SYNTHESIS OF DIASTEREOMERIC MIXTURE OF 15,19,23-TRIMETHYLHEPTATRAICYCLOHEXANE, CONTACT SEX PHEROMONE OF TSETSE FLY, Glossina morsitans morsitans WESTWOOD

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Abstract—A nine-step synthesis is described for a diastereomeric mixture of 15,19,23-trimethylheptatriacontane, a contact sex pheromone of Glossina morsitans morsitans Westwood. The compound has been synthesized by means of double alkylation of diethyl 3-oxoglutarate (DEOG) with 3-methyl-2-heptadecenyl methanesulfonate, which was readily prepared from 1-hexadecene, as the key step.

Key Words—Tsetse fly, Glossina morsitans morsitans, Diptera, Muscidae, sex pheromone, branched hydrocarbon, 15,19,23-trimethylheptatriacontane, diethyl 3-oxoglutarate, alkylation.

INTRODUCTION

Several workers have investigated the sex pheromones of tsetse flies, because the flies are major vectors of African trypanosomiases such as sleeping sickness and nagana. Of interest is that many insect pheromones include such compounds as alcohols, acetates, aldehydes, and hydrocarbons (Nelson, 1978; Sonnet, 1984). Carlson et al. (1978) isolated a group of sex pheromones from the

1This study constitutes Part XII of 'Selective Alkylation of Diethyl 3-Oxoglutarate.' Part XI of this series, see Naoshima et al. (1984).

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cuticle of the female tsetse fly, *Glossina morsitans morsitans* Westwood and identified the most active component as 15,19,23-trimethylheptatriacontane (I), a branched hydrocarbon. Compound I was synthesized either as a diastereomeric mixture by Carlson et al. (1978) and Hoshino and Mori (1980) or as the set of four stereoisomers by Helmchen and Schmierer (1983). These methods were complicated and suffered from low overall yields. A recent report on pheromone effects (Helmchen and Langley, 1981) has showed that all of the four stereoisomers of I were equally active on *Glossina morsitans morsitans* Westwood.

A number of pheromones have been prepared from diethyl 3-oxoglutarate, DEOG, through reaction with a variety of alkylating agents (Naoshima et al., 1983, 1984). We now report a synthetic approach toward a diastereomeric mixture of I, which is based on the double alkylation of DEOG with 3-methyl-2-heptadecenyl methanesulfonate (II) derived from 1-hexadecene. Pheromone I was synthesized with an improved overall yield, compared with the value reported previously, by use of both DEOG and 1-hexadecene as the starting materials.

**METHODS AND MATERIALS**

Column chromatography was carried out employing 230–400 mesh silica gel (Merck Kieselgel 60 Art 9385) according to the flash technique described by Still et al. (1978). All solvent systems were expressed in ratios by volume (v/v). IR spectra were determined on a Hitachi model 260-10 spectrometer. [1H]NMR spectra were obtained on a Hitachi model R-24B spectrometer in CDCl₃ solutions using Me₄Si as an internal standard. EI and CI mass spectra were recorded on a JEOL model JMS-D300 double-focusing mass spectrometer at 70 eV and 200 eV, respectively, using a direct insertion probe. GLC analysis for the determination of the purity of the pheromone I was made isothermally at 250°C (N₂, 60 ml/min), employing a Hitachi 163 gas chromatograph equipped with a 1-m × 3-mm glass column of 3% OV-1 on 80–100 mesh Chromosorb W AW DMCS. Sodium hydride (Aldrich Chemical Company, Inc., Milwaukee, Wisconsin) was weighed as a 60% dispersion in mineral oil and washed with dry n-hexane to remove the oil prior to use. Solvents were purified and dried by standard methods.

2-Hexadecanol (IIA). Compound IIA was readily synthesized from 1-hexadecene with a 97% yield by an oxymercuration-demercuration procedure (Brown and Geoghegan, 1970): mp 45–46°C (mp 41.5°C, see Messer, 1929).

2-Hexadecanone (IIB). Compound IIB was synthesized with a 96.5% yield by oxidizing IIA with sodium dichromate: mp 44–45°C (mp 43°C, see Ruzicka et al., 1928).

Ethyl 3-methyl-2-heptadecanoate (IIC). Compound IIC was synthesized by