New Degradation Products and a Pathway for the Degradation of Aminocarb [4-(Dimethylamino)-3-methylphenyl *N*-Methylcarbamate] in Purified Water

Daniel A. Leger and Victorin N. Mallet*

In this study we found that aminocarb in purified water was hydrolyzed to 4-(dimethylamino)-3-methylphenol. This compound in turn was converted to 2-methyl-1,4-benzoquinone either by direct means or via 2-methyl-1,4-dihydroquinone. The benzoquinone reacted readily with methylamine and dimethylamine present in solution to give four red chemicals. In addition mono- and diepoxides of 2-methyl-1,4-benzoquinone were formed. The presence and nature of these chemicals were determined by GC–MS.

Aminocarb, 4-(dimethylamino)-3-methylphenyl *N*-methylcarbamate, also known as MATACIL, is a broad-spectrum insecticide used throughout the world in agriculture and forestry. It is used extensively in Canada to control the spruce budworm (*Choristoneura fumiferana* Clem.), which is a defoliator of coniferous trees. Aminocarb has been studied by many authors, and the subject has been reviewed by the National Research Council of Canada (1982). Many degradation products have been found in various substrates, but not all have been identified. Thus one recommendation by the NRCC was that all the degradation products of aminocarb be identified.

We became interested in aminocarb for the above reason, but we were also intrigued by the reddish coloration that occurred in environmental water extracts from samples collected during a spray operation in New Brunswick in 1985. In a previous paper (Leger and Mallet, 1985), four red degradation products partially responsible for the red coloration of aqueous solutions of aminocarb were identified. These were 6-(dimethylamino)-2-methyl-1,4-benzoquinone (6-DMAQ), 6-(methylamino)-2-methyl-1,4-benzoquinone (6-MAQ), 5-(dimethylamino)-2-methyl-1,4-benzoquinone (5-DMAQ), and 5-(methylamino)-2-methyl-1,4-benzoquinone (5-MAQ). At the time other degradation products were detected but their identities not determined.

This paper reports on the identification of new degradation products of aminocarb in purified water, leading to the proposal of a possible degradation pathway.

EXPERIMENTAL SECTION

Materials and Methods. The degradation of aminocarb in purified water (normal procedure) was given in Leger and Mallet (1985).

An aqueous solution of aminocarb (analytical standard, 99.9% from Chemagro Ltd.) was prepared by dissolving 100.0 mg in 1 L of purified water (pH 6.4) in a 1-L volumetric flask, which was then covered with an aluminum foil and kept at 25 °C in a water bath. A few milliliters of methanol was added to help dissolve aminocarb. The purified water was obtained by passing twice distilled and deionized water through a 0.45-μm filter and a chromatographic column to remove trace organics. After 30 days a 250-mL aliquot was extracted with 2 × 50 mL of ethyl acetate and the solvent was evaporated to 1 mL.

An aliquot of the extract was analyzed with a Finnigan 4021 GC–MS with Incos data system, using a 30-m DB-5 fused silica capillary column. Approximately 0.5 μL of the solution was injected (splitless) at 50 °C, held at that temperature for 1 min, and then raised to 200 °C at 20 °C/min. The electromultiplier was set at 1400 V, the electron energy was set at 70 eV, and scanning was done from 40 to 300 amu at 1.5 s/scan.

Synthesis of Diepoxides. Moore (1967) synthesized monoepoxy-1,4-benzoquinones by the direct oxidation of the corresponding quinone with a stoichiometric amount of *tert*-butyl hydroperoxide in absolute ethanol–1,4-dioxane (1:1) using Triton B (30% methanolic benzyltrimethylammonium hydroxide) as base catalyst. Because these chemicals were not available at the time, we used a 30% solution of hydrogen peroxide in aqueous ethanol as suggested by Moore (1967).

To 5 g of 2-methyl-1,4-benzoquinone in 40 mL of methanol was added 12 mL of 30% hydrogen peroxide. Then, over 1 h, 4 mL of 6 M NaOH was added while the temperature of the reaction was maintained between 15 and 20 °C. After the addition of NaOH, mixing was continued for 1 h. Water (40 mL) was added and the resulting mixture extracted with 2 × 40 mL of diethyl ether and dried with anhydrous sodium sulfate. The diluted solution (0.1 mL of extract in 100 mL of ethyl acetate) was analyzed by GC–MS.

RESULTS

An extract of an aqueous solution of aminocarb (100 mg/L) aged for 30 days and analyzed by GC–MS gives an ion chromatogram such as that shown in Figure 1. There are at least 11 peaks, and interpretation of the corresponding mass spectra is very revealing. The mass spectra of peaks m/z 476, 490, 512, and 521 are identical with those of 5-MAQ, 6-MAQ, 5-DMAQ, and 6-DMAQ, already identified in a previous paper (Leger and Mallet, 1985). The mass spectral data are reproduced in Table I for comparison purposes.

The mass spectrum of peak 696 shows a M^+ peak of m/z 208, a base peak of m/z 151, and fragments of masses 150, 136, 120, 107, and 77. These values correspond to those of the parent compound aminocarb as already published (NRCC, 1982; Jankowski and Paré, 1980). The spectrum is identical with that of a standard of aminocarb.

The mass spectrum corresponding to peak 414 shows a M^+ at m/z 151 and fragments with masses of 150, 136, 120, 107, and 77, corresponding to those published for aminocarb phenol (NRCC, 1982; Jankowski and Paré, 1980) except that there is an additional peak at m/z 124. The mass spectrum of a standard of aminocarb phenol, under the same conditions, is identical except for the peak at m/z 124. Thus, it is concluded that aminocarb phenol is responsible for peak 414. However, it is clear from Figure 1 that there is another component, peak 418, that would

Department of Chemistry and Biochemistry, Université de Moncton, Moncton, NB, Canada E1A 3E9.

0021-8561/88/1436-0185$01.50/0

Table I. Mass Spectral Data of Aminocarb and Several Degradation Products

peak no.[a]	mass, m/z (% intensity)							
	M^+							
521	165 (100)	150 (34)	137 (20)	122 (23)	108 (17)	94 (27)	82 (24)	69 (40)
490	151 (100)	136 (7.9)	123 (37)	108 (11)	94 (29)	82 (29)	68 (36)	55 (64)
512	165 (100)	150 (38)	137 (6.7)	122 (37)	108 (16)	94 (14)	82 (22)	69 (38)
476	151 (100)	136 (4.4)	123 (14)	108 (13)	94 (19)	82 (39)	68 (30)	55 (78)
696	208 (17)	151 (100)	136 (43)	120 (16)	107 (6)	77 (9)		
414	151 (100)	150 (67)	136 (53)	120 (16)	107 (11)	77 (17)		
193	122 (100)	94 (67)	82 (66)	68 (36)	66 (56)	54 (79)		
219	138 (42)	123 (100)	110 (7)	95 (22)	82 (18)	69 (26)	54 (39)	53 (25)
265	138 (78)	123 (69)	110 (30)	95 (5)	82 (23)	69 (100)	54 (21)	53 (31)
271	154 (24)	139 (26)	111 (17)	69 (37)	55 (12)			

[a] With reference to the ion chromatogram shown in Figure 1.

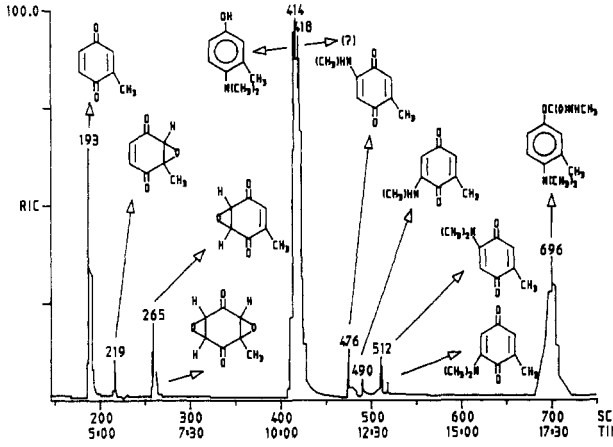

Figure 1. Ion chromatogram of a water extract showing the presence of aminocarb and several degradation products.

interfere with the mass spectrum of peak 414. Presumably the ion peak of m/z 124 originates from this second peak at 418 on the ion chromatogram (see Figure 1). The nature of peak 418 and m/z 124 will be explained later.

The mass spectrum corresponding to peak 193 was matched with that of 2-methyl-1,4-benzoquinone obtained from the Environmental Protection Agency data bank. The spectral data shown in Table I also correspond to those already published for 2-methyl-1,4-benzoquinone (Bowie et al., 1966; MSDC, 1974). Its fragmentation pattern is characteristic of benzoquinones (Bowie et al., 1966), i.e., loss of CO (m/z 94) and ions of m/z 68, 54, 82, and 40 coming from an A, B, C, D type of fragmentation. The spectrum of a standard of 2-methyl-1,4-benzoquinone under the same conditions is identical.

The mass spectral data for peaks 219 and 265 are very similar (Table I). The fragmentation patterns are essentially the same, but the intensities of the ions vary (Figures 2 and 3). There is also some similarity between the mass spectra of peaks 219 and 265 and that of 2-methyl-1,4-benzoquinone, e.g. loss of CO and 2 CO, suggesting that the compounds may be 1,4-benzoquinones. Supposing that m/z 138 is the molecular ion for both products, it is 16 amu or one oxygen atom more than that of 2-methyl-1,4-benzoquinone. With these inferences, several structures of a hydroxy-2-methyl-1,4-benzoquinone were considered, but the published spectrum (Bowie et al., 1966) of 5-hydroxy-2-methyl-1,4-benzoquinone though very similar does not correspond exactly to the spectra of peaks 219 and 265. The fragment at m/z 123, in particular, is absent from the hydroxy compound but very prominent in the mass spectra of peaks 219 and 265 (see Figures 2 and 3). Keeping in mind the low molecular weight and the relation with a 1,4-benzoquinone structure, the other alternative is an epoxide structure. Thus two structures namely 6-methyl-7-oxabicyclo[4.1.0]-3-heptene-2,5-dione and 3-methyl-7-oxabicyclo[4.1.0]-3-heptene-2,5-dione were considered (see Figures 2 and 3).

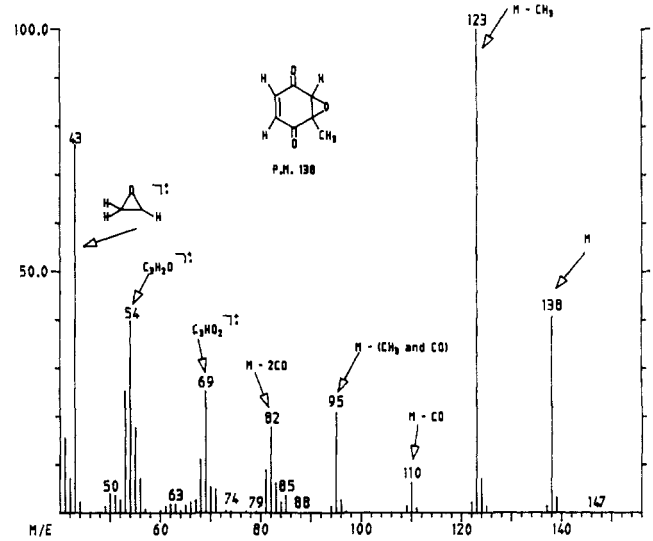

Figure 2. Mass spectrum of peak 219 (see Figure 1) corresponding to 6-methyl-7-oxabicyclo[4.1.0]-3-heptene-2,5-dione.

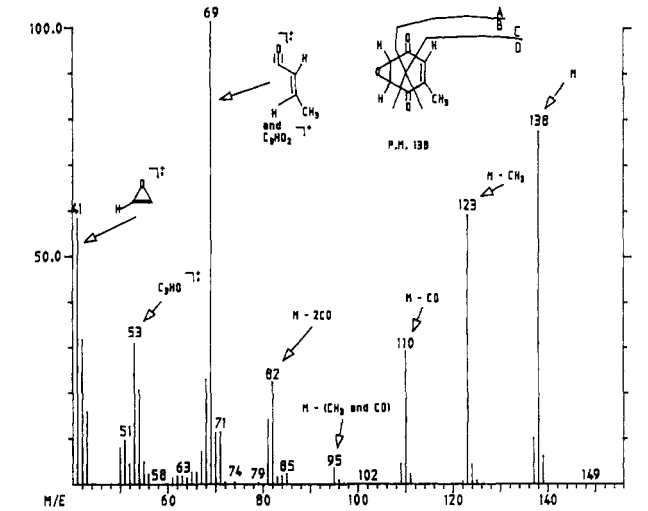

Figure 3. Mass spectrum of peak 265 (see Figure 1) corresponding to 3-methyl-7-oxabicyclo[4.1.0]-3-heptene-2,5-dione.

The mass spectrum of peak 219 (Figure 1) shows fragments characteristic of 1,4-benzoquinone, e.g. M – CO (m/z 110) and M – 2 CO (m/z 82) (Bowie et al., 1966). The base peak m/z 123 shows the easy loss of a methyl group, indicating a stabilizing group in proximity, supporting the possibility of an epoxy ring in positions 2 and 3 of 2-methyl-1,4-benzoquinone. This hypothesis is strongly supported by the intense fragment at m/z 43, which is characteristic of a molecule of the type methyl oxa bicyclo

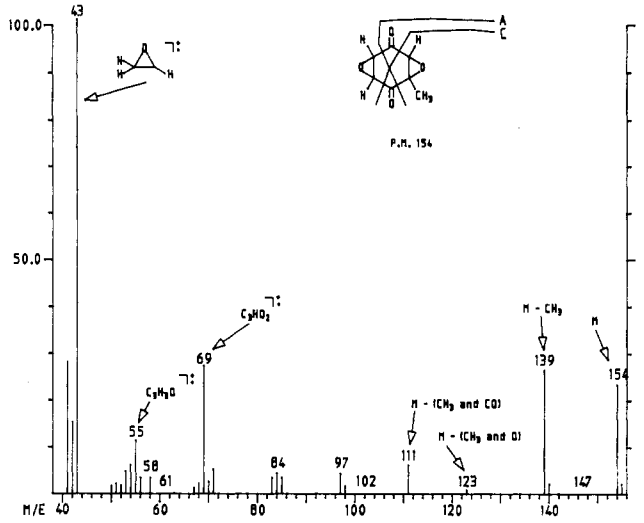

Figure 4. Mass spectrum of peak 271 (see Figure 1) corresponding to 5-methyl-4,8-dioxatricyclo[5.1.0.0]octane-2,6-dione.

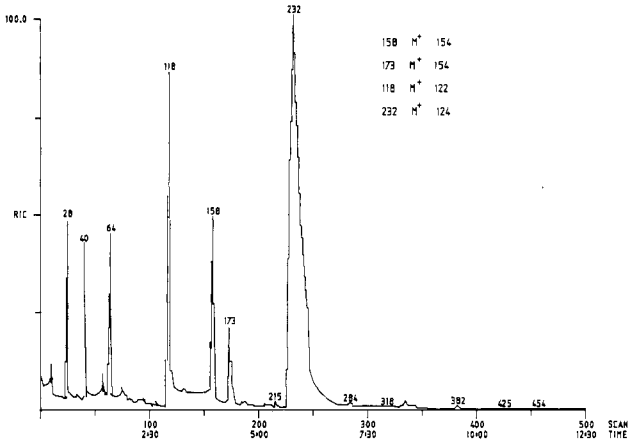

Figure 5. Ion chromatogram of the extract of reaction between 2-methyl-1,4-benzoquinone and H_2O_2 in water.

where the methyl group is directly attached to the epoxide ring (Heller and Milne, 1978; Strong et al., 1969). The fragment at m/z 54 also supports the hypothesis of an epoxy ring in positions 2 and 3 since it is characteristic of an unsubstituted benzoquinone in positions 5 and 6 (Bowie et al., 1966). The other principal fragments in the mass spectra of peak 219 are consistent with the proposed structure. It was thus concluded at this point that peak 219 was 6-methyl-7-oxabicyclo[4.1.0]-3-heptene-2,5-dione.

The mass spectrum of peak 265 (Figure 3) also shows fragments characteristic of 1,4-benzoquinones, e.g. M – CO (m/z 110) and M – 2 CO (m/z 82). It should be noted that a fragment at m/z 123 (loss of a methyl group) is also present but less intense than for peak 219 (see Figure 2), indicating that the stabilizing group is not in proximity to the methyl group. The weak intensity of fragment m/z 54 suggests that positions 5 and 6 of the benzoquinone are occupied presumably by an epoxide ring. This hypothesis is confirmed by the intense fragment at m/z 41, which is characteristic of a methyl oxa bicyclo molecule where the methyl group is not attached to the epoxide ring (Roberts et al., 1971). The base peak at m/z 69 is consistent with such a structure since four fragmentations (A–D, Figure 3) may give such an ion. It was thus concluded that peak 265 (Figure 3) was an isomer of peak 219 (Figure 2) and the suggested structure is 3-methyl-7-oxabicyclo[4.1.0]-3-heptene-2,5-dione.

The structure of peak 271 (Figure 4) was discovered by a similar approach. Considering the fragment at m/z 154 as the molecular ion, it is 32 amu more than 2-methyl-1,4-benzoquinone (equivalent to two oxygen atoms) or 16 amu more (one oxygen atom) than the monoepoxide of 2-methyl-1,4-benzoquinone. This suggests the presence of a diepoxide of 2-methyl-1,4-benzoquinone, and only one structure is possible: 5-methyl-4,8-dioxatricyclo[5.1.0.0]-octane-2,6-dione (see Figure 4). The fragment at m/z 139 in the mass spectrum of peak 271 confirms the presence of a methyl group and that of a stabilizing group in proximity, presumably that of an epoxy group as was the case with product 219 (Figure 2). The fragment at m/z 111 (loss of a methyl group and a carbonyl) supports the hypothesis that the product is a methylbenzoquinone. The strong intensity of the base peak at m/z 43 also supports this structure since this fragment indicates an epoxy group in the molecule (Heller and Milne, 1978; Figure 2). On the basis of the evidence presented and the presence in the extract of 2-methyl-1,4-benzoquinone and the two monoepoxides already discussed, it is concluded that product 271 is 5-methyl-4,8-dioxatricyclo[5.1.0.0]octane-2,6-dione.

Confirmation of the Formation of Epoxides in Purified Water. The evidence presented above points to the formation of epoxides of 2-methyl-1,4-benzoquinone as a result of the degradation of aminocarb in water. To our knowledge such degradation products of aminocarb or, for that matter, other carbamates have never been reported in the literature. However, there is ample evidence of epoxide formation from quinones. In fact, quinone epoxides seem to be very important natural products in the biosynthetic pathways of chemicals by fungi (Kirimaya et al., 1977). Highly oxygenated cyclohexane derivatives with antibiotic or cytotoxic properties have also been isolated from fungi and higher plants (Ichihara et al., 1979).

The mono- and diepoxy-1,4-benzoquinones are thought to have biological importance as antibiotics and as biosynthetic intermediates to naturally occurring hydroxyquinones. Their synthesis by direct base-catalyzed peroxide oxidation of the corresponding 1,4-quinones has been described (Moore, 1967).

We reacted 2-methylbenzoquinone with hydrogen peroxide in aqueous basic medium. The ethyl acetate extract of the reaction mixture was analyzed by GC–MS, and the ion chromatogram is shown in Figure 5. Interpretation of the mass spectra confirmed the presence of the parent compound 2-methyl-1,4-benzoquinone (M^+, m/z 122, peak 118) and of the corresponding 1,4-hydroquinone (M^+, m/z 124, peak 232). Two other peaks (m/z 158, 173) with molecular ion masses of 154 had identical mass spectra except for peak intensities. Their spectra corresponded almost exactly with that of peak 271 (Figure 4) discussed earlier, indicating formation of two diepoxides. The formation of two isomers should be expected in a synthetic reaction, since both the trans and the cis forms of the diepoxides are possible. We did not try to identify which was cis or trans. One isomer seemed to be twice as concentrated as the other, if ion peak height is any indication.

The presence of the monoepoxides was not detected in the extract, and this was expected because the reaction was done with H_2O_2/NaOH in water, which is too exhaustive. The monoepoxides should be obtainable with *tert*-butyl hydroperoxide as the oxidizing agent, Triton B as a base, and absolute ethanol–1,4-dioxane as the solvent as suggested by Moore (1967). For our purpose the fact that the diepoxy was there and by the inference that the monoepoxybenzoquinone may be synthesized in water is conclusive evidence that they are formed in water as a result of the degradation of aminocarb. We have also determined in a subsequent study (not shown here) that the epoxides are

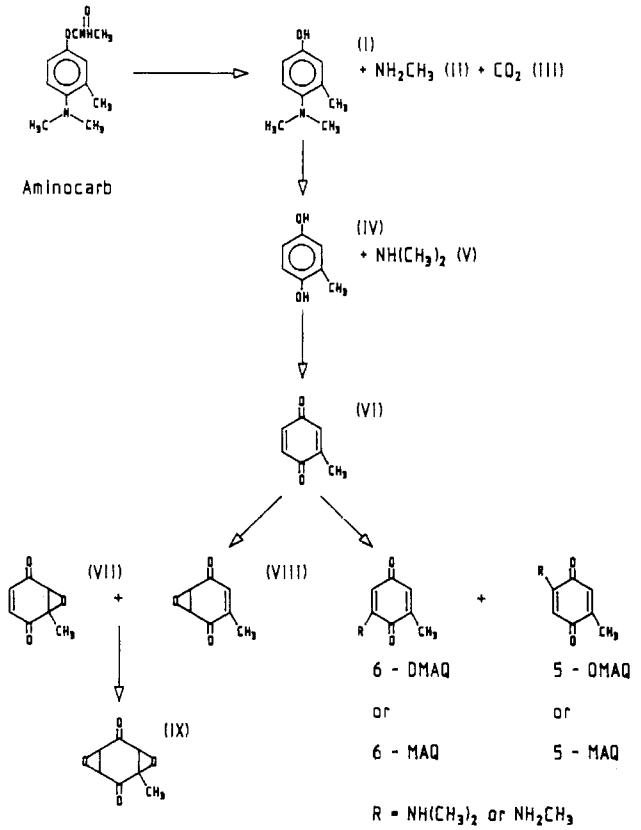

Figure 6. Schematic representation of the degradation of aminocarb in water by a quinolic pathway.

also formed in water with 2-methyl-1,4-benzoquinone or 4-(dimethylamino)-3-methylphenol as starting material.

DISCUSSION

(1) Pathway for the Degradation of Aminocarb in Purified Water. The discovery of new degradation products of aminocarb has led us to propose a pathway to explain their formation. This pathway shown in Figure 6 applies to the degradation of aminocarb in purified water in the dark at 25 °C. It is based not only on our results but also on information available in the literature on the degradation of aminocarb and the chemistry of quinones.

The first step is the hydrolysis of aminocarb to the corresponding phenol (I), methylamine (II), and CO_2 (III) as already documented (NRCC, 1982). The second step is the conversion of the phenol to 2-methyl-1,4-benzoquinone, possibly via the hydroquinone-liberating dimethylamine. Evidence for the presence of 1,4-dihydroquinone is strong. In Figure 1, ion peak 418 gives a spectrum with a M^+ of m/z 124. The structure of the hydroquinone could not be derived from the said spectrum because of interfering peaks from the spectrum of ion peak 414 (see Figure 1). However, the presence of the hydroquinone was detected in aqueous solutions of 2-methyl-1,4-benzoquinone, and the mass spectrum matched to some degree that obtained from peak 418 (Figure 1). It is suspected that the latter equilibrate between the quinone and hydroquinone structures (Coffey, 1974; Roberts et al., 1971). The 1,4-dihydroquinone was also detected as a result of the synthesis of the diepoxides discussed earlier.

The subsequent steps are all based upon the reactions of 2-methyl-1,4-benzoquinone. Thus, the formation of 5- and 6-DMAQ and 5- and 6-MAQ by the reactions of the quinone with methyl and dimethylamine have already been demonstrated (Leger and Mallet, 1985). The epoxyquinones would also originate from 2-methyl-1,4-benzoquinone as supported by the evidence presented here. These epoxides are thermally stable (Alder et al., 1960; Ichwhara et al., 1979), which explains why they were well separated by GC–MS and they may be obtained rather easily from the corresponding benzoquinones in water.

In addition, benzoquinones in solution may also equilibrate to the corresponding hydroxyquinones or to partially reduced states such as semiquinones. Thus, it is probable that these products may also exist in the reaction medium. Experiments are presently being done to determine what happens to the quinones and epoxides in water.

(2) Comparison with Mexacarbate (Zectran). Although 2-methyl-1,4-benzoquinone has never been reported for aminocarb in water, the dimethyl analogue and others have been reported for Zectran (Williams et al., 1964; Hosler, 1974; Roberts et al., 1978; Mauck et al., 1977), which contains one additional methyl group in position 5 of the aromatic ring.

Thus, Williams et al. (1964) reported that Zectran applied to broccoli plants yielded several quinones (ortho and para) and hydroquinones, which formed conjugates with the lignin of the plant. They also discovered the corresponding quinone in dog.

In vitro studies by Hosler (1974e) showed the presence of 2-hydroxy-3,5-dimethyl-1,4-benzoquinone in aqueous medium (pH 9.5). This product has also been claimed by Roberts et al. (1978), and he postulated a scheme for the degradation of Zectran in water.

Finally, Mauck et al. (1977) reported that Zectran in basic aqueous medium yielded at least four products: the corresponding phenol, 3,5-dimethyl-1,4-benzoquinone, 3,5-dimethyl-1,4-dihydroquinone, and 4-amino-3,5-dimethylphenol.

Thus there seems to exist a strong resemblance between the degradation of Zectran and that of aminocarb in water even thought the reaction conditions were different. This may be said because the degradation products of Zectran, namely 3,5-dimethyl-1,4-benzoquinone and Zectran phenol, are analogous to those obtained for aminocarb. However, the pathway proposed here is significantly different from that proposed by Roberts et al. (1978). We have not found yet with aminocarb in purified water evidence of oxidation of the dimethylamino group or of the carbamate moiety. We have not found orthoquinones either. According to our studies it seems that the formation of the quinones from aminocarb or Zectran proceeds via the phenol. In fact, Mauck et al. (1977) obtained the corresponding phenol and quinone with Zectran and they proposed a degradation pathway similar to ours. The above authors, however, never reported the presence of epoxides with Zectran in water although it is most probable that they are formed.

CONCLUSION

The discovery of 2-methyl-1,4-benzoquinone as a degradation product of aminocarb in water supports the formation of quinone epoxides detected in this study. The methylbenzoquinone is also a precursor of the colored (aminomethyl)benzoquinones reported by us in an earlier study (Leger and Mallet, 1985). From the discovery of all these degradation products we have proposed a quinolic oxidative degradation pathway for the degradation of aminocarb in water.

Since the conditions to extract and analyze these degradation products are now known, quantitative analyses to determine the importance of each should be possible, not only in purified water but also in environmental water.

Presently we are studying the degradation of 4-(dimethylamino)-3-methylphenol and 2-methyl-1,4-benzoquinone in water to determine the extent of the degradation in an enclosed system and identify further breakdown

products. It is our intention to pursue these experiments under actual spray operations to determine whether the same degradation products may be obtained and to confirm that the degradation pathway is also oxidative via the quinones.

ACKNOWLEDGMENT

This project was funded by the Natural Sciences and Engineering Research Council of Canada.

Registry No. I, 14143-25-0; VI, 553-97-9; VII, 55164-59-5; VIII, 15254-70-3; IX, 111662-54-5; aminocarb, 2032-59-9; 1,4-dihydroquinone, 123-31-9.

LITERATURE CITED

Alder, K.; Flock, F. H.; Beumling, H. *Chem. Ber.* **1960**, *93*, 1896.
Bowie, J. H.; Cameron, D. W.; Giles, R. G. F.; Williams, D. H. *J. Chem. Soc. B* **1966**, 335.
Coffey, S., Ed. *Rodd's Chemistry of Carbon Compounds*, 2nd ed.; Elsevier: New York, 1974; p 31.
Heller, S. R.; Milne, G. W. A. *EPA/NHI Mass Spectral Data Base*; U.S. GPO: Washington, DC, 1978; p 124, 137, 139, 1099.
Hosler, C. F., Jr. *Bull. Environ. Contamin. Toxicol.* **1974**, *12*, 599.
Ichihara, A.; Kobayaski, M.; Oda, K.; Sakamura, S.; Sakai, R. *Tetrahedron* **1979**, *35*, 2861.
Jankowski, K.; Paré, J. R. *Eur. J. Mass Spectrom. Med. Environ. Res.* **1980**, *1*, 141.
Kirimaya, N.; Higuchi, Y.; Yamamoto, Y. *Chem. Pharm. Bull.* **1977**, *25*, 1265.
Leger, D. A.; Mallet, V. N. *J. Agric. Food Chem.* **1985**, *33*, 7481.
Mass Spectrometry Data Centre *Eight Peak Index of Mass Spectra*, 2nd ed.; Pendragon House: Palo Alto, CA, 1974; Vol. 1, p 94.
Mauck, W. L.; Olson, L. E.; Hogan, J. W. *Arch. Environ. Contamin. Toxicol.* **1977**, *6*, 385.
Moore, H. W. *J. Org. Chem.* **1967**, *32*, 1996.
National Research Council of Canada *Aminocarb: The Effects of Its Use on the Forest and the Human Environment*, Publ. No. 18979; NRCC: Ottawa, Canada, 1982; p 19.
Roberts, J. D.; Stewart, R.; Caserio, M. C. *Organic Chemistry*; W. A. Benjamin: Meslo Park, CA, 1971; p 638.
Roberts, R. B.; Look, M.; Haddon, W. F.; Dickerson, T. C. *J. Agric. Food Chem.* **1978**, *26*, 55.
Strong, M. K.; Brown, P.; Djerassi, C. *Org. Mass Spectrom.* **1969**, *2*, 1201.
Williams, E.; Meikle, R. M.; Redeman, C. T. *J. Agric. Food Chem.* **1964**, *12*, 453.

Received for review September 10, 1986. Revised manuscript received May 11, 1987. Accepted October 7, 1987.

Metabolic Fate of Fenvalerate in Wheat Plants

Philip W. Lee,* Stephen M. Stearns, and Walter R. Powell

The metabolic fate of [*chlorophenyl*-^{14}C]- and [*phenoxyphenyl*-^{14}C]fenvalerate on wheat plants after foliar treatment was examined. The half-life of fenvalerate on foliar surfaces at an exaggerated application rate of 1 lb/acre, under outdoor conditions, was approximately 3 weeks. Systemic movement of [^{14}C]fenvalerate and its metabolite(s) was not observed. The amount of ^{14}C residue in the grain and hull (mature plants harvested 10 weeks posttreatment) was below the limit of reliable measurement (<0.03 ppm). Undegraded [^{14}C]fenvalerate was the major product recovered in the foliage or straw at each sampling interval. Individual degradation products accounting for greater than 1% of the applied radioactivity were not present. Important degradation pathways included decarboxylation and ester cleavage. Formation of water-soluble conjugates was only of minor significance in the wheat plants. The isomeric composition between the [^{14}C]fenvalerate treatment solution and the "aged" parent recovered from the treated plants was unchanged.

Fenvalerate [1, cyano(3-phenoxyphenyl)methyl 4-chloro-α-(1-methylethyl)benzeneacetate, PYDRIN insecticide, a registered product of Du Pont] is an effective synthetic pyrethroid insecticide possessing excellent insecticidal activity and also favorable environmental stability (Miyamoto and Mikami, 1983). The environmental fate of fenvalerate (Lee, 1985; Caplan et al., 1984; Reed et al., 1983; Ohkawa et al., 1980a; Mikami et al., 1980) and its metabolism in the soil (Mikami et al., 1984; Ohkawa et al., 1978), animals (Lee et al., 1985; Kaneko et al., 1984; Kaneko et al., 1981; Ohkawa et al., 1979), and insects (Soderlund et al., 1983) have been reported. Plant metabolism studies have been conducted with the kidney bean (Ohkawa et al., 1980b) and cabbage (Mikami et al., 1985). The increased wide use pattern of fenvalerate and its extended field residual activity warrant further understanding of its metabolic fate in other crop species, especially in the grain cereals. This report describes the dissipation rate, characterization of the residue distribution pattern, and structural elucidation of significant fenvalerate degradation products in mature wheat plants following foliar application.

Agricultural Products Department, Experimental Station, E. I. du Pont de Nemours & Company, Inc., Wilmington, Delaware 19898.

EXPERIMENTAL SECTION

Test Materials and Reference Standards. Radiolabeled fenvalerate and appropriate reference standards were synthesized by the Biological Science Research Center (BSRC), Shell Agricultural Chemical Co. Two preparations of [^{14}C]fenvalerate, one labeled at the chlorophenyl and the other at the phenoxyphenyl moiety, were used. Both compounds had a radiochemical purity of greater than 99.5%, as determined by thin-layer chromatography (TLC), autoradiography, and liquid scintillation counting (LSC). Authentic standards included CPIA [**2**, 4-chloro-α-(1-methylethyl)benzeneacetic acid], 4′-hydroxyfenvalerate [**3**, cyano[3-(4-hydroxyphenoxy)phenyl]methyl 4-chloro-α-(1-methylethyl)benzeneacetic acid], decarb-

0021-8561/88/1436-0189$01.50/0