Nematocidal Activities of Halogenoalkylcarboxylic Acid Esters

By Katsura MUNAKATA, Akio HARADA and Tsutomu NISHIZAWA*

Department of Agricultural Chemistry and Department of Agronomy,
Faculty of Agriculture, Nagoya University*

Received January 30, 1959

About 40 halogenoalkylcarboxylic acid esters were synthesized and their nematocidal activities were tested against the rice white tip nematode, *Aphelenoides besseyi*.

Allyl esters of halogenoacetic acids were found to inhibit completely the growth of nematode at the 8 p.p.m. level, and the most effective one was allyl bromoacetate inhibiting at the 2 p.p.m. level, while sodium N-methyldithiocarbamate, a commercial nematocide inhibited at the 16 p.p.m. level.

The relationship of variation of the acid and alcohol moieties of esters to the nematocidal activity was discussed.

The relationship of the chemical structure and the nematocidal activity is very obscure, and most of commercial nematocides are rather harmful for plants.

For the study to find out new herbicidal chemicals, the authors had synthesized about 120 esters of halogenoalkylcarboxylic acids. As these compounds had shown various extents of herbicidal activities, the idea to test these compounds against nematodes occurred. In this paper a preliminary investigation to evaluate the activity of selected 37 esters against the rice white tip nematode, *Aphelenoides besseyi*, is reported.

Geltler et al.¹⁾ also reported about screening tests on 53 bromoacetic acid esters as nematocides of *Rhabditis* sp. and *Panagrellus* sp., and octyl, 4-bicyclohexyl, heptyl, decyl, 4-*sec*-butylcyclohexyl and hexyl esters were shown to be effective at the 2 p.p.m. level.

METHODS AND RESULTS

The esters were prepared by the reaction of alcohols or phenols with the appropriate acids using sulfuric acid or hydrogen chloride gas as catalyst, and in other case alcohols or phenols were reacted with appropriate acid halides in pyridine.

The vinyl esters were prepared by the reaction of acids and acetylene gas according to Wileys method²⁾.

The chemical and physical properties of these compound will be reported separately with other compounds of this group.

All compounds to be tested were formulated in an aqueous preparations, and those insoluble in water were suitably dispersed or emulsified.

Furthermore, several nonhalogenocarboxylic acid esters, halogenoacids, alcohols, phenols and a commercial nematocide, sodium N-methyldithiocarbamate (Vapum), were also tested for comparison.

The evaluation of compounds against the nematode was carried as follows³⁾.

One hundred rice white tip nematodes cultivated on artificial medium⁴⁾ were poured with 3 ml of a definite concentration of the liquid preparations of esters, and kept at 27°C for 24 hours, and the lethal percentage was measured. The test was triplicated.

The results of evaluations are shown in Table I, and the figures in Table are the lethal percentage, 100 showing complete kill of the nematode and zero showing complete lack of nematocidal activity.

DISCUSSIONS

From the result of test shown in the Table I, several facts were evident.

2) R.H. Wiley, *Org. Synth.*, **28**, 94 (1948).

* This report was presented at the Meeting of the Agricultural Chemical Society of Japan at Kyoto University, May, 1958.

1) S. L. Gertler, J. Feldmesser and R. V. Rebois, *J. Agri. Food Chem.*, **6**, 843 (1958).

3) K. Iyatomi, "Shin-Noyaku Kenkuhō," Nankōdō, Co., 1958 p. 465.

4) K. Iyatomi and T. Nishizawa, *Jap. Jour. Appl. Zool.*, **19**, 8, (1954).

TABLE I. NEMATOCIDAL ACTIVITIES OF HALOGENOALKYLCARBOXYLIC ACID ESTERS

Conc. in p.p.m.	256	128	64	32	16	8	4	2
Methyl chloroacetate	100	100	100	100	75	5	0	—
Ethyl "	100	100	100	98	43	3	0	—
Propyl "	100	100	100	100	95	30	0	—
Isopropyl "	100	100	50	13	3	0	0	—
Isobutyl "	100	100	90	0	0	0	0	—
Vinyl "	75	5	0	0	0	0	0	—
Allyl "	100	100	100	100	100	100	70	—
Furfuryl "	100	100	51	5	0	0	0	—
Tetrahydrofurfuryl "	100	90	22	5	0	0	0	—
Benzyl "	100	66	56	45	23	16	12	—
Phenyl "	100	100	100	52	—	—	—	—
<i>o</i> -Chlorophenyl "	30	15	3	0	0	0	0	—
<i>m</i> -Chlorophenyl "	100	100	100	100	52	30	—	—
<i>p</i> -Chlorophenyl "	100	100	0	0	0	0	0	0
2,4-Dichlorophenyl "	100	60	7	0	0	0	0	—
2,4,5-Trichlorophenyl "	100	100	100	100	78	30	0	—
2,4,6-Trichlorophenyl "	100	100	60	25	9	0	0	—
2-Methyl-4-chlorophenyl "	100	100	63	26	8	0	0	—
<i>p</i> -Bromophenyl "	100	100	100	100	95	85	65	—
<i>p</i> -Iodophenyl "	0	0	0	0	0	0	0	—
<i>p</i> -Nitrophenyl "	0	0	0	0	0	0	0	—
Butoxyethyl "	100	100	100	100	63	0	0	—
Allyl bromoacetate	100	100	100	100	100	100	100	99
Benzyl "	100	100	100	100	100	100	90	—
Butoxyethyl "	100	100	100	100	100	100	96	10
Allyl iodoacetate "	100	100	100	100	100	100	83	—
Benzyl "	100	100	100	100	100	100	96	—
Butoxyethyl "	100	100	100	100	100	100	69	—
Allyl 1,1-dichloro-propionate	100	100	98	61	34	0	0	—
Allyl 2,3-dichloro-isobutyrate	100	100	95	74	43	37	0	—
Benzyl "	100	83	72	68	50	14	0	—
Butoxyethyl "	100	99	80	47	43	24	0	—
Allyl trichloroacetate	100	55	8	0	0	0	0	—
Allyl acetate	100	100	100	100	90	26	0	—
Benzyl "	100	0	0	0	0	0	0	—
Butoxyethyl "	0	0	0	0	0	0	0	—
Sodium acetate	0	0	0	0	0	0	0	—
Sodium chloroacetate	16	0	0	0	0	0	0	—
Sodium bromoacetate	74	8	0	0	0	0	0	—
Sodium iodoacetate	100	12	0	0	0	0	0	—
Sodium methylthiocarbamate	100	100	100	100	100	44	0	—
Allyl alcohol	100	100	100	60	26	0	0	—
Benzyl alcohol	0	0	0	0	0	0	0	—
Butoxyethyl alcohol	0	0	0	0	0	0	0	—
Phenol	0	0	0	0	0	0	0	—
<i>o</i> -Chlorophenol	0	0	0	0	0	0	0	—
<i>m</i> -Chlorophenol	8	0	0	0	0	0	0	—
<i>p</i> -Chlorophenol	27	0	0	0	0	0	0	—
2,4-Dichlorophenol	70	0	0	0	0	0	0	—
2,4,5-Trichlorophenol	100	90	28	0	—	—	—	—
2,4,6-Trichlorophenol	7	5	3	0	—	—	—	—
Pentachlorophenol	10	4	0	0	—	—	—	—
<i>p</i> -Bromophenol	40	14	3	0	—	—	—	—
<i>p</i> -Iodophenol	0	0	0	0	—	—	—	—
<i>p</i> -Nitrophenol	17	0	0	0	—	—	—	—
<i>p</i> -Cresole	0	0	0	0	—	0	0	0

In the case of chloroacetates, the variation in alcohol moiety of esters gave some effects for nematocidal activities, and allyl moiety showed the strongest activity.

It is worthy to note that also allyl alcohol itself showed rather strong activity, while aryl moiety such as benzyl, phenyl or substituted phenyl alcohols did not show so much increase in activities.

About the acid moiety of esters, the strongest activity was found in the case of bromoacetic acid, and the extreme strong activity was showed also by allyl bromoacetate.

The activity did not increase with the length of the carboxylic acid chain as in the case of propionic acid or iso butyric acid. From the results on sodium acetate, allyl alcohol and allyl acetate, it is clear that allyl acetate showed the strongest activity.

Accordingly, the formation of ester may contribute to the strengthening of activity.

The esters containing bromine atom which showed strong activities included *p*-bromophenyl chloroacetate, and allyl, benzyl or butoxyethyl bromoacetate.

The phenols did not show so strong nematocidal activities in spite of their strong activities against microorganisms.

Further experiments are being conducted about nematocidal activities of related compounds, and about the toxicity for other nematodes.

Acknowledgment The authors wish to thank Prof. Y. Sumiki of the University of Tokyo for his advice and encouragement, Prof. T. Tamura and Prof. K. Iyatomi for their helpful discussions, and Miss N. Ôkubo for her technical assistance in nematocide screening tests.