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SYNTHESIS OF OPTICALLY ACTIVE FORMS OF (*Z*)-14-METHYLHEXADEC-8-ENAL

THE PHEROMONE OF FEMALE DERMESTID BEETLE[a]

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Abstract—The both enantiomers of (*Z*)-14-methylhexadec-8-enal were synthesized starting from (*R*)-(+)-citronellol. The (*R*)-(−)-enantiomer (**1**) was about 250 times more active than its amtipode (**1'**) when tested on dermestid beetle.

In 1969, Burkholder, *et al.*[1] studied the sex pheromone of the female dermestid beetle, *Trogoderma inclusum* Le Conte, and isolated (*Z*)-(−)-14-methylhexadec-8-en-1-ol **16**, and methyl (*Z*)-(−)-14-methylhexadec-8-enoate by extracting whole insects. The absolute configuration of these pheromone components was determined by us to be *R* by synthesizing their antipodes from (*S*)-(−)-2-methylbutan-1-ol.[2] Very recently Rossi and Carpita critically traced our synthesis confirming the reported $[\alpha]_D$ value of (*S*, *Z*)-(+)-14-methylhexadec-8-en-1-ol.[3]

In 1976, Cross *et al.* isolated the genuine sex pheromone of *T. inclusum* and *T. variabile* by aeration of the female beetles and identified it as (*Z*)-14-methylhexadec-8-enal (**1** and **1'**).[4] We therefore decided to synthesize both enantiomers (**1** and **1'**) of the pheromone to clarify the relationship between chirality and pheromone activity.[5] In the present work we tried to circumvent the ambiguity concerning the optical and/or chemical purities of (*S*)-(−)-2-methylbutan-1-ol, the starting material in our previous synthesis.[c,2,3] This required us to employ (*R*)-(+)-citronellol **2a** as the common starting material for the both enantiomers (**1** and **1'**). Since the optical purity of our (*R*)-(+)-citronellol **2a** was high,[6,cf 7] the synthesis described below enabled us to secure highly pure **1** and **1'**.

The tosylate **2b** of (*R*)-(+)-citronellol was oxidized with *m*-chloroperbenzoic acid to give an epoxide **3**. This was cleaved with HIO_4 to an aldehyde **4** whose reduction with LAH yielded gas chromatographically pure (*S*)-(+)-4-methylhexan-1-ol **5a**, $[\alpha]_D^{20}$ + 6.63° (neat). The corresponding tosylate **5b** was treated with LiBr to give a bromide **6**. The coupling of the Grignard reagent prepared from **6** with allyl bromide afforded an optically active olefin **7'** with *S* absolute configuration.

The enantiomeric *R*-olefin **7** was prepared as follows. The acetate **2c** of (*R*)-(+)-citronellol was oxidized with *m*-chloroperbenzoic acid to give an epoxide **8**. This was treated with selenophenol followed by hydrogen peroxide[8] to give a crude alcohol **9a**. After acetylation to **9b**, the olefinic alcohol was oxidized with *m*-chloroperbenzoic acid yielding an epoxide **10**. Oxidation with HIO_4

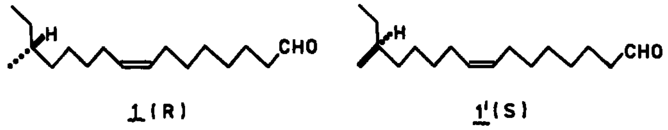

Fig. 1.

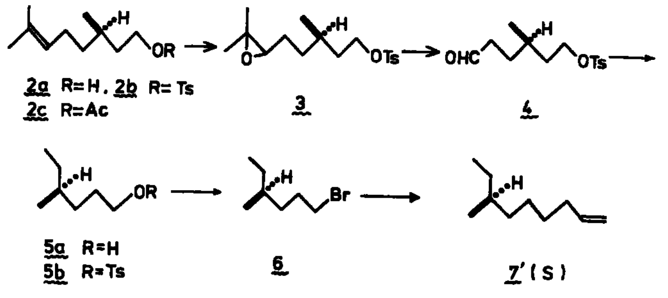

Fig. 2.

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[a] Pheromone Synthesis XXIII. This work was presented at 175th ACS National Meeting in Anaheim, Calif., on 16 March 1978, as a part of K.M.'s lecture in a Symposium entitled *Stereochemical Aspects of Pesticide Chemistry*. The experimental part of this work was taken from the forthcoming doctoral dissertation of T.S. Part XXII, K. Mori, S. Masuda and M. Matsui, *Agric. Biol. Chem.* **42**, 1015 (1978).

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[c] Another drawback of this starting material was the unavailability of its (*R*)-(+)-isomer.

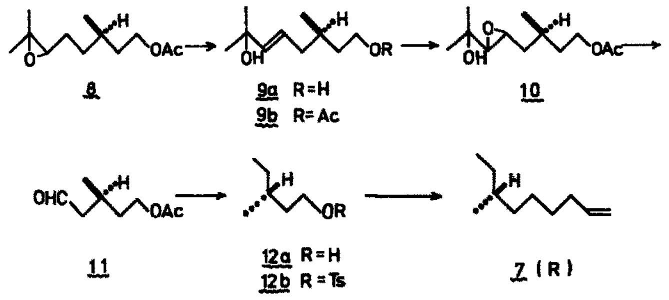

Fig. 3.

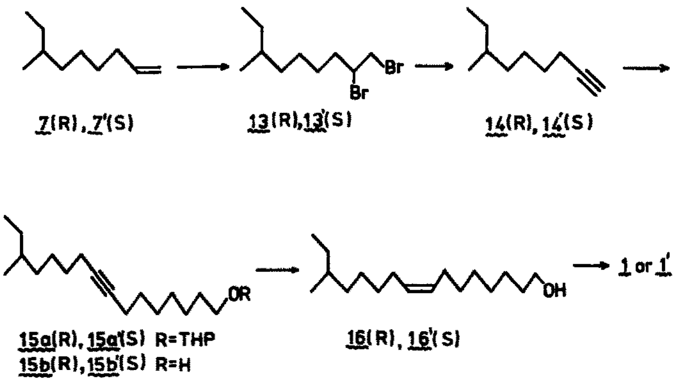

Fig. 4.

cleaved the epoxide to an aldehyde **11**. The Wolff–Kishner reduction of **11** gave gas chromatographically pure (*R*)-(−)-3-methylpentan-1-ol **12a**, $[\alpha]_D^{22}$ −5.42° (neat). The corresponding tosylate **12b** was coupled in the presence of Li_2CuCl_4[9] with a Grignard reagent prepared from but-3-enyl bromide to give the required *R*-olefin **7**. Throughout these synthetic sequences the absolute configuration of the asymmetric C atom of citronellol was fully retained as later shown by the $[\alpha]_D$ values of the final products (**1** and **1'**), although GLC analyses revealed the presence of unidentified impurities in our **7** and **7'**.

The olefins **7** and **7'** were converted by the addition of Br_2 to dibromides **13** and **13'**, respectively. Dehydrobromination of **13** and **13'** with $NaNH_2$ in liq NH_3 gave acetylenes **14** and **14'**. The (*S*)-(+)-acetylene **14'**, $[\alpha]_D^{19}$ + 8.84 (neat), was 95% pure as shown by GLC. The (*R*)-(−)-acetylene **14**, however, was about 80% pure with $[\alpha]_D^{21}$ value of −5.94° (neat). The acetylenes **14** and **14'** in THF were treated with n-BuLi and the resulting carbanion was alkylated with 1-tetrahydropyranyloxy-7-iodoheptane in HMPA. The products **15a** and **15a'**, were treated with *p*-TsOH in MeOH to give alcohols **15b** and **15b'**, respectively. The semi-hydrogenation of **15b** and **15b'** was followed by chromatographic purification over SiO_2–$AgNO_3$ to give **16** and **16'**, respectively. The GLC analysis revealed the (*R*)-alcohol **16**, $[\alpha]_D^{20}$ −5.43° ($CHCl_3$), to be 96% pure. The antipodal (*S*)-alcohol **16'**, $[\alpha]_D^{22}$ + 5.57° ($CHCl_3$), was also 96% pure by GLC analysis. The reported $[\alpha]_D$ values for this alcohol **16'** in the same solvent were +5.31° (Mori)[2] and +5.33° (Rossi and Carpita).[3] Rossi and Carpita estimated their alcohol **16'** to be 92.5% optically pure by comparing the rotation value of their intermediate with that of the optically pure authentic material. Our alcohols were therefore throught to be highly optically pure (>92.5%). Oxidation of **16** and **16'** with CrO_3·C_5H_5NHCl[10] yielded the final products, (*R*, *Z*)-14-methylhexadec-8-enal **1**, $[\alpha]_D^{21}$ − 5.94° ($CHCl_3$), and (*S*, *Z*) − **1'**, $[\alpha]_D^{21}$ + 6.02° ($CHCl_3$). The GLC analyses revealed their purities to be 94% for **1** and >98% for **1'**, respectively. The IR, NMR and mass spectra of our **1** and **1'** were entirely identical with the published charts of the natural pheromone.[4] Rossi and Carpita reported the rotation value of **1'** to be $[\alpha]_D^{25}$ + 6.05° (ether).[3]

In conclusion we synthesized the both enantiomers of the dermestid beetle pheromone in highly optically pure states. The biological evaluation of our material was kindly carried out by Prof. W. E. Burkholder, University of Wisconsin, employing *Trogoderma inclusum* Le Conte as the test animal. The 50% response threshold dose for the (*R*)-pheromone (**1**) was 9.6×10^{-4} μg per male insect, while that of the (*S*)-isomer (**1'**) was 3.9×10^{-2} μg. The (*R*)-enantiomer was therefore about 250 times more active than its antipode. The (*S*)-isomer showed no inhibitory effect when mixed with the (*R*)-isomer. This may mean that the (*S*)-isomer is biologically inactive, since it is highly probable that its weak activity is due to the contamination of a trace amount of the (*R*)-isomer.[d]

EXPERIMENTAL

All b.ps were uncorrected. IR spectra refer to films and were determined on a Jasco IRA-1 spectrometer. NMR spectra were recorded as CCl_4 solns at 60 MHz with TMS as an internal standard on a Hitachi R-24A spectrometer. Optical rotations

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[d] At the time when this work was almost completed except for the later stages in the synthesis of (*S*)-(+)-**1'**, Rossi orally reported his synthesis of (*R*)-(−)-**1** from (*R*)-(+)-citronellol **2a** at the EUCHEM Conference on Mono- and Sesquiterpenoids, Varenna, Lake Como, Italy, on 27 August 1977. K.M. expresses his thanks to Prof. G. Jommi (Milan) for having invited him to that Conference.

were measured on a Jasco DIP-4 polarimeter. GLC analyses were performed on a Yanaco G 80 gas chromatograph.

(R)-(+)-*Citronellol tosylate* **2b**. Powdered tosyl chloride (41.4 g) was added portionwise to a stirred and cooled soln of **2a** (26.5 g; prepd from (*R*)-(+)-citronellic acid with $[\alpha]_D^{23}+11.2°$ ($c = 2.8$, $CHCl_3$) by reduction with LAH) in dry pyridine (150 ml) at 0–5°. The mixture was stirred for 2 hr under ice-cooling, poured into ice-water–dil HCl and extracted with ether. The ether soln was washed with dil HCl, water, $NaHCO_3$ aq and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The resulting crude tosylate **2b** (49g) was employed for the next step without further purification, ν_{max} 2910 (s), 1600 (m), 1195 (s), 1180 (s) cm^{-1}.

(R)-*Epoxycitronellol tosylate* **3**. *m*-Chloroperbenzoic acid (74% purity, 42 g) was added portionwise to a stirred and ice-cooled soln of **2b** (49 g) in dry CH_2Cl_2 (200 ml). After the addition, the mixture was stirred for 2 hr and then filtered to remove precipitated *m*-chlorobenzoic acid. The CH_2Cl_2 soln was washed with $NaHSO_3$ aq, dil Na_2CO_3 aq and brine, dried ($MgSO_4$) and concentrated *in vacuo* to give crude **3** (51 g), ν_{max} 2980 (s), 2940 (s), 1600 (m), 1200 (s), 1185 (s) cm^{-1}; δ0.87 (3H, d, J = 6 Hz), 1.16 (3H, s), 1.20 (3H, s), 2.44 (3H, s), 4.04 (2H, t, J = 6 Hz), 7.34 (2H, d, J = 9 Hz), 7.78 (2H, d, J = 9 Hz). This was employed for the next step without further purification.

(R)-6-*Tosyloxy-4-methylhexanal* **4**. A soln of $HIO_4.2H_2O$ (40 g) in THF (100 ml) was added dropwise to a stirred and ice-cooled soln of **3** (51 g) in ether (300 ml). After stirring for 1 hr, the mixture was poured into ice-water and extracted with ether. The ether soln was washed with water, $NaHCO_3$ aq, $Na_2S_2O_3$ aq and brine, dried ($MgSO_4$) and concentrated to give crude **4** (43 g), ν_{max} 2970 (s), 2940 (s), 2880 (m), 2720 (w), 1730 (vs), 1600 (m), 1365 (vs), 1195 (vs), 1185 (vs) cm^{-1}; δ 0.82 (3H, d, J = 5 Hz), 2.40 (3H, s), 4.00 (2H, t, J = 6 Hz), 7.40 (2H, d, J = 9 Hz), 7.82 (2H, d, J = 9 Hz), 9.74 (1H, t, J = 1.5 Hz). This was employed for the next step without further purification.

(S)-(+)-4-*Methylhexan*-1-*ol* **5a**. A soln of **4** (43 g) in dry ether (30 ml) was gradually added to a stirred and ice-cooled suspension of LAH (17 g) in dry ether (1000 ml). The mixture was stirred for 12 hr at room temp. Then water was added dropwise to the stirred and ice-cooled mixture to destroy the excess of LAH. The mixture was poured into ice-dil HCl. The ether layer was separated and the aqueous layer was extracted with ether. The combined ether soln was washed with water, $NaHCO_3$ aq and brine, dried ($MgSO_4$) and concentrated. The residue was distilled to give 11.62 g (54% from **2a**) of **5a**, b.p. 87–92°/26 mm, n_D^{20} 1.4278; $[\alpha]_D^{20}+6.63°$ (neat); ν_{max} ~3320 (s), 2970 (s), 2940 (s), 2870 (s), 1460 (m), 1390 (m), 1060 (s), 900 (w) cm^{-1}; δ 0.88 (6H, deformed t, br.), ~1.35 (7H, br), 3.50 (2H, t, J = 6 Hz), 4.28 (1H, s); MS: *m/e* 116 (M^+); GLC (Column, 5% LAC 2R-446, 1.5 m × 3 mm i.d. at 80°; Carrier gas, N_2, 1 kg/cm^2): Rt 2.8 min. (Found: C, 72.30; H, 13.59. $C_7H_{16}O$ requires: C, 72.35; H, 13.88%).

(S)-(+)-1-*Bromo-4-methylhexane* **6**. Powdered tosyl chloride (14.6 g) was added portionwise to a stirred and ice-cooled soln of **5a** (7.44 g) in dry pyridine (70 ml). The mixture was stirred for 2 hr at 0–5°. Subsequent work-up as described for **2b** gave 18.8 g of **5b**, ν_{max}, 2960 (s), 2920 (s), 2880 (s), 1600 (m), 1200 (s), 1185 (s) cm^{-1}. This was dissolved in acetone (100 ml). LiBr (15.1 g) was added to the soln. The mixture was heated under reflux for 1 hr and then stirred for 12 hr at room temp. After pouring into ice-water, the mixture was extracted with ether. The ether soln was washed with water and $NaHCO_3$ aq, dried ($CaCl_2$) and concentrated. The residue was distilled to give 8.3 g (72.4% from **5a**) of **6**, b.p. 67–72°/28 mm, n_D^{21} 1.4484; $[\alpha]_D^{21}+11.0°$ (neat); ν_{max} 2960 (s), 2920 (s), 2860 (s), 1460 (m), 1380 (m), 1250 (m), 1210 (m) cm^{-1}; δ 0.88 (6H, br), ~1.32 (4H, m), ~1.80 (3H, m), 3.32 (2H, t, J = 6 Hz); MS: 180, 178 (M^+); GLC (Column, 5% LAC 2R-446, 1.5 m × 3 mm i.d. at 60°; Carrier gas, N_2, 1 kg/cm^2): Rt 2.6 min. (Found: C, 48.85; H, 8.79. $C_7H_{15}Br$ requires: C, 46.94; H, 8.44%. This bromide unfortunately did not give correct analytical data).

(S)-(+)-7-*Methylnon*-1-*ene* **7'**. A Grignard reagent was prepared from **6** (12.8 g) and Mg (1.74 g) in dry ether (40 ml). Allyl bromide (9.5 g) was added dropwise to the reagent under ice-cooling and then the mixture was heated under reflux for 2 hr. These operations were carried out under Ar. The mixture was poured into ice-water and extracted with ether. The ether soln was dried ($CaCl_2$) and fractionally distilled to give 7.1 g (71%) of **7'**, b.p. 158–162°, n_D^{23} 1.4225; $[\alpha]_D^{23}+7.14°$ (neat); ν_{max} 3090 (w), 2970 (s), 2940 (s), 2890 (s), 2860 (s), 1645 (m), 1470 (m), 1390 (m), 995 (m), 910 (s) cm^{-1}; δ 0.88 (6H, br), ~1.28 (9H, br), ~2.05 (2H, br. d), ~4.8–~5.2 (2H, m), 5.48–~6.2 (1H, m); GLC (Column, 3% SE-30, 2.25 m × 3 mm i.d. at 60°; Carrier gas, N_2, 1 kg/cm^2): Rt 4.7 min (80%), impurity at Rt 3.5 min. MS: *m/e* 140 (M^+).

(R)-(+)-*Citronellol acetate* **2c**. Ac_2O (52 ml) was added to a soln of **2a** (26 g) in dry pyridine (26 ml) and the mixture was heated on a boiling water bath for 3 hr. Then it was poured into water and extracted with ether. The ether soln was washed with water, dil HCl, $NaHCO_3$ aq and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was distilled to give 31 g (94%) of **2c**, b.p. 88–93°/3 mm. This was employed for the next step without further purification.

(R)-(+)-*Epoxycitronellol acetate* **8**. *m*-Chloroperbenzoic acid (80% purity, 32.5 g) was added portionwise to a stirred and ice-cooled soln of **2c** (27 g) in CH_2Cl_2 (200 ml) at 5–10°. The mixture was stirred for 2 hr at 0–5°. Then it was washed with Na_2CO_3 aq and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was distilled to give 26.6 g (91%) of **8**, b.p. 94–104°/3 mm, $n_D^{21.5}$ 1.4366; $[\alpha]_D^{22}+2.26°$ (neat); ν_{max} 2960 (s), 2930 (s), 2880 (m), 1745 (s), 1460 (m), 1385 (m), 1375 (m), 1250 (s), 1060 (m), 1040 (m) cm^{-1}; δ 0.95 (3H, d, J = 6 Hz), 1.18 (3H, s), 1.20 (3H, s), ~1.45 (7H, br), 1.96 (3H, s), 2.50 (1H, t, J = 4 Hz), 4.05 (2H, t, J = 6 Hz); GLC (Column, 5% LAC 2R-446, 1.5 m × 3 mm at 120°; Carrier gas, N_2, 1 kg/cm^2): Rt 7.7 min. (Found: C, 66.94; H, 10.21. $C_{12}H_{22}O_3$ requires: C, 67.26; H, 10.35%).

(S)-(+)-3,7-*Dimethyloct*-5-*ene*-1,7-*diol* 1-*acetate* **9b**. A soln of C_6H_5SeNa was prepared by the addition of $NaBH_4$ (8g) to a suspension of $C_6H_5SeSe_6H_5$ (29.35 g) in EtOH (300 ml) under N_2. To this was added a soln of **8** (35 g) in EtOH (30 ml). The mixture was stirred and heated under reflux for 2 hr. After cooling and dilution with THF (200 ml), 30% H_2O_2 (130 ml) was added dropwise to the stirred and cooled mixture during 1 hr below 20°. The stirring was continued for 5 hr at room temp. Then the mixture was diluted with water and extracted with ether. The ether soln was washed with Na_2CO_3 aq and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residual crude **9a**, ν_{max} 3360 (s), 2980 (s), 2930 (s), 1060 (s) cm^{-1}, was mixed with dry pyridine (24 ml) and Ac_2O (48 g). The mixture was left to stand overnight at room temp. Then it was poured into water and extracted with ether. The ether soln was washed with water, dil HCl, $NaHCO_3$ aq and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was distilled to give 25.5 g (72% from **8**) of **9b**, b.p. 113–118°/1.1 mm, $n_D^{22.5}$ 1.4486: $[\alpha]_D^{22.5}+2.22°$ (neat); ν_{max} 3410 (m), 2960 (s), 2920 (s), 2860 (m), 1740 (s), 1660 (w), 1460 (m), 1370 (s), 1245 (s), 1150 (m), 1040 (m), 970 (m) cm^{-1}; δ 0.96 (3H, d, J = 6 Hz), 1.23 (6H, s), 1.54 (5H, m), 1.99 (3H, s), 2.66 (1H, s), 4.03 (2H, t, J = 6 Hz), 5.53 (2H, br. s): GLC (Column, 5% LAC 2R-446, 1.5 m × 3 mm i.d. at 120°; Carrier gas, N_2, 1.0 kg/cm^2): Rt 15.2 min; MS: *m/e* 214 (M^+).

(S)-(+)-5,6-*Epoxy*-3,7-*dimethyloctane*-1,7-*diol* 1-*acetate* **10**. *m*-Chloroperbenzoic acid (75% purity, 30.15 g) was gradually added to a stirred and cooled soln of **9b** (25.5 g) in CH_2Cl_2 (200 ml) at 5–10°. The mixture was stirred for 2 hr at 0–5° and filtered to remove the precipitated *m*-chlorobenzoic acid. The filtrate was washed with Na_2CO_3 soln, dried ($MgSO_4$) and concentrated *in vacuo* to give 26 g of crude **10**, ν_{max} 3480 (m), 2980 (s), 2940 (s), 2880 (m), 1745 (s), 1465 (m), 1380 (s), 1250 (s), 1050 (m) cm^{-1}; δ 1.03 (3H, d, J = 6 Hz), 1.18 (3H, s), 1.22 (3H; s), ~1.5 (5H, m), 1.99 (3H, s), 2.26 (1H, s), 2.58 (1H, d, J = 2 Hz) 2.90 (1H, dt, $J_1 = 6$, $J_2 = 2$ Hz), 4.08 (2H, t, J = 6 Hz). This was employed for the next step without further purification.

(S)-(−)-5-*Acetoxy*-3-*methylpentanal* **11**. A soln of $HIO_4 \cdot 2H_2O$ (50 g) in THF (100 ml) was added dropwise to a stirred and ice-cooled soln of **10** (26 g) in ether (100 ml). After the addition, the mixture was stirred for 8 hr at 0–5°. Then it was poured into water and extracted with ether. The ether soln was washed with water, $NaHCO_3$ aq, $Na_2S_2O_3$ aq and brine, dried ($MgSO_4$) and concentrated. The residue was distilled to give 7.43 g (40%) of **11**, b.p. 104–115°/11 mm, n_D^{22} 1.4347; $[\alpha]_D^{22}-4.90°$ (neat); ν_{max} 2970 (s), 2940 (s), 2880 (m), 2720 (w), 1740 (s), 1730 (sh), 1460 (m), 1380 (s), 1240 (s), 1060 (m), 1030 (m) cm^{-1}; δ 0.98 (3H, d, J = 6 Hz), ~1.6 (3H, m), 1.97 (3H, s), 2.30 (2H, br, s), 4.03 (2H, t, J = 6 Hz), 9.75 (1H, t, J = 2 Hz); GLC (Column, 5% LAC 2R-446, 1.5 m × 3 mm i.d. at 80°; Carrier gas, N_2, 1 kg/cm^2): Rt 7.5 min; MS: *m/e* 158 (M^+).

(R)-(−)-3-*Methylpentan*-1-*ol* **12a**. A mixture of **11** (4 g), 85% $N_2H_4 \cdot H_2O$ (10 ml) and diethylene glycol (16 ml) was heated under reflux for 30 min. Then KOH (8 g) in water (10 ml) was added and the mixture was heated under reflux for another 30 min. Then the bath temp was gradually raised to 200°. Water (50 ml) was added portionwise to the mixture during 2 hr. This effected the steam-distillation of the reduction product. The distillate was extracted with ether. The ether soln was washed with water and brine, dried ($MgSO_4$) and concentrated. The residue was distilled to give 1.6 g (62%) of **12a**, b.p. 63–67°/17 mm, n_D^{22} 1.4185; $[\alpha]_D^{22}$ − 5.42° (neat); ν_{max} 3330 (s), 2960 (s), 2940 (s), 2880 (s), 1465 (m), 1390 (m), 1070 (s), 1030 (m) cm^{-1}; δ 0.90 (6H, br), ~1.45 (5H, br), 3.55 (2H, t, J = 6 Hz), 3.55 (1H, s, –OH); MS: *m/e* 102 (M^+); GLC (5% LAC 2R-446, 1.5 m × 3 mm i.d. at 60°; Carrier gas, N_2 1 kg/cm^2): Rt 3.8 min. (Found: C, 70.13; H, 14.02. $C_6H_{14}O$ requires: C, 70.53; H, 13.81%).

(R)-3-*Methylpentyl tosylate* **12b**. Powdered tosyl chloride (7.19 g) was added to a stirred and ice-cooled soln of **12a** (3.5 g) in dry pyridine (40 ml). The mixture was stirred for 2 hr at 0–5°. Then it was poured into ice-dil HCl and extracted with ether. The ether soln was washed with dil HCl, water, $NaHCO_3$ aq and brine, dried ($MgSO_4$) and concentrated *in vacuo* to give 8 g of crude **12b**, ν_{max} 2960 (s), 2920 (s), 2870 (m), 1600 (m), 1460 (m), 1365 (s), 1180 (s), 1100 (m), 940 (s), 890 (s), 860 (m) cm^{-1}; δ 0.85 (6H, m), ~1.0–~2.0 (5H, m), 2.42 (3H, s), 4.00 (2H, t, J = 6 Hz), 7.38 (2H, d, J = 9 Hz), 7.80 (2H, d, J = 9 Hz). This was employed for the next step without further purification.

(R)-(−)-7-*Methylnon*-1-*ene* **7**. A soln of **12b** (8 g) in THF (30 ml) was gradually added at −78° under Ar to the Grignard reagent prepared from but-3-enyl bromide (9.2 g) and Mg (2.1 g) in dry ether (50 ml). Subsequently 1.77 ml of 0.1 M–Li_2CuCl_4 in THF was added to the mixture. The reaction temp was raised during 2 hr to room temp and the mixture was stirred for 12 hr. Then it was poured into ice-dil H_2SO_4. The organic layer was separated, washed with water, dried ($CaCl_2$) and fractionally distilled to give 3.3 g (50% yield) of crude **7**, b.p. 158–162°, n_D^{20} 1.4226; $[\alpha]_D^{21}$ − 4.92° (neat); GLC (3% SE-30, 2.25 m × 3 mm i.d. at 60°; Carrier gas, N_2, 0.6 kg/cm^2): Rt 4.7 min (69.0%), impurity at 3.4 min; MS: *m/e* 140 (M^+). The IR and NMR spectra of **7** were identical with those described for **7′**.

(S)-(+)-1,2-*Dibromo*-7-*methylnonane* **13′**. A soln of Br_2 (6.4 g) in CH_2Cl_2 (20 ml) was added dropwise to a stirred soln of **7′** (5.6 g) in CH_2Cl_2 (50 ml) under ice-cooling. After the addition the mixture was washed with $Na_2S_2O_3$ aq, dried ($CaCl_2$) and concentrated. The residue was distilled to give 10.0 g (83%) of **13′**, b.p. 108–112°/6 mm, $n_D^{21.5}$ 1.4934; $[\alpha]_D^{23}$ + 7.20° (neat); ν_{max} 2970 (s), 2940 (s), 2860 (s), 1465 (m), 1440 (m), 1390 (m), 1150 (m) cm^{-1}; δ 0.88 (6H, br), ~1.1–~2.5 (11 H, br), ~3.3–~4.5 (3H, m); GLC (5% LAC 2R-446, 1.5 m × 3 mm i.d. at 120°; Carrier gas, N_2, 1.0 kg/cm^2): Rt 6.0 min (single peak); MS: *m/e* 219 and 221 (M^+–Br).

(R)-(−)-1,2-*Dibromo*-7-*methylnonane* **13**. Similarly **7** gave crude **13** (72% yield), b.p. 122–130°/6 mm, n_D^{21} 1.5019; $[\alpha]_D^{21}$ − 5.76° (neat); GLC (5% LAC 2R-446, 1.5 m × 3 mm i.d. at 120°; Carrier gas, N_2, 1.0 kg/cm^2): Rt 6.0 min (80%), impurity at 8.7 min, MS: *m/e* 219 and 221 (M^+–Br).

(S)-(+)-7-*Methylnon*-1-*yne* **14′**. A soln of **13′** (10 g) in dry ether (10 ml) was added dropwise at −33° to a suspension of $NaNH_2$ (from 3.0 g of Na) in liq NH_3 (50 ml). The mixture was stirred for 4 hr at −40°, then left to stand at room temp. to remove NH_3, poured into ice-water and extracted with ether. The ether soln was washed with water and brine, dried ($MgSO_4$) and fractionally distilled to give 3.5 g (76%) of **14**, b.p. 96–98°/84 mm, $n_D^{21.5}$ 1.4262; $[\alpha]_D^{19}$ + 8.84° (neat); ν_{max} 3300 (s), 2930 (s), 2860 (s), 2110 (m), 1460 (m), 1430 (w), 1380 (m) cm^{-1}; δ 0.90 (6H, deformed t, J = 6 Hz), ~1.36 (9H, br), 1.77 (1H, t, J = 3 Hz), ~2.18 (2H, br); GLC (5% LAC 2R-446, 1.5 m × 3 mm i.d. at 60°; Carrier gas, N_2, 1.0 kg/cm^2): Rt 1.35 min (95%), impurity at 0.8 min; MS: *m/e* 138 (M^+). Rossi and Carpita reported n_D^{25} 1.4255 and $[\alpha]_D^{20}$ + 9.55° (neat) for this compound.[3] However, their NMR data [δ 5.16 (2H, m), 3.51 (2H, t), 3.20 (1H, s), 1.97 (4H, m), ~1.33 (19H, br), 0.88 (3H, t) and 0.88 (3H, t)] were inconsistent with the structure **14′** and differed from ours. (Rossi's data showed 34 protons while **14′** requires only 18 protons.)

(R)-(−)-7-*Methylnon*-1-*yne* **14**. Similarly **13** gave **14** (64% yield), b.p. 146–158°, n_D^{21} 1.4270; $[\alpha]_D^{21}$ − 5.94° (neat); GLC (5% LAC 2R-446, 1.5 m × 3 mm i.d. at 60°; Carrier gas, N_2, 1 kg/cm^2): Rt 1.36 min (80%), impurity at 2.8 min. This enantiomer was impure compared with the (*S*)-isomer.

(S)-(+)-14-*Methylhexadec*-8-*yn*-1-*ol* **15b′**. A soln of *n*-BuLi in n-hexane (1.5N, 18.3 ml) was added to a stirred soln of **14′** (3.5 g) in dry THF (25 ml) at −40° under Ar. The mixture was stirred for 15 min to complete the formation of the anion. To this was added a soln of 1-tetrahydropyranyloxy-7-iodoheptane (9.0 g) in dry HMPA (25 ml) and the mixture was stirred for 30 min at 20–25°. Then it was poured into ice-water and extracted with n-hexane. The hexane soln was washed with water and brine, dried ($MgSO_4$) and concentrated *in vacuo* to give crude **15a′**. This was dissolved in MeOH (40 ml) containing *p*-TsOH (350 mg) and the soln was stirred for 1 hr at 60–65°. This was poured into water and extracted with ether. The ether soln was washed with water, $NaHCO_3$ aq and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was distilled to give 3.7 g (58%) of **15b′**, b.p. 138–141°/0.5 mm, n_D^{22} 1.4624; $[\alpha]_D^{20}$ + 5.97° (*c* = 3.29, MeOH); ν_{max} 3340 (m), 2945 (s), 2860 (s), 1465 (m), 1390 (m), 1360 (m), 1340 (w), 1070 (m), 780 (vw), 730 (w) cm^{-1}; δ 0.90 (6H, br), ~1.37 (19H, br), ~2.08 (4H, br), 2.68 (1H, s), 3.50 (2H, t, J = 6 Hz); GLC (Column, 3% SE-30, 1.5 m × 3 mm i.d. at 160°; Carrier gas, N_2, 1 kg/cm^2): Rt 9.2 min (single peak); MS: *m/e* 252 (M^+).

(R)-(−)-14-*Methylhexadec*-8-*yn*-1-*ol* **15b**. A similar reaction of **14** with 1-tetrahydropyranyloxy-7-iodoheptane gave **15b** (58% yield), b.p. 144–148°/0.7 mm, n_D^{22} 1.4660; $[\alpha]_D^{22}$ − 5.11° (*c* = 2.79, MeOH); GLC (Column, 5% LAC-2R-446, 1.5 m × 3 mm i.d. at 160°; Carrier gas, N_2, 1 kg/cm^2); Rt 13.3 min (92%), impurity at 5.8 min.

(S)-(+)-14-*Methylhexadec*-8-*en*-1-*ol* **16′**. 5% Pd-$BaSO_4$ (273 mg) and quinoline (3 drops) were added to a soln of **15b′** (1.6 g) in MeOH (30 ml) and the mixture was shaken under H_2 at room temp. H_2 uptake (130 ml) ceased after 40 min. The catalyst was filtered off and the filtrate was concentrated *in vacuo* to give crude **16′**. This was chromatographed over SiO_2–$AgNO_3$ (prepared from 30 g of Mallinckrodt AR 100 mesh SiO_2 and 2.5 g of $AgNO_3$ in 7 ml of H_2O) in n-hexane. Elution with n-hexane yielded 1.18 g (73%) of **16′**, b.p. 152–155°/0.65 mm, n_D^{22} 1.4596; $[\alpha]_D^{22}$ + 5.57° (*c* = 2.86, $CHCl_3$); ν_{max} 3360 (m), 3010 (m), 2960 (sh), 2940 (s), 2860 (s), 1660 (w), 1470 (m), 1380 (m), 1060 (m), 960 (w), 730 (w) cm^{-1}; δ ~0.90 (6H, br), ~1.32 (19 H, br), ~2.00 (5H, br), 3.52 (2H, t, J = 6 Hz), 5.37 (2H, t, J = 6 Hz); TLC (Silicagel G, n-hexane-ether 3:1): R_f 0.49; GLC (Column, 5% LAC 2R-446, 1.5 m × 3 mm i.d. at 160°; Carrier gas, N_2, 1 kg/cm^2); Rt 8.4 min (96%), impurity at 11.6 min; MS: *m/e* 254 (M^+). The spectral data (IR, NMR and MS) were identical with those previously reported by us.[2] (Found: C, 79.84; H, 13.38. $C_{17}H_{34}O$ requires: C, 80.24; H, 13.42%).

(R)-(−)-14-*Methylhexadec*-8-*en*-1-*ol* **16**. Similarly **15b** gave **16** (77% yield), b.p. 144–148°/0.8 mm, n_D^{20} 1.4588; $[\alpha]_D^{20}$ − 5.43° (*c* = 2.20, $CHCl_3$); GLC (5% LAC 2R-446, 1.5 m × 3 mm i.d. at 160°; Carrier gas, N_2, 1 kg/cm^2): Rt 7.9 min (96%), impurity at 11.0 min; MS: *m/e* 254 (M^+).

(S)-(+)-14-*Methylhexadec*-8-*enal* **1′**. A soln of **16′** (1.1 g) in dry CH_2Cl_2 (10 ml) was added dropwise to a stirred and ice-cooled suspension of $CrO_3 \cdot C_5H_5NHCl$ (2.0 g) and NaOAc (156 mg) in dry CH_2Cl_2 (20 ml). The mixture was stirred for 1 hr and diluted with dry ether (60 ml). The organic soln was filtered through a Florisil column. The inorganic residue was washed with dry ether (20 ml × 2) and the ether soln was also filtered through a Florisil column. The organic soln was combined and concentrated *in vacuo*. The residue was distilled to give 620 mg (57%) of **1′**, b.p. 140–141°/1.5 mm, n_D^{22} 1.4570; $[\alpha]_D^{21}$ + 6.02° (*c* = 3.24, $CHCl_3$); ν_{max} 3010 (w), 2940 (s), 2860 (s), 2710 (w), 1740 (s), 1660 (w), 1470 (m), 1415 (m), 1400 (w), 1385 (m), 1160 (w), 1100 (w), 1025 (w), 970 (w), 730 (w) cm^{-1}; δ (100 MHz) 0.85 (6H, m), 1.21 (17 H, br), 1.84 (4 H, br. d, J = 6 Hz), 2.24 (2H, t, J = 6 Hz), 5.12 (2H, t, J = 6 Hz), 9.41 (1 H, t, J = 1 Hz); TLC (Silica gel G, n-hexane-ether 20; 1): R_f 0.52 GLC (3% SE-30, 1.5 m × 3 mm i.d. at 160°; Carrier gas, N_2, 1.2 kg/cm^2): Rt 9.0 min (single peak); MS: *m/e* 252 (M^+), 234, 223, 205. (Found: C, 80.39; H, 12.89. $C_{17}H_{32}O$ requires: C, 80.89; H, 12.78%).

(R)-(−)-14-*Methylhexadec-8-enal* **1**. Similarly **16** gave **1** (52% yield), b.p. 127–128°/0.65 mm, n_D^{21} 1.4539 $[\alpha]_D^{21}$ −5.94° (*c* = 1.06, $CHCl_3$); MS (70 eV): *m/e* 55.0550 (C_4H_7, 100%), 56.0624 (C_4H_8, 40.4%), 57.0713 (C_4H_9, 68.6%), 67.0556 (C_5H_7, 58.4%), 68.0619 (C_5H_8, 24.7%), 70.0783 (C_5H_{10}, 100%), 71.0863 (C_5H_{11}, 38.4%), 81.0711 (C_6H_9, 59.2%), 82.0779 (C_6H_{10}, 34.1%), 83.0862 (C_6H_{11}, 53.3%), 84.0936 (C_6H_{12}, 21.6%), 93.0699 (C_7H_9, 20.0%), 95.0855 (C_7H_{11}, 45.9%), 96.0932 (C_7H_{12}, 28.2%), 97.1015 (C_7H_{13}, 31.0%), 98.0731 ($C_6H_{10}O$, 26.7%), 109.1023 (C_8H_{13}, 24.7%), 121.1026 (C_9H_{13}, 15.3%), 123.1173 (C_9H_{15}, 14.5%), 135.1163 ($C_{10}H_{15}$, 14.1%), 149.1348 ($C_{11}H_{17}$, 6.7%), 205.1962 ($C_{15}H_{25}$, 3.53%), 223.2100 ($C_{15}H_{27}O$, 4.3%), 234.2337 ($C_{17}H_{30}$, 6.3%), 252.2434 ($C_{17}H_{32}O = M^+$, 5.5%); TLC (Silica gel G, n-hexane-ether 20:1): R_f 0.52; GLC (5% LAC 2R-446, 1.5 m × 3 mm i.d. at 160°; Carrier gas, N_2, 15 ml/min): Rt 3.5 min (94%), impurity at 5.0 min. (Found: C, 80.10; H, 12.85. $C_{17}H_{32}O$ requires: C, 80.89; H, 12.78%).

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