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

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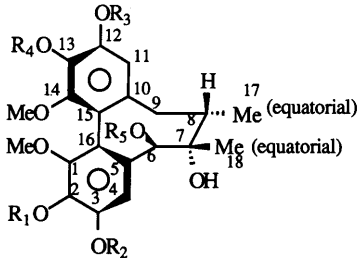
**Two new dibenzocyclooctadiene lignans, benzoylgomisin Q (1) and benzoylgomisin P (2) were isolated from the fruits of *Schisandra sphenanthera* REHD. *et* WILS. (Schisandraceae) together with angeloylgomisin P (8), tigloylgomisin P (9), and (+)-gomisin $K_3$ (10) which were the components of *Schisandra chinensis* BAILL. The structures of 1 and 2 were determined by spectral studies and chemical correlation with schisantherin A (3) and 8, respectively.**

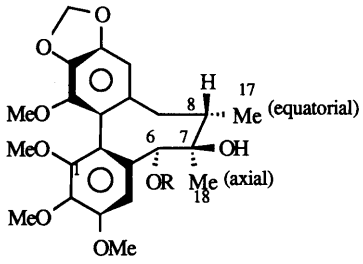
**Keywords** *Schisandra sphenanthera*; Schisandraceae; dibenzocyclooctadiene; lignan; benzoylgomisin Q; benzoylgomisin P; angeloylgomisin P; tigloylgomisin P; (+)-gomisin $K_3$

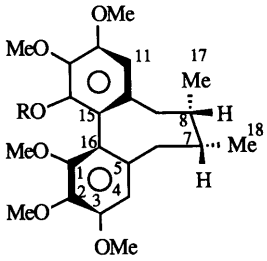
The fruits of *Schisandra sphenanthera* REHD. *et* WILS. (Schisandraceae) are used as an antitussive, tonic and sedative agent under the name of Wuweizi[1] in Chinese traditional medicine together with the fruits of *Schisandra chinensis* BAILL. Six dibenzocyclooctadiene lignans (deoxyschizandrin and 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 $K_3$ (**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 schisantherins A, B, C, D, and E, respectively, isolated by Liu *et al.*[3] and the carbon shifts in the $^{13}$C-nuclear magnetic resonance ($^{13}$C-NMR) spectra of these compounds were assigned as shown in Table II on the basis of $^{13}$C-NMR spectral studies of dibenzocyclooctadiene lignans.[8] Compounds **8**, **9**, and **10** were identified as angeloylgomisin P,[9] tigloylgomisin P,[10] and (+)-gomisin $K_3$ by direct comparison with authentic samples obtained from *Schisandra chinensis*.

Benzoylgomisin Q (**1**) was isolated as a white amorphous powder, $C_{31}H_{36}O_9$, $[\alpha]_D$ −118° ($CHCl_3$) and possessed the characteristic ultraviolet (UV) spectrum ($\lambda_{max}$ 221.7, 255sh, and 289 nm) of a dibenzocyclooctadiene lignan. Its circular dichroism (CD) spectrum ($[\theta]_{216}$ +60700, $[\theta]_{235}$ −138000, $[\theta]_{250}$ −67600sh) indicated that **1** had an *S*-biphenyl configuration.[11] $^1$H-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




**1** : $R_1=R_2=R_3=R_4=Me$, $R_5=-CO-$(Ph)

**3** : $R_1=R_2=Me$, $R_3+R_4=CH_2$, $R_5=-CO-$(Ph)

**3a** : $R_1=R_2=Me$, $R_3=R_4=H$, $R_5=-CO-$(Ph)

**4** : $R_1=R_2=Me$, $R_3+R_4=CH_2$, $R_5=-CO-C(Me)=C(Me)H$

**5** : $R_1=R_2=Me$, $R_3+R_4=CH_2$, $R_5=-CO-C(H)=C(Me)Me$

**6** : $R_1+R_2=CH_2$, $R_3+R_4=CH_2$, $R_5=-CO-$(Ph)

**7** : $R_1=R_2=R_4=Me$, $R_3=H$, $R_5=-CO-$(Ph)

**2** : $R=-CO-$(Ph)

**2a** : $R=H$

**8** : $R=-CO-C(Me)=C(Me)H$

**9** : $R=-CO-C(H)=C(Me)Me$

**10** : $R=H$

**10a** : $R=COCH_3$

Chart 1

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

| Compound | H-4, s H-11, s | H-6α s | H-6β ($J$=Hz) | H-9α, dd ($J$=Hz) | H-9β, dd ($J$=Hz) | H–C(8)–Me m | d ($J$=Hz) | HO[a]–C(7)–Me br s | s | OMe s | $OCH_2O$ d ($J$=Hz) | $C_6H_5CO$– m |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 6.83 | 5.96 | — | 2.43 | 2.29, d | 2.16 | 1.21 | 1.60 | 1.36 | 3.17, 3.39, 3.59, | — | 7.21—7.51 (5H) |
| | 6.69 | | | (14, 9.6) | (14) | | (7) | | | 3.89, 3.94, 3.99 | | |
| **3** | 6.82 | 5.82 | — | 2.36 | 2.22, d | 2.12 | 1.18 | 1.53 | 1.38 | 3.30, 3.57, 3.89, | 5.65 (1.5) | 7.27—7.55 (5H) |
| | 6.56 | | | (13, 9, 9.5) | (13.9) | | (7) | | | 3.92 | 5.78 (1.5) | |
| **3a** | 6.82 | 6.08 | — | 2.41 | 2.26, d | 2.13 | 1.18 | 2.05 | 1.35 | 2.82, 3.48, 3.90 | — | 7.14—7.54 (5H) |
| | 6.87 | | | (13, 9) | (13) | | (7.1) | | | 3.96 | | |
| **2** | 6.97 | — | 5.72 | 2.11 | 2.23 | 1.94 | 1.17 | 1.94 | 1.21 | 3.62, 3.85 (×2), | 5.99 (2H, s) | 7.31—7.57 (3H) |
| | 6.53 | | | (13.5, 9) | (13.5, 1) | | (7) | | | 3.90 | | 8.02—8.07 (2H) |
| **8**[b] | 6.89 | — | 5.59 | 2.07 | 2.18 | 1.88 | 1.11 | | 1.10 | 3.62, 3.82, 3.88, | 5.98 (2H, s) | — |
| | 6.50 | | | (13.7, 9.3) | (13.7, 1.5) | | (6.6) | | | 3.91 | | |

*a*) Hydroxyl signals were confirmed by addition of $D_2O$. *b*) Other signals: $Me\overset{\beta}{>}C=C\overset{\alpha}{<}CO-Me$: **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. $^{13}$C-NMR Spectral Data for **1**, **3**, **3a**, **4**, **5**, **7**, **2**, and **8** ($\delta$ 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, — |
| $OCH_2O$ | | 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 ($M^+ - C_6H_5COOH$) and 105 ($C_6H_5CO^+$) also supported the presence of a benzoyloxyl group in **1**. The $^1$H-NMR spectrum of **1** is very similar to that of **3** having C-6β-benzoyloxyl, C-7β-tertiary methyl and C-8α-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 $^1$H- and $^{13}$C-NMR spectra with those of **3** (Tables I and II), it was assumed that the methylenedioxyl 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 methylenedioxyl moiety with lead tetraacetate [$Pb(OAc)_4$] in dry benzene. Treatment of **3** with $Pb(OAc)_4$ in dry benzene afforded a diphenol (**3a**), $C_{29}H_{32}H_9$. Methylation of **3a** afforded a dimethyl ether, which was identified as benzoylgomisin Q (**1**) by direct comparison ($[\alpha]_D$, infrared (IR), $^1$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 (6*S*,7*S*,8*S*,*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, $C_{30}H_{32}O_9$, $[\alpha]_D$ −22.1° ($CHCl_3$). Its UV, IR, $^1$H-NMR (Table I) spectral analyses indicated that **2** was a dibenzocyclooctadiene lignan possessing a methylenedioxyl

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 benzoyloxyl group on the cyclooctadiene ring. The CD spectrum ($[\theta]_{211}$ +89800, $[\theta]_{252}$ −652000) indicated that **2** had an *S*-biphenyl configuration. In the $^1$H-NMR spectra of **2** and **3**, the tertiary methyl group ($\delta$ 1.21) of **2** appeared at higher field than that of **3** ($\delta$ 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 $^1$H- and $^{13}$C-NMR data of **2** and angeloylgomisin P (**8**) having C-6α-angeloxyl, C-7α-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**), $C_{23}H_{28}O_8$. Compound **2a** was identified as gomisin P[6] which had been obtained by hydrolysis of **8** and had two hydroxyl groups at the C-6α and C-7β positions. The singlet at $\delta$ 4.34 in the $^1$H-NMR spectrum of **2a**, which appeared at $\delta$ 5.72 in **2**, was assigned to a benzylic methine, indicating that the benzoyl group in **2** was linked to a C-6α 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 detecter.

**Extraction** Dried fruits (475 g) of *Schisandra sphenanthera* REHD. *et* WILS. collected in October 1987, were pulverized and extracted with hexane (1.5 l × 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. × 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° (*c*=1.81, $CHCl_3$). *Anal.* Calcd for $C_{25}H_{32}O_7$: C, 67.55; H, 7.26. Found: C, 67.63; H, 7.26. $^1$H-NMR $\delta$ in $CDCl_3$: 0.78 (3H, d, *J*=7 Hz), 0.99 (3H, d, *J*=7 Hz), 1.72—2.00 (2H, m, 2 × CH), 1.94 (3H, s, $COCH_3$), 3.62, 3.85, 3.86, 3.89, 3.90 (each 3H, s, 5 × OMe), 6.51, 6.70 (each 1H, s, 2 × 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° (*c*=0.890, $CHCl_3$). IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3520 (OH), 1720, 1700 (C=O), 1598, 712 (aromatic ring). UV $\lambda_{max}^{EtOH}$ 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 ($M^+ - C_6H_5COOH$, 44), 360 (13), 105 ($C_6H_5CO^+$, 100), 77 (26). High-resolution MS, Calcd for $C_{31}H_{36}O_9(M^+)$: 552.2359. Found: 552.2356.

**Benzoylgomisin P (2)** A white amorphous powder, $[\alpha]_D^{24}$ −22.1° (*c*=0.453, $CHCl_3$). IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3524 (OH), 1724 (C=O), 1622, 1600, 710 (aromatic ring). UV $\lambda_{max}^{EtOH}$ 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 ($M^+ - C_6H_5COOH$, 24), 343 (32), 342 (24), 105 ($C_6H_5CO^+$, 100), 77 (46). High-resolution MS, Calcd for $C_{30}H_{32}O_9(M^+)$: 536.2046. Found: 536.2049.

**Schisantherin A (3)** Colorless prisms (from MeOH), mp 122—124 °C, $[\alpha]_D^{23}$ −187° (*c*=1.74, $CHCl_3$). IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3388 (OH), 1728 (C=O), 1620, 1598, 712 (aromatic ring). MS *m/z* (%): 536 ($M^+$, 44), 414 ($M^+ - C_6H_5COOH$, 47), 343 (63), 342 (45), 105 ($C_5H_5CO^+$, 100), 77 (36). *Anal.* Calcd for $C_{30}H_{32}O_9 \cdot 1/2CH_3OH$: 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° (*c*=0.31, $CHCl_3$). IR $\nu_{max}^{KBr}$ 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 [$CH_3CH=C(CH_3)CO^+$, 87], 55 (100). High-resolution MS, Calcd for $C_{28}H_{34}O_9(M^+)$: 514.2203. Found: 514.2205. *Anal.* Calcd for $C_{28}H_{34}O_9 \cdot 1/2CH_3OH$: 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° (*c*=2.88, $CHCl_3$). IR $\nu_{max}^{KBr}$ 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 [$CH_3CH=C(CH_3)CO^+$, 77], 55 (89). High-resolution MS, Calcd for $C_{28}H_{34}O_9(M^+)$: 514.2203. Found: 514.2200. *Anal.* Calcd for $C_{28}H_{34}O_9 \cdot 1/2CH_3OH$: 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° (*c*=0.978, $CHCl_3$). IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3408 (OH), 1722 (C=O), 1622, 712 (aromatic ring). MS *m/z* (%): 520 ($M^+$, 32), 398 (42), 326 (74), 277 (35), 105 ($C_6H_5CO^+$, 100), 77 (48). High-resolution MS, Calcd for $C_{29}H_{28}O_9(M^+)$: 520.1733. Found: 520.1743.

**Schisantherin E (7)** Colorless needles (from $CH_2Cl_2$–benzene), mp 219—220.5 °C, $[\alpha]_D^{24}$ −186° (*c*=0.526, $CHCl_3$). IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3488, 3392 (OH), 1704 (C=O), 1584, 712 (aromatic ring). UV $\lambda_{max}^{EtOH}$ nm (log ε): 220 (4.67), 257 (sh 4.05), 285 (sh 3.55). MS *m/z* (%): 538 ($M^+$, 42), 416 ($M^+ - C_6H_5COOH$, 49), 345 (36), 105 ($C_6H_5CO^+$, 100), 77 (34). High-resolution MS, Calcd for $C_{30}H_{34}O_9(M^+)$: 538.2203. Found: 538.2204. *Anal.* Calcd for $C_{30}H_{34}O_9$: 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° (*c*=1.68, $CHCl_3$). IR $\nu_{max}^{KBr}$ 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 [$CH_3CH=C(CH_3)CO^+$, 74], 55 (100). High-resolution MS, Calcd for $C_{28}H_{34}O_9(M^+)$: 514.2203. Found: 514.2198.

**Tigloylgomisin P (9)** A white amorphous powder, $[\alpha]_D^{24}$ −56.1° (*c*=0.980, $CHCl_3$). IR $\nu_{max}^{KBr}$ 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 [$CH_3CH=C(CH_3)CO^+$, 74], 55 (66). High-resolution MS, Calcd for $C_{28}H_{34}O_9(M^+)$: 514.2203. Found: 514.2212.

**(+)-Gomisin $K_3$ (10)** Colorless needles (from ether–hexane), mp 99—100 °C, $[\alpha]_D^{24}$ +56.5° (*c*=1.70, $CHCl_3$). IR $\nu_{max}^{KBr}$ 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 $C_{23}H_{28}O_6(M^+)$: 402.2042. Found: 402.2046.

**Treatment of 3 with $Pb(OAc)_4$ in Benzene** A solution of **3** (84 mg) and $Pb(OAc)_4$ (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 (*Rf* 0.22, 19 mg) and unchanged **3** (*Rf* 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° (*c*=0.466, $CHCl_3$). IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3476 (OH), 1720 (C=O), 1600, 712 (aromatic ring). MS *m/z* (%): 524 ($M^+$, 11), 402 (22), 330 (8.0), 105 ($C_6H_5CO^+$, 100), 77 (59). High-resolution MS, Calcd for $C_{29}H_{32}O_9(M^+)$: 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 $H_2O$, dried over $Na_2SO_4$ 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, $[\alpha]_D^{24}$ −115° ($c$=0.285, $CHCl_3$). High-resolution MS, Calcd for $C_{31}H_{36}O_9$ ($M^+$): 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 $^1$H-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 $H_2O$ (15 ml) and extracted with ether (15 ml × 3). The combined ethereal extract was washed with $H_2O$, dried over $Na_2SO_4$ 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, $[\alpha]_D^{24}$ −97.4° ($c$=0.390, $CHCl_3$). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 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 $C_{23}H_{28}O_8$($M^+$): 432.1784. Found: 432.1780. $^1$H-NMR $\delta$ in $CDCl_3$: 1.10 (3H, s), 1.10 (3H, d, $J$=7.1 Hz), 1.80 (1H, m), 1.99 (2H, br s, $D_2O$ 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 $^1$H-NMR).

The aqueous solution was acidified with 1 N HCl and extracted with ether. The ethereal extract was washed with $H_2O$, dried over $Na_2SO_4$ 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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**References and Notes**

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