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Preparation and Insect Attractant Activity of Some Alkoxy Styrene Derivatives

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The synthesis of hydroxy- and alkoxy styrene derivatives was studied and 15 derivatives were prepared from inexpensive, naturally occurring reagents. These compounds were evaluated as fruit fly attractants in an outdoor olfactometer, and several were moderately attractive to male Mediterranean fruit flies. Others were moderately to strongly attractive to male oriental fruit flies. Several derivatives were moderately attractive to female Mediterranean fruit flies or melon flies, and 4-hydroxy-3-methoxystyrene benzoate was moderately attractive to both male and female melon flies. Effective female attractants are not available currently for these three insect pests.

Use of insect attractants to determine movement of insect populations and optimum time for insecticide application is important to proper crop management

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(Beroza, 1972). Attractants also have been used with insecticides so that insects could be eradicated from an area with a minimum amount of insecticide (Steiner et al., 1965). The need for potent and longer lasting attractants continues, and, for many damaging insects, adequate attractants remain to be found.

Attractants have been studied extensively for Mediterranean (*Ceratitis capitata*) and oriental (*Dacus dorsalis*) fruit flies and melon flies (*Dacus cucurbitae*), three of the world's worst insect pests of fruit crops (Beroza, 1972). Powerful attractants for males of each of the three species are known, but no effective attractants have been

found which are specific for the females.

We report the synthesis of hydroxy- and alkoxy-styrene derivatives and their attractiveness to male and female Mediterranean and oriental fruit flies and melon flies. Some structure-activity relationships of the compounds are also reported.

EXPERIMENTAL SECTION

Synthetic Methods. We used one of two methods, A (Shono et al., 1959) and B, to synthesize from their corresponding cinnamic acids most of the derivatives listed in Table I. Some samples were commercial preparations, and others were synthesized from styrene derivatives.

Method A. A 25-g sample of cinnamic acid derivative in 50 ml of quinoline and 0.25 g of either hydroquinone or Cu powder were heated to 210–240 °C for 20 min. The mixture was cooled, and 500 ml of benzene was added. The solution was filtered (if Cu catalyst was used), and washed with two 120-ml portions each of 1 N HCl, saturated Na₂CO₃ solution, and water, and then dried over Na₂SO₄ and concentrated. The dark, oily residue was distilled at 1.0–1.5 mmHg pressure to afford the corresponding styrene derivative. One derivative, 3-hydroxy-4-methoxystyrene (7), was further purified by preparative thin-layer chromatography (TLC) on silica gel H plates with 95:5 benzene-acetone as the developing solvent. The uv-absorbing material was eluted and sublimed, mp 57–58 °C, for use as an attractant in screening tests.

Method B. A 5.0-g sample of cinnamic acid derivative and 0.1 g of Cu powder were placed in a 50-ml round-bottomed flask and heated in an oil bath. The flask was equipped with a thermometer and an air-cooled condenser by way of a 75° three-way connecting tube (Corning Glass Works, Corning, N.Y.). The sample was heated until bubbling was vigorous (oil bath temperature indicated in Table I) at atmospheric pressure and then distilled at that temperature under vacuum at ca. 50 mmHg pressure until bubbling ceased (20–60 min). The distilling head, condenser, and receiver were removed, and the partially solidified distillate was rinsed into a separatory funnel with 30–40 ml of ether. The ether solution was washed with 3 N NaOH and water, dried over Na₂SO₄, and concentrated. The residue was distilled at 1.0–1.5 mmHg pressure in a short-path (3 cm) distillation apparatus.

The acetate (9) and benzoate (10) esters of 4-hydroxy-3-methoxystyrene (8) were prepared from 8 in pyridine with acetic anhydride and benzoyl chloride, respectively. The crystalline benzoate ester (10) after recrystallization from acetone-hexane had mp 109.5–110 °C.

3,4-Dimethoxystyrene was prepared from 4-hydroxy-3-methoxystyrene by treatment with diazomethane in ether and was purified by distillation with a short-path apparatus as described above.

Analytical Methods. Melting points were not corrected. Infrared spectra were determined of samples as films or in micro KBr disks (for solids). Mass spectra were determined at 70 eV with a DuPont 21-490 mass spectrometer.

Gas-liquid chromatographic (GLC) analyses were performed on a Hewlett-Packard Model 7620 gas chromatograph equipped with a thermal conductivity detector and a 0.20 in. i.d. × 20 ft stainless steel column packed with 20% UCW-98 on 60–80 mesh Gas-Chrom P. The column temperature was 100 °C initially and then raised to 225 °C at 4 °C per min. The samples were injected directly onto the column, detector temperature was 275 °C, and helium flow was 100 ml/min.

Table I. Preparation and Screening of Alkoxy- and Hydroxystyrene Derivatives as Attractants of Male and Female Fruit Flies

No.	Compound	Method of preparation	Bath temp, °C	Yield, %	Mass spectral data ^c	Class ratings ^d					
						Mediterranean fruit fly		Melon fly		Oriental fruit fly	
						♂	♀	♂	♀	♂	♀
1	3,5-Dimethoxy-4-hydroxystyrene	A	220	2	180, 108, 167, 165, 94, 101, 122	1	1	1	1	1	1
2	2,4-Dimethoxystyrene	A, B	210	6, 13	129, 142, 141, 121, 164, 102, 78	2	1	1	1	1	1
3	2,5-Dimethoxystyrene	B	275	2	164, 121, 149, 91, 78, 77, 178 ^d	1	1	1	1	1	1
4	3,4-Dimethoxystyrene			69	164, 129, 149, 77, 91, 121, 103	1	1	1	1	3	1
5	3,5-Dimethoxystyrene	B	245	8	164, 135, 91, 78, 105, 134, 121	1	1	1	1	1	1
6	4-Ethoxy-3-methoxystyrene	B	230	21	178, 150, 135, 107, 91, 77, 76	1	1	1	1	2	1
7	3-Hydroxy-4-methoxystyrene	A	240	5	135, 150, 106, 77, 79, 55, 57	1	1	1	1	1	1
8	4-Hydroxy-3-methoxystyrene	A	210	98	150, 135, 107, 77, 45, 46, 39	2	2	1	1	2	1
9	4-Hydroxy-3-methoxystyrene acetate			55	150, 142, 141, 135, 108, 115, 107... 192	2	2	2	2	2	2
10	4-Hydroxy-3-methoxystyrene benzoate			66	105, 77, 254, 106, 51, 78, 91	1	2	2	2	1	1
11	4-Hydroxystyrene ^e					2	1	1	1	1	1
12	3-Methoxystyrene	B	310	16	134, 91, 65, 104, 78, 103, 105	2	2	1	2	1	1
13	4-Methoxystyrene ^f					2	1	1	1	1	1
14	3,4-Methylenedioxy-styrene	B	270	14	148, 147, 89, 63, 91, 90, 62	2	1	1	1	1	1
15	3,4,5-Trimethoxystyrene	B	300	33	194, 179, 151, 136, 91, 65, 121	2	1	1	1	2	1

^a Based on olfactometer tests. ^b Temperature of oil bath needed for decarboxylation. ^c Peaks are listed in decreasing order of intensity with M⁺ in italics. ^d Peak due to impurity. ^e Oxford Organic Chemicals, Oxford, England. ^f IGCN Life Sciences Group, Plainview, N.Y.

Silica gel G plates were used for TLC, with 95:5 benzene-acetone as the developing solvent. Anisaldehyde was the spray reagent (Berry and Tatum, 1965).

Olfactometer Tests. Candidate attractants were tested as 0.1% aqueous emulsions in glass traps. Class ratings as listed in Table I are derived from the Attractancy Indices, which are the quotients of the number of insects caught with the candidate attractant divided by the number caught with water alone (Christenson et al., 1963). The ratings are as follows:

Class	Attractancy index	Degree of attraction
3	>50	Strong
2	11-50	Moderate
1	<11	Little or none

Wick tests were conducted with 0.2-ml quantities of several of the candidate attractants according to Christenson et al. (1963). The level of attractiveness of the candidates was compared with that of either methyleugenol or trimedlure, the standard attractants for males of the oriental and Mediterranean fruit flies, respectively (Steiner, 1952; Beroza et al., 1961).

RESULTS AND DISCUSSION

The compounds screened were chosen for two reasons. First, one derivative studied, 4-hydroxy-3-methoxystyrene (8) (4-vinylguaiacol), has been identified as a decomposition product responsible for an overripe flavor in orange juice (Tatum et al., 1975) and some insect pests are attracted to overripe fruit. Secondly, the dimethoxy derivative (4) of 4-vinylguaiacol is an analog of methyleugenol, a potent attractant of the oriental fruit fly (Steiner, 1952). Table I lists synthesis and screening information for the styrene derivatives.

Most styrene derivatives were prepared by decarboxylation of their corresponding cinnamic acids. Method A afforded an excellent yield of 4-hydroxy-3-methoxystyrene (8) from 4-hydroxy-3-methoxycinnamic acid but furnished comparatively poor yields or none of other derivatives. Thus, method B was developed. Although yields varied and were generally low, the method did permit heating of the reaction mixture to temperatures high enough for decarboxylation (generally >240 °C required). The highest temperature possible in method A was that of boiling quinoline (ca. 235 °C), not high enough for decarboxylation of many cinnamic acid derivatives.

All compounds listed in Table I were pure according to TLC but not GLC. Some derivatives, e.g., 3,4-dimethoxystyrene (4), decomposed under the conditions of GLC as evidenced by several sharp, unresolved, nonreproducible peaks; others, however, e.g., 3-methoxystyrene, were stable. Thus, GLC could not be used for monitoring purity of all the styrene derivatives.

Male Mediterranean fruit flies were moderately attracted to compounds 2, 8, 11, and 14 (Table I). Male oriental fruit flies were strongly attracted to compound 4 and moderately attracted to compounds 6, 8, and 9. Some of the more promising derivatives were evaluated in wick tests (Table II) and were only 10–20% as attractive as trimedlure or methyleugenol are to male Mediterranean and oriental fruit flies, respectively. Since many compounds are moderately attractive to male Mediterranean and oriental fruit flies, these derivatives were not further evaluated with males of those two species. The apparent differences in relative activity of candidate lures to oriental and Mediterranean fruit flies, as indicated in Tables I and II, are not uncommon in fruit fly bioassays. In practice, only candidate compounds which show outstanding ac-

Table II. Attraction of Male Mediterranean or Oriental Fruit Flies to Wicks Baited with Candidate Attractants

Treatment	Estimated no. responding after 15-min exposure	
	Mediterranean fruit fly	Oriental fruit fly
3,4-Dimethoxy-styrene (4)	150	75
4-Hydroxy-3-methoxystyrene (8)	100	30
4-Ethoxy-3-methoxystyrene (6)	0	250
4-Methoxystyrene (13)	0	50
4-Hydroxystyrene (11)	50	
Methyleugenol ^a	0	500
Trimedlure ^b	500	0

^a Standard attractant for male oriental fruit flies.

^b Standard attractant for male Mediterranean fruit flies.

tivity in both glass traps and wick tests are further evaluated in the field.

Compounds that attract male melon flies or females of all three species are much less common. Of the derivatives listed in Table I, compounds 9, 10, and 12 were moderately attractive to female Mediterranean fruit flies, compounds 9, 10, 12, and 15 were moderately so to female melon flies, and compound 10 was moderately attractive to male melon flies, as well. However, in wick tests these compounds attracted neither male nor female melon flies. None of the derivatives tested were moderately or strongly attractive to female oriental fruit flies.

Several structure-activity relationships were noted in this study. One of the stronger attractants of male Mediterranean and oriental fruit flies was 4-hydroxy-3-methoxystyrene (8). However, its isomer (7), with hydroxyl and methoxyl groups interchanged, was not active. 3,4-Dimethoxystyrene (4), the only compound in this study with class 3 activity, is an analog of methyleugenol. Acetate 9 was more attractive than the parent compound (8) to female melon and Mediterranean fruit flies. As compared to 8, the benzoate ester 10 was more attractive to male melon flies, but less so to male Mediterranean and oriental fruit flies. All compounds moderately attractive to female Mediterranean fruit flies and melon flies possessed a 3-methoxyl group, and two of the compounds (9 and 10) had an esterified 4-hydroxyl group. Other derivatives suggested by this study that might be active toward female flies of all three species and to male melon flies are 3-methoxy-4-hydroxystyrene derivatives esterified with other acids. The acids chosen might be those that have activity in their own right.

Several of the 15 hydroxy- and methoxystyrene derivatives screened as fruit fly attractants were moderately to strongly attractive to male Mediterranean or oriental fruit flies. Others were moderately so to female Mediterranean fruit flies and melon flies, and one, to male melon flies. None of the derivatives was as attractive as currently used compounds.

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Mass Spectral Confirmation and Analysis by the Hall Detector of Mirex and Photomirex in Herring Gulls from Lake Ontario

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Mirex, 1,2,3,4,5,5,6,7,8,9,10,10-dodecachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane, and a monohydro Mirex, 1,2,3,4,5,5,6,7,9,10,10-undecachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane (photomirex), were discovered in the whole body lipid of Herring Gulls from Pigeon Island, Lake Ontario. PCBs, which were evident in high concentrations, coeluted with Mirex and photomirex in residue cleanup procedures, and interfered with their determination by electron-capture gas chromatography (EC-GC) using standard analytical columns. Samples were perchlorinated to remove this interference, and structures were confirmed by gas chromatography/mass spectrometry (GC/MS). The Hall electrolytic conductivity detector was shown to be useful as a specific detector to monitor residues of Mirex and photomirex in the presence of high PCB interference. Eggs of Herring Gulls proved to be useful as indicators of these compounds in Lake Ontario.

Mirex has recently been recognized by gas chromatography/mass spectrometry (GC/MS) as a contaminant of Lake Ontario fish (Kaiser, 1974). The adult Herring Gull is a widespread aquatic feeding carnivore which is relatively nonmigratory on Lake Ontario (Kaldec and Drury, 1968). Lake fish comprise the bulk of the bird's diet, although garbage is sometimes eaten. Herring Gulls on Lake Ontario have been found to contain high levels of organochlorines such as DDE and PCBs (Gilbertson, 1974; Frank et al., 1975); therefore we wished to determine if Mirex and other undiscovered compounds were also present.

It is difficult to determine Mirex and other organochlorine residues in the presence of high levels of PCBs and DDE because of interference in electron-capture gas chromatography (EC-GC) using standard analytical columns. The recently developed Hall electrolytic conductivity detector was reported to have a low specificity in the chloride mode for PCBs, while having a high specificity for highly chlorinated, nonaromatic compounds such as Mirex (Hall, 1974). The use of the Hall detector was therefore investigated for routine analysis of trace organochlorine pollutants in the heavily PCB-contaminated Herring Gull lipid.

Existing column chromatography procedures (Reynolds, 1971; Berg et al., 1972) were not effective in separating PCBs from Mirex and related compounds for confirmation of the latter by GC/MS. This was overcome by perchlorinating samples to convert interfering PCBs to decachlorobiphenyl.

EXPERIMENTAL SECTION

Reagents and Solvents. Florisil (60-100 mesh) obtained from Floridin Corp. was heated at 300 °C overnight to remove any electron capturing contaminants and used

in the activated form for extraction. For column chromatography it was deactivated with 1.2% by weight glass distilled water.

HCB (hexachlorobenzene), BHC (1,2,3,4,5,6-hexachlorocyclohexane), and *p,p'*-DDT (1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane) were obtained from Chem Services Inc.

Mirex (1,2,3,4,5,5,6,7,8,9,10,10-dodecachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane), *p,p'*-DDE (1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene), heptachlor epoxide (1,4,5,6,7,8,8-heptachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-endomethanoindene), and dieldrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-endo-1,4-*exo*-5,8-dimethanonaphthalene) were obtained from U.S. EPA, Research Triangle Park, N.C.

Decachlorobiphenyl was obtained from Analabs Inc. Aroclor 1260 was obtained from Monsanto Corp.

All solvents used were glass distilled, nanograde quality from Caledon Laboratories.

Preparation of Environmental Samples. Sixteen adult Herring Gulls were obtained in 1973 from a colony located on Pigeon Island, Lake Ontario. The gulls were plucked, macerated in a Hobart chopper, freeze dried, and extracted in a Soxhlet apparatus (extra-large size, Corning Glass Works) with hexane/acetone azeotrope. The solvent was removed, yielding approximately 1 kg of lipid. The lipid comprised approximately 10% of the whole body weight.

Herring Gull eggs were obtained from Scotch Bonnet Island, Lake Ontario in the spring of 1972, and from Muggs Island, Lake Ontario in the spring of 1974 and 1975. They were ground in precleaned sodium sulfate and extracted with hexane in a column. The lipid extracted comprised approximately 5% of the fresh weight of the eggs.

Extraction of Organochlorine Compounds. The acetonitrile-hexane partition method of Porter and Burke (1973) was modified as follows: The lipid (8 g) was mixed with Florisil as stipulated in the method, but the residues were eluted with 5% water in acetonitrile. This eluate was placed in a large separatory funnel and shaken with 100 ml of hexane. The sample was then partitioned with 800

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