(two sets of d, J = 2.3 Hz, H_1'), 5.86 (br s, NH_2), 5.54, 5.47 (two sets of dd, J = 2.3, 6.3 Hz, H_2'), 4.95 (dd, H_3'), 4.56 (m, H_4'), 3.78 (m, CH), 2.70 (m, CH), 2.20–1.37 (m, H_5', $(CH_2)_2$), 1.60, 1.37 (2 s, $C(CH_3)_2$). Mass spectrum (desorption CI, rel intensity): m/e 609 (MH^+, 8.4).

5'-(6-Amino-6-carboxy-1-phenyl-1-hexyn-3-yl)-5'-deoxyadenosine (4). A crude sample of **4** (41.6 mg) was obtained from 140 mg of **39** by using a similar method to that described for the preparation of **15**. This crude product was purified by preparative reverse-phase HPLC with gradient elution of 0–100% solvent A (6:4 CH_3CN/H_2O) in solvent B (H_2O) to give 20.6 mg (70% yield from **38**) of the desired **4** as a foam. UV (MeOH): λ_{max} = 251 nm, λ_{min} = 240 nm. ^1H NMR (CD_3OD, δ): 8.25, 8.24, 8.21, 8.20 (4 s, 2 H, H_8, H_2), 7.30 (m, 5 H, ArH), 5.98 (two sets of d, 1 H, H_1'), 4.85 (overlapping with HOD peak, H_2'), 4.40 (m, 1 H, H_4'), 4.25 (m, 1 H, H_3'), 3.59 (m, 1 H, CH), 2.86 (m, 1 H, CH), 2.28–1.60 (m, 6 H, H_5', $(CH_2)_2$). ^{13}C NMR (CD_3OD, ppm): 174.38 (C=O), 157.37 (C_4), 153.94 (C_2), 150.62 (C_6), 141.78, 141.49 (C_8), 132.65, 132.58, 132.65, 128.94, 120.77 (Ar), 124.95 (C_5), 92.77, 92.16, 92.09 (Ar-*C*≡), 90.61, 90.55, 90.20 (C_1'), 84.44, 84.40 (C_4'), 83.86, 83.74, 83.70 (≡C), 75.42, 75.23 (*R* and *S* CH), 74.94, 74.90 (C_3'), 56.17, 56.13 (C_2'), 40.43, 40.11, 39.96 (C_5', CH_2), 32.36, 31.39, 31.20, 30.58, 30.47, 30.07 (CH_2, *R* and *S* CH). FAB mass spectrum (rel intensity): m/e 467 (MH^+, 16.8). HR mass spectrum (desorption CI) calcd for $(MH - CO_2)^+$ m/e $C_{22}H_{27}N_6O_3$ 423.2145, obsd m/e 423.2139.

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Supplementary Material Available: Procedures for the synthesis of **23a**, **23c**, **24a**, **25a**, **30a**, **32a**, and **33a** with complete spectral data (3 pages). Ordering information is given on any current masthead page.

Total Synthesis and Absolute Stereochemistry of (+)-Xestoquinone and Xestoquinol

Nobuyuki Harada,*[1a] Tatsuo Sugioka,[1a,b] Hisashi Uda,[1a] and Takeo Kuriki[1b]

Chemical Research Institute of Nonaqueous Solutions, Tohoku University, 2-1-1 Katahira, Aoba, Sendai 980, Japan, and Pharma Research Laboratory, Hoechst Japan, Ltd., 1-3-2 Minamidai, Kawagoe, Saitama 350, Japan

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The first total synthesis of (+)-xestoquinone **1**, a biologically active marine natural product isolated from tropical marine sponges, was achieved. Optically pure hydroxymethyl ketone derivative (4a*R*,5*S*,8a*R*)-(+)-**8** was converted to enone (+)-**15** via the reactions of eight steps. The Diels–Alder reaction of (+)-**15** with 3,6-dimethoxybenzocyclobutene (**16**) afforded an adduct (+)-**17** of a tetracyclic system, which was converted to (12b*S*)-xestoquinone **1** via a series of five-step reactions. The CD spectrum of the synthetic sample was identical with that of the natural xestoquinone (+)-**1**. Therefore, the absolute stereochemistry of (+)-xestoquinone **1** was determined to be 12b*S*. Finally, xestoquinone (12b*S*)-(+)-**1** was converted to xestoquinol (12b*S*)-**2**, although xestoquinol **2** itself has not been isolated yet as a natural product. The absolute configuration of xestoquinone **1** was also established by the comparison of the CD spectrum of naphthalene–diene derivative **22** with the theoretically calculated CD curve of a model compound (12b*S*)-**23**.

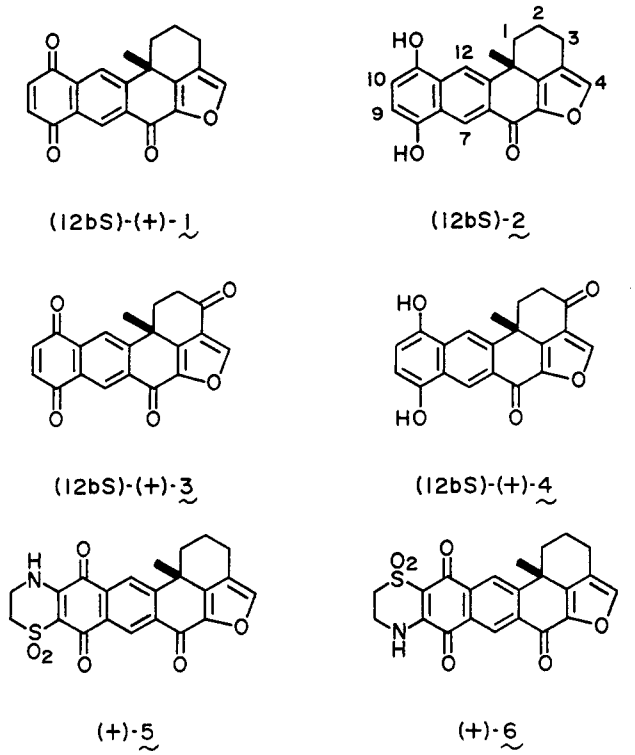
A variety of novel quinone and hydroquinone compounds with biological activites have been isolated from tropical marine sponges (Chart I). Xestoquinone (+)-**1** was isolated from the Okinawan sponge *Xestospongia sapra* as a cardiotonic constituent by Nakamura.[2] From the same Okinawan sponge, Kitagawa[3] isolated halenaquinol (+)-**4** together with its sulfate ester, and hydroquinone (+)-**4** was easily oxidized to give halenaquinone (+)-**3**, which had been originally isolated from the sponge *Xestospongia exigua* in Western Caroline Islands by Scheuer.[4] From the view point of the instability of the hydroquinone compound, Kitagawa[3] suggested that halenaquinone **3** might be a secondary product of halenaquinol isolation. If so, xestoquinol **2** may be a genuine natural product instead of xestoquinone **1**. Recently, Schmitz[5] isolated adociaquinone A ((+)-**5**), adociaquinone B ((+)-**6**), and related compounds from sponges of the genus *Adocia* in Truk Lagoon.

We and Kitagawa have previously determined the absolute stereochemistry of halenaquinone (+)-**3** and halenaquinol (+)-**4** as shown in Chart I by the theoretical calculation of the CD spectra of pertinent derivatives.[6] Furthermore, we experimentally showed that the absolute stereostructures of (+)-**3** and (+)-**4** determined theoretically were confirmed by the total synthesis[7] of halenaquinone (+)-**3** and halenaquinol (+)-**4**. On the other hand, the absolute stereochemistry of xestoquinone has remained undetermined. Here, we report the first total synthesis of xestoquinone (+)-**1** and xestoquinol **2** and the experimental determination of their absolute stereostructures. In addition, we also describe the theoretical confirmation of the absolute configuration of the xestoquinone series on the basis of the CD spectra of naphthalene–diene derivatives with a twisted π-electron system.

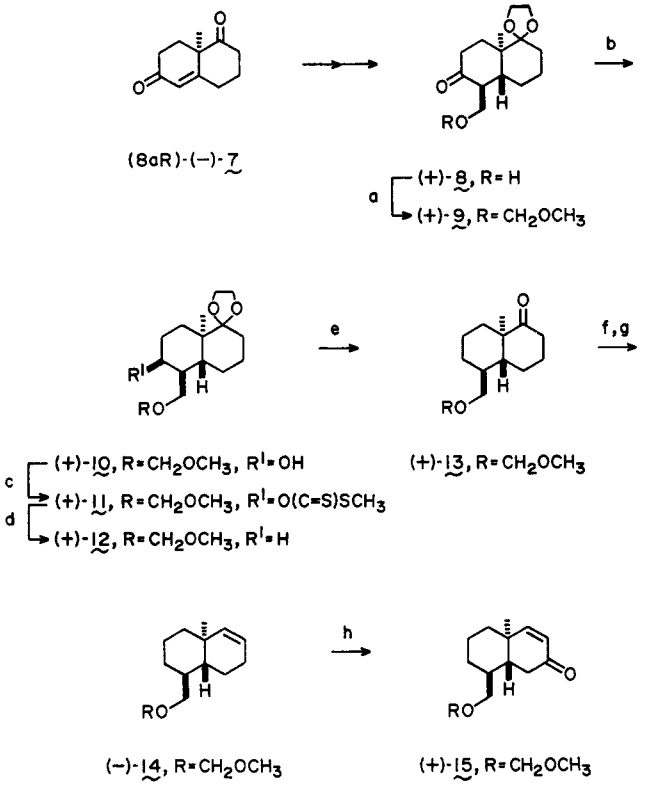
(1) (a) Tohoku University. (b) Hoechst Japan Ltd.
(2) Nakamura, H.; Kobayashi, J.; Kobayashi, M.; Ohizumi, Y.; Hirata, Y. *Chem. Lett.* **1985**, 713.
(3) Kobayashi, M.; Shimizu, N.; Kyogoku, Y.; Kitagawa, I. *Chem. Pharm. Bull.* **1985**, *33*, 1305.
(4) Roll, D. M.; Scheuer, P. J.; Matsumoto, G. K.; Clardy, J. *J. Am. Chem. Soc.* **1983**, *105*, 6177.
(5) Schmitz, F. J.; Bloor, S. J. *J. Org. Chem.* **1988**, *53*, 3922.
(6) Kobayashi, M.; Shimizu, N.; Kitagawa, I.; Kyogoku, Y.; Harada, N.; Uda, H. *Tetrahedron Lett.* **1985**, *26*, 3833. Harada, N.; Uda, H.; Kobayashi, M.; Shimizu, N.; Kitagawa, I. *J. Am. Chem. Soc.* **1989**, *111*, 5668.
(7) Harada, N.; Sugioka, T.; Ando, Y.; Uda, H.; Kuriki, T. *J. Am. Chem. Soc.* **1988**, *110*, 8483.

0022-3263/90/1955-3158$02.50/0

Chart I



Scheme I[a]



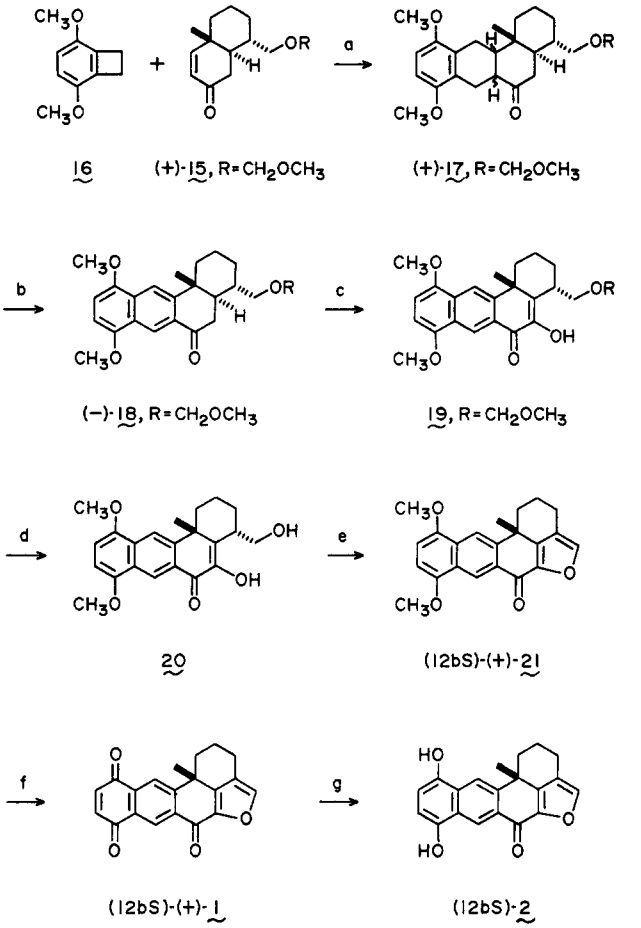
[a] (a) $ClCH_2OCH_3$, $(i\text{-}Pr)_2NEt$, CH_2Cl_2; (b) $Li(s\text{-}Bu)_3BH$, tetrahydrofuran (THF); (c) BuLi, THF, CS_2, and then CH_3I; (d) Bu_3SnH, α,α'-azobisisobutyronitrile (AIBN), toluene; (e) *p*-toluenesulfonic acid (*p*-TsOH), acetone, water; (f) *p*-toluenesulfonohydrazide, EtOH; (g) MeLi, THF; (h) CrO_3, 3,5-dimethylpyrazole, CH_2Cl_2.

Results and Discussion

Total Synthesis of (+)-Xestoquinone and Xestoquinol. As a synthetic strategy, the route shown in Schemes I and II was adopted. Although the absolute configuration of xestoquinone **1** had not been determined, we assumed that xestoquinone had the same absolute configuration as halenaquinone (+)-**3**. The absolute configuration of (+)-**3** was previously determined to be 12b*S* by the theoretical calculation of the CD spectrum[6] and also by the total synthesis.[7] Therefore, we started from hydroxymethyl ketone (4a*R*,5*S*,8a*R*)-(+)-**8**,[7] $[\alpha]^{20}_D$ +3.6° (*c* 1.707, $CHCl_3$), which was easily derived from Wieland–Miescher ketone (8a*R*)-(−)-**7**[8] via selective acetalization and reductive hydroxymethylation (Scheme I).

The hydroxyl group of (+)-**8** was protected as a methoxymethyl ether to give ether (+)-**9** in 80% yield (Scheme I). To reduce the carbonyl group of (+)-**9** to a methylene moiety of **12**, we tried the thioacetal reduction method. However, the attempt was unsuccessful because of the exchange of the acetal group at the 1-position by a thioacetal group.[9] So, we adopted the method of radical reduction of xanthate **11** instead.[10] Ketone (+)-**9** was stereoselectively reduced with lithium tri-*sec*-butylboro-

Scheme II[a]



[a] (a) 150–210 °C, 3 h and then 210–220 °C, 10 h; (b) 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), benzene; (c) *t*-BuOK, *t*-BuOH, O_2; (d) HCl, MeOH; (e) activated MnO_2, $CHCl_3$, and then *p*-TsOH; (f) $(NH_4)_2Ce(NO_3)_6$, water, CH_3CN; (g) $Na_2S_2O_4$, water, acetone.

(8) For the preparation of the optically pure Wieland–Miescher ketone, see: Harada, N.; Sugioka, T.; Uda, H.; Kuriki, T. *Synthesis* **1990**, 53. Buchschacher, P.; Fürst, A. *Org. Synth.* **1986**, *63*, 37. Buchschacher, P.; Fürst, A.; Gutzwiller, J. *Organic Syntheses*; Wiley: New York, Collect. Vol. 7, in press.

(9) Although we also tried the Huang–Minlon reduction of a similar compound, the method was inapplicable.

(10) Barton, D. H. R.; Motherwell, W. B. *Pure Appl. Chem.* **1981**, *53*, 15.

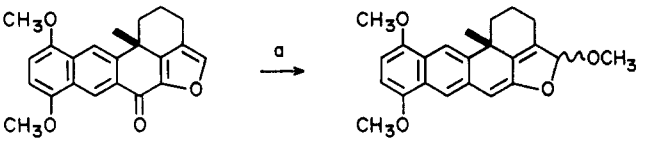
hydride (L-Selectride), yielding axial alcohol (+)-**10** in 92% yield, which was then converted to xanthate (+)-**11** in quantitative yield by treatment of lithium alkoxide of the alcohol with carbon disulfide and then with iodomethane. Xanthate (+)-**11** was next reduced with tributyltin hydride, giving the desired compound (+)-**12** in 92% yield. After deprotection of the acetal group of (+)-**12** (98% yield), ketone (+)-**13** was converted to olefin (−)-**14** in 98% yield by formation of tosylhydrazone followed by treatment with methyllithium. The allylic methylene moiety of olefin (−)-**14** was oxidized with CrO_3 and 3,5-dimethylpyrazole,[11] yielding conjugated enone (+)-**15** in 55% yield.

The Diels–Alder reaction to construct the molecular skeleton of the tetracyclic system was carried out by heating a mixture of 3,6-dimethoxybenzocyclobutene (**16**)[7] and enone (+)-**15** at 210–220 °C for 10 h, affording the desired adduct (+)-**17** in 40% yield (Scheme II). The ^{13}C NMR spectrum of (+)-**17** indicated that the product was composed of a single stereoisomer. Tetrahydronaphthalene derivative (+)-**17** was dehydrogenated with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), giving naphthalene derivative (−)-**18** in 80% yield. To construct the furan ring system, ketone (−)-**18** was next subjected to an air oxidation in the presence of a base. Oxygen gas was bubbled into a solution of **18** and potassium *tert*-butoxide in *tert*-butyl alcohol, yielding diosphenol **19**. The ^1H NMR spectrum of **19** showed a sharp singlet peak at δ 7.095 characteristic of the intramolecular hydrogen-bonded hydroxyl group of a diosphenol moiety.[12] Deprotection of the methoxymethyl group of **19** by treatment with concentrated hydrochloric acid in methanol gave alcohol **20**. To perform the next oxidation reaction of the primary hydroxyl group of **20** to aldehyde and successive cyclization to form a furan ring, we at first tried the dimethyl sulfoxide (DMSO)/1,3-dicyclohexylcarbodiimide (DCC) oxidation method, which was successful in the case of the total synthesis of halenaquinol series.[7] However, all attempts employing DMSO and various auxiliary reagents (DCC, acetic anhydride, and oxalyl chloride), pyridinium chlorochromate, pyridinium dichromate, and *N*-bromosuccinimide were unsuccessful. The method of oxidation with activated manganese(IV) oxide, followed by successive treatment with *p*-toluenesulfonic acid, was finally found to give the desired xestoquinol dimethyl ether (+)-**21** as crystals in 24% overall yield from **18**.

The hydroquinone dimethyl ether moiety of (+)-**21** was oxidatively cleaved with ammonium cerium(IV) nitrate ($(NH_4)_2Ce(NO_3)_6$), yielding xestoquinone (12bS)-**1** as crystals: mp 213–216 °C dec; natural[2] mp 212–214 °C dec. All of the spectroscopic data of the synthetic sample of (12bS)-**1**, including CD data, were identical with those of the natural xestoquinone (+)-**1** (see Experimental Section). Since it is evident that the absolute configuration of the synthetic xestoquinone **1** is 12b*S*, because we started from the Wieland–Miescher ketone (8a*R*)-(−)-**7**, the results described above lead to the conclusion that natural xestoquinone (+)-**1** also has the 12b*S* absolute configuration. Xestoquinone ((12b*S*)-(+)-**1**) was finally reduced with sodium hydrosulfite to afford xestoquinol ((12b*S*)-**2**) in an almost quantitative yield. Although xestquinol **2** has not been isolated yet as a natural product, the spectroscopic data of the synthetic sample reasonably support its structure. The first total synthesis of (+)-xestoquinone and xestoquinol has been thus achieved, and their absolute configuration was unambiguously determined to be 12b*S*.

Since xestoquinone (+)-**1** was converted to adociaquinones A (**5**) and B (**6**) by Schmitz,[5] our total synthesis of (+)-**1** also implies the formal total synthesis of these hexacyclic metabolites **5** and **6**.

Scheme III[a]



(12bS)-(+)-21 (4ξ,12bS)-22

[a] (a) $CeCl_3 \cdot 7H_2O$, $NaBH_4$, MeOH, and then pyridinium *p*-toluenesulfonate, MeOH.

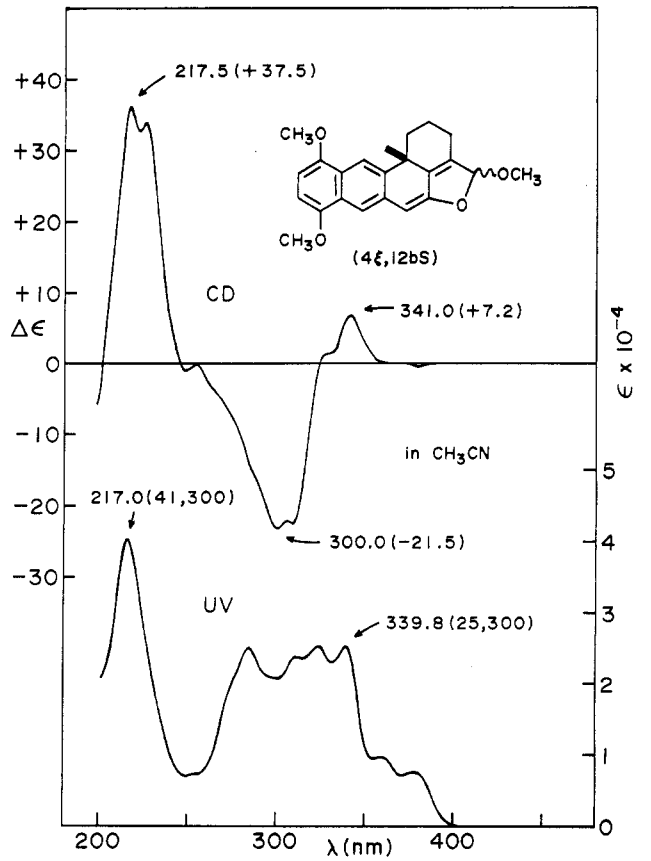


Figure 1. CD and UV spectra of xestoquinol naphthalene–diene derivative (4ξ,12b*S*)-**22** in acetonitrile.

CD Spectrum and Absolute Stereochemistry of Naphthalene–Diene Derivative. We and Kitagawa have previously determined the absolute stereochemistry of halenaquinone (+)-**3** and halenaquinol (+)-**4** by theoretical calculation of CD spectra of naphthalene–diene derivatives.[6] To apply the same method to the present xestoquinone compounds, xestoquinol dimethyl ether (+)-**21** was converted to naphthalene–diene derivative **22** by reduction with sodium borohydride in the presence of cerium(III) chloride[14] and methanol, followed by treatment with pyridinium *p*-toluenesulfonate and methanol (Scheme III). The product obtained was a mixture of two stereoisomers of the methoxyl group at the 4-position, from which a single isomer **22** was isolated as crystals.[15] Al-

(11) Salmond, W. G.; Barta, M. A.; Havens, J. L. *J. Org. Chem.* **1978**, *43*, 2057.

(12) The ^1H NMR spectrum of the diosphenol moiety generally exhibits a singlet peak of hydroxyl group proton around δ 6.9–7.6; see refs 7 and 13.

(13) Kreiser, W.; Ulrich, W. *Liebigs Ann. Chem.* **1972**, *761*, 121.

(14) Gemal, A. L.; Luche, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 5454.

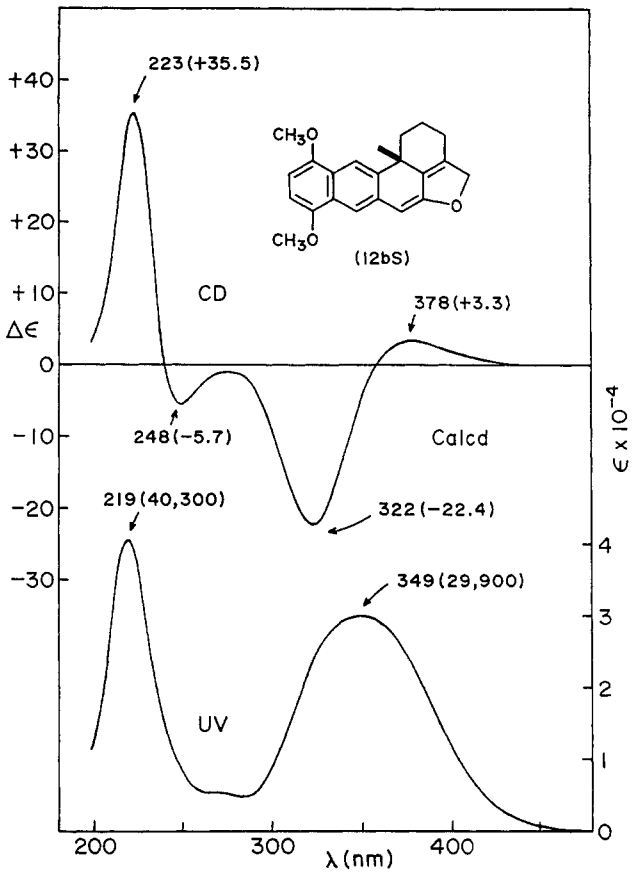


Figure 2. CD and UV curves of xestoquinol naphthalene–diene derivative (12b*S*)-**23** calculated by the π-electron SCF-CI-DV MO method.

though the relative stereochemistry of the methoxyl group at the 4-position of **22** has remained undetermined, it is a minor problem for the present situation because the chiroptical properties of the twisted conjugated π-electron system composed of naphthalene, conjugated diene, and lone-pair orbitals of three ether oxygens are little affected by the chirality at the 4-position. In fact, the basic pattern of CD spectrum of **22** shown in Figure 1 is quite similar to those of naphthalene–diene derivatives of halenaquinol series that we have previously prepared starting from natural halenaquinol.[6]

We have previously performed[6] the theoretical calculation of the CD and UV spectra of a model compound (**23**) with 12b*S* absolute configuration by the application of the π-electron SCF-CI-dipole velocity MO method[16] (Figure 2). Since the observed CD and UV spectra of xestoquinol naphthalene–diene derivatives **22** (Figure 1) are in a good agreement with the theoretically obtained CD and UV curves of the model compound (12b*S*)-**23** (Figure 2), it is evident that compound **22** has a 12b*S* absolute configuration. The absolute stereochemistry of compounds in the xestoquinone series was thus established.

Experimental Section

General Procedures. Melting points are uncorrected. IR spectra were obtained as KBr disks or $CHCl_3$ solutions by using a JEOL JIR-100 or a Hitachi 285 spectrophotometer. ^1H NMR spectra were recorded on a JEOL FX90Q (89.55-MHz) or a JEOL JNM-GX400 (399.8-MHz) spectrometer. ^{13}C NMR spectra were obtained on a JEOL FX90Q (22.5-MHz). The assignment of the peaks of methyl (CH_3), methylene (CH_2), methine (CH), and unprotonated (C) carbons in ^{13}C NMR spectra was performed by the DEPT measurements (θ = 135°, 90°). All NMR data are reported δ downfield from tetramethylsilane. Optical rotations $[\alpha]_D$ were measured on a Jasco DIP-370 spectropolarimeter. UV and CD spectra were recorded on Jasco UVDEC-505 or Ubest-50 and Jasco J-400X spectrometers, respectively. MS spectra were obtained with a JEOL JMS DX-300/JMA-3100/3500 spectrometer by the electron ionization procedure (70 eV), unless otherwise noted. The purity of all title compounds was shown to be ≥95% by ^1H NMR, TLC, HPLC, and/or elemental analysis.

(4a*R*,5*S*,8a*R*)-3,4,4a,5,8,8a-Hexahydro-5-[(methoxymethoxy)methyl]-8a-methyl-1,6(2*H*,7*H*)-naphthalenedione 1-Ethylene Acetal ((+)-9). To a solution of (4a*R*,5*S*,8a*R*)-3,4,4a,5,8,8a-hexahydro-5-(hydroxymethyl)-8a-methyl-1,6-(2*H*,7*H*)-naphthalenedione 1-ethylene acetal ((+)-8)[7] (10.0 g, 39.3 mmol) in dry dichloromethane (300 mL) were added successively, under nitrogen, *N*,*N*-diisopropylethylamine (60.9 g, 471 mmol) and chloromethyl methyl ether (19.0 g, 236 mmol). After the mixture was stirred at room temperature overnight, the reaction mixture was poured into ice water and extracted with dichloromethane. The organic layer was washed with water and then with brine, dried over anhydrous Na_2SO_4, and evaporated to dryness. The residue was chromatographed on silica gel (hexane/EtOAc, 3:1) to give methoxymethyl ether (+)-**9** (9.36 g, 80%) as crystals: mp 77.0–77.5 °C; IR ($CHCl_3$) ν_{max} 2950, 2880, 1710, 1440, 1180, 1145, 1105, 1072, 1038, 945 cm^{-1}; ^1H NMR (89.55 MHz, $CDCl_3$) δ 1.201 (3 H, s), 1.4–2.5 (12 H, m), 3.352 (3 H, s), 3.65 (1 H, dd, J = 10.0, 3.3 Hz), 3.8–4.0 (5 H, m), 4.542 (1 H, d, J = 6.6 Hz), 4.631 (1 H, d, J = 6.6 Hz); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 14.1 (CH_3), 22.7 (CH_2), 25.0 (CH_2), 29.8 (CH_2), 30.0 (CH_2), 37.6 (CH_2), 42.1 (C), 42.6 (CH), 51.0 (CH), 55.3 (CH_3), 63.5 (CH_2), 65.0 (CH_2), 65.2 (CH_2), 96.9 (CH_2), 112.5 (C), 210.0 (C); $[\alpha]^{20}_D$ +3.8° (*c* 1.4735, $CHCl_3$). Anal. Calcd for $C_{16}H_{26}O_5$: C, 64.41; H, 8.78. Found: C, 64.33; H, 8.51.

(4a*R*,5*S*,6*S*,8a*R*)-3,4,4a,5,6,7,8,8a-Octahydro-6-hydroxy-5-[(methoxymethoxy)methyl]-8a-methyl-1(2*H*)-naphthalenone 1-Ethylene Acetal ((+)-10). To a solution of ketone **9** (9.36 g, 31.4 mmol) in dry tetrahydrofuran (THF; 200 mL) cooled to 0 °C was added a solution of lithium tri-*sec*-butylborohydride (L-Selectride) in THF (1.0 M solution, 38.0 mL, 38.0 mmol), and the reaction mixture was stirred at 0 °C for 35 min. An aqueous sodium hydroxide solution (1.0 M, 90 mL) and an aqueous hydrogen peroxide solution (35%, 90 mL) were added dropwise under ice cooling. After the mixture was stirred for 30 min at room temperature, the reaction mixture was poured into ice water and extracted with ethyl acetate. The organic layers were washed with brine and evaporated to dryness. The residue (9.651 g) was subjected to a column chromatography on silica gel (EtOAc), giving alcohol (+)-**10** (8.63 g, 92%) as a syrup: IR ($CHCl_3$) ν_{max} 3500, 2940, 2875, 1440, 1380, 1180, 1145, 1100, 1085, 1030, 948, 905 cm^{-1}; ^1H NMR (89.55 MHz, $CDCl_3$) δ 0.990 (3 H, s), 1.0–2.3 (12 H, m), 2.77 (1 H, br s), 3.361 (3 H, s), 3.673 (1 H, s), 3.722 (1 H, d, J = 2.2 Hz), 3.934 (4 H, m), 4.07 (1 H, m), 4.565 (1 H, d, J = 6.9 Hz), 4.628 (1 H, d, J = 6.9 Hz); $[\alpha]^{20}_D$ +14.9° (*c* 1.838, $CHCl_3$); high-resolution mass spectrum, calcd for $C_{16}H_{28}O_5$ 300.193 66, found 300.193 64.

***O*-[(4a*R*,5*S*,6*S*,8a*R*)-3,4,4a,5,6,7,8,8a-Octahydro-5-[(methoxymethoxy)methyl]-8a-methyl-1(2*H*)-oxonaphthalen-6-yl] *S*-Methyl Dithiocarbonate Ethylene Acetal ((+)-11).** To a solution of alcohol (+)-**10** (4.0 g, 13.3 mmol) in dry THF (60 mL) cooled to −78 °C was added a solution of butyllithium in hexane (1.6 M, 10.9 mL, 17.4 mmol), and the mixture was stirred at −78 °C for 30 min and then at 0 °C for 20 min. Carbon disulfide (1.52 g, 20.0 mmol) was added dropwise, and the reddish yellow reaction mixture was stirred at 0 °C for 40 min. Iodomethane (7.60 g, 53.5 mmol) was added, and the reaction mixture was stirred at 0 °C for 20 min and then at room temperature for 30 min. It was then poured into ice water and extracted with ethyl acetate. The organic layers were washed with aqueous NH_4Cl and with brine and evaporated to dryness. The residue was chroamtographed on silica gel (hexane/EtOAc, 3:1) to give xanthate (+)-**11** (5.20 g, 100%) as a syrup: IR ($CHCl_3$) ν_{max} 2945,

(15) It was rather difficult to purify naphthalene–diene derivative **22** because of its instability. The separation of two stereoisomers was checked by an HPLC (Nucleosil 50-5 column; hexane/EtOAc, 30:1).

(16) Harada, N.; Nakanishi, K. *Circular Dichroic Spectroscopy—Exciton Coupling in Organic Stereochemistry*; University Science Books: Mill Valley, CA, 1983.

2880, 1255, 1230, 1180, 1145, 1105, 1085, 1045, 997, 946, 915, 870 cm^{-1}; ^1H NMR (89.55 MHz, $CDCl_3$) δ 1.042 (3 H, s), 1.1–2.3 (12 H, m), 2.552 (3 H, s), 3.300 (3 H, s), 3.31 (1 H, dd, J = 10.0, 8.0 Hz), 3.57 (1 H, dd, J = 10.0, 5.1 Hz), 3.922 (4 H, m), 4.493 (1 H, d, J = 6.6 Hz), 4.581 (1 H, d, J = 6.6 Hz), 5.922 (1 H, br q); $[\alpha]^{20}_D$ +12.2° (c 1.3345, $CHCl_3$). Anal. Calcd for $C_{18}H_{30}O_5S_2$: C, 55.36; H, 7.74; S, 16.42. Found: C, 55.41; H, 7.90; S, 16.16.

(4a*R*,5*S*,8a*R*)-3,4,4a,5,6,7,8,8a-Octahydro-5-[(methoxymethoxy)methyl]-8a-methyl-1(2*H*)-naphthalenone 1-Ethylene Acetal ((+)-12). To a solution of xanthate (+)-**11** (5.20 g, 13.3 mmol) in dry toluene (80 mL) heated at 90 °C was added dropwise, over 1.5 h, a solution of tributyltin hydride (12.8 g, 44.0 mmol) and α,α'-azobisisobutyronitrile (AIBN; 1.35 g, 8.22 mmol) in dry toluene (80 mL). The turbid reaction mixture was stirred for additional 30 min and then evaporated in vacuo to dryness. The residue was subjected to a column chromatography on silica gel (hexane/EtOAc, 3:1) to give (+)-**12** (3.48 g, 92%) as a syrup: IR ($CHCl_3$) ν_{max} 2930, 2870, 1443, 1380, 1178, 1140, 1105, 1082, 1035, 1005, 948, 908, 865 cm^{-1}; ^1H NMR (89.55 MHz, $CDCl_3$) δ 1.001 (3 H, s), 1.1–1.9 (14 H, m), 3.2–3.7 (2 H, m), 3.336 (3 H, s), 3.928 (4 H, m), 4.580 (2 H, s); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 14.6 (CH_3), 21.0 (CH_2), 22.9 (CH_2), 23.6 (CH_2), 30.0 (CH_2), 30.3 (CH_2), 30.8 (CH_2), 37.2 (CH), 42.8 (C), 43.4 (CH), 55.0 (CH_3), 65.0 (CH_2), 65.2 (CH_2), 71.4 (CH_2), 96.7 (CH_2), 113.0 (C); $[\alpha]^{20}_D$ +34.2° (c 1.8125, $CHCl_3$). Anal. Calcd for $C_{16}H_{28}O_4$: C, 67.57; H, 9.92. Found: C, 67.66; H, 10.04.

(4a*R*,5*S*,8a*R*)-3,4,4a,5,6,7,8,8a-Octahydro-5-[(methoxymethoxy)methyl]-8a-methyl-1(2*H*)-naphthalenone ((+)-13). A mixture of acetal **12** (3.48 g, 12.2 mmol), p-toluenesulfonic acid monohydrate (0.30 g, 1.58 mmol), water (50 mL), and acetone (100 mL) was stirred at room temperature for 14 h, during which time the starting material gradually dissolved to afford a clear solution. The reaction mixture was poured into water and extracted with ethyl acetate. The organic layers were washed with water and brine and evaporated to dryness, giving ketone (+)-**13** (2.88 g, 98%) as a syrup: IR ($CHCl_3$) ν_{max} 2930, 2860, 1698, 1446, 1375, 1310, 1145, 1105, 1033, 970, 910 cm^{-1}; ^1H NMR (89.55 MHz, $CDCl_3$) δ 1.125 (3 H, s), 1.2–1.9 (11 H, m), 1.9–2.3 (2 H, m), 2.3–2.8 (1 H, m), 3.344 (3 H, s), 3.49 (2 H, d, J = 4.4 Hz), 4.588 (2 H, s); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 16.6 (CH_3), 20.7 (CH_2), 23.4 (CH_2), 25.9 (CH_2), 30.5 (CH_2), 32.6 (CH_2), 37.0 (CH), 37.3 (CH_2), 47.5 (CH), 48.6 (C), 55.2 (CH_3), 70.9 (CH_2), 96.8 (CH_2), 215.6 (C); $[\alpha]^{20}_D$ +59.2° (c 1.7785, $CHCl_3$). Anal. Calcd for $C_{14}H_{24}O_3$: C, 69.96; H, 10.06. Found: C, 70.23; H, 9.95.

[(1*S*,4a*S*,8a*R*)-1,2,3,4,4a,7,8,8a-Octahydro-4a-methylnaphthalen-1-yl]methyl Methoxymethyl Ether ((−)-14). A solution of ketone (+)-**13** (3.18 g, 13.2 mmol) and p-toluenesulfonhydrazide (2.96 g, 15.9 mmol) in ethanol (200 mL) was refluxed for 4 h, during which time ethanol was gradually distilled. The reaction mixture was evaporated in vacuo, and the residue was subjected to a short-column chromatography on silica gel (EtOAc), yielding tosylhydrazone: IR ($CHCl_3$) ν_{max} 2930, 2860, 1595, 1445, 1380, 1330, 1160, 1105, 1090, 1035, 990, 910, 550 cm^{-1}; ^1H NMR (89.55 MHz, $CDCl_3$) δ 0.963 (3 H, s), 1.0–2.7 (14 H, m), 2.425 (3 H, s), 3.320 (3 H, s), 3.40 (2 H, m), 4.556 (2 H, s), 7.30 (2 H, d, J = 8.2 Hz), 7.83 (2 H, d, J = 8.2 Hz).

The tosylhydrazone obtained was dissolved in dry THF (100 mL), and to the solution cooled at 0 °C was added a methyllithium solution in diethyl ether (1.4 M, 25 mL, 35 mmol) under nitrogen. After the reaction mixture was stirred at 0 °C for 1 h and then at room temperature for 1 h, the mixture was poured into ice water and extracted with ethyl acetate. The organic layer was wahsed with water and brine and evaporated to dryness. The residue was chromatographed on silica gel (hexane/EtOAc, 3:1), giving olefin (−)-**14** (2.91 g, 98% based on **13**) as a syrup: IR ($CHCl_3$) ν_{max} 2925, 1440, 1368, 1125, 1105, 1035, 945, 912 cm^{-1}; ^1H NMR (89.55 MHz, $CDCl_3$) δ 0.909 (3 H, s), 1.0–2.2 (12 H, m), 3.347 (3 H, s), 3.38 (1 H, dd, J = 10.3, 5.1 Hz), 3.52 (1 H, dd, J = 10.3, 4.1 Hz), 4.593 (2 H, s), 5.431 (2 H, s); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 19.8 (CH_3), 20.9 (CH_2), 21.4 (CH_2), 26.3 (CH_2), 31.4 (CH_2), 34.9 (C), 36.7 (CH), 39.3 (CH_2), 45.0 (CH), 55.0 (CH_3), 71.1 (CH_2), 96.8 (CH_2), 123.7 (CH), 139.7 (CH); $[\alpha]^{20}_D$ −43.1° (c 2.2085, $CHCl_3$). Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 74.94; H, 10.51.

(4a*S*,8*S*,8a*R*)-4a,5,6,7,8,8a-Hexahydro-8-[(methoxymethoxy)methyl]-4a-methyl-2(1*H*)-naphthalenone ((+)-15). To a suspension of chromium(VI) oxide (CrO_3; 25.9 g, 259 mmol) in dichloromethane (100 mL) cooled at −20 °C was added 3,5-dimethylpyrazole (24.9 g, 259 mmol) in one portion, and the mixture was stirred at that temperature for 20 min. A solution of olefin (−)-**14** (2.91 g, 12.9 mmol) in dichloromethane (100 mL) was added, and the reaction mixture was stirred at −20 °C for 2.5 h. After an aqueous sodium hydroxide solution (5 M, 100 mL) was added, the mixture was stirred at 0 °C for 1 h, poured into water, and extracted with dichloromethane. The organic layer was filtered with Celite, washed with dilute hydrochloric acid and brine, and then evaporated to dryness. The residue was chromatographed on silica gel (hexane/EtOAc, 3:1) to give enone (+)-**15** (1.70 g, 55%) as a syrup: IR ($CHCl_3$) ν_{max} 2925, 1670, 1445, 1385, 1370, 1145, 1102, 1032, 913 cm^{-1}; ^1H NMR (89.55 MHz, $CDCl_3$) δ 1.081 (3 H, s), 1.1–2.7 (10 H, m), 3.342 (3 H, s), 3.436 (2 H, d, J = 3.7 Hz), 4.573 (2 H, s), 5.833 (1 H, dd, J = 9.9, 0.7 Hz), 6.735 (1 H, d, J = 9.9 Hz); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 17.1 (CH_3), 20.9 (CH_2), 30.0 (CH_2), 36.3 (C), 36.8 (CH), 37.6 (CH_2), 37.7 (CH_2), 44.4 (CH), 55.2 (CH_3), 69.9 (CH_2), 96.7 (CH_2), 126.6 (CH), 161.5 (CH), 199.5 (C); $[\alpha]^{20}_D$ +2.9° (c 1.7085, $CHCl_3$); MS m/z 238 (parent, 8%), 206 (78%), 191 (34%), 175 (100%), 161 (65%), 147 (20%), 135 (35%), 121 (45%); high-resolution mass spectrum, calcd for $C_{14}H_{22}O_3$ 238.156 88, found 238.156 81. Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.56; H, 9.30. Found: C, 70.50; H, 9.44.

(4*S*,4a*R*,6aξ,12aξ,12b*R*)-1,2,3,4,4a,6a,7,12,12a,12b-Decahydro-8,11-dimethoxy-4-[(methoxymethoxy)methyl]-12b-methyl-6(5*H*)-benz[*a*]anthracenone ((+)-17). A solution of enone (+)-**15** (0.300 g, 1.26 mmol) and 3,6-dimethoxybenzocyclobutene (**16**;[7] 0.620 g, 3.78 mmol) in benzene (1.0 mL) was placed in a pressure ampule, and the solvent was evaporated in vacuo. The ampule was sealed and heated in an oil bath. The temperature was gradually raised from 150 to 210 °C over 3 h and then kept around 210–220 °C for 10 h. The reaction mixture was dissolved in a small amount of chloroform, which was subjected to HPLC on silica gel (hexane/EtOAc, 3:1), yielding the Diels–Alder adduct (+)-**17** (0.203 g, 40%) as crystals: mp 146 °C; IR (KBr) ν_{max} 2940, 1710, 1480, 1440, 1257, 1145, 1115, 1078, 1040, 920, 800, 720 cm^{-1}; ^1H NMR (89.55 MHz, $CDCl_3$) δ 1.304 (3 H, s), 1.2–3.6 (18 H, m), 3.322 (3 H, s), 3.729 (3 H, s), 3.766 (3 H, s), 4.543 (2 H, s), 6.557 (2 H, s); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 19.1, 21.0, 21.3, 22.3, 30.1, 35.1, 37.0, 38.1, 41.6, 41.6, 44.1, 47.0, 55.3, 55.4, 55.6, 70.3, 96.7, 106.5 106.8, 124.9, 125.0, 151.1, 151.4, 210.6; $[\alpha]^{20}_D$ +142.4° (c 1.240, $CHCl_3$); high-resolution mass spectrum, calcd for $C_{24}H_{34}O_5$ 402.240 61, found 402.240 75. Anal. Calcd for $C_{24}H_{34}O_5$: C, 71.61; H, 8.51. Found: C, 71.39; H, 8.77.

(4*S*,4a*R*,12b*R*)-1,2,3,4,4a,12b-Hexahydro-8,11-dimethoxy-4-[(methoxymethoxy)methyl]-12b-methyl-6(5*H*)-benz[*a*]anthracenone ((−)-18). A solution of adduct (+)-**17** (0.203 g, 0.504 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ; 0.241 g, 1.06 mmol) in benzene (30 mL) was refluxed for 4 h. The reaction mixture was chroamtographed on basic alumina (EtOAc) to remove excess DDQ and hydroquinone formed. The crude product obtained was further purified by HPLC on silica gel (hexane/EtOAc, 3:1), giving naphthalene derivative (−)-**18** (0.161 g, 80%) as a syrup: IR ($CHCl_3$) ν_{max} 3000, 2945, 2840, 1680, 1630, 1590, 1465, 1438, 1345, 1335, 1272, 1150, 1115, 1095, 1035, 972 cm^{-1}; ^1H NMR (89.55 MHz, $CDCl_3$) δ 1.238 (3 H, s), 1.3–2.6 (8 H, m), 2.51 (1 H, dd, J = 18.0, 12.6 Hz), 2.92 (1 H, dd, J = 18.0, 4.9 Hz), 3.349 (3 H, s), 3.51 (2 H, d, J = 3.3 Hz), 3.940 (3 H, s), 3.955 (3 H, s), 4.593 (2 H, s), 6.60 (1 H, d, J = 8.5 Hz), 6.77 (1 H, d, J = 8.5 Hz), 8.170 (1 H, s), 8.933 (1 H, s); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 21.6, 22.2, 30.2, 37.3, 38.1, 39.0, 42.5, 55.2, 55.6, 55.7, 70.3, 96.8, 103.1, 106.1, 116.6, 123.6, 124.5, 128.9, 129.4, 149.1, 149.9, 151.0, 198.3; $[\alpha]^{20}_D$ −17.6° (c 1.3085, $CHCl_3$); MS m/z 398 (parent, 100%), 383 (23%), 321 (9%); high-resolution mass spectrum, calcd for $C_{24}H_{30}O_5$ 398.209 31, found 398.209 28.

(4*S*,12b*S*)-1,2,3,4-Tetrahydro-5-hydroxy-8,11-dimethoxy-4-[(methoxymethoxy)methyl]-12b-methyl-6(12b*H*)-benz[*a*]anthracenone (19). Into a solution of ketone (−)-**18** (0.100 g, 0.251 mmol) and potassium *tert*-butoxide (0.141 g, 1.26 mmol) in *tert*-butyl alcohol (10 mL) was bubbled oxygen gas for 4 h at room temperature. The reaction mixture was acidified with an aqueous ammonium chloride solution and extracted with chloroform. The organic layer was washed with brine and evaporated to dryness, yielding diosphenol **19** as a syrup: ^1H NMR (89.55 MHz, $CDCl_3$) δ 1.1–3.2 (7 H, m), 1.675 (3 H, s), 3.419 (3 H, s),

3.939 (6 H, s), 3.8–4.1 (1 H, m), 4.35 (1 H, dd, J = 9.8, 4.6 Hz), 4.740 (2 H, s), 6.52 (1 H, d, J = 8.0 Hz), 6.64 (1 H, d, J = 8.0 Hz), 7.095 (1 H, s, OH), 8.375 (1 H, s), 9.116 (1 H, s); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 22.4, 27.1, 31.9, 41.1, 41.6, 43.4, 55.2, 55.6, 55.6, 70.8, 96.9, 102.9, 105.7, 119.7, 122.6, 124.8, 125.2, 128.5, 134.9, 141.6, 148.1, 148.7, 150.6, 180.9; MS m/z 412 (parent, 19%), 335 (100%); high-resolution mass spectrum, calcd for $C_{24}H_{28}O_6$ 412.188 57, found 412.188 17.

(4*S*,12b*S*)-1,2,3,4-Tetrahydro-5-hydroxy-4-(hydroxymethyl)-8,11-dimethoxy-12b-methyl-6(12b*H*)-benz[*a*]anthracenone (20). Diosphenol **19** obtained above was dissolved in methanol (15 mL), and concentrated hydrochloric acid (0.02 mL) was added. The reaction mixture was stirred at 70 °C for 3 h, poured into water, and extracted with ethyl acetate. The organic layer was washed with brine and evaporated to give alcohol **20** (0.092 g) as a syrup: ^{1}H NMR (89.55 MHz, $CDCl_3$) δ 1.64 (3 H, s), 1.1–3.0 (7 H, m), 3.53 (1 H, t, J = 7.8 Hz, disappeared in D_2O), 3.6–4.3 (2 H, m), 3.98 (6 H, s), 6.60 (1 H, d, J = 8.6 Hz), 6.75 (1 H, d, J = 8.6 Hz), 7.67 (1 H, s, disappeared in D_2O), 8.38 (1 H, s), 9.13 (1 H, s).

(12b*S*)-2,3-Dihydro-8,11-dimethoxy-12b-methyl-1*H*-benzo[6,7]phenanthro[10,1-*bc*]furan-6(12b*H*)-one ((+)-21). A mixture of alcohol **20** (0.092 g, 0.25 mmol) obtained above and activated manganese(IV) oxide (4.0 g, 46 mmol) in chloroform (15 mL) was stirred at room temperature for 30 min. The mixture was stirred with water (15 mL) for 5 min in order to allow the fine particle of manganese oxide to coagulate, and then the precipitation was filtered with Celite and washed with chloroform. The combined filtrate was washed well with water and concentrated in vacuo to ca. 20 mL. To the solution obtained was added *p*-toluenesulfonic acid monohydrate (0.002 g, 0.01 mmol), and the mixture was stirred at room temperature for 30 min, poured into water, and extracted with chloroform. The organic layer was washed with water, dried over anhydrous sodium sulfate, and evaporated to dryness. The residue was subjected to HPLC on silica gel (hexane/EtOAc, 1:1) to give xestoquinol dimethyl ether (+)-**21** (0.021 g, 24% based on **18**) as crystals: mp 243 °C dec; IR (KBr) ν_{max} 3101, 2964, 2947, 2835, 1659, 1628, 1612, 1533, 1470, 1443, 1423, 1394, 1363, 1358, 1340, 1323, 1267, 1244, 1190, 1161, 1144, 1111, 1090, 1066, 1043, 970, 931, 906, 866, 802, 754, 719 cm^{-1}; ^{1}H NMR (399.8 MHz, $CDCl_3$) δ 1.540 (3 H, s), 1.834 (1 H, ddd, J = 13.2, 13.2, 4.1 Hz), 2.10–2.20 (1 H, m), 2.20–2.34 (1 H, m), 2.58–2.68 (2 H, m), 2.878 (1 H, dd, J = 16.7, 7.7 Hz), 3.983 (3 H, s), 3.989 (3 H, s), 6.704 (1 H, d, J = 8.4 Hz), 6.816 (1 H, d, J = 8.4 Hz), 7.482 (1 H, br t, J = 1.4 Hz), 8.279 (1 H, s), 9.282 (1 H, s); $[\alpha]^{20}_D$ +93.7° (c 0.6500, $CHCl_3$); MS m/z 348 (parent, 71%), 333 (100%), 318 (18%), 303 (37%); high-resolution mass spectrum, calcd for $C_{22}H_{20}O_4$ 348.136 15, found 348.136 21. Anal. Calcd for $C_{22}H_{20}O_4$: C, 75.84; H, 5.79. Found: C, 75.86; H, 5.59.

(12b*S*)-2,3-Dihydro-12b-methyl-1*H*-benzo[6,7]phenanthro[10,1-*bc*]furan-6,8,11(12b*H*)-trione ((+)-1). To a solution of xestoquinol dimethyl ether (+)-**21** (0.010 g, 0.029 mmol) in acetonitrile (6.0 mL) was added an aqueous solution of ammonium cerium(IV) nitrate ($(NH_4)_2Ce(NO_3)_6$; 0.075 g, 0.14 mmol) in water (0.5 mL) under ice cooling. After the solution was stirred at 0 °C for 20 min, the reaction mixture was poured into water and extracted with chloroform. The organic layer was washed with brine and evaporated to dryness. The residue was subjected to a short-column chromatography on silica gel (EtOAc) and then to HPLC (hexane/EtOAc, 3:2), yielding xestoquinone (+)-**1** (0.0050 g, 55%) as crystals: mp 213–216 °C dec; natural[2] mp 212–214 °C dec; IR (KBr) ν_{max} 3105, 2958, 1670, 1606, 1454, 1321, 1136, 850, 582, 432 cm^{-1}; ^{1}H NMR (399.8 MHz, $CDCl_3$) δ 1.537 (3 H, s, 12b-CH_3), 1.756 (1 H, ddd, J = 13.0, 13.0, 4.5 Hz, 1_{ax}-H), 2.19 (1 H, m, 2_{eq}-H), 2.28 (1 H, m, 2_{ax}-H), 2.580 (1 H, ddd, J = 13.0, 4.1, 3.0 Hz, 1_{eq}-H), 2.640 (1 H, dddd, J = 17.0, 9.9, 8.4, 1.5 Hz, 3_{ax}-H), 2.883 (1 H, dddd, J = 17.0, 8.0, 2.2, 1.5 Hz, 3_{eq}-H), 7.028 (1 H, d, J = 10.4 Hz, 9-H or 10-H), 7.060 (1 H, d, J = 10.4 Hz, 10-H or 9-H), 7.538 (1 H, br t, J = 1.5 Hz, 4-H), 8.247 (1 H, s, 12-H), 9.058 (1 H, s, 7-H); UV (CH_3CN) λ_{max} 345.0 nm (sh) (ϵ 7200), 294.5 (14 800), 259.0 (sh) (21 000), 252.0 (22 300), 217.0 (20 500); natural[17] UV (CH_3CN) λ_{max} 345.0 nm (sh) (ϵ 6700), 294.0 (13 700), 259.0 (sh) (20 100), 251.5 (21 400), 216.5 (19 900); CD (CH_3CN) λ_{ext} 350.0 nm ($\Delta\epsilon$ +2.7), 309.0 (−3.2), 278.0 (+0.9), 269.0 (−0.8), 236.5 (−13.4), 213.0 (+5.1); natural[17] CD (CH_3CN) λ_{ext} 352.0 nm ($\Delta\epsilon$ +2.7), 309 (−2.6), 278.0 (+1.1), 258.0 (+0.6), 236.0 (−12.2), 214.0 (+5.5); MS m/z 318 (parent, 31%), 303 (100%); high-resolution mass spectrum, calcd for $C_{20}H_{14}O_4$ 318.089 20, found 318.089 24.

(12b*S*)-2,3-Dihydro-8,11-dihydroxy-12b-methyl-1*H*-benzo[6,7]phenanthro[10,1-*bc*]furan-6(12b*H*)-one (2). To a solution of xestoquinone **1** (0.0035 g, 0.011 mmol) in acetone (10 mL) was added saturated aqueous sodium hydrosulfite ($Na_2S_2O_4$; 0.5 mL), and the mixture was stirred at room temperature for 30 min. After addition of dichloromethane (20 mL) and anhydrous sodium sulfate, the organic layer was separated and evaporated in vacuo, yielding xestoquinol **2** (0.0035 g, 100%): thin-layer chromatography on silica gel (TLC) R_f 0.14 (hexane/EtOAc, 3:2); ^{1}H NMR (89.55 MHz, DMSO-d_6) δ 1.48 (3 H, s), 1.5–3.0 (6 H, m), 6.70 (1 H, d, J = 8.5 Hz), 6.83 (1 H, d, J = 8.5 Hz), 7.86 (1 H, s), 8.16 (1 H, s), 8.93 (1 H, s), 9.2–9.9 (2 H, br s, disappeared in D_2O/DMSO-d_6); UV (CH_3CN) λ_{max} 400.0 nm, 306.8, 275.0, 223.5; MS m/z 320 (parent, 32%), 305 (93%), 303 (100%); high-resolution mass spectrum, calcd for $C_{20}H_{16}O_4$ 320.104 85, found 320.104 88.

(4ξ,12b*S*)-1,2,3,12b-Tetrahydro-8,11-dimethoxy-12b-methyl-4*H*-benzo[6,7]phenanthro[10,1-*bc*]furan-4-yl Methyl Ether (22). To a solution of xestoquinol dimethyl ether (+)-**21** (0.014 g, 0.040 mmol) in dichloromethane (1.5 mL) and methanol (1.5 mL) was added cerium(III) chloride ($CeCl_3 \cdot 7H_2O$; 0.150 g, 0.403 mmol). After the mixture was stirred at room temperature for 10 min, $NaBH_4$ (0.0076 g, 0.20 mmol) was added. After the mixture was stirred for 15 min, water (0.07 mL) was added, and then the mixture was subjected to a short-column chromatography on silica gel (EtOAc). The eluent was evaporated, and the residue was dissolved into methanol (4.0 mL). After pyridinium *p*-toluenesulfonate (0.002 g, 0.008 mmol) was added, the mixture was stirred for 20 min, poured into water, and extracted with ethyl acetate. The organic layer was washed with water, dried over anhydrous Na_2SO_4, and evaporated to dryness. The residue was subjected to HPLC on silica gel (hexane/EtOAc, 3:1), giving a mixture of two epimers of naphthalene–diene derivative, which was treated with petroleum ether and then recrystallized from diethyl ether/hexane to give a single isomer **22** (0.005 g, 34%) as crystals: mp 185–187 °C; IR (KBr) ν_{max} 2991, 2935, 2833, 1649, 1599, 1458, 1379, 1335, 1311, 1269, 1255, 1200, 1146, 1115, 1092, 1066, 972, 906, 899, 885, 850, 843, 802, 725 cm^{-1}; ^{1}H NMR (89.55 MHz, $CDCl_3$) δ 1.365 (3 H, s), 1.6–2.6 (6 H, m), 3.496 (3 H, s), 3.933 (6 H, s), 5.833 (2 H, s), 6.589 (2 H, s), 7.766 (1 H, s), 7.950 (1 H, s); UV (CH_3CN) λ_{max} 380.8 nm (ϵ 7700), 362.8 (9800), 339.8 (25 300), 324.6 (25 100), 313.0 (23 700), 286.4 (24 900), 217.0 (41 300); CD (CH_3CN) λ_{ext} 380.0 nm ($\Delta\epsilon$ −0.4), 341.0 (+7.2), 327.5 (+2.1), 309.5 (−20.8), 300.0 (−21.5), 227.0 (+35.2), 217.5 (+37.5); MS m/z 364 (parent, 100%), 349 (28%), 334 (45%), 321 (30%), 319 (74%), 318 (59%), 303 (33%), 288 (29%), 275 (12%), 153 (12%); high-resolution mass spectrum, calcd for $C_{23}H_{24}O_4$ 364.167 45, found 364.167 72.

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Supplementary Material Available: Spectral data (IR, ^{13}C NMR, $[\alpha]_D$ values, MS, and/or high-resolution mass spectra) for compounds (+)-**8**, (+)-**9**, (+)-**10**, (+)-**11**, (+)-**12**, (+)-**13**, tosylhydrazone of **13**, (−)-**14**, and **20** (3 pages). Ordering information is given on any current masthead page.

(17) The sample of natural xestoquinone used for IR, UV, and CD measurements was supplied by Dr. H. Nakamura, Mitsubishi-Kasei Institute of Life Sciences.

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