

Toxicity of Parathion and Several of its Photoalteration Products to Boll Weevils

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Exposure of parathion to light results in the formation of cholinesterase inhibitors chromatographically different from parathion (2). In 1958, Frawley et al. (5) found a mixture of parathion, paraoxon, and oxidation and degradation products resulting from the exposure of parathion to ultraviolet light. Gar and Kapiiani (6), Koivistoinen (8), and El-Rafai and Hopkins (4) reported mixtures containing parathion, paraoxon, S-ethyl parathion, S-phenyl parathion and a variety of unidentified products from parathion exposed to various light treatments.

Joiner and Baetcke (7) have found up to 12 identifiable photoalteration products resulting from treatment of parathion with high intensity ultraviolet light. No more than 5 identifiable photoalteration products from ultraviolet treatment of parathion have been previously reported (4,5,6,8). The purpose of the study reported here was to determine the toxicity of some of these products as compared to the parent compound.

EXPERIMENTAL

Samples of parathion and potential photoalteration products (Table 1) were verified by infrared spectroscopy and thin layer chromatography. Toxicity studies were conducted with 4-day-old, laboratory-reared boll weevils, Anthonomus grandis Boheman (Texas A&M strain). Insects (minimum of 100 per dose; average weight of 13.5 milligrams per insect) were treated topically with one microliter of insecticide solution in acetone, and mortality was determined 24 hours posttreatment. LD₅₀ and slope values were determined by log-probit analysis (3) on a UNIVAC 1106 computer (Sperry-Rand Corporation, Holyoke, Mass.). Chemicals

TABLE 1

Nomenclature and Chemical Structure of Compounds Tested^{a/}

Compound Number	Chemical	Structure
1	O,O-diethyl O-4-nitrophenyl phosphorothioate b/	$(\text{CH}_3\text{CH}_2\text{O})_2-\text{P}(=\text{S})-\text{O}-\text{C}_6\text{H}_4\text{NO}_2$
2	O,O-diethyl O-4-nitrophenyl phosphate b/	$(\text{CH}_3\text{CH}_2\text{O})_2-\text{P}(=\text{O})-\text{O}-\text{C}_6\text{H}_4\text{NO}_2$
3	O,S-diethyl O-4-nitrophenyl phosphorothioate c/	$\text{CH}_3\text{CH}_2\text{S}-\text{P}(=\text{O})(\text{OCH}_2\text{CH}_3)-\text{O}-\text{C}_6\text{H}_4\text{NO}_2$
4	O,O-diethyl S-4-nitrophenyl phosphorothioate c/	$(\text{CH}_3\text{CH}_2\text{O})_2-\text{P}(=\text{O})-\text{S}-\text{C}_6\text{H}_4\text{NO}_2$
5	O,O-bis(4-nitrophenyl) O-ethyl phosphorothioate c/	$\text{CH}_3\text{CH}_2\text{O}-\text{P}(=\text{S})(\text{OC}_6\text{H}_4\text{NO}_2)_2$
6	O,O-bis(4-nitrophenyl) O-ethyl phosphate c/	$\text{CH}_3\text{CH}_2\text{O}-\text{P}(=\text{O})(\text{OC}_6\text{H}_4\text{NO}_2)_2$
7	O,O-diethyl O-phenyl phosphorothioate b/	$(\text{CH}_3\text{CH}_2\text{O})_2-\text{P}(=\text{S})-\text{O}-\text{C}_6\text{H}_5$
8	O,O-diethyl O-phenyl phosphate b/	$(\text{CH}_3\text{CH}_2\text{O})_2-\text{P}(=\text{O})-\text{O}-\text{C}_6\text{H}_5$

^{a/}All compound label purities were between 98.5 and 99.5%.^{b/}American Cyanamide Co., USA.^{c/}Farben Fabriken Bayer AG, Germany.

yielding less than 50% mortality at a dosage of 1500 micrograms per gram body weight (approximately 500 times the LD₅₀ of parathion) are reported as having an LD₅₀ >1500.

RESULTS AND DISCUSSION

Conversion of parathion to paraoxon resulted in no appreciable change in toxicity of these compounds to boll weevils (Table 2). Similar results have been noted in comparison of methyl parathion and methyl paraoxon (1). The LD₅₀ values of methyl parathion and methyl paraoxon in boll weevils were 2.54 ± 0.34 and 2.28 ± 0.43 micrograms per gram body weight, respectively (these LD₅₀ values were appreciably lower than the LD₅₀ values reported in this study for ethyl paraoxon). In mammals, ethyl paraoxon and methyl paraoxon have been shown to be generally more toxic than the parent compounds (10). The greater innate toxicity of these oxygen analogs is apparently offset, in insects, by a more rapid metabolic detoxication (11).

Rearrangement of parathion to the S-ethyl (Compound 3) and S-phenyl (Compound 4) analogs resulted in significantly decreased toxicity. The S-phenyl derivative was about twice as toxic as the S-ethyl derivative, but only one-sixteenth as toxic as the parent compound. The lower toxicity of the S-ethyl analog has also been observed in mammals, but the S-phenyl analog was found to be of about the same toxicity as parathion to mice via subcutaneous injection (10).

Both products containing two 4-nitrophenyl moieties (Compounds 5 and 6) were virtually nontoxic to the test organism. Similarly, loss of the nitro group (Compounds 7 and 8) resulted in essentially complete detoxication. Compounds resulting from photolysis (diethyl phosphate and diethyl phosphorothionate) were not assayed but were assumed to be noninsecticidal (9).

Photoalteration of parathion leads to only partial detoxication of the insecticide, with several products retaining significant toxicity to both insects and mammals. It is clear, therefore, that residue determinations of parathion, and presumably other organophosphorus pesticides, should include biological as well as chemical assays in order to establish the potential hazard of such residues.

TABLE 2

DOSAGE-MORTALITY DATA ON PARATHION AND POTENTIAL
PHOTOALTERATION PRODUCTS

Compound Number	Chemical	LD ₅₀ ^{a/}	Slope
1	Parathion(O,O-diethyl O-4-nitrophenyl phos- phorothionate)	12.3 ± 3.3	2.91
2	Paraoxon(O,O-diethyl O-4-nitrophenyl phos- phate)	13.8 ± 1.3	2.13
3	O,S-diethyl O-4-nitro- phenyl phosphorothioate	416.0 ± 61.5	1.85
4	O,O-diethyl S-4-nitro- phenyl phosphorothioate	207.5 ± 64.0	3.12
5	O,O-bis(4-nitrophenyl) O-ethyl phosphorothioate	>1500	—
6	O,O-bis(4-nitrophenyl) O-ethyl phosphate	>1500	—
7	O,O-diethyl O-phenyl phosphorothioate	>1500	—
8	O,O-diethyl O-phenyl phosphate	>1500	—

^{a/} LD₅₀ (microgram per gram of body weight) ± 95% con-
fidence limits.

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