

RELATIVE TOXICITY OF SELECTED COMPOUNDS AS RESIDUAL SPRAYS AGAINST ADULTS OF *ANOPHELES QUADRIMACULATUS* SAY

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INTRODUCTION. The Orlando, Florida, laboratory of the Entomology Research Division has maintained a continuing program for the evaluation of new insecticides and residual applications for the control of mosquitoes, particularly anophelines, in buildings. Since the development of resistance to chlorinated hydrocarbon insecticides by several important species, interest has centered in the organophosphorus compounds and carbamates.

In recent experiments with *Anopheles quadrimaculatus* Say, Hercules AC-5727 (Union Carbide 10854) (*m*-isopropylphenyl methylcarbamate) and Sevin (1-phthalyl *N*-methylcarbamate) were the best of the carbamates to show outstanding promise (LaBrecque *et al.* 1960; Gahan *et al.* 1961a). Later, Gahan *et al.* (1961b) found that Bayer 39007 (*o*-isopropoxyphenyl methylcarbamate) and Bayer 41831 (Sumithion) (*O,O*-dimethyl 4-nitro-*m*-tolyl phosphorothioate) were also highly effective. Deposits of 100 mg. of these compounds per square foot on plywood panels were still producing at least 90 percent mortality within 24 hours after exposures of 60 minutes or less on residues aged for 24 to 32 weeks. Georgiou and Metcalf (1961) also found *m*-isopropylphenyl methylcarbamate (Hercules AC-5727) and *o*-isopropoxyphenyl ethylcarbamate (Bayer 39007) highly effective against adults of *Culex quinquefasciatus* and *Anopheles albimanus* Wiedemann. This paper presents additional laboratory results obtained with these four materials and an initial report on 10 new compounds that have been effective at least

28 weeks as residues on plywood panels.

LABORATORY TESTS. In conducting these tests acetone solutions or water suspensions of the compounds were sprayed on plywood panels at 100 mg. of the technical compound per square foot. At intervals after treatment approximately 40 adult females of *Anopheles quadrimaculatus* Say were exposed on the treated surfaces under half sections of Petri dishes. After exposure, the mosquitoes were transferred to untreated screen holding cages, furnished cotton that had been saturated with 10 percent honey solution and held for 24 hour mortality counts.

Mosquitoes were exposed initially on the treated surfaces 1 week after the panels were sprayed. If the mortality was high enough, additional exposures were made the fourth week and at 4-week intervals thereafter throughout the first year. The interval between testing was increased to 8 weeks for the second year and 16 weeks for the third year.

To increase the number of materials that could be evaluated, only a 1-hour exposure was used in most experiments instead of the 4 or 5 different exposures employed in the experiments reported in the papers cited above. However, fast action is a highly desirable characteristic for such compounds, particularly if used in malaria eradication programs, and therefore deposits that gave 100 percent knockdown in 30 minutes the first week after treatment were tested again with exposures of 1, 5, and 15 minutes on the following day.

Six of the materials were methylcarbamates. In addition to the *m*-isopropylphenyl (Hercules AC-5727) and *o*-isopropoxyphenyl (Bayer 39007) esters already mentioned, the 6-chloro-*m*-cumenyl (Hercules 7522 G and H), 6-chloro-3,5-xylyl

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(Upjohn U-12927), 4-(methylthio)-3,5-xylyl (Bayer 37344), and 1-naphthyl (Sevin) esters were tested. All of these compounds are grayish, pinkish, or white crystalline materials, are readily soluble in acetone, and have a mild odor. Hercules 7522 and Hercules AC-5727 were also tested at 100 mg. per square foot in combination with 1,000 mg. of piperonyl butoxide per square foot.

Seven materials were organophosphorus compounds; Bayer 41831 (Sumithion) (*O,O*-dimethyl *O*-4-nitro-*m*-tolyl phosphorothioate), Bayer 23248 (3-chloropropyl 2,2-dichlorovinyl ethyl phosphate), Bayer 30468 (*O*-ethyl *O,p*-(ethylthio)phenyl methylphosphonothioate), Bayer 29952 (*O*-ethyl *O,p*-(methylthio)phenyl methylphosphonothioate) and Bayer 34042 (*O*-ethyl *O*-(4-methylthio-*m*-tolyl) methylphosphoramidothioate) were yellowish or brown liquids, and Ciodrin (Shell SD-4294) (dimethyl 2-(*alpha* methylbenzyl-oxycarbonyl)-1-methylvinyl phosphate) was a clear liquid. None of these materials had any strong objectionable odors. Bayer 30237 (*O*-methyl *O,p*-(methylthio)phenyl

methyl phosphonothioate) was a brown liquid with a strong, disagreeable odor.

The other compound, Telodrin (Shell SD-4402) (1,3,4,5,6,7,8,8-octachloro-1,3,3a,4,7,7a-hexahydro-4,7-methanoisobenzofuran), is a brown crystal with a milodor.

The results are summarized in Table 1 which lists the number of weeks of aging during which each treatment caused at least 70 percent mortality among mosquitoes exposed on the treatment for 1 hour, the range of mortality in tests during that period, and the percent knockdown in 3 minutes in tests after 1 week of aging.

Six of the seven most effective compounds were carbamates. Except for a 3 percent kill the second week, Sevin consistently gave kills of 92 to 100 percent for 84 weeks, and above 70 percent for 9 weeks. Bayer 39007 produced 100 percent mortality for 72 weeks, then lost toxicity rapidly. Upjohn U-12927 and Bayer 37344 were still causing 98 to 100 percent mortality approximately 1 year after treatment and eventually may prove to be the most durable of the group. Bayer 41831, a

TABLE 1.—Residual effectiveness of insecticides on plywood panels in tests with *Anopheles quadrimaculatus*. ("Plus" signs indicate panels that were still effective at the end of the period indicated.)

| Insecticide | Weeks panels caused 70-100 percent mortality | Mortality range above 70 percent | Initial knockdown in 30 mi (percent) |
|---|--|----------------------------------|--------------------------------------|
| Sevin | 96 | 85-100 | 0 |
| Bayer 39007 | 72 | 100 | 100 |
| Upjohn U-12927 | 56+ | 100 | 100 |
| Bayer 37344 | 48+ | 98-100 | 0 |
| Bayer 41831 | 64 | 80-100 | 37 |
| Hercules AC-5727 | 60 | 100 | 100 |
| | 48 | 100 | 100 |
| Hercules 5727 plus piperonyl butoxide | 120+ | 100 | 100 |
| Hercules 7522-G | 64 | 90-100 | 100 |
| 7522-H | 28 | 100 | 100 |
| Hercules 7522-H plus piperonyl butoxide | 44+ | 100 | 100 |
| Shell SD-4294 | 44 | 75-100 | 0 |
| Shell SD-4402 | 36 | 85-100 | 13 |
| Bayer 23248 | 36 | 100 | 100 |
| Bayer 30468 | 36 | 98-100 | 20 |
| Bayer 30237 | 36 | 70-100 | 73 |
| Bayer 29952 | 31 | 100 | 37 |
| Bayer 34042 | 28 | 93-100 | 0 |

organophosphorus compound, dropped below 70 percent after 64 weeks. Hercules AC-5727 continued to kill all the mosquitoes for 48 weeks in one experiment and 0 weeks in another, but the mortality decreased to 5-10 percent the next time an exposure was made. The status of Hercules 7522 is not clear at this time; one sample remained highly effective for 64 weeks but another lost its toxicity rapidly after the 28th week.

In addition to their durability, the outstanding characteristic of four of these carbamates—Bayer 39007, Upjohn U-2927, Hercules AC-5727 and Hercules 7522—was the rapidity with which they produced knockdown and the short period of contact required for the mosquitoes to pick up a lethal dose of the chemical. Fresh treatments applied at 100 mg. per square foot caused 100 percent knockdown within 5 minutes after exposure started and exposures as short as 1 minute killed all the mosquitoes in 24 hours. The other carbamates—Sevin and Bayer 37344—caused no knockdown in 30 minutes. Bayer 41831 (Sumithion) caused no knockdown in 30 minutes.

Piperonyl butoxide was used in combination with Hercules AC-5727 and Hercules 7522 sprays to determine its synergistic effect with these carbamates. Residues applied at the rate of 100 mg. of insecticide plus 1,000 mg. of piperonyl butoxide per square foot outlasted 100 mg. of the insecticide alone and were still highly effective at the time this paper was written. The Hercules 7522 used in this test was the sample that lost toxicity rapidly after the 28th week. The combination was still killing all mosquitoes exposed to it after 44 weeks. A treatment containing both Hercules AC-5727 and piperonyl butoxide was still highly effective more than 2 years after application, whereas the insecticide alone lasted 48 weeks. Piperonyl butoxide would not be practical for use at this rate of application, but lower dosages of piperonyl butoxide or one of the other insecticide synergists may substantially improve the effectiveness of carba-

mate insecticides and be inexpensive enough to use.

Toxicological information on rats or mice obtained from the manufacturers or from B. A. Butt, entomologist of this Division, at Brownsville, Texas, indicated that at least four and possibly all of these compounds would be safe for use in actual control work. The acute oral LD-50 to rats and/or mice is about 500-700 mg./kg. for Sevin, 50-300 mg./kg. for Upjohn U-12927, 95-200 mg./kg. for Bayer 39007, 200 mg./kg. for Bayer 41831, 15-63 mg./kg. for Hercules AC-5727, 250 mg./kg. for Bayer 37344, and approximately 45 mg./kg. for Hercules 7522. Applications of Bayer 39007 at 1000 mg./kg. as an oil suspension to the shaved bellies of rats produced no symptoms or irritation during a 4-hour exposure or afterwards.

The remaining organophosphorus compounds and Telodrin were less durable than the seven materials already discussed although they remained highly effective for intervals ranging between 28 and 44 weeks. Bayer 23248 was the only compound that acted rapidly enough to cause 100 percent knockdown in 30 minutes. Shell SD-4294 has an oral LD-50 to rats of 98 mg./kg. of body weight and was sufficiently effective to justify evaluation against natural populations of *Anopheles* mosquitoes, but the other materials have oral LD-50's or LD-100's ranging from 1 mg. to 10 mg./kg. of body weight and probably are too toxic to use in buildings inhabited by warm-blooded animals.

FIELD TESTS. The year 1961 was unfavorable for conducting field tests in Central Florida because of abnormally low rainfall, which eliminated many favorable breeding areas for *Anopheles* mosquitoes. Bayer 39007 was applied to the only barn in the area that was found heavily infested with adults of *Anopheles quadrimaculatus*. It was sprayed as a wettable powder at the rate of 100 mg. per square foot. Pretreatment counts made on two occasions within 1 month of the spray application averaged 197 adults per observation period. During

the first 12 weeks after treatment not a single mosquito was seen in this building. By the 17th week the control had dropped to 84 percent. Additional counts made during the 21st and 25th weeks indicated that the control had increased again to 90-96 percent. These latter observations were made during the winter when *Anopheles* populations are normally low, so probably do not correctly indicate the effect of these compounds on the mosquito infestation. It was obvious, nevertheless, that the treatment remained highly effective for more than 3 months.

In a previous paper, Gahan *et al.* (1961b) reported that Hercules AC-5727 at 100 mg. per square foot eliminated all the mosquitoes from treated buildings during the first 9 to 11 weeks, and that the control remained above 90 percent for at least 25 to 28 weeks. A deposit of 50 mg. per square foot eliminated all mosquitoes for 9 weeks but was not highly effective after 11 weeks. Sevin was much less effective than Hercules AC-5727; at each observation some *Anopheles* mosquitoes were present in the treated buildings and the control deteriorated rapidly. The Sevin was applied as a water emulsion prepared with a concentrate obtained from the manufacturer. Later, the company reported that this concentrate was an unsatisfactory formulation.²

² From a paper by R. W. Bagley and R. C. Back, "Preliminary Tests with Sevin Insecticide for the Control of Adult Mosquitoes," read at meeting of the American Mosquito Control Association, Galveston, Texas, March 5, 1962.

SUMMARY. Six of the seven most effective materials in laboratory tests with 14 compounds were derivatives of methyl carbamic acid. Deposits of 100 mg./sq. ft. on plywood remained effective (70 percent kills of *Anopheles quadrimaculatus* Say exposed for 1 hour) for the following numbers of weeks: Sevin (1-naphthyl *N*-methylcarbamate), 96; Bayer 39007 (isopropoxyphenyl methylcarbamate), 7; Upjohn U-12927 (6-chloro-3,5-xylyl methylcarbamate), more than 56; Bayer 3734 (4-(methylthio)-3,5-xylyl methylcarbamate), more than 48; Bayer 41831 (S-mithion) (*O,O*-dimethyl *O*-4-nitro-*m*-tol phosphorothioate) 64; Hercules AC-5727 (*m*-isopropylphenyl methylcarbamate), 2 to 60; and Hercules 7522 G and H (chloro-*m*-cumenyl methylcarbamate), 28-64. The last two compounds were highly synergized by piperonyl butoxide. Bayer 39007 at 100 mg./sq. ft. gave control of natural infestation of *A. quadrimaculatus* in an infested barn for more than months.

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