extracted with $CHCl_3$. When the $CHCl_3$ solution was dried ($MgSO_4$) and distilled to dryness, it yielded 2.25 g of crystalline product. Recrystallization from acetone and hexane gave an analytical sample, mp 172°, nmr peak at 65 (C-13 methyl) cps.

Anal. Calcd for $C_{19}H_{26}O_4$: C, 71.67; H, 8.23. Found: C, 71.47; H, 8.12.

3-Methoxyestra-1,3,5(10)-triene-11β,16β,17β-triol 16,17-Acetonide (7).—A solution of 50 mg of **6d** and 5 mg of *p*-toluenesulfonic acid in 10 ml of acetone was refluxed for several minutes, cooled, neutralized with pyridine, and evaporated to dryness. The crystalline residue was triturated with MeOH and collected by filtration. Recrystallization of the crude product from Et_2O and hexane gave an analytical sample: mp 184–186°; nmr peaks at 66.5, 80, and 90 (3 methyl groups) cps.

Anal. Calcd for $C_{22}H_{30}O_4$: C, 73.71; H, 8.44. Found: C, 73.48; H, 8.33.

17α-Ethynylestra-1,3,5(10)-triene-3,11β,17β-triol (8a).—To a mixture of 17 g of lithium acetylide—ethylenediamine complex in 100 ml of DMSO at 25° was added with stirring a solution of 8 g of **4b** in 150 ml of DMSO. The mixture was stirred for 2 hr and then added with vigorous stirring to a mixture of 200 g of ice and 1 l. of cold H_2O. The solution was diluted with H_2O to 2 l. and then adjusted to about pH 7 with 4 *M* HCl. The crude product was collected by filtration, washed with H_2O, and dried *in vacuo* at 60°. It weighed 6.3 g and melted at 265–272°. Crystallization of the crude product from MeOH–CH_2Cl_2 gave an analytical sample: mp 279–281° (lit.[9] mp 294°); $[\alpha]_D$ +111.5 (pyridine); λ_{max} (KBr) 2.83, 2.99, 3.01, 6.15, and 6.29 μ.

Anal. Calcd for $C_{20}H_{24}O_3$: C, 76.89; H, 7.74. Found: C, 76.70; H, 7.78.

3-Methoxy-17α-ethynylestra-1,3,5(10)-trien-11β-ol (8b).—When 3 g of **4d** was ethynylated according to the procedure described for the preparation of **8a**, 2.75 g of crude product, mp 172–175°, was obtained. Recrystallization from acetone and hexane gave an analytical sample: mp 176–177°; $[\alpha]_D$ +79°; λ_{max} 2.77, 3.03, and 6.22 μ.

Anal. Calcd for $C_{21}H_{26}O_3$: C, 77.27; H, 8.03. Found: C, 77.24; H, 7.92.

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Insect Sex Attractants. VII. 5,9-Tridecadien-1-ol Acetates[1]

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The stereochemical configuration of insect attractants often determines their activity. For example, the sex attractant of the silkworm moth, *Bombyx mori* L., is the *trans, cis* isomer of 10,12-hexadecadien-1-ol; the other three isomers are much less active.[2–6] When the sex attractant of the pink bollworm moth was elucidated as 10-propyl-*trans*-5,9-tridecadien-1-ol acetate by Jones, *et al.*,[7] we decided to prepare analogs to evaluate attractancy and structure–activity relationships.[8]

The method used to prepare the 5,9-tridecadienyl acetates is shown in Chart I. The tetrahydropyranyl ether of 5-hexyn-1-ol was alkylated with the *cis* or *trans* isomer of 1-bromo-3-heptene (**2**) in dioxane by using lithium amide. Reduction of the isomers (**3**) in sodium–liquid ammonia or by hydrogenation over poisoned Pd–$CaCO_3$ yielded the tetrahydropyranyl ethers of 5,9-tridecadien-1-ol (**4**). Prolonged refluxing of these ethers with acetic acid–acetyl chloride cleaved the tetrahydropyran group to form the desired 5,9-tridecadienyl acetates (**5**).

CHART I

$RO(CH_2)_4C{\equiv}CH + Br(CH_2)_2CH{=}CH(CH_2)_2CH_3 \longrightarrow$

1

2a, *cis*
b, *trans*

$RO(CH_2)_4C{\equiv}C(CH_2)_2CH{=}CH(CH_2)_2CH_3 \longrightarrow$

3a, *cis*
b, *trans*

$RO(CH_2)_4CH{=}CH(CH_2)_2CH{=}CH(CH_2)_2CH_3 \longrightarrow$

4a, *cis*-5, *cis*-9
b, *cis*-5, *trans*-9
c, *trans*-5, *cis*-9
d, *trans*-5, *trans*-9

$CH_3CO_2(CH_2)_4CH{=}CH(CH_2)_2CH{=}CH(CH_2)_2CH_3$

5a, *cis*-5, *cis*-9
b, *cis*-5, *trans*-9
c, *trans*-5, *cis*-9
d, *trans*-5, *trans*-9

R = 2-tetrahydropyranyl

The 5,9-tridecadienyl acetates were colorless liquids with similar infrared spectra, except that intensities varied for the *trans* peak at 960 cm^{-1} and the *cis* peak at 720 cm^{-1}. Since each isomer contained certain amounts of the three remaining isomers as impurities, the *trans* content of each acetate was determined by infrared spectroscopy,[9] using elaidyl acetate as a standard. The results obtained are shown in Table I.

Attractancy Tests.—The acetates **5** were evaluated as attractants for male and female Mexican fruit flies, *Anastrepha ludens* (Lowe); Mediterranean fruit flies, *Ceratitis capitata* (Wiedemann); oriental fruit flies, *Dacus dorsalis* (Hendel); melon flies, *D. cucurbitae* Coquillet; male fall armyworms, *Spodoptera frugiperda* (J. E. Smith); codling moths, *Carpocapsa pomonella* L.; gypsy moths, *Porthetria dispar* L.; cabbage loopers, *Trichoplusia ni* (Hübner); and pink bollworm moths. The *cis*-5,*cis*-9 and *trans*-5,*cis*-9 acetates were attractive to fall armyworms in the laboratory and the *cis*-5, *trans*-9 acetate caused copulatory behavior in male cabbage looper moths. All other test results were negative.

Experimental Section[10]

2-(5-Hexynyloxy)tetrahydropyran (1).—Dihydropyran (25.2 g, 0.30 mole) was added to 24.5 g (0.25 mole) of 5-hexyn-1-ol and 5 drops of concentrated HCl, with stirring. The solution was cooled to keep the temperature below 40° and then stirred at room temperature for 3 hr. Excess Na_2CO_3 was added to the

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(10) Infrared spectra were obtained with a Perkin-Elmer 521 spectrophotometer. Gas chromatographic analyses were performed on a F and M Model 500 gas chromatograph with a flame ionization detector by using a column of 5% Carbowax 20M on 60–80 mesh base-washed Chromosorb W (60.9 × 0.03 cm). An approximate flow rate of 75 ml of N_2/min was maintained. Company and trade names are given for identification purposes only and do not constitute endorsement by the U. S. Department of Agriculture.

Table I

Content of *trans* Unsaturation in 5,9-Tridecadien-1-ol Acetate Isomers

Isomer	*trans* unsaturation, %
5a	10.6
5b	39.0
5c	50.0
5d	91.0

solution, and stirring was continued for an additional 1 hr. After filtration, the filtrate was distilled to yield, after a small forerun, 42.4 g (93%) of colorless liquid, bp 55–60° (0.05 mm), $n^{25}\mathrm{D}$ 1.4575 (lit.[7] bp 70–80° (0.3 mm), $n^{25}\mathrm{D}$ 1.4556).

1-Bromo-*cis*-3-heptene (2a).—Reaction between *cis*-3-hepten-1-ol and PBr_3 by the procedure of Crombie[11] gave **2a** (68.5%), bp 69–72° (18 mm), $n^{25}\mathrm{D}$ 1.4671 (lit.[11] bp 68–72° (15 mm), $n^{25}\mathrm{D}$ 1.4705).

1-Bromo-*trans*-3-heptene (2b).—In like manner, reaction between *trans*-3-hepten-1-ol and PBr_3 gave **2b** (50%), bp 70–74° (18 mm), $n^{24}\mathrm{D}$ 1.4678 (lit.[11] bp 172–175°, $n^{25}\mathrm{D}$ 1.4641).

Tetrahydro-2-(*cis*-9-tridecen-5-ynyloxy)pyran (3a).—Compound 1 (5.2 g, 0.028 mole) was added with stirring to a mixture of 0.65 g (0.028 mole) of $LiNH_2$ and 31.4 ml of dry purified dioxane under N_2. The reaction mixture was refluxed for 3.5 hr and cooled, and 5.0 g (0.028 mole) of 1-bromo-*cis*-3-heptene (**2a**) was added dropwise. Refluxing was continued for 17 hr; then H_2O (57 ml) was added to the mixture. The solution was extracted three times with ether, and the ether extracts were washed (NaCl solution). The combined ether extracts were dried (Na_2SO_4) and distilled to give, after a small forerun, 3.4 g (43%) of colorless liquid: bp 110–112° (0.07 mm); $n^{25}\mathrm{D}$ 1.4735; ir, 715 (*cis* CH=CH), 2930 (broad CH), and 1200–1040 cm^{-1} (tetrahydropyranyl); gas chromatographic analysis, sharp peak, retention time 427 sec, column at 135°.

Anal. Calcd for $C_{18}H_{30}O_2$: C, 77.65; H, 10.86. Found: C, 77.59; H, 10.92.

Tetrahydro-2-(*trans*-9-tridecen-5-ynyloxy)pyran (3b).—Reaction between 1 and 1-bromo-*trans*-3-heptene (**2b**) by the previous procedure gave **3b** (41%): bp 119° (0.05 mm); $n^{25}\mathrm{D}$ 1.4719; ir, 967 cm^{-1} (*trans* CH=CH) instead of at 715 cm^{-1}, as well as for the other groups described for **3a**; gas chromatographic analyses, sharp peaks with retention times of 312 and 420 sec at 140 and 135°, respectively.

Anal. Calcd for $C_{18}H_{30}O_2$: C, 77.65; H, 10.86. Found: C, 77.50; H, 10.70.

Tetrahydro-2-(*cis*-5,*cis*-9-tridecadienyloxy)pyran (4a).—A solution of 5.0 g (0.018 mole) of **3a** in 20 ml of absolute EtOH was hydrogenated at room temperature, by using 0.35 g of 5% Pd–$CaCO_3$ and 2 drops of quinoline. When the required amount of H_2 for one double bond had been absorbed (445 ml at 29° (760 mm)), the reaction was interrupted. The mixture was filtered, freed of solvent, and distilled to yield 3.7 g (73%) of colorless liquid, bp 106–107.5° (0.03 mm), $n^{25}\mathrm{D}$ 1.4682; ir, increased absorption at 720 cm^{-1} for *cis* double bonds over that found in **3a**; gas chromatography, sharp peak, retention time 216 sec at 135°.

Anal. Calcd for $C_{18}H_{32}O_2$: C, 77.09; H, 11.50. Found: C, 76.86; H, 11.43.

Tetrahydro-2-(*cis*-5,*trans*-9-tridecadienyloxy)pyran (4b).—Reduction of **3b** by the procedure used to obtain **4a**, with 3% by weight of catalyst, gave **4b** (84%), bp 104.5–108.5° (0.03 mm), $n^{27}\mathrm{D}$ 1.4670. The infrared spectrum was identical with that of **3b** except for the additional absorption of the *cis* double bond at 720 cm^{-1}; gas chromatography, sharp peak, retention time 228 sec at 135°.

Anal. Calcd for $C_{18}H_{32}O_2$: C, 77.09; H, 11.50. Found: C, 77.19; H, 11.54.

Tetrahydro-2-(*trans*-5,*cis*-9-tridecadienyloxy)pyran (4c).—To a mixture of 2.0 g (0.090 g-atom) of Na in approximately 200 ml of liquid NH_3 was added dropwise, with stirring, 5.0 g (0.018 mole) of **3a** at −76°. Ether (10 ml) was added, and the NH_3 was allowed to reflux for 5 hr. The reaction mixture was again cooled to −76°, and excess NH_4Cl and 20 ml of ether were added. After the mixture stood overnight, 50 ml of ether and H_2O (25 ml) were added under N_2. The aqueous phase was extracted twice with ether; the combined ether layers were washed (cold H_2O, cold 5% HCl, 5% Na_2CO_3, NaCl solution). The ether solution was dried (Na_2SO_4) and distilled to give 4.0 g (80%) of colorless liquid, bp 106–110° (0.03 mm), $n^{28}\mathrm{D}$ 1.4667. The infrared spectrum of the product was identical with that of **4b**; gas chromatography, sharp peak, retention time 240 sec at 135°.

Anal. Calcd for $C_{18}H_{32}O_2$: C, 77.09; H, 11.50. Found: C, 76.90; H, 11.50.

Tetrahydro-2-(*trans*-5,*trans*-9-tridecadienyloxy)pyran (4d).—Reduction of **3b** by the previous procedure gave the desired product (72%): bp 105–109° (0.03 mm); $n^{25}\mathrm{D}$ 1.4660; ir, identical with that of **3b** except for increased *trans* double bond absorption at 965 cm^{-1}; gas chromatography, sharp peak, retention time 180 sec at 140°.

Anal. Calcd for $C_{18}H_{32}O_2$: C, 77.09; H, 11.50. Found: C, 76.80; H, 11.66.

***cis*-5,*cis*-9-Tridecadien-1-ol Acetate (5a).**—A solution of 3.3 g (0.012 mole) of **4a**, 12 ml of AcOH, and 3.3 g (0.042 mole) of AcCl was refluxed for 7 hr and then allowed to stand overnight. The solution was poured onto ice diluted to about 100 ml with saturated NaCl and extracted three times with ether. The combined ether layers were washed (three times with H_2O and with 5% Na_2CO_3 and then twice with NaCl), and the ether extract was dried (Na_2SO_4) and distilled to yield 2.3 g of colorless liquid.

The remaining three geometrical isomers were prepared in the same manner. All isomers showed satisfactory analyses for $C_{15}H_{26}O_2$. Table II lists the physical properties of the four isomers obtained.

Table II

Geometric Isomers of 5,9-Tridecadien-1-ol Acetate

Isomer	Bp, °C (mm)	$n\mathrm{D}$ (°C)	% yield	Ir, cm^{-1}	Glc (125°) retention, sec
5a	81–85 (0.02)	1.4540 (26)	80	720	126
5b	80–85 (0.05)	1.4540 (25)	84	970	120
5c	87–89 (0.03)	1.4534 (26)	86	970	126
5d	74–76 (0.02)	1.4522 (26)	63	967	120

Elaidyl Acetate.—Elaidic acid (Hormel) was reduced with $LiAlH_4$.[12] The resulting alcohol was acetylated with an acetic acid–acetyl chloride mixture.

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