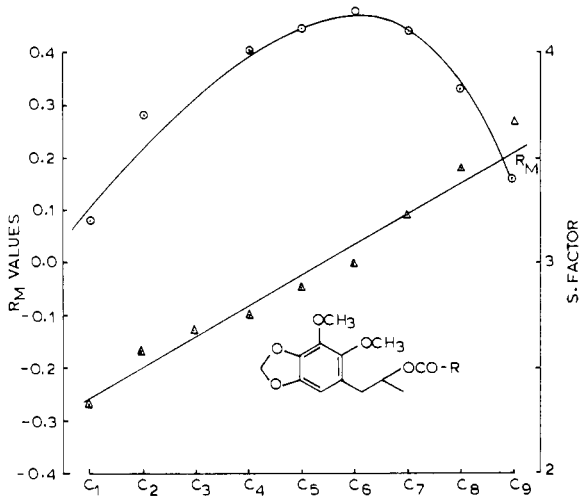

Figure 2. Relationship among the length of acyl moiety of esters from propan-2-ol (III), R_M values, and factors of synergism. (Δ–Δ) R_M value; (O–O) factor of synergism.

mercuration with sodium borohydride. Both these alcohols as well as the esters derived from them showed no significant toxicity up to 1% concentration against the test insect *T. castaneum*.

In studies on synergistic activity, all of them showed different degrees of synergism. The factors of synergism ranged from 1.5 to 4.2 as compared to 2.0 for the standard reference synergist, piperonyl butoxide. A perusal of the data given in Table I shows that the esters XV–XXV derived from propan-2-ol (III) are more active than the corresponding esters IV–XIV, derived from propan-1-ol (II). Further, a comparison of synergistic activity of these compounds and their lipophilicity shows that the latter alone is not the criterion for better synergism. Thus in both the homologous series in compounds IV to XII (Figure 1) and XV to XXIII (Figure 2), the synergistic factor increases with increasing lipophilicity only up to a maximum of six or seven carbon atoms in the ester chain. Higher molecular weight esters in both the series, although more lipophilic, are less potent synergists. Similar results have been observed earlier in a series of substituted cinnamic esters (Vaidyanathaswami et al., 1977) and alkoxy derivatives from dillapiole (Tomar et al., 1979a), but these showed a maximum of synergistic activity with only two or three carbon atoms in the side chain.

As seen from Table I, other esters like benzoates and chloroacetates of these alcohols show poor synergism.

Supplementary Material Available: A listing of data from IR and NMR spectra and elemental analysis of esters IV–XXV (8 pages). Ordering information is given on any current masthead page.

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Determination of (*Z*)-9-Tetradecen-1-ol Formate, a *Heliothis* spp. Mating Disruptant, in Air by Electron-Capture Gas Chromatography following Photolytic Cleanup

Joseph H. Caro,* Horatio P. Freeman, and Barbara A. Bierl-Leonhardt

A sensitive method for determination of (*Z*)-9-tetradecen-1-ol formate (*Z*-9-tdf) in air has been developed. The compound is trapped on a bed of Chromosorb 102, eluted from the bed with hexane, and reacted with bromine to form the *vic*-dibromide. The latter is subjected to two clean-up procedures—silica gel microcolumn chromatography, followed by thin-film ultraviolet light irradiation—and is then determined by electron-capture gas chromatography. Recovery through the method after correction for a consistent 40% loss of dibromide during UV cleanup is about 89%, and the quantitative limit in unpolluted air is less than 3 ng/m^3. Identity of the *Z*-9-tdf-dibromide may be confirmed at levels of 40 ng/m^3 and above by saponification and reaction with acetyl chloride to form the corresponding acetate.

The principle of insect control by air permeation with synthetic sex attractants or mating disruptants is now firmly established. Although not a component of the natural sex attractant emitted by the female moths, (*Z*)-9-tetradecen-1-ol formate (*Z*-9-tdf), when vaporized into the atmosphere, effectively disrupts mating of several species of Lepidoptera, principally in the *Heliothis* genus—*H. zea*, the corn earworm or cotton bollworm, and *H. virescens*, the tobacco budworm (Mitchell et al., 1975; Gothilf et al., 1978). For emission into the air in the field,

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Z-9-tdf is normally dispensed in a controlled-release formulation, such as microcapsules, plastic laminates, or hollow fibers. Since the important characteristic for success with the air permeation technique is the maintenance of some critical concentration of the disruptive chemical in the air per given area of land (McLaughlin et al., 1975), an analytical method is needed to quantify this level and to show how air concentrations vary not only with the type of formulation, but also with time and with location beneath the crop canopy. Biologically effective application rates of disruptive chemicals like Z-9-tdf are typically low, ca. 50 g/ha or less, so high sensitivity is a requisite if an analytical method is to be used successfully in air permeation work.

A method is presented here that accurately and sensitively measures air concentrations of Z-9-tdf and is useful even when the air being sampled is contaminated with emissions that would normally cause severe difficulty in analysis. The key to the general utility of the method is the use of ultraviolet (UV) irradiation as a clean-up technique. The UV irradiation of either solutions or solids has been reported for both identification of pesticides (Banks and Bills, 1968; Glotfelty, 1972) and for extract cleanup (Caro, 1971; Leavitt et al., 1973).

Although applied here only to Z-9-tdf, the analytical approach may be applicable to determinations of a wide variety of alkenyl pheromones in the atmosphere.

EXPERIMENTAL SECTION

Adsorbent Selection. Because porous polymeric adsorbents are recognized as being especially well suited to the trapping of organic compounds from air (Butler and Burke, 1976), several of these materials were evaluated before Chromosorb 102 was selected as the medium of choice for Z-9-tdf analysis. Tests were made of Tenax; Porapak Q; heat-treated Porapak Q; the Amberlites XAD-2, XAD-4, and XAD-7; and Chromosorb 101 as well as Chromosorb 102. The criteria included cleanliness of blanks, sampling efficiency and capacity, ease of desorption of the trapped Z-9-tdf, and cost. Although none of the adsorbents gave unacceptable results, Chromosorb 102, which has been reported as being ideal for sampling pesticides in air (Thomas and Seiber, 1974), provided the best overall performance.

Air Sampling. The air sampler is a 65-mm length of 15.9-mm ($^5/_8$ in.) i.d. glass tubing fused at one end to a 25-mm length of 6.4-mm ($^1/_4$ in.) i.d. tubing. A plug of glass wool was placed in the throat of the sampler, which was then filled with a 30-mm-deep bed (2.0 g) of 60–80-mesh Chromosorb 102 porous polymeric adsorbent (Supelco, Inc., Bellefonte, PA) and topped with a second plug of glass wool to hold the adsorbent in place. The Chromosorb 102 was purified before use by Soxhlet extraction with 1:1 hexane–acetone for 16 h. The narrow end of the sampler was connected to a vacuum pump (Gast 4.0 cfm or equivalent) by rubber or Tygon tubing and air drawn through, at a rate of 1–2 m^3/h as measured with a rotameter, for the desired time interval. Total volume of air should not exceed 10 m^3. In field experiments with Z-9-tdf conducted by the authors (Caro et al., 1979) typical air flow rates were 20–25 L/min (1.2–1.5 m^3/h) and sampling time periods were 1–4 h.

Analytical Procedure. To elute the Z-9-tdf from the adsorbent, the air sampler was placed in a vertical position and 50 mL of hexane poured in, the eluate being caught in a Kuderna-Danish (K-D) apparatus (Kontes Glass Co, Vineland, NJ) fitted with a 500-mL flask and 10-mL receiver. The eluate was concentrated to ca. 10 mL on a steam bath, with a 3-ball Snyder column (Kontes Glass Co.) joined to the K-D apparatus. The concentrate was cooled to room temperature and transferrd quantitatively by Pasteur pipet to a 125-mL separatory funnel. To remove water-soluble contaminants, the concentrate was shaken 1 min with each of two 80-mL volumes of H_2O, and the aqueous phases were discarded.

The hexane was transferred quantitatively to a graduated 10-mL K-D receiver and concentrated to ca. 1 mL under a stream of purified N_2 or other inert gas. A 0.5-mL volume of Br_2 solution was added, and the reactants were mixed 15 s on a Vortex mixer. The Br_2 solution, 0.04 mL of Br_2 (4 drops from a Pasteur pipet) in 5 mL of CS_2, was prepared daily. The mixture, now containing the *vic*-dibromide of Z-9-tdf, was transferred to a 125-mL separatory funnel, 8 mL of hexane and 50 mL of H_2O were added, and the solution was shaken for 1 min. The aqueous phase was discarded and the hexane phase was transferred quantitatively to a graduated 10-mL K-D receiver and concentrated to 0.5 mL under a stream of inert gas.

For cleanup by column chromatography, a microcolumn was prepared in a Pasteur pipet by placing a small glass wool plug in the throat of the pipet, adding, with the aid of an electric vibrator, a 35-mm (0.4-g) layer of 70–150-mesh Woelm silica gel (ICN Pharmaceuticals, Cleveland OH) previously adjusted to activity grade IV with H_2O, and topping with a 5–7-mm layer of anhydrous Na_2SO_4. The microcolumn was prewet with hexane, the 0.5-mL sample extract was transferred quantitatively onto the column, 10 mL of hexane was eluted through the column, and the eluate was discarded. The addition of a 10-mL volume of liquid to the small column was facilitated by attaching a 10- to 12-mL glass chamber to the top of the column with a short length of rigid Teflon tubing. A graduated 4-mL K-D receiver was next placed to receive the eluate and the column was eluted with 2 mL of benzene.

For the next step, cleanup by UV irradiation, the benzene eluate was concentrated to ca. 0.2 mL under a stream of inert gas, and the concentrate was transferred quantitatively to a 25-mm diameter watch glass. The solution was allowed to evaporate to dryness and the watch glass was exposed to a germicidal UV lamp (254-nm radiation, 17 $\mu W/cm^2$ intensity at 1 m) at a distance of 10 cm for 30 min. The residue was washed off the watch glass into a K-D receiver with 2 mL of benzene.

For quantitation, an aliquot of the benzene solution was injected with a 10-μL syringe into a gas chromatograph. A Tracor Model 222 instrument fitted with a ^{63}Ni electron-capture detector was used. The column was glass, 180 cm × 2 mm i.d., packed with a mixture of 1.5% OV-17 and 1.95% OV-210 on 100–150-mesh Chromosorb WHP (Supelco, Inc., Bellefonte, PA). Column temperature was 205 °C and carrier gas (95:5, argon–methane) flow rate was 37 mL/min. Under these conditions, the retention time of Z-9-tdf-dibromide was 5.0 min.

Confirmation of Identity. The 2-mL benzene solution obtained after final cleanup was transferred to a 125-mL boiling flask, 5 mL of aqueous NaOH solution (4 mg/mL) was added, and the mixture was refluxed 30 min with magnetic stirring. The cooled mixture was transferred to a 125-mL separatory funnel, 5 mL of hexane was added, the solution was shaken for 1 min with each of two 50-mL volumes of H_2O, and the aqueous phases were discarded. The hexane layer was transferred to a K-D receiver and concentrated to ca. 1 mL under a stream of inert gas. Two drops pyridine and 2 drops acetyl chloride were added with a Pasteur pipet. The solution was stirred 15 s on a Vortex

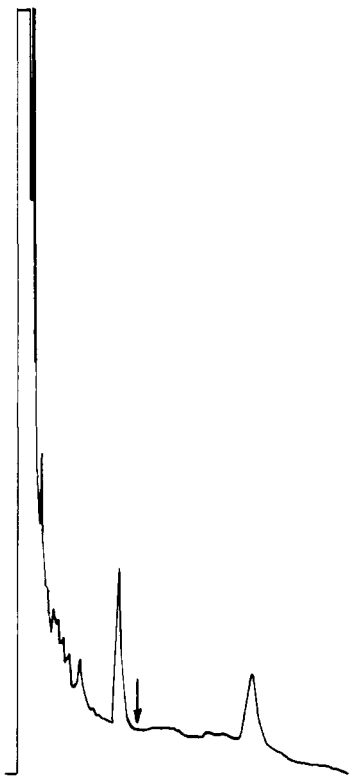

Figure 1. Reagent blank chromatogram (extract of Chromosorb 102 not exposed to air). Vertical arrow indicates retention time of Z-9-tdf-dibromide.

mixer, let stand 30 min at ca. 50 °C, and transferred to a 125-mL separatory funnel. Five milliliters of hexane was added and the mixture was shaken for 1 min with each of two 50-mL volumes of H_2O. The volume of the hexane layer was adjusted to give, on injection of a 2–8-μL aliquot into a gas chromatograph, a well-defined peak for the dibromide of (Z)-9-tetradecen-1-ol acetate. When the same GC conditions were used as in the Z-9-tdf determination above, retention time of the acetate analogue was 1.25 relative to that of the Z-9-tdf-dibromide.

RESULTS AND DISCUSSION

No breakthrough of Z-9-tdf through the 2-g bed of Chromosorb 102 was noted, even with volumes of sampled air as high as 10 m^3. Larger air volumes could probably be sampled quantitatively, but no attempts were made to extend measurements to ultimate breakthrough because the sampling of 10 m^3 of air or less is sufficient for determinations down to the quantitative limit of the method.

Tests showed that as little as 10 ng of Z-9-tdf adsorbed on the Chromosorb 102 may be quantitatively desorbed by elution with hexane. Not only is elution a far more rapid and simple extraction technique than the widely used Soxhlet procedure, it is also less vigorous, so that strongly bound organic impurities are less efficiently removed from the adsorbent.

The conversion of Z-9-tdf to its *vic*-dibromide, a derivative giving a strong electron-capture response, is similar to the previously published bromination of disparlure, the synthetic gypsy moth sex attractant (Caro et al., 1978). A dilute solution of bromine in a suitable solvent, like carbon disulfide, reacted quantitatively and almost instantaneously with Z-9-tdf. Since the derivative was water insoluble, stable in both hexane and benzene, and did not volatilize when deposited from solutions as a thin film, quantitation through the several steps of the analytical

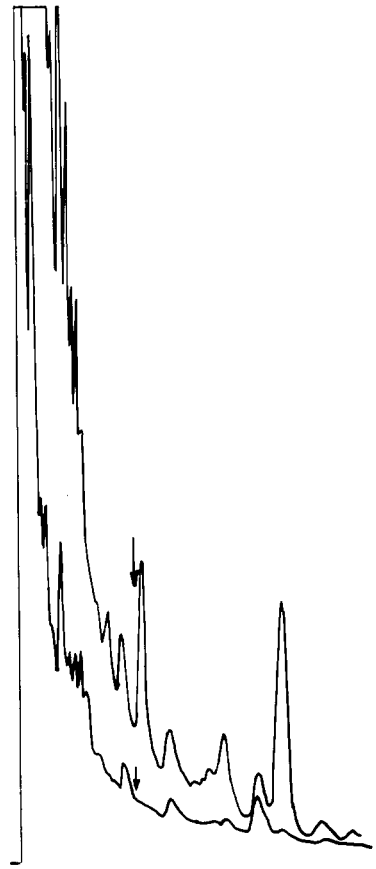

Figure 2. Chromatograms of an extract from air within the crop canopy in an untreated corn field at Gainesville, FL. Volume of air sampled, 4.7 m^3. Upper curve, before UV cleanup; lower curve, after UV cleanup. Vertical arrows indicate retention time of Z-9-tdf-dibromide.

method was unambiguous. The structure of the derivative as 9,10-dibromotetradecan-1-ol formate was verified by chemical ionization mass spectrometry (CIMS) and infrared spectrophotometry. CIMS was used because electron-impact mass spectrometry of authentic organic dibromides did not show the molecular ion that would confirm the presence of bromine in the molecules.

Elution through the silica gel microcolumn gave variable degrees of cleanup from sample to sample because of the difficulty in exactly reproducing the activity grade of the silica gel and the degree of packing of the column. Thus, the two major peaks that appeared in all reagent blank chromatograms at retention times of 0.84 and 1.95 relative to that of Z-9-tdf-dibromide (Figure 1) varied considerably in size. However, Z-9-tdf added to the adsorbent before extraction was consistently recovered, irrespective of the degree of cleanup.

UV photolysis as a clean-up technique in quantitative analysis can be used only when the compound of interest resists degradation entirely or degrades at a predictable rate. The latter held true when a thin film of Z-9-tdf-dibromide was exposed. Table I shows the results of a series of replicate experiments with authentic Z-9-tdf-dibromide, in which solutions containing 100 ng of the derivative were evaporated to dryness on watch glasses and exposed to the germicidal lamp at 10-cm distance for different time periods. Reproducibility was quite satisfactory and, after the 30-min period required to remove major interferences from field air extracts, only 40% of the compound had degraded. The same degree of degradation was observed in UV treatments of spiked field air samples. Valid quantitation of Z-9-tdf in field air could

Table I. Rates of Degradation of Thin Films of Z-9-tdf-dibromide on Exposure to a Germicidal Ultraviolet Lamp[a]

experiment no.	% of original Z-9-tdf-dibromide remaining					
	min of UV irradiation					
	0	2	5	10	20	30
1	100.0	97.1	91.8	80.0	67.2	59.1
2	99.6	95.1	91.5	78.3	64.5	60.9
3	99.6	91.4	84.2	77.4	60.4	59.9
mean	99.7	94.5	89.2	78.6	64.0	60.0

[a] Lamp specifications described in the Experimental Section. Distance of films from lamp, 10 cm.

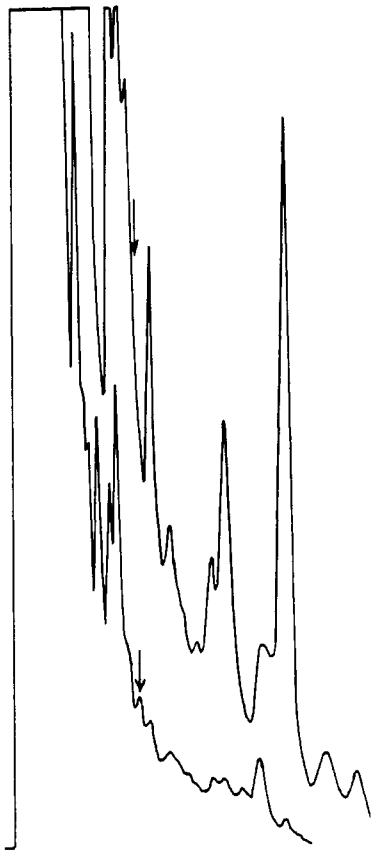

Figure 3. Chromatograms of an extract from air within the crop canopy in a corn field treated with Z-9-tdf at Aberdeen, MD. Volume of air sampled, 2.3 m^3. Upper curve, before UV cleanup; lower curve, after UV cleanup. Vertical arrows indicate retention time of Z-9-tdf-dibromide.

then be achieved by correction for this loss.

The importance of photolytic cleanup in the quantitation of Z-9-tdf in field air is illustrated in Figures 2 and 3. In Figure 2, chromatograms are shown for relatively clean air taken from a corn field near Gainesville, FL, for which a later experiment with Z-9-tdf was planned. Without UV cleanup, the large peak immediately following the retention time of Z-9-tdf-dibromide would clearly interfere with quantitation of any Z-9-tdf present; after UV cleanup, this peak was completely degraded. In Figure 3, an example is shown of air sampled in a Z-9-tdf field experiment at Aberdeen, MD, that was badly contaminated by emissions from an unknown source. The small but quantifiable Z-9-tdf-dibromide peak appearing after UV cleanup was, before the cleanup, completely hidden in the high background.

Recovery of Z-9-tdf through the method was established in 12 determinations made at various times in the laboratory with use of the air flow technique described in an earlier paper (Caro et al., 1978). In each case, 100 ng of Z-9-tdf was applied to the source, which consisted of glass fiber filter paper clippings lying directly on the bed of Chromosorb 102. Air (1–9 m^3) was passed through the apparatus at rates ranging from 0.8 to 2.0 m^3/h. Recoveries ranged from 79 to 101% and averaged 89 ± 2%.

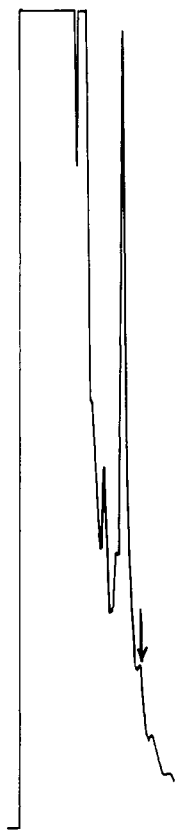

Figure 4. Chromatogram of an air extract from the Aberdeen, MD, field, showing a Z-9-tdf-dibromide peak near the limit of quantitation. Volume of air sampled, 6.7 m^3.

Z-9-tdf in the polluted air of the Aberdeen experiment could be quantitated down to nanogram-per-cubic meter levels. In Figure 4, an example is shown of quantitation near the limit of the method, the small Z-9-tdf-dibromide peak being equivalent to a Z-9-tdf concentration in air of 3 ng/m^3. It is likely that the quantitative limit would be 1 ng/m^3 or less in uncontaminated field air.

No effort has been made to date to optimize the procedure for confirming the identity of Z-9-tdf by conversion of its dibromide to the tetradecenyl acetate analogue. Conversions made as described in the Experimental Section gave recoveries that were variable and averaged only 50 or 60%. Since, in addition, the electron-capture response to the acetate dibromide is less than half that of the formate dibromide, a minimum of ca. 40 ng of Z-9-tdf was required in the sample before positive identification of the compound could be made.

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Susceptibility of Stored-Product Insects to Pyridyl Ether Analogues of Juvenile Hormone

Karl J. Kramer,* Harrison E. McGregor, and Kenji Mori

Four pyridyl ether analogues of juvenile hormones were each mixed separately with whole wheat or ground wheat medium and tested for activity against stored product insects. (*E*)-5{[5-(3-butyl-3-methyloxiranyl)-3-methyl-2-pentenyl]oxy}-2-ethylpyridine was effective at 2 and 0.1 ppm in preventing larval and adult development, respectively, from eggs of *Tribolium confusum* Jacquelin duVal. The ID_{95} doses of 0.04–50 ppm also suppressed the development of adult progeny of *Plodia interpunctella* (Hubner), *Ephestia cautella* (Walker), *Sitotroga cerealella* (Olivier), *Rhyzopertha dominica* (F.), *Oryzaephilus surinamensis* (L.), and *Sitophilus oryzae* (L.). Other compounds were less effective. Addition of a propyl substituent on the epoxide terminus of (*E*)-5-{[5-(3,3-dimethyloxiranyl)-3-methyl-2-pentenyl]oxy}-2-ethylpyridine increased activity about tenfold.

One of the most active insect growth regulators (IGR) against stored-product insects is the pyridyl ether analogue of juvenile hormone, (*E*)-5-{[5-(3,3-dimethyloxiranyl)-3-methyl-2-pentenyl]oxy}-2-ethylpyridine (Figure 1, compound III; Solli et al., 1976; Kramer and McGregor, 1978). Although compound III was highly effective as a progeny suppressant against external grain feeders (ID_{95} < 100 ppm), such as the confused flour beetle, *Tribolium confusum* Jacquelin duVal, red flour beetle, *T. castaneum* (Herbst), sawtoothed grain beetle, *Oryzaephilus surinamensis* (L.), Indian meal moth, *Plodia interpunctella* (Hubner), and almond moth, *Ephestia cautella* (Walker), it was much less effective against most of the internal grain feeders (ID_{95} > 100 ppm) such as the rice weevil *Sitophilus oryzae* (L.) and Angoumois grain moth, *Sitotroga cerealella* (Olivier).

In order to improve the activity of the pyridyl ether juvenile hormone mimic, we lengthened the molecular chain from 15 to 18 atoms by synthesizing analogues extended by a propyl substituent at the epoxide terminus. A length of 17–18 atoms is usually optimal for IGR activity, depending on the particular derivative being studied (Kiguchi et al., 1974; Mori et al., 1975). The activities of two 18-atom analogues against seven species of stored product insects is reported here.

EXPERIMENTAL SECTION

Chemicals. The chemicals (Figure 1) evaluated were (I) 5-{[5-(3-butyl-3-methyloxiranyl)-3-methyl-2-pentenyl]oxy}-2-ethylpyridine, (II) (*E,E*)-5-[(3,7-dimethyl-2,6-undecadienyl)oxy]-2-ethylpyridine, (III) (*E*)-5-{[(3,3-dimethyloxiranyl)-3-methyl-2-pentenyl]oxy}-2-ethylpyridine (93%, AI3-70644, Stauffer Chemical Co.), (IV) (*E*)-5-[(3,7-dimethyl-2,6-octadienyl)oxy]-2-ethylpyridine (91.5%, AI3-70643, Stauffer). The synthesis of compounds I and II will be described in a separate paper.

Screening Procedure. All insects were obtained from cultures maintained at the U.S. Grain Marketing Research Laboratory. "Chanute" wheat was used in all tests and was obtained from a commercial source. Kernels were cleaned and tempered to a moisture of 12.5 ± 0.5% as determined by a Motomco moisture meter (Motomco, Inc., Electronics Division, Clark, NJ).

The insects were exposed to juvenile hormone analogues admixed with diet. Appropriate stock solutions of chemicals were prepared in water to provide 0.01–100 ppm dosages of insect growth regulator (w/w) when applied to whole wheat or to ground wheat moth medium (Kinsinger, 1975). The kernels were treated as described by McGregor and Kramer (1975, 1976). The chemicals were applied to the grain by uniformly pipetting 5 mL of the appropriate stock solution onto the inside surface of a rotating jar containing 100 g of medium. Then the jar was rotated for 20 min on a mechanical tumbler operating at 40 rpm. The treated diet was allowed to equilibrate for at least 24 h before insects were added. The whole wheat or ground wheat moth medium (100 g) was infested with 50 adult Coleoptera or 50 lepidopteran eggs. Activity was evaluated on the basis of the degree of acute toxicity after 21 days of exposure or the inhibition of progeny development after 9 weeks. All experiments were conducted at 27 °C and 60% RH. The average number of insects found in four replicate samples (minus the number of parent insects when appropriate) was determined. When the numbers of progeny were reduced significantly, the samples were held an additional 6–12 weeks, examined every 2 weeks, and progeny were recorded. The ID_{95} was then expressed as the ppm per weight of grain necessary to obtain 95% inhibition of progeny development when compared with solvent only treated samples. Probit analyses of the data were conducted according to Finney (1952).

RESULTS AND DISCUSSION

Table I shows the biological activity of the pyridyl ether juvenile hormone mimics when they were homogeneously mixed with diet and exposed to stored-product Lepi-

U.S. Grain Marketing Research Laboratory, Agricultural Research, Science and Education Administration, U.S. Department of Agriculture, Manhattan, Kansas 66502 (K.J.K., H.E.M.), and the Department of Agricultural Chemistry, The University of Tokyo, Tokyo 113, Japan (K.M.).

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