New Triterpene Constituents, Foliasalacins A₁–A₄, B₁–B₃, and C, from the Leaves of *Salacia chinensis*

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Four dammarane-type, three lupane-type, and an oleanane-type triterpenes named foliasalacins A₁ (1), A₂ (2), A₃ (3), A₄ (4), B₁ (5), B₂ (6), B₃ (7), and C (8) were isolated from the leaves of *Salacia chinensis* LINN. collected in Thailand. The structures of new triterpene constituents (1–8) were characterized on the basis of chemical and physicochemical evidence.

Key words *Salacia chinensis*; Hippocrateaceae; foliasalacin; dammarane type triterpene; lupane type triterpene; oleanane type triterpene

During the course of our characterization studies on bioactive constituents from *Salacia* species,^{1–13} we have reported the isolation and absolute stereostructure elucidation of thirteen megastigmane glycosides, foliasalaciosides A₁, A₂, B₁, B₂, C, D, E₁, E₂, E₃, F, G, H, and I, and seven new phenolic glycosides, foliachinenosides A₁, A₂, A₃, B₁, B₂, C, and D, from the leaves of *Salacia chinensis* LINN. (Hippocrateaceae) together with twenty known constituents.^{14–16} As a continuing study on the leaves of *S. chinensis*, we have isolated four dammarane-type, three lupane-type, and an oleanane-type triterpenes named foliasalacins A₁ (1), A₂ (2), A₃ (3), A₄ (4), B₁ (5), B₂ (6), B₃ (7), and C (8) from the less polar fraction of the leaves. This paper deals with the isolation and structure elucidation of these eight new triterpenes.

The dried leaves of *S. chinensis*, which were collected at Nakhon Si Thammarat province, Thailand, were finely cut and extracted with methanol (MeOH) to furnish a methanolic extract (13.0%). The MeOH extract was partitioned into an EtOAc–H₂O (1:1, v/v) mixture to furnish an EtOAc-soluble fraction (4.1%) and an aqueous phase as previously reported.^{14–16} From the EtOAc-soluble fraction, foliasalacins A₁ (1, 0.00038%), A₂ (2, 0.00018%), A₃ (3, 0.00038%), A₄ (4, 0.00011%), B₁ (5, 0.00073%), B₂ (6, 0.00076%), B₃ (7, 0.00070%), and C (8, 0.00005%), were isolated using normal-, and reverse-phase silica gel column chromatography, and finally HPLC (Chart 1).

Structures of Dammarane-Type Triterpenes, Foliasalacins A₁, A₂, A₃, and A₄ Foliasalacin A₁ (1), [α]_D²⁶ +33.1° (CHCl₃), was isolated as a white powder. The IR spectrum of 1 showed absorption bands at 3424 and 1646 cm^{–1} ascribable to hydroxyl and olefin functions. The electron ionization (EI) MS of 1 exhibited a molecular ion peak at *m/z* 458, and the high resolution (HR) EI-MS analysis revealed the molecular formula of 1 to be C₃₁H₅₄O₂. The ¹H- (CDCl₃) and ¹³C-NMR (Table 1) spectra¹⁷ of 1 showed signals assignable to eight methyls [δ 0.77, 0.85, 0.87, 0.96, 0.97, 1.12, 1.65 (1.647) (3H each, all s, H₃-29, 19, 18, 30, 28, 21, 27), 1.02 (1.019, 3H, d, *J*=6.7 Hz, H₃-31)], a methine bearing an oxygen function [δ 3.20 (1H, dd, *J*=4.8, 11.7 Hz, H-3)], a terminal double bond [δ 4.68 (4.678, 2H, m, H₂-26)], together with ten methylenes, five methines, and six quaternary carbons. The spectral data of 1 were similar to those of a dammarane triterpene with an unusual and extra methyl group at the 24-position, carnaubadiol (9),¹⁸ except

for the signals due to the side chain part (C-23–27, 31). As shown in Fig. 1, the ¹H–¹H correlation spectroscopy (¹H–¹H COSY) experiment on 1 indicated the presence of partial structures written in bold lines, and in a heteronuclear multiple-bond correlation (HMBC) experiment, long-range correlations were observed between the following protons and carbons: H-5 and C-1, 7; H₃-18 and C-8, 13–15; H₃-19 and C-1, 5, 9, 10; H₃-21 and C-17, 20, 22; H₂-26 and C-24, 25, 27; H₃-27 and C-24–26; H₃-28 and C-3–5, 29; H₃-29 and C-3–5, 28; H₃-31 and C-23–25. Next, the stereochemistry of the tetracyclic carbon skeleton structure (C-1–19, 28–30) in 1 was clarified using nuclear Overhauser enhancement spectroscopy (NOESY) experiment, which showed NOE correlations between the following proton pairs: H α -1 and H-3, H-9; H β -1 and H₃-19; H-3 and H-5, H₃-28; H-5 and H-9; H-

Chart 1. Structures of New Foliasalacins from the Leaves of *Salacia chinensis*

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9 and H₃-18; H-13 and H₃-21, H₃-30; H-17 and H₃-18. On the basis of above mentioned evidence, **1** was presumed to be the 24-isomer of **9**. By comparing the chemical shifts of the 20—22 carbons of **1** [δ_C 25.5 (C-21), 39.1 (C-22), 75.3 (C-20)] with those of the 20-epimers of dammarane type compounds, dammarenediol I (**10**, 20*R*) [δ_C 23.5 (C-21), 41.8 (C-22), 75.8 (C-20)]¹⁹ and dammarenediol II (**11**, 20*S*) [δ_C 24.9 (C-21), 40.5 (C-22), 75.4 (C-20)],¹⁹ which measured in the same solvent (CDCl₃) as **1**, the stereostructure of the 20-posi-

tion in **1** was certificated to be *S** orientation. Finally, the stereostructure of the 24-position in **1** was determined to be *S** by the application of the reported NMR method.^{20,21} Namely, the configuration at the 24-position in **1** was characterized by comparison of the $\Delta\delta$ values of the side chain protons (H-26—27, H-26—31, and H-27—31) in the ¹H-NMR (CDCl₃) spectrum of **1** with those of known compounds, codisterol (**12**) [(24*S*)-methylcholesta-5,25-dien-3 β -ol], epicodisterol (**13**) [(24*R*)-methylcholesta-5,25-dien-3 β -ol], and leucastrin (**14**) [(3*S*,17*S*,20*S*,24*S*)-3,20-dihydroxy-24-methylprotost-25-ene]. As shown in Table 2, the $\Delta\delta$ values of the 26- and 27-protons, the 26- and 31-protons, and the 27- and 31-protons in **1** were approximated to those of codisterol (**12**) and leucastrin (**14**), thus the configuration at the 24-position in **1** was elucidated to be *S** orientation. On the basis of this evidence and comparison of the ¹H- and ¹³C-NMR data of **1** with those of **9**, foliasalacin A₁ (**1**) was characterized to be the 24-isomer of carnaubadiol (**9**).

Foliasalacin A₂ (**2**), [α_D^{25} +22.0° (CHCl₃)], was isolated as a white powder. The IR spectrum of **2** showed absorption bands at 3423 and 1647 cm⁻¹ assignable to hydroxyl and olefin functions, respectively. Its molecular formula

Table 1. ¹³C-NMR Data for **1**—**4**

Position	1	2	3	4
1	39.1	39.1	39.2	39.1
2	27.4	27.4	27.4	27.4
3	79.0	79.0	78.9	79.0
4	39.0	39.0	39.0	39.0
5	55.9	55.9	55.7	55.9
6	18.3	18.3	18.2	18.3
7	35.2	35.3	36.3	35.2
8	40.4	40.4	40.9	40.4
9	50.7	50.6	51.4	50.7
10	37.1	37.1	37.3	37.1
11	21.6	21.5	21.3	21.6
12	24.7	25.4	24.9	24.8
13	42.3	42.2	43.5	42.4
14	50.4	50.0	50.5	50.4
15	31.2	31.1	74.0	31.2
16	27.6	27.6	38.7	27.5
17	49.5	49.3	45.3	49.8
18	16.5	16.4	9.1	16.5
19	16.2	16.2	16.4	16.2
20	75.3	75.7	152.2	75.4
21	25.5	23.8	107.8	25.4
22	39.1	40.2	32.3	39.4
23	28.9	28.4	33.6	28.4
24	41.7	41.7	41.0	156.5
25	149.9	149.9	149.8	34.0
26	109.6	109.6	109.6	21.94
27	18.8	18.8	18.9	21.96
28	28.0	28.0	28.0	28.0
29	15.4	15.4	15.4	15.4
30	15.5	15.5	15.7	15.5
31	20.0	20.0	19.8	106.2

Measured in CDCl₃ at 125 MHz.

Fig. 1. Selected ¹H—¹H COSY, HMBC, and NOE Correlations of **1**—**4**

Chart 2

Table 2. Comparison of ^1H Chemical Shifts of Compounds of **1**–**3**, **12**–**14**

H	1	2	3	12	13	14
26	4.678	4.680	4.688	4.658	4.654	4.674
27	1.647	1.647	1.647	1.635	1.649	1.646
31	1.019	1.016	1.020	0.990	0.984	1.014
$\Delta\delta$						
26–27	3.031	3.033	3.131	3.023	3.005	3.028
26–31	3.659	3.664	3.668	3.668	3.670	3.660
27–31	0.628	0.631	0.627	0.645	0.665	0.632

Measured in CDCl_3 at 500 MHz.

$\text{C}_{31}\text{H}_{54}\text{O}_2$, the same as that of **1**, was determined from the molecular ion peak at m/z 458 and by HR-EI-MS measurement. The ^1H - (CDCl_3) and ^{13}C -NMR (Table 1) spectra¹⁷⁾ of **2** showed signals assignable to eight methyls [δ 0.78, 0.85, 0.88, 0.97, 0.98, 1.10, 1.65 (1.647) (3H each, all s, H_3 -29, 19, 18, 30, 28, 21, 27), 1.02 (1.016, 3H, d, $J=6.7$ Hz, H_3 -31)], a methine bearing an oxygen function [δ 3.20 (1H, dd, $J=5.2$, 11.6 Hz, H-3)], a terminal double bond [δ 4.68 (4.680, 2H, m, H_2 -26)], together with ten methylenes, five methines, and six quaternary carbons. The proton and carbon signals in the ^1H - and ^{13}C -NMR spectra of **2** were superimposable on those of **1**, except for the signals due to the 20–22-positions. The ^1H - ^1H COSY, HMBC, and NOESY experiments on **2** (shown in Fig. 1) indicated that **2** was the 20-isomer of **1**. By comparing the chemical shifts of the 20–22 carbons of **2** with those of the 20-epimers of dammarane type triterpenes, dammarenediol I (**10**, 20*R*) and dammarenediol II (**11**, 20*S*),¹⁹⁾ the stereostructure of the 20-position in **2** was elucidated as *R** form. On the other hand, the 24-position in **2** was confirmed to be *S** orientation by the same method²¹⁾ as that for **1** (the $\Delta\delta$ values of H-26–27, H-26–31, and H-27–31 of **2** were shown in Table 2). Consequently, the structure of **2** was elucidated as shown.

Foliasalacin **A**₃ (**3**), $[\alpha]_{\text{D}}^{27} +31.4^\circ$ (CHCl_3), was isolated as a white powder. The molecular formula, $\text{C}_{31}\text{H}_{52}\text{O}_2$, was determined by EI and HR-EI-MS measurement. The ^1H - (CDCl_3) and ^{13}C -NMR (Table 1) spectra¹⁷⁾ of **3** showed signals ascribable to seven methyls [δ 0.78, 0.86, 0.95, 0.98, 1.06, 1.65 (1.647) (3H each, all s, H_3 -29, 19, 18, 28, 30, 27), 1.02 (1.020, 3H, d, $J=6.7$ Hz, H_3 -31)], two methines bearing an oxygen function [δ 3.21 (1H, dd, $J=4.9$, 11.6 Hz, H-3)], 4.26 (1H, dd, $J=8.6$, 8.6 Hz, H-15), two terminal double bonds [δ 4.69 (4.688, 2H, m, H_2 -26), [4.70 (1H, m), 4.71 (1H, brs), H_2 -21]], together with nine methylenes, five methines, and five quaternary carbons. As shown in Fig. 1, the ^1H - ^1H COSY experiment on **3** indicated the presence of partial structure written in bold lines, and in the HMBC experiment, long-range correlations were observed between the following proton and carbon pairs: H-5 and C-1, 7; H-15 and C-13, 17, 18, H_3 -18 and C-8, 13–15; H_3 -19 and C-1, 5, 9, 10; H_2 -21 and C-17, 20, 22; H_2 -26 and C-24, 25, 27; H_3 -27 and C-24–26; H_3 -28 and C-3–5, 29; H_3 -29 and C-3–5, 28; H_3 -31 and C-23–25. The above-mentioned evidence indicated that **3** was a dammarane-type triterpene with the 24-methyl and the 20- and 25-*exo*-methylenes at the side chain. In the NOESY experiment, NOE correlations were observed between $\text{H}\alpha$ -1 and H-3, H-9; $\text{H}\beta$ -1 and H_3 -19; H-3 and H-5,

H_3 -28; H-5 and H-9; H-9 and H_3 -18; H-13 and H-15, H_3 -30; H-15 and H_3 -30; H_3 -18 and $\text{H}\alpha$ -17, so that the stereostructure of **3** including the 3β and 15α -hydroxyl groups was clarified. On the other hand, the stereostructure of the 24-position was presumed to be *S** by the same NMR method as that for **1** and **2** (Table 2). Those findings led us to formulate the structure of **3** as shown.

Foliasalacin **A**₄ (**4**), $[\alpha]_{\text{D}}^{27} +25.9^\circ$ (CHCl_3), was also obtained as a white powder. The IR spectrum of **4** showed absorption bands at 3422 and 1647 cm^{-1} ascribable to hydroxyl and olefin functions, respectively. Its molecular formula, $\text{C}_{31}\text{H}_{54}\text{O}_2$, was determined from the molecular ion peak at m/z 458 and by HR-EI-MS measurement. The ^1H - (CDCl_3) and ^{13}C -NMR (Table 1) spectra¹⁷⁾ of **4** showed signals assignable to eight methyls [δ 0.78, 0.85, 0.89, 0.96, 0.98, 1.16 (3H each, all s, H_3 -29, 19, 18, 30, 28, 21), 1.04, 1.04 (3H each, both d, $J=6.9$ Hz, H_3 -26, 27)], a methine bearing an oxygen function [δ 3.20 (1H, dd, $J=4.2$, 11.0 Hz, H-3)], a terminal double bond [δ 4.69, 4.75 (1H each, both brs, H_2 -31)], together with ten methylenes, five methines, and five quaternary carbons. The proton and carbon signals in the ^1H - and ^{13}C -NMR spectra of **4** were superimposable on those of foliasalacin **A**₁ (**1**), except for the signals due to the 24–27- and 31-positions in the side chain. By comparison of the chemical shift values of the 20–23 carbons in the ^{13}C -NMR of **4** with those of **1**, the stereostructure at the 20-position in **4** was clarified to be the same as that of **1**. Furthermore, as shown in Fig. 1, long-range correlations were observed between the following protons and carbons: H_2 -26 and C-24, 25, 27; H_3 -27 and C-24–26; H_2 -31 and C-23–25, the structure of the side chain part was determined as shown. On the basis of above-mentioned evidence and detail examination of various NMR data as shown in Fig. 1, the structure of foliasalacin **A**₄ (**4**) was characterized.

Structures of Lupane-Type Triterpenes, Foliasalacins

B₁ and **B**₂ Foliasalacin **B**₁ (**5**) was obtained as a white powder with positive optical rotation ($[\alpha]_{\text{D}}^{29} +9.4^\circ$ in CHCl_3), and showed absorption bands at 3422 and 1717 cm^{-1} due to hydroxyl and carbonyl functions in the IR spectrum. The molecular formula, $\text{C}_{30}\text{H}_{50}\text{O}_2$, of **5** was determined from the EI-MS [m/z 442 (M^+)], and by HR-EI-MS analysis. The ^1H - (CDCl_3) and ^{13}C -NMR (Table 3) spectra¹⁷⁾ of **5** showed seven methyls [δ 0.75, 0.94, 0.94, 1.03, 1.08, 1.08 (3H each, all s, H_3 -28, 25, 27, 24, 23, 26), 0.97 (3H, d, $J=6.8$ Hz, H_3 -30)], a methene bearing an oxygen function [δ 3.41 (1H, dd, $J=8.1$, 11.1 Hz), 3.82 (1H, dd, $J=4.5$, 11.1 Hz), H_2 -29], a carbonyl function [δ_{C} 218.3 (C-3)], together with ten methylenes, five methines, and four quaternary carbons. The ^1H - ^1H COSY experiment on **5** indicated the presence of partial structures written in bold lines (Fig. 2), and in HMBC experiment, the long-range correlations were observed between H-1 and C-3, 5; H-2 and C-3, 10; H_3 -23 and C-3–5, 24; H_3 -24 and C-3–5, 23; H_3 -25 and C-1, 5, 9, 10; H_3 -26 and C-7–9, 14; H_3 -27 and C-8, 13–15; H_3 -28 and C-16–18, 22; H_2 -29 and C-19, 20, 30; H_3 -30 and C-19, 20, 29. The relative stereostructure of **5** was determined on the NOESY experiment, which showed NOE correlations between H-1 α and H-2 α ; H-1 β and H-2 β , H_3 -25; H-2 β and H_3 -24, H_3 -25; H-5 and H-9, H_3 -23; H-9 and H_3 -27; H-12 α and H_2 -29, H_3 -30; H-13 and H_3 -26, H_3 -28; H-18 and H_3 -27, H_2 -29, H_3 -30; H-19 and H_3 -28. Finally, reduction of **5** with NaBH_4 in anhydrous MeOH gave

Table 3. ^{13}C -NMR Data of **5**–**8** and Related Compounds (**5a** and **6a**)

Position	5	5a	6	6a	7	8
1	39.5	38.7	39.6	38.7	39.5	38.8
2	34.2	27.4	34.2	27.4	34.1	27.3
3	218.3	79.0	218.3	79.0	218.3	79.0
4	47.3	38.9	47.4	38.9	47.3	38.8
5	54.8	55.2	54.9	55.2	54.8	55.0
6	19.7	18.3	19.7	18.3	19.7	18.6
7	33.6	34.3	33.6	34.3	33.7	37.9
8	40.8	40.9	40.8	40.9	40.8	42.4
9	49.4	50.0	49.4	50.0	49.3	50.5
10	36.8	37.1	36.8	37.1	36.8	37.4
11	21.5	20.9	21.4	20.8	21.5	21.7
12	27.2	27.2	26.9	26.9	27.0	25.1
13	38.0	37.9	37.9	38.0	37.8	133.6
14	43.1	43.0	43.1	42.9	43.1	50.7
15	27.3	27.3	27.3	27.3	27.3	67.0
16	35.4	35.5	35.4	35.5	35.3	46.2
17	43.1	43.1	42.9	43.0	43.0	36.2
18	47.4	47.5	47.2	47.2	48.6	133.4
19	43.6	43.6	39.2	39.2	43.5	39.0
20	38.0	38.0	37.9	37.8	42.0	33.3
21	23.1	23.1	21.9	21.9	23.8	35.1
22	40.1	40.1	40.5	40.6	39.7	39.0
23	26.7	28.0	26.7	28.0	26.7	28.0
24	21.0	15.4	21.1	15.4	21.0	15.5
25	15.9	16.1	15.8	16.0	16.0	16.3
26	15.8	16.0	15.9	16.1	15.8	18.1
27	14.4	14.4	14.3	14.4	14.4	13.8
28	17.6	17.6	18.1	18.1	17.8	24.2
29	64.5	64.5	68.2	68.4	181.8	32.3
30	18.0	18.0	10.3	10.3	17.1	24.1

Measured in CDCl_3 at 125 MHz. Fig. 2. Selected ^1H – ^1H COSY, HMBC, and NOE Correlations of **5**, **7** and **8**

a known compound, (20*R*)-lupane-3 β ,29-diol (**5a**)²² (Fig. 3). Thus, the stereostructure of **5** was characterized as shown.

Foliasalacin B₂ (**6**) was isolated as a white powder with

Reagents and conditions: i) NaBH_4 / MeOH , r.t.; ii) CrO_3 / pyridine , r.t.

Fig. 3

positive optical rotation ($[\alpha]_D^{26} +17.2^\circ$ in CHCl_3). The molecular formula, $\text{C}_{30}\text{H}_{50}\text{O}_2$, was determined from the EI-MS [m/z 442 (M^+)] and by HR-EI-MS measurement. The ^1H - (CDCl_3) and ^{13}C -NMR (Table 3) spectra¹⁷ of **6** [δ 0.78 (3H, s, H_3 -28), 0.80 (3H, d, $J=6.8$ Hz, H_3 -30), 1.22, 1.59 (1H each, both m, H_2 -21), 1.95 (1H, m, H-19), 3.42 (2H, m, H_2 -29); δ_C 10.3 (C-30), 18.1 (C-28), 21.9 (C-21), 39.2 (C-19), 68.2 (C-29)] were very similar to those of **5**, except for the protons of 19-, 21-, and 28–30-positions. Finally, the reduction of **6** with NaBH_4 afforded a known compound (20*S*)-lupane-3 β ,29-diol (**6a**)²² (Fig. 3). On the basis of this evidence and detail NMR analysis (Fig. 2), the stereostructure of foliasalacin B₂ (**6**) was determined as shown.

Foliasalacin B₃ (**7**) was isolated as a white powder with negative optical rotation ($[\alpha]_D^{27} -26.4^\circ$ in CHCl_3). The EI-MS of **7** exhibited a molecular ion peak at m/z 456, and the HR-EI-MS analysis revealed the molecular formula of **7** to be $\text{C}_{30}\text{H}_{48}\text{O}_3$. The ^1H - (CDCl_3) and ^{13}C -NMR (Table 3) spectra of **7** showed seven methyls [δ 0.76, 0.93, 0.94, 1.03, 1.08, 1.08 (3H each, all s, H_3 -28, 27, 25, 24, 23, 26), 1.15 (3H, d, $J=6.9$ Hz, H_3 -30)], two carbonyl functions [δ_C 181.8 (C-29), 218.3 (C-3)], together with ten methylenes, five methines, and four quaternary carbons. The planar and relative stereostructures of **7** were determined by various NMR experiment as shown in Fig. 2.¹⁷ By comparison of the chemical shift values of the 28- and 30-protons in **7** with known compounds, 20(*R*)- and 20(*S*)-3 β -hydroxylupane-29-oic acid (**15**, **16**) [20(*R*): 0.74 (3H, s, H_3 -28), 1.15 (3H, d, $J=6.5$ Hz, H_3 -30); 20(*S*): 0.77 (3H, s, H_3 -28), 1.05 (d, $J=6.5$ Hz, H_3 -30)],²² the stereostructure of the 20-position in **7** was clarified to be *R** orientation. Finally, **7** was derived by oxidation of **5** with chromium trioxide (CrO_3) in pyridine, so that the stereostructure of foliasalacin B₃ (**7**) was clarified as shown.

Structure of Oleanane-Type Triterpene, Foliasalacin C
Foliasalacin C (**8**) was obtained as a white powder with negative optical rotation ($[\alpha]_D^{28} -25.1^\circ$ in CHCl_3) and the IR spectrum of **8** showed absorption bands at 3422 and 1636 cm^{-1} due to hydroxyl and olefin functions. The molecular formula, $\text{C}_{30}\text{H}_{50}\text{O}_2$, was determined from the EI-MS [m/z 442 (M^+)] and by HR-EI-MS analysis. The ^1H - (CDCl_3) and ^{13}C -NMR (Table 3) spectra¹⁷ of **5** showed eight methyls [δ 0.70, 0.77, 0.86, 0.90, 0.94, 0.98, 1.07, 1.17 (3H each, all s, H_3 -30, 24, 25, 26, 29, 24, 28, 27)], two methines bearing an oxygen function [δ 3.23 (1H, dd, $J=4.1$, 11.0 Hz, H-3), 4.13 (1H, dd, $J=8.3$, 8.3 Hz, H-15)], a tetra-substituted double

bond [δ_C 133.4 (C-18), 133.6 (C-13)], together with ten methylenes, two methines, and five quaternary carbons. The ^1H - ^1H COSY experiment on **8** indicated the presence of partial structures written in bold lines, and in the HMBC experiment, long-range correlations were observed between the following proton and carbon pairs: H₂-11 and C-13; H₂-12 and C-18; H₂-22 and C-18; H₃-23 and C-3—5, 24; H₃-24 and C-3—5, 23; H₃-25 and C-1, 5, 9, 10; H₃-26 and C-7—9, 14; H₃-27 and C-8, 13—15; H₃-28 and C-16—18, 22; H₂-29 and C-19—21, 30; H₃-30 and C-19—21, 29. On the basis of above mentioned evidence, **8** was elucidated to be an olean-13-ene-type triterpene with the 3- and 15-hydroxyl groups. The stereostructures of the 3- and 15-positions in **8** were determined on the NOESY experiment, which showed NOE correlations between the following proton pairs: H α -1 and H α -2, H-3, H-9; H α -2 and H-3; H-3 and H-5, H₃-23; H-9 and H α -12, H₃-27; H α -11 and H α -12; H α -12 and H α -19; H-15 and H₃-26, H₃-28; H α -19 and H₃-29. Consequently, the 3- and 15-hydroxyl functions were elucidated to be β and α -configurations, respectively, and the stereostructure of foliasalacin C (**8**) was characterized as shown in Fig. 2.

Experimental

General Experimental Procedures The following instruments were used to obtain physical data: specific rotations, Horiba SEPA-300 digital polarimeter ($l=5$ cm); CD spectra, JASCO J-720WI spectrometer; UV spectra, Shimadzu UV-1600 spectrometer; IR spectra, Shimadzu FTIR-8100 spectrometer; EI-MS and high-resolution MS, JEOL JMS-GCMATE mass spectrometer; ^1H -NMR spectra, JEOL EX-270 (270 MHz) and JNM-LA500 (500 MHz) spectrometers; ^{13}C -NMR spectra, JEOL EX-270 (68 MHz) and JNM-LA500 (125 MHz) spectrometers with tetramethylsilane as an internal standard; and HPLC detector, Shimadzu RID-6A refractive index and SPD-10Avp UV-VIS detectors. HPLC column, Cosmosil 5C₁₈-MS-II (Nacalai Tesque Inc., 250 $\times$ 4.6 mm i.d.) and (250 $\times$ 20 mm i.d.) columns were used for analytical and preparative purposes, respectively.

The following experimental conditions were used for chromatography: ordinary-phase silica gel column chromatography, Silica gel BW-200 (Fuji Silysia Chemical, Ltd., Aichi, Japan, 150—350 mesh); reversed-phase silica gel column chromatography, Chromatorex ODS DM1020T (Fuji Silysia Chemical, Ltd., Aichi, Japan, 100—200 mesh); TLC plates and precoated TLC plates with Silica gel 60F₂₅₄ (Merck, 0.25 mm) (ordinary phase) and Silica gel RP-18 F_{254S} (Merck, 0.25 mm) (reversed phase); reversed-phase HPTLC, with Silica gel RP-18 WF_{254S} (Merck, 0.25 mm); and detection was achieved by spraying with 1% Ce(SO₄)₂–10% aqueous H₂SO₄ followed by heating.

Plant Material The dried leaves of *S. chinensis* were collected at Nakhon Si Thammarat province, Thailand in 2006 and identified by one of authors (Rajamangala University of Technology Srivijaya, Pongpiriyadacha Y.). A voucher of the plant is on file in our laboratory (2006, Thai-06).

Extraction and Isolation The dried leaves of *S. chinensis* LINN. (5.8 kg) were finely cut and extracted 3 times with methanol (MeOH) under reflux for 3 h. Evaporation of the solvent under reduced pressure provided a methanolic extract (756 g, 13.0%). The MeOH extract (712 g) was partitioned into an EtOAc–H₂O (1 : 1, v/v) mixture to furnish an EtOAc-soluble fraction (222 g, 4.1%) and an aqueous phase. The EtOAc fraction (200 g) was subjected to ordinary-phase silica gel column chromatography [3.8 kg, hexane–EtOAc (40 : 1 $\rightarrow$ 10 : 1 $\rightarrow$ 5 : 1 $\rightarrow$ 1 : 1, v/v) $\rightarrow$ CHCl₃–MeOH–H₂O (10 : 3 : 1, v/v/v, lower layer) $\rightarrow$ MeOH] to give sixteen fractions [Fr. 1 (0.7 g), Fr. 2 (1.3 g), Fr. 3 (28.3 g), Fr. 4 (0.9 g), Fr. 5 (9.0 g), Fr. 6 (14.9 g), Fr. 7 (3.2 g), Fr. 8 (10.7 g), Fr. 9 (9.1 g), Fr. 10 (6.2 g), Fr. 11 (4.2 g), Fr. 12 (13.8 g), Fr. 13 (4.1 g), Fr. 14 (43.2 g), Fr. 15 (16.9 g), Fr. 16 (26.3 g)]. Fraction 10 (6.2 g) was subjected to Sephadex LH-20 column chromatography [200 g, MeOH–CHCl₃ (1 : 1, v/v)] to give two fractions [Fr. 10-1 (2400 mg), Fr. 10-2 (3600 mg)]. Fraction 10-2 (3600 mg) was subjected to reversed-phase silica gel column chromatography [120 g, CH₃CN–H₂O (75 : 25 $\rightarrow$ 85 : 15 $\rightarrow$ 90 : 10 $\rightarrow$ 100 : 5, v/v) $\rightarrow$ CH₃CN $\rightarrow$ CHCl₃] to give nine fractions [Fr. 10-2-1 (150 mg), Fr. 10-2-2 (164 mg), Fr. 10-2-3 (192 mg), Fr. 10-2-4 (817 mg), Fr. 10-2-5 (204 mg), Fr. 10-2-6 (70 mg), Fr. 10-2-7 (49 mg), Fr. 10-2-8 (159 mg), Fr. 10-2-9 (583 mg)]. Fraction 10-2-3 (192 mg) was purified by HPLC [MeOH–H₂O (92 : 8, v/v)] and finally HPLC [MeOH–H₂O

(88 : 12, v/v)] to furnish foliasalacins A₃ (**3**, 9.1 mg, 0.00020%) and B₃ (**7**, 31.8 mg, 0.00070%). Fraction 10-2-4 (817 mg) was subjected to HPLC [MeOH–H₂O (92 : 8, v/v)] and HPLC [MeOH–H₂O (88 : 12, v/v)] to furnish foliasalacins A₃ (**3**, 2.1 mg, 0.00005%) and C (**8**, 2.1 mg, 0.00005%). Fraction 10-2-5 (204 mg) was purified by HPLC [MeOH–H₂O (92 : 8, v/v)] and finally HPLC [MeOH–H₂O (88 : 12, v/v)] to afford foliasalacins A₁ (**1**, 17.0 mg, 0.00038%), A₂ (**2**, 8.2 mg, 0.00018%), A₄ (**4**, 4.9 mg, 0.00011%), and B₁ (**5**, 16.8 mg, 0.00037%). Fraction 11 (4.2 g) was subjected to reversed-phase silica gel column chromatography [150 g, MeOH–H₂O (70 : 30 $\rightarrow$ 80 : 20 $\rightarrow$ 90 : 10, v/v) $\rightarrow$ MeOH $\rightarrow$ CHCl₃] to afford five fractions [Fr. 11-1 (45 mg), Fr. 11-2 (54 mg), Fr. 11-3 (40 mg), Fr. 11-4 (799 mg), Fr. 11-5 (1960 mg)]. Fraction 11-4 (799 mg) was separated by HPLC [MeOH–H₂O (92 : 8, v/v)] to give sixteen fractions [Fr. 11-4-1 (5.0 mg), Fr. 11-4-2 (9.1 mg), Fr. 11-4-3 (7.1 mg), Fr. 11-4-4 (55.9 mg), Fr. 11-4-5 (18.5 mg), Fr. 11-4-6 (107.7 mg), Fr. 11-4-7 (17.7 mg), Fr. 11-4-8 (29.2 mg), Fr. 11-4-9 (34.5 mg), Fr. 11-4-10 (54.7 mg), Fr. 11-4-11 (64.5 mg), Fr. 11-4-12 (78.6 mg), Fr. 11-4-13 (32.2 mg), Fr. 11-4-14 (15.7 mg), Fr. 11-4-15 (18.1 mg), Fr. 11-4-16 (16.2 mg)]. Fractions 11-4-13 and 11-4-16 were identified as foliasalacins B₁ (**5**, 16.2 mg, 0.00036%) and B₂ (**6**, 32.2 mg, 0.00072%), respectively. Fraction 11-4-7 (17.7 mg) was purified by HPLC [MeOH–H₂O (88 : 12, v/v)] to furnish foliasalacin A₃ (**3**, 5.8 mg, 0.00013%). Fraction 11-4-14 (15.7 mg) was purified by HPLC [MeOH–H₂O (88 : 12, v/v)] to furnish foliasalacin B₂ (**6**, 1.9 mg, 0.00004%).

Foliasalacin A₁ (**1**): A white powder; [α]_D²⁶ +33.1° ($c=0.85$, CHCl₃); IR (KBr) ν_{max} 3424, 2941, 2872, 1705, 1646, 1456, 1377, 756 cm⁻¹; ^1H -NMR (500 MHz, CDCl₃) δ 0.73 (1H, dd, $J=2.0$, 11.7 Hz, H-5), 0.77, 0.85, 0.87, 0.96, 0.97, 1.12 (3H each, all s, H₃-29, 19, 18, 30, 28, 21), 0.95 (1H, m, H-1 α), 1.02 (3H, $J=6.7$ Hz, H₃-31), 1.32 (1H, m, H-9), 1.63 (1H, m, H-1 β), 1.64 (1H, m, H-13), 1.65 (3H, brs, H₃-27), 1.70 (1H, m, H-17), 3.20 (1H, dd, $J=4.8$, 11.7 Hz, H-3), 4.68 (2H, m, H₂-26); ^{13}C -NMR data (125 MHz, CDCl₃) δ_C : see Table 1; EI-MS m/z 458 (M)⁺ (0.4), 440 (5), 422 (4), 379 (4), 141 (43), 123 (100); HR-EI-MS m/z 458.4132 [Calcd for C₃₁H₅₄O₂ (M)⁺, 458.4124].

Foliasalacin A₂ (**2**): A white powder; [α]_D²⁵ +22.0° ($c=0.21$, CHCl₃); IR (KBr) ν_{max} 3423, 2933, 2870, 1647, 1338, 887 cm⁻¹; ^1H -NMR (500 MHz, CDCl₃) δ 0.73 (1H, dd, $J=2.2$, 11.9 Hz, H-5), 0.78, 0.85, 0.88, 0.97, 0.98, 1.10 (3H each, all s, H₃-29, 19, 18, 30, 28, 21), 0.97 (1H, m, H-1 α), 1.02 (3H, $J=6.7$ Hz, H₃-31), 1.31 (1H, m, H-9), 1.69 (1H, m, H-1 β), 1.69 (1H, m, H-17), 1.65 (3H, brs, H₃-27), 1.71 (1H, m, H-13), 3.20 (1H, dd, $J=5.2$, 11.6 Hz, H-3), 4.68 (2H, m, H₂-26); ^{13}C -NMR data (125 MHz, CDCl₃) δ_C : see Table 1; EI-MS m/z 458 (M)⁺ (2), 440 (35), 422 (50), 379 (69), 141 (88), 123 (100); HR-EI-MS m/z 458.4120 [Calcd for C₃₁H₅₄O₂ (M)⁺, 458.4124].

Foliasalacin A₃ (**3**): A white powder; [α]_D²⁷ +31.4° ($c=0.58$, CHCl₃); IR (KBr) ν_{max} 3422, 2933, 2870, 1705, 1636, 1215, 887, 754 cm⁻¹; ^1H -NMR (500 MHz, CDCl₃) δ 0.74 (1H, dd, $J=2.2$, 11.6 Hz, H-5), 0.78, 0.86, 0.95, 0.98, 1.06 (3H each, all s, H₃-29, 19, 18, 28, 30), 0.94 (1H, m, H-1 α), 1.02 (3H, $J=6.7$ Hz, H₃-31), 1.28 (1H, dd, $J=2.8$, 11.9 Hz, H-9), 1.65 (3H, brs, H₃-27), 1.68 (1H, m, H-1 β), 2.21 (1H, m, H-17), 3.21 (1H, dd, $J=4.9$, 11.6 Hz, H-3), 4.26 (1H, dd, $J=8.6$, 8.6 Hz, H-15), 4.69 (2H, m, H₂-26), 4.70 (1H, m, Ha-21), 4.71 (1H, brs, Hb-21); ^{13}C -NMR data (125 MHz, CDCl₃) δ_C : see Table 1; EI-MS m/z 456 (M)⁺ (6), 438 (14), 420 (13), 395 (20), 306 (40), 205 (100); HR-EI-MS m/z 456.3973 [Calcd for C₃₁H₅₂O₂ (M)⁺, 456.3967].

Foliasalacin A₄ (**4**): A white powder; [α]_D²⁷ +25.9° ($c=0.20$, CHCl₃); IR (KBr) ν_{max} 3422, 2933, 2872, 1647, 889, 803, 754 cm⁻¹; ^1H -NMR (500 MHz, CDCl₃) δ 0.73 (1H, dd, $J=2.2$, 11.9 Hz, H-5), 0.78, 0.85, 0.89, 0.96, 0.98, 1.16 (3H each, all s, H₃-29, 19, 18, 30, 28, 21), 0.99 (1H, m, H-1 α), 1.04, 1.04 (3H each, both d, $J=6.9$ Hz, H₃-26, 27), 1.31 (1H, m, H-9), 1.70 (1H, m, H-1 β), 1.71 (1H, m, H-17), 3.20 (1H, dd, $J=4.2$, 11.0 Hz, H-3), 4.69, 4.75 (1H each, both brs, H₂-31); ^{13}C -NMR data (125 MHz, CDCl₃) δ_C : see Table 1; EI-MS m/z 458 (M)⁺ (4), 440 (44), 422 (43), 379 (43), 190 (34), 141 (100); HR-EI-MS m/z 458.4117 [Calcd for C₃₁H₅₄O₂ (M)⁺, 458.4124].

Foliasalacin B₁ (**5**): A white powder; [α]_D²⁹ +9.4° ($c=0.79$, CHCl₃); IR (KBr) ν_{max} 3422, 2936, 2870, 1717, 756 cm⁻¹; ^1H -NMR (500 MHz, CDCl₃) δ 0.75, 0.94, 0.94, 1.03, 1.08, 1.08 (3H each, all s, H₃-28, 25, 27, 24, 23, 26), 0.97 (3H, d, $J=6.8$ Hz, H₃-30), 1.29 (1H, m, H-18), 1.33 (1H, m, H-5), 1.37 (1H, m), 1.68 (1H, m, H₂-21), 1.37 (1H, m, H-9), 1.37 (1H, m, H-12 α), 1.40 (1H, m, H-1 α), 1.68 (1H, m, H-12 β), 1.70 (1H, m, H-13), 1.77 (1H, m, H-19), 1.92 (1H, m, H-1 β), 2.43 (1H, ddd, $J=4.3$, 7.3, 15.6 Hz, H-2 α), 2.49 (1H, ddd, $J=7.7$, 9.5, 15.6 Hz, H-2 β), 3.41 (1H, dd, $J=8.1$, 11.1 Hz), 3.82 (1H, dd, $J=4.5$, 11.1 Hz, H₂-29); ^{13}C -NMR data (125 MHz, CDCl₃) δ_C : see Table 3; EI-MS m/z 442 (M)⁺ (63), 427 (23), 424 (24), 411

(11), 409 (16), 383 (41), 205 (100); HR-EI-MS m/z 442.3815 [Calcd for $C_{30}H_{50}O_2$ (M)⁺, 442.3811].

Foliasalacin B₃ (**6**): A white powder; $[\alpha]_D^{26} +17.2^\circ$ ($c=1.70$, $CHCl_3$); IR (KBr) ν_{max} 3415, 2935, 2870, 1717, 754 cm^{-1} ; 1H -NMR (500 MHz, $CDCl_3$) δ 0.78, 0.95, 0.95, 1.03, 1.08, 1.08 (3H each, all s, H₃-28, 25, 27, 24, 23, 26), 0.80 (3H, d, $J=6.8$ Hz, H₃-30), [1.22 (1H, m), 1.59 (1H, m), H₂-21], 1.24 (1H, m, H-18), 1.32 (1H, m, H-5), 1.36 (1H, m, H-12 α), 1.37 (1H, m, H-9), 1.42 (1H, m, H-1 α), 1.68 (1H, m, H-12 β), 1.72 (1H, m, H-13), 1.92 (1H, m, H-1 β), 1.95 (1H, m, H-19), 2.40 (1H, ddd, $J=4.3, 7.3, 15.6$ Hz, H-2 α), 2.49 (1H, ddd, $J=7.7, 9.5, 15.6$ Hz, H-2 β), 3.42 (2H, m, H₂-29); ^{13}C -NMR data (125 MHz, $CDCl_3$) δ_C : see Table 3; EI-MS m/z 442 (M)⁺ (64), 427 (19), 424 (27), 411 (7), 409 (12), 383 (31), 205 (100); HR-EI-MS m/z 442.3818 [Calcd for $C_{30}H_{50}O_2$ (M)⁺, 442.3811].

Foliasalacin B₃ (**7**): A white powder; $[\alpha]_D^{27} -26.4^\circ$ ($c=0.97$, $CHCl_3$); IR (KBr) ν_{max} 2936, 2869, 1707, 1460, 1381, 1229, 1115 cm^{-1} ; 1H -NMR (500 MHz, $CDCl_3$) δ 0.76, 0.93, 0.94, 1.03, 1.08, 1.08 (3H each, all s, H₃-28, 27, 25, 24, 23, 26), 1.15 (3H, d, $J=6.8$ Hz, H₃-30), 1.44 (1H, m, H-18), 1.32 (1H, m, H-5), 1.41 (1H, m, H-9), 1.52 (1H, m, H-12 α), 1.43 (1H, m, H-1 α), 1.56 (1H, m, H-12 β), 1.73 (1H, m, H-13), 1.78 (1H, m, H-19), 1.92 (1H, m, H-1 β), 2.42 (1H, ddd, $J=4.8, 7.6, 15.8$ Hz, H-2 α), 2.48 (1H, m, H-2 β); ^{13}C -NMR data (125 MHz, $CDCl_3$) δ_C : see Table 3; EI-MS: m/z 456 (M)⁺ (21), 441 (11), 438 (19), 423 (10), 383 (100), 358 (3), 221 (23), 205 (55), 163 (61); HR-EI-MS m/z 456.3601 [Calcd for $C_{30}H_{50}O_2$ (M)⁺, 456.3603].

Foliasalacin C (**8**): A white powder; $[\alpha]_D^{28} -25.1^\circ$ ($c=0.11$, $CHCl_3$); IR (KBr) ν_{max} 3422, 2941, 2870, 1636, 756 cm^{-1} ; 1H -NMR (500 MHz, $CDCl_3$) δ 0.76 (1H, m, H-5), 0.70, 0.77, 0.86, 0.90, 0.94, 0.98, 1.07, 1.17 (3H each, all s, H₃-30, 24, 25, 26, 29, 23, 28, 27), 0.96 (1H, m, H-1 α), 1.25 (1H, m, H-11 α), 1.44 (1H, m, H-9), 1.47 (1H, m, H-11 β), 1.58 (1H, m, H-2 β), 1.60 (1H, m, H-19 β), 1.66 (1H, m, H-2 α), 1.70 (1H, m, H-1 β), 1.94 (1H, m, H-12 β), 2.25 (1H, dd, $J=2.7, 14.5$ Hz, H-19 α), 2.67 (1H, m, H-12 α), 3.23 (1H, dd, $J=4.1, 11.0$ Hz, H-3), 4.13 (1H, dd, $J=8.3, 8.3$ Hz, H-15); ^{13}C -NMR data (125 MHz, $CDCl_3$) δ_C : see Table 3; EI-MS: m/z 442 (M)⁺ (18), 424 (18), 409 (16), 406 (6), 391 (6), 255 (7), 234 (29), 203 (100), 189 (34); HR-EI-MS m/z 442.3807 [Calcd for $C_{30}H_{50}O_2$ (M)⁺, 442.3811].

NaBH₄ Reduction of Foliasalacin B₁ (5**)** A solution of foliasalacin B₁ (**5**) (5.5 mg) in dehydrated MeOH (1.0 ml) was treated with sodium borohydride (NaBH₄, 1.0 mg) and the mixture was stirred at room temperature for 1 h. The reaction mixture was quenched in acetone, and then removal of the solvent under reduced pressure yielded a reaction mixture, which was purified by normal-phase silica gel CC [500 mg, hexane–EtOAc (3 : 1, v/v)] to furnish (20*R*)-lupane-3 β ,29-diol (**5a**, 5.1 mg, 92.6%). The obtained compound **5a** was identified by comparison of their physical data ($[\alpha]_D$, 1H -NMR, MS) with reported values.

(20*R*)-Lupane-3 β ,29-diol (**5a**): A white powder; $[\alpha]_D^{30} -4.0^\circ$ ($c=0.48$, $CHCl_3$; lit: $[\alpha]_D^{30} -14.1^\circ$); ^{13}C -NMR data (125 MHz, $CDCl_3$) δ_C : see Table 3; EI-MS: m/z 444 (M)⁺ (20), 426 (18), 207 (100), 189 (84).

CrO₃–Pyridine Oxidation of Foliasalacin B₁ (5**)** A solution of foliasalacin B₁ (**5**) (3.9 mg) in pyridine (0.5 ml) was treated with chromium trioxide (CrO₃, 2.0 mg)–pyridine (0.5 ml) mixture, and the mixture was stirred at room temperature for 2.0 h. Removal of the solvent under reduced pressure to a residue, which was purified by HPLC [MeOH–H₂O (92 : 8, v/v)] to give foliasalacin B₃ (**7**) (1.0 mg, 24.8%). The obtained **7** was identified by comparison of their physical data ($[\alpha]_D$, 1H -NMR, ^{13}C -NMR, MS) with the values of isolated foliasalacin B₃ (**7**).

NaBH₄ Reduction of Foliasalacin B₂ (6**)** A solution of foliasalacin B₂ (**6**) (5.6 mg) in dehydrated MeOH (1.0 ml) was treated with NaBH₄ (1.0 mg) and the mixture was stirred at room temperature for 1 h. Workup of the reac-

tion mixture as described above to give (20*S*)-lupane-3 β ,29-diol (**6a**, 5.3 mg, 94.6%). The obtained compound **6a** was identified by comparison of their physical data ($[\alpha]_D$, 1H -NMR, MS) with reported values.

(20*S*)-Lupane-3 β ,29-diol (**6a**): A white powder; $[\alpha]_D^{30} -2.0^\circ$ ($c=0.05$, $CHCl_3$; lit: $[\alpha]_D^{30} -5.8^\circ$); ^{13}C -NMR data (125 MHz, $CDCl_3$) δ_C : see Table 3; EI-MS: m/z 444 (M)⁺ (13), 426 (21), 207 (100), 189 (93).

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