Morinins L—P, Five New Phenylpropanol Derivatives from *Morina chinensis*

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Five new phenylpropanol derivatives, called morinins L—P (1—5), along with two known compounds, 3, 4-dimethoxycinnamylalcohol methyl ether (6) and *p*-methoxycinnamaldehyde (7), have been isolated from the roots of the medicinal Chinese plant, *Morina chinensis*. The structures of all the new compounds were determined on the basis of spectral evidence, especially by 2D-NMR and HREIMS. Alkaline hydrolytic degradation confirmed the structure of compound 5.

Key words *Morina chinensis*; Dipsacaceae; phenylpropanol derivatives; morinin L—P

Sterols, triterpenes, saponins, alkaloids and flavanoids had been found from the *Morina* genus.[1—5] A Chinese traditional medicinal plant, *Morina chinensis* (Dipsacaceae) has been used for the treatment of many diseases since ancient times[6]; it is mainly distributed in northwestern China, and has also been used in Tibetan medicine. However, the chemical constituents of this plant have not yet been studied. We report here the isolation and structure elucidation of five new phenylpropanol derivatives, called morinins L—P (**1**—**5**), as well as two known compounds, 3,4-dimethoxycinnamylalcohol methyl ether (**6**) and *p*-methoxycinnamaldehyde (**7**), from the methanol extracts of the roots of the medicinal Chinese plant, *M. chinensis*.

The methanol extracts of the roots of *M. chinensis* were partitioned between water and chloroform first, and then between water and *n*-butanol. The chloroform extracts were separated using repeated silica gel column chromatography, HPLC and GPC (General Permeation Chromatography), to give compounds **1**—**7**.

Compound **1**, obtained as a colourless oil. The high-resolution electron impact-mass spectra (HREIMS) showed the molecular ion peak at *m/z* 374.1708 $[M]^+$, which, together with its ^{1}H- (Table 1), ^{13}C-NMR and distortionless enhancement by polarigation transfer (DEPT) (Table 2) spectral data, suggested the molecular formula to be $C_{21}H_{26}O_6$. The ^{1}H-NMR spectrum of **1** displayed the presence of a 1,3,4-trisubstituted benzene ring at δ_H 6.94 (1H, d, J=1.6 Hz, H-2), 6.83 (1H, d, J=8.0 Hz, H-5), 6.93 (1H, dd, J=8.0, 1.6 Hz, H-6), a double bond at δ_H 6.61 (1H, d, J=15.8 Hz, H-7) and 6.18 (1H, dt, J=15.8, 6.5 Hz, H-8), a methylene which connected with the double bond (confirmed by the correlations of ^{1}H–^{1}H correlation spectroscopy (COSY) and heteronuclear multiple bond correlation (HMBC)) and oxygen at δ_H 4.83 (2H, d, J=6.5 Hz, H-9), two methoxy groups at δ_H 3.89 and 3.91, typical signals of two angeloyl groups[7,8] at δ_H 6.47 (1H, br q, J=7.2 Hz, H-3′), 6.03 (1H, dq, J=7.2, 1.1 Hz, H-3″), 2.13 (3H, d, J=7.2 Hz, H-4′), 1.94 (3H, dd, J=7.2, 1.1 Hz, H-4″), 4.86 (2H, s, H-5′) and 1.86 (3H, br s, H-5″). ^{13}C-NMR and DEPT data were in complete agreement with the above analysis. The C-5′ methyl of one angeloyl group has been oxygenated as a methylene according to its ^{1}H- (δ_H 4.86, 2H, s, H-5′) and ^{13}C-NMR (δ_C 65.3, CH_2, C-5′) spectral data.

In the HMBC spectrum of **1**, the correlations of δ_H 3.89 and 3.91 (OMe) with δ_C 149.4 (C-4) and 149.2 (C-3); δ_H 6.61 (H-7) with δ_C 129.4 (C-1), 109.1 (C-2), 120.1 (C-6) and 65.2 (C-9); δ_H 4.83 (H-9) with δ_C 134.4 (C-7), 121.2 (C-8) and 165.9 (C-1′, the carbonyl of the inner angeloyl group),

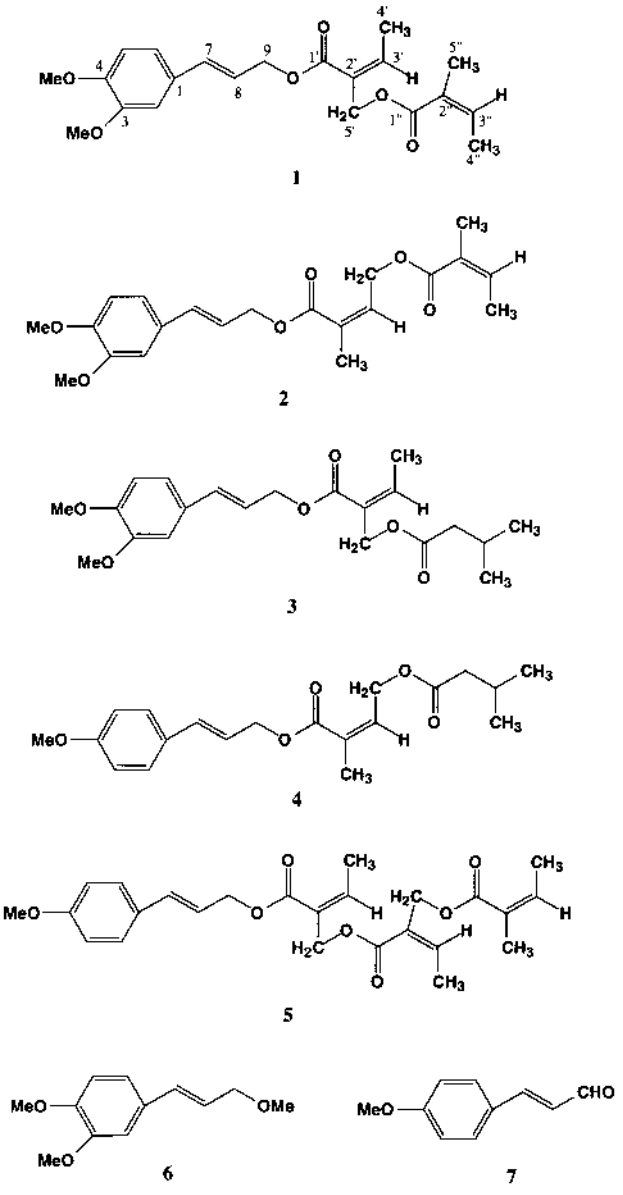

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Table 1. ^{1}H-NMR Spectral Data of Compounds **1**—**5**

No.	1	2	3	4	5
2	6.94, d (1.6)	6.97, d (1.6)	6.95, d (1.7)	7.35, d (8.7)	7.33, d (8.6)
3				6.87, d (8.7)	6.86, d (8.6)
5	6.83, d (8.0)	6.83, d (8.0)	6.83, d (8.0)	6.87, d (8.7)	6.86, d (8.6)
6	6.93, dd (8.0, 1.6)	6.96, dd (8.0, 1.6)	6.94, dd (8.0, 1.7)	7.35, d (8.7)	7.33, d (8.6)
7	6.61, d (15.8)	6.63, d (15.8)	6.62, d (15.8)	6.64, d (15.8)	6.62, d (15.8)
8	6.18, dt (15.8, 6.5)	6.20, dt (15.8, 6.5)	6.19, dt (15.8, 6.5)	6.19, dt (15.8, 6.4)	6.17, dt (15.8, 6.6)
9	4.83, d (6.5)	4.82, d (6.5)	4.83, dd (6.5, 0.8)	4.81, d (6.4)	4.81, d (6.6)
3′	6.47, br q(7.2)	6.10, m	6.45, br q (7.2)	6.02, dq (7.2, 1.4)	6.46, br q (7.2)
4′	2.13, d (7.2)	5.14, dd (7.2, 1.4)	2.12, d (7.2)	5.06, dd (7.2, 1.6)	2.11, d (7.2)
5′	4.86, s	1.98, d (1.4)	4.77, s	1.97, d (1.6)	4.88, br s
2″			2.18, d (7.1)	2.21, d (7.1)	
3″	6.03, dq (7.2, 1.1)	6.10, m	2.06, m	2.11, m	6.41, br q (7.3)
4″	1.94, dd (7.2, 1.1)	2.00, dd (7.2, 1.3)	0.92, d (6.6)	0.98, d (5.6)	2.05, d (7.3)
5″	1.86, br s	1.91, d (1.3)	0.92, d (6.6)	0.98, d (5.6)	4.71, br s
3‴					6.05, br q (7.0)
4‴					1.94, d (7.0)
5‴					1.86, s
OMe	3.89, 3.91	3.89, 3.91	3.89, 3.91	3.82	3.81

$CDCl_3$ as solvents, TMS as int. standard. Figures in parentheses are coupling constants in Hz. (400 MHz, δ, ppm).

Table 2. ^{13}C-NMR and DEPT Spectral Data of Compounds **1**—**5**

No.	1	2	3	4	5
1	129.4 s	129.3 s	129.4 s	129.1 s	129.1 s
2	109.1 d	109.0 d	109.1 d	128.0 d	128.0 d
3	149.2 s[a)]	149.1 s[a)]	149.2 s[a)]	114.1 d	114.1 d
4	149.4 s[a)]	149.3 s[a)]	149.4 s[a)]	159.6 s	159.7 s
5	111.2 d	111.1 d	111.2 d	128.0 d	128.0 d
6	120.1 d	120.1 d	120.1 d	114.1 d	114.1 d
7	134.4 d	134.5 d	134.4 d	134.3 d	134.2 d
8	121.2 d	121.1 d	121.2 d	120.8 d	120.8 d
9	65.2 t	65.6 t	65.3 t	65.6 t	65.1 t
1′	165.9 s	166.9 s	165.9 s	166.9 s	165.6 s
2′	128.0 s	128.6 s	127.9 s	128.0 s	127.6 s
3′	143.5 d	138.4 d	143.8 d	138.7 d	143.9 d
4′	15.9 q	62.9 t	15.9 q	62.9 t	15.9 q
5′	65.3 t	20.0 q	65.4 t	20.0 q	65.4 t
1″	167.7 s	167.9 s	172.8 s	171.2 s	165.7 s
2″	127.8 s	127.7 s	43.5 t	43.4 t	127.8 s
3″	138.1 d	139.2 d	25.8 d	25.5 d	143.5 d
4″	15.8 q	15.9 q	22.4 q	22.5 q	15.8 q
5″	20.6 q	20.7 q	22.4 q	22.5 q	65.4 t
1‴					167.6 s
2‴					127.8 s
3‴					138.2 d
4‴					15.7 q
5‴					20.6 q
OMe	55.9, 56.0	55.9, 56.0	55.9, 56.0	55.4	55.4

$CDCl_3$ as solvents, TMS as int. standard. *a*) Assignments maybe interchangeable in the same column. (100 MHz, δ, ppm).

δ_H 4.86 (H-5′ of the first angeloyl group) with δ_C 165.9 (C-1′, the carbonyl of the first angeloyl group), 128.0 (C-2′), 143.5 (C-3′) and 167.7 (C-1″, the carbonyl of the terminal angeloyl group), indicated the C-5′ methyl of the first angeloyl group has been oxygenated by the second angeloyl group, while the first one connected with C-9. All of the ^{1}H- and ^{13}C-NMR spectral data were assigned according to the correlations of ^{1}H–^{1}H COSY, heteronuclear single quantum coherence (HSQC), HMBC and nuclear Overhauser enhancement and exchange spectroscopy (NOESY). Thus, the structure of compound **1** has been determined as shown, and termed morinin L.

Compound **2**, obtained as a colourless oil. Its NMR spectral data were very similar to those of **1**, and HREIMS (374.1721) gave the same molecular formula of $C_{21}H_{26}O_6$ as that of **1**. In the ^{1}H-NMR spectra of **1** and **2**, the evident differences between them were the signals of methyls belonging to the angeloyl groups. In compound **1**, two methyls (δ_H 2.13, d, J=7.2 Hz, H-4′; δ_H 1.94, dd, J=7.2, 1.1 Hz, H-4″) showed larger coupling constants, which were coupled with H-3′ and H-3″, respectively, and only one methyl (δ_H 1.86, br s, H-5″) showed as a singlet. However, for compound **2**, only a methyl (δ_H 2.00, dd, J=7.2, 1.3 Hz, H-4″) showed a larger coupling constant, and the other two methyls (δ_H 1.98, s, H-5′; δ_H 1.91, d, J=1.3 Hz, H-5″) showed the small coupling constants. This suggested the difference between compounds **2** and **1** should be the linkage position of two angeloyl groups.

In the HMBC spectrum of compound **2**, the correlations of δ_H 4.82 (H-9) with δ_C 166.9 (C-1′), 134.5 (C-7) and 121.1 (C-8), suggested the first angeloyl group connected with C-9 just like that in **1**, and the correlations of δ_H 5.14 (H-4′) with δ_C 167.9 (C-1″), 128.6 (C-2′) and 138.4 (C-3′) suggested the second angeloyl group connected with the C-4′ of the first one while the linkage was at C-5′ in **1**. All of the ^{1}H- and ^{13}C-NMR spectra data were assigned according to the correlations of ^{1}H–^{1}H COSY, HSQC and HMBC. So, compound **2** was an isomer of compound **1**, termed morinin M.

Compound **3**, obtained as a colourless oil. The HREIMS (376.1902) gave the molecular formula of $C_{21}H_{28}O_6$. Its ^{1}H- and ^{13}C-NMR spectral data were similar to those of **1**, the evident difference between **3** and **1** was the signals of one isovaleryl group[9] (^{1}H-NMR: δ_H 2.18, d, J=7.1 Hz, H-2″; δ_H 2.06, m, H-3″; δ_H 0.92, d, J=6.6 Hz, H-4″ and H-5″; ^{13}C-NMR: δ_C 172.8, C-1″; δ_C 43.5, C-2″; δ_C 24.8, C-3″; δ_C 22.4, C-4″ and C-5″) in **3** instead of the signals of the second angeloyl group in **1**. The existence of this isovaleryl group was confirmed by the correlation of ^{1}H–^{1}H COSY and HMBC.

In the HMBC spectrum of compound **3**, the correlations of δ_H 4.83 (H-9) with δ_C 165.9 (C-1′), 134.4 (C-7) and 121.2 (C-8), δ_H 4.77 (H-5′ of the angeloyl group) with δ_C 165.9 (C-1′, the carbonyl of the angeloyl group), 127.9 (C-2′),

143.8 (C-3′) and 172.8 (C-1″, the carbonyl of the isovaleryl group), suggested the angeloyl group connected with C-9 just like those in **1** and **2**, and the isovaleryl group was connected with the C-5′ of the angeloyl group. Thus, the structure of compound **3** has been determined as shown, and called morinin N.

Compound **4**, obtained as a colourless oil. Both ^{1}H- (δ_H 7.35, 2H, d, J=8.7 Hz, H-2 and H-6; δ_H 6.87, 2H, d, J=8.7 Hz, H-3 and H-5) and ^{13}C-NMR (δ_C 129.1, C-1; δ_C 128.0, C-2 and C-6; δ_C 114.1, C-3 and C-5) spectral data indicated the aromatic ring of compound **4** was *p*-substituted, and also displayed only one methoxyl group (δ_H 3.82 and δ_C 55.4) in compound **4**. Its HREIMS (346.1776) gave the molecular formula of $C_{20}H_{26}O_5$. The NMR spectral data of compound **4** also showed the existence of angeloyl and isovaleryl groups. However, the isovaleryl group was connected with C-4′ of the angeloyl group according to the ^{1}H-NMR spectral data (δ_H 5.06, 2H, dd, J=7.2, 1.6 Hz, H-4′; δ_H 1.97, 3H, d, J=1.6 Hz, H-5′) of the angeloyl group, and further confirmed by the HMBC correlation of δ_H 5.06 (H -4′) with δ_C 171.2 (C-1″, the carbonyl of the isovaleryl group). Hence, we detetmined the structure of compound **4** as shown, termed morinin O.

Compound **5**, obtained as a colourless oil. Its HREIMS (442.2009) gave the molecular formula of $C_{25}H_{30}O_7$. Both ^{1}H- and ^{13}C-NMR spectral data of compound **5** indicated the aromatic ring was *p*-substituted, and there were three angeloyl groups in its structure. In the ^{1}H-NMR spectrum of compound **5**, three methyls (δ_H 2.11, d, J=7.2 Hz, H-4′; δ_H 2.05, d, J=7.3 Hz, H-4″; δ_H 1.94, d, J=7.0 Hz, H-4‴) of angeloyl groups showed larger coupling constants, which were coupled with H-3′, H-3″ and H-3‴, respectively, and only one methyl (δ_H 1.86, s, H-5″) belonging to the terminal angeloyl group showed as singlet, suggested the second angeloyl group was connected with the C-5′ of the first angeloyl group and the terminal one was connected with the C-5″ of the second one. These linkages were confirmed by the correlations of HMBC.

In the HMBC spectrum of compound **5**, the correlations of δ_H 3.81 (OMe) with δ_C 159.7 (C-4) and 114.1 (C-3 and C-5); δ_H 4.81 (H-9) with δ_C 165.6 (C-1′, the carbonyl of the first angeloyl group), 134.2 (C-7) and 120.8 (C-8); δ_H 4.88 (H-5′) with δ_C 165.6 (C-1′), 127.6 (C-2′), 143.9 (C-3′) and 165.7 (C-1″, the carbonyl of the second angeloyl group); δ_H 4.71 (H-5″) with δ_C 165.7 (C-1″), 127.8 (C-2″), 143.5 (C-3″) and 167.6 (C-1‴, the carbonyl of the terminal angeloyl group), suggested the structure of compound **5** as shown, called morinin P.

The angeloyl group is a very common substituent in natural compounds, but in compounds **1**—**5**, the methyls of the angeloyl group were further oxygenated. The angeloyl and isovaleryl groups connected to each other is unusual for natural products. To further confirm the structures, we hydrolyzed compound **5** under an alkaline condition, and 4-*O*-methylcinnamyl alcohol, 5-hydroxyangelic acid and angelic acid were obtained.

Although 3,4-dimethoxycinnamylalcohol has been isolated from *Asiasarum heterotropoides* var. *mandshuricum*,[10] to the best of our knowledge, 3,4-dimethoxycinnamylalcohol methyl ether (**6**) has not been previously reported. *p*-Methoxycinnamaldehyde (**7**) was synthesised[11] and prepared as a derivative of *p*-hydroxycinnamaldehyde,[12] this is the first time to isolate compound **7** from the natural plant. The NMR spectral data of compounds **6** and **7** are given in the Experimental section.

Experimental

General Experimental Procedures NMR (400 MHz for ^{1}H-NMR, 100 MHz for ^{13}C-NMR, both use tetramethylsilane (TMS) as internal standard) were measured on a Bruker AM 400 spectrometer and MS spectra on a JEOL JMSD-300 instrument; CC: Silica gel 60 (Merck); HPLC: GPC (Shodex H-2001, 2002, $CHCl_3$), Silica gel (Si 60, Hibar RT 250-25). IR spectra were recorded on a 1720 infrared Fourier transform spectrometer (Perkin-Elmer), UV spectra on a UV2100 UV-Vis recording spectrometer (Shimadzu). Optical rotations were measured with a JASCO DIP-370 digital polarimeter.

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

Extraction and Isolation of Compounds The powder of air dried roots of *M. chinensis* were extracted with MeOH (15 l each time) at a temperature of about 60 °C for three times, 6 h each time. After concentration of the combined extracts under reduced pressure, the residue (200 g) was diluted with water, 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 with pure acetone and MeOH eluted, respectively). Thirteen fractions were obtained. Fraction 1 (0.8 g) was chromatographed over a silica gel column (2.0×70 cm) and eluted with hexane–EtOAc (10 : 1), to give 8 fractions (Fr1. 1—Fr1. 8). The mixture of Fr. 1.3 and Fr. 1.4 was separated by GPC ($CHCl_3$), and gave a further 7 fractions (Fr. 1.3.1—Fr. 1.3.7), compound **4** (3 mg) was obtained after the purification of Fr. 1.3.4 using HPLC (silica, hexane–EtOAc, 10 : 1). Fraction 4 (1.9 g) was chromatographed over a silica gel column (3.5×15 cm) and eluted with hexane–EtOAc (8 : 1), to give 5 fractions (Fr. 4.1—Fr. 4.5). Fr. 4.4 was isolated by GPC ($CHCl_3$), to give 6 fractions (Fr. 4.4.1—Fr. 4.4.6). Fr. 4.4.4 and Fr. 4.4.6 were purified by GPC ($CHCl_3$), and gave compounds **6** (54 mg) and **7** (33 mg), respectively. Then, Fr. 4.4.1 was isolated by HPLC (silica, hexane–EtOAc, 4 : 1), giving compound **2** (3 mg) and a mixture (11 mg) of compounds **1** and **3**; this mixture was again purified by HPLC (silica, hexane–EtOAc, 10 : 1), and gave pure compounds **1** (3.8 mg) and **3** (4.3 mg). Fr. 4.2 was isolated by HPLC (silica, hexane–EtOAc, 4 : 1), obtained 8 fractions (Fr. 4.2.1—Fr. 4.2.8). Fr. 4.2.6 was then purified by GPC ($CHCl_3$), giving compound **5** (20 mg).

Morinin L (**1**): $[\alpha]_D^{25}$ +1.56° (c=0.39, $CHCl_3$); IR ($CHCl_3$) ν_{max} cm^{-1}: 2937, 1713, 1515, 1466, 1265, 1235, 1230, 1209, 1203, 1159, 1141, 1027, 966, 856; UV $\lambda_{max}^{CHCl_3}$ nm (log ε): 239.7 (sh, 3.23), 271.2 (3.72), 304.5 (br, 2.98); EI-MS *m/z* (rel. int.): 374 $[M]^+$ (92.2), 274 (21.7), 193 (86.6), 181 (23.6), 177 (98.4), 146 (44.6), 131 (14.7), 119 (14.3), 99 (22.0), 83 (100), 82 (55.2), 55 (45.7); HREIMS *m/z* 374.1708 (Calcd for $C_{21}H_{26}O_6$, 374.1729); ^{1}H-NMR data see Table 1; ^{13}C-NMR and DEPT data see Table 2.

Morinin M (**2**): $[\alpha]_D^{25}$ −3.16° (c=0.25, $CHCl_3$); IR ($CHCl_3$) ν_{max} cm^{-1}: 3013, 2932, 1713, 1604, 1515, 1466, 1353, 1267, 1230, 1214, 1202, 1141, 1027, 966, 856; UV $\lambda_{max}^{CHCl_3}$ nm (log ε): 239.5 (sh, 3.29), 271.3 (3.78), 304.2 (br, 2.90); EI-MS *m/z* (rel. int.): 374 $[M]^+$ (78.9), 193 (56.2), 192 (100), 177 (78.0), 149 (48.4), 121 (17.4), 97 (16.6), 83 (81.4), 71 (23.1), 55 (49.2), 43 (32.5); HREIMS *m/z* 374.1721 (Calcd for $C_{21}H_{26}O_6$, 374.1729); ^{1}H-NMR data see Table 1; ^{13}C-NMR and DEPT data see Table 2.

Morinin N (**3**): $[\alpha]_D^{25}$ +1.14° (c=0.35, $CHCl_3$); IR ($CHCl_3$) ν_{max} cm^{-1}: 3025, 3013, 2962, 1718, 1604, 1515, 1466, 1421, 1265, 1231, 1200, 1160, 1141, 1027, 965, 857, 801, 796; UV $\lambda_{max}^{CHCl_3}$ nm (log ε): 239.0 (sh, 3.20), 270.8 (3.82), 304.0 (br, 3.12); EI-MS *m/z* (rel. int.): 376 $[M]^+$ (63.1), 274 (17.9), 193 (56.7), 183 (28.7), 177 (100), 165 (8.9), 147 (9.8), 146 (35.6), 131 (14.6), 119 (19.2), 99 (13.6), 85 (65.8), 82 (46.3), 57 (44.2), 54 (23.6), 41 (17.2); HREIMS *m/z* 376.1902 (Calcd for $C_{21}H_{28}O_6$, 376.1886); ^{1}H-NMR data see Table 1; ^{13}C-NMR and DEPT data see Table 2.

Morinin O (**4**): $[\alpha]_D^{25}$ +2.67° (c=0.23, $CHCl_3$); IR ($CHCl_3$) ν_{max} cm^{-1}: 2962, 2931, 2360, 1718, 1609, 1514, 1466, 1379, 1250, 1231, 1203, 1148, 1035, 801, 796; UV $\lambda_{max}^{CHCl_3}$ nm (log ε): 240.5 (sh, 3.28), 265.7 (br, 3.80); EI-MS *m/z* (rel. int.): 346 (25.1), 245 (3.9), 244 (31.0), 216 (4.3), 215 (5.3), 181 (5.4), 163 (61.7), 162 (82.0), 147 (94.7), 135 (18.5), 131 (18.6), 121 (13.0),

115 (14.2), 104 (12.1), 103 (13.3), 99 (13.3), 91 (14.8), 85 (53.0), 83 (28.4), 82 (100), 78 (5.4), 77 (8.3), 69 (13.5), 57 (56.2), 55 (15.6), 43 (17.4), 41 (20.9); HREIMS *m/z* 346.1776 (Calcd for $C_{20}H_{26}O_5$, 346.1780); ^{1}H-NMR data see Table 1; ^{13}C-NMR and DEPT data see Table 2.

Motinin P (**5**): $[\alpha]_D^{25}$ +2.31° (*c*=0.95, $CHCl_3$); IR ($CHCl_3$) ν_{max} cm^{-1}: 2958, 1713, 1654, 1609, 1513, 1458, 1387, 1235, 1230, 1215, 1209, 1203, 1175, 1037, 968, 852, 757; UV $\lambda_{max}^{CHCl_3}$ nm (log ε): 266.3 (3.92); EI-MS *m/z* (rel. int.): 442 $[M]^+$ (51.8), 279 (45.8), 245 (23.7), 244(100), 216 (14.5), 215 (10.7), 198 (11.6), 197 (87.7), 185 (13.1), 181 (97.1), 180 (98.6), 163 (98.4), 161 (36.9), 148 (46.5), 147 (96.5), 135 (24.5), 131 (30.9), 121 (26.1), 115 (43.5), 103 (32.8), 99 (85.6), 91 (47.3), 83 (94.5), 82 (96.9), 69 (19.1), 55 (94.5), 54 (97.0), 53 (41.8), 43 (22.8); HREIMS *m/z* 442.2009 (Calcd for $C_{25}H_{30}O_7$, 442.1992); ^{1}H-NMR data see Table 1; ^{13}C-NMR and DEPT data see Table 2.

3,4-Dimethoxycinnamylalcohol Methyl Ether (**6**): ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 3.37 (3H, s, 9-OMe), 3.85 (3H, s, OMe), 3.87 (3H, s, OMe), 4.06 (2H, d, *J*=6.1 Hz, H-9), 6.14 (1H, dt, *J*=15.8, 6.1 Hz, H-8), 6.53 (1H, d, *J*=15.8 Hz, H-7), 6.79 (1H, d, *J*=8.2 Hz, H-5), 6.90 (1H, dd, *J*=8.2, 1.5 Hz, H-6), 6.94 (1H, d, *J*=1.5 Hz, H-2). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 55.7, 55.8, 57.9 (q, OMe), 73.1 (t, C-9), 108.8 (d, C-2), 111.0 (d, C-5), 119.7 (d, C-6), 123.9 (d, C-8), 132.3 (d, C-7), 129.7 (s, C-1), 148.8, 148.9 (s, C-3, C-4).

p-Methoxycinnamaldehyde (**7**): ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 3.85 (3H, s, OMe), 9.64 (1H, d, *J*=6.7 Hz, H-9), 6.60 (1H, dd, *J*=15.9, 6.7 Hz, H-8), 7.42 (1H, d, *J*=15.9 Hz, H-7), 6.94 (2H, d, *J*=8.7 Hz, H-3 and H-5), 7.51 (2H, d, *J*=8.7 Hz, H-2 and H-6). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 55.5 (q, OMe), 193.7 (d, C-9), 130.4 (d, C-2 and C-6), 114.6 (d, C-3 and C-5), 126.5 (d, C-8), 152.8 (d, C-7), 126.8 (s, C-1), 162.2 (s, C-4).

Alkaline Hydrolysis of Compound 5 5.6 mg of compound **5** was dissolved in 1 N NaOMe solution (4 ml), hydrolyzed for 1 h under refluxing, then adjusted the pH value of the mixture to 3.0 using 1 N HCl. 5 ml H_2O was added to the mixture after evaporating MeOH under reduced pressure, then extracted with $CHCl_3$ (3×7 ml). 4-*O*-Methylcinnamyl alcohol, 5-hydroxyangelic acid and angelic acid were obtained after purifing the $CHCl_3$ extract using GPC ($CHCl_3$). ^{1}H-NMR (400 MHz, $CDCl_3$) data of 4-*O*-methylcinnamyl alcohol: δ 7.33 (2H, d, *J*=8.6 Hz, H-2 and H-6), 6.87 (2H, d, *J*=8.6 Hz, H-3 and H-5), 6.58 (1H, d, *J*=15.9 Hz, H-7), 6.25 (1H, dt, *J*=15.9, 6.0 Hz, H-8), 4.31 (2H, d, *J*=6.0 Hz, H-9), 3.82 (3H, br s, OMe); ^{1}H-NMR (400 MHz, $CDCl_3$) data of 5-hydroxyangelic acid: δ 6.42 (1H, br q, *J*=7.2 Hz, H-3), 4.23 (2H, br s, H-5), 1.98 (3H, d, *J*=7.2 Hz, H-4); ^{1}H-NMR (400 MHz, $CDCl_3$) data of angelic acid: δ 6.24 (1H, dq, *J*=7.2, 1.2 Hz, H-3), 2.05 (3H, d, *J*=7.2 Hz, H-4), 1.92 (3H, br s, H-5).

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