double bond impurity. Gas chromatography revealed a single sharp peak, retention time 282 sec at 170° and 30 cc of N_2/min.

Anal. Calcd for $C_{16}H_{30}O_2$: C, 75.53; H, 11.89. Found: C, 75.37; H, 12.02.

Acknowledgment.—The author wishes to thank Mr. Martin Jacobson of this division, Beltsville, Md., for helpful suggestions and discussions.

Insect Sex Attractants. X. 5-Dodecen-1-ol Acetates, Analogs of the Cabbage Looper Sex Attractant[1]

DAVID WARTHEN AND MARTIN JACOBSON

Entomology Research Division, U. S. Department of Agriculture, Beltsville, Maryland 20705

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In a continuing investigation of sex attractants for the control of insect pests,[2] the *cis* and *trans* isomers of 5-dodecen-1-ol acetate were synthesized. These compounds are analogs of *cis*-7-dodecen-1-ol acetate, the sex attractant produced by the female cabbage looper, *Trichoplusia ni* (Hübner), and synthesized by Berger and Green, *et al.*[3,4]

The method used to prepare the 5-dodecen-1-ol acetates is shown in Chart I. The tetrahydropyranyl

CHART I

$$\underset{\mathbf{1}}{RO(CH_2)_4C{\equiv}CH} \xrightarrow[\text{dioxane}]{C_6H_{13}Br,\ LiNH_2} \underset{\mathbf{2}}{RO(CH_2)_4C{\equiv}C(CH_2)_5CH_3} \xrightarrow[H_2,\ Pd\text{-}CaCO_3]{Na\text{–}NH_3\ or}$$

$$RO(CH_2)_4CH{=}CH(CH_2)_5CH_3 \xrightarrow{AcOH\text{–}AcCl} CH_3CO_2(CH_2)_4CH{=}CH(CH_2)_5CH_3$$

3a, *cis*-5; **b**, *trans*-5 — **4a**, *cis*-5; **b**, *trans*-5

R = 2-tetrahydropyranyl

ether of 5-hexyn-1-ol was alkylated with hexyl bromide. Reduction of **2** in sodium–liquid ammonia or in the presence of poisoned Pd–$CaCO_3$ yielded almost exclusively the *trans* or *cis* isomer,[5-7] respectively, of the tetrahydropyranyl ethers of 5-dodecen-1-ol (**3**). Subsequent refluxing with acetic acid–acetyl chloride cleaved the tetrahydropyranyl group to form the desired 5-dodecen-1-ol acetates (**4**).

The acetates **4a** and **4b** were evaluated as attractants for male and female Mexican fruit flies, *Anastrepha ludens* (Loew); Mediterranean fruit flies, *Ceratitis capitata* (Wiedemann); oriental fruit flies, *Dacus dorsalis* (Hendel); melon flies, *Dacus cucurbitae* (Coquillet); male fall armyworm, *Spodoptera frugiperda* (J. E. Smith); codling moths, *Carpocapsa pomonella* L.; gypsy moths, *Porthetria dispar* L.; cabbage loopers and pink bollworm moths, *Pectinophora gossypiella* (Saunders). The *cis* and *trans* isomers of 5-dodecen-1-ol acetate were found in laboratory tests to be less attractive to cabbage loopers than *cis*-7-dodecen-1-ol acetate. All other test results were negative.

Experimental Section[8,9]

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 $NaHCO_3$ was added to the solution, and stirring was continued for an additional 1 hr. After filtration, the filtrate was distilled to yield, after a small forerun, 42.6 g (93%) of colorless liquid, bp 52–57° (0.03 mm), $n^{25}D$ 1.4579 (lit.[10] bp 70–80° (0.3 mm), $n^{25}D$ 1.4556).

2-(5-Dodecynyloxy)tetrahydropyran (2).—Compound 1 (40.0 g, 0.22 mole) was added with stirring to a mixture of 5.1 g (0.22 mole) of $LiNH_2$ and 250 ml of dry dioxane (purified by refluxing over Na and then distilling) under N_2. The reaction mixture was refluxed for 3.5 hr and cooled, and 36.3 g (0.22 mole) of hexyl bromide was added dropwise. Refluxing was continued for 17 hr; then H_2O (250 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, 27.2 g (47%) of colorless liquid: bp 105–108° (0.06 mm); $n^{24}D$ 1.4630; ir, 2930 (broad CH) and 1200–1040 cm^{-1} (tetrahydropyranyl); gas chromatography, single sharp peak, retention time 336 sec at 150° and 40 cc of N_2/min.

Anal. Calcd for $C_{17}H_{30}O_2$: C, 76.64; H, 11.35. Found: C, 76.50; H, 11.41.

2-(*cis*-5-Dodecenyloxy)tetrahydropyran (3a).—A solution of 10.0 g (0.038 mole) of **2** in 40 ml of absolute EtOH was hydrogenated at room temperature, by using 300 mg of 5% Pd–$CaCO_3$ and 2 drops of quinoline. When the required amount of H_2 for one double bond had been absorbed (920 ml at 26° and 760 mm), the reaction was interrupted. The mixture was filtered, freed of solvent, and distilled to yield 8.8 g (87%) of colorless liquid, bp 96–99° (0.04 mm), $n^{25}D$ 1.4578. The ir spectrum showed absorption at 720 cm^{-1} (*cis* CH=CH) and a very weak bond at 965 cm^{-1} representing *trans* double bond impurity. Gas chromatography showed a single sharp peak, retention time 102 sec at 150° and 40 cc of N_2/min.

Anal. Calcd for $C_{17}H_{32}O_2$: C, 76.06; H, 12.02. Found: C, 75.86; H, 12.04.

2-(*trans*-5-Dodecenyloxy)tetrahydropyran (3b).—To a mixture of 4.0 g (0.18 g-atom) of Na in about 400 ml of liquid NH_3 was added dropwise, with stirring, 10.0 g (0.038 mole) of **2** at −76°. Ether (20 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 40 ml of ether were added. After the mixture stood overnight, 100 ml of ether and H_2O (50 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, and NaCl solution). The ether solution was dried (Na_2SO_4) and distilled to give 9.2 g (91%) of colorless liquid, bp 94–96° (0.03 mm), $n^{25}D$ 1.4569, ir absorption at 965 (*trans* CH=CH) and a very weak bond at 720 cm^{-1} representing *cis* double bond impurity. Gas chromatographic analyses showed single sharp peaks, retention times 114 and 108 sec at 150° and 40 and 55 cc of N_2/min, respectively.

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(6) K. N. Campbell and L. T. Eby, *J. Am. Chem. Soc.*, **63**, 216 (1941).

(7) R. L. Augustine, "Catalytic Hydrogenation," Marcel Dekker, Inc., New York, N. Y., 1965, p 71.

(8) Boiling points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Infrared spectra were obtained with a Perkin-Elmer 521 spectrophotometer. Gas chromatographic analyses were performed on a Varian Aerograph Autoprep 700 gas chromatograph with a thermal conductivity detector by using a column of 5% Carbowax 20M on 60–80 mesh base-washed Chromosorb W (60.9 × 0.03 cm) and helium as the carrier gas.

(9) Company and trade names are given for identification purposes only and do not constitute endorsement by the U. S. Department of Agriculture.

(10) W. A. Jones, M. Jacobson, and D. F. Martin, *Science*, **152**, 1516 (1966).

Anal. Calcd for $C_{15}H_{32}O_2$: C, 76.06; H, 12.02. Found: C, 76.32; H, 12.27.

***cis*-5-Dodecen-1-ol Acetate (4a).**—A solution of 7.0 g (0.026 mole) of **3a**, 28 ml of AcOH, and 7.0 ml (0.098 mole) of AcCl was refluxed for 7 hr and then allowed to stand overnight. The solution was poured onto ice diluted to about 200 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 5.4 g (92%) of colorless liquid: bp 78–83° (0.06 mm); $n^{26}D$ 1.4422; ir absorption at 2920 (CH), 1740 and 1230 (primary acetate), and at 720 cm^{-1} (*cis*-CH=CH). A weak band at 965 cm^{-1} represented *trans* double bond impurity. Gas chromatography revealed a single sharp peak, retention time 54 sec at 150° and 40 cc of N_2/min.

Anal. Calcd for $C_{14}H_{26}O_2$: C, 74.28; H, 11.58. Found: C, 74.47; H, 11.45.

***trans*-5-Dodecen-1-ol Acetate (4b).**—Reaction between **3b** and AcCl by the procedure used to obtain **4a** gave the desired product (90%, I, bp 71–74° (0.05 mm), $n^{25}D$ 1.4419. The ir spectrum was identical with that for **4a** except for a more intense *trans* double bond absorption at 970 cm^{-1} and a less intense double bond absorption at 720 cm^{-1} that represented *cis* impurity. Gas chromatography showed a single sharp peak, retention time of 54 sec at 150° and 55 cc of N_2/min.

Anal. Calcd for $C_{14}H_{26}O$: C, 74.28; H, 11.58. Found: C, 74.43; H, 11.76.

Acknowledgments.—Attractancy tests were conducted at various laboratories of the Entomology Research Division under the supervision of J. W. Balock, Mexico City, Mexico (*A. ludens*); L. F. Steiner, Honolulu, Hawaii (*C. capitata*, *D. dorsalis*, *D. cucurbitae*); A. L. Sparks, Tifton, Georgia (*S. frugiperda*); B. A. Butt, Yakima, Washington (*C. pomonella*); A. N. Kishaba, Riverside, California (*T. ni*); M. T. Ouye, Brownsville, Texas (*P. gossypiella*); and by C. W. Collier, Plant Pest Control Division, Falmouth, Massachusetts (*P. dispar*).

Compounds Related to 2,4-Dichlorophenoxyacetic Acid and Its Derivatives

JORGE R. BARRIO

Departamento de Química Orgánica, Facultad de Farmacia y Bioquímica, Universidad de Buenos Aires, Buenos Aires, Argentina

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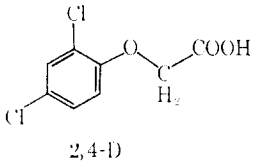
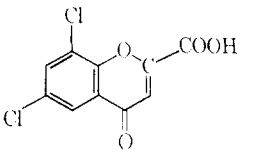
2,4-Dichlorophenoxyacetic acid (2,4-D) and its derivatives, whose phytohormonal activity is as intense as that of indolebutyric acid or even greater,[1] effectively promote plant growth and also appear to be the most important organic herbicides acting through growth regulation rather than through necrotic or toxic effects.[2] 2-Carboxy-6,8-dichloro-γ-chromone (I) structurally related to 2,4-D and some derivatives have been prepared and tested for phytohormonal activity.[3] There are three differences in 2,4-D and I. One is the presence of the acrylic-type unsaturation; second, there is the presence of the keto group; and third is the fact that in I the molecule should be largely planar and the O–C–CO_2H chain is "tied" down by being part of a ring. In 2,4-D the molecule is not planar and the OCH_2CO_2H is free to rotate. The general process of synthesis is shown in Scheme I.

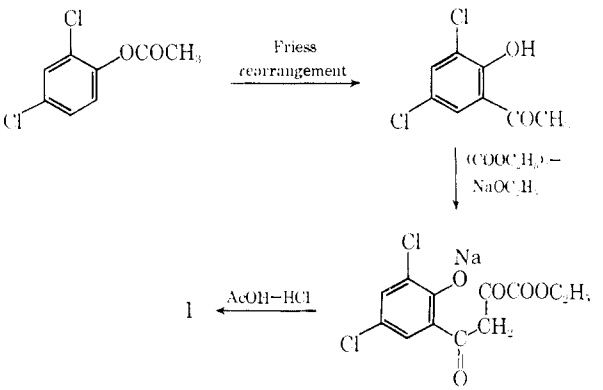


2,4-D



I

SCHEME I

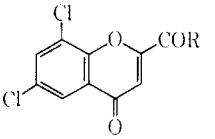


Biological Activity.—Phytoactivity assays of I, V, and VI were carried out on sunflower, wheat, yellow maize, and grain sorghum. I was neutralized with 0.1 *N* NaOH in order to increase its solubility. VI could not be tested because of its insolubility in water.

Tests were performed as follows. (a) For tests on germinating seeds, in Koenig germinators, Hoagland nutrient solution was used with addition of the test substance at a concentration of 20 or 40 mg/100 ml. (b) Germination tests were performed on seeds in the conditions described above, with 24 hr of previous soaking in Hoagland nutrient solution with the addition of the test substance at a concentration of 20 or 40 mg/100 ml. (c) Tests were made on seeds treated as in b, then planted, and the young plants were sprayed with the same solution in aerosol form.

The compounds tested showed no phytohormonal activity. In tests on wheat, slightly less development was seen in the initial growth phase, as compared with controls. However, no significant difference was observed during later development.

TABLE I



Compd	R	Mp, °C	Yield, %	Formula	Analyses
I	OH	254–255	56	$C_{10}H_4Cl_2O_4$	C, H, Cl
II	OC_2H_5	123–124	77	$C_{12}H_8Cl_2O_4$	C, H; Cl[a]
III	$O(CH_2)_2CH_3$	97–98	77	$C_{13}H_{10}Cl_2O_4$	C, H, Cl
IV	$OCH(CH_3)_2$	138–139	82	$C_{13}H_{10}Cl_2O_4$	C, H, Cl
V	$O(CH_2)_3CH_3$	117–118	87	$C_{14}H_{12}Cl_2O_4$	C, H; Cl[b]
VI	$N(C_2H_5)_2$	155–156	61	$C_{14}H_{13}Cl_2NO_3$	C, H, N
VII	Cl	131–132	6	$C_9H_3Cl_3O_3$	C, H

[a] Cl: calcd, 24.73; found, 24.20. [b] Cl: calcd, 22.54; found, 22.09.

(1) F. A. Gilbert, *Chem. Rev.*, **39**, 99 (1946).

(2) E. M. Hildebrand, *Science*, **103**, 465 (1946).

(3) Phytohormonal assays were performed by E. Vomsch, Facultad de Agronomía y Veterinaria, Universidad de Buenos Aires.