Structures of New Friedelane- and Norfriedelane-Type Triterpenes and Polyacylated Eudesmane-Type Sesquiterpene from *Salacia chinensis* LINN. (*S. prinoides* DC., Hippocrateaceae) and Radical Scavenging Activities of Principal Constituents

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Two new friedelane-type triterpenes, salasones D and E, a new norfriedelane-type triterpene, salaquinone B, and a new polyacylated eudesmane-type sesquiterpene, salasol B, were isolated from the stems of *Salacia chinensis* LINN. (*S. prinoides* DC., Hippocrateaceae) collected in Thailand. Their stereostructures were elucidated on the basis of chemical and physicochemical evidence. Some norfriedelane-type triterpene, lignan, and catechin constituents were found to show radical scavenging activity.

Key words salasone; salaquinone; salasol; antioxidant; *Salacia chinensis*; radical scavenger

Previously, we reported that the extracts of several *Salacia* species such as *Salacia reticulata*,[1—6] *S. oblonga*,[7] and *S. chinensis* (synonyms *S. prinoides*),[8,9] showed hypoglycemic effects in oral sucrose- and maltose-loaded rats, inhibitory activities against α-glucosidases (*e.g.* sucrase, maltase, and isomaltase) and rat lens aldose reductase, hepatoprotective effect on CCl_4-induced liver injury, antioxidative activity, and anti-obese activity. As their active constituents, thiosugar sulfonium sulfates named salacinol and kotalanol, friedelane-type triterpenes, eudesmane-type sesquiterpenes, and phenolic compounds were isolated from the extracts. As a continuation of the characterization studies on bioactive constituents of *Salacia* species plants, we have isolated two friedelane-type triterpene, salasones D (**1**) and E (**2**), a norfriedelane-type triterpene, salaquinone B (**3**), and a eudesmane-type sesquiterpene, salasol B (**4**) from the stems of *S. chinensis* collected in Thailand. This paper deals with the isolation and structure elucidation of four new constituents (**1**—**4**) and radical scavenging activity of the principal constituents from *S. chinensis*.

The 80% aqueous methanolic extract from the stems of *S. chinensis* (collected in Phiphun district, Nakhon si thammarat province, Thailand) was partitioned into a mixture of ethyl acetate (EtOAc) and water to furnish the EtOAc-soluble fraction and H_2O-soluble fraction. The EtOAc-soluble fraction was separated by silica gel and octadecyl silica gel (ODS) column chromatography and finally HPLC (ODS) to give salasones D (**1**, 0.0012% from the natural medicine) and E (**2**, 0.0010%), salaquinone B (**3**, 0.0003%), and salasol B (**4**, 0.0014%).

Structures of Salasons D (1) and E (2) Salasone D (**1**) was obtained as a white powder with negative optical rotation ($[\alpha]_D^{22}$ −19.6°, $CHCl_3$). The IR spectrum of **1** showed absorption bands at 3453 and 1717 cm^{-1} ascribable to hydroxyl and carbonyl functions. In the electron impact (EI)-MS of **1**, the molecular ion peak was observed at *m/z* 458 (M^+) and the high resolution EI-MS analysis revealed the molecular formula of **1** to be $C_{30}H_{50}O_3$. The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 1) spectra of **1**, which were assigned by various NMR experiments,[10] showed signals assignable to seven methyls [δ 0.80, 1.00, 1.07, 1.09, 1.31, 1.57 (3H each, all s, 24, 30, 29, 27, 25, 28-H_3), 0.97 (3H, d, J=6.7 Hz, 23-H_3)], a methine and methylene bearing a hydroxyl group [δ 4.22 (1H, d, J=7.3 Hz, 15-H), 4.24, 4.89 (1H each, both d, J=11.6 Hz, 26-H_2)], and a carbonyl group [δ_C 211.9 (3-C)] together with ten methylenes (1, 2, 6, 7, 11, 12, 16, 19, 21, 22-C), four methines (4, 8, 10, 18-C), and six quaternary carbons (5, 9, 13, 14, 17, 20-C). The proton and carbon signals in the ^{1}H- and ^{13}C-NMR spectra of **1** were superimposable on those of a known friedelane-type triterpene, kokoonol (**1a**),[11] which was isolated from *S. reticulata*, except for the signals due to the 15-hydroxyl group. The planar structure of **1** was elucidated on the basis of homo-correlation spectroscopy (^{1}H–^{1}H COSY) and heteronuclear multiple bond connectivity (HMBC) experiments. Namely, the ^{1}H–^{1}H COSY experiment on **1** indicated the presence of seven partial structures shown in bold lines in Fig. 1 (10–1–2-C, 4–23-C, 6–8-C, 11–12-C, 15–16-C, 18–19-C, and 21–22-C). In the HMBC experiment, long-range correlations were observed between the following proton and carbon pairs (4-H and 2, 3, 5, 23-C; 15-H and 14-

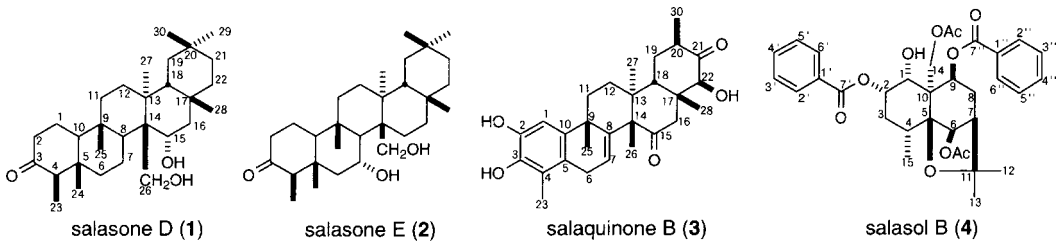

Chart 1

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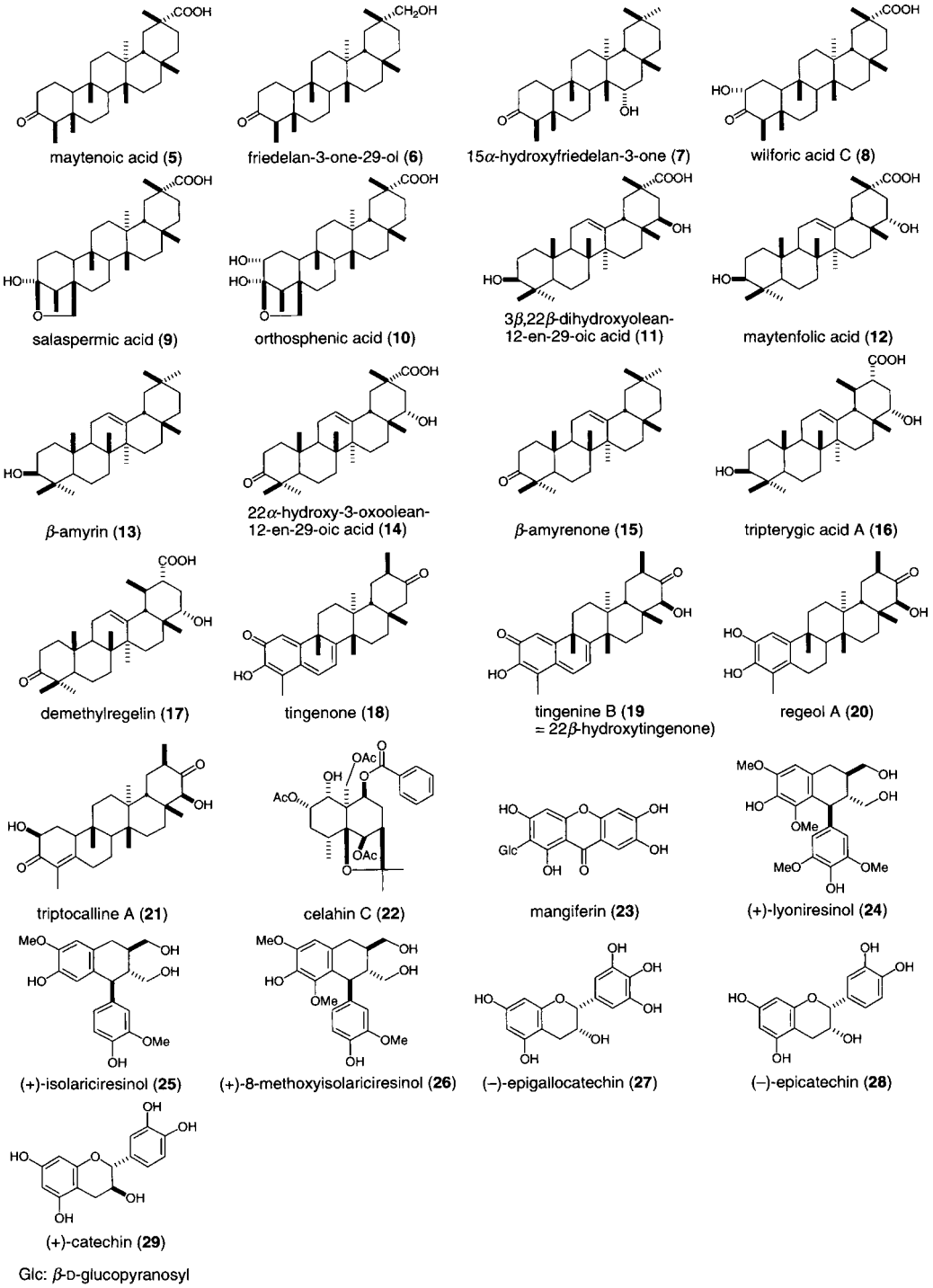

Chart 2

C; 23-H_3 and 3–5-C; 24-H_3 and 4–6, 10-C; 25-H_3 and 8–11-C; 26-H_3 and 8, 13–15-C; 27-H_3 and 12–14, 18-C; 28-H_3 and 16–18, 22-C; 29-H_3 and 19–21, 30-C; 30-H_3 and 19–21, 29-C) as shown in Fig. 1. The above evidence led us to clarify the connectivities of the quaternary carbons and the positions of the carbonyl and hydroxyl groups in **1**. The stereostructure of **1** including the 15α-hydroxyl group was confirmed by nuclear Overhauser enhancement spectroscopy (NOESY) experiment, which showed NOE correlations between the following proton pairs (15-H and 26-H_2, 28-H_3; 18-H and 28, 30-H_3; 23-H_3 and 24-H_3; 24-H_3 and 25-H_3; 25-H_3 and 26-H_2; 26-H_2 and 28-H_3; 28-H_3 and 30-H_3). Consequently, the stereostructure of **1** was determined as 3-oxofriedelane-15α,26-diol.

Salasone E (**2**) was obtained as a white powder with negative optical rotation ($[\alpha]_D^{23}$ −18.5°, $CHCl_3$). The IR spectrum of **2** indicated the presence of hydroxyl and carboxyl functions at 3453 and 1734 cm^{-1}. The molecular formula $C_{30}H_{50}O_3$ of **2**, which was the same as that of **1**, was determined from the molecular ion peaks at *m/z* 458 (M^+) in EI-MS and by high resolution EI-MS measurements. The ^{1}H-NMR ($CDCl_3$) and ^{13}C-NMR (Table 1) spectra[10] of **2** showed

signals assignable to seven methyls [δ 0.81, 0.95, 0.97, 1.07, 1.11, 1.17 (3H each, all s, 24, 29, 30, 25, 27, 28-H_3), 0.91 (3H, d, J=6.8 Hz, 23-H_3)], a methylene and a methine bearing an oxygen function [δ 4.16 (2H, br s, 26-H_2), 4.29 (1H, ddd, J=2.6, 10.6, 10.6 Hz, 7-H)], and a carbonyl group [δ_C 212.4 (3-C)] together with ten methylenes (1, 2, 6, 11, 12, 15, 16, 19, 21, 22-C), four methines (4, 8, 10, 18-C), and six quaternary carbons (5, 9, 13, 14, 17, 20-C). The proton and carbon signals in the ^{1}H- and ^{13}C-NMR spectra of **2** resembled those of **1a**, except for the signals ascribable to the 7-hydroxyl group. As shown in Fig. 1, the ^{1}H–^{1}H COSY experiment on **2** showed the presence of the similar functional structures to those of **1**, except for the position of a secondary hydroxyl group. In the HMBC experiment of **2**, long-range correlations were observed between the following proton and carbon pairs (4-H and 2, 3, 5, 23-C; 23-H_3 and 3–5-C; 24-H_3 and 4–6, 10-C; 25-H_3 and 8–11-C; 26-H_3 and 8, 13–15-C; 27-H_3 and 12–14, 18-C; 28-H_3 and 16–18, 22-C; 29-H_3 and 19–21, 30-C; 30-H_3 and 19–21, 29-C) as shown in Fig. 1. The above evidence indicated the positions of the 3-carbonyl and 7-hydroxyl functions in the fridelane skeleton. Furthermore, the stereostructure of the 7α-hydroxyl group in **2** was determined by NOESY experiment, which showed the NOE correlations between the following proton pairs (7-H and 24, 25-H_3, 26-H_2; 18-H and 28, 30-H_3; 23-H_3 and 24-H_3; 24-H_3 and 25-H_3; 25-H_3 and 26-H_2; 26-H_2 and 28-H_3; 28-H_3 and 30-H_3). On the basis of this evidence, the stereostructure of **2** was confirmed as 3-oxofriedelane-7α,26-diol.

Table 1. ^{13}C-NMR Data of Salasones D (**1**) and E (**2**), Salaquinone B (**3**), and Salasol B (**4**)

	1[a)]	**2**[b)]	**3**[b)]		**4**[b)]
C-1	22.8	35.6	107.7	C-1	69.3
C-2	42.7	41.1	141.6	C-2	73.9
C-3	211.9	212.4	139.5	C-3	31.2
C-4	57.8	58.1	120.9	C-4	33.3
C-5	42.4	42.5	125.7	C-5	89.3
C-6	41.7	50.4	27.8	C-6	78.3
C-7	22.7	69.2	126.0	C-7	48.9
C-8	54.4	58.2	139.0	C-8	34.4
C-9	38.0	38.8	36.2	C-9	69.4
C-10	59.8	59.3	140.0	C-10	54.5
C-11	37.1	36.0	33.0	C-11	82.6
C-12	31.6	29.9	29.4	C-12	30.3
C-13	41.0	40.3	43.5	C-13	26.0
C-14	46.8	44.2	58.0	C-14	65.7
C-15	75.5	27.0	211.4	C-15	18.2
C-16	48.4	35.5	47.5	2-BzO-	
C-17	30.9	30.1	49.4	C-1′	130.4
C-18	42.6	43.3	44.3	C-2′,6′	129.6
C-19	32.2	21.9	30.7	C-3′,5′	128.6
C-20	28.4	28.3	40.0	C-4′	133.1
C-21	36.2	32.4	212.4	C-7′	165.4
C-22	39.5	39.2	77.8	9-BzO-	
C-23	7.2	6.9	11.6	C-1″	129.6
C-24	14.4	15.9		C-2″,6″	129.7
C-25	16.9	18.8	33.4	C-3″,5″	128.6
C-26	65.8	64.2	25.6	C-4″	133.3
C-27	19.7	20.1	21.4	C-7″	167.0
C-28	32.7	31.2	24.6	6-AcO-	170.0
C-29	35.7	34.7			21.3
C-30	31.0	31.1	14.8	14-AcO-	170.8
					21.2

Measured in *a*) pyridine-d_5 and *b*) $CDCl_3$ at 125 MHz.

Structure of Salaquinone B (3) Salaquinone B (**3**) was obtained as an amorphous powder with positive optical rotation ($[\alpha]_D^{26}$ +69.4°, $CHCl_3$). The IR spectrum of **3** showed absorption bands at 3432 and 1709 cm^{-1} ascribable to hydroxyl and carbonyl functions. In the UV spectrum of **3**, absorption maxima were observed at 223 nm (log ε 3.9), 246 nm (3.7), and 416 nm (3.7). The molecular formula $C_{28}H_{36}O_5$ of **3** was characterized from the EI-MS and by high resolution EI-MS measurement. The ^{1}H-NMR ($CDCl_3$) and ^{13}C-NMR (Table 1) spectra[10] of **3** showed signals assignable to six methyls [δ 1.01, 1.05, 1.27, 1.69, 2.16 (3H each, all s, 27, 28, 25, 26, 23-H_3), 1.11 (3H, d, J=8.4 Hz, 30-H_3)], a methine bearing an oxygen function [δ 4.42 (1H, br s, 22-H)], two olefins [δ 6.31 (1H, d, J=5.1 Hz, 7-H), 6.71 (1H, s, 1-H)], and two carbonyl groups [δ_C 211.4 (15-C), 212.4 (21-C)] together with five methylenes (6, 11, 12, 16, 19-C), two methines (18, 20-C), and ten quaternary carbons (2–5, 8–10, 13, 14, 17-C). The proton and carbon signals in the ^{1}H- and ^{13}C-NMR spectra of **3** were very similar to those of a known

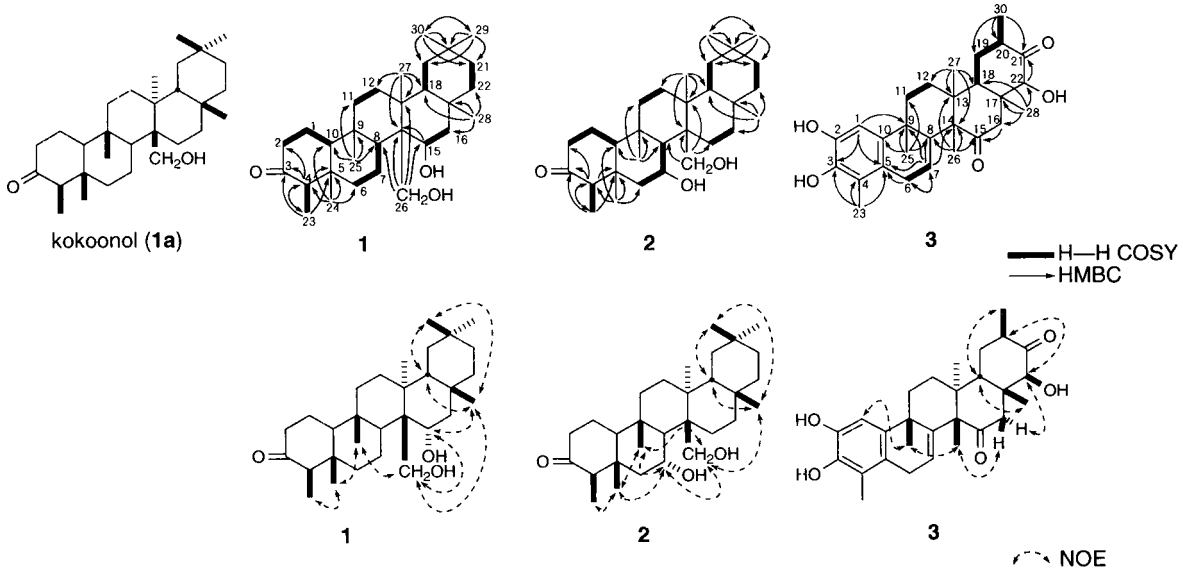

Fig. 1. H–H COSY, HMBC, and NOE Correlations of **1**—**3**

29-norfriedelane-type triterpene, regeol A (**20**), except for the signals due to the 15-carbonyl group. As shown in Fig. 1, the ^{1}H–^{1}H COSY experiment of **3** indicated the presence of three partial structures shown in bold lines (6–7-C, 11–12-C, 18–20–30-C). In the HMBC experiment of **3**, long-range correlations were observed between the following proton and carbon pairs (1-H and 3, 5, 9-C; 6-H_2 and 5, 7-C; 7-H and 5, 6, 9, 14-C; 16-H_2 and 15-C; 22-H and 21-C; 23-H_3 and 3–5-C; 25-H_3 and 8–11-C; 26-H_3 and 8, 13–15-C; 27-H_3 and 12–14, 18-C; 28-H_3 and 16–18, 22-C; 30-H_3 and 19–21-C), so that the positions of the carbonyl and olefin functions and quaternary carbons of **3** were clarified as shown in Fig. 2. The stereostructure of **3** including the 22β-hydroxyl group was confirmed by NOESY experiment. Namely, the NOE correlations of **3** were observed between the following proton pairs (1-H and 25-H_3; 16α-H and 22-H; 16β-H and 26-H_3; 18-H and 28, 30-H_3; 20-H and 22-H; 25-H_3 and 26-H_3). The above mentioned evidence led us to characterize the stereostructure of salaquinone B as **3**.

Structure of Salasol B (4) Salasol B (**4**) was isolated as a white powder with positive optical rotation ($[\alpha]_D^{26}$ +59.0°, $CHCl_3$). The molecular formula $C_{33}H_{38}O_{10}$ of **4** was determined from the molecular ion peak observed in the EI-MS and by high resolution EI-MS measurement. The IR spectrum of **4** showed absorption bands at 3475, 1744, 1719, 1368, 1244, and 1099 cm^{-1} ascribable to hydroxyl, carbonyl, and aromatic functions. In the UV spectrum of **4**, absorption maxima were observed at 230 nm (log ε 4.2) and 273 nm (3.4) suggestive of a benzoyl group. The ^{1}H-NMR ($CDCl_3$) and ^{13}C-NMR (Table 1)[10] spectra of **4** indicated the presence of three methyls [δ 1.21 (3H, d, J=7.4 Hz, 15-H_3), 1.45, 1.52 (3H each, both s, 12, 13-H_3)], two acetyl groups [δ 2.07, 2.19 (3H each, both s, 6, 14-OAc)], a methylene and four methine bearing an oxygen function [δ 4.50, 5.18 (1H each, both d, J=12.5 Hz, 14-H_2), 4.85 (1H, br s, 1-H), 5.52 (1H, d, J=7.4 Hz, 9-H), 5.61 (1H, br s, 2-H), 5.91 (1H, s, 6-H)], and two benzoyl groups [δ 7.46, 7.47 (2H each, both dd-like, 3′, 5′-, 3″, 5″-H), 7.56 (2H, t-like, 4′, 4″-H), 8.08 (2H, d, J=7.1 Hz, 2′, 6′-H), 8.09 (2H, d, J=7.3 Hz, 2″, 6″-H)] together with two methylenes (3, 8-C), two methines (4, 7-C), and three quaternary carbons (5, 10, 11-C). The alkaline hydrolysis of **4** with 5% aqueous potasium hydroxide (KOH) in 1,4-dioxane yielded a known eudesmane-type sesquiterpene, 3,4-dideoxymaytol (**4a**),[12] which was also obtained by the alkaline hydrolysis of celahin C (**22**).[9] The ^{1}H–^{1}H COSY experiment on **4** indicated the presence of four partial structure written in bold lines, as shown in Fig. 2. The positions of acetyl and benzoyl groups in **4** were clarified by HMBC experiment. Namely, long-range correlations in the HMBC experiment were observed between the following protons and carbons of **4** (2-H and 7′-C; 6-H and 5-C, 6-OAc; 9-H and 10, 7″-C; 12-H_3 and 7, 11, 13-C; 13-H_3 and 7, 11, 12-C; 14-H_2 and 1, 5, 9, 10-C, 14-OAc). Finally, comparison of the spectral data for **4** with those for the related sesquiterpenes led us to elucidate the stereostructure of **4**.

DPPH Radical Scavenging Activities of the Constituents from *S. chinensis* The DPPH radical, which is stable and shows an absorption at 517 nm, has been used as a convenient tool for the radical scavenge assay, and this assay is independent of any enzyme activity.[13,14] When this compound accepts an electron or hydrogen radical to become a more stable compound, the absorption vanishes. Previously, we reported the DPPH radical and/or superoxide anion radical ($^{\bullet}O_2^-$) scavenging activities of several natural medicines, such as the fruit hulls of *Garcinia mangostana*,[15] the rhizomes of *Rheum undulatum*,[16] the whole plants of *Cyperus longus*,[17] and the flowers of *Prunus mume*.[18] In our continuing studies on antioxidative principles from natural medicines, DPPH radical scavenging activities of the aqueous methanolic extract of *S. chinensis* and isolated constituents were examined. As a result, the aqueous methanolic extract of *S. chinensis* (SC_{50}=13 μg/ml) and following ten constituents were found to show scavenging activities as shown in Table 2, norfriedelane-type triterpenes: tigenone (**18**, SC_{50}=13 μM), tingenine B (**19**, 8.5 μM), and regeol A (**20**, 10 μM); xanthone: mangiferin (**23**, 5.9 μM); lignans: (+)-lyoniresinol (**24**, 6.6 μM), (+)-isolariciresinol (**25**, 12 μM), and (+)-8-methoxyisolariciresinol (**26**, 15 μM); and flavan-3-ols:

Table 2. DPPH Radical Scavenging Activity of Chemical Constituents from *Salacia chinensis*

	DPPH radical SC_{50} (μM)[a]
Friedelane Type Triterpenes	
Maytenoic acid (**5**)	>40
Friedelane-3-one-29-ol (**6**)	>40
15α-Hydroxyfriedelane-3-one (**7**)	>40
Wilfolic acid C (**8**)	>40
Salaspermic acid (**9**)	>40
Orthosphenic acid (**10**)	>40
Oleanane Type Triterpenes	
3β,22β-Dihydroxyolean-12-en-29-oic acid (**11**)	>40
Maytenfolic acid (**12**)	>40
β-Amyrin (**13**)	>40
22α-Hydroxy-3-oxoolean-12-en-29-oic acid (**14**)	>40
β-Amyrenone (**15**)	>40
Ursan Type Triterpenes	
Tripterygic acid A (**16**)	>40
Demethylregelin (**17**)	>40
Norfriedelane Type Triterpenes	
Tingenone (**18**)	13
Tingenine B (**19**)	8.5
Regeol A (**20**)	10
Triptocalline A (**21**)	>40
Agarofuran Type Sesquiterpenes	
Celahin C (**22**)	>40
Others	
Mangiferin (**23**)	5.9
(+)-Lyoniresinol (**24**)	6.6
(+)-Isolariciresinol (**25**)	12
(+)-8-Methoxyisolariciresinol (**26**)	15
(−)-Epigallocatechin (**27**)	2.5
(−)-Epicatechin (**28**)	4.1
(+)-Catechin (**29**)	5.9

a) Concentration required for 50% reduction of 40 μM DPPH radical.

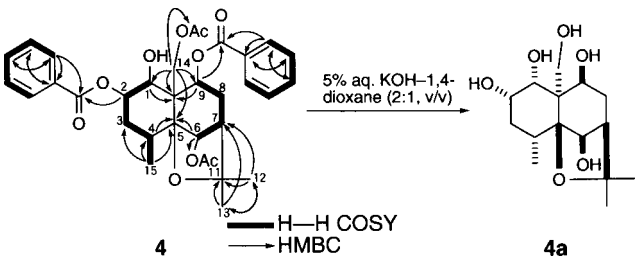

Fig. 2. H–H COSY and HMBC Correlations of **4**

(−)-epigallocatechin (**27**, 2.5 μM), (−)-epicatechin (**28**, 4.1 μM), and (+)-catechin (**29**, 5.9 μM).

Experimental

The following instruments were used to obtain physical data: specific rotations, Horiba SEPA-300 digital polarimeter (l=5 cm); UV spectra, Shimadzu UV-1600 spectrometer; IR spectra, Shimadzu FTIR-8100 spectrometer; EI-MS and high-resolution MS, JEOL JMS-GCMATE mass spectrometer; ^{1}H-NMR spectra, JNM-LA500 (500 MHz) spectrometer; ^{13}C-NMR spectra, JNM-LA500 (125 MHz) spectrometer with tetramethylsilane as an internal standard; HPLC detector, Shimadzu RID-6A refractive index detector.

The following experimental conditions were used for chromatography: ordinary-phase silica gel column chromatography, Silica gel BW-200 (Fuji Silysia Chemical, Ltd., 150—350 mesh); reversed-phase silica gel column chromatography, Chromatorex ODS DM1020T (Fuji Silysia Chemical, Ltd., 100—200 mesh); TLC, pre-coated TLC plates with Silica gel 60F_{254} (Merck, 0.25 mm) (ordinary phase) and Silica gel RP-18 F_{254S} (Merck, 0.25 mm) (reversed phase); reversed-phase HPTLC, pre-coated TLC plates with Silica gel RP-18 WF_{254S} (Merck, 0.25 mm); detection was achieved by spraying with 1% $Ce(SO_4)_2$–10% aqueous H_2SO_4 followed by heating.

Extraction and Isolation of Salasones D (1) and E (2), Salaquinone B (3), and Salasol B (4) from the Stems of *Salacia chinensis* L. The dried stems of *S. chinensis* (5 kg) were crushed and extracted three times with 80% aqueous methanol under reflux. Evaporation of the solvent under reduced pressure provided the 80% aqueous methanolic extract (551 g, 11.0%), and it (538 g) was partitioned into the EtOAc–H_2O (1 : 1) mixture. Removal of the solvent under reduced pressure from the EtOAc- and water-soluble portion yielded 66.6 g (1.4%) and 471.4 g (9.6%) of residue, respectively. The EtOAc-soluble portion (58.7 g) was subjected to normal-phase silica gel column chromatography [1.8 kg, *n*-hexane–EtOAc (10 : 1→5 : 1→2 : 1→1 : 1, v/v)→$CHCl_3$–MeOH–H_2O (10 : 3 : 0.5, v/v)→MeOH] to give nine fractions {Fr. 1 [squalene (596 mg, 0.014%)], Fr. 2 (1.2 g), Fr. 3 (3.6 g), Fr. 4 (3.4 g), Fr. 5 (4.5 g), Fr. 6 (2.8 g), Fr. 7 (6.3 g), Fr. 8 (17.6 g), Fr. 9 (18.7 g)}. Fraction 5 (3.0 g) was further separated by HPLC [YMC-Pack ODS-A (YMC Co., Ltd., 250×20 mm i.d.), MeOH–1% aqueous AcOH (95 : 5, v/v)] to give ten fractions [Fr. 5-1 (146 mg), Fr. 5-2 (318 mg), Fr. 5-3 (298 mg), Fr. 5-4 (273 mg), Fr. 5-5 (238 mg), Fr. 5-6 (206 mg), Fr. 5-7 (387 mg), Fr. 5-8 (173 mg), Fr. 5-9 (164 mg), Fr. 5-10 (157 mg)]. Fraction 5-2 (318 mg) was purified by HPLC [MeOH–H_2O (75 : 25, v/v)] to give salasol B (**4**, 38 mg, 0.0014%). Fraction 5-8 (173 mg) was purified by normal-phase silica gel column chromatography [i) 17 g, $CHCl_3$–MeOH (100 : 1, v/v)→MeOH, ii) 10 g, benzene–acetone (40 : 1→20 : 1→10 : 1, v/v)→MeOH] to give salasones D (**1**, 34 mg, 0.0012%) and E (2, 27 mg, 0.0010%) together with salasone B (14 mg, 0.0005%).[9] Fraction 7 (6.0 g) was further separated by reversed-phase silica gel column chromatography [180 g, MeOH–H_2O (40 : 60→50 : 50→70 : 30→80 : 20→90 : 10, v/v)→MeOH] to give five fractions [Fr. 7-1 (1.8 g), Fr. 7-2 (1.5 g), Fr. 7-3 (1.0 g), Fr. 7-4 (703 mg), Fr. 7-5 (924 mg)]. Fraction 7-2 (1.5 g) was purified by normal-phase silica gel column chromatography [75 g, $CHCl_3$–MeOH (100 : 1, v/v)→MeOH] and HPLC [i) MeOH–1% aqueous AcOH (75 : 25, v/v), ii) CH_3CN–H_2O (55 : 45, v/v)] to give salaquinone B (**3**, 12 mg, 0.0003%) together with salaquinone A (24 mg, 0.0006%)[9] and salasol A (26 mg).[9]

Salasone D (**1**): A white powder, $[\alpha]_D^{22}$ −19.6° (c=0.50, $CHCl_3$). High-resolution EI-MS: Calcd for $C_{30}H_{50}O_3$ (M^+): 458.3760. Found: 458.3773. IR (KBr): 3453, 2930, 1717, 1458, 1391 cm^{-1}. ^{1}H-NMR (500 MHz, pyridine-d_5) δ: 0.80, 1.00, 1.07, 1.09, 1.31, 1.57 (3H each, all s, 24, 30, 29, 27, 25, 28-H_3), 0.97 (3H, d, J=6.7 Hz, 23-H_3), 1.73 (1H, dd-like, 18-H), [1.80 (1H, br d, J=*ca.* 16 Hz), 2.22 (1H, dd, J=7.3, 15.5 Hz), 16-H_2], 2.25 (1H, m, 4-H), 4.22 (1H, d, J=7.3 Hz, 15-H), 4.24, 4.89 (1H each, both d, J=11.6 Hz, 26-H_2). ^{13}C-NMR (pyridine-d_5) δ_C: given in Table 1. EI-MS: m/z 458 (M^+, 7), 109 (100).

Salasone E (**2**): A white powder, $[\alpha]_D^{23}$ −18.5° (c=0.50, $CHCl_3$). High-resolution EI-MS: Calcd for $C_{30}H_{50}O_3$ (M^+): 458.3760. Found: 458.3789. IR (KBr): 3453, 2924, 1734, 1458, 1390 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 0.81, 0.95, 0.97, 1.07, 1.11, 1.17 (3H each, all s, 24, 29, 30, 25, 27, 28-H_3), 0.91 (3H, d, J=6.8 Hz, 23-H_3), 1.42 (1H, m, 18-H), 2.31 (1H, q, J=6.8 Hz, 4-H), 4.16 (2H, br s, 26-H_2), 4.29 (1H, ddd, J=2.6, 10.6, 10.6 Hz, 7-H). ^{13}C-NMR ($CDCl_3$) δ_C: given in Table 1. EI-MS: m/z 458 (M^+, 8), 109 (100).

Salaquinone B (**3**): An amorphous powder, $[\alpha]_D^{26}$ +69.4° (c=0.20, $CHCl_3$). High-resolution EI-MS: Calcd for $C_{28}H_{36}O_5$ (M^+): 452.2563. Found: 452.2547. UV [MeOH, nm (log ε)]: 223 (3.9), 246 (3.7), 416 (3.7). IR (KBr): 3432, 2924, 1709, 1595, 1439, 1381 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.01, 1.05, 1.27, 1.69, 2.16 (3H each, all s, 27, 28, 25, 26, 23-H_3), 1.11 (3H, d, J=8.4 Hz, 30-H_3), 2.22 (1H, m, 18-H), 2.64 (1H, m, 20-H), 2.75, 2.87 (1H each, both d, J=15.0 Hz, 16-H_2), [3.00 (1H, br d, J=*ca.* 20 Hz), 3.41 (dd, J=5.1, 20.1 Hz), 6-H_2], 4.42 (1H, br s, 22-H), 6.31 (1H, d, J=5.1 Hz, 7-H), 6.71 (1H, s, 1-H). ^{13}C-NMR ($CDCl_3$) δ_C: given in Table 1. EI-MS: m/z 452 (M^+, 27), 57 (100).

Salasol B (**4**): A white powder, $[\alpha]_D^{26}$ +59.0° (c=0.10, $CHCl_3$). High-resolution EI-MS: Calcd for $C_{33}H_{38}O_{10}$ (M^+): 594.2464. Found: 594.2468. UV [MeOH, nm (log ε)]: 230 (4.2), 273 (3.4). IR (KBr): 3475, 3025, 2930, 1744, 1719, 1368, 1271, 1244, 1099, 712 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.21 (3H, d, J=7.4 Hz, 15-H_3), 1.45, 1.52 (3H each, both s, 12, 13-H_3), [1.99 (1H, br d, J=*ca.* 15 Hz), 2.46 (1H, ddd-like), 3-H_2], 2.07, 2.19 (3H each, both s, 6, 14-OAc), 2.27 (1H, ddd-like, 7-H), [2.32 (1H, dd, J=3.1, 16.2 Hz), 2.58 (1H, ddd, J=3.6, 7.4, 16.2 Hz), 8-H_2], 2.40 (1H, m, 4-H), 4.50, 5.18 (1H each, both d, J=12.5 Hz, 14-H_2), 4.85 (1H, br s, 1-H), 5.52 (1H, d, J=7.4 Hz, 9-H), 5.61 (1H, br s, 2-H), 5.91 (1H, s, 6-H), 7.46, 7.47 (2H each, both dd-like, 3′, 5′-, 3″, 5″-H), 7.56 (2H, t-like, 4′, 4″-H), 8.08 (2H, d, J=7.1 Hz, 2′, 6′-H), 8.09 (2H, d, J=7.3 Hz, 2″, 6″-H). ^{13}C-NMR ($CDCl_3$) δ_C: given in Table 1. EI-MS: m/z 594 (M^+, 2), 105 (100).

Alkaline Hydrolysis of Salasol B (4) A solution of **4** (4.9 mg) in 5% aqueous KOH–1,4-dioxane (2 : 1, v/v, 1.5 ml) was stirred at room temperature (25 °C) for 4 h. The reaction mixture was neutralized with Dowex HCR W2 (H^+ form) and the resin was removed by filtration. After removal of the solvent from the filtrate *in vacuo*, the residue was separated by normal-phase silica gel column chromatography [500 mg, $CHCl_3$–MeOH–H_2O (30 : 3 : 1, lower layer, v/v)] to give 3,4-dideoxymaytol (**4a**, 2.3 mg, 92%). Compound **4a** was identified by comparison of physical data ($[\alpha]_D$, IR, ^{1}H-NMR, MS) with reported values.[9,12]

Bioassay. DPPH Radical Scavenging Activity The free radical scavenging activity of the constituents was assessed using the DPPH radical.[13,14] An ethanol solution of DPPH (100 μM, 1.0 ml) was mixed with different concentrations of each test compound (0—200 μM, 0.5 ml) and 0.1 M acetate buffer (pH 5.5, 1.0 ml), and the absorbance change at 517 nm was measured 30 min later. The reaction solution without DPPH was used as a blank test. Measurements were performed in duplicate, and the concentration required for a 50% reduction (50% scavenging concentration, SC_{50}) of 40 μM DPPH radical solution was determined graphically.

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