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TWO LIGNANS FROM *SCHISANDRA SPHENANTHERA**

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Key Word Index—*Schisandra sphenanthera*; Schisandraceae; dibenzocyclooctadiene; lignan; benzoylgomisin U; tigloylgomisin O; isoschizandrin.

Abstract—Two new dibenzocyclooctadiene lignans, benzoylgomisin U and tigloylgomisin O were isolated from the fruits of *Schisandra sphenanthera* together with known lignans, gomisin U and epigomisin O. Their structures were determined by chemical and spectral studies. The structure of isoschizandrin was also revised by advanced chemical and spectral studies.

INTRODUCTION

The fruits of *Schisandra sphenanthera* Rehd. et Wils. are used as an antitussive, tonic, and sedative agent under the name of Wuweizi in Chinese traditional medicine together with the fruits of *S. chinensis* Baill. Eleven dibenzocyclooctadiene lignans [1, 2] have been isolated from this plant. In this paper we report the isolation of two new lignans, benzoylgomisin U(**1a**) and tigloylgomisin O(**2a**) together with two known lignans, gomisin U(**1b**) and epigomisin O(**2b**) from *S. sphenanthera* collected in the province of Shangxi in China, and the revised stereostructure of isoschizandrin (**3a**) [3] from *S. chinensis*.

RESULTS AND DISCUSSION

Compound **1b**, named gomisin U was identified as 6β-hydroxy compound [4] of (−)-gomisin K_1 (**1c**) by direct comparison with an authentic sample. Compound **2b** was identified as epigomisin O [5] by direction comparison with an authentic sample obtained from *S. chinensis*.

Benzoylgomisin U (**1a**) was obtained as needles, $C_{30}H_{34}O_8$, $[\alpha]_D$ −61.6° ($CHCl_3$) and possessed the characteristic UV spectrum (λ_{max} 215.2, 255 sh, and 289 sh nm) of dibenzocyclooctadiene lignans [6]. Its CD spectrum ($[\theta]_{213.1}$ +86 200, $[\theta]_{235.0}$ −98 500, and $[\theta]_{248.6}$ −55 100 sh) indicated that **1a** has a *S*-biphenyl configuration [7]. The ^{1}H NMR spectral analyses (Table 1) showed that **1a** has one phenolic hydroxyl and five methoxyl groups on the aromatic rings, and a benzoyloxyl and two secondary methyl groups. The mass spectrum with peaks at *m/z* 522 $[M]^+$, 400 $[M-C_6H_5CO_2H]^+$ and 105 $[C_6H_5CO]^+$ [8], and ^{13}C NMR spectrum (Table 2) also supported the presence of a benzoyloyl group in **1a**.

On hydrolysis with 3% ethanolic potassium hydroxide, **1a** afforded a benzoic acid and **1b**. The doublet at δ4.42 in the ^{1}H NMR spectrum of **1b**, which appeared at δ6.01 in **1a**, was assigned to the C-6 benzylic methine. This showed that the benzoyl group in **1a** is linked to the C-6 hydroxyl group in **1b**.

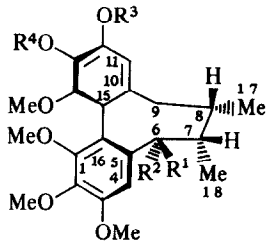
The structure of **1a** was confirmed by the two-dimensional nuclear Overhauser effects spectroscopy (NOESY) spectrum of **1a** in chloroform-*d* (Fig. 1). The NOESY spectrum showed appreciable NOE between the C-3 methoxyl signal at δ3.89 and the lower-field aromatic proton (H-4) signal at δ6.80, and between the H-4 and the C-6 benzylic methine signal, but no NOE between the higher-field aromatic proton (H-11) signal at δ6.67 and any methoxyl signal. These findings indicated that the phenolic hydroxyl group is located adjacent to H-11, and that the C-6 benzylic methine proton is α-oriented. The NOESY spectrum also showed appreciable NOE between the C-7 methyl signal at δ0.84 and the H-4 signal, and between the H-8 signal and the H-11 signal, indicating that both C-7 and C-8 methyl groups are α-oriented. On the basis of the above results, the structure of benzoylgomisin U was determined as (6*R*,7*S*,8*S*,*S*-biar)-6-benzoyloxy-6,7,8,9-tetrahydro-1,2,3,13,14-heptamethoxy-7,8-dimethyl-12-dibenzo [*a*, *c*]-cyclooctenol (**1a**) (Fig. 1).

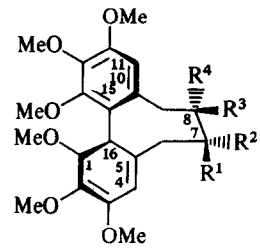
Tigloylgomisin O(**2a**) was obtained as an amorphous powder, $C_{28}H_{34}O_8$, $[\alpha]_D$ −22° ($CHCl_3$) and possessed the characteristic UV spectrum (λ_{max} 215.2, 258 sh, and 293 sh nm) of dibenzocyclooctadiene lignan. Its CD spectrum ($[\theta]_{229.4}$ +5 700, $[\theta]_{241.1}$ −57 200, $[\theta]_{249.1}$ −47 200 sh) indicated that **2a** has an *S*-biphenyl configuration [7]. The ^{1}H NMR spectrum (Table 1) showed that **2a** has a methylenedioxyl and four methoxyl groups on the aromatic rings, and a tigloyloxyl and two secondary methyl groups. The ^{13}C NMR spectrum (Table 2) also supported the presence of tigloyl group [δ11.2 (α-Me), 14.2 (β-Me), 128.4, 137.1 (C=C), and 166.9 (C=O)].

On hydrolysis with 3% ethanolic potassium hydroxide, **2a** afforded a tiglic acid and **2c**, which was identified as gomisin O [5] by direct comparison with an authentic sample. The doublet at δ4.34 in the ^{1}H NMR spectrum of **2c**, which appeared at δ5.76 in **2a**, was assigned to the C-6 benzylic methine. This showed that the tigloyl group in **2a** is linked to the C-6 hydroxyl group in **2c**.

The structure of **2a** was confirmed by the NOESY spectrum in chloroform-*d* (Fig. 2). The NOESY spectrum

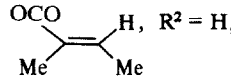
* Part 17 in the series 'The Constituents of *Schisandra* Species'. For Part 16 see ref. [2].



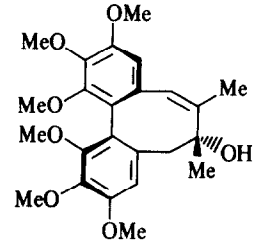


1a R^1 = OCO-(C$_6$H$_5$), $R^2 = R^3$ = H, R^4 = Me
1b R^1 = OH, $R^2 = R^3$ = H, R^4 = Me
1c $R^1 = R^2 = R^3$ = H, R^4 = Me

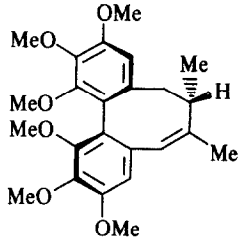
3a $R^1 = R^4$ = Me, R^2 = OH, R^3 = H
3b $R^1 = R^3$ = Me, R^2 = OH, R^3 = H
4a R^1 = OH, $R^2 = R^4$ = Me, R^3 = H
4c $R^1 + R^2 = CH_2$, R^3 = H, R^4 = Me

2a R^1 =  , R^2 = H, $R^3 + R^4 = CH_2$

2b R^1 = H, R^2 = OH, $R^3 + R^4 = CH_2$
2c R^1 = OH, R^2 = H, $R^3 + R^4 = CH_2$



4b



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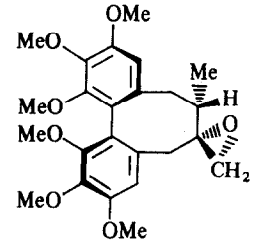

4e

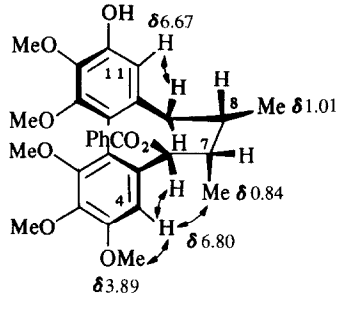

Fig. 1. NOE (↔) in the NOESY spectrum of compound **1a** (in $CDCl_3$).

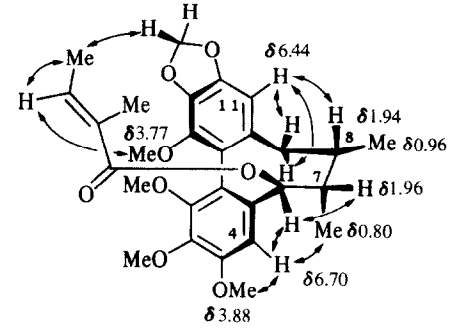

Fig. 2. NOE (↔) in the NOESY spectrum of compound **2a** (in $CDCl_3$).

showed appreciable NOE between the C-3 methoxyl signal at δ3.88 and the lower-field aromatic proton (H-4) signal at δ6.70, and between the H-4 and the C-6 benzylic methine signal, indicating that the C-6 benzylic methine proton is α-oriented. The NOESY spectrum also showed appreciable NOE between the C-7 methyl signal at δ0.80 and the H-4 signal, and between the H-8 signal and the H-11 signal, indicating that both C-7 and C-8 methyl groups are α-oriented. On the basis of above results, the structure of tigloylgomisin O was determined as (6*R*,7*S*,8*S*,*S*-biar)-

Table 1. ^{1}H NMR spectral data of compounds **1a**, **1b**, **2a**, **2b**, **2c**, **3a**, **4c**, and **4e** ($CDCl_3$, 500 MHz)

Compound	H-4, *s* H-11, *s*	H-6α (*J* = Hz)	H-6β (*J* = Hz)	H-9α, *dd* (*J* = Hz)	H-9β, *dd* (*J* = Hz)	H-7 (*J* = Hz)	H-8 (*J* = Hz)	C-7-Me (*J* = Hz)	C-8-Me *a* (*J* = Hz)	OMe *s*
1a*	6.80 6.67	6.01 *d* (7.7)		2.22 *br t*†	2.30 *br d*†	2.09 *m*	2.09 *m*	0.84 *d* (6.8)	1.01 (6.9)	3.38, 3.53, 3.75, 3.89 3.92, 5.80 1H, *s* (OH)
1b	6.55 6.59	4.42 *d* (7.7)		2.06 (12.7, 10.0)	2.27 (12.7, 4.0)	1.76 *m*	1.88 *m*	0.88 *d* (6.9)	0.94 (7.1)	3.53, 3.71, 3.89, 3.90 3.94, 5.78 1H, *s* (OH)
2a*	6.70 6.44	5.76 *d* (7.8)		2.15 (13.4, 9.4)	2.22 (13.4, 3.8)	1.96 *m*	1.94 *m*	0.80 *d* (6.9)	0.96 (7.1)	3.52, 3.77, 3.89 (×2) 5.92 and 5.96 each 1H, *d* (1.5 Hz, OCH_2O)
2b	7.01 6.44	1.09 *br s* (OH)	4.57 *d* (1.2)	2.12 (13.4, 4.9)	1.95 *d* (13.4)	1.85–2.05 *m*	1.85–2.05 *m*	0.70 *d* (6.8)	1.00 (6.8)	3.55, 3.85, 3.91 (×2) 5.94 2H, *s* (OCH_2O)
2c	6.57 6.42	4.34 *d* (8.3)		2.02 (13.0, 4.9)	2.32 (13.0, 5.5)	1.67 *m*	1.85 *m*	0.92 *d* (5.1)	0.90 (5.6)	3.53, 3.89, 3.90, 3.91 5.95 and 5.97 each 1H, *d* (1.5 Hz, OCH_2O)
3a	6.61 6.54	2.82 *d* (13.1)	2.32 *dd* (13.1, 1.1)	2.52 (14.1, 6.5)	2.55 (14.1, 3.2)		1.90 *m*	1.19 *s*	0.88 (7.1)	3.55, 3.56, 3.88 (×2) 3.89 (×2)
4c	6.65 6.55	2.93 *d*[a] (12.3)	3.00 *d*[a] (12.3)	2.52 (13.5, 5.4)	2.56 (13.5, 2.7)		2.70 *ddd* (7.2, 5.4, 2.7)	4.72 1H, *d* (2.0) 4.86 1H, *d* (2.0)	1.02 (7.2)	3.60, 3.62, 3.87, 3.88 (×2), 3.90
4e	6.48[a] 6.58[a]	3.02 *dd* (13.3, 1.5)	1.95 *dd* (13.3, 0.9)	2.59 (13.7, 6.9)	2.69 (13.7, 1.7)		1.52 *m*	2.54 1H, *dd* (4.5, 1.5) 2.98 1H, *d* (4.5)	1.00 (7.1)	3.59, 3.60, 3.88 (×2) 3.90 (×2)

*Other signals: **1a**, C_6H_5CO—: 7.29 (2H, *m*), 7.45 (1H, *m*), 7.57 (2H, *br*); **2a**, Tigloyl: 1.62 (3H, *quin*, *J* = 1.2 Hz, α-Me), 1.67 (3H, *dq*, *J* = 7.0, 1.2 Hz, β-Me), 6.27 (1H, *br q*, *J* = 7.0 Hz).
†In case of 200 MHz ^{1}H NMR spectrum, these signals were shown at δ2.20 (*dd*, *J* = 13.0, 10.0 Hz) and 2.30 (*dd*, *J* = 13.0, 4.0 Hz).
[a] Assignments of these signals may be reversed.

Table 2. ^{13}C NMR spectral data of compounds **1a**, **1b**, **2a**, and **2c** ($CDCl_3$, 50 MHz)

C		1a*	1b	2a*†	2c
1		152.0	152.0[a]	152.0	151.9
2		142.0	141.6	141.8[a]	141.7[a]
3		151.8	151.9[a]	151.7	152.1
4		111.0	110.1	110.8	110.1
5		132.1	136.4[b]	132.6	137.0
6		81.4	81.4	80.9	81.4
7		37.6	40.0	37.4	40.0
8		36.4	36.8	36.5	37.0
9		36.8	37.3	36.9	38.0
10		137.6	137.7[b]	135.5	135.5
11		109.6	109.8	102.4	102.5
12		148.9	149.4	148.6	149.2
13		137.5	137.7	134.5	134.6
14		150.3	150.6	141.4[a]	141.5[a]
15		122.2[a]	122.0[c]	121.9[b]	122.2[b]
16		123.2[a]	120.8[c]	123.2[b]	120.6[b]
17		20.3	18.3	19.2	17.5[c]
18		14.2	15.7	14.2	16.5[c]
	C-1, 14	60.5[b], 59.7	60.4, 60.2	60.5, 59.2	60.4, 59.5
OMe	C-2, 13	60.9, 60.6[b]	60.9, 60.9	60.9, —	60.9, —
	C-3, 12	56.0,	56.0, —	56.0, —	56.0, —
OCH_2O		—	—	100.6	100.8

*Other signals: 1a, 128.1 (3′, 5′), 129.7 (2′, 6′), 130.3 (1′), 132.8 (4′), 165.5 (C=O) (C_6H_5CO–); 2a, 11.7 (α-Me), 14.2 (β-Me), 128.4 (α-olephin), 137.1 (β-olephin), 166.9 (C=O) (Tigloyl).

†This compound was measured at 125 MHz and assignments were confirmed by ^1H–^{13}C COSY spectrum.

[a,b,c]Assignments within any vertical column may be reversed.

6,7,8,9-tetrahydro-1,2,3,14-tetramethoxy-7,8-dimethyl--12,13-methylenedioxy-6-tigloyloxy-dibenzo[*a*, *c*] cyclooctene (**2a**) (Fig. 2).

Previously, the structure of isoschizandrin isolated from *S. chinensis* was proposed as **3b** having a C-8β secondary methyl group on the basis of spectral studies and chemical correlation with **4b** derived from schizandrin (**4a**) [3]. However, this structural re-investigation showed that the structure of isoschizandrin is **3a** having the C-8α secondary methyl group as follows. The NOESY spectrum of **3a** (Fig. 3) showed appreciable NOE between the H-11 signal at δ6.54 and the C-8 secondary methyl signal at δ0.88, indicating that the C-8 secondary methyl group is α-oriented. The configuration of the C-8 position in **3a** was confirmed by the transformation of schizandrin (**4a**) to **3a**.

Treatment of **4a** with hydrochloric acid afforded **4c** and **4d** and some minor compounds. The physical and spectroscopic properties of **4c** and **4d** were identical with those of authentic samples, respectively [3]. Oxidation of **4c** with *m*-chloroperbenzoic acid afforded an epoxide **4e**. The presence of a methylene signal (δ2.54, 1H, *dd*, $J=4.5$, 1.5 Hz; 2.98, 1H, *d*, $J=4.5$ Hz) and no exo-methylene signal in the ^1H NMR spectrum of **4e** indicated that an epoxide ring in **4e** is formed by oxidation of exo-methylene group in **4c**. Reduction of **4e** with $LiAlH_4$ afforded **3a**. These findings indicate that isoschizandrin is the C-7 epimer of **4a**. From these spectral and chemical data, the structure of isoschizandrin was revised to (7*R*,8*S*,*R*-biar)-6,7,8,9-tetrahydro-1,2,3,12,13,14-hexamethoxy-7,8-dimethyl-7-dibenzo[*a*, *c*]cyclooctenol (**3a**).

EXPERIMENTAL

General. See ref. [2]. 10% $AgNO_3$–impregnated silica gel (Merck Kieselgel $60F_{254}$) was used for argentic prep. TLC.

2D-NOESY. 2D-NOE data were obtained from the phase sensitive NOESY using the standard DISNMR software package (Bruker): data were collected in 2K t_2 data with 4 scans and 1K t_1 increments. A mixing time of 2.5 sec was randomly modulated by ±10% in order to eliminate coherent magnetization transfer. The total experimental time was 10 hr. The data were filtered through a squared sinebell window filter (SSB2 = 2) and doubly transformed in a 2 × 1K data matrix (real + imaginary) with a digital resolution of 2.68 Hz per point in the ω_2 and ω_1 domain.

Plant material. Dried fruits of *Schisandra sphenanthera* Rehd. et Wils. collected in October 1987, were provided from the Institute of Medicine and Pharmacy Shanxi Province.

Extraction and isolation. The dried fruits (475 g) of *S. sphenanthera* were pulverized and extracted with *n*-hexane (1.5 l × 3, 3 hr each) under reflux. The *n*-hexane extracts were concd to give a brown mass (79.5 g). This afforded 12 frs (frs 1–12) on silica gel CC with *n*-hexane–EtOAc. Fr. 8 (2.87 g) was rechromatographed on silica gel (3 cm i.d. × 16 cm) with C_6H_6–Et_2O (9:1). The first eluate (200 ml) was concd to give a residue. This residue was

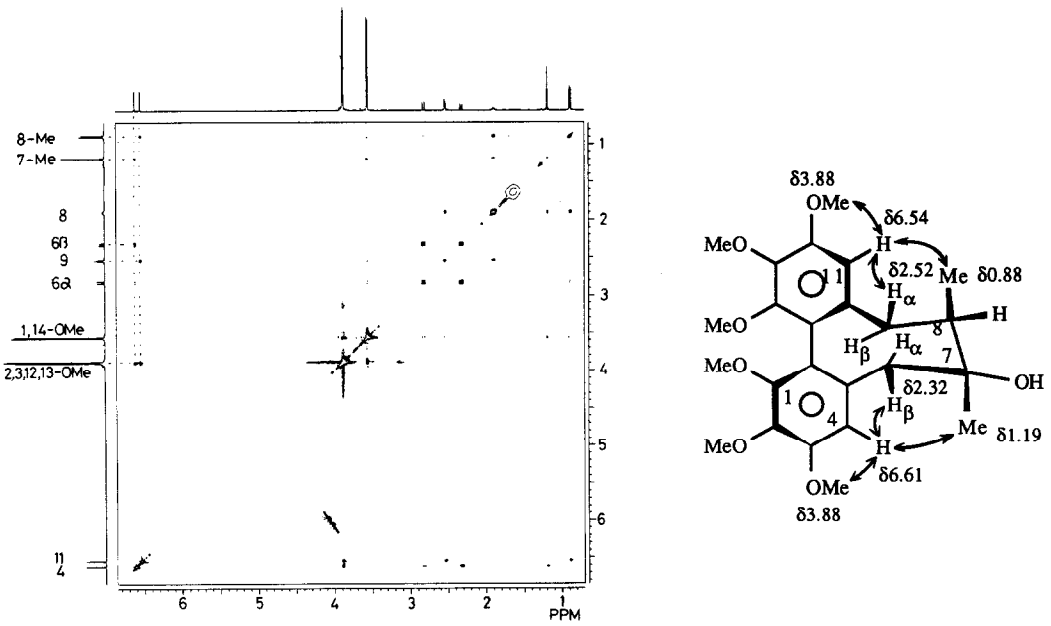

Fig. 3. NOE (↔) in the NOESY spectrum of compound **3a** (in $CDCl_3$).

purified by prep. TLC [C_6H_6–Et_2O (4:1), R_f 0.48] to give **2a** (24 mg, yield 0.0051%). Fr. 10 (0.81 g) was purified by repeated prep. TLC [1st: C_6H_6–Et_2O (3:2), R_f 0.69; 2nd: *n*-hexane–$CHCl_3$–EtOH (5:14:1), R_f 0.65] to give **1a** (22 mg, yield 0.0046%). Fr. 11 (2.985 g) was rechromatographed on silica gel (3 cm i.d. × 19 cm) with C_6H_6–Et_2O. The C_6H_6–Et_2O (85:15) eluate (1.74 g) was purified by repeated prep. TLC [1st: C_6H_6–Et_2O (3:2), R_f 0.40; 2nd: *n*-hexane–$CHCl_3$–EtOH (10:10:1), R_f 0.47] to give **2b** (22 mg, yield 0.0046%). Fr. 12 (0.173 g) was purified by repeated prep. TLC [1st: C_6H_6–Et_2O (3:2), R_f 0.19; 2nd: *n*-hexane–Me_2CO (7:2), R_f 0.25] to give **1a** (12.5 mg, yield 0.00026%).

Compounds **1b** and **2b** were identified by direct comparison with authentic samples [4, 5].

Benzoylgomisin U (**1a**). Needles from *n*-hexane–Et_2O, mp 166–167.5°, $[\alpha]_D^{24}$ −61.6° ($CHCl_3$; *c* 0.730). IR ν_{max}^{KBr} cm^{-1}: 3404 (OH), 1708 (C=O), 1582, 720, 712 (aromatic ring). UV λ_{max}^{EtOH} nm (log ε): 215.2 (4.72), 255 (sh 4.09), 289 (sh 3.49). EIMS *m/z* (rel. int.): 522 $[M]^+$ (37), 400 (100), 385 (13), 122 (23), 105 (75), 77 (37). High resolution MS *m/z*: 522.2248 (calc. for $C_{30}H_{34}O_8$: 522.2254). CD (*c* 0.0122, MeOH) $[\theta]^{24}$ (nm): 0 (203.7), +86 200 (213.1), 0 (222.6), −98 500 (235.0), −55 100 sh (248.6).

Tigloylgomisin O (**2a**). Amorphous powder, $[\alpha]_D^{24}$ −22.0° ($CHCl_3$; *c* 0.830). IR ν_{max}^{KBr} cm^{-1}: 1702 (C=O), 1650 (C=C), 1620, 1598 (aromatic ring). UV λ_{max}^{EtOH} nm (log ε): 215.2 (4.74), 258 (sh 4.94), 293 (sh 3.42). EIMS *m/z* (rel. int.): 498 $[M]^+$ (100), 399 (33), 398 (73), 342 (13), 83 (79), 55 (68). High resolution MS *m/z*: 498.2263 (calc. for 498.2254). CD (*c* 0.0117, MeOH) $[\theta]^{24}$ (nm): −4 800 (217.1), +5 700 (229.4), −57 200 (241.1), −47 200 sh (249.1), −11 700 sh (273.8).

Hydrolysis of compound **1a**. A soln of **1a** (10 mg) in 3% KOH–EtOH (1 ml) was kept at 65° for 3 hr, then diluted with H_2O (15 ml), and extracted with Et_2O. The Et_2O extract was washed with H_2O, dried over Na_2SO_4, and concd. The residue was purified by prep. TLC [C_6H_6–Et_2O (2:1)] to give **1c** (6.5 mg) as an amorphous powder, $[\alpha]_D^{24}$ −43.9° ($CHCl_3$; *c* 0.210). High resolution MS *m/z*: 418.1994 (calc. for $C_{23}H_{30}O_7$: 418.1992). This compound was identified as gomisin U (**1c**) by direct comparison with an authentic sample ($[\alpha]_D$, IR, EIMS, and ^1H NMR). The aq. soln was acidified with 1 M HCl and extracted with Et_2O. The Et_2O extract was washed with H_2O, dried over Na_2SO_4, and evapd. The residue was purified by prep. TLC [*n*-hexane–EtOAc (3:1)] to give benzoic acid as an amorphous powder, which was identical with an authentic sample by HPLC [HPLC conditions: column, YMC Pack A-312ODS (6 mm i.d. × 150 mm); mobile phase, 20 mM KH_2PO_4–MeCN (4:1); flow rate, 1 ml min^{-1}; detection, UV 215 nm; benzoic acid, RR_t (min), 11.8].

Hydrolysis of compound **2a**. A soln of **2a** (14 mg) in 3% KOH–EtOH (2 ml) was kept at 65° for 4 hr, then extracted with Et_2O. The Et_2O extract was washed with H_2O, dried over Na_2SO_4, and evapd. The residue was purified by prep. TLC [*n*-hexane–Me_2CO (7:3)] to give **2c** (8 mg) as prisms from *n*-hexane–Et_2O, mp 144–145.5°, $[\alpha]_D^{24}$ −35.3° ($CHCl_3$; *c* 0.340). High resolution MS *m/z*: 416.1842 (calc. for $C_{23}H_{28}O_7$: 416.1835). This compound was identified as gomisin O (**2c**) by direct comparison with an authentic sample ($[\alpha]_D$, IR, EIMS, and m mp). The aq. soln was treated as described for hydrolysis of **1a** to give tiglic acid (1 mg) as an amorphous powder, which was identical with an authentic sample by GC [GC conditions: column, 20% FFAP on Chromosorb WAW 80–100 mesh (3 mm i.d. × 2 m); column temp., 60°; inj. temp., 180°; carrier gas, He, 50 ml min^{-1}; tiglic acid, RR_t (min), 6.4].

Dehydration of schizandrin (**4a**) *with* HCl. Schizandrin (**4a**) (2.5 g) was dissolved in a mixture of 1 M HCl (50 ml) and dioxane (50 ml), and the soln was heated at 90° for 4 hr. After cooling, the reaction mixture was diluted with Et_2O and washed with H_2O. The Et_2O soln was dried over Na_2SO_4 and evapd. The residue was chromatographed on silica gel (4 cm i.d. × 18 cm) with *n*-hexane–Me_2CO. The fraction eluted with *n*-hexane–Me_2CO (4:1) was evapd to give **4a** (441 mg). The fraction eluted with *n*-hexane–acetone (17:3) was evapd to give a residue, which was purified by argentic prep. TLC [*n*-hexane–Et_2O (1:1)] to give **4c** (63 mg) and **4d** (137 mg) [9]. Compound **4c**: prisms from *n*-hexane–Et_2O, mp 115–117°, $[\alpha]_D^{24}$ +178° ($CHCl_3$; *c* 1.06) (found: C, 69.33; H, 7.42. Calc. for $C_{24}H_{30}O_6$: C, 69.54; H,

7.30%). This compound was identical ($[\alpha]_D$, IR, ^{1}H NMR, and m mp) with an authentic sample [3]. Compound **4d**: needles from *n*-hexane–Et_2O, mp 122–122.5°, $[\alpha]_D^{24}$ −104° ($CHCl_3$; *c* 1.36) (found: C, 69.45; H, 7.31. Calc. for $C_{24}H_{30}O_6$: C, 69. 54; H, 7.30%). This compound was identical ($[\alpha]_D$, IR, ^{1}H NMR, and m mp) with an authentic sample [3].

Oxidation of **4c** *with* m-*chloroperbenzoic acid.* Compound **4c** (60 mg) and *m*-chloroperbenzoic acid (60 mg) were dissolved in $CHCl_3$ (2 ml) and the soln was stirred at room temp. for 3 hr. The reaction mixture was diluted with EtOAc, washed 5% $NaHCO_3$ and H_2O, and evapd. The residue was purified by prep. TLC [*n*-hexane–Et_2O (2:3)] to give **4e** (22 mg) as an amorphous powder, $[\alpha]_D^{24}$ +123° ($CHCl_3$; *c* 0.72). IR ν_{max}^{KBr} cm^{-1}: 1598 (aromatic ring). EIMS *m/z* (rel. int.): 430 $[M]^+$ (100), 402 (27), 400 (14), 399 (17), 360 (11), 359 (14). High resolution MS *m/z*: 430.1984 (calc. for $C_{24}H_{30}O_7$: 430.1991).

Reduction of **4e** *with* $LiAlH_4$. $LiAlH_4$ (15 mg) was added to a soln of **4e** (16 mg) in dry THF (3 ml). The reaction mixture was stirred at room temp. for 3 hr, and then wet Et_2O added. The reaction mixture was purified by prep. TLC [*n*-hexane–EtOAc (3:2)] to give **3a** (7 mg) as an amorphous powder, $[\alpha]_D^{24}$ +85° ($CHCl_3$; *c* 0.275). High resolution MS *m/z*: 432.2125 (calc. for $C_{24}H_{32}O_7$: 432.2147). This compound was identified as isoschizandrin by direct comparison with an authentic sample ($[\alpha]_D$, IR, EIMS, and ^{1}H NMR).

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