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SYNTHESIS OF THE OPTICALLY ACTIVE FORMS OF 4,10-DIHYDROXY-1,7-DIOXASPIRO[5.5]UNDECANE AND THEIR CONVERSION TO THE ENANTIOMERS OF 1,7-DIOXASPIRO[5.5]UNDECANE, THE OLIVE FLY PHEROMONE†

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Abstract—Both the enantiomers of 1,7-dioxaspiro[5.5]undecane, the major component of the pheromone of the olive fly (*Dacus oleae*), were synthesized from (*S*)-malic acid.

The olive fruit fly, *Dacus oleae* Gmelin, is the major pest of olive in Mediterranean countries such as Greece, Israel, Italy and Spain. Haniotakis was the first to show that the female of this species produces a pheromone that attracts males.[1] Subsequently Rossi claimed that (*Z*)-6-nonen-1-ol was active as an attractant.[2] The claim, however, was later challenged by Baker, Francke and their respective co-workers.[3] They found 1,7-dioxaspiro[5.5]undecane **1** to be the major component of the sex pheromone of the olive fly.[3] The proposed structure **1** was confirmed by the synthesis of its racemate, which was active as an attractant against the olive fly.[3,4] The spiroacetal **1** was also obtained as a minor component of the secretion of male Tephritid fruit fly, *Dacus cucumis*.[5] Nothing is known, however, concerning the absolute configuration of the natural pheromone itself. We therefore became interested in synthesizing both the enantiomers of **1** so as to provide reference samples for the determination of the stereochemistry of the natural pheromone. This paper describes the full account of our synthesis of the enantiomers of **1** *via* 4,10-dihydroxy-1,7-dioxaspiro[5.5]undecane **3a**.[6] At the time when we began this work, only a synthesis of (*R*)-spirobi-1,4-dioxane from D-fructose had been recorded.[7] After the completion of the present work, Redlich and Francke preliminarily reported the synthesis of both the enantiomers of **1** starting from D-glucose.[8]

1,7-Dioxaspiro[5.5]undecane **1** is the proto-type of several spiroacetals isolated from insects,[9] fungi,[10] and bacteria.[11] In the case of the substituted spiroacetals such as 2,8-dimethyl-1,7-dioxaspiro-[5.5]undecane **2**, its stable conformation is that which is depicted as **2** with two equatorial Me groups.[12] The absolute configuration of its spiro carbon atom is fixed due to the oxygen anomeric effect.[13] It therefore should be possible to synthesize the enantiomers of **1**, if one can temporarily attach substituents on the tetrahydropyranyl rings to control the stereochemistry at the spiro center. The substituent must be removed readily without causing any racemization at the spiro center. As such a substituent we chose an OH group, whose reductive removal is a well-established process. Consequently, (4*S*,6*S*,10*S*)-4,10-dihydroxy-1,7-dioxaspiro[5.5]undecane **3a** and its antipode were the key-intermediates in the present synthesis as shown in Fig. 1. An immediate precursor of **3a** must be a tetrahydroxy ketone **14**, which could be prepared from (*S*)-(−)-malic acid **4a** *via* **8a**.

Our conversion of the readily available (*S*)-(−)-**4a** to the dihydroxy spiroacetal **3a** is shown in Fig. 2. The natural enantiomer of malic acid **4a** was treated successively with AcCl followed by EtOH to give a known half ester **4b** after chromatographic purification.[14] Reduction of **4b** with $BH_3 \cdot THF$ yielded **5a**. To obtain **6**, **5a** was submitted to the ester-exchange with NaOEt/EtOH to give **5b** contaminated with a γ-lactone **7a**. Treatment of the crude **5b** with 2,2-dimethoxypropane and TsOH gave **5d**, which was contaminated with a considerable amount of **7b** and therefore unsuitable for further manipulation. The successful preparation of **6** was accomplished as follows. Firstly, protection of the primary OH group of **5a** was effected with 2-methoxypropene and PPTS to give **5c**. Then treatment of **5c** with NaOEt/EtOH gave **5d**, which gradually isomerized to **6** during the storage. Therefore without isolation, **5d** was treated with a small amount of $BF_3 \cdot Et_2O$ in ether to give **6**. An attempt to isolate **6** resulted in a poor yield owing to the high volatility of **6**. To circumvent this, the reaction mixture containing **6** and $BF_3 \cdot Et_2O$ in ether was neutralized with solid $NaHCO_3$ and added to LAH suspension in ether to give **8a**, which could be isolated in a good yield. Conventional tosylation of **8a** gave crystalline **8b**, which gave an iodide **9** upon treatment with NaI in acetone in the presence of $NaHCO_3$. The overall yield of **9** from **4a** was 35.9%. Alkylation of 7,8-dimethyl-1,5-

† Pheromone Synthesis—74. Part 73, K. Mori, M. Kato and S. Kuwahara, *Liebigs Ann. Chem.* (1985), in press. This work was presented by K.M. as a part of his lecture at XVIIth International Congress of Entomology, Hamburg, F.R.G. (August 1984) and at the International Symposium on Recent Advances in the Chemistry of Insect Control, Cambridge, U.K. (September 1984). The chemical experimental part of this work was taken from the doctoral dissertation of T.U. The X-ray crystallographic work was done by K.Y. and M.M.

‡ Research Fellow on leave from Sumitomo Chemical Co., Ltd. (1981–1983).

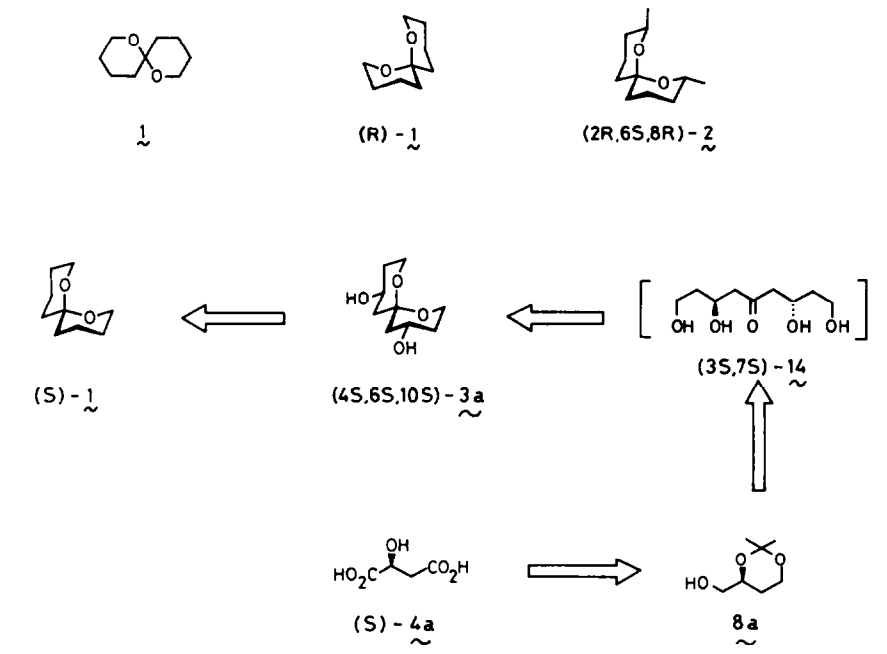

Fig. 1. Synthetic plan.

dihydro-2,4-benzodithiepin[15] with **9** using n-BuLi as the base gave **10** in 60% yield. It should be added that the alkylation of the conventional Corey–Seebach's 1,3-dithiane[16] with **9** using n-BuLi as the base gave the alkylation product in only 12.6% yield. Further alkylation of **10** with **9** gave **11**. Treatment of **11** with $CuCl_2 \cdot 2H_2O$ and CuO in aq acetone under reflux[17] gave the key-intermediate (4*S*,6*S*,10*S*)-**3a**, m.p. 153–154°; $[\alpha]_D^{21.5} + 121.4°$ (acetone), as a single crystalline product in 28.7% overall yield from **9**. The depicted structure **3a** was confirmed by an X-ray analysis. The structure was solved by MULTAN 11/82 with the final agreement values of $R = 0.033$ and $R_w = 0.051$.[18] The ORTEP computer drawing of (4*S*,6*S*,10*S*)-**3a** is shown in Fig. 3a. The known (*S*)-configuration at C-4 and C-10 enabled us to assign (*S*)-configuration to the spiro center at C-6. The crystal structure of (4*S*,6*S*,10*S*)-**3a** is shown in Fig. 3b. The OH groups of (4*S*,6*S*,10*S*)-**3a** participate in intermolecular hydrogen bonds [O(12)—H(12) . . . O(13) = 2.708(3) and O(13)—H(13) . . . O(12) = 2.775(3) Å]. The high m.p. of the crystal must be due to this intermolecular hydrogen bonding. The optical purity of (4*S*,6*S*,10*S*)-**3a** was estimated to be 100% by the HPLC analysis of the corresponding bis-MTPA ester **3b**.

The next task was to find out a proper condition for the successful deoxygenation of (4*S*,6*S*,10*S*)-**3a** to (*S*)-**1**. As shown in Fig. 4, various attempts were made in vain.

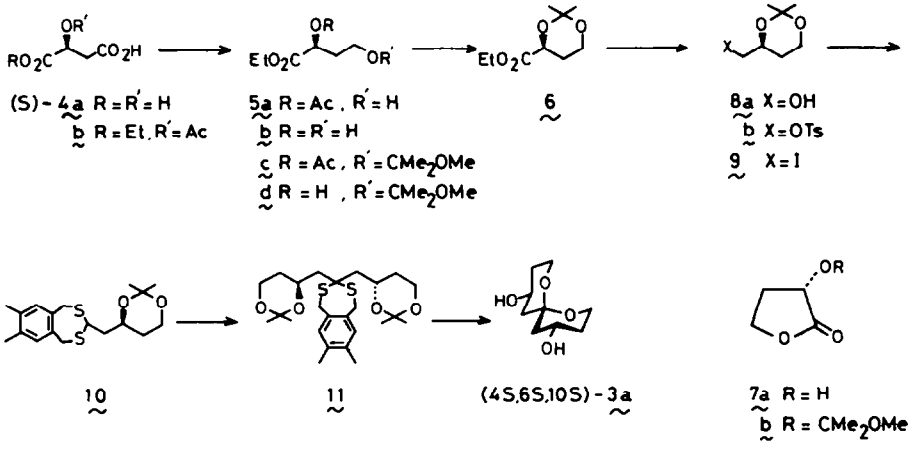

Fig. 2. Synthesis of (4*S*,6*S*,10*S*)-**3a**.

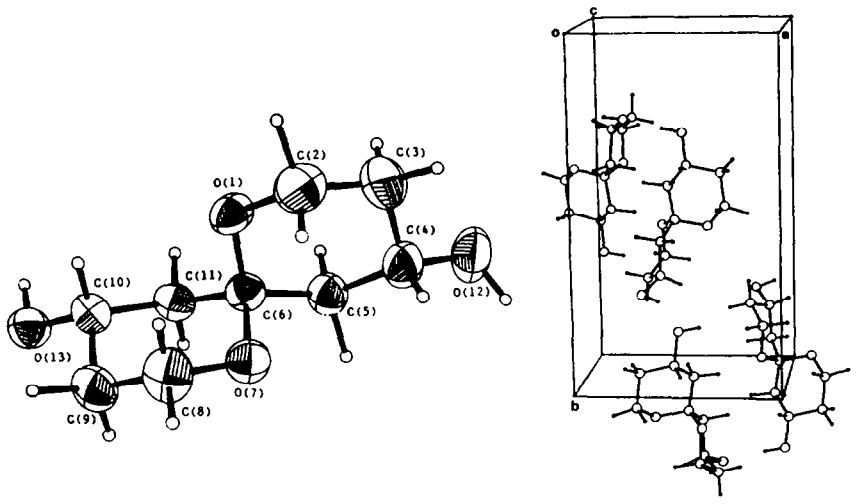

Fig. 3. a. (left) The molecular and b. (right) crystal structures of (4*S*,6*S*,10*S*)-**3a**.

First, tosylation of **3a** was followed by the LAH reduction of the resulting ditosylate **3c**, which did not work to give (*S*)-**1**. Attempted replacement of the TsO group in **3c** with LiI to yield the corresponding axial diiodide resulted in the recovery of **3c**. Radical-type deoxygenation of neither a xanthate **3d**[cf 19] nor a thiocarbonyl diimidazole derivative **3e**[cf 20] with n-Bu_3SnH was successful. We then turned our attention to the reduction of a crystalline diketone **12a** readily available by the pyridinium chlorochromate (PCC) oxidation[21] of **3a**. The attempted Wolff–Kishner reduction of **12a** with N_2H_4–KOH[cf 22] was unsuccessful. Then the diketone **12a** was converted to the corresponding bistosylhydrazone **12b** and its reduction with catecholborane[23] was attempted in vain. Attempted conversion of **12b** to a diene mixture by the Shapiro reaction with n-BuLi as the base[cf 24] was again unsuccessful.

With a hope that the axial ditosylate **13b** might be reduced successfully, the diketone **12a** was treated with $LiB(sec\text{-}Bu)_3H$ and the reaction mixture was worked up under alkaline condition to give a crystalline diol (4*R*,6*S*,10*R*)-**13a**, m.p. 57–61°; $[\alpha]_D^{23}+111.1°$ ($CHCl_3$), in 58% yield. The depicted structure **13a** with two axial OH groups was supported by an X-ray analysis with the final agreement values of $R = 0.045$

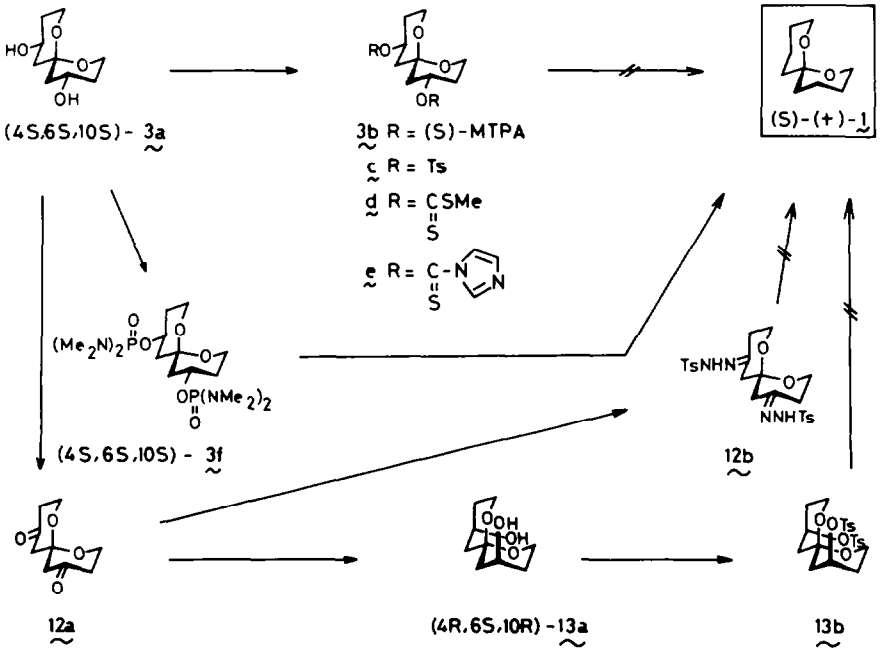

Fig. 4. Conversion of (4*S*,6*S*,10*S*)-**3a** to (*S*)-(+)-**1**.

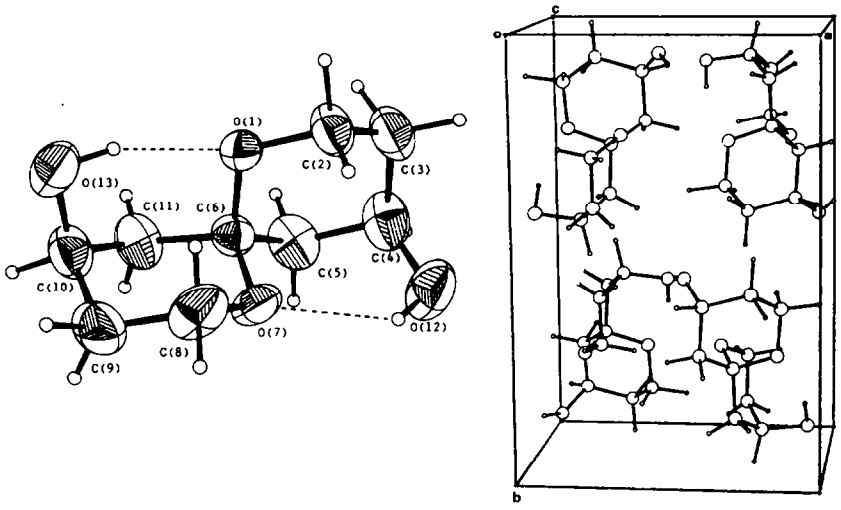

Fig. 5. a. (left) The molecular and b. (right) crystal structures of (4*R*,6*S*,10*R*)-**13a**.

and $R_w = 0.065$. The ORTEP drawing of (4*R*,6*S*,10*R*)-**13a** is shown in Fig. 5a. The crystal structure of (4*R*,6*S*,10*R*)-**13a** is shown in Fig. 5b. The OH groups in (4*R*,6*S*,10*R*)-**13a** participate in intramolecular hydrogen bonds [O(12)—H(12)...O(13) = 2.860(4) and O(13)—H(13)...O(12) = 2.837(3) Å], which stabilize the axial orientation of the OH groups. Intermolecular hydrogen bonds are not observed in the crystal of (4*R*,6*S*,10*R*)-**13a**. Hence the crystal showed the low m.p. The existence of an intramolecular hydrogen bond in a similar system was also reported by Ley.[25] The corresponding ditosylate **13b**, however, did not yield **1** upon reduction with LAH.

The final solution to this deoxygenation problem was brought about by another observation in our group[6,26] that the deoxygenation of 4-hydroxy-1,7-dioxaspiro[5.5]undecane to **1** was possible by the reduction of its N,N,N',N'-tetramethylphosphorodiamidate with $Li/EtNH_2$ according to the method of Ireland *et al.*[27] Thus, (4*S*,6*S*,10*S*)-**3a** was first treated with n-BuLi and $(Me_2N)_2POCl$ in THF–TMEDA to give **3f**. Reduction of **3f** with $Li/EtNH_2$–t-BuOH–THF gave (*S*)-1,7-dioxaspiro[5.5]undecane **1**, $[\alpha]_D^{23} + 109.3°$ (n-pentane), in 73% yield. The overall yield of (*S*)-(+)-**1** from (*S*)-(−)-malic acid **4a** was 6.1% in 13 steps.

With this success in hand, the synthesis of (*R*)-(−)-**1** was accomplished as shown in Fig. 6. The key-step of the synthesis was the facile acid-catalyzed conversion of the thermodynamically unstable (4*R*,6*S*,10*R*)-**13a** to the more stable (4*R*,6*R*,10*R*)-**3a** *via* **14**. When (4*R*,6*S*,10*R*)-**13a** was treated with dil HCl in THF, or when the reaction mixture after the reduction of **12a** with $LiB(sec\text{-}Bu)_3H$ was worked up under acid

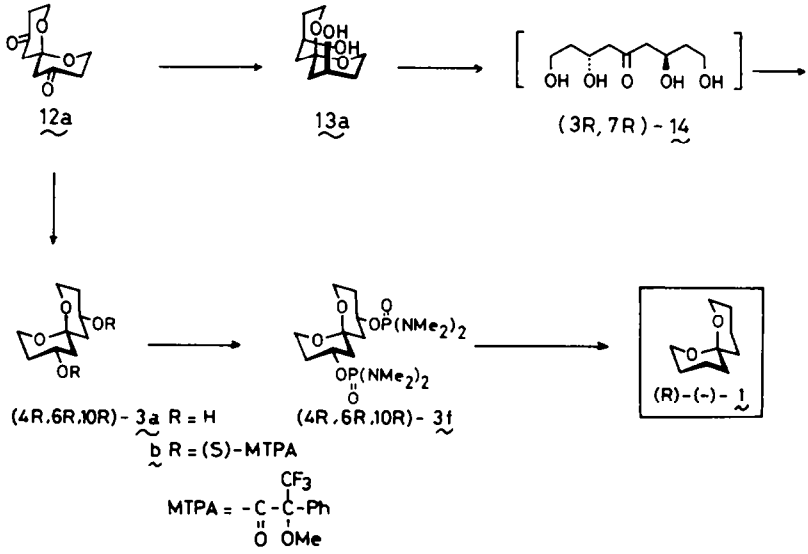

Fig. 6. Conversion of **13a** to (*R*)-(−)-**1**.

condition (pH 3), (4*R*,6*R*,10*R*)-**3a**, m.p. 150–151°; $[\alpha]_D^{23}$ −121.7° (acetone), was obtained in 60% yield, whose IR and ^{1}H-NMR spectra were identical with those of (4*S*,6*S*,10*S*)-**3a**, The optical purity of (4*R*,6*R*,10*R*)-**3a** was estimated to be 100% by the HPLC analysis of the corresponding bis-MTPA ester **3b**. Deoxygenation of (4*R*,6*R*,10*R*)-**3a** by Ireland's method proceeded without any accident *via* (4*R*,6*R*,10*R*)-**3f** to give (*R*)-**1**, $[\alpha]_D^{21}$ −121.6° (n-pentane). The overall yield of (*R*)-(−)-**1** was 21% from (4*S*,6*S*,10*S*)-**3a**, or 2.2% from (*S*)-(−)-malic acid **4a** in 15 steps. The ^{1}H- and ^{13}C-NMR (δ 19.4, 26.2, 36.6, 60.6, 95.3) data of both (*R*)- and (*S*)-**1** were in good accord with the published data by Baker *et al.*[3] The MS of (*R*)-**1** coincided with the authentic spectrum provided by Dr T. E. Bellas. Prof. V. Schurig kindly determined the optical purities of our (*R*)- and (*S*)-**1** by his complexation GLC technique, and found them to be 73% and 100%, respectively. The observed low optical purity of (*R*)-**1** might be due to the racemization during the storage of the sample prior to the GLC analysis.

In conclusion, we synthesized both the enantiomers of 1,7-dioxaspiro[5.5]undecane starting from the natural enantiomer of malic acid as the single chiral starting material. Our alternative synthesis of both (*R*)- and (*S*)-**1** *via* 4-hydroxy-1,7-dioxaspiro[5.5]undecane in 99.5 and 92% optical purities will be reported in due course.[25] Bioassay of the enantiomers of **1** from both the Hamburg[8] and the Tokyo[6] groups is now under way by Dr G. Haniotakis of Greek Atomic Energy Commission.

EXPERIMENTAL

All b.ps and m.ps were uncorrected. IR spectra were measured as film for oils and as Nujol mull for solids on a Jasco A-102 spectrometer. NMR spectra were recorded 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-140 or DIP-180 polarimeters. GLC analyses were performed on a Jeol JGC-20K, Yanaco GCG-550F or Hitachi GC-163 gas chromatographs. MS were recorded on a Hitachi RMU-6L or a Shimadzu-LKB-9000 mass spectrometers.

(S)-2-Acetoxybutanedioic acid 1-ethyl ester **4b**

(*S*)-(−)-**4a** (100 g, 0.75 mol) was added to AcCl (320 ml) and the mixture was stirred and heated under reflux at 55°. Crystals of **4a** gradually disappeared with evolution of HCl. The heating and stirring was continued for 4 hr until the evolution of HCl ceased. The soln was concentrated *in vacuo*. The residue was mixed with C_6H_6 (200 ml) and the mixture was concentrated *in vacuo* to remove C_6H_6 and AcOH. AcOH was further removed by heating and stirring at 70° *in vacuo*. After cooling to room temp, the residue was mixed with dry EtOH (100 ml) with vigorous shaking. At the end of the exothermic reaction, which sometimes needed cooling, the mixture was heated for 10 min at 70–75° and for 10 hr at 50–55°. Then the solvent was removed *in vacuo* [40–45° (bath temp)/0.5–1 mm]. The crude residue was chromatographed over SiO_2 (Merck Kieselgel 60, 1 kg) in CH_2Cl_2. Elution with CH_2Cl_2–MeOH (50:1) gave (*S*)-**4b** (110 g, 72%), m.p. 50–51°; $[\alpha]_D^{19}$ −29.6° (*c* = 1.1, EtOH) [lit.[14] m.p. 50–51°; $[\alpha]_D^{22}$ −29.1° (*c* = 10.5, EtOH)]; ν_{max} 3150 (m), 1740 (s), 1200 (br s), 1180 (s) cm^{-1}; δ ($CDCl_3$) 1.30 (3H, t, J = 7 Hz), 2.15 (3H, s), 3.00 (2H, d, J = 6 Hz), 4.30 (2H, q, J = 7 Hz), 5.55 (1H, t, J = 6 Hz), 10.90 (1H, s). For the complete separation of the unwanted regioisomer (*S*)-3-acetoxybutanedioic acid 1-ethyl ester, it is essential to pack the SiO_2 column with CH_2Cl_2. Then a soln of the mixture in CH_2Cl_2 was adsorbed on the column. Use of the CH_2Cl_2–MeOH mixture for the packing of the column resulted in non-separation of the mixture.

Ethyl (S)-2-acetoxy-4-hydroxybutanoate **5a**

A soln of BH_3·THF (1 M soln in THF, Aldrich, 700 ml, 0.7 mol) was added dropwise to a stirred and ice-cooled soln of **4b** (136 g, 0.67 mol) in dry ether (1000 ml). The mixture was stirred overnight at 35°. Then excess BH_3·THF was destroyed by careful and dropwise addition of water (400 ml) to the stirred and ice-cooled mixture. The ether soln was washed with sat $NaHCO_3$ aq, water and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was distilled to give 106.4 g (84%) of **5a**, b.p. 89.5°/0.12 mm, $n_D^{20.8}$ 1.4316; $[\alpha]_D^{20.8}$ −52.3° (*c* = 2.3, EtOH); ν_{max} 3500 (m), 1745 (s), 1220 (s) cm^{-1}; δ (CCl_4) 1.24 (3H, t, J = 7 Hz), 1.70–2.10 (2H, m), 2.09 (3H, s), 3.14 (1H, br s), 3.58 (2H, t, J = 6 Hz), 4.10 (2H, q, J = 7 Hz), 4.94 (1H, t, J = 7 Hz); MS: *m/z* 191 ($M^+ + 1$), 145 (M − EtO), 117 (M − CO_2Et).

Ethyl (S)-2-acetoxy-4-(1′,1′-dimethyl-1′-methoxy)methoxybutanoate **5c**

A trace amount of PPTS was added to a stirred and ice-cooled soln of **5a** (56.4 g, 296 mmol) in 2-methoxypropene (100 ml). The ice-bath was removed after 30 min and the mixture was stirred for 20 hr at room temp. The excess 2-methoxypropene was removed *in vacuo* and the residue was dissolved in ether. The ether soln was washed with water, dried ($MgSO_4$) and concentrated *in vacuo* to give 70.1 g (90%) of **5c**. This was directly employed in the next step without further purification. A purified analytical sample was obtained by SiO_2 chromatography, n_D^{21} 1.4248; $[\alpha]_D^{21}$ −26.5° (*c* = 2.2, $CHCl_3$); ν_{max} 1750 (s), 1375 (s), 1220 (s), 1085 (s), 1055 (s) cm^{-1}; δ (CCl_4) 1.20 (6H, s), 1.24 (3H, t, J = 7 Hz), 1.70–2.20 (2H, m), 2.05 (3H, s), 3.08 (3H, s), 3.42 (2H, t, J = 6 Hz), 4.14 (2H, q, J = 7 Hz), 4.98 (1H, t, J = 6 Hz); MS: *m/z* 231 (M − MeO), 230 (M − MeOH), 173 (M − $OCMe_2OMe$).

Ethyl (S)-2-hydroxy-4-(1′,1′-dimethyl-1′-methoxy)methoxybutanoate **5d**

(*S*)-**5c** (70.1 g, 270 mmol) was added to a stirred soln of NaOEt [from 1.0 g (43 mg atom) of Na] in dry EtOH (500 ml). The soln was stirred for 30 min at room temp. It was then poured into sat NH_4Cl aq (200 ml). The mixture was concentrated *in vacuo* to remove EtOH. The residue was diluted with water to dissolve inorganic salt and extracted with ether. The ether soln was washed with brine, dried ($MgSO_4$) and concentrated *in vacuo* to give 55.2 g (94%) of **5d**, ν_{max} 3500 (m), 1740 (s), 1215 (s), 1190 (s), 1155 (s), 1125 (s), 1080 (s), 1050 (s) cm^{-1}; δ 1.27 (6H, s), 1.30 (3H, t, J = 7 Hz), 1.70–2.20 (2H, m), 3.16 (3H, s), 3.52 (2H, t, J = 6 Hz), 4.25 (2H, q, J = 7 Hz), 4.00–4.30 (1H, overlapped with the 2H-signal at δ 4.25). This gradually isomerized to **6** and was used immediately for the next reaction.

Ethyl (S)-2,4-dihydroxybutanoate 2,4-acetonide **6**

Ten drops of $BF_3 \cdot Et_2O$ (47% in Et_2O) was added to a soln of **5d** (55 g, 0.25 mol) in dry ether (400 ml). The soln was stirred overnight at room temp. Then $NaHCO_3$ powder (5 g) was added to the soln and the mixture was stirred for 2 hr. This ether soln of **6** was filtered and the filtrate was directly employed in the next step. Isolation of **6** in another run resulted in 28% yield to give **6** as a volatile oil, ν_{max} 1760 (s), 1730 (s), 1190 (s), 1115 (s) cm^{-1}; δ 1.28 (3H, t, J = 7 Hz), 1.35 (3H, s), 1.40 (3H, s), 1.50–2.00 (2H, m), 4.12 (2H, q, J = 7 Hz), 3.70–4.45 (3H, m).

(S)-Butane-1,2,4-triol 2,4-acetonide **8a**

To a stirred and ice-cooled suspension of LAH (19 g) in dry ether (200 ml) was added a soln of **6** (prepd from 55 g of **5d** as described above) in dry ether (400 ml). The mixture was stirred for 1 hr at room temp. The excess LAH was destroyed by the successive addition of water (19 ml), 15% NaOH aq (57 ml) and water (19 ml) to the stirred and ice-cooled mixture. The stirring was continued for 3 hr at room temp. The mixture was filtered. The filter-cake was heated with CH_2Cl_2 for 30 min and filtered again. The combined filtrate was concentrated *in vacuo*. The residue was mixed with C_6H_6 and the mixture was concentrated *in vacuo* to give 30 g (82% from **5d**) of **8a**. This was

directly employed in the next step. An analytical sample was obtained by chromatographic purification over SiO_2 (elution with ether), n_D^{21} 1.4487; $[\alpha]_D^{21} + 16.3°$ (c = 3.2, $CHCl_3$); ν_{max} 3450 (s), 1385 (s), 1370 (s), 1200 (s), 1165 (s), 1100 (s) cm^{-1}; δ (CCl_4) 1.30 (3H, s), 1.42 (3H, s), 1.40–2.00 (2H, m), 3.20–3.60 (3H, m), 3.70–4.30 (3H, m); MS: m/z 147 ($M^+ + 1$), 131 ($M - Me$), 115 ($M - CH_2OH$).

(S)-*Butane*-1,2,4-*triol* 2,4-*acetonide* 1-*tosylate* **8b**

A soln of TsCl (15.6 g, 81.8 mmol) in dry C_5H_5N (20 ml) was added dropwise to a soln of **8a** (10 g, 68.4 mmol) in dry C_5H_5N (8 ml) with stirring and ice-cooling under Ar. After stirring for 3 hr at 0–5°, the mixture was poured into iced sat NH_4Cl aq (100 ml) and extracted with $CHCl_3$. The $CHCl_3$ soln was washed with sat $CuSO_4$ aq, sat $NaHCO_3$ aq and brine, dried ($MgSO_4$) and concentrated *in vacuo* to give 19.2 g (93%) of **8b**, m.p. 57.5–59°; $[\alpha]_D^{22} + 1.7°$ (c = 1.2, $CHCl_3$); ν_{max} 1600 (m), 1500 (w), 1360 (s), 1190 (s), 1170 (s), 1110 (s), 1100 (m), 990 (s), 975 (s), 875 (m), 840 (m), 835 (m), 820 (m), 810 (m) cm^{-1}; δ ($CDCl_3$) 1.28 (3H, s), 1.37 (3H, s), 1.30–1.70 (2H, m), 2.43 (3H, s), 3.60–4.30 (5H, m), 7.32 (2H, d, J = 8 Hz), 7.80 (2H, d, J = 8 Hz). (Found: C, 56.00; H, 6.70. Calc for $C_{14}H_{20}O_5S$: C, 55.97; H, 6.72%.)

(S)-1-*Iodobutane*-2,4-*diol acetonide* **9**

$NaHCO_3$ (55 g, 656 mmol) and **8b** (19.7 g, 65.6 mmol) were added to a soln of NaI (98.3 g, 656 mmol) in dry acetone (300 ml). The mixture was vigorously stirred and heated under reflux for 12 hr. It was then concentrated *in vacuo*. The residue was diluted with $CHCl_3$ and filtered. The filter-cake was washed with $CHCl_3$. The combined $CHCl_3$ soln was washed with water, 10% $Na_2S_2O_5$ aq, water and sat $NaHCO_3$ aq, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was distilled to give 15.5 g (92%) of **9**, b.p. 94–95°/9 mm, n_D^{22} 1.5114; $[\alpha]_D^{21.3} + 24.3°$ (c = 2.3, $CHCl_3$); ν_{max} 1380 (s), 1240 (s), 1195 (s), 1150 (s), 1120 (s), 1090 (s), 970 (s) cm^{-1}; δ (CCl_4) 1.30 (3H, s), 1.38 (3H, s), 1.50–1.90 (2H, m), 2.90–3.30 (2H, m), 3.60–4.20 (3H, m). (Found: C, 32.71; H, 5.17. Calc for $C_7H_{13}O_2I$: C, 32.83; H, 5.13%.) In this reaction, the vigorous stirring and a great excess of NaI were essential in realizing a good yield. Without vigorous stirring, **8b** decomposed to give butane-1,2,4-triol 1-tosylate and other unidentified products.

3-[(S)-2',4'-*Dihydroxybutyl*]-7,8-*dimethyl*-1,5-*dihydro*-2,4-*benzodithiepin* 2',4'-*acetonide* **10**

A soln of n-BuLi in n-hexane (1.5 N, 32 ml, 47.5 mmol) was added dropwise to a stirred and ice-cooled suspension of 7,8-dimethyl-1,5-dihydro-2,4-benzodithiepin (10.0 g, 47.5 mmol) in dry THF (50 ml) under Ar. After stirring for 1 hr at 0–3°, the mixture was cooled to −35°. To this was added dropwise **9** (12.2 g, 47.6 mmol). After 5 min, the reaction temp was raised to 0–3°. The stirring was continued for 30 min at 0–3° and for 1 hr at room temp. The mixture was concentrated *in vacuo* at 35°. The residue was diluted with water, neutralized with AcOH, and extracted with $CHCl_3$. The $CHCl_3$ soln was washed with sat $NaHCO_3$ aq, water and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed over SiO_2 (500 g). Elution with n-hexane–EtOAc (9:1) gave 9.63 g (60%) of **10** as a pale yellow glassy material (1.3 g of starting dithiepine was recovered), $[\alpha]_D^{21} + 23.7°$ (c = 1.1, $CHCl_3$); ν_{max} 1510 (m), 1380 (s), 1370 (s), 1270 (s), 1240 (s), 1200 (s), 1160 (s), 1125 (s), 1100 (s) cm^{-1}; δ (CCl_4) 1.33 (3H, s), 1.43 (3H, s), 1.50–2.00 (4H, m), 2.23 (6H, s), 3.86 (4H, s), 3.50–4.50 (4H, m), 6.96 (2H, s). (Found: C, 63.76; H, 7.70. Calc for $C_{18}H_{26}O_2S_2$: C, 68.86; H, 7.74%.)

3,3-*Bis*[(S)-2',4'-*dihydroxybutyl*]-7,8-*dimethyl*-1,5-*dihydro*-2,4-*benzodithiepin di*-2',4'-*acetonide* **11**

A soln of n-BuLi in n-hexane (1.5 N, 18.5 ml, 27.8 mmol) was added dropwise over 3 min to a stirred and cooled soln of **10** (9.46 g, 27.9 mmol) in THF (84 ml) at −10° under Ar. Subsequently **9** (10.7 g, 41.9 mmol) was added dropwise over 1 min. The mixture was stirred for 2 hr at 0°. It was then poured into ice-water (100 ml), neutralized with AcOH and extracted with $CHCl_3$. The $CHCl_3$ soln was washed with sat $NaHCO_3$ aq and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed over SiO_2 (400 g). Elution with n-hexane–EtOAc (9:1) gave 7.1 g (55%) of **11** (2.4 g of **9** and 2.8 g of **10** were recovered), $[\alpha]_D^{21.5} + 15.9°$ (c = 1.5, $CHCl_3$); ν_{max} 1510 (w), 1200 (s), 1165 (m), 1125 (m), 1095 (m), 970 (m) cm^{-1}; δ (CCl_4) 1.25 (6H, s), 1.35 (6H, s), 1.00–2.5 (8H, m), 2.15 (6H, s), 3.75 (4H, s), 3.80–4.30 (6H, m), 6.82 (2H, s). This was employed in the next step without further purification.

(4*S*, 6*S*, 10*S*)-(+)-4,10-*Dihydroxy*-1,7-*dioxaspiro*[5.5]*undecane* **3a**

$CuCl_2 \cdot 2H_2O$ (5.1 g, 30 mmol) and CuO (4.7 g, 60 mmol) were added to a stirred soln of **11** (7.0 g, 15 mmol) in acetone–water (99:1, 190 ml). The mixture was stirred and heated under reflux for 30 min, and filtered through Celite. The Celite layer was washed thoroughly with hot acetone. SiO_2 (30 g) was added to the acetone soln and the mixture was concentrated *in vacuo*. The SiO_2 containing **3a** was put on the top of a SiO_2 column (200 g). Elution with ether–MeOH (19:1) gave 2.46 g (87.2%) of **3a**. This was recrystallized from acetone to give pure (4*S*,6*S*,10*S*)-**3a**, m.p. 153–154° (in a sealed capillary tube. Sublimable!), $[\alpha]_D^{21.5} + 121.4°$ (c = 0.5 acetone); ν_{max} 3300 (s), 1260 (m), 1245 (m), 1180 (s), 1160 (w), 1130 (w), 1105 (m), 1080 (w), 1055 (s), 1030 (s), 980 (s), 950 (w), 940 (m), 885 (m), 860 (m), 800 (m), 760 (m) cm^{-1}; δ (acetone-d_6) 0.95–2.10 (8H, m), 3.30–4.40 (6H, m); ^{13}C-NMR (25 MHz, acetone-d_6) 36.07, 46.10, 59.31, 63.99, 99.81. (Found: C, 57.11; H, 8.53. Calc for $C_9H_{16}O_4$: C, 57.42; H, 8.58%.) The corresponding ditosylate **3c** was prepared in the conventional manner, m.p. 94–105° (dec); $[\alpha]_D^{22} + 33.4°$ (c = 1.3, $CHCl_3$). (Found: C, 56.11; H, 5.72. Calc for $C_{23}H_{28}O_8S_2$: C, 55.62; H, 5.69%.) The xanthate **3d** was obtained as an oil, $[\alpha]_D^{21} + 14.6°$ (c = 2.0, $CHCl_3$). The imidazolylthiocarbonyl derivative **3e** was an oil, $[\alpha]_D^{21} + 37.6°$ (c = 2.2, $CHCl_3$).

(S)-1,7-*Dioxaspiro*[5.5]*undecane*-4,10-*dione* **12a**

PCC (13.3 g, 62 mmol) was added to a stirred and ice-cooled suspension of (4*S*,6*S*,10*S*)-**3a** (0.7 g, 3.7 mmol) in dry CH_2Cl_2 (63 ml). The mixture was stirred vigorously for 1 hr at 5–10° and for 5 hr at room temp. Florisil (60–100 mesh, 30 g) was then added to the mixture and the stirring was continued for 30 min. The mixture was diluted with ether (100 ml) and stirred for 10 min. It was then filtered through Florisil (100 g). The column was washed with ether. The combined organic soln was concentrated *in vacuo* to give 0.59 g (86%) of **12a**. This was recrystallized from EtOH to give pure **12a**, m.p. 146.5° (in a sealed capillary tube. Sublimable!), $[\alpha]_D^{22} + 203.4°$ (c = 1.0, $CHCl_3$); ν_{max} 1724 (s), 1258 (m), 1238 (s), 1180 (m), 1154 (m), 1140 (m), 1074 (m), 1048 (s), 986 (m), 940 (m), 870 (m), 764 (m) cm^{-1}; δ (90 MHz, $CDCl_3$) 2.00–2.90 (8H, m), 3.70–4.20 (4H, m); MS: m/z 184 (M^+). (Found: C, 58.65; H, 6.72. Calc for $C_9H_{12}O_4$: C, 58.68; H, 6.58%.) The corresponding bistosylhydrazone **12b** was prepared in the usual manner, m.p. 130–131°; $[\alpha]_D^{23} + 24.1°$ (c = 1.1, MeOH). (Found: C, 52.55; H, 5.71; N, 10.35. Calc for $C_{23}H_{28}O_6N_4S_2$: C, 53.06; H, 5.42; N, 10.76%.)

(4R,6S,10R)-4,10-*Dihydroxy*-1,7-*dioxaspiro*[5.5]*undecane* **13a**

A soln of LiB(sec-Bu)$_3$H in THF (Aldrich, 1M, 9.2 ml, 9.2 mmol) was added dropwise to a stirred and cooled soln of **12a** (570 mg, 3.1 mmol) in dry THF (8 ml) at −74° under N_2. The mixture was stirred for 1 hr at −74° and for 3 hr at room temp. The gelatinous mixture was diluted with dry THF (20 ml) and stirred for 1 hr. The excess hydride was destroyed by the careful dropwise addition of 1M NaOAc aq (4 ml) to the stirred and ice-cooled mixture. NaOAc (2 g) was then added. Subsequently 30% H_2O_2 (*ca* 9 ml) was added dropwise at 3–5° until the exothermic reaction ceased. The mixture remained strongly basic. After stirring for 5 hr, the mixture was extracted with $CHCl_3$. The $CHCl_3$ soln was washed with sat $NaHCO_3$ aq and brine, dried (Na_2SO_4) and concentrated *in vacuo*. The residue was chromatographed over SiO_2 (25 g). Elution with $CHCl_3$–MeOH (19:1) gave 340 mg (58%) of **13a**.

This was recrystallized from n-hexane to give pure **13a**, m.p. 57–61°, $[\alpha]_D^{23}$ + 111.1° (*c* = 0.38, $CHCl_3$); $[\alpha]_D^{23}$ + 125.5° (*c* = 1.34, acetone); ν_{max} 3524 (s), 1240 (m), 1206 (m), 1174 (s), 1144 (s), 1104 (s), 1060 (s), 1030 (s), 1004 (s), 972 (m), 928 (m), 902 (m), 888 (m), 822 (m), 802 (s) cm^{-1}; δ (90 MHz, $CDCl_3$) 1.50–2.10 (8H, m), 3.60–4.30 (6H, m). (Found: C, 57.74; H, 8.93. Calc for $C_9H_{16}O_4$: C, 57.42; H, 8.58%.) The corresponding ditosylate **13b** was prepared in the usual manner, m.p. 97° (dec), $[\alpha]_D^{22}$ + 59.2° (*c* = 0.52, $CHCl_3$). (Found: C, 55.71; H, 5.73; S, 13.11. Calc for $C_{23}H_{28}O_8S_2$: C, 55.62; H, 5.69; S, 12.91%.)

(4S,6S,10S)-(+)-1,7-*Dioxaspiro*[5.5]*undecane*-4,10-*diol bis*-N,N,N',N'-*tetramethylphosphorodiamidate* **3f**

A soln of n-BuLi in n-hexane (1.67 N, 1.6 ml, 2.7 mmol) was added dropwise to a stirred and ice-cooled soln of **3a** (150 mg, 0.8 mmol) in dry THF–N,N,N',N'-tetramethylethylenediamine (4:1, 6 ml) under Ar. During the addition, white precipitates of the Li salt appeared. The mixture was stirred for 30 min at room temp and for 1 hr at 40°. It was then ice-cooled and to it was added $(Me_2N)_2POCl$ (1.3 ml, 8.8 mmol). The stirring was continued for 12 hr at room temp. The reaction was quenched by the addition of water (5 ml). After stirring for 30 min, the mixture was poured into sat $NaHCO_3$ aq (10 ml). It was stirred for 1 hr and extracted with $CHCl_3$. The $CHCl_3$ soln was washed with sat $NaHCO_3$ aq and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by medium pressure LC over Merck Lobar Column (Grosse B). Elution with EtOAc–MeOH (9:1) gave 296 mg (81.4%) of **3f**, n_D^{21} 1.4432; $[\alpha]_D^{23}$ + 39.9° (*c* = 0.8, $CHCl_3$); ν_{max} 1306 (m), 1228 (s), 1190 (m), 1058 (m), 1024 (s), 986 (s), 912 (s), 752 (s) cm^{-1}; δ (90 MHz, $CDCl_3$) 1.35–2.30 (8H, m), 2.58 (12H, s), 2.71 (12H, s), 3.50–3.70 (4H, m), 4.40–4.90 (2H, m). This was employed directly in the next step.

(S)-(+)-1,7-*Dioxaspiro*[5.5]*undecane* **1**

Li (91 mg, 13 mg atom) was dissolved in dry $EtNH_2$ (15 ml) at −74° under Ar. A soln of (4*S*,6*S*,10*S*)-**3f** (296 mg, 0.66 mmol) in dry THF (1 ml) and t-BuOH (0.4 g) was added dropwise to the stirred Li/$EtNH_2$ at −74°. The stirring was continued for 1 hr at −74°. The reaction was quenched with water (1 ml), and the temp was raised to room temp. The mixture was poured into water (10 ml) and extracted with n-pentane (30 ml × 4). The pentane soln was washed with water and brine, dried ($MgSO_4$) and concentrated *in vacuo* (20 mmHg) under ice-cooling. The residue was chromatographed over SiO_2 (3 g). Elution with n-pentane and n-pentane–ether (1:1) gave 74 mg (72%) of (*S*)-(+)-**1**, n_D^{21} 1.4432; $[\alpha]_D^{23}$ + 109.3° (*c* = 0.28, n-pentane); ν_{max} 2944 (s), 2872 (s), 1454 (m), 1440 (m), 1386 (m), 1372 (m), 1352 (m), 1336 (w), 1280 (m), 1256 (w), 1230 (m), 1208 (m), 1180 (m), 1110 (m), 1096 (s), 1060 (s), 1040 (s), 990 (s), 934 (m), 914 (w), 876 (m), 796 (m) cm^{-1}; ^{1}H-NMR (90 MHz, benzene-d_6) 0.60–2.30 (12H, m), 3.30–3.90 (4H, m); ^{13}C-NMR (22.4 MHz, benzene-d_6) δ 19.41, 26.19, 36.59, 60.56, 95.30; MS: *m/z* 157 (1%, M^+ + 1), 156 (16%, M^+, $C_9H_{16}O_2$ = 156), 129 (1%), 128 (11%), 127 (1%), 126 (3%), 125 (1%), 114 (1%), 112 (2%), 111 (20%), 109 (1%), 102 (5%), 101 (98%), 100 (50%), 99 (7%), 98 (100%, base peak), 97 (3%), 95 (2%), 86 (1%), 85 (22%), 84 (4%), 83 (32%), 82 (2%), 81 (1%), 79 (2%), 77 (1%), 72 (1%), 71 (6%), 70 (8%), 69 (1%), 68 (1%), 67 (7%), 66 (1%), 65 (1%), 59 (9%), 58 (3%), 44 (6%), 43 (34%), 42 (18%), 41 (72%), 40 (7%), 39 (32%), 38 (1%), 31 (7%), 30 (4%), 29 (27%), 28 (20%), 27 (37%), 26 (4%), 18 (2%), 15 (4%).

(4R,6R,10R)-(−)-4,10-*Dihydroxy*-1,7-*dioxaspiro*[5.5]*undecane* **3a**

(a) A soln of LiB(sec-Bu)$_3$H in THF (Aldrich, 1M, 10.8 ml, 11 mmol) was added dropwise to a stirred and cooled soln of **12a** (500 mg, 2.7 mmol) in dry THF (8 ml) at −74° under N_2. The mixture was stirred for 1 hr at −74° and for 3 hr at room temp. The gelatinous mixture was diluted with dry THF (20 ml) and stirred for 1 hr. The excess hydride was destroyed by the careful and dropwise addition of 1M NaOAc aq to the stirred and ice-cooled mixture. When the vigorous evolution of gas ceased, 30% H_2O_2 (*ca* 10 ml) was added dropwise to the mixture at 5–25°. The mixture was stirred for 2 hr. The pH of the mixture was *ca* 3 during this period. It was then extracted with $CHCl_3$. The $CHCl_3$ soln was washed with sat $NaHCO_3$ aq and brine, dried (Na_2SO_4) and concentrated *in vacuo*. The residue was chromatographed over SiO_2 (25 g). Elution with $CHCl_3$–MeOH (19:1) gave 308 mg (60%) of (4*R*,6*R*,10*R*)-**3a**. This was recrystallized from acetone to give pure (4*R*,6*R*,10*R*)-**3a**, m.p. 150–151° (in a sealed capillary tube. Sublimable!), $[\alpha]_D^{23}$ − 121.7° (*c* = 0.5, acetone). (Found: C, 57.73; H, 8.85. Calc for $C_9H_{16}O_4$: C, 57.42; H, 8.58%.) The spectral data of (4*R*,6*R*,10*R*)-**3a** were identical with those of (4*S*,6*S*,10*S*)-**3a**.

(b) To a soln of (4*R*,6*S*,10*R*)-**13a** (600 mg) in THF (10 ml) was added two drops of conc HCl, and the mixture was stirred for 48 hr at room temp. It was then neutralized by the addition of solid K_2CO_3 and filtered. The filtrate was concentrated *in vacuo*. The residue was recrystallized from ether to give 450 mg (75%) of (4*R*,6*R*,10*R*)-**3a**, m.p. 150–151°, $[\alpha]_D^{23.5}$ − 121.3° (*c* = 1.22, acetone). The spectral data of this sample was identical with those of (4*R*,6*R*,10*R*)-**3a** prepared by the method (a).

(4R,6R,10R)-(−)-1,7-*Dioxaspiro*[5.5]*undecane*-4,10-*diol bis*-N,N,N',N'-*tetramethylphosphorodiamidate* **3f**

In the same manner as described for (4*S*,6*S*,10*S*)-**3f**, (4*R*,6*R*,10*R*)-**3a** (140 mg, 0.74 mmol) yielded 270 mg (79.5%) of (4*R*,6*R*,10*R*)-**3f**, n_D^{21} 1.4762; $[\alpha]_D^{23}$ − 44.0° (*c* = 1.0, $CHCl_3$). The spectral data of (4*R*,6*R*,10*R*)-**3f** were identical with those of (4*S*,6*S*,10*S*)-**3f**.

(R)-(−)-1,7-*Dioxaspiro*[5.5]*undecane* **1**

In the same manner as described for the preparation of (*S*)-(+)-**1**, 270 mg (0.59 mmol) of (4*R*,6*R*,10*R*)-**3f** yielded 47.1 mg (51%) of (*R*)-(−)-**1**, n_D^{21} 1.4552; $[\alpha]_D^{23}$ − 121.6° (*c* = 0.1, n-pentane); MS: *m/z* 156 (M^+, $C_9H_{16}O_2$ = 156). The spectral data (^{1}H-NMR, ^{13}C-NMR and MS) of (*R*)-(−)-**1** were identical with those of (*S*)-(+)-**1**.

Determination of the optical purities of the enantiomers of **3a**

The bis-(*S*)-MTPA esters **3b** of (4*R*,6*R*,10*R*)- and (4*S*,6*S*,10*S*)-**3a** were prepared in the usual manner,[28] and analyzed by HPLC (Column, Nucleosil® 50–5, 25 cm × 4.6 mm; Solvent, n-hexane–THF (10:1), 1.1 ml/min; Detection at 254 nm): R_t 14.69 min [(4*S*,6*S*,10*S*)-**3b**], 19.54 min [(4*R*,6*R*,10*R*)-**3b**]. The optical purities of (4*S*,6*S*,10*S*)- and (4*R*,6*R*,10*R*)-**3b** were 100%.

Determination of optical purities of the enantiomers of **1**

The analysis was carried out by Prof. V. Schurig and will be published separately by him. GLC (Column, Ni-bis(hfb-monoterpenoate) in OV 101; Oven temp 70°; Injection temp 150°; Carrier gas, N_2, 1 atm): R_t *ca* 42.8 min [(*S*)-**1**], 44.5 min [(*R*)-**1**]. Our (*R*)-**1** was of 73% e.e. and (*S*)-**1** was of 100% e.e.

X-ray analyses of **3a** *and* **13a**

The crystals were mounted in glass capillaries. Unit-cell dimensions and orientation matrices were obtained by least-squares methods from the setting angles of 25 reflections. Intensities were collected on an Enraf-Nonius CAD 4 diffractometer at room temp. Data were corrected for Lorentz-polarization effects. Absorption corrections were not applied. The crystal data and data collection parameters are summarized in Table 1.

The structures were solved by direct methods using MULTAN 11/82.[18] All hydrogen atoms were located on difference Fourier maps. Full-matric least-squares refinement included anisotropic thermal parameters for non-hydrogen atoms as well as isotropic thermal parameters for hydrogen atoms. Convergence was reached at R = 0.033 and Rw = 0.051 for **3a** and R = 0.045 and Rw = 0.065 for **13a**.

All calculations were performed on a PDP 11/34 computer using Enraf–Nonius SDP-PLUS programs.

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Table 1. Summary of crystal data and data collection parameters

	3a	13a
formula	$C_{19}H_{16}O_4$	$C_{19}H_{16}O_4$
mol. wt.	188.23	188.23
crystal size, mm	0.10 × 0.23 × 0.33	0.30 × 0.30 × 0.50
space group	$P2_12_12_1$	$P2_12_12_1$
a, Å	8.800 (1)	9.138 (2)
b, Å	15.367 (1)	13.557 (2)
c, Å	7.496 (1)	7.731 (2)
V, Å^3	1013.7	957.7
d_{calcd}, g/cm^3	1.233	1.291
Z	4	4
diffractometer	Enraf-Nonius CAD 4	
monochrometer	graphite	
radiation	Cu Kα	Mo Kα
scan type	$\omega/2\theta$	$\omega/2\theta$
$2\theta_{max}$, deg	140	50
no. of unique data	1135	1003
no. of data used in refinement	923 ($I > 3\sigma(I)$)	740 ($I > 3\sigma(I)$)
final R	0.033	0.045
final Rw	0.051	0.065

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