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Synthesis and Resolution of the Enantiomeric *trans,trans*-Spiro[5.5]undecane-1,7-diols and Determination of their Absolute Configuration; (*S*)-(–)-Spiro[5.5]undecane-1,7-dione

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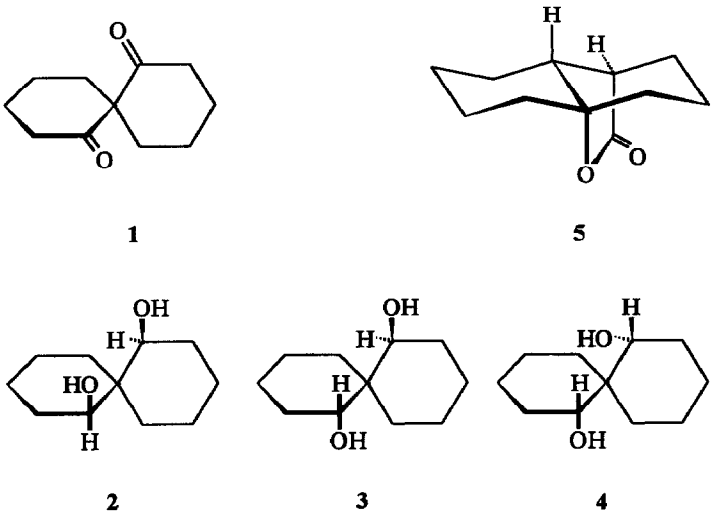
Abstract: Syntheses of spiro[5.5]undecane-1,7-dione (**1**) and the three diastereomeric spiro[5.5]undecane-1,7-diols (**2**, **3** and **4**) with *cis,cis*-, *cis,trans*- and *trans,trans*-configuration are described. The structure of the lactone side product (±)-**5** was elucidated by NMR spectroscopy. Resolution of the *trans,trans*-diol (±)-**4** was accomplished via the diastereomeric (1*S*,4*R*)-camphanoates (–)-**6** and (+)-**7** to give (–)-**4** and (+)-**4**. Oxidation of (–)-**4** by the method of Swern yielded the optically active dione (–)-**1**. An X-ray crystal structure of (–)-**6** allowed assignment of the absolute configuration of (1*R*,6*S*,7*R*)-(–)-**4** and hence of (*S*)-(–)-**1**. The chiroptical properties of the bis(4-bromobenzoate) (–)-**8** derived from (–)-**4** also prove the (1*R*,6*S*,7*R*)-configuration.

There exist several methods to prepare optically active spiro[4.4]nonane-1,6-dione[1] and the corresponding diastereomeric diols[1]. The *cis,cis*-diol has been used as a chiral auxiliary ligand in metal catalyzed asymmetric transformations[2]. The homologous (±)-spiro[5.5]undecane-1,7-dione [(±)-**1**] has been prepared only once[3] in very low yield and is not well characterized. There is no description of the three diastereomeric spiro[5.5]undecane-1,7-diols (**2**, **3** and **4**) with *cis,cis*-, *cis,trans*- and *trans,trans*-configuration in the literature. We have repeated the synthesis of (±)-**1** from 5-(2-oxocyclohexyl)-pentanoic acid by acid catalyzed Claisen condensation (cp. lit.[1b]) and could improve the yield of (±)-**1** to 26 % using amberlyst 15, a strongly acidic ion exchanger, as the catalyst in boiling toluene. The ^{13}C NMR spectrum of the dione **1** shows six signals in accordance with its rotational symmetric C_2 structure. As a side product the lactone (±)-**5**[4] of 4a-hydroxy-(4a*r*,8a*t*)-decahydro-[1*c*]naphthoic acid was isolated in 7 % yield. Its structure could be deduced by detailed analysis of the NMR spectra. This lactone (±)-**5** with mp 76.6—77.6 °C has already been prepared by Nazarov et al.[4] and differs from the diastereomeric lactone with mp 73—74 °C described by Stork et al.[5] When we used 1-naphthalene sulphonic acid in boiling xylene according to lit.[3] to effect this reaction only 9 % of (±)-**1** and 12 % of the lactone (±)-**5** could be isolated.[6]



Scheme 1

Reduction of the dione **1** with $LiAlH_4$ in diethyl ether afforded the diastereomeric diols **2**, **3** and **4** in the approximate ratio 1 : 1 : 2 and their structures could be deduced from their properties. The diol **4** can be separated from the diols **2** and **3** by column chromatography. The less polar *cis,cis*-diol **2** and *cis,trans*-diol **3** form isopropylidene acetals by treatment with 2-methoxypropene. These acetals can be separated by chromatography and they afford the diols **2** and **3** after methanolysis. In the more polar *trans,trans*-diol **4** no intramolecular acetal can be formed, because the hydroxy groups are too far apart. The ^{13}C NMR spectrum of the C_2 symmetric diol **2** shows 6 signals while the ^{13}C NMR of diol **3** shows 11 signals in accordance with its asymmetric C_1 structure. These observations determine the configurations of the three diols **2**, **3** and **4** unequivocally.

The *trans,trans*-diol (±)-**4** was esterified with (1*S*,4*R*)-(–)-camphanoyl chloride[7,8] to yield the diastereomeric esters (–)-**6** and (+)-**7**. They could be separated by column chromatography on silica gel (R_f 0.40 and 0.26) with CH_2Cl_2/AcOEt (19 : 1) as eluant. The more polar biscamphanoate (–)-**6** is practically insoluble in cyclohexane and can therefore easily be isolated pure from the ester mixture by extraction with hot cyclohexane and recrystallization of the insoluble residue from cyclohexane/AcOEt. The ^{13}C NMR spectra of **6** and **7** show specific differences, therefore both derivatives are diastereomerically pure.

An X-ray crystal structure[9] was obtained from the more polar biscamphanoate (–)-**6** (Figure 1). The *trans,trans*-configuration of the acyloxy groups in the spirocyclane moiety is clearly seen in the figure. Because the absolute configuration in the (1*S*,4*R*)-camphanoyl parts of the bisester is known, the (1*R*,6*S*,7*R*)-configuration for the spiro[5.5]undecane-1,7-diol part can be deduced. The two camphanoyloxy groups occupy equatorial positions in the chair,chair-conformation of the spirocyclane system. The ester functions themselves are in an antiplanar arrangement and the C-O bonds in 1,7-position define a torsion angle of ca. – 110°. It can be assumed that other esters e. g. bis(4-bromobenzoates) will arrange predominantly in this very stable conformation.

X-ray crystal structure of (−)-**6**

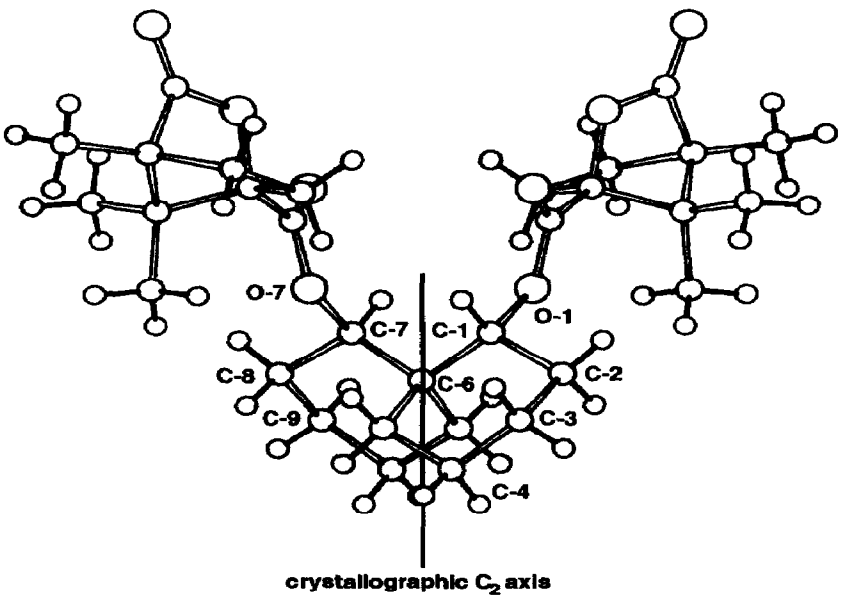
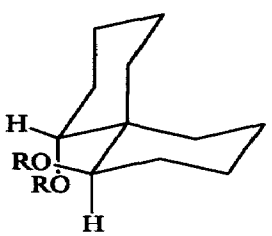
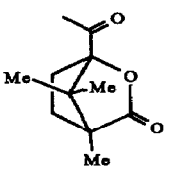


Figure 1

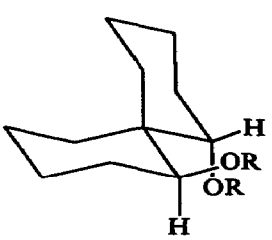


(-)-**4** R = H

(-)-**6** R =

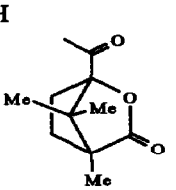


(-)-**8** R = 4-BrC_6H_4CO



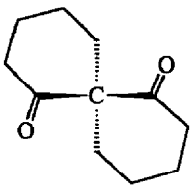
(+)-**4** R = H

(+)-**7** R =



Scheme 2

Transesterification of the biscamphanoate (–)-**6** with methanol/sodium methoxide yielded the enantiomerically pure (1*R*,6*S*,7*R*)-(–)-spiro[5.5]undecane-1,7-diol [(–)-**4**]. The latter optically active diol was converted into the bis(4-bromobenzoate) (–)-**8**. If the two chromophoric 4-bromobenzoyl groups are arranged with a torsion angle of ca. – 110° (cp. X-ray structure of **6**) the bisbenzoate rule[10] can be applied to derive the absolute configuration of the molecules from the chiroptical properties. In the CD spectrum two Cotton effects with opposite sign are created by the dipole-dipole interaction of the two chromophores. The minimum at 250 nm ($\Delta\varepsilon_{max}$ = – 41.4) corresponds to the in-phase coupling transition with lower energy, the maximum at 233 nm ($\Delta\varepsilon_{max}$ = + 6.85) represents the out-of-phase coupling with higher energy. If a negative Cotton effect is followed by a positive one, a torsion angle with negative twist sense between the two benzoate chromophores can be deduced nonempirically according to Nakanishi et al.[10] This confirms the (1*R*,6*S*,7*R*)-configuration for (–)-**8** and (–)-**4** deduced from the X-ray crystal structure of (–)-**6**.



Fischer projection of (*S*)-(–)-**1**

Scheme 3

Oxidation of the *trans,trans*-diol (–)-**4** by the method of Swern[11] yielded the (*S*)-(–)-spiro[5.5]undecane-1,7-dione [(–)-**1**] with known absolute configuration with a mp of 69.6—71.9 °C appreciably higher than the mp of (±)-**1** (41.8—43.9 °C). The chiroptical properties of the 1,3-dicarbonyl compound (–)-**1** are outstanding. A high specific rotation, $[\alpha]_D^{20}$ = – 236, $[\alpha]_{365}^{20}$ = – 2410, and a strong Cotton effect, $\Delta\varepsilon_{max}$ = – 5.35 (316 nm), are probably due to the interaction between the two carbonyl groups. There is no corresponding absorption enhancement in the UV spectrum.

EXPERIMENTAL SECTION

^{1}H (500.13 and 270.17 MHz) and ^{13}C (125.77 and 67.94 MHz) NMR spectra were recorded on a Bruker AM-500-FT and a Jeol JNM-EX 270 instrument (δ in ppm referenced to residual solvent signal, with chemical shifts referred to TMS; *J* in Hz, multiplicities as determined from DEPT spectra). Optical rotations were measured on a Perkin Elmer 241 polarimeter. IR spectra were recorded on a Perkin Elmer 297 instrument. UV spectra were obtained using a Kontron Uvikon 930 and a Kontron Uvikon 860 instrument. CD spectra were recorded on a JASCO J 600 dichrograph. Melting points were determined on a Büchi 510 melting point apparatus. Kieselgel 60 F_{254} glass plates (from Merck) were used for TLC, compounds were visualized by conc. H_2SO_4/5 min 160 °C. All solvents were distilled before use. Ether and THF were filtered through ICN Alumina B. Elemental analyses were performed by the microanalytical laboratory of Ilse Beetz, D 96317 Kronach.

(±)-Spiro[5.5]undecane-1,7-dione [(±)-**1**]: A mixture of (±)-5-(2-oxocyclohexyl)pentanoic acid[12] (10.14 g; 51.1 mmol), amberlyst 15 (9.26 g) and 1000 ml of toluene was refluxed for 67 h (Dean-Stark trap). After cooling the catalyst was filtered off, the filtrate was washed twice with 50 ml of 1 M K_2CO_3 and 50 ml of water respectively, dried (Na_2SO_4) and evaporated. The residue (5.96 g) was chromatographed on silica gel (1000 g; cyclohexane/AcOEt 4 : 1) yielding (±)-**1** (2.370 g, 25.7 %) as a pale yellow oil which solidified upon standing overnight (mp 29—34 °C, after two subsequent distillations at 65 °C in high vacuo: mp 41.8—43.9 °C [lit.[3]: 38—40 °C]), R_f = 0.50. – IR (CCl_4): $\tilde{\nu}$ 2930, 2855, 1715, 1700. – ^{1}H NMR (C_6D_6): δ 1.08 (dddd, J = 14.7, 10.0, 4.6, 0.8, 2 H, 5-H_a, 11-H_a), 1.17—1.28 (4 H, 3-H_a, 4-H_e, 9-H_a, 10-H_e), 1.41 (dtd, J = 12.9, 6.0, 1.8, 2 H, 3-H_e, 9-H_e), 1.52 (dtdd, J = 16.3, 10.1, 4.2, 2 H, 4-H_a, 10-H_a), 2.19 (dd, J = 8.5, 5.8, 4 H, 2-H, 8-H), 2.20 (dddd, J = 14.7, 6.0, 4.2, 1.8, 2 H, 5-H_e, 11-H_e). – ^{13}C NMR (C_6D_6): δ 21.4 (t, C-4, C-10), 27.7 (t, C-3, C-9), 36.4 (t, C-5, C-11), 40.8 (t, C-2, C-8), 64.5 (s, C-6), 209.2 (s, C-1, C-7).

(±)-(1SR,6RS,7RS)-11-Oxa-tricyclo[5.3.2.0^{1,6}]dodecan-12-one (lactone of (±)-4a-hydroxy-(4ar,8at)-decahydro-[1c]naphthoic acid) [(±)-**5**]: The more polar fractions of the chromatography described above afforded 670 mg (7.3 %) (±)-**5** as colourless crystals, mp 68.8—71.6 °C, after recrystallization from pentane: mp 76.6—77.6 °C(lit.[4]: mp 80—81 °C), R_f = 0.42. – IR (CCl_4): $\tilde{\nu}$ 2930, 2850, 1780, 1175, 1145, 940. – ^{1}H NMR ($CDCl_3$): δ 1.07 (dddd, J = 14.0, 8.8, 7.0, 2.0, 1 H, 3-H_a), 1.18 (ddddd, J = 13.3, 13.2, 12.8, 3.5, 3.5, 1 H, 9-H_a), 1.34 (ddd, J = 14.6, 12.8, 5.2, 1 H, 2-H_a), 1.44 (ddd, J = 14.1, 13.3, 5.5, 1 H, 10-H_a), 1.49 (ddddd, J = 12.9, 12.8, 12.8, 3.6, 3.1, 1 H, 4-H_a), 1.57 (m, 1 H, 4-H_e), 1.60 (dddd, J = 12.8, 10.4, 7.9, 2.2, 1 H, 8-H_a), 1.68 (m, 1 H, 9-H_e), 1.65—1.75 (4 H, 2-H_e, 5-H, 6-H_a), 1.79 (dm, J = 13.4, 1 H, 10-H_e), 1.91 (dm, J = 10.4, 1 H, 8-H_e), 1.99 (dm, J = 14.6, 1 H, 2-H_e), 2.41 (dd, J = 4.9, 2.2, 1 H, 7-H_e). – ^{13}C NMR ($CDCl_3$) δ 19.4 (t, J = 130, C-5), 20.5 (t, J = 125, C-4), 23.6 (t, J = 126, C-9), 26.2 (t, J = 130, C-8), 27.0 (t, J = 127, C-3), 32.6 (t, J = 126, C-2), 35.5 (t, J = 130, C-10), 47.3 (d, J = 137, C-6), 48.5 (d, J = 144, C-7), 85.1 (quint, J = 6, C-1), 179.3 (t, J = 8, CO).

(±)-trans,trans-Spiro[5.5]undecane-1,7-diol [(±)-**4**]: A solution of (±)-**1** (917 mg; 5.09 mmol) in dry Et_2O (30 ml) was added dropwise (30 min) to a boiling suspension of 1.01 g (96 %; 25.6 mmol) $LiAlH_4$ in dry Et_2O (80 ml). After boiling and stirring for 3 h the reaction mixture was quenched with satd. K_2CO_3 (6 ml). The clear solution was decanted and the precipitate was washed twice with ether (100 ml). The ethereal solutions were dried (Na_2SO_4), evaporated and the residue was chromatographed on 100 g of silica gel (cyclohexane/AcOEt 1 : 1) to give 382 mg of crude (±)-**4** which was recrystallized from benzene (5.5 ml); 301 mg (32.1 %) (±)-**4** as colourless crystals, mp 151.9—154.3 °C, R_f = 0.21. – IR ($CHCl_3$): $\tilde{\nu}$ 3600, 3500—3200 (br), 2930, 2855, 1050, 1025. – ^{1}H NMR ($[CD_3]_2CO$): δ 1.22 (qt, J = 12.9, 4.2, 2 H, 3-H_a, 9-H_a), 1.27—1.37 (4 H, 4-H_e, 5-H_a, 10-H_e, 11-H_a), 1.37—1.42 (2 H, 5-H_e, 11-H_e), 1.45 (dddd, J = 16.3, 11.4, 9.2, 1.2, 2 H, 2-H_a, 8-H_a), 1.60 (ddtd, J = 16.3, 4.2, 3.9, 1.6, 2 H, 2-H_e, 8-H_e), 1.64—1.69 (4 H, 3-H_e, 4-H_a, 9-H_e, 10-H_a), 3.18 (d, J = 5.4, 2 H, OH), 3.83 (dt, J = 11.4, 5.0, 2 H, 1-H_a, 7-H_a). – ^{13}C NMR ($[CD_3]_2CO$): δ 21.0 (t, C-4, C-10), 23.9 (t, C-5, C-11), 25.6 (t, C-3, C-9), 30.8 (t, C-2, C-8), 43.7 (s, C-6), 70.4 (d, C-1, C-7). – Anal. calcd. for $C_{11}H_{20}O_2$ (184.28): C, 71.70; H, 10.94. Found C, 71.64; H, 10.88.

(±)-cis,trans-Spiro[5.5]undecane-1,7-diol [(±)-**3**]: The less polar fractions of several chromatographic separations contained both additional diastereomeric diols as a mixture (9.282 g, mp 67—102 °C, R_f = 0.45). This

was recrystallized from 75 ml of cyclohexane (3.117 g, mp 115—140 °C) and again from 40 ml of cyclohexane yielding 2.64 g (±)-**3** as colourless crystals, mp 117.0—121.8 °C. – IR ($CHCl_3$): $\tilde{\nu}$ 3600, 3500—3100 (br), 2920, 2850, 1000, 980, 945, 865. – ^{1}H NMR (C_5D_5N): δ 0.68—0.79 (1 H, 5-H_a), 1.15—1.47 (6 H, 3-H_a, 4-H, 9-H_e, 10-H), 1.59—1.78 (5 H, 2-H, 8-H_a, 9-H_a, 11-H_e), 1.82 (m, 1 H, 8-H_e), 1.85 (ddd, J = 13.5, 5.0, 3.5, 1 H, 5-H_e), 1.99 (m, 1 H, 3-H_e), 2.21 (td, J = 13.2, 4.0, 1 H, 11-H_a), 3.80—3.88 (2 H, 1-H_e, 7-H_a), 6.47 (s, 1 H, 7-OH), 6.74 (s, 1 H, 1-OH). – ^{13}C NMR (C_5D_5N): δ 20.1 (t, C-11), 20.3 (t, C-3), 20.60 (t, C-10), 20.65 (t, C-4), 25.1 (t, C-9), 29.5 (t, C-2), 30.4 (t, C-8), 30.5 (t, C-5), 40.8 (s, C-6), 78.0 (d, C-1), 78.3 (d, C-7). – Anal. calcd. for $C_{11}H_{20}O_2$ (184.28): C, 71.70; H, 10.94. Found C, 71.72; H, 10.90.

(±)-cis,cis-Spiro[5.5]undecane-1,7-diol [(±)-**2**]: The mixture of the diastereomeric diols (R_f = 0.45; 605 mg; 3.28 mmol) was stirred together with 2-methoxypropene (2.0 ml; 21 mmol) and p-TsOH (50 mg; 0.26 mmol) for 1 h at room temp. The reaction mixture was diluted with cyclohexane (10 ml), filtrated over 3 cm of alumina B (ICN), eluted with cyclohexane (100 ml) and evaporated. The residue (735 mg, yellow oil) was chromatographed on 1.6 kg of silica gel (hexane/AcOEt 19 : 1). The less polar fractions (R_f = 0.28) contained 140 mg of the acetonide of the *cis,cis*-diol (as judged by ^{13}C NMR). After mixed fractions (150 mg) the more polar fractions (R_f = 0.27) containing 373 mg of the *cis,trans*-acetonide were eluted. A solution of the *cis,cis*-acetonide (140 mg) in MeOH (20 ml) was refluxed with p-TsOH (10 mg) for 30 min and evaporated. After addition of AcOEt (50 ml) the organic layer was washed with 1 M K_2CO_3 (20 ml), dried (Na_2SO_4) and evaporated. The residue (104 mg, light yellow oil) was chromatographed (20 g of silica gel; cyclohexane/AcOEt 1 : 1) to afford 79 mg (±)-**2** as a pale yellow, viscous oil, R_f = 0.45 (cyclohexane/AcOEt 1 : 1), bp. 80 °C/10^{-2} Torr. – IR ($CHCl_3$): $\tilde{\nu}$ 3600, 3500—3100, 2920, 2855, 1000, 975. – ^{1}H NMR (C_6D_6): δ 0.84 (dt, J = 13.8, 5.9, 2 H, 5-H_e, 11-H_e), 1.21—1.29 (6 H, 3-H_e, 4-H, 9-H_e, 10-H), 1.48—1.54 (4 H, 2-H, 8-H), 1.60—1.69 (2 H, 3-H_a, 9-H_a), 1.85—1.95 (2 H, 5-H_a, 11-H_a), 2.52 (br, 2 H, OH), 3.62 (t, J = 4.4, 2 H, 1-H_e, 7-H_e). – ^{13}C NMR (C_6D_6): δ 20.8 (t, C-4, C-10), 22.2 (t, br, C-3, C-9), 29.8 (t, C-2, C-8), 30.7 (t, br, C-5, C-11), 39.9 (s, C-6), 73.9 (d, br, C-1, C-7). – Anal. calcd. for $C_{11}H_{20}O_2$ (184.28): C, 71.70; H, 10.94. Found C, 71.65; H, 10.87.

(1R,6S,7R)-(–)-Spiro[5.5]undecane-1,7-diyl-bis-(1S,4R)-camphanoate [(–)-**6**]: A solution of (±)-**4** (2.070 g; 11.23 mmol) in dry pyridine (10 ml; 124 mmol) was added with stirring to a solution of (1*S*,4*R*)-(–)-camphanoyl chloride[7,8] (5.99 g; 27.6 mmol) in dry pyridine (10 ml; 124 mmol) under Ar. After 19 h at room temp the resulting slurry was poured into 2 N H_2SO_4 (300 ml) and extracted twice with AcOEt (100 ml). The extracts were washed with 2 N H_2SO_4 (100 ml), 1 M K_2CO_3 (100 ml) and water (20 ml), dried (Na_2SO_4) and evaporated. The residue (6.081 g, mp 195—> 250 °C) was boiled with 200 ml of cyclohexane for 40 min. The solution was removed and the insoluble residue was boiled again twice with 70 ml of cyclohexane. The residue (2.197 g) was then recrystallized from 340 ml of cyclohexane/AcOEt (3 : 2) affording 1.690 g (27.6 %) (–)-**6** as colourless crystals, mp > 280 °C, R_f = 0.26 (CH_2Cl_2/AcOEt 19 : 1), $[\alpha]_D^{20}$ = – 38 (c = 1.06, MeCN). – IR ($CHCl_3$): $\tilde{\nu}$ 2930, 1780, 1740, 1725, 1275, 1170, 1105, 1065, 1020, 995. – ^{13}C NMR (C_6D_6): δ 9.8 (q, C-9'), 16.6 (q, C-10'), 16.8 (q, C-8'), 19.8 (t, C-4), 24.5 (t, C-3), 25.0 (t, C-5), 26.7 (t, C-2), 28.8 (t, C-6'), 31.3 (t, C-5'), 41.3 (s, C-6), 54.0 (s, C-7'), 54.8 (s, C-1'), 74.5 (d, C-1), 91.0 (s, C-4'), 167.1 (s, C-3'), 177.4 (s, C-2').

(1S,6R,7S)-(+)-Spiro[5.5]undecane-1,7-diyl-bis-(1S,4R)-camphanoate [(+)-7]: The evaporation residue of the last two cyclohexane extractions from above (588 mg) was chromatographed on silica gel (300 g; CH_2Cl_2/AcOEt 19 : 1) yielding 275 mg of (+)-7, mp 218—221 °C (from cyclohexane), R_f = 0.40 (CH_2Cl_2/AcOEt 19 : 1), $[\alpha]_D^{20}$ = + 30 (c = 1.22, MeCN). – IR ($CHCl_3$): $\tilde{\nu}$ 2930, 1780, 1725, 1275, 1170, 1105, 1065, 1025, 1015, 995. – ^{13}C NMR (C_6D_6): δ 9.8 (q, C-9'), 16.6 (q, C-10'), 16.7 (q, C-8'), 19.8 (t, C-4), 24.4 (t, C-3), 24.8 (t, C-5), 26.7 (t, C-2), 28.8 (t, C-6'), 31.2 (t, C-5'), 41.7 (s, C-6), 53.8 (s, C-7'), 54.7 (s, C-1'), 74.4 (d, C-1), 90.9 (s, C-4'), 167.3 (s, C-3'), 177.5 (s, C-2').
From the more polar fractions 293 mg of (–)-**6**, R_f = 0.26 (CH_2Cl_2/AcOEt 19 : 1), could be obtained.

(1R,6S,7R)-(–)-Spiro[5.5]undecane-1,7-diol [(–)-**4**]: A solution of (–)-**6** (1.027 g; 1.885 mmol) in 100 ml 0.06 M NaOMe in MeOH was boiled under reflux for 15 h. After cooling 10 ml of methanolic HCl (from 0.4 ml of AcCl and 10 ml of MeOH) was added and the mixture was evaporated. The residue was chromatographed on silica gel (100 g; cyclohexane/AcOEt 1 : 2) affording 374 mg which were sublimed at 10^{-3} Torr; 326 mg (94 %) (–)-**4** as colourless crystals, mp 181.4—182.7 °C, R_f = 0.25, $[\alpha]_D^{20}$ = – 36 (c = 1.15, EtOH).

(1R,6S,7R)-(–)-Spiro[5.5]undecane-1,7-diyl-bis(4-bromobenzoate) [(–)-**8**]: A solution of 69 mg (0.37 mmol) of (–)-**4** in dry pyridine (2 ml) was added to a stirred solution of 4-bromobenzoyl chloride (0.40 g; 1.8 mmol) in dry pyridine (1 ml), the resulting slurry was stirred overnight at room temp and then poured into 1 M H_2SO_4. The mixture was extracted twice with Et_2O/AcOEt (2 : 1), the extracts were washed twice with 1 M K_2CO_3 (100 ml) and water (20 ml). After drying (Na_2SO_4) and evaporating, the residue (412 mg) was dissolved in 100 ml of CH_2Cl_2/AcOEt (1 : 1), water (10 ml) was added and the mixture was stirred for 3 days at room temp. After washing with 1 M K_2CO_3 (40 ml), drying (Na_2SO_4) and evaporating, the residue (341 mg) was chromatographed on silica gel (100 g; cyclohexane/CH_2Cl_2 1 : 2); 204 mg (99 %) (–)-**8**, colourless oil which solidified upon standing, mp 122.7—124.3 °C (colourless crystals from cyclohexane), R_f = 0.58, $[\alpha]_D^{20}$ = – 180 (c = 1.01, dioxane), UV (MeCN): $\lambda_{max}(\varepsilon)$ = 244 nm (34700), CD (MeCN): $\Delta\varepsilon_{max}$(nm) = – 41.4 (250), + 6.85 (233), – 4.1 (210), + 29 (201).

(1S,6R,7S)-(+)-Spiro[5.5]undecane-1,7-diol [(+)-**4**]: Similarly prepared as (–)-**4** from (+)-7 (residue of the first filtrate of the cyclohexane extractions, 230 mg; 0.422 mmol) yielding 71 mg (91 %) (+)-**4** (75 % ee); $[\alpha]_D^{20}$ = + 27 (c = 1.19, EtOH), other physical properties identical to (–)-**4**.

(S)-(–)-Spiro[5.5]undecane-1,7-dione [(–)-**1**]: Under N_2 atmosphere a solution of DMSO (1.6 ml; 23 mmol) in 5 ml of dry AcOEt was dropped to a solution of oxalyl chloride (1.0 ml; 12 mmol) in 10 ml of dry AcOEt at – 78 °C. After 15 min 280 mg (1.52 mmol) of (–)-**4** in 20 ml of dry AcOEt were added dropwise within 30 min. After an additional 60 min at – 78 °C NEt_3 (7.0 ml; 50 mmol) was added rapidly and the mixture was warmed to room temp. Water (40 ml) was added and the mixture was partitioned between 2 N H_2SO_4 (100 ml) and 100 ml of AcOEt. The organic layer was washed with 2 M $KHCO_3$ (20 ml), dried (Na_2SO_4) and evaporated. The residue (446 mg) was chromatographed on 100 g of silica gel (cyclohexane/AcOEt 4 : 1) yielding 265 mg (97 %) of (-)-1 as colourless crystals, mp 69.6—71.9 °C, R_f = 0.48, $[\alpha]_D^{20}$ = – 236, $[\alpha]_{578}^{20}$ = – 251, $[\alpha]_{546}^{20}$ = – 301, $[\alpha]_{436}^{20}$ = – 734, $[\alpha]_{365}^{20}$ = – 2410 (c = 0.36, cyclohexane), UV (cyclohexane): $\lambda_{max}(\varepsilon)$ = 310 nm (73), CD (cyclohexane): $\Delta\varepsilon_{max}$(316 nm) = – 5.35.

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