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The Constituents of *Schizandra chinensis* Baill. II.[1] The Structure of a New Lignan, Gomisin D[2]

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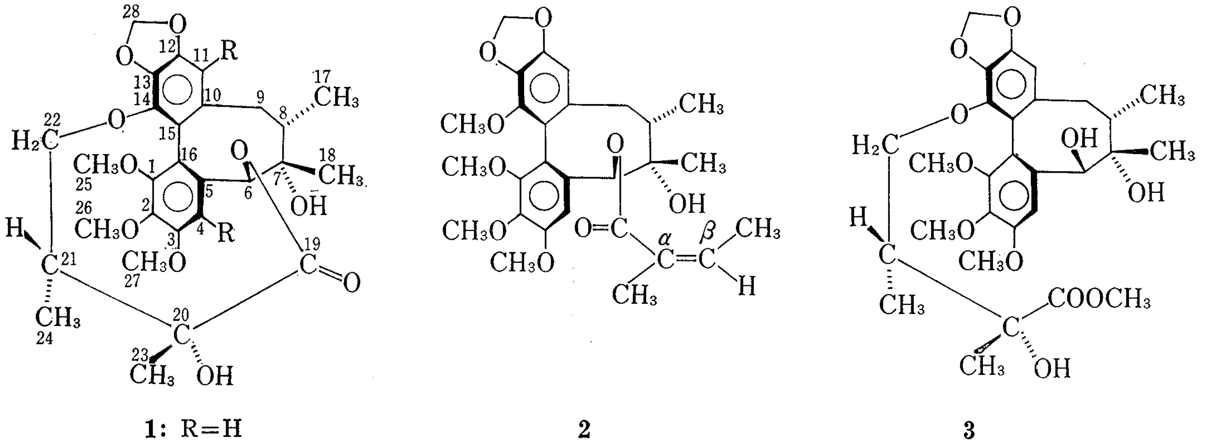
A new dibenzocyclooctadiene lignan, named gomisin D (1), was isolated from the petroleum ether extract of the fruits of *Schizandra chinensis* Baill. (Schizandraceae), and its structure was elucidated on the basis of chemical and spectral evidence. The absolute structure of gomisin D was determined by X-ray analysis of its 4,11-dibromo-derivative (4).

Keywords——*Schizandra chinensis* Baill.; Schizandraceae; dibenzocyclooctadiene lignan; gomisin D; NMR spectra; NOE; mass spectra; CD spectra; X-ray analysis

In the preceding paper,[1] we reported the structures of five new dibenzocyclooctadiene lignans, gomisins A, B, C, F and G, together with the absolute structure of schizandrin[4] isolated from the fruits of *Schizandra chinensis* Baill. (Schizandraceae). The present paper describes the structure of a new dibenzocyclooctadiene lignan named gomisin D (**1**), isolated from the same source (yield 0.016%).

Gomisin D (**1**), $C_{28}H_{34}O_{10}$, mp 194°, $[\alpha]_D^{25}$ $-58.8°$ ($CHCl_3$), was isolated as colorless prisms. The ultraviolet (UV) spectrum of **1**, with absorption maxima at 216 (log ε 4.57), 256 (sh 3.94) and 294 nm (3.68), closely resembled that of schizandrin, and the infrared (IR) spectrum showed two hydroxyl bands (3505 and 3450 cm^{-1}) and an ester band (1720 cm^{-1}), indicating that **1** is a dibenzocyclooctadiene lignan having two hydroxyls and an ester linkage. Analysis of the proton nuclear magnetic resonance (PMR) spectrum of **1** compared with that of gomisin B (**2**) suggested that **1** has the same skeleton as **2**, differing in the functional groups on the aromatic rings and the ester moiety. As shown in Table I, **1** has a methylenedioxyl group,



1: R=H
4: R=Br

2

3

Chart 1

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1) Y. Ikeya, H. Taguchi, I. Yosioka, and H. Kobayashi, *Chem. Pharm. Bull.* (Tokyo), **27**, 1383 (1979).

2) Preliminary communication of this work: Y. Ikeya, H. Taguchi, and Y. Iitaka, *Tetrahedron Lett.*, **1976**, 1359.

3) Location: *a) Izumi 1421, Komae-shi, Tokyo 201, Japan*; *b) Hongo, Bunkyo-ku, Tokyo 113, Japan.*

4) N.K. Kochetkov, O.S. Chizhov, and V.I. Sheichenko, *Tetrahedron Lett.*, **1961**, 730.

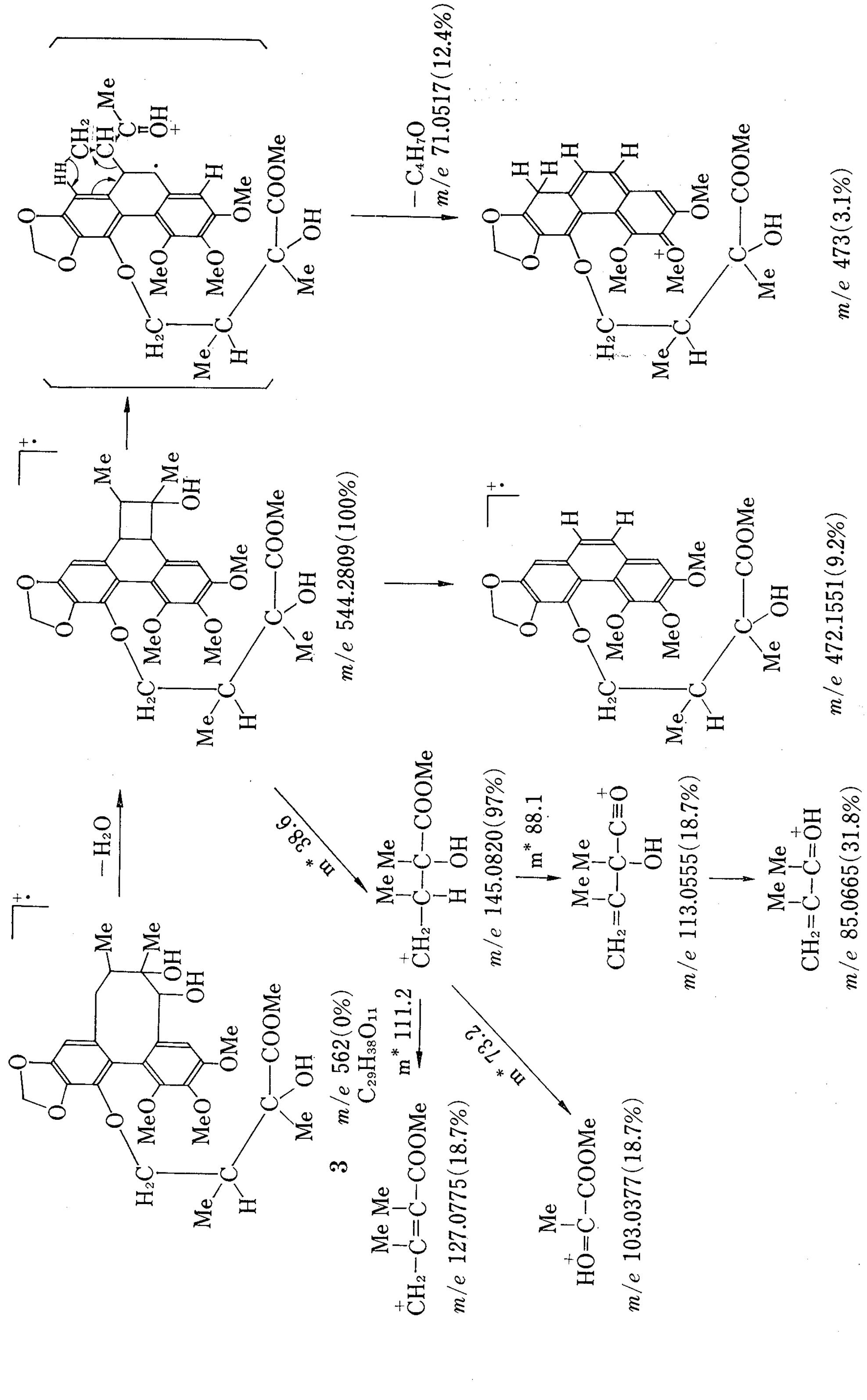

Chart 2. High Resolution Mass Spectral Data for 3

Table I. PMR Spectral Data for Gomisin D(**1**) and Gomisin B (**2**)[1a)] (δ ppm in $CDCl_3$)

Compound	4-H, s 11-H, s	6-H, s	$-OCH_2O-$ (J=Hz)	OCH_3, s	9α-H (J=Hz)	9β-H (J=Hz)	7-OH	8-H, m	18-H, s (3H, s)
1	6.80 6.43	5.71	5.90, d, (1) 5.99, d, (1)	3.56, 3.86 3.92	2.43d,d (14/8)	1.95d,d (14/1)	1.73	1.72	1.20
2	6.83 6.48	5.70	5.90 s	3.57, 3.75 3.85, 3.93	2.00—2.45m		1.60	1.90	1.33

Compound	17-H (3H, d, J=Hz)	22-H (2H, m)	20-OH	21-H (1H, m)	23-H (3H, s)	24-H (3H, d, J=7 Hz)	Angeloyl-		
							vinyl-H	β-methyl	α-methyl
1	1.02(7)	3.4—4.0	3.10	1.63	1.26	1.10	—	—	—
2	1.13(7)	—	—	—	—	—	6.00	1.86	1.40

three methoxyls and a methyleneoxyl group (δ 3.4—4.0, m, $-CH_2O-$) on the aromatic rings, and also has a secondary methyl (δ 1.10), a tertiary methyl (δ 1.26) and a hydroxyl (δ 3.10) in the ester moiety.

Hydrolysis of **1** with 3% ethanolic potassium hydroxide followed by methylation with diazomethane afforded compound **3**, $C_{29}H_{38}O_{11}$, mp 127—128°, $[\alpha]_D^{22}$ $-39.1°$ ($CHCl_3$), IR (in KBr): 3430 (OH), 1730 (ester), which gave a positive test for a 1,2-diol moiety (KIO_4–$AgNO_3$).[5)] The structure of **3** including the side chain [$ArOCH_2-\dot{C}H(CH_3)-\dot{C}(OH)-COOCH_3$] was confirmed by analysis of the mass spectrum as shown in Chart 2. The structure of **3** was also confirmed by analysis of the PMR spectrum with the aid of double resonance experiments (in C_6D_6). On irradiation at δ 2.08 (1H, m, $C_{(8)}$–H), the doublet methyl at δ 0.97 changed to a singlet, and the signal around δ 1.9—2.5 (2H, m,) was deformed, indicating the presence of the partial structure [$ArCH_2-CH(CH_3)-$]. On irradiation at δ 2.35 (1H, m), the doublet methyl at δ 1.10 changed to a singlet, and the ABX octet around δ 4.1—4.6 changed to an AB quartet, indicating the presence of the partial structure [$ArOCH_2CH(CH_3)-$] in **3**. On the other hand, the singlet at δ 5.71 in **1**, which was assigned to the C-6 methine, was shifted to δ 3.72 (in C_6D_6) (δ 3.17 in $CDCl_3$) in **3**, indicating that the carboxyl terminal of the side chain in **3** is linked to the C-6 hydroxyl group in **1**.

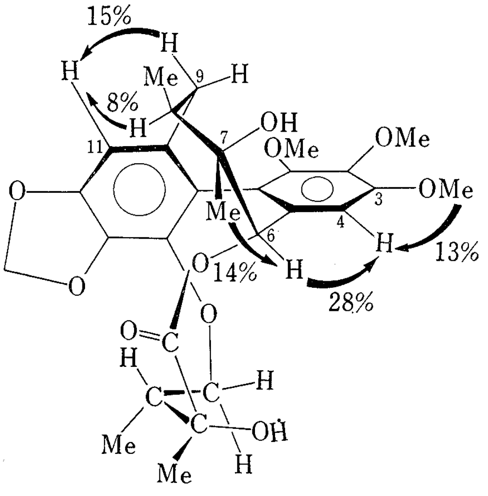

Fig. 1. NOE of **1** in $CDCl_3$

The structure of **1** was elucidated by measurements of intramolecular nuclear Overhauser effects (NOE) in **1** (in $CDCl_3$).[1,6)] As shown in Fig. 1, irradiation of methoxyl (δ 3.86) and proton (δ 5.71, $C_{(6)}$–H) signals caused 13% and 28% increases in the integrated intensity of the lower aromatic proton (δ 6.80, $C_{(4)}$–H), respectively. On the other hand, irradiation of a tertiary methyl signal (δ 1.20, $C_{(18)}$–H) caused a 14% increase in the integrated intensity of the proton (δ 5.71, $C_{(6)}$–H), while no enhancement of the signal intensities in the aromatic protons was

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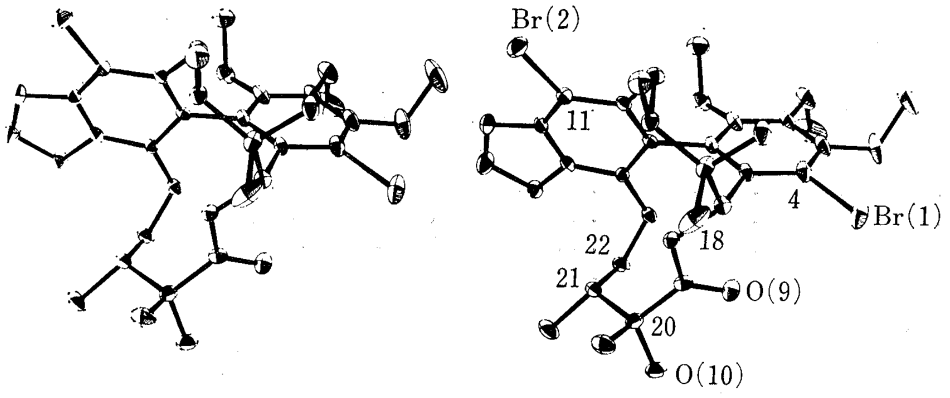

Fig. 2. Stereoscopic Drawing of the Molecule produced by the ORTEP Program

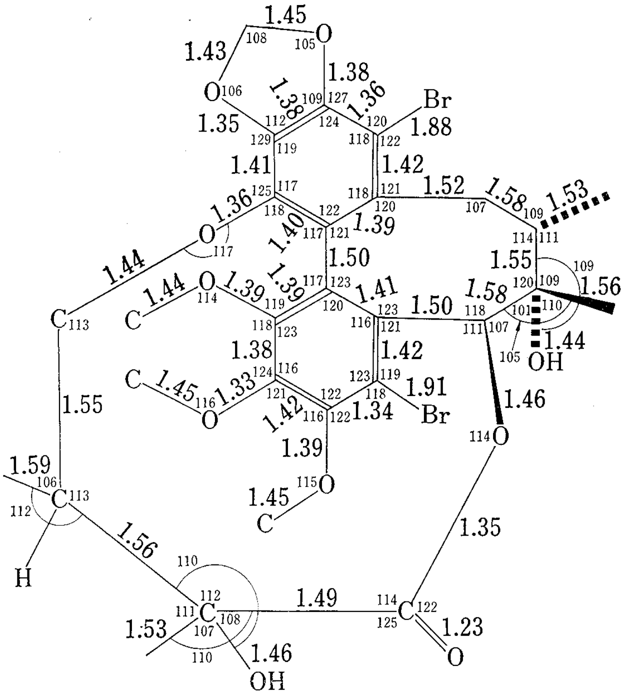

Fig. 3. Bond Lengths (Å) and Angles (°) of **4**

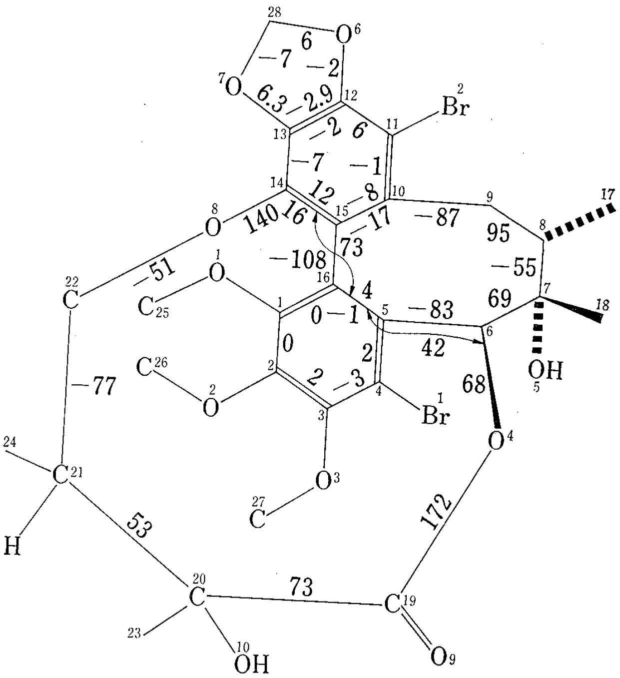

Fig. 4. Endocyclic Torsion Rotation Angles (°) of **4**

Table II. Distribution of Observed and Calculated Intensity Ratios between Friedel Pairs

$b=\|\mathrm{Fo}(hkl)\|/\|\mathrm{Fo}(h\bar{k}l)\|$	$a=\|\mathrm{Fc}(hkl)\|/\|Fc(h\bar{k}l)\|$					
	$a\geqq1.10$	$1.10>a\geqq1.05$	$1.05>a\geqq1.03$	$0.95<a\leqq0.97$	$0.90<a\leqq0.95$	$a\leqq0.90$
$b\geqq1.10$	25	18	9	2	0	1
$1.10>b\geqq1.05$	1	18	5	0	0	0
$1.05>b\geqq1.03$	0	0	0	0	0	0
$0.95<b\leqq0.97$	0	0	0	0	0	0
$0.90<b\leqq0.95$	0	0	0	1	10	3
$b\leqq0.90$	0	1	0	1	6	13
R for $\|\mathrm{Fo}(hkl)\|-\|\mathrm{Fc}(hkl)\|$	0.097	0.099	0.090	0.118	0.072	0.178
R for $\|\mathrm{Fo}(hkl)\|-\|\mathrm{Fc}(h\bar{k}l)\|$	0.172	0.123	0.103	0.113	0.099	0.188

The numerals are the numbers of pairs having intensity ratios in the indicated ranges.
The Structure Factors were calculated by assuming $\Delta f'=-0.767$, $\Delta f''=1.283$.

TABLE III. Final Atomic Parameters of **4**

Temperature factors are of the form $T=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$

	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br(01)	0.50909(9)	0.17147(9)	0.66367(14)	0.00469(6)	0.00519(5)	0.01124(14)	−0.00077(5)	−0.00152(8)	0.00360(8)
Br(02)	0.64795(9)	0.33425(8)	−0.12144(14)	0.00452(5)	0.00417(4)	0.01239(14)	0.00050(5)	0.00286(8)	0.00160(7)
C(1)	0.4172(7)	0.1370(5)	0.2191(13)	0.0040(5)	0.0013(2)	0.0146(16)	0.0003(3)	−0.0016(16)	0.0003(5)
C(2)	0.4093(8)	0.0855(5)	0.3108(15)	0.0049(6)	0.0012(2)	0.0172(18)	0.0000(3)	0.0000(9)	0.0014(5)
C(3)	0.4421(9)	0.0987(5)	0.4439(15)	0.0054(6)	0.0016(2)	0.0168(18)	0.0001(3)	0.0003(10)	0.0035(6)
C(4)	0.4756(6)	0.1579(6)	0.4782(12)	0.0022(4)	0.0028(3)	0.0127(14)	0.0003(3)	−0.0001(6)	0.0025(6)
C(5)	0.4852(6)	0.2106(4)	0.3842(11)	0.0024(4)	0.0017(2)	0.0101(11)	0.0002(2)	−0.0004(6)	0.0014(4)
C(6)	0.5217(6)	0.2765(5)	0.4280(11)	0.0024(4)	0.0020(2)	0.0090(11)	−0.0003(3)	−0.0004(6)	0.0003(4)
C(7)	0.6242(6)	0.2929(5)	0.3954(11)	0.0021(4)	0.0028(3)	0.0080(11)	−0.0007(3)	−0.0003(6)	0.0007(5)
C(8)	0.6552(7)	0.3045(5)	0.2475(11)	0.0032(4)	0.0021(2)	0.0088(11)	−0.0004(3)	0.0005(6)	0.0004(4)
C(9)	0.6304(7)	0.2459(5)	0.1477(11)	0.0028(4)	0.0021(2)	0.0103(12)	0.0005(3)	−0.0002(6)	0.0003(5)
C(10)	0.5418(6)	0.2640(4)	0.0793(10)	0.0031(4)	0.0015(2)	0.0081(11)	0.0006(3)	−0.0003(6)	0.0000(4)
C(11)	0.5406(7)	0.3047(5)	−0.0381(11)	0.0045(5)	0.0019(2)	0.0081(11)	0.0005(3)	0.0002(7)	0.0001(4)
C(12)	0.4588(7)	0.3253(4)	−0.0863(10)	0.0052(5)	0.0013(2)	0.0070(10)	0.0004(3)	−0.0003(6)	0.0000(4)
C(13)	0.3777(6)	0.3144(4)	−0.0212(10)	0.0035(4)	0.0013(2)	0.0084(10)	0.0003(2)	−0.0016(6)	−0.0001(4)
C(14)	0.3776(6)	0.2777(4)	0.1001(10)	0.0034(4)	0.0012(2)	0.0068(10)	−0.0001(2)	0.0000(6)	0.0001(4)
C(15)	0.4593(6)	0.2484(4)	0.1043(4)	0.0031(4)	0.0011(2)	0.0082(11)	0.0001(2)	000000(6)	−0.0003(4)
C(16)	0.4539(7)	0.1981(4)	0.2520(11)	0.0034(4)	0.0014(2)	0.0086(11)	0.0001(3)	−0.0005(6)	0.0008(4)
C(17)	0.7571(7)	0.3170(6)	0.2418(15)	0.0027(4)	0.0034(4)	0.0144(16)	−0.0004(7)	0.0004(7)	0.0008(7)
C(18)	0.6459(11)	0.3558(8)	0.4821(14)	0.0082(9)	0.0046(5)	0.0107(15)	−0.0036(6)	0.0029(10)	−0.0027(7)
C(19)	0.3830(6)	0.3346(5)	0.4265(11)	0.0028(4)	0.0020(2)	0.0093(11)	−0.0003(3)	0.0008(6)	−0.0008(5)
C(20)	0.3329(7)	0.3955(5)	0.3855(11)	0.0041(5)	0.0022(2)	0.0084(11)	0.0001(3)	0.0012(7)	−0.0004(5)
C(21)	0.3018(8)	0.3923(5)	0.2344(11)	0.0048(6)	0.0018(2)	0.0085(11)	0.0009(3)	0.0000(7)	0.0000(4)
C(22)	0.2477(7)	0.3288(5)	0.2001(12)	0.0039(5)	0.0020(2)	0.0108(13)	0.0009(3)	0.0003(6)	−0.0002(5)
C(23)	0.3925(9)	0.4566(5)	0.4098(15)	0.0064(7)	0.0019(3)	0.0158(18)	−0.0004(4)	0.0004(10)	−0.0017(6)
C(24)	0.2373(12)	0.4524(7)	0.1958(17)	0.0101(11)	0.0029(4)	0.0152(19)	0.0033(5)	−0.0018(13)	0.0005(7)
C(25)	0.4380(13)	0.0898(8)	0.0008(17)	0.0094(11)	0.0043(5)	0.0143(20)	0.0031(6)	0.0008(13)	−0.0011(9)
C(26)	0.2798(12)	0.0167(8)	0.2973(34)	0.0064(9)	0.0036(5)	0.0536(64)	−0.0020(6)	0.0039(22)	−0.0044(16)
C(27)	0.4960(14)	−0.0031(9)	0.5370(29)	0.0101(13)	0.0042(5)	0.0414(50)	0.0018(7)	−0.0002(23)	0.0088(14)
C(28)	0.3462(9)	0.3771(8)	−0.1997(14)	0.0052(7)	0.0045(5)	0.0116(16)	0.0008(5)	0.0001(9)	0.0030(7)
O(1)	0.3809(6)	0.1277(4)	0.0899(9)	0.0055(4)	0.0020(2)	0.0137(11)	0.0000(2)	−0.0020(6)	−0.0006(4)
O(2)	0.3765(7)	0.0258(4)	0.2789(12)	0.0072(5)	0.0014(2)	0.0223(16)	−0.0006(3)	0.0003(8)	0.0012(5)
O(3)	0.4286(8)	0.0490(5)	0.5389(12)	0.0094(7)	0.0029(2)	0.0220(17)	−0.0009(4)	−0.0021(10)	0.0053(6)
O(4)	0.4668(4)	0.3307(3)	0.3737(7)	0.0030(3)	0.0017(1)	0.0078(7)	−0.0003(2)	0.0006(4)	0.0001(3)
O(5)	0.6690(5)	0.2359(4)	0.4524(9)	0.0030(3)	0.0036(3)	0.0126(10)	0.0004(2)	−0.0003(5)	0.0032(4)
O(6)	0.4434(5)	0.3656(4)	−0.1977(7)	0.0053(4)	0.0026(2)	0.0074(8)	0.0000(2)	−0.0007(5)	0.0011(3)
O(7)	0.3089(5)	0.3478(4)	−0.0797(8)	0.0036(3)	0.0024(2)	0.0095(8)	0.0005(2)	−0.0013(5)	0.0010(3)
O(8)	0.3053(4)	0.2714(3)	0.1845(8)	0.0027(3)	0.0017(1)	0.0106(8)	0.0001(2)	−0.0002(4)	0.0005(3)
O(9)	0.3544(5)	0.2931(4)	0.5077(8)	0.0030(3)	0.0031(2)	0.0106(9)	−0.0005(2)	0.0001(5)	0.0011(4)
O(10)	0.2543(6)	0.4018(4)	0.4746(9)	0.0047(4)	0.0031(2)	0.0111(10)	0.0008(3)	0.0020(6)	−0.0009(4)

observed. A higher field aromatic proton (δ 6.43, $C_{(11)}$–H) was affected by irradiation of the higher field benzylic methylene proton (δ 1.95 d, d, $J=14/1$ Hz) and a methine proton (δ 1.72, $C_{(8)}$–H), while it was unaffected by irradiation of each methoxyl signal or the secondary methyl signals.

Based on the above results and Dreiding model examination, the structure of gomisin D, including the conformation of the cyclooctadiene ring could be expressed as **1** (Fig. 1) except for the configurations at C-20 and 21. The J values between the C-8 proton and C-9 methylene protons in the PMR spectrum of **1**($J_{8,9\alpha}=8$ Hz, $\phi_{8,9\alpha}\fallingdotseq 150°$; $J_{8,9\beta}=1$ Hz, $\phi_{8,9\beta}\fallingdotseq 90°$) are compatible with the structure **1**.

X-Ray Analysis of 4,11-Dibromo-gomisin D(4)

The absolute structure of gomisin D was elucidated by X-ray crystallographic analysis of the 4,11-dibromo derivative (**4**) of **1**, which was prepared by treatment of **1** with bromine in carbon tetrachloride, as described in the Experimental section. The molecular structure of **4** produced by the ORTEP program is shown in Fig. 2. The bond lengths and angles lie in the normal range, as shown in Fig. 3, and the endocyclic torsion angles of **4** are shown in Fig. 4. These data are in good agreement with the chemical and physical data of 1. Therefore, the chemical structure of gomisin D (**1**) is deduced to be as given in Fig. 1.

The absolute configurations were determined to be 6*S*, 7*S*, 8*S*, 20*R* and 21*R*, respectively, and that of the biphenyl group was *S* with a dihedral angle of 73°. The configurations of the biphenyl groups in schizandrin, and gomisins A, B, C, F and G have been correlated by comparison of the circular dichroism (CD) spectra with that of **3**, which was derived from gomisin D, as described in the preceding paper,[1] and it has been found that gomisin A and schizandrin possess the *R*-biphenyl configuration, while gomisins B, C, F and G possess the *S*-biphenyl configuration.

Experimental

All melting points were determined on a Yanagimoto micromelting point apparatus (a hot stage type) and are uncorrected. The UV spectra were recorded with a Hitachi 624 digital spectrophotometer and the IR spectra with a Hitachi EPI-G2 machine. The PMR spectra were recorded with Varian T-60 and JEOL PS-100 spectrometers with tetramethylsilane as an internal standard. The mass spectra were measured with a Hitachi double focusing mass spectrometer and a JEOL JMS-01SG-2 unit. The specific rotations were measured with a JASCO DIP-SL unit and the CD spectra with a JASCO J-20 spectrophotometer. Silica gel (Kieselgel 60, Merck) was used for column chromatography. Thin-layer chromatography (TLC) was carried out on Merck plates precoated with Kieselgel 60 F_{254}. Preparative layer chromatography (PLC) was carried out on plates (20×20 cm, 0.75 mm thick) coated with Kieselgel GF_{254} (Merck).

Isolation of Gomisin D(1)——In the preceding paper,[1] it was reported that the petro. ether extract of the fruits of *Schizandra chinensi* (4.67 kg) afforded twelve fractions (fr. 1—12) on silica gel column chromatography using *n*-hexane–benzene and acetone-benzene solvent systems. Fr. 10 (6.07 g) was rechromatographed on silica gel(120 g) using acetone–*n*-hexane to give a gum (162 g), which was purified by PLC using $CHCl_3$–EtOH (19: 1). The zone with *Rf* 0.52 was further purified by PLC using *n*-hexane–EtOAc (1: 2) to give **1** as colorless prisms (from ether–*n*-hexane) (yield 740 mg, 0.016%), mp 194°, $[\alpha]_D^{25}$ −58.8° ($c=0.265$, $CHCl_3$). CD ($c=0.0137$, MeOH), $[\theta]^{23}$ (nm): +116000 (230), −3900 (248). UV λ_{max}^{EtOH} nm (log ε): 216 (4.57), 256 (sh 3.94), 294 (3.68). IR ν_{max}^{KBr} cm^{-1}: 3505, 3450 (OH), 1720 (ester). High resolution mass spectrum (MS), Calcd. for $C_{28}H_{34}O_{10}$ (M^+): 530.2156. Found: 530.2144. *Anal.* Calcd. for $C_{28}H_{34}O_{10}$: C, 63.39; H, 6.46. Found: C, 63.60; H, 6.51.

Preparation of 3——A solution of **1** (82 mg) in 3% KOH–EtOH (4 ml) was kept at 70° for 3 hr. The reaction mixture was cooled, acidified with 5% HCl and extracted with ether. The ethereal extract was washed with H_2O, dried over Na_2SO_4 and concentrated. The residue was methylated with ethereal diazomethane for 3 hr and the product was purified by PLC using benzene–ether (1: 1) to give **3** (56 mg) as colorless needles (from *n*-hexane–ether), mp 127—128°, $[\alpha]_D^{22}$ +39.1° ($c=0.307$, $CHCl_3$). CD ($c=0.0229$, MeOH), $[\theta]^{23}$ (nm): +54000 (216), −78500 (240), −72400 (sh 249). IR ν_{max}^{KBr} cm^{-1}: 3430 (OH), 1730 (ester). UV λ_{max}^{EtOH} nm (log ε): 217 (4.68), 255 (sh 3.97), 278—280 (sh 3.53). PMR (δ in C_6D_6): 0.97 (3H, d, 17-H), 1.02 (3H, s, $C\underline{H}_3$–$\overset{|}{\underset{|}{C}}$–OH), 1.10 (3H, d, $J=7$ Hz, 24-H), 1.30 (3H, s, $C\underline{H}_3$–$\overset{|}{\underset{|}{C}}$–OH), 2.08 (1H, m, 8-H), 2.20 (1H, br s, OH), 2.35 (1H, m, 21-H), 1.9—2.5 (2H, m, 9-H), 3.30 (1H, s, OH), 3.35, 3.38, 3.55, 3.97 (each 3H, s, 4×OCH_3), 3.72 (1H, s, 6-H; 3.17 in $CDCl_3$), 4.25 (1H, d, d, $J=9/7$ Hz), 4.50 (1H, d, d, $J=9/5$ Hz) (22-H), 5.33 (2H, q, $J=1.5$ Hz, –OCH_2O–), 6.50 (1H, s, 11-H) and 7.02 (1H, s, 4-H). MS data are given in Chart 2.

Bromination of 1⁷⁾——Bromine (0.2 ml) was added to a solution of **1** (65 mg) in CCl_4 saturated with H_2O (40 ml) at 25° in a dark room, and the reaction mixture was stirred for 2 hr. After decomposition of excess bromine with 10% $Na_2S_2O_3$, the reaction mixture was diluted with H_2O and then extracted with $CHCl_3$. The $CHCl_3$ extract was washed with H_2O, dried over Na_2SO_4 and concentrated under reduced pressure to give a gum, which was purified by PLC using benzene–ether (1:1) to give **4** (57 mg) as colorless plates, mp 246—247°, $[\alpha]_D^{23}$ −3.6° (c=1.12, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3502 (OH), 1720 (ester). PMR (δ in $CDCl_3$): 0.95 (3H, d, J=7 Hz, $C\underline{H}_3$–CH), 1.25 (3H, s, $C\underline{H}_3$–C–OH), 1.27 (3H, d, J=7 Hz, $C\underline{H}_3$–CH), 1.37 (3H, s, $C\underline{H}_3$–C–OH), 1.70 (1H, m, –CH), 1.87 (1H, m, –CH), 1.92 (1H, s, OH), 2.58 (center) (2H, m, 9-H), 3.32 (1H, s, OH), 3.55, 3.90, 3.98 (each 3H, s, 3×OCH_3), 3.65—4.32 (2H, m, 22-H), 6.00 (1H, d, J=1 Hz), 6.08 (1H, d, J=1 Hz) (–OCH_2O–), 6.30 (1H, s, 6-H). MS, *m/e* (%): 690 (57), 689 (36), 688 (100), 687 (18), 686 ($C_{28}H_{32}$-$^{79}Br_2O_{10}$, 52). *Anal.* Calcd. for $C_{28}H_{32}Br_2O_{10}$: C, 48.85; H, 4.69. Found: C, 49.06; H, 4.75.

X-Ray Crystallographic Analysis of 4——Recrystallization of **4** from ether–petro.ether afforded colorless plates flattened on the (010) plane. The density was measured by the flotation method using aqueous potassium iodide solution.

Crystal data: $C_{28}H_{32}Br_2O_{10}$, MW. 686, orthorhombic, space group P $2_12_12_1$. a=14.756 (7), b=20.172 (10), c=9.854 (5) Å, U=2933.13 Å³, Dm=1.54 g·cm⁻³, Dx=1.513 g·cm⁻³, Z=4, λ for CuKα=1.54178 Å.

The intensity data were measured with a Philips four-circle diffractometer with graphite-monochromated CuKα radiation using an ω-2θ scan method. The crystal dimensions were about 0.6×0.1×0.4 mm. The space group was determined from Weissenberg photographs. Out of the total of 3119 independent reflections within a 2θ value of 156°, 3036 reflections having intensities above the $2\sigma(\pm)$ level were used for structure determination. The intensities of 1074 Friedel pairs were also measured on the diffractometer. These intensities were corrected for Lorentz and polarization effects and were placed on an absolute scale by Wilson's method. No absorption correction was made.

Determination of the Structure——The structure of **4** was determined by the heavy atom method. The coordinates of the two bromine atoms were determined from the Patterson map, and Fourier synthesis phased by the two bromine atoms indicated the positions of 35 light atoms on the electron density map. Subsequent difference Fourier synthesis enabled us to identify the locations of the 3 remaining atoms and also to assign the atomic species. Refinement was carried out by the block-diagonal least-squares method using an HBLS program.⁸⁾ The final R value was 0.089 without hydrogen atoms. The absolute structure was established by using the anomalous dispersion effect of bromine for CuKα radiation. Intensities were measured based on a right-handed axial system. The observed and calculated intensity ratios between the Friedel pair reflections are compared in Table II. The ratios were only taken for the reflections with values of [|Fobs(hkl)|−|Fobs($\bar{h}\bar{k}\bar{l}$)|] greater than 3σ[Fobs(hkl)]. Out of the 117 planes, 113 planes showed consistent values for |Fobs(hkl)|/|Fobs($\bar{h}\bar{k}\bar{l}$)| and |Fcal(hkl)|/|Fcal($\bar{h}\bar{k}\bar{l}$)| when the atomic coordinates were referred to the right-handed system. Consequently, the absolute structure of **4** is as shown in Fig. 4. The final atomic parameters are listed in Table III.

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