MAGUIRE

Environment Canada

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National Water Research Institute

Institut National de Recherche sur les Eaux

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R. James Maguire
Process Research Division
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Canada Centre for Inland Waters
Environment Canada
P.O. Box 5050, Burlington, Ontario
Canada L7R 4A6

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INTRODUCTION

Of the thousands of methylcarbamates synthesized by various chemical companies in the last twenty years, only about a dozen have reached sizable production as commercial insecticides. One of the oldest methylcarbamate insecticides is aminocarb (4-dimethylamino-3-methylphenyl-N-methylcarbamate; p-dimethylamino-m-tolyl-N-methylcarbamate; Bayer 44646) which was introduced in 1963 as Matacil by Bayer Leverkusen and researched in the United States by the Chemagro Division of Baychem Corporation. This chapter summarizes the available literature on the physical and chemical properties, biological and environmental transformations, and the chemical analysis of aminocarb.

Physical and Chemical Properties

Figures 1 and 2 show the chemical structures of aminocarb and some of its biological and environmental "metabolites". Aminocarb is a white crystalline solid, mp 93-94°C, mw 208, quite soluble in most polar organic solvents, moderately soluble in aromatic solvents (1), and soluble to at least 100 ppm in water at pH 7.0 and 25°C (2). It is "partially decomposed" when held for several days as dilute solutions in acetone, carbon tetrachloride, chloroform or methylene chloride, but it is stable when held for comparable periods in acetonitrile, benzene, 95% ethanol, n-hexane and toluene (3). The extraction p-values (the p-value, determined by distributing a solute between equal volumes of two immiscible phases, is defined as the fraction of the total solute partitioning into the upper phase) for aminocarb in six binary solvent systems are given in Table 1 (4). Aminocarb can be

prepared in three ways, by reacting the parent phenol with (i) methyl isocyanate, (ii) phosgene, followed by methylamine, or (iii) methylcarbamoyl chloride (5). Synthetic methods for some of aminocarb's metabolites have been reported (3,6). Tables 2-5 summarize the data on the (i) proton magnetic resonance, (ii) infrared absorption frequencies, (iii) ultraviolet absorption, fluorescence and phosphorescence characteristics, and (iv) electron impact, chemical ionization, and negative ion mass spectra of aminocarb, respectively. The half-life for the hydrolysis of aminocarb in pH 9.3 buffer (unspecified temperature) has been reported to be 4 hours (14). The rate of evaporation of aminocarb from a glass surface under fluorescent light at 25°C has been studied (14). The rate of loss curve (plotted on a semi-logarithmic scale) was approximately linear for the first few hours only (50% loss time was 1.6 hours) and, in the period of 4 to 12 hours after application, it developed a considerably lower slope, indicative of a change to less volatile products on exposure to air and light. Thin layer chromatographic analysis of the residue revealed three unidentified degradation products.

Biological and Environmental Reactions

Critical interpretation of toxicology and residue studies on an insecticide is possible only when the chemical, biological and environmental metabolism of the compound is understood. Biologically active metabolites may be formed, particularly if the modification on the molecule occurs at a site other than that which is necessary for insecticidal activity. In this

respect, metabolites formed by mechanisms other than initial hydrolysis at the carbamic ester site may be of importance.

Hydrolysis predominates in the metabolism of aminocarb in rats (15). About 70% of a ^{14}C-carbonyl-labeled dose of aminocarb injected into rats was expired as $^{14}CO_2$ after 48 hours; 25% of the administered radiocarbon was eliminated in the urine and 4% was voided in the feces. There was, however, no identification of the metabolites in this study.

Several metabolic studies have been done using rat and human liver enzyme systems and housefly enzyme preparations (16-21). The major metabolites, apart from the initial hydrolysis products methylamine (IV) and 4-dimethylamino-3-methylphenol (III) have been identified as 4-dimethylamino-m-tolyl-N-hydroxymethylcarbamate (II), 4-methylamino-m-tolyl-N-methylcarbamate (VI), 4-amino-m-tolyl-N-methylcarbamate (VII) and 4-formamido-m-tolyl-N-methylcarbamate (IX) and there may be at least 7 more unidentified metabolites which are present in smaller amounts. The N-hydroxymethyl derivative is as potent a plasma cholinesterase inhibitor as aminocarb, and the 4-amino and 4-methylamino derivatives are ten times more potent than aminocarb (19). Some of the unidentified metabolites are 1 - 10 times more active than aminocarb as anti-cholinesterase agents (19). Human liver enzymes do not produce the N-hydroxymethyl derivative as readily as rat liver fractions (21). Balba and Saha (6) have used the ascorbic acid oxidation system (L-ascorbic acid, ferrous ion, ethylenediaminetetraacetic acid and soluble oxygen) to oxidize aminocarb in an attempt to simulate biological oxidation processes. There were about 12 oxidation products, of which 5 were identified as 4-dimethylamino-m-tolyl

-N-hydroxymethylcarbamate (II), 4-methylamino-m-tolyl-N-methylcarbamate (VI), 4-amino-m-tolyl-N-methylcarbamate (VII), 4-dimethylamino-3-methylphenol (III), and a derivative of aminocarb in which an hydroxyl group had been added to the ring in an unspecified position (V). It appears that this simulation approach may be useful in studying the biological oxidation of carbamates.

The major products of aminocarb resulting from injection into bean plants are similar to, or the same as, those resulting from animal systems: the 4-methylamino, 4-amino, 4-formamido and 4-methylformamido (VIII) derivatives (14). The authors noted that the phenol was probably conjugated and that there was no 4-dimethylamino-m-tolyl-N-hydroxymethylcarbamate formed. Continued metabolism in plants results in most of the terminal residues being in a form which cannot be extracted from the plant tissues. For example, when ^{14}C-carbonyl-labeled aminocarb was injected into bean plants, 70% of the administered dose was unextractable after 6 days (22). Unidentified water-soluble metabolites (conjugates with carbohydrates which could be hydrolyzed with β-glucosidase) accounted for 8% of the applied dose, and 2% of the dose was present as unidentified organo-extractable compounds.

The photolysis of aminocarb was first examined by Crosby et al. (23); they irradiated solutions of aminocarb in absolute ethanol or hexane with laboratory ultraviolet light (peak radiation at 254 nm) and sunlight, and noted transformation to 3-5 unidentified plasma cholinesterase inhibitors. Addison et al. (8) determined that the major product of photolysis in absolute ethanol or hexane, using either light of wavelength 254nm or ">300 nm" was 4-dimethylamino-3-methylphenol. In this regard, Kuhr and Dorough (5) have advised caution on two features of the

photochemical decomposition of carbamates, i.e., (i) illumination from the sun does not involve light of 254 nm, but includes a spectral range of wavelengths from 300 to 450 nm, and (ii) dissolution of the carbamate in a solvent makes practically every molecule a potential target, whereas carbamates coated onto silica gel, plant foliage, or other surfaces are not as readily available.

Abdel-Wahab et al. (14) identified 4 of 8 products observed on bean leaves after irradiation with short wavelength (254 nm) ultraviolet light; these were the 4-formamido, 4-methylformamido, 4-amino and 4-methylamino derivatives. Aminocarb did not degrade under fluorescent or long wavelength ultraviolet light (366 nm). A later report by the same authors (3) used an environmentally more relevant light source, i.e., sunlight, in the photooxidation of aminocarb on bean leaves. Although ultraviolet light (254 nm) produces more products than sunlight, in both cases the 4 major metabolites (of about 11) are those just mentioned. The proposed scheme for sunlight photodecomposition of aminocarb is shown in Fig. 3. Despite the ease of breakdown of aminocarb, several of the derivatives retain considerable toxicity; thus, in the end it is the stability of these products which determines the environmental safety of aminocarb, and the stability of these products is, at present, unknown.

The persistence of aminocarb added to a sample of river water (maintained in the laboratory) has been examined (24). Aliquots of whole water were extracted and analyzed for aminocarb from time to time; the results showed that 60% of the parent compound remained after 1 week, 10% after 2 weeks, and none remained after 3 weeks. The identities of the

degradation products were not determined. Sundaram et al (25) studied the persistence of only the parent compound in pond and stream water after a forest spray; they found rough "half-lives" of 4-9 days, with no traces remaining after 32 days. Sundaram and Hopewell (26) also studied the rate of disappearance of aminocarb from spruce foliage and forest soil under natural meteorological conditions. Initial concentrations of about 10 ppm in foliage and 7 ppm in soil had "half-lives" of 6 and 2 days, respectively, and had dropped to trace or non-detectable levels within 47 and 27 days, respectively; as in the previous study, the identities of the degradation products were not determined.

Several research areas on aminocarb which require further study (and which reflect the author's bias) are (i) the persistence and distribution of solvent oils and carriers in the context of forest spraying operations, (ii) the photolysis of aminocarb in natural waters, and (iii) the distribution, persistence and fate of aminocarb and its metabolites in natural waters, sediments and suspended solids.

Chemical Analysis for Aminocarb

Carbamate residue methodology requires a high degree of skill on the part of the residue chemist because carbamates in general cannot be manipulated in the same manner as most other pesticides. For example, the gas-liquid chromatographic (glc) analysis of most pesticides is a relatively simple matter once suitable extraction and cleanup methods have been perfected. The parent compounds and toxic metabolites are merely injected

into the gas chromatograph and the materials generally elute intact. However, even if extraction efficiency and cleanup are found to be excellent, carbamates often degrade during gas chromatography (5). This may partially be prevented by special column preparations and by selecting just the right glc parameters (27, 28) but even then the results are not always satisfactory.

One approach used to circumvent thermal degradation of the intact carbamate is its derivatization to a thermally more stable form. In the case of phenyl N-methylcarbamates such as aminocarb, derivatization sometimes involves hydrolysis of the carbamate ester and reaction of the released phenol with a reagent to yield a product which can be detected by glc. This technique is not without certain inherent problems (5). For example, one can never be sure whether the phenol originated from chemical or metabolic degradation of the carbamate or if it occurred naturally in the substrate being analyzed. Since phenols are usually less toxic to animals than the parent insecticides, it is essential that they be separated from the intact carbamates prior to derivatization. Otherwise, the final results cannot be properly interpreted. Another problem in the derivatization of phenols (from carbamates) relates to interfering materials (29). Derivatizing agents are susceptible to attack by polar co-extractives; for example, phenols occur ubiquitously in nature and often survive cleanup procedures to form derivatives which make the quantitation of the insecticides difficult. So while cleanup is nearly always a significant problem in pesticide residue analysis its magnitude is often much greater with the carbamates. A point on cleanup worth stressing with regard to carbamates such as aminocarb which have a

p-dimethylamino group which can be protonated is that aminocarb cannot be extracted quantitatively from acidified aqueous solutions (25,26,30,31); the pH of the medium should first be adjusted to neutrality.

Even though considerable problems are involved in the gas chromatographic analysis of N-methylcarbamate insecticide residues, it appears to be the method currently preferred by most residue chemists. High pressure liquid chromatography (lc), a relatively new and expensive technique, has, however, shown considerable potential for methylcarbamate insecticide analysis because of its mild operating conditions (eliminating the need for derivatization against thermal degradation), specificity, and possibilities for automation; in the future, liquid chromatography may well prove to be the best method for the analysis of carbamates and their degradation or transformation products.

Table 6 lists various methods which have been used in the analysis of aminocarb, and the minimum detectable limit (absolute weight) or minimum residue level capable of detection, where these are reported. These analytical methods have only been applied to the parent aminocarb and its hydrolysis products, both the phenol and the methylamine; no other degradation or transformation products were considered.

It is apparent that poor reporting techniques on the part of pesticide residue chemists have made it difficult to extract unambiguous information from Table 6. In general, one wishes to have information both on (a) the absolute amount of a pesticide, and (b) the residue level of a particular pesticide from a given substrate, which can be detected by a particular technique. The

residue level which can be detected includes information both on (a) and on the interfering material from whatever substrate is being analyzed; thus a sensitivity level for corn, using detector A, is not readily translated into a sensitivity level for spruce foliage, using detector B.

In general it appears that enzymic, colorimetric and most tlc-fluorescence methods are not as sensitive as gc or lc techniques, although the fluorometric method which uses a dansyl derivative (52) shows fair sensitivity. On an absolute weight basis, the most sensitive method shown in Table 6 is that employing a trichloroacetylated phenol derivative (32); however, it should again be emphasized that the nature of the substrate will probably affect the minimum residue level obtained.

The use of trimethylamine as a catalyst in the derivatization of aminocarb with heptafluorobutyric anhydride (39) speeds the reaction considerably so that it is complete in 15-20 min. at room temperature compared with 2 hours at 120°C for the uncatalyzed derivatization. Unfortunately this derivative is stable at best for a few days (25). The time-consuming production of such unstable derivatives serves to reinforce the advantages of liquid chromatography in situations which require hundreds of samples to be analyzed.

In addition to the methods shown in Table 6 there is a method which has been applied to other carbamates and which might be adapted to aminocarb: N-methylation of the carbamate using sodium hydride-methyl iodide (55,56). The dialkylated derivatives of N-methylcarbamates are somewhat more stable thermally, and detection limits are about 5 ppb using a Coulson electrolytic conductivity detector in the nitrogen mode.

Despite what has been said about the difficulties involved in performing gc analyses on underivatized carbamates in general, this technique will probably continue to be popular with pesticide chemists who are dissatisfied with derivatization methods, yet cannot afford a high pressure liquid chromatograph. For example, Brun (57) has been able to chromatograph underivatized aminocarb on a six-foot 3% OV-17 column at 190°C (Hall detector); he reports sensitivities of 0.5 ppb in water and 0.5 ppm in sediment, and apparently no on-column decomposition of aminocarb.

No gc methods have been published for metabolites of aminocarb per se, apart from the phenol and methylamine hydrolysis products. However, most of the metabolites, with or without derivatization, would probably exhibit retention times different than that of the parent aminocarb. Note that if the presence of the N-hydroxymethyl derivative (II in Fig. 1) is suspected, it obviously cannot be shown by chromatographing the corresponding derivatized phenol; the proper approach would be to chromatograph it directly or derivatize the intact metabolite.

A note on sampling natural waters for aminocarb is appropriate here. Mallet (58) claims that aminocarb can be collected and preserved using XAD-4 resin, stored with no loss for at least one month, and eluted from the resin using a suitable solvent, e.g., ethyl acetate. A mixed resin column of XAD-4 for the relatively non-polar parent aminocarb, and XAD-8 for the more polar metabolites, might prove useful for water sampling and collection. Of course, the extraction efficiencies of the resin materials for the various compounds, and the "lifetime" of the compounds on the resin materials, should be investigated before this method is used in the field. This method, if

feasible, would obviate the need to bring large amounts of flammable solvent into the field when collecting water samples for aminocarb analysis; in addition the method could be refined so that it could be carried out by relatively unskilled personnel.

Finally, a note of caution regarding cleanup procedures is appropriate. Appreciable losses of aminocarb during freezing and storage have been noted (14), and Brun (57) has noted significant losses of aminocarb from environmental samples in the rotary and Kuderna-Danish evaporators.

In conclusion, this section on analysis has demonstrated that extraction and chromatographic procedures are more complex and require more care for carbamates than for other classes of pesticides. The techniques of liquid and gas chromatography appear to be the most promising for the separation and quantitation of aminocarb. Derivatization methods prior to gas chromatography do appear tedious, however, and efforts are being made to develop suitably sensitive gas chromatographic methods which do not require derivatization.

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TABLE 1

p-Values of Aminocarb Determined Gravimetrically by Single Distribution between Immiscible Phases at 25.5°C (4).

Solvent System	p-Value
hexane:acetonitrile	0.03
isooctane:dimethylformamide	0.02
isooctane:85% dimethylformamide	0.02
hexane:90% dimethylsulfoxide	0.01
heptane:90% ethanol	0.07
isooctane:80% acetone	0.27

TABLE 2

Proton Magnetic Resonance Data on Aminocarb

Protons	Signal Patterns	$\tau^{1,2}$	$\tau^{1,3}$
ring methyl	singlet	7.71	7.62
ring dimethylamino	singlet	7.37	7.28
carbamate N-methyl	doublet	7.26	7.05
carbamate N-H	unresolved	4.6	-
ring protons	multiplet	3.1	3.12-2.92

[1] ppm downfield from tetramethylsilane internal standard; sample dissolved in $CDCl_3$.

[2] ref. 7.

[3] ref. 8.

TABLE 3

Infrared Absorption Frequencies (cm^{-1}) of Aminocarb (9)

Characteristic	Solution Frequency[1]	Solid Frequency[2]
NH stretching	3436 (m)	3333 (m)
C=O stretching	1745 (s)	1709 (s)
NH in-plane deformation	-	1524 (m)
C-N stretching	1276 (wm)	1277 (m)
C-O-C asymmetric stretching	1217 (s)	1255 (s)
C-O-C symmetric stretching	1166 (s), 1155 (s)	1168 (s)
NH out of plane deformation, secondary	-	636 (m)

[1] CS_2 solvent; s = strong, m = medium, w = weak.

[2] in KBr.

TABLE 4

Ultraviolet Absorption, Fluorescence and Phosphorescence Date on Aminocarb

Method	Characteristics
ultraviolet [1]	in C_2H_5OH λ_{max} = 248 nm ($\varepsilon = 6.67 \times 10^4$ ℓ mole^{-1} cm^{-1}) $\varepsilon_{300} = 7.32 \times 10^3$ ℓ mole^{-1} cm^{-1}
fluorescence [2]	major excitation peak at 262 nm; emission peak at 375 nm (5.3% relative intensity in 95% ethanol)
phosphorescence [2]	at 77°K major excitation peak at 253 nm; emission peak at 460 nm (1.15% relative intensity in absolute ethanol, 0.55 s decay time)

[1] ref. 8.

[2] ref. 10.

TABLE 5

Mass Spectra of Aminocarb

Electron Impact[1]		Chemical Ionization[2]		Negative Ion[3]	
m/e	intensity	m/e	intensity	m/e	intensity
15	17	83	7.0	16	2
27	3	150	7.0	26	2
29	2	151	37.7	42	4
39	2	152	100.0	74	2
40	8	153	9.8	150	100
41	2	180	9.8	151	8
42	3	207	21.3		
43	4	208	30.6		
44	4	209	83.6		
45	8	210	10.9		
51	7	237	8.2		
52	5				
53	5				
55	3				
58	15				
63	4				
65	5				
66	7				

...continued

m/e	intensity	m/e	intensity	m/e	intensity
77	13				
79	7				
81	2				
89	1				
91	3				
92	2				
121	8				
134	8				
136	35				
150	50				
151	100				
208	22				

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[1] ref. 11.

[2] ref. 12, methane as reagent gas.

[3] ref. 13.

TABLE 6

Analytical Methods for Aminocarb

Method	Features	MDL (or MRL)[1]	Ref.
gc	ECD, DC-200, 180°C trichloroacetylation of phenol	10 pg	32
gc	ECD, XE-60, 165°C chloroacetylation of phenol	-	33
gc	FID, no derivative OV-17 or SE 30 + carbowax 20 M appreciable breakdown	-	34
gc	ECD, XE-60, 190°C 2,4-dinitroaniline derivative of methylamine	0.2 ppm in spinach (85% recovery)	35
gc	ECD, SE-30 (160 - 230°C) trifluoroacetyl derivative of intact aminocarb	<2 ng	36
gc	ECD, pentafluoropropionic anhydride derivative of intact aminocarb	<80 pg	37

....continued

gc	ECD, 220°C 2,5-dichlorobenzenesulfonate derivative of phenol (reacts with intact aminocarb)	<1 ng	38
	FPD (S-mode) other conditions as above	10 ng	
gc	ECD, SE-30, 190°C heptafluorobutyryl derivative of parent aminocarb	0.1 ppm in soil 0.5 ppm in foliage 0.1 ppb in water	25
gc	Coulson conductivity detector halogen (reductive) mode heptafluorobutyryl derivative of parent aminocarb OV-1, 210°C	0.2 ng (est)	39
	trifluoroacetyl derivative, otherwise same conditions as above	0.4 ng (est)	
gc	no derivative Hall detector (N-mode) SE-30, 210°C	0. 2 ppm in soil 0.2 ppm in conifer foliage	26
gc	FPD (S-mode) pentafluorobenzene sulfonyl chloride derivative of phenol	0.5 ppb in water 0.5 ppm in soil or sediment	40
lc	reversed phase Partisil-10 ODS column with carriers of various polarities UV detector (254 nm)	0.35 $\frac{\text{A units}}{\mu g}$	41

..... continued

lc	Li Chrosorb Si 60 column 5% 2-propanol in isooctanol as carrier phase UV detector (254 nm)	0.8 ng	42
colori-metric	oxidation of carbamate $N-CH_3$ group followed by Schiff base formation with p-dimethylaminobenzaldehyde	10 - 100 µg	43
colori-metric	cholinesterase inhibition	0.2 µg	44
spectro-photofluoro-metric	λ_{ex} = 256 nm λ_{em} = 375 nm	0.8 ppm in milk	10
tlc-colori-metric	reaction with diphenylpicryl-hydrazyl solution	0.1 µg	45
tlc-enzyme inhibition	steer liver esterase no derivative	500 ng	46
tlc-spectro-photometric	p-dimethylaminobenzaldehyde derivative (uncertain structure) of phenol; λ_{max} = 248 nm	5 µg	47
tlc-enzyme inhibition	pig liver esterase	10 ng	48
tlc-fluoro-metric	flavone derivatives	0.01 - 0.06 µg	49
tlc-fluoro-metric	derivatization of phenol with dansyl chloride	1 ng/spot	50

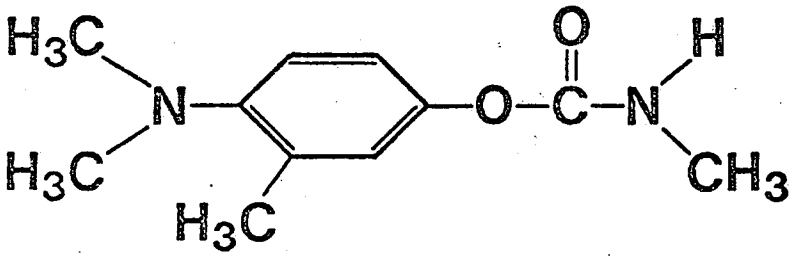
...continued

FIGURE CAPTIONS

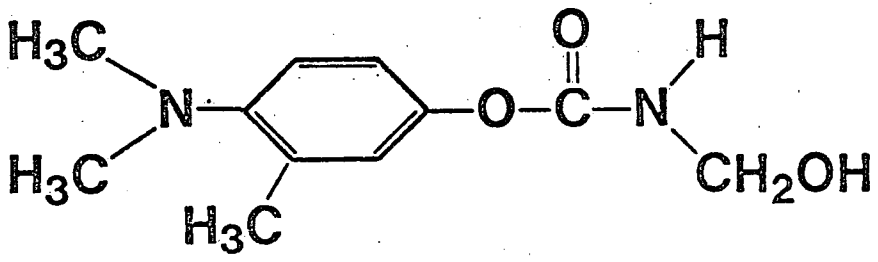
Fig. 1 Chemical structure of aminocarb and some metabolites; I, aminocarb; II, 4-dimethylamino-m-tolyl-N-hydroxymethyl-carbamate; III, 4-dimethylamino-3-methylphenol; IV, methylamine; V, ring-hydroxylated aminocarb (in unspecified position).

Fig. 2 Chemical structures of some metabolites of aminocarb: VI, 4-methylamino-m-tolyl-N-methylcarbamate; VII, 4-amino-m-tolyl-N-methylcarbamate; VIII, 4-methylformamido-m-tolyl -N-methylcarbamate; IX, 4-formamido-m-tolyl-N-methylcarbamate.

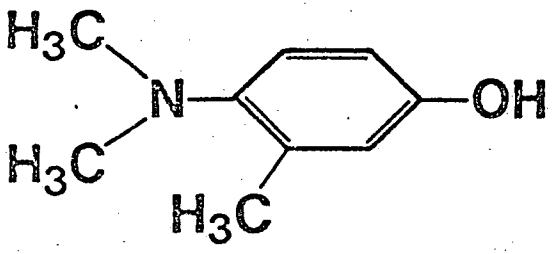
Fig. 3 Proposed Scheme for Sunlight Photodecomposition of Aminocarb (3).



I



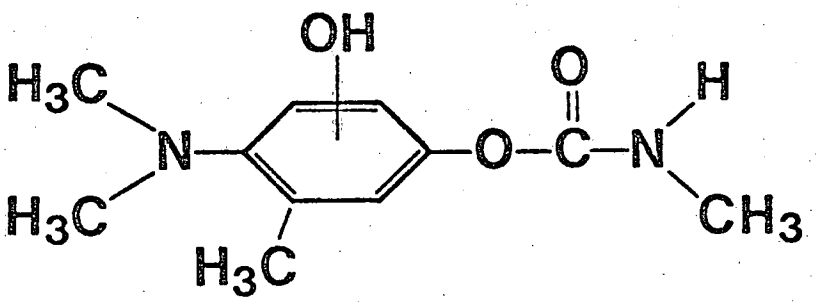
II



III

CH_3NH_2

IV



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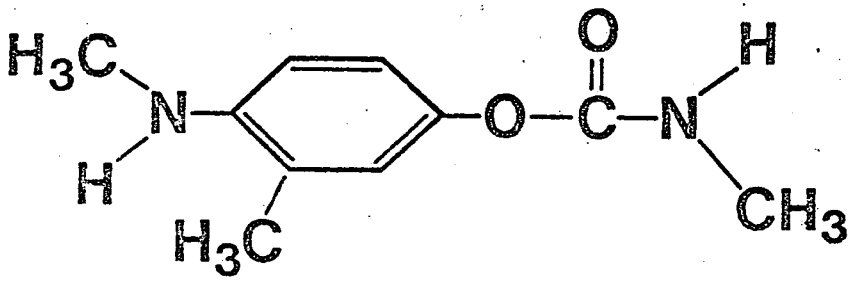
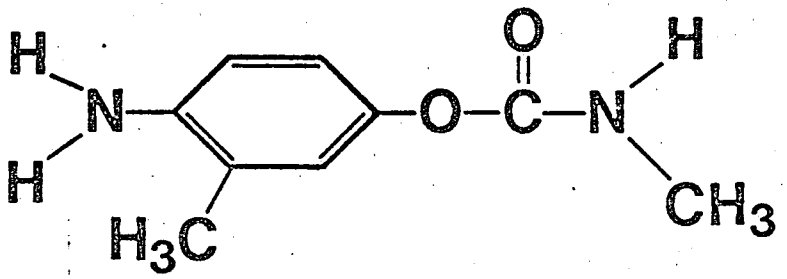
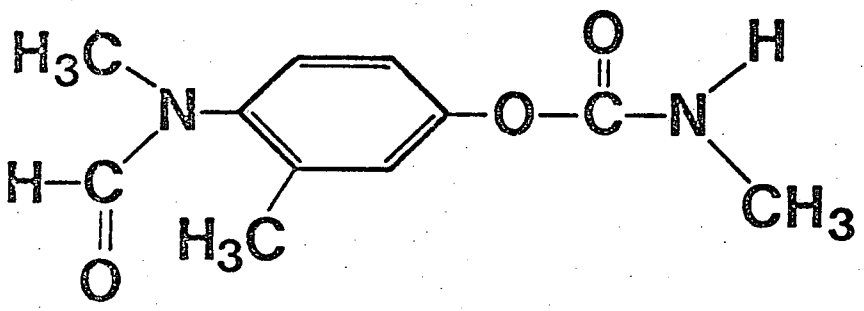


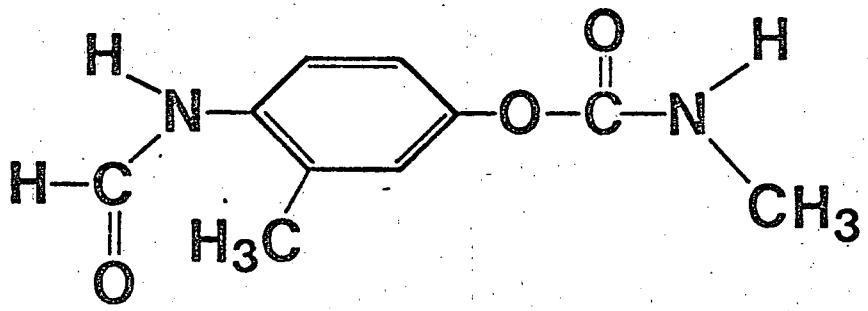
VI



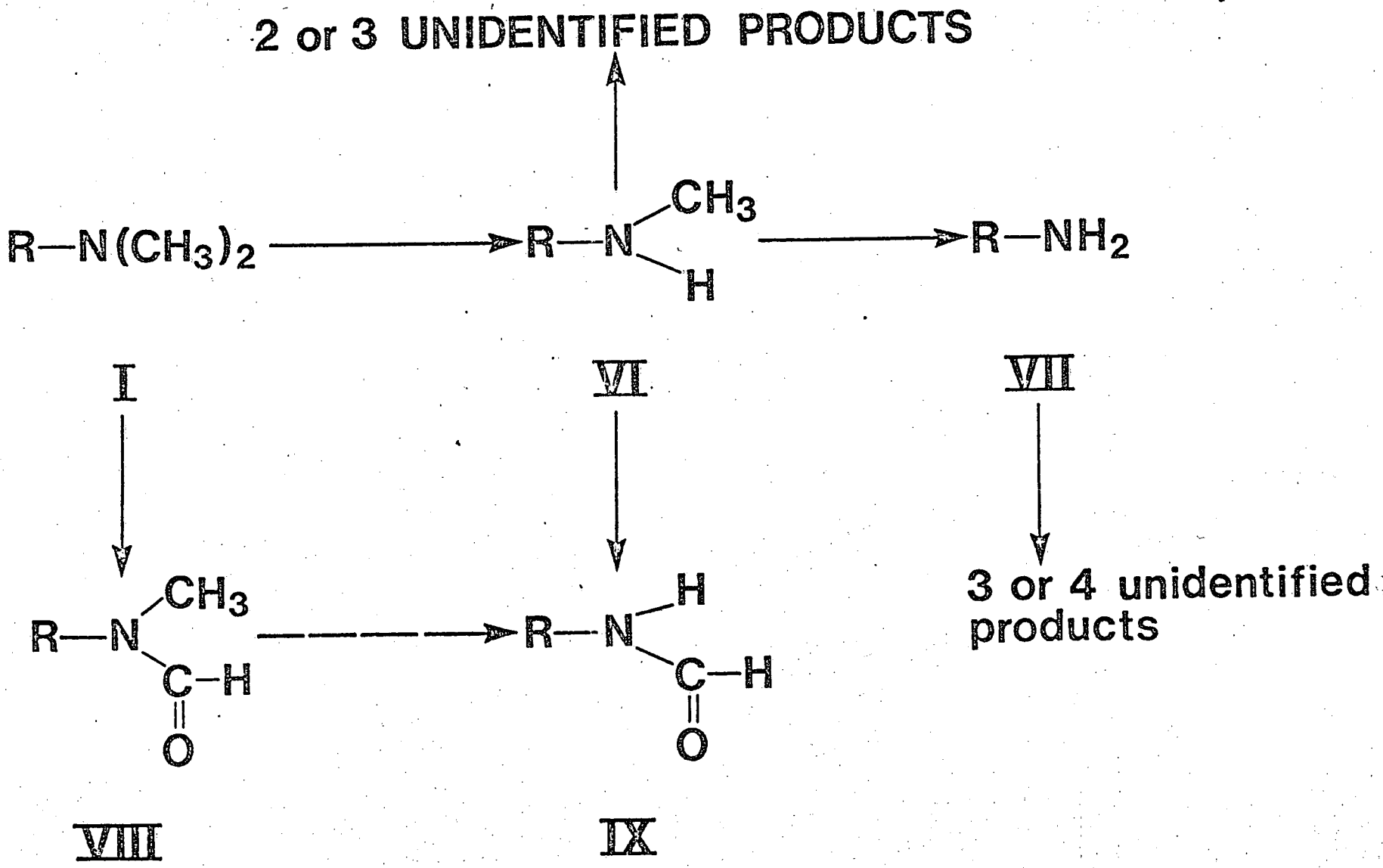
VII

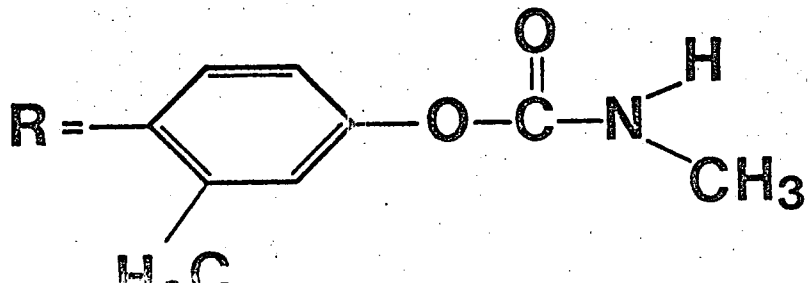


VIII



IX


2 or 3 UNIDENTIFIED PRODUCTS
R—N(CH3)2
R—N
CH3
H
R—NH2
I
VI
VII
3 or 4 unidentified products
R—N
CH3
C—H
O
R—N
H
C—H
O
VIII
IX


R =
O
C
O
N
H
CH3
H3C

tlc-fluoro-metric	dansyl derivative of phenol	-	51
tlc-fluoro-metric	dansyl derivative of phenol (methylamine is also derivatized)	<1 ng	52
tlc-fluoro-metric	π-complex derivatives with nitro-substituted fluorenes	0.5 - 5 µg	53
tlc-fluoro-metric	natural fluorescence on acidic alumina layers λ_{ex} = 372 nm λ_{em} = 473 nm	0.2 µg	54

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[1]Abbreviations: MDL, minimum detectable limit; MRL, minimum residue level; ECD, election capture detector; FID, flame ionization detector; FPD, flame photometric detector; UV, ultraviolet; gc, gas-liquid chromatography; lc, high pressure liquid chromatography; tlc, thin layer chromatography; dansyl, 1-dimethylaminonaphthalene-5-sulfonate.