Terpenoids from the Stems of *Cipadessa baccifera*

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In our systematical investigation on Chinese Meliaceae plants, the stems of *Cipadessa baccifera* collected in Yunnan province were studied. Two new tetranortriterpenoids, cipadessalide (**1**) and rubralin D (**2**), one new pregnane, 3β,4β-dihydroxy-2β-acetoxypregnan-16-one (**3**), and two new sesquiterpenoids, bacciferins A (**4**) and B (**5**), along with 10 known compounds were isolated. Their structures were elucidated by 1D and 2D NMR spectra and other spectroscopic studies, as well as chemical conversion.

The genus *Cipadessa* belongs to the Trichileae tribe of the Meliodeae subfamily of the Meliaceae family.[1,2] The folk medicine "Ya Luo Qing", derived from the leaves and roots of *Cipadessa* plants, was used to treat dysentery, skin itch, malaria, and burns by a Chinese minority-ethnic Dai.[3–5] In this paper, we describe the phytochemical investigation of *C. baccifera*, a *Cipadessa* species distributed widely in the southwest of China.[2] Previous studies on the seeds of this plant revealed the occurrence of 13 mexicanolide-type tetranortriterpenoids, two pregnanes, and two heneicosenes.[5,6] Herein, we report the identification of two new tetranortriterpenoids, cipadessalide (**1**) and rubralin D (**2**), one new pregnane, 3β,4β-dihydroxy-2β-acetoxypregnan-16-one (**3**), and two new sesquiterpenoids, bacciferin A (**4**) and B (**5**).

Results and Discussion

Cipadessalide (**1**), obtained as white amorphous powder, possessed the molecular formula $C_{33}H_{42}O_{12}$ as indicated by the $[M+Na]^+$ peak at *m/z* 653.2583 in the HRESIMS and its ^{13}C NMR spectrum. Thus, 13 unsaturation degrees were determined for **1**. The IR spectrum showed absorption bands at 3448 and 1732 cm^{-1} ascribable to hydroxy and lactone functionalities, respectively. The ^1H NMR spectrum of **1** (Table 1) revealed the presence of a β-substituted furan ring (δ_H 7.24, s; 6.25, d, $J = 0.8$; 7.39, s), a formate group (δ_H 8.14, s), three methyl singlets (δ_H 1.00; 1.13; 1.81) and a 2-hydroxy-3-methylpentanoate group (δ_H 3.23, m; 0.83, d, $J = 6.8$; 0.78, t, $J = 7.4$). The ^{13}C NMR spectrum showed 33 resonances (Table 1), which were classified by DEPT as five methyl, six methylene (two oxygenated), 12 methine (three olefinic and five oxygenated), and 10 quaternary carbons (four carbonyl, three olefinic, and one oxygenated carbon). Besides the formate and 2-hydroxy-3-methylpentanoate groups, **1** contained 26 carbons and was assumed to be a tetranortriterpenoid.[7,8] Comparison of the ^1H and ^{13}C NMR data of **1** and mombasol[7] indicated that the CDE ring systems of **1** were similar to those of mombasol, which was further supported by HSQC and HMBC experiments (Figure 1). An olefinic double bond was assigned at C-8/C-14 by HMBC correlations between C-8 (δ_C 127.5) and H-9 (δ_H 2.84, d, $J = 7.8$), as well as C-14 (δ_C 148.2) and H-9, H-16b (δ_H 1.94, m), and H_3-18 (δ_H 1.00, s). Furthermore, the cross peaks from the oxymethine proton (δ_H 4.86, d, $J = 6.3$) to C-8 and C-17 (δ_C 43.4) assigned it as H-15. In the HMBC spectrum, the correlations between H_2-28 (δ_H 4.28, d, $J = 4.8$; 4.17, d, $J = 4.8$) and C-4 (δ_C 80.6), C-5 (δ_C 39.4), C-7 (δ_C 173.7), and C-29 (δ_C 24.0), as well as H-5 (δ_H 2.96, m) and C-1 (δ_C 80.9), C-7, C-19 (δ_C 18.5), and C-28 (δ_C 75.3), constructed a six-membered lactone ring fused at C-4 and C-5. Such a structural moiety resembled the AA′ ring systems of rohituka 3.[8] The obvious low-field shift of H_3-29 (δ_H 1.81, s) in comparison with the corresponding signal of mombasol (δ_H 1.31, s) further supported the above conclusion. The oxygenated methylene (δ_H 5.03, d, $J = 12.2$; 3.77, d, $J = 12.2$; δ_C 69.2) was assigned at C-30 by HMBC correlations between H_2-30 and C-8, C-9 (δ_C 53.2), and C-14. The HMBC correlation from H_2-30 to C-1 constructed the 1,30-oxygen bridge to form a tetrahydropyrano ring. The relative configuration of **1** was determined by its ROESY spectrum (Figure 1). The NOE interaction between H-15 and H_3-18 placed OH-15 in a β-orientation. H-11 and H-12 were deduced to be trans-diaxially oriented by the characteristic coupling constant ($J_{11,12} = 11.9$).[7,8] The NOE correlation of H-12/H-17 indicated H-12 was β-orientated, while the NOE correlation pairs H-11/H_3-18 and H-11/H_3-19 suggested α-orientation for H-11. In addition, the NOE interactions between H-5 and H-12 and H_3-29 indicated that H-5 and H_3-29 were β-cofacially oriented. The NOE correlation between H-1 and H_3-19 revealed that H-1 was α-oriented. The relative configuration of the 2-hydroxy-3-methylpentanoate moiety is undefined. Therefore, the structure of **1** was established.

The proposed biogenetic relationship between compound **1** and mombasol is shown in Figure 2. Compound **1** is the first sample of a tetranortriterpenoid that contains an oxygen bridge between C-1 and C-30. It is also the first prieurianin-type tetranortriterpenoid from *Cipadessa* plants.

Rubralin D (**2**) was obtained as white amorphous powder. The molecular formula, $C_{41}H_{58}O_{14}$, was inferred from its HRESIMS (*m/z* 797.3738 $[M+Na]^+$), with 13 unsaturation degrees. The IR absorption bands at 3385 and 1771 cm^{-1} suggested the presence of hydroxy and ester functionalities. The ^1H and ^{13}C NMR spectra of **2**, similar to those of rubralin B,[9] suggested the presence of a β-substituted furan ring, two acetyl, five methyl singlets, two methyl doublets, one methyl triplet, one trisubstituted double bond, and three carbonyl carbons (Table 2). $^1H-^1H$ COSY and HMBC spectra revealed the presence of a 2-hydroxy-3-methylbutyrate, a 2,3-dihydroxy-3-methylvalerate and two acetate groups. Twelve of 14 oxygen atoms accounted for the above moieties. The remaining two oxygen atoms were found to form a lactone ring, which was supported by the carbonyl carbon (δ_C 169.1) in the ^{13}C NMR spectrum. These data were indicative of an evodulone-type tetranortriterpenoid structure for **2**. The relative configuration was determined by the ROESY experiment and by biogenetic considerations. The detailed assignments of the ^1H and ^{13}C NMR signals of **2** were deduced by HSQC, HMBC, and ROESY spectra. Compound **2** is the first evodulone-type tetranortriterpenoid from *Cipadessa* plants.

3β,4β-Dihydroxy-2β-acetoxypregnan-16-one (**3**) was obtained as colorless cubic crystals. The HRESIMS indicated the molecular formula as $C_{23}H_{36}O_5$ (*m/z* 415.2443 $[M+Na]^+$). The IR spectrum indicated the presence of hydroxy (3539 cm^{-1}), ester carbonyl (1738 cm^{-1}), and ketonic carbonyl (1711 cm^{-1}) groups. The ^1H and ^{13}C NMR spectra (Table 3) showed signals for two tertiary methyl (δ_H 2.08, 1.19), a primary methyl (δ_H 1.00, $J = 7.2$), an acetyl (δ_H 2.08; δ_C 21.5, 171.3), a ketonic carbonyl (δ_C 219.5), and three

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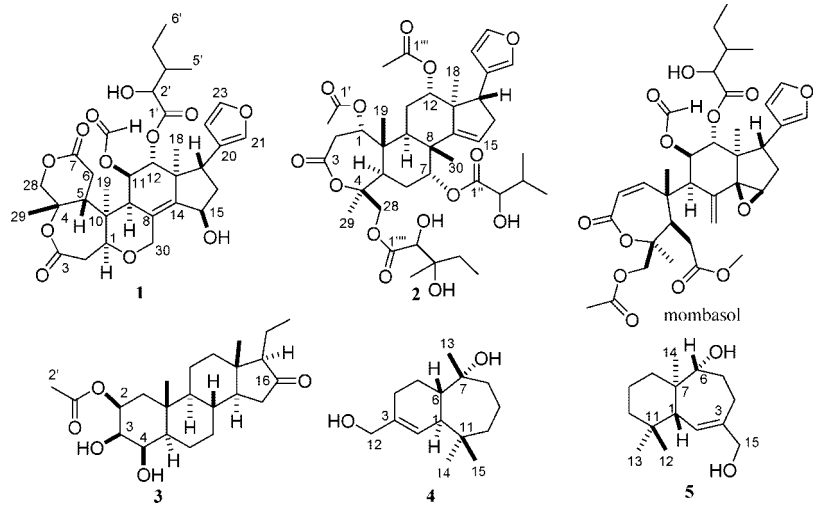

Table 1. ^{1}H and ^{13}C NMR Data of Compound **1** (in $CDCl_3$, 400 MHz, ppm)

C	δ_H (mult, *J*)	δ_C	C	δ_H (mult, *J*)	δ_C
1	3.62, d (5.1)	80.9 CH	18	1.00, s	17.0 CH_3
2a	3.34, m	40.3 CH_2	19	1.13, s	18.5 CH_3
2b	2.96, m		20		122.4 C
3		170.6 C	21	7.24, s	140.3 CH
4		80.6 C	22	6.25, d (0.8)	110.5 CH
5	2.96, m	39.4 CH	23	7.39, s	142.8 CH
6a	3.20, m	31.2 CH_2	28a	4.28, d (4.8)	75.3 CH_2
6b	3.08, m		28b	4.17, d (4.8)	
7		173.7 C	29	1.81, s	24.0 CH_3
8		127.5 C	30a	3.77, d (12.2)	69.2 CH_2
9	2.84, d (7.8)	53.2 CH	30b	5.03, d (12.2)	
10		49.5 C	11′	8.14, s	160.8 CH
11	5.66, dd (7.9, 11.8)	69.6 CH	1′		174.7 C
12	5.37, d (11.9)	75.0 CH	2′	3.23, m	74.7 CH
13		49.4 C	3′	1.52, m	38.2 CH
14		148.2 C	4′	1.08, m	23.5 CH_2
15	4.86, d (6.3)	68.8 CH	4′	1.10, m	
16a	2.32, m	41.2 CH_2	5′	0.83, d (6.8)	15.2 CH_3
16b	1.94, m		6′	0.78, t (7.4)	11.6 CH_3
17	3.12, m	43.4 CH			

oxygenated methine groups (δ_H 5.30, dd, J = 3.2, 6.4; 3.85, bs; 3.68, m), which were similar to those of 2β,3β,4β-trihydroxypregnan-16-one.[5,10] Three oxymethine protons were assigned to H-2, H-3, and H-4 by the ^{1}H−^{1}H COSY spectrum (bold lines in Figure 3a). The HMBC correlation between H-2 and C-1′ indicated the acetyl group at C-2, which was supported by the downfield shift of H-2 relative to the corresponding signal of 2β,3β,4β-trihydroxypregnan-16-one (δ_H 4.54). The relative configuration of **3** was fixed by the ROESY experiment (broken arrows in Figure 3b). The NOE correlation pairs of OH-4/H_3-19 and H_3-2′/H_3-19 suggested H-2 and H-4 were α-cofacially oriented. The cross peak between H-3 and H-5 indicated that the hydroxyl group at C-3 was also β-oriented. Compound **3** was thus assigned as 3β,4β-dihydroxy-2β-acetoxypregnan-16-one. The structure was further confirmed by hydrolysis of **3** with potassium hydroxide in methanol to give a major compound, whose ^{1}H NMR data and TLC behavior were identical with those of 2β,3β,4β-trihydroxypregnan-16-one.

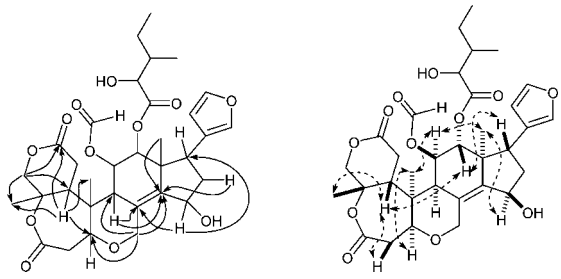

Figure 1. Important HMBC correlations (arrows) and key NOE correlations (broken arrows) for **1**.

The molecular formula of bacciferin A (**4**) was established as $C_{15}H_{26}O_2$ according to the ion peak at *m*/*z* 238.1928 in its HREIMS. The IR absorption at 3361 cm^{-1} indicated the presence of hydroxy groups. The ^{13}C NMR spectrum of **4** revealed 15 resonances. The ^{1}H NMR spectrum showed signals of three methyls (δ_H 1.26, s; 1.02, s; 0.86, s), an olefinic proton (δ_H 5.87, dd, J = 2.6, 3.2) and an oxygenated methylene (δ_H 4.01, 2H, s). These data suggested a bicyclic sesquiterpenoid with a double bond and two hydroxy groups. The NMR data of **4** were similar to those of (1*S*,6*S*,7*R*)-1,11,11-trimethylbicyclo[5,4,0]undec-2-ene-6,7,12-triol[11] except for a methine (δ_H 1.74, m; δ_C 51.9) in **4**, which replaced the oxygenated quaternary carbon (δ_C 78.8, C-6) in (1*S*,6*S*,7*R*)-1,11,11-trimethylbicyclo[5,4,0]undec-2-ene-6,7,12-triol. The structure of **4** was confirmed by ^{1}H−^{1}H COSY and HMBC experiments. Its relative configuration was fixed by a ROESY experiment as the same as that of (1*S*,6*S*,7*R*)-1,11,11-trimethylbicyclo[5,4,0]undec-2-ene-6,7,12-triol.

Bacciferin B (**5**) was obtained as white amorphous powder. The HREIMS of **5**, exhibiting the ion peak at *m*/*z* 238.1934, established the molecular formula as $C_{15}H_{26}O_2$. The strong IR absorption at 3365 cm^{-1} indicated the presence of hydroxy groups. The ^{1}H and ^{13}C NMR spectra of **5** showed signals of three methyls, an oxymethine, an oxymethylene, and a trisubstituted double bond (Table 3). The NMR data of **5** resembled those of tsangane A[12]

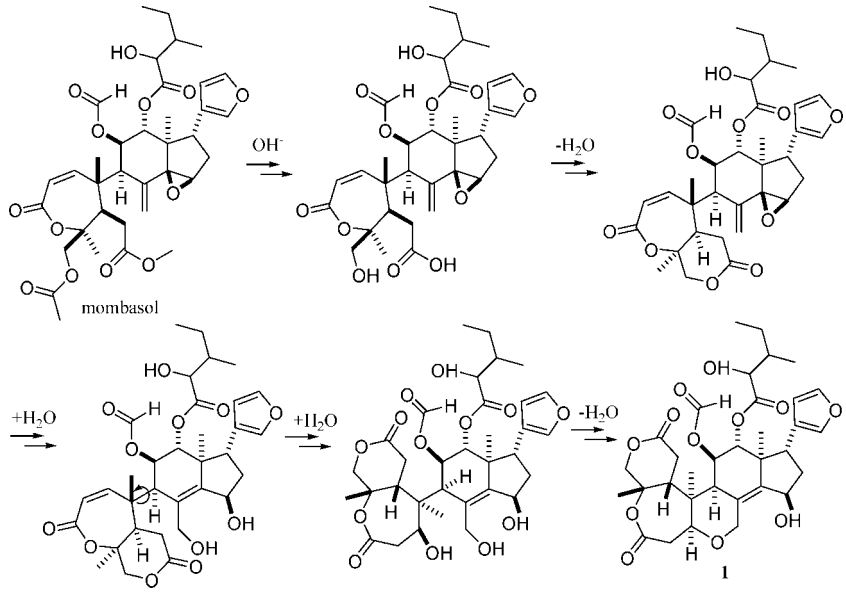

Figure 2. Proposed biosynthetic relationship between **1** and mombasol.

Table 2. ^{1}H and ^{13}C NMR Data of Compound **2** (in $CDCl_3$, 400 MHz, ppm)

C	δ_H (mult, *J*)	δ_C	C	δ_H (mult, *J*)	δ_C
1	4.75, d (6.1)	70.4 CH	21	7.18, s	140.2 CH
2a	3.19, dd (6.1, 15.5)	35.0 CH_2	22	6.20, s	111.5 CH
2b	3.28, d (15.5)		23	7.35, t (1.7)	142.2 CH
3		169.1 C	28	1.45, s	29.7 CH_3
4		85.3 C	29	5.12, d (14.8)	65.4 CH_2
5	2.55, dd (2.1, 12.6)	44.3 CH	29	3.94, d (14.9)	
6a	2.03, m	26.3 CH_2	30	1.24, s	29.1 CH_3
6b	2.11, m		1′		169.4 C
7	5.29, bs	75.1 CH	2′	2.08, s	20.7 CH_3
8		41.4 C	1′		172.9 C
9	2.70, dd (8.6, 11.8)	37.2 CH	2″	4.04, s	75.4 CH
10		44.1 C	3″	2.08, m	31.7 CH
11a	1.21, m	25.3 CH_2	4″	1.09, d (6.8)	19.3 CH_3
11b	2.12, m		5″	0.86, d (6.8)	15.7 CH_3
12	5.05, t (8.4)	76.5 CH	1‴		170.8 C
13		51.2 C	2‴	1.94, s	21.3 CH_3
14		155.0 C	1⁗		173.9 C
15	5.50, s	122.4 CH	2⁗	4.08, s	75.9 CH
16a	2.38, d (11.3)	36.7 CH_2	3⁗		74.5 C
16b	2.43, dd (3.3, 11.3)		4⁗	1.69, m	31.3 CH_2
17	3.01, dd (8.0, 10.5)	49.7 CH	4⁗	1.60, m	
18	0.94, s	14.6 CH_3	5⁗	0.95, t (7.5)	8.0 CH_3
19	1.20, s	15.4 CH_3	6⁗	1.18, s	22.1 CH_3
20		124.1 C			

except for a methylene in **5** replacing the oxymethine (C-4) in tsangane A. The structure of **5** was further confirmed by HMBC and HSQC experiments. The relative configuration of **5** was the same as that of tsangane A by the ROESY spectrum.

Ten known compounds were identified as mombasol,[7] 2β,3β,4β-trihydroxypregnan-16-one,[5,10] 2α,3α,4β-trihydroxypregnan-16-one,[10] 2β,3β-dihydroxy-5α-pregnan-16-one,[13] 3β,16α,18*S**-trihydroxypregnane,[14] meliavosin,[15] 9β-hydroxyaphanamol II,[16] guaianediol,[17] cryptomeridiol,[18] and 4(15)-eudesmene-1β,6α-diol[19] by comparison of the NMR data with those of known compounds. All these compounds, except 2β,3β,4β-trihydroxy-pregnan-16-one, were isolated from *Cipadessa* genus for the first time.

Experimental Section

General Experimental Procedures. Optical rotations were recorded on a Perkin-Elmer 341 polarimeter. IR spectra were recorded on Nicolet Magna FT-IR 750 spectrophotometer using KBr disks. NMR spectra were recorded on Bruker AM-400 and INVOR-600 NMR spectrometers. The chemical shift (δ) values are given in parts per million with TMS as internal standard, and coupling constants (*J*) are in hertz. EIMS and HREIMS spectra were recorded on Finnigan MAT-95 mass spectrometer. ESIMS and HRESIMS spectra were recorded on Micromass LC-MS-MS mass spectrometer. All solvents were of analytical grade (Shanghai Chemical Plant, Shanghai, China). Si gel used for flash chromatography and precoated Si gel GF254 plates used for TLC were produced by Qingdao Marine Chemical Industrials. TLC spots were viewed at 254 nm and visualized by spraying with 5% H_2SO_4 in EtOH containing 10 mg/mL vanillin. Sephadex LH-20 gel (Amersham Biosciences) and MCI gel (CHP20P, 75–150 μm, Mitsubishi Chemical Industries Ltd.) were used for column chromatography (CC). Preparative HPLC was performed on a Varian SD1 instrument with a 320 single wave detector. Chromatographic separation was carried out on a C18 column (220 × 25 mm, 10 μm, Merck), using a gradient solvent system comprised of H_2O (A) and CH_3CN (B) at a flow rate of 15 mL/min.

Plant Material. The stems of *C. baccifera* (9.56 kg) were collected in Xishuangbanna, Yunnan province, and identified by Professor Jin-Gui Shen of Shanghai Institute of Materia Medica, Chinese Academy of Sciences. A voucher specimen (YYE-20060201) was deposited at the Herbarium of Shanghai Institute of Materia Medica, Chinese Academy of Sciences.

Table 3. ^{1}H and ^{13}C NMR Data of Compounds **3**−**5** (in $CDCl_3$, 400 MHz, ppm)

	3		**4**		**5**	
C	δ_H (mult, *J*)	δ_C	δ_H (mult, *J*)	δ_C	δ_H (mult, *J*)	δ_C
1	a 1.26, m; b 2.20, m	40.4	2.39, bs	43.0	1.72, m	48.9
2	5.30, dd (3.2, 6.4)	72.9	5.87, dd (2.6, 3.2)	127.4	5.56, d (5.7)	128.0
3	3.68, m	74.6		137.0		141.3
4	3.85, bs	71.0	2.12, m; 1.64, m	27.2	2.11, m; 2.05, m	25.6
5	1.18, m	48.9	1.74, m; 1.63, m	21.7	1.70, m; 1.37, d (13.6)	31.6
6	a 1.92, m; b 1.48, m	25.1	1.74, m	51.9	3.22, dd (3.4, 11.3)	86.0
7	a 1.76, m; b 1.01, m	32.4		76.0		39.8
8	1.52, m	34.0	2.11, m; 1.72, m	36.3	1.94, t (13.2); 1.10, m	38.7
9	0.81, dt (3.9, 10.5)	56.0	1.65, m; 1.57, m	19.7	1.46, m, 2H	18.2
10		35.0	1.89, dt (3.6, 10.4); 1.40, dt (3.5, 12.3)	41.3	1.45, m; 1.11, m	42.2
11	a 1.38, m; b 1.62, m	20.1		38.2		33.3
12	a 1.89, m; b 1.34, m	38.1	4.01, s, 2H	67.7	0.83, s	33.3
13		42.1	1.26, s	32.6	1.02, s	22.6
14	1.42, m	50.5	1.02, s	33.3	0.79, s	13.7
15a	2.22, dd (7.7, 11.0)	38.5	0.86, s	26.7	4.03, s, 2H	68.4
15b	1.78, m					
16		219.5				
17	1.68, m	65.3				
18	0.68, s	13.6				
19	1.19, s	16.2				
20	1.65, m; 1.23, m	17.6				
21	1.00, t (7.2)	13.5				
1′		171.3				
2′	2.08, s	21.5				

Extraction and Isolation. The air-dried stems of *C. baccifera* were ground into powder and extracted with 95% EtOH (×3). After evaporation of the collected percolate, the crude extract (487.5 g) was suspended in H_2O (2.5 L) and extracted with petroleum ether (PE) (1 L × 3), $CHCl_3$ (1 L × 3) and *n*-BuOH (1 L × 3), successively. The $CHCl_3$ extract (210 g) was subjected to CC over Si gel eluted with $CHCl_3$–CH_3OH (100:1 to 4:1) to yield 10 fractions (CBC1 to CBC10). Fractions CBC3, CBC5, and CBC7 were subjected to an MCI gel column eluted with H_2O/CH_3OH (1:1 to 0:1), respectively, to afford a series of subfractions (3-A to 3-F; 5-A to 5-H; 7-A to 7-F). Subfraction 3-B was further purified by preparative HPLC (H_2O/CH_3CN from 3:2 to 3:7), affording 4(15)-eudesmene-1*β*,6α-diol (22 mg), guaianediol (61 mg) and **4** (26 mg). Subfraction 3-D was subjected to a Si gel column eluted with PE/acetone (9:1 to 4:1) to yield nine subfractions (3-D1 to 3-D9). Subfractin 3-D7 was purified by CC over Sephadex LH-20 ($CHCl_3$/CH_3OH 1:1) to give 2*β*,3*β*-dihydroxy-5α-pregnan-16-one (256 mg). Compound **3** (286 mg) was crystallized (PE/acetone) from subfraction 3-D9 and its mother liquor was further purified by a Sephadex LH-20 column ($CHCl_3$/CH_3OH 1:1) to yield mombasol (142 mg). Subfraction 5-E was separated by CC over Si gel (PE/acetone 7:1 to 2:1) to afford five subfractions (5-E1 to 5-E5). Subfraction 5-E1 yielded bacciferin B (**5**, 37 mg) by CC over Sephadex LH-20. Subfractin 5-E3 was separated by preparative HPLC (H_2O/CH_3CN 55:45 to 3:7) to give cryptomeridiol (41 mg) and 9*β*-hydroxyaphanamol II (14 mg). Subfraction 5-E5 was subjected to a Si gel column eluted with PE/acetone (3:1) to obtain **1** (13 mg). Subfraction 5-G was subjected to a Si gel column chromatography (PE/acetone 5:1 to 2:1) to give five subfractions (5-G1 to 5-G5). Subfraction 5-G4 was separated by preparative HPLC (H_2O/CH_3CN 11:9 to 7:13), affording 3*β*,16α,18*S**-trihydroxypregnane (3 mg), **2** (4 mg) and meliavosin (8 mg). Subfraction 7-C was subjected to CC over Si gel (PE/acetone 4:1 to 2:1) to yield 2*β*,3*β*,4*β*-trihydroxypregnan-16-one (524 mg), and 2α,3α,4*β*-trihydroxypregnan-16-one (13 mg).

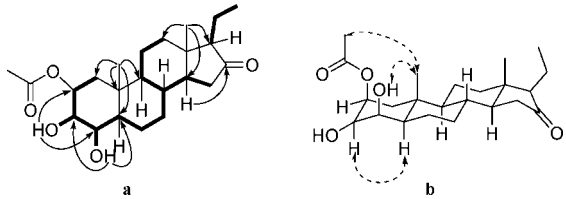

Figure 3. (a) Important ^{1}H−^{1}H COSY (bold lines) and HMBC correlations (arrows) for **3**; (b) key NOE correlations (broken arrows) and possible conformation for **3**.

Cipadessalide (1). White amorphous powder; $[\alpha]^{20}_D$ −30 (*c* 0.25, $CHCl_3$); IR ν_{max} (KBr) 3448 (strong, broad), 1732 (strong, sharp), 1165, 1105, 1072 cm^{-1}; ^{1}H and ^{13}C NMR data, Table 1; ESIMS *m*/*z* 653.1 $[M+Na]^+$, 675.3 $[M+HCOO^-]^-$; HRESIMS *m*/*z* 653.2583 (calcd for $C_{33}H_{42}O_{12}Na$, 653.2574).

Rubralin D (2). White amorphous powder; $[\alpha]^{20}_D$ −18 (*c* 0.20, $CHCl_3$); IR ν_{max} (KBr) 3450 (strong, broad), 1750 (strong, sharp), 1160, 1105, 1072 cm^{-1}; ^{1}H and ^{13}C NMR data, Table 2; ESIMS *m*/*z* 797.3 $[M+Na]^+$, 819.4 $[M+HCOO^-]^-$; HRESIMS *m*/*z* 797.3738 (calcd for $C_{41}H_{58}O_{14}Na$, 797.3724).

3*β*,4*β*-Dihydroxy-2*β*-acetoxypregnan-16-one (3). White cubes (PE/acetone); mp 215–218 °C; $[\alpha]^{20}_D$ −94 (*c* 0.40, $CHCl_3$); IR ν_{max} (KBr) 3539, 1738, 1711, 1385, 1267, 1082, 1063, 1011 cm^{-1}; ^{1}H and ^{13}C NMR data, Table 3; ESIMS *m*/*z* 415.0 $[M+Na]^+$, 437.1 $[M+HCOO^-]^-$; HRESIMS *m*/*z* 415.2443 (calcd for $C_{23}H_{36}O_5Na$, 415.2460).

Bacciferin A (4). White amorphous powder; $[\alpha]^{20}_D$ −3.3 (*c* 0.30, $CHCl_3$); IR ν_{max} (KBr) 3361 (strong, broad), 1456, 1387, 1362, 1148, 1072, 1051, 1016 cm^{-1}; ^{1}H and ^{13}C NMR data, Table 3; EIMS*m*/*z* 238 $[M]^+$, 220 $[M-H_2O]^+$, 202 $[M-H_2O-H_2O]^+$, 189, 177, 159, 135, 109, 105, 93, 79; ESIMS *m*/*z* 261.0 $[M+Na]^+$; HREIMS *m*/*z*238.1928 (calcd for $C_{15}H_{26}O_2$, 238.1933).

Bacciferin B (5). White amorphous powder; $[\alpha]^{20}_D$ −2.0 (*c* 0.30, $CHCl_3$); IR ν_{max} (KBr) 3358 (strong, broad), 1458, 1194, 1051, 939 cm^{-1}; ^{1}H and ^{13}C NMR data, Table 3; EIMS *m*/*z* 238 $[M]^+$, 220 $[M-H_2O]^+$, 205, 187, 177, 159, 135, 123, 107, 105, 93, 81; ESIMS *m*/*z* 261.0 $[M+Na]^+$; HREIMS *m*/*z* 238.1934 (calcd for $C_{15}H_{26}O_2$, 238.1935).

Hydrolysis of 3*β*,4*β*-dihydroxy-2*β*-acetoxypregnan-16-one (3). A solution of **3** (40 mg) in 5% methanolic KOH (5 mL) was heated at 50 °C in a H_2O bath for 10 min. After acidification and removal of the methanol in vacuo, the residue was separated by CC over Si gel eluted with PE/acetone (3:1) to give the product (24 mg), which was identified as 2*β*,3*β*,4*β*-trihydroxypregnan-16-one (TLC and ^{1}H NMR).

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Supporting Information Available: ^{1}H and ^{13}C NMR and MS spectra of **1**–**5** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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