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STEREOCONTROLLED SYNTHESIS OF ALL OF THE POSSIBLE STEREOISOMERS OF 3, 11-DIMETHYLNONACOSAN-2-ONE AND 29-HYDROXY-3, 11-DIMETHYLNONACOSAN-2-ONE

THE FEMALE SEX PHEROMONE OF THE GERMAN COCKROACH†

KENJI MORI,* SATORU MASUDA and TOSHIO SUGURO
Department of Agricultural Chemistry, The University of Tokyo, Yayoi 1-1-1, Bunkyo-ku, Tokyo 113, Japan

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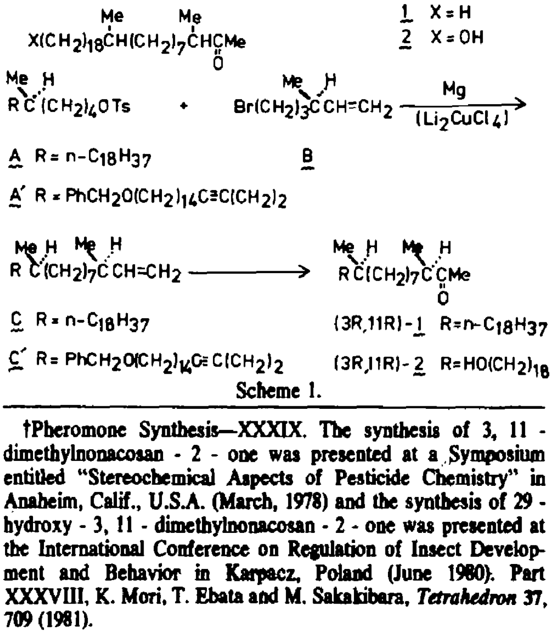
Abstract—All of the possible stereoisomers of 3, 11 - dimethylnonacosan - 2 - one **1** and 29 - hydroxy - 3, 11 - dimethylnonacosan - 2 - one **2** were synthesized from (*R*)-(+)- citronellic acid as the chiral source. The natural pheromones were shown to be (3*S*, 11*S*) – **1** and (3*S*, 11*S*) – **2** by direct comparisons.

From the cuticular wax of sexually mature females of the German cockroach (*Blattella germanica*), Fukami *et al.* isolated 3, 11-dimethylnonacosan-2-one **1** and 29 - hydroxy - 3, 11 - dimethylnonacosan - 2 - one **2** as the sex pheromones which, upon contact with antennae, elicited wing-raising and direction- turning response from the male adults at the first stage of their sequential courtship behavior.[1-3] Both **1** and **2** were synthesized in several ways as a mixture of all of the possible stereoisomers.[1,4-10] However, no synthesis of optically pure pheromones was reported to date except an unsuccessful attempt to that goal by Rossi *et al.*[11] We have now completed the synthesis of all of the possible stereoisomers of **1** and **2** in optically pure forms and established the hitherto unknown absolute configuration of the natural pheromones to be 3*S*, 11*S* as described below.[12]



Scheme 1.

Synthetic plan and the starting material. The key step in our synthesis was the coupling of a chiral tosylate **A** or **A′** with a chiral Grignard reagent derived from **B** to give an olefin **C** or **C′** which was converted to **1** or **2** in a standard manner. The success of this scheme was dependent on our ability to prepare optically pure fragments **A**, **A′** and **B** from readily available starting material. (*R*)-(+)- Citronellic acid **4a** served for this purpose. All of the stereoisomers of **1** and **2** were synthesized from this single chiral source. It was prepared from (–)-isopulegol **3** and its optical purity was estimated to be ~92% by the HPLC analysis of the corresponding amide **4b**. The two diastereomeric amides resulting from (*R*)-(+)-**4a** and a trace amount of the contaminating (*S*)-(–)-citronellic acid were completely separable on a Zorbax SIL column (see Experimental).[13] (*R*)-(+)-Citronellic acid **4a** of this optical purity (~92%) was the common starting material for our syntheses of optically active pheromones such as (3*R*, 4*R*) - 4 - methylheptan - 3 - ol.[14] (*Z*)-trogodermal,[15] (*E*)-trogodermal,[16] 10-methyldodecyl acetate[17] and the pine sawfly pheromone.[18] These synthetic pheromones were therefore of ~92% optical purities, since we carefully planned the synthetic routes to retain the molecular asymmetry of the starting material. Details of the determination of the optical purities of this and related compounds by hplc will be reported separately as our reply to Rossi's criticism concerning the optical purities of our trogodermal enantiomers.[19]‡

Synthesis of 3, 11 - *dimethylnonacosan* - 2 - *one* **1**. The preparation of the fragment **A** was carried out as follows by the elongation of the carbon chain of citronellol **5a**. (*R*) - (+) - Citronellic acid **4a** was reduced with LAH to (*R*) - (+) - citronellol **5a**.[15] The corresponding tosylate **5b** was treated with NaI in acetone to give an iodide **6**. By the standard malonic ester synthesis it was converted to a carboxylic acid **8** *via* a malonate **7**. This was reduced with LAH to **9a** whose acetylation gave an acetate **9b**. An epoxide **10** was obtained by oxidizing **9b** with *m*-chloroperbenzoic acid. Oxidation of **10** with HIO_4 yielded an aldehyde **11**. The Wittig reaction between **11** and a phosphorane generated from $n\text{-}C_{15}H_{31}P^+Ph_3Br^-$ gave an olefinic alcohol **12**. This was hydrogenated over Pd–C to give a crystalline alcohol (*R*)-**13a**, $[\alpha]_D^{20}$ +1.01 ± 0.1° (ether), which could be purified by recrystallization. The corresponding tosylate **13b** (= **A**) was prepared in the conventional manner. The antipode of the above described fragment **A** was prepared by lengthening the OH-side of the starting (*R*)-(+)-citronellol **5a**, since optically pure (*S*) - (–) - citronellol was not available in Japan.

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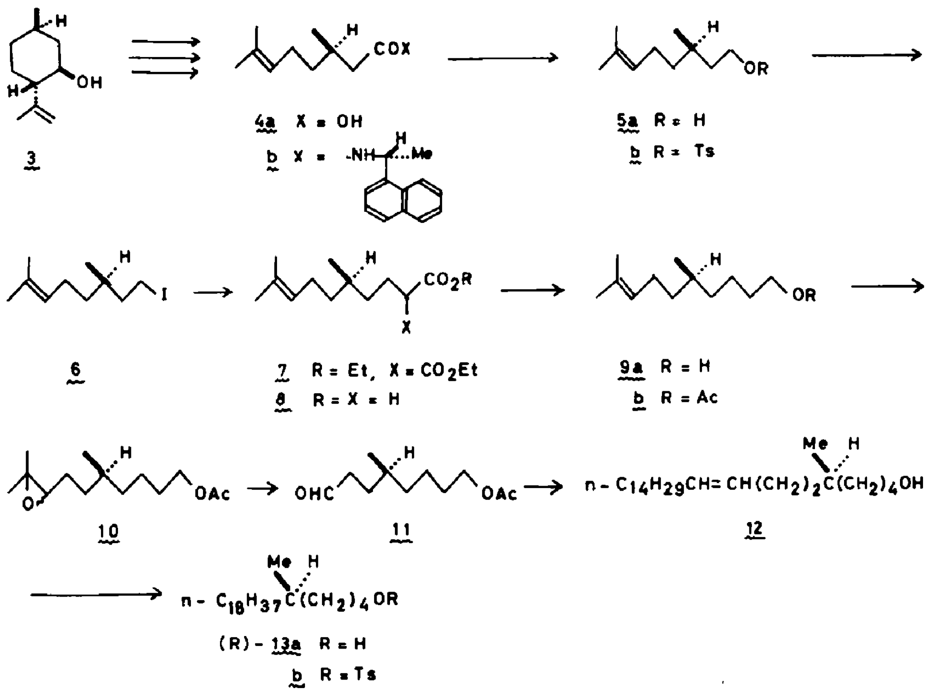
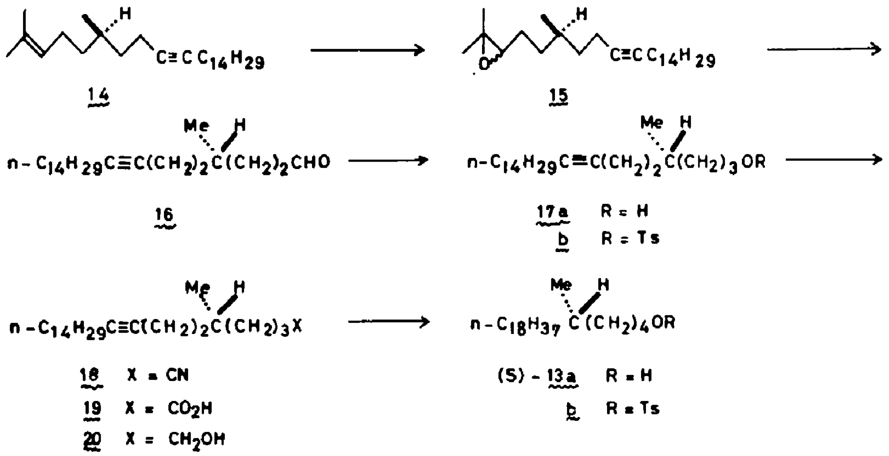
†Pheromone Synthesis—XXXIX. The synthesis of 3, 11 - dimethylnonacosan - 2 - one was presented at a Symposium entitled "Stereochemical Aspects of Pesticide Chemistry" in Anaheim, Calif., U.S.A. (March, 1978) and the synthesis of 29 - hydroxy - 3, 11 - dimethylnonacosan - 2 - one was presented at the International Conference on Regulation of Insect Development and Behavior in Karpacz, Poland (June 1980). Part XXXVIII, K. Mori, T. Ebata and M. Sakakibara, *Tetrahedron* 37, 709 (1981).

‡Here we just would like to emphasize that the determination of optical purities of our pheromone intermediates is based on the NMR or chromatographic analyses of their diastereomeric derivatives whenever possible, while Rossi entirely depends on the comparison of $[\alpha]_D$ values. Contrary to Rossi's claim that (*S*) - trogodermal was far more active than the (*R*) - enantiomer when tested on male khapra beetles by the method of Levinson,[19] Prof. Levinson himself found that our (*R*) - trogodermal was definitely more active (× 10^2 ~ 10^3) than the (*S*) - enantiomer by the same test on the same species.[20]



Scheme 2.

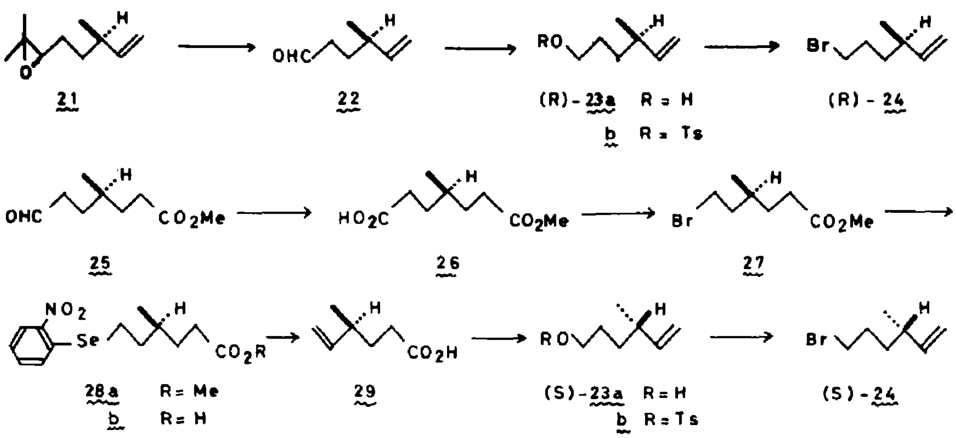


Scheme 3.

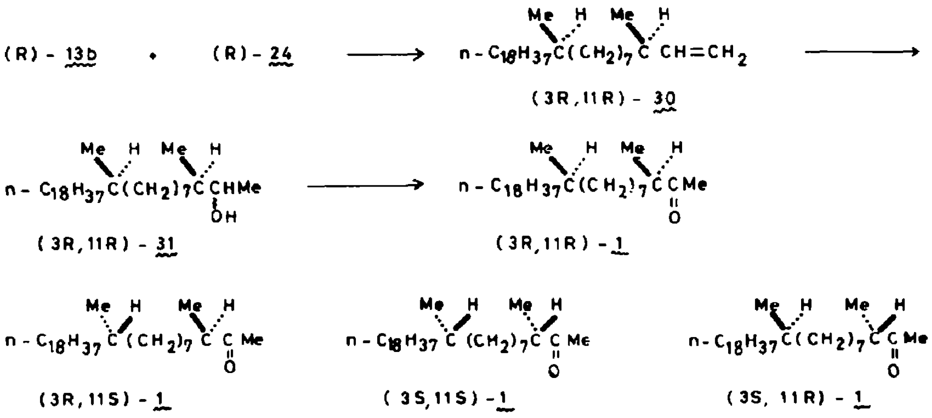
Alkylation of hexadec-1-yne with (R)-(−)-citronellyl iodide **6** gave an acetylene **14**. This was epoxidized to **15**. Oxidation of **15** with HIO$_4$ cleaved it to give **16**. LAH reduction of **16** gave an alcohol **17a**. The corresponding tosylate **17b** was converted to a nitrile **18**. Alkaline hydrolysis of **18** gave an acid **19**, which was reduced with LAH to give an alcohol **20**. This was hydrogenated (H$_2$/Pd–C) to afford the desired alcohol (S)-**13a**, $[\alpha]_D^{20}$ − 1.01 ± 0.08° (ether), as crystals. The corresponding tosylate (S)-**13b** (=antipode of **A**) was prepared in the conventional manner.

The next task was the preparation of the fragment **B**, the other half of the molecule. The synthesis of its (R)-isomer started from the known epoxide **21**.[21] Oxidation of **21** with HIO$_4$ gave an aldehyde **22**. This was reduced with LAH to give an alcohol (R)-**23a**. The corresponding tosylate (R)-**23b** was treated with LiBr in acetone to give a bromide (R)-**24** (=**B**), α_D^{19} − 12.6° (neat, l = 1 dm). The preparation of (S)-**24** was more complicated. The known aldo ester **25**[18] was oxidized with CrO$_3$ to a half ester **26**. Its Ag salt was submitted to the Hunsdiecker reaction (Br$_2$ in CCl$_4$) to give a bromo ester **27**. This was reacted with *o*-nitroselenophenol[22] to yield a selenide **28a**. The corresponding acid **28b** was treated with H$_2$O$_2$ to effect the oxidative elimination of the selenophenyl group yielding an olefinic acid **29**. This was reduced with LAH to give an alcohol (S)-**23a**. The corresponding tosylate (S)-**23b** was converted to the desired bromide (S)-**24** (= antipode of **B**), $\alpha_D^{20.5}$ + 13.2° (neat, l = 1 dm) in the conventional manner.

The coupling of (R)-**13b** with the Grignard reagent derived from (R)-**24** was successfully carried out in the presence of Li$_2$CuCl$_4$ in THF–ether[23] The Markownikoff hydration of the resulting olefin (3R, 11R)-**30** by oxymercuration–demercuration with Hg(OAc)$_2$ and NaBH$_4$[24] gave an alcohol (3R, 11R)-**31** as a waxy solid. This was oxidized with CrO$_3$ to give (3R, 11R)-(−)-**1** after three recrystallizations from EtOH. In the same manner,



Scheme 4.



* NATURAL PHEROMONE

Scheme 5.

(*S*)-**13b** and (*R*)-**24** gave (3*R*, 11*S*) - (−) - **1**, (*S*) - **13b** and (*S*)-**24** gave (3*S*, 11*S*) - (+) - **1**, and (*R*)-**13b** and (*S*)-**24** gave (3*S*, 11*R*) - (+) - **1**. The IR and NMR spectra of the natural pheromone were entirely identical with those of (3*R*, 11*R*)- and (3*S*, 11*S*)-isomers. Specific rotations and m.ps of the natural pheromone **1** and the four synthetic stereoisomers and their mixture m.ps with natural pheromone **1** are listed in Table 1. The natural pheromone was identified as (3*S*, 11*S*)-**1** by the mixture m.p. determination showing no m.p. depression. The specific rotation of our synthetic (3*S*, 11*S*)-**1** was in good agreement with that of the natural pheromone. The bioassay of the synthetic stereoisomers was kindly carried out by Prof. Fukami and Dr. Yamaoka of Kyoto University. The natural and the synthetic four stereoisomers showed the same range of pheromone activity when tested on the males of German cockroach at 50 μg/ml dose. Thus the pheromone receptor of the male German cockroach seems to be devoid of stereospecificity.

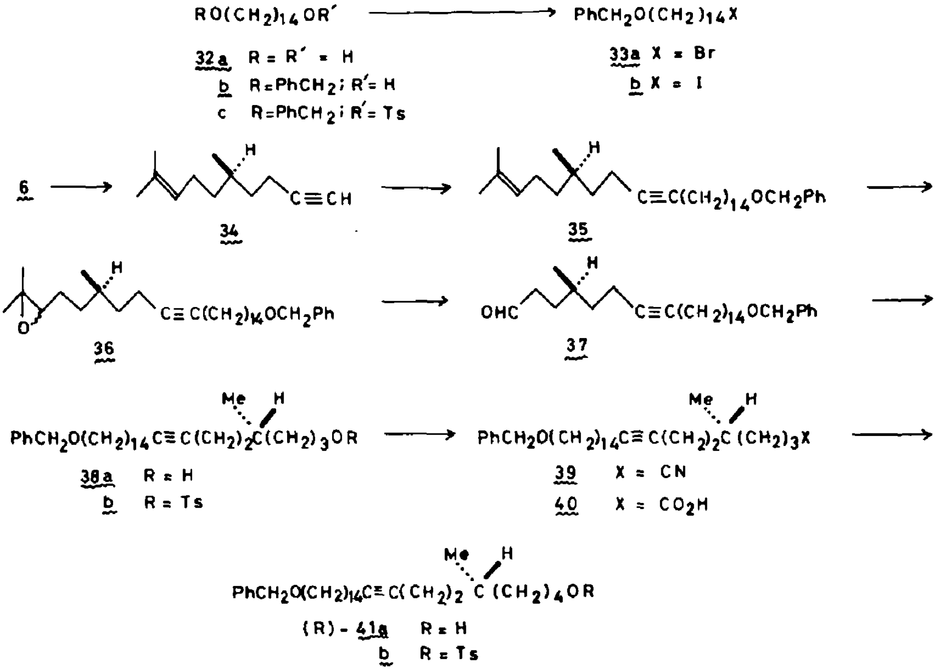
Synthesis of 29 - *hydroxy* - 3, 11 - *dimethylnonacosan* - 2 - *one* **2**. The strategy used for the synthesis of 29 - hydroxy - 3, 11 - dimethylnonacosan - 2 - one **2** was same as that described above for the synthesis of **1**. However, instead of the fragment A, a compound A′ with an ω-benzyloxy group had to be employed so as to introduce

Table 1. Optical rotations and m.ps of natural and synthetic stereoisomers of **1** and their mixture m.p. with natural **1**

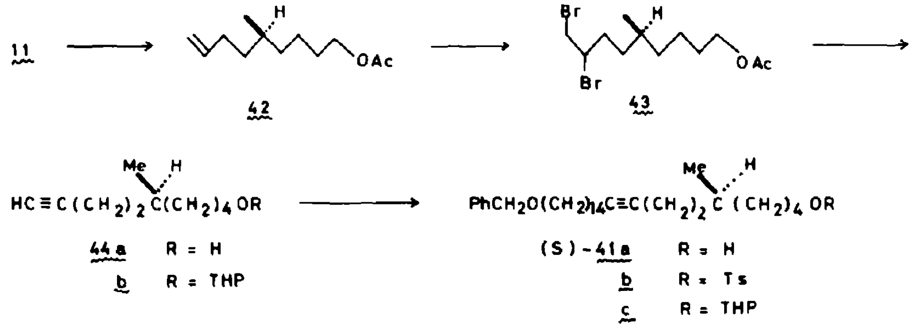
Compound **1**	$[\alpha]_D$ (in n-hexane)	m.p.*	Mixture m.p. with the natural pheromone*
Natural	+5.1° (c=3.54)³	45-46°	——
3S, 11S	+5.98° (c=0.9)	44-44.5°	44-45°
3S, 11R	+5.73° (c=2.04)	38-38.5°	33.5-35°
3R, 11R	-5.63° (c=4.1)	44.5-45°	35-37.5°
3R, 11S	-5.68° (c=4.0)	39-39.5°	34.5-35.5°

* Measured by Dr. Yamaoka of Prof. Fukami's laboratory.

the ω-OH group. Both enantiomers of A′ were synthesized from (*R*) - (+) - citronellol **5a** and tetradecane - 1, 14 - diol **32a** in the following manner.



Scheme 6.

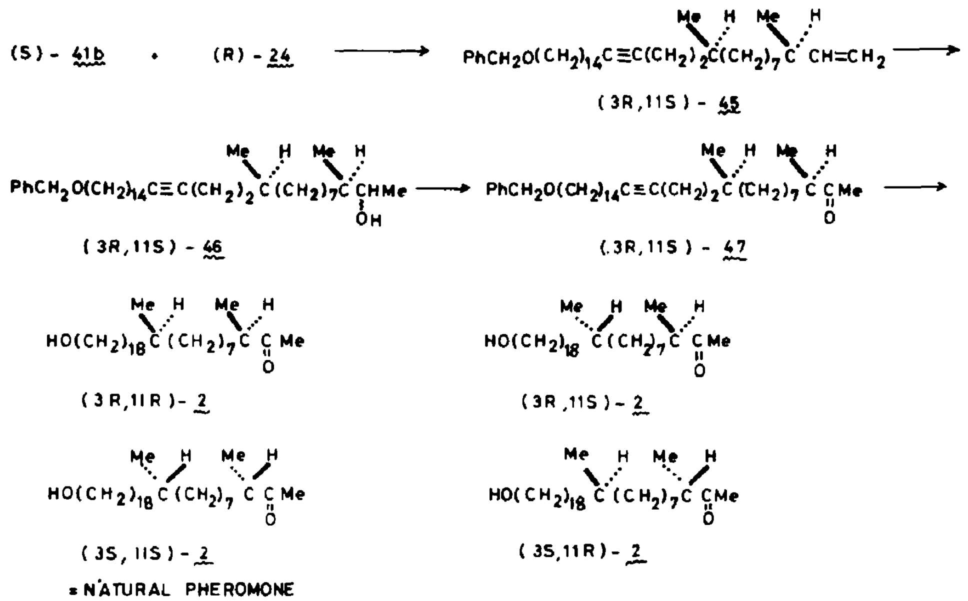


Scheme 7.

Tetradecane - 1, 14 - diol **32a** was converted into the corresponding monobenzyl ether **32b**. Its tosylate **32c** was treated with LiBr to give a bromide **33a**. Halogen exchange of **33a** with NaI gave an iodide **33b**. This was used for the alkylation of an acetylene **34**, derived from (*R*) - (−) - citronellyl iodide **6**. The alkylation product **35** was epoxidized with *m*-chloroperbenzoic acid to give an epoxide **36**, whose triple bond remained intact. Oxidation of **36** with HIO_4 gave an aldehyde **37**. One-carbon elongation of the aldehyde **37** was executed in the conventional manner. Reduction of **37** with LAH gave an alcohol **38a**. The corresponding tosylate **38b** was treated with NaCN to give a nitrile **39**. This was hydrolyzed to a carboxylic acid **40**. The (*R*) - alcohol **41a**, α_D^{20} +0.44° (neat, $l = 1$ dm), was obtained by the reduction of **40** with LAH. Conventional tosylation of **41a** gave the corresponding tosylate (*R*)-**41b** (= fragment A′).

A simpler route was available for the synthesis (*S*)-**41b**. The aldehyde **11** was converted to an olefin **42** by the Wittig reaction. Addition of Br_2 to **42** yielded a dibromide **43**. This was treated with $NaNH_2$ in liq NH_3 to give an acetylene **44a**. The corresponding THP ether **44b** was alkylated with **33b** yielding (*S*)-**41c**. Acid treatment of (*S*)-**41c** gave an alcohol (*S*)-**41a**, α_D^{22} −0.41° (neat, $l = 1$ dm), whose tosylation yielded the desired tosylate (*S*)-**41b** (= A′).

The coupling of (*S*)-**41b** with the Grignard reagent derived from (*R*)-**24** took place smoothly to give an enyne (3*R*, 11*S*)-**45**. The Markownikoff hydration of **45** by oxymercuration–demercuration gave an alcohol (3*R*, 11*S*)-**46**. This was oxidized with CrO_3 to give a ketone (3*R*, 11*S*)-**47**. Hydrogenation of **47** over Pd-C effected the debenzylation and the saturation of the triple bond to give (3*R*, 11*R*)-(−)-**2** as crystals. In the same manner (*R*)-**41b** and (*R*)-**24** gave (3*R*, 11*S*)-(−)-**2**, (*R*)-**41b** and (*S*)-**24** gave (3*S*, 11*S*)-(+)-**2** and (*S*)-**41b** and (*S*)-**24** gave (3*S*, 11*R*)-(+)-**2**. The spectral data of (3*R*, 11*R*)-**2** and (3*S*, 11*S*)-**2** were in good accord with those described for the natural pheromone. Table 2 shows specific rotations and m.ps of the natural pheromone **2** and the four synthetic stereoisomers and their mixture m.ps with natural pheromone **2**. In this case, too, the natural product was identified as the (3*S*, 11*S*)-isomer by the



Scheme 8.

Table 2. Optical rotations and m.ps of natural and synthetic stereoisomers of 2 and their mixture m.p. with natural 2

Compound 2	$[\alpha]_D$ (in n-hexane)	m.p.	Mixture m.p. with the natural pheromone*
Natural	+7.1° (c=0.35)[3]	42.5-43°*	—
3S, 11S	+6.1° (c=0.65)	41-42°*	41 - 42.5°
3S, 11R	+6.4° (c=0.55)	40-40.5°*	36 - 37°
3R, 11R	-6.5° (c=0.38)	38-40°	—
3R, 11S	-6.8° (c=1.0)	39-40°	—

*Measured by Dr. Nishida of Prof. Fukami's Laboratory.

mixture m.p. determination showing no m.p. depression. The stereochemistry at C-3 of natural 2 had previously been assigned as *S* on the basis of its ORD.[3] The optical rotation of the synthetic (3*S*, 11*S*)-2 was in accord with that of the natural pheromone. The biological activity of our synthetic materials will be reported in due course.

In conclusion we were able to establish unambiguously the absolute configurations of the two German cockroach pheromones to be 3*S*, 11*S* by synthesizing all of the possible stereoisomers.

EXPERIMENTAL

All b.ps and m.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 unless otherwise stated. Optical rotations were measured on a Jasco DIP-4 polarimeter. GLC analyses were performed on a Yanaco G 80 gas chromatographs.

(R)-(+)-*Citronellic acid* **4a**. (−)-Isopulegol 3, the starting material, was kindly provided by Takasago Perfumery Co., and recrystallized three times from an equal volume of ligroin at −20° to give fine needles of pure 3, b.p. 67–69°/4 mm; α_D^{22} −20.3° (neat, 1 = 1 dm). Jones CrO_3 (260 ml) was added dropwise during 1 hr to a stirred and ice-cooled soln of 3 (105 g) in acetone (1l) keeping the inner temp below 20°. After the addition, the mixture was stirred for 5 min and the excess CrO_3 was destroyed by the addition of MeOH. The mixture was concentrated *in vacuo*, diluted with water and extracted with ether. The ether extract was washed with water, $NaHCO_3$ aq and NaCl aq, dried ($MgSO_4$) and concentrated *in vacuo* to give 82.9 g (80%) of isopulegone. Dry HCl gas was bubbled through this crude isopulegone (82.9 g) to give a chloroketone. This was added to a vigorously stirred soln of 5% NaOH in water (2l). The stirring was continued for 3 hr at room temp. Then the mixture was extracted with ether to remove neutral substances containing pulegone. The aq layer was acidified with conc HCl (200 ml) and extracted with ether. The ether extract was washed with water and NaCl aq, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was distilled to give 32.5 g (28% from 3) of **4a**, b.p. 130–134° (4 mm), n_D^{21} 1.4538; $[\alpha]_D^{22}$ + 11.7° (*c* = 1.58, $CHCl_3$); glc (Column, 3% SE-30, 1.5 m × 2 mm i.d. at 140–200° (+6°/min); Carrier gas, N_2, 1.05 kg/cm^2): R_t 2.1 min (single peak).

Determination of the optical purity of (R)-(+)-*citronellic acid.* Oxalyl chloride (0.32 ml) was added to a soln of the above described (*R*)-(+)-citronellic acid (263 mg) in dry benzene (5 ml). The mixture was stirred and heated under reflux for 30 min and then concentrated *in vacuo*. The residue was distilled to give 225.5 mg (77%) of the acyl chloride, b.p. 60–62°/4 mm. This was added to a soln of (*R*)-(+) - α - (1-naphthyl)ethylamine (donated by Sumitomo Chemical Co. and 98.4% optically pure as determined by the Analytical Division, Institute of Biological Science, Sumitomo Chemical Co., 410 mg) in dry ether (15 ml). Subsequent work-up gave the crude amide **4b**. Its diastereomeric composition was analyzed by hplc (Shimadzu LC-2; Zorbax SIL column, 25 cm × 6.2 mm; Solvent, *n*-hexane–THF (4:1), 0.2 ml/min; Pressure, 1.0–2.0 kg/cm^2; Detector, 254 nm). The retention times of (*R* acid, *R*)-**4b** and (*S* acid, *R*)-**4b** were 55.5 (96%) and 60.2 (4%) min, respectively. The optical purity of **4a** was therefore 92%.

(R)-(+)-*Citronellol* **5a**. A soln of **4a** (32.5 g) in dry ether (50 ml) was added dropwise to a stirred and ice-cooled suspension of LAH (8 g) in dry ether (1 l). After the addition, the mixture was stirred for 3 hr at room temp. Then it was poured into ice-dil HCl and ether layer was separated. The aq layer was extracted with ether. The ether soln was washed with water, $NaHCO_3$ aq and NaCl aq, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was distilled to give 27.0 g (92%) of **5a**, b.p. 92–95°/4 mm n_D^{23} 1.4536; α_D^{20} + 4.92° (neat, l = 1 dm); ν_{max} 3340 (s), 2980 (s), 2940 (s), 2880 (s), 1455 (m), 1390 (m), 1060 (m), 825 (w) cm^{-1}; δ 0.92 (3H, d, J = 6Hz), ~ 1.25 (6H, m, J = 6Hz), 1.58 (3H, s), 1.63 (3H, s), 1.90 (1H, m, J = 6.0 Hz), 3.54 (2H, t, J = 6Hz), 3.85 (1H, s), 5.05 (1H, t, J = 6Hz).

(R)-(+)-*Citronellyl tosylate* **5b**. *p*-Toluenesulfonyl chloride (41.4 g) was added portionwise to a stirred and ice-cooled soln of **5a** (26.5 g) in dry pyridine (150 ml). After the addition 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 NaCl aq, dried ($MgSO_4$), and concentrated *in vacuo* to give 49 g (quantitative) of crude **5b**, ν_{max} 2910 (s), 1600 (m), 1195 (s), 1180 (s) cm^{-1}. This was employed for the next step without further purification.

(R)-(−)-*Citronellyl iodide* **6**. Sodium iodide (56.4 g) was added to a soln of **5b** (prepd from 29.3 g of **5a**) in acetone (300 ml). The mixture was stirred and heated under reflux for 4 hr and stirred at room temp for 14 hr. Then it was poured into water and extracted with ether. The ether soln was washed with water, $Na_2S_2O_3$ aq and NaCl aq, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was distilled to give (42.5 g (85%) of **6**, b.p. 110–115°/12 mm, $n_D^{20.5}$ 1.4995; $\alpha_D^{20.5}$ −14.34° (neat, l = 1 dm); ν_{max} 2960 (s), 2920 (s), 2860 (s), 1450 (m), 1380 (m), 1180 (m) cm^{-1}; δ0.88 (3H, d, J = 6 Hz), ~1.25 (4H, m), 1.58 (3H, s), 1.65 (3H, s), 1.97 (4H, m), 3.15 (2H, t, J = 6Hz), 5.02 (1H, t, J = 6Hz); glc (Column, 3% SE-30, 2.25 m × 2 mm at 130°; Carrier gas, N_2, 1.0 kg/cm^2) R_t 3.5 min. (Found: C, 45.03; H, 7.14. $C_{10}H_{19}I$ requires: C, 45.13; H, 7.20%).

Diethyl (R)-(−)-*Citronellylmalonate* **7**. A soln of diethyl malonate (48 g) in dry EtOH (50 ml) was added to a stirred and ice-cooled soln of NaOEt (prepd from 7g of Na) in dry EtOH (150 ml). To this was added a soln of **6** (67 g) in dry EtOH (50 ml). The mixture was stirred for 1 hr at 0–5° and then stirred and heated under reflux for 4 hr. EtOH was removed *in vacuo* and the residue was acidified with dil AcOH. The mixture was extracted with ether. The ether soln was washed with water, $Na_2S_2O_3$ aq, $NaHCO_3$ aq and NaCl aq, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was distilled to give 58.5g (78%) of **7**, b.p. 156–161°/4 mm, n_D^{20} 1.4481; α_D^{20} − 5.02° (neat, l = 1 dm); ν_{max} 2990 (s), 2920 (s), 2860 (m), 1750 (s), 1740 (s), 1280 (m), 1250 (m), 1190 (m), 1180 (m), 1040 (m) cm^{-1}; δ0.92 (3H, d, J = 6Hz), 1.28 (6H, t, J = 7Hz), 1.61 (3H, s), 1.68 (3H, s), 3.15 (1H, t, J = 7Hz), 4.16 (4H, q, J = 7Hz), 5.08 (1H, t, J = 7Hz). (Found: C, 68.32; H, 10.17. $C_{17}H_{30}O_4$ requires: C, 68.42; H, 10.13%).

(S)-(−)-5,9 - *Dimethyldec* - 8 - *enoic acid* **8**. A soln of **7** (58 g) in 95% EtOH (100 ml) was added to KOH aq (58 g in 140 ml H_2O) and the mixture was stirred and heated under reflux for 2.5 hr. It was concentrated *in vacuo* to remove EtOH. AcOH (140 ml) was added to the residue and the resulting soln was stirred and heated under reflux for 2 days. After cooling, the mixture was diluted with water and extracted with ether. The ether soln was washed with water and NaCl aq, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was distilled to give 35.5 g (92%) of **8** b.p. 150–160°/5 mm, n_D^{20} 1.4563, α_D^{20} − 2.06° (neat, l = 1 dm); ν_{max} ~ 3200 (br), 2970 (s), 2920 (s), 2860 (s), ~ 2650 (br), 1710 (s), ~ 1280 (m), 935 cm^{-1}; δ 0.85 (3H, d, J = 6Hz), 1.53 (3H, s), 1.62 (3H, s), 5.00 (1H, t, J = 6Hz), 12.10 (1H, s). (Found: C, 72.68; H, 11.40. $C_{12}H_{22}O_2$ requires: C, 72.68; H, 11.18%).

(S)-(+)-5, 9-*Dimethyldec*-8-*en*-1-*o*l **9a**. A soln of **8** (35.5 g) in dry ether (200 ml) was added dropwise to a stirred and ice-cooled suspension of LAH (10 g) in dry ether (500 ml). The mixture was stirred for 4 hr at room temp and then poured into ice-dil HCl. The ether layer was separated and the aq layer was extracted with ether. The combined ether soln was washed with water, $NaHCO_3$ aq and NaCl aq, dried (K_2CO_3) and concentrated *in vacuo*. The residue was distilled to give 30.4 g (92%) of **9a**, b.p. 110–112°/2.5 mm, n_D^{20} 1.4578; α_D^{20} + 0.27° (neat, l = 1 dm); ν_{max} 3300 (m), 2950 (sh), 2910 (s), 2840 (s), 1450 (m), 1380 (m), 1070 (m), 1050 (m) cm^{-1}; δ0.84 (3H, d, J = 6Hz), 1.52 (3H, s), 1.60 (3H, s), 2.96 (1H, s, –OH), 3.46 (2H, br, t), 4.99 (1H, t, J = 6 Hz). (Found: C, 78.03; H, 13.32. $C_{12}H_{24}O$ requires: C, 78.19; H, 13.13%).

(S)-5, 9-*Dimethyldec*-8-*enyl acetate* **9b**. Ac_2O (60 ml) was added to a soln of **9a** (30.4 g) in dry pyridine (60 ml). The mixture was stirred at room temp for 5 hr, poured into ice-water and extracted with ether. The ether soln was washed with water, $CuSO_4$ aq, water and NaCl aq, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was distilled to give 36.0 g (96.5%) of **9b**, b.p. 115–118°/1.5 mm, n_D^{20} 1.4461; ν_{max} 2940 (s), 2890 (s), 2830 (s), 1730 (s), 1230 (s), 1020 (m) cm^{-1}; δ0.88 (3H, d, J = 6Hz), 1.60 (3H, s), 1.67 (3H, s), 1.98 (3H, s), 4.02 (2H, t, br, J = 6Hz), 5.10 (1H, t, J = 6Hz). (Found: C, 73.86; H, 11.73. $C_{14}H_{26}O_2$ requires: C, 74.28; H, 11.58%).

(5S, 8RS) - 8, 9 - *Oxido* - 5, 9 - *dimethyldecyl acetate* **10**. *m*-Chloroperbenzoic acid (85% purity, 33 g) was added portionwise to a stirred and ice-cooled soln of **9b** (36 g) in $CHCl_3$ (400 ml). The mixture was left to stand overnight in a refrigerator and filtered to remove precipitated *m*-chlorobenzoic acid. The filter cake was washed with n-hexane. The combined filtrate and washings were washed with Na_2CO_3 aq and NaCl aq, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was distilled to give 34.5 g (90%) of **10**, b.p. 125–130°/1.5 mm, n_D^{19} 1.4416; α_D^{19} + 0.31° (neat, l = 1 dm); ν_{max} 2960 (s), 2930 (s), 2860 (s), 1745 (s), 1240 (vs), 1125 (m), 1040 (s), 895 (m), 870 (m) cm^{-1}; δ0.85 (3H, d, J = 6Hz), 1.15 (3H, s), 1.20 (3H, s), 1.93 (3H, s), 2.45 (1H), 3.96 (2H, t, J = 7Hz). (Found: C, 69.11; H, 10.95. $C_{14}H_{26}O_3$ requires: C, 69.38; H, 10.81%).

(S)-(+)-8-*Acetoxy*-4-*methyloctanal* **11**. A soln of **10** (34.5 g) in ether (100 ml) was added to a stirred and ice-cooled soln of $HIO_4 \cdot 2H_2O$ (35 g) in THF (100 ml). The mixture was stirred for 1 hr at room temp, poured into water and extracted with ether. The ether soln was washed with water, $NaHCO_3$ aq and NaCl aq., dried ($MgSO_4$) and concentrated *in vacuo*. The residue was distilled to give 23.0 g (81%) of **11**, b.p. 115–120°/1.5 mm, n_D^{19} 1.4420; α_D^{20} + 1.45° (neat, l = 1 dm); ν_{max} 2920 (s), 2860 (s), 2700 (w), 1740 (s), 1720 (s), 1250 (s), 1035 (m) cm^{-1}; δ0.85 (3H, br, d, J = 6Hz), 1.94 (3H, s), 3.95 (2H, t, J = 7Hz), 9.68 (1H, t, J = 2Hz). (Found: C, 66.34; H, 10.18. $C_{11}H_{20}O_3$ requires: C, 65.97; H, 10.07%).

(S)-(−)-5-*Methyltricos*-8-*en*-1-*o*l **12**. A phosphorane soln was prepared under Ar by the addition of n-BuLi (1.5 N in n-hexane, 92 ml) to a stirred and ice-cooled soln of n-$C_{15}H_{31}P^+(Br^-)Ph_3$ (80 g) in dry THF (100 ml). The mixture was stirred for 1 hr at 20° to give a deep red soln. This was added to a stirred and cooled soln of **11** (23 g) in dry THF (200 ml) during 1.5 hr at −20 to −30° under Ar. The inner temp. was gradually raised to room temp during 1 hr and the stirring was continued for 1.5 hr at room temp. Then a soln of NaOH (30 g) in MeOH (100 ml)-H_2O (30 ml) was added to the mixture to effect hydrolysis of acetate. The mixture was left to stand overnight at room temp, diluted with water and extracted with n-hexane. The extract was washed with 50% MeOH (100 ml) and water, dried ($MgSO_4$) and concentrated *in vacuo* to give 65 g of a crude material. This was chromatographed over Merck Kieselgel 60 (70–230 mesh, 500 g, 45 × 5.5 cm) in n-hexane. Elution with n-hexane removed hydrocarbon impurities. Subsequent elution with n-hexane-ether (9:1 ~ 4:1) gave 8.6 g (22%) of pure **12**, n_D^{20} 1.4646, α_D^{20} −0.90° (neat, l = 1 dm); ν_{max} 3300 (m), 3000 (w), 2920 (s), 2850 (s), 1650 (w), 1465 (m), 1380 (m), 1050 (m), 960 (w), 720 (w) cm^{-1}; δ ~ 0.90 (6H, m), ~ 1.25 (~ 32H), ~ 2.00 (4H, m), 3.54 (2H, m), 5.30 (2H, t, J = 5Hz). (Found: C, 81.62; H, 13.73. $C_{24}H_{48}O$ requires: C, 81.74; H, 13.72%).

(R)-(+)-5-*Methyltricosan*-1-*ol* (*R*)-**13a**. 10% Pd-C (2g) was added to a soln of **12** (8.6 g) in n-hexane (100 ml) and 95% EtOH (50 ml). The mixture was shaken under H_2(1 atm) for 2 hr at room temp. Then the catalyst was removed by filtration and washed with n-hexane. The combined filtrate and washings were concentrated *in vacuo* to give crystals of **13a**. This was recrystallized from n-hexane yielding 7.0 g (81%) of **13a** as prisms, m.p. 47.0–47.5°, $[\alpha]_D^{20} + 1.01 \pm 0.1°$ (c = 4.065, ether); ν_{max} 3360 (m), 2920 (s), 2850 (s), 1465 (m), 1380 (m), 1050 (m), 730 (m), 720 (m) cm^{-1}; δ0.90 (6H, m), ~1.25 (~42H, br), 3.67 (2H, t, J = 6Hz). (Found: C, 80.84; H, 14.37. $C_{24}H_{50}O$ requires: C, 81.28; H, 14.21%).

(R)-5-*Methyltricosyl tosylate* (*R*)-**13b**. *p*-Toluenesulfonyl chloride (2.0 g) was added to a stirred and ice-cooled soln of (*R*)-**13a** (2.5 g) in dry pyridine (20 ml). The stirring was continued for 1 hr at 0–5° and then for 2 hr at room temp. The mixture was poured into ice-water and extracted with ether. The ether extract was washed with water, $CuSO_4$aq, water and NaCl aq, dried ($MgSO_4$) and concentrated *in vacuo* to give 3.5 g (quantitative) of crude (*R*)-**13b**, ν_{max} 1600 (m), 1190 (s), 1180 (s), 1100 (m), 960 (m), 930 (s) cm^{-1}. This was employed for the next step without further purification.

(R)-(+)-2, 6-*Dimethyltetracos-2-en-9-yne* **14**. A soln of n-BuLi in n-hexane (1.5 M, 118 ml) was added to a stirred and cooled soln of hexadec-1-yne (32.55 g) in dry THF (150 ml) at −10° under Ar. The stirring was continued for 30 min. Then a soln of **6** (39 g) in dry HMPA (180 ml) was gradually added to the acetylide soln at −10°. The cooling bath was removed after the addition and the stirring was continued for 12 hr at room temp. The mixture was poured into ice-water and extracted with n-hexane. The hexane soln was washed with water and NaCl aq, dried ($CaCl_2$) and concentrated *in vacuo*. The residue was chromatographed over Merck Kieselgel 60 (150 g) in petroleum ether. The yield of pure **14** after distillation was 34.7 g (60%), b.p. 192–196°/0.8 mm, n_D^{20} 1.4643; $\alpha_D^{20} + 2.76°$ (neat, 1 = 1 dm); ν_{max} 2920 (s), 2860 (s), 1475 (m), 1382 (m), 1340 (w), 1120 (w), 1085 (w), 825 (w), 720 (w) cm^{-1}; δ0.87 (6H, m), ~1.24 (29H, br), 1.57 (3H, s), ~2.04 (4H, m), 5.02 (1H, t, J = 6Hz); glc (Column, 3% SE-30, 2.25 m × 2 mm at 220°; Carrier gas, N_2, 1.0 kg/cm^2) Rt 8.2 min. (Found: C, 86.47; H, 13.69. $C_{26}H_{46}$ requires: C, 86.59; H, 13.41%).

(S)-(+)-4-*Methyldodecos-7-yn-1-al* **16**. Epoxydation of **14** with *m*-chloroperbenzoic acid in the same manner as described for the prepn of **10** yielded **15**. This was cleaved with $HIO_4 \cdot 2H_2O$ in the same manner as described for the prepn of **11** to give **16**. The crude **16** was purified by SiO_2 chromatography to give 14.0 g (63% from **14**) of fairly pure **16**, $n_D^{20.5}$ 1.4628; $\alpha_D^{20.5} + 1.45°$ (neat, l = 1 dm); ν_{max} 2920 (s) 2850 (s), 2700 (m), 1730 (s), 1460 (m), 1380 (m), 1330 (w), 1220 (w), 1110 (vw), 1030 (w), 720 (m), 670 (m) cm^{-1}; δ0.90 (6H, m), ~1.24 (29H, br), ~2.05 (4H, m), 2.22 (2H, m), 9.65 (1H, t, J = 1.8Hz). (Found: C, 81.61; H, 1250. $C_{23}H_{42}O$ requires: C, 82.57; H, 12.65%). This was employed for the next step without further purification.

(S)-(+)-4-*Methyldodecos-7-yn-1-ol* **17a**. A soln of **16** (14 g) in dry ether (20 ml) was added to a stirred and ice-cooled suspension of LAH (5.0 g) in dry ether (300 ml). The crude **17a** obtained by the subsequent work-up was purified by chromatography over Merck Kieselgel 60 (150 g) in petroleum ether–ether (10:1) to give 12.7 g (67.6%) of pure **17a**, n_D^{20} 1.4644; $\alpha_D^{20} + 1.02°$ (neat, 1 = 1 dm); ν_{max} 3310 (m), 2910 (s), 2850 (s), 1460 (m), 1435 (vw), 1380 (m), 1330 (w), 1055 (m), 890 (w), 720 (w) cm^{-1}; δ0.82 (3H, t, J = 6 Hz), 0.90 (3H, d, J = Hz), 1.24 (31 H, br), 1.75 (1H, s), 2.17 (4H, br), 3.47 (2H, t, J = 6Hz); tlc (Silca gel G, petroleum ether–ether 2:1) Rf 0.63. (Found: C, 81.80; H, 13.04. $C_{23}H_{44}O$ requires: C, 82.07; H, 13.18%).

(S)-(+)-4-*Methyldodecos-7-ynyl tosylate* **17b**. The alcohol **17a** (13.9 g) was converted into **17b** in the usual manner, ν_{max} 1600 (w), 1190 (s), 1180 (s) cm^{-1}. This was employed for the next step without further purification.

(R)-(+)-1-*Cyano-5-methyldodecos-8-yne* **18**. NaCN (4.0 g) was added to a soln of **17b** (17.3 g) in DMSO (40 ml). The mixture was stirred and heated at 60° for 3 hr. Then it was poured into ice-water and extracted with ether. The ether soln was washed with water and NaCl aq, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed over Merck Kieselgel 60 (180 g, 30 × 3.5 cm) in n-hexane-ether (30:1). The yield of pure **18** was 9.2 g (49%), n_D^{20} 1.4635; $\alpha_D^{20} + 4.10°$ (neat, 1 = 1 dm); ν_{max} 2920 (s), 2840 (s), 2240 (w), 1460 (m), 1430 (sh), 1380 (w), 1325 (w), 720 (w) cm^{-1}; δ0.92 (6H, m), ~1.25 (31H, br), 2.15 (6H, br). (Found: C, 83.26; H, 12.77; N, 3.81. $C_{24}H_{43}N$ requires: C, 83.41; H, 12.54; N, 4.05%).

(R)-(+)-*Methyltricos-8-ynoic acid* **19**. A soln of **18** (9.2 g) and NaOH (10.6 g) in EtOH–H_2O (103 ml, 60:43, v/v) was stirred and heated under reflux for 24 hr. After cooling, the mixture was acidified with dil HCl-ice and extracted with ether. The ether soln was washed with water and NaCl aq, dried (MgSO) and concentrated *in vacuo*. The residue was chromatographed over Merck Kieselgel 60 (14 cm × 3.5 cm) in petroleum ether–ether (2:1) to give 8.8 g (91%) of **19**, m.p. 20–21°, $[\alpha]_D^{19} + 4.06°$ (c = 2.29, ether); ν_{max} ~3200 br, 2940 (s), 2870 (s), ~2640 (br), 1720 (s), 1470 (m), 1440 (m), 1420 (w), 1380 (w), 1300 (w), 1280 (w), 1220 (w), 1100 (w), 930 (m), 720 (w) cm^{-1}; δ0.90 (6H, m), ~1.30 (31H, br), 2.15 (6H, m), 11.98 (1H, s). (Found: C, 78.99; H, 12.34. $C_{24}H_{44}O_2$ requires: C, 79.06; H, 12.16%).

(R)-5-*Methyltricos-8-yn-1-ol* **20**. A soln of **19** (8.2 g) in dry ether (50 ml) was added to a stirred and ice-cooled suspension of LAH (2.5 g) in dry ether (150 ml). The mixture was stirred overnight at room temp. A small amount of water was added gradually to destroy the excess LAH. Then the mixture was poured into ice-dil HCl and extracted with ether. The ether soln was washed with water, $NaHCO_3$ aq and NaCl aq, dried (K_2CO_3) and concentrated *in vacuo* to give 8.0 g (quantitative) of crude **20**, ν_{max} 3300 (m), 2920 (s), 2840 (s), 1460 (m), 1380 (m), 1330 (w), 1120 (w), 1070 (w), 1050 (m), 720 (w) cm^{-1}. This was employed for the next step without further purification.

(S)-(−)-5-*Methyltricosan-1-ol* (S)-**13a**. 10% Pd–C (2 g) was added to a soln of **20** (7.5 g) in n-hexane (100 ml) and 95% EtOH (50 ml) and the mixture was shaken under H_2. Subsequent work-up as described for the prepn of (*R*)-**13a** gave 6.5 g (87%) of (*S*)-**13a**, m.p. 47.0 − 47.5°; $[\alpha]_D^{20}$ −1.01 ± 0.08° (*c* = 5.37, ether); ν_{max} 3360 (m), 2920 (s), 2850 (s), 1465 (m), 1380 (m), 1050 (m), 730 (m), 720 (m) cm^{-1}; δ0.90 (6H, m), ~1.25 (~42H, br), 3.67 (2H, t, J = 6Hz). (Found: C, 80.89; H, 13.90. $C_{24}H_{50}O$ requires: C, 81.28; H, 14.21%).

(R)-(−)-4-*Methylhex-5-en-1-ol* (R)-**23a**. Oxidation of **21** with $HIO_4 \cdot 2H_2O$ was carried out in the same manner as described for the prepn of **11** to give the known aldehyde **22**.[21] A soln of **22** (4.3 g) in dry ether (5 ml) was added to a stirred and ice-cooled suspension of LAH (3.3 g) in dry ether (40 ml). The mixture was stirred for 3 hr at room temp. Then the mixture was poured into ice-dil HCl and extracted with ether. The ether soln was washed with water, $NaHCO_3$ aq and NaCl aq, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was distilled to give 4.0 g (91.4%) of (*R*)-**23a**, b.p. 79 ~ 81°/25 mm, n_D^{19} 1.4371; α_D^{19} −15.5° (neat, 1 = 1 dm); ν_{max} 3330 (s), 3080 (m), 2940 (s), 2860 (s), 1640 (m), 1450 (m), 1420 (m), 1380 (m), 1055 (s), 995 (m), 905 (s) cm^{-1}; δ0.98 (3H, d, J = 6Hz), 1.41 (4H, m), 2.10 (1H, m), 3.27 (1H, s, –OH), 3.45 (2H, t, J = 6Hz), ~4.70–~5.10 (2H, m), ~5.30 – ~5.92 (1H, m); MS: *m/e* 114 (M^+); glc (Column, 3% SE-30, 1.5 m × 2 mm at 50°; Carrier gas, N_2, 0.7 kg/cm^2) R_t 3.7 min.

(R)-(−)-4-*Methylhex-5-enyl bromide* (R)-**24**. *p*-Toluenesulfonyl chloride (7.7 g) was added to a stirred and ice-cooled soln of (*R*)-**23a** (3.8 g) in dry pyridine (25 ml). The mixture was stirred for 1.5 hr at 0–5°. Then it was poured into ice-water and extracted with ether. The ether soln was washed with water, $CuSO_4$aq, $NaHCO_3$ aq and NaClaq, dried ($MgSO_4$) and concentrated *in vacuo* to give 8.2 g (quantitative) of crude (*R*)-**23b**. This was dissolved in acetone (100 ml). LiBr (7.2 g) was added to the soln and the mixture was stirred and heated under reflux for 1.5 hr and then stirred overnight at room temp. It was poured into water and extracted with ether. The ether soln was washed with water, $NaHCO_3$ aq and NaCl aq, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was distilled to give 4.46 g (75.6% from (*R*)-**23a**) of (*R*)-**24**, b.p. 81–84°/34 mm, n_D^{19} 1.4597; α_D^{19} −12.6° (neat, 1 = 1 dm); ν_{max} 3080 (m), 2970 (s), 2940 (s), 2880 (s), 1640 (m), 1460 (m), 1440 (w), 1420 (w), 1380 (m), 1300 (w), 1280 (w), 1255 (w), 1215 (m), 998 (m), 910 (s) cm^{-1}; δ0.98 (3H, d, J = 6Hz), ~1.20 – ~2.40 (5H, m), 3.28 (2H, t, J = 7Hz), ~4.68 – ~5.10 (2H, m), ~5.27 – ~5.90 (1H, m); glc (Column, 3% SE-30, 1.5 m × 2 mm at 50°; Carrier gas, N_2, 0.7 kg/cm^2) R_t 5.3 min. (Found: C, 46.85; H, 7.35. $C_7H_{13}Br$ requires: C, 47.48; H, 7.40%).

(R)-(+)-4-*Methylheptanedioic acid monomethyl ester* **26**. Jones CrO_3 (12.9 ml) was added dropwise to a soln of **25** (13.58 g) in acetone (180.1 ml) with stirring and ice-cooling. The mixture was stirred for 10 min at room temp. Then MeOH was added to destroy excess CrO_3. The mixture was concentrated *in vacuo*. The residue was diluted with water and extracted with ether. The ether soln was washed with water and NaCl aq, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was distilled to give 10.38 g (70%) of **26**, b.p. 125–132°/4 mm, n_D^{21} 1.4468; $\alpha_D^{21}+0.9°$ (neat, l = 1 dm); ν_{max} ~3200 (m), 2950 (s), 2870 (m), ~2600 (m), 1740 (vs), 1710 (vs), 1400 (m), 1280 (m), 1200 (s), 1080 (s), 1100 (m) cm^{-1}; δ0.8–1.1 (3H, br), 1.3–1.8 (5H, br), 2.1–2.5 (4H, br), 3.6 (3H, s), 11.4 (1H, s). (Found: C, 57.58; H, 8.65. $C_9H_{16}O_4$ requires: C, 57.43; H, 8.57%).

Methyl (S)-(+)-*6-bromo-4-methylhexanoate* **27**. Ag_2O (7.7 g) was added to a stirred soln of **26** (12.43 g) in distilled water (177.3 ml) contained in a flask wrapped with aluminum foil. After stirring for 4 hr at 40°, the crystalline Ag salt was collected on a Buchner funnel, washed with hot MeOH and dried *in vacuo* at 50° over P_2O_5. The dried solid (15.9 g) was put into a dried flask and the Ag salt was further dried *in vacuo* for 30 hr at 100–110°. Subsequent Hunsdiecker reaction was carried out under Ar. The Ag salt was suspended in dry CCl_4 (dried over P_2O_5 and distilled, 114.1 ml). Br_2 (dried over P_2O_5, 8.6 g) was added dropwise to the stirred and ice-cooled suspension. The mixture was stirred and heated under reflux for 1 hr and filtered. The filtrate was washed with 10% Na_2CO_3 aq, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was distilled to give 9.64 g (65.4%) of **27**, b.p. 97–101°/7 mm, n_D^{20} 1.4648; $\alpha_D^{20}+6.6°$ (neat, l = 1 dm); ν_{max} 2960 (m), 2930 (m), 2860 (m), 1745 (s), 1440 (m), 1270 (m), 1200 (m), 1180 (m) cm^{-1}; δ0.92 (3H, distorted d, J = 6Hz), ~1.55 – ~2.00 (5H, m), 2.30 (2H, t, J = 6Hz), 3.40 (2H, t, J = 6Hz), 3.62 (3H, s); glc (Column, 3% SE-30, 1.5 m × 2 mm at 108°; Carrier gas, N_2, 1.3 kg/cm^2) R_t 3.7 min. (Found: C, 42.83; H, 6.69. $C_8H_{15}O_2Br$ requires: C, 43.07; H, 6.78%).

Methyl (S)-6-(o-*nitrophenylseleno*)-4-*methylhexanoate* **28a**. To a soln of *o*-nitrophenylseleno cyanate (9.8 g) in dry EtOH (232.4 ml), $NaBH_4$ (1.96 g) was gradually added with stirring and ice-cooling under Ar. The mixture was stirred for 30 min to yield a dark red soln. A soln of **27** (9.64 g) in dry EtOH (23.5 ml) was added to this red soln and the mixture was stirred for 8 hr at room temp. Then it was concentrated *in vacuo*, poured into water and extracted with ether. The ether soln was washed with water and NaCl aq, dried ($MgSO_4$) and concentrated *in vacuo* to give 14.75 g of crude **28a**, ν_{max} 2940 (m), 1735 (s), 1585 (m), 1560 (m), 1510 (s), 1330 (s), 1305 (s), 725 (m) cm^{-1}. This was employed for the next step without further purification.

(S)-6-(o-*Nitrophenylseleno*)-4-*methylhexanoic acid* **28b**. The crude **28a** (11 g) was mixed with 20% NaOH aq (19.2 g) and MeOH (2 ml) and the mixture was stirred and heated under reflux for 1.5 hr. Then it was diluted with water, acidified with conc HCl and extracted with ether. The ether soln was washed with water, dried ($MgSO_4$) and concentrated *in vacuo* to give 10.98 g of crude **28b**, ν_{max} ~3400 (m), 2970 (s), 2920 (s), 2860 (m), 1710 (s), 1590 (m), 1560 (m), 1515 (s), 1335 (s), 1305 (s), 730 (s) cm^{-1}. This was employed for the next step without further purification.

(S)-(+)-*4-Methylhex-5-enoic acid* **29**. 35% H_2O_2 (9.8 ml) was added dropwise to a stirred and ice-cooled soln of **28b** (10.6 g) in THF (250 ml). The stirring was continued for 30 min at 0–5° and 10 hr at room temp. Then the soln concentrated *in vacuo*. The residue was diluted with water and extracted with ether. The ether soln was washed with water and NaCl aq, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was distilled to give 2.97 g (72.4% from **27**) of **29**, b.p. 124–130°/33 mm, $n_D^{20.5}$ 1.4346; $\alpha_D^{20.5}+14.42°$ (neat, l = 1 dm); ν_{max} ~3100 (m), 2960 (s), 2930 (s), 2880 (m), ~2680 (m), 1715 (s), 1645 (w), 1420 (m), 1285 (m), 1225 (m), 995 (m), 915 (s) cm^{-1}; δ1.04 (3H, d, J = 6Hz), 1.68 (2H, m), 2.24 (2H, q, J = 7 Hz), ~2.0 – ~2.6 (1H, m), ~4.7 – ~5.9 (3H, m), 11.3 (1H, s). (Found: C, 64.81; H, 9.48. $C_7H_{12}O_2$ requires: C, 65.60; H, 9.44%).

(S)-(+)-*4-Methylhex-5-en-1-ol* (S)-**23a**. A soln of **29** (3.18 g) in dry ether (20 ml) was added dropwise to a suspension of LAH (1.35 g) in dry ether (89.5 ml) with stirring and ice-cooling. The mixture was stirred for 3 hr at room temp. Subsequent conventional work-up followed by distillation gave 2.48 g (87.6%) of (*S*)-**23a**, b.p. 76–79°/18 mm, n_D^{20} 1.4351; $\alpha_D^{20}+15.6°$ (neat, l = 1 dm); ν_{max} 3320 (s), 3085 (m), 2960 (s), 2940 (s), 2880 (s), 1640 (m), 1460 (m), 1420 (m), 1380 (m), 1065 (s), 1040 (m), 1000 (s), 910 (s) cm^{-1}; δ0.96 (3H, d, J = 6 Hz), ~1.2 – ~1.7 (4H), ~1.85 – ~2.40 (1H, m), 3.48 (2H, t, J = 6Hz), 3.55 (1H, s, –OH), ~4.2 – ~5.9 (3H, m); glc (3% SE-30, 1.5 m × 2 mm at 45°; Carrier gas, N_2, 0.8 kg/cm^2): R_t 5.5 min; MS: *m/e* 114 (M^+). These spectral data are in good accord with that of (*R*)-**23a**.

(S)-*4-Methylhex-5-enyl tosylate* (S)-**23b**. This was prepared in the conventional manner to give 7.7 g of (*S*)-**23b** from 3.28 g of (*S*)-**23a** and employed for the next step without further purification.

(S)-(+)-*4-Methylhex-5-enyl bromide* (S)-**24**. This was prepared in the same manner as described in the prepn of (*R*)-**24** to give 3.61 g (70.8% from (*S*)-**23a**) of (*S*)-**24** from 7.7 g of (*S*)-**23b**, b.p. 74–79°/47 mm, $n_D^{20.5}$ 1.4623; $\alpha_D^{20.5}+13.48°$ (neat, l = 1 dm); ν_{max} 3090 (m), 2980 (s), 2940 (s), 2880 (m), 1645 (m), 1460 (m), 1260 (m), 1215 (m), 1000 (m), 915 (s) cm^{-1}; δ0.98 (3H, d, J = 6Hz), ~1.20 – ~2.40 (5H, m), 3.28 (2H, t, J = 7 Hz), ~4.70 – ~5.10 (2H, m), ~5.30 – ~5.90 (1H, m); glc (Column, 3% SE-30, 1.5 m × 2 mm at 56°; Carrier gas, N_2, 0.8 kg/cm^2) R_t 5.2 min. (Found: C, 47.71; H, 7.49. $C_7H_{13}Br$ requires: C, 47.48; H, 7.40%).

(3R, 11R)-3 11-*Dimethylnonacos*-1-*ene* (3R, 11R)-**30**. A Grignard reagent was prepared from (*R*)-**24** (2.1 g) and Mg (0.44 g) in dry ether (15 ml). A soln of (*R*)-**13b** (*ca* 3.5 g prepd from 2.5 g of (*R*)-**13a**) in dry THF (20 ml) was added to the stirred and cooled Grignard soln at −78° under Ar. 0.1 M–Li_2CuCl_4 in THF (0.35 ml) was added to the pasty mixture. Then the temp was gradually raised during 2 hr to room temp and the stirring was continued for 20 hr. The mixture was poured into ice-dil H_2SO_4 and extracted with ether. The ether soln was washed with water and NaCl aq, dried (K_2CO_3) and concentrated *in vacuo* to give 2.9 g (94%) of oily (3*R*, 11*R*)-**30**, ν_{max} 3080 (w), 2940 (s), 2860 (s), 1645 (m), 1470 (m), 1380 (m), 1080 (m), 1000 (m), 910 (m) cm^{-1}. This was employed for the next step without further purification.

(3R, 11R)-3, 11-*Dimethylnonacosan-2-ol* (3R, 11R)-**31**. A soln of (3*R*, 11*R*)-**30** (2.9 g) in THF (10 ml) was added to a stirred suspension of Hg $(OAc)_2$ (4.1 g) in THF (25 ml) and H_2O (12 ml) and the mixture was stirred overnight at room temp yielding an orange soln with some suspended materials. Then NaOH aq (1.5 g NaOH in 12.5 ml H_2O) followed by $NaBH_4$ (0.25 g) and NaOH (1.5 g) in water (12.5 ml) were added to the mixture and the stirring was continued for 30 min. The mixture was saturated with NaCl by adding solid NaCl and extracted with ether. The ether soln was washed with NaCl aq, dried (K_2CO_3) and concentrated *in vacuo*. The residue was chromatographed over Merck Kieselgel 60 (70–230 mesh, 50 g, 31 × 2.5 cm) in *n*-hexane. Elution with n-hexane removed hydrocarbon impurities. Subsequent elution with n-hexane-ether (9:1) gave 1.2 g (41% from **30**) of (3*R*, 11*R*)-**31** as a waxy solid, m.p. 29–32°, ν_{max} 3300 (m), 2960 (s), 2920 (s), 2850 (s), 1470 (m), 1380 (m), 1100 (m), 1065 (m), 960 (w), 930 (m), 880 (w), 720 (m) cm^{-1}. (Found: C, 81.96; H, 14.52. $C_{31}H_{64}O$ requires: C, 82.22; H, 14.25%).

(3R, 11R)-(−)-3, 11-*Dimethylnonacosan-2-one* (3R, 11R)-**1**. Jones CrO_3 (2 ml) was added to a stirred soln of (3*R*, 11*R*)-**31** (1.2 g) in acetone (50 ml). The mixture was left to stand for 5 min at room temp. Then MeOH was added to destroy excess CrO_3. The mixture was poured into water and extracted with ether. The ether soln was washed with water and NaCl aq, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed over Merck Kieselgel 60 (70 ~ 230 mesh, 20 g, 14 × 2.5 cm) in n-hexane. Elution with n-hexane–ether (19:1) gave 0.9 g (75%) of (3*R*, 11*R*)-**1**. This was recrystallized three times from 99% EtOH to give 600 mg of needles, m. p. 44.5–45°, $[\alpha]_D^{21}-5.63\pm0.1°$ (c = 4.101, n-hexane); ν_{max} (nujol) 1715 (vs), 1300 (w), 1280 (w), 1250 (w), 1220 (w), 1210 (w), 1190 (m), 1175 (w), 1150 (m), 1100 (w), 1080 (w), 1060 (w), 1040 (w), 1020 (w), 950 (w), 880 (w), 870 (w), 730 (m), 720 (m) cm^{-1}; δ(100 MHz, CCl_4) 0.84 (6H, m), 1.07 (3H, d, J = 7Hz), 1.25 (~48 H), 2.10 (3H, s), ~2.40 (1H, m); MS: *m/e* 450 (M^+). (Found: C, 82.39; H, 13.74. $C_{31}H_{62}O$ requires: C, 82.59; H, 13.86%).

(3S, 11S)-(+)-3, 11-*Dimethylnonacosan-2-one* (3S, 11S)-**1**. This was prepared from (*S*)-**13b** and (*S*)-**24** in the same manner as described for the prepn of (3*R*, 11*R*)-**1**. After recrystallization from 99% EtOH, 30.5 mg of (3*S*, 11*S*)-**1** was obtained as needles, m.p. 44.0–44.5°; $[\alpha]_D^{21}+5.98\pm0.30°$ (c = 0.90, n-hexane). The IR and NMR spectra were identical with those of (3*R*, 11*R*)-**1** and the natural pheromone. MS (70eV): *m/e* 41.0365 (C_3H_5, 23.1%), 42.0434 (C_3H_6, 5.5%), 43.0163 (C_2H_3O, 54.9%), 43.0525 (C_3H_7, 53.3%), 53.0389 (C_4H_5, 4.7%), 55.0559 (C_4H_7, 43.5%), 56.0632 (C_4H_8, 17.6%), 57.0362 (C_3H_5O, 5.1%), 57.0712 (C_4H_9, 58%), 59.0482 (C_3H_7O, 4.3%), 59.0543 (C_3H_7O, 4.3%), 67.0559 (C_5H_7, 7.1%), 68.0622 (C_5H_8, 5.5%), 69.0707 (C_5H_9, 26.7%), 70.0779 (C_5H_{10}, 14.9%), 71.0502 (C_4H_7O, 6.3%), 71.0861 (C_5H_{11}, 29.0%), 72.0572 (C_4H_8O, 100%), 73.0616 (C_4H_9O, 21.0%), 81.0694 (C_6H_9, 9.0%), 82.0768 (C_6H_{10}, 9.4%), 83.0859 (C_6H_{11}, 20.0%), 84.0918 (C_6H_{12}, 5.1%), 85.0644 (C_5H_9O, 36.5%), 85.1017 (C_6H_{13}, 15.7%), 95.0846 (C_7H_{11}, 11.4%), 96.0939 (C_7H_{12}, 7.8%), 97.1008 (C_7H_{13}, 18.4%). 99.1130 (C_7H_{15}, 5.5%), 109.1029 (C_8H_{13}, 9.4%), 110.1083 (C_8H_{14}, 5.1%), 111.1159 (C_8H_{15}, 9.0%), 123.1153 (C_9H_{15}, 4.7%), 125.1323 (C_9H_{17}, 3.9%). 127.1115 ($C_8H_{15}O$, 4.3%), 450.4806 ($C_{31}H_{62}O = M^+$, 16.1%). 451.4852 ($C_{31}H_{63}O$, 8.6%). (Found: C, 83.17; H, 13.95. $C_{31}H_{62}O$ requires: C, 82.59; H, 13.86%).

(3R, 11S)-(−)-3, 11-*Dimethylnonacosan-2-one* (3R, 11S)-**1**. This was prepared from (*S*)-**13b** and (*R*)-**24** in the same manner as described for the prepn of (3*R*, 11*R*)-**1**. After silica gel chromatography (Merck Kieselgel 60) and two recrystallizations from 99% EtOH, 750 mg (23% from (*S*)-**13a**) of (3*R*, 11*S*)-**1** was obtained as fine rhombic needles, m.p. 39.0–39.5°; $[\alpha]_D^{21}$ −5.68 ± 0.10° ($c = 3.996$, n-hexane); ν_{max} (nujol) 1705 (vs), 1305 (w), 1280 (w), 1270 (w), 1250 (w), 1210 (w), 1200 (w), 1190 (w), 1180 (w), 1140 (m), 955 (w), 890 (w), 850 (w), 730 (m), 720 (m) cm^{-1}; δ(100 MHz, CCl_4) 0.88 (6H, m), 1.07 (3H, d, J = 7 Hz), 1.25 (~48 H), 2.10 (3H, s), ~2.55 (1H, m). (Found: C, 82.50; H, 13.84. $C_{31}H_{62}O$ requires: C, 82.59; H, 13.86%).

(3S, 11R)-(+)-3, 11-*Dimethylnonacosan-2-one* (3S, 11R)-**1**. This was prepared from (*R*)-**13b** and (*S*)-**24** in the same manner as described for the prepn of (3*R*, 11*R*)-**1**. After silica gel chromatography (Merck Kieselgel 60) and recrystallization from 99% EtOH, 315 mg (11.7% from (*R*)-**13a**) of (3*S*, 11*R*)-**1** was obtained as needles, m.p. 38.0–38.5°; $[\alpha]_D^{21}$ + 5.73 ± 0.15° ($c =$ 2.049, n-hexane); The IR and NMR spectra were identical with those of (3*R*, 11*S*)-**1**. (Found: C, 82.55; H, 13.91. $C_{31}H_{62}O$ requires: C, 82.59; H, 13.86%).

Tetradecane-1, 14-*diol monobenzyl ether* **32b**. A mixture of **32a** (42.6 g), $PhCH_2Cl$ (23.4 g) and KOH (10.4 g) was heated at 110° for 4 hr with stirring. Then it was poured into ice-water and the precipitated crystals were collected on a filter. The crystals were washed with a small amount of ether and dried *in vacuo* over P_2O_5 to give 35.8 g of crude **32b**, ν_{max} (nujol) 3440 (s), 3400 (s), 3110 (m), 3100 (m), 3050 (m), 1510 (m), 1500 (m), 1480 (s), 1460 (s), 1420 (m), 1060 (s), 750 (s), 700 (s) cm^{-1}; MS: *m/e* 320 (M^+). This was employed for the next step without further purification.

14-*Benzyloxytetradecyl tosylate* **32c**. *p*-Toluenesulfonyl chloride (42.6 g) was added to a soln of **32b** (35.8 g) in dry pyridine (355 ml) with stirring and ice-cooling. The mixture was stirred for 2 hr and poured into ice-dil HCl. The precipitated crystals were collected on a filter, washed with water, and dried *in vacuo* over P_2O_5 to give 47.6 g of the tosylate **32c**, m.p. 39–40°; ν_{max} 3050 (m), 2950 (s), 2900 (s), 1600 (m), 1480 (m), 1460 (m), 1370 (s), 1195 (s), 1180 (s), 1105 (s), 950 (s), 840 (s), 815 (s) cm^{-1}. This was employed for the next step without further purification.

14-*Benzyloxytetradecyl bromide* **33a**. A soln of **32c** (47.6 g) and LiBr (27.2 g) in acetone (541 ml) was stirred and heated under reflux for 1 hr. Then it was poured into ice-water and extracted with ether. The ether soln was washed with water, $NaHCO_3$ aq and NaCl aq, dried ($CaCl_2$) and concentrated *in vacuo* to give 32.7 g of crude **33a**. This was purified by chromatography over Kieselgel 60 (360 g). Elution with n-hexane–ether gave 25.4 g (35.8%) of **33a**, m.p. 45–46°; ν_{max} 3090 (w), 3050 (w), 2940 (s), 2870 (s), 1510 (w), 1460 (m), 1375 (m), 1110 (s), 1030 (m), 740 (s), 705 (s) cm^{-1}; δ1.25 (24H, br. s), 3.25 (4H, m), 4.34 (2H, s), 7.10 (5H, s); MS: *m/e* 382 (M^+).

14-*Benzyloxytetradecyl iodide* **33b**. NaI (20 g) and **33a** (25.4 g) were dissolved in acetone (240 ml) and the mixture was heated under reflux for 24 hr. Then it was poured into ice-dil $NaHCO_3$ aq and extracted with ether. The ether soln was washed with water, dried ($MgSO_4$) and concentrated *in vacuo* to give 22 g of crude **33b**. This was employed for the next step without further purification. Its IR spectrum was very similar to that of **33a**.

(R)-(+)-5, 9-*Dimethyldec-8-en-1-yne* **34**. A suspension of $NaNH_2$ in liq NH_3 was prepared in the usual manner from Na (10.9 g) and liq NH_3 (300 ml). To this was bubbled acetylene for 3 hr. After evaporation of NH_3, dry DMSO (200 ml) was added. Then **6** (37.1 g) was added dropwise to the stirred acetylide soln at room temp. The stirring was continued for 4 hr. Then solid NH_4Cl was added to destroy excess NaC≡CH. The mixture was poured into ice-water and extracted with ether. The ether soln was washed with water and sat NaCl, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was distilled to give 14.3 g (62.3%) of **34**, b.p. 108–113°/43 mm, n_D^{22} 1.4476; α_D^{22} + 3.8° (neat, l = 1 dm); ν_{max} 3340 (m), 2995 (s), 2960 (s), 2880 (s), 2140 (w), 1460 (m), 1390 (m) cm^{-1}; δ0.87 (3H, d, J = 6Hz), 1.55 (3H, s) 1.62 (3H, s), 4.98 (1H, t, J = 6Hz). (Found: C, 87.12; H, 12.39. $C_{12}H_{20}$ requires: C, 87.73; H, 12.27%).

(R)-1-*Benzyloxy*-19,23-*dimethyltetracos-22-en-15-yne* **35**. A soln of n-BuLi in n-hexane (1.79 N, 27.3 ml) was added dropwise to a stirred and ice-cooled soln of **34** (8.0 g) in dry THF (70 ml) at −10° under Ar. The soln was stirred for 30 min at −10°. A soln of **33b** (21.0 g) in dry HMPA (61.8 ml) was added to the stirred and cooled soln of the acetylide at −10°. After the addition the stirring was continued for 1 hr at room temp. The mixture was poured into ice-water and extracted with n-hexane. The n-hexane soln was washed with water and NaCl aq, dried ($CaCl_2$) and concentrated *in vacuo* to give 22.8 g of crude **35**, ν_{max} 3100 (w), 3050 (w), 2960 (s), 2880 (s), 1465 (m), 1110 (m), 740 (m), 705 (m) cm^{-1}; δ0.90 (3H, deformed d, J = 6Hz), 1.25 (~29H, br. s), 1.55 (3H, s), 1.65 (3H, s), ~1.8 – ~2.2 (6H, m), 3.35 (2H, t, J = 6Hz), 4.35 (2H, s), 5.02 (1H), 7.15 (5H, s); MS: *m/e* 466 (M^+). This was employed for the next step without further purification.

19(S)-1-*Benzyloxy*-19, 23-*dimethyl*-22,23-*oxidotetracos*-15-*yne* **36**. *m*-Chloroperbenzoic acid (85% purity, 10.9 g) was added portionwise to a stirred and ice-cooled soln of **35** (22.8 g) in $CHCl_3$ (110 ml). The mixture was stirred for 2 hr at room temp, and filtered to remove *m*-chlorobenzoic acid. The solid was washed with n-hexane. The combined filtrate and washings were washed with $NaHSO_3$ aq and concentrated *in vacuo*. The residue was dissolved in ether. The ether soln was washed with Na_2CO_3 aq and NaCl aq, dried ($MgSO_4$) and concentrated *in vacuo* to give 22.7 g of crude **36**, whose NMR spectrum lacked signals due to $Me_2C{=}C\ddot{H}$ and showed a signal at δ2.50 (1H, t, J = 6Hz) due to the oxido-methine proton.

(S)-22-*Benzyloxy-4-methyldocos-7-ynal* **37**. A soln of crude **36** (22.7 g) in ether (76.2 ml) was added dropwise to a soln of $HIO_4 \cdot 2H_2O$ (14.0 g) in THF (75 ml) with stirring and ice-cooling. The mixture was stirred for 1.5 hr at room temp. Then it was poured into water and the ether layer was separated. The aq layer was extracted with ether. The ether soln was washed with water, $NaHCO_3$ aq and NaCl aq, dried ($MgSO_4$) and concentrated *in vacuo* to give 20.2 g of crude **37**, ν_{max} 3050 (w), 3020 (w), 2900 (s), 2840 (s), 2700 (w), 1725 (m), 1455 (m), 1100 (m), 1070 (m), 740 (m), 705 (m) cm^{-1}. This was employed for the next step without further purification.

(S)-(+)-22-*Benzyloxy-4-methyldocos-7-yn-1-ol* **38a**. A soln of crude **37** (20.7 g) in dry ether (55 ml) was added to a stirred and ice-cooled suspension of LAH (1.7 g) in dry ether (100 ml). The mixture was stirred for 4 hr at room temp. Then a small amount of water was added to the stirred and ice-cooled mixture to destroy the excess LAH. The ether layer was separated. The residue was acidified with ice-dil HCl and extracted with ether. The combined ether soln was washed with water and NaCl aq, dried ($MgSO_4$) and concentrated *in vacuo* to give 16.36 g of crude **38a**. This was chromatographed over Merck Kieselgel 60 (Art 7734, 160 g) in n-hexane-ether to give 9.65 g (45% from **34**) of **38a**, n_D^{21} 1.4931; $[\alpha]_D^{20}$ + 2.09° ($c = 3.25$, n-hexane); ν_{max} 3380 (m), 3050 (w), 3000 (w), 2900 (s), 2830 (s), 1450 (m), 1100 (m), 1020 (m), 730 (m), 695 (m) cm^{-1}; δ0.85 (3H, d, J = 6Hz), 1.22 (~30H), ~1.7 – ~2.3 (5H), ~3.4 (4H, m), 4.32 (2H, s), 7.12 (5H, s); MS: *m/e* 442 (M^+).

(S)-22-*Benzyloxy-4-methyldocos-7-ynyl tosylate* **38b**. *p*-Toluenesulfonyl chloride (8.3 g) was added portionwise to a stirred and ice-cooled soln of **38a** (9.65 g) in dry pyridine (79.4 ml). The stirring was continued for 1.5 hr at 0–5°. Then the mixture was poured into ice-dil HCl and extracted with ether.

The ether soln was washed with 10% HCl, water, $NaHCO_3$aq and NaClaq, dried ($MgSO_4$) and concentrated *in vacuo* to give 10.4 g of crude **38b**, ν_{max} 2900 (s), 2840 (s), 1595 (m), 1450 (m), 1365 (s), 1190 (s), 1180 (s), 1115 (m), 1095 (m), 960 (m), 915 (m), 815 (m), 740 (m) cm^{-1}.

(R)-22-*Benzyloxy-4-methyldocos-7-ynyl cyanide* **39**. A soln of **38b** (10.4 g) and NaCN (1.0 g) in DMSO (80 ml) was stirred and heated at 60–65° for 16 hr. Then it was poured into ice-water and extracted with ether. The ether soln was washed with water and NaClaq, dried ($MgSO_4$) and concentrated *in vacuo* to give 7.74 g of crude **39**, ν_{max} 2900 (s), 2820 (s), 2220 (w), 1450 (m), 1100 (m), 740 (m), 700 (m) cm^{-1}.

(R)-23-*Benzyloxy-5-methyltricos-8-ynoic acid* **40**. A soln of **39** (7.74 g) and NaOH (13.7 g) in EtOH (68.6 ml)–H_2O (54.8 ml) was stirred and heated under reflux for 17 hr. After the removal of EtOH *in vacuo*, the residue was acidified with ice-dil HCl and extracted with ether. The ether soln was washed with water and NaCl aq, dried ($MgSO_4$) and concentrated *in vacuo* to give 6.4 g of crude **40**, ν_{max} ~ 3600 – ~ 2400 (m), 2910 (s), 2840 (s), 1710 (s), 1460 (m), 1120 (s), 1105 (s), 740 (m), 700 (m) cm^{-1}.

(R)-(+)-23-*Benzyloxy-5-methyltricos-8-yn-1-ol* (*R*)-**41a**. A soln of **40** (6.4 g) in dry ether (22.5 ml) was added dropwise to a stirred and ice-cooled suspension of LAH (1.03 g) in dry ether (78.6 ml). The stirring was continued for 5 hr at room temp. Excess LAH was destroyed by the addition of a small amount of water with stirring and ice-cooling. The ether soln was separated and the residue was treated with ice-dil HCl. The aq soln was extracted with ether. The combined ether soln was washed with water, $NaHCO_3$ aq and NaCl aq, dried ($MgSO_4$) and concentrated *in vacuo* to give 5.78 g of crude **41a**. This was chromatographed over Kieselgel 60 (Art 7732, 50 g). Elution with n-hexane–ether gave 4.51 g (45.3% from **38a**), α_D^{20} + 0.44° (neat, 1 = 1 dm); ν_{max} ~ 3300 (m), 2920 (s), 2840 (s), 1500 (w), 1450 (m), 1100 (m), 1070 (m), 1050 (m), 1030 (m), 740 (m), 700 (m) cm^{-1}; δ0.88 (3H, d, J = 6Hz), 1.26 (~ 32H), ~ 1.9 – ~ 2.3 (~ 5H), ~ 3.4 (4H, m), 4.38 (2H, s), 7.16 (5H, S); MS: *m/e* 456 (M^+).

(R)-23-*Benzyloxy-5-methyltricos-8-ynyl tosylate* (R)-**41b**. *p*-Toluenesulfonyl chloride (2.0 g) was added to a soln of (*R*)-**41a** (2.4 g) in dry pyridine (25 ml) with stirring and ice-cooling. The mixture was stirred at 0–5° for 2 hr. Then it was poured into ice-dil HCl and extracted with ether. The ether soln was washed with 10% HCl, water, $NaHCO_3$aq and NaClaq, dried ($MgSO_4$) and concentration *in vacuo* to give 2.96 g of (*R*)-**41b**, ν_{max} 2920 (s), 2840 (s), 1590 (w), 1490 (w), 1450 (m), 1360 (s), 1190 (s), 1180 (s), 1100 (m), 960 (m), 930 (m), 810 (m), 730 (m), 700 (w) cm^{-1}. This was employed for the coupling reaction without further purification.

(S)-(−)-5-*Methylnon-8-enyl acetate* **42**. A phosphorane soln was prepared by the addition of n-BuLi in n-hexane (1.6N, 59.0 ml) to the stirred and cooled suspension of $Ph_3P(Me)Br$(38.3 g) in dry THF (342 ml) at −30° under Ar. The mixture was stirred at −20° for 40 min. This phosphorane soln was added dropwise to a soln of **11** (17.9 g) in dry THF (172 ml) with stirring and cooling at −50°. The reaction temperature was raised to −10° during 2 hr and then kept there for 1 hr. The stirring was further continued overnight at room temp. Then the mixture was poured into ice-NH_4Claq. The oranic layer was separated and concentrated *in vacuo*. The residue was diluted with n-hexane and filtered. The prevous NH_4Claq was extracted with n-hexane. The combined n-hexane soln was washed with water and NaClaq, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by filtration chromatography (SiO_2) and distillation to give 9.85 g (55.6%) of **42**, b.p. 101–106°/3 mm, n_D^{26} 1.4330; α_D^{25} −0.9° (neat, 1 = 1 dm); ν_{max} 3060 (m), 2920 (s), 2840 (s), 1740 (s), 1635 (m), 1240 (s), 1030 (m), 990 (m), 900 (m) cm^{-1}; δ0.86 (3H, d, J = 6Hz), ~ 1.1 – ~ 1.8 (~9H, m), 1.94 (3H, s), ~ 1.8 – ~ 2.3 (2H, m), 3.95 (2H, t, J = 6Hz), ~4.7 – ~5.2 (2H, m), ~ 5.3 – ~ 5.8 (1H, m). (Found: C, 72.85; H, 11.01. $C_{12}H_{22}O_2$ requires: C, 72.68; H, 11.18%).

(S)-(+)-9-*Acetoxy*-1, 2-*dibromo-5-methylnonane* **43**. A soln of Br_2 (8.0 g) in CH_2Cl_2 (25 ml) was added dropwise to a stirred and ice-cooled soln of **42** (9.85 g) in CH_2Cl_2 (128 ml). The soln was stirred for 1 hr, washed with $NaHSO_3$aq and water, dried ($CaCl_2$) and concentrated *in vacuo*. The residue was distilled to give 15.1 g (85%) of **43**, b.p. 134–137°/0.3 mm, n_D^{26} 1.4896; α_D^{26} + 2.2° (neat, 1 = 1 dm); ν_{max} 2920 (s), 2850 (s), 1735 (s), 1240 (s), 1030 (m) cm^{-1}; δ0.95 (3H, deformed d, J = 6Hz), ~ 1.4 (~ 11H, m), 1.95 (3H, s), ~ 3.4 – ~ 3.8 (3H, m), 4.0 (2H, t, J = 6Hz). (Found: C, 40.43; H, 6.26. $C_{12}H_{22}O_2Br_2$ requires: C, 40.25; H, 6.19%).

(S)-(+)-5-*Methylnon-8-yn-1-ol* **44a**. A soln of **43** (15.1 g) in dry ether (70 ml) was added to a stirred suspension of $NaNH_2$ (from 6.8 gof Na) in liq NH_3 (400 ml). The mixture was stirred for 1 hr. Then solid NH_4Cl was added to destroy excess $NaNH_2$ and NH_3 was allowed to evaporate. The residue was extracted with ether. The ether soln was washed with water and NH_4Claq, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was dissolved in MeOH (52 ml) and 10% NaOHaq (30 ml). The soln was stirred and heated under reflux for 30 min. MeOH was removed *in vacuo*. The residue was diluted with water and extracted with ether. The ether soln was washed with water and NaClaq, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was distilled to give 4.51 g (69.4%) of **44a**, b.p. 85–90°/0.5 mm, n_D^{26} 1.4565; α_D^{22} + 0.08° (neat, 1 = 1 dm); ν_{max} 3300 (br. s), 3280 (s), 2910 (s), 2840 (s), 2110 (m), 1460 (m), 1050 (m) cm^{-1}; δ0.88 (3H, d, J = 6Hz), ~ 1.35 (9H, br), 1.75 (1H, t, J = 3Hz), 2.15 (2H, dt, J_1 = 6, J_2 = 3 Hz), 2.30 (1H, s), 3.50 (2H, t, J = 6Hz). (Found: C, 77.36; H, 11.71. $C_{10}H_{18}O$ requires: C, 77.87; H, 11.76%).

(S)-1-*Tetrahydropyranyloxy-5-methylnon-8-yne* **44b**. Dihydropyran (2.51 g), **44a** (3.54 g) and *p*-TsOH (1.1 g) were dissolved in dry ether (170 ml). The soln was stirred overnight at room temp. Then it was washed with water, K_2CO_3 aq and NaCl aq, dried (K_2CO_3) and concentrated *in vacuo* to give 5.85 g of **44b**, ν_{max} 3280 (m), 2920 (s), 2840 (s), 1450 (m), 1440 (m), 1350 (m), 1200 (m), 1120 (s), 1070 (s), 1030 (s), 960 (m) cm^{-1}. This was employed for the next step without further purification.

(S)-23-*Benzyloxy-5-methyltricos-8-yn-1-ol tetrahydropyranyl ether* (S)-**41c**. A soln of n-BuLi in n-hexane (1.6N, 14.4 ml) was added dropwise to a stirred and cooled soln of **44b** (5.47 g) in dry THF (33.6 ml) at −10° under Ar. The soln was stirred for 30 min at −10°. A soln of **33b** (9.88 g) in dry HMPA (30.4 ml) was added dropwise to the stirred and cooled soln of the acetylide. Then the mixture was stirred for 1 hr at room temp. It was poured into ice-dil HCl and extracted with n-hexane. The hexane soln was washed with water and NaCl aq, dried (K_2CO_3) and concentrated *in vacuo* to give 13.2 g of crude **41c**, ν_{max} 2900 (s), 2820 (s), 1450 (m), 1110 (s), 1060 (s), 1020 (s), 980 (m), 730 (m), 690 (m) cm^{-1}. This was employed for the next step without further purification.

(S)-(−)-23-*Benzyloxy-5-methyltricos-8-yn-1-ol* (*s*)-**41a**. *p*-Toluenesulfonic acid (1.39 g) was added to a soln of (*S*)-**41c** (13.2 g) in MeOH (66 ml). The soln was stirred for 2 hr at 40–50°. MeOH was removed *in vacuo*. The residue was diluted with water and extracted with ether. The ether soln was washed with water, K_2CO_3 aq and NaCl aq, dried ($MgSO_4$) and concentrated *in vacuo* to give 10 g of crude (*S*)-**41a**. This was chromatographed over Merck Kieselgel 60 (Art 7734, 100 g). Elution with n-hexane-ether gave 4.3 g (41% from **44a**) of pure (*S*)-**41a**, n_D^{22} 1.4853; α_D^{22} − 0.41° (neat, 1 = 1 dm); ν_{max} ~ 3350 (m), 2920 (s), 2840 (s), 1450 (m), 1100 (m), 1070 (m), 1050 (m), 1030 (m), 740 (m), 700 (m) cm^{-1}; δ0.90 (3H, deformed d, J = 6Hz), 1.22 (~ 34H, br. s), 2.10 (4H, br), 3.40 (4H, m), 4.34 (2H, s), 7.10 (5H, s); MS: *m/e* 456 (M^+). (Found: C, 80.97; H, 11.58. $C_{31}H_{52}O_2$ requires: C, 81.52; H, 11.47%).

(S)-23-*Benzyloxy-5-methyltricos-8-ynyl tosylate* (S)-**41b**. *p*-Toluenesulfonyl chlororide (4.18 g) was added to a stirred and ice-cooled soln of (*S*)-**41a** (5.0 g) in dry pyridine (52.1 ml). The soln was stirred for 2 hr. Then it was poured into ice-dil HCl and extracted with ether. The ether soln was washed with 10% HCl, water, $NaHCO_3$ aq and NaCl aq, dried ($MgSO_4$) and concentrated *in vacuo* to give 5.32 g of crude (*S*)-**41b**, ν_{max} 3040 (w), 3000 (w), 2900 (s), 2840 (s), 1590 (m), 1490 (w), 1450 (m), 1360 (s), 1175 (s), 1100 (s), 925 (m), 810 (m), 730 (m) cm^{-1}. This was employed for the coupling reaction without further purification.

(3S, 11R)-(+)-29-*Benzyloxy*-3, 11-*dimethylnonacos*-1-*en*-14-*yne* (3S, 11R)-**45**. A Grignard reagent was prepared from (*S*)-**24** (0.87 g) and Mg (0.15 g) in dry ether (5.3 ml). A soln of (*R*)-**41b** (1.5 g) in dry THF (8.3 ml) was added dropwise to the stirred

Grignard soln at −60° under Ar. Then 0.1 M-Li_2CuCl_4 in THF (0.13 ml) was added. The reaction temp was gradually raised to −20 ~ −30° and kept there for 1 hr. Subsequently the mixture was stirred overnight at room temp. Then it was poured into ice-dil H_2SO_4 and extracted with ether. The ether soln was washed with water, $NaHCO_3$ aq and NaCl aq, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed over Kieselgel 60 (Art 7734, 30 g). Elution with n-hexane–ether gave 0.9 g (69.2%) of (3*S*, 11*R*)-**45**, α_D^{20} +4.5° (neat, 1 = 1 dm); ν_{max} 3040 (w), 3010 (w), 2900 (s), 2840 (s), 1640 (w), 1500 (w), 1460 (m), 1450 (m), 1100 (m), 905 (m), 735 (m), 700 (m) cm^{-1}; δ0.90 (3H, deformed d, J = 6 Hz), 1.10 (3H, deformed d, J = 6 Hz), 1.30 (42H, br, s), 2.10 (4H, m), 3.40 (2H, t, J = 6Hz), 4.42 (2H, s), ~4.7– ~5.8 (3H, m), 7.25 (5H, s); MS: *m/e* 536 (M^+).

(3R, 11R)-29-*Benzyloxy*-3, 11-*dimethylnonacos*-1-*en*-14-*yne* (3R, 11R)-**45**. In the same manner as described above, (*R*)-**24** (1.44 g) and (*R*)-**41b** (2.47 g) yielded (3*R*, 11*R*)-**45** (1.4 g, 64.5%), n_D^{20} 1.4847; α_D^{20} −4.68° (neat, 1 = 1 dm); ν_{max} 3040(w), 3010(w), 2900 (s), 2840 (s), 1640 (w), 1500 (w), 1450 (m), 1100 (m), 1030 (w), 990 (w) 900 (w), 740 (m), 700 (m) cm^{-1}; δ0.90 (3H, d, J = 6Hz), 1.02 (3H, d, J = 6Hz), 1.25 (42H, br, s), 2.10 (4H, m), 3.35 (2H, m), 4.40 (2H, s), ~4.7 – ~5.8 (3H, m), 7.20 (5H, s); MS: *m/e* 536 (M^+).

(3S, 11S)-(+)-29-*Benzyloxy*-3, 11-*dimethylnonacos*-1-*en*-14-*yne* (3S, 11S)-**45**. The coupling of (*S*)-**24** (1.89 g) and (*S*)-**41b** (2.6 g) yielded 1.83 g (80%) of (3*S*, 11*S*)-**45**, n_D^{23} 1.4821; α_D^{22} + 4.1° (neat, 1 = 1 dm); MS: *m/e* 536 (M^+). The IR and NMR spectra are identical with those of (3*R*, 11*R*)-**45**.

(3*R*, 11*S*)-(−)-29-*Benzylozy*-3, 11-*dimethylnonacos*-1-*en*-14-*yne* (3R, 11S)-**45**. The coupling of (R)-**24** (1.09 g) and (*S*)-**41b** (1.5 g) yielded 0.8 g (60.6%) of (3*R*, 11*S*)-**45**, n_D^{22} 1.4861; α_D^{22} − 4.4° (neat, 1 = 1 dm); MS: *m/e* 536 (M^+). The IR and NMR spectra were identical with those of (3*S*, 11*R*)-**45**.

(3*S*, 11*R*)-29-*Benzyloxy*-3, 11-*dimethylnonacos*-14-*yn*-2-*o*1 (3*S*, 11*R*)-**46**. A soln of (3*S*, 11*R*)-**45** (1.44 g) in THF (5 ml) was added to a suspension of $Hg(OAc)_2$ (1.03 g) in THF (8 ml) and H_2O (3.2 ml). The mixture was stirred for 3 hr at room temp. Then 12% (w/v) NaOH aq (2.7 ml) and $NaBH_4$-NaOH aq (2.7 ml of a soln containing 0.9 g of $NaBH_4$ and 1.2 g of NaOH in 10 ml H_2O) were added and the mixture was stirred for 30 min at room temp. The soln was saturated with NaCl and extracted with ether. The either soln was washed with NaCl aq, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed over Merck Kieselgel 60 (Art 7734) to give 320 mg of (3*S*, 11*R*)-**46**, ν_{max} 3380 (br. m), 2900 (s), 2840 (s), 1450 (m), 1360 (m), 1100 (m), 1070 (m), 1020(m), 740(w) 700(w) cm^{-1}; MS: *m/e* 536 (M^+–H_2O).

(3*R*, 11*R*)-29-*Benzyloxy*-3, 11-*dimethylnonacos*-14-*yn*-2-*o*1 (3*R*, 11*R*)-**46**. In the same manner as described above, (3*R*, 11*R*)-45 (1.4 g) gave 750 mg of (3*R*, 11*R*)-**46**, ν_{max} 3380 (m), 2900 (s), 2840 (s), 1450 (m), 1380 (w), 1360 (w), 1100 (m), 1070 (m), 1020 (m), 740 (w) 700 (w) cm^{+1}; MS: *m/e* 536 (M^+–H_2O).

(3S, 11S)-29-*Benzyloxy*-3, 11-*dimethylnonacos*-14-*yn*-2-*o*1 (3S, 11S)-**46**. Hydration of (3*S*, 11*S*)-**45** (1.83 g) gave (3*S*, 11*S*)-**46** (860 mg); MS: *m/e* 536 (M^+-H_2O). The IR spectrum was identical with that of (3*R*, 11*R*)-**46**.

(3R, 11S)-29-*Benzyloxy*-3, 11-*dimethylnonacos*-14-*yn*-2-*o*1 (3*R*, 11*S*)-**46**. Hydration of (3*R*, 11*S*)-**45** (0.8 g) gave (3*R*, 11*S*)-**46** (650 mg); MS: *m/e* 536 (M^+-H_2O). The IR spectrum was identical with that of (3*S*, 11*R*)-**46**.

(3S, 11R)-29-*Benzyloxy*-3, 11-*dimethylnonacos*-14-*yn*-2-*one* (3*S*, 11*R*)-**47**. Jones CrO_3 (0.6 ml) was added to a soln of (3*S*, 11*R*)-**46** (320 mg) in acetone (14 ml) with stirring and ice-cooling. The excess CrO_3 was destroyed with MeOH. The mixture was poured into ice-water and extracted with ether. The ether soln was washed with water and NaCl aq, dried ($MgSO_4$) and concentrated *in vacuo* to give 320 mg of crude (3*S*, 11*R*)-**47**, ν_{max} 3080 (w), 3030 (w), 2920 (s), 2850 (s), 1710 (s), 1460 (m), 1360 (m), 1120 (m), 1105 (m), 790 (m), 770 (w), 740 (w), 700 (w) cm^{-1}.

(3R, 11R)-29-*Benzylozy*-3, 11-*dimethylnonacos*-14-*yn*-2-*one* (3R, 11R)-**47**. In the same manner as described above (3*R*, 11*R*)-**46** (750 mg) gave (3*R*, 11*R*)-**47** (640 mg), ν_{max} 3080 (w), 3030(w), 2920(s), 2850(s), 1710(s), 1460(m), 1450(m), 1370(m), 1355(m), 1110(m), 1095(m), 1020(w), 730(m), 695(m) cm^{-1}.

(3S, 11S)-29-*Benzyloxy*-3, 11-*dimethylnonacos*-14-*yn*-2-*one* (3S, 11S)-**47**. Jones oxidation of (3*S*, 11*S*)-**46** (860 mg) gave (3*S*, 11*S*)-**47** (800 mg). Its IR spectrum spectrum was identical with that of (3*R*, 11*R*)-**47**.

(3R, 11S)-29-*Benzyloxy*-3, 11-*dimethylnonacos*-14-*yn*-2-*one* (3R, 11S)-**47**. Jones oxidation of (3*R*, 11*S*)-**46** (650 mg) gave 3*R*, 11*S*)-**47** (450 mg). Its IR spectrum was identical with that of (3*S*, 11*R*)-**47**.

(3S, 11S)-(+)-29-*Hydroxy*-3, 11-*dimethylnonacosan*-2-*one* (3S, 11S)-**2**. A mixture of 10% Pd–C (370 mg), (3*S*, 11*R*)-**47** (370 mg) and 95% EtOH (7 ml) was shaken under H_2 at room temp. The product was purified by preparative tlc (Kiesegel 60 F_{254} 20 × 2 × 0.2 cm; C_6H_6 = EtOAc = 5:1) and recrystallized from *n*-pentane to give 130 mg (10.4% from **45**) of (3*S*, 11*S*)-**2**, m.p. 41–42°, $[\alpha]_D^{20}$ + 6.1 ± 0.7° (*c* = 0.65, *n*-hexane); ν_{max} 3400 (s), 3360 (s), 2910(s), 2840(s), 1710(s), 1460(s), 1380(s), 1360(s), 1190(m), 1180(m), 1150(m), 1120(w), 1110(w), 1090(w), 1060(s), 1030(m), 1005(m), 985(w), 970(w), 730(s) cm^{-1}; δ (100MHz, $CDCl_3$) 0.80 (3H, deformed d, J = 6Hz), 1.03 (3H, d, J = 7Hz), 1.20 (~48H, s), 1.60 (2H, m), 2.08 (3H, s), 2.45 (1H, sextet, J = 7Hz), 3.56 (2H, t, J = 6.5Hz); MS: *m/e* 466 (M^+).

(3R, 11S)-(−)-29-*Hydroxy*-3, 11-*dimethylnonacosan*-2-*one* (3R, 11S)-**2**. In the same manner as described above, (3*R*, 11*R*)-**47** (640 mg) gave (3*R*, 11*S*)-**2** (121 mg, 10% from **45**), m.p. 39–40°, $[\alpha]_D^{20}$ −6.8 ± 0.3° (*c* = 1.0, *n*-hexane); ν_{mac} 3400 (s), 3360 (s), 2900(s), 2840(s), 1710(s), 1460(s), 1380(s), 1360(s), 1190(m), 1170(m), 1150(m), 1110(w), 1090(w), 1060(s), 1030(m), 1005(m), 985(w), 970(w), 730(s) cm^{-1}; δ (100 MHz, $CDCl_3$) 0.80 (3H, deformed d, J = 6Hz) 1.03 (3H, d, J = 7Hz), 1.22 (~48H, s), ~1.60 (2H, m), 2.08 (3H, s), 2.45 (1H septet J = 7Hz), 3.56 (2H, t, J = 6.5Hz); MS: *m/e* 466 (M^+).

(3S, 11R)-(+)-29-*Hydroxy*-3, 11-*dimethylnonacosan*-2-*one* (3S, 11R)-**2**. Hydrogenation of (3*S*, 11*S*)-**47** (800 mg) gave (3*S*, 11*R*)-**2** (70 mg, 4.32% from **45**), m.p. 40–40.5°; $[\alpha]_D^{22}$ + 6.4 ± 0.6° (*c* = 0.55, n-hexane); MS: *m/e* 466 (M^+). The IR and NMR spectra were identical with those of (3*R*, 11*S*)-**2**.

(3R, 11R)-(−)-29-*Hydroxy*-3, 11-*dimethylnonacosan*-2-*one* (3R, 11R)-**2**. Hydrogenation of (3*R*, 11*S*)-**47** (450 mg) gave (3*R*, 11*R*)-**2** (40 mg, 5.8% from **45**), m.p. 38–40°; $[\alpha]_D^{23}$ − 6.5 ± 0.5° (*c* = 0.38, n-hexane); MS: *m/e* 466 (M^+). Its IR and NMR spectra were identical with those of (3*S*, 11*S*)-**2**.

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