Novel Insecticidal Chrysanthemic Esters¹⁾

Sir:

In the previous papers,^{2~4)} the present authors reported the synthesis and bioassay of various, non-ketonic esters of chrysanthemic acid and pointed out that the allyl substituent in the alcoholic moiety plays a very important role in the insecticidal activity of chrysanthemates. We wish, at this time, to report some preliminary results of synthesis and bioassay of novel chrysanthemic esters containing propargyl group as an integral part of alcoholic components.

In place of the allyl group of allethrin, benathrin and japothrin in earlier works, propargyl group was introduced by the known methods of synthesis to cyclopentenolone, and benzyl and furfuryl alcohols to give 2-propargyl-4-hydroxy-3-methylcyclopentene-1-one, *p*-propargylbenzyl alcohol and 5-propargylfurfuryl alcohol, respectively. These alcohols

the resulting chrysanthemates fully substantiated the ester-structures proposed.

As can be seen from the data in Table II, the chrysanthemates I, II and propargyl-rethrin were highly toxic against common house fly and their activities were far superior than those of the allyl analogs previously reported. It is worthy of note that, of these novel chrysanthemates, the compound II, 5-propargylfurfuryl chrysanthemate,⁵⁾ is 11.6 to 29.0 times as toxic in knock-down as allethrin and exhibits low toxicity to mammals, the

TABLE I. BOILING POINTS AND REFRACTIVE INDICES OF THE CHRYSANTHEMATES

	Steric configuration of acid moiety	bp °C(mmHg)	n_D^{25}
I	<i>dl-cis, trans</i>	155~158 (0.30)	1.5309
II-1	<i>dl-cis, trans</i>	120~122 (0.20)	1.5048
II-2	<i>d-trans</i> (natural)	119~121 (0.18)	1.5051

were esterified by the standard method with isomeric chrysanthemoyl chlorides in the presence of organic bases. The IR spectra of

acute oral LD₅₀ being above 3.3 g/kg to mouse.

In contrast to the present finding with our sample of propargyl-rethrin, Gersdorff *et al.*⁶⁾ reported that propargyl-rethrin was 64% as

1) All rights reserved: The patent applications for these and related compounds have been filed.

2) Y. Katsuda and H. Ogami, *Botyu-Kagaku*, **31**, 30 (1966).

3) Y. Katsuda, H. Ogami, T. Kunishige and E. Togashi, *ibid.*, **31**, 82 (1966).

4) Y. Katsuda, H. Ogami, T. Kunishige and Y. Sugii, *Agr. Biol. Chem.*, **31**, 259 (1967).

5) For convenient sake, 5-propargylfurfuryl chrysanthemate is proposed to be designated as "Prothrin."

6) W. A. Gersdorff and P. G. Piquett, *J. Econ. Entomol.*, **54**, 1250 (1961).

TABLE II. EFFECTIVENESS OF THE CHRYSANTHEMATES TO ADULT COMMON HOUSE FLY, (*Musca domestica vicina* Macq.) IN COMPARISON WITH THOSE OF ALLETHRIN

(Applied Topically in Acetone Solution)

Material	Knock-down after 30 min		Mortality after 24 hr	
	KD 50	Relative effectiveness	LD 50	Relative effectiveness
I	0.13 γ /fly	4.46	0.10 γ /fly	12.80
II-1	0.05	11.60	0.15	8.53
II-2	0.03	19.33	0.06	21.33
Allethrin*	0.58	1.00	1.28	1.00
<i>d-trans</i> -Allethrin**	0.18	3.22	0.67	1.91
Propargyl-rethrin***	0.51	1.14	0.99	1.24

* *dl*-Allethronyl *dl-cis*, *trans*-chrysanthemate.** *dl*-Allethronyl *d-trans*-chrysanthemate.*** *dl*-2-Propargyl-4-hydroxy-3-methyl-cyclopentene-1-one ester of *dl-cis*, *trans*-chrysanthemic acid.

toxic as allethrin to house fly by the turntable method. This discrepancy in activity between the present and the Gersdorff's data may be attributed to the difference in purity of the samples and/or the method of bioassay applied. Experimental details will be published elsewhere in the near future.

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