Ethylene oxide, itself a biocide and soil sterilant, is well known to hydrolyze in aqueous solution to ethylene glycol (eq 5). The process is general acid or base catalyzed (Long and Pritchard, 1956). Clearly the rate of eq 5 is not enhanced by light. At pH 7 $t_{1/2}$ is approximately 10 days.

$$\overbrace{CH_2CH_2O} \xrightarrow[H_2O]{H^+, OH^-} HOCH_2CH_2OH \qquad (5)$$

The relative rates of reactions 3 and 4 compared to the rate of reduction of ferrioxalate are ($k_{RX}/k_{Fe^{III}O_X}$) 32 for EDB and 3.8 for bromoethanol, respectively. With sunlight irradiation, EDB reacts 2.7 times faster than ferrioxalate. An estimate of the rate for Br^- release from EDB based upon 53 days (and nights) of exposure to roof sunlight, (10% conversion) corresponds to a $t_{1/2}$ ~380 days or a ~15-fold rate enhancement over the dark reaction.

DISCUSSION

The general photo enhanced substitution observed here (eq 6) suggests cationic intermediates. These results

$$>C\text{-}Br \xrightarrow{ROH} >C\text{-}OR \qquad (6)$$

would accord with a variety of studies of the photolysis of primarily aliphatic iodides in polar millieu (Kropp, 1984) and with the products obtained and the paths of reaction of chloropicrin and methyl bromide (Castro and Belser, 1983). Quantum yields cannot be calculated from the data at hand. Nevertheless, the absorption spectrum of ferrioxalate solutions is well-known, and clearly the actinometer solution absorbs more light than the organic halides over the entire wavelength region generated by the medium-pressure lamp. For ferrioxalate the extinction coefficient at 218 nm (λ_{max} for EDB) is ca 10^4 (Parker, 1953) and the absorption of light by the salt extends well into the visible. The faster rates of decay of the less absorbing halides indicate quantum yields considerably above one. A chain reaction is implied and the reactions bear further mechanistic scrutiny.

The rate enhancement for the photo process noted here with EDB is remarkable (~10^5). The actual photohydrolysis of ethylene dibromide in the environment could be an important means of its decay. Moreover, it is conceivable that photoprocesses could be employed to destroy relatively substitution inert aliphatic halides in the environment.

Registry No. EDB, 106-93-4; bromoethanol, 540-51-2; ethylene oxide, 75-21-8; ethylene glycol, 107-21-1.

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Methiocarb Residues in Grapes and Wine and Their Fate during Vinification

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An analytical method developed for the determination of total methiocarb residues on grapes included initial extraction with acetonitrile, oxidation of residues to methiocarb sulfone with *m*-chloroperbenzoic acid, derivatization with methanesulfonyl chloride, and quantitation by sulfur specific flame photometric gas chromatography. Grape juice, pomace, and wine were analyzed to determine the fate of methiocarb during vinification. Samples were also analyzed for the individual metabolites of methiocarb by using similar methods but omitting the oxidation step. Total residue on Pinot noir grapes treated 4 times at 4.5 kg AI/ha was 46 ppm 7 days after a handgun application and 7.4 ppm if the material was applied by airplane. Residues on White Riesling grapes treated with a concentrate sprayer at the same rate ranged from 12 to 19 ppm 7 days after last application. About 50–80% of the residue on fruit was removed from the vinification process with pomace and additional reductions occurred during the settling of juice. Total residue in wines made from grapes treated 7 days before harvest was 4.9 ppm in White Riesling wine and 4.6 ppm in Pinot noir wine which represented 26 and 13% of the initial residue on grapes.

INTRODUCTION

Birds cause considerable damage to maturing grapes and growers suffer financial losses estimated to be over 4 million dollars annually (Crase et al., 1976). The usual techiques utilized to reduce bird damage, such as noise, netting, live trapping, and poisoning, are expensive and not always effective (Boudreau, 1972). Recently it has been found that chemicals which repel birds are more effective and more economical to use. One such chemical useful against bird depredation is methiocarb [mesurol, 3,5-dimethyl-4-(methylthio)phenyl methyl carbamate] (Schafer and Brunton, 1971; Bollingier et al., 1971; Bailey and Smith, 1979). However, before this compound could be used on grapes, the magnitude of residues on grapes and the fate of residues during the vinification process needed to be determined.

Methiocarb is metabolized to its sulfoxide and sulfone by plants (Abdel-Wahab et al., 1966), and since these compounds are also toxic, any analytical method developed for methiocarb should also detect the oxidative metabolites. Carbamates, such as methiocarb, are thermally

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unstable and decompose to the phenols and to methyl isocyanate under the usual gas chromatographic conditions (Zielinski and Fishbein, 1965). This problem has been eliminated by using heat stable derivatives. Numerous derivatization procedures have been published for methiocarb including silylation (Thornton and Dräger, 1973; Strankowski and Stanley, 1981), bromination (Van Middelem et al., 1965), hydrolysis to phenols (Bowman and Beroza, 1969), reaction with trifluoroacetic, pentafluoropropionic, and heptafluorobutyric anhydrides (Seiber, 1972; Greenhalgh et al., 1976; Greenhalgh et al., 1977), formation of 2,4-dinitrophenyl ether (Holden, 1973; Ernst et al., 1975), formation of 2,6-dinitro-4-trifluoromethyl ether (Ernst et al., 1975), and mesylation (Maitlen and McDonough, 1980; Maitlen, 1981). To simplify the analytical procedures and to improve sensitivity, methods have been developed where both the methiocarb and its sulfoxide were oxidized to the sulfone before derivatization and the total residue determined as the sulfone (Thornton and Dräger, 1973; Maitlen, 1981; Strankowski and Stanley, 1981).

In this paper two procedures were followed. One group of samples was analyzed by using the method outlined by Maitlen and McDonough (1980) in which the parent compound and the oxidative metabolites are analyzed individually. The other group of samples was analyzed by using a second procedure which included an oxidation step using *m*-chloroperbenzoic acid to convert all residues to the sulfone. Methiocarb residues on grapes resulting from different application methods were determined and the fate of methiocarb during the vinification process followed by analyzing grape juice, pomace, and wine. In addition, the reduction of residues of methiocarb and its metabolites during the processing of fortified White Riesling juice and the stability of residues during storage of Pinot noir wine were also studied.

EXPERIMENTAL SECTION

Treatment of Grapes. The plots of Pinot noir grapes were located at Forest Grove, OR, and were treated with Mesurol 75% WP formulation (Mobay Chemical Corp.) at weekly intervals. Three or four application were made by handgun, concentrate sprayer, or airplane at 4.5 kg active ingredient (AI) per ha. The last application was made Oct 4, 1978. The grapes from the plot receiving four applications by concentrate sprayer were processed into wine at the Oregon State University winery. In addition, plots of Pinot noir grapes located at Dundee, OR, were treated Oct 10 and 17, 1978, with 2.2 kg AI per ha of methiocarb using the same formulation and applying the material with a concentrate sprayer. These grapes were harvested one week after the last application and were processed into wine by a commercial winery in Oregon. The plots of White Riesling grapes were located at Forest Grove, OR, and Prosser, WA, and were treated four times at weekly intervals at the rate of 4.5 kg AI per ha with the Measurol 75% WP formulation applied by a concentrate sprayer. The last application at Forest Grove was made Oct 25, 1978 and at Prosser Oct 16, 1978. The grapes from the Forest Grove plot were taken for vinification at the Oregon State University winery. Random 1–2-kg samples of grapes were collected 1 or 7 days after the last application for residue analysis and were stored at −23 °C. Grapes for vinification were collected in 32–45 kg lots and were processed immediately.

Vinification of Grapes. Yeast Starter. A 2% inoculum of rehydrated dry wine yeast (Vin-A-Dry, Scott Laboratories, San Rafael, CA) was prepared in 1:1 grape juice–water at 41 °C. The rehydrated culture was incubated at room temperature for 3 h.

Processing of White Riesling Grapes. Untreated and treated grapes were crushed immediately after receiving from the vineyard at the Oregon State University winery. A portion of the untreated grape juice was fortified to 15 ppm of methiocarb by using the Mesurol 75% WP formulation. A 1% solution of potassium pyrosulfite was used to adjust the sulfur dioxide level to 50 ppm and the juices were allowed to settle overnight. The settled juice was racked into 19-L glass carboys, inoculated with the 2% yeast starter and the carboys sealed with fermentation locks. All wines were fermented to dryness at 15 °C, racked twice, and held at 3.5 °C until bottled. Wines were adjusted to 30 ppm free sulfur dioxide and bottled without filtration 11 months after crushing.

Processing of Pinot Noir Grapes. The grapes were crushed immediately after receiving and 50 ppm of sulfur dioxide was added. A portion of the untreated grapes was pressed and settled overnight, and the settled juice was fortified to 15 ppm of methiocarb with the Mesurol 75% WP formulation. A portion of the untreated must was also fortified in the same manner. All musts were inoculated with the 2% yeast starter. Musts were fermented until 2–3 °Brix, pressed, and fermented to dryness at 20 °C in 38-L plastic tubs. Wines were racked three times and held at 3.5 °C until bottled. Pinot noir grapes from a vineyard treated two times at 2.2 kg AI per ha were processed into wine by a commercial winery by fermenting the grapes on the skins for seven days before pressing and then following standard commercial practices of vinification.

Apparatus and Reagents. A Varian 3700 gas chromatograph equipped with a flame photometric detector was used for analysis. A Waters Associates liquid chromatograph Model ALC 202 equipped with a differential UV detector (254 nm) was utilized for the isolation of the methiocarb phenol. Gas chromatography–mass spectrometry studies were carried out on a Finnigan 4023 instrument. Standard laboratory glassware was used throughout the experiments. The analytical grade standards of methiocarb, methiocarb sulfoxide, methiocarb sulfone, methiocarb phenol, methiocarb sulfoxide phenol, and methiocarb sulfone phenol were obtained from the Agricultural Chemicals Division, Mobay Chemical Corp., Kansas City, MO. The *m*-chloroperbenzoic acid was supplied by Research Organic/Inorganic Chemicals Co., Sun Valley, CA, methanesulfonyl chloride by Eastman Organic Chemicals, Rochester, NY, and *N,O*-bis(trimethylsilyl)acetamide (BSA) by Pierce Chemical Co., Rockford, IL. All chemicals used were of reagent grade. All solvents were distilled in glass.

Gas Chromatography. A dual flame photometric detector operated with the 365-nm interference filter for sulfur was used. The detector temperature was 230 °C with the gas flows to the detector of 80, 170, and 140 mL/min, for air 1, air 2, and hydrogen, respectively. A 46 cm × 2 mm i.d. glass column packed with 5% OV-101 on 120/140 mesh Chromosorb WHP was used. Column temperature was 195 °C, injector temperature 200 °C, and nitrogen carrier gas flow 30 mL/min. The peak heights of methiocarb standards and samples were matched in triplicate. The square roots of peak height (cm) for each standard or sample were derived and compared to determine the total residue as methiocarb sulfone or the residues of individual metabolites in the sample. The retention times for methiocarb, its sulfoxide, or sulfone at 195 °C column temperature were 1.0, 2.5, and 2.6 min, respectively.

Liquid Chromatograpy (HPLC). A 25 cm × 4.6 mm i.d. stainless steel column packed with 5 μ Lichrosorb silica gel was used for the isolation of methiocarb phenol. The instrument was operated under isocratic conditions using 5% 2-propanol in trimethylpentane as the solvent. Methiocarb carbamate and phenol standards were used to determine the retention volumes.

Gas Chromatography–Mass Spectrometry (GC–MS). The column used for the separation of methiocarb and its sulfoxide and sulfone in the GC–MS studies was 180 cm × 2 mm i.d. glass packed with 3% OV-17 on 100/120 mesh Chromosorb WHP. Conditions for the mass spectral confirmation of the residues were ionizing voltage 70 eV, source temperature 300 °C, separator oven temperature 275 °C, column temperature 220 °C, and injector temperature 275 °C.

The column used for the determination of the methiocarb phenol was 180 cm × 2 mm i.d. glass packed with 3% OV-101 on 100/120 mesh Chromosorb WHP. Operating conditions were the same as described above with the exception of the column temperature which was 230 °C.

Analytical Procedures. Analysis for Total Residues as Methiocarb Sulfone. All samples were stored at −23 °C and were warmed to room temperature before extraction.

Extraction of Grapes. A 50-g random sample of grapes was blended with 50 mL of acetonitrile (Baker Resi-analyzed), 5 g of Hyflow Supercel (Johns-Mansville Co.), and 15 mL of precipitating solution (25 mL of concentrated phosphoric acid and 1.25 g of ammonium chloride/L) in an omnimixer for 1 min at high speed. The mixture was filtered under vacuum through Reeve Angle 202 filter paper. The filter cake was macerated again with 50 mL of acetonitrile and 15 mL of precipitating solution and filtered. The mixer cup and filter cake was washed with an additional 25 mL of acetonitrile, the extracts and washings were combined in a separatory funnel, and the acetonitrile phase (upper layer) was separated. The aqueous phase was extracted with 50- and 25-mL portions of acetonitrile. The combined acetonitrile phases were cooled to 4 °C and the water that separated was discarded. The acetonitrile solution was concentrated to about 5 mL on a rotary evaporator at 34 °C. Ten mL of a 2.5 N sodium hydroxide solution was added to the flask, the contents were transferred to a separatory funnel and extracted with three 10-mL portions of chloroform. The chloroform layers were separated and discarded. The aqueous phase was acidified with 15 mL of 1 N sulfuric acid and extracted with three 25-mL portions of chloroform. The chloroform extracts were combined and evaporated to dryness on a rotary evaporator at 34 °C.

Extraction of Grape Juice and Wine. Five grams of Hyflow Supercel was added to 50-mL of wine or juice samples and the samples were filtered through Reeve Angle 202 filter paper under vacuum. The filter cake was rinsed with 50 mL of acetonitrile and the filtrate and the acetonitrile layer were transferred to a separatory funnel. Ten grams of sodium chloride was added to the filtrate in the case of wine. An additional 50 mL of acetonitrile was added to the separatory funnel, the contents agitated for 30 s, and the acetonitrile layer separated. The remaining steps in the extraction procedure were identical with those utilized in the fruit extraction. Ten percent diethyl ether in acetonitrile was used for the extractions if problems developed with emulsions.

Oxidation. Methiocarb and its sulfoxide residues in fruit, juice, and wine samples were oxidized to the methiocarb sulfone by allowing the samples to stand for 30 min at room temperature with 4 mL of 1% *m*-chloroperbenzoic acid in chloroform. Twenty-five milliliters of a saturated sodium sulfite solution was added and the sample transferred to a separatory funnel. Twenty-five milliliters of a saturated sodium bicarbonate solution was added and the mixture agitated. This solution was extracted three times with 25-mL portions of chloroform and the combined chloroform extracts evaporated to dryness on a rotary evaporator at 34 °C.

Derivatization. The methiocarb sulfone was hydrolized and the phenol converted to the mesylate according to the procedure of Maitlen and McDonough (1980). One milliliter of 0.25 N potassium hydroxide solution in methanol was added to the oxidized residue and the solution was allowed to stand at room temperature for 15 min to hydrolize the sulfone to the corresponding phenol. Two milliliters of 5% pyridine in benzene and 1 mL of 1% acetophenone in benzene (keeper solution) were added. The solvents were removed under a dry airstream at room temperature. Two milliliters of 1% methanesulfonyl chloride in benzene was added and the samples allowed to stand at room temperature for 30 min. The samples were then evaporated to dryness under a stream of dry air, diluted with benzene to the required concentration, and analyzed by gas chromatography.

Analysis for Individual Residues of Methiocarb and Its Sulfoxide and Sulfone. Samples of grapes, pomace, grape juice, and wine were analyzed in addition to the total sulfone also for the parent compound (methiocarb). Cellar- and bottle-aged Pinot noir wine and samples obtained during the processing of White Riesling press juice fortified with methiocarb were analyzed for methiocarb and its sulfoxide and sulfone individually.

Extraction. The initial extraction of grape juice and wine was identical with that of total residue analysis, only 100-, 50- and 50-mL portions of acetonitrile were used. The combined acetonitrile extracts were transferred to a separatory funnel, 800 mL of water added and the solution extracted with two 50-mL portions of chloroform. The chloroform extract was dried with anhydrous sodium sulfate and evaporated to dryness on a rotary evaporator at 34 °C. The samples were then derivatized with methanesulfonyl chloride as described above.

Samples of fruit were analyzed for the parent compound only by using a modified extraction procedure. Three hundred grams of fruit were ground with an equal weight of dry ice in a Waring blender and stored at −23 °C in a freezer to permit sublimation of the dry ice. Ten percent diethyl ether in acetonitrile was used for the initial extraction and 10 g of sodium chloride was added to the aqueous phase before chloroform extraction. A 1:1 hexane (acetonitrile saturated)–acetonitrile backwash was used to remove the nonpolar oils. Cleanup was accomplished on a Florisil column to be described.

Frozen pomace samples were ground in a Hobart food chopper. A 50-g subsample was blended with 150 mL of acetonitrile, 25 mL of precipitating solution, and 5 g of Hyflow Supercel in an omnimixer at high speed for 1 min. The extract was recovered by filtering under vacuum and the filter cake reextracted with 140 mL of acetonitrile and 25 mL of precipitating solution, again recovering the extract by filtering under vacuum. Twenty–five milliliter aliquots of the treated samples and 50-mL aliquots of the controls were taken for analysis from the combined acetonitrile extracts. One hundred or 200 mL of water was added to each aliquot of the treated or control samples, respectively, and the aqueous phase was extracted with two

Table I. Recovery of Added Methiocarb and Its Metabolites from Untreated Samples

sample	fortification compound	fortification levels, ppm	no. of recoveries	average[a] recovery, %	range of recoveries, %	SD, %
		Total Sulfone Method				
Pinot noir grapes	methiocarb	0.5	10	78	71–90	5.5
Pinot noir grapes	sulfoxide	0.5	2	91	84–98	
Pinot noir grapes	sulfone	0.5	2	100	98–102	
White Riesling grapes	methiocarb	0.5	8	82	68–92	10.8
Pinot noir juice	methiocarb	0.5	2	83	83–83	
White Riesling juice	methiocarb	0.5	3	84	78–90	4.9
Pinot noir wine	methiocarb	0.5	2	86	78–94	
White Riesling wine	methiocarb	0.5–2.0	5	88	77–98	8.4
		Method for Individual Residues				
Pinot noir grapes	methiocarb	1.0–4.0	6	46	34–68	10.6
White Riesling grapes	methiocarb	1.0–4.0	4	50	39–71	14.8
Pinot noir pomace	methiocarb	6.0	1	71	71	
White Riesling pomace	methiocarb	6.0	1	64	64	
White Riesling sediment	methiocarb	2.1	1	51	51	
White Riesling sediment	sulfoxide	2.0	1	53	53	
White Riesling sediment	sulfone	2.1	1	97	97	
White Riesling juice	methiocarb	0.42–2.1	8	75	43–88	14.5
White Riesling juice	sulfoxide	0.4–2.0	4	86	77–105	11.3
White Riesling juice	sulfone	0.42–2.1	4	112	102–121	8.4
Pinot noir wine	methiocarb	2.0	1	62	62	
Pinot noir wine	sulfoxide	0.5	1	136	136	
Pinot noir wine	sulfone	0.5	1	92	92	
Pinot noir wine	methiocarb phenol	0.5	1	72	72	
Pinot noir wine	sulfoxide phenol	0.5	1	24	24	
Pinot noir wine	sulfone phenol	0.5	1	72	72	
White Riesling wine	methiocarb	0.42–1.26	7	70	56–92	13.9
White Riesling wine	sulfoxide	0.4–1.2	3	68	55–90	15.5
White Riesling wine	sulfone	0.42–1.26	3	94	81–105	10.0

[a] Corrected for background response if observed.

25-mL portions of chloroform. The combined chloroform extracts were taken to dryness and derivatized as described before. Moisture determinations (AOAC, 1975) were performed simultaneously with methiocarb analyses on each pomace sample.

Partitioning and Cleanup. A Florisil chromatography column was prepared as follows: a plug of glass wool, 1.5 cm of anhydrous sodium sulfate, 10 g of activated Florisil (Floridin Co., Tallahasse, FL, 100/120 mesh, activated at 450 °C for 12 h and stored at 130 °C), and 1.5 cm of anhydrous sodium sulfate were successively added to an 18 mm i.d. glass chromatography column equipped with a Teflon stopcock. The column was packed with 50 mL of hexane. Derivatized residues were quantitatively transferred to the column with aliquots of dichloromethane. The methiocarb and its sulfone mesylates were eluted from the column with 80 mL of 10% acetone in dichloromethane. The methiocarb sulfoxide mesylate was eluted with 50 mL of 50% acetone in dichloromethane. The solvents were removed on a rotary evaporator, and residues dissolved in benzene and diluted as required for gas chromatographic analysis. The presence of methiocarb and its sulfoxide and sulfone was also confirmed by gas chromatography–mass spectrometry by comparing the spectra obtained with treated samples to those of analytical standards.

Determination of Methiocarb Phenol. Wines were extracted with acetonitrile and chloroform as described above. The chloroform extract was evaporated to dryness and the residue was quantitatively transferred with benzene to a graduated 10-mL centrifuge tube and concentrated to 0.25 mL under an air jet. Approximately 40% of the concentrate was injected into a liquid chromatograph and methiocarb phenol was collected off the column from successive injections totaling 100 μL. The HPLC solvent was removed and the residue transferred with benzene to a graduated screw-cap vial and concentrated to 0.5 mL under an air jet. Twenty-five microliters of BSA were added and the methiocarb phenol quantitatively determined as the trimethylsilyl derivative by GC–MS by comparison of the m/z 240 peak with that of a standard.

RESULTS AND DISCUSSION

The reliability of the analytical method was tested by adding known amounts of methiocarb and its metabolites to the various substrates prior to extraction and analysis. The range of fortifications and recoveries is shown in Table I. The overall average recovery was 77%, however the range of recoveries varied from a low of 24% for the sulfoxide phenol to a high of 136% for the sulfoxide metabolite in Pinot noir wine. Recoveries of methiocarb from Pinot noir and White Riesling grapes when analyzed for this compound alone averaged only 46% and 50%, respectively. Greenhalgh et al. (1977) have reported that oxidation of methiocarb can occur during the analysis causing low recoveries if the solution is allowed to go to dryness during the concentration steps. In addition, it is possible for extracted plant material to occlude pesiticides (Bowman and Beroza, 1969). In this study there was no evidence of methiocarb loss during residue partitioning or on Florisil columns.

Initially the grapes were analyzed for methiocarb alone by using a procedure identical with that used for the total sulfone analysis but omitting the oxidation step. Because low recoveries were encountered, an attempt was made to improve the recoveries by modifying the extraction procedure. The grapes were ground with dry ice before blending with acetonitrile to provide a more finely divided sample and 10% diethyl ether in acetonitrile was used as the extraction solvent to reduce emulsification during

Table II. Total Residues of Methiocarb Measured as the Sulfone (in ppm)[a] on Grapes Resulting from Different Application Methods

variety	location of plots	application method	no.[b]	days after last application 1	3	7
Pinot noir	Forest Grove, OR	handgun	4	58	40	46
Pinot noir	Forest Grove, OR	handgun	3	3.6	4.1	4.6
Pinot noir[c]	Forest Grove, OR	concentrate sprayer	4	22		36
Pinot noir	Forest Grove, OR	concentrate sprayer	3	26	32	48
Pinot noir	Forest Grove, OR	airplane	3	6.1		7.4
White Riesling[c]	Forest Grove, OR	concentrate sprayer	4	25		19
White Riesling	Prosser, WA	concentrate sprayer	4	17		12

[a] Average of two replications with the following exceptions: three replications for the airplane application plot and no replications for the Pinot noir four applications by concetrate sprayer plot and for the White Riesling Forest Grove plot. [b] Mesurol 75% WP formulation (Mobay Chemical Corp.) applied at weekly intervals at 4.5 kg AI per ha. Last application to Pinot noir grapes Oct 4, 1978, and to White Riesling grapes at Forest Grove Oct 25, 1978, and at Prosser Oct 16, 1978. [c] Grapes from this plot were processed into wine by the Oregon State University winery.

blending. These modifications of the extraction procedure failed to improve the recoveries. Both extraction procedures when used for analyzing the samples for methiocarb residues gave low recoveries and the second procedure was used.

The method for grape juice and wine was also modified for the analysis of the individual metabolites. The step involving concentration of the acetonitrile extract followed by uptake in aqueous base, chloroform wash, acidification and extraction of residue into chloroform was replaced by dilution of the acetonitrile extract with water and extraction with chloroform. This shortened the analytical procedure since the concentration of the acetonitrile extract was time consuming.

Methiocarb residues in grapes expressed as total sulfone and resulting from different application methods are summarized in Table II. As expected, the handgun application resulted in highest residues, followed by concentrate sprayer and airplane. The 10-fold reduction in residue in the plot treated three times with a handgun as compared to the four handgun applications is not readily explained and is most likely due to an application error. The increase in residues from 1 day to 7 days after application in some of the Pinot noir plots is probably due to drying of the grapes on the vine.

The fate of methiocarb during the vinification process is shown in Table III. Grapes from the field-treated plots were analyzed by two techniques: all samples were analyzed for the parent compound (methiocarb) and most of the samples were also analyzed for the total residue by oxidizing all residues to the sulfone. The results shown have not been corrected for recoveries and the data indicate that the residues determined by the two techniques were similar. A greater discrepency between the two techniques was noted when these values were corrected for recoveries because of the low recoveries for the methiocarb method. Residue levels in all plots treated with the concentrate sprayer were comparable as shown in Table II. Because of the late treatment date the residues found on grapes were high; there was no dilution of residues due to growth and the cold weather in late fall also retarded degradation. In contrast, Bailey and Smith (1979) observed a gradual reduction of methiocarb residues on Gordo grapes during the summer in Australia, total residues declined from 28 ppm to 1.3 ppm in 28 days. Greenhalgh et al. (1977) reported a similar loss of methiocarb on lowbush blueberries.

About 52–84% reduction in the concentration of total residues was observed when the residues in juice were compared to those on grapes. Pomace, which is the dry material left after the juice is pressed from the grapes, was analyzed for methiocarb residues only and not for sulfoxide or sulfone. The results indicated high residues of parent compound in pomace ranging from 53 to 142 ppm on dry weight basis. The lower concentration of residues in grape juice and the high residues in pomace suggest that a substantial portion of the residue was removed from the vinification process with pomace. Further losses of residues occurred when the juice was fermented into wine. It is likely that some of the methiocarb and its metabolites settled out with the lees and were discarded when the wine was racked. The average percent of the initial total residue on grapes retained in White Riesling wine was 29% (range 26–32%) and in Pinot noir wine 28% (range 13–49%). Total residues in wines made from grapes treated 1–7 days before harvest ranged from 4.6 to 9.7 ppm; similar residues have been reported by Noble (1980) in wines resulting from identical field treatments of Gamay Beaujolais and Pinot Blanc grapes.

Table III. Residues (in ppm)[a] of Methiocarb and Total Methiocarb Sulfone Found during the Vinification of Field-Treated Grapes

sample	appl rate,[b] kg AI/ha	days after last application 1 MS[c]	1 MSO_2[d]	7 MS[c]	7 MSO_2[d]
Pinot noir grapes	4.5	22	22	16	36
Pinot noir grapes	2.2			12	
White Riesling grapes	4.5	38	25	25	19
Pinot noir must	4.5	10	9.9	7.1	5.7
Pinot noir must	2.2			4.9	
White Riesling juice	4.5	15	12	5.1	8.8
Pinot noir pomace	4.5	28		16	
Pinot noir pomace	2.2			26	
White Riesling pomace	4.5	40			
Pinot noir wine	4.5	7.4	9.7	7.9	4.6
Pinot noir wine	2.2			3.6	
White Riesling wine	4.5	4.8	8.0	3.3	4.9

[a] Analyses not replicated. [b] Mesurol 75% WP formulation (Mobay Chemical Corp.) applied by concentrate sprayer at weekly intervals. Plots receiving 4.5 kg AI/ha were treated four times, the plot receiving 2.2 kg AI/ha two times. [c] Residue of parent compound only. [d] Residues oxidized to sulfone and expressed as total sulfone.

Data presented in Table IV illustrate the fate of methiocarb added to pressed juice of White Riesling grapes and carried through the vinification process. Sedimentation overnight reduced the total methiocarb residue in juice to 6.2 ppm, indicating that the sedimentation step used in white table wine production provides an important route of residue reduction. Here the data suggest that contrary to previous findings, the lees removed during fermentation did not contain significant methiocarb residues: half-fermented juice and wine contained identical residues. Oxidation of the methiocarb to the sulfoxide or sulfone was

Table IV. Fate of Methiocarb during Vinification of White Riesling Juice[a]

sample	residue, ppm[b]		
	methiocarb	methiocarb sulfoxide	methiocarb sulfone
juice	10.4	0.6	0.1
sediment	29.3	0.7	0.5
settled juice	6.2	0.2	0.9
half-fermented juice	2.7	0.2	0.1
wine	2.7	0.2	0.1

[a] Juice fortified to 15 ppm AI with Mesurol 75% WP formulation. [b] Analyses not replicated.

Table V. Methiocarb Residues[a] in Pinot Noir Juice and Wine Obtained from Juice Fortification,[b] Must Fortification,[b] and Commercial Trials

trial	residue, ppm			
	juice		wine	
	fermented[c] on skins	press juice	first racking	cold[d] stabilized
press juice fortification	4.5[e]	6.0	3.8	5.1
must fortification	3.3		5.2	4.0
commercial trial	4.9	4.2	3.3	3.6

[a] Analyses not replicated. [b] Fortified to 15 ppm AI with Mesurol 75% WP formulation. [c] Prior to pressing. [d] Wine stored at 3.5 °C for 6 months. [e] Settled juice.

minimal during processing, sulfoxide and sulfone accounted for only about 10% of the total residue in wine. Methiocarb residues in must, juice, and in wine at first racking and after 6 months of storage at 3.5 °C were unchanged in Pinot noir commercial, pressed juice fortification, and must fortification trials (Table V).

In comparison, Kawar et al. (1978) found 8.8 ppm of parathion in finished wine derived from reconstituted Semillion grape juice concentrate fortified to 25 ppm; fermentation lees in this case contained 156 ppm parathion. Hydrolysis of parathion to *p*-nitrophenol was an important step in lowering of the pesticide level in wine while oxidation was not a significant factor. Similar evaluations were conducted by Kawar et al. (1979) with diluted Zinfandel concentrates fortified to 25 ppm with dimethoate, dialifor, and methidathion. Residues of dimethoate remained constant going from must to the finished wine. Wine prior to bottling contained 10% of the dialifor and 46% of the methidathion added to the grape juice. Chiba and Doornbos (1971) analyzed wines made from grapes treated in the field with DDT and found only traces of DDT in 1 month old wine. Residues in wine were below 0.0002 ppm after 4 month of storage.

The hydrolytic and oxidative stability of methiocarb in finished wine is an important consideration in evaluating the safety of this pesticide, because the sulfoxide is known to be a more potent cholinesterase inhibitor than the parent compound (Oonnithan and Casida, 1966; Metcalf et al., 1967). Data presented in Table VI show over 2 ppm of the sulfoxide present in cellar- or bottle-aged wine, amounting to about 20% of the total residue. Residues

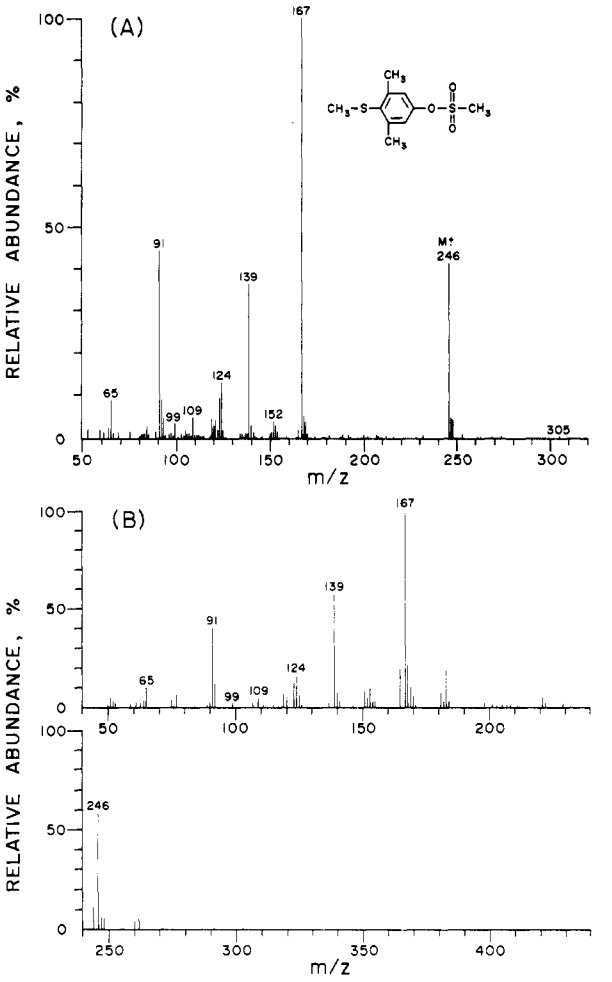

Figure 1. Electron impact spectra of mesylated methiocarb. Spectra obtained on a Finnigan 4023 instrument. Ionization voltage was 70 eV. (A) Standard. (B) Isolated from combined White Riesling and Pinot noir wines produced from field-treated grapes.

of methiocarb and its sulfoxide and sulfone were nearly identical in both wines, and were in agreement with the 9.7 ppm residue detected as total sulfone in 1-day Pinot noir wine prior to bottling. Recoveries were 62% for methiocarb, 136% for the sulfoxide, and 92% for the sulfone, suggesting that oxidation may have taken place during the analytical procedure. This also suggests that oxidation during analysis may account for the sulfoxide and sulfone residues in treated samples, but since oxidation can also take place in the field, the origin of sulfoxide and sulfone residues reported in Table VI is difficult to determine. The possibility that the phenolic metabolites may be determined together with the carbamates was checked by fortifying untreated wine to 0.5 ppm with methiocarb and its sulfoxide and sulfone phenols, followed by extraction as described for the carbamates and silylation for mass spectrometric analysis. Recoveries were calculated by comparing the intensity of selected ions produced by

Table VI. Methiocarb and Its Phenol, Sulfoxide, and Sulfone Residues[a] in Cellar- and Bottle-Aged Wine Produced from Field-Treated Pinot Noir Grapes[b]

sample	methiocarb	methiocarb phenol	methiocarb sulfoxide	methiocarb sulfone	total sulfone
before storage	7.4				9.7
cellar[c]	7.3	0.05	2.1	0.8	
bottle[d]	8.0	0.05	2.1	0.8	

[a] Analyses not replicated. [b] Grapes harvested 1 day after last application. Treated four times at 4.5 kg AI/ha with Measurol 75% WP formulation at weekly intervals. [c] Stored 2 months at 13 °C, 6 months at 3.5 °C. [d] Stored 2 months at 13 °C, 6 months at 3.5 °C, and 2 months in bottles at 13 °C.

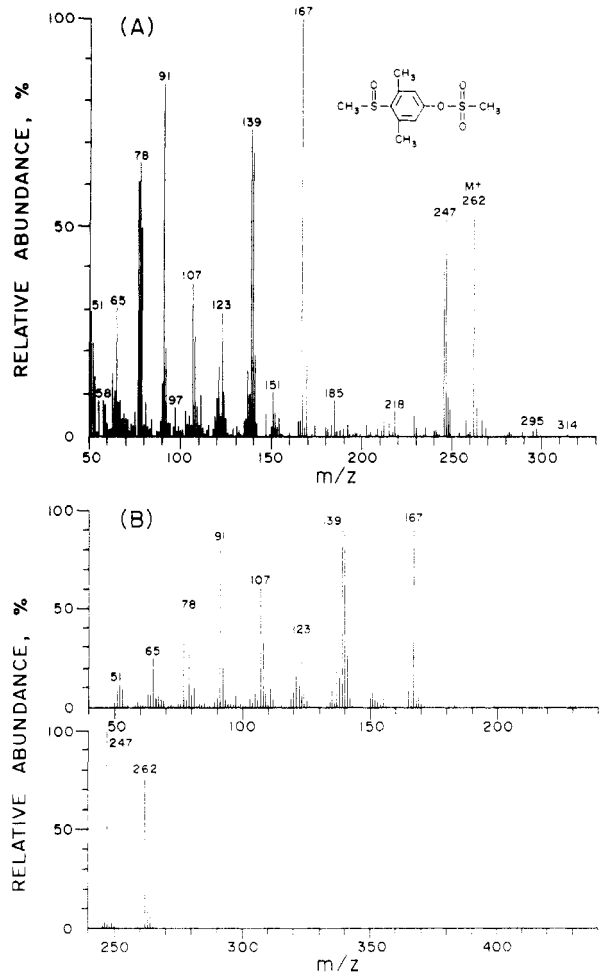

Figure 2. Electron impact spectra of mesylated methiocarb sulfoxide. Spectra obtained on a Finnigan 4023 instrument. Ionization voltage was 70 eV. (A) Standard. (B) Isolated from combined White Riesling and Pinot noir wines produced from field-treated grapes.

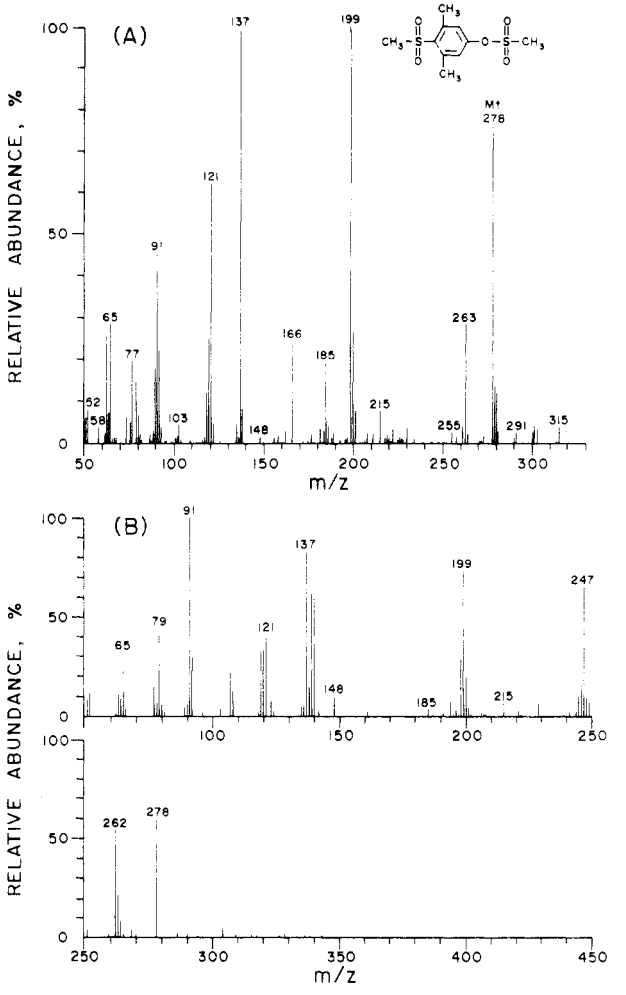

Figure 3. Electron impact spectra of mesylated methiocarb sulfone. Spectra obtained on a Finnigan 4023 instrument. Ionization voltage was 70 eV. (A) Standard. (B) Isolated from combined White Riesling and Pinot noir wines produced from field-treated grapes.

the mass spectrometer to those of standards. Seventy-two percent of the methiocarb and its sulfone phenols were recovered and 24% of the sulfoxide phenol added was detected. It is therefore apparent that the extraction procedure utilized for the carbamate analysis also recovers phenols and because the carbamates were hydrolyzed to the corresponding phenols prior to derivatization, all carbamate residues determined would also contain the corresponding phenols. To determine the extent of phenols present in aged wines, samples of cold stabilized and bottled wines were analyzed for methiocarb phenol by collecting the phenol peak off a HPLC column and then analyzing the sample by mass spectrometry. Data in Table VI indicate that only 0.05 ppm of the methiocarb phenol was present in finished wine.

The mass spectra of methiocarb and its sulfoxide and sulfone mesylates obtained by combining the final extracts of the two wines and those of the corresponding standards are shown in Figure 1–3. The presence of m/z 247 and 262 ions in the wine sulfone mesylate spectrum (Figure 3 part B) indicates incomplete separation of the sulfoxide from methiocarb and its sulfone during Florisil cleanup.

In summary, residues on grapes following 3–4 applications at 4.5 kg AI/ha varied from 3.6 to 58 ppm depending on the application method and treatment to harvest interval. Considerable loss of residue occurred when the juice was pressed from the grapes, about half to $^4/_5$ of the residue on fruit was removed from the vinification process with pomace. Total residues in the finished wine prior to bottling ranged from 4.6 to 9.7 ppm which represented 26–32% of the initial residue on grapes for White Riesling wine and 13–49% of the initial residue for the Pinot noir wine. Methiocarb residue in a fortified White Riesling press juice was reduced by settling and oxidation during processing was minimal. Residues of methiocarb and its sulfoxide and sulfone were not affected by storage at cellar temperatures, and only trace amounts of methiocarb phenol were detected in finished wine.

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Registry No. Methiocarb, 2032-65-7; methiocarb sulfoxide, 2635-10-1; methiocarb sulfone, 2179-25-1; methiocarb phenol, 7379-51-3.

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Aerobic and Anaerobic Degradation of Aldicarb Sulfone in Soils

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[*S-methyl*-^{14}C]Aldicarb sulfone [2-methyl-2-(methylsulfonyl)proprionaldehyde *O*-(methylcarbamonyl)oxime] was incubated under aerobic and anaerobic conditions in surface and subsurface soils from Florida and Georgia. Evolution of $^{14}CO_2$, formation of metabolites, and amounts of extractable and nonextractable ^{14}C were measured in soils incubated with [^{14}C]aldicarb sulfone. Mineralization and disappearance of the carbamate varied greatly from soil to soil. Under aerobic conditions, half-lives in the surface soils from two Florida sites (Lake Hamilton and Oviedo) were shorter than in the corresponding subsurface soils. Aldicarb sulfone nitrile and aldicarb sulfone acid were the two major metabolites. In addition, a TLC polar product, aldicarb sulfone oxime, and three unidentified products were detected.

Aldicarb sulfone [2-methyl-2-(methylsulfonyl)propionaldehyde *O*-(methylcarbamoyl)oxime] and aldicarb sulfoxide [2-methyl-2-(methylsulfinyl)propionaldehyde *O*-(methylcarbamoyl)oxime] are the primary oxidation products of the pesticide aldicarb [2-methyl-2-(methylthio)propionaldehyde *O*-(methylcarbamoyl)oxime] in soils. Aldicarb is rapidly oxidized to aldicarb sulfoxide, which is subsequently oxidized to aldicarb sulfone. Both oxidation products have a toxicity similar to that of the parent aldicarb. Since aldicarb is rapidly degraded in soils (Bromilow et al., 1980; Coppedge et al., 1967; Smelt et al., 1978; Ou et al., 1985), the two oxidation products should contribute to the pesticidal activity. Aldicarb sulfone oxime was also detected in aldicarb treated soils (Bull et al., 1970; Ou et al., 1985). This indicated that aldicarb sulfone, similar to aldicarb and to aldicarb sulfoxide, underwent hydrolysis to the oxime. This should further degrade to the nitrile and eventually to CO_2.

Limited information is available on the degradation rates and half-lives of aldicarb sulfone in soils. Smelt et al. (1978) reported that half-lives under aerobic incubation at 15 °C varied greatly from soil to soil, ranging from 18 days in a clay loam to 154 days in a peaty sand. Disappearance of aldicarb sulfone in subsoil samples was considerably slower than in soil samples from corresponding surface horizons. Half-lives for aldicarb sulfone in soils incubated under anaerobic conditions were substantially shorter (Smelt et al., 1983).

This work was initiated to supplement an earlier study on aldicarb degradation (Ou et al., 1985). Mineralization and disappearance of aldicarb sulfone, and formation of metabolites in surface and subsurface soils collected from Florida and Georgia, were determined under both aerobic and anaerobic conditions.

MATERIALS AND METHODS

Soils. Surface and subsurface soils used in this investigation were the same as those used by Ou et al. (1985). Soil samples were collected from three locations: Lake Hamilton, FL (0–30 and 152–183 cm); Oviedo, FL (0–15 and 107–114 cm); Dougherty Plains, GA (Profile I = 0–27 and 27–57 cm, Profile II = 0–20 and 20–40 cm). Detailed descriptions of the sampling sites and selected properties of these soils have been reported previously (Ou et al., 1985).

Pesticides. Analytical grade aldicarb sulfone was supplied by USEPA (Research Triangle Park, NC). [*S-methyl*-^{14}C]aldicarb sulfone with a specific activity of 7.1

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