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SYNTHESIS OF OPTICALLY ACTIVE FORMS OF METHYL (*E*)-2,4,5-TETRADECATRIENOATE, THE PHEROMONE OF THE MALE DRIED BEAN BEETLE†

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Abstract—Both enantiomers of methyl (*E*)-2,4,5,-tetradecatrienoate were synthesized with 125–127% the rotatory power of the natural product which was isolated as the pheromone of *Acanthoscelides obtectus*. The absolute configuration of the levorotatory natural pheromone was confirmed to be *R*.

In 1970 Horler isolated methyl (*E*)-(−)-2,4,5-tetradecatrienoate **1** as the sex pheromone produced by the male dried bean beetle, *Acanthoscelides obtectus* (Say).[1] This unique allenic structure attracted attention of many synthetic chemists and several syntheses of its racemate were reported.[2-7] However, due to the difficulty in generating the axial chirality of the allenic system in a well-defined manner,[8] only one synthesis of the optically active forms of **1** has been reported. Thus Pirkle and Boeder obtained the pheromone enantiomers with 74–77% the rotatory power of the natural product employing organocopper chemistry.[9] Herein we report a new synthesis of both (*R*)-(−)-and (*S*)-(+)-**1** possessing 125 ~ 127% the roratory power of the natural pheromone.

The key step in our synthesis is the ortho ester Claisen rearrangement reaction (**A** → **B**) with transfer of the central chirality of the asymmetric carbon atom in A into the axial chirality of the allenic linkage in **B**. As depicted in the Scheme, an (*S*)-acetylenic alcohol **A** gives stereoselectively an (*S*)-allene **B** via the transition state **C** with two bulky substituents (OEt and R=n–C_8H_{17}) in pseudo-equatorial position. Although the synthesis of chiral allenes via Claisen-type rearrangement was first recorded in 1965,[10] this is a new example of the application of the ortho ester method in the preparation of highly optically pure allenes. It should be added that the stereoselectivity of the ortho ester method is known to be higher than that of the classical Claisen rearrangement.[11]

In order to secure the optically active forms of the starting alcohol **2a** of the known absolute configuration, we adopted the classical resolution technique which was more reliable at the time when we started this work than other methods such as microbial resolution[12] or asymmetric synthesis.[13] The racemic alcohol **2a**[2,4,6] was converted into the corresponding phthalic half ester **2b**. This was resolved with (*R*)-(+)-1-(α-naphthyl)ethylamine to give a crystalline salt, m.p. 102–106°, $[\alpha]_D^{22}+29.3°$ ($CHCl_3$), after repeated recrystallization from MeOH-ether. Acidification of the salt with dil HCl liberated the resolved half ester whose saponification with NaOH soln gave (+)-**2a**, $[\alpha]_D^{22}+14.8°$ (ether). In the same manner resolution with (*S*)-(−)-1-(α-naphthyl)ethylamine gave another crystalline salt, m.p. 101–104°, $[\alpha]_D^{22}-29.7°$ ($CHCl_3$), which yielded (−)-**2a**, $[\alpha]_D^{21}-15.0°$ (ether). The absolute configuration of (+)-**2a** was shown to be *R* by its hydrogenation to (+)-undecan-3-ol, whose stereochemistry had been determined as *S* by Levene and Rothen.[14] The optical purities of the resolved acetylenic alcohols (*R*)-(+)-**2a** and (*S*)-(−)-**2a** were determined by analyzing the diastereomeric ratio of their corresponding (*S*)-(−)-α-methoxy-α-trifluoromethylphenylacetic acid (MTPA) ester.[15] The NMR analysis of (*S*)-(−)-MTPA ester of (*R*)-(+)-**2a** in the presence of $Eu(fod)_3$ revealed the optical purity of (*R*)-(+)-**2a** to be ~90%. The GLC analysis, however, was more decisive and the optical purities of (*R*)-(+)-**2a** and (*S*)-(−)-**2a** were determined to be 92% and 93%, respectively.

The crucial ortho ester Claisen rearrangement reaction was carried out by heating (*R*)-(+)-**2a** with excess triethyl orthoacetate in the presence of a small amount of propionic acid at 110° for 7 hr to give an optically active allene (*R*)-(−)-**3**, $[\alpha]_D^{22}-47.0°$ (ether), in 88% yield. Although we were unable to directly determine the optical purity of (*R*)-(−)-**3**, the success of this chirality transfer reaction was revealed by its later conversion into (*R*, *E*)-(−)-**1** with optical rotatory power greater than that of the natural pheromone.

The remaining problems are the one-carbon elongation of the carbon chain and the introduction of a double bond α to the ester group. For the purpose of one-carbon homologation, the ester (*R*)-(−)-**3** was reduced with diisobutylaluminum hydride to give an allenic alcohol (*R*)-(−)-**4a**, $[\alpha]_D^{24}-66.3°$ (ether), in 77% yield.‡ The corresponding tosylate (*R*)-**4b** was treated with NaCN in DMSO to give a nitrile (*R*)-**5**. Alkaline hydrolysis of (*R*)-**5** yielded a carboxylic acid (*R*)-**6a**, which was esterified with CH_2N_2 to give (*R*)-(−)-**6b**, $[\alpha]_D^{22}-63.3°$ (n-hexane). Pirkle's (*R*)-(−)-**6b** was reported to exhibit $[\alpha]_D$ value of −45.0° (n-hexane).[9]

Introduction of the third double bond was achieved as

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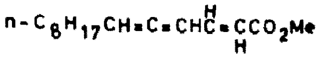
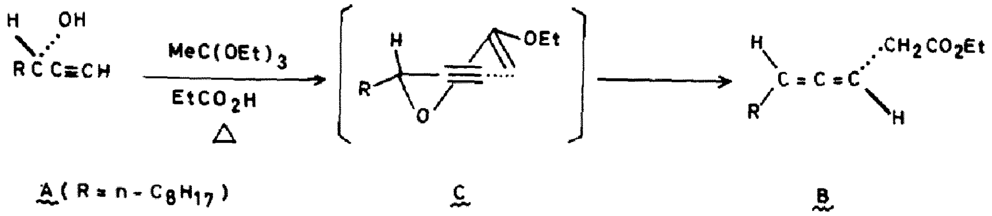
†Pheromone Synthesis—XLII. The experimental part of this work was mainly taken from the M.Sc. thesis of T.N. (March 1980, Present address: Institute of Physical and Chemical Research, Wako-shi, Saitama 351). This work was presented by K.M. as a part of his lectures at the Korea–Japan Joint Symposium on Organic Reactions and Synthethes in Seoul, Korea (26 April 1980) and at the International Conference on Regulation of Insect Development and Behaviour in Karpacz, Poland (23 June 1980). Part XLI, K. Mori, *Tetrahedron* T-J 1326 (1981).

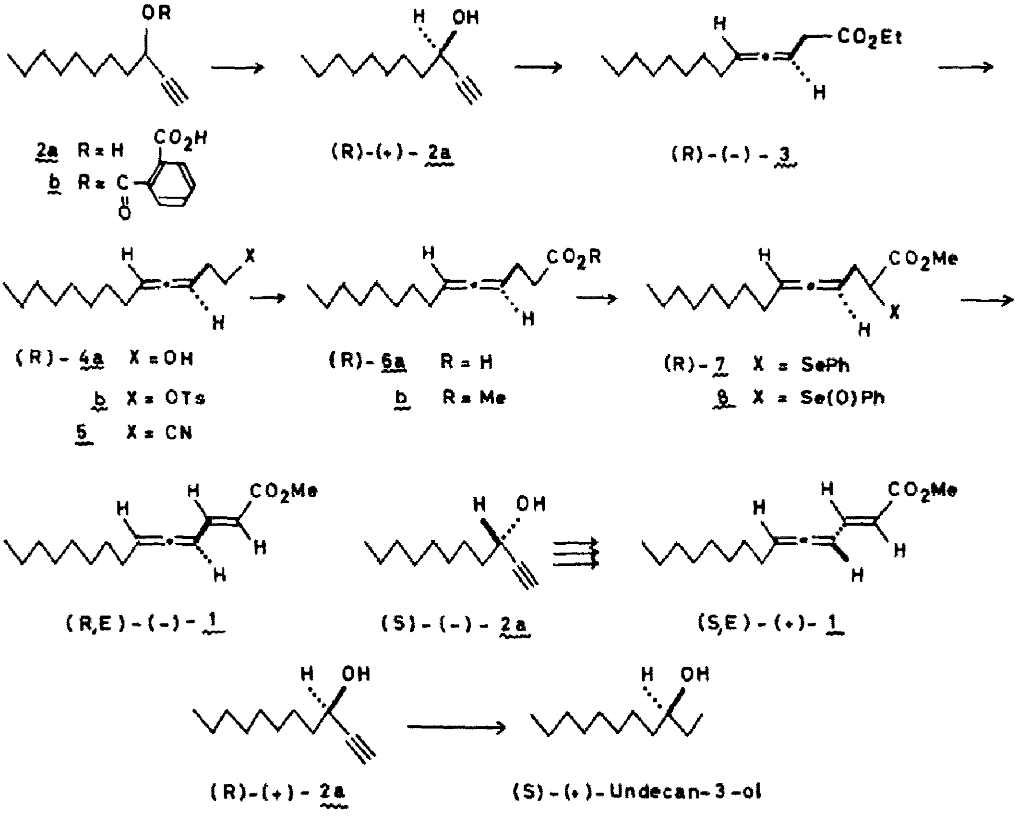
‡Neither MTPA ester method nor chiral shift reagent method was successful in establishing the optical purity of this allenic alcohol **4a**.



$n\text{-}C_8H_{17}CH{=}C{=}CH\overset{H}{C}{=}\underset{H}{C}CO_2Me$

1





described previously by others[6,9] utilizing organoselenium chemistry.[14] α-Phenylselenation of the ester **6b** yielded an α-phenylseleno ester **7**. This was treated with NaIO$_4$ to give a selenoxide **8**, which smoothly gave the desired final product (*R*, *E*)-(−)-**1**, $[\alpha]_D^{23}$ −162°(n-hexane). The spectral data (IR and NMR) of our allenic ester (*R*, *E*)-(−)-**1** were in excellent agreement with those reported previously for the natural and synthetic pheromones.[1-3,6,9] In the same manner (*S*)-(−)-**2a** yielded (*S*, *E*)-(+)-**1**, $[\alpha]_D^{22}$ + 160° (n-hexane).

The natural pheromone is known to be levorotatory. Its absolute configuration is therefore *R* as proposed by Pirkle and Boeder.[9] Our synthetic pheromone (*R*, *E*)-(−)-**1**, $[\alpha]_D^{23}$ −162° (n-hexane), has 127% the rotatory power of the naturally occurring material with $[\alpha]_D^{23}$ −128° (n-hexane). Since our starting material (*R*)-(+)-**2a** is of 92% optical purity, the $[\alpha]_D$ value of optically pure (*R*, *E*)-(−)-**1** should be no less than −176°, which is 137.5% the rotatory power of the natural pheromone. This suggests the possibility of chemical and/or enantiomeric heterogeneity of the natural pheromone which can only be clarified after its reisolation from the insect. Pirkle's synthetic (*R*, *E*)-(−)-**1** showed $[\alpha]_D$ value of only −98.3° (n-hexane), which is 77% the rotatory power of the natural pheromone or 61% the rotatory power of our synthetic (*R*, *E*)-(−)-**1**. This clearly manifests the superiority of the ortho ester Claisen rearrangement to S$_N$2′-type substitution with an organocopper reagent in generating chiral allenes.

In conclusion we were able to synthesize both enantiomers of the dried bean beetle pheromone in high optical purity confirming the *R*-configuration of the levorotatory natural pheromone. The bioassay of our products is under way by Prof. H. Z. Levinson of Max-Planck-Institut für Verhaltensphysiologie, Seewiesen.

EXPERIMENTAL

All b.ps and m.ps were uncorrected. IR spectra refer to films unless otherwise specified and were determined on a Jasco IRA-1 spectrometer. NMR spectra were recorded at 60 MHz with TMS as an internal standard on a Hitachi R-24A spectrometer. Optical rotations were measured on a Jasco DIP-4 polarimeter. Glc analyses were performed on a Yanaco G 80 or on a Yanaco G 180 gas chromatographs.

(±)-1-*Undecyn-3-ol hemiphthalate*(±)-**2b**. A soln of **2a** (111 g) and phthalic anhydride (127 g) in dry pyridine (170 ml) was stirred at 30° for 2 days. This was poured into cooled 2N HCl (1500 ml). The pH of the mixture was adjusted to <4 by the dropwise addition of conc. HCl. Then it was extracted with ether. The ether soln was cooled and shaken with N-NH_3 aq (2500 ml). The aq layer was separated and the ether layer was washed with a small amount of N-NH_3 aq. The combined aq layer was acidified with conc. HCl and extracted with ether. The ether soln was washed with water and brine, dried ($MgSO_4$) and concentrated *in vacuo* to give crude (±)-**2b** (193 g, 92%), ν_{max} 3260 (s), 2900 (s), 2830 (s), 2640 (m), 2510 (m), 2100 (w), 1730 (s), 1695 (s), 1590 (m), 1570 (m), 1485 (m), 1450 (m), 1410 (s), 1370 (m), 1285 (s), 1260 (s), 1160 (w), 1140 (m), 1120 (s), 1070 (s), 950 (m, br), 790 (m), 740 (m) cm^{-1}. This was employed for the next step without further purification.

Optical resolution of (±)-**2b**

(*a*) *Formation of the amine-salt.* (*R*)-(+)-1-(α-Naphthyl)ethylamine (Sumitomo Chemical Co., ~98% optical purity, 100 g) was gradually added to a stirred and cooled soln of (±)-**2b** (219 g) in MeOH (400 ml). The stirring was discontinued after the addition and the soln was left to stand overnight at room temp. The separated crystals were collected on a filter and washed with n-hexane–ether (1:1). The amine-salt was recrystallized several times from MeOH–ether until its specific rotation became constant. Thus 62.2 g (37%) of pure amine salt [(*R*)-half ester +(*R*)-amine] was obtained, m.p. 102–106°; $[\alpha]_D^{22}$ +29.3° (c = 1.01, $CHCl_3$); ν_{max} (nujol) 3340 (m), 2960 (s, br), 2720 (m, br), 2560 (w), 2320 (w), 1990 (w), 1960 (w), 1740 (m), 1640 (s, br), 1610 (m), 1590 (w), 1570 (w), 1540 (m), 1480 (s), 1430 (m), 1410 (m), 1390 (m), 1380 (m), 1310 (m), 1280 (s), 1190 (w), 1180 (w), 1170 (w), 1160 (w), 1150 (m), 1120 (w), 1080 (m), 1030 (w), 1010 (w), 980 (w), 900 (w), 870 (w), 850 (w), 830 (w), 810 (m), 790 (m), 770 (m), 750 (w), 730 (w), 720 (w), 710 (w), 680 (w), 660 (w) cm^{-1}. (Found: C, 76.41; H, 7.71; N, 2.88. Calc. for $C_{31}H_{37}O_4N$: C, 76.35; H, 7.65; N, 2.87%). The mother liquors during the course of preparation of pure (*R*)-half ester-(*R*)-amine salt were combined and acidified to give **2b** (184 g) enriched in (*S*)-half ester. This was dissolved in MeOH (400 ml) and mixed with (S)-(−)-1-(α-naphthyl)ethylamine (Sumitomo Chemical Co., ~98% optical purity, 50 g). The precipitated crystalline salt was repeatedly recrystallized from MeOH–ether to give pure (*S*)-half ester-(*S*)-amine salt (62.8 g, 37.4%), m.p. 101–104°; $[\alpha]_D^{22}$ −29.7° (c = 1.00, $CHCl_3$). (Found: C, 76.59; H, 7.66; N, 2.84. Calc. for $C_{31}H_{37}O_4N$: C, 76.36; H, 7.65; N, 2.87%).

(*b*) *Liberation of the resolved alcohol* **2a**. (*R*)-Half ester-(*R*)-amine salt (62.2 g) was added to a stirred and ice-cooled mixture of ether (250 ml) and 0.4N HCl (350 ml). The mixture was stirred for 3 hr under ice-cooling and extracted with ether. The ether soln was washed with a small amount of water and brine, dried ($MgSO_4$) and concentrated *in vacuo* to give (*R*)-**2b**. This was mixed under stirring and ice-cooling with ether (200 ml) and NaOH soln (15 g in 250 ml of water). The mixture was stirred overnight under ice-cooling and extracted with ether. The ether soln was washed with water and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was distilled to give 16.8 g (83% from the salt) of (*R*)-(+)-**2a**, b.p. 73°/0.06 mm, n_D^{21} 1.4454; $[\alpha]_D^{22}$ +14.8° (c = 1.04, ether); ν_{max} ~3300 (s, br), 3280 (s), 2910 (s), 2840 (s), 2120 (w), 1460 (m), 1380 (m), ~1300 (m), 1120 (w), 1020 (m), 890 (w), 730 (m), 660 (m) cm^{-1}; δ 0.90 (3H, distorted, t, J = 7 Hz), ~1.1-~2.0 (14H, br), 2.30 (1H, d, J = 2 Hz), 2.45 (1H, s), 4.25 (1H, m); glc (Column, 3% SE-30, 1.5 m × 2 mm at 100°; Carrier gas, N_2, 1.4 kg/cm^2): R_t 4.1 min. (Found: C, 78.23; H, 11.93. Calc. for $C_{11}H_{20}O$: C, 78.51; H, 11.98%). In the same manner (*S*)-half ester-(*S*)-amine salt (62.8 g) yielded 13.5 g (66.7% yield from the salt) of (*S*)-(−)-**2a**, b.p. 73°/0.06 mm, n_D^{21} 1.4457; $[\alpha]_D^{21}$ −15.0° (c = 1.02, ether). (Found: C, 78.46; H, 12.15. Calc. for $C_{11}H_{20}O$: C, 78.51; H, 11.98%).

Hydrogenation of (R)-(+)-**2a** *to* (S)-(+)-*undecan-3-ol.* 5% Pd–C (100 mg) was added to a soln of (*R*)-(+)-**2a** (100 mg) in 95% EtOH (10 ml) and the mixture was shaken under H_2. Subsequently the catalyst was filtered off and the filtrate was concentrated *in vacuo*. The residue was purified by silica gel chromatography to give 42 mg (41%) of (*S*)-(+)-undecan-3-ol, $[\alpha]_D^{22}$ +6.2° (c = 0.42, EtOH) [lit.[17] for (−)-isomer; $[\alpha]_D^{20}$-6.22° (EtOH)]; ν_{max} 3380 (s, br), 2940 (s), 2860 (s), 1470 (m), 1390 (m), 1120 (m), 1090 (m), 1050 (m), 970 (m), 930 (w), 880 (w), 730 (w) cm^{-1}; δ 0.96 (6H, distorted t, J = 6 Hz), 1.01 ~ 1.70 (16H, br), 2.05 (1H, s, –OH), 3.10 ~ 3.60 (1H, m); glc (Column, 3% SE-30, 1.5 m × 2 mm at 100°; Carrier gas, N_2, 1.0 kg/cm^2): R_t 4.8 min; MS; m/e 154 (M–H_2O).

Determination of the optical purities of (R)-(+)-**2a** *and* (S)-(−)-**2a**. The (*S*)-(−)-MTPA ester of (*R*)-(+)-**2a** ($[\alpha]_D^{22}$ +14.0° (c = 1.128, ether)) was prepared in the usual manner[15] and its NMR spectrum was measured in the presence of Eu(fod)$_3$: δ 4.65 (O*Me*, 5%), 5.08 (O*Me*, 95%). This sample was therefore of 90% optical purity. The (*S*)-(−)-MTPA esters of (±)-**2a**. (*R*)-(+)-**2a** ($[\alpha]_D^{22}$ +14.8° (c = 1.04, ether)) and (*S*)-(−)-**2a** ($[\alpha]_D^{21}$ −15.0° (c = 1.02, ether)) were prepared in the usual manner[15] and analyzed by glc. Glc of (±)-**2a** MTPA ester (Column, Thermon 1000, 30 m × 0.3 mm at 200°; Carrier gas, N_2, 40 ml/min): R_t 846 sec, 948 sec (1:1). Glc of (*R*)-(+)-**2a** MTPA ester (same conditions as above): R_t 868 sec (4%), 980 sec (96%) ∴ optical purity = 92%. Glc of (*S*)-(−)-**2a** MTPA ester (same conditions as above): R_t 796 sec (96.5%), 914 sec (3.5%) ∴ optical purity = 93%.

Ethyl 3,4-*tridecadienoate* 3

(*a*) (R)-(−)-*Isomer.* A mixture of (*R*)-(+)-**2a** (16.8 g), $EtCO_2H$ (0.4 g) and $MeC(OEt)_3$ (113.3 g) was heated at 110° for 7 hr under Ar, when no starting **2a** could be detected by glc. The mixture was concentrated *in vacuo* and the residue was diluted with ether. The ether soln was washed with $NaHCO_3$ aq and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was distilled to give 21.0 g (88%) of (*R*)-(−)-3, b.p. 95–98°/0.17 mm, n_D^{22} 1.4568; $[\alpha]_D^{22}$ −47.0° (c = 1.00, ether); ν_{max} 2940 (s, sh), 2910 (s), 2840 (s), 1970 (w), 1740 (s), 1460 (m), 1410 (w), 1370 (m), 1250 (m), 1200 (m), 1160 (s), 1040 (m), 940 (w), 870 (w), 730 (w) cm^{-1}; δ 0.90 (3H, distorted t, J = 6 Hz), 1.10 ~ 1.73 (15H, br), 1.73–2.30 (2H, m), 2.93 (2H, dd, J_1 = 6, J_2 = 4 Hz), 4.10 (2H, q, J = 7 Hz), 4.98–5.38 (2H, m); MS: m/e 238 (M^+); glc (Colunm, 3% SE-30, 1.5 m × 2 mm at 100° + 16°/min; Carrier gas, N_2, 15 ml/min): R_t 10.0 min. (Found: C, 75.43; H, 10.82. Calc. for $C_{15}H_{26}O_2$: C, 75.56; H, 11.01%).

(*b*) (S)-(+)-*Isomer.* In the same manner as above, (*S*)-(−)-**2a** (13.5 g), $EtCO_2H$ (0.4 g) and $MeC(OEt)_3$ (91.3 g) yielded 17.3 g (90%) of (*S*)-(+)-3, b.p. 95–100°/0.2 mm, n_D^{22} 1.4561; $[\alpha]_D^{22}$ +48.1° (c = 0.77, ether). The IR and NMR data were identical with those described for (*R*)-(−)-3.

3,4-*Tridecadien*-1-*ol* **4a**

(*a*) (R)-(−)-*Isomer.* A soln of (*R*)-(−)-3 (10.0 g) in dry C_6H_6 (40 ml) was added dropwise at −3 ~ 3° to a stirred and cooled soln of i-Bu_2AlH in n-hexane (25 w/v%, 50 ml) under Ar. After the addition, the mixture was stirred for 1 hr at 0°. i-PrOH (20 ml) was added dropwise to the stirred and cooled mixture at 5–10° to destroy excess i-Bu_2AlH. Then well-cooled 3N H_2SO_4 (100 ml) was added to dissolve Al as $Al_2(SO_4)_3$. More acid was added to dissolve solid, if necessary. The mixture was extracted with ether. The ether soln was washed with $NaHCO_3$ soln and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was distilled to give 6.0 g (77%) of (*R*)-(−)-**4a**, b.p. 90–93°/0.11 mm, n_D^{24} 1.4678; $[\alpha]_D^{20}$ −66.3° (c = 1.17, ether); ν_{max} ~3300 (s, br), 2900 (s), 2840 (s), 1960 (m), 1460 (s), 1380 (m), 1340 (m), 1290 (m), 1180 (m), 1110 (m), 1050 (s), 870 (m), 720 (m) cm^{-1}; δ 0.90 (3H, distorted t, J = 6 Hz), 1.10–1.70 (12H, br), 1.70 (1H, s, –OH), 1.70–2.40 (4H, m), 3.63 (2H, t, J = 7 Hz), 4.90–5.30 (2H, m); glc (Column, 3% SE-30, 1.5 m × 2 mm at 100° + 16°/min; Carrier gas, N_2, 1.2 kg/cm^2); R_t 7.6 min; MS (20 eV): m/e 55 (59%), 65 (79%), 68 (100%), 98 (70%), 196 (0.8%, M^+). (Found: C, 78.99; H, 12.29. Calc. for $C_{15}H_{24}O$: C, 79.50; H, 12.34%).

(*b*) (S)-(+)-*Isomer*. In exactly the same manner as above, (*S*)-(+)-3 (10.0 g) yielded 6.0 g (77%) of (*S*)-(+)-**4a**, b.p. 90–95°/0.1 mm, n_D^{24} 1.4674; $[\alpha]_D^{24}+66.9°$ ($c=1.20$, ether). The IR and NMR spectra were identical with those of (*R*)-(−)-3.

3,4-*Tridecadien*-1-*yl cyanide* 5

(*a*) (R)-*Isomer*. *p*-TsCl (25.0 g) was added to a stirred and ice-cooled soln of (*R*)-(−)-**4a** (10.0 g) in pyridine (150 ml). The stirring was continued for 2 hr at 0°. The mixture was poured into ice-water and extracted with ether. The ether soln was washed with $CuSO_4$ soln, water and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residual crude tosylate **4b**, ν_{max} 2900 (s), 2840 (s), 1960 (w), 1590 (m), 1490 (w), 1460 (m), 1370 (s), 1310 (w), 1300 (w), 1210 (w), 1180 (s), 1120 (w), 1100 (m), 970 (m), 910 (m), 810 (m), 765 (m), 670 (m) cm^{-1}, was dissolved in dry DMSO (70 ml) and NaCN (3.0 g) was added to the soln. The mixture was stirred 2 days at room temp under Ar. Then it was diluted with water and extracted with ether. The ether soln was washed with water and brine, dried ($MgSO_4$) and concentrated *in vacuo* to give 9.5 g (91%) of crude (*R*)-5, ν_{max} 2940 (s, sh), 2900 (s), 2840 (s), 2240 (w), 1970 (w), 1460 (m), 1380 (w), 1340 (w), 1330 (w), 870 (m), 725 (w) cm^{-1}; δ 0.90 (3H, distorted t, J = 6 Hz), 1.13–1.75 (12H, br), 1.75–2.70 (6H, m), 4.90–5.50 (2H, m). This was employed for the next step without further purification.

(*b*) (S)-*Isomer*. In the same manner as above, (*S*)-(+)-**4a** (6.0 g) yielded 5.3 g (84%) of (*S*)-5.

Methyl 4,5-tetradecadienoate 6b

(*a*) (R)-(−)-*Isomer*. A mixture of (*R*)-5 (9.5 g), 95% EtOH (130 ml) and NaOH soln (30 g in 40 ml water) was stirred and heated under reflux overnight. The mixture was concentrated *in vacuo* and the residue was diluted with water. The aq soln was extracted with ether to remove neutral impurities. The aq layer was acidified with conc. HCl to pH 2 and extracted with ether. The ether soln was washed with water and brine, dried ($MgSO_4$) and concentrated *in vacuo* to give 9.0 g of crude (*R*)-**6a**, ν_{max} ~ 3000 (m, br) 2900 (s), 2840 (s), ~2640 (m), 1960 (w), 1710 (s), 1430 (m, br), 1280 (m), 1250 (m), 1210 (m), 1170 (w), 930 (w, br), 870 (w) cm^{-1}. This was dissolved in ether and treated with CH_2N_2 in ether prepared from 25 g of N-nitroso-N-methylurea. The ice-cooled ether soln was stirred for 5 min and treated with a small amount of AcOH to destroy excess CH_2N_2. The ether soln was washed with $NaHCO_3$ soln and brine, dried ($MgSO_4$) and concentrated *in vacuo* to give 10.5 g of crude (*R*)-**6b**. This was chromatographed over silica gel (Mallinckrodt SILICAR CC-7, 105 g). Elution with n-hexane-ether 1:0–20:1 gave (*R*)-**6b**. This was distilled to give 7.75 g (64.0% from (*R*)-(−)-**4a**) of (*R*)-(−)-**6b**, b.p. 118–122°/0.83 mm, n_D^{22} 1.4588; $[\alpha]_D^{22}-63.3°$ ($c=2.07$, *n*-hexane); ν_{max} 2940 (s, sh), 2910 (s), 2840 (s), 1965 (w), 1745 (s), 1460 (m, sh), 1435 (m), 1360 (m), 1340 (m), 1300 (m), 1255 (m), 1230 (m), 1200 (m), 1160 (s), 1050 (w), 1020 (w), 990 (w), 870 (m), 720 (w) cm^{-1}; δ 0.90 (3H, distorted t, J = 6 Hz), ~1.27 (12H, br), 1.65–2.10 (2H, m), 2.10–2.50 (4H, m), 3.59 (3H, s), 4.80–5.35 (2H, m); glc (Column, Thermon 1000, 30 m × 0.3 mm at 162°; Carrier gas, N_2, 35 ml/min): R_t 10.9 min (single peak). (Found: C, 75.63; H, 10.87. Calc. for $C_{15}H_{26}O_2$: C, 75.57; H, 10.99%).

(*b*) (S)-(+)-*Isomer*. In the same manner as described above, (*S*)-5, (5.3 g) yielded 2.61 g (35.8% from (*S*)-(+)-**4a**) of (*S*)-(+)-**6b**, b.p. 129–132°/2.3 mm, n_D^{22} 1.4589; $[\alpha]_D^{22}+63.3°$ ($c=2.17$, *n*-hexane); glc (Column, Thermon 1000, 30 m × 0.3 mm at 162°; Carrier gas, N_2, 35 ml/min): R_t 11.0 min (single peak). The IR and NMR spectra were identical with those of (*R*)-(−)-**6b**.

Methyl 2-phenylseleno-4,5-tetradecadienoate 7

(*a*) (R)-*Isomer*. A soln of i-Pr_2NLi was prepared by the addition of n-BuLi in n-hexane (1.67N, 3.77 ml) to a stirred and cooled soln of i-Pr_2NH (2 ml) in dry THF (1 ml) at −65 to −53° under Ar. The mixture was stirred for 30 min at −65° after the addition. To this was added (*R*)-(−)-**6b** (500 mg) in dry THF (2 ml) with stirring and cooling at −65 to −63°. The stirring was continued for 30 min at −65°. Subsequently a soln of PhSeSePh (918 mg) in dry THF (2 ml) was added dropwise to the stirred soln at −65 to −60°. After stirring for 1 hr, the dry ice-acetone bath was removed and sat NH_4Cl aq (5 ml) was added dropwise to the mixture. Then it was extracted with ether. The ether soln was washed with Na_2CO_3 aq and brine, dried ($MgSO_4$) and concentrated *in vacuo* to give 1.35 g of crude **7**. This was chromatographed over silica gel (Mallinckrodt SILICAR CC-7, 35 g). Elution with *n*-hexane gave 394 mg of pure (*R*)-7 and 440 mg of a mixture of (*R*)-**6b** and (*R*)-7. Pure (*R*)-7 showed the following IR spectrum: ν_{max} 3040 (w), 2910 (s), 2840 (s), 1965 (w), 1730 (s), 1570 (w), 1470 (m), 1455 (m), 1430 (s), 1380 (w), 1340 (m), 1300 (m), 1270 (m), 1250 (m), 1230 (s), 1190 (m), 1160 (s), 1140 (m), 1065 (w), 1030 (m), 1020 (m), 1000 (w), 970 (w), 910 (w), 870 (m), 840 (w), 740 (s), 695 (m) cm^{-1}.

(*b*) (S)-*Isomer*. In the same manner as above (*S*)-(+)-**6b** (500 mg) yielded 394 mg of (*S*)-7 and 430 mg of a mixture of (*S*)-**6b** and (*S*)-7. (*S*)-7.

Methyl (E)-2,4,5-*tetradecatrienoate* 1

(*a*) (R, E)-(−)-*Isomer*. A soln of $NaIO_4$ (536 mg) in hot water (3 ml) was added to a soln of (*R*)-7 (394 mg) in THF (7 ml). The mixture was stirred for 10 hr at room temp and diluted with ether. The organic layer was separated and the aq layer was extracted with ether. The combined organic soln was washed with Na_2CO_3 soln and brine, dried (Na_2SO_4) and concentrated *in vacuo* to give 370 mg of crude (*R*, *E*)-1. This was chromatographed over silica gel (Mallinckrodt SILICAR CC-7, 8 g). Elution with n-hexane yielded 209 mg (42.1% from (*R*)-**6b**) of pure (*R*, *E*)-(−)-1, $[\alpha]_D^{23}-162°$ ($c=0.95$, n-hexane); ν_{max} 2940 (s, sh), 2910 (s), 2840 (s), 1945 (m), 1720 (s), 1630 (s), 1460 (m), 1435 (m), 1410 (w), 1380 (w), 1330 (m, sh), 1310 (s), 1270 (s), 1245 (s), 1210 (w), 1190 (m), 1180 (s), 1140 (s), 1120 (m), 1090 (w), 1035 (m), 1015 (w), 980 (m), 880 (m), 855 (m), 760 (w), 720 (w), 700 (w) cm^{-1}; δ 0.89 (3H, distorted t, J = 6 Hz), ~1.28 (12H, br), 1.70–2.38 (2H, m), 3.63 (3H, s), 5.13–6.05 (3H, m), 7.06 (1H, dd, $J_1=15$, $J_2=10$ Hz); glc (Yanaco 550F; Column, 3% SE-30, 1.5 m × 2 mm at 140°; Carrier gas, N_2, 1.2 kg/cm^2): R_t 7.5 min (98.4%), impurities at 0.5 min (0.9%) and 0.85 min (0.6%).

(*b*) (S, E)-(+)-*Isomer*. In the same manner as described above, (*S*)-7 (394 mg) yielded 196 mg (39.5% from (*S*)-**6b**) of pure (*S*, *E*)-(+)-1, $[\alpha]_D^{22}+160°$ ($c=0.75$, n-hexane); glc (Yanaco 550F; Column, 3% SE-30, 1.5 m × 2 mm at 140°; Carrier gas, N_2, 1.2 kg/cm^2): R_t 7.2 min (99.2%), impurities at 0.5 min (0.4%) and 0.8 min (0.4%).

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