AN ECONOMICAL SYNTHESIS OF THE MAJOR SEX ATTRACTANT OF THE OAK LEAF ROLLER—-cis-10-TETRADECENYL ACETATE¹

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Abstract—The major sex attractant of the oak leaf roller (Archips semiferanus Walker), cis-10-tetradecenyl acetate (I), was synthesized in 55-62% overall yield by a highly economical route from inexpensive azelaic acid (II).

Key Words—synthesis, cis-10-tetradecenyl acetate (I), Archips semiferanus, oak leaf roller, sex attractant, pheromone.

INTRODUCTION

The oak leaf roller moth, Archips semiferanus Walker, is a tree-defoliating insect which has destroyed over \$70 million worth of timber in the northeastern United States. In Pennsylvania alone, 60–90% of the trees in over 1 million acres of forest land have been destroyed; it has been termed the worst forest-insect disaster in the history of this state.

Efforts to control the pest were initiated with a study of the sexual communication system in the adult moths (Hendry et al., 1973). Over 20 active principles (Hendry et al., 1974b; 1975) have been identified in the adult female which attract male moths in field tests (Hendry et al., 1974a). The most active component has been shown to be *cis*-10-tetradecenyl acetate (I) (Hendry et al., 1974c).

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Initial syntheses of compound I were conducted according to scheme A, similar to those previously reported (Hendry et al., 1974c). The yield of compound I by this route was poor (<10%) despite numerous efforts to improve the overall yield. An alternative economical method is reported here (scheme B). The overall yield from inexpensive azelaic acid (II) was 55-62%.

METHODS AND MATERIALS

Instruments

Vapour phase chromatography was performed on a Hewlett-Packard 7610A chromatograph using helium as a carrier gas at 30 ml/min on a 6 mm OD, 2 mm ID, 6-ft glass U-tube column of 10% DEGS on Chromosorb WAW. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian A-60. Signals are reported downfield from tetramethylsilane (δ). Infrared (IR) spectra were recorded on a Perkin-Elmer model 257 grating spectrometer and are reported in cm⁻¹. Mass spectra (MS) were run on a Finnigan 3000 GC-MS system with 6000 digital computer.



(I)

Dimethyl Azelate (1,9-nonanedioic Acid, Dimethylester)

The diester was prepared by a method similar to that of Vogel (1934) in 93% yield, bp 109°C at 2 mm. Analysis of the diester by IR,⁴ NMR,⁴ and MS identified the product as dimethyl azelate.

1,9-Nonanediol

Through a modified procedure of Huber (1951; Nystrom and Brown, 1947), the diol was prepared in 94% yield as a clear, colorless oil which crystallized on standing and was identical (IR, NMR)⁴ to an authentic sample (Aldrich Chemical Co.), mp 43.5–45.8°C (Huber, 1951).

9-Bromo-1-nonanol

One half kg (3.13 mol) of 1,9-nonanediol was dissolved in 2500 ml of 48% aqueous HBr (22.2 mol) in a 5-liter flask and heated at 80°C (Butenandt et al., 1962). The reaction mixture was extracted continuously with a liquid-liquid extractor using refluxing *n*-hepatane. The heptane in the collection flask was changed 3 times at 24-h intervals. After neutralization of the heptane extracts with saturated NaHCO₃ solution and washing once with distilled water, the heptane was evaporated. Fractional distillation of the reaction product yielded 531 g of a clear colorless oil (76% distilled yield), bp 113°C at 0.75 mm.

The crude reaction mixture could also be purified by recrystallization of the solid formed when the heptane extracts were cooled for several hours at 0°C. Recrystallization from hexane gave colorless needles, mp 32.5–33°C (Butenandt et al., 1962; Chuit and Hausser, 1929) in slightly lower yield than the distillation.

IR: γ^{neat} 3350, --OH

- NMR: δ^{CC1_4} 3.42 (center of two overlapping triplets, 4H); 2.29 (s, 1H) 1.36 (s, broad, 14H)
- MS: *m/e* 224, 222 (M); 206 (M—H₂O)

10-Tetradecyn-1-ol

A solution of 170 g of freshly distilled 1-pentyne (2.5 mol, Farchan) in 1000 ml of dry THF was treated with 2.5 mol of *n*-butyl lithium in hexane at 0-5°C under a nitrogen atmosphere. After the yellow mixture was stirred for 2 h, a solution of 1 mol (223 g) of 9-bromo-1-nonanol in 750 ml of hexamethylphosphoramide (HMPA, distilled from molecular sieves prior to ^{*}These spectra were identical to those in the Sadtler files. use) was added slowly to the lithium acetylide. The temperature was kept $<5^{\circ}$ C during the addition. The reaction mixture was then allowed to warm up to room temperature and stirred for 8 h. Ice water (1 liter) was added slowly and the aqueous solution extracted with pentane (4 × 500 ml). The combined pentane extracts were washed with a saturated NaCl solution, dried over anh. Na₂SO₄, and the solvent was removed leaving 191 g (91%) of the desired product, bp 127°C at 0.5 mm.

IR : γ^{neat} 3350, —OH NMR: δ^{CCl_4} 3.45 (*m*, 3H); 2.08 (*m*, 4H); 1.71–1.16 (*s*, broad, 16H); 0.96 (*t*, 3H, $J \sim 5-6$ cps) MS: *m/e* 192 (M—H₂O)

(Z)-10-Tetradecen-1-ol

10-Tetradecyn-1-ol (100 g, 0.476 mol) was hydrogenated (Cram and Allinger, 1956) with 1 g of 5% palladium-on-barium sulfate in 1 liter of absolute methanol to which 1 g of quinoline was added. The solution was kept at 400 psi of H_2 for 30 min with the total uptake of hydrogen being 0.476 mol. After the catalyst was removed, the methanol was evaporated leaving 94.9 g of alkenol (94%), bp 122°C at 0.40 mm.

IR: γ^{neat} 3350, -OH; 1668; 711 (*cis* out of plane bend) NMR: δ^{CC1_4} 5.29 (*t*, 2H, $J \sim 4-5$ cps); 3.52 (*m*, 3H); 1.96 (*m*, 4H); 1.63-1.15 (*s*, broad, 16H); 0.91 (*t*, 3H, $J \sim 5$ cps) MS: m/e 212 (M); 194 (M-H₂O)

(Z)-10-Tetradecenyl Acetate

To 100 g (0.472 mol) of (Z)-10-tetradecenol in a 500-ml RB flask equipped with dropping funnel, reflux condenser, and magnetic stirrer, 50 ml of acetyl chloride (50% excess) was added dropwise (reaction was highly exothermic). After the addition was completed, the resulting dark red solution was stirred for 1 hr at room temperature. 100 g of ice water was added cautiously followed by 200 ml of diethyl ether. The phases were separated, the ether layer neutralized with NaHCO₃, and washed with distilled water. The aqueous layers were combined and washed with three 50-ml portions of ether. The ethereal extracts were dried over anh. Na₂SO₄ and the ether removed by roto evaporation. The product was distilled through a short-path column, bp 125–126.5°C at 0.5 mm, yielding 114 g (95%) of the desired product as a clear, colorless liquid. IR: $\gamma^{CH_2CI_2}$ 1729 (C=O); 1634 (C=C); 1233 (C=O); 710 (*cis*-C=C) NMR: δ^{CCI_4} 5.28 (*m*, 2H); 3.96 (*t*, 2H, $J \sim 6$ cps); 1.96 (*s*, 3H); 1.64–1.12 (*s*, broad, 16H); 0.91 (*t*, 3H, $J \sim 6$ cps)

MS: m/e 254 (M); 194 (M—HOAc); 166; 152; 138; 82 (base peak)

An analysis for purity was carried out on a computerized gas chromatograph-mass spectrometer on a 2 mm ID, 150 cm 10% diethylene glycol succinate glass U-tube column (100-120 mesh Chromosorb W) at 135°C; the product was >95% of the *cis* isomer.

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