standard in the bioassays. Discovery of these attractants offers a good potential and a new tool for the control of *Hippelates* eye gnats.

ACKNOWLEDGMENT

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Synthesis and Laboratory and Field Evaluation of a New, Highly Active and Stable Insect Growth Regulator

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The insect growth regulator 6,7-epoxy-1-(*p*-ethylphenoxy)-3-ethyl-7-methylnonane (Ro 10-3108) is an efficient agent for plant protection. Stability studies in the laboratory (uv, hydrolysis) and persistency studies outdoors show that this compound, in contrast to most known insect growth regulators, is sufficiently stable for practical purposes. Ro 10-3108 gave good control of natural populations of summerfruit tortrix moth and scale insects. The favorable toxicological data as well as the biodegradability of Ro 10-3108 make this compound a promising candidate for several fields of application. A technically feasible synthesis of the compound is given.

In the last several years compounds which mimic the effects of insect juvenile hormones by preventing adult development have received a great deal of attention as possible insect control agents. Hundreds of chemical structures with juvenile hormone activity have been synthesized and investigated (Menn and Beroza, 1972; Sláma et al., 1974). Efforts of chemists and entomologists have been directed mostly toward four classes of insect growth regulators (IGR's): derivatives of juvabione and dehydrojuvabione (Suchý et al., 1968), compounds having a farnesyl type skeleton (Mori, 1971), alkyl 3,7,11-trimethyl-2,4-dodecadienoates (Henrick et al., 1973), and aromatic ethers with a geranyl type side chain (cf. Bowers, 1971; Pallos et al., 1971; Sarmiento et al., 1973). We concentrated our efforts on compounds of the latter type, keeping in mind that any successful IGR must have a better field stability than the previously described candidates (cf. Bagley and Bauernfeind, 1972; Sláma et al., 1974, pp 275 ff).

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MATERIALS AND METHODS

Synthesis. Compounds 1 (Wright et al., 1974), 2, and 3 (cf. Table I) were synthesized by hydrogenation of the unsaturated compounds which result from alkylation of *p*-ethylphenol with the appropriate allylic bromide followed by epoxidation (cf. Bowers, 1969). In addition, a synthetic scheme was adopted for compound 3 (Ro 10-3108) which allows its preparation in kilogram quantities and which avoids major purification steps (cf. Figure 1). Starting from 7-methyl-6-nonen-3-one (Hoffmann et al.,

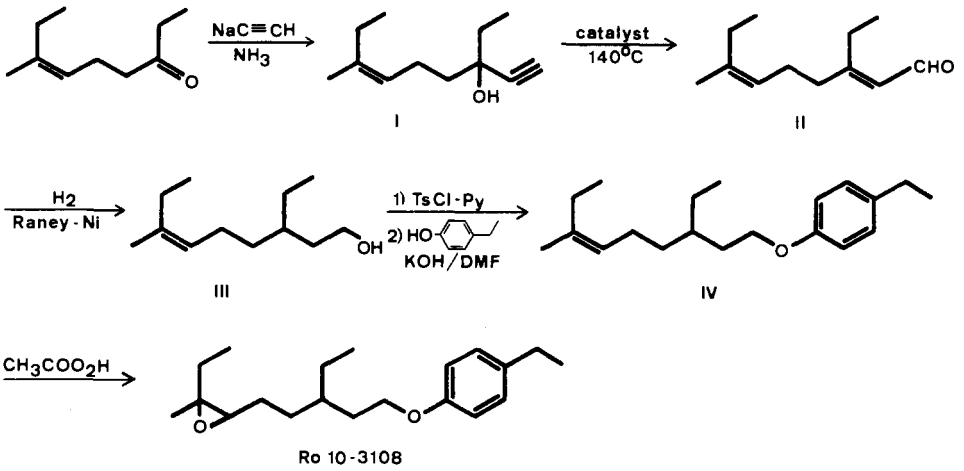


Figure 1. Preparation of Ro 10-3108.

1969; Pfiffner, 1971) the acetylenic carbinol was prepared by the usual ethynylation procedure. For the conversion into the α, β-unsaturated aldehyde we made use of a new process for the isomerization of acetylenic carbinols (Pauling, 1972; Hindley and Andrews, 1974) using a vanadyl *n*-propylate and silanol catalyst composition. Uptake of 2 mol of hydrogen converted the aldehyde (II) to the saturated alcohol (III), which by tosylation, reaction with *p*-ethylphenol in the presence of powdered potassium hydroxide, and peracetic acid treatment was converted to the final product with an overall yield of 46% for the six steps.

PHYSICO-CHEMICAL PROCEDURES

(a) **Determination of the Uv Stability.** The uv stability was determined with a "Spectrotest" apparatus (Original-Hanau) equipped with an 800-W Xenon lamp and a filter UG-11 for solar energy distribution in the near-uv (ca. 370 to 290 nm). The light intensity at the sample surface was approximately ten times that of the sun. The compounds to be tested were applied to commercial thin-layer plates (silica gel 60, Merck) as 0.1% solutions in dioxane. Spots of ca. 0.4 cm^2 were obtained which contained 2 μg of the compound, corresponding to an average area density of 5×10^{-6} g/cm^2. These spots were illuminated for varying periods of time, after which the amount of unaltered material was determined directly on the plates by quantitative thin-layer chromatography using a chromatogram scanner (Carl Zeiss). From these values the time ($t_{1/2}$), in which half of the substance originally present in a spot was degraded by the uv radiation, was ascertained by extrapolation.

(b) **Determination of the Stability in Aqueous Emulsion under Outdoor Conditions.** Emulsions of the compounds studied (20 ppm of active ingredient) in pukka water = standard synthetic field water according to WHO (1964) containing 5000 ppm of urea, 80 ppm of free ammonia, 120 ppm of sodium chloride, 10 ppm of soap, and as much acetic acid as needed to adjust the pH to 7.0) were kept outdoors in glass dishes for 1 week. Initially and after 1 week, known amounts of an internal standard were added to an aliquot of the emulsion and the aqueous phase extracted with ether. The ether solutions were concentrated and the amount of unaltered material determined by gas chromatography on a glass capillary column coated with SF-96 silicone oil.

(c) **Determination of the Hydrolytic Stability.** The relative hydrolytic stabilities were determined in aqueous emulsion of pH 4 at room temperature in the dark. Pairs of compounds were assayed in order to assure absolutely identical conditions for both compounds. In this way the hydrolysis rates obtained could be compared directly. The emulsions therefore contained 10 ppm each of the two compounds investigated and 10 ppm of a nonhydrolyzable internal standard in addition to 30 ppm of an emulsifying agent (Arkopal N-090, Hoechst). Aliquots from these emulsions were drawn at predetermined intervals, extracted with ether, the extracts concentrated, and the amount of unaltered material determined by GC. The hydrolysis rates of the compounds studied were determined relative to the nonhydrolyzable internal standard and were found to follow a first-order law. The half-life times were renormalized to give a relative stability of unity for the least stable of the compounds investigated. A relative stability of 1 corresponds to a half-life time ($t_{1/2}$) $\simeq$ 5–10 hr at pH 4 under the above conditions (absolute values of $t_{1/2}$ vary according to the pair of compounds studied while relative values are independent as determined by double checks).

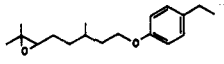
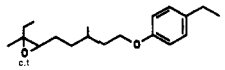
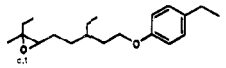
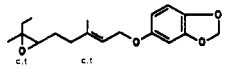
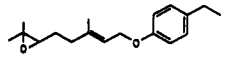
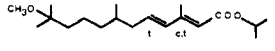
(d) **Determination of the Relative Persistency on Leaves.** Bean leaves were treated with solutions of 0.1% test compound and 0.1% DDT (as internal standard) in acetone. The resulting area densities were ca. 10^{-5} g/cm^2. After 1 week the leaves were extracted with dichloromethane and assayed by capillary GLC. The results were expressed as percent material recovered relative to DDT as internal standard. The absolute values of recovered material relative to the original deposit were lower due to volatility and degradation of DDT (Harrison et al., 1967).

BIOLOGICAL TRIALS

(a) **Effect on Metamorphosis of Summerfruit Tortrix Moth (*Adoxophyes orana*) in the Laboratory.** The bottoms of two petri dishes were treated with acetone solutions of the test compound to give a dosage of 10^{-5}–10^{-10} g of active ingredient/cm^2. After 1 hr, 10 last instar larvae were introduced into each dish fed with artificial diet and incubated at 26°C and 60% relative humidity. After hatching of the adults, the activity was calculated after Abbott (1925) as percent reduction of the total number of adults showing no visible morphogenetic defects (normal imagines). Permament and supernumerary larvae, larval–pupal and pupal–adult intermediates, and dead pupae as well as adults exhibiting any signs of morphogenetic disturbance were considered to be affected, i.e. abnormal.

(b) **Effect on Metamorphosis of Summerfruit Tortrix Moth (*Adoxophyes orana*) in the Field.** *Artificial Infestation.* Eighteen apple trees per variant were sprayed with a 0.1% active ingredient emulsion to the run-off point. Ten days after treatment, a total of 22–27 branches per variant were artificially infested with 5 last

Table I. Results Obtained from Physico-chemical Investigations

Compound			a, $t_{1/2}$, min	b, % material recovered after 1 week (water)	c, rel hydrolytic stability	d, % material recovered after 1 week (plant)
No.	Structure	Code				
1		Ro 10-3109[e]	60		1	
2		Ro 10-6976	60		3	30[i]
3		Ro 10-3108	80	85	6	65
4		Ro 20-3600[f]	1	Traces	~1	~15
5		Ro 08-9801[g]	7	15	1	35[i]
6		Ro 10-6425[h]	13	0	>6	40[i]

[a] Uv stability. [b] Stability in aqueous emulsion under field conditions. [c] Relative hydrolytic stability. [d] Persistency on leaves. For more details see Material and Methods. [e] ENT 34'979. [f] ENT 70'357. [g] R 20'458, ENT 70'221. [h] The related all-trans isomer is identical with ZR-515. [i] Not significantly different in Duncan's multiple range test ($P = 0.05$).

instar larvae trapped in a gauze bag. After hatching of the adults, the activity was calculated after Abbott (1925) as percent reduction of normal imagines (adults with no visible morphogenetic defects); location, Valais, Switzerland.

Natural Population. Thirty apple trees carrying a natural population of summerfruit tortrix moth larvae were treated with a 0.1% active ingredient emulsion of Ro 10-3108 16 days after the officially recommended spraying date for conventional insecticides. When the first larvae started to pupate (14 days after treatment) as many larvae as possible of all stages were collected and fed in the laboratory with leaves from the same plots. After hatching of the adults, the total number of imagines showing no visible signs of morphogenetic disturbances (= normal adults) was counted. Orthene (51% acephate) was used as a standard; location, Valais, Switzerland.

(c) **Effect on a Natural Population of San José Scale (*Quadraspidiotus perniciosus*) in the Field.** Four 3-year-old apple trees (starkrimson variety) carrying a well synchronized population of hibernated first instar larvae were treated with a 0.1% active ingredient emulsion to the run-off point. At regular intervals, the number of crawlers was recorded for each tree; location, Valais, Switzerland.

(d) **Effect on a Natural Population of Citrus Snow Scale (*Unaspis citri*) in the Field.** The trial plot consisted of three white grapefruit trees per variant. On each tree three 1-in. square areas were cleaned of all scales by brushing over a 1-in. square template with a toothbrush 1 week prior to treatment. The first counts of resettled scales were made on the day of treatment to determine the infestation ability of the population. The squares were recleaned and the trees sprayed to run-off (ca. 10 gal per tree). The number of resettled scales was recorded at regular intervals. Ethion was used as a standard; location, Vero Beach, Fla.

RESULTS AND DISCUSSION

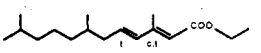
The results of the physico-chemical investigations are summarized in Table I. The review of all the data shows the advantage of Ro 10-3108 over the other compounds tested in this series. It is interesting to note (Table I, column a) that the three saturated compounds **1**, **2**, and **3** proved to be much more stable against uv light than the unsaturated phenyl ethers **4** and **5** as well as the dienoate **6** which has been studied in detail recently (Schooley et al., 1975; Quistad et al., 1975). When compound **3** was tested in water under outdoor conditions, the same superiority could be demonstrated (Table I, column b). Although it is known that replacement of the epoxide by an alkoxy group increases hydrolytic stability (Table I, column c), it could be clearly demonstrated that the epoxides **2** and especially **3** possess a remarkably improved hydrolytic stability in comparison to the other epoxides. We explain this fact by the presence of the ethyl groups in positions 3 and 7. The data in Table I, column d demonstrate that the hydrolytic stability is not the only factor to affect the persistency of a compound on plant material. A good overall chemical stability is an essential prerequisite for the good performance of a compound on plant material. The data from all physico-chemical investigations therefore resulted in the decision to select Ro 10-3108 from the three saturated phenyl ethers for biological studies and to compare its activity with the performance of compounds **4**, **5**, **6**, and **7**.

The data in Tables II, III, and IV show that Ro 10-3108 gives 100% control of summerfruit tortrix moth by inhibiting normal metamorphosis in the laboratory as well as in the field. The same control could also be achieved with this compound if sprayed as a 0.1% active ingredient emulsion to natural populations of the grape berry moth (*Lobesia botrana*) and the larch tortrix moth (*Zeiraphera diniana*).

If tested on a natural San José scale population, Ro 10-3108 was found to be as active as Pacol (3% ethylparathion, 78% mineral oil) (Figure 2). Scheurer and Ruzette (1974) found the sensitive stage toward IGR's in *Aspidiotus nerii* and *Parthenolecanium cornii* to be the second instar in females and the nymphal stage in males. On the other hand, Staal (1975) reported high sensitivity of all stages of *Hemiberlesia lataniae*. Our physiological investigations in the laboratory showed that Ro 10-3108 interferes with the larval molt, with the metamorphosis of males, and with the fertility of females (Vogel et al., 1975).

Similar effects could be demonstrated in field trials on two species of mealy bugs (*Planococcus citri*, *Pseudococcus comstocki*) and on citrus snow scale (*Unaspis citri*). Table

Table II. Effect of Several IGR's on *Adoxophyes orana* in the Laboratory

Compound No.	Code	Structure[a]	Dosage, 10^{-x} g of a.i./cm², x =	% reduction of adults showing no visible morphogenetic defects[b] Trial 1	Trial 2
3	Ro 10-3108		5	100	
			6	100	
			7	100	
			8	100	100
			9		56
			10		44
4	Ro 20-3600[c]		5	100	
			6	100	
			7	100	
			8	68	44
			9		44
			10		0
5	Ro 08-9801[d]		5	100	
			6	100	
			7	67	60
			8		0
			9		0
			10		0
6	Ro 10-6425[e]		5	100	
			6	100	
			7	80	
			8	40	0
			9		0
			10		0
7	Ro 10-2202[f]		5	100	
			6	100	
			7	100	
			8	40	71
			9		0
			10		0

[a] For structures, see Table I. [b] For details see Materials and Methods. [c] ENT 70'357. [d] R 20458, ENT 70'221. [e] The related all-trans isomer is identical with ZR-515 (Methoprene). [f] The related all-trans isomer is identical with ZR-512 (Hydroprene).

Table III. Effect of Different Compounds on Last Instar Larvae of *Adoxophyes orana* in the Field

Compound	Dosage, %	No. bags	Mean no. adults showing no visible morphogenetic defects (normal adults) per bag ± SE
Control		22	3.2 ± 0.3
Ro 10-3108	0.1	22	0 ± 0.0
Ro 20-3600	0.1	26	0.7 ± 0.15
Ro 08-9801	0.1	27	2.3 ± 0.2

Table IV. Effect of Ro 10-3108 on a Natural Population of Summerfruit Tortrix Moth (*Adoxophyes orana*)

Compound	Dosage, %	Total no. of larvae collected	Total no. of normal adults
Control		71	68
Ro 10-3108	0.1	75	0
Orthene	0.1	0[a]	

[a] Orthene is a "knock down" larvicide. All larvae were killed immediately after treatment and dropped to the ground before collection took place.

V shows that Ro 10-3108 is as active against citrus snow scales as Ethion, a standard organophosphate scalecide.

Furthermore, during our 1974 field trials we observed a good side effect of Ro 10-3108 on the population development of rosy apple aphids (*Dysaphis plantaginea*). After treatment of 21 apple trees with 0.1% active ingredient emulsion, only 185 branches became infested with this pest as compared to 942 attacked branches in the case of the untreated control. This observation was fully confirmed by data obtained in specially arranged field

Table V. Effect of Ro 10-3108 on Citrus Snow Scale (*Unaspis citri*) in the Field

Compound	Dosage, %	Mean accumulative no. resettled scales per tree (weeks after treatment) 0	3	6	12	36
Control		185	56	674	>1000	>1000
Ro 10-3108	0.1	117	0	1	24	122
Ethion	0.08	77	0	7	14	104

trials (Meier et al., 1975) with *Acyrthosiphon pisum* and *Phorodon humuli*. It was demonstrated by these authors that Ro 10-3108 performed as well as ZR-777 or ZR-512 against these two aphid species.

Detailed investigations performed by Frischknecht (1975) revealed that Ro 10-3108 stabilizes aphid populations by causing superlarvae (cf. Hangartner et al., 1971) and by preventing normal molt in 4th instar larvae.

In the case of stored product pests, Hoppe and Suchý (1975) found that Ro 10-3108 is able to fully control a population of *Ephestia kühniella* (Mediterranean flour moth), *Plodia interpunctella* (Indian meal moth), *Rhizopertha dominica* (Lesser grain borer), and *Tribolium castaneum* (Red flour beetle) at a dosage of 10 ppm for at least 1 year if the treated material (wheat grain) was stored at normal storage conditions.

As far as the effect on nontarget organisms such as freshwater eels (*Auguilla sp.*), mosquito fish (*Gambusia sp.*), shrimps (*Nontantia sp.*), skimmers (*Sympetrum sp.*), diving beetles (*Columbetes sp.*), and water fleas (*Gammarus sp.*) is concerned, Ro 10-3108 compares favorably with standard insecticides (Hoppe, 1975). Furthermore, Frischknecht (1975) found that the compound does not harm the parasitic wasps *Habrobracon sp.*, predators of

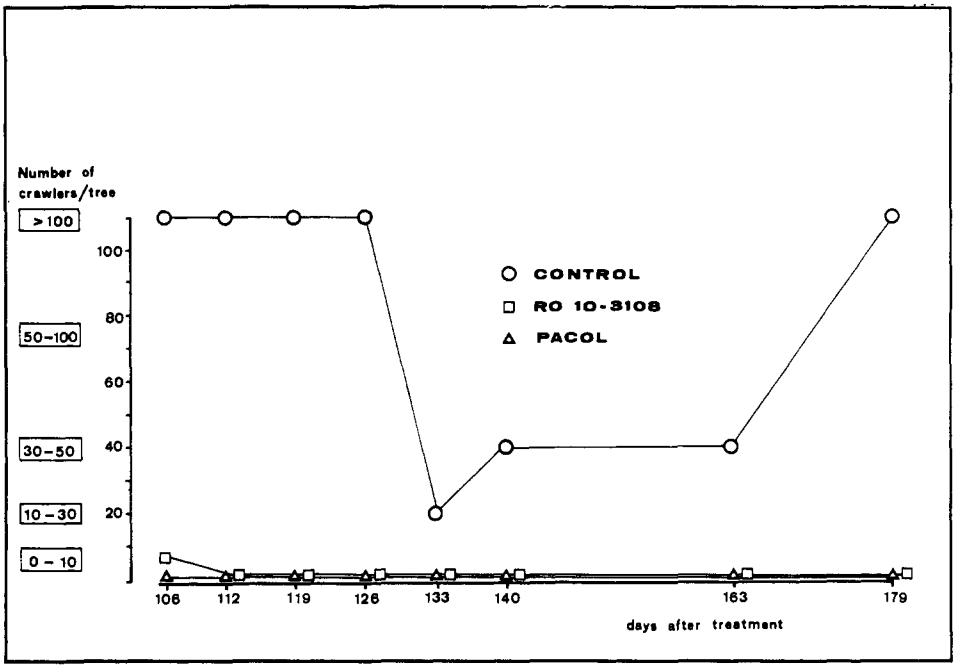


Figure 2. Average number of crawlers of San José scale recorded per tree after treatment with a 0.1% emulsion of Ro 10-3108 in comparison to a 2% emulsion of pacol.

greenhouse white flies, nor does it disturb normal development of *Prospaltella* sp., predator of San José scale. Gerig (1975) demonstrated that honeybees from three beehives placed in a rape field which had been sprayed 4 times during blossom with 1 kg of Ro 10-3108/ha per treatment were not influenced at all. No significant difference in the behavior of the bee colonies or in the quality and quantity of the brood could be observed in comparison to control colonies in this praxis-oriented trial.

Encouraging results were also obtained in the case of mammals. The acute oral LD_{50} values for mice and rats were in excess of 8000 mg/kg. The LD_{50} values after 5 oral administrations at daily intervals were 5400 ± 450 mg/kg for mice and higher than 8000 mg/kg for rats. In addition, skin and eye irritation tests gave favorable results and guppies and rainbow trouts survived a 96-hr exposure to a 5000-ppm suspension of Ro 10-3108. Additional toxicological studies including a long-term feeding study are in progress.

To demonstrate its biodegradability, Ro 10-3108 was exposed to air and sunlight in polluted water for 4 weeks. Five important degradation products (Figure 3) found in this experiment result from physico-chemical or biological attack on the epoxide moiety leading to hydration or rearrangement and from α oxidation of the ethyl group on the aromatic ring (cf. Hoffmann et al., 1973; Gill et al., 1974; Hammock et al., 1974). The results of a detailed study of the metabolism of Ro 10-3108 will be published later (Dorn et al., 1976).

CONCLUSIONS

We were able to demonstrate that Ro 10-3108 is sufficiently stable to be used in plant protection programs without sophisticated formulations. Furthermore, it could be shown in practice that the application of an IGR can inhibit crop damage in two ways: (a) the whole population to be controlled is eliminated as the result of the morphogenetic effect of the compound applied (model: summerfruit tortrix moth); (b) the initial population is not completely controlled but stabilized below the damage level (model: San José scale). The additional positive properties of Ro 10-3108, namely the favorable toxicological data as well as the biodegradability, should be considered as a stimulus for further intensive research in this area.

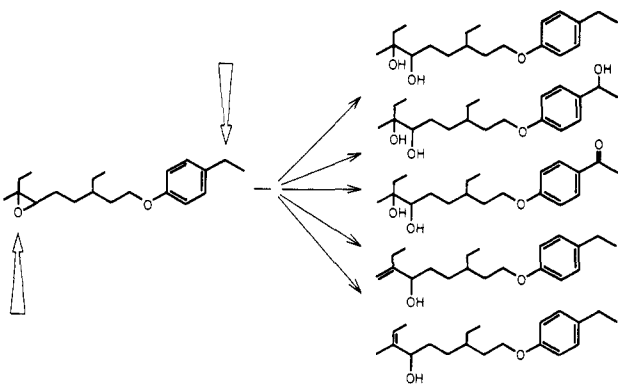


Figure 3. Major degradation products of Ro 10-3108 after exposure to air and sunlight in polluted water for 4 weeks.

EXPERIMENTAL SECTION

3-Ethyl-7-methyl-6-nonen-1-yn-3-ol (I). A well-dried 1.5-l. four-necked flask equipped with a gas inlet tube, a mechanical stirrer, an addition funnel, and dry ice condenser was filled under cooling with approximately 1000 ml of liquid ammonia. While introducing acetylene at a fast rate 7.8 g of potassium and 46 g of sodium were added in small portions. After the metal had dissolved the cooling bath was removed and while still introducing acetylene 300 g of 7-methyl-6-nonen-3-one was added dropwise over 1 hr. The reaction mixture was allowed to reflux for 2 hr. Ammonium chloride (120 g) was added in small portions with caution and the ammonia was allowed to evaporate overnight. The next day 600 ml of ether was added and the remaining ammonia was removed at room temperature. After 600 ml of water had been added the ethereal layer was separated and washed twice with a total of 1000 ml of 0.5 *N* sulfuric acid and twice with a total of 600 ml of water. The aqueous solutions were reextracted with ether and the combined organic solution dried (Na_2SO_4) and evaporated. The crude product was distilled through a Fenske column giving 306 g (87.5%) of carbinol (I), 96.5% pure by GLC (cis/trans ratio, 35.7/60.8): bp 107–109°C (12 Torr); NMR ($CDCl_3$) δ 0.82–1.18 (triplets, 6, C-3 and

C-7 CH_2CH_3 cis and trans isomers), 1.60–1.70 (broad signal, 3, C-7 CH_3 cis and trans), 2.44 (s, 1, C≡C*H*), 5.17 (t, 1, J = 7 Hz, H-6). Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.63; H, 11.21.

3-Ethyl-7-methyl-2,6-nonadien-1-al (II). A mixture of 100 g of 3-ethyl-7-methyl-6-nonen-1-yn-3-ol (I), 33 g of triphenylsilanol, 2.4 g of tri-*n*-propyl orthovanadate, 2 g of stearic acid, and 1000 ml of paraffin oil (high melting point) was heated 4.5 hr at 140°C under argon. The aldehyde was distilled off under high vacuum (ca. 0.5 Torr). The crude product was purified by fractional distillation using a 60-cm column. The major fraction, 72.8 g (73%), had a boiling point of 84–87°C (0.08 Torr): purity by GLC (cis/trans mixture) 96%; NMR ($CDCl_3$) δ 0.98, 1.11, and 1.18 (t, 6, J = 7 Hz, C-3 and C-7 CH_2CH_3 cis/trans isomers), 1.61 and 1.68 (d, 3, J = 1 Hz, C-7 CH_3 cis and trans), 5.10 (broad signal, 1, H-2), 5.85 (d, 1, J = 8 Hz, H-6), 9.99 and 10.04 (d, 1, J = 8 Hz, C*H*O cis and trans). Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.78, H, 11.20.

3-Ethyl-7-methyl-6-nonen-1-ol (III). To a solution of 37.8 g of aldehyde (II) and 80 ml of ethanol, 1 g of sodium carbonate and 4 ml of water were added. After 3 g of Raney nickel had been added the mixture was hydrogenated until the uptake of hydrogen had ceased. After removal of the catalyst by filtration the solution was concentrated in a rotary evaporator and the residue dissolved in 100 ml of hexane. The solution was washed four times with water, the aqueous solutions were reextracted with hexane, and the combined organic solution was dried (Na_2SO_4) and evaporated to give 39.3 g of product sufficiently pure to be used for the next step: purity by GLC 95.7%; bp 125°C (10 Torr); NMR ($CDCl_3$) δ 0.88 (t, 3, J = 6, 5 Hz, C-3 CH_2CH_3), 0.98 (t, 3, J = 6, 5 Hz, C-7 CH_2CH_3), 1.61 and 1.68 (d, 3, J = 1 Hz, C-7 CH_3 cis and trans), 3.65 (t, 2, J = 6, 5 Hz, OCH_2), 5.10 (t, 1, J = 6, 5 Hz, H-6). Anal. Calcd for $C_{12}H_{24}O$: C, 78.19; H, 13.13. Found: C, 77.97; H, 13.37.

3-Ethyl-7-methyl-6-(*cis/trans*)-nonen-1-ol *p*-Toluenesulfonate. To a stirred mixture of 55.6 g of 3-ethyl-7-methyl-6-nonen-1-ol and 50 ml of pyridine cooled in an ice bath, 65 g of *p*-toluenesulfonyl chloride was added in small portions over 50 min. After being stirred for 5 hr at 0–5°C, the reaction mixture was poured into a mixture of 250 ml of ice–water and 90 ml of concentrated hydrochloric acid and extracted three times with ether. The ether layer was thoroughly washed with water and brine, dried (Na_2SO_4–K_2CO_3), and evaporated to give 97.6 g of crude product which was used without further purification for the next step. An analytical sample was prepared by chromatography on silica gel using a mixture of hexane–ether containing 0.1% pyridine as eluent: ir (film) 1175, 1190, 1360, and 1600 cm^{-1}; NMR ($CDCl_3$) δ 2.48 (s, 3, $ArCH_3$), 4.10 (t, 2, J = 6, 5 Hz, OCH_2), 5.07 (t, 1, J = 7 Hz, H-6), 7.39, 7.86 (2 d, 4, J = 8.5 Hz, aromatic H). Anal. Calcd for $C_{19}H_{30}O_3S$: C, 67.41; H, 8.93; S, 9.47. Found: C, 67.32; H, 9.05; S, 9.66.

1-(*p*-Ethylphenoxy)-3-ethyl-7-methyl-6-(*cis/trans*)-nonene (IV). To a stirred solution of 44 g of *p*-ethylphenol in 135 ml of dimethylformamide, cooled in an ice bath, 22 g of potassium hydroxide (freshly pulverized) was added in small portions over 1 hr under nitrogen. After 4 hr stirring at room temperature, the mixture was cooled to 0°C and a solution of 97.6 g of crude tosylate in 35 ml of dimethylformamide was added dropwise over 1 hr. Stirring was continued for 40 hr at room temperature; the reaction mixture was then poured into 400 ml of ice–water and extracted three times with a total of 500 ml of hexane. The hexane layer was washed several times with water and dried over sodium sulfate. The dried solution was filtered through a column of 150 g of silica gel in hexane and hexane–ethyl acetate (98:2) and the resulting product was dried under high vacuum to give 64.5 g (77.5%) of crude product, 96.7% pure by GLC analysis, the major impurity being the *p*-toluenesulfonate of *p*-ethylphenol: bp 126°C (0.04 Torr); NMR ($CDCl_3$) δ 0.89 and 0.97 (2 t, 6, J = 5.5 Hz, C-3 and C-7 CH_2CH_3), 1.20 (t, 3, J = 7 Hz, $ArCH_2CH_3$), 1.60 (d, 3, J = 1 Hz, C-7 CH_3), 2.58 (q, 2, J = 7 Hz, $ArCH_2CH_3$), 3.95 (t, 2, J = 6.5 Hz, OCH_2), 5.11 (t, 1, J = 7 Hz, H-6), 6.78, 7.11 (2 d, 4, J = 8.5 Hz, aromatic H). Anal. Calcd for $C_{20}H_{32}O$: C, 83.27; H, 11.18. Found: C, 83.61; H, 11.06.

6,7-Epoxy-1-(*p*-ethylphenoxy)-3-ethyl-7-methylnonane (Ro 10-3108). To a stirred mixture of 22 g of 1-(*p*-ethylphenoxy)-3-ethyl-7-methyl-6-(*cis/trans*)-nonene, 5 g of sodium acetate, and 100 ml of chloroform, cooled in an ice bath, was added 15.3 ml of peracetic acid (40%) dropwise over 90 min. After being stirred for another 30 min at 0°C the reaction mixture was poured into 600 ml of ice–water. The organic layer was separated and washed twice with 10% aqueous sodium bicarbonate, 10% aqueous sodium thiosulfate, and brine. The aqueous solutions were reextracted with chloroform and the combined chloroform solutions dried and evaporated to constant weight. The product, 22.2 g (95%), gave a correct elemental analysis. Its purity by TLC was estimated to be 92–95% (98% by GLC). The three major impurities were identified as the starting material (IV), the *p*-toluenesulfonate of *p*-ethylphenol, and 3-ethyl-7-methylnonyl *p*-ethylphenyl ether, obviously due to some overhydrogenation to 3-ethyl-7-methylnonan-1-ol which was subsequently carried through the reaction sequence. The product is a colorless liquid boiling at 132–134°C (0.02 Torr): $n^{20}D$ 1.4955; NMR ($CDCl_3$) δ 1.20 (t, 3, J = 7 Hz, $ArCH_2CH_3$), 1.23 (s, 3, C-7 CH_3), 2.62 (q, 2, J = 7 Hz, $ArCH_2CH_3$), 2.73 (t, 1, J = 5 Hz, H-6), 3.95 (t, 2, J = 6.5 Hz, OCH_2), 6.80, 7.12 (2 d, 4, J = 8.5 Hz, aromatic H). Anal. Calcd for $C_{20}H_{32}O_2$: C, 78.90; H, 10.59. Found: C, 78.78; H, 10.59.

6,7-Epoxy-1-(*p*-ethylphenoxy)-3,7-dimethylnonane (Ro 10-6976). 6,7-Epoxy-1-(*p*-ethylphenoxy)-3,7-dimethyl-2-nonene (5 g) was dissolved in 100 ml of ethyl acetate and hydrogenated in the presence of 0.1 g of platinum oxide until no more uptake of hydrogen could be observed. The catalyst was then filtered off and the filtrate evaporated. The crude product containing minor amounts of by-products arising from hydrogenolysis was purified by column chromatography on silica gel. The fractions eluted with hexane–ether (19:1) contained 4.2 g (84%) of product (99% pure by GLC, mixture of *cis*- and *trans*-epoxide): bp 125°C (0.02 Torr); $n^{20}D$ 1.4905; NMR ($CDCl_3$) δ 0.92 (t, 3, J = 7 Hz, CH_3CH_2), 0.95 (d, 3, J = 7 Hz, C-3 CH_3), 1.17 (t, 3, J = 7 Hz, $ArCH_2CH_3$), 1.21 and 1.25 (2 s, 3, C-7 CH_3 cis and trans), 2.56 (q, 2, J = 7 Hz, $ArCH_2CH_3$), 2.67 (t, 1, J = 7 Hz, H-6), 3.95 (t, 2, J = 6.5 Hz, OCH_2), 6.78 and 7.08 (2 d, 4, J = 8.5 Hz, aromatic H). Anal. Calcd for $C_{19}H_{30}O_2$: C, 78.57; H, 10.41. Found: C, 78.97; H, 10.58.

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Volatile Components of Pecan Leaves and Nuts, *Carya illinoensis* Koch

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The volatile constituents of leaves and immature pecan nuts (including the shucks), *Carya illinoensis* Koch (Juglandaceae), were analyzed by GLC–MS and found to contain 38 compounds including 7 monoterpene hydrocarbons, 7 sesquiterpene hydrocarbons, 11 terpene alcohols, 1 terpene aldehyde, 1 terpene ketone, and 11 other aldehydes, ketones, alcohols, and esters. These studies were initiated to identify those constituents that could conceivably attract the pecan weevil, *Curculio caryae* Horn, to the leaves and nuts, their primary food source. The constituents could also be precursors of the pecan weevil sex pheromone.

Pecans, *Carya illinoensis* Koch (Juglandaceae), are commercially grown in a "Belt" across the southern United States that includes North Carolina, South Carolina, Georgia, Florida, Alabama, Mississippi, Louisiana, Arkansas, Oklahoma, Texas, New Mexico, and Arizona. The pecan trees are attacked by several insects including the pecan weevil, *Curculio caryae* Horn. Indeed, in one central Mississippi orchard (Neel, 1970), 30–40% of the pecans were infested. Likewise, the average weevil population per tree in an Oklahoma orchard in 1968 and 1969 was estimated to be 1962 and 6130, respectively (Raney et al., 1970).

The work reported herein was a survey of the volatile components from pecan leaves and nuts made in anticipation of a further effort to determine any role in plant attraction and nutrition of the pecan weevil. The preliminary work on the pecan weevil sex attractant was reported recently by Mody et al. (1973).

A search of the literature revealed that mature pecan leaves and nuts have been analyzed for various constituents and properties including sterols and choline, carbohydrates, fatty acids in the oil, trace elements, growth regulators, amino acids and proteins, minerals, and vitamins. However, the only study of volatile constituents was made with roasted pecans by Wang and Odell (1972). They found 19 carbonyl compounds, pyridine, 8 pyrazines, 7 acids, 5 alcohols, and 1 lactone. The presence of most of these components is due to roasting, because except for 2-furfuraldehyde they are not found in unroasted pecans.

EXPERIMENTAL SECTION

Preparation of Essential Oil. Fresh, mature pecan leaves of the cultivar Stuart were gathered in July. Green nuts with shucks (involucre) and shells that had not hardened and with kernels that were in the water stage were gathered in August. Both the leaves and the nuts

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