# Sesquiterpenoids and Phenylpropanoids from *Chloranthus serratus*

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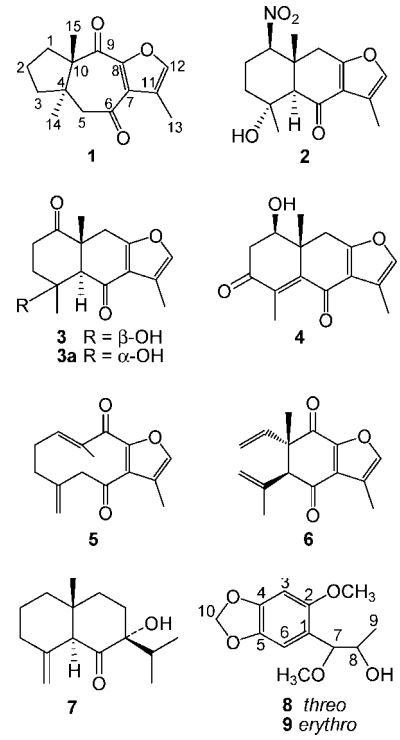
Seven new sesquiterpenoids, chlorantenes A−G (**1**−**7**), two new phenylpropanoids (**8** and **9**), and six known sesquiterpenoids were isolated from the whole plants of *Chloranthus serratus*. Their structures were elucidated on the basis of spectroscopic analyses. Chlorantene A (**1**) was a sesquiterpene with a unique C-4 and C-10 linkage, and chlorantene B (**2**) possessed a nitro group at C-1. The structure of a eudesmane-type sesquiterpene previously isolated from *Chloranthus henryi* was revised as its 4-epimer (**3a**).

Plants of the genus *Chloranthus* (Chloranthaceae) are mainly distributed in eastern Asia,[1] with 13 species and five varieties occurring in China.[2] Some plants of this genus have been used in Chinese folk medicine for treatment of bone fractures.[3] A variety of sesquiterpenoids[4] and sesquiterpenoid oligomers have been isolated from this genus.[5] *Chloranthus serratus* (Thunb.) Roem. et Schult. is a perennial herb found in southern China,[2] which has been used to activate blood circulation against stasis in Chinese folk medicine.[6] Chemical studies conducted previously on *C. serratus* reported the presence of amides,[7] sesquiterpenoids,[8] and sesquiterpenoid dimers.[9] In the current study, seven new sesquiterpenoids (**1**−**7**), two new phenylpropanoids (**8** and **9**), and six known compounds were isolated from the whole plants of *C. serratus*. The structure of a eudesmane-type sesquiterpene, 4$\beta$-hydroxy-8,12-epoxyeudesma-7,11-diene-1,6-dione,[10] previously isolated from *Chloranthus henryi,* was revised (**3a**). We present herein the isolation, structural elucidation, and antimicrobial test of the new compounds.




## Results and Discussion

Chlorantene A (**1**), a white amorphous powder, displayed a molecular formula of $C_{15}H_{18}O_3$ as determined by HREIMS at *m/z* 246.1251 $[M]^+$ (calcd 246.1256) and indicating 7 degrees of unsaturation. Its IR absorptions implied the presence of conjugated carbonyls (1674, 1653 $cm^{-1}$). The $^1H$ NMR spectrum of **1** (Table 1) showed three methyl groups [$\delta_H$ 1.06, 1.33 (each 3H, s), 2.25 (3H, d, $J = 1.0$ Hz)] and an olefinic proton at $\delta_H$ 7.41 (1H, q, $J =$ 1.0 Hz, H-12). The $^{13}C$ NMR spectrum (with DEPT experiments, Table 1) revealed the presence of 15 carbon resonances comprising three methyl, four methylene, one olefinic methine, and seven quaternary carbons (two of which are carbonyl and three olefinic carbons). The ketone groups and double bonds accounted for 4 out of the 7 degrees of unsaturation, the remaining 3 degrees of unsaturation required compound **1** to be tricyclic.

The scaffold of compound **1** was constructed by a combination of 2D NMR analysis. The $^1H$ and $^{13}C$ NMR and HSQC spectra first allowed the assignment of all the protons to their bonding carbons. In the HMBC spectrum, the mutual correlations of $H_3$-15/C-1, C-4, and C-10; H-2/C-1, C-3, C-4, and C-10; and $H_3$-14/C-3, C-4, and C-10 indicated the presence of five-membered ring A (Figure S1-1, Supporting Information) bearing methyl groups at C-4 and C-10, respectively. The HMBC correlations from $H_3$-13 to C-7, C-11, and C-12 and from H-12 to C-7, C-8, and C-11 enabled the establishment of a furan ring C. The HMBC correlations from $H_2$-5 to C-4, C-6 ($\delta_C$ 195.7), C-7, and C-10 allowed the linkage of rings A and C via the C-5 and C-6 unit, and the HMBC correlations from H-1 and $H_3$-15 to C-9 ($\delta_C$ 192.9) permitted the attachment of C-9 carbonyl to C-10. The "loose ends" of C-8 and C-9 were tentatively connected under the requirement of the tricyclic feature of **1** as indicated. The relative configuration of **1** was established by a NOESY experiment, in which the correlations from $H_3$-15 to H-1$\beta$, H-3$\beta$, and H-5$\beta$ indicated that they were cofacial and were arbitrarily assigned having a $\beta$-configuration. Consequently, the NOESY correlations of $H_3$-14/H-1$\alpha$, H-3$\alpha$, and H-5$\alpha$ showed that they were $\alpha$-oriented.

Chlorantene B (**2**), a white amorphous powder, had the molecular formula $C_{15}H_{19}NO_5$ as determined by HREIMS. The ESIMS ion at *m/z* 316.1 $[M + Na]^+$ supported this assignment. The IR spectrum exhibited the absorption bands for OH (3502 $cm^{-1}$), conjugated ketone (1656 $cm^{-1}$), and nitro groups (1544 and 1363 $cm^{-1}$). The $^1H$ and $^{13}C$ NMR (Table 1) spectra of **2** showed the signals of three methyl groups [$\delta_H$ 1.10, 1.54 (3H, both s, 14 and 15-Me), 2.19 (3H, d, $J = 1.1$ Hz, 13-Me)], a trisubstituted furan ring [$\delta_H$ 7.12 (brs); $\delta_C$ 119.0 (C-7), 164.8 (C-8), 119.2 (C-11), 140.1 (C-12)], and three methylene, two methine, and three quaternary carbons. The NMR data of **2** showed high similarity to those of curcolonol,[11] except that C-1 ($\delta_C$ 92.9) of **2** was severely downfield shifted as

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**Table 1.** $^1$H NMR and $^{13}$C NMR Data of Compounds **1**, **2**, **4**, and **5**

| | **1**[a] | | **2**[a] | | **4**[b] | | **5**[a] | |
|---|---|---|---|---|---|---|---|---|
| no. | $\delta_C$ | $\delta_H$ (mult., *J* in Hz) | $\delta_C$ | $\delta_H$ (mult., *J* in Hz) | $\delta_C$ | $\delta_H$ (mult., *J* in Hz) | $\delta_C$ | $\delta_H$ (mult., *J* in Hz) |
| 1 | 33.1 | 2.55, m<br>1.79, m | 92.9 | 4.63, dd (12.6, 4.0) | 72.9 | 4.19, dd (11.3, 5.9) | 140.3 | 6.27, dd (7.2, 7.2) |
| 2 | 17.5 | 1.76, m (2H) | 23.4 | 2.30, m<br>2.13, m | 43.0 | 2.70, dd (16.2, 11.3)<br>2.65, dd (16.2, 5.9) | 29.1 | 2.40, m (2H) |
| 3 | 40.0 | 1.89, m<br>1.64, m | 37.4 | 1.91, ddd (13.8, 7.2, 3.6)<br>1.62, ddd (14.3, 13.8, 4.1) | 198.5 | | 34.8 | 2.42, m (2H) |
| 4 | 43.1[c] | | 70.5 | | 138.2 | | 140.7 | |
| 5 | 52.0 | 3.05, d (17.6)<br>2.79, d (17.6) | 61.9 | 2.64, s | 150.7 | | 51.8 | 3.45, s (2H) |
| 6 | 195.7 | | 194.9 | | 187.0 | | 198.4 | |
| 7 | 126.7 | | 119.0 | | 120.9 | | 137.8 | |
| 8 | 150.8 | | 164.8 | | 165.7 | | 148.4 | |
| 9 | 192.9 | | 40.1 | 3.10, d (17.1)<br>2.97, d (17.1) | 36.6 | 3.19, d (17.6)<br>3.04, d (17.6) | 185.3 | |
| 10 | 58.9[c] | | 43.2 | | 45.5 | | 139.4 | |
| 11 | 123.9 | | 119.2 | | 119.6 | | 121.0 | |
| 12 | 143.6 | 7.41, q (1.0) | 140.1 | 7.12, brs | 141.1 | 7.39, brs | 143.9 | 7.39, q (1.0) |
| 13 | 10.3 | 2.25, d (3H, 1.0) | 8.9 | 2.19, d (3H, 1.1) | 8.7 | 2.21, s (3H) | 8.6 | 2.02, d (3H, 1.0) |
| 14 | 22.5 | 1.06, s (3H) | 24.2 | 1.54, s (3H) | 13.2 | 2.03, s (3H) | 118.8 | 5.14, s<br>4.98, s |
| 15 | 23.2 | 1.33, s (3H) | 16.2 | 1.10, s (3H) | 18.0 | 1.28, s (3H) | 13.3 | 1.88, s (3H) |

[a] Data were measured in $CDCl_3$ at 400 MHz ($^1$H) and 100 MHz ($^{13}$C). [b] Data were measured in $CD_3COCD_3$ at 400 MHz ($^1$H) and 100 MHz ($^{13}$C). [c] Signals may be exchangeable.

**Table 2.** $^1$H NMR and $^{13}$C NMR Data of Compounds **3a** and **3**

| | **3a**[a] | | **3a**[b] | | **3**[a] | | **3**[b] | |
|---|---|---|---|---|---|---|---|---|
| no. | $\delta_C$ | $\delta_H$ (mult., *J* in Hz) | $\delta_C$ | $\delta_H$ (mult., *J* in Hz) | $\delta_C$ | $\delta_H$ (mult., *J* in Hz) | $\delta_C$ | $\delta_H$ (mult., *J* in Hz) |
| 1 | 210.9 | | 211.0 | | 212.8 | | 212.4 | |
| 2 | 34.6 | 2.75, ddd (15.2, 14.7, 6.0)<br>2.47, ddd (15.2, 4.6, 2.9) | 34.6 | 2.83, m<br>2.24, m | 33.6 | 3.09, ddd (14.1, 14.1, 5.5)<br>2.20, ddd (14.1,5.6, 3.6) | 33.5 | 2.96, m<br>2.08, m |
| 3 | 38.8 | 2.04, ddd (13.4,6.0, 2.9)<br>1.92, ddd (14.7, 13.4, 4.6) | 38.9 | 1.80, m<br>1.78, m | 39.5 | 2.14, ddd (13.3, 5.5, 3.6)<br>1.74, ddd (14.1, 13.3, 5.6) | 38.9 | 1.82, m<br>1.76, m |
| 4 | 70.2 | | 69.4 | | 69.6 | | 68.6 | |
| 5 | 62.0 | 2.91, s | 61.1 | 3.11, s | 60.6 | 2.78, s | 59.3 | 3.03, s |
| 6 | 195.3 | | 194.9 | | 196.1 | | 194.3 | |
| 7 | 118.9 | | 118.8 | | 120.3 | | 119.4 | |
| 8 | 165.7 | | 165.4 | | 164.9 | | 164.4 | |
| 9 | 35.5 | 3.09, d (17.7)<br>2.96, d (17.7) | 34.9 | 3.16, d (17.8)<br>2.79, d (17.8) | 34.7 | 3.14, d (17.9)<br>2.77, d (17.9) | 34.1 | 3.13, d (17.6)<br>2.67, d (17.6) |
| 10 | 51.0 | | 50.5 | | 52.5 | | 51.7 | |
| 11 | 119.2 | | 118.1 | | 118.6 | | 118.0 | |
| 12 | 140.1 | 7.14, brs | 140.6 | 7.45, brs | 140.0 | 7.09, brs | 140.4 | 7.42, brs |
| 13 | 8.9 | 2.21, d (3H, 1.3) | 8.8 | 2.10, d (3H, 1.2) | 8.7 | 2.16, d (3H, 1.0) | 8.7 | 2.09, d (3H, 1.6) |
| 14 | 23.7 | 1.74, s (3H) | 23.4 | 1.59, s (3H) | 30.2 | 1.50, s (3H) | 29.5 | 1.47, s (3H) |
| 15 | 20.2 | 1.28, s (3H) | 20.0 | 1.12, s (3H) | 20.0 | 1.39, s (3H) | 20.2 | 1.26, s (3H) |

[a] Data were measured in $CDCl_3$ at 400 MHz ($^1$H) and 100 MHz ($^{13}$C). [b] Data were measured in DMSO-$d_6$ at 400 MHz ($^1$H) and 100 MHz ($^{13}$C).

compared with C-1 ($\delta_C$ 77.9) of curcolonol, bearing a C-1-OH, suggesting that the nitro group was attached to C-1 of **2**. Analyses of 2D NMR spectra of **2**, including HSQC and HMBC, verified this assignment.

The relative configuration of **2** was established by a ROESY experiment. ROESY correlations of H-2$\beta$/Me-14 and Me-15, and Me-15/Me-14 and H-9$\beta$, indicated that they were cofacial and randomly assigned as $\beta$-configured. The ROESY correlations of H-3$\alpha$/H-1$\alpha$ and H-5, and H-9$\alpha$/H-5, then enabled the assignment of H-1 and H-5 being $\alpha$-directed.

Compound **3a** was obtained as a white amorphous powder with the molecular formula $C_{15}H_{18}O_4$ as assigned by HREIMS. IR absorptions showed the presence of OH (3525 cm$^{-1}$), ketone (1711 cm$^{-1}$), and conjugated ketone (1666 cm$^{-1}$) groups. The $^1$H and $^{13}$C NMR data (Table 2) of **3a** displayed three methyl groups and a furan ring and two carbonyl, three methylene, one methine, and two quaternary carbons. Analysis of the NMR data indicated that the structure of **3a** was similar to that of **2**, with the only difference being the presence of a C-1 ketone group in **3a**, which was verified by 2D NMR (HSQC, HMBC, and ROESY) experiments. The ROESY correlations of H-2$\beta$ (2.75, ddd, $J$ = 15.2, 14.7, 6.0 Hz)/Me-14 (1.74, s) and Me-15 (1.28, s), and Me-14/Me-15, revealed that they were cofacial and arbitrarily assigned as $\beta$-configured. The H-5 was consequently assigned as $\alpha$-oriented by the ROESY correlations of H-5/H-3$\alpha$ and H-9$\alpha$ of H-5. The structure of **3a** was thus elucidated to be 4$\alpha$-hydroxy-8,12-epoxyeudesma-7,11-diene-1,6-dione. However, 4$\beta$-hydroxy-8,12-epoxyeudesma-7,11-diene-1,6-dione[10] shared the same NMR data with those of **3a**, which was assigned as the 4-epimer of **3a**. The $^1$H NMR data of the sesquiterpene reported in the literature[10] were recorded in DMSO-$d_6$, but they were actually identical with those of **3a** measured in $CDCl_3$ in our study. To clarify this uncertainty, the NMR data of **3a** were also recorded in DMSO-$d_6$ (see Table 2). The differences of NMR data of **3a** recorded in $CDCl_3$ and DMSO-$d_6$ were obvious, suggesting that the data in the literature were likely recorded in $CDCl_3$ rather than DMSO-$d_6$.

Fortunately, the 4-epimer of **3a**, 4$\beta$-hydroxy-8,12-epoxyeudesma-7,11-diene-1,6-dione, namely, chlorantene C (**3**), was also isolated. The only structural difference between **3** and **3a** was the configuration at C-4, which caused the distinct changes of chemical shifts of carbons and protons near C-4 (see Table 2). The relative configuration of **3** was also established by a ROESY experiment,

**Table 3.** $^1$H NMR and $^{13}$C NMR Data of Compounds **6**−**9**[a]

| | **6** | | **7** | | **8** | | **9** | |
|---|---|---|---|---|---|---|---|---|
| no. | $\delta_C$ | $\delta_H$ (mult., *J* in Hz) | $\delta_C$ | $\delta_H$ (mult., *J* in Hz) | $\delta_C$ | $\delta_H$ (mult., *J* in Hz) | $\delta_C$ | $\delta_H$ (mult., *J* in Hz) |
| 1 | 141.7 | 5.81, dd (17.4, 10.6) | 41.8 | 1.58, m (2H) | 119.1 | | 118.5 | |
| 2 | 116.3 | 5.13, dd (17.4, 8.3)<br>5.09, dd (10.6, 8.3) | 23.4 | 1.60, m (2H) | 153.3 | | 152.8 | |
| 3 | 117.7 | 4.82, s<br>5.01, s | 38.2 | 2.22, m<br>1.94, m | 94.4 | 6.52, s | 94.3 | 6.53, s |
| 4 | 139.8 | | 142.3 | | 147.6 | | 147.4 | |
| 5 | 70.0 | 3.52, s | 54.4 | 3.80, s | 141.4 | | 141.4 | |
| 6 | 193.7 | | 211.1 | | 106.8 | 6.76, s | 107.2 | 6.85, s |
| 7 | 130.0 | | 80.5 | | 81.4 | 4.38, d (7.8) | 80.6 | 4.58, d (4.2) |
| 8 | 154.0 | | 32.1 | 1.89, m<br>1.69, m | 71.5 | 3.74, m | 69.7 | 3.94, m |
| 9 | 187.7 | | 35.4 | 1.98, m<br>1.39, m | 17.5 | 0.98, d (3H, 6.2) | 17.5 | 1.04, d (3H, 6.6) |
| 10 | 55.3 | | 43.9 | | 101.1 | 5.93, d (1.4)<br>5.90, d (1.4) | 101.1 | 5.94, d (1.3)<br>5.91, d (1.3) |
| 11(2-$OCH_3$) | 120.8 | | 31.4 | 2.18, m | 56.3 | 3.74, s (3H) | 56.2 | 3.75, s (3H) |
| 12(7-$OCH_3$) | 145.5 | 7.46, q (1.0) | 16.9 | 0.91, d (3H, 6.7) | 56.5 | 3.20, s (3H) | 57.1 | 3.27, s (3H) |
| 13 | 8.5 | 2.24, d (3H, 1.0) | 16.6 | 0.88, d (3H, 6.7) | | | | |
| 14 | 22.9 | 1.62, s (3H) | 111.2 | 5.77, s<br>4.99, s | | | | |
| 15 | 19.0 | 1.33, s (3H) | 17.1 | 0.73, s (3H) | | | | |

[a] Data were measured in $CDCl_3$ at 400 MHz ($^1$H) and 100 MHz ($^{13}$C).

in which the correlations of Me-15/H-2$\beta$ and H-9$\beta$ indicated that they were cofacial and were randomly fixed as $\beta$-oriented. As a consequence, the mutual correlations of Me-14/H-3α and H-5, and H-3α/H-5, indicated that they were α-oriented. These results indicated that the NMR data reported in the literature[10] corresponded to the structure **3a** rather than **3**. Therefore, the structure of 4$\beta$-hydroxy-8,12-epoxyeudesma-7,11-diene-1,6-dione reported in the literature[10] was revised as its 4-epimer (**3a**), and chlorantene C (**3**) was assigned as 4$\beta$-hydroxy-8,12-epoxyeudesma-7,11-diene-1,6-dione.

Chlorantene D (**4**), a yellow amorphous powder, had the molecular formula $C_{15}H_{16}O_4$ as determined by HREIMS, with 8 degrees of unsaturation. IR absorptions displayed the presence of OH (3429 cm$^{-1}$) and conjugated ketone (1680 and 1643 cm$^{-1}$) groups. The $^{13}$C NMR spectrum (Table 1) showed 15 carbon resonances assignable to two carbonyls [$\delta_C$ 198.5 (C-3) and 187.0 (C-6)], a trisubstituted furan ring, a tetrasubstituted double bond [$\delta_C$ 138.2 (C-4) and 150.7 (C-5)], and three methyl, two methylene, one oxygenated methine [$\delta_C$ 72.9 (C-1)], and one quaternary carbon [$\delta_C$ 45.5 (C-10)]. Fifteen proton resonances were observed in the $^1$H NMR spectrum, and the only missing one was attributable to the exchangeable OH proton. The data suggested that **4** was a eudesmane-type sesquiterpene having the same B and C rings as compounds **2** and **3** and that differences were in the A ring. The planar structure of **4** was determined on the basis of spectroscopic analyses and confirmed by HMBC. The relative configuration of **4** was assigned by a ROESY experiment in which correlations of Me-15/H-2$\beta$ and H-9$\beta$ and of H-1/H-9α were observed.

Chlorantene E (**5**) had the molecular formula $C_{15}H_{16}O_3$ as determined by HREIMS. The $^1$H and $^{13}$C NMR spectra (Table 1) of **5** displayed signals indicating two methyl groups [$\delta_H$ 1.88 (3H, s) and 2.02 (3H, d, $J$ = 1.0 Hz)], a trisubstituted furan ring, an exocyclic double bond at $\delta_H$ 4.98 and 5.14 (each 1H, s), an olefinic proton assignable to a trisubstituted double bond, and two conjugated ketone groups [$\delta_C$ 198.4 (C-6) and 185.3 (C-9)]. The HMBC spectrum revealed a germacrane-type furanosesquiterpene for compound **5** with ketone groups located at C-6 and C-9, and $\Delta^{4(14)}$ and $\Delta^{1(10)}$ double bonds. ROESY correlations of H-1/H-3$\beta$ and of $H_3$-15/H-2α, $H_2$-5 indicated that the $\Delta^{1(10)}$ double bond had *E*-geometry and that the preferred conformation for **5** in solution was as depicted.

Chlorantene F (**6**) was a yellow oil with the molecular formula $C_{15}H_{16}O_3$ (HREIMS). Its IR absorptions implied the presence of carbonyl groups (1768, 1685 cm$^{-1}$). The $^1$H and $^{13}$C NMR spectra of **6** (Table 3) showed three methyls, a trisubstituted furan ring, two terminal double bonds, two conjugated ketones, one methine, and a quaternary carbon. Comparison of the NMR data of **6** with those of curzerenone[12] indicated that they were analogues, and the only difference was that compound **6** had a C-9 ketone group instead of the C-9 methylene of curzerenone. Analysis of the HMBC spectrum confirmed this assignment. The relative configuration of **6** was tentatively assigned by comparing the NMR data with that of curzerenone.[12]

Chlorantene G (**7**) was obtained as a white amorphous powder with the molecular formula $C_{15}H_{24}O_2$ (HREIMS), 16 mass units more than that of acolamone.[4c] The IR absorptions revealed the presence of OH (3521 cm$^{-1}$) and carbonyl (1708 cm$^{-1}$) groups. The $^1$H NMR data of **7** (Table 3) showed high similarity to those of acolamone and indicated that the only difference was likely the presence of one more OH group in **7**. An oxygenated quaternary carbon resonance at $\delta_C$ 80.5 was assigned to C-7 bearing an OH group by the HMBC correlations from H-8 and H-11 to C-7. The relative configuration of **7** was established by a ROESY experiment, in which the correlations from H-5 to H-1α, H-3α, and H-9α indicated that they were cofacial and were randomly fixed as α-oriented; the correlations from Me-15 to H-2$\beta$ and H-8$\beta$ and from Me-12 (or Me-13) to H-8$\beta$ consequently indicated that they were $\beta$-directed.

*threo*-1-(1-Methoxy-2-hydroxypropyl)-2-methoxy-4,5-methylenedioxybenzene (**8**) and *erythro*-1-(1-methoxy-2-hydroxypropyl)-2-methoxy-4,5-methylenedioxybenzene (**9**) shared the same molecular formula of $C_{12}H_{16}O_5$ as determined by HREIMS. The highly similar $^1$H and $^{13}$C NMR data (Table 3) indicated that they were stereoisomers. This was confirmed by their HMBC spectra, in which methoxy groups were located at C-2 and C-7 by the correlations of their corresponding protons to C-2 and C-7, respectively. A methylenedioxy group was attached to C-4 and C-5 by the correlations from $H_2$-10 to C-4 and C-5, and an OH group was attached to C-8 by the correlations from H-7 and $H_3$-9 to C-8. The planar structure of **8** and **9** was therefore elucidated as depicted. The *threo* and *erythro* diastereomers could be distinguished by the coupling constants of the vicinal protons, and the coupling constants of *threo* and *erythro* of anethole glycol reported in the literature[13] were 7.8 and 4.5 Hz, respectively. Therefore, compounds **8** and **9** were assigned as *threo* and *erythro* diastereomers on the basis of

coupling constants of the vicinal protons (**8**, $J_{7,8}$ = 7.8 Hz; **9**, $J_{7,8}$ = 4.2 Hz), respectively.

Five known sesquiterpenoids were identified as furanodienone,[14] zederone,[4c] curzerenone,[12] 7α-hydroxyneoacolamone,[4c] and curcolonol[11] on the basis of spectroscopic data ($^1$H, $^{13}$C NMR and EIMS).

All of the new compounds were tested for their antimicrobial activities against 13 microorganisms *in vitro*. Compounds **4**−**7** showed moderate activities only against *Helicobacter pylori*-SS1 with MICs of 25−50 μg/mL.

## Experimental Section

**General Experimental Procedures.** IR spectra were recorded on a Perkin-Elmer 577 spectrometer with a KBr disk. UV spectra were measured on a Shimadzu UV-2550 UV−visible spectrophotometer. Optical rotations were made on a Perkin-Elmer 341 polarimeter at room temperature. NMR spectra were measured on a Bruker AM-400 spectrometer with TMS as internal standard. EIMS (70 eV) and ESIMS were carried out on a Finnigan MAT 95 mass spectrometer and an Esquire 3000plus LC-MS instrument, respectively. Semipreparative HPLC was performed on a Waters 515 pump equipped with a Waters 2487 UV detector (254 nm) and an YMC-Pack ODS-A column (250 × 10 mm, S-5 μm, 12 nm). All solvents used were of analytical grade (Shanghai Chemical Plant, Shanghai, People's Republic of China). Silica gel (300−400 mesh), C18 reversed-phase silica gel (150−200 mesh, Merck), Sephadex LH-20 gel (Amersham Biosciences), and MCI gel (CHP20P, 75−150 μM, Mitsubishi Chemical Industries Ltd.) were used for column chromatography, and precoated silica gel GF254 plates (Qingdao Marine Chemical Plant, Qingdao, People's Republic of China) were used for TLC.

**Plant Material.** Whole plants of *C. serratus* were collected from Guilin area of Guangxi Zhuang Autonomous Region of China and were authenticated by Professor Shao-Qing Tang of Guangxi Normal University. A voucher specimen (CSE-2006-1Y) has been deposited in the Shanghai Institute of Materia Medica.

**Extraction and Isolation.** The air-dried powder of whole plants (5 kg) of *C. serratus* was extracted with 95% EtOH at room temperature to obtain 600 g of crude extract, which was then partitioned between EtOAc and $H_2O$ to give an EtOAc-soluble fraction (260 g). The EtOAc-soluble fraction was chromatographed over a column of MCI gel (MeOH/$H_2O$, 50:50 to 90:10) to yield five fractions (A−E). Fraction A was subjected to silica gel chromatography (CC) eluted with petroleum ether/acetone (10:1 to 1:1) in gradient to obtain six fractions (A1−A6). Fraction A2 was chromatographed over a column of reversed-phase $C_{18}$ silica gel eluted with MeOH/$H_2O$ (MeOH/$H_2O$, 45:55 to 70:30) to give five subfractions (A2a−A2e). Fraction A2c was purified by CC using petroleum ether/EtOAc (4:1) to yield compound **8** (41 mg). Purification of fraction A2d by semipreparative HPLC (MeOH/$H_2O$, 50:50, 3 mL/min) gave **9** (17 mg). Fraction C was subjected to CC eluting with petroleum ether/acetone (50:1 to 1:1) to give five fractions (C1−C5). Fraction C2 was chromatographed over a column of RP-18 silica gel (MeOH/$H_2O$, 65:35) to give four subfractions (C2a−C2d). Fraction C2a was separated on a column of Sephadex LH-20 eluted with MeOH to give compound **6** (12 mg) and furanodienone (538 mg). Fraction C2b was subjected to a column of Sephadex LH-20 eluted with MeOH to yield 7α-hydroxyneoacolamone (43 mg) and curzerenone (25 mg). Fraction C2c was chromatographed on a column of RP-18 silica gel (MeOH/$H_2O$, 65:35) to give compound **3** (22 mg) and zederone (80 mg). Purification of C2d by CC eluted with petroleum ether/EtOAc (15:1) gave compounds **1** (10 mg) and **7** (11 mg). Fraction C5 was subjected to a column of RP-18 silica gel (MeOH/$H_2O$, 5:5 to 7:3) to give six subfractions (C5a−C5f). Fraction C5a was purified on a column of Sephadex LH-20 eluted with MeOH to give compound **4** (5 mg). Fraction C5d was subjected to CC eluted with petroleum ether/EtOAc (10:1) to give compounds **3a** (20 mg) and **5** (30 mg). Fraction C5f was subjected to CC on silica gel eluted with petroleum ether/EtOAc (6:1) to give compound **2** (8 mg) and curcolonol (5 mg).

**Chlorantene A (1):** white, amorphous powder; $[\alpha]^{20}_D$ −7 (*c* 0.200, $CHCl_3$); UV (MeOH) $\lambda_{max}$ (log ε) 307 (3.56), 211 (4.23) nm; IR (KBr) $\nu_{max}$ 2968, 1674, 1653, 1504, 1377, 1223, 1043 cm$^{-1}$; for $^1$H NMR and $^{13}$C NMR data, see Table 1; ESIMS *m/z* 269.1 [M + Na]$^+$; EIMS *m/z* 246 [M]$^+$ (100), 231 (89), 203 (28), 190 (32), 177 (69), 161 (23), 109 (35), 95 (18), 81 (16), 53 (12); HREIMS *m/z* 246.1251 (calcd for $C_{15}H_{18}O_3$ 246.1256).

**Chlorantene B (2):** white, amorphous powder; $[\alpha]^{20}_D$ −19 (*c* 0.125, $CHCl_3$); UV (MeOH) $\lambda_{max}$ (log ε) 271 (3.85), 205 (4.56) nm; IR (KBr) $\nu_{max}$ 3502, 1656, 1544, 1363, 1064 cm$^{-1}$; for $^1$H NMR and $^{13}$C NMR data, see Table 1; ESIMS *m/z* 316.1 [M + Na]$^+$; EIMS *m/z* 293 [M]$^+$ (25), 278 (25), 245 (17), 227 (16), 163 (100), 139 (21), 122 (47), 91 (10), 77 (5), 65 (6); HREIMS *m/z* 293.1259 (calcd for $C_{15}H_{19}NO_5$ 293.1263).

**4α-Hydroxy-8,12-epoxyeudesma-7,11-diene-1,6-dione (3a):** white, amorphous powder; $[\alpha]^{20}_D$ +4 (*c* 0.175, $CHCl_3$); UV (MeOH) $\lambda_{max}$ (log ε) 271 (3.82), 205 (4.41) nm; IR (KBr) $\nu_{max}$ 3525, 2976, 1711, 1666, 1558, 1425, 1379, 1238, 1070, 887, 769 cm$^{-1}$; for $^1$H NMR and $^{13}$C NMR data, see Table 2; ESIMS *m/z* 285 [M + Na]$^+$; EIMS *m/z* 262 (54) [M]$^+$, 244 (36), 201 (60), 191 (54), 163 (100), 122 (100), 94 (24), 91 (19), 77 (2); HREIMS *m/z* 262.1198 [M]$^+$ (calcd for $C_{15}H_{18}O_4$ 262.1205).

**Chlorantene C (3):** white, amorphous powder; $[\alpha]^{20}_D$ ~0 (*c* 0.150, $CHCl_3$); UV (MeOH) $\lambda_{max}$ (log ε) 265 (3.78), 206 (4.38) nm; IR (KBr) $\nu_{max}$ 3486, 2966, 1703, 1670, 1434, 1375, 1114, 754 cm$^{-1}$; for $^1$H NMR and $^{13}$C NMR data, see Table 2; ESIMS *m/z* 285 [M + Na]$^+$; EIMS *m/z* 262 [M]$^+$ (34), 244 (53), 217 (36), 201 (100), 191 (67), 163 (50), 122 (57), 94 (16), 77 (9); HREIMS *m/z* 262.1201 [M]$^+$ (calcd. for $C_{15}H_{18}O_4$ 262.1205).

**Chlorantene D (4):** yellow, amorphous powder; $[\alpha]^{20}_D$ +5 (*c* 0.185, $CHCl_3$); UV (MeOH) $\lambda_{max}$ (log ε) 314 (3.30), 262 (3.77) nm; IR (KBr) $\nu_{max}$ 3429, 2978, 1680, 1643, 1568, 1439, 1327, 1094, 1059, 1003, 916, 795 cm$^{-1}$; for $^1$H NMR and $^{13}$C NMR data, see Table 1; ESIMS *m/z* 261 [M + H]$^+$; EIMS *m/z* 260 (88) [M]$^+$, 242 (4), 216 (32), 201 (42), 189 (100), 173 (36), 145 (26), 115 (18), 94 (7), 91 (11); HREIMS *m/z* 260.1051 [M]$^+$ (calcd for $C_{15}H_{16}O_4$ 260.1049).

**Chlorantene E (5):** colorless oil; UV (MeOH) $\lambda_{max}$ (log ε) 289 (3.75); IR (KBr) $\nu_{max}$ 2933, 1768, 1685, 1371, 1002 cm$^{-1}$; for $^1$H NMR and $^{13}$C NMR data, see Table 1; ESIMS *m/z* 267 [M + Na]$^+$; EIMS *m/z* 244 [M]$^+$ (23), 229 (33), 216 (60), 201 (65), 187 (48), 164 (100), 108 (43), 91 (42), 82 (44); HREIMS *m/z* 244.1101 [M]$^+$ (calcd. for $C_{15}H_{16}O_3$ 244.1099).

**Chlorantene F (6):** yellow oil; $[\alpha]^{20}_D$ ~0 (*c* 0.500, $CHCl_3$); UV (MeOH) $\lambda_{max}$ (log ε) 306 (3.69), 218 (4.13) nm; IR (KBr) $\nu_{max}$ 3135, 3087, 2935, 1768, 1685, 1527, 1355, 1051, 929 cm$^{-1}$; for $^1$H NMR and $^{13}$C NMR data, see Table 3; EIMS *m/z* 244 [M]$^+$ (55), 229 (81), 216 (100), 201 (64), 187 (35), 173 (46), 145 (28), 108 (80), 91 (43), 77(33); HREIMS *m/z* 244.1100 [M]$^+$ (calcd for $C_{15}H_{16}O_3$ 244.1099).

**Chlorantene G (7):** white, amorphous powder; $[\alpha]^{20}_D$ +135 (*c* 0.150, $CHCl_3$); IR (KBr) $\nu_{max}$ 3521, 2937, 1708, 1390, 1199, 1002, 902 cm$^{-1}$; for $^1$H NMR and $^{13}$C NMR data, see Table 3; EIMS *m/z* 236 [M]$^+$ (18), 218 (8), 137 (26), 109 (100), 81 (12), 67 (10); HREIMS *m/z* 236.1764 [M]$^+$ (calcd for $C_{15}H_{24}O_2$ 236.1776).

***threo*-1-(1-Methoxy-2-hydroxypropyl)-2-methoxy-4,5-methylenedioxybenzene (8):** white, amorphous powder; $[\alpha]^{20}_D$ −1 (*c* 0.250, $CHCl_3$); UV (MeOH) $\lambda_{max}$ (log ε) 300 (4.18), 236 (4.16), 204 (4.78) nm; IR (KBr) $\nu_{max}$ 3463, 2939, 1627, 1488, 1193, 871, 609 cm$^{-1}$; for $^1$H NMR and $^{13}$C NMR data, see Table 3; EIMS *m/z* 240 [M]$^+$ (5), 195 (100), 180 (5), 165(6), 151 (2); HREIMS *m/z* 240.1001 [M]$^+$ (calcd for $C_{12}H_{16}O_5$ 240.0998).

***erythro*-1-(1-Methoxy-2-hydroxypropyl)-2-methoxy-4,5-methylenedioxybenzene (9):** white, amorphous powder; $[\alpha]^{20}_D$ −1 (*c* 0.150, $CHCl_3$); UV (MeOH) $\lambda_{max}$ (log ε) 299 (4.16), 232 (4.23), 202 (4.80) nm; IR (KBr) $\nu_{max}$ 3469, 1618, 1485, 1423, 1191, 929, 615 cm$^{-1}$; for $^1$H NMR and $^{13}$C NMR data, see Table 3; EIMS *m/z* 240 [M]$^+$ (6), 195 (100), 180 (5), 165 (10), 151 (2); HREIMS *m/z* 240.1003 [M]$^+$ (calcd for $C_{12}H_{16}O_5$ 240.0998).

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**Supporting Information Available:** Key HMBC and ROESY correlations of **1**−**9** and selected $^1$H, $^{13}$C NMR and 2D NMR spectra of compounds **1**−**9** are available free of charge via the Internet at http://pubs.acs.org.

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