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Received for review July 18, 1977. Accepted September 8, 1977. This paper was presented in part at the Division of Agricultural and Food Chemistry, 172nd National Meeting of the American Chemical Society, San Francisco, Calif., Aug 1976.

Insecticidal Aminothio Derivatives of the Pesticidal Carbamate Methomyl

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The insecticidal activities of a series of aminothio derivatives of methomyl were investigated. In general, the spectrum of activity of the compounds closely paralleled that of the parent, methomyl, often being equitoxic to the southern armyworm (*Spodoptera eridania* Cramer), cabbage looper (*Trichoplusia ni* Hübner), cotton bollworm (*Heliothis zea* Boddie), tobacco budworm (*Heliothus virescens* Fabricius), and boll weevil (*Anthonomus grandis* Boheman) but less active against the house fly (*Musca domestica* L.) and house cricket (*Acheta domesticus* L.). Additional biological parameters of a single compound, U-46,855, methyl [[[methyl-(4-morpholinothio)amino]carbonyl]oxy]ethanimidothioate, were compared to those of methomyl in the laboratory. U-46,855 demonstrated a marked increase in foliar residual life, lower mammalian toxicity, and greater crop selectivity while methomyl was much more resistant to mechanical loss due to rain. Evaluation of chemicals for the control of the bollworm complex in Alabama demonstrated that U-46,855 produced significantly higher cotton yields than methomyl.

In recent years certain substituents attached to the carbamate nitrogen of *N*-methylcarbamate insecticides have resulted in the production of compounds with improved ancillary properties over the parent. Certain arylthio and acyl derivatives of carbofuran, propoxur, carbaryl, aldicarb, and other *N*-methylcarbamates exhibit reduced mammalian toxicity and, in some cases, increased insecticidal activity (Reay and Lewis, 1966: Brown and Kohn, 1972; Black et al., 1973a). The selective toxicity was initially attributed to differential metabolism (Black et al., 1973b) but upon further examination these authors were unable to substantiate this (Chiu et al., 1975).

A consideration of carbamate insecticides reveals that few are highly effective against lepidopterous insects. Methomyl, an oxime carbamate, proves to be an exception. However methomyl suffers shortcomings with regard to its mammalian toxicity, crop safety, and residual action. Sulfenylated derivatives of methomyl are reported in the patent literature (Durden and Sousa, 1976; Union Carbide Corp., 1976) as showing improvements in these undesirable properties. The main thrust of this article is to report the results of our investigations of aminothio derivatives of methomyl.

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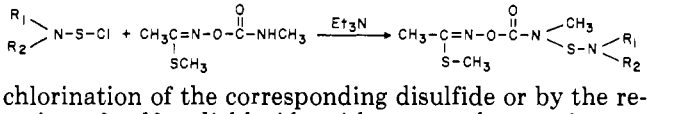
SYNTHESIS OF COMPOUNDS

The aminothio derivatives (Table I) were prepared by the reaction of an appropriate chlorothioamine with methomyl. The chlorothioamines were obtained by the



chlorination of the corresponding disulfide or by the reaction of sulfur dichloride with a secondary amine according to standard procedures (Kühle, 1970; Farbenfabriken Bayer A.G., 1958).

CAUTION: N-Chlorothioamines have been reported to detonate on attempted distillation (Davis and Skibo, 1976); a severe explosion resulting in personal injury and fire has occurred in these laboratories on attempted distillation of *N*-chlorothiopiperidine. Care in assuring purity of starting

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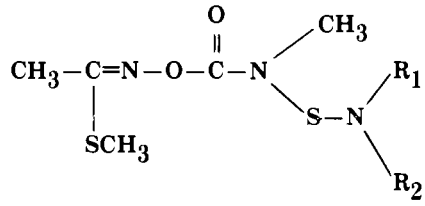
Table I. Chemical Data[a] and Insecticidal Activities of Aminothio Derivatives of Methomyl.



Compound	R_1	R_2	mp	Rate[b]	Percent Mortality BW[c]	HC[d]	HF[e]	YFM[f]	SAW[g]	CL[h]	CBW[i]	TB[j]
I	CH_3	CH_3	68-70	A	0	27	10	5	33	13		
				B	65	100	50	0	100	53		
				C	94	100	100	0	100	93		
II	i-C_3H_7	i-C_3H_7	81-2	A	0	50	5	0	7	0		
				B	47	100	35	0	93	60		
				C	94	100	100	0	100	93		
III	n-C_4H_9	n-C_4H_9	Oil	A	6	0	15	11	47	7		
				B	65	23	50	32	100	33		
				C	88	100	100	32	100	80		
IV	$-CH_2-(CH_2)_3-CH_2$		53-4	A	0	23	5	0	27	27		
				B	82	60	45	5	87	60		
				C	82	100	95	5	93	100		
V	$CH_2-CH_2-O-CH_2-CH_2$		128-9	A	6	13	5	0	40	53	17	13
				B	71	10	70	0	93	80	42	60
				C	94	63	95	0	100	93	92	93
VI	$CH_2-CH(CH_3)-O-CH(CH_3)-CH_2$		65-7	A	0	3	5	0	13	20		
				B	65	20	55	0	93	53		
				C	94	100	100	0	100	100		
Methomyl				A	0	100	45	0	60	20	16	13
				B	94	100	90	0	93	67	42	57
				C	88	100	100	0	100	87	83	93
		LSD	(0.05)		27	25	23	16	24	34	27	24

[a]Satisfactory elemental analyses were obtained for all compounds

[b]All rates are expressed in ppm except for the house cricket test which is expressed as μg/100 cm^2

Rate	BW[c]	HC[d]	HF[e]	YFM[f]	SAW[g]	CL[h]	CBW[i]	TB[j]
A	3	3	3	0.07	7	20	3	3
B	10	10	10	0.2	20	60	9	9
C	30	30	30	0.6	60	180	27	27

[c]Boll weevil [*Anthonomus grandis* Boheman] [d]House cricket [*Acheta domesticus* (Linnaeus)] [e]House fly [*Musca domestica* (Linnaeus)] [f]Yellow-fever mosquito [*Aedes aegypti* (Linnaeus)] [g]Southern armyworm [*Spodoptera eridania* (Cramer)] [h]Cabbage looper [*Trichoplusia ni* (Hübner)] [i]Cotton bollworm [*Heliothis zea* (Boddie)] [j]Tobacco budworm [*Heliothis virescens* (Fabricius)]

materials for the preparation of the chlorothioamines results in a product adequate for the preparation of these derivatives and makes the dangerous distillation procedure unnecessary.

The following procedure for the preparation of methyl *N*-[[[methyl(4-morpholinothio)amino]carbonyl]oxy]-ethanimidothioate (V = U-46,855) is typical. A solution of 1.89 g (18.7 mmol) of triethylamine in 5 mL of acetonitrile was added to a cold (0–5 °C) solution of 2.88 g (17.8 mmol) of methomyl and 2.88 g (18.7 mmol) of *N*-chlorothiomorpholine in 20 mL of acetonitrile over 7 min. The mixture was allowed to warm to room temperature over 2 h and then diluted with 75 mL of water. The resultant precipitate was collected and dried to give 3.03 g of a white solid. A second crop of 1.16 g was obtained from the mother liquors. The combined crops were recrystallized from methanol to afford 3.79 g (76%) of white needles, mp 129–30 °C. The ^1H NMR spectrum showed the following absorptions: (chloroform-*d*, Me_4Si) 3.65 (m, 4 H, OCH_2), 3.45 (s, 3 H, NCH_3), 3.35 (m, 4 H, NCH_2), 2.42 (s, 3 H, SCH_3), 2.31 (s, 3 H, $CH_3(S)C=$). The IR spectrum showed $\tilde{\nu}_{C=O}$ at 1725 cm^{-1}.

BIOLOGICAL TESTS

Insecticidal Assays. The laboratory screening procedures are similar to those reported by Friedman and Gemrich (1971) and are outlined in Table II. In all cases, test organisms of uniform age and size were randomly selected from a large population of mixed sexes. Data were subjected to one-way analysis of variance and the least significant difference between treatments determined. Average values of all replicates were corrected by use of Abbott's formula (Finney, 1964).

Residual Tests. Selected compounds were evaluated for their foliar residual properties in both the absence and presence of simulated rain. In the former situation,

Table II. Synopsis of Insecticidal Assay Procedures

Insect	Stage[i]	Principal mode of contact	Method of application	Time post-treatment in days to evaluation
Boll weevil[a]	A	Feeding	Treated 10% sugar solution	2
House cricket[b]	N	Residual contact	Glass residue	1
House fly[c]	A	Feeding	Treated 10% sugar solution	2
Yellow-fever mosquito[d]	L	Contact	Treated larval water	2
Southern armyworm[e]	L	Residual contact-feeding	Leaf[j] dip	2
Cabbage looper[f]	L	Residual contact-feeding	Leaf[j] dip	2
Bollworm[g]	L	Residual contact-feeding	Leaf[k] dip	4
Tobacco budworm[h]	L	Residual contact-feeding	Leaf[k] dip	3

[a] *Anthonomus grandis.* [b] *Acheta domesticus.* [c] *Musca domestica.* [d] *Aedes aegypti.* [e] *Spodoptera eridania.* [f] *Trichoplusia ni.* [g] *Heliothis zea.* [h] *Heliothis virescens.* [i] Stage: A = adult, N = nymph, L = larva. [j] Lima bean, *Phaseolus vulgaris* var *Jackson wonder.* [k] Cotton, *Gossypium hursutum* var. *Deltapine 16.*

Table III. Foliar Residual Activity of Aminothio Derivatives of Methomyl

Compound	ppm AI	Average percent corrected 2-day SAW[a] mortality at indicated days posttreatment							
		0	10	14	21	28	34	41	49
III	200	100	93	80	27	7	0	0	0
V	200	100	100	100	100	100	100	100	100
VI	200	100	100	100	67	87	13	33	33
Methomyl	200	100	100	20	20	0	7	13	0

[a] SAW = southern armyworm fourth-instar larvae.

seedling lima bean plants in the fully expanded primary leaf stage were sprayed to "wet", allowed to dry, and held in the greenhouse. At various times posttreatment, leaves were removed and offered to southern armyworm larvae. In the latter case, only the upper leaf surfaces were sprayed. Immediately after the spray deposits had dried, 6 mm of simulated rain was applied to the leaves. After drying, the leaves were removed and offered to southern armyworm larvae.

Phytotoxicity Studies. Six full coverage sprays were applied weekly to seedling lima beans, *Phaseolus vulgaris* var. *Jackson Wonder*; cotton, *Gossypium hirsutum* var. *Deltapine 16*; eggplant, *Solanum melongena* var. *Black Beauty*; pepper, *Capsicum frutescens* var. *Yolo Wonder*; tobacco, *Nicotinana tobaccum* var. *McNair*; and tomato, *Lycopersicon esculentum* var. *Rutgers*. The plants were maintained in the greenhouse at temperatures between 16–32 °C. Water and fertilizer were supplied via subirrigation. Although weekly phytotoxicity ratings were recorded, only the results observed following six spray applications are presented.

Cotton Field Trial. In 1976 a 2-ha field of cotton (McNair 511) growing in Alabama was randomly blocked into 0.0056-ha plots for field evaluation of chemicals, including V (U-46,855) for the control of the bollworm complex, *Heliothis* sp. Six-foot alleys were maintained between the plots and each treatment was replicated three times. Applications were made on a 3 to 5 day schedule beginning on July 26 and ending 11 applications later on September 8. Sprays were applied using a high clearance application of 114 L of water/ha. In addition, five applications of azinphosmethyl were applied for boll weevil control. Although a number of parameters were monitored throughout the test, including bollworm damaged terminals, live larvae per square, and bloom ratings, best measurements of control were obtained using the percent damaged squares and bolls as well as plot yields.

RESULTS AND DISCUSSION

The insecticidal activities of the aminothio derivatives paralleled those of the parent methomyl (Table I). Methomyl proved to be significantly more toxic than all of the compounds against house flies and house crickets while it was more toxic than some (I, II, VI) but not all (III, IV, V) of the compounds against the southern armyworm and boll weevil. While methomyl was not significantly more effective than any of the compounds in test against the cabbage looper, V proved to be more active than I, II, III and gave evidence of being more toxic than IV, VI, and methomyl. A further comparison of the activity of V vs. methomyl against two important cotton insect pests, the bollworm and the tobacco budworm, demonstrated that both were essentially equitoxic based on foliar contact-feeding tests. On the basis of inherent insecticidal activity it would appear that V and the other derivatives offer no major control advantage over methomyl with the possible exception of reduced toxicity to predators. Methomyl has been implicated in secondary outbreaks of insects due to suppression of parasites (Oatman and Kennedy, 1976). Methomyl is highly toxic to mammalian systems (oral rat LD_{50} = 17–24 mg/kg compared to 105 mg/kg for V), has a limited foliar residual effective life, and is phytotoxic to some crops, e.g., cotton, limiting its utility.

The foliar residual effectiveness of three derivatives was compared to methomyl (Table III). Though all of the compounds proved to have a greater foliar residual activity than methomyl, V demonstrated at least four times the residual life of methomyl under the conditions of no weathering. In a test designed to determine whether or not this residual activity could be maintained under the conditions of simulated rain, we observed (Table IV) that unlike V, which was readily washed off under as little as 6 mm of rain, methomyl retained a high level of toxicity. Subsequent studies not reported here have shown that methomyl can undergo much heavier applications of rain with minimal loss in toxicity. Methomyl appears to be taken up or bound by the leaf rapidly and then degraded over a relatively short period of time. This conclusion is supported by the plant metabolism studies of Harvey and Reiser (1973). On the other hand, V is probably not readily absorbed by the plant, or bound, degraded, or volatilized at the plant surface, but is readily subject to mechanical loss.

If a compound rests in a relatively "inert" condition on foliage, it may well be expected to be nonphytotoxic. The plant safety of V was compared to methomyl in the

Table IV. Influence of Simulated Rain on the Foliar Residual Activity of Methyl N-[[[Methyl(4-morpholinothio)amino]carbonyl]oxy]-ethanimidothioate Compared to Methomyl

Compound	g of AI/ha	Average percent corrected SAW[a] mortality 2 days posttreatment	
		No rain	6 mm rain
V[b]	70	0	0
V[b]	140	100	14
V[b]	280	100	0
V[b]	560	100	14
Methomyl[c]	70	0	0
Methomyl[c]	140	4	0
Methomyl[c]	280	100	100
Methomyl[c]	560	100	100

[a] SAW = southern armyworm third-instar larvae. [b] Formulated as a 75WP. [c] Lannate 90SP.

greenhouse (Table V). Clearly, V had a much greater margin of safety than methomyl, especially to eggplant and cotton. The apparent reverse relationship between dose and slight injury noted for V has been confirmed in additional studies, and although it is not fully understood, it is believed to be associated with a decrease in spreading properties of the formulation at the lower concentrations. As the nature of cotton insect control most generally requires numerous and frequent applications of pesticides to the newly developing terminals, a highly insecticidal yet phytotoxic compound like methomyl has limited utility.

The laboratory evaluations revealed both similar and divergent properties for methomyl and V. While methomyl had a higher level of broad spectrum insecticidal activity and showed increased resistance to weathering, the compounds possessed similar lepidopterous larvicidal activities in residual contact tests and V displayed reduced mammalian toxicity, increased foliar residual properties, and greater crop selectivity. The question still remained, how would they compare under field conditions.

Tobacco budworm and especially bollworm pressure were exceedingly severe in the Alabama trial while boll weevil activity was light and held in check with the applications of azinphosmethyl; the conditions were excellent for a definitive test. A comparison of the results (Table VI) between V and methomyl as well as several other cotton insecticides demonstrated the ability of both compounds to check effectively severe bollworm pressure as revealed by the marked reductions noted in both square and boll damage. However, an examination of the yield data point to a performance advantage for V in the range of 50% over methomyl, equivalent to ca. 1.5 bales of lint cotton/ha increase. Although there is a correlation between square and boll damage and yield, the problem in emphasizing damaged squares and bolls is that there is no indication of the total number of squares and bolls remaining on the plant at the time of evaluation; therefore, compounds demonstrating similar boll and square damage ratings may, at times, produce dissimilar yield data. The yield differences observed between methomyl and V may, in fact, be due in part to variations in field toxicity to the target species, residual activity, or actions on nontarget organisms, but the authors feel that much of the difference is due to plant injury. Within 1 day posttreatment following the first application, all methomyl-treated plots displayed phytotoxic symptoms in the form of reddened leaves. The emerging growth was usually not injured but following repeated applications the level of injury got progressively worse, lower leaves dropped prematurely and the plants were slightly stunted. Slight injury was detected after the sixth application of compound V which persisted following five additional applications.

Clearly, these data demonstrate that methyl *N*-[[[methyl(4-morpholinothio)amino]carbonyl]oxy]ethan-

Table V. Plant Safety of Methyl *N*-[[[Methyl(4-morpholinothio)amino]carbonyl]oxy]ethanimidothioate Compared to Methomyl

Compound	ppm AI[b]	Phytotoxicity index[a] following 6 applications					
		Bean	Cotton	Eggplant	Pepper	Tobacco	Tomato
V[c]	150	0.0	1.0	1.5	0.0	0.0	0.0
V[c]	300	0.0	0.5	2.5	0.0	0.0	0.0
V[c]	600	0.0	0.0	0.0	0.0	0.0	0.0
Methomyl[d]	150	0.5	5.5	5.0	0.5	0.0	1.0
Methomyl[d]	300	1.0	6.0	6.5	1.0	1.5	1.5
Methomyl[d]	600	3.0	8.5	8.5	2.0	3.5	2.5
Untreated		0.0	0.0	0.0	0.0	0.0	0.0

[a] Index: 0 = no injury, 10 = complete kill of plant. [b] Applied as full coverage sprays. [c] Formulated as 75W. [d] Lannate 90SP.

Table VI. Field Activity of Methyl *N*-[[[Methyl(4-morpholinothio)amino]carbonyl]oxy]ethanimidothioate against the Bollworm Complex Compared to Methomyl and Other Insecticides

Treatment	kg of AI/ha	Average percent damaged		kg of seed cotton/ha
		Squares	Bolls	
Compound V[a]	0.28	7	6	3007
Compound V[a]	0.56	0	4	2757
Compound V[a]	0.84	2	2	3184
Methomyl[b]	0.28	5	12	1815
Methomyl[b]	0.56	5	6	2214
Methomyl[b]	0.84	6	7	1842
Chlordimeform[c]	0.07	13	16	1067
Chlordimeform[c]	0.14	8	13	1902
Chlordimeform[c]	0.28	10	12	1948
Tox + MP[d]	1.12 + 0.56	23	24	1150
Tox + MP[d]	2.24 + 1.12	3	8	1748
Untreated		70	39	136
	LSD (0.05)	28	15	1117

[a] Formulated as 50WP. [b] Lannate 90SP. [c] Galecron 4E. [d] Toxaphene + methyl parathion 6-3EC.

imidothioate (V, U-46,855) is a potentially useful insect control agent and that modification of a good insecticidal chemical can result in the production of compounds with improved toxicological and biological parameters.

ACKNOWLEDGMENT

We wish to acknowledge the assistance of E. Vande-Streek, G. H. Smith, L. H. Hope, and R. H. Tiller in the biological evaluations of some of these compounds and T. E. Weddon and M. M. Gargano in the toxicological investigations.

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Received for review July 11, 1977. Accepted October 28, 1977.

Determination of FMC 33297 Residues in Plant, Animal, and Soil Matrices by Gas Chromatography

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Analytical procedures are described for the determination of FMC 33297 residues in/on various food and fiber crops, soils, and animal tissues and fats. The quantitative methods involve extraction of residues from the sample matrices using hexane, hexane–isopropanol, or methanol–water, depending on sample type followed by cleanup on Florisil. Samples containing oils and lipids are eluted through a gel permeation column prior to Florisil column cleanup. Residues of FMC 33297 are detected by gas–liquid chromatography utilizing either a ^{63}Ni electron-capture detector of a Coulson electrolytic conductivity detector operating in the halogen mode. Adequate recoveries are obtained from fortified check samples spiked at the 0.05 ppm level with each isomer of FMC 33297 in all sample types analyzed.

FMC 33297, 3-phenoxybenzyl (±)-*cis,trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate, is a synthetic pyrethroid insecticide currently being developed by FMC Corporation. FMC 33297 (Figure 1), also known as NRDC 143 and permethrin, has been described by Elliot et al. (1973). FMC 33297 has a cis,trans isomer ratio of: minimum 35% (±)-cis and maximum 65% (±)-trans.

As part of the development process, analytical procedures were required for the determination of FMC 33297 residues in/on various food and fiber crops. Williams (1976) reported an analytical procedure for the analysis of permethrin in potato tubers without separation of the *cis,trans*-permethrin isomers. This paper describes analytical procedures developed by FMC Corporation for the analysis of FMC 33297 residues with isomer separation in/on various food and fiber crops, soils, and animal fats and tissues.

The analytical procedures involve extraction of residues from the sample matrices using organic solvents followed by cleanup on activated Florisil. Samples containing high oil or lipid content are subjected to gel permeation cleanup prior to elution through Florisil. The use of gel permeation chromatography for pesticide–lipid separation was reported by Stalling et al. (1972, 1974). Tindle and Stalling (1972) described an automated gel permeation system capable of processing 23 samples unattended. Griffitt and Craun (1974) evaluated the automated system and found it to be an efficient tool for fat–pesticide separation.

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EXPERIMENTAL SECTION

Reagents. All reagents used were purchased commercially as pesticide quality or equivalent from Burdick and Jackson Laboratories, Inc., and from Mallinckrodt Chemical Co. Florisil, PR Grade, 60–100 mesh, Floridin Co., was activated overnight at 135 °C prior to use.

Apparatus. An automated gel permeation system, GPC Autoprep 1001, Analytical Biochemistry Laboratories, Inc., was used. The columm, 2.5 cm × 30 cm, was packed with 50 g of Bio-Beads S-X3, 200–400 mesh, Bio-Rad Laboratories, compressed to a bed length of 27 cm using Kontes Organic Solvent plunger assemblies (K-422353-0025). A 1:3 mixture of hexane–ethyl acetate was used as the eluting solvent with a flow rate of 5 mL/min. Operating time parameters for the dump, collect, and wash cycles were 17, 8, and 4 min, respectively.

A Tracor MT-220 gas chromatograph equipped with both a ^{63}Ni electron-capture detector (ECD) and a Coulson electrolytic conductivity detector (CCD) operating in the halogen mode was used. A noise filter, Spectrum Model 1021, was placed in-line between the ECD and the strip chart recorder to increase baseline stability. The ECD was connected to a 6 ft × 2 mm i.d. glass column packed with Supelcoport, 80/100 mesh, coated with 1% SP-2330. The

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