

Benzoylgomisin Q and Benzoylgomisin P, Two New Lignans from *Schisandra sphenanthera* REHD. et WILS.

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Two new dibenzocyclooctadiene lignans, benzoylgomisin Q (1) and benzoylgomisin P (2) were isolated from the fruits of *Schisandra sphenanthera* REHD. et WILS. (Schisandraceae) together with angeloylgomisin P (8), tigloylgomisin P (9), and (+)-gomisin K₃ (10) which were the components of *Schisandra chinensis* BAILL. The structures of 1 and 2 were determined by spectral studies and chemical correlation with schisantherin A (3) and 8, respectively.

Keywords *Schisandra sphenanthera*; Schisandraceae; dibenzocyclooctadiene; lignan; benzoylgomisin Q; benzoylgomisin P; angeloylgomisin P; tigloylgomisin P; (+)-gomisin K₃

The fruits of *Schisandra sphenanthera* REHD. et WILS. (Schisandraceae) are used as an antitussive, tonic and sedative agent under the name of Wuweizi¹⁾ in Chinese traditional medicine together with the fruits of *Schisandra chinensis* BAILL. Six dibenzocyclooctadiene lignans (deoxyschizandrin and schisantherins A (3), B (4), C (5), D (6), and E (7)), a diarylbutane lignan (*dl*-wulignan), a 4-aryltetralone lignan (schisandrone), and a tetrahydrofuran lignan (*d*-epigalbacin) have been isolated from this plant by Liu *et al.*,^{2,3)} Li *et al.*,⁴⁾ and Huang *et al.*⁵⁾ This paper deals with the structures of two new dibenzocyclooctadiene lignans, benzoylgomisin Q (1) and benzoylgomisin P (2), and the isolation of eight known dibenzocyclooctadiene lignans, 3, 4, 5, 6, 7, angeloylgomisin P (8), tigloylgomisin P (9)⁶⁾ and (+)-gomisin K₃ (10)⁷⁾ from the fruits of *Schisandra sphenanthera* collected in the province of Shangxi in China.

Compounds 3, 4, 5, 6, and 7 were identified as schisan-

therins A, B, C, D, and E, respectively, isolated by Liu *et al.*³⁾ and the carbon shifts in the ¹³C-nuclear magnetic resonance (¹³C-NMR) spectra of these compounds were assigned as shown in Table II on the basis of ¹³C-NMR spectral studies of dibenzocyclooctadiene lignans.⁸⁾ Compounds 8, 9, and 10 were identified as angeloylgomisin P,⁹⁾ tigloylgomisin P,¹⁰⁾ and (+)-gomisin K₃ by direct comparison with authentic samples obtained from *Schisandra chinensis*.

Benzoylgomisin Q (1) was isolated as a white amorphous powder, C₃₁H₃₆O₉, [α]_D -118° (CHCl₃) and possessed the characteristic ultraviolet (UV) spectrum (λ_{max} 221.7, 255sh, and 289 nm) of a dibenzocyclooctadiene lignan. Its circular dichroism (CD) spectrum ([θ]₂₁₆ +60700, [θ]₂₃₅ -138000, [θ]₂₅₀ -67600sh) indicated that 1 had an *S*-biphenyl configuration.¹¹⁾ ¹H-NMR spectral analyses of it (Table I) showed the presence of six methoxyl groups on the aromatic rings, and a benzoyloxyl group, a secondary methyl

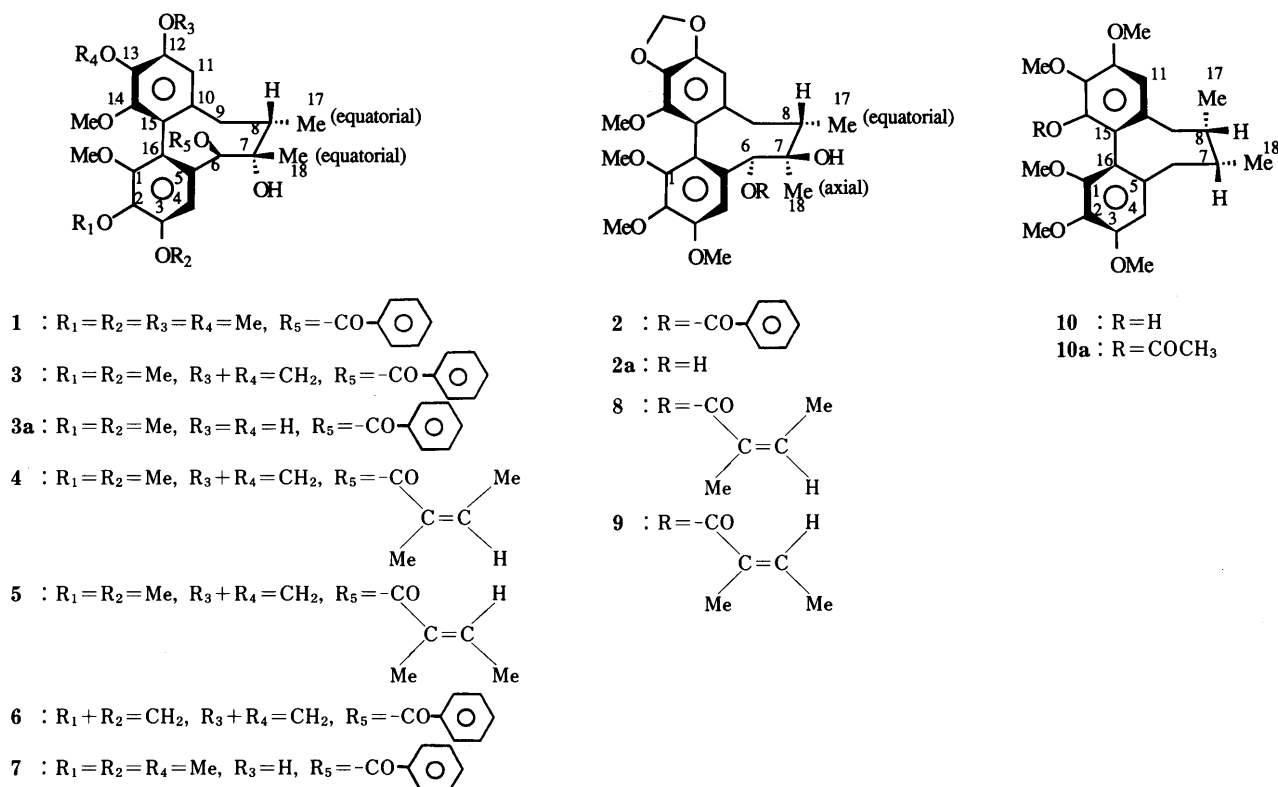


Chart 1

TABLE I. $^1\text{H-NMR}$ Spectral Data for 1, 3, 3a, 2, and 8 (δ in CDCl_3 , 200 MHz)

Com- pound	H-4, s H-11, s	H-6 α s	H-6 β ($J=\text{Hz}$)	H-9 α , dd ($J=\text{Hz}$)	H-9 β , dd ($J=\text{Hz}$)	H-C ₍₈₎ -Me m d ($J=\text{Hz}$)	HO-C ₍₇₎ -Me br s	OMe s	OCH ₂ O d ($J=\text{Hz}$)	C ₆ H ₅ CO- m
1	6.83 6.69	5.96	—	2.43 (14, 9.6)	2.29, d (14)	2.16 1.21 (7)	1.60 1.36	3.17, 3.39, 3.59, 3.89, 3.94, 3.99	—	7.21—7.51 (5H)
3	6.82 6.56	5.82	—	2.36 (13, 9, 9.5)	2.22, d (13.9)	2.12 1.18 (7)	1.53 1.38	3.30, 3.57, 3.89, 3.92	5.65 (1.5) 5.78 (1.5)	7.27—7.55 (5H)
3a	6.82 6.87	6.08	—	2.41 (13, 9)	2.26, d (13)	2.13 1.18 (7.1)	2.05 1.35	2.82, 3.48, 3.90 3.96	—	7.14—7.54 (5H)
2	6.97 6.53	—	5.72	2.11 (13.5, 9)	2.23 (13.5, 1)	1.94 1.17 (7)	1.94 1.21	3.62, 3.85 ($\times 2$), 3.90	5.99 (2H, s)	7.31—7.57 (3H) 8.02—8.07 (2H)
8 ^b	6.89 6.50	—	5.59	2.07 (13.7, 9.3)	2.18 (13.7, 1.5)	1.88 1.11 (6.6)	1.10	3.62, 3.82, 3.88, 3.91	5.98 (2H, s)	—

a) Hydroxyl signals were confirmed by addition of D_2O . b) Other signals: $\text{Me}-\overset{\beta}{\underset{\alpha}{\text{C}}}=\overset{\gamma}{\text{C}}-\text{CO}-\text{Me}$: 8, 2.00 (6H, m, α - and β -Me), 6.08 (1H, m, β -H). c) Abbreviations: br=broad, d=doublet, m=multiplet, q=quartet, s=singlet, t=triplet.

TABLE II. $^{13}\text{C-NMR}$ Spectral Data for 1, 3, 3a, 4, 5, 7, 2, and 8 (δ in CDCl_3 , ^{13}C at 50 MHz)

Carbon	1	3	3a	4 ^a	5 ^a	7	2 ^a	8 ^a
1	152.3	152.2	152.1	152.1	152.0	152.2	151.2	151.0
2	142.1	141.8 ^b	142.4	141.8 ^b	141.7 ^b	142.1	141.1 ^b	141.0 ^b
3	152.0	151.9	152.1	151.9	151.8	152.0	152.4	152.3
4	110.2	110.0	110.0	110.0	110.3	110.4	106.2	106.4
5	130.0	130.4	130.2	130.6	131.0	130.1	132.8	132.9
6	84.5	84.8	84.0	84.4	84.2	84.6	78.3	77.3
7	72.5	72.3	72.6	72.2	72.2	72.6	75.2	75.2
8	42.3	42.7	42.4	42.5	42.5	42.4	46.6	46.7
9	36.8	36.4	36.1	36.5	36.4	36.4	36.7	36.7
10	136.3	135.2	133.4	135.2	135.4	137.1	136.7	136.7
11	107.2	102.4	111.1	102.7	102.5	109.8	103.1	103.0
12	153.3	148.8	144.2	148.7	148.6	149.1	149.5	149.3
13	140.0	134.1	134.3	134.3	134.3	137.5	135.7	135.6
14	150.7	140.2 ^b	143.7	140.6 ^b	140.6 ^b	149.3	141.7 ^b	141.4 ^b
15	122.5	122.2 ^c	122.2 ^b	122.3 ^c	122.1 ^c	122.4 ^b	123.0 ^c	122.9 ^c
16	122.5	121.1 ^c	120.2 ^b	121.2 ^c	121.6 ^c	121.5 ^b	119.6 ^c	119.5 ^c
17	19.0	18.9	18.9	18.9	18.9	18.9	18.8	18.8
18	28.1	28.2	28.1	28.2	28.1	28.1	17.7	17.5
OMe 1,14	60.2, ^b 59.8 ^b	60.7, ^d 58.6	60.9, 59.2	60.6, 59.0	60.6, 58.9	59.9, ^c 58.9 ^c	60.6, 60.6	60.6, 59.9
2,13	60.9, ^c 60.7 ^c	60.8, ^d —	61.1, —	60.8, —	60.8, —	60.9, ^d 60.7 ^d	60.9, —	60.9, —
3,12	56.0, ^d 56.2 ^d	55.9, —	56.1, —	55.9, —	55.7, —	56.0, —	56.0, —	55.8, —
OCH ₂ O		100.4	—	100.5	100.5	—	101.1	101.0
Benzoyl 1'		129.3	129.1			129.3	130.3	
2',6'		129.5	129.6			129.6	129.5	
3',5'		127.9	128.2			128.1	128.5	
4'		132.9	133.3			133.4	133.1	
C=O		164.8	165.1			164.9	165.2	

a) Other signals: Angeloyl: 4, 15.7 (q, β -Me), 19.7 (q, α -Me), 121.7 (s), 139.8 (d) (C=C), 165.8 (s, C=O); 8, 15.8 (q, β -Me), 20.7 (q, α -Me), 127.5 (s), 138.7 (d) (C=C), 166.4 (s, C=O). Tigloyl: 5, 11.5 (q, α -Me), 14.2 (q, β -Me), 127.6 (s), 137.5 (d) (C=C), 166.3 (C=O). b—d) Assignments within any vertical column may be reversed.

group and a tertiary methyl group attached to a carbon carrying a hydroxyl group. The mass spectrum (MS) with peaks at m/z 552 (M^+), 430 ($\text{M}^+ - \text{C}_6\text{H}_5\text{COOH}$) and 105 ($\text{C}_6\text{H}_5\text{CO}^+$) also supported the presence of a benzoyloxyl group in 1. The $^1\text{H-NMR}$ spectrum of 1 is very similar to that of 3 having C-6 β -benzoyloxyl, C-7 β -tertiary methyl and C-8 α -secondary methyl groups and the twist-boat-chair conformation of the cyclooctadiene ring, except for the functional groups on the aromatic rings. By comparisons of its ^1H - and $^{13}\text{C-NMR}$ spectra with those of 3 (Tables I and II), it was assumed that the methylenedioxy moiety at C-12 and -13 positions in 3 was replaced by two methoxyl groups in 1. Finally, the structure of 1 was confirmed by the chemical correlation with 3 as described below.

In a previous paper,¹²⁾ we reported on the selective cleavage of methylenedioxy moiety with lead tetraacetate

[$\text{Pb}(\text{OAc})_4$] in dry benzene. Treatment of 3 with $\text{Pb}(\text{OAc})_4$ in dry benzene afforded a diphenol (3a), $\text{C}_{29}\text{H}_{32}\text{H}_9$. Methylation of 3a afforded a dimethyl ether, which was identified as benzoylgomisin Q (1) by direct comparison ($[\alpha]_D$, infrared (IR), $^1\text{H-NMR}$, and MS). This fact indicated that the configurations of C-6-benzoyloxyl, C-7-tertiary methyl and C-8-secondary methyl groups in 1 were the same as those in 3.

Thus, the structure of benzoylgomisin Q was determined as (6S,7S,8S,S-biar)-6-benzoyloxy-6,7,8,9-tetrahydro-1,2,3,12,13,14-hexamethoxy-7,8-dimethyl-7-dibenzo[a,c]-cyclooctenol (1).

Benzoylgomisin P (2) was isolated as a white amorphous powder, $\text{C}_{30}\text{H}_{32}\text{O}_9$, $[\alpha]_D -22.1^\circ$ (CHCl_3). Its UV, IR, $^1\text{H-NMR}$ (Table I) spectral analyses indicated that 2 was a dibenzocyclooctadiene lignan possessing a methylenedioxy

moiety and four methoxyl groups on the aromatic rings, and a secondary methyl group, a tertiary methyl group attached to a carbon carrying a hydroxyl group and a benzoyloxy group on the cyclooctadiene ring. The CD spectrum ($[\theta]_{211} + 89800$, $[\theta]_{252} - 652000$) indicated that **2** had an *S*-biphenyl configuration. In the ^1H -NMR spectra of **2** and **3**, the tertiary methyl group (δ 1.21) of **2** appeared at higher field than that of **3** (δ 1.36), indicating that it was shielded by the aromatic ring. This suggested the C-7-tertiary methyl group in **2** was α -configuration (axial orientation), different from that in **3** (equatorial orientation). The C-8-secondary methyl group in **2** appeared at the same region as that in **3**, suggesting that the C-8-secondary methyl group in **2** was the same α -configuration as that in **3**. Comparison of the ^1H - and ^{13}C -NMR data of **2** and angeloylgomisins **P** (**8**) having C-6 α -angeloxyl, C-7 α -tertiary methyl and C-8-secondary methyl groups, suggested that these compounds differed by acid moiety at the C-6 position.

On hydrolysis with 3% ethanolic potassium hydroxide, **2** gave benzoic acid and a diol (**2a**), $\text{C}_{23}\text{H}_{28}\text{O}_8$. Compound **2a** was identified as gomisin **P**⁶⁾ which had been obtained by hydrolysis of **8** and had two hydroxyl groups at the C-6 α and C-7 β positions. The singlet at δ 4.34 in the ^1H -NMR spectrum of **2a**, which appeared at δ 5.72 in **2**, was assigned to a benzylic methine, indicating that the benzoyl group in **2** was linked to a C-6 α hydroxyl group of **2a**. Thus, the structure of benzoylgomisin **P** was determined as (6*R*,7*R*,8*S*,*S*-biar)-6-benzoyloxy-6,7,8,9-tetrahydro-1,2,3,14-tetramethoxy-7,8-dimethyl-12,13-methylenedioxy-7-dibenzo-*[a,c]*cyclooctenol (**2**).

Experimental

Details of the instruments and chromatographic conditions used throughout this work are the same as described in the previous paper,¹³⁾ except for the following. Gas liquid chromatography (GLC) was carried out on a Shimadzu gas chromatograph GC-9A with hydrogen flame ionization detector.

Extraction Dried fruits (475 g) of *Schisandra sphenanthera* REHD. et WILS. collected in October 1987, were pulverized and extracted with hexane (1.5 l $\times$ 3, 3 h each) under reflux. The hexane extracts were concentrated to give a brown mass (79.50 g). This residue was chromatographed on silica gel (6 cm i.d. $\times$ 20 cm), developing with hexane-EtOAc to give twelve fractions; I (0.08 g), II (9.20 g), III (24.51 g), IV (19.37 g), V (1.14 g), VI (5.54 g), VII (4.31 g), VIII (2.87 g), IX (0.31 g), X (0.81 g), XI (2.98 g) and XII (0.17 g).

Fractions IX and XII were repeatedly chromatographed on silica gel with various solvent systems to give **8** (40 mg) and **7** (17 mg, yield 0.0046%). Fraction XI was rechromatographed on silica gel using benzene-ether. The fraction eluted with benzene-ether (85:15) was concentrated to give a residue (1.736 g). This residue was repeatedly chromatographed on silica gel with various solvent systems to give **1** (23 mg, yield 0.0048%), **3** (1.332 g, yield 0.29%), **4** (32 mg, yield 0.0069%), and **5** (199 mg, yield 0.042%). Fraction X was repeatedly chromatographed on silica gel with various solvent systems to give **2** (17.5 mg, yield 0.0037%), **6** (4.1 mg, yield 0.0009%), **8** (82 mg, total 122 mg, yield 0.026%), **9** (12 mg, yield 0.0025%), and crude **10** (80 mg). Crude **10** (80 mg) was acetylated with a mixture of Ac_2O (0.3 ml) and pyridine (0.5 ml) at room temperature overnight to give a monoacetate (**10a**, 54 mg) as colorless needles (from ether-hexane), mp 159–160.5°C, $[\alpha]_D^{24} + 54^\circ$ ($c=1.81$, CHCl_3). Anal. Calcd for $\text{C}_{25}\text{H}_{32}\text{O}_7$: C, 67.55; H, 7.26. Found: C, 67.63; H, 7.26. ^1H -NMR δ in CDCl_3 : 0.78 (3H, d, $J=7$ Hz), 0.99 (3H, d, $J=7$ Hz), 1.72–2.00 (2H, m, 2 $\times$ CH), 1.94 (3H, s, COCH_3), 3.62, 3.85, 3.86, 3.89, 3.90 (each 3H, s, 5 $\times$ OMe), 6.51, 6.70 (each 1H, s, 2 $\times$ aromatic H). Compound **10a** (50 mg) was dissolved in 3% KOH-EtOH (2 ml) and the reaction mixture was kept at 50°C for 1 h, then diluted with ether. The ethereal solution was washed with H_2O , dried over Na_2SO_4 and concentrated to give **10** (37 mg, yield 0.0078%).

Benzoylgomisin Q (**1**) A white amorphous powder, $[\alpha]_D^{23} - 118^\circ$

($c=0.890$, CHCl_3). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3520 (OH), 1720, 1700 (C=O), 1598, 712 (aromatic ring). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 221.7 (4.70), 255 (sh 4.10), 289 (sh 3.36). CD ($c=0.0115$, MeOH) $[\theta]^{26}$ (nm): +60700 (216), 0 (223), -138000 (235), -67600 (sh 250). MS m/z (%): 552 (M^+ , 66), 430 ($\text{M}^+ - \text{C}_6\text{H}_5\text{COOH}$, 44), 360 (13), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 100), 77 (26). High-resolution MS, Calcd for $\text{C}_{31}\text{H}_{36}\text{O}_9(\text{M}^+)$: 552.2359. Found: 552.2356.

Benzoylgomisin P (**2**) A white amorphous powder, $[\alpha]_D^{24} - 22.1^\circ$ ($c=0.453$, CHCl_3). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3524 (OH), 1724 (C=O), 1622, 1600, 710 (aromatic ring). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 222.8 (4.71), 280.6 (3.63), 289.8 (3.56). CD ($c=0.0112$, MeOH) $[\theta]^{28}$ (nm): +89800 (211), 0 (236), -65200 (252). MS m/z (%): 536 (M^+ , 13), 414 ($\text{M}^+ - \text{C}_6\text{H}_5\text{COOH}$, 24), 343 (32), 342 (24), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 100), 77 (46). High-resolution MS, Calcd for $\text{C}_{30}\text{H}_{32}\text{O}_9(\text{M}^+)$: 536.2046. Found: 536.2049.

Schisantherin A (**3**) Colorless prisms (from MeOH), mp 122–124°C, $[\alpha]_D^{23} - 187^\circ$ ($c=1.74$, CHCl_3). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3388 (OH), 1728 (C=O), 1620, 1598, 712 (aromatic ring). MS m/z (%): 536 (M^+ , 44), 414 ($\text{M}^+ - \text{C}_6\text{H}_5\text{COOH}$, 47), 343 (63), 342 (45), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 100), 77 (36). Anal. Calcd for $\text{C}_{30}\text{H}_{32}\text{O}_9 \cdot 1/2\text{CH}_3\text{OH}$: C, 69.29; H, 6.20. Found: C, 69.29; H, 6.21.

Schisantherin B (**4**) Colorless prisms (from MeOH), mp 90–91°C, $[\alpha]_D^{24} - 25.8^\circ$ ($c=0.31$, CHCl_3). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3548 (OH), 1696 (C=O), 1644 (C=C), 1620, 1600 (aromatic ring). MS m/z (%): 514 (M^+ , 42), 414 (75), 371 (32), 343 (93), 83 [$\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{CO}^+$, 87], 55 (100). High-resolution MS, Calcd for $\text{C}_{28}\text{H}_{34}\text{O}_9(\text{M}^+)$: 514.2203. Found: 514.2205. Anal. Calcd for $\text{C}_{28}\text{H}_{34}\text{O}_9 \cdot 1/2\text{CH}_3\text{OH}$: C, 64.52; H, 6.84. Found: C, 64.77; H, 6.76.

Schisantherin C (**5**) Colorless prisms (from MeOH), mp 99–101°C, $[\alpha]_D^{25} - 150.3^\circ$ ($c=2.88$, CHCl_3). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3524 (OH), 1710, 1692 (C=O), 1648 (C=C), 1622, 1598 (aromatic ring). MS m/z (%): 514 (M^+ , 46), 414 (72), 371 (20), 343 (100), 83 [$\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{CO}^+$, 77], 55 (89). High-resolution MS, Calcd for $\text{C}_{28}\text{H}_{34}\text{O}_9(\text{M}^+)$: 514.2203. Found: 514.2200. Anal. Calcd for $\text{C}_{28}\text{H}_{34}\text{O}_9 \cdot 1/2\text{CH}_3\text{OH}$: C, 64.52; H, 6.84. Found: C, 64.80; H, 6.77.

Schisantherin D (**6**) Colorless prisms (from MeOH), mp 122–125°C, $[\alpha]_D^{24} - 150^\circ$ ($c=0.978$, CHCl_3). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3408 (OH), 1722 (C=O), 1622, 712 (aromatic ring). MS m/z (%): 520 (M^+ , 32), 398 (42), 326 (74), 277 (35), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 100), 77 (48). High-resolution MS, Calcd for $\text{C}_{29}\text{H}_{28}\text{O}_9(\text{M}^+)$: 520.1733. Found: 520.1743.

Schisantherin E (**7**) Colorless needles (from CH_2Cl_2 -benzene), mp 219–220.5°C, $[\alpha]_D^{24} - 186^\circ$ ($c=0.526$, CHCl_3). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3488, 3392 (OH), 1704 (C=O), 1584, 712 (aromatic ring). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 220 (4.67), 257 (sh 4.05), 285 (sh 3.55). MS m/z (%): 538 (M^+ , 42), 416 ($\text{M}^+ - \text{C}_6\text{H}_5\text{COOH}$, 49), 345 (36), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 100), 77 (34). High-resolution MS, Calcd for $\text{C}_{30}\text{H}_{34}\text{O}_9(\text{M}^+)$: 538.2203. Found: 538.2204. Anal. Calcd for $\text{C}_{30}\text{H}_{34}\text{O}_9$: C, 66.90; H, 6.36. Found: C, 66.77; H, 6.40.

Angeloylgomisin P (**8**) A white amorphous powder, $[\alpha]_D^{24} - 93.5^\circ$ ($c=1.68$, CHCl_3). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3528 (OH), 1720 (C=O), 1646 (C=C), 1622, 1598 (aromatic ring). MS m/z (%): 514 (M^+ , 25), 414 (54), 343 (76), 300 (54), 83 [$\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{CO}^+$, 74], 55 (100). High-resolution MS, Calcd for $\text{C}_{28}\text{H}_{34}\text{O}_9(\text{M}^+)$: 514.2203. Found: 514.2198.

Tigloylgomisin P (**9**) A white amorphous powder, $[\alpha]_D^{24} - 56.1^\circ$ ($c=0.980$, CHCl_3). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3524 (OH), 1714 (C=O), 1648 (C=C), 1622, 1598 (aromatic ring). MS m/z (%): 514 (M^+ , 30), 414 (82), 371 (18), 343 (100), 300 (47), 83 [$\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{CO}^+$, 74], 55 (66). High-resolution MS, Calcd for $\text{C}_{28}\text{H}_{34}\text{O}_9(\text{M}^+)$: 514.2203. Found: 514.2212.

(+)-Gomisin K₃ (**10**) Colorless needles (from ether-hexane), mp 99–100°C, $[\alpha]_D^{24} + 56.5^\circ$ ($c=1.70$, CHCl_3). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3546 (OH), 1614, 1598, 1582 (aromatic ring). MS m/z (%): 402 (M^+ , 100), 370 (4.5), 356 (10), 345 (7.7), 221 (7.7). High-resolution MS, Calcd for $\text{C}_{23}\text{H}_{28}\text{O}_6(\text{M}^+)$: 402.2042. Found: 402.2046.

Treatment of 3 with $\text{Pb}(\text{OAc})_4$ in Benzene A solution of **3** (84 mg) and $\text{Pb}(\text{OAc})_4$ (126 mg) in dry benzene (4 ml) was stirred at 50°C for 8 h, then diluted with ether. The total mixture was washed with H_2O , dried over Na_2SO_4 and concentrated. The residue was purified by preparative thin layer chromatography (prep. TLC) [hexane-acetone (7:3)] to give an oxidative product (R_f 0.22, 19 mg) and unchanged **3** (R_f 0.25, 27 mg). A solution of the oxidative product in 80% AcOH (1 ml) was stirred at room temperature for 1 h. The reaction mixture was purified by prep. TLC [hexane-acetone (3:2)] to give **3a** (12 mg) as a white amorphous powder (from ether-hexane), mp 185–186°C, $[\alpha]_D^{25} - 182^\circ$ ($c=0.466$, CHCl_3). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3476 (OH), 1720 (C=O), 1600, 712 (aromatic ring). MS m/z (%): 524 (M^+ , 11), 402 (22), 330 (8.0), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 100), 77 (59). High-resolution MS, Calcd for $\text{C}_{29}\text{H}_{32}\text{O}_9(\text{M}^+)$: 524.2046. Found: 524.2043.

Methylation of 3a Me_2SO_4 (0.1 ml) and K_2CO_3 (50 mg) were added to a solution of **3a** (10 mg) in dry acetone (1 ml). The reaction mixture was

stirred at 45 °C for 4 h, then diluted with ether. The ethereal solution was washed with H₂O, dried over Na₂SO₄ and concentrated. The residue was purified by prep. TLC [hexane-acetone (7:3)] to give a dimethyl ether (6.7 mg) as a white amorphous powder, $[\alpha]_D^{25}$ -115° (*c*=0.285, CHCl₃). High-resolution MS, Calcd for C₃₁H₃₆O₉ (M⁺): 552.2359. Found: 552.2368. This compound was identified as benzoylgomisin Q (1) by direct comparison with an authentic sample ($[\alpha]_D$, IR, MS, and ¹H-NMR).

Hydrolysis of 2 A solution of 2 (12 mg) in 3% KOH-EtOH (1.5 ml) was kept at 65 °C for 3 h, then diluted with H₂O (15 ml) and extracted with ether (15 ml × 3). The combined ethereal extract was washed with H₂O, dried over Na₂SO₄ and concentrated to give a residue. This residue was purified by prep. TLC [benzene-ether (3:2)] to give a diol (2a), colorless needles (from ether-hexane), mp 113–115 °C, $[\alpha]_D^{25}$ -97.4° (*c*=0.390, CHCl₃). IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3504, 3388 (OH), 1614, 1600 (aromatic ring). MS *m/z* (%): 432 (M⁺, 79), 414 (69), 360 (20), 343 (100), 342 (68), 312 (47). High-resolution MS, Calcd for C₂₃H₂₈O₈ (M⁺): 432.1784. Found: 432.1780. ¹H-NMR δ in CDCl₃: 1.10 (3H, s), 1.10 (3H, d, *J*=7.1 Hz), 1.80 (1H, m), 1.99 (2H, br s, D₂O exchangeable), 2.07 (1H, dd, *J*=13.9, 9.6 Hz), 2.14 (1H, dd, *J*=13.9, 1 Hz), 3.58, 3.83, 3.91, 3.92 (each 3H, s), 4.34 (1H, s), 5.94 (1H, d, *J*=1.5 Hz), 5.95 (1H, d, *J*=1.5 Hz), 6.17 (1H, s), 7.10 (1H, s). This compound was identified as gomisin P (2a)⁶⁾ by direct comparison with an authentic sample (mixed melting point, $[\alpha]_D$, IR and ¹H-NMR).

The aqueous solution was acidified with 1 N HCl and extracted with ether. The ethereal extract was washed with H₂O, dried over Na₂SO₄ and concentrated to give a residue (1 mg). This compound was identified as benzoic acid by direct comparison (GLC) with an authentic sample [GLC conditions: column, 20% FFAP on Chromosorb WAW (80–100 mesh) 3 mm i.d. × 2 m; column temperature, 70 °C; injection temperature, 180 °C; carrier gas, He, 50 ml/min; benzoic acid, *t_R* (min), 6.8].

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