Tetrahedron Vol. 35, pp. 1279 to 1284

0040-4020/79/0515-1279/$02.00/0

STEREOCONTROLLED SYNTHESIS OF ALL OF THE FOUR POSSIBLE STEREOISOMERS OF *ERYTHRO*-3,7-DIMETHYL-PENTADEC-2-YL ACETATE AND PROPIONATE, THE SEX PHEROMONE OF THE PINE SAWFLIES[a]

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(*Received in Japan* 11 *October* 1978)

Abstract—All of the four possible stereoisomers of 2,3-*erythro*-3,7-dimethylpentadecan-2-ol **1** were synthesized by a stereospecific S_N2 oxirane cleavage of (2*S*,3*S*)-2,3-epoxybutane or its antipode with lithium di[(*R*)- or (*S*)-4-methyldodecyl]cuprate. Their acetates or propionates were prepared to test their pheromone activity.

In 1976, Jewett *et al.* identified 3,7-dimethylpentadecan-2-ol **1** as the free alcohol in three species from two genera of pine sawflies (Hymenoptera: Diprionidae).[1] The acetate **2** or propionate **3** of this alcohol are the sex pheromones of these insects. In *Neodiprion lecontei* and *N. sertifer*, the acetate **2** is the major component of their sex attractant, while in *Diprion similis*, it is the propionate **3**.[1] The alcohol **1** possesses three asymmetric C atoms and therefore can exist in eight stereoisomeric forms. Five syntheses of a stereoisomeric mixture of **1** were reported.[2-6] The C-2:C-3 *erythro* structure, as illustrated in **1a**, was suggested in the course of the structure elucidation[1] and later confirmed by the synthesis of (±)-*erythro*-**1**.[5] This reduced the numbers of the possible stereoisomers to four.

Jewett *et al.* suggested that the subtle pheromone specificity existing at the level of the genus might be due to optical isomerism in the alcohol moiety.[1] In order to prove or disprove this, one must synthesize all of the four possible stereoisomers of the each of the pheromones **2** and **3** in optically pure forms. Recently a synthesis of *erythro*-**1** was reported with unknown configuration at C-7.[7] However, when we undertook this study, no synthesis of highly optically pure **1** had been achieved with rigorously defined absolute stereochemistry. Herein we describe in detail our synthesis of **1** based on a stereospecific oxirane cleavage reaction (**A** + **B** → **1a**).[8] The key concept of our synthesis was the S_N2 attack of a chiral organocopper reagent **B** to a chiral epoxide **A** providing the chiral alcohol **1a**. The isomeric alcohols **1a'**, **1b** and **1b'** were also obtainable by employing stereoisomers of **A** and/or **B**.

The both enantiomers of the epoxide **A** were prepared from tartaric acids, **4a** and **4a'**. Diethyl D-tartrate **4b** was converted to the corresponding acetonide **5**.[9] This was reduced with LAH to a diol **6a**. The corresponding tosylate **6b** was highly crystalline and readily purified by recrystallization. This was converted to an iodide **7a**, whose hydrogenation to **7b** followed by acid hydrolysis directly gave **8**, $[\alpha]_D^{22} - 12.48°$ (neat) in 57% yield from **7a**.[10] Treatment of **8** with HBr–AcOH gave an acetoxy bromide **9**. This was heated with KOH aq soln to give (2*R*,3*R*)-(+)-2,3-epoxybutane **10**, $[\alpha]_D^{20} + 58.0°$ (ether).[11] The net retention of the (2*R*,3*R*)-configuration of **8** was the result of the Walden iversions in the steps **8**–**9** and **9**–**10**. This epoxide **10** was previously prepared by a different route starting from **8** obtained by fermentation and reported to exhibit α_D (obs. at 25°) + 46.75°.[12] In the same manner, L-(+)-tartaric acid yielded **8'**, $[\alpha]_D^{21} + 12.14°$ (neat), whose conversion via **9'** afforded (2*S*,3*S*)-(−)-2,3-epoxybutane **10'**, $[\alpha]_D^{20.5} - 61.5°$ (ether). The method of preparation of these epoxides[11] ensured their high stereochemical purities which were supported by very clean NMR spectra, δ 1.20 (6H, d, J = 5 Hz), 2.51 (2H, dq, J_1 = 1.5 Hz, J_2 = 5 Hz), indicating no contamination with the *erythro*-isomer.

Another part of the molecule, the chiral bromide **19** or **19'**, was prepared from (*R*)-(+)-citronellol **11a** derived from highly optically pure isopulegol.[13] The tosylate **11b** was treated with NaCN in DMSO to give a nitrile **12**. Hydrolysis of **12** gave an acid **13a** which was treated with CH_2N_2 to give an ester **13b**. Epoxidation of **13b** with *m*-chloroperbenzoic acid yielded an epoxide **14** which was cleaved with HIO_4 to an aldehyde **15**. This was reduced with $NaBH_4$ to give an alcohol **16a**. The chain-elongation of **16a** was accomplished by the treatment of the corresponding tosylate **16b** with $(n\text{-}C_5H_{11})_2CuLi$ to give an ester **17**. LAH reduction of **17** gave an alcohol **18a**. The corresponding tosylate **18b** was treated with LiBr to give (*R*)-(−)-1-bromo-4-methyldodecane **19**, $[\alpha]_D^{22} - 2.16°$ (neat). The (*S*)-enantiomer **19'** was synthesized in the simpler manner. Citronellyl tosylate **11b** was treated with $(n\text{-}C_6H_{13})_2CuLi$ to give an olefin **20**. This was oxidized with O_3 and the ozonide was reduced with $NaBH_4$ and LAH to give the (*S*)-alcohol **18a'**. The (*S*)-bromide **19'**, $[\alpha]_D^{21} + 2.29°$ (neat), was obtained via **18b'** in the same manner as described for the preparation of **19**.

The coupling reaction (**A** + **B**) was best accomplished by employing R_2CuLi-type reagents.[13,14] Thus the (*R*)-bromide **19** in ether was converted to R_2CuLi reagent and reacted with the epoxide **10** in ether at −50 to −40° for 3 hr to give (2*R*,3*R*,7*R*)-**1a**, $[\alpha]_D^{20} + 9.72°$ (neat), in 53% yield after chromatographic purification and distillation. The yield was very susceptible to the subtle change in reaction conditions and some unidentified by-products with C=O absorption in IR were often obtained in 20–

[a]Pheromone Synthesis XXVIII. Part XXVII, T. Suguro and K. Mori, *Agric. Biol. Chem.* 43, 409 (1979).

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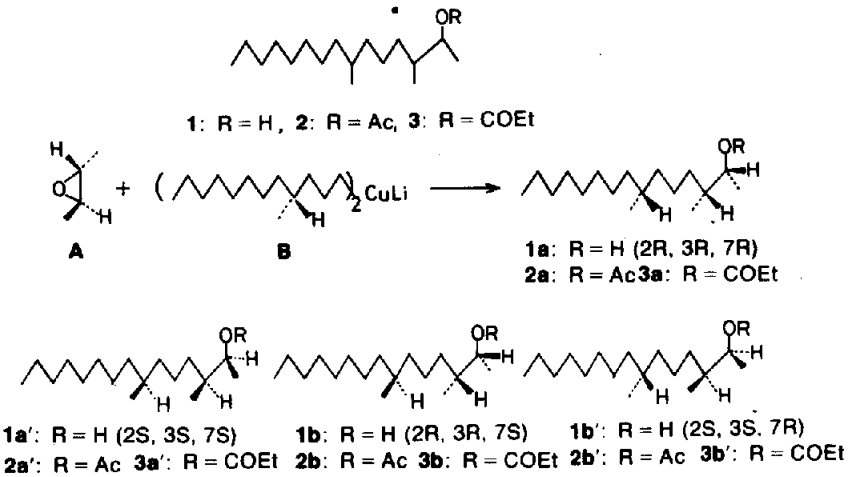


Fig. 1.

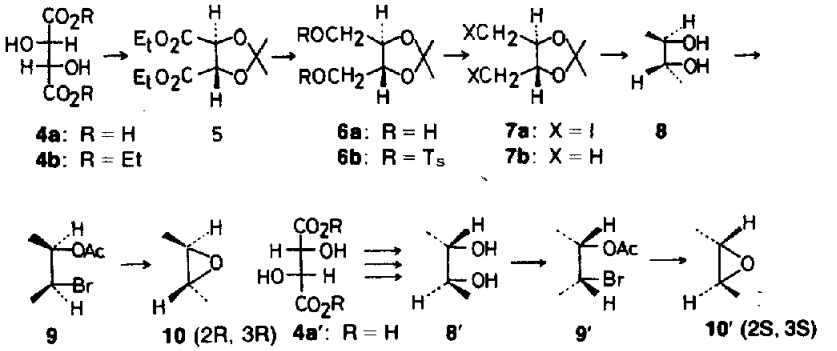


Fig. 2.

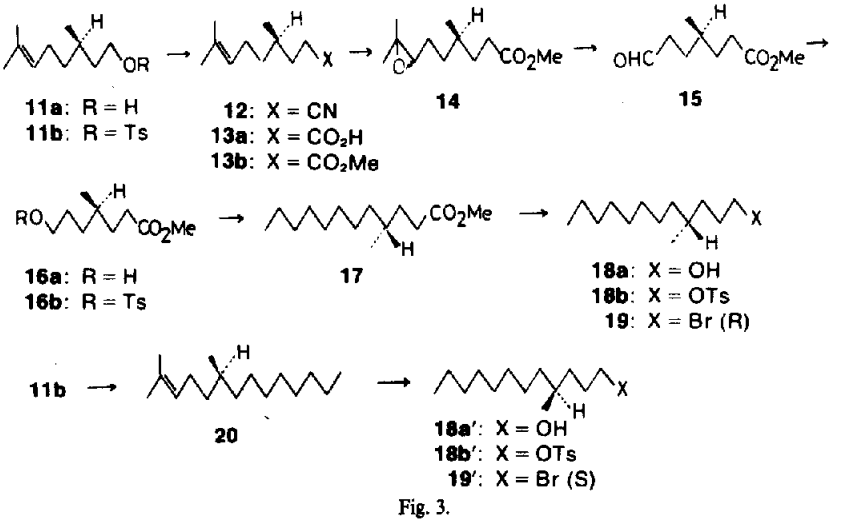


Fig. 3.

30% yield when the reaction was allowed to proceed for 10–15 hr at −20°. In the same manner, **19'** and **10'** gave (2*S*,3*S*,7*S*)-**1a'**, $[\alpha]_D^{20}$ − 9.86° (neat), in 74% yield; **19'** and **10** gave (2*R*,3*R*,7*S*)-**1b**, $[\alpha]_D^{20}$ + 10.77° (neat) in 92% yield; **19** and **10'** gave (2*S*,3*S*,7*R*) **1b'**, $[\alpha]_D^{20}$ − 11.10° (neat) in 43% yield. These alcohols were converted to the acetates (**2a**, **2a'**, **2b** and **2b'**) and propionates (**3a**, **3a'**, **3b** and **3b'**) in the usual manner.

The stereochemical and optical purities of these products were fully examined by GLC, ^{1}H NMR and ^{13}C NMR. The following physical measurements were made to prove that our synthetic alcohols **1a**, **1a'**, **1b** and **1b'** were 100% pure *erythro*-isomers. As a reference sample, a diastereomeric mixture of **1** was synthesized and converted to the corresponding acetate **2**.[6] The mixture **1** or **2** was gas chromatographically inseparable on an SE-30

or SF-96 column. However, on a PEG-20M column (50 m × 0.28 mm), it was separable and shown to be a mixture of *erythro* and *threo* isomers in about 1:1 ratio. The glc analysis of our synthetic alcohols **1a**, **1a'**, **1b** and **1b'** showed all of them to be 100% pure 2,3-*erythro* compounds. Secondly, the ^{1}H NMR analysis of **1a** and **1a'** was carried out in the presence of Eu(fod)$_3$.† The (2*R*,3*R*,7*R*)-isomer **1a** showed two pairs of 3H-doublets at δ 1.35 and 2.00, while the *erythro–threo* mixture **1** suffered separation of the signals to exhibit four pairs of doublets at δ 1.55 (1.4H, d), 1.72 (1.6H, d), 2.26 (1.4H, d) and 2.39 (1.6H, d). The third piece of evidence was obtained by measuring the ^{1}H NMR spectra of **2a**, **2a'**, **2b** and **2b'** in benzene-d_6. These acetates showed a 3H-doublet at $\delta \sim 1.07$ ($J = 6$ Hz), while the *erythro–threo* mixture exhibited a pair of doublets at δ 0.98 (1.4H, d, $J = 6$ Hz) and 1.07 (1.6H, d, $J = 6$ Hz). Fourthly, the ^{13}C NMR spectra of these acetates showed a sharp signal due to CHOAc at δ 72.802 (**2a**), 72.852 (**2a'**), 72.852 (**2b**) and 72.899 (**2b'**) ppm, while the *erythro–threo* mixture exhibited signals at δ 72.802 and 73.191 ppm.[5]

In order to check the optical purities of the products, the ^{1}H NMR spectra of **1a** and **1a'** were measured in the presence of Eu(hfbc)$_3$‡ to reveal no separation of the signal due to C-1 Me confirming the high optical purities. A 1:1 mixture of **1a** and **1a'** showed two pairs of doublets at δ 3.27 (1.5H) and 3.31 (1.5H) in the presence of Eu(hfbc)$_3$. The ^{1}H NMR spectra of the (*S*)-(−)-MTPA§ esters of **1a** and **1b** were measured in the presence of Eu(fod)$_3$ to reveal no splitting of the signals due to OMe protons. This also supported the high optical purities (>98%) of our synthetic products.

The biological activity of our samples is now under estimation in several entomological laboratories both in Europe and in the U.S.A.

EXPERIMENTAL

All b.ps and m.ps were uncorrected. IR spectra refer to films for oils or Nujol mulls for solids 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 were measured on a Jasco DIP-4 polarimeter. Glc analyses were performed on a Yanaco G 80 gas chromatograph.

2,3 - O - *Isopropylidene* - D - *threitol* **6a**. A soln of **5** (73 g, prepd according to lit.[9]) in dry ether (100 ml) was added dropwise to a stirred and ice-cooled suspension of LAH (17 g) in dry ether (900 ml). The mixture was stirred for 1 hr at room temp. and then left to stand overnight at room temp. Water (17 ml), 5% NaOH aq (17 ml) and water (50 ml) were added successively to the stirred and ice-cooled mixture. After stirring for 1 hr, the mixture was filtered. The filter cake was thoroughly washed with acetone. The filtrate and washings were combined and concentrated *in vacuo*. The residue was distilled to give 30.5 g (63%) of **6a**, b.p. 110–120°/0.5 mm, n_D^{20} 1.4574; ν_{max} 3400 (s), 2980 (s), 2940 (s), 2880 (s), 1460 (m), 1390 (s), 1375 (s), 1260 (s), 1220 (s), 1175 (s), 1120 (s), 1050 (vs), 980 (m), 900 (m), 880 (m), 850 (s), 800 (w) cm^{-1}; δ ($CDCl_3$) 1.40 (6H, s), 3.68 (~6H, br), 3.90 (~2H, br).

2,3 - O - *Isopropylidene* - L - *threitol* **6a'**. This was prepared in the same manner as described above for **6a**.

1,4 - *Ditosyl* - 2,3 - O - *isopropylidene* - D - *threitol* **6b**. This was prepared from **6a** by the method of Carmack and Kelley,[9] m.p. 85–86°, $[\alpha]_D^{21}$ + 12.0° ($c = 4.555$, $CHCl_3$); ν_{max} 1595 (m), 1380 (s), 1360 (s), 1195 (s), 1180 (s), 1175 (s), 1100 (m), 1060 (m), 990 (s), 970 (s), 890 (m), 850 (m), 830 (m), 820 (m), 810 (s), 785 (m), 670 (m) cm^{-1}; δ ($CDCl_3$) 1.30 (6H, s), 2.47 (6H, s), 4.12 (6H, br.s), 7.44 (2H, d, $J = 8$ Hz), 7.90 (2H, d, $J = 8$ Hz). (Found: C, 53.20; H, 5.46. Calc. for $C_{21}H_{26}O_8S_2$: C, 53.60; H, 5.57%).

1,4 - *Ditosyl* - 2,3 - O - *isopropylidene* - L - *threitol* **6b'**. This was prepared from **6a'** by the known method,[9] m.p. 85–87°, $[\alpha]_D^{22}$ − 12.6° ($c = 4.257$, $CHCl_3$).

1,4 - *Dideoxy* - 1,4 - *diiodo* - 2,3 - O - *isopropylidene* - D - *threitol* **7a**. A soln of **6b** (164 g) and NaI (250 g) in acetone (1200 ml) was stirred and heated under reflux for 2 days. The mixture was filtered and the solid was washed with acetone. The combined acetone soln was concentrated *in vacuo*. The residue was shaken with ether and water. The ether soln was washed with $Na_2S_2O_4$ aq and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was distilled to give 125 g (94%) of **7a**, b.p. 105–110°/0.8 mm, n_D^{22} 1.5721; $[\alpha]_D^{22}$ + 17.6° ($c = 3.52$, MeOH); ν_{max} 2960 (m), 2910 (m), 2830 (m), 1375 (s), 1365 (s), 1230 (s), 1200 (s), 1170 (m), 1150 (m), 1100 (m), 1035 (vs), 875 (s) cm^{-1}; δ 1.40 (6H, s), 3.25 (4H, d, $J = 6$ Hz), 3.70 (2H, m). (Found: C, 22.05; H, 3.09. Calc. for $C_7H_{12}O_2I_2$: C, 22.01; H, 3.16%).

1,4 - *Dideoxy* - 1,4 - *diiodo* - 2,3 - O - *isopropylidene* - L - *threitol* **7a'**. This was prepared in the same manner as described above for **7a**, b.p. 98–108°/0.5 mm, n_D^{21} 1.5706; $[\alpha]_D^{21}$ − 17.6° ($c = 3.23$, MeOH).

(2R,3R) - (−) - *Butane* - 2,3 - *diol* **8**. 10% Pd–C (15 g) and KOH aq (24 g in 250 ml) were added to a soln of **7a** (74.5 g) in MeOH (300 ml) and the mixture was shaken under H_2 atm at room temp. When the H_2 uptake (*ca* 8 l) ceased, the mixture was filtered to remove the catalyst. The filtrate containing **7b** was acidified with conc HCl (Congo red) and left to stand overnight at room temp. Then K_2CO_3 powder was added to saturate the soln. The separated MeOH layer was dried over K_2CO_3 and the aqueous layer was extracted with MeOH. The MeOH extract was dried over K_2CO_3. The combined MeOH soln was concentrated *in vacuo*. The residue was triturated with EtOH–MeOH and filtered to remove inorganic salts. The filtrate was concentrated *in vacuo* and the residue was triturated with EtOH–MeOH. The filtrate was concentrated *in vacuo*. This operation was repeated two additional times. The final dark residue was distilled to give 9.5 g (57%) of **8**, b.p. 70–73°/4 mm, n_D^{20} 1.4311; $[\alpha]_D^{22}$ − 12.48° (neat) (lit.[12] $[\alpha]_D^{25}$ − 13.09°); ν_{max} 3350 (s), 2980 (s), 2940 (m), 2880 (m), 1120 (m), 1090 (m), 1060 (s) cm^{-1}; δ ($CDCl_3$) 1.15 (6H, d, $J = 6$ Hz), 3.5 (2H, m), 3.70 (2H, s, –OH).

(2S,3S) - (+) - *Butane* - 2,3 - *diol* **8'**. This was prepared in the same manner as described above for **8**, b.p. 70–80°/5 mm, n_D^{21} 1.4344; $[\alpha]_D^{21}$ + 12.14° (neat) (lit.[10] $[\alpha]_D^{25}$ + 12.4°).

(2R,3S) - 2 - *Acetoxy* - 3 - *bromobutane* **9**. 30% dry HBr in AcOH (150 ml) was added to the ice-cooled and stirred **8** (19 g). The soln was stirred for 30 min at 0–5° and then for 1 hr at 40–50°. After cooling, it was poured into ice-water and extracted with ether. The ether soln was washed with water and Na_2CO_3 aq, dried ($MgSO_4$) and concentrated *in vacuo* to give 37 g (86%) of **9**, ν_{max} 3000 (m), 2950 (m), 1750 (vs), 1390 (s), 1380 (s), 1220 (vs), 1120 (vs), 1030 (s), 850 (m) cm^{-1}. This was employed for the next step without further purification.

(2S,3R) - 2 - *Acetoxy* - 3 - *bromobutane* **9'**. This was prepared in the same manner as described above for **9** in 93% yield and directly used for the next step.

(2R,3R) - (+) - 2,3 - *Epoxybutane* **10**. The acetoxy bromide **9** (32.5 g) was added dropwise to a vigorously stirred KOH aq (100 g in 100 ml H_2O) at 100°. After the addition, the bath temp. was raised to 120–130° to distill off the epoxide. A fraction boiling at 50–68° was collected, dried over KOH pellets and redistilled to give 5.0 g (42%) of **10**, b.p. 56–58°, $n_D^{20.5}$ 1.3729; $[\alpha]_D^{20}$ + 58.0° ($c = 2.31$, ether); ν_{max} 2990 (s), 2940 (m), 1490 (m), 1450 (s), 1380 (s), 1335 (m), 1280 (w), 1260 (w), 1150 (w), 1110 (s), 1020 (vs), 950 (w), 880 (s), 810 (s), 735 (m), 720 (m) cm^{-1}; δ 1.20 (6H, d, $J = 5$ Hz), 2.51 (2H, dq, $J_1 = 1.5$ Hz, $J_2 = 5$ Hz); MS: *m/e* 72 (M^+).

(2S,3S) - (−) - 2,3 - *Epoxybutane* **10'**. This was prepared in the same manner as described above for **10** in 48% yield, b.p. 56–58°, $n_D^{20.5}$ 1.3728, $[\alpha]_D^{20.5}$ − 61.5° ($c = 2.11$, ether).

(R) - (+) - *Citronellyl cyanide* **12**. *p*-TsCl (49.5 g) was added to a stirred and ice-cooled soln of **11a** (34 g) in dry C_5H_5N (150 ml). The mixture was stirred for 4–5 hr, poured into ice-water and

†Tris(6,6,7,7,8,8,8 - heptafluoro - 2,2 - dimethyl - 3,5 - octanedionato) - europium(III).

‡Tris(3 - heptafluorobutyryl - *d* - camphorato) - europium(III).

§α - Methoxy - α - trifluoromethylphenylacetic acid.

extracted with ether. The ether soln was washed with sat $CuSO_4$ aq, water, sat $NaHCO_3$ aq, water and brine, dried ($MgSO_4$) and concentrated *in vacuo* to give 64 g (quantitative) of crude **11b**, ν_{max} 1600 (m), 1365 (s), 1195 (vs), 1185 (vs), 1100 (m), 945 (s), 890 (m), 815 (s), 765 (m), 670 (s) cm^{-1}. This was dissolved in DMSO (170 ml) and NaCN (14 g) was added. The mixture was stirred and heated at 60° for 10 hr, poured into ice-water and extracted with ether. The ether soln was washed with water and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed over SiO_2 and the fraction containing the nitrile was distilled to give 29 g (85%) of **12**, b.p. 78–80°/3 mm, n_D^{21} 1.4508; $[\alpha]_D^{21}$ +4.41° (neat); ν_{max} 2960 (s), 2920 (s), 2860 (s), 2250 (m), 1670 (w), 1450 (m), 1385 (m), 1115 (m), 1085 (w), 980 (w), 830 (m) cm^{-1}; δ 0.93 (3H, d, J = 6 Hz), 1.60 (3H, s), 1.67 (3H, s), 5.05 (1H, t, J = 6 Hz). (Found: C, 79.95; H, 11.44; N, 8.33. $C_{11}H_{19}N$ requires: C, 79.94; H, 11.57, N, 8.47%).

(R) - (−) - 4,8 - *Dimethylnon* - 7 - *enoic acid* **13a**. A soln of **12** (22.5 g) and NaOH (108 g) in 60% EtOH (350 ml) was heated under reflux for 30 hr. Then it was concentrated *in vacuo* to remove EtOH, diluted with water, acidified with conc HCl and extracted with ether. The ether soln was washed with water and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was distilled to give 23.5 g (94%) of **13a**, b.p. 115–118°/2.5 mm, n_D^{22} 1.4554, $[\alpha]_D^{22}$ −3.64° (neat); ν_{max} ~3200 (m), 2920 (s), ~2650 (m), 1710 (vs), 1460 (m), 1420 (m), 1385 (m), 1295 (m), 1220 (m), 940 (m), 830 (w) cm^{-1}; δ 0.90 (3H, d, J = 6 Hz), 1.58 (3H, s), 1.67 (3H, s), 5.06 (1H, t, J = 6 Hz), 11.96 (1H, s). (Found: C, 71.35; H, 10.76. $C_{11}H_{20}O_2$ requires: C, 71.75; H, 10.86%).

Methyl (R) - (−) - 4,8 - *dimethylnon* - 7 - *enoate* **13b**. A soln of **13a** (22 g) in ether was treated with CH_2N_2 in ether to give 20.5 g (87%) of **13b**, b.p. 76–78°/2 mm, n_D^{22} 1.4444; $[\alpha]_D^{22}$ −0.98° (neat); ν_{max} 2960 (s), 2920 (s), 2870 (s), 1745 (vs), 1440 (m), 1380 (m), 1260 (m), 1195 (s), 1175 (s), 1115 (m), 1095 (m), 1020 (w), 990 (w), 830 (w) cm^{-1}; δ 0.88 (3H, d, J = 6 Hz), 1.58 (3H, s), 1.66 (3H, s), 3.62 (3H, s), 5.05 (1H, t, J = 6 Hz). (Found: C, 72.32; H, 11.02. $C_{12}H_{22}O_2$ requires: C, 72.69; H, 11.17%).

Methyl (4R) - (−) - 7,8 - *epoxy* - 4,8 - *dimethylnonanoate* **14**. *m*-Chloroperbenzoic acid (85% purity, 65.9 g) was added portionwise to a stirred and ice-cooled soln of **13b** (66 g) in dry CH_2Cl_2 (400 ml). The mixture was stirred for 3 hr and filtered. The filtrate was washed with sat Na_2CO_3 aq, water and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed over Merck silica gel C-60 (60 g). The fractions containing **14** were combined and concentrated *in vacuo*. The residue was distilled to give 57 g (81%) of **14**, b.p. 102–106°/4 mm, n_D^{19} 1.4394; $[\alpha]_D^{19}$ −0.12° (±0.02°, neat); ν_{max} 2960 (s), 2920 (s), 2870 (m), 1740 (s), 1460 (m), 1440 (m), 1380 (s), 1260 (s), 1200 (s), 1180 (s), 1120 (m), 1020 (w), 990 (w), 870 (m), 850 (w), 800 (w), 760 (w), 740 (w) cm^{-1}; δ 0.90 (3H, d, J = 6 Hz), 1.20 (3H, s), 1.22 (3H, s), 3.60 (3H, s). (Found: C, 66.92; H, 10.26. $C_{12}H_{22}O_3$ requires: C, 67.26; H, 10.34%).

Methyl (R) - (−) - 7 - *oxo* - 4 - *methylheptanoate* **15**. A soln of $HIO_4 \cdot 2H_2O$ (20.1 g) in THF (100 ml) was added dropwise during 30 min to a soln of **14** (15.8 g) in ether (100 ml). The mixture was stirred for 2 hr, poured into ice-water and extracted with ether. The ether soln was washed with water, sat $NaHCO_3$ aq, water and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was distilled to give 11 g (87%) of **15**, b.p. 68–74°/2 mm, n_D^{22} 1.4385; $[\alpha]_D^{22}$ −0.71° (±0.02°, neat); ν_{max} 2960 (m), 2940 (m), 2880 (m), 2720 (w), 1740 (s), 1440 (m), 1390 (m), 1260 (m), 1200 (s), 1170 (s), 1105 (m), 1020 (m), 890 (w), 850 (w) cm^{-1}; δ 0.90 (3H, d, J = ~6 Hz), 1.10–1.90 (5H, m), 2.10–2.60 (4H, m), 3.60 (3H, s), 9.80 (1H, t, J = 2 Hz). (Found: C, 62.66; H, 9.45. $C_9H_{16}O_3$ requires: C, 62.77; H, 9.35%).

Methyl (R) - (−) - 7 - *hydroxy* - 4 - *methylheptanoate* **16a**. $NaBH_4$ (1.22 g) was added to a stirred and ice-cooled soln of **15** (11 g) in MeOH (60 ml). The mixture was stirred for 40 min, acidified (pH 4) with AcOH, poured into water and extracted with ether. The ether soln was washed with water, sat $NaHCO_3$ aq and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was distilled to give 9.4 g (84.5%) of **16a**, b.p. 105–109°/3 mm, n_D^{21} 1.4420; $[\alpha]_D^{21}$ −0.98° (±0.02°, neat); ν_{max} 3360 (m), 2920 (s), 2860 (s), 1440 (s), 1380 (m), 1340 (m), 1280 (m), 1205 (s), 1175 (s), 1105 (m), 1060 (s), 1020 (m), 895 (w) cm^{-1}; δ 0.90 (3H, d, J = 6 Hz), 1.00–1.80 (7H, m), 2.27 (2H, t, J = 6 Hz), 2.55 (1H, s), 3.52 (2H, t, J = 6 Hz), 3.62 (3H, s). (Found: C, 62.04; H, 10.35. $C_9H_{18}O_3$ requires: C, 62.04; H, 10.40%).

Methyl (R) - 7 - *tosyloxy* - 4 - *methylheptanoate* **16b**. *p*-TsCl (12.3 g) was added to a stirred and ice-cooled soln of **16a** (8.9 g) in dry C_5H_5N (30 ml). The mixture was left to stand at 0–5° for 4 hr, poured into ice-water and extracted with ether. The ether soln was washed with cold N HCl, sat $NaHCO_3$ and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residual crude **16b** (15.3 g, quantitative) was dried *in vacuo* (P_2O_5), ν_{max} 2960 (m), 2930 (m), 2880 (m), 1745 (s), 1600 (m), 1365 (s), 1200 (vs), 1185 (vs), 1100 (m), 965 (m), 920 (m), 820 (m), 670 (m) cm^{-1}. This was employed for the next step without further purification.

Methyl (R) - (+) - 4 - *methyldodecanoate* **17**. A soln of **16b** (15.3 g) in dry ether (40 ml) was added to a stirred and cooled soln of $(n\text{-}C_5H_{11})_2CuLi$ (150 mM) in dry ether (220 ml) at −35 to −40° under Ar. The mixture was stirred for 4 hr at −35 to −40°, then warmed to −10° and poured into sat NH_4Cl aq (300 ml). The mixture was stirred for 2 hr and extracted with ether. The ether soln was washed with water and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was distilled to give 8.0 g (68%) of **17**, b.p. 88–91°/2 mm, $n_D^{21.5}$ 1.4338; $[\alpha]_D^{21}$ +0.49° (±0.01°, neat); ν_{max} 2960 (s), 2925 (s), 2860 (s), 1750 (s), 1200 (m), 1180 (m) cm^{-1}; δ 0.70–1.05 (6H, m), 1.05–1.80 (17H, m), 2.25 (2H, t, J = 6 Hz), 3.63 (3H, s); Glc (Column, 5% SE-30, 2.5 m × 3 mm at 205°; Carrier gas N_2, 1 kg/cm^2): R_t 5 min. (Found: C, 73.21; H, 12.25. $C_{14}H_{28}O_2$ requires: C, 73.64; H, 12.34%).

(R) - (+) - 4 - *Methyldodecan* - 1 - *ol* **18a**. A soln of **17** (7.5 g) in dry ether (40 ml) was added to a stirred and ice-cooled suspension of LAH (1.19 g) in dry ether (100 ml). The mixture was stirred for 2 hr at 0–5° and then left to stand several hr. The mixture was ice-cooled again. Water (1 ml), 10% NaOH aq (1 ml) and water (3 ml) were added successively to the stirred and ice-cooled mixture. After stirring for 1.5 hr the mixture was filtered. The filter cake was thoroughly washed with ether. The filtrate and washings were combined and concentrated *in vacuo*. The residue was distilled to give 6.35 g (91%) of **18a**, b.p. 93–94°/0.25 mm, n_D^{22} 1.4433; $[\alpha]_D^{22}$ +1.88° (neat); ν_{max} 3340 (m), 2960 (s), 2940 (s), 2860 (s), 1470 (m), 1390 (m), 1065 (m), 900 (w), 730 (w) cm^{-1}; δ 0.75–1.05 (6H, m), 1.05–1.80 (19H, br), 2.35 (1H, s), 3.53 (2H, t, J = 6 Hz). (Found: C, 77.85; H, 13.86. $C_{13}H_{28}O$ requires: C, 77.93; H, 14.07%).

(R) - 4 - *Methyldodec* - 1 - *yl tosylate* **18b**. *p*-TsCl (7.18 g) was added to a stirred and ice-cooled soln of **18a** (6.3 g) in dry C_5H_5N (20 ml). The mixture was stirred at 0–5° for 4 hr, poured into ice-water and extracted with ether. The ether soln was washed with dil HCl, sat $NaHCO_3$ aq and brine, dried ($MgSO_4$) and concentrated *in vacuo* to give 11 g (quantitative) of **18b**, ν_{max} 2960 (s), 2930 (s), 2860 (s), 1600 (m), 1370 (s), 1195 (s), 1185 (s), 1100 (m), 970 (m), 920 (m), 820 (m), 670 (m) cm^{-1}. This was employed for the next step without further purification.

(R) - (−) - 1 - *Bromo* - 4 - *methyldodecane* **19**. LiBr (5.16 g) was added to a soln of **18b** (11 g) in acetone (100 ml). The mixture was concentrated *in vacuo*, diluted with water and extracted with ether. The ether soln was washed with water and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed over Merck silica gel C-60. Elution with *n*-hexane gave 6.2 g (75%) of **19**, b.p. 91–96°/2 mm, n_D^{22} 1.4575; $[\alpha]_D^{22}$ −2.16° (±0.02°, neat); ν_{max} 2940 (s), 2910 (s), 2840 (s), 1460 (m), 1375 (m), 1260 (m), 1200 (w), 920 (w) cm^{-1}; δ 0.75–1.05 (6H, m), 1.05–1.60 (17H, br), 1.60–2.10 (2H, m), 3.35 (2H, t, J = 6 Hz). (Found: C, 60.14; H, 10.62. $C_{13}H_{27}Br$ requires: C, 59.32; H, 10.33%).

(S) - (−) - 2,6 - *Dimethyltetradec* - 2 - *ene* **20**. A soln of $(n\text{-}C_6H_{13})_2CuLi$ was prepared by adding $n\text{-}C_6H_{13}Li$ (1.2 N, 333 ml ether soln) to a stirred suspension of CuI (38 g) in dry ether (150 ml) at −30 to −25° under Ar. A soln of **11b** (31 g) in dry ether (120 ml) was added to the stirred and cooled $(n\text{-}C_6H_{13})_2CuLi$ at −60 to −50°. The mixture was stirred at −50° for 2 hr. The reaction temp was gradually raised to −10° and kept there for 1 hr. Then the mixture was poured into sat NH_4Cl aq, stirred for 1–2 hr and extracted with ether. The ether extract was washed with water and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was distilled to give 17.8 g (80%) of **20**, b.p. 98–102°/1.3 mm, $n_D^{21.5}$ 1.4441; $[\alpha]_D^{21.5}$ −1.26° (±0.02°, neat); ν_{max}

(9H, m, 0.82, 0.88, 0.92, 0.95), 1.00–1.80 (28H, m, 1.07, 1.09, 1.18, 1.22), 2.22 (2H, q, J = 8 Hz), 4.55–5.00 (1H, m); glc (Column, 3% SE-30, 1.5 m × 2 mm at 170°; Carrier gas, N_2, 15 ml/min): R_t 7.55 min (>98.5% purity). (Found: C, 76.11; H, 12.82. $C_{20}H_{40}O_2$ requires: C, 76.87; H, 12.88%).

(2S,3S,7R) - (−) - erythro - 3,7 - *Dimethylpentadec* - 2 - *yl propionate* **3b'**. This was prepared in the same manner as described above. Starting from 0.55 g of **1b'**, 0.499 g (74%) of **3b'** was obtained, b.p. 130–131°/0.3 mm, n_D^{20} 1.4411; $[\alpha]_D^{20}$ −5.86° (±0.02°, neat). The IR, NMR and glc retention time on the SE-30 Column were identical with those of **3b**. The purity was >99.5% by the glc analysis. (Found: C, 76.64; H, 12.87. $C_{20}H_{40}O_2$ requires: C, 76.87; H, 12.88%).

(2R,3R,7R) - (+) - erythro - 3,7 - *Dimethylpentadec* - 2 - *yl propionate* **3a**. This was prepared in the same manner as described above for **3b**. Starting from 0.8 g of **1a**, 0.93 g (95%) of **3a** was obtained, b.p. 126–128°/0.25 mm, n_D^{20} 1.4410; $[\alpha]_D^{20}$ +5.44° (±0.02°, neat). The IR, NMR and glc retention time on the SE-30 column were indistinguishable from those of **3b**. The purity was >99.5% by the glc analysis. (Found: C, 76.72; H, 12.80. $C_{26}H_{40}O_2$ requires: C, 76.87; H, 12.88%).

(2S,3S,7S) - (−) - erythro - 3,7 - *Dimethylpentadec* - 2 - *yl propionate* **3a'**. This was prepared in the same manner as described above for **3b**. Starting from 1.0 g of **1a'**, 0.95 (78%) of **3a'** was obtained, b.p. 136–138°/0.5 mm, n_D^{20} 1.4409; $[\alpha]_D^{20}$ −5.52° (±0.02°, neat). The IR, NMR and glc retention time on the SE-30 column were identical with those of **3a**. The purity was >98.5% (R_t 7.55 min) with a small amount of impurity (1%, R_t 4.8 min). (Found: C, 76.55; H, 12.79. $C_{20}H_{40}O_2$ requires: C, 76.87; H, 12.8%).

Glc analysis of **1a**, **1a'**, **1b**, **1b'** *and an* erythro-threo *mixture* **1**. The analysis was performed on a PEG 20M Golay column (50 m × 0.28 mm at 180°). The retention times were as follows: **1a**, 21.46 min; **1a'**, 22.29 min; **1b**, 22.10 min: **1b'** 22.10 min; **1** (*erythro–threo* mixture) 21.53 min, 22.28 min (4:5). The alcohols **1a**, **1a'**, **1b** and **1b'** were homogeneous.

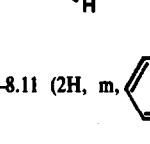
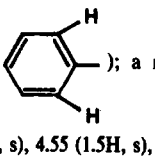
^1H *NMR analysis of* **1a**, **1a'** *and* **1** (erythro–threo *mixture*) *in the presence of* Eu(fod)$_3$. The alcohol **1a**, **1a'** or **1** (20 mg) and Eu(fod)$_3$ (8 mg) were dissolved in CCl_4 (0.4 ml) and the ^1H NMR was measured at 100 MHz. **1a**, δ 1.35 (3H, d, J = 6 Hz, Me at C-3), 2.00 (3H, d, J = 6 Hz, C-1-Me); **1a'** δ 1.68 (3H, d, J = 6 Hz, Me at C-3), 2.45 (3H, d, J = 6 Hz); **1** δ 1.55 (1.4H, d, J = 6 Hz), 1.72 (1.6H, d, J = 6 Hz), 2.26 (1.4H, d, J = 6 Hz), 2.39 (1.6H, d, J = 6 Hz).

^{13}C *NMR analysis of* **2a**, **2a'**, **2b**, **2b'** *and* **2** (erythro–threo *mixture*). The acetate **2a**, **2a'**, **2b**, **2b'** or **2** (100 mg) was dissolved in C_6H_6-d_6 (0.35 ml) and the ^{13}C NMR was recorded on a Jeol JNM-FX 100 spectrometer at 25.05 MHz, pulse interval 1.0000 sec, accum. point 8192, accum. times 40. **2a** δ 72.807 (ÇHOAc), 168.606 (ÇOCH$_3$); **2a'** δ 72.852 (ÇHOAc), 168.606 (ÇOCH$_3$); **2b** δ 72.852 (ÇHOAc), 168.606 (ÇOCH$_3$); **2b'** δ 72.899 (ÇHOAc), 168.660 (ÇOCH$_3$); **2** (*erythro–threo* mixture) δ 72.802 (ÇHOAc), 73.191 (ÇHOAc), 168,513 (ÇOCH$_3$).

^1H *NMR analysis of* **1a** *and* **1a'** *in the presence of* Eu(hfbc)$_3$. The alcohol **1a** or **1a'** (20 mg) and Eu(hfbc)$_3$ (15 mg) were dissolved in $CDCl_3$ (0.5 ml) and ^1H NMR was observed at 100 MHz. **1a** δ 0.92 (3H, t, J = 6 Hz, 15-Me), 1.06 (3H, d, J = 6 Hz, Me at C-7), 2.39 (3H, d, J = 6 Hz, Me at C-3), 3.39 (3H, d, J = 6 Hz, 1-Me); **1a'** δ 0.85 (3H, t, J = 6 Hz, 15-Me), 0.96 (3H, d, J = 6 Hz, Me at C-7), 2.07 (3H, d, J = 6 Hz, Me at C-3), 2.93 (3H, d, J = 6 Hz, 1-Me); **1a** (10 mg) + **1a'** (10 mg) δ 3.27 (1.5H, d, J = 6 Hz, 1-Me), 3.31 (1.5 H, d, J = 6 Hz, 1-Me). Other signals were not so separated as these signals.

(S) - (−) - *MTPA ester of* (2S,3S,7S) - (−) - erythro - 3,7 - *dimethylpentadecan* - 2 - *ol*. A soln of (*S*)-(−)-MTPA Cl (150 mg) in dry CCl_4 (1 ml) was added dropwise to an ice-cooled soln of **1a'** (100 mg) in dry C_5H_5N (1.3 ml) and dry CCl_4 (1.2 ml). The mixture was left to stand overnight at room temp. Excess $Et_2N(CH_2)_3NH_2$ (100 μl) was added and the mixture was left to stand for 5 min. Then it was diluted with ether (50 ml). The ether soln was washed with N HCl, water, sat $NaHCO_3$ aq, water and brine, dried ($MgSO_4$) and concentrated *in vacuo* to give 0.17 g of the MTPA ester, ν_{max} 2940 (s), 2860 (s), 1750 (s), 1500 (w), 1450 (m), 1380 (m), 1300 (m), 1280 (s), 1190 (s), 1175 (s), 1125 (m), 1080 (w), 1020 (m), 990 (w), 960 (w), 915 (w), 860 (w), 760 (w), 720 (m), 700 (w) cm^{-1}; δ ~0.7 to ~1.05 (9H, m), ~1.05 to ~2.0 (26H, br), 3.51 (3H, s), 5.10 (1H, m, br), 7.42 (5H, m).

(S) - (−) - *MTPA ester of* (2R,3R,7S) - (+) - erythro - 3,7 - *dimethylpentadecan* - 2 - *ol*. This was prepared in the same manner as described above from 100 mg of **1b** to give 150 mg of the MTPA ester. The IR and NMR spectra were almost identical with those of the MTPA ester of **1a'**.

^1H *NMR analysis of the MTPA esters in the presence of* Eu(fod)$_3$. The MTPA ester (110 mg) and Eu(fod)$_3$ (20 mg) were dissolved in CCl_4 (0.4 ml) and the ^1H NMR was recorded at 100 MHz. The MTPA-ester of **1a'**. δ 4.71 (3H, s, –OMe), 8.12–8.47 (2H, m, ); the MTPA-ester of **1b**. δ 4.22 (3H, s, –OMe), 7.75–8.11 (2H, m, ); a mixture of the both MTPA esters. δ 4.08 (1.5H, s), 4.55 (1.5H, s), 7.69–8.01 (1H, m), 8.01–8.36 (1H, m).

Acknowledgements—We thank Emeritus Prof. M. Matsui for his encouragements. We are grateful to Mr. S. Muraki of Takasago Perfumery Co., Tokyo, for his kind supply of isopulegol. Thanks are due to Dr. Y. Takagi, Messers T. Somei and T. Hanyu, Hasegawa Perfume Industry Co., Kawasaki, for glc analyses. We thank Dr. K. Aizawa and Ms. Y. Naito of this Department for analytical works. This work was supported by a grant-in-aid for scientific research (Grant No. 247104), Ministry of Education, Japan.

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2970 (s), 2930 (s), 2860 (s), 1470 (m), 1380 (m), 830 (w), 725 (w) cm^{-1}; $\delta \sim 0.7$ to ~ 1.0 (6H, m), ~ 1.0 to ~ 1.5 (17H, br), 1.58 (3H, s), 1.66 (3H, s), 1.95 (2H, q, J = 7 Hz), 5.08 (1H, t, J = 7 Hz); Glc (Column, 5% SE-30, 2.5 m × 3 mm at 184°; Carrier gas, N_2, 1 kg/cm^2): R_t 7.1 min. (Found: C, 85.54; H, 14.18. $C_{16}H_{32}$ requires: C, 85.63; H, 14.36%).

(S) - (−) - 4 - *Methyldodecan* - 1 - *ol* **18a'**. O_3 was bubbled into a cooled soln of **20** (5.5 g) in $CHCl_3$ (50 ml) at −20° until saturation (violet color). To this soln of the ozonide, a soln of $NaBH_4$ (9.1 g) in 50% EtOH aq (50 ml) was added at −20° with stirring. After the addition the mixture was stirred and heated at 50° for 1 hr. The mixture was acidified with 10% H_2SO_4 aq and extracted with $CHCl_3$. The $CHCl_3$ soln was washed with water, dried ($MgSO_4$) and concentrated *in vacuo*. The residue exhibited C=O absorption in its IR spectrum. This was dissolved in dry ether (50 ml) and added dropwise to a stirred and ice-cooled suspension of LAH (1.5 g) in dry ether (50 ml). The mixture was stirred for 3 hr at 0–5°. Water (1.5 ml), 10% NaOH (1.5 ml) and water (4.5 ml) were added successively to the stirred and ice-cooled mixture. The stirring was continued for 1 hr. The mixture was filtered and the filter cake was washed with ether. The ether soln was concentrated *in vacuo*. The residue was distilled to give 4.4 g (89%) of **18a'**, b.p. 105–108°/0.4 mm, n_D^{22} 1.4427; $[\alpha]_D^{22}$ −1.54° (neat). The IR and NMR spectra were identical with those of **18a**. (Found: C, 77.65; H, 13.95. $C_{13}H_{28}O$ requires: C, 77.93; H, 14.07%).

(S) - (+) - 1 - *Bromo* - 4 - *methyldodecane* **19'**. This was prepared in the same manner as described for **19**. Thus **18a'** (4.2 g) gave **18b'** (7.5 g). This was converted to **19** (4 g,, 80%), b.p. 96–102°/2.5 mm; n_D^{21} 1.4580; $[\alpha]_D^{21}$ +2.29° (±0.01, neat). The IR and NMR spectra were identical with those of **19**. (Found: C, 59.59; H, 10.38. $C_{13}H_{27}Br$ requires: C, 59.32; H, 10.33%).

(2S,3S,7S) - (−) - erythro - 3,7 - *Dimethylpentadecan* - 2 - *ol* **1a'**. An RLi reagent was prepared from **19'** (17 g) and Li (2.24 g) in dry ether to give 0.55 N soln. This soln (36 ml) was added dropwise during 10–15 min to a stirred and cooled suspension of CuI (1.9 g) in dry ether (15 ml) at −20 to −15° under Ar. The resulting clear gray soln was cooled to −50 to −40°. A soln of **10'** (1.4 g) in dry ether (10 ml) was added dropwise to the R_2CuLi soln at −50 to −40°. The mixture was stirred at −50 to −40° for 2 hr and left to stand overnight at −20°. This was poured into sat NH_4Cl aq and extracted with ether. The ether soln was washed with water and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed over Merck silica gel C-60 (140 g). Elution with *n*-hexane–ether (100:1–20:1) gave impure **1a'** with C=O absorption in IR spectrum. This was further purified by preparative tlc (Merck Art 5717) to give pure **1a'**. This was distilled to give 1.89 g (74%) of **1a'**, b.p. 114–116°/0.25 mm, n_D^{20} 1.4509; $[\alpha]_D^{20}$ −9.86° (±0.02°, neat); ν_{max} 3340 (m), 2960 (s), 2900 (s), 2840 (s), 1460 (m), 1380 (m), 1300 (w), 1150 (w), 1080 (m), 995 (w), 920 (w), 880 (w), 720 (w) cm^{-1}; δ (100 MHz, $CDCl_3$), 0.80 (3H, d, J = 6 Hz), 0.84 (3H, t, J = 6 Hz), 0.85 (3H, d, J = 6 Hz), 1.10 (3H, d, J = 6 Hz), ~1.0 to ~1.5 (~22H, br, 1.23), 1.60 (1H, s), 3.56 (1H, m); Glc (Column, 3% SE-30, 1.5 m × 2 mm at 170°, Carrier gas N_2, 12 ml/min): R_t 3.6 min (>99.5%). (Found: C, 79.41; H, 14.30. $C_{17}H_{36}O$ requires: C, 79.62; H, 14.13%).

(2R,3R,7S) - (+) - erythro - 3,7 - *Dimethylpentadecan* - 2 - *ol* **1b**. An RLi soln was prepared from **19'** (17 g) and Li (2.24 g) in dry ether. This RLi soln (0.55 N, 36 ml) was added to a suspension of CuI (1.9 g) in dry ether as described above. A soln of **10** (1.4 g) in dry ether was added to the R_2CuLi soln. Subsequent work-up as described above for **1a'** gave 2.35 g (92%) of **1b**, b.p. 119–120°/0.3 mm, n_D^{20} 1.4512; $[\alpha]_D^{20}$ +10.77° (±0.02°, neat). The IR, NMR and glc were indistinguishable from those of **1a'**. (Found: C, 79.17; H, 14.26. $C_{17}H_{36}O$ requires: C, 79.62; H, 14.13%).

(2S,3S,7R) - (−) - erythro - 3,7 - *Dimethylpentadecan* - 2 - *ol* **1b'**. An RLi soln was prepared from **19** (19 g) and Li (2.5 g) in dry ether. This RLi soln (0.50 N, 40 ml) was added dropwise to a stirred and cooled suspension of CuI (1.9 g) in dry ether (15 ml) at −20 to −15°. The resulting clear gray soln was cooled to −50 to −40°. A soln of **10'** (1.6 g) in dry ether (5 ml) was added to the stirred and ice-cooled R_2CuLi soln at −50 to −40° under Ar. The mixture was stirred for 3 hr at −50 to −40°. The reaction temp was gradually raised to −10°. Then the mixture was poured into ice-NH_4Cl aq, stirred for 2 hr and extracted with ether. The ether extract was washed with water and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed over Merck silica gel C-60 (120 g). Elution with n-hexane–ether (100:1–20:1) gave pure **1b'**. This was distilled to give 1.1 g (43%) of **1b'**, b.p. 127–129°/0.5 mm, n_D^{20} 1.4519; $[\alpha]_D^{20}$ −11.10° (±0.02°, neat). The IR, NMR and glc were indistinguishable from those of **1a'**. (Found: C, 79.32; H, 14.15. $C_{17}H_{36}O$ requires: C, 79.62; H, 14.13%).

(2R,3R,7R) - (−) - erythro - 3,7 - *Dimethylpentadecan* - 2 - *ol* **1a**. An RLi soln was prepared from **19** (19 g) and Li (2.5 g) in dry ether. This RLi soln (0.50 N, 40 ml) was added to a suspension of CuI (1.9 g) in dry ether as described above. A soln of **10** (1.6 g) in dry ether was added to the R_2CuLi soln. Subsequent work-up as described above for **1b'** gave 1.35 g (53%) of **1a**, b.p. 125–127°/0.5 mm, n_D^{18} 1.4527; $[\alpha]_D^{20}$ +9.72° (±0.02°, neat). The IR, NMR and glc were identical with those of **1a'**. (Found: C, 79.29; H, 14.35. $C_{17}H_{36}O$ requires: C, 79.62; H, 14.13%).

(2R,3R,7R) - (+) - erythro - 3,7 - *Dimethylpentadec* - 2 - *yl acetate* **2a**. Ac_2O (1.3 g) was added to an ice-cooled soln of **1a** (0.8 g) in dry C_5H_5N (4 ml). The mixture was left to stand overnight at room temp. and diluted with ether (50 ml). The ether soln was washed with 5% HCl, water sat $NaHCO_3$ aq and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was distilled to give 0.85 g (93%) of **2a**, b.p. 120–121°/0.3 mm, $n_D^{19.5}$ 1.4402; $[\alpha]_D^{19.5}$ +5.64° (±0.02°, neat); ν_{max} 2960 (s), 2930 (s), 2860 (s), 1745 (s), 1470 (s), 1380 (m), 1255 (s), 1160 (w), 1140 (w), 1125 (w), 1080 (w), 1050 (w), 1025 (m), 950 (w), 860 (w), 730 (w) cm^{-1}; δ (100 MHz, C_6H_6-d_6) 0.78–1.00 (9H, m), 1.06 (3H, d, J = 6 Hz), 1.12–1.60 (22H, br), 1.68 (3H, s), 4.48 (1H, m). The NMR spectrum of an *erythro–threo* mixture[6] showed a pair of doublets at δ 0.98 (1.4H, d, J = 6 Hz) and 1.07 (1.6H, d, J = 6 Hz). δ (60 MHz, CCl_4) 0.72–1.02 (9H, m), 1.13 (3H, d, J = 6 Hz), 1.20–1.63 (22H), 1.95 (3H, s), 4.60–4.95 (1H, m); glc (Column; 3% SE-30, 1.5 m × 3 mm at 170°, Carrier gas, N_2, 15 ml/min): R_t 5.2 min (>99.5%). (Found: C, 76.05; H, 12.75. $C_{19}H_{38}O_2$ requires: C, 76.45; H, 12.82%).

(2S,3S,7S) - (−) - erythro - 3,7 - *Dimethylpentadec* - 2 - *yl acetate* **2a'**. Ac_2O (1.3 g) was added to **1a'** (0.8 g) in dry C_5H_5N (4 ml). Subsequent workup gave crude **2a'**. This was purified by preparative tlc to give pure **2a'**, which was distilled to give 0.82 g (89%) of **2a'**, b.p. 117–118°/0.2 mm, n_D^{20} 1.4404; $[\alpha]_D^{20}$ −5.76° (±0.02°, neat). The IR, NMR and glc retention time on the SE-30 column were identical with those of **2a**. (Found: C, 76.70; H, 12.95. $C_{19}H_{38}O_2$ requires: C, 76.45; H, 12.82%).

(2R,3R,7S) - (+) - erythro - 3,7 - *Dimethylpentadec* - 2 - *yl acetate* **2b**. This was prepared from **1b** (0.8 g) in the same manner as described for **2a'**. The distilled pure **2b** weighed 0.63 g (66%), b.p. 133–134°/0.55 mm, $n_D^{20.5}$ 1.4406; $[\alpha]_D^{20.5}$ +6.08° (±0.02°, neat). The IR, NMR and glc retention time on the SE-30 column were indistinguishable with those of **2a**. (Found: C, 76.16; H, 12.77. $C_{19}H_{38}O_2$ requires: C, 76.45; H, 12.82%).

(2S,3S,7R) - (−) - erythro - 3,7 - *Dimethylpentadec* - 2 - *yl acetate* **2b'**. This was prepared from **1b'** (0.6 g) in the same manner as described for **2a**. The distilled pure **2b'** weighed 0.58 g (61%), b.p. 113–115°/0.2 mm, n_D^{20} 1.4405; $[\alpha]_D^{20}$ −6.18° (±0.02°, neat). The IR, NMR and glc retention time on the SE-30 column were identical with those of **2b**. (Found: C, 76.59; H, 12.87. $C_{19}H_{38}O_2$ requires: C, 76.45; H, 12.82%).

(2R,3R,7S) - (+) - erythro - 3,7 - *Dimethylpentadec* - 2 - *yl propionate* **3b**. A soln of EtCOCl (0.74 g) in dry CCl_4 (2 ml) was added dropwise to a stirred and ice-cooled soln of **1b** (1.28 g) in dry C_5H_5N (5 ml) and dry CCl_4 (5 ml) at 0–5°. The mixture was left to stand overnight at room temp. and then diluted with ether (70 ml). The ether soln was washed with N HCl, water, sat $NaHCO_3$ and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed over Merck silica gel C-60 (15 g). Elution with n-hexane–ether (30:1) gave **3b**. This was distilled to give 1.1 g (71%) of pure **3b**, b.p. 124–126°/0.2 mm, n_D^{20} 1.4409; $[\alpha]_D^{20}$ +5.90° (±0.02° neat); ν_{max} 2965 (s), 2940 (s), 2860 (s), 1745 (s), 1470 (m), 1430 (w), 1385 (m), 1345 (w), 1330 (w), 1285 (w), 1200 (s), 1140 (w), 1120 (w), 1090 (m), 1070 (m), 1020 (w), 920 (w), 895 (w), 865 (w), 810 (w), 740 (w), 725 (w) cm^{-1}; δ 0.65–1.00