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Identification of Four New Degradation Products of Aminocarb [4-(Dimethylamino)-3-methylphenyl *N*-Methylcarbamate] in Water

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In this study we have found that aminocarb, a forestry insecticide, gives four colored degradation products in purified water. They were identified as 6-(dimethylamino)-2-methyl-1,4-benzoquinone, 5-(dimethylamino)-2-methyl-1,4-benzoquinone, 6-(methylamino)-2-methyl-1,4-benzoquinone, and 5-(methylamino)-2-methyl-1,4-benzoquinone. The four chemicals were extracted from water, then separated, and purified by chromatographic methods. Identification was achieved by nuclear magnetic resonance, mass spectrometry, and X-ray crystallography.

INTRODUCTION

Aminocarb, [4-(dimethylamino)-3-methylphenyl *N*-methylcarbamate], also known as MATACIL, is a broad spectrum insecticide used throughout the world for the control of agricultural and forest pests. In Canada, it is used extensively to protect coniferous trees from *Choristoneura fumiferana* Clem., better known as the spruce budworm. Thus, the National Research Council of Canada (NRCC) is interested to know the fate of this chemical in the Canadian ecosystem and in a recent review of the subject (NRCC, 1982) it has recommended that further studies be done to establish the nature of all the degradation products of aminocarb.

Many researchers have studied the fate of aminocarb in various substrates (Abdel-Wahab et al., 1966; Krishna and Casida, 1966; Abdel-Wahab and Casida, 1967; Balba and Saha, 1974; Addison et al., 1974; Sundaram and Szeto, 1979; Sundaram et al., 1980; Cool and Jankowski, 1982). Several degradation products have been identified, namely, 4-(dimethylamino)-3-methylphenol, 4-amino-3-methylphenol, 4-(dimethylamino)-3-methylphenyl *N*-(hydroxymethyl)carbamate, 4-(methylamino)-3-methylphenyl *N*-methylcarbamate, and 4-(formamido)-3-methylphenyl *N*-methylcarbamate, to name but a few.

It is now generally accepted that aminocarb hydrolyzes readily in alkaline medium (Maguire, 1979) and under environmental conditions (Davidson and Dorais, 1981) to give the corresponding phenol. A recent study by Mallet and Levesque (1983) has established that several parameters such as pH, temperature, and dissolved oxygen may accelerate the degradation of aminocarb in water but no attempt was made to detect degradation products other than the corresponding phenol.

In an attempt to identify new degradation products of aminocarb in water, our attention was focused on a pink-reddish coloration that develops in aging aqueous solutions. This coloration has been reported by Vassilieff and Ecobichon (1982) who suggested that it could be caused by an equilibrium between protonated and unprotonated species. This tentative explanation seemed unsatisfactory since the

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Table I. Mass Spectral Data for the Red Colored Chemicals

chem no.	mass (% intensity)							
	M^+	m/z	m/z	m/z	m/z	m/z	m/z	m/z
1	165 (100)	150 (34)	137 (20)	122 (23)	108 (17)	94 (27)	82 (24)	69 (40)
2	151 (100)	136 (7.9)	123 (37)	108 (11)	94 (29)	82 (29)	68 (36)	55 (64)
3	165 (100)	150 (38)	137 (6.7)	122 (37)	108 (16)	94 (14)	82 (22)	69 (38)
4	151 (100)	136 (4.4)	123 (14)	108 (13)	94 (19)	82 (39)	68 (30)	55 (78)

coloration was not reversible by a change in pH.

Thus the aim of this research was to isolate and identify those degradation products responsible for the coloration of aging aqueous standard solutions of aminocarb.

EXPERIMENTAL SECTION

Materials and Methods. (1) Degradation of Aminocarb in Purified Water (Normal Procedure). 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. 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 (Millipore Norganic Kit).

(2) Degradation of Aminocarb in Purified Water (Preparative Procedure). To obtain more rapidly, larger quantities of the desired degradation products of aminocarb an accelerated degradation procedure was developed. Exactly 1.0 g of aminocarb, 1.5 L of purified water, and 2.0 mL of NaOH (3 M) were added to a 2-L Erlenmeyer flask. The solution of pH ~10 was heated and kept at 35–40 °C while stirring for 3 h and then neutralized to pH 7.0 by adding HCl (3 M). Finally 1.5 g of potassium chromate was added to oxidize the liberated phenol and the solution was stirred for 7 h at 30–35 °C.

(3) Extraction of Aqueous Solutions. The red colored solution resulting from either degradation method just described was extracted with ethyl acetate (2 × 50 mL for 250 mL of water solution). About 1 g of NaCl was added to reduce emulsions and to reduce the solubility of ethyl acetate in water. The extract was dried over anhydrous Na_2SO_4 and evaporated almost to dryness with a rotary evaporator.

(4) Thin-Layer Chromatography (TLC). The concentrated extract obtained above was spotted as a band on a silica gel thin-layer plate (20 × 20 cm, PK6F, 0.5 mm thick, Whatman Chem. Sepn. Inc.) which was eluted with ether–*n*-hexane (40:10). Following development to 10 cm each colored band of adsorbant was scraped and placed in a disposable Pasteur pipet (14.5 cm × 0.8 cm i.d., Canlab Chem. Co.) thus forming a small column. Each column was eluted with ethyl acetate until all the colored substance had been collected. Each colored eluate was evaporated to dryness.

(5) High-Performance Liquid Chromatography (HPLC). Each crystalline colored product from the TLC separation was purified further by HPLC with a Spectra Physics SP8000B equipped with a preparative column (Partisil M9, 10/25 RPODS, Whatman) and a UV detector (254 nm). The mobile phase was water and acetonitrile (80:20) at 3.0 mL/min, isocratic mode. Each colored substance was extracted from 75 mL of aqueous medium with 2 × 15 mL of methyl isobutyl ketone (MIBK) which was then removed completely by rotary evaporation yielding pure crystalline solids.

(6) Gas Chromatography (GC). The gas chromatograph was a Tracor 560 equipped with a flame ionization detector (FID) and a 1.8 m × 4 mm i.d. glass column containing 3% OV-17 on Chromosorb W, DMCS, 80–100 mesh. The operating conditions were column temperature 100 °C for 5 min, then 100–180 °C at 5 °C/min, injection temperature 150 °C, detector temperature 190 °C, at a flow rate of 34 mL/min with N_2 as carrier gas.

(7) Spectral and Other Instrumental Analyses. MS were recorded on a Finnigan 4021, NMR with a Varian XL 200, and X-ray crystallography on a Pika FACS-I. NMR spectra were recorded in deuterated chloroform.

(8) Synthesis of 5-(Dimethylamino)-2-methyl-1,4-benzoquinone (5-DMAQ) and 6-(Dimethylamino)-2-methyl-1,4-benzoquinone (6-DMAQ). Both chemicals were synthesized by reacting 2-methyl-1,4-benzoquinone with dimethylamine according to Shaikh (1977). The compounds were separated by TLC and purified by HPLC as described earlier. Both chemicals are red crystalline solids 5-DMAQ: λ_{max} 275, ϵ 10 400; λ_{max} 487, ϵ 3800; mp 83 °C. 6-DMAQ: λ_{max} 277, ϵ 10 400; λ_{max} 385, ϵ 4800; mp 102 °C.

RESULTS AND DISCUSSION

An aqueous solution of aminocarb (100 mg/L) kept in the dark at 25 °C becomes reddish after 12 days and intensely red colored after 30 days. An aliquot extracted after 17 days, which corresponds approximately to the half-life (Mallet and Levesque, 1983), yields 8 spots on TLC. The spot at the origin (spot 0) is dark brown while spots 1–4 are reddish. The others (5–7) are only visible under UV light. A control, without aminocarb, does not give any spot.

The objective of this study was to determine the cause of the reddish coloration of aging aqueous solutions of aminocarb. Thus attempts were made to identify the chemicals corresponding to spots 1–4. However, the quantities obtained from the normal degradation procedure were small even though 100 mg/L were used. So a preparative procedure was developed that gave sufficient quantities (1–2 mg) of the desired products in a relatively short time. Verification was made by TLC, GC, HPLC, and eventually by GC–MS that the same four chemicals were obtained by both procedures.

The four red colored chemicals obtained from the degradation of aminocarb in water were analyzed by MS, by direct injection. The data are presented in Table I. The chemical responsible for spot no. 3 has a molecular ion of m/z 165. The fragment at m/z 150 represents the loss of a methyl group from the molecular ion. The peak at m/z 137 may be attributed to the loss of a carbonyl group from the molecular ion. This is the first evidence that the structure is a benzoquinone and it is supported by Coffey (1974) and Bowie et al. (1966). The intense peak at m/z 122 corresponds to the successive loss of a carbonyl group and a methyl group from M^+. Further support for the quinone structure are the fragments at m/z 69 and 68, as suggested by Coffey (1974) and Bowie et al. (1966).

The proton NMR data for the four chemicals are presented in Table II. The data for chemical no. 3 indicate the presence of an olefenic proton coupled to a methyl group. The former appears as a quartet at 6.30 ppm and the latter as a doublet at 1.96 ppm. These values and a coupling constant of 1.6 are typical of 2-methylbenzoquinones (Norris and Sternhell, 1966). The presence of

Table II. H-1 NMR Data for the Red Colored Chemicals[a]

chem no.	chemical shifts, ppm, and coupling constants, Hz				
	H-3	CH_3	H-5 or 6	$N(CH_3)$	NH
1	6.40 (1 H, m, 1.6 Hz)	1.96 (3 H, d)	5.49 (1 H, d)	3.07 (6 H, S)	
2	6.46 (1 H, m, 1.6 Hz)	1.99 (3 H, d, 1.6 Hz)	5.41 (1 H, d)	2.83 (3 H, d)	5.64 (1 H, br)
3	6.30 (1 H, q, 1.6 Hz)	1.96 (3 H, d, 1.6 Hz)	5.50 (1 H, S)	3.07 (6 H, S)	
4	6.43 (1 H, q, 1.6 Hz)	2.05 (3 H, d)	5.43 (1 H, S)	2.82 (3 H, d)	5.63 (1 H, br)

[a] s = singlet; d = doublet; q = quartet; br = broad band; m = multiplet.

Table III. C-13 NMR Data for Chemicals No. 1 and 3

carbon or group	NMR signal, ppm	
	no. 1	no. 3
C-1	185.6	185.4
C-2	142.7	147.3
C-3	134.5	131.1
C-4	185.9	185.3
C-5	104.5	150.6
C-6	151.1	104.3
R–CH_3	15.8	15.7
$N(CH_3)_2$	42.3	42.3

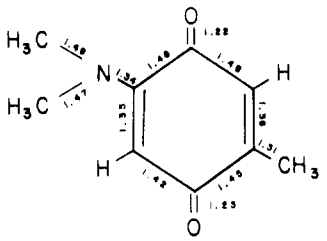

Figure 1. Structure of 5-(dimethylamino)-2-methyl-1,4-benzoquinone (5-DMAQ) with bond lengths as determined by X-ray crystallography.

an uncoupled proton is indicated by a singlet at 5.50 ppm and the signal at 3.07 ppm corresponding to six protons indicates clearly the presence of a dimethylamino group.

The C-13 NMR data for chemicals 1 and 3 are given in Table III. The values obtained for the six ring carbons are in agreement with those of substituted quinones (Berger and Rieker (1972); Hollenstein and von Philipsborn (1972)). Thus the signals for C-1 and C-4 have similar chemical shifts typical of carbonyl groups. Evidence for the two substituents, dimethylamine and methyl groups, is given by the respective signals at 42.3 (N–O) and 15.7 ppm (CH_3).

Thus the information presented above supported the structure of a benzoquinone substituted with a methyl group next to a proton and having a dimethylamino group also next to a proton. Still the ambiguity as to whether the structure was 1,2-benzoquinone or a 1,4-benzoquinone persisted even though the C-13 NMR data supported the latter. X-ray crystallography provided the final answer (Figure 1) and chemical 3 was identified as 5-(dimethylamino)-2-methyl-1,4-benzoquinone (5-DMAQ). Confirmation was achieved by synthesizing 5-DMAQ by another route and comparing its MS data with those of chemical 3. The spectra were identical.

The MS data for chemical no. 1 (see Table I) indicate that the molecular ion is also of m/z 165 and the breakdown pattern is identical except for peak intensities with that obtained with chemical 3, suggesting an isomer. The NMR data for chemical 1 (see Table II) suggest a methyl group (1.96 ppm, d, 3 H) next to a proton as was the case for chemical 3. The presence of a dimethylamino group is also evident at 3.07 ppm (6 H). Therefore if chemical 1 is an isomer of chemical 3, the dimethylamino group must be in position 6. Thus, all the evidence pointed to the chemical 6-(dimethylamino)-2-methyl-1,4-benzoquinone (6-DMAQ). Confirmation was obtained by synthesizing 6-DMAQ by another route and comparing its MS with that of chemical 1. The spectra were identical.

Table IV. R_f Values and GLC and HPLC Retention Times of Colored Degradation Products of Aminocarb in Water

chemical	R_f values	retention time, min	
		GC	HPLC
1 (6-DMAQ)	0.29	23.9	25.2
2 (6-MAQ)	0.36	22.5	14.1
3 (5-DMAQ)	0.40	23.0	27.9
4 (5-MAQ)	0.47	21.6	15.6

Once the structures of 5-DMAQ and 6-DMAQ were established it was easier to deduce the structures of chemicals 2 and 4. According to their mass spectral data (Table I) they are isomers of molecular weight 151 (M_r). The mass spectral data indicate loss of a methyl group (m/z 136), loss of a carbonyl group (m/z 136), and successive losses of a carbonyl and a methyl groups (m/z 108).

The proton NMR data [The C-13 NMR were not done because of the limited quantities of isolated degradation products.] show a doublet (3 H) at 2.8 ppm and a broad signal at 5.6 ppm suggesting a coupling with NH. The presence of a methyl group next to a proton is also evident. All this information plus the similarities of the coupling constants between protons of chemical 2 and 6-DMAQ on one hand and between chemical 4 and 5-DMAQ on the other, lead to the conclusion that chemical 2 is 6-(methylamino)-2-methyl-1,4-benzoquinone (6-MAQ) and chemical 4 is 5-(methylamino)-2-methyl-1,4-benzoquinone (5-MAQ).

To the best of our knowledge, these four chemicals are new degradation products of aminocarb and have never been reported in the literature. Their R_f values and GC and HPLC retention times are given in Table IV for reference purposes. These values are exactly the same for either the isolated degradation products or the synthesized products, as applicable.

CONCLUSION

As a result of this study four new degradation products of aminocarb were identified. It is too early to tell whether these chemicals are important in terms of the environment. Obviously they are formed in an enclosed system where the reactants and products can interact with one another. Work is presently under way to determine the relative quantities of these chemicals in relation to the parent compound. At the moment they are thought to be minor constituents. Other degradation products are presently being identified and it is expected that they will shed light as to the probable degradation pathway. Once all of the degradation products are known and the reaction pathway is understood it should be possible to undertake a similar study under environmental conditions and the information gathered in this study will provide a base for comparison.

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Conformer-Restriction Analysis: Pyrethroids Containing Dibenzofuran Alcohol Moieties

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In an undertaking of conformer-restriction analysis, seven pyrethroids have been synthesized in which the alcohol moieties are hydroxymethyl (or the α-cyano derivative) substituted dibenzofurans. The acid moiety of each pyrethroid ester was *d-trans*-chrysanthemic acid. The various dibenzofuran alcohols synthesized represent the two planar conformational extremes associated with both 3-phenoxybenzyl alcohol and 1,1′-biphenyl-3-methanol, both of which are potent pyrethroid alcohols. The new pyrethroid esters were found to have very little or no insecticidal activity against the various species tested. It is concluded that planar conformations of the flexible (or twistable) aromatic alcohol moieties of potent pyrethroids are incompatible with binding to an insect receptor site.

INTRODUCTION

During recent years synthetic pyrethroids have attracted considerable attention as potential replacements for naturally occurring pyrethrins and other types of synthetic insecticides (Elliott, 1977; Wilkerson and Norton, 1981; Sheppard and Norton, 1980). Most of the recent successful studies have been primarily concerned with the synthesis of either photostabilized alcohol moieties or the replacement of the isobutenyl groups of the acid moiety by functions that are resistant to oxidative degradation (Sheppard and Norton, 1980; Soderlund and Casida, 1977).

Other studies involving compositional variations of the cyclopropane ring (e.g., an appropriately substituted aziridine ring) have been less successful in producing potent insecticides (Sheppard and Norton, 1980; Casida and Berteau, 1969). Structural and configurational requirements for both the acid and alcohol moieties of active pyrethroids have been extensively studied, and general guidelines have been given which relate to optimal structure/activity relationships (Elliott, 1977). Conformation/activity relationships among pyrethroids is also an important consideration. Insecticidal action is presently interpreted to involve an ability of the active molecule to adopt a conformation in which the structural components necessary for potency are properly oriented with respect to each other and to a complementary receptor (Elliott, 1970; 1977).

In conformational studies of the pyrethroid, decamethrin, the bond rotations of all pertinent single bonds have been determined by calculation (for the free molecule) and by X-ray analysis (the crystalline form) (Elliott and Janes, 1977). In the bonds associated with the ether linkage of the alcohol moiety, bonds a and b were both calculated to be rotated 90° for the free molecule (best rotation to minimize interdependent interference). On the other hand, the rotational angles are 44° and 19° for bonds a and b, respectively, in the crystalline form. It is not known how significant these bond angle preferences are for insecticidal activity. Sharp NMR signals for pyrethroids in solution indicate that the various conformers are interconverted rapidly. At the site of action the forces of binding undoubtedly influence the conformational status of the pyrethroid as it accommodates itself to the binding site.

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