CHIRALITY OF SYNERGISTIC SEX PHEROMONE COMPONENTS OF THE WESTERN HEMLOCK LOOPER
Lambdina fiscellaria lugubrosa (HULST) (LEPIDOPTERA: GEOMETRIDAE)

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Abstract—Bakers' yeast reduction of (2E)-3-(2'-furanyl)-2-methyl-2-propanal yielded the synthetic intermediate, (2S)-3-(2'-furanyl)-2-methylpropanol, of high chiral purity (>97% ee) for the synthesis of the enantiomers of 2,5-dimethylheptadecane and 7-methylheptadecane, two synergistic sex pheromone components of the western hemlock looper (WHL), Lambdina fiscellaria lugubrosa Hulst. In electrophysiological bioassays, (7S)- but not (7R)-7-methylheptadecane elicited strong antennal responses by male WHL antennae. In field trapping experiments, addition of (7S)- but not (7R)-7-methylheptadecane to (5R,11S)-5,11-dimethylheptadecane, the major sex pheromone component of WHL, increased attraction. Attraction to (5R,11S)-5,11-dimethylheptadecane in combination with (7S)-7-methylheptadecane was further enhanced by the addition of (5S)- but not (5R)-2,5-dimethylheptadecane. Similarly, attraction to (5R,11S)-5,11-dimethylheptadecane combined with (5S)-2,5-dimethylheptadecane increased when (7S)- but not (7R)-7-methylheptadecane was added as a third component. We conclude that (7S)-7-methylheptadecane and (5S)-2,5-dimethylheptadecane are the synergistic sex pheromone components of WHL. The synthetic methodology described is applicable to the synthesis of chiral methyl-branched pheromones in other orders of the Insecta, particularly Coleoptera, Diptera and Orthoptera.

Key Words—Sex pheromone, enantiomer, Lepidoptera, Geometridae, western hemlock looper, (5R)-2,5-dimethylheptadecane, (5S)-2,5-dimethylheptadecane, (7R)-7-methylheptadecane, (7S)-7-methylheptadecane, chirality.

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INTRODUCTION

5,11-Dimethylheptadecane (5,11-dime-17Hy) is the major sex pheromone component of the eastern hemlock looper (EHL), Lambdina fiscellaria fiscellaria (Guen.) (Gries et al., 1991a,b) and the western hemlock looper (WHL) L. f. lugubrosa (Hulst) (Gries et al., 1993a). As shown in recent electrophysiological studies and field trapping experiments, of the four stereoisomers of 5,11-dime-17Hy, only (5R,11S)-5,11-dime-17-Hy elicited antennal responses by male EHLs and WHLs and attracted male loopers in the field (Li et al., 1993).

2,5-Dimethylheptadecane (2,5-dime-17Hy) is a synergistic sex pheromone component in both EHL and WHL. While 7-methylheptadecane (7-me-17Hy) is present in the EHL, it is a third synergistic pheromone component only in the WHL (Gries et al., 1993a). Biotransformation is widely used in the synthesis of chiral synthons of high chiral purity, and it provides many ways to chiral natural products (Fuganti, 1990). We report the bakers’ yeast synthesis of and antennal responses and field attraction to the enantiomers of 7-me-17Hy and 2,5-dime-17Hy in the WHL.

METHODS AND MATERIALS

General Procedures for Synthesis and Characterization

Evaporations were carried out under reduced pressure below 45°C. Infrared spectra (Perkin-Elmer 599B spectrophotometer) were obtained from a neat film or suspension of the pure compound in Nujol on NaCl plates. Gas–liquid chromatography (GLC) was conducted employing a Hewlett Packard 5880 gas chromatograph equipped with a fused silica column (30 m × 0.25 mm ID) coated with DB-1 (J&W Scientific, Folsom, California). Thin-layer chromatography (TLC) plates were prepared from silica gel 60G. For detection of compounds, plates were sprayed with 10% sulfuric acid and heated. Chromatographic separations were carried out as previously described (Still et al., 1978). Optical rotations were measured on an Autopol II automatic polarimeter. Concentrations for optical rotations were reported in grams per 100 ml of solvent. Nuclear magnetic resonance (NMR) spectra (Bruker WU-400 spectrometer) were taken in CDCl₃ at 400 MHz (J values in hertz). Mass spectra were obtained on a Hewlett Packard 5985B mass spectrometer equipped with a fused silica column (30 m × 0.25 mm ID) coated with DB-1. High-resolution mass spectra were generated on Kretos M580 mass spectrometer.

Syntheses of Individual Compounds

(2S)-3-(2'-Furanyl)-2-methylpropanyl p-toluenesulfonate 4 (Scheme 1). This compound was synthesized as previously reported (Fuganti et al., 1988): [α]D⁰ + 6.9 (c 6.4, CHCl₃).