TECHNICAL PAPERS

Insecticidal Activity of 2,2-*bis*-(2-Chlorothienyl)-1,1,1-Trichloroethane

ROBERT L. METCALF

University of California Citrus Experiment Station, Riverside, California

The preparation of several thienyl analogues of DDT was recorded by Metcalf and Gunther (*1*), who found that in residue tests 2,2-*bis*-(2-chlorothienyl)-1,1,1-trichloroethane was about 1/100 as toxic as *p, p'*-DDT on a weight basis to the greenhouse thrips, *Heliothrips haemorrhoidalis* (Bouché), and less than 1/1,000 as toxic to *Drosophila melanogaster* Meig. Subsequently, Truitt, *et al.* (*4*) repeated the preparation of this compound and stated that it was as active as DDT against cockroaches (unspecified species). Inasmuch as DDT is comparatively ineffective against the German cockroach, *Blatella germanica* (L.), we feel that this comparison is misleading with respect to the insecticidal potency of the compound and wish to record additional experimental data. The effectiveness of this thienyl-isoster of DDT is also of interest in clarifying the mode of action of DDT.

Toxicity tests were made on 10 species of insects as described in Table 1. In every case the insects were exposed to equivalent amounts of 2,2-*bis*-(*p*-chlorophenyl)-1,1,1-trichloroethane (m.p., 108–109° C), and 2,2-*bis*-(2-chlorothienyl)-1,1,1-trichloroethane (m.p., 65–66° C), in paired experiments carried out under identical conditions. The residue tests were made by placing the insects on crystalline deposits of the compounds on filter paper, deposited from standard acetone solutions. The tests using dusts were carried out with leaves dusted in a precision dusting tower. The potency of the thienyl analogue was comparable to that of DDT in tests with the German cockroach, red harvester ant, honey bee, and milkweed bug. Against the other species, DDT was markedly more effective. It is interesting that the insects against which the thienyl analogue was most effective are, with the possible exception of the honey bee, highly resistant to the action of DDT as compared with other chlorinated hydrocarbon insecticides. This is graphically shown in Table 2, where the activity of DDT is compared with chlordan (1,2,4,5,6,7,8,8-octachloro-4,7-methano-3a,4,7,7a-tetrahydroindane) and γ-hexachlorocyclohexane in the case of the ant and cockroach. It is evident that, compared in this way, chlordan and γ-hexachlorocyclohexane are each more than 1,000 times as toxic as DDT, on a weight basis, to these insects.

TABLE 1

RELATIVE EFFECTIVENESS OF *p,p'*-DDT AND 2,2-*bis*-(2-CHLOROTHIENYL)-1,1,1-TRICHLOROETHANE TO VARIOUS INSECTS

Species	How tested	Mortality	
		DDT	Thienyl analogue
Apis mellifera L.—adult honey bee	Residue—1 mg/cm²	45%—5 hrs	40%—5 hrs
Pogonomyrmex barbatus (F. Smith)—adult red harvester ant	Residue—1 mg/cm²	35%—24 hrs	30%—24 hrs
Lucilia sericata Meig.—adult greenbottle fly	Residue—1 mg/cm²	100%—18 hrs	5%—18 hrs
Blatella germanica (L.)—adult German cockroach	Residue—1.3 mg/cm²	40%—120 hrs	50%—120 hrs
Oncopeltus faciatus (Dall.)—adult large milkweed bug	Residue—1.3 mg/cm²	90%—72 hrs	60%—72 hrs
Phryganidia californica Pack.—California oakworm, last larval instar	5% dust at 0.2 mg/cm²	75%—96 hrs	None—96 hrs
	oak leaves	No feeding	Heavy feeding
Listroderes obliquus Klug.—adult vegetable weevil	5% dust at 0.2 mg/cm²	70%—96 hrs	None—96 hrs
	malva leaves	No feeding	Heavy feeding
Apantesis proxima G. M.—last instar larvae	10% moist bran bait; fed 1 gm/larva	65%—96 hrs	2%—96 hrs
Tribolium confusum Duv.—adult confused flour beetle	(a) 2% in flour medium	100%—120 hrs	10%—120 hrs
	(b) Residue—1.5 mg/cm²	100%—48 hrs	2%—48 hrs
Aonidiella aurantii (Mask.)—first instar California red scale	Residue on grapefruit from xylene-water spray		
	0.4 gm/liter	98.8%—3 weeks	1%—3 weeks
	0.2 gm/liter	97.1%—3 weeks	None—3 weeks

From the standpoint of the method of action of DDT, the behavior of the thienyl-isoster is of special interest. The dimensions of the thiophene molecule are nearly identical with those of benzene (*2*), and if it can be shown that the substitution can be made without altering the qualitative biological behavior of the compound, it may be indicative of the role of the aromatic rings as

"spacers" for orienting the compound in some biological system. A few experiments were carried out using the American cockroach, *Periplaneta americana* (L.), as a test animal and applying measured dosages of the thienyl compound exteriorly and by intra-abdominal injection. Tobias, *et al.* (*3*) determined the LD_{50} of DDT applied to *P. americana* in acetone as 10 μg/gm in 120 hrs. For DDT injected intra-abdominally the figure was 5–8 μg/gm. Using identical technics and amounts of acetone per insect, we obtained no response in 120 hrs from the application of 125 μg/gm of 2,2-*bis*-(2-chlorothienyl)-1,1,1-trichloroethane on the dorsum of the thorax near the point of attachment of the wings, nor from the intra-abdominal injection of 125 μg/gm of the compound between the third and fourth abdominal sternites. Thus, DDT is much more effective to this insect both by contact and by injection than is its thienyl-isoster, and the failure of the latter to produce symptoms at equivalent dosage cannot be due to poor penetration into the insect.

TABLE 2

COMPARATIVE EFFECTIVENESS OF DDT, CHLORDAN, AND γ-HEXACHLOROCYCLOHEXANE TO GERMAN COCKROACH AND RED HARVESTER ANT

Insect	Toxicant as residue (μg/cm²)	Per cent mortality in 120 hrs		
		DDT	γ-Hexachlorocyclohexane (m.p., 112° C)	Chlordan (b.p., 175°/2 mm)
B. germanica	1,300	50	...	...
	13	0	100	100
	1.3	..	90	70
	0.13	..	10	10
		Per cent mortality in 48 hrs		
P. barbatus	500	0		
	13	..	90	65
	1.3	..	45	30
	0.13	..	10	15

Yeager and Munson (*5*) studied the site of action of DDT in *P. americana* and found evidence that DDT acted at a site common to the insect leg and body, viz., the myoneural junctions of nerve fibers. A significant portion of their evidence was the action of DDT in causing tremors and convulsions when applied to severed insect legs. The application of the thienyl-isoster to the severed legs of *P. americana* at a dose of 100 μg/leg resulted in unmistakable DDT-like, repeated, and spasmodic contractions of three-fourths of the legs treated. The duration and intensity of the movement was, however, much less than that produced by similar applications of DDT at 10 μg/leg. This appears to demonstrate that 2,2-*bis*-(2-chlorothienyl)-1,1,1-trichloroethane affects insect nerves in a manner similar, if not identical, to the action of DDT, but that the intensity of action is much less than one-tenth that of DDT.

It may be concluded that 2,2-*bis*-(2-chlorothienyl)-1,1,1-trichloroethane is considerably less potent insecticidally than DDT, except when tested against insects highly resistant to DDT. However, qualitatively it resembles DDT in its mode of action and appears to affect the same locus in the insect nervous system. This is evidence, therefore, that the phenyl rings are not essential in producing the biochemical effects of the DDT-type molecule.

References

1. METCALF, R. L., and GUNTHER, F. A. *J. Amer. chem. Soc.*, 1947, **69**, 2579.
2. SCHOMAKER, V., and PAULING, L. *J. Amer. chem. Soc.*, 1939, **61**, 1769.
3. TOBIAS, J., KOLLROS, J., and SAVIT, J. *J. Pharm. exp. Therap.*, 1946, **86**, 287–293.
4. TRUITT, P., MATTISON, M., and RICHARDSON, E. *J. Amer. chem. Soc.*, 1948, **70**, 79.
5. YEAGER, J. F., and MUNSON, S. C. *Science*, 1945, **102**, 305–307.

A Theory of Herbicidal Action

A. S. CRAFTS[1]

Division of Agronomy and Horticulture,
Puerto Rico Agricultural Experiment Station,
Rio Piedras

Because there are many herbicides and many mechanisms involved in their action, generalization concerning them is hazardous. However, the contact sprays and soil sterilants are so dependent upon uptake by the plant that the mechanism of absorption is paramount to their effectiveness.

A theory proposing that nonpolar compounds can pass through the cuticle of leaves readily, whereas polar compounds enter with difficulty, has been published (*3*). Evidence is presented that nonpolar phenols in water, or in oil, are more toxic than their salts in water. Because such compounds (dinitrocresol, dinitrobutyl and amyl-phenols, pentachlorophenol, etc.) are more soluble in oil than in water, they are used to prepare either fortified oils or fortified oil emulsion sprays. Salts of these compounds in water are selective because, by differential wetting, they will kill broad-leafed weeds with no injury to grain, flax, etc. Lowering the polarity of the toxicants of such solutions by addition of acid salts (activation) or by using the ammonium salts increases their toxicity. Active absorption of the phenol molecules explains this increased toxicity where complete conversion to undissociated parent molecules is not accomplished.

Early testing confirmed this mechanism for 2,4-D compounds (*5*). The esters were more toxic than the ammonium salt, which exceeded the sodium salt. Many published results substantiate this relation. Early herbicides such as iron sulfate, sulfuric acid, sodium arsenite, and sodium chlorate entered plants because of their high concentration or corrosive action. Modern herbicides, such as dinitro- and chlorophenols, phenoxy compounds, and carbamates, are used at low concentrations; their entry from sprays into the plant depends upon their com-

[1] On leave from the College of Agriculture, University of California, Davis.

A. Emanuelli, assistant agronomist in the Puerto Rico Agricultural Experiment Station, has cooperated in the current research reported in this paper.