Phenylpropanol Derivatives from *Morina chinensis*

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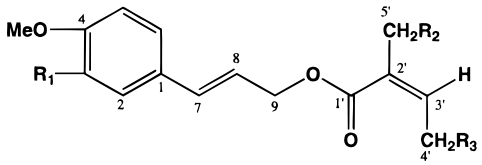
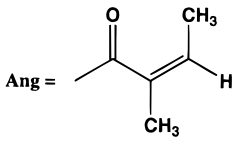
Received March 8, 1999

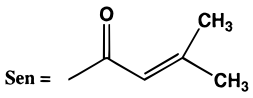
Seven new phenylpropanol derivatives, named morinins A−G (**1**−**7**), along with five known compounds, 4-*O*-methylcinnamyl alcohol, 4-*O*-methylcinnamyl methyl ether, 4-*O*-methylcinnamyl acetate, *p*-methoxybenzaldehyde, and 4-*O*-methyl-(*E*)-coniferyl alcohol, have been isolated from the roots of the medicinal Chinese plant, *Morina chinensis*. Their structures were determined on the basis of spectral data, especially 2D NMR and HRMS.

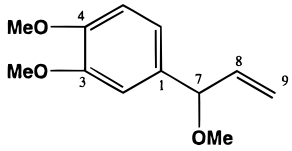
The chemical constituents of only four species of the genus *Morina* have been reported; these are *Morina longfolia*, *Morina*, *M. persica*, and *M. kokanica*.[1−5] Sterols, triterpenes, saponins, alkaloids, and flavanoids had been isolated from these plants. As a Chinese traditional medicinal plant, *Morina chinensis* has been used for the treatment of many diseases such as arthritis and stomach trouble etc. since ancient times.[6] It is mainly distributed in Northwestern China and has also been used in Tibetan medicine. We now report the isolation and structure elucidation of seven new phenylpropanol derivatives, named morinins A−G (**1**−**7**), as well as five known compounds, 4-*O*-methylcinnamyl alcohol, 4-*O*-methylcinnamyl methyl ether, 4-*O*-methylcinnamyl acetate, *p*-methoxybenzaldehyde, and 4-*O*-methyl-(*E*)-coniferyl alcohol, which have been isolated from a MeOH extract of the roots of the Chinese *Morina chinensis*.



1 $R_1 = R_2 = R_3 = H$
2 $R_1 = OMe$ $R_2 = R_3 = H$
3 $R_1 = OMe$ $R_2 = OH$ $R_3 = H$
4 $R_1 = R_3 = H$ $R_2 = OAng$
5 $R_1 = R_2 = H$ $R_3 = OAng$
6 $R_1 = R_3 = H$ $R_2 = OSen$







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Results and Discussion

The MeOH extract of the roots of *M. chinensis* was partitioned between H_2O and $CHCl_3$, and then between H_2O and *n*-butanol. The $CHCl_3$ extract was fractionated using repeated silica gel column chromatography, HPLC, and GPC to give compounds **1**−**7**.

Compound **1** (morinin A) showed a molecular ion peak in HREIMS at *m/z* 246.1280, suggesting a molecular formula of $C_{15}H_{18}O_3$. ^{1}H NMR spectrum of **1** showed the presence of a para-substituted benzene ring at δ_H 7.34 (2H, d, J = 8.6 Hz, H-2 and H-6), 6.86 (2H, d, J = 8.6 Hz, H-3 and H-5), a double bond at δ_H 6.63 (1H, br d, J = 15.8 Hz, H-7) and 6.21 (1H, dt, J = 15.8, 6.5 Hz, H-8), an oxygenated allylic methylene at δ_H 4.80 (2H, d, J = 6.5 Hz, H-9), typical signals of an angeloyl group[7−9] at δ_H 6.08 (1H, br q, J = 7.1 Hz, H-3′), 2.01 (3H, br d, J = 7.1 Hz, H-4′), and 1.92 (3H, br s, H-5′) and the signal of methoxy group at δ_H 3.81. ^{13}C NMR and DEPT spectral data were in good agreement with the above assignments. However, the signal of C-1 (δ_C 127.9) overlapped with the signals of C-2 and C-6 when $CDCl_3$ was used as solvent, but was separated (C-1, δ_C 129.1; C-2 and C-6, δ_C 128.8) when CD_3OD was used as solvent.

In the HMBC spectrum of **1**, the correlations of δ_H 3.81 (OMe) with δ_C 159.6 (C-4); δ_H 6.63 (H-7) with δ_C 127.9 (C-1, C-2, C-6) and 65.0 (C-9); δ_H 4.80 (H-9) with δ_C 133.6 (C-7), 121.3 (C-8), and 167.9 (C-1′, the carbonyl of angeloyl group), indicated **1** was a cinnamyl alcohol derivative, and that the methoxy and angeloyl groups were connected with C-4 and C-9, respectively. ^{1}H and ^{13}C NMR signals were assigned according to ^{1}H−^{1}H COSY and HSQC. Thus, morinin A (**1**) has been determined to be 4-*O*-methylcinnamyl angelic acid ester.

Compound **2** (morinin B) displayed NMR spectrum similar to that of **1**. ^{1}H NMR of **2** showed a 1,3,4-trisubstituted benzene ring at δ_H 6.94 (1H, dd, J = 8.2, 1.6 Hz, H-6), 6.82 (1H, d, J = 8.2 Hz, H-5), and 6.96 (1H, br s, H-2), and two methoxyl groups at δ_H 3.89 and 3.91, indicating that a second methoxyl group was attached at C-3 of aromatic ring in **2**. ^{13}C NMR and DEPT data also suggested there were three aromatic quaternary carbons and two methoxyl groups in **2**, and the angeloyl signals were similar to those of **1**. The HREIMS (276.1367) indicated the molecular formula to be $C_{16}H_{20}O_4$. In the HMBC spectrum of **2**, the correlations of δ_H 6.62 (H-7) with δ_C 129.4 (C-1), 108.9 (C-2), 120.0 (C-6), and 65.0 (C-9); δ_H 4.80 (H-9) with δ_C 134.0 (C-7), 120.0 (C-8), and 168.0 (C-1′, the carbonyl of angeloyl group), together with the correlations of ^{1}H−^{1}H COSY and HSQC, indicated the structure of morinin B (**2**) to be 4-*O*-methyl-(*E*)-coniferyl angelic acid ester.

Compound **3** (morinin C), showed NMR data quite similar to those of **2**. The evident difference between **3** and **2** was the disappearance of the signal of 5′-Me of angeloyl

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10.1021/np990091h CCC: $18.00
Published on Web 09/08/1999

group and the appearance of an oxygenated methylene signal at δ_H 4.27 (2H, br s, H-5′). Instead, this signal correlated with the signals at δ_H 6.43 (1H, br q, H-3′) and 2.11 (3H, br d, H-4′) in the $^1H-^1H$ COSY spectrum. The ^{13}C NMR and DEPT data of **3** confirmed the existence of an oxygenated methylene. Thus, a hydroxyl should be attached to C-5′. The HREIMS spectrum gave the molecular ion peak at *m*/*z* 292.1317, confirmed the molecular formula to be $C_{16}H_{20}O_5$. Furthermore, in the EIMS spectrum of **3**, an intense cleavage fragment peak at *m*/*z* 99 supported a hydroxyl group at C-5′ in **3**. Thus, the structure of morinin C (**3**) was determined to be 4-*O*-methyl-(*E*)-coniferyl 5′-hydroxyangelic acid ester.

Compound **4** (morinin D) showed NMR spectral data common to those of compounds **1** and **3** in addition to signals of a second angeloyl residue. HREIMS gave the molecular ion peak at *m*/*z* 344.1642, suggesting a molecular formula of $C_{20}H_{24}O_5$. The ^1H NMR spectrum of **4** showed the signals of another angeloyl group in addition to the angeloyl signals of compound **3**. The ^{13}C NMR data also indicated two angeloyl groups in compound **4**. As in compound **3**, C-5′ of one angeloyl group is oxygenated according to the ^1H NMR (δ_H 4.84, br s, H-5′) and ^{13}C NMR (δ_C 65.0, CH_2, C-5′) spectral data. The ^1H and ^{13}C NMR signals were assigned on the basis of $^1H-^1H$ COSY, HSQC, and HMBC. In the HMBC spectrum of **4**, the correlations of δ_H 4.81 (H-9) with δ_C 165.5 (C-1′), 133.7 (C-7), and 120.5 (C-8), suggested that the first angeloyl group was connected with C-9, and the correlations of δ_H 4.84 (H-5′) with δ_C 167.2 (C-1″), 165.5 (C-1′), 128.7 (C-2′), and 143.2 (C-3′), suggested that the second angeloyl group was connected with the C-5′ of the first one. The correlation of δ_H 4.84 (H-5′) with 1.85 (H-5″) in the NOESY spectrum confirmed this linkage. Hence, the structure of morinin D (**4**) is 4-*O*-methylcinnamyl 5′-angeloylangelic acid ester.

Compound **5** (morinin E) showed NMR data very similar to those of **4**. HREIMS (344.1639) gave the same molecular formula ($C_{20}H_{24}O_5$) as **4**. The evident difference in the ^1H NMR spectra of **5** and **4** were the signals of methyls belonging to the angeloyl groups. In compound **4**, two methyls (δ_H 2.12, br d, J = 7.2 Hz, H-4′; δ_H 1.94, dd, J = 7.3, 1.3 Hz, H-4″) showed the bigger coupling constants, which were coupled with H-3′ and H-3″, respectively, and a methyl (δ_H 1.85, br d, J = 1.3 Hz, H-5″) showed a small coupling constant, which should be coupled with H-3″. However, for compound **5**, only a methyl (δ_H 2.00, dd, J = 7.2, 1.3 Hz, H-4″) showed a bigger coupling constant, and the other two methyls (δ_H 1.91, br s, H-5′; δ_H 1.97, br d, J = 1.3 Hz, H-5″) showed small coupling constants. This suggested that the difference between **5** and **4** should be in the position of linkage of the two angeloyl groups. In the HMBC spectrum of compound **5**, the correlations of δ_H 4.81 (H-9) with δ_C 166.8 (C-1′), 134.2 (C-7), and 120.8 (C-8), suggested that the first angeloyl group was connected with C-9 just like in **4**, and the correlations of δ_H 5.14 (H-4′) with δ_C 167.8 (C-1″), 128.7 (C-2′), and 138.9 (C-3′) suggested that the second angeloyl group was connected at C-4′ in **5**. All of the ^1H and ^{13}C NMR signals were assigned according to the correlations of $^1H-^1H$ COSY, HSQC and HMBC. Thus, morinin E (**5**) is 4-*O*-methylcinnamyl 4′-angeloylangelic acid ester.

Compound **6** (morinin F) gave NMR signals similar to those of **4**. HREIMS (344.1609) indicated molecular formula of $C_{20}H_{24}O_5$. Comparison of the ^1H NMR spectra of **6** and **4**, indicated that the two ester substituents were an angeloyl group and a senecioyl group in **6**. The existence of a senecioyl group in **6** was supported not only by ^1H NMR spectral data, but also by ^{13}C NMR spectral data.[9,10] In the HMBC spectrum of compound **6**, the correlations of δ_H 4.82 (H-9) with δ_C 166.3 (C-1′), 133.8 (C-7), and 121.0 (C-8), suggested that the angeloyl group was connected with C-9, and the correlations of δ_H 4.77 (H-5′) with δ_C 166.0 (C-1″), 166.3 (C-1′), 128.1 (C-2′), and 143.4 (C-3′), suggested that the senecioyl group was attached to C-5′ of the angeloyl group. All of the ^1H and ^{13}C NMR signals were assigned according to the correlations of $^1H-^1H$ COSY, HSQC, and HMBC. Thus, morinin F (**6**) has been determined to be 4-*O*-methylcinnamyl 5′-senecioylangelic acid ester.

Compound **7** (morinin G) showed a molecular ion peak at *m*/*z* 208.1095 (HREIMS), suggesting a morlecular formula of $C_{12}H_{16}O_3$. The ^1H NMR spectrum of **7** showed three aromatic protons, three olefinic protons, an oxygenated methine proton and three methoxyl groups. ^{13}C NMR and DEPT data were in good agreement with the above assignments, and indicated a terminal double bond (δ_C 115.9, C-9). In the HMBC spectrum of **7**, the correlations of δ_H 3.29 (7-OMe) with δ_C 84.2 (C-7), δ_H 4.54 (H-7) with δ_C 133.2 (C-1), 109.4 (C-2), 119.1 (C-6), 138.6 (C-8), and 115.9 (C-9), which, together with the correlations of $^1H-^1H$ COSY and HSQC confirmed the structure as shown. Thus, morinin G (**7**) is 3-(3′,4′-dimethoxyphenyl)-3-methoxy-1-propene.

The angeloyl group is a very common substituent in natural compounds, but no reports were encountered about the methyls of angeloyl group being oxygenated further, as in compounds **3**−**6**. The angeloyl and senecioyl groups connected to each other is also unusual for natural products, although Bohlmann et al.[11,12] reported some guaianolides and rearranged guaianolides with the methyls of tigloate groups being oxygenated as acetyl esters.

The structures of the known compounds 4-*O*-methylcinnamyl alcohol, 4-*O*-methylcinnamyl methyl ether, 4-*O*-methylcinnamyl acetate, *p*-methoxybenzaldehyde, and 4-*O*-methyl-(*E*)-coniferyl alcohol, were identified according to their ^1H, ^{13}C NMR and EIMS data or by comparison of their spectral data with those published in the literature.[13−15] 4-*O*-Methylcinnamyl methyl ether and 4-*O*-methylcinnamyl acetate have been reported as synthetic compounds but have not been previously reported as natural products.

Experimental Section

General Experimental Procedures. NMR (400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR, both in TMS) were measured on a Bruker AM 400 spectrometer and MS spectra on a JEOLJMSD-300 instrument; CC: silica gel 60 (Merck); HPLC: GPC (shodex H-2001, 2002, $CHCl_3$), Si gel (Si 60, Hibar RT 250-25). IR spectra were recorded on a 1720 Infrared Fourier Transform spectrometer (Perkin-Elmer) and UV spectra on a UV2100 UV−vis recording spectrometer (shimadzu). Optical rotations were measured with a JASCD DIP-370 digital polarimeter.

Plant Material. The whole plant (including 1.8 kg of roots and 3.0 kg of stems and leaves) of *M. chinensis* was collected in the south of Qinghai province, China, in August 1998. It was identified by Dr. Wang Hengshan, Department of Biology, Lanzhou University, China. The voucher specimen (MC-99-08) has been preserved at the Herbarium of the Faculty of Pharmaceutical Sciences, Tokushima University, Japan.

Extraction and Isolation of Compounds. The powder of air-dried roots of *M. chinensis* was extracted with MeOH (15 L each time) at the temprature about 60 °C for three times, 6 h each. After concentration of the combined extracts under reduced pressure, the residue (200 g) was diluted with H_2O and then extracted with $CHCl_3$ and *n*-butanol, respectively.

The $CHCl_3$ extract (120 g) was chromatographed over a silica gel column (11 × 100 cm, Merck silica gel 60, 1.6 kg) and eluted with *n*-hexane−acetone (15:1 to 1:1), then pure

acetone and finally MeOH. Thirteen fractions were obtained. Fraction 1 (0.8 g) was chromatographed over a silica gel column (2.0 × 70 cm) eluting with hexanes−EtOAc (10:1), to give 8 fractions (1.1−1.8). Fraction 1.1 was purified by preparative TLC, on silica gel plates with hexane-$CHCl_3$ (1:1), to give compound **1** (20 mg). Fraction 1.2 was further purified over a silica gel column (1.5 × 75 cm), eluting with hexane−$CHCl_3$−acetone (10:5:0.5), to give 6 fractions (1.2.1−1.2.6). Fraction 1.2.5 was purified by GPC (gel permeation chromatography, Shodex H-2001, 2002, $CHCl_3$), to give 4-*O*-methylcinnamyl methyl ether (10 mg). Fraction 1.4 was purified by GPC ($CHCl_3$), to give 7 fractions (1.4.1−1.4.7). Fraction 1.4.4 was further purified by HPLC (silica, hexane−EtOAc, 10:1), to obtain compound **5** (12 mg). Fraction 2 (1.2 g) was chromatographed over a silica gel column (3.5 × 60 cm), eluting with hexane−EtOAc (10:1), to give 4 fractions (2.1−2.4). Fraction 2.1 was separated by GPC ($CHCl_3$), to give compound **5** (13 mg) and 4-*O*-methylcinnamyl alcohol (13 mg). Fraction 3 (1.4 g) was fractionated by GPC ($CHCl_3$), to give 10 fractions (3.1−3.10). Fraction 3.5 was separated by HPLC (silica, hexane−EtOAc, 8:1), to obtain 13 fractions (3.5.1−3.5.13). Compounds **2** (17 mg) and **6** (18 mg) were obtained after separation of fraction 3.5.13 by GPC ($CHCl_3$) and fraction 3.5.7 by HPLC (silica, hexane−EtOAc, 7:1), respectively. Fraction 3.6 was was further separated by HPLC (silica, hexane−EtOAc, 7:1), to obtain compound **7** (191 mg) and 4-*O*-methylcinnamyl acetate (11 mg); in the same way, compound **4** (86 mg) and *p*-methoxybenzaldehyde (16 mg) were obtained from fractions 3.5 and 3.8, respectively. Fraction 12 (6.32 g) was separated by medium-pressure column chromatography on silica gel column (3.5 × 45 cm, 200 g), eluting with $CHCl_3$−MeOH (50:1 to 1:1), to give 10 fractions (12.1−12.10). The combined 12.1 + 12.2 fractions were rechromatographed over a silica gel column (3.5 × 65 cm), eluting with hexane−acetone (3:1), to give **7** fractions (12.1.1−12.1.7). Compound **3** (4 mg) and 4-*O*-methyl-(*E*)-coniferyl alcohol (24 mg) were obtained after purification of fraction 12.1.1 by GPC ($CHCl_3$).

Morinin A (1): $[\alpha]_D^{25}$ +0.24° (*c* 0.85, $CHCl_3$); UV ($CHCl_3$) λ_{max} (log ϵ) 266.1 (3.81) nm; IR (KBr) ν_{max} 2955, 2369, 1713, 1655, 1609, 1579, 1513, 1459, 1388, 1352, 1252, 1232, 1155, 1038, 967, 846, 758, 523 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.34 (2H, d, J = 8.6 Hz, H-2 and H-6), 6.86 (2H, d, J = 8.6 Hz, H-3 and H-5), 6.63 (1H, d, J = 15.8 Hz, H-7), 6.21 (1H, dt, J = 15.8, 6.5 Hz, H-8), 6.08 (1H, br q, J = 7.1 Hz, H-3′), 4.80 (2H, d, J = 6.5 Hz, H-9), 3.81 (3H, s, OMe), 2.01 (3H, br d, J = 7.1 Hz, H-4′), 1.92 (3H, br s, H-5′); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.9 (s, C-1′), 159.6 (s, C-4), 138.0 (d, C-3′), 133.6 (d, C-7), 129.1 (s, C-2′), 127.9 (overlapped, s, C-1; d, C-2 and C-6), 121.3 (d, C-8), 114.0 (d, C-3 and C-5), 65.0 (t, C-9), 55.3 (q, OMe), 20.7 (q, C-5′), 15.8 (q, C-4′); ^{13}C NMR (CD_3OD, 100 MHz) δ 169.3 (s, C-1′), 161.1 (s, C-4), 138.8 (d, C-3′), 135.0 (d, C-7), 130.4 (s, C-2′), 129.1 (s, C-1), 128.8 (d, C-2 and C-6), 122.0 (d, C-8), 115.0 (d, C-3 and C-5), 66.0 (t, C-9), 55.7 (q, OMe), 20.7 (q, C-5′), 15.9 (q, C-4′); EIMS *m*/*z* (rel int.) 246 $[M]^+$ (43.6), 201 (2.9), 164 (4.0), 163 (17.2), 148 (22.5), 147 (100), 146 (11.6), 135 (19.2), 132 (15.5), 131 (31.6), 115 (36.2), 104 (21.8), 103 (42.5), 91 (37.9), 83 (98.2), 77 (22.0), 55 (52.2), 51 (10.4), 39 (19.5); HREIMS *m*/*z* 246.1680 (calcd for $C_{15}H_{18}O_3$, 246.1652).

Morinin B (2): $[\alpha]_D^{25}$ +7.52° (*c* 1.41, $CHCl_3$); UV ($CHCl_3$) λ_{max} (log ϵ) 295.2 (2.98), 271.9 (3.25), 267.1 (3.25), 242.0 (3.04) nm; IR (KBr) ν_{max} 2933, 1713, 1649, 1603, 1586, 1516, 1460, 1420, 1385, 1351, 1267, 1232, 1159, 1029, 965, 855, 798, 758, 597 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.96 (1H, br s, H-2), 6.94 (1H, dd, J = 8.2, 1.6 Hz, H-6), 6.82 (1H, d, J = 8.2 Hz, H-5), 6.62 (1H, d, J = 15.8 Hz, H-7), 6.21 (1H, dt, J = 15.8, 6.5 Hz, H-8), 6.08 (1H, qq, J = 7.2, 1.2 Hz, H-3′), 4.80 (2H, d, J = 6.5 Hz, H-9), 3.91, 3.89 (each 3H, s, OMe), 2.01 (3H, dd, J = 7.2, 1.2 Hz, H-4′), 1.93 (3H, br s, H-5′); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.0 (s, C-1′), 149.2, 149.1 (s, C-4 and C-3), 138.2 (d, C-3′), 134.0 (d, C-7), 129.4 (s, C-1), 127.9 (s, C-2′), 120.0 (d, C-6 and C-8), 111.1 (d, C-5), 108.9 (d, C-2), 65.0 (t, C-9), 56.0, 55.9 (q, OMe), 20.7 (q, C-5′), 15.9 (q, C-4′); EIMS *m*/*z* (rel int.) 276 $[M]^+$ (96.2), 193 (37.8), 178 (44.5), 177 (94.7), 165 (45.2), 146 (97.1), 133 (32.3), 131 (52.5), 119 (46.0), 115 (39.8), 103 (41.6), 91 (57.7), 77 (36.0), 65 (29.8), 57 (42.1), 55 (91.8), 43 (68.7); HREIMS *m*/*z* 276.1367 (calcd for $C_{15}H_{18}O_3$, 276.1362).

Morinin C (3): $[\alpha]_D^{25}$ −28.00° (*c* 0.10, $CHCl_3$); UV ($CHCl_3$) λ_{max} (log ϵ) 270.4 (3.75) nm; IR (KBr) ν_{max} 3621, 3570, 2922, 2851, 1719, 1703, 1678, 1656, 1639, 1604, 1517, 1460, 1160, 1141, 1026, 861, 759, 596 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.96 (1H, br s, H-2), 6.95 (1H, d, J = 8.5 Hz, H-6), 6.83 (1H, d, J = 8.5 Hz, H-5), 6.63 (1H, d, J = 15.7 Hz, H-7), 6.43 (1H, br q, J = 7.2 Hz, H-3′), 6.22 (1H, dt, J = 15.7, 6.8 Hz, H-8), 4.86 (2H, d, J = 6.8 Hz, H-9), 4.27 (2H, br s, H-5′), 3.91, 3.89 (each 3H, s, OMe), 2.11 (3H, br d, J = 7.2 Hz, H-4′); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.0 (s, C-1′), 149.3, 149.1 (s, C-4 and C-3), 141.7 (d, C-3′), 134.7 (d, C-7), 131.6 (s, C-2′), 128.7 (s, C-1), 120.9 (d, C-8), 120.1 (d, C-6), 111.1 (d, C-5), 108.9 (d, C-2), 66.4 (t, C-5′), 66.3 (t, C-9), 56.0, 55.9 (q, OMe), 15.9 (q, C-4′); EIMS *m*/*z* (rel int.) 292 $[M]^+$ (85.7), 195 (11.6), 194 (80.2), 193 (20.8), 178 (24.6), 177 (100), 165 (24.7), 161 (16.7), 147 (20.9), 146 (54.5), 131 (26.9), 119 (20.9), 99 (79.0), 54 (18.0), 53 (17.5), 41 (26.3); HREIMS *m*/*z* 292.1317 (calcd for $C_{16}H_{20}O_5$, 292.1311).

Morinin D (4): $[\alpha]_D^{25}$ +0.53° (*c* 1.14, $CHCl_3$); UV ($CHCl_3$) λ_{max} (log ϵ) 267.3 (4.23) nm; IR (KBr) ν_{max} 2980, 2940, 2925, 1724, 1651, 1608, 1515, 1459, 1386, 1358, 1262, 1169, 1036, 968, 848, 521, 424 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.31 (2H, d, J = 8.7 Hz, H-2 and H-6), 6.87 (2H, d, J = 8.7 Hz, H-3 and H-5), 6.61 (1H, d, J = 15.7 Hz, H-7), 6.45 (1H, br q, J = 7.2 Hz, H-3′), 6.17 (1H, dt, J = 15.7, 6.5 Hz, H-8), 6.02 (1H, qq, J = 7.3, 1.2 Hz, H-3″), 4.84 (2H, br s, H-5′), 4.81 (2H, dd, J = 6.5, 0.7 Hz, H-9), 3.80 (3H, s, OMe), 2.12 (3H, br d, J = 7.2 Hz, H-4′), 1.94 (3H, d q, J = 7.3, 1.3 Hz, H-4″), 1.85 (3H, br d, J = 1.3 Hz, H-5″); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.2 (s, C-1″), 165.5 (s, C-1′), 159.4 (s, C-4), 143.2 (d, C-3′), 137.8 (d, C-3″), 133.7 (d, C-7), 128.7 (s, C-2′), 127.8 (s, C-2″), 127.6 (d, C-2 and C-6), 127.5 (s, C-1), 120.5 (d, C-8), 113.8 (d, C-3 and C-5), 65.0 (t, C-5′), 64.9 (t, C-9), 54.9 (q, OMe), 20.3 (q, C-5″), 15.6 (q, C-4″), 15.5 (q, C-4′); EIMS *m*/*z* (rel int.) 344 (18.4), 245 (3.9), 244 (20.9), 216 (6.7), 215 (5.1), 185 (10.5), 181 (20.2), 163 (56.9), 147 (131.5), 131 (33.0), 121 (13.0), 115 (57.9), 104 (30.9), 103 (51.1), 99 (14.5), 91 (55.3), 83 (69.3), 82 (54.2), 78 (23.8), 77 (23.3), 55 (100), 54 (51.7), 53 (39.6), 41 (17.3); HREIMS *m*/*z* 344.1642 (calcd for $C_{20}H_{24}O_5$, 344.1624).

Morinin E (5): $[\alpha]_D^{25}$ −0.64° (*c* 0.94, $CHCl_3$); UV ($CHCl_3$) λ_{max} (log ϵ) 266.4 (3.90) nm; IR (KBr) ν_{max} 3423, 2930, 1713, 1654, 1609, 1514, 1458, 1384, 1353, 1252, 1142, 1039, 970, 847, 758, 523 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.35 (2H, d, J = 8.6 Hz, H-2 and H-6), 6.87 (2H, d, J = 8.6 Hz, H-3 and H-5), 6.63 (1H, d, J = 15.9 Hz, H-7), 6.19 (1H, dt, J = 15.9, 6.6 Hz, H-8), 6.07 (2H, m, H-3′ and H-3″), 5.14 (2H, d q, J = 7.2, 1.2 Hz, H-4′), 4.81 (2H, d, J = 6.6 Hz, H-9), 3.81 (3H, s, OMe), 2.00 (3H, d q, J = 7.2, 1.3 Hz, H-4″), 1.97 (3H, br d, J = 1.3 Hz, H-5″), 1.91 (3H, br s, H-5′); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.8 (s, C-1″), 166.8 (s, C-1′), 159.7 (s, C-4), 138.9 (d, C-3′), 138.3 (d, C-3″), 134.2 (d, C-7), 129.0 (s, C-2″), 128.7 (s, C-2′), 128.0 (d, C-2 and C-6), 127.7 (s, C-1), 120.8 (d, C-8), 114.1 (d, C-3 and C-5), 65.6 (t, C-9), 62.8 (t, C-4′), 55.3 (q, OMe), 20.6 (q, C-5″), 19.9 (q, C-5′), 15.8 (q, C-4″); EIMS *m*/*z* (rel int.) 344 $[M]^+$ (21.4), 245 (5.6), 244 (37.3), 164 (5.2), 163 (52.9), 162 (62.7), 148 (11.9), 147 (100), 131 (18.6), 115 (22.3), 103 (19.4), 91 (19.2), 83 (69.2), 82 (73.4), 55 (42.7), 39 (11.4); HREIMS *m*/*z* 344.1639 (calcd for $C_{20}H_{24}O_5$, 344.1624).

Morinin F (6): $[\alpha]_D^{25}$ +8.16° (*c* 0.74, $CHCl_3$); UV ($CHCl_3$) λ_{max} (log ϵ) 266.3 (3.85) nm; IR (KBr) ν_{max} 2936, 1719, 1654, 1609, 1514, 1445, 1381, 1251, 1142, 1076, 1034, 969, 850 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.32 (2H, d, J = 8.7 Hz, H-2 and H-6), 6.86 (2H, d, J = 8.7 Hz, H-3 and H-5), 6.62 (1H, d, J = 15.9 Hz, H-7), 6.43 (1H, br q, J = 7.3 Hz, H-3′), 6.17 (1H, dt, J = 15.9, 6.5 Hz, H-8), 5.67 (1H, qq, J = 0.7, 0.7 Hz, H-2″), 4.82 (2H, dd, J = 6.5, 0.9 Hz, H-9), 4.77 (2H, br s, H-5′), 3.82 (3H, s, OMe), 2.14 (3H, d, J = 0.7 Hz, H-4″), 2.11 (3H, br d, J = 7.3 Hz, H-4′), 1.85 (3H, d, J = 0.7 Hz, H-5″); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.3 (s, C-1′), 166.0 (s, C-1″), 159.6 (s, C-4), 157.3 (s, C-3″), 143.4 (d, C-3′), 133.8 (d, C-7), 129.1 (s, C-1), 128.1 (s, C-2′), 127.9 (d, C-2 and C-6), 121.0 (d, C-8), 115.9 (d, C-2″), 114.1 (d, C-3 and C-5), 65.2 (t, C-5′), 64.6 (t, C-9), 55.4 (q, OMe), 27.5 (q, C-5″), 20.3 (q, C-4″), 15.9 (q, C-4′); EIMS

m/z (rel int.) 344 $[M]^+$ (72.8), 245 (29.0), 244 (100), 229 (41.6), 181 (98.5), 177 (97.7), 163 (98.0), 145 (40.2), 133 (49.3), 121 (85.5), 115 (98.9), 105 (60.1), 99 (74.9), 81 (54.2), 71 (98.4), 55 (96.2), 43 (96.0); HREIMS *m/z* 344.1609 (calcd for $C_{20}H_{24}O_5$, 344.1624).

Morinin G (7): $[\alpha]_D^{25}$ −1.16° (*c* 1.38, $CHCl_3$); UV ($CHCl_3$) λ_{max} (log ϵ) 280.0 (3.35), 243.2 (3.59) nm; IR (KBr) ν_{max} 3590, 3570, 3420, 2936, 2839, 2368, 2346, 1511, 1460, 1263, 1235, 1139, 1085, 1029 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.85 (1H, br s, H-2), 6.83 (1H, dd, J = 8.5, 1.5 Hz, H-6), 6.82 (1H, d, J = 8.5 Hz, H-5), 5.91 (1H, ddd, J = 17.3, 10.3, 6.5 Hz, H-8), 5.24 (1H, dd, J = 17.3, 1.2 Hz, H-9), 5.17 (1H, dd, J = 10.3, 1.2 Hz, H-9), 4.45 (1H, d, J = 6.5 Hz, H-7), 3.85, 3.83, 3.29 (each 3H, s, OMe); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.9 (s, C-4), 148.3 (s, C-3), 138.6 (d, C-8), 133.2 (s, C-1), 119.1 (d, C-6), 115.9 (t, C-9), 110.7 (d, C-5), 109.4 (d, C-2), 84.2 (d, C-7), 56.0, 55.7, 55.6 (q, OMe); EIMS *m/z* (rel int.) 208 $[M]^+$ (77.3), 193 (10.3), 181 (46.2), 177 (100), 165 (20.3), 146 (46.0), 131 (14.1), 119 (14.3), 115 (13.4), 103 (13.6), 91 (21.7), 77 (17.0), 63 (10.8), 65 (14.6), 55 (13.5), 39 (10.5); HREIMS *m/z* 208.1095 (calcd for $C_{12}H_{16}O_3$, 208.1099).

Acknowledgment. The authors thank Dr. Hengshan Wang, Department of Biology, Lanzhou University, China, for helping with the collection of the plant material.

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NP990091H