Absolute Conformation and Chiroptical Properties. VI. 2,2′,3,3′-Tetramethoxy-9,9′-bitriptycyl: A Stereochemical Analog of 1,2-Disubstituted Ethane with Identical Substituents[1,2)]

Shinji Toyota, Akihiro Yasutomi, Hiroharu Kojima, Yuko Igarashi, Mitsuhiro Asakura, and Michinori Ōki*

Department of Chemistry, Faculty of Science, Okayama University of Science, Ridai-cho Okayama 700-0005

(Received June 22, 1998)

The title compound was prepared by addition of 4,5-dimethoxybenzyne to 9,9′-bianthryl. The rotational isomers, *ap* and ±*sc*, were separated by HPLC. The ±*sc* isomers were treated with sodium ethanethiolate to produce 3,3′-dihydroxy-2,2′-dimethoxy-9,9′-bitriptycyl, which was converted to the ester of (1*S*,5*R*,7*R*)-4-[(2-carboxy)benzoyl]-3-thia-4-azatricyclo[5.2.1.0^{1,5}]decane 3,3-dioxide. The resulting diastereomers were separated by HPLC. The isomers were hydrolyzed and methylated with dimethyl sulfate to yield optically active 2,2′,3,3′-tetramethoxy-9,9′-bitriptycyl. The absolute conformation of the tetramethoxy compound was determined by X-ray structure analysis of 3′-ester of (1*S*,5*R*,7*R*)-4-(2-carboxybenzoyl)-3-thia-4-azatricyclo[5.2.1.0^{1,5}]decane 3,3-dioxide derived from 3-hydroxy-2,2′,3′-trimethoxy-9,9′-bitriptycyl, followed by hydrolysis and then methylation. The CD spectrum of *Msc*-2,2′,3,3′-tetramethoxy-9,9′-bitriptycyl is reported.

While we have been reporting absolute conformations and chiroptical properties of rotational isomers,[3—5)] which do not carry a stereogenic element other than internal rotation about a single C–C bond, the examples so far have been confined to compounds of which *ap* conformation has the symmetry of C_s. If an example of a higher symmetry than C_s becomes available, it will be an interesting addition to this series.

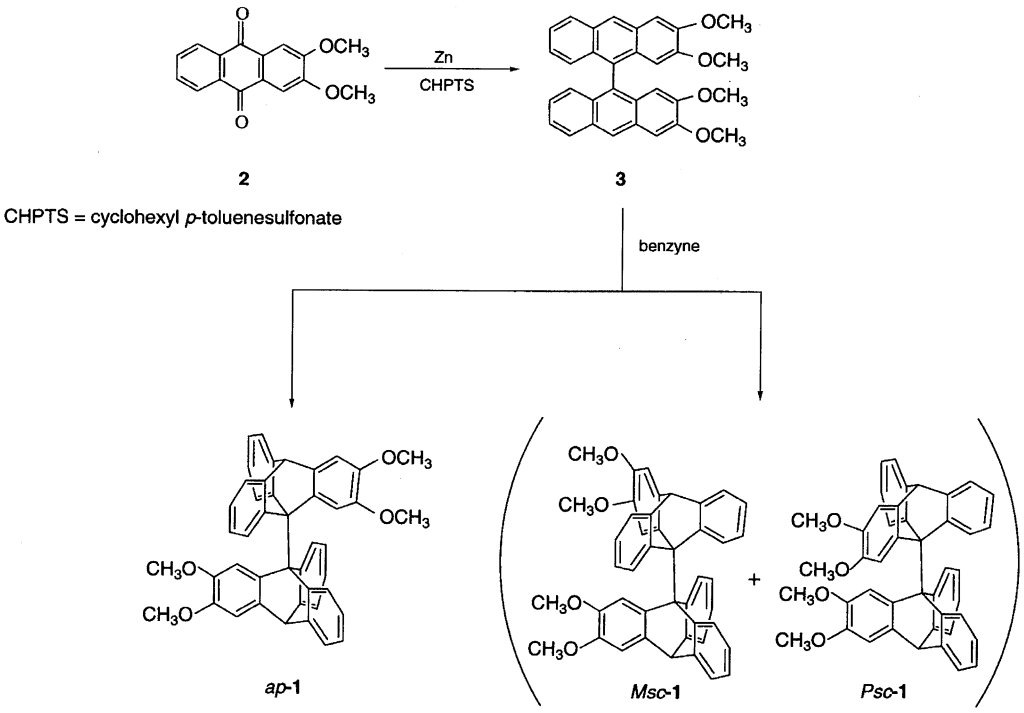
We selected compounds, of which *ap* conformation has C_{2h} symmetry, because the stereochemically most fundamental organic compounds such as butane or 1,2-dichloroethane belong to this symmetry. 9,9′-Bitriptycyl derivatives are suitable compounds because this series of compounds is known to exhibit a very high barrier to rotation, > 55 kcal mol^{-1} (1 cal = 4.184 J).[6)] In contrast, compounds of the type in which two *t*-butyl groups are hooked, show 16 kcal mol^{-1} barrier at the highest[7)] and, if we wish to freeze rotation about a single bond at room temperature, we must try to synthesize very special compounds.[8)]

The 9,9′-bitriptycyl must carry at least one substituent to distinguish one of the three benzeno bridges in each half of the bitriptycyl. The substituent should work as a key for optical resolution in the later stage. Thus we selected 2,2′,3,3′-tetramethoxy-9,9′-bitriptycyl (**1**) as a target molecule for the synthesis. Although Schwartz et al. synthesized a partially optically active bitriptycyl and an *ap* form of the same compound, their interest was only on the height of the rotational barrier, and thus they did not try to purify the optically active compound.[6)]

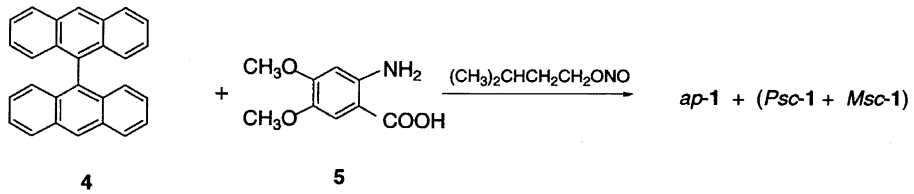
At the outset of the investigation, we utilized the synthetic strategy of reacting 2,2′,3,3′-tetramethoxy-9,9′-bianthryl (**3**) with benzyne. Compound **3** could be prepared by the method originally developed by Keely and Shannon[9)] and successfully applied to the synthesis of 2,2′,6,6′-tetramethoxy-9,9′-bianthryl by Cameron and Schüts.[10)] That is, reduction of 2,3-dimethoxyanthraquinone (**2**) with zinc and cyclohexyl *p*-toluenesulfonate gave **3** in ca. 60% yield. The reaction of **3** with benzyne afforded the desired compound in ca. 15% yield in total of *ap* and *sc* isomers (Scheme 1). In the later stage of investigation, we found that 4,5-dimethoxyanthranilic acid (**5**) was commercially available and the reaction of 4,5-dimethoxybenzyne generated from the anthranilic acid with 9,9′-bianthryl (**4**) afforded the desired compound in ca. 15% yield (Scheme 2). This almost the same with or even a little better yield of **1** by the reaction of **4** with 4,5-dimethoxybenzyne than the reaction of **3** with benzyne made the former method our choice of the synthesis of **1**, because of the fewer steps of synthesis and easier handling of the intermediates.

The structures of *sc*- and *ap*-**1** were determined by ^{13}C NMR spectra. Due to the C_{2h} symmetry for the *ap* isomer, four benzeno bridges in the compound are magnetically identical, as are the two benzeno bridges which carry two methoxyl groups each. Thus 12 lines are expected for aromatic carbons in *ap*-**1**. By contrast, although the two benzeno bridges which carry methoxyl groups are identical, two benzeno bridges in one of the triptycyl moiety are not identical in the *sc* form. Thus *sc*-**1** should give 18 lines for the aromatic carbons. In the actual ^{13}C NMR spectra, one compound showed 12 lines and the other 17 lines for aromatic carbons. These results establish the structures of **1**.

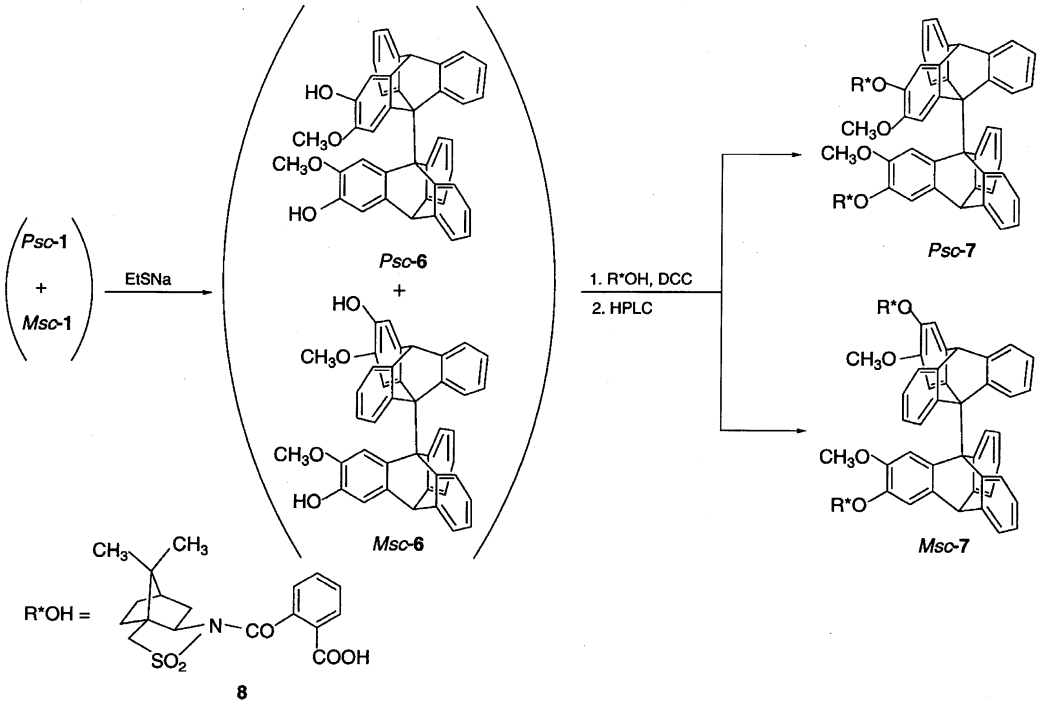
For the resolution of compound *sc*-**1**, we used (1*S*,5*R*,7*R*)-4-(2-carboxybenzoyl)-3-thia-4-azatricyclo[5.2.1.0^{1,5}]decane 3,3-dioxide (**8**), which was prepared by treating phthalic



Scheme 1.



Scheme 2.



Scheme 3.

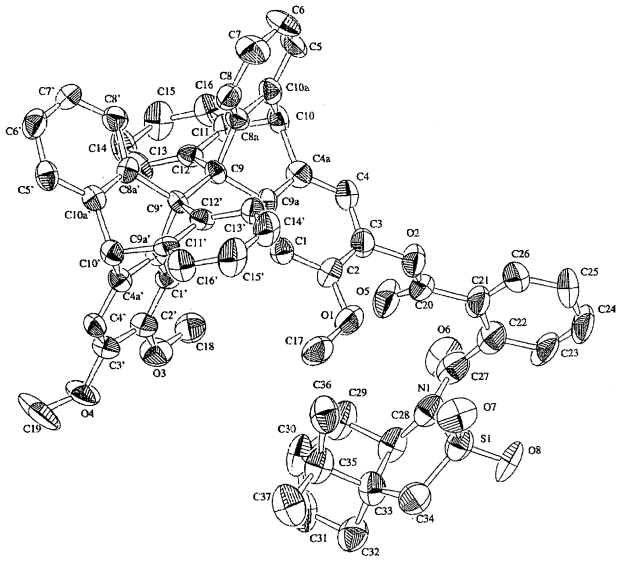


Fig. 1. An ORTEP drawing of *Msc*-**10** with thermal ellipsoids at 50% probability.

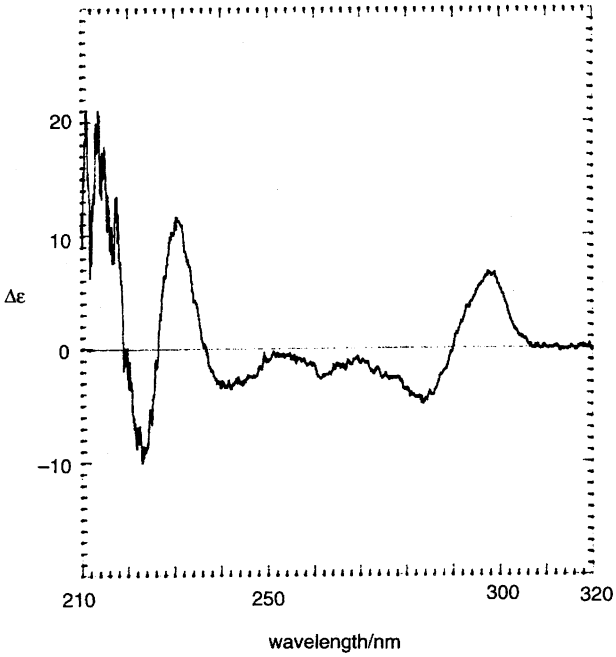
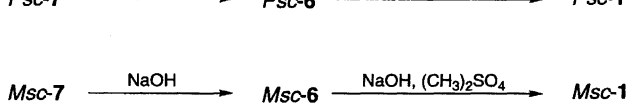


Fig. 2. The CD spectrum of *Msc*-**1**.

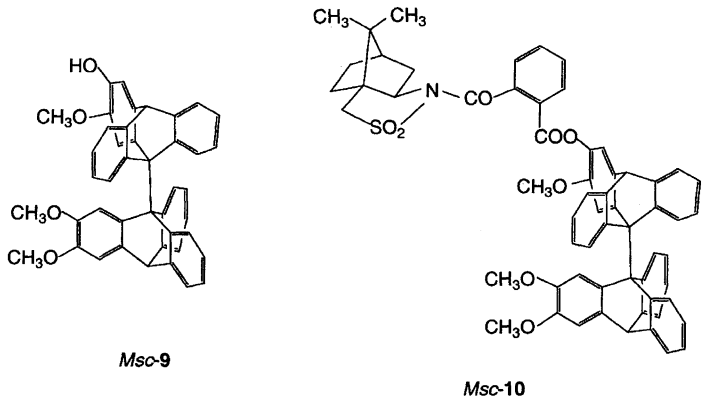


Scheme 4.

anhydride with sodium 10,2-camphorsultamate.[11] 3,3′-Dihydroxy-2,2′-dimethoxy-9,9′-bitriptycyl (**6**), which was prepared by treating compound **1** with sodium ethanethiolate,[12] was treated with compound **8** in the presence of dicyclohexylcarbodiimide and 4-(dimethylamino)pyridine to form the corresponding ester (**7**). Thanks to the steric effects, only 3- and 3′-methoxy groups were demethylated. Finally the diastereomeric mixture of the ester **7** was separated by HPLC (Scheme 3). The respective isomers, *Msc*-**7** and *Psc*-**7**, were hydrolyzed to produce the biphenolic compounds **6**, which were methylated with dimethyl sulfate in the presence of sodium hydroxide (Scheme 4). Compound **1** derived from the more easily eluted fraction of *sc*-**7** showed the specific rotation of −7.6°, whereas that from the less easily eluted isomer of *sc*-**7** showed +7.8°. The isomer which was levorotatory was found to be *Msc*, as is discussed later in this paper.

If one of the diastereomers of compound **7** gave good crystals for X-ray investigation, the story would have been much simpler. However, all the attempts to obtain single crystals large enough for an X-ray investigation have not been successful. Following Professor Harada's suggestion, we decided to use a compound which contained only one of the camphorsultam moieties. The tetramethoxy compound was treated in the same way as for the demethylation with shorter period of the treatment. This gave mono-demethylated compound **9**, which was converted to the camphorsultam derivative **10**, in a reasonable yield (Scheme 5). The first-eluted compound afforded good crystals for X-ray analysis, when grown from nitromethane.

An ORTEP drawing of the compound is shown in Fig. 1. Clearly it has the *Msc* structure at the C(9)–C(9′) bond. This *Msc*-**10** was hydrolyzed as before and the obtained *Msc*-**9** was methylated with dimethyl sulfate in the presence of sodium hydroxide to afford *Msc*-**1**. The CD spectrum of *Msc*-**1** is



Scheme 5.

shown in Fig. 2. Comparison of the CD spectra showed that the tetramethoxy compound **1** which was obtained by hydrolysis followed by methylation of the first-eluted isomer of **7** had the same absolute conformation with *Msc*-**1**. Thus it seems that the *Msc* forms, irrespective of the number of camphorsultam moieties, are eluted first in this series of compounds.

The positive Cotton effects observed at the longest wavelength region (ca. 300 nm) of compound *Msc*-**1** are interesting, because in no triptycene compounds has this type of Cotton effects been observed.[5] One report shows that 1,2-dimethoxybenzene has an absorption maximum at 274 nm in the UV region.[13] However, examination of the UV absorption spectra of compound **1** and even of a half of the molecule **1**, 2,3-dimethoxytriptycene, discovers such an absorption. The UV absorption of triptycene is known to be placed in a longer wavelength than triphenylmethane or *o*-xylene. This is interpreted by assuming electronic interactions among the benzene rings.[14] We believe the Cotton effect and the UV absorption of compound **1** at a longer wavelength than the absorption of 1,2-dimethoxybenzene can be attributed to the same interactions.

Experimental

^{1}H NMR spectra were obtained on a Varian Gemini-300 spectrometer which operated at 300.1 MHz and ^{13}C NMR spectra on a Bruker AMX-R400 which operated at 100 MHz. UV spectra and CD spectra were recorded on a Hitachi U-2000 and a JASCO J-600 spectropolarimeter, respectively. The HPLC machines used for separation of the isomers were either a Hitachi L-6250 or a Shimadzu LC-8A with UV detectors at 254 nm. For the Hitachi machine, Chemcopack column 10×300(W) was used with Chemcosorb 7Si stationary phase, and for the Shimadzu machine Develosil Packed column 20×250(W) with Develosil 60-5 packings. Elemental analyses were performed on a Perkin–Elmer 240C analyzer. Melting points are not corrected.

2,2′,3,3′-Tetramethoxy-9,9′-bitriptycyl (1). To a solution of 2.0 g (4.6 mmol) of 9,9′-bianthryl (**4**)[15] in 180 mL of diisopropyl ketone, was added 1.3 mL (1.1 g or 9.6 mmol) of isopentyl nitrite and the whole was heated under reflux. To this solution were added simultaneously from two dropping funnels a solution of 8.8 g (46 mmol) of 4,5-dimethoxyanthranilic acid (**5**) in 10 mL of 1,2-dimethoxyethane and another solution of 6.4 mL (5.4 g or 46 mmol) of isopentyl nitrite in 10 mL of diisopropyl ketone during the period of 3 h. After the completion of the addition, the mixture was further heated under reflux for 1 h and cooled. The product was roughly separated by chromatography on silica gel with from hexane to 6 : 1 hexane–ethyl acetate eluents. The products were further separated on alumina column with 10 : 1 hexane–ethyl acetate and the eluate was separated by HPLC with 10 : 3 hexane–ethyl acetate eluent, 30 mL min^{-1} flow rate, and 49 kg cm^{-2} pressure. This HPLC afforded many peaks and it was found that the peak at retention time of 11 min was the *ap*-isomer and that at retention time of 19 min it was the *sc*-isomer. The yields were 3 and 10%, respectively for *ap*-**1** and *sc*-**1**.

***ap*-1:** Recrystallized from tetrahydrofuran, nitrobenzene, benzene, and finally hexane–ethyl acetate, mp > 400 °C. Found: C, 84.33; H, 5.17%. Calcd for $C_{44}H_{34}O_4$: C, 84.32; H, 5.48%. ^{1}H NMR ($CDCl_3$) δ = 2.91 (6H, s), 3.90 (6H, s), 5.53 (2H, s), 6.46 (2H, s), 6.62 (4H, dt, J = 1.3 and 7.9 Hz), 6.90 (4H, d, J = 7.9 Hz), 6.99 (4H, t, J = 8.4 Hz), 7.11 (2H, s), 7.50 (4H, d, J = 7.3 Hz). ^{13}C NMR ($CDCl_3$) δ = 55.3, 55.5, 55.9, 58.1, 106.8, 117.2, 122.1, 122.7, 124.9, 131.2, 134.9, 140.1, 143.1, 143.2, 146.0, 147.2.

***sc*-1:** Recrystallized from hexane–ethyl acetate, mp 345—346 °C. Found: C, 84.58; H. 5.17%. Calcd for $C_{44}H_{34}O_4$: C, 84.32; H, 5.48%. ^{1}H NMR ($CDCl_3$) δ = 2.94 (6H, s), 3.90 (6H, s), 5.53 (2H, s), 6.48 (2H, s), 6.60 (4H, dt, J = 1.3 and 7.9 Hz), 6.89 (4H, dd, J = 7.5 and 4.9 Hz), 6.92—7.02 (4H, m), 7.10 (2H, s), 7.56 (4H, d, J = 7.4 Hz). ^{13}C NMR ($CDCl_3$) δ = 55.3, 55.7, 55.9, 58.2, 106.8, 117.5, 122.1, 122.3, 122.8, 124.8, 124.9, 131.0, 131.2, 135.1, 140.4, 142.9, 143.0, 143.1, 146.1, 147.1, 147.2.

2,2′,3,3′-Tetramethoxy-9,9′-bianthryl (3). To a mixture of 5.0 g (19 mmol) of 2,3-dimethoxyanthraquinone (**2**),[16] 37 g (0.57 mol) of zinc powder, and 250 mL of 1,2,4-trichlorobenzene, which was heated at 150—160 °C, was added 65 g (0.26 mol) of cyclohexyl *p*-toluenesulfonate[17] rapidly but maintaining the temperature above 150 °C. The resulting mixture was heated for a further 10 min at the temperature. The mixture was cooled, insoluble materials were removed by filtration, and the filtrate was washed with water, aqueous sodium hydrogencarbonate, and then water. After drying over magnesium sulfate, the solvent was removed by distillation under reduced pressure from the organic solution and the residue was submitted to column chromatography on silica gel with a hexane–ethyl acetate eluent. The desired compound was obtained in 62% yield as yellow crystals which were recrystallized from hexane-dichloromethane, mp 309.5—310.5 °C. Found: C, 80.98; H, 5.53%. Calcd for $C_{32}H_{26}O_4$: C, 80.99; H, 5.52%. ^{1}H NMR ($CDCl_3$) δ = 3.34 (6H, s), 4.07 (6H, s), 6.31 (2H, s), 6.98—7.12 (4H, m), 7.32—7.42 (4H, m), 8.07 (2H, d, J = 8.7 Hz), 8.46 (2H, s).

2,3-Dimethoxyanthracene, mp 204.0—205.0 °C, was obtained in 20% yield as a forerunner of the bianthryl in the chromatography: literature[18] mp 200—202 °C. ^{1}H NMR ($CDCl_3$) δ = 4.05 (6H, s), 7.20 (2H, s), 7.93 and 7.45 (4H, app dd, J = 6.5 and 3.3 Hz), 8.22 (2H, s).

Reaction of 2,2′,3,3′-Tetramethoxy-9,9′-bianthryl with Benzyne. This reaction was similarly carried out with use of 1.5 g (3.2 mmol) of the bianthryl **3**, 4.07 g (34.7 mmol) of isopentyl nitrite, and 4.4 g (32 mmol) of anthranilic acid in total of 150 mL of 1,2-dimethoxyethane. After HPLC under the same conditions as described above, *ap* and *sc* isomers of the desired compound **1** were obtained in 7 and 9% yields, respectively. ^{1}H NMR spectra of these compounds were identical with those of *ap*-**1** and *sc*-**1** described above.

***sc*-3,3′-Dihydroxy-2,2′-dimethoxy-9,9′-bitriptycyl (6).** A mixture of 77 mg (1.9 mmol) of sodium hydride suspension in oil (60%), 140 μL (1.99 mmol) of ethanethiol, and 3 mL of *N*,*N*-dimethylformamide (DMF) was stirred with ice-cooling for 10 min. A solution of 230 mg (0.37 mmol) of compound *sc*-**1** in 3 mL of DMF was added and the whole was stirred at room temperature for 10 min and then heated under reflux for 16 h. After cooling, 1 mol dm^{-3} hydrochloric acid was added and the mixture was extracted with ethyl acetate. The extracts were combined, washed with aqueous sodium hydrogencarbonate, and dried over magnesium sulfate. After evaporation of the solvent, the residue was purified by HPLC under the following conditions: chloroform eluent, flow rate 3.5 mL min^{-1}, pressure 24 kg cm^{-2}. The retention time of the desired product was 51 min. Yield 68%. Mp > 400 °C. ^{1}H NMR ($CDCl_3$) δ = 2.98 (6H, s), 5.41 (2H, s), 5.49 (2H, s), 6.42 (2H, s), 6.62 (4H, dt, J = 7.7 and 1.8 Hz), 6.91 (4H, d, J = 7.8 Hz), 6.98—7.02 (4H, m), 7.12 (2H, s), 7.49 (4H, d, J = 7.3 Hz).

***sc*-3-Hydroxy-2,2′,3′-trimethoxy-9,9′-bitriptycyl (9).** A

mixture of 60 μL (0.80 mmol) of ethanethiol, 36.5 mg (0.91 mmol) of a 60% oil suspension of sodium hydride, and 3 mL of DMF was stirred at room temperature for 10 min and then mixed with a suspension of 96.0 mg (154 μmol) of *sc*-**1** in 5 mL of DMF. The mixture was stirred at room temperature for 15 min and then heated under reflux for 50 min. After the mixture was cooled, it was acidified with 1 mol dm^{-3} hydrochloric acid and the mixture was extracted with ethyl acetate. The organic layer was washed with sodium hydrogencarbonate and dried. After evaporation of the solvent, the obtained solid was taken up in dichloromethane and submitted to HPLC under the following conditions: 100:1 dichloromethane–ethyl acetate eluent, flow rate 15 mL min^{-1}, pressure 70 kg cm^{-2}. The desired compound showed the retention time of 72 min, while the dihydroxy compound **6** gave 66 min. The yields of **9** and **6** were 43 and 12%, respectively. *sc*-**9** showed the following physical properties: Mp 354—356 °C. ^{1}H NMR ($CDCl_3$) δ = 2.94 (3H, s), 2.97 (3H, s), 3.91 (3H, s), 5.41 (1H, s), 5.49 (1H, s), 5.52 (1H, s), 6.41 (1H, s), 6.48 (1H, s), 6.60—6.64 (4H, m), 6.86—7.02 (8H, m), 7.11 (2H, s), 7.48—7.52 (4H, m).

sc-2,2′-Dimethoxy-3,3′-bis{2-[(1*S*,5*R*,7*R*)-3,3-dioxo-3-thia-4-azatricyclo[5.2.1.0^{1,5}]decan-4-ylcarbonyl]benzoyloxy}-9,9′-bitriptycyls (7). To a solution of 200 mg (0.92 mmol) of camphorsultam in 3 mL of benzene, was added 80 mg (2.0 mmol) of a 60% sodium hydride suspension in oil and the mixture was stirred for 30 min at room temperature. To this mixture was added 136 mg (0.92 mmol) of phthalic anhydride and the whole was stirred for 40 min. The mixture was quenched by 1 mol dm^{-3} hydrochloric acid and the organic layer was washed with water. Evaporation of the solvent followed by recrystallization from hexane-chloroform afforded (1*S*,5*R*,7*R*)-4-(2-carboxybenzoyl)-3-thia-4-azatricyclo[5.2.1.0^{1,5}]decane 3,3-dioxide (**8**) in 96% yield.

To a solution of 73 mg (0.20 mmol) of the **8** in 5 mL of tetrahydrofuran were added 186 mg (0.90 mmol) of dicyclohexylcarbodiimide, 24 mg (0.20 mmol) of 4-(dimethylamino)pyridine, and 40 mg (0.067 mmol) of *sc*-**6**, and the mixture was stirred for 20 h at room temperature. The solvent was removed in vacuo and the residue was shaken with chloroform. The insoluble materials were removed by filtration and the filtrate was washed with 1 mol dm^{-3} hydrochloric acid, aqueous sodium hydrogencarbonate and then water. The product was roughly purified by HPLC with chloroform (3.5 mL min^{-1} flow rate, 24 kg cm^{-2} pressure, and 43 min retention time) and the eluate was further separated by HPLC with a 3 : 2 hexane–ethyl acetate (4 mL min^{-1} flow rate, pressure 128 kg cm^{-2}), when two compounds, *Msc*-**7** and *Psc*-**7**, with retention times of 32 min and 42 min, respectively, were obtained, the yields of the two products being 20% each. The *Msc* form, mp 323.0—323.5 °C, $[\alpha]_D^{25}$ −67.9° (*c* = 1.3, $CHCl_3$). Found: C, 72.37; H, 5.52; N, 2.04%. Calcd for $C_{78}H_{68}N_2O_{12}S_2$: C, 72.60; H, 5.31; N, 2.17%. ^{1}H NMR ($CDCl_3$) δ = 0.79 (6H, s), 0.88 (6H, s), 1.21—1.27 (2H, m), 1.56—1.59 (4H, m), 1.70—1.72 (4H, m), 1.93—2.10 (4H, m), 2.86 (6H, s), 3.33 and 3.44 (4H, ABq, *J* = 13.8 Hz), 3.95—3.96 (2H, m), 5.56 (2H, s), 6.46 (2H, s), 6.65—6.71 (4H, m), 7.00—7.06 (8H, m), 7.44—7.63 (12H, m), 8.13 (2H, dd, *J* = 6.6 and 1.1 Hz).

***Psc*-7:** Mp 327—328 °C, $[\alpha]_D^{25}$ −86.3° (*c* = 1.3, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ = 1.01 (6H, s), 1.15 (6H, s), 1.30—1.47 (4H, m), 1.85—2.00 (4H, m), 2.00—2.18 (2H, m), 2.31—2.42 (2H, m), 2.88 (6H, s), 3.40 and 3.46 (4H, ABq, *J* = 14.0 Hz), 4.03—4.11 (2H, m), 5.52 (2H, s), 6.52 (2H, s), 6.64—6.72 (4H, m), 6.93—7.07 (8H, m), 7.32 (2H, s), 7.47—7.57 (8H, m), 7.61—7.66 (2H, s), 8.20 (2H, d, *J* = 7.6 Hz).

sc-2,2′,3-Trimethoxy-3′-{2-[(1*S*,5*R*,7*R*)-3,3-dioxo-3-thia-4-azatricyclo[5.2.1.0^{1,5}]decan-4-ylcarbonyl]benzoyloxy}-9,9′-bitriptycyls (10). These compounds were similarly prepared as described for the synthesis of **7** and separated by HPLC under the following conditions: eluent 50 : 1 dichloromethane–ethyl acetate, flow rate 5 mL min^{-1}, pressure 54 kg cm^{-2}. Under these conditions, the retention times of *Msc*-**10** and *Psc*-**10** were 72 and 75 min, respectively. The yields were 33 and 35% for *Msc*-**10** and *Psc*-**10**, respectively.

***Msc*-10:** Mp 300—312 °C (decomp), $[\alpha]_D^{25}$ −17.7° (*c* = 1.0, $CHCl_3$). Found: C, 76.32; H, 5.35; N, 1.56%. Calcd for $C_{61}H_{51}NO_8S$: C, 76.50; H, 5.37; N, 1.46%. ^{1}H NMR ($CDCl_3$) δ = 0.98 (3H, s), 1.12 (3H, s), 1.25—1.48 (2H, m), 1.80—1.98 (3H, m), 1.98—2.15 (1H, m), 2.28—2.42 (1H, m), 2.87 (3H, s), 2.96 (3H, s), 3.39 and 3.45 (2H, ABq, *J* = 13.8 Hz), 3.91 (3H, s), 4.02—4.12 (1H, m), 5.51 (1H, s), 5.53 (1H, s), 6.44 (1H, s), 6.57 (1H, s), 6.57—6.72 (4H, m), 6.87—7.07 (8H, m), 7.10 (1H, s), 7.31 (1H, s), 7.46—7.69 (7H, m), 8.21 (1H, dd, *J* = 7.7 and 1.1 Hz).

***Psc*-10:** Mp 297—305 °C (decomp), $[\alpha]_D^{25}$ −37.4° (*c* = 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ = 0.81 (3H, s), 0.94 (3H, s), 1.15—1.50 (3H, m), 1.50—1.70 (1H, m), 1.70—2.25 (3H, m), 2.89 (3H, s), 2.94 (3H, s), 3.40 and 3.43 (2H, ABq, *J* = 13.8 Hz), 3.89 (3H, s), 3.90—4.10 (1H, m), 5.53 (1H, s), 5.55 (1H, s), 6.42 (1H, s), 6.57 (1H, s), 6.57—6.70 (4H, m), 6.87—7.77 (8H, m), 7.10 (1H, s), 7.28 (1H, s), 7.46—7.67 (7H, m), 8.16 (1H, dd, *J* = 7.8 and 1.2 Hz).

9(9′)-*Msc*-2,2′,3,3′-Tetramethoxy-9,9′-bitriptycyls (*Msc*-1). A 0.25 mol dm^{-3} aqueous solution of sodium hydroxide (0.5 mL) was added to a solution of 67 mg (0.051 mmol) of *Msc*-**7** in 5 mL of tetrahydrofuran and the resulting solution was stirred at room temperature for 30 min. To the solution was added 13 μL (0.14 mmol) of dimethyl sulfate and the mixture was heated under reflux for 30 min. After cooling, the mixture was acidified with 1 mol dm^{-3} hydrochloric acid and extracted with ethyl acetate after adding aqueous sodium chloride. The product was purified by HPLC on silica gel (10 : 3 hexane–ethyl acetate, 5 mL min^{-1} flow rate, 49 kg cm^{-2} pressure). A white solid was obtained in 18 mg (58%) yield, the retention time being 28 min. Mp 347—348 °C, $[\alpha]_D^{25}$ −7.6° (*c* = 1.4, $CHCl_3$). Found: C, 84.68; H, 5.51%. Calcd for $C_{44}H_{34}O_4$: C, 84.32; H, 5.48%. ^{1}H NMR spectrum of this compound was identical with that of the racemic mixture.

This compound was also obtained by hydrolysis of *Msc*-**10** with potassium hydroxide followed by methylation with dimethyl sulfate.

9(9′)-*Psc*-1. This compound was similarly prepared as above, from *Psc*-**7**. The yield was 47%. Mp 352—353 °C, $[\alpha]_D^{25}$ +7.8° (*c* = 1.1, $CHCl_3$). Found: C, 84.13; H, 5.47%. Calcd for $C_{44}H_{34}O_4$: C, 84.32; H, 5.48%. This compound showed an identical ^{1}H NMR spectrum with the racemic mixture of **1**.

UV Absorption Spectra. These were recorded with methanol solutions of 1.00×10^{-5} mol dm^{-3} for 2,3-dimethoxytriptycene and 0.500×10^{-5} mol dm^{-3} for compound **1**. Because of solubility problems, ethanol had to be used for *ap*-**1**. The following absorption maxima were recorded (wavelength/nm and log ε given). 2,3-Dimethoxytriptycene; 204 (4.82), 218 (shoulder 4.74), 281 (3.84), 291 (3.88). *ap*-**1**; 202 (5.18), 218 (shoulder 5.01), 287 (4.11). *sc*-**1**; 203 (5.15), 217 (shoulder 5.02), 283 (4.07), 291 (4.09).

CD Spectrum of *Msc*-1. These were also recorded on methanol solutions with concentrations of 1.00×10^{-5} mol dm^{-3}. A cell of 1.0 mm was used for the wavelength region of 210—320 nm. The spectra were recorded eight times; the integrated spectrum is shown in Fig. 2. The following peaks and troughs were recorded (wavelength and $\Delta\varepsilon$ are given): 223.2 (−9.8), 230.5 (11.9), 240.1 (−3.5), 283.5 (−4.8), 297.5 (6.6).

X-Ray Crystallography.[19] The crystals suitable for X-ray diffraction were obtained when they were grown from the forerunner in HPLC of *sc*-**7** in nitromethane. The size of the crystal submitted for data collection was $0.13\times0.13\times0.28$ mm^3. The data were collected on a Rigaku AFC7R four circle diffractometer with Cu $K\alpha$ radiation (λ = 1.54178 Å), using the ω–2θ scan technique to a maximum of 120.2°. Scans of $(1.63+0.30\tan\theta)°$ were made at a speed of 10.0° min^{-1} in omega. The weak reflections were scanned three times. Of the 4061 reflections collected, 3939 were judged unique, and 3481 were used for the structure determination. The linear absorption coefficient was 10.7 cm^{-1}. The structure was solved by direct methods using the teXsan program. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The function minimized was $\Sigma[w(|F_o|-|F_c|)^2]$ where $w=(\sigma_c^2|F_o|+p^2/4|F_o|^2)^{-1}$. The crystal and analysis data were as follows: Empirical formula $C_{61}H_{51}NO_8S$, formula weight 958.14, crystal system monoclinic, space group $P2_1$, a = 8.398(2), b = 20.379(4), c = 14.390(4) Å, β = 96.50(2)°, V = 2446(1) Å^3, Z = 2, D_c = 1.300 g cm^{-3}, R = 0.078, R_w = 0.072.

This work was partially supported by a Special Fund administered by Japan Private School Promotion Foundation. The authors thanks are also due to Professor K. Takeda and Y. Moriyama for their help in measuring the CD spectra.

References

1) For Part V of the series, see Ref. 5.

2) A preliminary note has been published: S. Toyota, A. Yasutomi, and M. Ōki, *Tetrahedron Lett.*, **36**, 6297 (1995).

3) S. Toyota, H. Yamane, and M. Ōki, *Bull. Chem. Soc. Jpn.*, **66**, 212 (1993).

4) S. Toyota, T. Miyasaka, Y. Matsumoto, T. Matsuo, and M. Ōki, *Bull. Chem. Soc. Jpn.*, **67**, 1680 (1994).

5) S. Toyota, T. Akinaga, H. Kojima, M. Aki, and M. Ōki, *J. Am. Chem. Soc.*, **118**, 11460 (1996).

6) L. H. Schwartz, C. Koukotus, P. Kukkola, and C. S. Yu, *J. Org. Chem.*, **51**, 955 (1986).

7) B. L. Hawkins, W. Bremser, S. Borcic, and J. D. Roberts, *J. Am. Chem. Soc.*, **93**, 4472 (1971).

8) S. Brownstein, J. Dunogues, D. Lindsay, and K. U. Ingold, *J. Am. Chem. Soc.*, **99**, 2073 (1977); M. A. Falmm-ter Meer, H.-D. Beckhaus, K. Peters, H.-G. von Schnering, H. Fritz, and C. Rüchardt, *Chem. Ber.*, **119**, 1492 (1986).

9) W. Keely and J. S. Shannon, *Aust. J. Chem.*, **13**, 103 (1960).

10) D. W. Cameron and P. E. Schüts, *J. Chem. Soc. C*, **1967**, 2121.

11) G. I. Feutrill and R. N. Mirrington, *Tetrahedron Lett.*, **1970**, 1327; G. I. Feutrill and R. N. Mirrington, *Aust. J. Chem.*, **25**, 1719 (1972); G. I. Feutrill and R. N. Mirrington, *Aust. J. Chem.*, **25**, 1731 (1972).

12) N. Harada, T. Nehira, T. Soutome, N. Hiyoshi, and F. Kido, *Enantiomer*, **1**, 35 (1996).

13) A. Kiss, J. Molnár, and C. Sándorfy, *Compt. Rend.*, **227**, 724 (1948).

14) J. de Wit and H. Wynberg, *Tetrahedron*, **29**, 1379 (1973).

15) F. Bell and D. H. Waring, *J. Chem. Soc.*, **1949**, 267.

16) K. Lagodzinski, *Ber.*, **28**, 116 (1895); K. Lagodzinski, *Justus Liebigs Ann. Chem.*, **342**, 90 (1905).

17) W. Hückel, O. Neunhoeffer, A. Gerke, and E. Frank, *Justus Liebigs Ann. Chem.*, **477**, 99 (1930); R. S. Topson, M. A. Clapp, and L. H. Cretcher, *J. Org. Chem.*, **12**, 133 (1947); S. Winstein, F. Grunwald, R. E. Buckles, and C. Hanson, *J. Am. Chem. Soc.*, **70**, 816 (1948).

18) S. T. Cristol, D. G. Seapy, and E. O. Aeling, *J. Am. Chem. Soc.*, **105**, 7337 (1983).

19) Tables of atomic coordinates, anisotropic thermal parameters for non-hydrogen atoms, complete F_o-F_c data, bond lengths, bond angles, torsion angles, and experimental details are deposited as Document No. 71057 at the Office of the Editor of Bull. Chem. Soc. Jpn.