Syntheses of Racemic and Diastereomeric Mixtures of 3,7,11,15-Tetramethylhentriacontane and 4,8,12,16-Tetramethyldotriacontane, the Cuticular Tetramethylalkanes of the Tsetse Fly, Glossina brevipalpis†

Chié SHIBATA, Ayako FURUKAWA, and Kenji MORI††

Department of Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka 1-3, Shinjuku-ku, Tokyo 162-8601, Japan

Received October 1, 2001; Accepted October 30, 2001

Cuticular hydrocarbons of the tsetse fly, Glossina brevipalpis, contain 3,7,11,15-tetramethylhentriacontane and 4,8,12,16-tetramethyldotriacontane as possible candidates for its contact sex pheromone. These were synthesized as racemic and diastereomeric mixtures starting from racemic citronellol and employing phenylsulfone-mediated chain-elongation as the key reaction.

Key words: cuticular hydrocarbon; Glossina brevipalpis; methyl-branched alkane; optically active alkane; pheromone

The tsetse fly is known to spread the notorious sleeping sickness in Africa, and is therefore a hazard to the health of humans and cattle there. Their pheromones are of considerable research interest among medical entomologists, and a number of methyl-branched hydrocarbons have been isolated as their contact sex pheromones.1) We have been engaged since 1980 in the synthesis of such tsetse fly pheromones as those of Glossina morsitans morsitans,2) Glossina pallidipes,3) Glossina tachinoides,4) and Glossina austeni.5) The synthesized pheromones were all methyl-branched hydrocarbons with two3–5) or three2) branchings.

Tetramethylalkanes are significant components of the cuticular hydrocarbons of G. brevipalpis, while in other tsetse flies, they are only minor components.3,5) 3,7,11,15-Tetramethylhentriacontane (I) and 4,8,12,16-tetramethyldotriacontane (2) are present in both male and female G. brevipalpis,6) although their biological role is not yet clear. In order to clarify this, sufficient amounts of I and 2 are required for subsequent biotesting. We therefore undertook the syntheses of 1 and 2.

The presence of four stereogenic centers in 1 and 2 means that they exist in sixteen stereoisomeric forms. To avoid complication, we decided to synthesize both 1 and 2 as racemic and diastereomeric mixtures. If there is no stereoisomer to inhibit the bioactivity of other isomer(s), we can expect good bioassay results even with the stereoisomeric mixture of a pheromone.7) Indeed, in the case of G. tachinoides, a racemic and diastereomeric mixture of 11,23-dimethylheptatriacontane was active as the sex stimulant against male flies.8) As shown in Scheme 1, our synthetic plan for 1 and 2 is very simple. Target molecules I and 2 with four methyl branchings are to be dissected into two building blocks, A and B, each of them possessing two methyl branchings. Alkylation of phenylsulfone B with iodide A builds up the carbon skeleton of I and 2.5,9) Both A and B can be synthesized from commercially available (±)-citronellol (C).

Scheme 2 summarizes our syntheses of 1 and 2. The preparation of building block 10 (one of A) will be discussed first. (±)-Citronellol (3) was converted to the known (±)-2,6-dimethyl-1,8-diacetoxy-2-phenylsulfonate 10.

Scheme 1. Structures of the Cuticular Hydrocarbons of the Tsetse Fly, Glossina brevipalpis, and Their Retrosynthetic Analysis.

†† To whom correspondence should be addressed at the following: Insect Pheromone and Traps Division, Fuji Flavor Co., Ltd., Midorigaoka 3-5-8, Hamura-City, Tokyo 205-8053, Japan. Fax: 81-42-555-7920
octene (6) via (-)-citronellyl acetate (4) and alcohol (-)-5 according to the method of Kefalas and Ragoussis, who prepared (S)-5. Treatment of (-)-6 with methylmagnesium bromide in the presence of dilithium tetrachlorocuprate afforded alcohol (-)-7. Hydrogenation of (-)-7 over palladium-carbon gave alcohol 8 as a racemic and diastereomeric mixture. It should be added that (3R,7R)-8 and (3R,7S)-8 are known compounds. 

Alcohol 8 furnished iodide 10 (one of A) via tosylate 9. The overall yield of 10 was 26% based on 7 (seven steps). In the same manner, except that ethyllithium was employed for the conversion of 6 to 11, iodide 14 (the other of A) was synthesized from 3 in a 24% overall yield (seven steps) via 11, 12 and 13. Four optically active forms of 12 and 14 are known compounds.

Another building block 21 (B) was also prepared. Chain-elongation of (+)-citronellyl tosylate (15) with tetradecylmagnesium bromide under Schlosser conditions afforded (+)-2,6-dimethyl-2-docosene (16), whose (S)-isomer is a known compound. Oxidation of (+)-16 with selenium dioxide and t-butyl hydroperoxide was followed by sodium borohydride reduction of the resulting alpha, beta-unsaturated aldehyde to give allylic alcohol (+)-17. Since hydrogenation of 17 over palladium-charcoal or platinum oxide was unsuccessful under atmospheric pressure, 17 was hydrogenated under medium pressure (3-4 kg/cm²) over Raney nickel (W 7) to give saturated alcohol 18 as a racemic and diastereomeric mixture. Alcohol 18 was then tosylated to give 19, which was converted to phenylsulfone 21 via iodide 20. The overall yield of 21 was 29% based on (+)-citronellol (3, seven steps).

With the two building blocks A (10 or 14) and B (21) in hand, these two were connected by alklylation of the anion of phenylsulfone 21 with iodide 10 or 14 to give new phenylsulfonyl 22 or 23 in a 99% or 93% yield. Finally, reductive removal of the phenylsulfonic group of 22 and that of 23 with lithium in ethylamine yielded the target molecules, 3,7,11,15-tetramethylhentriacontane (1) and 4,8,12,16-tetramethylodotriacontane (2), in 83% and 81% yields, respectively. The overall yield of 1 was 21% (nine steps via 10) or 24% (nine steps via 21), and that of 2 was 17% (nine steps via 14) or 8% (nine steps via 21) based on (+)-citronellol (3). Both 1 and 2 showed spectral (1H-NMR and MS) properties and elemental analytical data in good agreement with the structures.

In conclusion, racemic and diastereomeric mixtures of the two cuticular hydrocarbons, 1 and 2, of the tsetse fly, Glossina brevipalpis, were synthesized. Biological studies on 1 and 2 are now in progress by Dr. D. A. Carlson at U.S. Department of Agriculture.

Experimental

Melting point (mp) data were measured with a Yanaco MP-12 instrument and are uncorrected. IR data were measured with a Jasco FT/IR-410 spectrometer. 1H-NMR data were measured with a Jeol JNM-AL300 (300 MHz), Jeol JNM-LA400 (400 MHz) or Jeol JNM-LA500 (500 MHz) spectrometer (TMS at δH = 0.00 or CDCl3 at δH = 7.26 was used as the internal standard). MS data were measured with a Jeol JMS-AX 505 HA spectrometer, and refractive index (nD) data were measured with an Atago DMT-1 refractometer.

(+)-[(E)-2,6-Dimethyl-1,8-diacetoxy-2-octene [(-)-6]] to a stirred and ice-cooled solution of (+)-5 (10.2 g, 47.7 mmol) in CH2Cl2 (40 ml) and pyridine (11.6 ml, 143 mmol) was added Ac2O (6.80 ml, 71.5 mmol). After stirring for 5 h at room tempera-
ture, the mixture was poured into 1 M HCl and extracted with CH2Cl2. The combined organic phases were successively washed with 1 M HCl, water, a saturated aqueous NaHCO3 solution and brine, dried with MgSO4, and concentrated in vacuo. The residue was chromatographed on silica gel (200 g; hexane/ AcOEt, 20:1) to give 11.7 g of (±-6) (95%) as a yellow oil, nD25 1.4521 (lit.12) nD20 1.4530. IR vmax (film) cm\(^{-1}\): 1740 (s, C=O), 1240 (C=C (O) = O), NMR δH (400 MHz, CDCl3): 0.92 (3H, d, J = 6.7 Hz, 6-Me), 1.16-1.27 (1H, m, 6-H), 1.34-1.57 (4H, m, 5-H, 7-H), 1.61 (3H, s, 2-Me), 1.95 (3H, s, 1-Ac), 2.07 (3H, s, 8-Ac), 4.12-4.21 (2H, m, -OH), 5.44 (1H, t, J = 7.7 Hz, 3-H). The IR and \(^1\)H-NMR spectra are identical to those in the literature.9)

(±)-3,7-Dimethylnonyl Tosylate ([±]-9). To a stirred and ice-cooled solution of (±)-8 (2.10 g, 12.2 mmol) in CH2Cl2 (20 ml) and pyridine (3.10 ml, 36.6 mmol) was added p-toluene sulfonyl chloride (3.92 g, 20.6 mmol) in one portion. After stirring for 17 h at 4°C, the mixture was poured into water, and the resulting mixture was extracted with Et2O. The combined ethereal extracts were successively washed with 1 M HCl, a saturated NaHCO3 solution and brine, dried with MgSO4, and concentrated in vacuo to give 4.26 g of crude (±)-9. IR vmax (film) cm\(^{-1}\): 1600 (m, aromatic), 1365 (m, S–O–C). NMR δH (400 MHz, CDCl3): 0.80-0.86 (9H, m, 3-Me, 7-Me, 9-H), 1.00-1.33 (10H, m, 3-H, 4-H, 5-H, 6-H, 7-H, 8-H), 1.40-1.49 (1H, m, 2-H), 1.64-1.67 (1H, m, 2-H), 2.45 (3H, s, Ar-Me), 4.04-4.08 (2H, m, 1-H), 7.34 (2H, d, J = 8.4 Hz, aromatic), 7.79 (2H, d, J = 8.4 Hz, aromatic). This compound was employed in the next step without further purification. Its IR spectrum is identical to that in the literature.12)

(±)-3,7-Dimethylnonyl Iodide ([±]-10). To a solution of crude (±)-9 (4.26 g) in N,N-dimethylformamide (DMF, 30 ml) was added NaI (10.0 g, 66.5 mmol). After stirring at 50°C for 2 h, the mixture was poured into water and extracted with Et2O. The combined ethereal extracts were successively washed with a saturated aqueous Na2S2O3 solution, water and brine, dried with MgSO4, and concentrated in vacuo. The residue was chromatographed on silica gel (160 g; hexane/AcOEt, 1:1) to give 3.33 g (2 steps, 95%) of 10 as a colorless oil, nD25 1.4808. IR vmax (film) cm\(^{-1}\): 1175 (m, CH2–I). NMR δH (400 MHz, CDCl3): 0.85-0.90 (9H, m, 3-Me, 7-Me, 9-H), 1.04-1.57 (10H, m, 2-H, 4-H, 5-H, 6-H, 8-H), 1.59-1.68 (1H, m, 7-H), 1.82-1.92 (1H, m, 3-H), 3.14-3.28 (2H, m, 1-H). This compound was employed in the next step without further purification.

(±)-3,7-Dimethyl-6-decen-1-ol ([±]-11). In a similar manner to that described for the preparation of (±)-7, except that EtMgBr in dry THF (0.94 ml, 2.60 ml, 2.44 mmol) was employed for this conversion, (±)-6 (730 mg, 2.85 mmol) yielded 370 mg (70%) of (±)-11 as a colorless oil, nD25 1.4547. IR vmax (film) cm\(^{-1}\): 3420 (w, O–H), 1050 (m, C–O). NMR δH (400 MHz, CDCl3): 0.85 (3H, t, J = 7.2 Hz, 10-H) 0.91 (3H, d, J = 7.2 Hz, 3-Me), 1.15-1.25 (2H, m, 9-H), 1.30-1.45 (3H, m, 4-H, O–H), 1.57 (3H, seemingly d, J = 5.1 Hz, 7-Me), 1.61-1.70 (3H, m, 2-H, C–O).
3-H), 1.90–2.10 (4H, m, 5-H, 8-H), 3.67 (2H, m, 1-H), 5.10 (1H, t, \( J = 6.4 \) Hz, 6-H). Anal. Found: C, 78.20; H, 13.12%. Calcd. for C\(_{12}\)H\(_20\)O: C, 77.72; H, 13.32%.

(\(\pm\)-3,7-Dimethyldecan-1-ol [\(\pm\)]-12). In the same manner as that described for the preparation of (\(\pm\)-8), (\(\pm\)-11) (1.80 g, 9.80 mmol) yielded 1.60 g (90% of) (\(\pm\)-12) as a colorless oil, \(n\)\(_D\) \(1.4426\) [lit.\(^{15}\) \(n\)\(_D\) \(1.4430\) ([3R,7R]-12)]. IR \(\nu_{\text{max}}\) (film) \(cm^{-1}\): 3420 (m, O–H), 1055 (m, C–O). NMR \(\delta_{\text{H}}\) (500 MHz, CDCl\(_3\)): 0.84 (3H, d, \( J = 6.6 \) Hz, 7-Me), 0.87 (3H, t, \( J = 7.3 \) Hz, 10-H), 0.89 (3H, d, \( J = 6.3 \) Hz, 3-Me), 1.06–1.39 (12H, m, 3-H, 4-H, 5-H, 6-H, 7-H, 8-H, 9-H), 1.61 (2H, m, 2-H), 3.68 (2H, m, 1-H). IR \(\nu_{\text{max}}\) (film) \(cm^{-1}\): 3420 (w, O–H), 2930 (s, C–H), 1460 (m, C–H). NMR \(\delta_{\text{H}}\) (400 MHz, CDCl\(_3\)): 0.83–0.90 (9H, m, 3-Me, 7-Me, 10-Me), 1.32 (12H, m, 3-H, 4-H, 5-H, 6-H, 7-H, 8-H, 9-H), 2.45 (3H, s, Ar-Me), 4.07 (2H, m, 1-H), 7.34 (2H, d, \( J = 8.0 \) Hz, aromatic), 7.79 (2H, d, \( J = 8.2 \) Hz, aromatic). This compound was employed in the next step without further purification.

(\(\pm\)-3,7-Dimethyldecyld Iodide [\(\pm\)]-13). In the same manner as that described for the preparation of (\(\pm\)-9), (\(\pm\)-12) (1.30 g, 6.98 mmol) yielded 3.05 g of crude (\(\pm\)-13) as a colorless oil, \(n\)\(_D\) \(1.4983\). IR \(\nu_{\text{max}}\) (film) \(cm^{-1}\): 1360 (s, SO\(_2\)), 1180 (s, SO\(_2\)). NMR \(\delta_{\text{H}}\) (500 MHz, CDCl\(_3\)): 0.80 (3H, d, \( J = 6.8 \) Hz, 7-Me), 0.83 (3H, d, \( J = 6.7 \) Hz, 10-H), 0.88 (3H, d, \( J = 7.0 \) Hz, 3-Me), 1.19–1.26 (14H, m, 2-H, 3-H, 4-H, 5-H, 6-H, 7-H, 8-H, 9-H), 2.45 (3H, s, Ar-Me), 4.07 (2H, m, 1-H), 7.34 (2H, d, \( J = 8.0 \) Hz, aromatic), 7.79 (2H, d, \( J = 8.2 \) Hz, aromatic). The residue was chromatographed on silica gel (53 g; hexane/AcOEt, 9:1) to give 10.2 g of (\(\pm\)-17) (53%) as a colorless waxy solid, mp 25–30°C. IR \(\nu_{\text{max}}\) (film) \(cm^{-1}\): 3325 (s, O–H), 1040 (m, C–O). NMR \(\delta_{\text{H}}\) (500 MHz, CDCl\(_3\)): 0.86 (3H, d, \( J = 7.0 \) Hz, 6-Me), 0.88 (3H, t, \( J = 7.0 \) Hz, 22-H), 1.23–1.37 (34H, m, 5-H, 6-H, 7-H, 8-H, 9-H, 10-H, 11-H, 12-H, 13-H, 14-H, 15-H, 16-H, 17-H, 18-H, 19-H, 20-H, 21-H, –OH), 1.67 (3H, s, 2-Me), 2.06 (2H, m, 4-H), 3.99 (2H, s, 1-H), 5.40 (1H, m, 3-H). Anal. Found: C, 81.41; H, 13.77%. Calcd. for C\(_{25}\)H\(_{58}\)O: C, 81.74; H, 13.72%.

(\(\pm\)-2,6-Dimethyldecosan-1-ol [\(\pm\)]-18). A solution of (\(\pm\)-17) (2.90 g, 8.63 mmol) in 99.5% EtOH (5 ml) was shaken in an H\(_2\) (3–4 kg/m\(^3\)) atmosphere in the presence of Raney nickel (W 7; 500 mg) for 18 h at room temperature. The catalyst was removed by filtration through a Celite pad, and the filtrate was concentrated in vacuo. The residue was chromatographed on silica gel (55 g; hexane/AcOEt, 50:1) to give 2.92 g of (\(\pm\)-18) (quant.) as a colorless waxy solid, mp 25–30°C. IR \(\nu_{\text{max}}\) (film) \(cm^{-1}\): 3395 (s, O–H), 1010 (m, C–O). NMR \(\delta_{\text{H}}\) (400 MHz, CDCl\(_3\)): 0.83–0.93 (9H, m, 2-Me, 6-Me, 22-H), 1.08–1.43 (37H, m, 3-H, 4-H, 5-H, 6-H, 7-H, 8-H, 9-H, 10-H, 11-H, 12-H, 13-H, 14-H, 15-H, 16-H, 17-H, 18-H, 19-H, 20-H, 21-H, –OH), 1.55–1.61 (2H, m, 2-H), 3.39–3.52 (2H, m, 1-H). Anal. Found: C, 81.17; H, 14.49%. Calcd. for C\(_{25}\)H\(_{58}\)O: C, 81.28; H, 14.21%.

(\(\pm\)-2,6-Dimethyldecosyl Iodide [\(\pm\)]-19). In the same manner as that described for the preparation of (\(\pm\)-9), (\(\pm\)-18) (500 mg, 0.99 mmol) yielded 464 mg (93%) of (\(\pm\)-19) as a colorless oil, \(n\)\(_D\) \(1.4806\). IR \(\nu_{\text{max}}\) (film) \(cm^{-1}\): 1600 (m, aromatic), 1365 (m, S–O–C). NMR \(\delta_{\text{H}}\) (400 MHz, CDCl\(_3\)): 0.80 (3H, d, \( J = 6.8 \) Hz, 6-Me), 0.86–0.90 (6H, m, 2-Me, 22-H), 0.95–1.34 (38H, m, 2-H, 3-H, 4-H, 5-H, 6-H, 7-H, 8-H, 9-H, 10-H, 11-H, 12-H, 13-H, 14-H, 15-H, 16-H, 17-H, 18-H, 19-H, 20-H, 21-H, –OH), 2.45 (3H, s, Ar-Me), 3.78–3.89 (2H, m, 1-H), 7.33 (2H, d, \( J = 8.4 \) Hz, aromatic), 7.79 (2H, d, \( J = 8.4 \) Hz, aromatic). Anal. Found: C, 72.89; H, 11.36%. Calcd. for C\(_{25}\)H\(_{56}\)I\(_3\)O\(_3\): C, 73.17; H, 11.09%.

(\(\pm\)-2,6-Dimethyldecosyl Iodide [\(\pm\)]-20). In the same manner as that described for the preparation of (\(\pm\)-10), (\(\pm\)-19) (250 mg, 0.50 mmol) yielded 191 mg (82%) of (\(\pm\)-20) as a colorless oil, \(n\)\(_D\) \(1.4377\). IR \(\nu_{\text{max}}\)}
in dry THF (3 ml) was added dropwise to the mixture.

\[ \text{IR} \ \text{cm}^{-1} : 2920 (s, \text{C–H}), 1460 (m, \text{O–C}) \]
\[ \text{NMR} \ \text{H} (400 MHz, CDCl₃): 0.79–0.89 (18H, m, 2-Me, 4-H, 5-H, 6-H, 7-H, 8-H, 9-H, 10-H, 11-H, 12-H, 13-H, 14-H, 15-H, 16-H, 17-H, 18-H, 19-H, 20-H, 21-H), 2.89–3.11 (2H, m, 1-H), 7.56 (2H, t, \ J = 7.7 Hz, aromatic), 7.63 (1H, t, \ J = 7.7 Hz, aromatic), 7.92 (2H, d, \ J = 7.7 Hz, aromatic). \]

**C. Shibata et al.**

(±)-2,6-Dimethyl-1-phenylsulfonyledocosane ([±]-21). To a stirred solution of (±)-20 (0.25 mmol) in dry THF (3 ml) was added n-BuLi in hexane (1.56 M, 0.70 ml, 1.09 mmol) at −78°C under argon. The solution was stirred at −50°C for 15 min and then cooled to −78°C. A solution of (±)-10 (200 mg, 0.71 mmol) in dry THF (3 ml) was added dropwise to the mixture at −78°C while stirring. The mixture was stirred at 0°C for 4 h, poured into a saturated aqueous NH₄Cl solution at 0°C, and extracted with Et₂O. The combined ethereal extracts were successively washed with water and brine, dried with MgSO₄, and concentrated in vacuo. The residue was chromatographed on silica gel (4 g; hexane/AcOEt, 50:1) to give 97.2 mg (83%) of (±)-22 as a colorless oil, \( n^\circ_2 = 1.4562 \) IR \( \text{v}_{\text{max}} \) (film) \( \text{cm}^{-1} \): 2925 (s, C–H), 2855 (s, C–H), 1465 (m, CH₂), 1375 (m, CH₂), 126.9 (86), 195.8 (61), 196.8 (80), 266.7 (61), 321.7 (34). NMR \( \delta_{\text{H}} \) (500 MHz, CDCl₃): 0.72–0.87 (18H, m, 2-Me, 3-Me, 7-Me, 11-Me, 15-Me, 31-H), 1.11–1.31 (52H, m, 2-H, 3-H, 4-H, 5-H, 6-H, 7-H, 8-H, 9-H, 11-H, 12-H, 13-H, 14-H, 15-H, 16-H, 17-H, 18-H, 19-H, 20-H, 21-H, 22-H, 23-H, 24-H, 25-H, 26-H, 27-H, 28-H, 29-H, 30-H, 31-H). 2.87–2.88 (1H, m, 10-H), 7.56 (2H, t, \ J = 7.8 Hz, aromatic), 7.63 (1H, t, \ J = 7.8 Hz, aromatic), 7.89 (2H, d, \ J = 7.8 Hz, aromatic). **Anal. Found:** C, 77.94; H, 12.24%. Calcd. for C₄₂H₇₈O₂S: C, 77.78; H, 12.10%.

4,8,12,16-Tetramethyl-11-phenylsulfonyledotriacontane ([±]-23). In a similar manner to that described for the preparation of (±)-22, except that (±)-14 (627 mg, 2.12 mmol) was employed for this conversion, (±)-21 (676 mg, 1.41 mmol) yielded 781 mg (85%) of (±)-23 as a colorless oil, \( n^\circ_2 = 1.4848 \) IR \( \text{v}_{\text{max}} \) (film) \( \text{cm}^{-1} \): 1310 (s, SO₂), 1150 (s, SO₂). NMR \( \delta_{\text{H}} \) (400 MHz, CDCl₃): 0.79–0.89 (18H, m, 2-Me, 4-Me, 8-Me, 12-Me, 16-Me, 32-H), 1.21–1.25 (54H, m, 2-H, 3-H, 4-H, 5-H, 6-H, 7-H, 9-H, 10-H, 11-H, 12-H, 13-H, 14-H, 15-H, 16-H, 17-H, 18-H, 19-H, 20-H, 21-H, 22-H, 23-H, 24-H, 25-H, 26-H, 27-H, 28-H, 29-H, 30-H, 31-H). 2.88 (1H, m, 11-H), 7.57 (3H, t, \ J = 8.0 Hz, aromatic) 7.89 (2H, d, \ J = 7.3 Hz, aromatic). **Anal. Found:** C, 78.02; H, 12.23%. Calcd. for C₄₂H₇₈O₂S: C, 77.95; H, 12.15; O, 4.94; S, 4.96%.

3,7,11,15-Tetramethyl-10-phenylsulfonylhexadecane ([±]-I). Lithium wire (145 mg, 20.9 mmol) was dissolved in EtNH₂ (10 ml) at −50°C under argon. To the stirred and cooled solution of lithium, a solution of (±)-22 (150 mg, 0.24 mmol) in dry THF (1.5 ml) was added dropwise at −60°C. After stirring at −50°C for 2 h, the reaction was quenched with NH₄Cl. After removing EtNH₂, the mixture was poured into a saturated aqueous NH₄Cl solution and extracted with hexane. The combined organic phases were washed with water and brine, dried with MgSO₄, and concentrated in vacuo. The residue was chromatographed on silica gel (4 g; hexane) to give 97.2 mg (83%) of (±)-I as a colorless oil, \( n^\circ_2 = 1.4562 \) IR \( \text{v}_{\text{max}} \) (film) \( \text{cm}^{-1} \): 2925 (s, C–H), 2855 (s, C–H), 1465 (m, CH₂), 1375 (m, CH₂), 126.9 (86), 195.8 (61), 196.8 (80), 266.7 (61), 321.7 (34). NMR \( \delta_{\text{H}} \) (500 MHz, CDCl₃): 0.72–0.87 (18H, m, 1-H, 3-Me, 7-Me, 11-Me, 15-Me, 31-H), 0.89–1.36 (54H, m, 2-H, 3-H, 4-H, 5-H, 6-H, 7-H, 8-H, 9-H, 10-H, 11-H, 12-H, 13-H, 14-H, 15-H, 16-H, 17-H, 18-H, 19-H, 20-H, 21-H, 22-H, 23-H, 24-H, 25-H, 26-H, 27-H, 28-H, 29-H, 29-H, 30-H, 31-H). MS (EI) \( m/z \) (relative intensity): 56.9 (94), 70.9 (100), 126.9 (86), 195.8 (61), 196.8 (80), 266.7 (61), 321.7 (63), 322.7 (81), 392.7 (71), 448.6 (14), 462.6 (31), 476.6 (23), 491.5 (M⁻, 16). GC [NB-5× column (0.25 mm × 30 m), 60 + 28°C/min to 180°C, and 180 + 3°C/min to 320°C; He carrier gas at 1.0 kg/cm²], \( t_R = 52.2 \) min. (1, >98% chemical purity). **Anal. Found:** C, 85.08; H, 15.05%. Calcd. for C₃₂H₆₀: C, 85.28; H, 14.72%.

4,8,12,16-Tetramethyldotriacontane ([±]-2I). In the same manner as that described for the preparation of (±)-1, (±)-23 (720 mg, 1.11 mmol) yielded 456 mg (81%) of (±)-2 as a colorless oil, \( n^\circ_2 = 1.4767 \) IR \( \text{v}_{\text{max}} \) (film) \( \text{cm}^{-1} \): 2920 (s, C–H), 1460 (m,
Syntheses of Two Tetramethylalkanes of the Tsetse Fly


Acknowledgment

We thank Dr. David A. Carlson (U.S. Department of Agriculture) for discussions. Financial support for this work from Mitsubishi Gas Chemical Co. and Nitto Denko Co. is acknowledged with thanks.

References
