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Structure and Chemistry of Some Ophiobolin D Derivatives

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Two different types of transannular reactions occurred in the eight-membered rings of ophiobolin D derivatives during decarboxylation and mild base treatment of the decarboxylated product. Possible reaction mechanisms, together with the chemical and spectral properties of these compounds, are presented on the basis of the configuration and conformation of two key compounds determined by X-ray crystallographic analyses.

Keywords——fungal metabolite; sesterterpene; transannular reaction; eight-membered ring; pyrolytic decarboxylation; intramolecular Michael-type reaction

Introduction

Ophiobolin D is a sesterterpenic metabolite isolated from a fungus, *Cephalosporium caerulens*, which is known to produce a protostane antibiotic, helvolic acid, as a major product.[2] The structure and the absolute configuration of ophiobolin D were established as **1** by X-ray crystallographic analysis.[3] The chemistry and the spectral properties of some derivatives of ophiobolin D were reported previously in preliminary communications.[4,5] The present paper describes in detail the chemical transformation of ophiobolin D, including two different types of transannular reactions in the eight-membered ring. One is a double bond migration reaction and the other is a facile cyclization reaction leading to a novel ring system consisting of four fused five-membered rings. Details of the structure determination of the two key compounds by X-ray crystallographic studies were described in the preceding paper.[6] This paper also includes a revision of the structure of compound **6**, which was erroneously assigned in a previous paper.[5]

Pyrolysis Products of Dehydroophiobolin D

Dehydroophiobolin D (**2**), obtained by Kiliani oxidation of **1**, was readily decarboxylated with evolution of carbon dioxide by heating above its melting point (112°) to afford a mixture of pyrolysis products. The products were purified by silica gel column chromatography to give three crystalline compounds, **4**, **5**, and **6**. The ratio of **4**, **5**, and **6** varied depending on the pyrolytic conditions. When the reaction was carried out by heating at 130° for 40 minutes in a thin glass tube, the ratio was 65 : 10 : 25. The mass spectra of these products exhibited the same molecular ion peak at *m/e* 354 ($C_{24}H_{34}O_2$) and gave almost identical fragmentation patterns showing intense peaks at *m/e* 339, 336, 311, and 285. The isomeric nature of these

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5) S. Nozoe, A. Itai, and Y. Iitaka, *J. Chem. Soc.*, sect. D, **1971**, 872.

6) A. Itai, Y. Iitaka, and S. Nozoe, *Chem. Pharm. Bull.*, **28**, 1035 (1980).

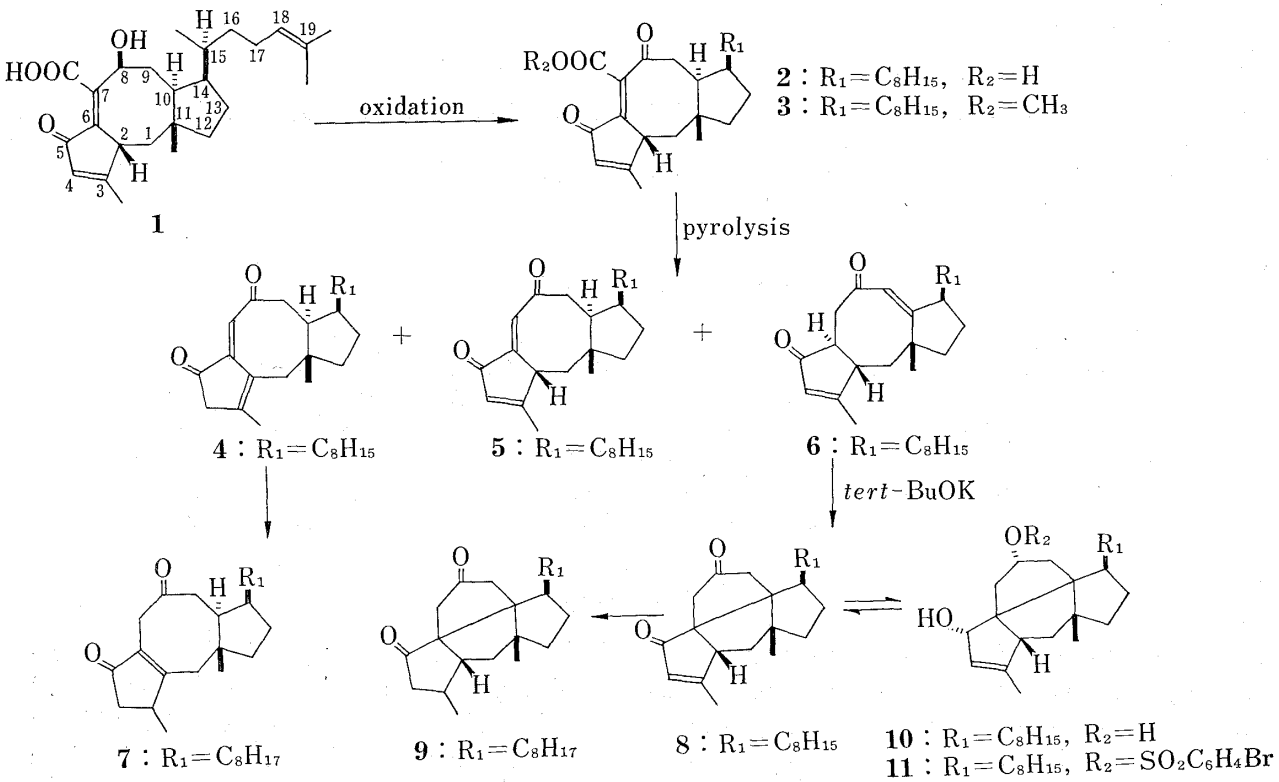

Chart 1

products was indicated by their thermal interconversion *i.e.*, heating of **4** afforded a mixture of **6** and **5**, and heating of **5** yielded a mixture of **6** and **4**, albeit in low yields. Compound **6** is thermally stable, so that the starting material was recovered under the same pyrolytic conditions.

Compound **4**, mp 102—103°, showed two carbonyl absorption bands in the IR spectrum at 1666 and 1750 cm^{-1} and UV absorption maxima at 219.5 nm (ε, 12500) and 314 nm (ε, 8800). The NMR spectrum of **4** showed an α-proton signal of an α,β-unsaturated ketone system at 6.12 and a methyl group on a double bond conjugated with a carbonyl group at 1.93. Catalytic hydrogenation over a Pd catalyst gave a tetrahydro derivative **7**, which showed IR absorption peaks at 1640, 1710, and 1717 cm^{-1} and a UV absorption maximum at 243.5 nm (ε, 10300). These data indicate the structure **4**, containing a dienone system, for this product. The fact that the IR absorption of the unsaturated five-membered ring ketone is the same as that of a normal saturated ketone on a five-membered ring can be explained in terms of the lack of cross-conjugation between the C_5 ketone and the $O_2{=}C_3{-}C_7{=}C_6{-}C_2{=}C_3$ conjugate system.

The presence of two α,β-unsaturated ketone systems in both **5** and **6** was shown by their IR and NMR spectra. Compound **5** showed IR bands at 1610, 1671, and 1699 cm^{-1} and **6** at 1617, 1668, and 1696 cm^{-1}. In the NMR spectra, **5** showed signals at 6.63 and 6.15 due to the α-protons of an α,β-unsaturated ketone and at 2.10 due to a methyl group on a double bond, while **6** showed the corresponding proton signals at 5.98, 5.64, and 2.07.

As shown in Table I, in which the chemical shifts and solvent shifts of the protons of compounds **4**, **5**, and **6** are summarized, the NMR spectrum of compound **5** shows a close resemblance to that of **3** throughout the spectrum. In particular, the C_2–H signal at 3.20 (1H, broad doublet, J=12) in **3**, which is characteristic of structures containing the carbon skeleton and ring junction of the original ophiobolin D system, such as **1**, **2**, and **3**, appeared in **5** at 3.31. Moreover, the former has an absorption maximum at 255.5 nm (ε, 15500) in the UV spectrum, which is close to those of **1** (λ_{max}: 259 nm) and **2** (λ_{max}: 258 nm). We therefore assigned the directly decarboxylated structure to compound **5**. In compound **6** the peak appears at

Table I. Chemical Shifts δ (ppm) and Solvent Shifts ($\Delta=\delta_{CDCl_3}-\delta_{C_6D_6}$) of the Protons of Three Pyrolysis Products

Compound	Solvent	C_2–H	C_3–CH_3	C_4–H	C_7–H	C_9–H	C_{11}–CH_3	C_{15}–CH_3	C_{18}–H	C_{19}–CH_3	
3	$CDCl_3$	3.20 d	2.11	6.10	—	—	0.94	0.87 d	5.10 t	1.66	1.58
4	$CDCl_3$	—	1.93	2.90 d 2.98 d	6.12	—	0.93	0.83 d	5.07 t	1.65	1.57
5	$CDCl_3$	3.31 d	2.10	6.15	6.63	—	0.96	0.84 d	5.07 t	1.67	1.58
6	$CDCl_3$	—	2.07	5.98	—	5.64	1.10	0.81 d	5.07 t	1.69	1.60
6	C_5D_5N	—	1.95	6.03	—	5.68	1.06	0.78 d	5.22 t	1.71	1.62
6	C_6D_6	—	1.48	5.75	—	5.38	0.91	0.76 d	5.24 t	1.71	1.62
6	Δ	—	+0.59	+0.23	—	+0.26	+0.19	+0.05	−0.17	−0.02	−0.02

232 nm (ε, 16600), which indicates the lack of a *cisoid* enone chromophore (C_5 ketone and C_6, C_7 double bond). Though we have already reported that compound **6** might be a stereoisomer of compound **5** with respect to the C_2–H configuration, we carried out X-ray crystallographic analysis in order to confirm this structure. As described in the preceding paper, compound **6** was determined to have a double bond between C_9 and C_{10} instead of between C_6 and C_7 as in **1**, **2**, and **5**. The ring junction at C_2 and C_6 between the eight-membered ring and a five-membered ring is *trans*, as the hydrogen at C_6 was α, while that at C_2 retained β-orientation. The α,β-unsaturated ketone system in the eight-membered ring is not coplanar. The planes of ketone and the double bond have an interplanar angle of 53.1°. The CD and ORD spectra of the three pyrolysis products are shown in Fig. 1; it can be seen that **5** and **6** exhibit rather symmetrical curves. The abnormally intense positive ellipticity in the CD spectrum of **6** ($[\theta]=+140000$, at 238 nm), shown in Fig. 1, is well explained by the large clockwise chirality of the *transoid* enone chromophore[7] (C_8 ketone and C_9, C_{10} double bond).

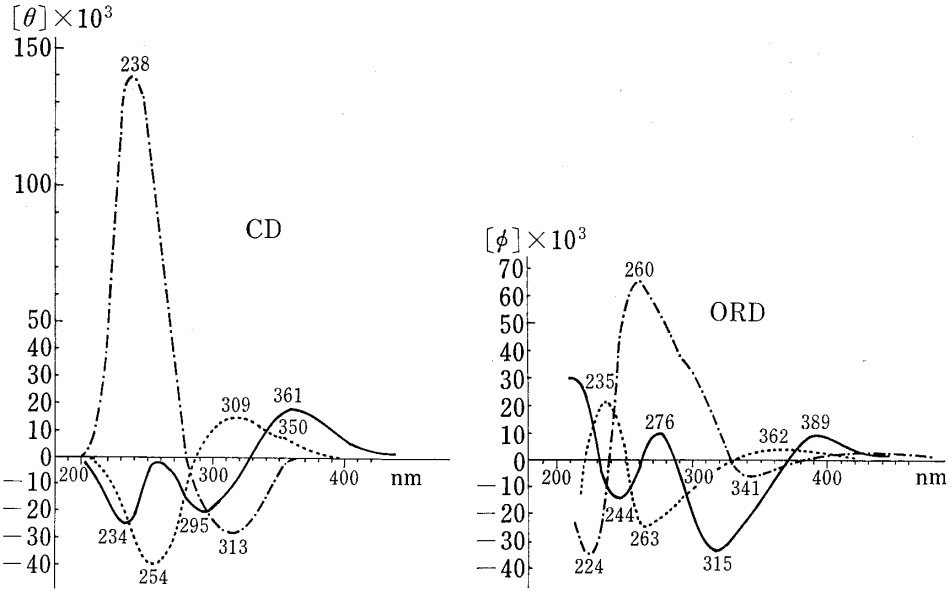

Fig. 1. CD and ORD Spectra of the Compounds **4**, **5**, and **6**
——; for **4**, – – –; for **5**, —·—·—; for **6**.

Cyclization of a Pyrolysis Product

Treatment of the thermally stable compound **6** with a trace amount of *tert*-BuOK at room temperature caused a facile transformation giving rise to a compound, mp 92—93°, possessing

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a molecular formula $C_{24}H_{34}O_2$, which is the same as that of the starting diketone. Compounds **4** and **5** did not afford the same product on treatment under the same or even more rigorous conditions. The product gave a mass fragmentation almost identical with those of **4**, **5**, and **6**. The IR spectrum of the product exhibited a new absorption band at 1743 cm^{-1} due to a saturated five-membered ring ketone. Catalytic hydrogenation proceeded with the absorption of two moles of hydrogen to give a saturated diketone **9**, M^+ at *m/e* 358 ($C_{24}H_{38}O_2$). These data indicate that a new saturated five-membered ring was formed. A deuterium exchange experiment showed the presence of nine exchangeable hydrogens. The retension of the β-methyl-α,β-unsaturated five-membered ring ketone in compound **8** is evident from its IR (1696, 1622 cm^{-1}), UV (λ_{max} 236 nm), and NMR (2.07, 5.75) spectra. Double resonance experiments revealed the presence of two AB quartet signals, both of which were further split by long range couplings. These signals originate from the methylene groups adjacent to a ketone group and the fine splittings can be attributed to long range couplings through the C_8 carbonyl carbon. The triplet centered at 3.11 is coupled by long range interaction with the signals at 5.75 (J= 1.3 Hz) and 2.07 (J=0.9 Hz) and is attributable to C_2–H. Upon irradiation at the tertiary

TABLE II. Chemical Shifts δ (ppm) and Solvent Shifts ($\Delta=\delta_{CDCl_3}-\delta_{C_6D_6}$) of the Protons of **8**, together with the Coupling Constants (Hz)

Solvent	C_2–H	C_3–CH_3	C_4–H	C_7–Hα	C_7–Hβ	C_9–Hα
$CDCl_3$	3.11 t	2.07	5.75	2.80 d	2.42 d	2.57 d
C_6D_6	2.44 t	1.46	5.50	2.81 d	2.17 d	2.50 d
Δ	+0.67	+0.61	+0.25	−0.01	+0.25	+0.07

Solvent	C_9–Hβ	C_{11}–CH_3	C_{15}–CH_3	C_{18}–H	C_{19}–CH_3	
$CDCl_3$	2.32 d	0.95	0.72 d	5.08 t	1.66	1.59
C_6D_6	2.18 d	0.72	0.59 d	5.29 t	1.71	1.64
Δ	+0.14	+0.23	+0.13	−0.21	−0.05	−0.05

$J_{4\text{-}3CH_3}$=1.3; $J_{4\text{-}2}$=1.3; $J_{2\text{-}3CH_3}$=0.9; $J_{1\alpha\text{-}2}$=9; $J_{1\beta\text{-}2}$=9; $J_{7\alpha\text{-}7\beta}$=19.5; $J_{9\alpha\text{-}9\beta}$=18; $J_{7\alpha\text{-}9\alpha}$=1.2; $J_{7\beta\text{-}9\beta}$=1.7.

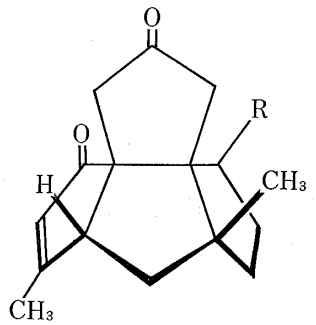

Fig. 2. Molecular Structure of **8**

methyl signal (δ, 0.95), a nuclear Overhauser effect was observed for only one proton out of four methylene protons (about 5—8% increase). The chemical shift and the coupling constant as well as the solvent shifts of the protons of **8** are summarized in the Table II. The results mentioned above indicate that the product has the structure **8**, which might be formed by a transannular Michael-type cyclization between C_6 and C_{10}. Reduction of the diketone **8** with an excess of $LiAlH_4$ gave the diol **10**, mp 141—142°, M^+=358, whose NMR spectrum showed signals at δ 4.15 (quintet, J=8), 4.74 (broad, s) and 5.41 (broad, s).

Inspection of a molecular model of this compound showed that all the rings must have *cis* junctions as shown in Fig. 2 (a *trans* fused compound would have extremely large strain). This conclusion was confirmed by X-ray crystal structure analysis of the mono-*p*-bromobenzenesulfonate **11**, mp 88°, $C_{30}H_{41}O_4SBr$, obtained by esterification of the diol. The NMR spectrum of the mono-*p*-bromobenzenesulfonate **11** showed signals at δ 4.70, 4.66, and 5.37. The only significant change in the spectrum was that the signal at 4.15 in **10** shifted to 4.70 in **11**. This observation and the fact that the diol **10** gave the starting diketone upon CrO_3

oxidation indicate that **8** and **11** have the same carbon skeleton. As shown in Fig. 3, compound **8** showed a negative Cotton effect at 236 nm ([θ]=−40000) and a positive one at 325 nm ([θ]=+4000), and the saturated diketone **9** showed a negative Cotton effect at 301 nm ([θ]=−14900), which is larger in ellipticity and higher in wavelength than those of isolated and saturated five-membered ring ketones except for *trans* indanone type ketones. This suggests that a new chromophore was formed by the interaction of the two neighboring carbonyl chromophores.

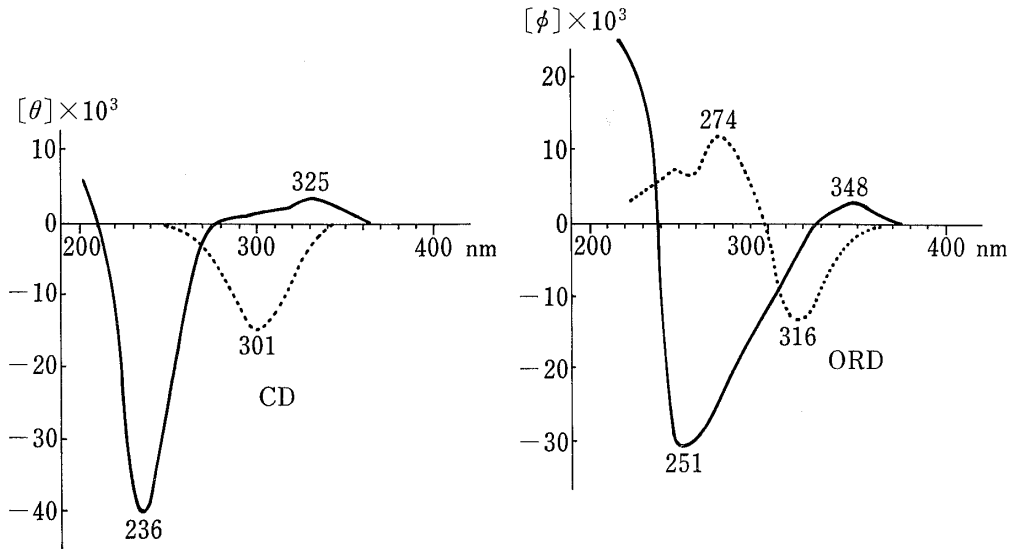

Fig. 3. CD and ORD Spectra for the Compounds **8** and **9**
—— for **8**; ------ for **9**.

Mechanism of Transannular Reactions

It is probable that compound **5** is formed first by the decarboxylation of **2**. From an inspection of the chemical structures of three pyrolysis products and the results of the interconversion experiments among them, the reaction is thought to proceed as follows during pyrolysis. Compound **4** is formed from **5** reversibly, while the thermally stable compound **6** is formed from **5** irreversibly. The conformation of **6** observed in the crystal and that of **5**, expected at the temperature of pyrolysis, are schematically shown in Fig. 4. Both structures show a mirror image relationship with respect to the ring skeletons and junctions. Based on spectroscopic observations, compound **5** appeared to adopt a more stable conformation with a planar α,β-unsaturated ketone in the eight-membered ring, but the postulated conformation might easily appear at higher temperatures. In that conformation, the planes of the C_8 carbonyl and C_6, C_7 double bond are not coplanar and the hydrogen at C_{10} come close to C_6, leading to an intramolecular transannular hydrogen migration. This is supported by the fact that the product having β-hydrogen at C_6 was not isolated, though it should be less strained than **6**. A probable reaction scheme is shown below, in which the hydrogen at C_{10} migrates to C_6 *via* an intermediate such as **12**.

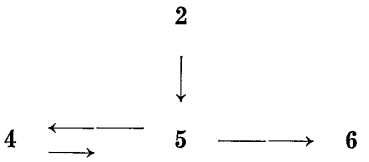

Chart 2

The second transannular reaction leading to a tetracyclic compound **8** from **6** on mild base treatment is easily explicable in terms of an intramolecular Michael-type addition reaction. We have carried out the reaction using isopropanol-d_8 as a solvent, observing the NMR spectra periodically. This experiment showed that the rates of enolization of C_5 carbonyl to C_6 and C_8

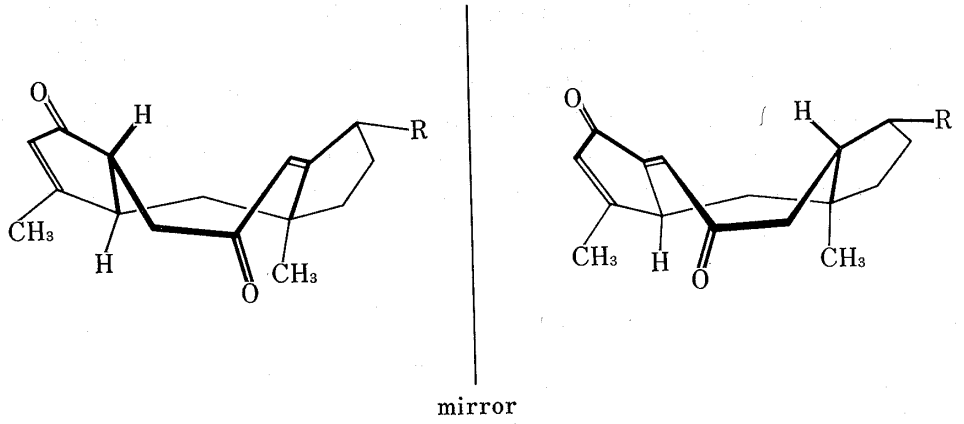

Fig. 4. Schematic Drawing of the Conformation of the eight-membered Ring

Left: observed conformation of **6** in the crystal, right: hypothetical conformation of **5** at the temperature of pyrolysis.

carbonyl to C_7 are much larger than that of cyclization, and that the deuterium exchange of the hydrogens at C_2, C_4, and C_9 occurred after completion of the cyclization. The deuterium exchange of C_3 methyl hydrogens proceeds a little faster than cyclization. The resulting carbanion at C_6 attacks transannularly at C_{10}, which is subject to nucleophilic attack due to the presence of the C_8 carbonyl. As the interactomic distance between C_6 and C_{10} is small, 3.20 Å, in the crystal of **6** as determined by X-ray structure analysis, such a conformation is thought to be one of the most stable in solution under the reaction conditions used.

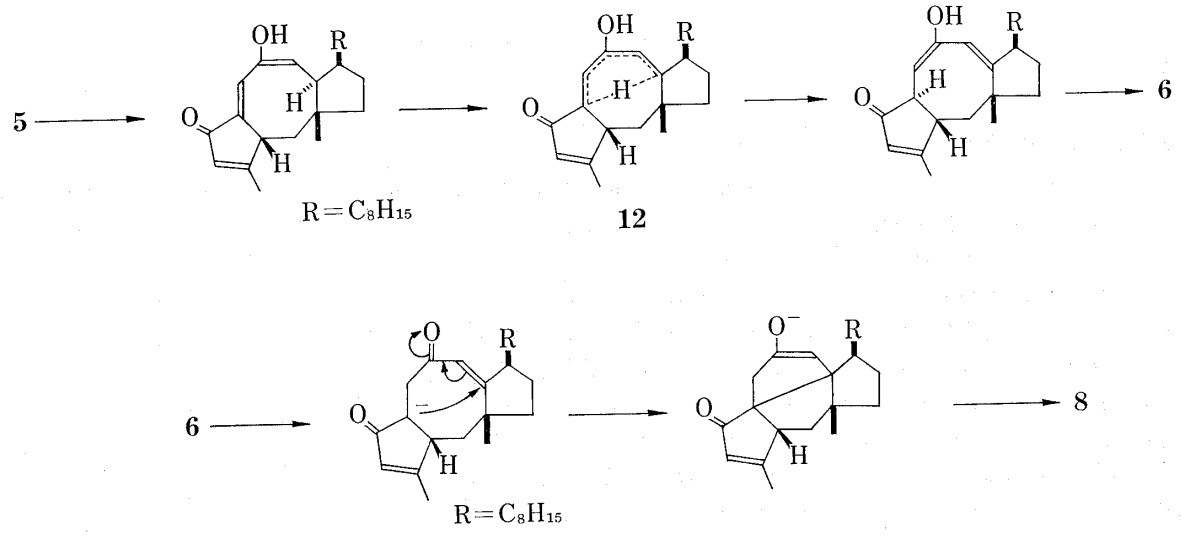

Chart 3

Experimental

NMR spectra were obtained using a JEOL 100 Mc instrument and double resonance and NOE experiments were carried out on a Varian HA-100 instrument. Chemical shifts are reported in ppm downfield from internal TMS (δ). IR spectra were measured on a JASCO DS-301 machine in $CHCl_3$ solution unless otherwise stated. IR frequencies are reported in wave numbers (cm^{-1}). UV spectra were measured on a Shimadzu SV-50 spectrometer. Absorption maxima are reported as wavelengths (in nm) followed by the molar extinction coefficient (ε) in parentheses. Mass spectra (MS) were determined on a Hitachi RMU-6D instrument at 70 eV utilizing a direct inlet system. Melting points are uncorrected. ORD and CD spectra were measured on a JASCO ORD-UV5 machine in EtOH solution. Elemental analyses were performed by the Microanalytical Laboratory, Institute of Applied Microbiology, University of Tokyo.

Oxidation of Ophiobolin D——Kiliani's reagent was added dropwise to a soln. of 4.0 g of ophiobolin D (**1**) in 30 ml of acetone until the color of the reagent persisted. After removal of the green precipitate, the

filtrate was diluted with water and extracted with Et_2O (150 ml×3). The dried Et_2O extracts were concentrated under reduced pressure to give 3.3 g of the crystalline product **2**. For analysis a sample was recrystallized three times from EtOH and dried, mp 112—113°. (*Anal.* Calcd for $C_{25}H_{34}O_4$: C, 75.34; H, 8.60. Found: C, 75.54; H, 8.57.). IR 1571, 1631, 1705. UV (EtOH) 258.5 (16000). NMR ($CDCl_3$) 6.03 (1H, s), 5.1 (1H, t, J=7), 3.3 (1H, d, J=12), 2.45, 2.57 (2H, AB q, J=10), 2.23, 1.71, 1.62, 0.97 (3H each, s), 0.88 (3H, d, J=7).

The methyl ester **3**, obtained by treatment with diazomethane, gave mp 120—121°, (*Anal.* Calcd for $C_{26}H_{36}O_4$: C, 75.69; H, 8.80. Found: C, 75.72; H, 8.73.). IR 1612, 1672, 1699, 1745. UV (EtOH) 258 (16000). NMR ($CDCl_3$) 6.10 (1H, s), 5.10 (1H, t, J=6), 3.20 (1H, d, J=12), 2.58, 2.68 (2H, AB q, J=14), 3.84 (3H, s), 2.11, 1.66, 1.58, 0.94 (3H each, s), 0.87 (3H, d).

Pyrolysis of Dehydroophiobolin D (2)——Dehydroophiobolin D (680 mg) was heated in a glass tube in an oil bath at 160° until evolution of carbon dioxide ceased (15 min). The resulting mixture was cooled and subjected to chromatography on silica gel (12 g) with *n*-hexane–benzene–Et_2O mixtures as eluting solvents. From the fractions eluted with benzene–hexane (9: 1), 65 mg of crystalline **4** was obtained. An analytical sample was recrystallized from MeOH and dried, mp 102—103° (*Anal.* Calcd for $C_{24}H_{34}O_2$: C, 81.31; H, 9.67. Found: C, 81.25; H, 9.67.). The product **4** showed the following spectral properties. IR (Nujol) 1618, 1666, 1750. UV (EtOH) 219.5 (12500), 314 (8800). NMR ($CDCl_3$) 6.12 (1H, s), 2.6—3.2 (2H, AB q), 5.07 (1H, t, J=6), 1.93, 1.65, 1.57, 0.93 (3H each, s), 0.83 (3H, d, J=7). MS *m/e* 354 (parent peak), 339, 336, 326, 211, 285. ORD, CD see "Discussion."

From the combined fractions eluted with benzene, 200 mg of the crystalline product **5** was obtained. An analytical sample was recrystallized from MeOH, mp 80—81° (*Anal.* Calcd for $C_{24}H_{34}O_2$: C, 81.31; H, 9.67; O, 9.03. Found: C, 81.38; H, 9.65; O, 9.68.). IR (Nujol) 1610, 1671, 1699. UV (EtOH) 255.5 (15500). NMR ($CDCl_3$) 6.63 (1H, s), 6.15 (1H, s), 5.07 (1H, t, J=6), 3.31 (1H, d, J=12), 2.10, 1.67, 1.58, 0.96 (3H each, s), 0.84 (3H, d, J=7). MS *m/e* 354 (parent peak) 339, 336, 326, 321, 285, 211.

The fractions eluted with benzene–EtO_2 mixture (99: 1) afforded a third crystalline product **6** in a yield of 80 mg (13%) and a mixture of **5** and **6** (80 mg). An analytical sample was recrystallized from MeOH and dried, mp 89—90°. (*Anal.* Calcd for $C_{24}H_{34}O_2$: C, 81.31; H, 9.67; O, 9.03. Found: C, 81.19; H, 9.68; O, 8.98.). The spectral properties of **6** were as follows: IR (Nujol) 1617, 1668, 1696. UV (EtOH) 232 (16600). NMR ($CDCl_3$) 5.98 (1H, s), 5.64 (1H, s), 5.07 (1H, t, J=6), 2.07, 1.69, 1.60, 1.10 (3H each, s), 0.81 (3H, d, J=7). MS *m/e* 354 (parent peak), 339, 336, 311, 297, 285.

Heating of dehydroophiobolin D (180 mg) in a glass tube at 130° for 40 min followed by chromatographic separation using the procedures described above yielded 95 mg (53%) of **4**, 15 mg (8%) of **5** and 37 mg (20%) of **6**.

Catalytic hydrogenation of 4——The diketone **4** (50 mg) was dissolved in EtOH (2 ml) and hydrogenated over a Pd-C catalyst (15 mg) until sufficient hydrogen (2 mol) was absorbed. After removal of the catalyst by filtration, the filtrate was concentrated under reduced pressure. The resulting oily product was purified by column chromatography on silica gel (600 mg), eluting with *n*-hexane–benzene mixtures. From the fractions eluted from *n*-hexane–benzene (1: 4), 30 mg of chromatographically homogeneous product **7** was obtained as a colorless liquid. IR (cap.) 1640, 1710. UV (EtOH) 243.5 (10300). MS *m/e* 358 (parent peak for $C_{24}H_{38}O_2$). NMR 0.70—1.00 (15H, five methyls); no signal was observed below 3.00.

Base Treatment of Diketone 6——A mixture. of a soln of **6** (200 mg) in *tert*-BuOH (5 ml) and *tert*-BuOK (16 ml) was allowed to stand for 30 min at room temperature, then diluted with water and extracted with Et_2O. The ethereal layer was washed with water and dried. The solvent was removed under reduced pressure, and the residue was taken up in MeOH. In this manner, 150 mg of crystalline product **8** was obtained. An analytical sample was recrystallized from MeOH, mp 92—93° (*Anal.* Calcd for $C_{24}H_{34}O_2$: C, 81.31; H, 9.67. Found: C, 80.97; H, 9.59). The product **8** had the following spectral properties: IR 1622, 1696, 1743. UV (EtOH) 236 (10900). NMR ($CDCl_3$) 5.75 (1H, s), 5.07 (1H, t, J=6), 3.07 (1H, t, J=9), 2.04, 1.67, 1.59, 0.92 (3H each, s), 0.71 (3H, d, J=7). MS *m/e* 354 (parent peak), 339, 336, 311, 285, 272, 245, 149, 121.

Catalytic Hydrogenation of 8——A solution of the diketone **8** (50 mg) in EtOH (10 ml) was shaken under hydrogen over a Pt catalyst to afford a tetrahydro derivative in quantitative yield, absorbing two moles of hydrogen. The oily product was purified by column chromatography to give the tetrahydro derivative **9**, colorless liquid; IR ($CHCl_3$) 1745. NMR ($CDCl_3$) 0.70—1.00 (15H, five methyls), 1.80—2.90; no signal was observed below 3.00.

Lithium Aluminum Hydride Reduction of the Diketone 8——The diketone was dissolved in dry Et_2O (100 mg, 2 ml) and $LiAlH_4$ (20 mg) in ether (1 ml) was added slowly under cooling. The mixture was allowed to stand for 1 hr. The product **10** (80 mg), obtained as crystals, was recrystallized from acetone, mp 141—142°, MS *m/e* 358 (parent peak for $C_{24}H_{34}O_2$), IR 3460, NMR ($CDCl_3$) 5.41 (1H, s), 5.13 (1H, t, J=6), 4.74 (1H, s), 4.15 (1H, quint, J=8), 1.69 (6H, 2 methyls), 1.61, 0.97 (3H, each, s, 2 methyls), and 0.72 (3H, d, J=7). Oxidation of **10** with Kiliani's reagent in acetone gave the starting diketone **8**.

Mono-*p*-bromobenzenesulfonate Ester of the Diol 10——A solution of the diol **10** (15 mg) in pyridine (0.5 ml) was treated with a solution of *p*-bromobenzenesulfonyl chloride (14 mg) in pyridine (0.5 ml), and the mixture was allowed to stand for 2 hr at room temperature. The resulting pyridine solution was poured

into ice-water and the product was extracted with ether. The ethereal layer was washed with a dilute aqueous solution of copper sulfate and water, dried and concentrated to give crystalline mono-*p*-bromobenzenesulfonate **11**, (16.1 mg). Recrystallization from ether gave a pure sample of **11**, (11.5 mg); mp 88—89°. (*Anal.* Calcd for $C_{30}H_{41}BrO_4S$: C, 62.41; H, 7.10; S, 5.55; Br, 13.84. Found: C, 62.11; H, 7.22; S, 5.05; Br, 12.85). IR (Nujol) 3605, 1352, 1186, 1580. MS *m/e* 340 (M—BsOH), 322 (M—BsOH—H_2O), NMR ($CDCl_3$) 5.09 (1H, s), 4.66 (1H, s), 4.70 (1H, m), 5.37 (1H, s), 0.85, 1.59, 1.67, 1.67 (3H each, s), 0.59 (3H, d, J=7), 7.74 (4H, AB-type).

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