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Microbial Degradation of the Carbamate Pesticides Desmedipham, Phenmedipham, Promecarb, and Propamocarb[1]

Charles O. Knowles and Herman J. Benezet

Department of Entomology, University of Missouri, Columbia, MO 65211

Many chemicals used to control pests come into contact with soil where they are attacked by various chemical and biological agents that can influence their bioactivity and persistence. Soil microorganisms play an important role in this connection. Depending upon the molecular configuration of the pesticide, microbial attack can increase or decrease bioactivity. With regard to persistence, the life of a given pesticide in soil usually is decreased by microbial attack. In fact, with some compounds, degradation is so extensive that the molecule is mineralized. In this paper, we describe the action of several soil microorganisms on four carbamate pesticides; the herbicides desmedipham and phenmedipham, the insecticide/acaricide promecarb, and the fungicide, propamocarb.

MATERIALS AND METHODS

The following radioactive pesticides were provided by NOR-AM Agricultural Products, Inc., Woodstock, Illinois: ethyl m-hydroxycarbanilate carbanilate or desmedipham labeled with radiocarbon in the m-aminophenol moiety (specific activity 1.95 mCi/mmole), methyl m-hydroxycarbanilate m-methylcarbanilate or phenmedipham labeled with radiocarbon in the m-aminophenol moiety (specific activity 1.95 mCi/mmole), m-cym-5-yl methylcarbamate or promecarb labeled with radiocarbon at ring position five (specific activity 3.3 mCi/mmole), and propyl[3-(dimethylamino)propyl]carbamate monohydrochloride or propamocarb labeled with radiocarbon at carbon one of the N-propyl moiety (specific activity 12.18 mCi/mmole). Structures and sources of nonradioactive standards have been reported previously (GRAY & KNOWLES 1981, KNOWLES & JOHANNSEN 1976, KNOWLES & SONAWANE 1972, SONAWANE & KNOWLES 1971).

The source of the microbes listed in Table 1 has been reported (BENEZET & KNOWLES 1981). Pure cultures of microorganisms were grown on 10 ml of yeast-mannitol media for 24 hr prior to amending with 10 µl of a 1 x 10^{-3}M ethanol solution of radioactive pesticide. Following a 28 day incubation period, each culture was extracted

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with ethyl acetate (2 x 10 ml), and duplicate aliquots of the aqueous and ethyl acetate fractions were radioassayed (Beckman LS 7500). An aliquot of the ethyl acetate fraction also was subjected to TLC, autoradiography, and radioassay to separate and quantitate its components. The adsorbent for TLC was silica gel GF_{254}; the solvent systems were benzene-ethanol (9:1) for desmedipham (KNOWLES & SONAWANE 1972), chloroform-acetonitrile (4:1) for phenmedipham, ethyl ether-n-hexane-ethanol (77:20:3) for promecarb, and methanol-ammonium hydroxide (9:1) for propamocarb (GRAY & KNOWLES 1981).

RESULTS

Table 1 presents a comparison of carbamate pesticide degradation by the eleven species of microorganisms. Desmedipham was very susceptible to microbial attack, being extensively degraded by all species with the exception of B. megaterium. Phenmedipham was attacked by all except A. liquefaciens and B. megaterium, and promecarb was attacked by all except A. versicolor, P. cyclopium, and B. megaterium. Propamocarb was resistant to attack by all eleven microbial species.

Table 2 presents the quantitative aspects of carbamate pesticide degradation by microorganisms. In the case of desmedipham, there was appreciable non-microbial degradation in the control, since only 29.8% of the parent compound remained after 28 days. However, in the presence of the microbes <0.4% of the parent remained after 28 days. The major metabolite in the organic fraction was ethyl-N-(3-hydroxyphenyl) carbamate (EHPC) exceeding control levels with each of the microbial species. Appreciable radiocarbon was present in the aqueous fraction, especially with P. putida and Flavobacter sp.; this material was not identified. The behavior of phenmedipham in the presence of the same three microbial species was similar to that of desmedipham; <0.6% of the parent compound remained after 28 days. Methyl-N-(3-hydroxyphenyl) carbamate (MHPC) was the major component of the organic fraction, and appreciable unidentified radiocarbon was present in the aqueous fraction. In the case of promecarb, 84.3% of the parent compound remained in the control after 28 days, while in the presence of P. putida, Flavobacter sp., and A. liquefaciens only 5.7, 1.7, and 16.8%, respectively, of the parent compound remained. The major metabolite in the organic fraction was isothymol with all three species. Other unidentified radiocarbon also was present in the organic and in the aqueous fractions.

DISCUSSION

Although desmedipham, phenmedipham, promecarb, and propamocarb are carbamates, they differ appreciably in structure. Within this small group of eleven species of microorganisms, there existed a relationship between carbamate structure and susceptibility to degradation. Desmedipham and phenmedipham, the herbicides with two aryl moieties, were most susceptible to degradation; seven of the eleven species showed high activity for these compounds. Promecarb,

TABLE 1

Comparison of Carbamate Pesticide Degradation by Microorganisms[a]

Microorganism	Pesticide			
	Desmedipham	Phenmedipham	Promecarb	Propamocarb
Aerobacter aerogenes	++	+	+	-
Aeromonas liquefaciens	++	-	++	-
Bacillus cereus	++	++	++	-
Bacillus megaterium	-	-	-	-
Bacillus subtilis	++	++	+	-
Flavobacter sp.	++	++	++	-
Proteus vulgaris	++	++	++	-
Pseudomonas putida	++	++	++	-
Aspergillus versicolor	++	++	-	-
Penicillium cyclopium	++	+	-	-
Torula rosea	++	++	+	-

[a]Degradative capacity evaluated on arbitrary scale with ++ = high activity, + = moderate activity, and - = low activity or no activity following incubation of pesticide with microorganism for 28 days as compared to sterile controls containing medium and pesticide.

the insecticide/acaricide with one aryl moiety was intermediate; four of the eleven species showed high activity for this pesticide. Propamocarb, the aliphatic fungicide, was least susceptible to attack; in fact, there was little, if any, degradation of propamocarb by any of the microorganisms studied.

TABLE 2

Degradation of Carbamate Pesticides by Several Microorganisms[a]

Microorganism	% Recovered radiocarbon in indicated fraction			
	Organic			Aqueous
	Parent	Metabolite	Other	
	Desmedipham			
Pseudomonas putida	0.1	70.3	0.5	29.1
Flavobacter sp.	<0.1	73.4	1.0	29.6
Aspergillus versicolor	0.4	88.6	2.9	8.1
Control	29.8	69.5	<0.1	0.3
	Phenmedipham			
Pseudomonas putida	0.3	67.4	0.4	31.9
Flavobacter sp.	0.6	62.0	1.7	35.7
Aspergillus versicolor	<0.1	47.8	4.6	47.6
Control	29.8	68.1	0.9	1.2
	Promecarb			
Pseudomonas putida	5.7	69.3	11.4	13.6
Flavobacter sp.	1.7	64.8	12.2	21.3
Aeromonas liquefaciens	16.8	65.6	9.0	8.6
Control	84.3	3.5	10.5	1.7

[a]Pesticides were incubated with microorganisms for 28 days. Recoveries of applied radiocarbon averaged greater than 96% in presence and absence (controls) of microorganisms. Compounds in organic fraction were separated by TLC yielding in each case parent compound, one major metabolite (EHPC for desmedipham, MHPC for phenmedipham, and isothymol for promecarb), and other material which consisted of the remainder of the radiocarbon on the TLC plate, some of which was at the origin.

Degradation products resulting from microbial action on the pesticides were formed by cleavage of the ester linkage. Desmedipham and phenmedipham were converted to EHPC and MHPC, respectively, while promecarb was converted to isothymol. Unidentified radiocarbon-containing compounds also were present in the aqueous fraction from the three carbamates.

It seemed that the presence of at least one aromatic moiety in the carbamate pesticide molecule markedly enhanced its susceptibility to microbial degradation.

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