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CHIRAL SYNTHESIS OF (2*S*,3*S*,7*S*)-3,7-DIMETHYLPENTADECAN-2-YL ACETATE AND PROPIONATE, POTENTIAL SEX PHEROMONE COMPONENTS OF THE PINE SAW-FLY *NEODIPRION SERTIFER* (GEOFF.)

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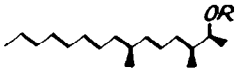
Abstract - A synthesis of (2*S*,3*S*,7*S*)-3,7-dimethylpentadecan-2-yl acetate (2) and propionate (3) is described. (2*S*)-2-Methyldecan-1-yl lithium (5) was reacted with (3*S*,4*S*)-3,4-dimethyl-γ-butyrolactone (6) to yield the ketoalcohol 19 which upon Huang-Minlon reduction furnished (2*S*,3*S*,7*S*)-3,7-dimethylpentadecan-2-ol (1). Acylations gave the esters 2 and 3. The (2*S*)-2-methyldecan-1-yl lithium was obtained *via* asymmetric synthesis. The chiral lactone 6 was obtained from (2*S*,3*S*)-*trans*-2,3-epoxybutane and dimethyl malonate.

The European pine saw-fly *Neodiprion sertifer* (Geoff.) is a pest on Scandinavian pine trees. The identification and synthesis of the pheromones of this and related species are essential for the development of selective methods for the monitoring and control of the populations of these insects.



1 : R=H
2 : R=COCH$_3$
3 : R=COC$_2$H$_5$

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The major pheromone components of the diprionoid saw-flies have been identified by Jewett and Coppel and were found to be esters of *erythro*-3,7-dimethylpentadecan-2-ol (1 or diastereoisomers).[1] The acetate is the most active in the *Neodiprion* species whereas the propionate is preferred by the *Diprion* species.[1,2] The esters of the (2*S*,3*S*,7*S*)-alcohol 1 are the active stereoisomers both in field tests[3,4] and by electroantennography.[5]

trans-Perillenal (4) has recently been isolated[6] from the lateral glands of *Neodiprion sertifer* and has also been synthesised[6,7] in this laboratory. Biological studies of its effects on the behaviour of the insects are in progress.

Several syntheses of mixtures of diastereoisomers of 3,7-dimethylpentadecan-2-ol have been reported.[2,8,9] Magnusson[10] has synthesised a mixture of isomers having the 2,3-*erythro*-configuration. A synthesis leading to the chiral alcohol 1 with controlled stereochemistry at carbons number 2 and 3 but not at carbon 7 has been published.[3,11] Mori[12] recently described a synthesis of all the four possible stereoisomers having *erythro*-configuration.

We now report a new synthesis of (2*S*,3*S*,7*S*)-3,7-dimethylpentadecan-2-ol and its esters 2 and 3.* The key intermediates chosen for this synthesis were the alkyl lithium 5 and the chiral lactone 6 (see Fig. 1.). Coupling of these should furnish the carbon skeleton of the target molecule with correct stereochemistry.

The chiral alkyl lithium 5 was obtained as

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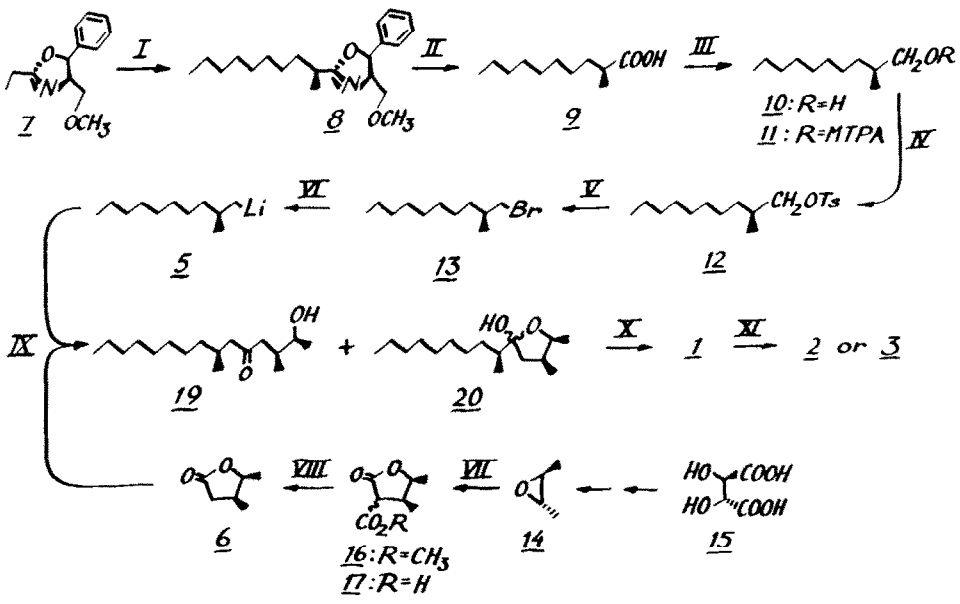


Fig. 1. I: a) LDA, -80°, THF. b) (*n*)-$C_8H_{17}I$, -100°. II: 4 M H_2SO_4, Δ_x, 4 h. III: LAH, Et_2O. IV: TsCl, C_5H_5N. V: LiCl, $(CH_3)_2CO$. VI: Li, Et_2O, -20°. VII: a) $(CH_3OCO)_2CH_2$, NaH, MeOH. b) KOH, H_2O, MeOH, Δ_x. c) H^+. VIII: C_5H_5N, Δ_x. IX: Cpds 5 and 6 mixed at -80°. X: N_2H_4, KOH, $H(OCH_2CH_2)_2OH$, 210°. XI: $(RCO)_2O$, C_5H_5N.

follows. Meyers[13] has developed an asymmetric synthesis which gives fair yields of 2-alkyl-alkanoic acids in high optical purities through alkylation of a chiral oxazoline anion followed by acid hydrolysis. In our hands alkylation of the anion of the known[13] chiral oxazoline 7 with octyl iodide gave the oxazoline 8, which was hydrolysed with dilute sulfuric acid to yield (*S*)-2-methyldecanoic acid (9) (60% overall yield) $[\alpha]_D^{20}$ +11.2° (neat). This corresponds to 72% e.e. (*cf* below and Experimental).

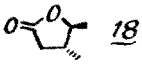
Lithium aluminium hydride reduction of the chiral acid 9 furnished (*S*)-2-methyldecan-1-ol (10) $[\alpha]_D^{20}$ -7.1° (neat) in 90% yield. This alcohol was esterified with both the enantiomers of 2-methoxy-2-trifluoromethyl-2-phenylacetyl chloride (MTPA-Cl).[21] The proton resonance spectra of these MTPA-esters 11 showed that the alcohol 10 was obtained in 72% e.e. (*cf* Experimental).

The alcohol 10 was converted to the tosylate 12 which was transformed to the bromide 13 by standard methods in 85% overall yield. The bromide was converted to the alkyl lithium compound 5 (*cf* below).

3,4-Dimethyl-γ-butyrolactone, the second building block in our synthesis of the alcohol 1, can be prepared in several ways, many of which only furnish diastereomeric mixtures. Provided that the pure *cis*-lactone is required, the method of choice is the stereospecific ring opening with inversion of *trans*-2,3-epoxybutane with a malonate ester anion followed by ester hydrolysis and decarboxylation. This method has been used for the preparation of the racemic *cis*-lactone 6.[14-16] (2*S*,3*S*)-*trans*-2,3-Epoxybutane (14) is available from (2*S*,3*S*)-(+)-tartaric acid (15) in a well documented reaction sequence.[12,17-20] The chiral epoxide 14 can then be used for the preparation of the chiral lactone 6.

The synthetically prepared epoxide 14 exhibited the optical rotation $[\alpha]_D^{20}$ -58.6° (lit.[19] $[\alpha]_D^{20}$ -58.8°). The optical purity was thus >99%. *meso*-*cis*-2,3-Epoxybutane could not be detected by GC. The chiral epoxide 14 was reacted with an excess of the sodium salt of dimethyl malonate in methanol. The product mixture containing the lactone ester 16 was hydrolysed with potassium hydroxide. The lactone acid 17 and malonic acid were isolated after acidification. When the mixture of acids was refluxed with pyridine, decarboxylation occured which furnished the desired lactone 6 in a 55% overall yield (based on the chiral epoxide 14) after chromatography and distillation.

The chiral *cis* lactone 6 showed $[\alpha]_D^{20}$ -54.9° (neat) and was free from contamination with the isomeric *trans*-lactone 18 as judged by GLC (*cf.* Experimental). For comparison, the racemic *trans*-lactone 18 was prepared from *cis*-2,3-epoxybutane and dimethyl malonate as described above.



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(*S*)-1-Bromo-2-methyldecane (13) was converted to the alkyl lithium 5 and reacted with (3*S*,4*S*)-*cis*-γ-butyrolactone (6) in diethyl ether at -80°. This gave a 5/1 mixture of the keto-alcohol 19 and its ring-closed isomeric form 20 (as judged by NMR in deuteriochloroform at room temperature) in 53% yield.

The mixture of compounds 19 and 20 was subjected to Huang-Minlon reduction with hydrazine in alkaline diethylene glycol which furnished the desired (2*S*,3*S*,7*S*)-3,7-dimethylpentadecan-2-ol in 76% yield after chromatography and distillation. The specific rotation, $[\alpha]_D^{20}$ -12.2° (neat), was slightly higher than that observed by Mori[12] for the same stereoisomer, $[\alpha]_D^{20}$ -9.88° (neat).

Acetylation and propionylation using standard procedures gave the (2*S*,3*S*,7*S*)-esters 2 and 3. These were purified by chromatography and distillation. Both esters were more than 99.5% pure as judged by gas chromatography. Since no epimerisation is likely to occur in the sequence of reaction steps starting with the coupling of the decanyl and the lactone moieties, the enantiomeric excesses of our esters were at least 99% at carbons number 2 and 3 and 72% at number 7 *i.e.* our samples are 86/14 mixtures of the (2*S*,3*S*,7*S*)-esters and the (2*S*,3*S*,7*R*)-esters.

Samples containing acetylated or propionylated mixtures of all the eight diastereoisomers of the alcohol 1 have been prepared and tested in the field.[2] The number of males caught was much lower than that expected on the basis of the content of the (2*S*,3*S*,7*S*)-ester in the sample.[2,3] However, it seems clear that the (2*S*,3*S*,7*R*)-isomer is not responsible for this inhibiting effect as this isomer was in fact found to be weakly attractive to *Neodiprion pinetum* in the field.[3,4]

The key step in Mori's[12] synthesis of the alcohol 1 is the attack of a chiral dialkyl lithium cuprate on one of the enantiomers of *trans*-2,3-epoxybutane (*e.g.* 14). In this way the four chiral 2,3-*erythro*-isomers of compound 1 were synthesised. Since *cis*-2,3-epoxybutane is a symmetric, non-chiral compound, the four possible *threo*-isomers of compound 1 cannot be prepared using Mori's method. The present synthesis, however, offers this possibility provided that the chiral *trans*-lactone 18 and its enantiomer are available.

EXPERIMENTAL

All reactions were carried out under dry nitrogen. The diethyl ether and tetrahydrofuran (THF) used as solvents were distilled from potassium/benzophenone under nitrogen immediately prior to use. The NMR spectra were recorded using tetramethyl silane as internal standard and deuteriochloroform as solvent.

(4S,5S)-2-(2-methyldecan-1-yl)-4-methoxymethyl-5-phenyl-2-oxazoline (8). (4*S*,5*S*)-2-Ethyl-4-methoxymethyl-5-phenyl-2-oxazoline (7) (53 g, 0.24 mol) in THF (400 ml) was stirred at -80°. Lithium diisopropyl amide (0.24 mol in THF, prepared from diisopropyl amine and butyl lithium) in THF (100 ml) was added during 0.5 h. After stirring for 1 h at -80° the temperature was lowered to -105°. Octyl iodide 58 g (0.24 mol) in THF (100 ml) was added during 8 h. Stirring at -100° was continued for an additional 12 h. The temperature was then slowly raised to -50° and the reaction mixture was poured into icewater. The mixture was extracted with diethyl ether and the ether layer was dried ($MgSO_4$) and concentrated to give a crude product which was used in the next step without purification. The product could be purified by bulb to bulb distillation which gave a colourless oil (air bath at 200°/0.01 mm). ^{1}H NMR (60 MHz): δ 0.08-1.0 (6H, m, $2CH_3$), 1.1-2.0 (18H, m, $-CH_2-$ and $CH-$), 3.1-3.5 (2H, m, $-CH_2-O-$), 3.3 (3H, s, OCH_3), 3.8-4.0 [1H, m, $C-(=N)CH-C$], 5.10 (1H, d, $C-(C_6H_5)CH-O-$), 7.20 (5H, broad s, C_6H_5).

(S)-(+)-2-Methylundecanoic acid (9). The crude product mentioned above was refluxed (4 h) with sulfuric acid (4 M, 400 ml). After cooling the product mixture was extracted with ether and the organic phase was washed several times with sodium carbonate solution. The combined carbonate phases were washed with ether and then acidified to pH 1. The oil that separated was extracted with diethyl ether. The extract was dried ($MgSO_4$) concentrated and distilled to give a colourless oil (27.2 g, 60%, b.p. 110-112°/0.5 mm). (Found: C 71.0 H 11.8 Calc. for $C_{11}H_{22}O_2$: C 70.9, H 11.9). n_D^{20} 1.4377. $[\alpha]_D$ +11.19° ± 0.05° (neat), +11.70° ± 0.05° (c 6, MeOH), +10.70° ± 0.05° (c 11, $CHCl_3$). Recently it was claimed that 2-methyldecanoic acid of 80% e.e. had been prepared showing the rotation $[\alpha]_D^{25}$ + 9.4 (c 10.4, $CHCl_3$).[23] Our acid should then be of 91% e.e. However, it is shown below that the $LiAlH_4$-reduction product, *i.e.* the (*S*)-(-)-alcohol 10 from our acid is obtained in 72% e.e. It is known that $LiAlH_4$-reduction of 2-methylpentanoic acid gives 2-methylpentan-1-ol with complete retention of configuration.[24] It seems highly unlikely that our acid should behave differently. Therefore our acid is in fact formed in 72% ee and pure (*S*)-(+)-2-methyldecanoic acid should show $[\alpha]_D^{20}$ +15.5° (neat).

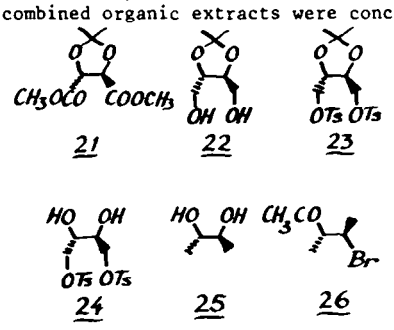
(S)-(-)-2-Methyldecan-2-ol (10). (*S*)-(+)-2-

-Methyldecanoic acid (9) (3.4 g, 18 mmol $[\alpha]_D^{20}$ +11.2°, neat) was dissolved in diethyl ether (20 ml) and slowly added to a stirred slurry of lithium aluminium hydride (1.25 g, 32 mmol) in diethyl ether (100 ml) during 0.5 h, and stirred for an additional h. The excess hydride was destroyed with $Na_2SO_4 \cdot 10H_2O$/celite. The resulting slurry was refluxed (1 h) and filtered. The solid was thoroughly washed with diethyl ether. The combined organic extracts were dried ($MgSO_4$) and concentrated to give a colourless oil after distillation (2.8 g, 90%, b.p. 92-94°/1 mm). (Found: C 76.9, H 14.0 Calc. for $C_{11}H_{24}O$: C 76.6, H 14.0). n_D^{20} 1.4409. $[\alpha]_D^{20}$ -7.07° ± 0.05° (neat) ^{1}H NMR (60 MHz): δ 0.8-1.0 (6H, m, 2-CH_3), 1.2-1.8 (15H, m), 1.55 (1H, broad s, -OH), 3.46 (2H, d, C-CH_2-O-). Both the possible diastereoisomers of the methoxytrifluorophenyl acetic acid esters 11 (MTPA-esters) of the (*S*)-Methyldecan-2-ol were prepared using the standard method described.[21,22] The ^{1}H NMR-spectrum (200 MHz) of the ester 11 from (-)-MTPA displayed a 10 line signal centered around δ 4.10 (2H, -(CH_3)CH-CH_2-O). Irradiation at δ 1.85 (1H, -(CH_3)CH-CH_2-O-) reduced the ten line signal to a five line signal consisting of a pair of doublets (J 10.5) and an apparent singlet unsymmetrically centered between the pair of doublets. The ratio between the integrals of the pair of doublets and that of the singlet is 86/14. The pair of doublets is ascribed to the (*S*)-2-methyldecan-2-yl diastereomer whereas the singlet must arise from the (*R*)-2-methyldecanyl ester isomer. In the decoupled spectrum of the ester 11 from (+)-MTPA the ratio of the integrals of the pair of doublets to that of the singlet is 14/86, thus confirming the assignment. Our (*S*)-2-methyldecan-1-ol (10) is thus obtained in 72% e.e. Tnerefore the specific rotation of pure (*S*)-10 should be $[\alpha]_D^{20}$ -9.8°.

(S)-1-Bromo-2-methyldecane (13). (*S*)-2-Methyldecan-1-ol (10) (10 g, 58 mmol) was dissolved in dry pyridine (75 ml, distilled from calcium hydride and stored under N_2 over molecular sieves 4 Å) and stirred at 0°. p-Toluenesulphonyl chloride (17.2 g, 89 mmol) was added and the mixture was stirred (3 h) and then kept at +5° overnight after which it was poured into ice and dilute hydrochloric acid and extracted with diethyl ether, wasned with water saturated sodium bicarbonate solution, brine, dried ($MgSO_4$) and concentrated to give 22 g of an oil consisting of the tosylate 12 mixed with a small amount of toluene sulphonyl chloride. This product mixture was dissolved in acetone (40 ml) and dried lithium bromide (25 g) in acetone (100 ml, dried over K_2CO_3 and distilled) was added and the resulting mixture was refluxed (16h). The mixture was poured into water and extracted with pentane. The pentane solution was washed with water, dried ($MgSO_4$), concentrated and chromatographed (silica gel, pentane as eluent) and then distilled to give a colourless oil (12.2 g, 91%, b.p. 91-92°/1 mm). (Found: C 56.5, H 9.86. Calc. for $C_{11}H_{23}Br$: C 56.2, H 9.9) $[\alpha]_D^{20}$ + 0.292° (neat). n_D^{20} 1.4587. ^{1}H NMR (60 MHz): δ 0.83 (3H, t, J 7 Hz, -CH_2-CH_3), 0.96 (3H, d, J 7 Hz, -CH(CH_3)-), 1.1-1.6 (14H, m), 1.6-1.7 (1H, m, C-CH(CH_3)-C), 3.28 (2H, d, J 5.6 Hz, -CH_2-Br).

(2R,3R)-Dimethyl-2,3-O-Isopropylidene-L-tartrate (21) was prepared from (2*R*,3*R*)-*L*-(+)-tartaric acid as described.[17]

(2R,3R)-2,3-O-Isopropylidene-L-threitol (22) The above ester ketal (21) was reduced with lithium aluminium hydride as described by Feit.[18] The work-up procedure was slightly modified. After completion of the reaction an excess of $Na_2SO_4 \cdot 10H_2O$/celite was carefully added and the mixture was refluxed (1 h) cooled and filtered. The solid obtained was exhaustively extracted in a Soxhlet extractor. The combined organic extracts were concentrated



21 22 23

24 25 26

and the residue was distilled (b.p. 100-102°/1 mm) through a 15 cm vacuum jacketed column packed with glass helices to give a 90% yield of the ketal diol 22.

(2S,3S)-1,4-Di-O-tosyl-2,3-O-isopropylidene-L-threitol (23) was prepared as described.[17,19] M.p. 92° (lit.[17] 92°).

(2S,3S)-1,4-Di-O-tosyl-L-threitol (24). Compound 23 was hydrolysed as described by Schurig.[19]

(2S,3S)-2,3-Butanediol (25). Compound 24 was reduced with $LiAlH_4$ according to Schurig.[19] The work-up procedure was, however, the same as that described for compound 22. Yield: 90%.

(2S,3R)-2-Acetoxy-3-bromobutane (26). The diol 25 was treated with hydrogen bromide in acetic acid as described by Golding.[20]

(2S,3S)-trans-2,3-Epoxybutane (14). The ester bromide 26 was treated with sodium pentylate in n-pentanol following the procedure used by Golding for the preparation of a diastereomeric mixture of 2,3-epoxybutanes.[20] The chiral epoxide was obtained in 76% yield. B.p. 54.0-54.5°. $[\alpha]_D^{20}$ -58.6° (neat). (Lit.[19]: $[\alpha]_D^{25}$ -58.8°). Gas chromatography (SF96 1%, Igepal 0.01%, 40 ml/min, 25°, packed column) showed that no *meso-cis*-epoxide was present.

meso-cis-*2,3-Epoxybutane.* This compound was prepared from *meso*-2,3-butanediol *via* the same sequence of reactions as above. B.p. 59-60°.

(4S,5S)-(-)-Dihydro-4,5-dimethylfuran-2(3H)-one or (3S,4S)-(-)-cis-dimethyl-γ-butyrolactone (6). Sodium (8.05 g, 0.35 mol) was dissolved in dry methanol (500 ml) and cooled to 0°. Dimethyl malonate (41 ml, 0.35 mol) in dry methanol (50 ml) was added dropwise. The solution was heated to reflux for 0.5 h and cooled to room temperature. (2*S*,3*S*)-2,3-Epoxybutane (14) (5.1 g, 0.072 mol) in dry methanol (20 ml) was added and the mixture was stirred overnight, followed by heating to 50° (8 h) and then heating at reflux overnight. Methanol (250 ml) was removed by distillation. The resulting mixture was cooled to room temperature and potassium hydroxide (28 g) in water (150 ml) was added. The mixture was refluxed (2 h) to hydrolyse the ester lactone 16 formed in the first step. The reaction mixture was cooled and conc. hydrochloric acid was cautiously added until the mixture was acidic. The solvent was evaporated off to give a mixture of inorganic salts, the acid lactone 17 and malonic acid. This mixture was exhaustively extracted with diethyl ether. The solution was dried and concentrated and the residue was refluxed in pyridine (8 h). The pyridine was removed by distillation through a 25 cm Vigreux column. The residue was dissolved

in diethyl ether (250 ml) and shaken with a hydrochloric acid solution (1M, 10 ml) saturated with sodium chloride followed by saturated potassium carbonate solution (10 ml). The water phases were back-extracted several times with diethyl ether. The combined organic extracts were dried ($MgSO_4$) and evaporated to give a residue which was chromatographed (silica gel, dry diethyl ether/pentane, 1/1 as eluent) and distilled (b.p. 105-107°/10 mm) to give a colourless oil (4.25 g, 53%). (Found: C 63.4, H 8.9. Calc. for $C_6H_{10}O_2$: C 63.1, H 8.8). $[\alpha]_D^{20}$ -54.9° (neat). n_D^{20} 1.4539. ^{1}H NMR (200 MHz): δ 1.03 (3H, d, J 6.8 Hz, C-CH(CH_3)-C), 1.30 (3H, d, J 6.6 Hz, C-CH(CH_3)-O), 2.1-2.4 (1H, m, -HCH-COO-), 2.5-2.8 (2H, m, -HCH-COO- and CH_2-CH(CH_3)-CH<), 4.67 (1H, d of q, J 6.0 and J 6.8 Hz, CH-C(CH_3)H-O). Irradiation at δ 2.25 did not change the signals at δ 1.03 whereas irradiation at δ 2.65 gave a singlet at δ 1.03. ^{13}C NMR: δ 13.87 (q, C-C(CH_3)-C), 15.35 (q, C-C(CH_3)-O), 33.37 (d, C-CH(C)-C), 36.89 (t, C-CH_2-C), 76.92 (d, C-C(C)-O) 176.86 (s, C-COO). Judging from these spectra the *cis*-lactone 6 was not contaminated with the *trans*-lactone 18. This was also confirmed by GLC: SF96, 1%, Igepal 0.01%, packed column, 0.25', 2.5 m, 40 ml N_2/min, 110°. Over 99.5% pure, ret. time 4.9 min. The maximum amount of the *trans*-lactone 17 (ret. time 4.0 min.) was 0.1%.

rac-trans-*Dihydro-4,5-dimethylfuran-2(3H)--one or* rac-trans-*3,4-Dimethyl-γ-butyrolactone (18).* *meso-cis*-Epoxybutane was reacted with dimethyl malonate as described above. This gave a 40% yield of the *trans*-lactone. B.p. 102-104°/10 mm. n_D^{20} 1.4291. ^{1}H NMR (200 MHz): δ 1.14 (3H, d, J 6.3 Hz, C-C(CH_3)H-C), 1.40 (3H, d, J 6.4 Hz, (C-C(CH_3)H-O), 2.1-2.4 (2H, m, CH-HCH-COO and C-HC(CH_3)-C), 2.6-2.8 (1H, m, CH-HCH-COO), 4.14 (1H, d of q, J 7.8 and 6.3 Hz, CH-C(CH_3)H-O). Irradiation at δ 4.14 gave a singlet at δ 1.40 and changed the multiplet at δ 2.1-2.4. ^{13}C NMR: δ 16.77, 19.10, 37.27, 38.19, 83.35 and 176.56. GLC: As above, ret. time 4.0 min (98.3%, *trans*-lactone 18) and 4.9 min (1.7%, *cis*-lactone 6).

(2S,3S,7S)-3,7-Dimethylpentadecan-2-ol-5-one (19). (*S*)-1-bromo-2-methyldecane (13) (3.96 g, 16.8 mmol) was added to finely cut strips of lithium wire (332 mg) in diethyl ether at -20°. After stirring (2 h) no additional lithium was consumed. The solution of alkyl lithium was removed from the excess lithium by a syringe. Judging from the amount of recovered lithium a maximum of 13 mmol of the alkyl lithium was formed. The chiral *cis*-lactone 6 (1.6 g, 14 mmol) was dissolved in diethyl ether (40 ml) and was stirred at -80°. The solution of the alkyl-lithium compound 5 was cooled and added during 1 h. Stirring at -80° was continued (1 h). The reaction was quenched with wet diethyl ether at -80° and then poured into water. The ether layer was washed with brine, dried ($MgSO_4$) and the solvent evaporated. The residue was chromatographed (silica gel, 5-20% ethyl acetate in pentane as eluent) and gave 1.98 g (53%) of a mixture of compound 19 and its ring-closed isomeric hemiketal form 20. ^{1}H NMR (60 MHz): δ 0.8-2.6 (32H, m), 3.6-4.0 [0.83H, m, -CH(CH_3)-OH of compound 19], 4.6-4.8 [0.17H, m, -CH(CH_3)-O-C of compound 20]. The 19/20 ratio is thus 4.7/1 at room temperature in chloroform.

(2S,3S,7S)-3,7-Dimethylpentadecan-2-ol (1). Potassium hydroxide (1.47 g) was dissolved in diethylene glycol (15 ml) and cooled to 90°. The mixture of the ol-one 19 and the hemiketal 20 (1.76 g, 6.5 mmol) was added followed by hydrazine hydrate (1.2 ml). The mixture was slowly heated (foaming) to 180° and maintained at this temperature for 1 h. The volatile components were allowed to distill off in a slow stream of nitrogen. The mixture was then heated to 210° (2 h), cooled, diluted with water and extracted with pentane. After washing with water the organic layer was dried ($MgSO_4$) and the solvent evaporated off. The residue was chromatographed (silica gel, 5-15% ethyl acetate in pentane) and distilled (b.p. 100-101°/0.02 mm) to give 1.26 g (76%) which was at least 99.5% pure by GLC (SE 30, capillary column, 70-180°). n_D^{20} 1.4514 (lit.[12] n_D^{20} 1.4509). $[\alpha]_D^{20}$ -12.15° ± 0.08° (neat) (lit[12] $[\alpha]_D^{20}$ -9.88°, neat). ^{1}H NMR (200 MHz): δ 0.84 (3H, d, J 6.3 Hz, C-CH(CH_3)-C), 0.88 (3H, t, J 6.3 Hz, -CH_2-CH_3), 0.89 [3H, d, J 6.6 Hz, C-CH(CH_3)-C], 1.15 [3H, d, J 6.2 Hz, C-CH(CH_3)-OH], 1.27 (22H, broad) 1.55 (1H, s, OH), 3.71 [1H, m, CH-C(CH_3)H-OH].

(2S,3S,7S)-3,7-Dimethylpentadecan-2-yl acetate (2). The alcohol 1 (0.9 g) was dissolved in acetic anhydride (2 ml) in pyridine (5 ml). After standing over night the solution was stirred with ice water (1 h). The mixture was extracted with pentane. The pentane layer was washed with hydrochloric acid (0.5 M), saturated sodium bicarbonate solution, brine, dried ($MgSO_4$) and the solvent evaporated off. The residue was chromatographed (silica gel, 1-2.5% ethyl acetate in pentane as eluent) to give an oil which was distilled (bulb to bulb/0.01 mm/150° air bath) to give 0.90 g (86%). The purity of this material was 99.5% as judged by GLC (SE30, capillary column). $[\alpha]_D^{20}$ -6.6° (neat) (lit.[12] $[\alpha]_D^{20}$ -5.76°, neat). n_D^{20} = 1.4419 (lit.[12] n_D^{20} 1.4404). The ^{1}H NMR spectrum was identical with that described.[12]

(2S,3S,7S)-3,7-Dimethylpentadecan-2-yl propionate (3). The propionate 3 was prepared as described for the acetate 2 but using propionic anhydride instead of acetic. Yield 93%. Purity, 99.5% by GLC (SE 30, capillary column). $[\alpha]_D^{20}$ -6.93° (c 18, hexane) (lit.[12] $[\alpha]_D^{20}$ -5.52°, neat). n_D^{20} 1.4423 (lit.[12] n_D^{20} 1.4409). The ^{1}H NMR spectrum was identical with that described.[12]

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