Hartley, 1969; Spencer and Cliath, 1970).

The transfer of relatively large quantities of bisazir to air can be ascribed to its relatively high vapor pressure. Jensen and Schall (1966) stated that "2,4-D and 2,4,5-T derivatives with a vapor pressure greater than 0.15 × 10^{-3} mm (0.15 μm) of Hg at 25 °C should be classified as highly volatile". All of the chemosterilants studied here are similar in molecular weight and can be considered quite volatile at room temperature. Hempa, a popular, particularly useful polar solvent, is even more volatile than bisazir. We suggest handling these materials with appropriate caution and ventilation.

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Received for review March 17, 1980. Accepted August 29, 1980. This paper reports the results of research only. Mention of a pesticide in this paper does not constitute a recommendation for use by the U.S. Department of Agriculture nor does it imply registration under FIFRA as amended. Mention of a proprietary product does not constitute a recommendation or endorsement by the U.S. Department of Agriculture.

Larvicidal Effects of Substituted Diamino- and Triamino-*s*-triazines

Albert B. DeMilo, Alexej B. Bořkovec,* Charles F. Cohen, and William E. Robbins

Larvicidal activity of 21 substituted 2,4-diamino-*s*-triazines and 14 substituted 2,4,6-triamino-*s*-triazines was determined in *Musca domestica* L., *Aedes aegypti* (L.), *Tribolium confusum* Jacquelin duVal, and *Plodia interpunctella* (Hübner). Some of the triazines examined in this study were previously reported to have insect chemosterilant activity. Larvicidal activity was highest in *M. domestica* and *A. aegypti*. Five of the compounds were more active than the larvicide 6-azido-*N*-cyclopropyl-*N'*-ethyl-1,3,5-triazine-2,4-diamine (CGA-19255) in *M. domestica*, and one was as active in *A. aegypti*.

The discovery of the insect sterilizing effects of diamino- and triamino-*s*-triazines (Borkovec and Terry, 1965; Borkovec and DeMilo, 1967; LaBrecque et al., 1968; Borkovec et al., 1972) presented a new type of inhibition of reproduction: when the female was treated, it mated and oviposited normally, and egg hatch was high, but the larvae died before reaching maturity. Apparently, the compounds or their metabolites disturbed the metabolism of the young larvae (Matolin and Landa, 1971). Recent reports on the larvicidal activity of 6-azido-*N*-cyclopropyl-*N'*-ethyl-1,3,5-triazine-2,4-diamine (AI3-70670; Ciba-Geigy CGA 19255) (Herzog and Brechbuehler, 1976; Christensen and Knapp, 1976; Miller et al., 1977) prompted us to determine the effects of 21 diamino- and 14 triamino-*s*-triazines on larvae of the yellow fever mosquito, *Aedes aegypti* (L.), housefly, *Musca domestica* L., Indianmeal moth, *Plodia interpunctella* (Hübner), and confused flour beetle, *Tribolium confusum* Jacquelin duVal. The results of these tests and the structure–activity correlations for the compounds are presented here.

EXPERIMENTAL SECTION

Materials. Except for the compound AI3-70670, which was supplied by the Ciba-Geigy Corp., all triazines shown in Table I were synthesized according to previously published procedures (Smolin and Rapoport, 1959; Nestler and Fuerst, 1963; Borkovec and DeMilo, 1967; DeMilo and Borkovec, 1968; DeMilo, 1970). New compounds (AI3-60019, -60108, -60209, -61516, -62414, -62415, and -62525) were analyzed (Galbraith Laboratories, Inc., Knoxville, TN) for carbon, hydrogen, and nitrogen with acceptable results (±0.3% of theory). Table I contains melting points of these materials. Compounds AI3-62414, AI3-62415, and AI3-62525 were prepared from 6-hydrazino-*N*,*N*,*N'*,*N'*-tetramethyl-1,3,5-triazine-2,4-diamine (DeMilo et al., 1973) and the appropriate aldehyde or isothiocyanate. Since many diamino and triamino-*s*-triazines are poorly soluble in water, several hydrochloride salts were tested; their activity was found to be comparable to that of the free bases. For convenience, some of the compounds listed in Table I were tested as hydrochlorides.

Biological Testing. All compounds were tested as additives to the diet of larvae of *A. aegypti* (A), *M. domestica* (M), *P. interpunctella* (P), and *T. confusum* (T). Testing procedures of Robbins et al. (1970) were used for A, M, and T, and the procedure of Cohen and Marks (1979) was used for P. Compounds that did not kill 75% or more of the test insects at their highest applied concentration (A, 10 ppm; M, 300 ppm; P, 1000 ppm; T, 3000 ppm) were considered inactive. All positive tests were replicated.

RESULTS AND DISCUSSION

Larvicidal activity of the *s*-triazines varied considerably among the four insect species, but the closest correlation could be made between the two Diptera: *M. domestica* and *A. aegypti* (Table I). In the series of 2-substituted-

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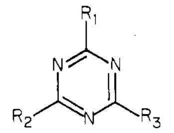
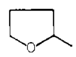
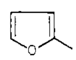
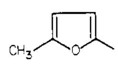
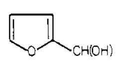
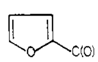
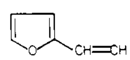
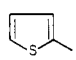
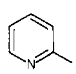
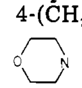
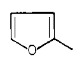
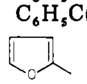
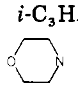
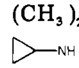
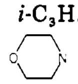
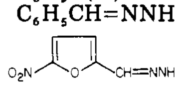
Table I. Concentrations of Substituted *s*-Triazines That Killed 75–100% of Larvae of *M. domestica* or *A. aegypti* When Added to Their Larval Media



AI3 No.	R_1	R_2	R_3	ppm in larval medium of[a] *M. domestica*	ppm in larval medium of[a] *A. aegypti*
		Diamino-*s*-triazines			
61080	Cl_3C	NH_2	NH_2	100	NA
60433[b]	*i*-C_3H_7	NH_2	NH_2	100	NA
60402	*i*-C_3H_7O	NH_2	NH_2	300	NA
62074	*i*-$C_3H_7C(O)$	NH_2	NH_2	NA	NA
60276[c]		NH_2	NH_2	300	NA
22641		NH_2	NH_2	1	10
60209[b,d]		NH_2	NH_2	30	NA
61994		NH_2	NH_2	NA	NA
62072		NH_2	NH_2	300	NA
60138		NH_2	NH_2	300	NA
60103		NH_2	NH_2	1	3
51408		NH_2	NH_2	100	10
62009	4-$ClC_6H_4CH(OH)$	NH_2	NH_2	300	NA
62050	4-$ClC_6H_4C(O)$	NH_2	NH_2	NA	NA
60025[b]	H	NH_2	4-$(CH_3O)C_6H_4NH$	300	NA
60368[b]	H	NH_2		NA	NA
60019[b,e]		NH_2	$(CH_3)_2N$	300	NA
62051	$C_6H_5CH(OH)$	NH_2	C_6H_5NH	NA	NA
62066	$C_6H_5C(O)$	NH_2	C_6H_5NH	NA	NA
62065	$C_6H_5C(O)$	NH_2	$(CH_3)_2N$	NA	NA
60108[b,f]		CH_3NH	CH_3NH	100	NA
		Triamino-*s*-triazines			
60008[b]	*i*-C_3H_7NH	NH_2	NH_2	1	1
51014		NH_2	NH_2	1	0.3
51146[b]	NH_2	$(CH_3)_2N$	$(CH_3)_2N$	100	NA
70670	N_3	C_2H_5NH		3	0.3
60352[b]	*i*-C_3H_7NH	*i*-C_3H_7NH	*i*-C_3H_7NH	0.3	1
60125[b]		CH_3NH	CH_3NH	100	10
61205	CH_3NH	$(CH_3)(CHO)N$	$(CH_3)(CHO)N$	NA	NA
61368	$(CHO)NH$	$(CH_3)_2N$	$(CH_3)_2N$	300	NA
61484[g]	$(CH_2COOH)NH$	$(CH_3)_2N$	$(CH_3)_2N$	NA	NA
61516[b,h]	$C_6H_5C(O)NH$	$(CH_3)_2N$	$(CH_3)_2N$	NA	NA
62525[i]	$C_6H_5CH{=}NNH$	$(CH_3)_2N$	$(CH_3)_2N$	NA	NA
62413		$(CH_3)_2N$	$(CH_3)_2N$	NA	NA
62415[j]	$CH_3NHC(S)NHNH$	$(CH_3)_2N$	$(CH_3)_2N$	30	NA
62414[k]	$C_6H_5NHC(S)NHNH$	$(CH_3)_2N$	$(CH_3)_2N$	NA	NA

[a] NA, no activity at the highest concentration tested. [b] Tested as the HCl salt. [c] Mp, 276–285 °C dec. [d] Mp of base, 277.5–281 °C. [e] Mp of HCl salt, 230–233 °C. [f] Mp of HCl salt, 233–235 °C. [g] Tested as the sodium salt. [h] Mp of base, 107–108 °C. [i] Mp, 155–156.5 °C. [j] Mp, 241–242 °C dec. [k] Mp, 181–182.5 °C.

4,6-diamino-*s*-triazines, the most effective substituents were the 2-thienyl and 2-furyl groups, but when the furyl group was substituted, saturated, or separated by one or two carbon atoms from the triazine ring, the larvicidal activity decreased. Substitutions on one or both of the amino groups also led to decreased activity. Less effective substituents on the s-triazine ring were Cl_3C, i-C_3H_7, and 2-pyridyl groups. In general, the mosquito was less susceptible than the housefly to the larvicidal effects of this series, but the most active compounds in *M. domestica* (A13-22641; AI3-60103) were also active in *A. aegypti*. In *T. confusum*, only AI3-61080 and AI3-60138 were active at the highest concentration; the same compounds were ineffective in *A. aegypti* and moderately effective in *M. domestica*. None of the compounds, except AI3-22641 at the highest concentration, were effective larvicides in *P. interpunctella*.

In the series of triamino-s-triazines (Table I), the susceptibility of the two dipterous species was again the highest. If the activity of the previously reported larvicide AI3-70670 (Herzog and Brechbuehler, 1976; Miller et al., 1977; Christensen and Knapp, 1976) is considered as a model, AI3-22641, AI3-60103, AI3-60008, AI3-51014, and AI3-60352 surpass its activity in *M. domestica* and AI3-51014 equals its activity in *A. aegypti*. Two of the most active triamino-s-triazines (AI3-60008; AI3-51014) are structurally similar to the most active diamino-s-triazines (AI3-22641; AI3-60103) by the presence of two free amino groups. Although AI3-70670 and AI3-60352 do not have free amino groups, it is conceivable that they could be dealkylated in the insect to more active compounds (Chang et al., 1968). There is a general similarity between the larvicidal and chemosterilant activities of amino-s-triazines in *M. domestica*. The compounds effective as sterilants in females, but ineffective in males, have either two free amino groups (Borkovec et al., 1972) or single substituents on the amino groups (LaBrecque et al., 1968); all the more effective larvicides in Table I belong to this group. On the other hand, compounds containing dimethylamino groups, which are necessary for sterilizing males, appear ineffective as larvicides. Because the detailed physiological effects of amino-s-triazines in insects are not known, further studies are required to determine whether the sterilizing and larvicidal activities of these compounds have a common basis.

Like the diamino-s-triazines, the triamino-s-triazines had low and erratic activity in *T. confusum*: AI3-51146, AI3-61205, and AI3-70670 were larvicidal only at the highest concentration. None was active in *P. interpunctella*.

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Metabolism of *cis*- and *trans*-Chlordane by a Soil Microorganism

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Chlordane is an environmentally persistent soil insecticde, particularly useful in the protection of wooden structures from termite damage. A slow change was found to occur in the composition of soil residues of technical chlordane, suggestive of chemical or biological transformation of certain components. An actinomycete (*Nocardiopsis* sp.) isolated from soil was capable of extensively degrading chlordane in pure culture. Growing broth cultures of *Nocardiopsis* metabolized pure *cis*- or *trans*-chlordane to at least eight solvent-soluble substances including dichlorochlordene, oxychlordane, heptachlor, heptachlor *endo*-epoxide, chlordene chlorohydrin, and 3-hydroxy-*trans*-chlordane. Identifications were based on gas chromatographic or mass spectroscopic analysis. Oxychlordane was metabolically inert, and accumulated in the mycelium as a terminal residue. Patterns of metabolic activity in microorganisms were compared to the residue patterns in chlordane-treated soil.

Chlordane is an environmentally persistent, all-purpose soil insecticide which has been used extensively in this country since about 1950. The agricultural uses of chlordane have been restricted in recent years because of a suspicion that this insecticide may be an environmental carcinogen (Environment Protection Agency, 1976; Epstein, 1976).

Any analysis of the environmental fate and impact of chlordane has been hindered by the complexity of the technical mixture. The two major components, *cis*- and *trans*-chlordane, together constitute only about half of the total weight of the technical material. The remainder is

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