

LIBRARY
STATE PLANT BOARD

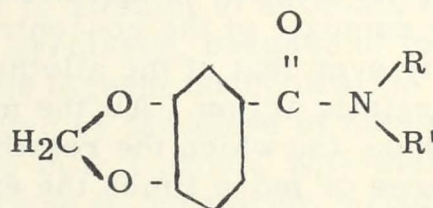
United States Department of Agriculture
Agricultural Research Administration
Bureau of Entomology and Plant Quarantine

PRELIMINARY TESTS WITH CERTAIN N-SUBSTITUTED
PIPERONYLAMIDES FOR SYNERGISTIC ACTION IN
ALLETHRIN FLY SPRAYS^{1/}

By W. A. Gersdorff, Norman Mitlin, and S. I. Gertler
Division of Insecticide Investigations

In previous work seeking synergists for pyrethrum in fly sprays it was found that certain N-substituted piperonylamides exhibited synergistic action when used in combination with pyrethrum solutions (Gertler *et al.* 3). The relative effectiveness of some of the best of these compounds was later determined (Gersdorff and Gertler 2). In the research described herein the joint action of compounds in this group and allethrin was studied.

These amides contain the methylenedioxyphenyl group appearing in most of the effective pyrethrum synergists. They have the general formula



R and R' may be hydrogen or an alkyl or cyclic group. When both are hydrogen, the compound is piperonylamide. The cyclic group may be substituted or unsubstituted. The compounds were prepared by reacting piperonyl chloride with the selected amines according to recognized procedures. They were all purified.

The compounds were incorporated in oil sprays, alone and in mixtures with 0.5 mg. of allethrin per milliliter. Even though acetone was used as an auxiliary solvent, the solubility of some of the compounds was so low that the desired concentration of the adjunct of 5 mg. per milliliter could not be attained. For these materials the concentration was 2.5 mg. per milliliter. The proportion of acetone to refined kerosene was 1 to 3 for all sprays.

Allethrin standards were prepared at concentrations of 0.25, 0.5, and 1 mg. per milliliter. The allethrin used was from a distilled sample of high purity (94 percent by the hydrogenolysis method).

^{1/} Previous publications in this series are E-805, E-828, and E-837.

The tests were made by the Campbell turntable method on adult house flies (Musca domestica L.) reared by standard laboratory procedure. Since knock-down of flies is increased by the addition of acetone, it was not estimated. Mortality only was determined for each spray. Approximately 100 flies averaging 3 1/2 days in age were used in each test. The mixed sprays were replicated four times, the sprays containing the adjuncts alone but twice. Since it was necessary to make the tests in several series, each with a different population of flies, mortalities in the different series would not be directly comparable. Therefore, the allethrin standard sprays were included in each series.

The adjuncts alone were nontoxic at the concentrations used. The mean mortalities obtained with the other sprays are given in table 1. A regression equation for the allethrin standards was obtained from the data in each series by the method of probit analysis as described by Finney (1). From this equation the logarithm of the allethrin equivalent was calculated for each of the four mortalities for all materials. From an analysis of variance of these log concentrations the allethrin equivalent required to show a significant increase in toxicity was calculated. The mean allethrin equivalents and those required to demonstrate synergism are also given. By comparison of the allethrin equivalent with the actual amount of allethrin in the mixture, 0.5 mg. per milliliter, ratios of toxicity may be obtained. Therefore, multiplying the allethrin equivalent by 2 gives the toxicity of the mixture relative to allethrin.

Since the adjuncts alone were nontoxic at the concentrations used, any significant increase in toxicity over that of the allethrin in each mixture may be ascribed to synergistic action. All the mixtures except one showed such an increase. Those for which the relative toxicity based on the allethrin equivalent was three or more times the expected contained the following amides:

- N-benzylpiperonylamide
- N-(o-bromophenyl)piperonylamide
- N-butylpiperonylamide
- N-cyclohexylpiperonylamide
- N,N-dibenzylpiperonylamide
- N,N-diethylpiperonylamide
- N-ethylpiperonylamide
- N-(o-nitrophenyl)piperonylamide
- N-phenylpiperonylamide
- N-propylpiperonylamide
- N-m-tolylpiperonylamide
- N-o-tolylpiperonylamide

The mixtures for which the relative toxicity was about twice the expected contained the following amides:

N-amylpiperonylamide
N-(m-bromophenyl)piperonylamide
N-(m-chlorophenyl)piperonylamide
N-(o-chlorophenyl)piperonylamide
N-methylpiperonylamide
N-p-tolylpiperonylamide

For four mixtures the increase in toxicity was less than twice the expected but still significant. The adjuncts in these mixtures were as follows:

N-(p-bromophenyl)piperonylamide
N-(p-chlorophenyl)piperonylamide
N-1-naphthylpiperonylamide
N-2-naphthylpiperonylamide

With the second and third compounds the increase in toxicity of the mixture was on the borderline of significance.

Unsubstituted piperonylamide was the only compound not affecting the toxicity when applied jointly with allethrin under these conditions.

It is not safe to attempt to estimate relative toxicity of compounds in the first groups precisely, because of too great extension of the standard curves beyond the highest concentration tested. Extrapolated points are too greatly affected by the slope of the determined curve. However, one of the compounds in this group, N,N-diethylpiperonylamide, was also one of the most effective in pyrethrum mixtures (Gersdorff and Gertler 2).

The least effective of the N-monoalkyl-substituted compounds was the methyl derivative.

The ortho-substituted compound was the most effective of the tolyl derivatives, and the para isomer the least. The same was true for the bromophenyl derivatives, but with the chlorophenyl derivatives the meta isomer was as effective as the ortho isomer. Gertler et al. (3) reported that in mixtures with pyrethrins tested by the same method the ortho-substituted aromatic piperonylamides appeared to be more effective than the corresponding meta or para derivatives.

Substitution of bromine in the ortho position on the phenyl derivative did not give a compound significantly different in effectiveness from the phenyl derivative itself. Substitution of chlorine, on the other hand, resulted in considerable decrease in effectiveness. The nitro group in this position on the phenyl derivative gave a synergist not so effective as the phenyl derivative but more effective than the corresponding chlorophenyl compound.

Methyl-substituted N-phenyl piperonylamides were more effective synergists than the other corresponding substituted phenyl derivatives.

Literature Cited

- (1) Finney, D. J.
1952. Probit analysis. 318 pp. Cambridge.
- (2) Gersdorff, W. A., and Gertler, S. I.
1944. Toxicity to house flies of certain N-substituted piperonylamides and benzamides combined with pyrethrins in oil base insect sprays. Soap and Sanit. Chem. 20(2): 123, 125.
- (3) Gertler, S. I., Fales, J. H., and Haller, H. L.
1943. A study of the synergistic action of N-substituted piperonylamides when incorporated in fly sprays. Soap and Sanit. Chem. 19(4): 105, 107.

Table 1. --Toxicity to house flies of space sprays containing certain N-substituted piperonylamides mixed with allethrin. Concentration of allethrin 0.5 mg., and of amides 5 mg. per milliliter unless otherwise indicated

Adjunct	Mean mortality in 1 day	Mean allethrin equivalent
	<u>Percent</u>	<u>Mg. per ml.</u>
Series 1		
Piperonylamide ^{1/}	42.6	0.540
Piperonylamide, N-butyl-	82.4	1.880
N-phenyl-	86.2	2.164
N-m-tolyl	76.0	1.339
N-o-tolyl-	98.9	>2
Allethrin standard, 1.0 mg. per ml.	65.6	0.972
0.5	41.4	.522
.25	15.8	.214
Required to demonstrate synergism ----		.769
Series 2		
Piperonylamide, N-o-chlorophenyl-	50.6	0.927
N-cyclohexyl-	67.2	1.341
N-1-naphthyl- ^{1/}	32.7	0.628
N-2-naphthyl-	44.7	.833
N-p-tolyl-	50.1	.916
Allethrin standard, 1.0 mg. per ml.	53.1	.976
0.5	27.7	.521
.25	5.3	.230
Required to demonstrate synergism ----		.639
Series 3		
Piperonylamide, N-benzyl-	76.8	1.298
N-p-chlorophenyl- ^{1/}	50.3	0.672
N-ethyl-	87.2	1.854
N-methyl-	71.8	1.106
N-propyl-	93.9	> 2
Allethrin standard, 1.0 mg. per ml.	67.6	1.007
0.5	37.9	0.507
.25	12.6	.241
Required to demonstrate synergism ----		.690



Table 1. --Continued.

Adjunct	Mean mortality in 1 day	Mean allethrin equivalent
	<u>Percent</u>	<u>Mg. per ml.</u>
Series 4		
Piperonylamide, N-amyl-	70.1	1.181
N-(<u>m</u> -bromophenyl)-	66.8	1.107
N-(<u>o</u> -bromophenyl)-	91.1	> 2
N-(<u>m</u> -chlorophenyl)-	59.3	0.944
N, N-diethyl-	97.1	> 2
Allethrin standard, 1.0 mg. per ml.	62.7	1.016
0.5	26.6	0.495
.25	6.1	.237
Required to demonstrate synergism ----		.649
Series 5		
Piperonylamide, N-(<u>p</u> -bromophenyl)- ^{1/}	42.9	0.695
N, N-dibenzyl-	82.5	1.647
N-(<u>o</u> -nitrophenyl)-	83.1	1.638
Allethrin standard, 1.0 mg. per ml.	58.1	0.928
0.5	35.2	.596
.25	4.0	.182
Required to demonstrate synergism ----		.668

^{1/} 2.5 mg. per ml.