Hibalactone (Savinin) as a Synergist for Pyrethrins and Allethrin

Sir:

In the previous paper¹⁾, the author made a report on the synergistic effect of hinokinin (I) on pyrethrins, and pointed out the necessity of the presence of a γ -lactone ring as a central nucleus for the cause of synergism.

It is an interesting problem to investigate that to what degree the pyrethrins and allethrin are activated by hibalactone (savinin) (II) which has recently been isolated independently by Masumura²⁾ from "chyabohiba", *Chamaecyparis obtusa* Sieb. et Zucc. in Japan, and by Schrecker et al.³⁾ from "sabina",

Juniperus sabina L. in America, because this compound is identical with hinokinin, both in its structure of the central nucleus and in its steric configuration as shown in (I) and (II).

The author has attempted to clarify the synergistic effect of hibalactone on pyrethrins and allethrin, and made investigations on the knock-down and lethal effectiveness of pyre-

throids-hibalactone emulsions against mosquito larvae, *Culex pipiens* var. *pallens* Coq., by means of the petri-dish method which was previously described by the author^{4,5)}, and also, on the knock-down effectiveness of pyrethroids-hibalactone dusts against house fly, *Musca domestica vicina* Macq., by means of the settling dust apparatus method of Nagasawa⁶⁾, comparing its synergistic activity with those of hinokinin and piperonyl butoxide.

Pyrethroid-synergist ratio in synergized emulsions and dusts were 1:8, such as 0.025:0.200 (ppm) in pyrethrins emulsions or 0.05:0.40 (%) in allethrin dusts. The degree of synergism (concentration of pyrethroid in pyrethroid only formulation divided by the concentration of pyrethroid in pyrethroid plus synergist formulation; median knock-down time of pyrethroid only divided by the median knock-down time of pyrethroid plus synergist) of the three compounds calculated from the median lethal concentration or median knock-down time by the probit method developed by Bliss, are given in Table I.

Hibalactone acts as a synergist for pyrethrins similarly to hinokinin, and the synergistic activity of the former is more effective than that of the latter in the knock-down test of dusts against house fly, but the former is, on the contrary, less effective than the latter in knock-down and lethal tests of emulsions against mosquito larvae.

Both hibalactone and hinokinin act effectively as a synergist for allethrin, and synergistic activity of the former is more effective than those of the latter and piperonyl butoxide against mosquito larvae, but the former is, on the contrary, less effective than the latter and

1) H. Matsubara, *Botyu Kagaku*, **15**, 21 (1950); **17**, 143 (1952).

2) M. Masumura, *J. Chem. Soc. Japan*, **76**, 423 (1955).

3) A.W. Schrecker and J.L. Hartwell, *J. Am. Chem. Soc.*, **76**, 4896 (1954).

4) H. Matsubara, *Botyu Kagaku*, **18**, 10 (1953).

5) H. Matsubara, *Res. Bull. Faculty of Agr. Gifu Univ.*, **6**, 124 (1956).

6) S. Nagasawa and T. Takano, *Botyu Kagaku*, **15**, 46 (1950).

TABLE I
THE DEGREE OF SYNERGISM OF HIBALACTONE, HINOKININ AND PIPERONYL BUTOXIDE
FOR PYRETHRINS AND ALLETHRIN, DETERMINED BY BIOASSAY WITH MOSQUITO LARVAE AND HOUSE FLY

Active ingredient	Synergist	Determined by knock-down effectiveness against				Determined by lethal effectiveness against	
		Mosquito larvae		House fly		Mosquito larvae	
		Degrees of synergism	Relative effectiveness	Degrees of synergism	Relative effectiveness	Degrees of synergism	Relative effectiveness
Pyrethrins	Hiballactone	1.70	1.00	1.54	1.00	1.49	1.00
	Hinokinin	1.92	1.13	1.09	0.71	1.62	1.08
	Piperonyl Butoxide	2.92	1.72	6.43	4.17	—	—
Allethrin	Hiballactone	3.50	1.00	3.21	1.00	2.46 ; 2.36	1.00 ; 1.00
	Hinokinin	3.21	0.92	3.69	1.15	1.88 ; —	0.76 ; —
	Piperonyl Butoxide	2.43	0.69	5.99	1.86	— ; 1.89	— ; 0.80

piperonyl butoxide against house fly.

From the bioassay of the synergized pyrethroids emulsions and dusts with hiballactone using two insects, it has been observed that the combination of allethrin with hiballactone; shows a higher order of synergism than the similar combination of pyrethrins with hiballactone furthermore, its synergistic activity for allethrin is 1.65~2.08 times as effective as that for pyrethrins.

By many investigators, it was found that the combinations of allethrin with synergists were in general, less effective than the similar combinations of pyrethrins, but the results shown in the present investigation did not agree with this finding.

The discovery of such unique synergistic

activity as exhibited by hiballactone provide us the hope of the research of some more powerful allethrin synergists which possess the methylenedioxyphenyl group. Other synthesized synergists with relation to hiballactone are now being investigated. A detailed observation on the relations between their chemical structures and synergistic activities for the pyrethroids will be described elsewhere.

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