Persistence and Metabolism of Folpet in Grapes and Wine

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The fate of folpet from the treatment on vine to the production of wine was studied. Sunlight degraded folpet to unknown products. Phthalimide was a minor metabolite formed on grapes from folpet. Folpet degraded in must, giving 80% phthalimide; the results obtained with model solutions showed that in must folpet can also give small amounts of phthalic acid. During wine-making folpet degraded completely, and at the end of fermentation phthalimide was only present in wine. This compound was stable in wine after several months. The presence of folpet in grapes inhibited the alcoholic fermentation of *Saccharomyces cerevisiae* and *Kloeckera apiculata* completely. Phthalimide, on the contrary, had no negative effect on the fermentative action of the two yeasts. GC and HPLC methods were developed to determine folpet and its metabolites.

Keywords: *Folpet; metabolites; residues; grapes; wine*

INTRODUCTION

Folpet, a contact fungicide belonging to the phthalimide family, has protective action against downy mildew (*Plasmopara viticola)*, powdery mildew *(Uncinula necator*), and gray mold (*Botrytis cinerea*) (Tomlin, 1994). The metabolic pathway in animals (Figure 1; FAO/WHO, 1970) is through the hydrolysis of folpet with cleavage of the sulfur−nitrogen bond to give phthalimide, which is hydrolyzed to phthalic acid. The metabolic pathway in plants is not described in the literature; nevertheless, it is reported to be the same as in animals (Tomlin, 1994). Studies on this pesticide are limited only to the active ingredients (AI). The degradative behavior of folpet in grapes and wine is reported in some recent reviews (Cabras et al., 1987; Zironi et al., 1991; Farris et al., 1992). The fact that the metabolism of folpet has never been studied could be due to the shortage of analytical methods for its determination. This work was aimed at contributing to the knowledge of the metabolic pathway of folpet in grapes and of the fate of the AI and its metabolites and/or degradation products during wine-making. The analytical methods and microbiological effects of folpet and its metabolites and/or degradation products are also studied.

EXPERIMENTAL PROCEDURES

Materials and Methods. The trial was carried out in a white grape vineyard (cv. Nuragus), located at Ussana, near Cagliari, Italy. A random-block scheme was used, with four replications for each test, and each block contained 100 plants. Treatment was carried out on September 14, 1995; Dipet (42.5% folpet) was a commercial formulation applied at the dose recommended by the manufacturer (250 g/hL; 6 hL/ha) with an F-320 portable motor sprayer (Fox Motori, Reggio Emilia, Italy). Samplings (on dry plants) started about 1 h after treatment: random 5-kg samples of grapes were collected from each plot and immediately analyzed for fungicide residues. The samplings and analyses were repeated weekly. The environmental conditions were continuously recorded with an AD-2 automatic weather station (Silimet, Modena, Italy). During the experiments it did not rain, and the maximum and minimum average temperatures were, respectively, 32.2 and 16.7 °C.

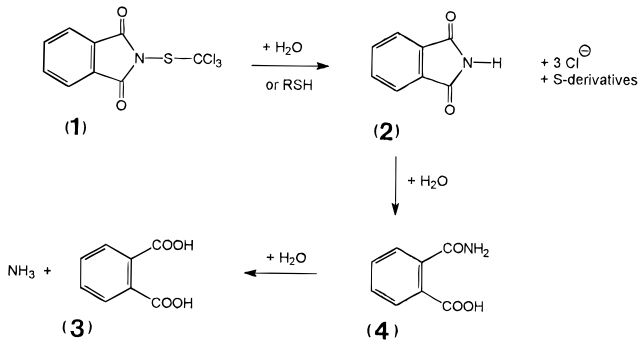

Figure 1. Folpet (**1**) and its metabolites: phthalimide (**2**), phthalic acid (**3**), and phthalamic acid (**4**).

Wine-Making. The wine-making scheme described in a previous paper (Cabras et al., 1995) was used. Briefly, all four grape samples per AI (*ca*. 20 kg) were pressed and stemmed together; 200 mg of sodium metabisulfite was added, and the mixed sample was divided into two equal parts. One part was allowed to ferment with the skins (vinification with maceration); the other was dripped and the resulting must was left to ferment (vinification without maceration). A 100-g aliquot of cloudy must was taken and centrifuged at 4000 rpm for 5 min to evaluate the amount of lees and the residue concentration in the clear must. To each sample was added 500 mg of dry yeast/kg of grapes. Fermentation had a regular course in all samples, and after 15 days the obtained wines were filtered and analyzed for fungicide residues.

Wine Clarification. Clarification tests were carried out on 1-L samples of residue-free assessed wine. The clarifying agents and the doses employed (usually applied in oenological practice) were as follows: 100 g/hL of bentonite (Dal Cin, Milano, Italy); 20 g/hL of charcoal (AEB, Brescia, Italy); 100 g/hL of potassium caseinate (Marescalchi, Alessandria, Italy); 80 g/hL of polyvinylpolypyrrolidone (Fluka, Milano, Italy). Two days after clarifying treatment, the clear wine and the control

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samples (without clarification) were analyzed for fungicide residues. Each clarification test was performed with four replications.

Chemicals. The pesticides were all analytical standards. Folpet and vinclozolin were purchased from Ehrenstorfer (Augsburg, Germany), and phthalimide, phthalic acid, and phthalamic acid were from Lancaster Synthesis (Muhlheim am Main, Germany) . Acetone and methanol were HPLC grade solvents (Carlo Erba), while petroleum ether (Carlo Erba) was a special reagent for pesticide determination. Anhydrous sodium metabisulfite and sodium sulfate were of analytical grade (Carlo Erba).

Stock standard solutions (*ca*. 300 ppm each) were prepared in methanol for folpet and phthalimide and in acetonitrile for phthalic and phthalamic acid. Working standard solutions were obtained by dilution with the extraction solution for GC determinations and with the mobile phase for HPLC determinations

Residue Analysis. *Gas Chromatographic Determination*. An HRGC Mega 5160 (Carlo Erba, Milano, Italy) gas chromatograph was employed, fitted with an ECD 400 detector, an AS 800 autosampler (Carlo Erba), and a split−splitless injector, connected to an HP 3396-II reporting integrator (Hewlett-Packard, Avondale, PA). A Durabond fused silica column (30 m × 0.32 mm i.d.) (J&W Scientific, Folsom, CA) was employed, with a DB 5 MS liquid phase (film thickness 0.25 μm). The injector and detector were operated at 250 and 320 °C, respectively. The sample (2 μL) was injected in the split mode (1:10), and the oven temperature was programmed as follows: 150 °C for 1 min, raised to 240 °C (5 °C/min), and held for 5 min. Helium was the carrier and make-up gas at 100 and 130 kPa, respectively. Calibration graphs for folpet and phthalimide were constructed with the internal standard (i.s.) method by measuring peak heights *vs* concentrations. Good linearities were achieved in the range 0−5 ppm, with correlation coefficients between 0.9994 and 0.9997.

HPLC Determination. An HP Model 1050 liquid chromatograph (Hewlett-Packard) was used, consisting of a pump, an autosampler with a 100-μL loop, and a variable-wavelength UV−vis detector. A Spherisorb S_5 C_8 column (250 × 4.6 mm i.d., 5 μm) (Phase Separations, Waddinxveen, The Netherlands) was employed. The gradient run used at the flow rate of 1 mL/min was as follows: 10% acetonitrile/90% H_2SO_4 10^{-3} N at time 0, 50% acetonitrile/50% H_2SO_4 10^{-3} N at time 10 min, 90% acetonitrile/10% H_2SO_4 10^{-3} N at time 15 min, held for 5 min and equilibrated at initial conditions for 10 min. The wavelengths were 200 nm at time 0, 215 nm at time 8.5 min, and 224 nm at time 12.5 min. Quantitative determinations were performed according to the external standard method by measuring peak heights *vs* concentrations. Good linearities were achieved in the range 0−5 ppm, with correlation coefficients between 0.9997 and 0.9999.

Extraction Procedure. A 10-g aliquot of grapes or 5 mL of must and wine was weighed in a 30-mL screw-capped flask; 4 g of NaCl and 10 mL of acetone/petroleum ether (50:50 v/v) containing vinclozolin at 0.6 ppm as the i.s. were added, and the tube was agitated in a rotary stirrer for 15 min. The phases were allowed to separate, and the organic layer was poured into another screw-capped tube containing 1 g of anhydrous sodium sulfate and injected for GC analysis.

Recovery Assays. Untreated grape, must, and wine samples were fortified with folpet and phthalimide and processed according to the above-described procedure. Recovery assays, carried out at 0.01, 0.50, and 3.00 ppm, showed values obtained from four replicates ranging between 93 and 101%, with a maximum coefficient of variation (CV) of 11.

Sunlight Photodegradation Test. Two-milliliter portions of 3 ppm folpet solutions in acetone were poured into 5 mL vials (i.d. = 1 cm) and evaporated under nitrogen stream at ambient temperature. The same was done for phthalimide and phthalamic and phthalic acids at 3 ppm. The screw-capped vials were then exposed to direct sunlight. At weekly intervals the vials were removed from the sunlight and stored at −25 °C until analyzed. The residue contained in the vial was dissolved with 2 mL of mobile phase (H_2O/CH_3CN 90:10 v/v) and injected for HPLC analysis. The test was carried out in triplicate; the ambient temperature ranged between 22 and 35 °C. Control samples were stored in the dark at room temperature and analyzed at the beginning and end of the test. Chromatographic analyses of control samples showed no degradation.

Folpet Analysis in Treatment Mixture. The treatment mixture was prepared with the commercial formulation Dipet at the dose recommended by the manufacturer (2.5 g/L). A 200-μL aliquot of this mixture was dissolved with acetone in a 10-mL flask. A 500-μL aliquot of this solution was diluted at 10 mL with the extraction solution and analyzed by GC.

Culture Media. Broth was made with 70 g/L yeast extract nitrogen base and 180 g/L glucose (YNBG) at pH 3.6. Each pesticide was dissolved in ethanol (5 mL) and added to 1 L of YNBG broth. Folpet at 4.1 and 2.0 ppm and phthalimide at 1.74 and 0.8 ppm were used. All media were sterilized by filtration through 0.22-μm membrane filters (Millipore).

Inoculation and Fermentation. The yeasts were *Saccharomyces cerevisiae* strain VER 1 and *Kloeckera apiculata* strain MON 2 from the collection of the Dipartimento di Scienze Ambientali Agrarie e Biotecnologie Agroalimentari, Università di Sassari, Italy. Precultures were prepared in GYEP substrate (2% glucose, 0.5% yeast extract, and 1% peptone) and agitated in a rotary shaker at 120 rpm for 48 h. The cells were then washed twice and suspended in 0.15 M NaCl. The amounts of the suspensions used as inocula were such to ensure 5×10^{-4} and 5×10^{6} cells/mL in each of the culture media. After inoculation, the culture media of each strain and each pesticide were apportioned into three 150-mL replications in 500-mL flasks. Two different controls were prepared, consisting respectively of 150 mL of each culture medium without inoculum (YNBG plus pesticide) to check pesticide chemical degradation, and inoculated (YNBG broth without pesticide) to check fermentation. Each experiment was carried out in triplicate. All flasks were rotary agitated in a thermostatically controlled chamber at 20 °C for 11 days.

Three samplings were carried out 0, 4, and 11 days after inoculation. The following analyses were made: pH, yeast cells per milliliter (microscopic count and cultural count), and CO_2 production (indirect weighing). Data were processed by a statistical package for analysis of variance.

RESULTS AND DISCUSSION

GC and HPLC methods for the determination of folpet and its metabolites were developed. The GC method was used to determine folpet and phthalimide in grapes, must, and wine (Figure 2a). The HPLC method was used to study folpet degradation in model solutions and when exposed to direct sunlight (Figure 2b).

Since the rapid degradation of folpet in water depends on its pH, and at pH 7 a half-time of 1.1 h was reported (Paster , 1992), we first studied the stability of folpet in the treatment mixture (pH 7.35) at the rate recommended by the manufacturer (2.5 g/L commercial formulation). The data reported in Table 1 showed that folpet degraded by a first-order kinetics ($r = -0.988$) and with a half-time ($t_{1/2}$) of 12 h. Phthalimide was present as *ca*. 3% of folpet and remained unchanged during the experiment. The obtained kinetic data did not agree with those reported by Wolfe et al. (1976) and Paster (1992), who respectively determined $t_{1/2}$ values of 1.4 and 1.1 h in water at pH 7. These decay rates were determined using only the active ingredient, while in our study the commercial formulation was used. The different rate could therefore be ascribed to the influence of the other ingredients in the formulation.

Residue in Grapes. After treatment, folpet and phthalimide residues were found in grapes (Table 2). The small amount of phthalimide in the treatment solution did not explain the determined residue (on average 0.56 mg/kg). Since the residues were analyzed a few hours after pressing, we supposed that they could be due to the degradative action of must (pH 3.3). To

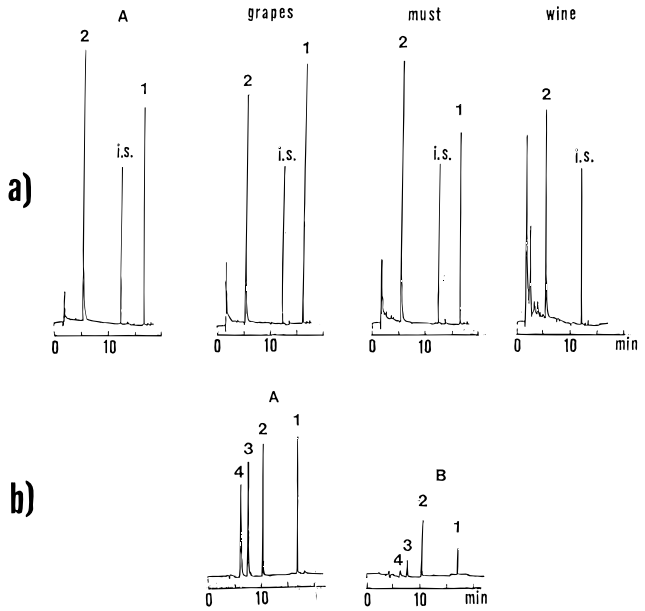

Figure 2. Chromatography of folpet (1) and its metabolites (**2**−**4**): **(a)** GC determination, standard solution (A, 1 = 1.6 ppm, 2 = 0.9 ppm), grapes, must, and wine samples; **(b)** HPLC determination, standard solution (A, concentration range 2.0−2.5 ppm; B, aqueous solution at pH 3). The operating conditions are reported under Experimental Procedures.

Table 1. Degradation of Folpet in the Treatment Mixture

time (h)	folpet (g/L)	phthalimide (g/L)
0	1.16 ± 0.08	0.03 ± 0.01
2	1.02 ± 0.02	0.03 ± 0.00
4	0.97 ± 0.10	0.03 ± 0.01
7	0.79 ± 0.15	0.03 ± 0.01

Table 2. Residues (Parts per Million ± SD) of Folpet and Phthalimide in Grapes, Must, and Wine

					wine	
pesticide	days after treatment	grapes	must	centrifuged must	without maceration	with maceration
folpet	0	2.83 ± 0.34	2.53	<0.01	<0.01	<0.01
phthalimide		0.56 ± 0.14	0.98	0.90	2.24	1.91
folpet	7	2.42 ± 0.59	2.42	<0.01	<0.01	<0.01
phthalimide		0.44 ± 0.28	0.77	0.52	1.94	1.82
folpet	14	1.79 ± 0.30	1.74	<0.01	<0.01	<0.01
phthalimide		0.46 ±0.09	0.60	0.35	1.32	1.23
folpet	21	1.73 ± 0.20	1.64	<0.01	<0.01	<0.01
phthalimide		0.71 ± 0.10	0.60	0.48	1.23	1.03
folpet	28	1.08 ± 0.28	1.11	<0.01	<0.01	<0.01
phthalimide		0.41 ± 0.20	0.38	0.11	0.98	0.74

verify this hypothesis, we added a known quantity of folpet to the untreated sample to study its degradative kinetics. The data reported in Table 3 showed that folpet degraded rapidly ($t_{1/2}$ = 18 h), yielding mainly phthalimide. After 9 h, phthalimide represented 85% of degraded folpet.

Having established that phthalimide residues were formed in must, we peformed extraction in the other samples immediately after pressing. Resuming the discussion on the degradation of folpet in grapes (Table 2), this showed a first-order kinetics ($r = -0.95$) with a half-time of 18 days. In calculating $t_{1/2}$ we did not include the residue at time zero for the above reasons. Phthalimide was found on the grapes in a concentration of *ca*. 0.5 ppm, which was steady in time during the experiments. Since the decrease in folpet was not completely balanced by the formation of phthalimide,

Table 3. Degradation of Folpet and Phthalimide (Parts per Million ± SD) in Grapes after Pressing

time (h)	folpet	formed phthalimide	phthalimide
0	3.14 ± 0.26	0	2.75 ± 0.01
2	2.76 ± 0.08	0.19 ± 0.03	2.60 ± 0.05
3	2.37 ± 0.05	0.34 ± 0.06	2.57 ± 0.08
6	2.30 ± 0.04	0.38 ± 0.09	2.49 ± 0,03
9.3	2.04 ± 0.06	0.46 ± 0.02	2.07 ± 0.03
22.5	1.96 ± 0.06	0.50 ± 0.03	2.11 ± 0.05

Table 4. Degradation of Folpet in Aqueous Solution at pH 3

time (days)	folpet	phthalimide	phthalamic acid	phthalic acid	total residues as folpet
0	2.82 ± 0.10				2.82 ± 0.10
1	0.35 ± 0.06	0.97 ± 0.04	0.18 ± 0.04	0.06 ± 0.00	2.73 ± 0.08
2	0.15 ± 0.01	1.08 ± 0.04	0.17± 0.00	0.11 ± 0.00	2.85 ± 0.08
3	nd[a]	1.07 ± 0.05	nd	0.17 ± 0.00	2.50 ± 0,10
4	nd	1.02 ± 0.06	nd	0.18 ± 0.02	2.41 ± 0.12
5	nd	1.05 ± 0.04	nd	0.15 ± 0.01	2.42 ± 0.08
6	nd	1.03 ± 0.06	nd	0.15 ± 0.01	2.34 ± 0.12
7	nd	1.03 ± 0.05	nd	0.16 ± 0.01	2.36 ± 0.10

[a] nd, not detectable.

we can assume that folpet also gave other compounds, which could not be determined with the analytical method used. To verify whether the degradation of folpet in must could be due to acidity, we studied its degradation in a model solution made up of an aqueous solution at pH 3 (H_2SO_4 10^{-3} N). The data in Table 4 showed that folpet degraded with a pseudo-first-order kinetics ($r = -0.97$) and a half-time of 10.5 h, yielding phthalimide, phthalamic acid, and phthalic acid. Phthalimide represented 80% of the degraded folpet and remained unchanged during the experiment. Phthalamic acid increased up to 12% of degraded folpet and disappeared when all of the folpet was degraded. Phthalic acid was 4% initially; while folpet degraded, it increased up to 10% of the degraded folpet and remained unchanged when no folpet or phthalamic acid was present in solution. This means that the degradation of folpet is not a series of subsequent reactions, as shown in Figure 1, but a series of parallel reactions yielding phthalimide on the one hand and phthalamic acid degrading to phthalic acid on the other. A confirmation was obtained from separate studies on the degradation of phthalimide, phthalamic acid, and phthalic acid. A similar degradative behavior in must and in aqueous acid solutions showed that acidity is responsible for the kinetic degradation of folpet. Experiments on the degradation of folpet in water at pH 7 showed that only phthalimide formed. These data indicate that in must folpet could also form small amounts of phthalic acid.

Wine-Making. After pressing, folpet and phthalimide residues in must were the same as in grapes (Table 2). After the centrifugation of must, folpet residues disappeared completely and phthalimide residues partially. This indicates that folpet is thoroughly adsorbed by the suspended solids in the must. At the end of fermentation only phthalimide residues were found in wine, in stoichiometric amounts compared to folpet in must. In wine obtained by vinification without skins, residues were 15% lower than in wine obtained by vinification with skins. Six months after vinification, phthalimide residues remained unchanged in wine. The presence of phthalimide in wine is not a toxicological problem, because phthalimide is considered nontoxic and is rapidly excreted by the organism (Paster, 1992).

Table 5. Effect of Folpet and Phthalimide on Fermentation Activity of *S. cerevisiae* and *K. apiculata* Yeasts

pesticide added	*S. cerevisiae*									*K. apiculata*								
	0 days after inoculation			4 days after inoculation			11 days after inoculation			0 days after inoculation			4 days after inoculation			11 days after inoculation		
(mgL)	cell/mL	pH	CO_2[a]	cell/mL	pH	CO_2[a]	cell/mL	pH	CO_2[a]	cell/mL	pH	CO_2[a]	cell/mL	pH	CO_2[a]	cell/mL	pH	CO_2[a]
control	5.0×10^4	3.6	nd	8.2×10^8	3.0	7.2	4.4×10^6	3.2	9.7	5.0×10^4	3.6	nd	8.7×10^8	3.3	4.2	3.9×10^4	3.4	4.3
	5.0×10^6	3.6	nd	8.8×10^8	3.0	7.4	4.6×10^6	3.4	9.1	5.0×10^6	3.6	nd	8.6×10^8	3.3	4.2	3.9×10^4	3.4	4.2
Folpet																		
4.1	5.0×10^4	3.6	nd	2.0×10^2	3.6	nd	0.9×10	3.6	nd	5.0×10^4	3.6	nd	4.0×10^2	3.6	nd	4.6×10	3.6	nd
	5.0×10^6	3.6	nd	3.0×10^4	3.6	nd	2.6×10^2	3.6	nd	5.0×10^6	3.6	nd	7.0×10^4	3.6	nd	3.8×10^2	3.6	nd
2.0	5.0×10^4	3.6	nd	2.3×10^2	3.6	nd	4.0×10	3.6	nd	5.0×10^4	3.6	nd	3.7×10^2	3.6	nd	2.2×10	3.6	nd
	5.0×10^6	3.6	nd	3.5×10^4	3.6	nd	2.4×10^2	3.6	nd	5.0×10^6	3.6	nd	5.7×10^4	3.6	nd	3.6×10^2	3.6	nd
Phthalimide																		
1.74	5.0×10^4	3.6	nd	8.2×10^8	3.0	7.2	4.4×10^6	3.2	9.7	5.0×10^4	3.6	nd	8.7×10^8	3.3	4.2	3.9×10^4	3.4	4.3
	5.0×10^6	3.6	nd	8.3×10^8	3.0	7.3	4.9×10^6	3.2	9.7	5.0×10^6	3.6	nd	8.7×10^8	3.3	4.8	3.6×10^4	3.4	4.7
0.80	5.0×10^4	3.6	nd	8.7×10^8	2.9	7.5	4.8×10^6	3.4	8.7	5.0×10^4	3.6	nd	8.5×10^8	3.3	3.6	$3.6 \times 1\,0^4$	3.4	3.6
	5.0×10^6	3.6	nd	8.8×10^8	3.0	7.4	4.6×10^6	3.4	9.1	5.0×10^6	3.6	nd	8.6×10^8	3.3	4.2	3.9×10^4	3.4	4.2

[a] Expressed as alcohol % (v/v). [b] nd, not detectable.

Wine Clarification. Since folpet was not present in wine, the clarification tests were carried out only on phthalimide at a concentration of 1.76 ppm. Charcoal showed a moderate adsorbent effect on phthalimide (decrease 23%), whereas bentonite, potassium caseinate, and polyvinylpolypyrrolidone were ineffective.

Effects on the Fermentative Microflora. The antiseptic activity on the fermentative microflora was studied by several authors and reviewed by Cabras et al. (1987). Folpet degradation in must, leading to phthalimide, brought up the question of whether antiseptic action was due to folpet, its metabolites, or both. To clarity this aspect, fermentation experiments were carried out with two yeasts (*Saccharomyces cerevisiae* and *Kloeckera apiculata*), in two different cell concentrations and in the presence of folpet and phthalimide. Folpet completely inhibited the fermentative activity of the yeasts on both cell concentrations (Table 5). The presence of phthalimide had no negative effect on the fermentative action of the two yeasts (Table 5). The fermentation course was regular according to the values of the species (8−9% alcohol after 11 days for *S. cerevisiae* and 3−5% alcohol for the *K. apiculata*), and no significative differences were observed between the samples and the control.

Photodegradation. Sunlight-irradiated folpet degraded with a half-time, calculated by a first-order kinetics ($r = -0.97$), of 18.9 days, similar to that determined on grapes. Chromatographic analysis did not show peaks assignable to known metabolites (phthalimide, phthalamic and phthalic acids). To establish whether the formation and degradation rates of these compounds were similar, experiments were carried out by exposing each compound to sunlight separately. Phthalimide and phthalic acid were stable throughout the exposure time, while phthalamic acid was fully trasformed in phthalic acid after 2 weeks. These data show that sunlight degrades folpet with a pathway different from those known so far.

Conclusions. The fact that folpet degrades slowly in the treatment mixture ensures that its concentration will not decrease significantly as long as the treatment is done a few hours after it is prepared. Sunlight degrades folpet to unknown products. Phthalimide is a minor metabolite formed on grapes by folpet. Folpet degraded in must, giving *ca.* 80% phthalimide. The results obtained with a model solution show that in must folpet can also give small amounts of phthalic acid. During wine-making, folpet degraded completely, and at the end of fermentation only phthalimide was present in wine. This compound was stable in wine after several months. The presence of folpet in must completely inibited the alcoholic fermentation of *S. cerevisiae* and *K. apiculata*. Using dry yeasts in large quantites, it was possible to obtain normal fermentation. Folpet can be removed completely from must by centrifugation. Phthalimide, on the contrary, had no negative effect on the fermentative action of the two yeasts.

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