Synthesis of Alkoxybenzenes and Alkoxyvinylbenzenes and Their Chemosterilizing and Toxic Activity on *Planococcus citri* (Hom., Pseudococcidae)

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Dialkoxy-, trialkoxy-, dialkoxyvinyl-, and trialkoxyvinylbenzenes were investigated for chemosterilant and toxic activity on *Planococcus citri*. The alkoxyvinylbenzenes were toxic; they reduced the egg production of the test insect. Dialkoxyvinylbenzenes decreased the number of eggs laid by females, but the chemosterilizing activity of the trialkoxy derivatives was not strong.

Larvae treated with 0.1% 1,5-diisopropoxy-4-vinylbenzene (**6**), 17% survived. The surviving females were strongly retarded in their growth (which was 56% of normal) and their egg production was reduced by 70%. Some of the small adults (43% of the surviving females) failed to form an ovisac and did not lay eggs at all.

Ageratochromenes isolated from *Ageratinae* species¹⁾ cause precocious metamorphosis in sensitive insect species,²⁾ and have been re-named "precocenes" (Table I: compounds **1~3**). Precocenes also interfere with other physiological processes that involve juvenile hormones and can produce sterility in insects. Bowers *et al.*³⁾ observed that insects with telotrophic ovarioles, such as *Dysdercus cingulatus*, *Oncopeltus fasciatus*, *Rhagoletis cerasi*, and *Epilancna varivestis*, become sterile after precocene treatment. Similar effects were observed by Zamorano *et al.*⁴⁾ for *Blatella germanica*, *Lygaeus militaris*, and *Pyrrhocoris apterus*. Treatment with **2** can produce sterility in ticks such as *Ornithodoros parkeri*⁵⁾ and *Rhipicephalus sanguineus*.⁶⁾

Saxena *et al.*⁷⁾ found beta-asarone (**20**) isolated from the sweet flag (*Acorus calamus*) to cause sterility without producing precocious metamorphosis.

Matolcsy *et al.*^{8,9)} synthesized 1,2-dimethoxy-5-isopropoxy-4-vinylbenzene (**7**) by the hybridization of beta-asarone (**20**) and **2**. Compound **7** is a precocene derivative with an open pyrane ring. This compound caused both precocious metamorphosis and a de-

crease in egg production by *D. cingulatus*.

In this paper we describe the synthesis and the sterilizing and toxic activities of other 5-isopropoxy-4-vinylbenzenes (**4~8**) and of alkoxybenzenes without double bond. Scale insects, which are seldom used in insect anti-hormone studies, were the test organisms.

The citrus mealybug (*Planococcus citri* Risso) is a major pest of citrus and other crops. Several other species of mealybugs that infect foliage and roots are also difficult to control on many field- and greenhouse crops.

The functions of natural juvenile hormones and juvenoids in the reproduction of scale insects are well known. After treatment of the first instar larvae of *P. citri* with kinoprene, methoprene, or hydroprene, numbers of progeny decreased significantly.¹⁰⁾ These insect usually initiate ovisac formation but eggs are not deposited there.¹¹⁾ In this case, histological observation of the ovarium showed decreased numbers of trophocytes, which have degenerated. Thus, the development of oocytes is

FIG. 1. General Scheme for Preparation of Alkoxybenzenes and Alkoxyvinylbenzenes.

completely inhibited.¹²⁾ After treatment of adults, the wax glands that secrete the ovisac cease to function and, as a consequence, the females lay eggs only in a single row and without any protective secretion.¹²⁾

The effects of insect-growth regulators on scale insects were summarized by Darvas and Varjas.¹³⁾

MATERIALS AND METHODS

Synthesis. The original procedure for the synthesis of alkoxyvinylbenzene derivatives was based on reduction of the appropriate acetophenone to the corresponding alcohol, the dehydration of which was expected to yield the vinylbenzene derivative (**K**).⁹⁾ This synthetic route was, however, not suitable because the dehydration gave very poor yields (5~7%). Other authors¹⁴⁾ have also reported failure in the dehydration of similar compounds, so we chose other ways (Fig. 1) to synthesize the derivatives.

For derivatives of 1-alkoxy-5-isopropoxy-4-vinylbenzene (**4~6**, $R=H$), we started from 2,4-dihydroxybenzene-1-carbaldehyde (**A**). The OH group in the ortho position forms a chelate ring and is hindered by the aldehyde group, so **A** can be selectively alkylated to afford 4-alkoxy-2-hydroxybenzene-1-carbaldehyde (**I**, $R'=H$). The isopropylation of **I** in the ortho position was not as easy as with the usual phenols owing to the difficulties described above.

We have tried a number of methods including sodium ethoxide in ethanol, potassium carbonate in acetone and in dimethylformamide (DMF), and liquid-liquid phase transfer systems using different catalysts, but none of them gave good yield. The solid-liquid phase-transfer system was the best. This method, giving an 80% yield, uses benzytributylammonium chloride (BAC) as the phase-transfer catalyst, potassium carbonate as the acid acceptor, and acetone as solvent. Other phase-transfer catalysts, triethylbenzylammonium chloride, methyltrialkyl-(C_8-C_{10})-ammonium chloride (Adogen 464), and cetylpyridinium bromide, were tried but BAC was most effective.

The double bond of alkoxyvinylbenzene (**K**) was formed by a simplified Wittig-Horner reaction in different media¹⁵⁾ by a solid-liquid transfer process. The corresponding aldehydes (**J**) were reacted with methyltriphenylphosphonium iodide in the presence of potassium carbonate in dioxane that contained a small amount of water.

Biological tests. Citrus mealybugs were maintained on etiolated potato sprouts in ventilated plastic boxes in an environment of 30°C, 60~80% relative humidity, and a cycle of 16 hr light, 8 h dark. The test compounds were diluted in acetone and sprayed onto the sprouts and tubers with a "Rofra" sprayer until drops ran off. To evaluate the toxicity of the compounds, 120 to 200 first-instar larvae

were placed onto a potato tuber in a plastic box. Twenty-three days later, the survivors were counted and the toxicity in terms of the percentage of larvae killed was calculated by the Henderson-Tilton formula. We expected fecundity to be affected after day 28 when the treated larvae became adults. Fecundity was measured by examining the ovisacs of 10 females for each treatment. In statistical treatment of the data (one way ANOVA), the lowest two values for egg production were discarded. Some female mealybugs lay eggs late, so the variation arising from difference in individual developmental time could be reduced by discarding extremes in data. Females much smaller than the acetone-treated controls were prepared by Wilkey's method¹⁶⁾ for microscopic examination, where body length was measured several different ways and the morphology of the antennae examined.

RESULTS AND DISCUSSION

Results are summarized in Table 1.

Precocenes **1~3** were only moderately toxic at the concentration of 0.1%. The alkoxyvinylbenzene derivatives (**4~8**) were more toxic. The vinylbenzenes with three alkoxy groups (**7~8**) were less toxic than those with two (**4~6**). At 0.05% the toxicity of **4~6** was lost. The alkoxybenzene derivatives without the double bond present in the precocenes and the vinylbenzenes were not toxic. The compounds without an isopropyl group in the meta position to another alkoxy group were moderately toxic except for 1,2,5-trimethoxybenzene (**11**), which was not at all toxic.

Of the surviving adults, many were males.

Of all the compounds examined for their sterilizing action only 1,5-diisopropyl-4-vinylbenzene (**6**) was effective. It reduced egg production by 70% compared with the untreated control. Dialkoxyvinylbenzenes **4**, **5**, and **6** also decreased the number of eggs laid by the females; the chemosterilizing activity of the trialkoxy derivatives **7~8** was not great.

Precocenes **1** and **3** reduced egg production somewhat, but **2** hardly of all.

The females treated with 0.1% **6** were strongly retarded in their growth. Their mean body length (1.35 ± 0.12) was only 56% of the length of the controls (2.43 ± 0.24 ; $p < 0.01$). The antennae of the insects had features char-

TABLE I. TOXIC AND CHEMOSTERILIZING ACTIVITY OF PRECOCENES, ALKOXYBENZENES AND ALKOXYVINYL BENZENES ON *P. citri*

No.	Structure	Concentration			
		0.1%		0.05%	
		Toxicity ^a (%)	Mean No. of eggs/female $\pm$ SE ^b	Toxicity ^a (%)	Mean No. of eggs/female $\pm$ SE ^b
1 (P1)		12	131.5 $\pm$ 40.5 BC	—	—
2 (P2)		49	205.8 $\pm$ 88.1 AB	—	—
3 (P3)		34	145.9 $\pm$ 15.2 B	—	—
4		84	124.3 $\pm$ 31.2 BC	9	126.1 $\pm$ 17.2 Y
5		70	143.5 $\pm$ 17.8 B	0	160.0 $\pm$ 28.0 XY
6		83	75.0 $\pm$ 10.1 C ^c	6	131.0 $\pm$ 40.0 Y
7		53	190.5 $\pm$ 42.4 AB	—	—
8		65	204.9 $\pm$ 37.2 AB	—	—
9		0	192.1 $\pm$ 58.6 AB	—	—
10		39	201.5 $\pm$ 47.8 AB	—	—
11		0	251.9 $\pm$ 22.7 A	—	—
12		35	230.3 $\pm$ 36.5 A	—	—
13		44	166.1 $\pm$ 34.5 B	—	—
14		0	202.5 $\pm$ 70.3 AB	—	—
15		0	207.6 $\pm$ 53.9 A	—	—
16		0	208.0 $\pm$ 43.8 AB	—	—
17		17	198.3 $\pm$ 35.4 AB	—	—

TABLE I. (continued).

No.	Structure	Concentration			
		0.1%		0.05%	
		Toxicity ^a (%)	Mean No. of eggs/female $\pm$ SE ^b	Toxicity ^a (%)	Mean No. of eggs/female $\pm$ SE ^b
18		51	206.9 $\pm$ 40.1 AB	—	—
19		87	208.5 $\pm$ 92.3 AB	28	131.6 $\pm$ 31.1 Y
Control		—	244.0 $\pm$ 49.8 A	—	172.6 $\pm$ 47.0 X
SD 1%			62.99		34.71
SD 5%					

^a The toxicity % calculated by the Henderson–Tilton formula on day 23 after 120 ~ 200 first-instar larvae placed on a treated surface.

^b Values labelled with the same letter in a column are not significantly different at the 1% (A, B, C) and 5% (X, Y) level, respectively (one way ANOVA).

^c We did not take into account the 43% of the surviving insects, that did not lay any eggs.

acteristic of adults, but the females did not form an ovisac and did not lay eggs within one week, the usual time for normal adults.

Neither of the compounds tested altered the secretion by wax glands.

Compounds **5** and **6** can be thought of as precocene derivatives the pyrane ring of which is opened; their mechanism of action may be similar to that of precocenes. However, the dialkoxy- and trialkoxybenzenes that lack the characteristic double bond needed for precocene activity are not representatives of precocenes.

Mealybugs (*Pseudococcidae*) are the oldest family of scale insects, a connecting link between the aphids and other families of scale insects.¹⁷⁾ The biological effects of precocenes have certain parallels between scale insects and their distant relatives, the aleyrodids and aphids. None of the precocenes (**1**~**3**) were very toxic for the aphids *Acyrtosiphon pisum* and *Myzus persicae* or for aleyrodids *aleyrodes brassicae* and *Trialeurodes vaporariorum*.¹⁸⁾ Treatment of *A. pisum*¹⁹⁾ and *Macrosiphum euphorbiae*²⁰⁾ with **2** increased the numbers of

alate forms. The same treatment of *M. persicae* increased the proportions of males²¹⁾ and of oviparous-viviparous adultoids.²²⁾

In our experiments, the toxicity of precocenes for *P. citri* was moderate, similar to that found for aphids and aleyrodids. The effects on the sexes was not different unlike juvenoids, which decrease the proportion of males.¹²⁾ These findings suggest that *P. citri* has a physiologically level of juvenile hormone different for the sexes. Males reacted to the rise in the level of juvenile hormone more than females; while females tolerated some decrease.

Another family of scale insects, the armored scale insects (*Diaspididae*), are much more sensitive to precocenes than mealybugs. When 0.1% **2** was used to treat the first instar larvae of *Quadraspidiotus perniciosus*, the insects died, and even on the 4th day after treatment, half of the animals did not survive on the treated surface.²³⁾

Precocenes are highly cytotoxic to the corpora allata, and cause the destruction of the gland responsible for production of juvenile

hormone. Precocenes themselves are pro-allatocidins, and their action probably arises from activation mediately cytochrome P-450. A highly reactive 3,4-epoxy-derivative is formed, which reacts with nucleophilic substrates in the gland, leading to the death of the corpora allata.²⁴⁻²⁶⁾

The precocene-like activity of **7**, 1,2-dimethoxy-5-isopropoxy-4-vinylbenzene, on *D. cingulatus* causes morphogenetical alteration, so such activity is not restricted to compounds with a chromene ring structure, but a double bond is an absolute requirement.⁸⁾ Compounds **4**~**8** did not affect the morphology of *P. citri*, but their toxic and sterilizing activities surpasses those of precocenes.

The presence of a double bond in a xenobiotic always provides a possibility for the organism to eliminate the chemical by an oxidative process *via* different oxygenases. Oxidative bioactivation of the double bond is probably involved in the mechanisms of **4**~**8**. many structures with a terminal π -bond inactivate cytochrome P-450 by alkylating its prosthetic heme group by the oxydation of a double bond.²⁷⁾ This probability seems likely because alkoxybenzenes without a vinyl group are inactive; the only exception is **19**, but the methylenedioxy structure is also an inhibitor of cytochrome P-450.

The biological action of **4**~**8** surpassing that of precocenes provides a new theoretical base for the development of novel insect-growth regulators.

EXPERIMENTAL

IR spectra were recorded with a Bruker IFS-113-VFI IR spectrometer. NMR spectra were made with a Bruker WM-250 FT spectrometer using 2,3,5,6-tetramethyl-*p*-xylene- α, α' -diol as an internal standard. Melting points are uncorrected. The results of elemental analysis found were in agreement with those calculated (within 0.3% error).

Compounds **A** and **D** were prepared with a Vilsmeier formulation of resorcinol and 1,3,6-trimethoxybenzene (**C**), respectively, as described elsewhere.^{28,29)} Compound **C** was synthesized by the simultaneous hydrolysis and methylation of 1,3,6-triacetoxybenzene²⁹⁾ obtained from

benzoquinone.³⁰⁾ The selective alkylations of the hydroxy group in the 3 position of **A** were done with the corresponding alkyl bromide or iodide in acetone in the presence of K_2CO_3 . Alkoxybenzenes **9**~**10** and **12**~**19** were synthesized from the appropriate phenols with the same alkylation method. We used procedure described elsewhere³¹⁾ for the acid-catalyzed oxidation of benzaldehydes with hydrogen peroxide to phenols for the preparation of **G**. The selective ortho demethylation of **D** was done with $AlCl_3$ in CH_2Cl_2 as described elsewhere.³²⁾

In the general procedure for the preparation of 4,5-dialkoxy-2-isopropoxybenzene-1-carboaldehyde (**J**), mixture of 2-hydroxybenzaldehyde derivative (**I**) (20 mmol), isopropyl bromide (9.84 g, 80 mmol), anhydrous K_2CO_3 (5.52 g, 40 mmol), and benzyltributylammonium chloride (1.9 g, 6 mmol) in 30 ml of dry acetone was refluxed and stirred for 5~6 hours. When the reaction (followed by TLC) ended, the mixture was no longer yellowish. Inorganic salts were filtered off by suction, and washed with acetone. The acetone solution was evaporated under reduced pressure. Ether and water were added to the remaining material, and the two phases were shaken and allowed to separate. The ether phase was washed with 5% NaOH solution twice and with water. The resultant solution was treated with charcoal and dried over Na_2SO_4 . after the ether was removed under reduced pressure, the product was distilled or recrystallized (if solid).

2-Isopropoxy-4-methoxybenzene-1-carboaldehyde (Ja). Yield: 83.9%, bp 115~116°C/0.8 Torr, IR (KBr): 1675 cm^{-1} ($\nu_{C=O}$), H NMR ($CDCl_3$): δ : 1.40 (6H, d, $J=8.0$ Hz), 3.86 (3H, s), 4.64 (1H, sp), 6.32 (1H, 2 $\times$ d), 6.45 (1H, d, $J=2.1$ Hz), 7.80 (1H, d, 8.5 Hz), 10.31 (1H, s).

4-Ethoxy-2-isopropoxybenzene-1-carboaldehyde (Jb). Yield: 83.1%, bp 119~120°C/0.3 Torr, IR (KBr): 1670 cm^{-1} ($\nu_{C=O}$), H NMR ($CDCl_3$): δ : 1.39 (6H, d, $J=8$ Hz), 1.43 (3H, t, $J=7$ Hz), 4.06 (2H, qu), 4.62 (1H, sp), 6.44 (1H, d, $J=2.2$ Hz), 6.60 (1H, 2 $\times$ d), 7.78 (1H, d, $J=8.7$ Hz), 10.31 (1H, s).

2,4-Diisopropoxybenzene-1-carboaldehyde (Jc). Yield: 81.3%, bp 125~126°C/0.4 Torr, IR (film): 1675 cm^{-1} ($\nu_{C=O}$), H NMR ($CDCl_3$): δ : 1.36 (6H, d, $J=8$ Hz), 1.39 (6H, d, $J=8$ Hz), 2 $\times$ 4.62 (2 $\times$ 1H, sp), 6.47 (1H, d, $J=1.6$ Hz), 6.48 (1H, 2 $\times$ d), 7.78 (1H, d, $J=8.7$ Hz), 10.30 (1H, s).

4,5-Dimethoxy-2-isopropoxybenzene-1-carboaldehyde (Jd). Yield: 78.6%, mp. 61~62°C (from hexane), IR (KBr): 1660 cm^{-1} ($\nu_{C=O}$), H NMR ($CDCl_3$): δ : 1.39 (6H, d, $J=6.1$ Hz), 3.88 (3H, s), 3.95 (3H, s), 4.4 (1H, sp), 6.52 (1H, s), 7.30 (1H, s), 10.32 (1H, s).

4-Ethoxy-2-isopropoxy-5-methoxybenzene-1-carboaldehyde (Je). $POCl_3$ (7.70 g, 37.2 mmol) was added dropwise to abs. DMF (15 ml) and stirred with ice-water cooling at 5~10°C. Then 1-ethoxy-3-isopropoxy-6-methoxybenzene (**H**) (6.3 g, 30 mm) dissolved in abs. DMF (15 ml) was added to this solution, and the stirring and cooling was continued. The mixture was then warmed at

40°C for two hours and poured into ice-water (120 ml). The solution was made basic with 10% NaOH, and the precipitate was filtered off with suction, washed with water, and recrystallized from water-ethanol (6:4). Yield: 80.6%, mp: 71~72°C, IR (KBr): 1664 cm⁻¹ ($\nu_{C=O}$), H NMR (CDCl₃): δ : 1.38 (6H, d, $J=6.1$ Hz), 1.51 (3H, t, $J=7$ Hz), 3.87 (3H, s), 4.16 (2H, qa), 4.57 (1H, sp), 6.51 (1H, s), 7.30 (1H, s), 10.31 (1H, s).

In the general method for the preparation of alkoxyvinylbenzenes (**K**), mixture of the appropriate benzaldehyde (**J**) (5 mmol), methyltriphenylphosphonium iodide (4.04 g, 10 mmol), and finely powdered K₂CO₃ (1.38 g, 10 mmol) in peroxide-free dioxane (5 ml) that contained 0.075 ml of water was refluxed with vigorous stirring for 6~10 hours. The reaction was monitored by TLC. The solids were filtered off with suction and washed with dioxane. The solvent was evaporated under reduced pressure, and the products obtained were purified by column chromatography. They were first put on a short column of silica gel in a small amount of dioxane and eluted with hexane only to remove triphenylphosphate oxide. Chromatography was then done on 200 ml of gel using hexane-acetone (10:1) for elution.

1-Methoxy-5-isopropoxy-4-vinylbenzene (**4**). Yield: 68.3%, IR (film): 1730 cm⁻¹ ($\nu_{C=C}$), H NMR (CDCl₃): δ : 1.34 (6H, d, $J=6$ Hz), 3.80 (3H, s), 4.50 (1H, sp), 5.10 (1H, 2×d), 5.62 (1H, 2×d), 6.45 (Ar 1H, d), 6.48 (Ar 1H, 2×d), 6.80 (1H, 2×d, $J=12.2$ and 17.2 Hz), 7.40 (Ar 1H, d, $J=9$ Hz).

1-Ethoxy-5-isopropoxy-4-vinylbenzene (**5**). Yield: 63.5%, IR (film): 1730 cm⁻¹ ($\nu_{C=C}$), H NMR (CDCl₃): δ : 1.34 (6H, d, $J=6.1$ Hz), 1.40 (3H, t, $J=7.1$ Hz), 4.02 (2H, qa), 4.50 (1H, sp), 5.1 (1H, 2×d), 5.62 (1H, 2×d), 6.45 (Ar 1H, d, $J=2.1$ Hz), 6.48 (Ar 1H, 2×d), 6.96 (1H, 2×d, $J=12.2$ and 17.1 Hz), 7.40 (Ar 1H, d, $J=9.0$ Hz).

1,5-Diisopropoxy-4-vinylbenzene (**6**). Yield: 61.6%, IR (film): 1729 cm⁻¹ ($\nu_{C=C}$), H NMR (CDCl₃): δ : 1.32 (6H, d, $J=6.1$ Hz), 1.34 (6H, d, $J=6.1$ Hz), 4.48 (1H, sp), 4.52 (1H, sp), 5.1 (1H, 2×d), 5.62 (1H, 2×d), 6.42 (Ar 1H, d, $J=2.0$ Hz), 6.46 (Ar 1H, 2×d), 6.97 (1H, 2×d, $J=12.2$ and 17.3 Hz), 7.40 (Ar 1H, d, $J=9.0$ Hz).

1,2-Dimethoxy-5-isopropoxy-4-vinylbenzene (**7**). Yield: 58.9%, IR (film): 1728 cm⁻¹ ($\nu_{C=C}$), H NMR (CDCl₃): α : 1.35 (6H, d, $J=6.2$ Hz), 3.85 (3H, s), 3.88 (3H, s), 5.00 (1H, 2×d), 5.21 (1H, 2×d), 6.45 (1H, s), 6.82 (1H, 2×d, $J=11.9$ and 17.3 Hz), 7.08 (1H, s).

1-Ethoxy-5-isopropoxy-2-methoxy-4-vinylbenzene (**8**). Yield: 57.9%, IR (film): 1726 cm⁻¹ ($\nu_{C=C}$), H NMR (CDCl₃): δ : 1.31 (6H, d, $J=6.3$ Hz), 1.45 (3H, t, $J=7.1$ Hz), 3.86 (3H, s), 4.07 (2H, qa), 4.35 (1H, sp), 5.13 (1H, 2×d), 6.51 (1H, s), 7.00 (1H, 2×d, $J=1.40$ and 11.2 Hz), 7.01 (1H, s).

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