

# Activity of Pyridyl and Phenyl Ether Analogues of Juvenile Hormone Against Coleoptera and Lepidoptera in Stored Grain<sup>1</sup>

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## ABSTRACT

Five pyridyl or phenyl ether analogues of juvenile hormone were each mixed separately with whole wheat or ground wheat medium and tested for activity against stored grain insects. The chemical (E)-5-[5-(3,3-dimethyl-2-oxiranyl)-3-methyl-2-pentenyl]oxy-2-ethylpyridine was effective at 100 ppm in preventing larval development from eggs of *Tribolium confusum* Jacquelin duVal, *T. castaneum* (Herbst), and *Sitophilus oryzae* (L.). The compound also suppressed adult progeny of *Rhyzopertha dominica* (F.), *Oryzaephilus surinamensis* (L.), *Plodia*

*interpunctella* (Hübner), *Cadra cautella* (Walker), and *Sitotroga cerealella* (Olivier) at doses of 10-250 ppm. Other compounds, (E)-5-[3,7-dimethyl-2,6-octadienyl]oxy-2-ethylpyridine, (E)-5-[3,7-dimethyl-2,6-octadienyl]oxy-2-methylpyridine, and 3-[5-(4-ethylphenoxy)-3-methyl-3-pentenyl]-2,2-dimethyloxirane, were less effective except in the case of *T. confusum* where a mixture of 2-ethyl-3-[3-ethyl-5-(4-ethylphenoxy)-pentyl]-2-methyloxirane and 2-ethyl-3-[5-(4-ethylphenoxy)-2,3-dimethyl-pentyl]-2-methyloxirane at 1 ppm was efficacious against adult progeny.

Many juvenile hormone mimics have a monoterpene or sesquiterpene moiety or a homologation of these moieties as part of their structure (Staal 1975). Some of the most active insect growth regulators (IGR) also contain an aromatic group, usually a benzene or pyridine ring in an ether linkage (Slama et al. 1974, Solli et al. 1976, Kramer 1976). We evaluated the activity of 5 pyridyl or phenyl ether analogues of juvenile hormone applied to wheat against several species of stored grain insects, and the results are reported here.

**MATERIALS AND METHODS.**—All insects were obtained from cultures that were maintained at the U.S. Grain Marketing Research Center and had no prior history of exposure to insecticides. 'Chanute' wheat that was used in the tests was obtained from a commercial source. Kernels were cleaned and tempered to a moisture of 12.5% as determined by a Motomco® moisture meter. The whole wheat or moth medium (W. H. McGaughey, unpublished) was treated with 1-250 ppm test material and subsequently infested with 50 lepidopteran eggs or adult coleopterans as described by McGregor and Kramer (1975, 1976).

The chemicals (Fig. 1) evaluated were: I.—(E)-5-[3,3-dimethyl-2-oxiranyl]-3-methyl-2-pentenyl-2-ethylpyridine (93%, AI3-70644, Stauffer Chem. Co.); II.—(E)-5-[3,7-dimethyl-2,6-octadienyl]oxy-2-ethylpyridine (91.5%, AI3-70643, Stauffer); III.—(E)-5-[3,7-dimethyl-2,6-octadienyl]oxy-2-methylpyridine (95.8%, AI3-70536, Stauffer); IV.—A mixture of 2-ethyl-3-[3-ethyl-5-(4-ethylphenoxy)pentyl]methyloxirane (75%) and 2-ethyl-3-[5-(4-ethylphenoxy)-2,3-dimethylpentyl]-2-methyloxirane (25%, AI3-70683, HLR Sciences, Inc., Hangartner et al. 1976); and V.—3-[5-(4-ethylphenoxy)-3-methyl-3-pentenyl]-2,2-dimethyloxirane (50% EC, AI3-70221, Stauffer).

All experiments were conducted at 27° and 60°

RH, and data are presented as the avg number of insects found in 4 replicate samples after 9 wk (minus the number of parent insects when appropriate). In cases where the numbers of progeny were reduced significantly, the tests were examined again after 6 mo.

**RESULTS AND DISCUSSION.**—Table 1 shows the biological effects on stored grain beetles of the aromatic juvenile hormone mimics mixed homogeneously with wheat. None of the compounds exhibited any acute toxic or knockdown effects, even after adult insects remained in treated grain for 3 wk. Also, when these insects were subsequently transferred to untreated grain for egg deposition, there was no latent effect on their progeny. The progeny derived from eggs laid in treated grain, however, were adversely affected (Table 1).

Compound IV was the most active insect growth regulator against progeny of confused flour beetle, *Tribolium confusum* Jacquelin duVal, and arrested adult development with 1 ppm. But the other 4 compounds were not as effective at less than 10 ppm. When 3rd and 4th instars were added to grain treated with compound I at 10 ppm, these insects completed larval development, but they subsequently died during pupation. Compound I acted similarly against the red flour beetle, *Tribolium castaneum* (Herbst), but had only 1/10th as much effect on the lesser grain borer, *Rhyzopertha dominica* (F.), and sawtoothed grain beetle, *Oryzaephilus surinamensis* (L.). Progeny of the rice weevil *Sitophilus oryzae* (L.), was the most difficult to suppress in whole grain. Large numbers developed at 100 ppm I, even when piperonyl butoxide, at 600 ppm also was added. Compounds II, IV, and V were even less effective.

In contrast, when adult weevils were placed in wheat that had been treated, ground, and formed into homogeneous pellets (McGregor and Kramer 1976), their progeny was completely suppressed. Apparently, for the JH mimics to be effective against the weevil, they have to penetrate into the kernel interior. In support of this conclusion, Rowlands (1976) reported that similar compounds were dis-

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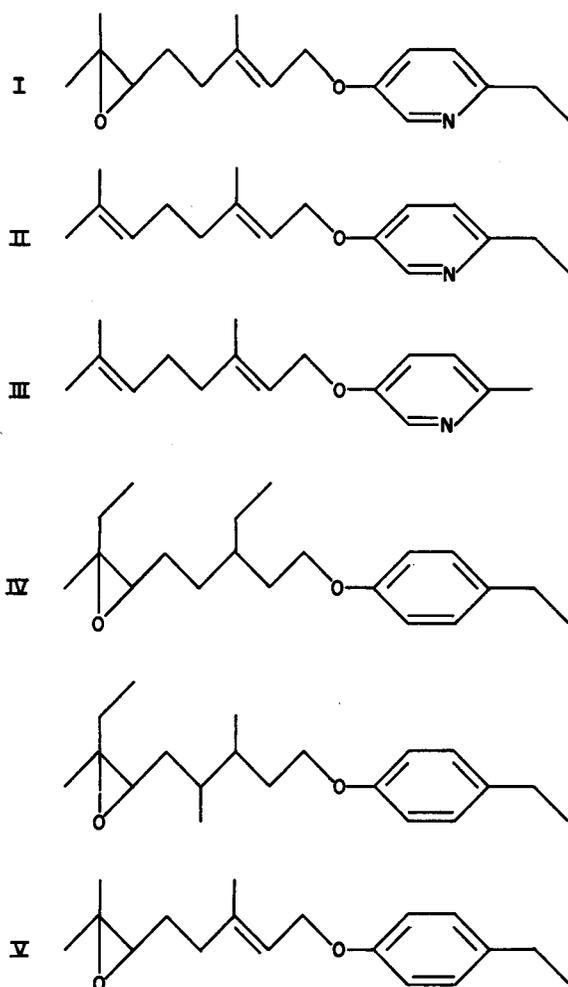


FIG. 1.—Pyridyl and phenyl ether analogues of juvenile hormone. See Materials and Methods for nomenclature.

tributed in the aleurone and germ layers but hardly at all in the endosperm where the weevil is found. Thus, obligatory in-kernel feeding insects that have a high dietary starch requirement may not contact sufficient amounts of these materials to be effective in whole grain. Visual inspection and x-ray analysis (Milner et al. 1950) revealed that no larvae developed and thus, virtually no grain damage occurred in samples treated with 100 ppm of compound I and infested with the confused flour beetle, red flour beetle, and rice weevil. We also have found that compound I kills eggs of these species at 100 ppm. Adult development was inhibited at 10 ppm, but larvae were present and they continued to consume grain. These insects eventually died during pupation as larval-pupal intermediates.

Table 2 shows the effect of the insect growth regulators on stored-grain lepidopterans. Eggs of the Indian meal moth, *Plodia interpunctella* (Hübner), almond moth, *Cadra cautella* (Walker), and Angoumois grain moth, *Sitotroga cerealella* (Olivier), were

Table 1.—Activity of JH mimics against coleopterans exposed from eggs in wheat.

Species	Compound no.	No. F <sub>1</sub> insects in untreated sample	% reduction of adult F <sub>1</sub> progeny at doses (ppm) of		
			1	10	100*
1. Confused flour beetle	I	266	90	100	100 L
Confused flour beetle	II	496	24	100	100
Confused flour beetle	III	195	14	100	100
Confused flour beetle	IV	228	100	100	
Confused flour beetle	V	190		100	
2. Red flour beetle	I	437	56	100	100 L
3. Lesser grain borer	I	1552	7	56	99
4. Sawtoothed grain beetle	I	945	4	0	100
5. Rice weevil	I	1588	3	21	50
Rice weevil <sup>b</sup>	I	1492	19	26	46
Rice weevil <sup>c</sup>	I	957		0	100 L
Rice weevil	II	1028	12	0	0
Rice weevil	IV	1141		5	4
Rice weevil	V	1875		5	

\* L denotes little or no larval development occurred.

<sup>b</sup> Piperonyl butoxide present at 600 ppm.

<sup>c</sup> Test performed using ground wheat pellets.

placed in moth medium or whole grain. Compounds I and V were the most effective inhibitors of Indian meal moth development at 1 and 10 ppm, respectively, but larvae developed in all experiments and caused damage. At higher doses, supernumerary instars were observed, but these insects died during pupation. Compounds II, III, and IV were less active than compound I.

The larval life of the Indian meal moth was lengthened from 25 days in control diet to 52 days in diet treated with 100 ppm of compound I. The almond moth and the Angoumois grain moth were less susceptible to compound I and required 100 and 250 ppm, respectively, for suppression of adult popula-

Table 2.—Activity of JH mimics against lepidopteran eggs in wheat or wheat based medium.

Species	Compound no.	No. moths found in untreated sample <sup>a</sup>	% reduction of adult insects at doses (ppm) of			
			1	10	100	250
1. Indian meal moth	I	42	99	100	100	
Indian meal moth	II	45	0	20	56	
Indian meal moth	III	41	5	0	20	
Indian meal moth	IV	40	30	98	100	
Indian meal moth	V	44		100		
2. Almond moth	I	32	3	0	100	100
Almond moth	IV	34	0	100		
3. Angoumois grain moth	I	31	0	26	45	100

<sup>a</sup> Fifty eggs added to 100 g of diet.

tion. No ovicidal effects were observed in any of the moth species. X-ray analysis revealed that the internally feeding Angoumois grain moth larvae were fully developed and that they died during the larval-pupal ecdysis. Hoppe (1976) found that 10 ppm of compound IV suppressed adult populations of *P. interpunctella*, *Ephestia kuehniella* (Zeller), *Rhyzopertha dominica*, and *T. castaneum* in wheat for at least 1 yr. Paulos et al. (1971) and Williams and Amos (1974) prevented adult development of *T. confusum* and *T. castaneum* in wheat flour at 5 ppm of compound V. The insect growth regulators examined here were active on wheat against stored-grain insects other than the rice weevil at doses of 1-250 ppm. The order of activity for the ether analogues of JH was as follows: confused flour beetle—IV > I > II, III; rice weevil—I > IV > II, V; and Indian meal moth—I > IV > II > III. The optimal structure for activity against *S. oryzae* and *P. interpunctella* was the pyridyl epoxy analogue I with the ethyl substituent in the *p*-position to the ether bond. For *T. confusum*, the phenyl epoxy derivative IV was the most active.

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#### REFERENCES CITED

- Hangartner, W. W., M. Suchy, H. Wipf, and R. C. Zurfueh. 1976. Synthesis and laboratory and field evaluation of a new, highly active and stable insect growth regulator. *J. Agric. Food Chem.* 24: 169-75.
- Hoppe, T. 1976. Microplot trial with an epoxyphenyl-ether (insect growth regulator) against several pests of stored wheat grain. *J. Stored Prod. Res.* 12: 205-9.
- Kramer, K. J. 1976. Selective biochemical approaches to insect control. P. 226-43. In R. B. Milles, L. A. Bulla, Jr., and S. Utida [eds.]. *Proc. U.S.-Jpn. Joint Semin. Stor. Prod. Insects* January 1976, Manhattan, Kans. 342 pp.
- McGregor, H. E., and K. J. Kramer. 1975. Activity of insect growth regulators, hydroprene and methoprene, on wheat and corn against several stored-grain insects. *J. Econ. Entomol.* 68: 668-70.
1976. Activity of Dimilin (TH-6040) against Coleoptera in stored wheat and corn. *Ibid.* 69: 479-80.
- Milner, M., M. R. Lee, and R. Katz. 1950. Application of x-ray technique to the detection of internal insect infestation of grain. *Ibid.* 43: 933-5.
- Paulos, F. M., J. J. Menn, P. E. Letchworth, and J. B. Miaullis. 1971. Synthetic mimics of insect juvenile hormone. *Nature* 232: 486-7.
- Rowlands, D. G. 1976. The uptake and metabolism by stored wheat grains of an insect juvenile hormone and two insect hormone mimics. *J. Stored Prod. Res.* 12: 35-41.
- Slama, K., M. Romanuk, and F. Sorm. 1974. *Insect Hormones and Bioanalogues*. Springer-Verlag, New York. pp. 90-302.
- Solli, H., H. B. Madsen, P. C. Holst, and P. D. Klemmensen. 1976. Pyridyl terpenoid ethers with high juvenile hormone activity. *Pestic. Sci.* 7: 503-11.
- Staal, G. B. 1975. Insect growth regulators with juvenile hormone activity. *Annu. Rev. Entomol.* 20: 417-60.
- Williams, P., and T. G. Amos. 1974. Some effects of synthetic juvenile insect hormones and hormone analogues on *Tribolium castaneum* (Herbst). *Aust. J. Zool.* 22: 147-153.