Pergamon

Tetrahedron: Asymmetry, Vol. 7, No. 7, pp. 1951-1956, 1996

0957-4166/96 $15.00 + 0.00

PII: S0957-4166(96)00234-0

Synthesis of (11*R*,17*S*)-11,17-Dimethylhentriacontane: a Communication Pheromone of Ant *Camponotus vagus*

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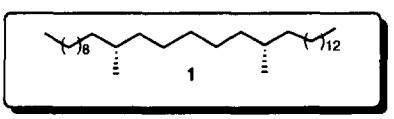
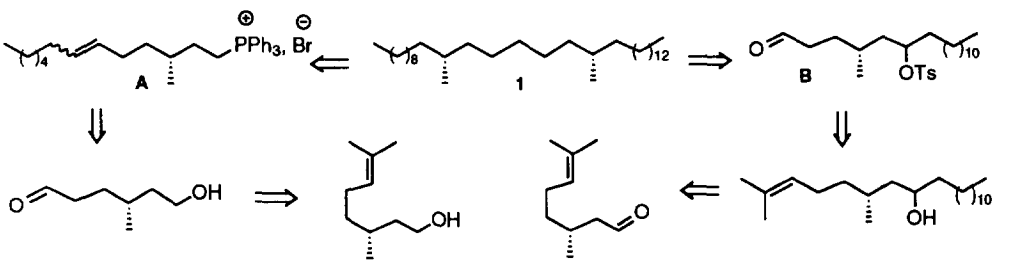
Abstract: The convergent synthesis in high enantiomeric and diastereoisomeric purity of (11*R*,17*S*)-11,17-dimethylhentriacontane, a communication pheromone of ant *Camponotus vagus* is described. The stereogenic centres were introduced from commercially available (*R*)-citronellol and (*R*)-citronellal. Copyright © 1996 Elsevier Science Ltd

Chiral methyl branched subunits are found in several classes of naturally occurring compounds and are particularly present in insect pheromones. During the last fifteen years, several chiral total syntheses[1] have been performed starting from natural products (citronellic acid, tartaric acid, ...), or using selective alkylations of chiral iron complexes,[2] enzymatic resolutions,[3,4] etc. Recently, Clément *et al.* identified, as ant *Camponotus vagus*'s communication pheromones, numerous long chain alkanes bearing one, two or three methyl groups.[5,6] Among them, 11,17-dimethylhentriacontane **1** seems to be the most important compound with respect to the activity of ant.[7]

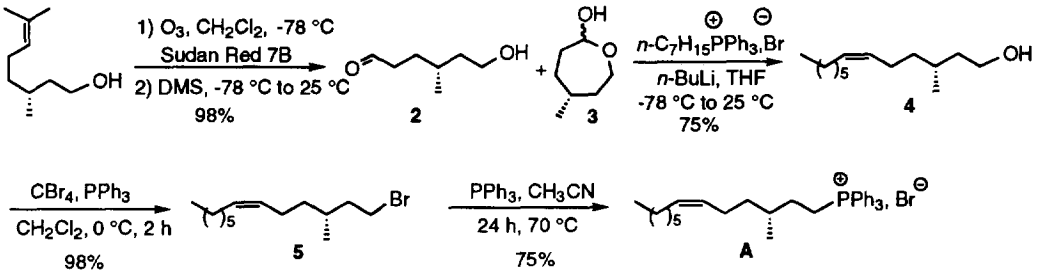


In order to precise the influence of dimethylhentriacontane and the absolute stereochemistry of the active pheromone, we planned the synthesis of the four possible stereoisomers of 11,17-dimethylhentriacontane. Moreover, a knowledge of the most active stereoisomer could be of great interest for the understanding of the biosynthesis of this type of pheromone. Our retrosynthetic strategy shown in scheme **1** is based on the coupling of two building blocks **A** and **B** both prepared from citronellic acid derivatives. The latter was chosen since both pure enantiomers are available.[8] A combination of different transformations (ozonolysis, alkylations, Wittig cross coupling, etc) on each ends of citronellol, should enable a rapid synthesis of all stereoisomers of 11,17-dimethylhentriacontane. In this paper, we focuse our attention on the synthesis of the (*R,S*)-isomer **1**, starting from the (*R*)-citronellol and (*R*)-citronellal.



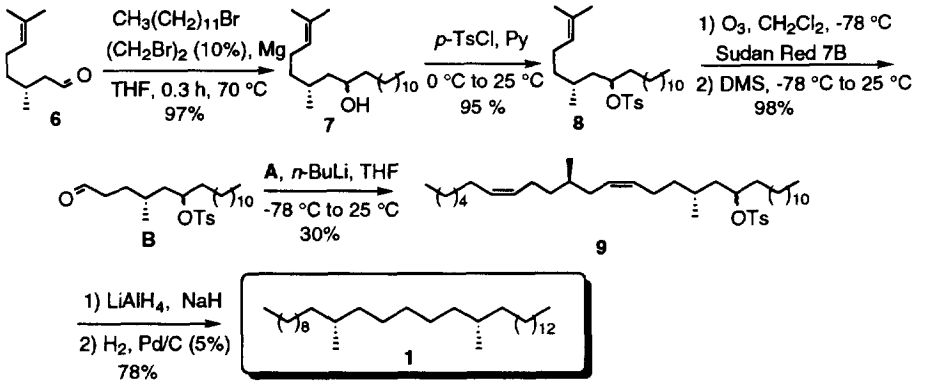
Scheme 1: Retrosynthetic strategy

Synthesis of fragment **A** (scheme **2**) started from (*R*)-citronellol which was converted by ozonolysis to a 1/1 mixture of aldehyde **2** and its hemiacetal form **3** in 98% yield.[9] The Wittig olefination of the mixture **2** + **3** with *n*-heptylidenetriphenylphosphorane gave the (*Z*)-ethylenic alcohol **4** as the major isomer in 75% yield.[10] Bromination under the well described conditions (tetrabromomethane/triphenylphosphine) of the alcohol **4** afforded the bromide **5** which was then converted into triphenylphosphonium salt **A** (74% yield from **4**).



Scheme 2: Synthesis of A fragment

Addition of dodecylmagnesium bromide to (*R*)-citronellal **6** led to a 1/1 mixture of two diastereoisomers of alcohol **7** in nearly quantitative yield. Alcohol **7** was then protected as its tosylate in conventional manner (*p*-tosylchloride/pyridine) in 95% yield. Finally fragment **B** was achieved by ozonolysis of alkene **8** in dichloromethane in 98% yield. We have chosen to remove the tosylate function after the elaboration of the hydrocarbon skeleton in order to permit an easy separation between **9** and the small amount of symmetric olefin (11,16-dimethylhexacos-7,13,19-triene) formed by oxidation of the phosphorane derived from **A**.[11]



Scheme 3: Synthesis of (11R,17S)-11,17-dimethylhentriacontane

A Wittig olefination between the phosphorane generated from **A** and the aldehyde **B** led in 30% yield to the required carbon skeleton. It should be noticed that the low yield of the reaction could be attributed to the long chain borne by the aldehyde.[12] Finally, (11*R*,17*S*)-11,17-dimethylhentriacontane **1** was obtained in a pure form in 78% yield by reduction of the tosylate function with lithium aluminium hydride and sodium hydride[13] followed by hydrogenation of the two double bonds using hydrogen and palladium on carbon in ethyl acetate. The overall yield is 13% from (*R*)-citronellol (seven steps) or 21% from (*R*)-citronellal (six steps).

This first total and stereocontroled synthesis of (*R*,*S*)-dimethylhentriacontane **1** shows the versatile and powerful worth of (*R*)-citronellol (or its derivatives) as chiral building block. Each end may be used separately to introduce any carbon atom long chain with or without a second chiral centre. Syntheses of other pure

enantiomers of branched long chain pheromones are underway. Biological tests are currently underway to investigate the activity and the real role of this pheromone.

Thanks to CNRS and MESR for financial support, Pr J.-L. Clément for fruitful discussions and "Conseil Régional PACA" for a grant (DP).

Experimental section

All reactions were carried out under argon atmosphere. Tetrahydrofuran and diethylether were dried and freshly distilled from sodium/benzophenone. Dichloromethane was dried by distillation over calcium hydride. Flash chromatography was carried out with Merck silica gel (silica gel, 230–400 Mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC 200 or a Bruker AMX 400 (nuclear magnetic resonance) spectrometer. Chemical shifts are given in ppm referring to Me_4Si used as internal standard for ^{1}H and ^{13}C NMR spectra (solvent = $CDCl_3$). Coupling constants are given in Hertz. The mass spectra were obtained on a Hewlett Packard apparatus (engine 5989A) in the GC/MS mode. IR spectra were recorded on a IR-FT Perkin Elmer 1600 apparatus and principal patterns are given in cm^{-1}.

(4*R*)-4-methyl-6-hydroxyhexan-1-al 2: 780 mg (5.0 mmol) of (*R*)-citronellol and 0.3 mg Sudan Red 7B in dichloromethane (50 mL) at -80 °C were submitted to a stream of ozone until the red colour disappear. The yellow solution was immediately purged of ozone by a stream of argon. Then, 1 mL (15.0 mmol) of dimethylsulfide was added; the solution was allowed to warm to room temperature, concentrated and purified by flash chromatography on silica gel which gave 648 mg (98% yield) a mixture (1/1) of **2** and its hemiacetal form **3**. R*f* = 0.26 (diethylether / petroleum ether: 1/1). IR (film): 3390, 2750, 1719, 1457, 1375, 1063. ^{1}H NMR δ: 0.89 (3H, d, *J* = 6.2); 1.35-1.74 (6H, m); 2.43 (1H, dddd, *J* = 1.7, 6.7, 8.4, 17.3); 2.47 (1H, dddd, *J* = 1.7, 6.3, 8.5, 17.3); 3.62-3.73 (2H, m); 9.76 (1H, t, *J* = 1.7). ^{13}C NMR δ: 19.3; 28.7; 29.2; 31.6; 41.6; 60.6; 203.1. hemiacetal **3**: ^{1}H NMR δ: 0.91 (3H, d, *J* = 6.2); 1.30-1.74 (8H, m); 3.53 (1H, dt, *J* = 3.4, 12.8); 3.90 (1H, bt, *J* = 12.8); 5.14 (1H, dd, *J* = 5.3, 9.2). ^{13}C NMR δ: 23.1; 30.9; 34.0; 36.4; 39.4; 60.2; 96.4.

heptyltriphenylphosphonium bromide: To a solution of 17.90 g (100 mmol) of 1-bromoheptane in acetonitrile (100 mL) were added 28.82 g of triphenylphosphine (110 mmol). After refluxing for 24 h, the mixture was concentrated, the crude product was diluted in dichloromethane (10 mL) then added dropwise to 3 L of diethylether. After stirring for 1 h, the precipitate was filtered and dried under vacuum affording 43.60 g (99% yield) of pure white solid. R*f* = 0.36 (5% methanol / CH_2Cl_2). mp: 165 °C. IR (CCl_4): 3054, 2984, 2305, 1424, 1265, 896. ^{1}H NMR δ: 0.78 (3H, t, *J* = 6.6); 1.17-1.21 (8H, m); 1.58-1.60 (2H, m); 3.74-3.81 (2H, m); 7.61-7.87 (15H, m). ^{13}C NMR δ: 13.9; 22.4 (d, J_{CP} = 4.8); 22.6 (d, J_{CP} = 50.2); 28.7; 30.1; 30.4; 31.2; 118.0 (3C, d, J_{CP} = 85); 130.5 (6C, d, J_{CP} = 11.5); 133.5 (6C, d, J_{CP} = 9.5); 135.1 (3C, d, J_{CP} = 3.5).

(*Z*)-(3*R*)-3-methyltridec-6-en-1-ol 4: To a suspension of 6.53 g (14.8 mmol) of heptyltriphenylphosphonium bromide (previously dried by three azeotropic distillations with benzene[14]) in tetrahydrofuran (37 mL) were added, at -40 °C, 8.8 mL (14.1 mmol) of *n*-butyllithium (1.6 M in hexane). The purple solution of ylide was slowly warm to room temperature and stirred for 2 h. After cooling to -80 °C, 490 mg (3.7 mmol) of mixture of **2** and **3** (previously dried by three azeotropic distillations with benzene) were added. The reaction mixture was then allowed to warm to room temperature, quenched by 10 mL of saturated solution of ammonium chloride, 10 mL of water, 10 mL of petroleum ether and extracted with diethylether (3 x 10 mL). The combined organic layers were washed with brine (3 x 10 mL) and dried over magnesium sulfate. After concentration, the crude product was purified by flash chromatography to give 587 mg (75% yield) of **4**

(*Z*/*E* = 9/1). R*f* = 0.39 (diethylether / petroleum ether: 1/1). IR (film): 3353, 2924, 1653, 1454, 1377, 1060, 967. ^{1}H NMR δ: 0.82-0.89 (6H, m); 1.20-1.40 (11H, m); 1.40-1.61 (2H, m); 1.95-2.02 (4H, M); 3.60-3.60 (2H, m); 5.28-5.34 (2H, m). (*Z*)-isomer: ^{13}C NMR δ: 14.1; 19.5; 22.7; 24.7; 27.3; 29.0; 29.2; 29.7; 31.8; 37.2; 39.8; 60.9; 129.7; 130.0; meaningful signals for (*E*)-isomer: 130.2; 130.4.

(*Z*)-(3*R*)-1-bromo-3-methyltridec-6-ene 5: To a mixture of 627 mg (2.9 mmol) of **4** and 2.45 g (7.4 mmol) of carbon tetrabromide in anhydrous dichloromethane (15 mL) was added, at 0 °C, 1.93 g (7.4 mmol) of triphenylphosphine. The reaction mixture was slowly allowed warm to room temperature. After stirring for 2 h, the reaction was checked by TLC (disappearance of alcohol) and concentrated. Purification by flash chromatography on silica gel gave 781 mg (98% yield) of **5**. $[\alpha]^{20;546}$- 11.4 (*c* 1, CH_2Cl_2). R*f* = 0.66 (diethylether / petroleum ether: 1/1). IR (film): 3004, 2925, 2854, 1651, 1459, 1378, 1264, 1217, 967. ^{1}H NMR δ: 0.78-0.93 (6H, m); 1.12-1.23 (1H, m); 1.23-1.39 (10H, m); 1.51-1.68 (1H, m); 1.79-1.89 (1H, m); 1.89-2.08 (4H, m); 3.30-3.47 (2H, m); 5.22-5.39 (2H, m). (*Z*)-isomer ^{13}C NMR δ: 14.2; 18.8; 22.7; 24.6; 27.3; 28.9; 29.7; 31.2; 31.8; 32.0; 36.4; 40.0; 129.4; 130.3; meaningful signals for (*E*)-isomer 129.9; 130.7.

(3*R*)-3-methyltridec-6-en-1-yl-triphenylphosphonium bromide A: To a solution of 427 mg (1.5 mmol) of **5** in acetonitrile (3.1 mL) were added 446 mg (1.7 mmol) of triphenylphosphine. After refluxing for 24 h, the mixture was concentrated and the crude material was chromatographed on silica gel giving 590 mg (75% yield) of **A**. $[\alpha]^{20;546}$- 8 (*c* 1, CH_2Cl_2). R*f* = 0.33 (5% methanol / CH_2Cl_2). IR (film): 3053, 2923, 2854, 1621, 1588, 1483, 1437, 1271, 1190, 1114, 996. ^{1}H NMR δ: 0.73-0.90 (3H, m); 0.90-1.06 (3H, m); 1.13-1.40 (11H, m); 1.50-1.71 (2H, m); 1.76-2.00 (4H, m); 3.70-3.86 (2H, m); 5.20-5.30 (2H, m); 7.63-7.93 (15H, m). ^{13}C NMR δ: 13.9; 18.8; 20.5 (d, J_{CP} = 50.0); 22.4; 24.2; 26.9; 28.6; 29.0 (d, J_{CP} = 5.5); 29.4; 31.4; 32.9 (d, J_{CP} = 14.9); 35.9; 118.3 (3C, d, J_{CP} = 85); 129.2; 130.3; 130.6 (6C, d, J_{CP} = 12.7); 133.7 (6C, d, J_{CP} = 10.2); 135.1 (3C, d, J_{CP} = 3.5); signals for (*E*)-isomer are surimposed with those of (*Z*)-isomer.

(6*R*)-2,6-dimethyleicos-2-en-8-ol 7: To 360 mg (15 at.gr.) of magnesium in tetrahydrofuran (1 mL) were added successively 1,2-dibromoethane (90 µL) and a mixture of 2.49 g (10 mmol) of 1-bromododecane and 1,2-dibromoethane (90 µL) in tetrahydrofuran (9 mL). Then, the reaction mixture was refluxed 20 min, cooled to 30 °C and 1.00 g (6.5 mmol) of (*R*)-citronellal **6** in tetrahydrofuran (6.5 mL) was added dropwise. After 30 min, the reaction was quenched by addition of 20 mL of satured solution of ammonium chloride and extracted with diethylether (3 x 15 mL). The combined organic layers were washed with brine (3 x 15 mL) and dried over magnesium sulfate. The residue was purified by flash chromatography on silica gel to give 2.05 g (97% yield) of **7** as a 1/1 mixture of diastereoisomers. R*f* = 0.40 (diethylether / petroleum ether: 1/4). IR (film): 3360, 2922, 2854, 1712, 1457, 1377, 1292, 1113, 835. ^{1}H NMR δ: 0.79-0.91 (6H, m); 1.23-1.39 (27H, m); 1.55 (3H, s); 1.58 (3H, s); 1.88-2.06 (2H, m); 3.59-3.73 (1H, m); 5.05-5.15 (1H, m). ^{13}C NMR δ: 14.1; 17.7; 19.2; 22.7; 25.4; 25.5; 25.7; 28.9; 29.4 (4C); 29.7 (3C); 32.0; 37.8; 38.5; 45.2; 69.9; 124.9; 131.1; meaningful signals for the other diastereoisomer: 36.7; 38.0; 45.0; 69.6.

(6*R*)-2,6-dimethyl-8-*p*-toluenesulfonyloxyeicos-2-ene 8: To a mixture of 3.05 g (16 mmol) of *p*-toluenesulfonyl chloride and 2.6 mL of pyridine, in 30 mL of dichloromethane under argon, at 0 °C, were added, dropwise 2.10 g (6.5 mmol) of **7** diluted in 12.5 mL of dichloromethane. After stirring for 30 min, the reaction mixture was allowed to warm to room temperature and stirred for 12 h. Then, the solution was pourred in 50 g of crushed ice, slowly warmed to room tempererature, extracted with diethylether (3 x 25 mL), successively washed with a 2N hydrochloric acid solution (20 mL), water (20 mL), brine (2 x 20 mL). After drying over magnesium sulfate and concentration, the crude mixture was purified by flash chromatography on

silica gel to give 2.95 g (95% yield) of **8** as a 1/1 mixture of diastereoisomers. R*f* = 0.48 (diethylether / petroleum ether: 1/4). IR (film): 2924, 2854, 1460, 1366, 1178, 1097, 896, 815. ^{1}H NMR δ: 0.64-0.98 (6H, m); 0.98-1.36 (27H, m); 1.65 (3H, s); 1.56 (3H, s); 1.73-2.04 (2H, m); 2.23-2.50 (3H, s); 4.50-4.71 (1H, m); 4.96-5.08 (1H, m); 7.27-7.31 (2H, d, *J* = 8.0); 7.74-7.78 (2H, d, *J* = 8.2). ^{13}C NMR δ: 14.2; 17.7; 19.7; 21.6; 22.7; 24.6; 25.3; 25.7; 29.0; 29.6; 29.4 (3C); 29.7 (3C); 32.0; 35.0; 37.3; 41.7; 83.1; 124.6; 127.8 (2C); 129.7 (2C); 131.3; 135.1; 144.3; meaningful signals for the other diastereoisomer: 19.3; 24.5; 25.2; 28.6; 34.3; 36.8; 82.9.

(4*R*)-4-methyl-6-*p*-toluenesulfonyloxyoctadecan-1-al B: 956 mg (2.0 mmol) of **8** and 0.4 mg of Sudan Red 7B in dichloromethane (20 mL), at -80 °C, were submitted to a stream of ozone until the red colour disappear. The yellow solution was immediately purged of ozone by a stream of argon. Then, 500 µL (6.0 mmol) of dimethylsulfide was added; the solution was allowed to warm to room temperature, concentrated and purified by flash chromatography on silica gel which gave 890 mg (98% yield) of **B**. R*f* = 0.41 (diethylether / petroleum ether: 1/1). IR (film): 2925, 2855, 1724, 1461, 1359, 1177, 1097, 897, 737. ^{1}H NMR δ: 0.70-1.00 (6H, m); 1.00-1.70 (27H, m); 2.22-2.44 (2H, m); 2.42 (3H, s); 4.52-4.70 (1H, m); 7.28-7.32 (2H, d, *J* = 8.2); 7.74-7.78 (2H, d, *J* = 8.1); 9.70 (1H, t, *J* = 1.6). ^{13}C NMR δ: 14.2; 19.6; 21.6; 22.7; 24.6; 28.3; 28.7; 29.4 (3C); 29.5; 29.7 (3C); 32.0; 35.0; 41.4; 41.6; 82.6; 127.8 (2C); 129.7 (2C); 134.7; 144.5; 202.2; meaningful signals for the other diastereoisomer: 19.0; 24.5; 28.6; 34.4; 41.3; 41.5; 82.4; 202.3.

(11*R*,17*R*)-11,17-dimethyl-19-*p*-toluenesulfonyloxyhentriacont-7,13-diene 9: To a suspension of 1.07 g (2.0 mmol) of **A** (previously dried by three azeotropic distillations with benzene) in tetrahydrofuran (12 mL) were added, at -60 °C, 1.3 mL (1.9 mmol) of *n*-butyllithium (1.6 M in hexane). The orange solution of ylide was slowly warm to room temperature and stirred for 2 h. After cooling to -80 °C, 508 mg (1.1 mmol) of **B** (previously dried by three azeotropic distillations with benzene) were added. The reaction mixture was then allowed to warm to room temperature, quenched by 10 mL of saturated solution of ammonium chloride, 10 mL of water, 10 mL of petroleum ether and extracted with diethylether (3 x 10 mL). The combined organic layers were washed with brine (3 x 10 mL) and dried over magnesium sulfate. After concentration, the crude product was purified by flash chromatography to give 365 mg (30% yield) of **9** as a 1/1 mixture of diastereoisomers. R*f* = 0.59 (diethylether / petroleum ether: 1/4). ^{1}H NMR δ: 0.68-0.98 (12H, m); 1.00-1.74 (38H, m); 1.74-2.14 (8H, m); 2.41 (3H, s); 4.52-4.75 (1H, m); 5.22-5.39 (4H, m); 7.53-7.64 (2H, d, *J* = 7.9); 7.75-7.79 (2H, d, *J* = 8.1). ^{13}C NMR δ: 14.2 (2C); 19.3; 19.6; 21.7; 22.7; 22.8; 24.7; 25.0; 27.3; 29.1; 29.4 (4C); 29.6 (2C); 29.8 (4C); 31.9; 32.1; 33.1; 34.4; 35.1; 36.8; 37.3; 41.8; 83.0; 127.8 (2C); 128.5; 129.7 (2C); 129.8; 129.9; 130.3; 135.1; 144.3; meaningful signals for the other diastereoisomer: 28.7; 34.6; 36.9; 82.9; 129.6 (2C); 135.0; 144.2.

(11*R*,17*S*)-11,17-dimethylhentriacont-7,13-diene: To a suspension of 14 mg (0.58 mmol) of sodium hydride were added 22 mg (0.58 mmol) of lithium aluminium hydride in anhydrous ether (2.3 mL). Then, 365 mg (0.58 mmol) of **9** were added. After stirring for 10 h at room temperature, the reaction was monitored by TLC (disappearance of starting material). The reaction was quenched by 3 mL of ethanol, filtered on celite 545 and 267 mg (98% yield) of diene was obtained after concentration. R*f* = 0.62 (petroleum ether). ^{1}H NMR δ: 0.60-0.91 (12H, m); 0.91-1.54 (40H, m); 1.65-2.11 (8H, m); 5.14-5.48 (4H, m). ^{13}C NMR δ: 14.2 (2C); 19.6; 19.7; 22.7; 22.8; 25.0 (2C); 27.2; 27.3; 29.1-30.3 (11C); 31.9; 32.0; 32.5; 33.1; 34.5; 36.8; 37.1 (2C); 128.1; 129.8; 129.9; 131.0.

(11*R*,17*S*)-11,17-dimethylhentriacontane 1: To 267 mg (0.57 mmol) of 11,17-dimethylhentriacont-7,13-diene in ethyl acetate (6 mL) were added 30 mg of palladium on carbon and submitted to hydrogen

atmosphere. The reaction was checked by TLC (disappearance of starting material). The reaction mixture was filtered on celite 545, concentred to give 215 mg (80% yield) of (*R*,*S*)-11,17-dimethylhentriacontane.$[\alpha]^{20;546}$- 4.5 (*c* 1, CH_2Cl_2). R*f* = 0.71 (petroleum ether). ^{1}H NMR δ: 0.79-0.88 (12H, bt); 1.23 (56H, bs). ^{13}C NMR δ: 14.2 (2C); 19.8 (2C); 22.8 (2C); 27.2(4C); 29.5-30.1 (14C); 30.5; 32.0 (2C); 32.8 (2C); 37.2 (4C). MS (70eV): m/z= 449 (M-15, 5); 323 (14); 239 (9); 267 (21); 224 (21); 168 (37); 169 (14); 141 (12); 127 (14); 125 (18); 113 (22); 99 (32); 97 (19); 85 (64); 71 (79); 57 (100); 55 (23). Analysis: calculated: C 85.26, H 14.74; found: C 85.34, H 14.52.

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(*Received in UK* 15 *April* 1996)