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Sex Pheromone of Pine Sawflies. Chiral Syntheses of some Active Minor Components Isolated from *Neodiprion sertifer* and of some Chiral Analogues of Diprionyl Acetate.

Erik Hedenström*[a], Hans-Erik Högberg[a], Ann-Britt Wassgren[b], Gunnar Bergström[b], Jan Löfqvist[c], Bill Hansson[c] and Olle Anderbrant[c]

[a]University College of Sundsvall/Härnösand, Box 860, S-851 24 Sundsvall, Sweden.
[b]Department of Chemical Ecology, University of Göteborg, S-413 20 Göteborg, Sweden.
[c]Department of Ecology, Animal Ecology, University of Lund, S-223 62 Lund, Sweden.

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Abstract: The chiral syntheses of some analogues, **2** - **7**, of 3,7-dimethyl-2-pentadecanol, **1** (diprionol), and of the corresponding acetates are described. The acetate of **1** is the main attractant in the sex pheromone of the *Neodiprion* genus (Diprionidae). Compounds **2** - **4** were identified as minor components isolated from females of *Neodiprion sertifer*. Synthetic intermediates were prepared either from chiral starting materials, *via* asymmetric syntheses, or by baker's yeast reductions.

The pine sawfly *Neodiprion sertifer*, Geoffrey (Diprionidae) is a pest on Scots pine in the northern parts of Europe, Asia and North America. A possible method for controlling and monitoring populations of this insect could be to utilize mixtures of synthetic pheromone components or analogues thereof. For some years we and others have been studying both synthetic approaches to, and biological activities of potential components of the sex pheromone of this insect, which uses 3,7-dimethyl-2-pentadecyl acetate, **1Ac** (diprionyl acetate) as main attractant. [1-9] The syntheses of the eight possible stereoisomers of **1Ac** in high stereochemical purities were recently described.[9] Biological studies both in the field and in the laboratory have established that *erythro*-(2*S*,3*S*,7*S*)-diprionyl acetate (**SSS-1Ac**) (Figure 1) is the main attractant in *Neodiprion sertifer* whereas one *threo*-isomer, **SRR-1Ac**, acts as an inhibitor of the former even at a very low concentration (≥0.5%).[10-12] Another *threo*-isomer, **SRS-1Ac**, can also function as an inhibitor, but a much higher concentration (~50%) is required.[12] In related genera the *threo*-isomer, **SRR-1Pr**, has been identified as the attractant for example in *Diprion similis*.[13]

We have recently isolated some active minor pheromone components after acetylation of extracts from biological material and have suggested the structures **2Ac**, **3Ac** and **4Ac** for these, or less likely other diastereomers, by electroantennography (EAG) in parallel with gas chromatography and mass spectrometry (GLC-MS).[14]

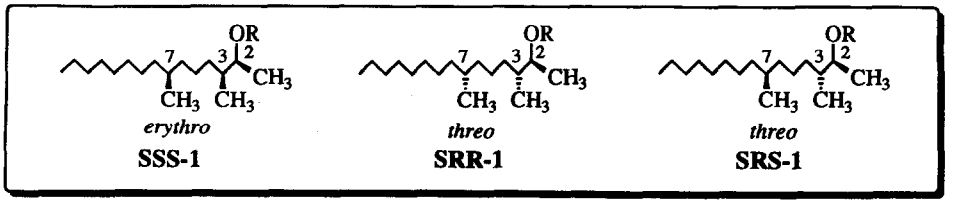


Figure 1. **1**: R = H; **1Ac**: R = $COCH_3$; **1Pr**: R = COC_2H_5

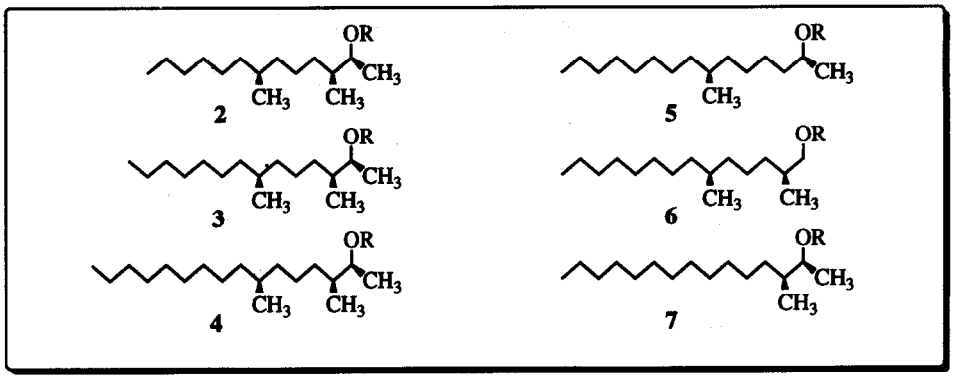


Figure 2. **2-7**: R = H. **2-7Ac**: R = $COCH_3$.

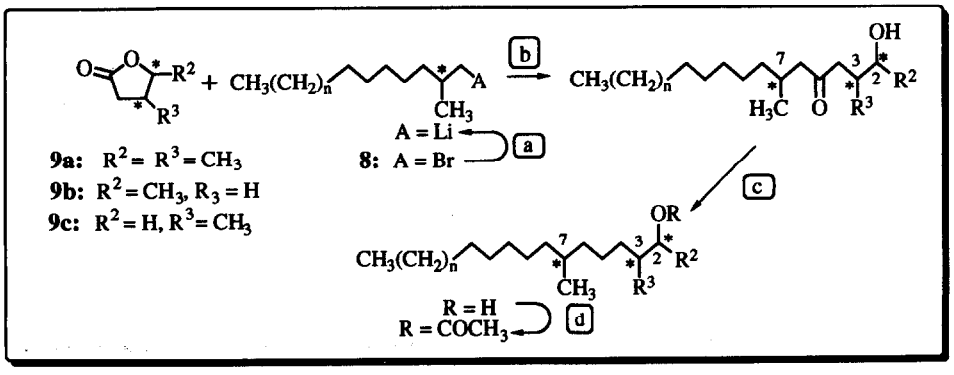
Acetylation of the extracts is necessary since the corresponding inactive alcohols **1-4** are the compounds isolated from body extracts, whereas the active esters are not found in this material.

We have also demonstrated that in *Neodiprion sertifer* different receptor cells respond to **SSS-1Ac** and **SRR-1Ac**.[15] How this stereochemical differentiation works is an intriguing problem. In order to clarify the effects of such subtle structural variation on the biological activity, it is necessary to have some closely related analogues of the active compounds available for biological tests.

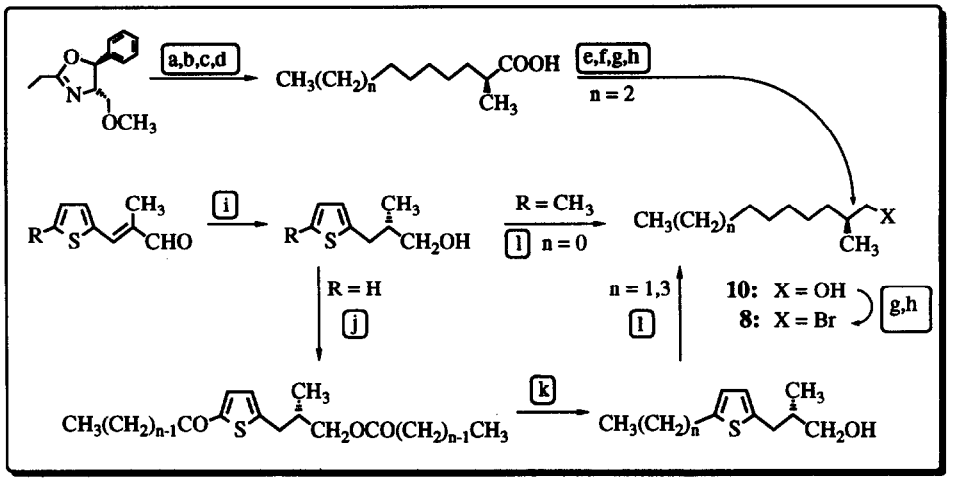
We now report the syntheses of the diprionyl acetate analogues **2-7** (Figure 2) and the probable identity of compounds **SSS-2**, **SSS-3** and **SSS-4** with the minor components recently isolated[14] from biological material.

Except for the analogue **7** (*vide infra*), we used a synthetic approach similar to that used by us previously.[2,9] This consisted of the attack of a chiral alkyllithium on a chiral lactone, followed by Huang-Minlon reduction of the ketoalcohol produced, to furnish the desired diprionol analogue, which was then acetylated as shown in Scheme 1.

The chiral-2-methyl-1-alkyllithiums were prepared from the corresponding (*S*)-1-bromo-2-methylalkanes **8**, which were in turn prepared from the (*S*)-alcohols *via* standard methods. The (*S*)-alcohol **10** (n = 2) was obtained by asymmetric synthesis (see Scheme 2) as has been described previously.[2,9] The (*S*)-alcohol **10** (n = 0) was prepared using a method developed by some of us.[16] 2-Methyl-3-(5-methyl-2-thiophene)propenal, on baker's yeast reduction furnished (*S*)-2-methyl-3-(5-methyl-2-thiophene)propanol in 94% ee. Treatment of this product with Raney nickel gave the saturated (*S*)-alcohol **10** (n = 0) in 87% ee. A slight variation of this method[16] was used for the preparation of (*S*)-alcohols **10** (n = 1 and 3). 2-Methyl-3-(2-thiophene)propenal gave (*S*)-



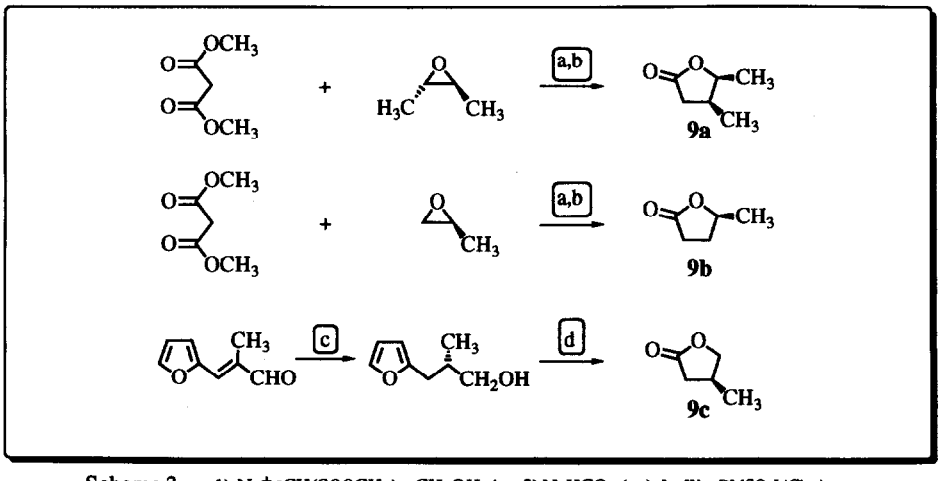
Scheme 1. **a**: Li, Et_2O, -20 °C. **b**: 1) Et_2O, -80 °C. 2) H_2O. **c**: N_2H_4, KOH, +100 - +210 °C. **d**: Ac_2O, pyridine.



Scheme 2. Synthesis of the (*S*)-1-bromo-2-methylalkanes **8**. **a**: LDA, THF, -80 °C. **b**: 1-iodooctane, -95 °C. **c**: 4M H_2SO_4, Δx. **d**: Cryst from acetone with (*R*)-2-phenylethylamine. **e**: $LiAlH_4$, Et_2O. **f**: H_3O^+. **g**: TsCl, pyridine. **h**: LiBr, acetone, Δx. **i**: Baker's yeast, 72 h 33%. **j**: $CH_3(CH_2)_{n-1}COCl$, $SnCl_4$, CH_2Cl_2, 0 °C, 1h, 90-94%. **k**: N_2H_4, KOH, diethylene glycol, 180 °C, 1 h, 210 °C, 2h, 87-91%. **l**: Raney nickel /H_2, methanol, 76-77%.

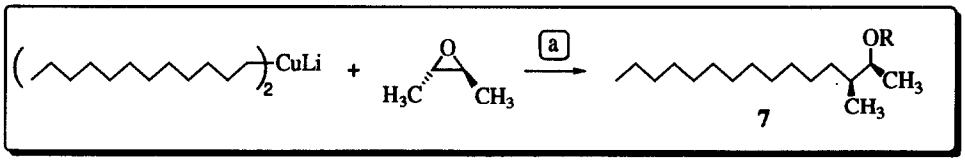
2-methyl-3-(2-thiophene)propanol in over 98% ee with baker's yeast reduction. The latter compound was acylated according to Friedel-Crafts and the product was subjected to Huang-Minlon reduction followed by Raney nickel treatment to give the desired (*S*)-alcohols **10** (n = 1 and 3) in >93% ee (for experimental details see ref.[16]).

As depicted in Scheme 3, the synthetic intermediates for the parts of the diprionol analogues containing the alcohol group, the lactones of type **9**, were prepared either from chiral epoxides (**9a** and **9b**) or from a chiral fermentation product (**9c**). (3*S*,4*S*)-(-)-*cis*-Dimethyl-γ-butyrolactone **9a** was prepared from optically pure (2*S*,3*S*)-epoxybutane as described by us,[9] and (*S*)-4-methyl-γ-butyrolactone **9b** in the same way from commercial (*S*)-epoxypropane of 95% ee. Baker's yeast fermentation of 2-methyl-3-(2-furyl)propenal gave (*S*)-2-methyl-3-(2-furyl)propanol, which on ozonisation furnished (*S*)-3-methyl-γ-butyrolactone **9c** in 99% ee as described by one of us in collaboration with an Italian group.[17]



Scheme 3. **a**: 1) $Na^+ {}^-CH(COOCH_3)_2$, CH_3OH, Δx. 2) $NaHCO_3$ (aq). **b**: Wet DMSO, LiCl, Δx. **c**: Baker's yeast. **d**: 1) Ozone, CH_2Cl_2. 2) H_2O_2, HCOOH.

The analogue **7**, lacking the methyl group in position 7, was prepared by treating the lithium cuprate prepared from bromododecane, lithium and cuprous iodide with (2*S*,3*S*)-epoxybutane (Scheme 4. Cf. Mori's method for diprionol synthesis[18]).



Scheme 4. **a**: Et_2O, -50 °C.

The N-isopropylcarbamates of compounds **2, 3** and **4** were prepared and subjected to capillary GLC on a tandem column including a chiral column of the König type using the method that we described previously.[9] This method cleanly separated the *threo*- from the *erythro*-isomers. The four individual *threo*-isomers of diprionol **1** were also separated, whereas only two peaks were obtained from the four *erythro*-isomers, one from 2*S*,3*S*,7*S*- and 2*S*,3*S*,7*R*-**1**, the other from 2*R*,3*R*,7*S*- and 2*R*,3*R*,7*R*-**1**. In the present work we found that the retention times of the N-isopropylcarbamates of the minor components responsible for the EAG-activities observed (after acetylation of the natural extract), had the same retention times as the synthetic carbamates. Therefore the configuration of the natural components should be 2*S*,3*S*-, and neither 2*R*,3*R*-, 2*S*,3*R*- nor 2*R*,3*S*-. The configuration in the 7-position could in theory be 7*R*- but this seems less likely, since 2*S*,3*S*,7*R*-**1** has neither been isolated from natural material nor is its acetate active in *Neodiprion sertifer*. Syntheses of all possible pairs of 2*S*,3*S*-isomers of alcohols **2 - 4** are probably needed to confirm the structural assignments.

We are at present studying the biological activities of the acetates **2 - 7Ac** in *Neodiprion sertifer*. The results will be discussed in a forthcoming paper.

Experimental

Commercially available chemicals were used as received, unless otherwise stated. Dry diethyl ether ($LiAlH_4$), pyridine (CaH_2), DMSO (CaH_2), and acetone (Na_2CO_3) were distilled from the indicated drying agents. Reactions sensitive to moisture and/or oxygen were carried out under argon. Preparative liquid chromatography was performed on straight phase silica gel (Merck 60, 230-400 mesh, 0.040 - 0.063 mm, 10 - 50g/g of mixture) using the gradient elution technique described in ref.[19] with an increasing concentration of distilled ethyl acetate in distilled hexane. Thin layer chromatography (TLC) was performed on silica gel plates (Merck 60, pre-coated aluminium foil) using ethyl acetate (20 or 40 %) in hexane as an eluent, and developed by means of ultraviolet irradiation and/or by spraying with vanillin in sulfuric acid and heating at 120 °C. Unless otherwise stated, GLC analyses were carried out using a capillary column (Hewlett-Packard, crosslinked 5% phenylmethylsilicone, SE54-type, 22 m x 0.31 mm I.D., d_f = 0.52 µm, carrier gas N_2 (10 psi), split ratio 1/20). Melting and boiling points are uncorrected and the latter are, unless otherwise stated, given as air bath temperatures (bath temp./mmHg) in a bulb to bulb (Büchi GKR-51) apparatus. Optical rotations were measured either neat in a 1 cm cell or in solution in a 1 dm cell using a Perkin Elmer 241 polarimeter. IR spectra were recorded neat between NaCl plates using a Perkin Elmer 782 infrared spectrometer. NMR spectra were recorded with tetramethylsilane as internal standard using either a Jeol PMX60SI (60MHz ^1H) or a Bruker AM400 (400 MHz ^1H and 376 MHz ^{19}F) spectrometer. Elemental analyses were carried out by Mikrokemi, Uppsala, Sweden.

Preparation of the diprionyl acetate analogues **2-7Ac**. All six analogues of diprionyl acetate were obtained on a 10 mg scale from the corresponding alcohols, using the method described in ref.[2] They were analysed by capillary GLC and were all obtained in >98.5% chemical purity.

(2S,3S,7S)-3,7-Dimethyl-2-tridecanol **2**. Using the method described below for **5**, compound **2** was prepared

from (3*S*,4*S*)-(-)-*cis*-dimethyl-γ-butyrolactone (**9a**, 0.12 g, 1.1 mmol) >99.9% ee and (*S*)-1-bromo-2-methyloctane (**S-8**, n = 0, 0.25 g, 1.21 mmol, >87% ee). Bulb to bulb distillation gave the tridecanol **2** (0.07 g, 0.3 mmol, 27%). Anal. calcd for $C_{15}H_{32}O$: C 78.9%, H:14.1%. Found: C 78.9%, H 14.1%. Physical data are presented in Table 1.

(2S,3S,7S)-3,7-Dimethyl-2-tetradecanol **3** and *(2S,3S,7S)-3,7-dimethyl-2-hexadecanol* **4** were prepared in the same way, starting with the same lactone **9a** >99.9% ee (0.11 g, 0.96 mmol) and either (*S*)-1-bromo-2-methylnonane (**S-8**, n = 1, 0.26 g, 1.2 mmol, >93.8% ee) or (*S*)-1-bromo-2-methylundecane (**S-8**, n = 3, 0.26 g, 1.0 mmol, >93.2% ee) respectively. Bulb to bulb distillation gave the tetradecanol **3**, (0.10 g, 0.40 mmol, 42%), (Anal. calcd for $C_{16}H_{34}O$: C 79.3%, H 14.1%. Found: C 79.9%, H 14.3%) or 0.07 g (0.30 mmol, 31%) of hexadecanol **4** (Anal. calcd for $C_{18}H_{38}O$: C 80.0%, H 14.2%. Found: C 80.4%, H 14.2%), respectively. Physical data for the title compounds see Table 1.

(2S,7S)-7-Methyl-2-pentadecanol **5**. This compound was prepared from (*S*)-(-)-4-methyl-γ-butyrolactone (**9b**, 95.0% ee) and (*S*)-1-bromo-2-methyldecane (**S-8**, n = 2) of >97% ee, using the method previously described for diprionol.[2,9] The alkyllithium (2.9 mmol) was formed from the bromide **S-8** (0.90 g, 3.8 mmol) and lithium (0.10 g, 14 mmol, 3% Na, freshly cut under Ar) in dry diethyl ether (10 ml) at -20 °C for 2h and then added to the lactone (0.26 g, 2.6 mmol) in dry diethyl ether at -80 °C. The solution was then stirred for 2 h before it was quenched with water. The slurry was allowed to reach ambient temperature, the organic phase was separated and the water phase was extracted with diethyl ether. The combined organic phase was washed with brine, dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography of the residue gave the expected ketoalcohol (0.32 g, 1.4 mmol, 54% based on the lactone), which was dissolved in diethylene glycol containing KOH (0.34 g, 6.0 mmol) and hydrazine (0.38 ml, 8.0 mmol) and the mixture was slowly heated to 180 °C and maintained there for 1h, after which it was slowly heated to 210 °C and maintained there for 2 h. After cooling, dilution with water, and diethyl ether extractions, the pooled organic extract was washed with water and dried ($MgSO_4$). Solvent evaporation gave an oil, which was subjected to flash chromatography followed by bulb to bulb distillation to give the desired alcohol **5** (0.26 g, 1.1 mmol, 42% based on the lactone). Anal. calcd for $C_{16}H_{34}O$: C 79.3%, H 14.1%. Found: C 79.1%, H 13.9%. For physical and spectral data see Table 1.

(2S,6S)-2,6-Dimethyl-1-tetradecanol **6**. This compound was prepared from (*S*)-(-)-3-methyl-γ-butyrolactone (**9c**) (0.15 g, 1.5 mmol, >98.6% ee, prepared according to ref.[17]) and (*S*)-1-bromo-2-methyldecane (**S-8**, n = 2) (0.52 g, 2.2 mmol) >97% ee using the same procedure as that described above. Yield of the tetradecanol **6** 0.17 g, (0.7 mmol, 47%). Anal. calcd for $C_{16}H_{34}O$: C 79.3%, H 14.1%. Found: C 79.2%, H 14.2%. For physical data see Table 1.

(2S,3S)-3-Methyl-2-pentadecanol **7**. 1-Bromododecane (2.0 g, 8.0 mmol) and lithium (0.11 g, 16 mmol, 3% Na, freshly cut under Ar) in dry diethyl ether (20 ml) was stirred at -20 °C for 2h and then purified cuprous iodide (0.76 g, 4.0 mmol) was added. The mixture was cooled to -50 °C and (2*S*,3*S*)-epoxybutane (0.29 g, 4.0 mmol, >99.9% ee, synthesized from (2*S*,3*S*)-(+)-tartaric acid as described by Byström et al[2]) was added. After stirring for 1h the mixture was allowed to reach 0 °C and the reaction was quenched with satd ammonium chloride solution. Extraction with diethyl ether, drying ($MgSO_4$) and flash chromatography gave the expected alcohol after bulb to bulb distillation, (0.29 g, 1.2 mmol, 30% based on the epoxide). Anal. calcd for $C_{16}H_{34}O$: C 79.3%, H 14.1%. Found: C 79.2%, H 14.1%. For physical data see Table 1.

(S)-1-Bromo-2-methyloctane **8** (n = 0). (*S*)-2-Methyl-1-octanol was prepared as described in ref.[16] The alcohol **10** (n = 0), (0.3g, 2.1 mmol, 87% ee) was dissolved in dry pyridine (5 ml) and stirred at 0 °C. *p*-Toluenesulfonyl chloride (0.52 g, 2.7 mmol) was added in one portion and the mixture was stirred overnight at 0 °C, after which it was poured into ice-water (10 ml, mixed with 6 M HCl, 5 ml). The resulting mixture was extracted with diethyl ether, washed ($NaHCO_3$, aq satd, and brine), and dried ($MgSO_4$). The organic solvent was evaporated to give an oil, which was dissolved in dry acetone (2 ml) and then added to a solution of dried

Table 1

Compound 2-7	Chemical purity by GLC (%)	$[\alpha]_D^{22}$ ° ±0.1 (hexane)	Boiling point (air bath) °C/mm Hg	n_D^{20} ±0.0002	NMR 400 MHz
SSS-2	>99.1	-14.2 (c 1.0)	90/0.07	1.4485	δ 0.84(3H,d,J=6.6 Hz), 0.87(3H,t,J=6.7 Hz), 0.88(3H,d,J=6.7 Hz), 1.15(3H,d,J=6.4 Hz), 1.02-1.46(19H,m), 3.70(1H,d of q,J=4.2 and 6.4 Hz)
SSS-3	>98.6	-13.5 (c 1.0)	100/0.07	1.4501	δ 0.84(3H,d,J=6.5 Hz), 0.87(3H,t,J=6.9 Hz), 0.88(3H,d,J=6.7 Hz), 1.15(3H,d,J=6.4 Hz), 1.02-1.47(21H,m), 3.70(1H,d of q,J=4.2 and 6.4 Hz)
SSS-4	>98.5	-12.1 (c 0.8)	130/0.07	1.4520	δ 0.84(3H,d,J=6.6 Hz), 0.88(3H,t,J=6,8 Hz), 0.89(3H,d,J=6.9 Hz), 1.15(3H,d,J=6.4 Hz), 1.03-1.46(24H,m), 1.55(1H,broad s), 3.71(1H,d of q,J=4.2 and 6.4 Hz)
SS-5	>99.9	+6.7 (c 1.3)	110/0.07	1.4480	δ 0.83(3H,t,J=6.5 Hz), 0.87(3H, d,J=6.9 Hz), 1.17(3H,d,J=6.2 Hz), 1.05-1.50(24H,m), 3.78(1H,sextet,J=6.1 Hz)
SS-6	>99.2	- 8.9 (c 1.2)	140/0.3	1.4503	δ 0.84(3H,d,J=6.5 Hz), 0.88(3H,t,J=6.8 Hz), 0.91(3H,d, J=6.7 Hz) 1.02-1.40(22H,m), 1.55-1.69(1H,m), 3.41(1H, d of d, J=10.5 and 6.6Hz), 3.50(1H d of d, J=10.5 and 5.8Hz)
SS-7	>98.6	-13.2 (c 1.0)	105/0.07	(m.p. 30-30.5 °C)	δ 0.87 (3H,d,J=6.8 Hz), 0.87(3H,t,J=6.8 Hz), 1.13(3H,d,J=6.4Hz), 1.07-1.44(24H,m), 3.69(1H, d of q J=4.2 and = 6.4 Hz)

(130 °C) lithium bromide (0.63 g, 7.3 mmol) in dry acetone (5 ml). The mixture was refluxed overnight. After dilution with water, extraction with pentane, washing with water, drying ($MgSO_4$), solvent evaporation and flash chromatography, followed by bulb to bulb distillation (60 °C/2 mm Hg), the bromide **8** (n = 0) was obtained in 70% yield (0.30 g, 1.4 mmol) and 95% chemical purity (contaminant: about 5% of the corresponding chloride). The identity of the bromide was checked by 60 MHz ^{1}H NMR and the bromide was then used without further characterisation.

(S)-1-Bromo-2-methylnonane **8** (n = 1) *and (S)-1-bromo-2-methylundecane* **8** (n = 3) were prepared in the same way, starting with (*S*)-2-methyl-1-nonanol[16] **10** (n = 1), (0.25 g, 1.6 mmol 93.8% ee) or (*S*)-2-methyl-1-undecanol[16] **10** (n = 3), (0.23 g, 1.24 mmol 93.2% ee), respectively. The products were distilled, bulb to bulb (70 °C/3 mm Hg, 0.27 g, 1.2 mmol, 75%) or (95 °C/3 mm Hg, 0.26 g, 1.1 mmol, 89%), respectively. The identities of the bromides were checked by 60 MHz ^{1}H NMR and these were then used without further purification or characterisation.

(3S,4S)-(-)-cis-Dimethyl-γ-butyrolactone (**9a**). Sodium (15 g, 0.652 mol) was dissolved in dry methanol (750 ml), the solution was cooled to 0 °C and distilled dimethyl malonate (76 ml, 0.65 mol) in dry methanol (100 ml) was added dropwise, after which the solution was refluxed for 0.5 h. (2*S*,3*S*)-epoxybutane, prepared according to literature[2,9] (8.58 g, 0.119 mol) was dissolved in dry methanol (40 ml) and added to the stirred solution of the anion of dimethyl malonate at room temperature. After stirring overnight the mixture was heated at 50 °C for 8h and then refluxed overnight. Quenching with acetic acid (37 ml), was followed by evaporation of the solvent to dryness. The residue was taken up in water (200 ml) then extracted with diethyl ether and the solvent evaporated off to give an oil, which contained the lactone ester and dimethyl malonate. The major portion of the dimethyl malonate was fractionally distilled off. The remaining mixture was decarbalkoxylated as de-

scribed by Krapcho *et al.* [20] Thus, it was refluxed for 3.5 h in DMSO / water (96 / 4, v / v, 150 ml) containing lithium chloride (24.0 g, 0.560 mol). Dilution with brine, followed by extraction with CH_2Cl_2, washing with brine and drying ($MgSO_4$), furnished an oil which was flash chromatographed and distilled (bulb to bulb 70 °C/2 mm Hg) to give the lactone **9a** (8.15 g, 71.5 mmol, 60%) with >99.9% ee (by GLC as amide, cf below) and containing less than 0.04% *trans*-lactone (by GLC). Spectroscopic and physical data were identical with those described.[2]

(4S)-(-)-Methyl-γ-butyrolactone (**9b**). This compound was prepared using the method described above for **9a** but starting from commercial (*S*)-epoxybutane of >95.0% ee. This furnished an oil which was flash chromatographed and distilled, (86 °C/11mm Hg), to give the lactone **9b**, >95.0% ee (by GLC as amide, cf below). $[\alpha]^{20}_D$ -36.8° ±0.1° (c 1.8, CH_2Cl_2) [Lit[21]: -29.6° (c 1.29 CH_2Cl_2), Lit.[22] (R)-isomer: +31.4° (c 1, CH_2Cl_2) and Lit.[23]: -36.8° (c 1.44, CH_2Cl_2)]. n^{20}_D 1.4376 ±0.0002. The ^1H NMR spectrum (60 MHz) was identical with that described.[21]

(3S)-(-)-Methyl-γ-butyrolactone (**9c**).This compound was prepared as described in ref.[17] which furnished the lactone **9c** with >98.6% ee (by GLC as amide acetate, cf. below). Spectroscopic and physical data were identical with those described earlier.[16,17,24,25]

Analyses of the enantiomeric excesses of the lactones 9 via their amides formed from (S)-1-phenylethylamine. The ring-opened hydroxyamides were prepared as described in ref.[9] from the lactones **9a**, **9b** and **9c**, i.e. the lactone (≈10 mg) and optically pure (*S*)-1-phenylethylamine (≈50 mg) were placed in a test tube, which was sealed under vacuum and heated for 24 h at 140°C. The viscous oil formed was taken up in diethyl ether, washed with aqueous hydrochloric acid, and dried ($MgSO_4$). The hydroxyamide prepared from lactone **9c** was esterified using acetic anhydride in pyridine[2], in order to enhance the resolution of the diastereomeric peaks when analysing as below. The solutions of the hydroxyamides and the acetoxyamide were analysed for enantiomeric excess (% ee) by GLC: Column: J &W DB-WAX (carbowax 20 M, 30 m x 0.32 mm I.D., d_f = 0.25 μm). Conditions: Isothermal 200 °C for the hydroxyamides and 210 °C for the acetoxyamide, carrier gas He(15 psi), split ratio 1/30. **9a-hydroxyamide** retention times: *SSS*(major): 26.65 min.; *SRR* (minor): 27.69 min. (99.9% ee). **9b-hydroxyamide**, retention times: *SS* (major): 26.67 min.; *SR* (minor): 27.02 min. (95.0% ee). **9c-acetoxyamide**, retention times: *SS* (major): 32.92 min.; *SR* (minor): 33.24 min. (98.6% ee).

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References

1. Ahlgren, G.; Bergström, G.; Löfqvist, J.; Jansson, A.; Norin, T. *J. Chem. Ecology,* **1979**, 5, 309-319.
2. Byström, S.; Högberg, H.-E.; Norin, T. *Tetrahedron,* **1981**, 37, 2249-2253.
3. Bæckström, P.; Okecha, S.; De Silva, N.; Wijekoon, D.; Norin, T. *Acta Chem. Scand.* **1982**, B 36, 31-36.
4. Norin, T. *Chemica Scripta,* **1985**, 25, 33-38.
5. Löfqvist, J. Species specificity in response to pheromone substances in diprionid sawflies. In *Mechanisms in Insect Olfaction*; Payne, T. L.; Birch, M. C.; Kennedy, C. E. J. Eds.; Oxford University Press.: Oxford, **1986**; pp. 123- 129.
6. Anderbrant, O.; Löfqvist, J.; Jönsson, J.; Marling, E. *J. Appl. Ent.*, **1989**, 107, 365-369.
7. Hallberg, E.; Löfqvist, J. *Can. J. Zool.*, **1981**, 59, 47-53.
8. Norin, T. *Pure & Appl. Chem.*, **1989**, 61, 547-550.
9. Högberg, H.-E.; Hedenström, E.; Wassgren, A.-B.; Hjalmarsson, M.; Bergström, G.; Löfqvist, J.; Norin, T. *Tetrahedron,* **1990**,

46, 3007-3018.

10. Kikukawa, T.; Matsumura, F.; Olaifa, J.; Kraemer, M.; Coppel H. C.; Tai, A. *J. Chem. Ecology,* **1983**, 9, 673-693.
11. Olaifa, J. I.; Matsumura, F.; Coppel, H. C. *J. Chem. Ecology,* **1987**, 13, 1395-1408.
12. Anderbrant, O.; Löfqvist, J.; Högberg, H.-E.; Hedenström, E.; Wassgren, A.-B.; Bergström, G.; Bengtsson M.; Magnusson, G. *Ent. Exp. Appl.*, **1992**, 46, in press.
13. Kikukawa, T.; Matsumura, F.; Kraemer, M.; Coppel H. C.; Tai, A. *J. Chem. Ecology,* **1982**, 8, 301-314.
14. Wassgren, A-B.; Anderbrant, O.; Löfqvist, J.; Hansson, B. S.; Bergström, G.; Hedenström, E.; Högberg, H.-E. Submitted to *J. of Insect Physiology.*
15. Hansson, B. S.; van der Pers, J. N. C.; Högberg, H.-E.; Hedenström, E.; Anderbrant, O.; Löfqvist, J. *J. Comp. Physiol. A,* **1991**, 168, 533-538.
16. Högberg, H.-E.; Hedenström, E.; Fägerhag J.; Servi, S. *J. Org. Chem.*, **1992**, 57, in press.
17. Fuganti, C.; Grasselli, P.; Servi S.; Högberg, H.-E. *J. Chem. Soc. Perkin Trans. I,* **1988**, 3061-3065.
18. Mori, K.; Tamada, S. *Tetrahedron,* **1979**, 35, 1279-1284.
19. Bœckström, P.; Stridh, K.; Li L.; Norin, T. *Acta Chem. Scand.*, **1987**, B 41, 442-447.
20. Krapcho, A. P.; Weimaster, J. F.; Eldridge, J. M.; Jahngen, Jr., E. G. E.; Lovey, A. J.; Stephens, W. P. *J. Org. Chem.*, **1978**, 43, 138-147.
21. Mori, K. *Tetrahedron,* **1975**, 31, 3011-3012.
22. Vigneron, J. P.; Bloy, V. *Tetrahedron Lett.*, **1980**, 21, 1735-1738.
23. Ohkuma, T.; Kitamura, M.; Noyori, R. *Tetrahedron Lett.*, **1990**, 31, 5509-5512.
24. Leuenberger, H. G.; Boguth, W.; Barner, R.; Schmid, M.; Zell, R. *Helv. Chim. Acta,* **1979**, 62, 455-463.
25. Mori, K. *Tetrahedron,* **1983**, 39, 3107-3109.