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SYSTEMIC INSECTICIDES

Heterocyclic Carbamates Having Systemic Insecticidal Action

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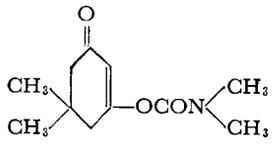
In the search for new insecticides certain heterocyclic dimethyl carbamates were found to have a high degree of systemic as well as a direct insecticidal action. The insecticidal action of 5,5-dimethyldihydroresorcinol dimethylcarbamate, 1-phenyl-3-methylpyrazolyl-(5)-dimethylcarbamate, and 1-isopropyl-3-methylpyrazolyl-(5)-dimethylcarbamate has been investigated. The last-named compound, also known as isolan, has a high degree of toxicity to insects and displays a strong systemic action against aphids. Field tests are under way to determine its practical value.

SYSTEMICS SYMPOSIUM

CERTAIN HETEROCYCLIC DIMETHYL CARBAMATES, like certain organic phosphates, have a high degree of systemic insecticidal action.

Dimetan

Gysin (*2*) reported that phenyl diethyl carbamate and the related 5,5-dimethyldihydroresorcinol diethyl carbamate had good insect-repellent action. However, when the closely related 5,5-dimethyldihydroresorcinol dimethyl carbamate was tested, there was practically no repellent action, but the compound was toxic to flies and some species of aphids. This compound is known under both the code number G-19258 and the common name dimetan. Wiesmann *et al.* (*4*) reported that it was effective against a number of species of aphids in concentrations of 0.02 to 0.04%. It was also translocated in certain plants and had a mild systemic insecticidal action.

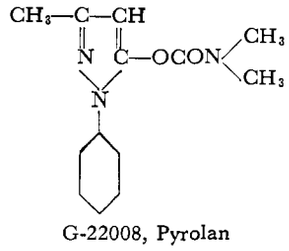


G-19258, Dimetan

None of numerous changes and substitutions in the carbamate or aliphatic portion of the above molecule enhanced insecticidal activity but rather tended to reduce it. For example, if the oxygen atoms of the carbamic acid radical were replaced by one or two sulfur atoms, the insecticidal activity was reduced. Other changes in the molecule resulted in the conclusion that the dimethyl urethanes were the most effective in the series.

Pyrolan

Attention was then directed to enolizable heterocyclic systems. The compound 1-phenyl-3-methylpyrazolyl-(5)-dimethyl carbamate, also known as G-22008 and pyrolan was found to be considerably more toxic to flies and other insects than dimetan, but it was also more toxic to warm-blooded animals. Wiesmann (*3*) reported on the insecticidal properties of pyrolan, and at the time considered it to have possibilities for combating flies in Europe that had developed resistance to DDT insecticides.



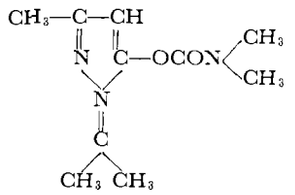
G-22008, Pyrolan

This compound was also found to have some systemic action against the green apple aphid (*Aphis pomi*). However, substitutions in the amine radical of the urethane group, additions to the phenyl group, substitutions for the hydrogen in the 4- position of the pyrazolone nucleus, or the replacement of the methyl group in the 3- position resulted in loss of insecticidal activity to a greater or lesser degree.

Isolan

It was surprising therefore to find that replacement of the phenyl nucleus with hydrogen or alkyl radicals resulted in some extremely effective insecticidal compounds. Toxicity to warm-blooded animals was also increased. Compounds of this group had a high degree of contact insecticidal action, but a rather short residual effect. They exhibited strong systemic action, however, with resulting longer residual effect as determined by applications to trunks of trees or stems of plants. The compound 1-isopropyl-3-methylpyrazolyl-(5)-dimethylcarbamate, also known by the code number G-23611 and the common name

isolan, has a very rapid toxic action to insects and a very marked systemic activity. It has been widely tested in Europe and the United States.



G-23611, Isolan

Extensive laboratory and field tests indicate that this compound is rather specific in its toxic action to aphids and certain other species of sucking insects. Its high degree of selectivity results in the advantage that it does not kill the beneficial parasites and predators by either contact or systemic action.

Table I shows the results of laboratory tests in which the action of isolan was compared with dimetan and pyrolan against five species of insects and two-spotted mites. The oral toxicity to mice for these three compounds is also indicated. It is apparent that isolan is considerably more effective against most of the species and that none of the three compounds is particularly toxic to two-spotted mites or southern army worms.

Although dimetan and pyrolan show some insecticidal action against green apple aphids, isolan has a much more pronounced action both in direct spray applications and in systemic action.

Systemic activity of isolan is easily demonstrated. In their laboratory, the authors submerged the roots of Windsor broad beans in aqueous solutions of isolan and then sealed the top of the jar around the stems of the plants with paraffin to prevent any fumigation effect. Pea aphids feeding on plants whose roots were submerged in solutions of isolan in concentrations as low as 0.005% were all killed in a few hours.

Results of field tests against the rosy apple aphid in New Jersey in 1952 are shown in Table II. At the time of application, the leaves were tightly rolled and the aphids were well protected from the spray. Although the possibility of fumigant action cannot be entirely discounted, the results are strongly suggestive that the high degree of kill was due largely to translocation through the leaves.

Grob (*1*) reported that treatment of potato seed pieces with isolan before planting resulted in potato plants free from aphids for about 6 weeks. When solutions of isolan and of a systemic organic phosphate were applied with a paint brush to the trunks of apple trees at dosages of 5 to 25 mg. per sq. cm. of trunk cross section, he concluded that against the green apple aphid isolan acts faster and at lower concentrations and has a longer residual effect than the phosphate.

A petroleum jelly containing 10% isolan was applied in thin bands to the trunks of apple trees in the vicinity of Yakima, Wash. Green apple aphids and wooly apple aphids were killed in 2 to 5 days after treatment and the trees remained free of aphids for from 2 months to the entire season. Some bark injury was noted from the application, but it is believed that this was due to the petroleum jelly rather than to the isolan. Aphid infestations on a black locust tree and a birch tree were eradicated by similar applications, but aphids on a maple tree were not controlled.

Aphids on plums, pears, and cabbage have also been controlled and the plants have remained free of aphids for several weeks. In some tests promising results have been obtained against thrips, but in no cases have mites been controlled.

Isolan is being made available to experiment stations and research workers for field tests in 1953 and it is hoped that as a result of further work a better picture will be obtained as to its possible utility in insect-control programs. The disadvantages of the compound are that it is highly toxic to warmblooded animals, and it is not effective against most species of mites. The pattern of toxicity to animals is similar to that of most organic phosphates, in that it shows cholinesterase inhibition as the primary toxic action. The advantages of the compound are that it shows a long period of protection against aphids at very low dosages, and has no adverse effect in observations to date on parasites and predators.

Table I. Effectiveness of Three Urethanes against Several Organisms in Laboratory Tests

Organism	Dosage, Ounces/100 Gal.	Dimetan, %	Pyrolan, %	Isolan, %
Two-spotted mites (nymphs)	32	13	43	6
Southern army worm (1st instar larvae)	32	25	35	10
Pea aphid (wingless adults)	32	100	100	100
	8	49	80	100
	2	5	6	70
Mexican bean beetle (1st instar larvae)	32	100	...	100
	8	85	...	100
	2	5	...	95
	Mg./Sq. Foot			
Housefly adults	200	100		
	50	97	100	100
	10	24	81	98
American cockroach (4th instar)	200	100	100	100
	50	100	100	100
	10	15	85	95
		Mg./Kg. Body Weight		
White mice (oral LD_{50})		140	90	18

Table II. Action of Isolan and Lindane against Rosy Apple Aphids

	Dosage Ounces/100 Gal.	% Dead, 24 Hours
Isolan	1	89.5
	4	98.0
Lindane	4	8.0

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