rate of disappearance of tebuconazole, after that period, does not fit the linear model described, such that a second constant rate of dissipation is not reached within 15 days. However, for both fungicides, a similar, two phase pattern of residue dissipation is evident.

What factors have contributed to the dissipation of propiconazole and tebuconazole? Only light rain was recorded at both sites over the periods of the first two applications. Irrigation and rain contributed a total of 60 and 78 mm of water at sites 1 and 2, respectively, after the final application of pesticides. Yet the rate of decrease remained high and relatively constant. This would suggest that the interactive effects of leaf surface, temperature, humidity, and sunlight are sufficient to effect a dramatic decrease in pesticide residues within the first 2 weeks.

For 15 days after the final application of fungicides, up until harvest, the slower rate of dissipation, detailed in Table 4, may relate to the systemic properties of propiconazole and tebuconazole. Up until that period, exposure to the weather may have completely removed residual pesticides from the leaf surfaces. Thereafter, the active ingredients remaining, which have been adsorbed into the leaf matrix, may be subject to a second combination of effects, such as metabolism and catabolism. It is these factors which may predominate to determine the second rate of disappearance of the pesticide residues over the remainder of the growing season.

Peppermint oils, produced from the steam distillation of samples from the final harvest, were analyzed for pesticide residues. The results, presented in Table 5, were used to calculate the percentage of residue which was carried over into the oil, relative to the levels detected in the peppermint before distillation. The amounts of 0.7% (SE ±0.1) propiconazole and 0.09% (SE ±0.02) tebuconazole were found to distill with the oil. As observed by Gould (1960) for dieldrin, aldrin, DDT, and dibrom in peppermint oil, the relationship between volatility and steam distillability is as expected. The

Table 5. Levels of Propiconazole and Tebuconazole Residues in Peppermint Oil

application rate	n	propiconazole, mg/kg mean ± SE	tebuconazole, mg/kg mean ± SE
site 1, 125 g ai/ha	3	0.017 ± 0.006	0.011 ± 0.001
site 1, 250 g ai/ha	3	0.039 ± 0.005	0.053 ± 0.008
site 2, 125 g ai/ha	3	0.029 ± 0.009	0.021 ± 0.005

percentage of propiconazole (vapor pressure $< 3 \times 10^{-6}$ mmHg at 20 °C) which co-distilled with the oil was higher than that recorded for tebuconazole (vapor pressure 0.01×10^{-6} mmHg at 20 °C). Also, as observed by Gould (1960), the amount of pesticide distilling with the oil was only poorly correlated to that present on the peppermint vegetative material.

Australian Food Standards Code (standard A14 schedule 1) specifies MRLs for propiconazole residues ranging from 0.01 to 2 mg/kg, depending on the product and its anticipated ADI, and 0.05 mg/kg of tebuconazole in barley and wheat. All relate to whole food products. The MRLs of propiconazole and tebuconazole in peppermint have not been set. However, the average daily intake anticipated for the flavor component, peppermint oil, is low. The levels of residues detected in the peppermint oil is well within the range set for propiconazole in food products and below the levels set for tebuconazole in barley and wheat. On the basis of these results, pesticide contamination in peppermint oil should not pose a significant risk to consumers, providing growers adhere to the recommended application rate of 125 g ai/ha.

ABBREVIATIONS USED

ai, active ingredient; NRA, National Registration Authority; MRL, maximim residue limit; ADI, average daily intake; TLC, thin layer chromatography; TID, thermionic nitrogen/phosphorus detectorl GC, gas chromatography; MSD, mass selective detector; GCMS, gas chromatography mass spectrometry; HRSIM, high-resolution selected ion monitoring; SD, standard deviation.

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