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Preparation of Alkyl-Substituted Indoles in the Benzene Portion. Part 11.[1] Total Synthesis of (6*R*,8*S*)-Herbindole A, (6*R*,8*S*)-Herbindole B, (6*R*,8*S*)-Herbindole C, (6*R*,8*S*)-*cis*-Trikentrin A, (6*R*,8*S*)-*cis*-Trikentrin B, (6*R*,8*R*)-*trans*-Trikentrin B, and (6*R*,8*R*)-iso-*trans*-Trikentrin B. Determination of the Absolute Structures of Natural Herbindoles and Trikentrins

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The key intermediate, (3*R*,5*S*)-3,5-dimethyl-1-cyclopentenylmethanol (13) for chiral syntheses of herbindoles and trikentrins, was prepared from the known Dields–Alder adduct 12. Employing pertinent methodologies developed in the previous model study (preceding paper), the title herbindoles 31, 34, and 38 as well as trikentrins 4, 6, 41, and 47 having (6*R*,8*S*)- or (6*R*,8*R*)-absolute configuration of the dimethyl groups on the 1,6,7,8-tetrahydrocyclopent[*g*]indole moiety were synthesized starting from 13 by way of precursor compounds 24b, 27a, and 27b for the crucial indole cyclization reaction. The following results were also obtained. (i) The proposed chemical structures of three herbindoles were confirmed. (ii) The absolute structures of herbindole A and *trans*-trikentrin B were established to be 1 and 7 by directly comparing optical properties between synthetic materials and the natural products. (iii) The absolute structures of herbindole B (2) and herbindole C (3) were assumed by analogy with 1. (iv) The absolute structures of *cis*-trikentrin B (6) and iso-*trans*-trikentrin B (8) were estimated by a circular dichroism (CD) analysis study. (v) Our previous proposal for the absolute configuration of *cis*-trikentrin A (4) was further confirmed.

Keywords chiral total synthesis; marine alkaloid; absolute configuration determination; herbindole; trikentrin; polyalkylindole synthesis

Indole alkaloids, herbindole A (**1**), herbindole B (**2**), and herbindole C (**3**), were isolated in 1990 from an orange-colored sponge, *Axinella* sp., collected in the Gulf of Exmouth, Western Australia, as substances exhibiting both cytotoxic activity against KB cells and general antifeedant activity against fish.[2] Their chemical structures have been proposed mainly on the basis of NMR studies to be 6,8-*cis*-4,5,6,8-tetramethyl-, 6,8-*cis*-4-ethyl-5,6,8-trimethyl-, and 6,8-*cis*-4-[(*E*)-1-butenyl]-5,6,8-trimethyl-1,6,7,8-tetrahydrocyclopent[*g*]indoles, respectively, in which the absolute configuration of the secondary methyl groups has remained unknown.[2] These structures resemble those of five trikentrins (**4**—**8**), constituents of the marine sponge *Trikentrion flabelliforme* collected at Darwin, Australia in 1986, which showed a growth-inhibitory activity against gram-positive bacteria[3] (Chart 1).

Several syntheses have been reported in the family of trikentrins, not only to confirm the chemical structures, but also to establish the absolute structures of *cis*- and *trans*-trikentrin A.[4] No total synthesis has been disclosed for herbindoles, since their structures with a fully alkyl-substituted benzene portion of the indole moiety are expected to make synthesis very difficult by conventional procedures. We embarked on an enantiospecific synthesis of herbindoles, based on the result of a preliminary study described in the preceding article,[1] and accomplished a total synthesis of (6*R*,8*S*)-herbindole A (**31**), (6*R*,8*S*)-herbindole B (**34**), and (6*R*,8*S*)-herbindole C (**38**). Furthermore the project was extended to the area of trikentrins, and (6*R*,8*S*)-*cis*-trikentrin A (**4**), (6*R*,8*S*)-*cis*-trikentrin B (**6**), (6*R*,8*R*)-*trans*-trikentrin B (**47**), and (6*R*,8*R*)-iso-*trans*-trikentrin B (**41**) were synthesized from a chirality-defined starting material. The following deductions were also made. (i) The proposed chemical structures of the three herbindoles were confirmed. (ii) The

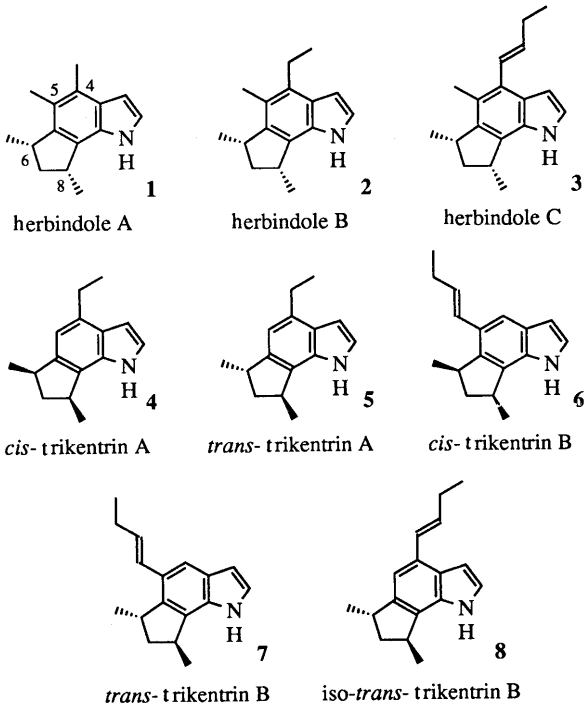

Chart 1

absolute structures of herbindole A and *trans*-trikentrin B were established to be **1** and **7** by directly comparing optical properties between synthetic materials and the natural products. (iii) The absolute structures of herbindole B (**2**) and herbindole C (**3**) were assumed by analogy with **1**. (iv) The absolute structures of *cis*-trikentrin B (**6**) and iso-*trans*-trikentrin B (**8**) were estimated by a circular dichroism (CD) analysis study. (v) Our previous proposal for the absolute configuration of *cis*-trikentrin A (**4**)[4b,e] was further confirmed. Here we present the full experimental details of our studies upon which these conclusions are based.[5]

Preparation of (3*R*,5*S*)-3,5-Dimethyl-1-cyclopentenylmethanol (13) As stated in the preceding preliminary study,[1] our synthetic plan for herbindoles A, B and C stemmed from the idea of preparing first pyrrole derivatives **9a** having a cyclopentane ring with the chiral dimethyl groups and then submitting **9a** to an acid-catalyzed cyclization reaction for the formation of indole derivatives **10a** (Chart 2). This indole formation process could be further applied to compounds **9b** and **9c**, and indole derivatives **10b** and **10c** thus formed might become suitable precursors for the synthesis of *cis*-trikentrin A, *cis*- and *trans*-trikentrins B, and iso-*trans*-trikentrin B. The preliminary study suggested that, if optically active 3,5-dimethyl-1-cyclopentenylmethanol (**13**) was obtainable from a chirality-defined starting material, preparation of **9** would be readily achieved by the Clasisen rearrangement of **13** to form **14** (R^1 = Me and H), followed by the condensation of **14** with 3-formyl-1-(phenylsulfonyl)pyrrole. We chose a Diels–Alder adduct **12** of cyclopentadiene with the ester **11** derived from (*E*)-3-bromoacrylic acid and (*S*)-3-hydroxy-1-methylsuccinimide[6,7] as a key starting material for the present study, assuming that herbindoles would possess the same absolute configuration of the dimethyl groups as *cis*-trikentrin A (**4**), and we sought an effective pathway to transform **12** into the (3*R*,5*S*)-dimethyl derivative **13**.

When starting from **12**, success of this transformation relied on the selection of both an ester group and a hetero-atom function on the bicycloheptene system, because, without this precaution, β-elimination of the hetero-atom would take place in part at every stage during the formation process of the *cis*-dimethyl function (Chart 3). Among the combinations of methyl, benzyl, and *tert*-butyl esters with bromine, methoxy, and benzyloxy groups, compound **16** bearing the benzyloxy and *tert*-butyl ester groups proved to be the only choice for this purpose. Thus the adduct **12** was hydrolyzed with diluted alkali and the resulting carboxylic acid was directly converted to the *tert*-butyl ester **15** in 60% yield, and then the bromine atom of **15** was replaced by the benzyloxy group under the literature conditions[8] to obtain **16** in 87% yield as a mixture of three isomers, whose ratio was determined to be 10 : 1 : 0.6 by HPLC analysis. For cleavage of the double bond of **16**, the usual procedure using a catalytic amount of osmium tetroxide and an excess of sodium metaperiodate was unsuitable in our case, since **16** afforded only a complex mixture of many intractable materials. This result was quite unexpected in view of the very mild nature of the reaction conditions. Probably, once the double bond of **16** was cleaved to afford two aldehydes, which were usually in equilibrium with their hydrate forms, an oxidation cycle due to a combination of osmium tetroxide and sodium metaperiodate would severely oxidize various kinds of intermediates composed of hemiacetals and hemilactols formed intramolecularly between two aldehydes themselves as well as between one of the aldehydes and the nearby ester group. To avoid this complication, it was necessary to isolate the diol **17** (96% yield) by oxidation with a catalytic amount of osmium tetroxide in the presence of trimethylamine *N*-oxide.

The diol **17** was further oxidized with an equivalent amount of sodium metaperiodate, and without purification of the intermediary dialdehyde, this was directly treated with ethanethiol in the presence of boron trifluoride to furnish the bisdithioacetal **18** in 76% yield, accompanied with a by-product **19** in 5% yield. Attempted isolation of the dialdehyde by chromatography over silica gel afforded a complex product, due to partial epimerization of the aldehyde groups. Reductive desulfurization of **18** was effected with Raney nickel (W-2) in a mixture of ethanol and dimethoxyethane (DME) (4 : 1), and the crude product

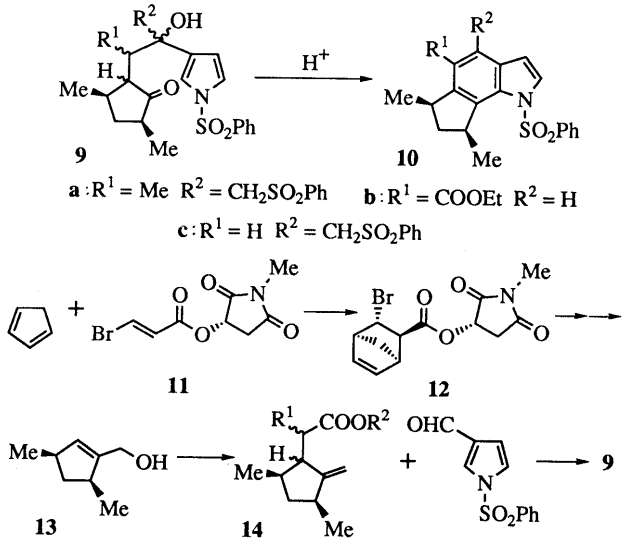

Chart 2

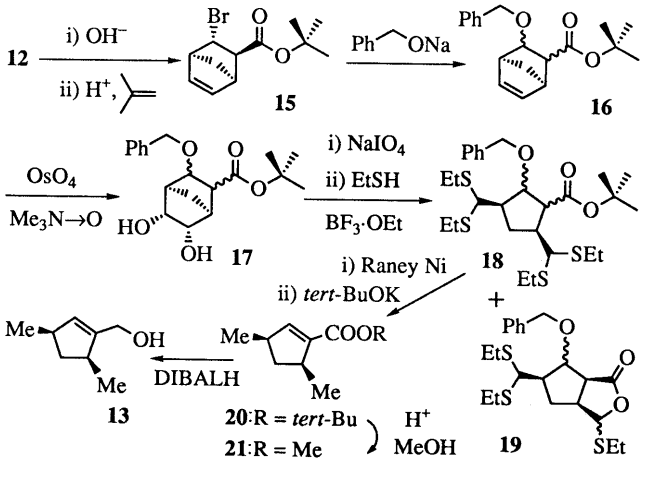

Chart 3

was treated with potassium *tert*-butoxide in tetrahydrofuran (THF) at 0 °C to provide a volatile α,β-unsaturated ester **20** in 76% yield as a single compound. The next task was the reduction of the ester group of **20** to the carbinol in **13**. This process, using various kinds of metal hydrides, turned out to be very difficult, due to both partial reduction to an α,β-unsaturated aldehyde, and concomitant initial reduction of the conjugate double bond, forming by-products such as a pair of epimers of saturated ester and saturated carbinol. This difficulty resulted entirely from the presence of the *tert*-butyl ester group, which had played an important role in the above transformation, but had become unnecessary at this stage, and therefore **20** was heated with 1% sulfuric acid in methanol to convert it into a volatile methyl ester **21** with an aromatic odor in 91% yield. Reduction of **21** with diisobutylaluminum hydride (DIBALH) at about −60 °C selectively afforded the required compound **13** in 96% yield.

Preparation of Precursor Compounds 24b, 27a, and 27b for the Indole Cyclization Reaction Chiral dimethylcyclopentenylmethanol **13** was treated with triethyl orthopropionate and triethyl orthoacetate, respectively, in the presence of pivalic acid for the Claisen rearrangement[9] (Chart 4). The reaction required rather forcing conditions, *i.e.*, heating **13** with the respective reagents in a sealed tube at 150—155 °C for 5 h, and **22a** and **22b** were obtained in 90% and 87% yields. These compounds, **22a** and **22b**, were then condensed with 3-formyl-1-(phenylsulfonyl)-pyrrole[10] (**23**) with the aid of lithium diisopropylamide (LDA) to afford **24a** and **24b** in 94% and 99% yields, respectively, based on **23**. One of these, **24b**, served as an important intermediate for the synthesis of (6*R*,8*S*)-*cis*-trikentrin B (**6**) and (6*R*,8*S*)-*trans*-trikentrin B (**47**).

Manganese dioxide oxidation of **24a** and **24b** in refluxing dichloromethane produced the β-ketoesters **25a** and **25b** in 81% and 84% yields. Deethoxycarbonylation of **25a** proceeded without difficulty with lithium chloride in aqueous hexamethylphosphoramide[11] (HMPA) to afford **26a** in 70% yield. In contrast to this expected result supported by the previous model study, deethoxycarbonylation of **25b** with either lithium chloride in HMPA-water or magnesium chloride in HMPA[12] afforded **26b** in only 50% or 33% yield. Here a classical procedure gave a better result, and the formation of **26b** was observed in 79% yield, when **25b** was refluxed in a 5% sodium hydroxide-containing DME–methanol–water (1 : 2 : 1) solution for 3 h, and the resulting material was treated with phenylsulfonyl chloride in the presence of sodium hydride. During the alkaline hydrolysis, both spontaneous decarboxylation and hydrolytic cleavage of the sulfonyl group had concomitantly taken place. The next task was introducion of the phenylsuflonylmethyl group into the ketone group of **26a** and **26b** in order to prepare common intermediates for the synthesis of (6*R*,8*S*)-herbindoles **31**, **34**, **38** and (6*R*,8*S*)-*cis*-trikentrin A (**4**). This was achieved quite readily by reaction of phenylsulfonylmethyllithium on **26a** and **26b**, affording **27a** and **27b** in 92% and 96% yields, respectively.

Total Synthesis of (6*R*,8*S*)-Herbindole A (31), (6*R*,8*S*)-Herbindole B (34), (6*R*,8*S*)-Herbindole C (38), (6*R*,8*S*)-*cis*-Trikentrin A (4), and (6*R*,8*R*)-iso-*trans*-Trikentrin B (41) Now the stage was set for the key step, the indole cyclization reaction. The requisite ketone group, essential for the acid-catalyzed cyclization, was unmasked from the *exo*-methylene group in **27a** and **27b** by oxidation with a

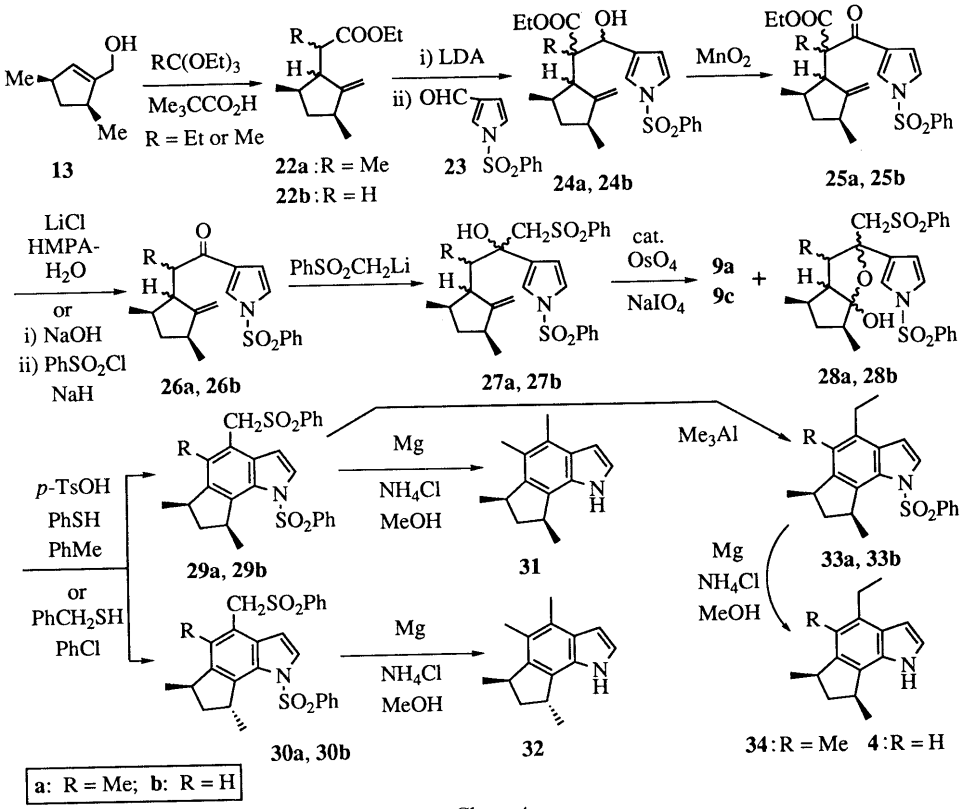

Chart 4

catalytic amount of osmium tetroxide and an excess of sodium metaperiodate. The resulting ketone derivatives **9a** and **9c** existed as mixtures with **28a** and **28b**, but without separation, these mixtures were directly heated in the presence of *p*-toluenesulfonic acid either in toluene with thiophenol at reflux for 5 h for the **a** series, R = Me, or in chlorobenzene with benzylthiol at reflux for 1.5 h for the **b** series of R = H. The expected indole derivatives **29a** and **29b** having *cis*-dimethyl groups were obtained in overall yields of 48% and 44% from **27a** and **27b**, accompanied with the formations of by-products **30a** and **30b** in 15% and 16% yields, after separation by HPLC. The latter derivatives having *trans*-dimethyl groups were produced by partial isomerization of the methyl group neighboring the ketone group in the intermediates **9a** and **9c** during this acid treatment.

As established in the previous model study, treatment of **29a** and **30a** with magnesium in methanol in the presence of ammonium chloride[13] removed reductively not only the indole-protecting sulfonyl group but also the phenylsulfonyl group at the side chain, and (6*R*,8*S*)-herbindole A (**31**), mp 134—136 °C (lit.[2] mp 120—122 °C for herbindole A), $[\alpha]_D^{21}$ +56.9° (*c* = 0.28, $CHCl_3$) and its *trans* isomer **32**, mp 84—86 °C, $[\alpha]_D^{22}$ −36.6° (*c* = 0.17, $CHCl_3$) were produced in 85% and 90% yields. An authentic sample of herbindole A (**1**), provided by Professor Scheuer, showed mp 132—134 °C, $[\alpha]_D^{21}$ −62° (*c* = 0.07, $CHCl_3$) after recrystallization from methanol–water, and identity of **31** with **1** was confirmed by comparison of their GCMS, ^{1}H- and ^{13}C-NMR and IR ($CHCl_3$) spectra, except for the enantiomeric nature of specific rotations. This latter characteer was further evidenced by comparison of the CD curves of **31** and **1**, which were in a mirror image relationship. Therefore the absolute structure of herbindole A was established as the (6*S*,8*R*)-structure **1**. As for herbindole B (**2**) and herbindole C (**3**), no optical data were available, so that the absolute configurations of the dimethyl group at 6 and 8 positions were estimated by analogy with those of herbindole A (**1**).

The common intermediates **29a** and **29b** were treated with trimethylaluminum at 0 °C for 1 h. Substitution of the side chain phenylsulfonyl group with the methyl group took place as expected from the previous study, and **33a** and **33b** were obtained in 92% and 95% yields, respectively. Removal of the indole-protecting group was carried out again with magnesium in methanol in the presence of ammonium chloride to furnish (6*R*,8*S*)-herbindole B (**34**), mp 131—133 °C (lit.[2] mp 118—120 °C for herbindole B), $[\alpha]_D^{21}$ +51.2° (*c* = 0.26, $CHCl_3$) and (6*R*,8*S*)-*cis*-trikentrin A (**4**), $[\alpha]_D^{24}$ +67.0° (*c* = 0.16, $CHCl_3$) in 92% and 91% yields, respectively. Identity of **34** as herbindole B (**2**), except for the absolute structure, was confirmed by comparing the GC-MS, ^{1}H- and ^{13}C-NMR and IR spectra of **34** with those of **2** described in the literature.[2] Spectral data of **4** were identical with those of (6*S*,8*R*)-*cis*-trikentrin A, $[\alpha]_D^{24}$ −68.6° (*c* = 1.03, $CHCl_3$), already synthesized by us from (*R*)-(+)-pulegone,[4b,e] and also with those of natural *cis*-trikentrin A, $[\alpha]_D$ +48° (*c* = 2.47, $CHCl_3$).[3] Thus the absolute structure of *cis*-trikentrin A was further confirmed to be **4**.

Compounds **29a**, **30a**, and **30b** were treated with allyltrimethylsilane in the presence of dichloroethylaluminum at −20 °C for 15 to 20 min for elongation of the three carbon unit (Chart 5). The reaction proceeded with extreme ease and **35**, **39a**, and **39b** were obtained in 92%, 90%, and 91% yields, respectively. Compounds **35** and **39b** were treated with rhodium chloride for migration of the double bond from the terminal part to the conjugate position as described before.[4e] Whereas **39b** afforded exclusively **40** in 92% yield by refluxing in ethanol with the catalyst for 8 h, **35** required prolonged heating in an ethanol solution with the catalyst at 100 °C for 50 h in a sealed tube. Even with these forcing reaction conditions, **37** was obtained in only 54% yield, together with the intermediary compound **36** in 38% yield, as a mixture of *E* and *Z* double bond isomers. Repeated treatment of the mixture **36** as above afforded a further crop of **37** in 50% yield, accompanied with recovered **36** in 40% yield. Alkaline hydrolysis of the phenylsulfonyl group in **37** and **40** provided (6*R*,8*S*)-herbindole C (**38**), $[\alpha]_D^{22}$ +19.9° (*c* = 0.18, $CHCl_3$) and (6*R*,8*R*)-iso-*trans*-trikentrin B (**41**), $[\alpha]_D^{24}$ *ca.* 0° (*c* = 0.11, $CHCl_3$) in 93% and 88% yields, respectively. Confirmation of the identity of **38** as herbindole C (**3**) except for the absolute structure was made by comparing the MS (DI), ^{1}H- and ^{13}C-NMR spectra of **38** with those of **3** described in the literature.[2] As for the synthesized **41**, identity with our synthetic (±)-iso-*trans*-trikentrin B[4e] was verified by comparison

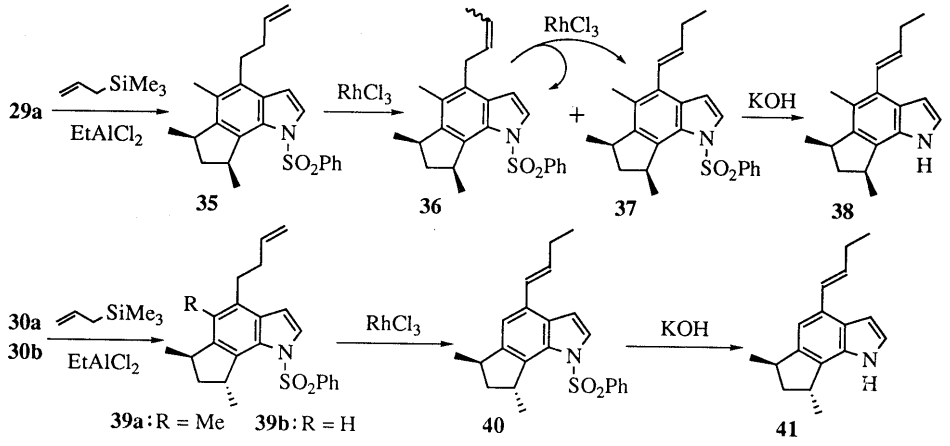

Chart 5

of their ^{1}H-NMR and IR spectra. However, natural iso-*trans*-trikentrin B was reported to be obtained as an inseparable mixture with *cis*-trikentrin B. Therefore estimation of their absolute structures is discussed later.

Total Synthesis of (6*R*,8*S*)-*cis*-Trikentrin B (6) and (6*R*,8*R*)-*trans*-Trikentrin B (47) The condensation product **24b** between the Claisen rearrangement product **22b** and 3-formylpyrrole derivative **23** was a starting material for the synthesis of these trikentrins B (Chart 6). The *exo*-methylene group of **24b** was oxidized as before by using a combination of a catalytic amount of osmium tetroxide and sodium metaperiodate, and, without isolation, the resulting ketone compound was further cyclized to an inseparable mixture of indole derivatives **42** in 41% yield by refluxing in chlorobenzene with *p*-toluenesulfonic acid and thiophenol. This mixture of **42** was reduced with lithium aluminum hydride at a low temperature of −20—0 °C to avoid further reductive removal of the phenylsulfonyl protecting group, and **43a** and **43b** were obtained in 73% and 17% yeilds after separation by HPLC. Following the result of the model study, the carbinols **43a** and **43b** were respectively oxidized with manganese dioxide in 89% and 87% yields to the aldehydes **44a** and **44b**, which were reacted with propylmagnesium bromide to afford a mixture of major (84% yield) and minor (*ca.* 4% yield) epimers of **45a** as well as a mixture of major (73% yield) and minor (*ca.* 8%) epimers of **45b**, all having unknown stereochemistry, accompanied with the formation of **43a** and **43b** in 10% and 18% yields. The combined epimers of **45a** and **45b** were respectively dehydrated by refluxing in benzene in the presence of a catalytic amount of *p*-toluenesulfonic acid to give the (*E*)-olefin derivatives **46a** and **46b** in 94% and 84% yields. The alkaline hydrolysis of the protecting group in **46a** and **46b** produced in 89% and 91% yeilds (6*R*,8*S*)-*cis*-trikentrin B (**6**), $[\alpha]_D^{24}$ +102° (c=0.18, $CHCl_3$) and (6*R*,8*R*)-*trans*-trikentrin B (**47**), $[\alpha]_D^{24}$ +24.3° (c=0.078, $CHCl_3$), whose IR and ^{1}H-NMR spectra were

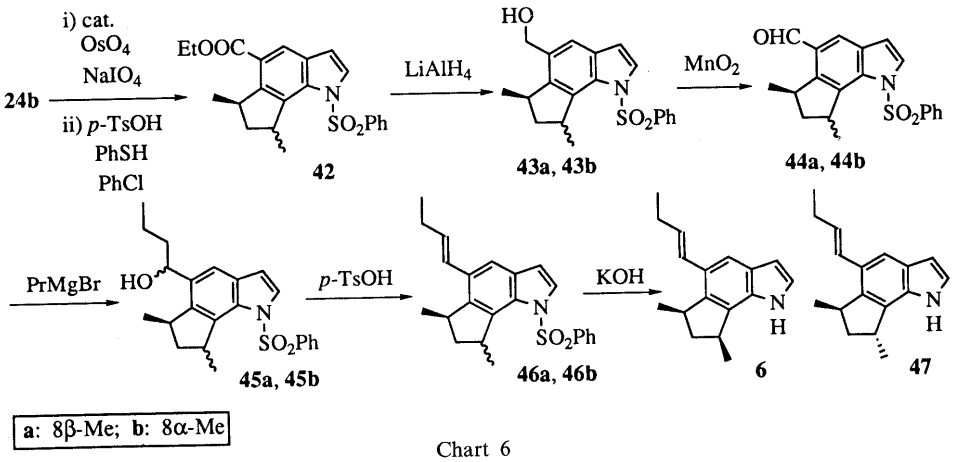

Chart 6

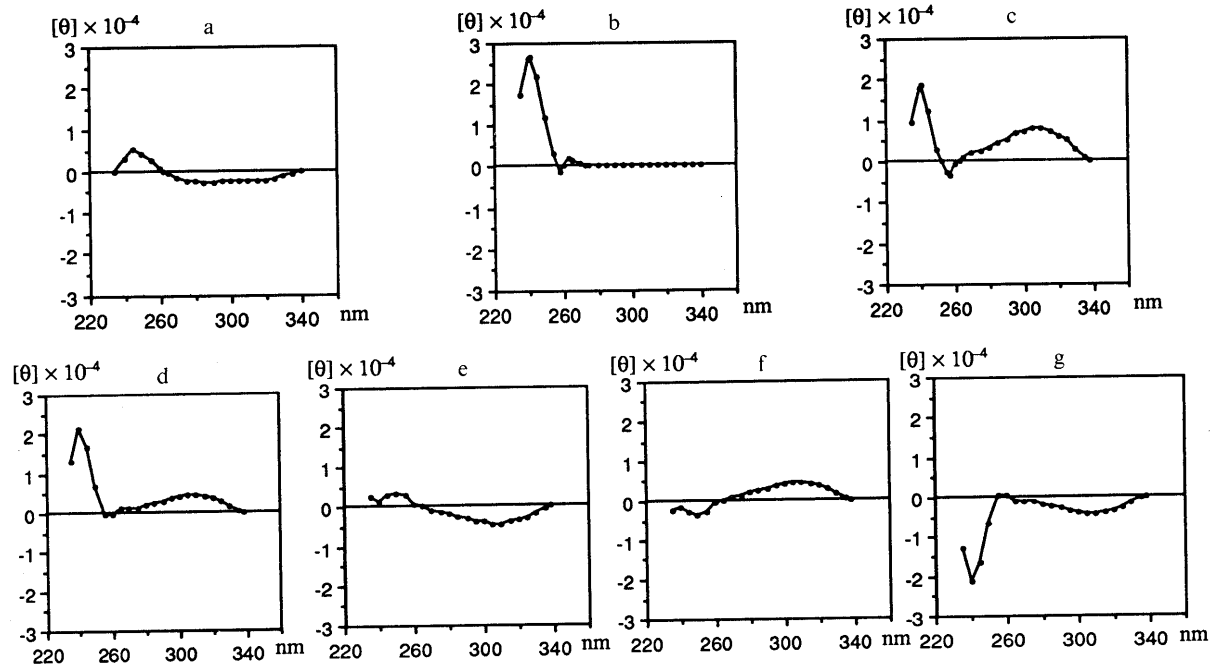

Fig. 1. CD Spectrum (a—c) and CD Curve (d—g). a, Mixture of Natural *cis*-Trikentrin B and iso-*trans*-Trikentrin B; b, (6*R*,8*S*)-*cis*-Trikentrin B (**6**); c, (6*R*,8*R*)-iso-*trans*-Trikentrin B (**41**). d, **6**+**41**; e, **6**+*ent*-**41**; f, *ent*-**6**+**41**; g, *ent* **6**+*ent*−**41**

identical with those of our synthetic (±)-*cis*-trikentrin B and (±)-*trans*-trikentrin B.[4e] Comparison of the optical rotational values of **47** and natural *trans*-trikentrin B,[3] $\{[\alpha]_D -13°$ ($c=1.97$, $CHCl_3$)$\}$, revealed that the natural product had the absolute structure of **7**.

From nature, *cis*-trikentrin B (**6**) and iso-*trans*-trikentrin B (**8**) were obtained as an inseparable mixture. At our request, Dr. Capon furnished us with the last remaining specimen of this mixture (*ca.* 0.5 mg) comprising **6** and **8** in a ratio of 44 : 56. The amount of the specimen was too small to allow any chemical reaction as a further attempt at separation. Therefore we decided to make a comparison of the CD spectral curve of this natural mixture (Fig. 1a) with calculated CD curves drawn from the measured CD curves of synthesized (6*R*,8*S*)-*cis*-trikentrin B (**6**) (Fig. 1b) and (6*R*,8*R*)-iso-*trans*-trikentrin B (**41**) (Fig. 1c) by taking into consideration that the addition rule for $[\theta]$'s is valid when two CD curves are combined.[14] Calculated curves (Fig. 1d, Fig. 1e, Fig. 1f, and Fig. 1g) were made for all possible combinations of **6**+**41**, **6**+*ent*-**41**, *ent*-**6**+**41**, and *ent*-**6**+*ent*-**41** by drawing as shown in Experimental. Among them, only the CD curve obtained from the combination of **6**+*ent*-**41** (Fig. 1e) resembled that of the natural mixture (Fig. 1a), so that the absolute structures of natural *cis*-trikentrin B and iso-*trans*-trikentrin B were estimated to be **6** and **8** (=*ent*-**41**).

In summary, starting from a chiral Diels–Alder adduct **12**, total syntheses of seven uniquely substituted indole derivatives, (6*R*,8*S*)-herbindole A (**31**), (6*R*,8*S*)-herbindole B (**34**), (6*R*,8*S*)-herbindole C (**38**), (6*R*,8*S*)-*cis*-trikentrin A (**4**), (6*R*,8*S*)-*cis*-trikentrin B (**6**), (6*R*,8*R*)-*trans*-trikentrin B (**47**), and (6*R*,8*R*)-iso-*trans*-trikentrin B (**41**), were achieved by applying the indole cyclization reaction **9**→**10** from pyrrole derivative. Together with the previous chiral syntheses of (6*S*,8*R*)-*cis*-trikentrin A and (6*R*,8*R*)-*trans*-trikentrin A,[4b,e] our synthetic studies have established the absolute structures of all eight herbindoles and trikentrins isolated from marine sponges as **1**—**8**.

Experimental

High-performance liquid chromatography (HPLC) was conducted on a TSK SiO_2-60 column (4.6 × 250 mm; Tosoh Co., Ltd.) with the eluting solvents indicated in parentheses; flow rate, 1 ml/min; detection, UV (254 nm). Specific rotations were measured on a JASCO DIP-370 digital polarimeter. CD spectra were taken on a JASCO J-500A. For other general descriptions, see the preceding paper.[1]

***tert*-Butyl [1*R*-(1α,2β,3α,4α)]-3-Bromobicyclo[2.2.1]hept-5-ene-2-carboxylate (15)** A solution of **12** (3.268 g, 9.96 mmol) in a mixture of 2N NaOH in H_2O (7 ml, 14.0 mmol), DME (14 ml) and MeOH (7 ml) was stirred at 0 °C for 1 h. The solution was made acidic (pH *ca.* 3) and extracted with Et_2O to afford the residue (2.57 g) after usual work-up. This was dissolved in CH_2Cl_2 (100 ml), and 95% H_2SO_4 (0.3 ml) was added at −20 °C. Isobutene gas (*ca.* 12 g, 214 mmol) was absorbed into this solution by bubbling at −20 °C for 2 h, and the solution was further stirred at room temperature for 48 h. This was poured into saturated $NaHCO_3$–H_2O and the whole was extracted with CH_2Cl_2. Usual work-up and purification by column chromatography [hexane–EtOAc (19 : 1)] afforded **15** (1.640 g, 60%) as a colorless oil. GC-MS *m/z*: 218, 216 (M^+, 6, 5), 137 (5), 119 (5), 91 (17), 66 (100), 57 (33). $[\alpha]_D^{24}$ +121° ($c=2.88$, $CHCl_3$). IR (neat) cm^{-1}: 1730. ^{1}H-NMR ($CDCl_3$) δ: 1.40 (9H, s), 1.68 (1H, br d, $J=9$ Hz), 2.01 (1H, d, $J=9$ Hz), 3.01—3.26 (3H, m), 3.98 (1H, dd, $J=2$, 2 Hz), 6.00—6.21 (2H, m).

***tert*-Butyl [1*R*-(1α,2ξ,3ξ,4α)]-3-Benzyloxybicyclo[2.2.1]hept-5-ene-2-carboxylate (16 Containing Three Isomers)** NaH in mineral oil (60%, 340 mg, 8.50 mmol) was added to a stirred solution of benzyl alcohol (1.15 ml, 11.1 mmol) in THF (8 ml) at 0 °C and the mixture was stirred under an Ar atmosphere for 20 min. A solution of **15** (1.010 g, 4.65 mmol) in THF (4 ml) was added dropwise to this and the whole was stirred at 0 °C for 3 h. It was poured into saturated $NaHCO_3$–H_2O, then the mixture was extracted with CH_2Cl_2, and usual work-up, followed by purification by column chromatography [hexane–EtOAc (49 : 1)], afforded **16** (969 mg, 87%) as a colorless oil, composed of three isomers in the ratio of 0.6 : 10 : 1, as determined by HPLC [hexane–EtOAc (59 : 1)], at the retention times (t_R) of 13.8, 15.6 and 16.7 min. GC-MS *m/z*: 235 (4), 179 (24), 153 (18), 149 (10), 107 (15), 91 (100), 57 (48). IR (neat) cm^{-1}: 1729. ^{1}H-NMR of the major isomer ($CDCl_3$) δ: 1.38 (9H, s), 1.59 (1H, br d, $J=9$ Hz), 1.88 (1H, d, $J=9$ Hz), 2.67 (1H, dd, $J=3$, 2 Hz), 2.93 (1H, br s), 3.03 (1H, br s), 3.79 (1H, dd, $J=2$, 2 Hz), 4.57 (2H, s), 6.00 (1H, dd, $J=5.5$, 3 Hz), 6.17 (1H, dd, $J=5.5$, 2.5 Hz), 7.13—7.45 (5H, m).

***tert*-Butyl [1*R*-(1α,2ξ,3ξ,4α,5α,6α)]-3-Benzyloxy-5,6-dihydroxybicyclo[2.2.1]heptane-2-carboxylate (17)** OsO_4 (4 mg, 0.016 mmol) was added to a solution of **16** (455 mg, 1.52 mmol) and $Me_3NO \cdot 2H_2O$ (210 mg, 1.89 mmol) in acetone (4.5 ml) and H_2O (0.5 ml), and the solution was stirred at room temperature for 15 h. Saturated $Na_2S_2O_3$–H_2O was added and the mixture was extracted with CH_2Cl_2. The CH_2Cl_2 solution was successively washed with saturated $CuSO_4$–H_2O, H_2O, saturated $NaHCO_3$–H_2O, and H_2O, and worked up as usual. Purification by PTLC [benzene–EtOAc (3 : 1)] afforded **17** (486 mg, 96%) as a colorless syrup, which became partially crystalline on standing. Repeated recrystallization from CH_2Cl_2–hexane gave the major isomer as colorless needles, mp 93.5—95.5 °C. *Anal.* Calcd for $C_{19}H_{26}O_5$: C, 68.24; H, 7.84. Found: C, 68.39; H, 7.77. HRMS Calcd for $C_{19}H_{26}O_5$: 334.1780. Found: 334.1795. MS *m/z*: 334 (M^+, 0.1), 277 (8), 171 (6), 169 (9), 153 (10), 91 (100), 57 (31). $[\alpha]_D^{24.5}$ +39.2° ($c=1.54$, $CHCl_3$). IR (neat) cm^{-1}: 1725. ^{1}H-NMR ($CDCl_3$) δ: 1.54 (9H, s), 1.59 (1H, d, $J=10.5$ Hz), 1.86 (1H, d, $J=10.5$ Hz), 2.34 (1H, br s), 2.34—2.63 (2H, m), 3.42—3.85 (3H + 2 × OH, m), 4.39 (1H, d, $J=12.5$ Hz), 4.53 (1H, d, $J=12.5$ Hz), 7.28 (5H, s).

***tert*-Butyl (1ξ,2ξ,3*R*,4*S*)-2-Benzyloxy-3,5-di[bis(ethylthio)methyl]-cyclopentanecarboxylate (18)** $NaIO_4$ (376 mg, 1.76 mmol) was added to a solution of **17** (544 mg, 1.63 mmol) in THF (18 ml) and H_2O (2 ml), and the mixture was stirred at 0 °C for 1 h. Water was added and the whole was extracted with CH_2Cl_2, then worked up as usual. The residual oil (540 mg) was dissolved in CH_2Cl_2 (15 ml), and EtSH (1.20 ml, 16.2 mmol) and $BF_3 \cdot OEt_2$ (0.10 ml, 0.81 mmol) were further added to this under an Ar atmosphere at 0 °C. This mixture was stirred at 0 °C for 18 h, then saturated $NaHCO_3$–H_2O was added, and the whole was extracted with CH_2Cl_2 and worked up as usual. Purification by column chromatography [hexane–EtOAc (19 : 1)] afforded **18** (672 mg, 76%). A by-product **19** (35 mg, 5%) was obtained from the more polar fractions. **18**: Colorless oil. HRMS Calcd for $C_{27}H_{44}O_3S_4$: 544.2173. Found: 544.2177. MS *m/z*: 544 (M^+, 3), 483 (3), 453 (6), 421 (8), 397 (5), 365 (37), 259 (18), 101 (62), 91 (100), 57 (50). IR ($CHCl_3$) cm^{-1}: 1717. ^{1}H-NMR ($CDCl_3$) δ: 1.03—1.38 (12H, m), 1.48 (9H, s), *ca.* 1.48—2.13 (1H, m), 2.13—2.93 (11H, m), 3.07 (1H, br d, $J=7$ Hz), 3.74 (1H, d, $J=7.5$ Hz), 4.10 (1H, br d, $J=4.5$ Hz), 4.18 (1H, d, $J=11$ Hz), 4.47 (1H, d, $J=11$ Hz), 4.66 (1H, d, $J=11$ Hz), 7.18—7.49 (5H, m). **19**: Colorless syrup. HRMS Calcd for $C_{21}H_{30}O_3S_3$: 426.1357. Found: 426.1334. MS *m/z*: 426 (M^+, 4), 365 (15), 259 (13), 101 (50), 91 (100). IR ($CHCl_3$) cm^{-1}: 1772. ^{1}H-NMR ($CDCl_3$) δ: 1.14 (3H, t, $J=7.5$ Hz), 1.22 (3H, t, $J=7.5$ Hz), 1.30 (3H, t, $J=7.5$ Hz), *ca.* 1.30—1.90 (1H, m), 2.14—3.06 (9H, m), 3.20 (1H, dd, $J=9$, 3 Hz), 3.76 (1H, d, $J=5$ Hz), 4.18 (1H, dd, $J=7$, 3 Hz), 4.56 (1H, d, $J=11$ Hz), 4.74 (1H, d, $J=11$ Hz), 5.41 (1H, s), 7.21—7.51 (5H, m).

***tert*-Butyl (3*R*,5*S*)-3,5-Dimethyl-1-cyclopentenecarboxylate (20)** A mixture of **18** (226 mg, 0.415 mmol) and Raney Ni (W-2) (1.5 ml) in EtOH (4 ml) and DME (1 ml) was refluxed with stirring for 2 h. After cooling, the mixture was filtered through a Celite bed and the Celite was washed thoroughly with CH_2Cl_2. The combined organic layer was evaporated to leave a residue (124 mg), which was dissolved in THF (4 ml) and the solution was cooled to 0 °C. *tert*-BuOK (93 mg, 0.83 mmol) was added and the mixture was stirred under an Ar atmosphere at 0 °C for 1 h. Saturated NH_4Cl–H_2O was added and the whole was extracted with CH_2Cl_2, and worked up as usual. Purification by PTLC [hexane–EtOAc (69 : 1)] gave **20** (62 mg, 76%) as a colorless oil. HPLC [hexane–EtOAc (69 : 1)] showed a single peak at $t_R=6.47$ min. GC-HRMS Calcd for $C_{12}H_{20}O_2$: 196.1463. Found: 196.1475. GC-MS *m/z*: 196 (M^+, 3), 141 (55), 140 (37), 123 (65), 95 (97), 57 (100). $[\alpha]_D^{22}$

+85.7° (c=3.12, $CHCl_3$). IR ($CHCl_3$) cm^{-1}: 1698, 1631. ^{1}H-NMR ($CDCl_3$) δ: *ca.* 0.82—1.29 (1H, m), 1.10 (3H, d, J=7 Hz), 1.18 (3H, d, J=7 Hz), 1.47 (9H, s), 2.38 (1H, ddd, J=12.5, 9, 9 Hz), 2.48—3.14 (2H, m), 6.48 (1H, dd, J=2, 2 Hz).

Methyl (3*R*,5*S*)-3,5-Dimethyl-1-cyclopentenecarboxylate (21) A solution of **20** (248 mg, 1.27 mmol) in 1% H_2SO_4–MeOH (5 ml) was gently refluxed with stirring for 3 h, then cooled in an ice bath. Saturated $NaHCO_3$–H_2O was added and the whole was extracted with CH_2Cl_2, and worked up as usual. Purification by PTLC [hexane–EtOAc (64 : 1)] gave **21** (178 mg, 91%) as a colorless oil. GC-HRMS Calcd for $C_9H_{14}O_2$: 154.0993. Found: 154.0992. GC-MS m/z: 154 (M^+, 10), 139 (11), 123 (17), 95 (100), 79 (33). $[\alpha]_D^{24}$ +98.0° (c=1.55, $CHCl_3$). IR ($CHCl_3$) cm^{-1}: 1712, 1630. ^{1}H-NMR ($CDCl_3$) δ: 0.89—1.28 (1H, m), 1.09 (3H, d, J=7 Hz), 1.18 (3H, d, J=7 Hz), 2.40 (1H, ddd, J=12.5, 8.5, 8.5 Hz), 2.54—3.11 (2H, m), 3.69 (3H, s), 6.51—6.65 (1H, m).

(3*R*,5*S*)-3,5-Dimethyl-1-cyclopentenylmethanol (13) A cooled (−65 °C) solution of **21** (166 mg, 1.08 mmol) in hexane (4 ml) was treated with 1.5 M DIBALH in toluene (2.16 ml, 3.24 mmol) under an Ar atmosphere and the mixture was stirred at −65——60 °C for 30 min. Saturated NH_4Cl–H_2O was added and the whole was filtered through a Celite bed. The Celite was washed with Et_2O and the combined organic layer was treated as usual. Purification by PTLC [hexane–EtOAc (9 : 1)] gave **13** (130 mg, 96%) as a colorless oil. GC-HRMS Calcd for $C_8H_{14}O$: 126.1044. Found: 126.1048. GC-MS m/z: 126 (M^+, 12), 111 (9), 95 (100). $[\alpha]_D^{24.5}$ +58.5° (c=2.60, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 0.77—1.13 (1H, m), 1.01 (3H, d, J=6.5 Hz), 1.04 (3H, d, J=6.5 Hz), 1.53 (1H, br s, OH), 2.35 (1H, ddd, J=12.5, 8.5, 8.5 Hz), 2.46—2.90 (2H, m), 4.07 (1H, d, J=14 Hz), 4.23 (1H, d, J=14 Hz), 5.40—5.56 (1H, m).

Ethyl (α*ξ*,1*ξ*,3*S*,5*R*)-2-Methylene-α,3,5-trimethylcyclopentaneacetate (22a) Pivalic acid (5 mg, 49.0 μmol) was added to a solution of **13** (75 mg, 0.595 mmol) and $EtC(OEt)_3$ (0.48 ml, 2.39 mmol) in toluene (1.5 ml) and the mixture was heated in a sealed tube under an Ar atmosphere at 150 °C for 5 h, then cooled in an ice bath. Saturated $NaHCO_3$–H_2O was added and the whole was extracted with CH_2Cl_2, and worked up as usual. Purification by PTLC [hexane–EtOAc (69 : 1)] gave **22a** (112 mg, 90%) as a colorless oil. GC-HRMS (80 °C, He 20 ml/min) Calcd for $C_{13}H_{22}O_2$: 210.1620. Found: 210.1617 (major isomer, t_R=8.0 min) and 210.1623 (minor isomer, t_R=10.5 min). GC-MS of major and minor isomers m/z: 210 (M^+, 0.6, 3), 195 (1, 6), 181 (0.5, 4), 165 (3, 6), 136 (13, 43),121 (16, 44), 109 (100, 100), 67 (15, 32). IR ($CHCl_3$) cm^{-1}: 1728, 1648. ^{1}H-NMR ($CDCl_3$) of major and minor isomers δ: *ca.* 0.70—1.38 (1H, m), 0.93 (3H, d, J=6 Hz), 1.05 (3H, d, J=6.5 Hz), 1.08 (3H, d, J=7 Hz), 1.23 (3H, t, J=7 Hz), 1.59—2.83 (5H, m), 4.10 and 4.12 (2H, q each, J=7 Hz), 4.63—4.96 (2H, m).

Ethyl (1*ξ*,3*S*,5*R*)-2-Methylene-3,5-dimethylcyclopentaneacetate (22b) In the same manner as above, **22b** (91 mg, 87%) was prepared from **13** (67 mg, 0.532 mmol), $MeC(OEt)_3$ (0.39 ml, 2.13 mmol) and pivalic acid (4 mg, 39 μmol) as a colorless oil. GC-HRMS (80 °C, He 20 ml/min) Calcd for $C_{12}H_{20}O_2$: 196.1463. Found: 196.1481 (major isomer, t_R= 5.6 min) and 196.1485 (minor isomer, t_R=7.0 min). GC-MS of major and minor isomers m/z: 196 (M^+, 6, 11), 181 (10, 23), 151 (12, 24), 122 (38, 63), 109 (69, 95), 108 (100, 100), 93 (32, 51), 29 (40, 55). IR ($CHCl_3$) cm^{-1}: 1729, 1647. ^{1}H-NMR ($CDCl_3$) δ: 0.83, 0.99, 1.07, and 1.09 (total 6H, d each, J=6.5 Hz), 1.24 (3H, 5, J=7 Hz), 4.13 (2H, q, J=7 Hz), 4.69—4.90 (2H, m).

Ethyl (α*ξ*,β*ξ*)-α-[(1*ξ*,3*S*,5*R*)-3,5-Dimethyl-2-methylenecyclopentyl]-β-hydroxy-α-methyl-1-(phenylsulfonyl)-1*H*-pyrrole-3-propanoate (24a) A THF solution (3 ml) of **22a** (238 mg, 1.13 mmol) was added at −68 °C to a THF solution (2.5 ml) of LDA, prepared from iso-Pr_2NH (0.21 ml, 1.50 mmol) and 15% BuLi–hexane (0.72 ml, 1.13 mmol), and the mixture was stirred at −68——65 °C for 40 min. It was cooled to −78 °C and a THF solution (2.5 ml) of **23** (161 mg, 0.685 mmol) was added dropwise. Stirring was continued at −78 °C for 40 min, then saturated NH_4Cl–H_2O was added and the whole was extracted with CH_2Cl_2. Usual work-up and purification by PTLC [hexane–EtOAc (5 : 1)] gave **24a** (287 mg, 94% based on **23**), together with recovery of **23** (3 mg, 2%) and **22a** (87 mg). **24a**: Colroelss syrup. HRMS Calcd for $C_{24}H_{31}NO_5S$: 445.1923. Found: 445.1935. MS m/z: 445 (M^+, 1), 304 (2), 286 (1), 235 (24), 141 (28), 109 (27), 77 (100). IR ($CHCl_3$) cm^{-1}: 1718, 1687, 1646. ^{1}H-NMR ($CDCl_3$) δ: 0.57—1.30 (13H, m), 1.74—2.52 (3H, m), 2.52—2.73 and 2.80—3.10 (total 1H, m each), 3.81, 4.00, and 4.03 (total 2H, q each, J=7 Hz), 4.27—5.31 (3H, m), 6.11 and 6.22 (total 1H, dd each, J=3.5, 2 and 2.5, 2.5 Hz), 6.89—7.12 (2H, m), 7.27—7.66 (3H, m), 7.66—7.89 (2H, m).

Ethyl (α*ξ*,β*ξ*)-α-[(1*ξ*,3*S*,5*R*)-3,5-Dimethyl-2-methylenecyclopentyl]-β-hydroxy-1-(phenylsulfonyl)-1*H*-pyrrole-3-propanoate (24b) In the same manner as above, **23** (116 mg, 0.494 mmol) was allowed to react with the Li enolate of **22b** (160 mg, 0.816 mmol) to give **24b** (211 mg, 99% based on **23**) with recovery of **22b** (61 mg). **24b**: Colorless syrup. HRMS Calcd for $C_{23}H_{29}NO_5S$: 431.1765. Found: 431.1749. MS m/z: 431 (M^+, 0.7), 413 (1), 340 (1), 321 (1), 272 (2), 235 (24), 141 (27), 77 (100), 51 (25). IR ($CHCl_3$) cm^{-1}: 1721, 1647. ^{1}H-NMR ($CDCl_3$) δ: 0.57—1.23 (10H, m), 1.66—3.27 (5H + OH, m), 3.43—4.13 (2H, m), 4.65—5.16 (3H, m), 6.14—6.36 (1H, m), 7.01—7.17 (2H, m), 7.26—7.68 (3H, m), 7.68—7.92 (2H, m).

Ethyl (α*ξ*)-α-[(1*ξ*,3*S*,5*R*)-3,5-Dimethyl-2-methylenecyclopentyl]-α-methyl-β-oxo-1-(phenylsulfonyl)-1*H*-pyrrole-3-propanoate (25a) A suspension of **24a** (287 mg, 0.645 mmol) and MnO_2 (2.244 g, 25.8 mmol) in CH_2Cl_2 (20 ml) was stirred under reflux for 2 h. The mixure was filtered through a Celite bed and the Celite was washed thoroughly with CH_2Cl_2. The combined organic layer was evaporated and the residue was purified by PTLC [hexane–CH_2Cl_2 (3 : 4)] to afford **25a** (232 g, 81%) as a colorless syrup. HRMS Calcd for $C_{24}H_{29}NO_5S$: 443.1766. Found: 443.1773. MS m/z: 443 (M^+, 5), 335 (12), 302 (15), 234 (100), 207 (17), 141 (33), 109 (21), 77 (91). IR ($CHCl_3$) cm^{-1}: 1731, 1672. ^{1}H-NMR ($CDCl_3$) δ: 0.67 and 0.84—1.14 (total 9H, d and m, J=6.5 Hz), 1.34 and 1.41 (total 3H, s each), 3.12 and 3.23 (total 1H, br d each, J=5 and 5.5 Hz), 3.83—4.21 and 3.96 (total 2H, m and q, J=7 Hz), 4.76, 4.83, and 5.11 (total 2H, br s each), 6.59 and 6.67 (total 1H, dd each, J=3.5, 1.5 Hz), 7.07 (1H, dd, J=3.5, 2.5 Hz), 7.34—7.82 (4H, m), 7.82—8.06 (2H, m).

Ethyl (α*ξ*)-α-[(1*ξ*,3*S*,5*R*)-3,5-Dimethyl-2-methylenecyclopentyl]-β-oxo-1-(phenylsulfonyl)-1*H*-pyrrole-3-propanoate (25b) In a similar manner, **24b** (60 mg, 0.139 mmol) was oxidized with MnO_2 (303 mg, 3.48 mmol) to yield **25b** (50 mg, 84%) as a colorless syrup. HRMS Calcd for $C_{23}H_{27}NO_5S$: 429.1610. Found: 429.1621. MS m/z: 429 (M^+, 2), 356 (3), 321 (6), 242 (4), 234 (100), 141 (27), 108 (31), 77 (70). IR ($CHCl_3$) cm^{-1}: 1733, 1679. ^{1}H-NMR ($CDCl_3$) δ: 0.51—1.29 (10H, m), 1.47—2.71 (3H, m), 2.81—3.06 and 3.36—3.66 (total 1H, m each), 3.88—4.24 and 4.30—4.39 (3H, m), 4.58—4.91 (2H, m), 6.60—6.82 (1H, m), 7.04—7.20 (1H, m), 7.37—7.69 (3H, m), 7.69—8.00 (3H, m).

3-[(2*ξ*)-2-[(1*ξ*,3*S*,5*R*)-3,5-Dimethyl-2-methylenecyclopentyl]-1-oxo]-propyl-1-(phenylsulfonyl)-1*H*-pyrrole (26a) A solution of **25a** (53 mg, 0.120 mmol) and LiCl (127 mg, 2.99 mmol) in HMPA (2.5 ml) and H_2O (54 μl, 3.00 mmol) was heated with stirring at 130—133 °C for 24 h, then cooled in an ice bath. Water was added and the whole was extracted with Et_2O, and worked up as usual. Purification by PTLC [hexane–Et_2O (9 : 1)] gave **26a** (31 mg, 70%) and recovered **25a** (2.5 mg, 5%). **26a**: Colorless syrup. HRMS Calcd for $C_{21}H_{25}NO_3S$: 371.1555. Found: 371.1528. MS m/z: 371 (M^+, 5), 263 (58), 234 (100), 141 (29), 77 (92), 69 (45). IR ($CHCl_3$) cm^{-1}: 1672. ^{1}H-NMR ($CDCl_3$) δ: 0.73—1.23 (10H, m), 1.39—2.61 (4H, m), 2.94—3.42 (1H, m), 4.65—4.93 (2H, m), 6.11—6.75 (1H, m), 7.08—7.22 (1H, m), 7.37—7.68 (3H, m), 7.68—7.81 (1H, m), 7.81—8.02 (2H, m).

3-[2-[(1*ξ*,3*S*,5*R*)-3,5-Dimethyl-2-methylenecyclopentyl]-1-oxo]ethyl-1-(phenylsulfonyl)-1*H*-pyrrole (26b) A solution of **25b** (76 mg, 0.177 mmol) in 5% NaOH/DME–MeOH–H_2O (1 : 2 : 1) (4 ml) was refluxed with stirring for 3 h, then cooled in an ice bath. The pH of the solution was adjusted to 4—5 with 0.5 N HCl–H_2O. Extraction with Et_2O and usual work-up gave a residue (36 mg). The residue and $PhSO_2Cl$ (88 mg, 0.50 mmol) were dissolved in THF (3 ml) and DMF (1 ml), and 60% NaH in mineral oil (20 mg, 0.50 mmol) was added under an Ar atmosphere at 0 °C. Stirring was continued for 2 h at the same temperature, then saturated NH_4Cl–H_2O was added and the whole was extracted with Et_2O, and worked up as usual. Purification by PTLC [hexane–CH_2Cl_2 (1 : 1)] gave **26b** (50 mg, 79%) as a colorless syrup. HRMS Calcd for $C_{20}H_{23}NO_3S$: 357.1397. Found: 357.1394. MS m/z: 357 (M^+, 5), 249 (16), 234 (100), 141 (33), 108 (27), 77 (90). IR ($CHCl_3$) cm^{-1}: 1679. ^{1}H-NMR ($CDCl_3$) δ: 0.70—1.18 (6H, m), 4.57—4.84 (2H, m), 6.67 (1H, dd, J=3, 1.5 Hz), 7.11 (1H, dd, J=3, 2 Hz), 7.36—7.71 (3H, m), 7.71 (1H, dd, J=2, 1.5 Hz), 7.79—8.01 (2H, m).

(α*ξ*)-α-[(1*ξ*)-1-[(1*ξ*,3*S*,5*R*)-3,5-Dimethyl-2-methylenecyclopentyl]-ethyl]-1-(phenylsulfonyl)-α-[(phenylsulfonyl)methyl]-1*H*-pyrrole-3-methanol (27a) A THF solution (4 ml) of $PhSO_2Me$ (192 mg, 1.23 mmol) was treated with 15% BuLi in hexane (0.79 ml, 1.23 mmol) at −73 °C for 5 min and at −20 °C for 30 min under an Ar atmosphere, and then cooled to −75 °C. A THF solution (3 ml) of **26a** (114 mg, 0.307 mmol) was added dropwise to this, and the mixture was stirred at −75——70 °C for 50 min. Saturated NH_4Cl–H_2O was added and the whole was

extracted with CH_2Cl_2, and worked up as usual. Purification by PTLC [benzene–EtOAc (29 : 1)] gave **27a** (149 mg, 92%) as a colorless amorphous powder. HRMS Calcd for $C_{28}H_{33}NO_5S_2$: 527.1800. Found: 527.1817. MS *m/z*: 527 (M^+, 0.3), 390 (16), 263 (27), 234 (45), 141 (40), 77 (100), 51 (22). IR ($CHCl_3$) cm^{-1}: 1643. ^{1}H-NMR ($CDCl_3$) δ: 0.16 and 0.66—1.08 (total 9H, d and m, J=6.5 Hz), 3.41—3.89 (2H, m), 4.31—4.43, 4.49—4.59, 4.75—4.89, and 5.18—5.35 (total 2H, m each), 5.47—5.66 (1H, m), 6.57—6.74 (1H, m), 6.93—7.08 (1H, m).

(αξ)-α-[(1ξ,3*S*,5*R*)-3,5-Dimethyl-2-methylenecyclopentyl]methyl-1-(phenylsulfonyl)-α-[(phenylsulfonyl)methyl]-1*H*-pyrrole-3-methanol (27b) In the same manner as above, **26b** (32 mg, 0.090 mmol) was treated with lithiomethyl phenyl sulfone, prepared from $PhSO_2Me$ (56 mg, 0.359 mmol) and 15% BuLi in hexane (0.23 ml, 0.359 mmol), to give **27b** (44 mg, 96%) as a colorless amorphous powder. HRMS Calcd for $C_{27}H_{31}NO_5S_2$: 513.1642. Found: 513.1626. MS *m/z*: 513 (M^+, 0.1), 390 (6), 372 (2), 357 (3), 354 (4), 234 (47), 141 (35), 77 (100), 51 (23). IR ($CHCl_3$) cm^{-1}: 1648. ^{1}H-NMR ($CDCl_3$) of major and minor isomers δ: 3.51 and 3.48 (total 1H, d each, J=11.5 Hz), 3.63 and 3.61 (total 1H, d each, J=11.5 Hz), 4.23—5.06 (2H + OH, m), 5.67—5.79 and 5.57—5.67 (total 1H, m each), 6.69—6.86 (1H, m), 7.00—7.13 (1H, m), 7.72—7.95 (2H, m).

(6*R*,8*S*)-1-(Phenylsulfonyl)-4-[(phenylsulfonyl)methyl]-1,6,7,8-tetrahydro-5,6,8-trimethylcyclopent[*g*]indole (29a) and (6*R*,8*R*)-1-(phenylsulfonyl)-4-[(phenylsulfonyl)methyl]-1,6,7,8-tetrahydro-5,6,8-trimethylcyclopent[*g*]indole (30a) $NaIO_4$ (171 mg, 0.799 mmol) was added to a solution of **27a** (42 mg, 0.080 mmol) and OsO_4 (2 mg, 7.9 μmol) in THF (4 ml) and H_2O (1 ml), and the mixture was stirred at room temperature for 19 h. After addition of saturated $Na_2S_2O_3$–H_2O, the whole was extracted with CH_2Cl_2, and worked up as usual to leave a residue (66 mg). A toluene solution (5 ml) of the residue, PhSH (82 μl, 0.745 mmol), and *p*-TsOH·H_2O (22 mg, 0.116 mmol) was refluxed with stirring for 5 h, and then cooled in an ice bath. Saturated $NaHCO_3$–H_2O was added and the whole was extracted with CH_2Cl_2, and worked up as usual. Purification by PTLC [hexane–DME (4 : 1)] afforded **29a** + **30a** (28 mg), which was separated by HPLC [column, Tosoh SiO_2-60, 21.5 × 300 mm; eluting solvent, hexane–EtOAc (4 : 1); flow rate, 5 ml/min; detection, UV (285 nm)] to yield **29a** (19 mg, 48%, t_R=90.6 min) and **30a** (6 mg, 15%, t_R=80.8 min). **29a**: Colorless syrup. HRMS Calcd for $C_{27}H_{27}NO_4S_2$: 493.1381. Found: 493.1371. MS *m/z*: 493 (M^+, 4), 352 (100), 196 (30), 181 (16), 141 (4), 77 (27), 51 (11). $[\alpha]_D^{21}$ +297° (c=0.946, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 1.21 (3H, d, J=7.5 Hz), 1.33 (3H, d, J=7 Hz), 1.56 (1H, d, J=12.5 Hz), 2.03 (3H, s), 2.48 (1H, ddd, J=12.5, 9, 9 Hz), 3.22 (1H, dq, J=9, 7.5 Hz), 4.12 (1H, dq, J=9, 7 Hz), 4.55 (1H, d, J=14.5 Hz), 4.61 (1H, d, J=14.5 Hz), 6.46 (1H, d, J=4 Hz), 7.26—7.32 (2H, m), 7.37—7.43 (2H, m), 7.47—7.56 (4H, m), 7.49 (1H, d, J=4 Hz), 7.58—7.63 (2H, m). **30a**: Colorless prisms, mp 207—209 °C (CH_2Cl_2–MeOH). *Anal.* Calcd for $C_{27}H_{27}NO_4S_2$: C, 65.69; H, 5.51; N, 2.84. Found: C, 65.71; H, 5.49; N, 2.93. HRMS Calcd for $C_{27}H_{27}NO_4S_2$: 493.1381. Found: 493.1357. MS *m/z*: 493 (M^+, 5), 352 (100), 196 (29), 181 (15), 141 (5), 77 (24), 51 (7). $[\alpha]_D^{21}$ −484° (c=0.379, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 1.06 (3H, d, J=6.5 Hz), 1.27 (3H, d, J=6.5 Hz), 1.85 (1H, ddd, J=12.5, 8, 6 Hz), 1.88 (3H, s), 1.98 (1H, ddd, J=12.5, 8, 4 Hz), 3.30 (1H, ddq, J=8, 4, 6.5 Hz), 4.20 (1H, ddq, J=8, 6, 6.5 Hz), 4.48 (1H, d, J=14 Hz), 4.53 (1H, d, J=14 Hz), 6.50 (1H, d, J=4 Hz), 7.24—7.31 (4H, m), 7.33—7.40 (2H, m), 7.38 (1H, d, J=4 Hz), 7.45—7.50 (1H, m), 7.51—7.60 (3H, m).

(6*R*,8*S*)-6,8-Dimethyl-1-(phenylsulfonyl)-4-(phenylsulfonyl)methyl-1,6,7,8-tetrahydrocyclopent[*g*]indole (29b) and (6*R*,8*R*)-6,8-dimethyl-1-(phenylsulfonyl)-4-(phenylsulfonyl)methyl-1,6,7,8-tetrahydrocyclopent-[*g*]indole (30b) A similar treatment of **27b** (41 mg, 0.080 mmol) with OsO_4 (2 mg, 7.9 μmol) and $NaIO_4$ (137 mg, 0.640 mmol) gave a residue (50 mg), which was dissolved in chlorobenzene (3 ml). $PhCH_2SH$ (75 μl, 0.64 mmol), and *p*-TsOH·H_2O (15 mg, 0.079 mmol) were added and the mixture was refluxed with stirring for 1.5 h. The same work-up as above, followed by PTLC [benzene–EtOAc (49 : 1)] afforded **29b** + **30b** (26 mg), which was separated by HPLC as described above [eluting solvent, hexane–EtOAc (7 : 2)] to yield **29b** (17 mg, 44%, t_R=92.8 min) and **30b** (6 mg, 16%, t_R=85.3 min). **29b**: Colorless syrup. HRMS Calcd for $C_{26}H_{25}NO_4S_2$: 479.1224. Found: 479.1222. MS *m/z*: 479 (M^+, 5), 338 (100), 182 (30), 167 (17), 77 (40), 51 (13). $[\alpha]_D^{24}$ +391° (c=0.934, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.14 (3H, d, J=7 Hz), 1.27 (3H, d, J=7 Hz), 1.36 (1H, ddd, J=13, 3.5, 3.5 Hz), 2.53 (1H, ddd, J=13, 9, 9 Hz), 2.89—3.29 (1H, m), 3.88—4.24 (1H, m), 4.34 (1H, d, J=14 Hz), 4.49 (1H, d, J=14 Hz), 6.46 (1H, d, J=4 Hz), 6.66 (1H, s), 7.09—7.68 (10H, m), 7.43 (1H, d, J=4 Hz). **30b**: Colorless syrup. HRMS Calcd for $C_{26}H_{25}NO_4S_2$: 479.1224. Found: 479.1224. MS *m/z*: 479 (M^+, 6), 338 (100), 182 (34), 167 (16), 77 (36), 51 (12). $[\alpha]_D^{24}$ −270° (c=0.503, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.01 (3H, d, J=6.5 Hz), 1.09 (3H, d, J=6.5 Hz), 1.60 (1H, ddd, J=12, 10.5, 7 Hz), 1.96 (1H, dd, J=12, 6.5 Hz), 3.20 (1H, ddq, J=10.5, 6.5, 6.5 Hz), 3.99 (1H, dq, J=7, 6.5 Hz), 4.46 (2H, s), 6.50 (1H, d, J=4 Hz), 6.67 (1H, s), 7.10—7.73 (10H, m), 7.56 (1H, d, J=4 Hz).

(6*R*,8*S*)-Herbindole A (31) Mg (37 mg, 1.54 mg atom) and NH_4Cl (4 mg, 0.075 mmol) were added to a MeOH solution (4 ml) of **29a** (15 mg, 0.030 mmol) and the mixture was stirred at room temperature for 2 h. Saturated NH_4Cl–H_2O was added and the whole was extracted with CH_2Cl_2, and worked up as usual. Purification by PTLC [hexane–EtOAc (14 : 1)] afforded crystalline **31** (5.5 mg, 85%), whose recrystallization from MeOH–H_2O gave colorless needles, mp 134—136 °C. GC-HRMS Calcd for $C_{15}H_{19}N$: 213.1517. Found: 213.1512. GC-MS *m/z*: 213 (M^+, 48), 198 (100), 183 (25), 168 (11). $[\alpha]_D^{21}$ +56.9° (c=0.28, $CHCl_3$). CD (c=0.47 × 10^{-3}, MeOH): $[\theta]_{264}^{20}$ 0, $[\theta]_{248}^{20}$, −3800, $[\theta]_{240}^{20}$, 0, $[\theta]_{225}^{20}$ +38900, $[\theta]_{213}^{20}$ 0. [CD of the recrystallized authentic sample (c=0.48 × 10^{-3}, MeOH): $[\theta]_{263}^{20}$ 0, $[\theta]_{248}^{20}$ +3300, $[\theta]_{241}^{20}$ 0, $[\theta]_{225}^{20}$ −38400, $[\theta]_{214}^{20}$ 0]. IR ($CHCl_3$) cm^{-1}: 3500 (s), 3005 (s), 2970 (s), 2940 (s), 2880 (s), 1619 (w), 1510 (w), 1483 (m), 1461 (w), 1452 (m), 1408 (m), 1399 (m), 1380 (m), 1353 (m), 1341 (w), 1321 (w), 1307 (w), 1280 (w), 1127 (m), 1095 (w), 1071 (w), 1061 (w), 910 (w), 845 (w), 720 (s). [IR of the recrystallized authentic sample ($CHCl_3$) cm^{-1}: 3500 (s), 3005 (s), 2970 (s), 2940 (s), 2875 (s), 1483 (m), 1461 (w), 1450 (m), 1408 (m), 1398 (m), 1377 (m), 1353 (m), 1340 (w), 1321 (w), 1305 (w), 1279 (w), 1126 (m), 1092 (w), 1072 (w), 1061 (w), 844 (w), 720 (s)]. ^{1}H-NMR (C_6D_6, 400 MHz) δ: 1.23 (3H, d, J=7 Hz), 1.35 (3H, d, J=7 Hz), 1.47 (1H, ddd, J=13, 2, 2 Hz), 2.28 (3H, s), 2.46 (3H, s), 2.60 (1H, ddd, J=13, 9, 9 Hz), 3.19 (1H, ddq, J=9, 2, 7 Hz), 3.35 (1H, ddq, J=9, 2, 7 Hz), 6.62 (1H, dd, J=3, 2 Hz), 6.66 (1H, dd, J=3, 2.5 Hz), 6.80 (1H, br s, NH). ^{13}C-NMR (C_6D_6, 100 MHz) δ: 15.4, 15.7, 22.9, 24.1, 37.3, 39.5, 42.2, 101.7, 122.6, 122.9, 126.4, 126.5, 128.6, 131.0, 141.8.

(6*R*,8*R*)-1,6,7,8-Tetrahydro-4,5,6,8-tetramethylcyclopent[*g*]indole (32) In the same manner as described above, **30a** (9 mg, 0.018 mmol) was reductively deprotected to afford **32** (3.5 mg, 90%) as colorless needles, mp 84—86 °C (MeOH–H_2O). GC-HRMS Calcd for $C_{15}H_{19}N$: 213.1517. Found: 213.1514. GC-MS *m/z*: 213 (M^+, 49), 198 (100), 183 (24). $[\alpha]_D^{22}$ −36.6° (c=0.17, $CHCl_3$). CD (c=0.48 × 10^{-3}, MeOH): $[\theta]_{298}^{22}$ 0, $[\theta]_{294}^{22}$ −1700, $[\theta]_{290}^{22}$ 0, $[\theta]_{269}^{22}$ +9200, $[\theta]_{246}^{22}$ +800, $[\theta]_{229}^{22}$ +22000, $[\theta]_{222}^{22}$ 0. ^{1}H-NMR (C_6D_6, 400 MHz) δ: 1.16 (3H, d, J=6.5 Hz), 1.19 (3H, d, J=7 Hz), 1.85 (1H, ddd, J=12, 9, 8 Hz), 1.95 (1H, ddd, J=12, 7, 1.5 Hz), 2.28 (3H, s), 2.46 (3H, s), 3.37 (1H, ddq, J=8, 1.5, 7 Hz), 3.45 (1H, ddq, J=9, 7, 6.5 Hz), 6.62 (1H, dd, J=3.5, 2 Hz), 6.68 (1H, dd, J=3.5, 2.5 Hz), 7.08 (1H, br s, NH).

(6*R*,8*S*)-4-Ethyl-1-(phenylsulfonyl)-1,6,7,8-tetrahydro-5,6,8-trimethylcyclopent[*g*]indole (33a) A solution of **29a** (20.5 mg, 0.042 mmol) in CH_2Cl_2 (3 ml) was stirred with 15% Me_3Al in hexane (0.18 ml, 0.247 mmol) under an Ar atmosphere at 0 °C for 1 h. Saturated NH_4Cl–H_2O was added and the whole was extracted with CH_2Cl_2, and worked up as usual. Purification by PTLC [hexane–EtOAc (29 : 1)] gave **33a** (14 mg, 92%) as a colorless syrup. HRMS Calcd for $C_{22}H_{25}NO_2S$: 367.1606. Found: 367.1602. MS *m/z*: 367 (M^+, 82), 352 (52), 226 (100), 211 (29), 197 (39), 196 (40), 182 (45), 77 (50), 51 (29). $[\alpha]_D^{22}$ +504° (c=0.705, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.11 (3H, t, J=7.5 Hz), 1.29 (3H, d, J=7 Hz), 1.30 (3H, d, J=7 Hz), 1.53 (1H, d, J=12.5 Hz), 2.26 (3H, s), 2.46 (1H, ddd, J=12.5, 9, 9 Hz), 2.75 (2H, q, J=7.5 Hz), 3.28 (1H, dq, J=9, 7 Hz), 4.06 (1H, dq, J=9, 7 Hz), 6.66 (1H, d, J=4 Hz), 7.13—7.48 (3H, m), 7.48—7.71 (2H, m), 7.54 (1H, d, J=4 Hz).

(6*R*,8*S*)-6,8-Dimethyl-4-ethyl-1-(phenylsulfonyl)-1,6,7,8-tetrahydrocyclopent[*g*]indole (33b) Similarly, treatment of **29b** (20 mg, 0.042 mmol) with 15% Me_3Al in hexane (0.18 ml, 0.247 mmol) under an Ar atmosphere at 0 °C for 1 h gave **33b** (14 mg, 95%) as a colorless syrup after purification by PTLC [hexane–EtOAc (19 : 1)]. HRMS Calcd for $C_{21}H_{23}NO_2S$: 353.1488. Found: 353.1429. MS *m/z*: 353 (M^+, 70), 338 (37), 212 (100), 183 (30), 168 (41), 77 (57), 51 (21). $[\alpha]_D^{24}$ +596° (c=0.608, $CHCl_3$). ^{1}H-NMR data were reported for the racemic form.[4e]

(6*R*,8*S*)-Herbindole B (34) In the same manner as described for the preparation of **31**, a MeOH solution of **33a** (7 mg, 0.019 mmol) was stirred with Mg (23 mg, 0.958 mg atom) and NH_4Cl (2 mg, 0.037 mmol) at room temperature for 3 h. The same work-up as before and PTLC [hexane–CH_2Cl_2 (3 : 1)] afforded crystalline **34** (4 mg, 92%) as colorless needles, mp 131—133 °C (MeOH–H_2O). *Anal.* Calcd for $C_{16}H_{21}N$: C, 84.53; H, 9.31; N, 6.16. Found: C, 84.14; H, 9.53; N, 6.07. GC-HRMS

Calcd for $C_{16}H_{21}N$: 227.1674. Found: 227.1673. GC-MS *m/z*: 227 (M^+, 56), 212 (100), 198 (7), 183 (21), 168 (12). $[\alpha]_D^{21}$ +51.2° (*c*=0.26, $CHCl_3$). CD (*c*=0.48×10^{-3}, MeOH): $[\theta]_{293}^{22}$ 0, $[\theta]_{275}^{22}$ −400, $[\theta]_{249}^{22}$ 0, $[\theta]_{225}^{22}$ +28800, $[\theta]_{213}^{22}$ 0. IR (KBr) cm^{-1}: 3400, 2970, 2930, 2875, 1454, 1405, 1127, 729. ^{1}H-NMR (C_6D_6, 400 MHz) *δ*: 1.22 (3H, d, *J*=7.5 Hz), 1.27 (3H, t, *J*=7.5 Hz), 1.35 (3H, d, *J*=7 Hz), 1.46 (1H, ddd, *J*=13, 2, 2 Hz), 2.34 (3H, s), 2.59 (1H, ddd, *J*=13, 9, 9 Hz), 2.97 (2H, q, *J*=7.5 Hz), 3.17 (1H, ddq, *J*=9, 2, 7.5 Hz), 3.34 (1H, ddq, *J*=9, 2, 7 Hz), 6.60 (1H, dd, *J*=3, 2 Hz), 6.65 (1H, dd, *J*=3, 2.5 Hz), 6.81 (1H, br s, NH). ^{13}C-NMR (C_6D_6, 100 MHz) *δ*: 14.8, 15.0, 22.9, 23.7, 24.1, 37.3, 39.6, 42.2, 101.4, 121.9, 122.8, 126.8, 128.5, 131.2, 133.0, 142.0.

(6*R*,8*S*)-*cis*-Trikentrin A (4) In the same manner as above, **33b** (10 mg, 0.028 mmol) was reductively deprotected to afford **4** (5.5 mg, 91%) as an unstable colorless oil. GC-HRMS Calcd for $C_{15}H_{19}N$: 213.1517. Found: 213.1508. GC-MS *m/z*: 213 (M^+, 56), 198 (100), 184 (15), 169 (20). $[\alpha]_D^{24}$ +67.0° (*c*=0.16, $CHCl_3$). CD (*c*=0.23×10^{-3}, MeOH): $[\theta]_{263}^{24}$ 0, $[\theta]_{248}^{24}$ +2600, $[\theta]_{239}^{24}$ 0, $[\theta]_{237}^{24}$ −2600, $[\theta]_{234}^{24}$ 0, $[\theta]_{220}^{24}$ +9500, $[\theta]_{210}^{24}$ 0. ^{1}H-NMR was reported for (6*S*,8*R*)-(−)-*cis*-trikentrin A.[4b,e]

(6*R*,8*S*)-4-(3-Butenyl)-1-(phenylsulfonyl)-1,6,7,8-tetrahydro-5,6,8-trimethylcyclopent[*g*]indole (35) A solution of **29a** (19 mg, 0.039 mmol) and allyltrimethylsilane (37 μl, 0.233 mmol) in CH_2Cl_2 (2 ml) was stirred with 0.95 M $EtAlCl_2$ in hexane (0.16 ml, 0.152 mmol) under an Ar atmosphere at −20 °C for 20 min. Saturated $NaHCO_3$–H_2O was added and the whole was extracted with CH_2Cl_2, and worked up as usual. Purification by PTLC [hexane–EtOAc (19 : 1)] gave **35** (14 mg, 92%) as a colorless syrup. HRMS Calcd for $C_{24}H_{27}NO_2S$: 393.1762. Found: 393.1765. MS *m/z*: 393 (M^+, 26), 352 (100), 252 (10), 211 (10), 210 (20), 196 (29), 180 (15), 77 (42), 69 (18), 51 (12), 41 (26). $[\alpha]_D^{21}$ +457° (*c*=0.708, $CHCl_3$). IR ($CHCl_3$) cm^{-1}: 1640. ^{1}H-NMR ($CDCl_3$) *δ*: 1.29 (3H, d, *J*=7 Hz), 1.31 (3H, d, *J*=7 Hz), 1.53 (1H, d, *J*=12.5 Hz), 2.04—2.38 (2H, m), 2.26 (3H, s), 2.47 (1H, ddd, *J*=12.5, 9, 9 Hz), 2.70—2.99 (2H, m), 3.28 (1H, dq, *J*=9, 7 Hz), 4.07 (1H, dq, *J*=9, 7 Hz), 4.92 (1H, br d, *J*=10 Hz), 4.97 (1H, br d, *J*=17 Hz), 5.82 (1H, ddt, *J*=17, 10, 6.5 Hz), 6.65 (1H, d, *J*=4 Hz), 7.17—7.48 (3H, m), 7.48—7.69 (2H, m), 7.54 (1H, d, *J*=4 Hz).

(6*R*,8*R*)-4-(3-Butenyl)-1-(phenylsulfonyl)-1,6,7,8-tetrahydro-5,6,8-trimethylcyclopent[*g*]indole (39a) In the same manner as above, a CH_2Cl_2 solution (1.5 ml) of **30a** (7 mg, 0.014 mmol) was treated with allyltrimethylsilane (18 μl, 0.114 mmol) and 0.95 M $EtAlCl_2$ in hexane (0.09 ml, 0.086 mmol) at −20 °C for 20 min to give **39a** (5 mg, 90%) as a colorless syrup. HRMS Calcd for $C_{24}H_{27}NO_2S$: 393.1762. Found: 393.1737. MS *m/z*: 393 (M^+, 27), 352 (100), 252 (10), 211 (10), 210 (20), 196 (26), 180 (14), 77 (34), 51 (12). $[\alpha]_D^{22}$ −522° (*c*=0.168, $CHCl_3$). IR ($CHCl_3$) cm^{-1}: 1640. ^{1}H-NMR ($CDCl_3$) *δ*: 1.18 (3H, d, *J*=6.5 Hz), 1.26 (3H, d, *J*=6.5 Hz), *ca.* 1.59—2.39 (4H, m), 2.24 (3H, s), 2.63—2.94 (2H, m), 3.20—3.61 (1H, m), 4.17 (1H, ddq, *J*=7, 7, 6.5 Hz), 4.87 (1H, br dd, *J*=9.5, 2 Hz), 4.93 (1H, br dd, *J*=17, 2 Hz), 5.72 (1H, dddd, *J*=17, 9.5, 6.5, 6.5 Hz), 6.58 (1H, d, *J*=4 Hz), 7.12—7.44 (3H, m), 7.35 (1H, d, *J*=4 Hz), 7.44—7.63 (2H, m).

(6*R*,8*R*)-4-(3-Butenyl)-6,8-dimethyl-1-(phenylsulfonyl)-1,6,7,8-tetrahydrocyclopent[*g*]indole (39b) In the same manner as above, **39b** (6.5 mg, 91%, coloress syrup) was obrained by reaction of **30b** (9 mg, 0.019 mmol) with allyltrimethylsilane (18 μl, 0.114 mmol) and 0.95 M $EtAlCl_2$ in hexane (0.08 ml, 0.076 mmol) in CH_2Cl_2 (1.5 ml) at −20 °C for 15 min. HRMS Calcd for $C_{23}H_{25}NO_2S$: 379.1605. Found: 379.1603. MS *m/z*: 379 (M^+, 46), 338 (100), 196 (40), 182 (30), 167 (23), 77 (47), 51 (14). $[\alpha]_D^{24}$ −335° (*c*=0.280, $CHCl_3$). IR ($CHCl_3$) cm^{-1}: 1636. ^{1}H-NMR ($CDCl_3$) *δ*: 1.05 (3H, d, *J*=6.5 Hz), 1.25 (3H, d, *J*=6.5 Hz), 1.62 (1H, ddd, *J*=11.5, 10, 7.5 Hz), 1.97 (1H, dd, *J*=11.5, 7 Hz), 2.18—2.56 (2H, m), 2.69—3.00 (2H, m), 3.09—3.51 (1H, m), 3.96 (1H, dq, *J*=7.5, 6.5 Hz), 4.94 (1H, br d, *J*=10 Hz), 4.99 (1H, br d, *J*=17.5 Hz), 5.82 (1H, ddt, *J*=17.5, 10, 6 Hz), 6.69 (1H, d, *J*=4 Hz), 7.19—7.79 (5H, m), 7.62 (1H, d, *J*=4 Hz).

(6*R*,8*S*)-4-[(ξ)-2-Butenyl]-1-(phenylsuflonyl)-1,6,7,8-tetrahydro-5,6,8-trimethylcyclopent[*g*]indole (36) and (6*R*,8*S*)-4-[(*E*)-1-Butenyl]-1-phenylsulfonyl)-1,6,7,8-tetrahydro-5,6,8-trimethylcyclopent[*g*]indole (37) An EtOH solution (1.5 ml) of **35** (13 mg, 0.033 mmol) and $RhCl_3 \cdot 3H_2O$ (0.7 mg, 2.7 μmol) was heated in a sealed tube under an Ar atmopshere at 100 °C for 50 h, then allowed to cool. Saturated $NaHCO_3$–H_2O was added and the whole was extracted with CH_2Cl_2, and worked up as usual. Separation and purification by PTLC [Merck SiO_2 60 F_{254} (20×20) plate, two sheets, hexane–EtOAc (69 : 1), three times development] gave **36** (5 mg, 38%) as a more polar substance and **37** (7 mg, 54%) as a less polar substance. **36**: Colorless syrup. HRMS Calcd for $C_{24}H_{27}NO_2S$: 393.1762. Found: 393.1764. MS *m/z*: 393 (M^+, 100), 378 (44), 252 (83), 222 (36), 210 (56), 182 (35), 167 (25), 77 (88), 51 (28). ^{1}H-NMR of major and minor isomers (($CDCl_3$) *δ*: 1.30 (3H, d, *J*=7 Hz), 1.33 (3H, d, *J*=7 Hz), 1.54 (1H, d, *J*=12.5 Hz), 1.57 and 1.77 (total 3H, d each, *J*=6.5 and 5.5 Hz), 2.25 (3H, s), 2.48 (1H, ddd, *J*=12.5, 8.5, 8.5 Hz), 3.09—3.62 (3H, m), 4.08 (1H, dq, *J*=8.5, 7 Hz), 5.01—5.67 (2H, m), 6.67 (1H, d, *J*=4 Hz), 7.18—7.50 (3H, m), 7.50—7.73 (3H, m). **37**: Colorless syrup. HRMS Calcd for $C_{24}H_{27}NO_2S$: 393.1762. Found: 393.1751. MS *m/z*: 393 (M^+, 61), 378 (19), 252 (100), 222 (16), 210 (16), 77 (56), 51 (16). $[\alpha]_D^{22}$ +401° (*c*=0.351, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) *δ*: 1.09 (3H, t, *J*=7 Hz), 1.29 (3H, d, *J*=7 Hz), 1.31 (3H, d, *J*=7 Hz), 1.53 (1H, d, *J*=12.5 Hz), 2.07—2.48 (2H, m), 2.24 (3H, s), 2.48 (1H, ddd, *J*=12.5, 8.5, 8.5 Hz), 3.28 (1H, dq, *J*=8.5, 7 Hz), 4.10 (1H, dq, *J*=8.5, 7 Hz), 5.87 (1H, dt, *J*=16, 6.5 Hz), 6.49 (1H, d, *J*=16 Hz), 6.78 (1H, d, *J*=4 Hz), 7.16—7.49 (3H, m), 7.49—7.70 (2H, m), 7.51 (1H, d, *J*=4 Hz). Repeated treatment of **36** (5 mg, 0.013 mmol) with $RhCl_3 \cdot 3H_2O$ (0.5 mg, 1.9 μmol) under the same conditions afforded **37** (2.5 mg, 50%) with recovery of **36** (2 mg, 40%).

(6*R*,8*R*)-4-[(*E*)-1-Butenyl]-6,8-dimethyl-1-(phenylsulfonyl)-1,6,7,8-tetrahydrocyclopent[*g*]indole (40) An EtOH solution (0.5 ml) of **39b** (6 mg, 0.016 mmol) and $RhCl_3 \cdot 3H_2O$ (0.5 mg, 1.9 μmol) was refluxed with stirring under an Ar atmosphere for 8 h. The same work-up as above and purification by PTLC [hexane–CH_2Cl_2 (4 : 1)] gave **40** (5.5 mg, 92%) as a colorless syrup. HRMS Calcd for $C_{23}H_{25}NO_2S$: 379.1605. Found: 379.1604. MS *m/z*: 379 (M^+, 81), 364 (23), 238 (100), 196 (33), 77 (60), 51 (18). $[\alpha]_D^{24}$ −304° (*c*=0.264, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) *δ*: 1.07 (3H, d, *J*=7 Hz), 1.10 (3H, t, *J*=7.5 Hz), 1.26 (3H, d, *J*=7 Hz), 1.63 (1H, ddd, *J*=11.5, 10, 7.5 Hz), 1.98 (1H, dd, *J*=11.5, 6.5 Hz), 2.26 (2H, dq, *J*=6, 7.5 Hz), 3.14—3.55 (1H, m), 3.99 (1H, dq, *J*=7.5, 7 Hz), 6.28 (1H, dt, *J*=16, 6 Hz), 6.67 (1H, d, *J*=16 Hz), 6.84 (1H, d, *J*=4 Hz), *ca.* 7.18—7.52 (3H, m), 7.52—7.76 (2H, m), 7.64 (1H, d, *J*=4 Hz).

(6*R*,8*S*)-Herbindole C (38) A solution of **37** (10 mg, 0.025 mmol) in 20% KOH in DME–MeOH–H_2O (1 : 1 : 1) (2.4 ml) was stirred under reflux for 6 h, then cooled in an ice bath. Saturated NH_4Cl–H_2O was added and the mixture was extracted with CH_2Cl_2, and worked up as usual. Purification by PTLC [hexane–EtOAc (14 : 1)] afforded **38** (6 mg, 93%) as an unstable colorless syrup. HRMS Calcd for $C_{18}H_{23}N$: 253.1830. Found: 253.1829. MS *m/z*: 253 (M^+, 76), 238 (100). $[\alpha]_D^{22}$ +19.9° (*c*=0.18, $CHCl_3$). CD (*c*=0.44×10^{-3}, MeOH): $[\theta]_{332}^{22}$ 0, $[\theta]_{294}^{22}$ −3700, $[\theta]_{251}^{22}$ 0, $[\theta]_{232}^{22}$ +25600, $[\theta]_{214}^{22}$ 0. IR ($CHCl_3$) cm^{-1}: 3500, 2970, 2940, 2880, 1463, 1378, 1280, 1131, 975. ^{1}H-NMR (C_6D_6, 400 MHz) *δ*: 1.08 (3H, t, *J*=7.5 Hz), 1.22 (3H, d, *J*=7.5 Hz), 1.33 (3H, d, *J*=7 Hz), 1.45 (1H, ddd, *J*=13, 2, 2 Hz), 2.25 (2H, ddq, *J*=6.5, 1.5, 7.5 Hz), 2.41 (3H, s), 2.58 (1H, ddd, *J*=13, 9, 9 Hz), 3.17 (1H, ddq, *J*=9, 2, 7.5 Hz), 3.33 (1H, ddq, *J*=9, 2, 7 Hz), 6.31 (1H, dt, *J*=16, 6.5 Hz), 6.69 (1H, dd, *J*=3, 2.5 Hz), 6.84 (1H, br s, NH), 6.89 (1H, dt, *J*=16, 1.5 Hz), 6.91 (1H, dd, *J*=3, 2 Hz). ^{13}C-NMR (C_6D_6, 100 MHz) *δ*: 14.4, 16.1, 22.9, 24.0, 27.2, 37.4, 39.4, 42.1, 103.1, 122.7, 123.1, 127.0, 127.3, 128.6, 129.0, 131.5, 135.8, 141.8.

(6*R*,8*R*)-iso-*trans*-Trikentrin B (41) In the same manner as above, **41** (2.5 mg, 88%, unstable colorless syrup) was obtained from **40** (4.5 mg, 0.012 mmol) after purification by PTLC [hexane–CH_2Cl_2 (7 : 2)]. GC-HRMS Calcd for $C_{17}H_{21}N$: 239.1673. Found: 239.1676. GC-MS *m/z*: 239 (M^+, 91), 224 (100), 169 (28), 154 (19). $[\alpha]_D^{24}$ *ca.* 0° (*c*=0.11, $CHCl_3$). CD (*c*=0.21×10^{-3}, MeOH): $[\theta]_{338}^{24}$ 0, $[\theta]_{310}^{24}$ +8000, $[\theta]_{263}^{24}$ 0, $[\theta]_{257}^{24}$ −3700, $[\theta]_{252}^{24}$ 0, $[\theta]_{241}^{24}$ +18700, $[\theta]_{230}^{24}$ 0. IR and ^{1}H-NMR spectra were reported for the racemate.[4e]

Ethyl (6*R*,8*S*)- and (6*R*,8*R*)-6,8-Dimethyl-1-(phenylsulfonyl)-1,6,7,8-tetrahydrocyclopent[*g*]indole-5-carboxylates (42) In a similar manner to that described for the preparation of **29a** and **30a**, a solution of **24b** (53 mg, 0.123 mmol) in THF (3 ml) and H_2O (1 ml) was stirred with OsO_4 (3 mg, 0.012 mmol) and $NaIO_4$ (263 mg, 1.23 mmol) at room temperature for 18 h. The same work-up as before, followed by separation by PTLC afforded a residue (43 mg). A chlorobenzene (3 ml) solution of the residue, PhSH (81 μl, 0.79 mmol) and *p*-TsOH·H_2O (19 mg, 0.100 mmol) was refluxed with stirring for 4 h. The same work-up as before and purification by PTLC [hexane–CH_2Cl_2 (3 : 2)] afforded a mixture of two isomers **42** (*cis*/*trans*=*ca.* 4) (20 mg, 41%) as a colorless syrup. HRMS Calcd for $C_{22}H_{23}NO_4S$: 397.1346. Found: 397.1342. MS *m/z*: 397 (M^+, 100), 382 (38), 368 (46), 256 (65), 210 (39), 168 (75), 77 (81), 51 (26), 29 (22). IR ($CHCl_3$) cm^{-1}: 1712. ^{1}H-NMR of the (6*R*,8*S*)-isomer ($CDCl_3$) *δ*: 1.57 (1H, d, *J*=13 Hz), 2.51 (1H, ddd, *J*=12, 9, 9 Hz), 4.33 (2H, q, *J*=7 Hz), 6.69 (1H, d, *J*=4 Hz), 7.64 (1H, d, *J*=4 Hz),

8.04 (1H, s). ^{1}H-NMR of the (6*R*,8*R*)-isomer ($CDCl_3$) δ: 1.91 (2H, dd, J=6.5, 6.5 Hz), 6.64 (1H, d, J=4 Hz), 7.83 (1H, s).

(6*R*,8*S*)-6,8-Dimethyl-1-(phenylsulfonyl)-1,6,7,8-tetrahydrocyclopent-[*g*]indole-5-methanol (43a) and (6*R*,8*R*)-6,8-Dimethyl-1-(phenylsulfonyl)-1,6,7,8-tetrahydrocyclopent[*g*]indole-5-methanol (43b) $LiAlH_4$ (10 mg, 0.263 mmol) was added to a THF solution (3 ml) of **42** (26 mg, 0.065 mmol) under an Ar atmosphere at −20 °C, and the mixture was stirred at −20 °C for 10 min and at 0 °C for 2 h. Saturated Rochelle salt in H_2O was added and the whole was extracted with CH_2Cl_2, and worked up as usual. PTLC [hexane–EtOAc (2 : 1)] gave a mixture of **43a** and **43b** (22 mg), which was further separated by HPLC as described for the separation of **29a** and **30a** [eluting solvent, hexane–EtOAc (5 : 2)] to yield **43a** (17 mg, 73%, t_R=96.8 min) and **43b** (4 mg, 17%, t_R=85.6 min). **43a**: Colorless scales, mp 161—162 °C (CH_2Cl_2–hexane). *Anal.* Calcd for $C_{20}H_{21}NO_3S$: C, 67.58; H, 5.96; N, 3.94. Found: C, 67.51; H, 6.00; N, 3.79. HRMS Calcd for $C_{20}H_{21}NO_3S$: 355.1242. Found: 355.1243. MS *m/z*: 355 (M^+, 91), 340 (43), 322 (22), 196 (100), 181 (42), 168 (37), 77 (59), 51 (24). $[\alpha]_D^{22}$ +658° (c=0.406, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.30 (3H, d, J=7 Hz), 1.32 (3H, d, J=7 Hz), 1.57 (1H, d, J=12.5 Hz), 1.63 (1H, s, OH), 2.50 (1H, ddd, J=12.5, 9, 9 Hz), 3.36 (1H, dq, J=9, 7 Hz), 4.10 (1H, dq, J=9, 7 Hz), 4.66 (1H, d, J=12.5 Hz), 4.80 (1H, d, J=12.5 Hz), 6.63 (1H, d, J=4 Hz), 7.16—7.48 (4H, m), 7.48—7.70 (2H, m), 7.57 (1H, d, J=4 Hz). **43b**: Colorless syrup. HRMS Calcd for $C_{20}H_{21}NO_3S$: 355.1242. Found: 355.1238. MS *m/z*: 355 (M^+, 91), 340 (40), 322 (24), 196 (100), 181 (44), 168 (38), 77 (57), 51 (28). $[\alpha]_D^{22}$ −624° (c=0.138, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.20 (3H, d, J=6.5 Hz), 1.24 (3H, d, J=6.5 Hz), 1.53 (1H, s, OH), 1.91 (2H, dd, J=6.5, 6.5 Hz), 3.50 (1H, tq, J=6.5, 6.5 Hz), 4.17 (1H, tq, J=6.5, 6.5 Hz), 4.68 (1H, d, J=14 Hz), 4.83 (1H, d, J=14 Hz), 6.61 (1H, d, J=4 Hz), 7.18—7.68 (5H, m), 7.32 (1H, s), 7.48 (1H, d, J=4 Hz).

(6*R*,8*S*)-6,8-Dimethyl-1-(phenylsulfonyl)-1,6,7,8-tetrahydrocyclopent-[*g*]indole-5-carboxaldehyde (44a) MnO_2 (44 mg, 0.506 mmol) was added to a CH_2Cl_2 solution (2.5 ml) of **43a** (9 mg, 0.025 mmol) and the mixture was stirred at room temperature for 1.5 h. The same work-up as for the preparation of **25a** and purification by PTLC [hexane–CH_2Cl_2 (1 : 1)] afforded **44a** (8 mg, 89%) as colorless prisms, mp 120—121 °C (CH_2Cl_2–hexane). *Anal.* Calcd for $C_{20}H_{19}NO_3S$: C, 67.96; H, 5.42; N, 3.96. Found: C, 67.64; H, 5.56; N, 4.01. HRMS Calcd for $C_{20}H_{19}NO_3S$: 353.1085. Found: 353.1092. MS *m/z*: 353 (M^+, 17), 212 (100), 168 (26), 77 (34), 51 (15). $[\alpha]_D^{22}$ +601° (c=0.233, $CHCl_3$). IR (KBr) cm^{-1}: 1690. ^{1}H-NMR ($CDCl_3$) δ: 1.33 (3H, d, J=7 Hz), 1.36 (3H, d, J=7 Hz), 1.64 (1H, d, J=13 Hz), 2.54 (1H, ddd, J=13, 9, 9 Hz), 3.88 (1H, dq, J=9, 7 Hz), 4.12 (1H, dq, J=9, 7 Hz), 6.76 (1H, d, J=4 Hz), 7.22—7.54 (3H, m), 7.54—7.78 (2H, m), 7.70 (1H, d, J=4 Hz), 7.86 (1H, s), 10.15 (1H, s).

(6*R*,8*R*)-6,8-Dimethyl-1-(phenylsulfonyl)-1,6,7,8-tetrahydrocyclopent-[*g*]indole-5-carboxaldehyde (44b) In the same manner as above, **43b** (7 mg, 0.020 mmol) was oxidized with MnO_2 (35 mg, 0.402 mmol) to yield **44b** (6 mg, 87%, colorless syrup) after purification by PTLC [hexane–CH_2Cl_2 (1 : 1)]. HRMS Calcd for $C_{20}H_{19}NO_3S$: 353.1085. Found: 353.1087. MS *m/z*: 353 (M^+, 18), 212 (100), 168 (25), 77 (6). $[\alpha]_D^{24}$ −645° (c=0.271, $CHCl_3$). IR ($CHCl_3$) cm^{-1}: 1692. ^{1}H-NMR ($CDCl_3$) δ: 1.23 (3H, d, J=6.5 Hz), 1.26 (3H, d, J=6.5 Hz), 1.99 (2H, dd, J=6.5, 6.5 Hz), 3.94 (1H, tq, J=6.5, 6.5 Hz), 4.20 (1H, tq, J=6.5, 6.5 Hz), 6.70 (1H, d, J=4 Hz), 7.17—7.69 (5H, m), 7.55 (1H, d, J=4 Hz), 7.76 (1H, s), 10.20 (1H, s).

(α*ξ*,6*R*,8*S*)-6,8-Dimethyl-1-(phenylsulfonyl)-α-propyl-1,6,7,8-tetrahydrocyclopent[*g*]indole-5-methanols (45a) A THF solution (2 ml) of **44a** (10 mg, 0.028 mmol) was treated with *ca.* 0.5 M PrMgBr (0.17 ml, 0.085 mmol) under an Ar atmosphere at −20 °C and the mixture was stirred at the same temperature for 20 min. Saturated NH_4Cl–H_2O was added and the whole was extracted with CH_2Cl_2, and worked up as usual. Purification by PTLC [hexane–EtOAc (4 : 1)] afforded **45a** (major isomer: 9.5 mg, 84% and minor isomer: *ca.* 0.5 mg, *ca.* 4%) and **43a** (1 mg, 10%). **45a** (major isomer): Colorless syrup. HRMS Calcd for $C_{23}H_{27}NO_3S$: 397.1710. Found: 397.1693. MS *m/z*: 397 (M^+, 53), 354 (100), 284 (18), 238 (30), 77 (63), 43 (31). ^{1}H-NMR ($CDCl_3$) δ: 0.84 (3H, dif. t, J=6.5 Hz), 1.30 (3H, d, J=7 Hz), 1.37 (3H, d, J=7 Hz), 1.56 (1H, d, J=12.5 Hz), 2.51 (1H, ddd, J=12.5, 8.5, 8.5 Hz), 3.33 (1H, dq, J=8.5, 7 Hz), 4.10 (1H, dq, J=8.5, 7 Hz), 4.92 (1H, dd, J=7, 5.5 Hz), 6.62 (1H, d, J=4 Hz), 7.21—7.70 (6H, m), 7.55 (1H, d, J=4 Hz). **45a** (minor isomer): Colorless syrup. HRMS Calcd for $C_{23}H_{27}NO_3S$: 397.1710. Found: 397.1731. MS *m/z*: 397 (M^+, 58), 354 (100), 284 (22), 238 (98), 77 (74), 51 (19).

(α*ξ*,6*R*,8*R*)-6,8-Dimethyl-1-(phenylsulfonyl)-α-propyl-1,6,7,8-tetrahydrocyclopent[*g*]indole-5-methanols (45b) In the same manner as above, treatment of **44b** (5.5 mg, 0.016 mmol) with *ca.* 0.5 M PrMgBr (0.10 ml, 0.050 mmol) at −20 °C for 20 min, followed by the same work-up and PTLC [hexane–EtOAc (4 : 1)] gave **45b** (major isomer: 4.5 mg, 73% and minor isomer: *ca.* 0.5 mg, *ca.* 8%) and **43b** (1 mg, 18%). **45b** (major isomer): Colorless syrup. HRMS Calcd for $C_{23}H_{27}NO_3S$: 397.1710. Found: 397.1710. MS *m/z*: 397 (M^+, 51), 354 (100), 284 (20), 238 (33), 77 (54), 43 (27). ^{1}H-NMR ($CDCl_3$) δ: 0.89 (3H, dif. t, J=7 Hz), 1.23 (3H, d, J=6.5 Hz), 1.27 (3H, d, J=6.5 Hz), 1.66 (1H, br s, OH), 3.21—3.64 (1H, m), 3.96—4.39 (1H, m), 4.96 (1H, dd, J=6, 6 Hz), 6.57 (1H, d, J=4 Hz), 7.12—7.63 (6H, m), 7.39 (1H, d, J=4 Hz). **45b** (minor isomer): Colorless syrup. HRMS Calcd for $C_{23}H_{27}NO_3S$: 397.1710. Found: 397.1714. MS *m/z*: 397 (M^+, 57), 354 (100), 284 (24), 238 (94), 77 (76), 43 (35).

(6*R*,8*S*)-5-[(*E*)-1-Butenyl]-6,8-dimethyl-1-(phenylsulfonyl)-1,6,7,8-tetrahydrocyclopent[*g*]indole (46a) A benzene solution (2.5 ml) of the combined two isomers of **45a** (10 mg, 0.025 mmol) and *p*-TsOH·H_2O (1 mg, 5.3 μmol) was stirred under reflux for 0.5 h, then allowed to cool. Saturated $NaHCO_3$–H_2O was added and the whole was extracted with CH_2Cl_2, and worked up as usual. Purification by PTLC [hexane–CH_2Cl_2 (2 : 1)] afforded **46a** (9 mg, 94%) as a colorless syrup. HRMS Calcd for $C_{23}H_{25}NO_2S$: 379.1605. Found: 379.1621. MS *m/z*: 379 (M^+, 100), 364 (53), 238 (90), 196 (35), 77 (83), 51 (26). $[\alpha]_D^{24.5}$ +470° (c=0.423, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.07 (3H, t, J=7.5 Hz), 1.30 (3H, d, J=7 Hz), 1.34 (3H, d, J=7 Hz), 1.54 (1H, d, J=12.5 Hz), 2.22 (2H, dq, J=6, 7.5 Hz), 2.49 (1H, ddd, J=12.5, 9, 9 Hz), 3.39 (1H, dq, J=9, 7 Hz), 4.11 (1H, dq, J=9, 7 Hz), 6.14 (1H, dt, J=16, 6 Hz), 6.50 (1H, d, J=16 Hz), 6.59 (1H, d, J=3.5 Hz), 7.15—7.47 (4H, m), 7.47—7.70 (2H, m), 7.51 (1H, d, J=3.5 Hz).

(6*R*,8*R*)-5-[(*E*)-1-Butenyl]-6,8-dimethyl-1-(phenylsulfonyl)-1,6,7,8-tetrahydrocyclopent[*g*]indole (46b) In the same manner as above, **45b** (major+minor isomers) (5 mg, 0.013 mmol) was dehydrated with *p*-TsOH·H_2O (0.5 mg, 2.6 μmol) to yield **46b** (4 mg, 84%) as a colorless syrup after purification by PTLC [hexane–CH_2Cl_2 (2 : 1)]. HRMS Calcd for $C_{23}H_{25}NO_2S$: 379.1605. Found: 379.1605. MS *m/z*: 379 (M^+, 100), 364 (50), 238 (90), 196 (36), 77 (59), 51 (17). $[\alpha]_D^{24}$ −455° (c=0.175, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.07 (3H, t, J=7 Hz), 1.20 (3H, d, J=6.5 Hz), 1.24 (3H, d, J=6.5 Hz), 1.91 (2H, dd, J=6.5, 6.5 Hz), 2.22 (2H, dq, J=6.5, 7 Hz), 3.50 (1H, tq, J=6.5, 6.5 Hz), 4.17 (1H, tq, J=6.5, 6.5 Hz), 6.08 (1H, dt, J=15.5, 6.5 Hz), 6.54 (1H, br d, J=15.5 Hz), 6.56 (1H, d, J=4 Hz), 7.14—7.67 (6H, m), 7.36 (1H, d, J=4 Hz).

(6*R*,8*S*)-*cis*-Trikentrin B (6) In the same manner as described for the preparation of **41**, **46a** (8 mg, 0.021 mmol) was hydrolyzed to afford **6** (4.5 mg, 89%) as an unstable colorless syrup. HRMS Calcd for $C_{17}H_{21}N$: 239.1674. Found: 239.1684. MS *m/z*: 239 (M^+, 92), 224 (100), 182 (30), 167 (18). $[\alpha]_D^{24}$ +102° (c=0.178, $CHCl_3$). CD (c=0.41 × 10^{-3}, MeOH): $[\theta]_{273}^{24}$ 0, $[\theta]_{263}^{24}$ +1700, $[\theta]_{260}^{24}$ 0, $[\theta]_{241}^{24}$ +26600, $[\theta]_{222}^{24}$ 0. IR and ^{1}H-NMR spectra were reported for the racemate.[4e]

(6*R*,8*R*)-*trans*-Trikentrin B (47) In the same way, **47** (2 mg, 91%) was obtained from **46b** (3.5 mg, 9.2 μmol). HRMS Calcd for $C_{17}H_{21}N$: 239.1674. Found: 239.1668. MS *m/z*: 239 (M^+, 95), 224 (100), 182 (32), 167 (21). $[\alpha]_D^{24}$ +24.3° (c=0.078, $CHCl_3$). CD (c=0.41 × 10^{-3}, MeOH): $[\theta]_{311}^{24}$ 0, $[\theta]_{293}^{24}$ −1900, $[\theta]_{281}^{24}$ 0, $[\theta]_{244}^{24}$ +28700, $[\theta]_{242}^{24}$ +2900, $[\theta]_{235}^{24}$ +4400, $[\theta]_{228}^{24}$ 0. IR and ^{1}H-NMR spectra were reported for the racemate.[4e]

Drawing of CD Curves in Fig. 1d—g After obtaining the CD curves of synthesized **6** (Fig. 1b) and **41** (Fig. 1c), CD curves of *ent*-**6** and *ent*-**41** were drawn by making mirror image curves of Fig. 1b and Fig. 1c. Then in the curves of **6**, **41**, *ent*-**6**, and *ent*-**41**, the $[\theta]$ value was measured at every 5 nm from 235 to 340 nm. At each wavelength of 235 nm, 240 nm and so forth, the sum of the $[\theta]$ values, for instance, 0.44 × {$[\theta]_{235}$ of **6**} + 0.56 × {$[\theta]_{235}$ of **41**}, reflecting the 44 : 56 ratio of the natural mixture, which was determined by comparison of integrated values of ^{1}H-NMR signals of the C-2 proton of the 1-butenyl side chain, was calculated for every combination of **6**+**41**, **6**+*ent*-**41**, *ent*-**6**+**41**, and *ent*-**6**+*ent*-**41**, and plotted to obtain the CD curves of Fig. 1d—g.

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