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The Constituents of *Schizandra chinensis* BAILL. XV.[1] Isolation and Structure Determination of Two New Lignans, Gomisin S and Gomisin T

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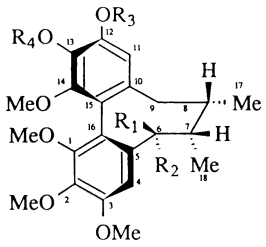
Two new dibenzocyclooctadiene lignans, gomisin S (**1**) and gomisin T (**2**), were isolated from the fruits of *Schizandra chinensis* BAILL. (Schizandraceae). On the basis of spectral methods and chemical transformations, the structures of **1** and **2** were elucidated as (6*S*,7*S*,8*S*,*S*-biar)-5,6,7,8-tetrahydro-1,2,10,11,12-pentamethoxy-6,7-dimethyl-3,8-dibenzo[*a*,*c*]cyclooctenediol and (6*S*,7*S*,*R*-biar)-5,6,7,8-tetrahydro-1,2,10,11,12-pentamethoxy-6,7-dimethyl-3,7-dibenzo[*a*,*c*]cyclooctenediol, respectively.

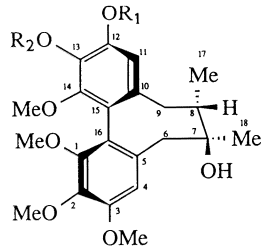
Keywords——*Schizandra chinensis*; Schizandraceae; dibenzocyclooctadiene; lignan; gomisin S; gomisin T; epigomisin O; (−)-gomisin K_1

In the previous papers of this series, we have reported a number of dibenzocyclooctadiene lignans isolated from the fruits of *Schizandra chinensis* BAILL. (Schizandraceae).[1] This paper deals with two additional new lignans, gomisin S (**1**, yield 0.001%) and gomisin T (**2**, 0.00024%) from the same source.

Gomisin S (**1**) was isolated as colorless prisms, $C_{23}H_{30}O_7$, mp 172—176 °C. The ultraviolet (UV), infrared (IR), ^{1}H- and ^{13}C-nuclear magnetic resonance (NMR) spectral analyses of **1** indicate that **1** is a dibenzocyclooctadiene lignan possessing a phenolic hydroxyl group and five methoxyl groups on the aromatic rings, and two secondary methyls on the cyclooctadiene ring. The circular dichroism (CD) spectrum ($[\theta]_{215}$ +110000, $[\theta]_{246}$ −88500) of **1** indicates that **1** has an *S*-biphenyl configuration.[2] The ^{1}H-NMR spectrum (Table I) of **1** closely resembles that of epigomisin O (**3**)[3] except for the functional groups on the aromatic rings, and shows that **1** has a C-6α-oriented hydroxyl group and a *cis*-dimethyl moiety on the cyclooctadiene ring, like **3**.

The position of the phenolic hydroxyl group in **1** was determined by comparison of the ^{13}C-NMR spectra (Table II) of **1** and its diacetate (**4**), $C_{27}H_{34}O_9$, with those of **3** and (−)-gomisin K_1 (**5**).[4] The appearance of an upfield methoxyl (δ 56.0) and four downfield methoxyl (δ 60.2—61.0) signals in the ^{13}C-NMR spectrum on **1**, indicates the presence of one methoxyl group and one hydroxyl group at the C-3 and C-12 positions in **1** as mentioned in the previous paper.[4] The protonated aromatic carbon signals (δ 106.4 in **1**, δ 106.2 in **4**) in **1** and **4**, which appear at essentially the same position as the C-4 signal of **3** (δ 106.4), are assignable to C-4, indicating that one methoxyl group (δ 56.0) of **1** is located at C-3. The other protonated aromatic carbon signal (δ 110.1) in **1** is consequently assigned to C-11, and is essentially at the same position as the C-11 signal of **5** possessing a hydroxyl group at C-12. When a hydroxyl group at the *ortho*-position relative to H-11 (or H-4) in the dibenzocyclooctadiene lignan is acetylated, the C-11 (or C-4) signal of the acetylated compound shows a downfield shift of *ca.* 7.5 ppm.[5] The C-11 signal of **4** shows a downfield shift of 7.5 ppm, indicating that the





1: $R_1=R_3=H$, $R_2=OH$, $R_4=Me$
3: $R_1=H$, $R_2=OH$, $R_3+R_4=CH_2$
4: $R_1=H$, $R_2=OCOMe$, $R_3=COMe$, $R_4=Me$
5: $R_1=R_2=R_3=H$, $R_4=Me$
6: $R_1=R_2=H$, $R_3+R_4=CH_2$
7: $R_1=OCOMe$, $R_2=H$, $R_3+R_4=CH_2$

2: $R_1=H$, $R_2=Me$
12: $R_1=R_2=Me$
13: $R_1=R_2=H$
14: $R_1=Me$, $R_2=H$

Chart 1

TABLE I. ^{1}H-NMR Spectral Data for **1**—**4**, **9**—**12**, **14** (δ in $CDCl_3$, 200 MHz)

Compd.	H-4, s H-11, s	H-6α (J=Hz)	H-6β (J=Hz)	H-9α (J=Hz)	H-9β (J=Hz)	H–C$_{(8)}$–Me[b] m	 (J=Hz)	H–C$_{(7)}$+Me[b] m	 (J=Hz)	OMe s	ArOH[a] br s
1	7.02 6.60	1.59 s OH[a]	4.59 d (1)	2.13 dd (13, 8.5)	1.98 dd (13, 1)	1.97	1.01 d (6.6)	2.00	0.70 d (6.4)	3.54, 3.62, 3.90, 3.91, 3.93	5.82
3[c]	6.98 6.43	1.93 s OH[a]	4.53 s	2.13 dd (13, 8)	1.93 dd (13, 1)	1.87	1.00 d (6)	1.87	0.70 d (7)	3.53, 3.82, 3.90, 3.90	—
4[c]	6.77[d] 6.72[d]	2.05 (3H, s) $COCH_3$	5.51 s	2.17 dd (14, 7.5)	2.0[e]	2.0	1.00 d (6.6)	2.0	0.76 d (6.6)	3.62 (×2), 3.87, 3.89, 3.92	—
9[e,f]	6.65 6.71	5.70 d (8.7)	1.78 (3H, s) $COCH_3$	2.35[e]	2.09 t (12.5)	1.85	0.94 d (7)	1.91	0.80 d (6.8)	3.56, 3.69, 3.87, 3.89, 3.90	—
10[f]	6.55[d] 6.58[d]	4.42 d (7.5)	 (OH)	2.06 dd (13, 10)	2.27 dd (13, 4.7)	1.89	0.94 d (7)	1.76	0.88 d (6.8)	3.53, 3.71, 3.90, 3.90, 3.94	5.78
11[f]	7.60 6.64	—	—	2.65 dd (12.9, 6.8)	2.18 t (12.5)	1.84	0.84 d (6.8)	2.68	1.04 d (6.6)	3.50, 3.60, 3.97, 3.97, 3.98	5.87
2	6.62[d] 6.63[d]	2.68 d (13.5)	2.37 d (13.5)	2.34 dd (14, 8)	2.61 dd (14, 2)	1.88	0.82 d (7)	1.88 s OH[a]	1.26 s	3.55, 3.56, 3.90, 3.91, 3.92	5.76
12	6.60 6.53	2.70 d (14)	2.32 d (14)	2.33 dd (14, 7)	2.68 dd (14, 2)	1.80	0.82 d (7)	1.86 s OH[a]	1.25 s	3.59 (×2), 3.90 (×2), 3.92 (×2)	—
14	6.64 6.55	2.69 d (13.5)	2.38 d (13.5)	2.36 dd (13.5, 8)	2.66 dd (13.5, 2)	1.87	0.82 d (7)	1.87 s OH[a]	1.27 s	3.43, 3.54, 3.90, 3.90, 3.91	5.61

a) Hydroxyl signals were confirmed by addition of D_2O. *b*) Confirmed by decoupling experiments. *c*) Other signals: **3**, δ 5.92 (2H, s, OCH_2O); **4**, δ 2.34 (3H, s, $COCH_3$); **9**, δ 2.35 (3H, s, $COCH_3$). *d*) Assignments may be reversed. *e*) These signals were unclear due to overlapping with the acetyl signal. *f*) These compounds were measured at 500 MHz. *g*) Abbreviations: br = broad, d = doublet, s = singlet, t = triplet.

hydroxyl group in **1** is located at C-12. On the basis of the above results and the J value between H-6β and H-7 ($J_{6\beta,7}=1$ Hz; $\phi_{6\beta,7}=90°$), the structure of gomisin S was suggested to be **1** possessing the twist-boat-chair conformation[6] of the cyclooctadiene ring. The structure

TABLE II. ^{13}C-NMR Spectral Data for **1**—**5**, **12**, **14** (δ in $CDCl_3$, 20 MHz)

Carbon	1	3	4	5	2[a]	12	14
1	151.1	151.2	151.2[b]	151.6	152.1	151.9[b]	152.0
2	140.0	140.8[b]	141.2	140.3	140.9	140.8[c]	141.1
3	152.3	152.3	152.5	151.7	152.4	152.3	152.6
4	106.4	106.4	106.2	110.8	110.2	110.5[d]	110.2[b]
5	136.4	136.5[c]	132.7	134.1	132.1	131.8	132.0
6	73.6	73.4	75.9	39.3	40.9	40.9	40.8
7	43.1	42.6	40.6	33.8	71.9	71.8	71.9
8	39.4	39.3	39.0	40.9	41.9	41.8	41.9
9	34.5	34.7	34.3	35.3	34.0	34.4	33.9
10	140.0	137.9[c]	138.9	140.0	134.6	133.8	129.5
11	110.1	102.8	117.6	110.0	113.1	110.1[d]	110.3[b]
12	149.3	149.2	144.2	148.8	147.8	152.0	146.3
13	137.6	134.6	142.9	137.5	137.8	140.3[c]	136.4
14	150.1	140.9[b]	151.9[b]	150.3	150.4	151.6[b]	145.2
15	119.8	119.6	126.2	121.6	122.0	122.8	122.0
16	121.3	121.3	121.4	123.4	124.1	124.2	124.0
17	22.1	22.0	21.9	21.7	15.8	15.9	15.8
18	7.7	7.8	8.5	12.8	29.8	29.7	29.9
OMe							
C-1, 14	60.2,[b] 60.5[b]	60.6, 59.6	60.6,[c] 60.7[c]	60.5,[b] 60.1[b]	60.6,[b] 60.1[b]	60.5 (×2)	60.7,[c] 60.3[c]
C-2, 13	61.0, 60.8	61.0, —	60.9, 60.7[c]	61.0,[c] 60.9[c]	61.0,[c] 60.9[c]	60.9 (×2)	61.0, —
C-3, 12	56.0, —	56.0, —	56.1, —	56.0, —	56.0, —	56.0 (×2)	56.1,[d] 56.2[d]
CO–CH_3	—	—	169.3, 20.8	—	—	—	—

a) This compound was measured at 50 MHz. *b*—*d*) Assignments within any column may be reversed.

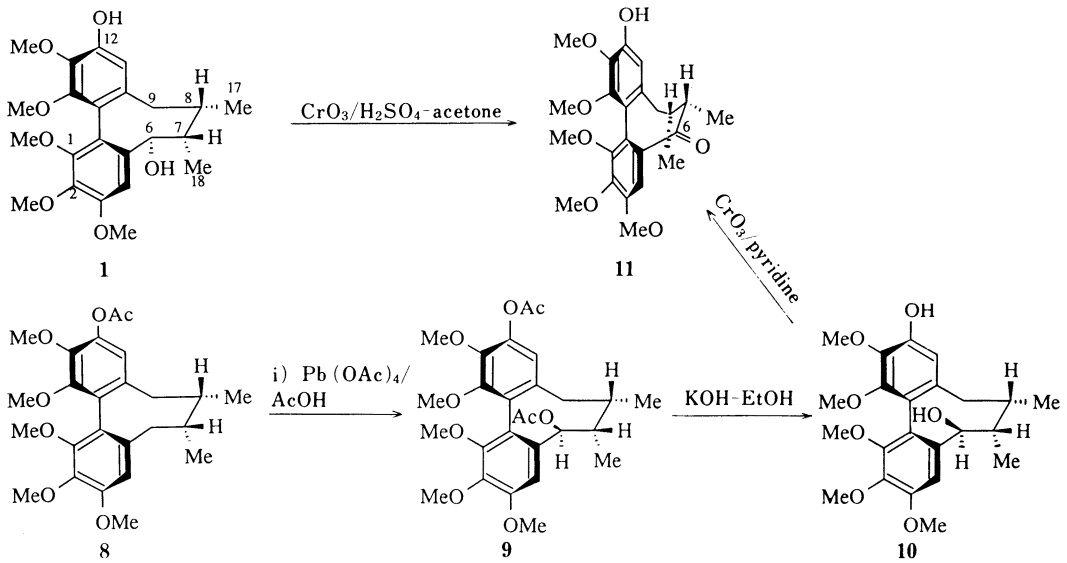


Chart 2

of **1** was confirmed by correlation with **5** as follows.

In the previous paper,[7] we reported that treatment of gomisin N (**6**) with Pb $(OAc)_4$ in AcOH gave 6β-acetoxygomisin N (**7**).[8] Treatment of (−)-gomisin K_1 acetate (**8**)[4] with Pb $(OAc)_4$ in AcOH gave a compound **9**. The ^{1}H-NMR spectrum (Table II) of **9** shows a new

acetoxyl signal (δ 1.78) and a new methine proton (H-6α) signal (δ 5.70). The J value ($J_{6\alpha,7}=8.7$ Hz; $\phi_{6\alpha,7}\fallingdotseq 30°$) between H-6$\alpha$ and H-7 indicates that **9** has the C-6β-oriented acetoxyl group. On hydrolysis with 3% ethanolic potassium hydroxide, **9** afforded a compound **10**. Next, oxidation of **10** with CrO_3 afforded a compound **11**, $C_{23}H_{28}O_7$, $[\alpha]_D$ +11° ($CHCl_3$), mp 142—145 °C. The IR spectrum of **11** shows a carbonyl band at 1648 cm^{-1} and the ^{1}H-NMR spectrum shows an extreme downfield shift (δ 7.60) of H-4, indicating that the carbonyl group is coplanar with the adjacent aromatic ring and that the cyclooctadiene ring has a boat conformation.[9] On the other hand, oxidation of **1** with CrO_3 afforded **11** too. This fact shows that **1** is the C-6 epimer of **9**. Thus, the structure of gomisin S (**1**) was determined as (6*S*,7*S*,8*S*,*S*-biar)-5,6,7,8-tetrahydro-1,2,10,11,12-pentamethoxy-6,7-dimethyl-3,8-dibenzo[*a*,*c*]cyclooctenediol.

Gomisin T(**2**) was isolated as a white amorphous powder, $C_{23}H_{30}O_7$, $[\alpha]_D$+60° ($CHCl_3$). Its UV, IR, and ^{1}H-NMR spectra indicate that **2** is a dibenzocyclooctadiene lignan possessing a phenolic hydroxyl group and five methoxyl groups on the aromatic rings and a hydroxyl group on the cyclooctadiene ring. On methylation, **2** gave a monomethyl ether (**12**), $C_{24}H_{32}O_7$, which was identified as schizandrin (mixed melting point, IR, and $[\alpha]_D$). These data indicate that **2** corresponds to the demethylated compound of schizandrin (**12**).

The position of the phenolic hydroxyl group in **2** was determined by comparison of the ^{13}C-NMR spectrum (Table II) of **2** with that of **12**. The appearance of an upfield methoxyl (δ 56.0) and four down field methoxyl (δ 60.1—61.0) signals in the ^{13}C-NMR spectrum of **2** indicates the presence of a methoxyl group and a hydroxyl group at C-3 and C-12 in **2**, as mentioned in the previous paper.[4] When a methoxyl group at the *ortho*-position relative to H-11 (or H-4) in a dibenzocyclooctadiene lignan is substituted by a hydroxyl group, the C-11 (or C-4) signal of the phenolic compound shows a downfield shift of *ca.* 3 ppm.[5] The protonated aromatic carbon signal (δ 110.2) in **2**, which appears at essentially the same position as the C-4 shift (δ 110.5) of 12, is assignable to C-4. The other protonated aromatic carbon signal (δ 113.1) in **2** is consequently assigned to C-11, which shows a downfield shift of 3 ppm in comparison with the C-11 signal of **12**.

On methylation with dimethyl sulfate and potassium carbonate at room temperature, the compound (**13**)[10] derived from gomisin A gave two methyl ethers, **2** and **14**. The $[\alpha]_D$, IR, ^{1}H-, and ^{13}C-NMR spectra of **2** were identical with those of gomisin T. In the ^{13}C-NMR spectrum (Table II) of **14**, two upfield methoxyl signals (δ 56.1 and 56.2) are assigned to the methoxyl groups at C-3 and C-12. This indicates that **14** corresponds to the C-12-O-methylated derivative of **13**. Furthermore, the aromatic carbon signals of **14** are reasonably assigned as shown in Table II based on a comparison of the chemical shifts with those of model compounds (2,6-dimethoxyphenol and 1,2,3-trimethoxybenzene) reported by Wenkert *et al.*[11]

Thus, the structure of gomisin T (**2**) was determined as (6*S*,7*S*,*R*-biar)-5,6,7,8-tetrahydro-1,2,10,11,12-pentamethoxy-6,7-dimethyl-3,7-dibenzo[*a*,*c*]cyclooctenediol.

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 270-30 infrared spectrophotometer. The ^{1}H-NMR and ^{13}C-NMR spectra were recorded with Bruker AM-500, JEOL JNM-FX-200, and Varian FT-80 NMR spectrometers using tetramethylsilane (TMS) as an internal standard. The specific rotations were measured with a JASCO DIP-360 digital poloarimeter and the mass spectra with a JEOL JNM-DX-300 mass spectrometer. The CD spectrum was recorded with a JASCO J-40. For silica gel column chromatography, Kieselgel 60 (Merck) was used. Kieselgel 60 F_{254} (Merck precoated plate) was used for preparative thin layer chromatography (prep. TLC) and spots were detected under UV (254 nm). For preparative high-performance liquid chromatography (prep. HPLC), a JASCO BIP-I high-pressure liquid chromatograph with a

TABLE III. Silica Gel Column Chromatography of Petroleum Ether Extract

Fraction No.	Solvent	Volume (l)	Yield (g)
1	Hexane–benzene (1 : 1)	11	76.2
2	Hexane–benzene (1 : 1)	3	473.2
	Hexane–benzene (1 : 9)	4	
	Benzene	1.3	
3	Benzene–acetone (98 : 2)	5	398.0
	Benzene–acetone (96 : 4)	5	
	Benzene–acetone (92 : 8)	3	
4	Benzene–acetone (9 : 1)	10	269.2
5	Benzene–acetone (9 : 1)	4	50.3
6	Benzene–acetone (88 : 12)	10	5.8
7	Benzene–acetone (85 : 15)	6	11.4
8	Benzene–acetone (8 : 2)	10	30.2
	Benzene–acetone (75 : 25)	6	
	Benzene–acetone (7 : 3)	1	
	Benzene–acetone (3 : 7)	3	
9	Acetone	6	23.5

UVIDEC-100-VI UV spectrophotometer was used.

Isolation of Gomisin S (1) and Gomisin T (2)——The dried fruits of *Schizandra chinensis* BAILL. (10 kg) were pulverized and extracted with petroleum ether (bp 37—39 °C) (40 l × 2, 7 h each) under reflux. The petroleum ethereal extract was concentrated to give a brown mass (1383 g), which ws chromatographed on silica gel (5 kg) with hexane–benzene, benzene, and then benzene–acetone. The details of this chromatography are given in Table III.

Fraction 8 (Table III) was rechromatographed on silica gel (5.5 cm i.d. × 45 cm) using hexane–acetone. The fractions eluted with hexane–acetone (80 : 20) were combined and concentrated to give a residue (4.91 g), which was purified by prep. TLC (hexane–EtOAc (1 : 2)). The zone with *Rf* 0.62 was extracted with $CHCl_3$–MeOH (4 : 1) and the extract was concentrated to give a residue (2.57 g), which was purified by prep. TLC ($CHCl_3$–EtOH (19 : 1)). The zone with *Rf* 0.41 was extracted with $CHCl_3$–MeOH (4 : 1) and the extract was concentrated to give **1** (101 mg, yield 0.001%) as colorless prisms from ether–hexane. On the other hand, the zone with *Rf* 0.47 was extracted with $CHCl_3$–MeOH (4 : 1) and the extract was concentrated to give a residue. This residue was purified by prep. HPLC to give **2** (24 mg, yield 0.0024%) as a white amorphous powder. Prep. HPLC conditions: column, YMC Pack S-345 I-15 ODS (20 mm i.d. × 250 mm); mobile phase, MeCN–MeOH–H_2O (11 : 11 : 16); flow rate, 5 ml/min; temp., room temperature; detection UV 254 nm; t_R, 34.0 min.

Gomisin S (1)——Colorless prisms, mp 172—176 °C, $[\alpha]_D^{23}$ −63° (*c* = 0.49, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1596, 1576 (aromatic ring). UV λ_{max}^{EtOH} nm (log ε): 216 (4.83), 249 (4.32), 276 (sh 3.58), 286 (3.52). CD (*c* = 0.0129, MeOH) $[\theta]^{24}$ (nm): +110000 (215), −88000 (246). Electron impact-mass spectra (EI-MS) *m/z* (%): 418 (M^+, 100), 401 (9.5), 400 (34), 362 (19), 224 (16), 222 (17). High-resolution MS, Calcd for $C_{23}H_{30}O_7H$ (M^+): 418.1991. Found: 418.2056. *Anal.* Calcd for $C_{23}H_{30}O_7$: C, 66.01; H, 7.23. Found: C, 65.76; H, 7.20.

Gomisin T (2)——A white amorphous powder, $[\alpha]_D^{23}$ +60° (*c* = 0.50, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3436 (OH), 1584 (aromatic ring), 1120, 1092. UV λ_{max}^{EtOH} nm (log ε): 215 (4.61), 251 (4.08), 288 (sh 3.39). EI-MS *m/z* (%): 418 (M^+, 100), 400 (6.2), 375 (14), 347 (11), 344 (21), 343 (14), 316 (32). High-resolution MS, Calcd for $C_{23}H_{30}O_7$ (M^+): 418.1990. Found: 418.1996. *Anal.* Calcd for $C_{23}H_{30}O_7$: C, 66.01; H, 7.23. Found: C, 65.83; H, 7.23.

Acetylation of 1——A solution of **1** (71 mg) in a mixture of Ac_2O (0.25 ml) and pyridine (0.5 ml) was allowed to stand at room temperature overnight, then diluted with ether. The ethereal solution was washed with 1 N HCl, 5% $NaHCO_3$, then H_2O, dried over Na_2SO_4 and concentrated to dryness. The residue was purified by prep. TLC (hexane–acetone (7 : 3)) to give a diacetate (**4**) as a white amorphous powder (53 mg), $[\alpha]_D^{25}$ −91° (*c* = 1.13, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 1765, 1740 (ester), 1595, 1576 (aromatic ring). EI-MS *m/z* (%): 502 (M^+, 100), 461 (27), 460 (92), 401 (18), 400 (57), 344 (12), 43 (63). High-resolution MS, Calcd for $C_{27}H_{34}O_9$ (M^+): 502.2203. Found: 502.2272.

Treatment of 8 with Pb (OAc)$_4$——$Pb(OAc)_4$ (180 mg) was added to a solution of **8** (145 mg) in AcOH (4 ml) and the reaction mixture was stirred at 12—16 °C for 18 h. The reaction mixture was diluted with ether, washed with 5% $NaHCO_3$, then H_2O, dried over Na_2SO_4 and concentrated to dryness. The residue was purified by prep. TLC (hexane–acetone (7 : 3), *Rf* 0.65) to give **9** as a white amorphous powder (33 mg), $[\alpha]_D^{26}$ +18° (*c* = 1.07, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 1765, 1730 (ester), 1590 (aromatic ring). UV λ_{max}^{EtOH} nm (log ε): 217 (4.65), 246 (sh 4.09), 283 (3.30). EI-MS *m/z* (%): 502 (M^+, 76), 460 (85), 442 ($M^+ - CH_3COOH$, 38), 401 (35), 400 (100), 385 (17), 43 (54). High-resolution MS, Calcd for $C_{27}H_{34}O_9$ (M^+): 502.2203. Found: 502.2249.

Hydrolysis of 9——A solution of **9** (33 mg) in 3% KOH–EtOH (2 ml) was kept at 60 °C for 3 h, then diluted with

H_2O (20 ml), neutralized with 1 N HCl and extracted with ether. The ethereal extract was washed with H_2O, dried over Na_2SO_4 and concentrated. The residue was purified by prep. TLC (hexane–acetone (7 : 3)) to give **10** as a white amorphous powder (18 mg). IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1580 (aromatic ring). EI-MS *m/z* (%): 418 (M^+, 100), 400 (33), 363 (12), 362 (55), 302 (13), 224 (26), 168 (25). High-resolution MS, Calcd for $C_{23}H_{30}O_7$ (M^+): 418.1981. Found: 418.1974.

Oxidation of 10 with CrO_3——CrO_3 (30 mg) was added to a solution of **10** (15 mg) in dry pyridine (0.5 ml). The reaction mixture was stirred at 24 °C for 1.5 h, then diluted with ether. The ethereal solution was washed with H_2O, dried over Na_2SO_4 and concentrated. The residue was purified by prep. TLC (hexane–EtOAc (1 : 1)) to give **11** (5 mg) as colorless needles (from ether–hexane), mp 142—145 °C, $[\alpha]_D^{25}$ +11° (*c* = 0.185, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3380 (OH), 1648 (C=O), 1576 (aromatic ring). EI-MS *m/z* (%): 416 (M^+, 100), 361 (4.6), 360 (14), 346 (7.1), 314 (6.9). High-resolution MS, Calcd for $C_{23}H_{28}O_7$ (M^+): 416.1935. Found: 416.1921.

Oxidation of 1 with CrO_3——An 8 N CrO_3 solution in 8 N H_2SO_4[12] (0.02 ml) was added to a solution of **1** (20 mg) in acetone (1.5 ml). The reaction mixture was stirred at 22 °C for 15 min. After addition of isopropanol (0.5 ml), the reaction mixture was diluted with ether. The ethereal solution was washed with H_2O, dried over Na_2SO_4, and concentrated. The residue was purified by prep. TLC (hexane–acetone (7 : 3)) to give **11** (7 mg) as colorless needles (from ether–hexane), mp 143—145.5 °C, $[\alpha]_D^{25}$ +12° (*c* = 0.35, $CHCl_3$). High resolution MS, Calcd for $C_{23}H_{28}O_7$ (M^+): 416.1835. Found: 416.1851. This compound was identified as **11** by direct comparison with an authentic sample prepared from **10** (IR, ^{1}H-NMR, mixed melting point, and $[\alpha]_D$).

Methylation of 2——$(CH_3)_2SO_4$ (0.1 ml) and K_2CO_3 (100 mg) were added to a solution of **2** (11 mg) in dry acetone (1.5 ml). The reaction mixture was stirred at 50 °C for 3 h, then diluted with H_2O, and extracted with ether. The ethereal extract was washed with H_2O, dried over Na_2SO_4 and concentrated. The residue was purified by prep. TLC (hexane–acetone (7 : 3), *Rf* 0.30) to give a methyl ether (**12**) as colorless prisms (from ether–hexane) (9.5 mg), mp 130—131.5 °C, $[\alpha]_D^{25}$ +88.3° (*c* = 0.283, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3524 (OH), 1600 (aromatic ring). *Anal.* Calcd for $C_{24}H_{32}O_7$: C, 66.65; H, 7.46. Found: C, 66.66; H, 7.32. This compound was identified as schizandrin (**12**) by direct comparison with an authentic sample (IR, $[\alpha]_D$, and mixed melting point).

Methylation of 13——$(CH_3)_2SO_4$ (0.3 ml) and K_2CO_3 (300 mg) were added to a solution of **13** (250 mg) in dry acetone (5 ml). The reaction mixture was stirred at room temperature for 7 h, then diluted with ether. The ethereal solution was washed with H_2O, dried over Na_2SO_4, and concentrated. The residue was purified by prep. TLC (hexane–acetone (7 : 3)). The zone with *Rf* 0.37 was extracted with $CHCl_3$–MeOH (4 : 1). The extract was concentrated to give **2** as a white amorphous powder (72 mg), $[\alpha]_D^{24}$ +67° (*c* = 1.04, $CHCl_3$). High-resolution MS, Calcd for $C_{23}H_{30}O_7$ (M^+): 418.1992. Found: 418.2057. This compound was identified as gomisin T (2) by direct comparison with an authentic sample (IR, ^{1}H-NMR, MS and $[\alpha]_D$).

The zone with *Rf* 0.32 was extracted with $CHCl_3$–MeOH (4 : 1). The extract was concentrated to give **14** as a white amorphous powder (71 mg), $[\alpha]_D^{24}$ +73° (*c* = 1.36, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3432 (OH), 1598 (aromatic ring). UV λ_{max}^{EtOH} nm (log ε): 216 (4.58), 255 (sh 4.03), 288 (sh 3.50). EI-MS *m/z* (%): 418 (M^+, 100), 375 (6.7), 347 (25), 344 (12), 334 (19), 316 (52), 315 (24). High-resolution MS, Calcd for $C_{23}H_{30}O_7$ (M^+): 418. 1992. Found: 418.1995.

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