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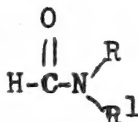
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PRELIMINARY TESTS OF SOME N-SUBSTITUTED FORMAMIDES
AS INSECTICIDES AND MITICIDES

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Thirty-two N-substituted formamides were tested as insecticides and miticides in the laboratory at Anaheim, Calif., from August 1952 to December 1953. These compounds may be represented by the general formula



where R or R¹ is a hydrogen, alkyl, cycloalkyl, aryl, substituted aryl, or cyclic group. These compounds were prepared by reacting various amines with formic acid under suitable conditions. The compounds were tested against four species of insects and two mites.

The following species were used:

- Armyworm (Pseudaletia unipuncta (Haw.))
- Bean weevil (Acanthoscelides obtectus (Say))
- Large milkweed bug (Oncopeltus fasciatus (Dall.))
- Pea aphid (Macrosiphum pisi (Harris))
- Citrus red mite (Metatetranychus citri (McG.))
- Two-spotted spider mite (Tetranychus bimaculatus Harvey)

The insects were reared in the laboratory and the mites were collected in the field.

The methods of testing against all but the bean weevil and the citrus red mite were described in the Bureau of Entomology and Plant Quarantine E-877. For the bean weevil, dry beans infested with the larvae were confined in 100-cc. petri dishes and exposed to the fumigating action of 0.2 gram per dish of the compound adsorbed on cotton. The citrus red mite was tested by spraying orange fruits infested with adults with an acetone solution of the compound.

The data for each species are tabulated in tables 1-6 with the compounds arranged in order of descending toxicity. The results with a standard spray are included in each table.

In the tests against armyworms (table 1) approximately half the compounds gave 100 percent kill at 5 percent concentration, but at 1 percent all were ineffective. There was no definite effect shown by varying the N-alkyl mono- or di- substitutions in either the formamides or the formamides. However, *o*-chloroformanilide was the most toxic, with the corresponding meta and para compounds showing much less toxicity. The 2,5-dichloro derivative was less toxic than the ortho compound but more toxic than the meta compound.

Fumigation tests with 26 of the compounds against the larvae of the bean weevil (table 2) showed the three lowest dialkyl formamides to be the most effective. The higher homologs were ineffective. Branching of the chain also had an adverse effect. The ethyl and propyl formamides showed moderate toxicity, and the higher members practically none. Only the *o*-chloroformanilide showed slight toxicity. The others showed none at all.

In tests against nymphs of the large milkweed bug (table 3) the higher monoalkyl formamides showed the highest toxicity at 5 and 1 percent. The tert- and dibutyl formamides were also rather toxic. About one-third of the compounds gave 100 percent kill at 5 percent, but only half of them showed much toxicity at 1 percent. The lower monoalkyl formamides up to the butyl group were completely nontoxic to the milkweed bug, but the corresponding formamides were toxic at 5 percent concentration.

The adult pea aphids (table 4) were most susceptible to 5 percent concentration of the higher members of the formamide series, such as dioctyl, dipentyl, and octyl, which also showed some toxicity at 1 percent. The pentyl and isopentyl formamides and the dibenzyl and phenethyl formamides were also toxic at 5 percent. The lower members of the series seemed to show the least toxicity. About one-fourth of the compounds tested were toxic to the pea aphid at 5 percent.

Of 15 compounds tested against the adult citrus red mite, about two-thirds were toxic at 1 percent, and about half at 0.5 percent (table 5). One, N-N-dibenzylformamide, gave 100 percent kill at 0.1 percent. Practically all the compounds were toxic at 5 percent.

The 17 compounds not tested against the citrus red mite were tested against adults of the two-spotted spider mite (table 6). About half these compounds showed over 90 percent kill at 5 percent, two compounds at 1

percent, and one at 0.5 percent. The most toxic formamides were the straight-chain monoalkyl-substituted ones above heptyl and the straight-chain dialkyl-substituted compounds above dibutyl. The lower members and the branched members of the series were distinctly less effective. Both the formanilides tested also showed toxicity at the higher concentrations.

In all the tests N,N-dibutylformamide and N,N-dipentylformamide gave 100 percent kill of three insects and one mite at 5 percent concentration. N,N-Diethylformamide also was effective against three insects, but somewhat less effective as a miticide. Six compounds were effective against two insects and a mite -- N-octylformamide, N,N-dioctylformamide, N,N-dibenzylformamide, o-chloroformanilide, N-ethylformanilide, and N-isopentylformanilide. N,N-Dipropylformamide and N-heptylformamide gave high kill of two insects. N-tert-Butylformamide, N-hexylformamide, N-phenethylformamide, and N-pentylformanilide were effective against one insect and one mite.

Although these preliminary tests show some rough trends in the effect of various substituents in formamides on the toxicity to individual species of insects or mites, it is still evident, as shown in previous work, that there is no consistency in effectiveness against all species.

Table 1.--Percent kill of third-instar larvae of the armyworm 2 days after confinement on foliage sprayed with various N-substituted 1/
formamides in acetone solution

Formamide	5-percent	1-percent
Formanilide, o-chloro-	100 -	7 xx
Formamide, N,N-dipentyl-	100 -	7 xxx
N-propyl-	100 -	3 xxx
N-butyl-	100 -	0 xx
N,N-dibutyl-	100 -	0 xx
N,N-diethyl-	100 -	0 xxx
N-isobutyl-	100 -	0 xxx
N,N-dipropyl-	100 -	0 xxx
N-(1-methylbutyl)-	100 -	0 xxx
N-heptyl-	100 -	0 xxx
N,N-dioctyl-	100 -	0 xxx
Formanilide, N-ethyl-	100 -	0 xxx
N-butyl-	100 -	0 xxx
N-pentyl-	100 -	0 xxx
N-isopentyl-	100 -	0 xxx
Formamide, N-phenethyl-	97 x	0 xxx
N-hexyl-	90 -	0 xx
N-octyl-	80 x	
Formanilide, 2,5-dichloro-	80 x	
Formamide, N-ethyl	67 xx	
N-(1-methylpentyl)-	50 x	
N,N-diisopropyl-	40 xx	
Formanilide, m-chloro-	40 xx	
Formamide, N,N-dibenzyl-	33 xx	
N-tert-butyl-	33 xx	
Formanilide, p-chloro-	17 xx	
p-Formophenetitide	13 xx	
Formamide, N,N-dicyclohexyl ^{2/}	7 xx	
N-sec-butyl-	0 xx	
p-Formanisidide	0 xx	
Formamide, N-(2-hydroxyethyl)-	0 xx	
N-(3-methoxypropyl)-	0 xxx	
DDT (0.025 percent)	85	

1/ Heavy feeding xxx, moderate xx, slight x, and no feeding -.

2/ Alcohol solution.

Table 2.--Percent kill of larvae of the bean weevil subjected to fumigation with 0.2 gram of N-substituted formamide for 21-24 days in 100-cc. petri dishes

Formamide	Percent kill
Formamide, N,N-dipropyl-	100
N,N-dibutyl-	95
N,N-diethyl-	90
N-ethyl-	57
N-propyl-	50
Formanilide, o-chloro-	44
Formamide, N-isobutyl-	42
N-butyl-	14
Formanilide, N-ethyl-	14
Formamide, N-sec-butyl-	0
N-(1-methylbutyl)-	0
N-(1-methylpentyl)-	0
N-heptyl-	0
N-octyl-	0
N,N-diisopropyl-	0
N,N-dipentyl-	0
N,N-dioctyl-	0
N,N-dibenzyl-	0
Formanilide, N-butyl-	0
N-pentyl-	0
N-isopentyl-	0
m-chloro-	0
p-chloro-	0
2,5-dichloro-	0
p-Formanisidide	0
p-Formophenetidide	0
Carbon bisulfide (0.2 gram)	88

Table 3.--Percent kill of fourth-instar nymphs of the large milkweed bug 2 days after being sprayed with various concentrations of N-substituted formamides in acetone solution

Formamide	5 percent	1 percent	0.5 percent
Formamide, N-heptyl-	100	95	15
N-octyl-	100	95	5
N-tert-butyl-	95	100	10
N,N-dibutyl-	100	90	35
N-hexyl-	100	60	
N,N-dipentyl-	100	35	
N,N-dibenzyl-	100	10	
Formanilide, o-chloro-	100	5	
N-butyl-	100	0	
Formamide, N,N-diethyl-	100	0	
Formanilide, N-ethyl-	100	0	
Formamide, N-(1-methylpentyl)-	95	20	
N,N-dicyclohexyl-	95	10	
N,N-dioctyl-	90	15	
N-(1-methylbutyl)-	90	0	
Formanilide, N-pentyl-	85		
N-isopentyl-	80		
m-chloro-	80		
Formamide, N-phenethyl-	75		
Formanilide, p-chloro-	40		
Formophenetidide	10		
Formamide, N,N-dipropyl-	5		
Formanilide, 2,5-dichloro-	5		
Formamide, N-propyl-	0		
N-ethyl-	0		
N-butyl-	0		
N-isobutyl-	0		
N-sec-butyl-	0		
N,N-diisopropyl-	0		
p-Formanisidide	0		
Formamide, N-(3-methoxypropyl)-	0		
N-(2-hydroxyethyl)-	0		
Lindane (0.005 percent)	95		

Table 4.--Percent kill of adult pea aphids 2 days after being sprayed with various concentrations of N-substituted formamides in acetone solution

Formamide	5 percent	1 percent	0.5 percent
Formamide, N,N-dioctyl-	100	92	61
N,N-dipentyl-	100	84	
N-octyl-	100	63	
N,N-dibenzyl-	100	32	
N-phenethyl-	100	34	
Formanilide, N-pentyl-	100	6	
N-isopentyl-	100	0	
Formamide, N-hexyl-	88		
N-heptyl-	83		
N,N-dibutyl-	78		
N-butyl-	67		
Formanilide, N-butyl-	58		
p-chloro-	57		
Formamide, N-2-hydroxyethyl-	54		
Formanilide, N-ethyl-	52		
m-chloro-	52		
Formamide, N-tert-butyl-	52		
N-(1-methylbutyl)-	51		
N-(1-methylpentyl)-	51		
N,N-dicyclohexyl-	38		
N-isobutyl-	37		
N,N-dipropyl-	32		
N,N-diethyl-	25		
N-propyl-	24		
N-(3-methoxypropyl)-	21		
N-sec-butyl-	17		
p-Formanisidide	15		
Formamide, N,N-diisopropyl-	11		
N-ethyl	0		
Formanilide, o-chloro-	0		
2,5-dichloro-	0		
p-Formophenetitide	0		
Parathion (0.025 percent)	91		

Table 5.--Percent kill of adult citrus red mites 2 days after being sprayed with various concentrations of N-substituted formamides in acetone solution

Formamide	5 per- cent	1 per- cent	0.5 per- cent	0.1 per- cent	0.05 per- cent
Formamide, N,N-dibenzyl-	100	100	100	100	18
N-(2-hydroxyethyl)-	100	100	--	76	
N-hexyl-	100	90	--	67	
N-(3-methoxypropyl)-	100	100	--	47	
N-tert-butyl-	100	90	--	45	
N-phenethyl-	100	100	--	37	
p-Formophenetitide	100	100	100	7	
Formamide, N,N-dicyclohexyl-	95	100	80		
Formanilide, p-chloro-	100	100	72		
p-Formanisidide	100	100	69		
Formanilide, m-chloro-	100	97	57		
N-pentyl-	100	74			
o-chloro-	100	54			
N-isopentyl-	100	38			
2,5,dichloro-	86				
Aramite (0.01 percent)	95				

Table 6.--Percent kill of adult two-spotted spider mites 2 days after being sprayed with various concentrations of N-substituted formamides in acetone solution

Formamide	5 per- cent	1 per- cent	0.5 per- cent	0.1 per- cent
Formamide, N,N-dioctyl-	100	100	100	27
N-octyl-	100	92	65	
N,N-dipentyl-	100	64		
N-heptyl-	100	64		
N,N-dibutyl-	100	54		
Formanilide, N-butyl-	100	35		
N-ethyl-	100	16		
Formamide, N-(1-methylpentyl)-	96	0		
N,N-diethyl-	92	0		
N-butyl-	72	8		
N-sec-butyl-	50	0		
N-(1-methylbutyl)-	50	0		
N-isobutyl-	40	0		
N,N-diisopropyl-	36	0		
N-propyl-	32	0		
N,N-dipropyl-	24	0		
N-ethyl-	18	0		
Aramite (0.01 percent)	92			

