Dihydrophenanthrenes from *Spiranthes sinensis*

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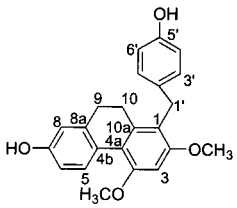
Received April 12, 2000

Six novel dihydrophenanthrene derivatives, sinensols A−F (**1**−**6**), were isolated from the aerial parts of *Spiranthesis sinensis*. Their structures were determined on the basis of various spectroscopic data, in particular those yielded by MS and 2D NMR techniques.

Spiranthes sinensis (Pers.) Ames. (Orchidaceae) has been used in Taiwan as a valuable folk drug for the treatment of hemoptysis, epistaxis, headache, chronic dysentery, and meningitis.[1,2] In the course of chemical studies on indigenous folk medicinal plants, we investigated the constituents of *S. sinensis*, which led to the isolation of five known dihydrophenanthrene derivatives—orchinol,[3] spiranthoquinone,[4] spiranthol-A,[4,5] spirasineol-A,[4,5] and shancidin[6]—and six novel dihydrophenanthrenes, sinensols A−F (**1**−**6**). This paper deals with the structural elucidation of compounds **1**−**6**.



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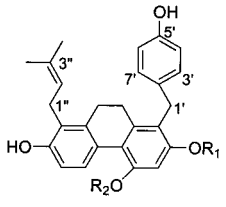

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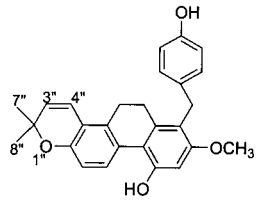
3: R_1=H, R_2=CH_3
7: R_1=CH_3, R_2=H



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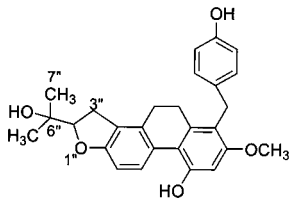

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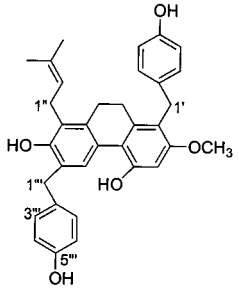

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Results and Discussion

An ethanolic extract of the aerial parts of *S. sinensis* was sucessively partitioned between *n*-BuOH and ethyl acetate. The EtOAc-soluble fraction showed moderate (42.5%) anti-hepatitis B virus e antigen (HBeAg) activity against hepatoma cell line MS-G2 at 100 μg/mL and was cytotoxic at 200 μg/mL. Repeated column chromatography of the EtOAc fraction led to the isolation of five known and six novel (**1**−**6**) dihydrophenanthrenes.

Sinensol A (**1**) was obtained as a colorless amorphous powder and showed UV absorptions at 270 (sh), 280, 296, and 312 (sh) nm. The IR spectrum revealed hydroxy (3400 and 1195 cm^{-1}) and aromatic ring (1615, 1596, 1575, and 1510 cm^{-1}) absorptions. The molecular formula, $C_{23}H_{22}O_4$, was assigned based on HREIMS. The ^{1}H NMR spectrum of **1** indicated two methylene groups attributable to the 9- and 10- protons of a dihydrophenanthrene at δ 2.60 and 2.63;[7] two methoxy methyl groups (δ 3.83 and 3.88); an A_2X_2 of typical 4-hydroxyphenyl protons [δ 6.66 and 6.95 (2H each, d, J = 8.1 Hz)]; an ABX system of aromatic protons at δ 6.63 (d, J = 2.1 Hz), 6.68 (dd, J = 8.7, 2.1 Hz), and 8.06 (d, J = 8.7 Hz); an isolated aromatic proton at δ 6.52; and a benzylic methylene at δ 3.99. The ^{13}C NMR indicated four oxygenated aromatic carbons (δ_C 153.4, 153.5, 156.0, 156.7). HMBC correlations of H-1′/C-1, -2 (δ_C 156.7), -10a, -2′, and -3′ (-7′); CH_3O (δ 3.83)/C-2; H-3′ (-7′)/C-4′ (-6′), -5′ (δ_C 153.4); H-10/C-1, -8a, -9, -10a, and -4a; H-6/C-4b, -5, -7 (δ_C 153.5) and -8; and H-3/C-1, -2, -4 (δ_C 156.0), and -4a determined the connectivity between the *p*-hydroxybenzyl and the dihydrophenanthrene, and the location of four oxygenated carbons. From these spectral data, sinensol A (**1**) was identified as 1-(4-hydroxybenzyl)-2,4-dimethoxy-7-hydroxy-9,10-dihydrophenanthrene. The locations of two methoxyl groups at C-2 and C-4 were confirmed by NOE experiments. Irradiation of the methoxyl at δ 3.88 enhanced the signals at H-3 (δ 6.52) and H-5 (δ 8.06), and the methoxyl at δ 3.83 caused NOE enhancements of the signals at H-1′ (δ 3.99) and H-3, respectively.

The EIMS of sinensol B (**2**) indicated a molecular ion at m/z 430, which gave a molecular formula of $C_{28}H_{30}O_4$ by HREIMS. The ^{1}H NMR spectrum of **2** revealed a 4-hydroxybenzyl group [δ 3.95 (2H, s), 6.64 and 6.90 (2H each, d, J = 9.0 Hz)], a 2-isopentenyl group [δ 3.38 (2H, d, J = 6.5 Hz), 5.07 (1H, t, J = 6.5 Hz), 1.66 and 1.76 (3H each, s)], two ortho-coupled aromatic protons [δ 6.63 and 7.84 (1H each, d, J = 8.5 Hz), an isolated aromatic proton (δ 6.64), two dihydrophenanthrene methylene protons [δ 2.53 (4H, s)], and two methoxyl groups (δ 3.85 and 3.87). Its UV absorption pattern was similar to that of **1**. The

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10.1021/np000170p CCC: $19.00
Published on Web 10/26/2000

differences between **2** and **1** were the *ortho*-phenylprotons and an additional isopentenyl moiety. The HMBC correlations of H-1″/C-7, -8, and -8a; H-1′/C-1, -2, and -10a; CH_3O (δ 3.87) and C-2; and CH_3O (δ 3.85)/C-4 aided in establishing the location of the isopentenyl, 4-hydroxylbenzyl, and two methoxyl groups on the dihydrophenanthrene skeleton. Compound **2** was determined to be 1-(4-hydroxybenzyl)-2,4-dimethoxy-7-hydroxy-8-isopentenyl-9,10-dihydrophenanthrene. Further confirmation was provided by NOESY correlations of H-1″/H-9, H-1′/H-10, CH_3O (δ 3.87), H-3/both CH_3O, and CH_3O (δ 3.85)/H-5.

Sinensol C (**3**) was isolated as a pale yellow amorphous powder, and its molecular formula, $C_{27}H_{28}O_4$, was suggested by ^{13}C NMR, DEPT, and HREIMS. The ^{1}H NMR revealed an isopentenyl group, a 4-hydroxybenzyl group, two ortho-coupled aromatic protons, an isolated aromatic proton, and one methoxyl group. Comparison of the NMR data of **3** and **2** indicated that they had the same skeleton, with the exception of a methoxyl group in **2** instead of a hydroxyl group in **3**. Comparison of its spectral data with spirasineol-A (**7**),[4,5] indicated that **3** was an isomer of **7**, and the only difference was the positions of the methoxyl and hydroxyl groups. The long-range HMBC correlations of H-3/C-2, -4 and -4a; CH_3O (δ 3.77)/C-4; and NOESY correlations of CH_3O/H-3 (δ 6.47) and -5 (δ 7.83) helped to confirm the location of the methoxyl group.

Sinensol D (**4**) was obtained as colorless amorphous powder, which was shown to have molecular formula $C_{27}H_{26}O_4$ by HREIMS and ^{13}C NMR. The IR spectrum showed hydroxyl (3400, 1200 cm^{-1}), aromatic (1616, 1510 cm^{-1}), and *gem*-dimethyl (1380, 1373 cm^{-1}) absorptions. A 2,2-dimethyl chromene moiety in **4** was revealed from its ^{1}H NMR [δ 1.39 (6H, s), 5.70 and 6.66 (1H each, d, J = 10.5 Hz)]. The structure of sinensol D (**4**) was elucidated as 1-(4-hydroxybenzyl)-2-methoxy-4-hydroxy-8-{2″,2″-dimethylpyrano[5″,6″:7,8]}dihydrophenanthrene from HMBC and NOESY correlations (see Experimental Section).

Sinensol E (**5**) had a molecular formula of $C_{27}H_{28}O_5$, as indicated by HREIMS and ^{13}C NMR. The UV spectrum of **5** was similar to that of **4**. Its IR spectrum showed hydroxyl (3380, 1196, 1050 cm^{-1}) and benzene ring (1616, 1600, 1515 cm^{-1}) absorptions. The ^{1}H NMR spectrum exhibited *ortho* aromatic protons (δ 6.73 and 7.74), a 4-hydroxylbenzyl group [δ (6.70 and 6.99)], an isolated phenyl proton (δ 6.48), a methoxyl group (δ 3.81), two phenolic hydroxyl groups (δ 4.68), and an aliphatic hydroxyl group (δ 5.45), which were similar to those of spirasineol-A (**7**); but the characteristic isopentenyl signals were absent. Instead, there were signals due to two *tert*-methyl signals (δ 1.27 and 1.38), a methylene signal (δ 3.12), and an oxygenated methine proton signal (δ 4.67). The data suggested that **5** was a derivative of spirasineol-A (**7**) with an oxidative cyclization between the isopentenyl group at C-8 and the hydroxyl group at C-7 forming a furan ring.[5] This assignment was supported by the appearance of a MS fragment ion peak at *m*/*z* 373 ($M^+ - C_3H_7O$). The key HMBC correlations of H-3″/C-7, -8, -8a, -2″, -6″; H-2″/C-3″, -4″, -5″, -6″, -8 confirmed the structural assignment for sinensol E (**5**).

Sinensol F (**6**) was obtained as pale yellow needles, mp 137−139 °C. Its molecular formula $C_{34}H_{34}O_5$ was established by HREIMS and ^{13}C NMR. The IR spectrum showed hydroxyl (3400, 1195 cm^{-1}) and aromatic ring (1600, 1515 cm^{-1}) absorptions. UV absorption peaks at 312 (sh), 300, 280, 271 (sh) nm were observed. The ^{1}H NMR revealed two 4-hydroxybenzyl groups, a 2-isopentenyl group, and two isolated aromatic protons. In comparison with the above compounds, the proton signals for the *ortho* aromatic protons disappeared; instead, an isolated aromatic proton (δ 7.90) and a 4-hydroxybenzyl group were present. The key HMBC correlations (Figure 1) of H-1″/C-7, -8, -8a; H-1′/C-1, -2, -2′, -3′(-7′), -10a; and H-1‴/C-5, -6, -7, -2‴, -3‴(-7‴) led to the identification and assignment of the isopentenyl and two 4-hydroxybenzyl groups on the dihydrophenanthrene skeleton. From the above analysis, compound **6** was given the structure 1,6-di(4-hydroxybenzyl)-2-methoxy-4,7-dihydroxy-8-isopentenyl-9,10-dihydrophenanthrene. The key NOESY correlations of H-1″/H-9; H-1′/H-10; OCH_3/H-1′, -3; and H-1‴/H-5 confirmed this conclusion. All the isolated dihydrophenanthrenes were confirmed active against the MS-G2 cell line and were cytotoxic at 20 μg/mL, but showed no anti-HBeAg effect at noncytotoxic (5 or 10 μg/mL) doses.

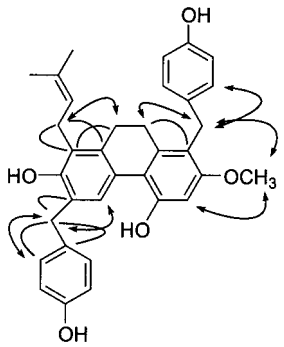

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Figure 1. Key NOESY (↔) and HMBC (⌒) correlations of **6**.

Experimental Section

General Experimental Procedures. Melting points were determined on Yanagimoto micromelting point apparatus and are uncorrected. Optical rotations were recorded on a JASCO DIP-370 polarimeter. IR spectra were recorded on a Perkin-Elmer 781 spectrophotometer. UV spectra were measured on a Hitachi U-3200 spectrophotometer. NMR were run on Bruker AC-300 and Varian unity INOVA-500 spectrometers. Mass spectra (EIMS and HREIMS) were obtained on a JEOL JMS-HX110 and a JEOL SX-102A instrument, respectively.

Plant Material. The aerial parts of *S. sinenesis* were purchased from a local herbal medicine store in Taipei, Taiwan, in April 1999. The plant was identified by comparison with the voucher specimens already deposited at the Herbarium of the Department of Botany, National Taiwan University, Taipei, Taiwan (no: TAI. 218182, collected on April 12, 1934).

Extraction and Isolation. The dried aerial parts of *S. sinenesis* (3 kg) were extracted with EtOH (each 50 mL × 3) at 50 °C. The EtOH extract was evaporated under reduced pressure. The concentrate was taken up in H_2O and partitioned successively between EtOAc and *n*-BuOH (each 1 L × 3). The EtOAc-soluble fraction (35 g) was subjected to column chromatography over Si gel using *n*-hexane−EtOAc gradient. The fractions (30−60% EtOAc in hexane) rich in dihydrophenanthrenes were rechromatogramed over a Si gel column eluted with *n*-hexane−EtOAc (2:1 and 1:1) and 5−10% MeOH/EtOAc to yield three fractions. The first two fractions were further fractionated on a Sephadex LH-20 column (EtOAc−MeOH, 1:1), then separated by preparative HPLC on a Si gel (Merck, Si 60, 7 μm) column using *n*-hexane−EtOAc, (2:1 or 1:1) to afford five known compounds: orchinol[3] (28 mg), spiranthoquinone[4] (12 mg), spiranthol-A (15 mg), spirasineol- A (42 mg), and shancidin (14 mg), plus compounds **1** (46 mg), **2** (15 mg), **3** (18 mg), **4** (15 mg), and **5** (24 mg); the third fraction was further separated using a Sephadex LH-20 column (EtOAc−MeOH, 1:1) to give **6** (28 mg).

Sinensol A (1): colorless amorphous powder; IR (KBr) ν_{max} 3400, 3005, 1615, 1596, 1574, 1230, 1195, 1095, 808 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 312 sh (4.08), 296 (4.16), 280 (4.42), 270 sh (4.36) nm; ^1H NMR ($CDCl_3$, 500 MHz) δ 2.60 and 2.63 (2H each, m, H-9, H-10), 3.83 and 3.88 (3H each, s, OCH_3), 3.99 (2H, s, H-1′), 6.52 (1H, s, H-3), 6.63 (1H, d, J = 2.1 Hz, H-8), 6.66 and 6.95 (2H each, d, J = 8.1 Hz, H-4′, H-6′, and H-3′,H-7′), 6.68 (1H, dd, J = 8.7, 2.1 Hz, H-6), 8.06 (1H, d, J = 8.7 Hz, H-5); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 26.2 (t, C-10), 29.7 (t, C-9), 30.1 (t, C-1′), 55.7 (q, OCH_3), 55.8 (q, OCH_3), 94.7 (d, C-3), 112.7 (d, C-6), 113.8 (d, C-8), 115.0 (d, C-4′, C-6′), 116.8 (s, C-4a), 118.7 (s, C-1), 125.9 (s, C-4b), 129.0 (d, C-3′, C-7′), 129.4 (d, C-5), 133.5 (s, C-2′), 139.7 (s, C-8a), 139.9 (s, C-10a), 153.4 (s, C-5′), 153.5 (s, C-7), 156.0 (s, C-4), 156.7 (s, C-2); HMBC correlations: H-3/C-1, -2, -4, -4a; H-5/C-4a, -4b, -8a, -6, -7; H-6/C-4b, -5, -7, -8; H-8/C-6, -7, -8a, -9, -4b; H-10/C-1, -4a, -8a, -9, -10a; H-1′/C-1, -2, -10a, -2′, -3′, -7′; OCH_3 (δ 3.88)/C-2; OCH_3(δ 3.83)/C-4; H-3′ (-7′)/C-1′, -2′, -4′ (-6′), C-5′; H-4′ (6′)/C-2′, -3′ (-7′), -5′; EIMS m/z 362 $[M]^+$ (100), 256 (30), 176 (5); HREIMS m/z 362.1519 (calcd for $C_{23}H_{22}O_4$, 362.1522).

Sinensol B (2): colorless amorphous powder; IR (KBr) ν_{max} 3450, 1615, 1590, 1515, 1240, 1200, 1175, 1100, 815 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 311 sh (4.06), 298 (4.16), 281 (4.40), 270 sh (4.35) nm; ^1H NMR (CD_3OD, 500 MHz) δ 1.66 and 1.76 (3H each, s, H-4″, -5″), 2.53 (4H, s, H-9, H-10), 3.38 (2H, d, J = 6.5 Hz, H-1″), 3.85 and 3.87 (3H each, s, OCH_3), 3.95 (2H, s, H-1′), 5.07 (1H, t, J = 6.5 Hz, H-2″), 6.63 and 7.84 (1H each, d, J = 8.5 Hz, H-6, H-5), 6.64 (1H, s, H-3), 6.64 and 6.90 (2H each, d, J = 9.0 Hz, H-4′, H-6′, and H-3′,H-7′); ^{13}C NMR (CD_3OD, 125 MHz) δ 18.0 (q, C-4″), 25.8 (q, C-5″), 25.9 (t, C-1″), 26.4 (t, C-9), 27.4 (t, C-10), 30.9 (t, C-1′), 56.2 (q, OCH_3), 56.3 (q, OCH_3), 96.3 (d, C-3), 113.0 (d, C-6), 115.9 (d, C-4′, C-6′), 117.5 (s, C-1), 119.0 (s, C-4a), 124.8 (s, C-4b), 124.8 (d, C-2″), 125.4 (d, C-5), 126.3 (s, C-8), 129.9 (d, C-3′, C-7′), 131.4 (s, C-3″), 133.7 (s, C-2′), 139.0 (s, C-8a), 140.7 (s, C-10a), 154.2 (s, C-7), 156.0 (s, C-4), 157.3 (s, C-5′), 158.0 (s, C-2); HMBC correlations: H-3/C-1, -2, -4, -4a; H-5/C-4a, -4b, -6, -7, -8a,; H-6/C-4b, -5, -7, -8; H-9 (-10)/C-1, -4a, -4b, -8, -8a, -9, -10, -10a; H-1′/C-1, -2, -10a, -2′, -3′ (-7′); OCH_3(δ 3.87)/C-2; OCH_3 (δ 3.85)/C-4; H-3′ (-7′)/C-1′, -2′, -4′ (-6′), C-5′; H-4′ (-6′)/C-2′, -3′ (-7′), -5′; H-1″/C-2″, -3″, -7, -8, -8a; EIMS m/z 430 $[M]^+$ (100), 416 (30), 325 (21), 269 (11); HREIMS m/z 430.2142 (calcd for $C_{28}H_{30}O_4$, 430.2145).

Sinensol C (3): pale yellow amorphous powder; IR (KBr) ν_{max} 3490, 3400, 1615, 1595, 1510, 1480, 1230, 1190, 1170, 1135, 1100, 820 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 297 sh (4.10), 282 (4.40), 273 sh (4.32) nm; ^1H NMR (CD_3OD, 500 MHz) δ 1.68 and 1.79 (3H each, s, H-4″, H-5″), 2.62 and 2.67 (2H each, m, H-9, H-10), 3.42 (2H, d, J = 6.5 Hz, H-1″), 3.77 (3H, s, OCH_3), 3.94 (2H, s, H-1′), 5.10 (1H, t, J = 6.5 Hz, H-2″), 6.47 (1H, s, H-3), 6.63 and 7.05 (2H each, d, J = 8.5 Hz, H-4′, -6′ and H-3′, H-7′), 6.67 and 7.83 (1H each, d, J = 9.0 Hz, H-6, H-5); ^{13}C NMR (CD_3OD, 125 MHz) δ 18.0 (q, C-4″), 25.9 (q, C-5″), 25.9 (t, C-1″), 26.8 (t, C-10), 28.9 (t, C-1′), 31.7 (t, C-9), 56.0 (q, OCH_3), 103.9 (d, C-3), 113.2 (d, C-6), 115.7 (d, C-4′, H-6′), 117.6 (s, C-4a), 118.6 (s, C-1), 124.8 (d, C-2″), 126.3 (s, C-4b), 126.5 (d, C-5), 126.6 (s, C-8), 130.4 (d, C-3′, H-7′), 131.5 (s, C-3″), 133.9 (s, C-2′), 139.0 (s, C-8a), 139.4 (s, C-10a), 153.0 (s, C-7), 154.2 (s, C-5′), 156.0 (s, C-2), 157.6 (s, C-4); HMBC correlations: H-3/C-1, -2, -4, -4a; H-5/C-4a, -4b, -6, -7, -8a; H-6/C-4b, -5, -7, -8; H-9/C-8, -8a, -4b, -10, -10a; H-10/C-1, -4a, -9, -8a; H-1″/C-7, -8, -8a, -2″, -3″; H-2″/C-1″, -3″, -4″, -5″, -8; H-1′/C-1, -2, -10a, -2′, -3′ (-7′); OCH_3/C-4; EIMS m/z 416 $[M]^+$ (100), 414 (30), 322 (10), 311 (15); HREIMS m/z 416.1986 (calcd for $C_{27}H_{28}O_4$, 416.1988).

Sinensol D (4): colorless amorphous powder; IR (KBr) ν_{max} 3400, 1616, 1510, 1460, 1380, 1373, 1200, 1100, 810 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 314 sh (4.00), 300 (4.01), 279 (4.25), 267 (4.35), 259 sh (4.28) nm; ^1H NMR (CD_3OD, 500 MHz) δ 1.39 (6H, s, H-7″, -8″), 2.59 (4H, s, H-9, -10), 3.79 (3H, s, OCH_3), 3.92 (2H, s, H-1′), 5.70 and 6.66 (1H each, d, J = 10.5 Hz, H-3″, H-4″), 6.48 (1H, s, H-3), 6.60 and 8.09 (1H each, d, J = 9.0 Hz, H-6, H-5), 6.65 and 6.90 (2H each, d, J = 8.5 Hz, H-4′, H-6′ and H-3′, H-7′); ^{13}C NMR (CD_3OD, 125 MHz) δ 25.1 (t, C-10), 27.1 (t, C-9), 27.9 (q, C-7″, C-8″), 30.8 (t, C-1′), 55.9 (q, OCH_3), 76.0 (s, C-2″), 99.0 (d, C-3), 114.5 (d, C-6), 115.9 (s, C-1), 116.0 (d, C-4′, C-6′), 116.3 (s, C-4a), 118.7 (s, C-10a), 118.8 (s, C-8), 120.4 (d, C-4″), 128.0 (s, C-8a), 129.9 (d, C-3′, C-7′), 130.1 (d, C-5), 133.8 (d, C-3″), 134.9 (s, C-4b), 140.4 (s, C-10a), 152.2 (s, C-7), 154.7 (s, C-4), 156.0 (s, C-5′), 158.1 (s, C-2); HMBC correlations: H-3/C-1, -2, -4, -4a; H-5/C-4a, -4b, -6, -7, -8a; H-6/C-4b, -5, -7, -8; H-9 (10)/C-1, -4a, -4b, -8, -8a; H-4″/C-7, -8, -8a, -2″, -3″; H-3″/C-2″, -4″, -7″, -8″, -8; H-1′/C-1, -2, -10a, -2′, -3′ (-7′); OCH_3/C-2; NOESY correlations: OCH_3/H-1′, -3; H-1′/OCH_3, H-10; H-4″/H-9, H-3″; H-3″/H-7″, -8″, -4″; EIMS m/z 414 $[M]^+$ (100), 413 (20), 309 (26), 257 (5), 177 (9); HREIMS m/z 414.1837 (calcd for $C_{27}H_{26}O_4$, 414.1832).

Sinensol E (5): colorless amorphous powder; $[\alpha]_D$ −4° (c 1.0, MeOH); IR (KBr) ν_{max} 3380, 1616, 1600, 1515, 1470, 1240, 1196, 1170, 1130, 1050, 815 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 318 sh (4.01), 303 (4.11), 281 (4.36), 274 sh (4.28) nm; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.27 (3H, d, J = 9.5 Hz, H-7″), 1.38 (3H, s, H-8″), 2.55 and 2.64 (2H each, m, H-9, H-10), 3.12 (2H, d, J = 8.5 Hz, H-3″), 3.81 (3H, s, OCH_3), 4.00 (2H, s, H-1′), 4.67 (1H, t, J = 9.5 Hz, H-2″), 4.68 (2H, br s, OH), 5.45 (1H, br s, OH), 6.48 (1H, s, H-3), 6.73 and 7.74 (1H each, d, J = 8.5 Hz, H-6, H-5), 6.70 and 6.99 (2H each, d, J = 8.5 Hz, H-4′, H-6′, and H-3′, H-7′); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 24.3 (q, C-7″), 26.1 (t, C-10), 26.4 (t, C-9), 29.9 (t, C-3″), 30.3 (t, C-1′), 55.9 (q, OCH_3), 72.1 (s, C-6″), 88.8 (d, C-2″), 98.5 (d, C-3), 107.0 (d, C-6), 115.3 (s, C-4a, 115.3 (d, C-4′, C-6′), 119.0 (s, C-1), 125.4 (d, C-5), 125.7 (s, C-8), 129.3 (s, C-4b), 129.3 (d, C-3′, C-7′), 133.7 (s, C-2′), 135.6 (s, C-8a), 139.6 (s, C-10a), 151.9 (s, C-4), 153.6 (s, C-5′), 157.2 (s, C-2), 158.2 (s, C-7); HMBC correlations: H-3/C-1, -2, -4, -4a; H-5/C-4a, -4b, -6, -7, -8a; H-6/C-4b, -5, -7, -8; H-9/C-8, -8a, -4b, -10, -10a; H-10/C-1, -4a, -9, -8a; H-3″/C-7 (-5″), -8 (-4″), -8a, -2″, -6″; H-2″/C-3″, -4″ (-8), -6″, -7″, -8″; H-1′/C-1, -2, -10a, -2′, -3′ (C-7′); OCH_3/C-2; EIMS m/z 432 $[M]^+$ (100), 373 (10), 361 (10), 267 (15), 107 (62), 59 (60); HREIMS m/z 432.1938 (calcd for $C_{27}H_{28}O_5$, 432.1937).

Sinensol F (6): pale yellow needles, mp 137−139 °C; IR (KBr) ν_{max} 3400, 3025, 1600, 1515, 1460, 1220, 1195, 1175, 820, 740 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 312 sh (4.11), 300 (4.17), 280 (4.38), 271 sh (4.28) nm; ^1H NMR (CD_3OD, 500 MHz) δ 1.66 and 1.76 (3H each, s, H-4″, H-5″), 2.51 (4H, s, H-9, H-10), 3.41 (2H, d, J = 6.5 Hz, H-1″), 3.77 (3H, s, OCH_3), 3.89 and 3.90 (2H each, s, H-1′, H-1‴), 5.07 (1H, J = 6.5 Hz, H-2″), 6.43 (1H, s, H-3), 6.63 and 6.89 (2H each, d, J = 8.5 Hz, H-4′, H-6′ and H-3′, H-7′), 6.69 and 7.07 (2H each, d, J = 8.5 Hz, H-4‴, H-6‴ and H-3‴, H-7‴), 7.90 (1H, s, H-5); ^{13}C NMR (CD_3OD, 125 MHz) δ 18.1 (q, C-4″), 25.9 (q, C-5″), 26.3 (t, C-9), 26.4 (t, C-1″), 27.5 (t, C-10), 30.8 (t, C-1′), 36.6 (t, C-1‴), 55.9 (q, OCH_3), 99.0 (d, C-3), 115.9 (d, C-4′, C-6′), 116.0 (d, C-4‴, H-6‴), 116.9 (s, C-4a), 118.6 (s, C-1), 124.8 (s, C-2″), 126.7 (s, C-8), 126.9 (s, C-6), 127.5 (s, C-4b), 129.4 (d, C-5), 129.9 (d, C-3′, C-7′), 130.9 (d, C-3‴, C-7‴), 131.7 (s, C-3″), 133.5 (s, C-2‴), 133.9 (s, C-2′). 136.5 (s, C-8a), 140.7 (s, C-10a), 151.1 (s, C-7), 154.4 (s, C-4), 156.0 (s, C-5′), 156.3 (s, C-5), 157.9 (s, C-2); HMBC and NOESY correlations, see Figure 1; EIMS m/z 522 $[M^+]$ (10), 456 (20), 416 (100), 368 (15), 348 (70), 248 (70), 107 (28), 69 (12); HREIMS m/z 522.2409 (calcd for $C_{34}H_{34}O_5$, 522.2407).

Acknowledgment. This work was supported by the National Science Council of the Republic of China (NSC 89-2314-B-077-012).

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NP000170P