Cipadesins A-C: Novel Tetranortriterpenoids from *Cipadessa cinerascens*

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Experimental Section

General Experimental Section. Melting points were measured in an X-6 melting point apparatus and are uncorrected. Optical rotations were measured on a Perkin-Elmer 341 automatic polarimeter. UV and IR spectra were measured on a Lambda 35 spectrometer and a Perkin-Elmer FT-IR spectrometer (KBr disk), respectively. Mass spectra were

obtained on a Finnigan-LCQDECA mass spectrometer (ESI-MS) and a Bruker Daltonics Bio TOF-Q mass spectrometer (HRESIMS). NMR spectra were recorded on a Bruker Avance 600 spectrometer with TMS as internal standard. Column chromatography (CC) was carried out on silica gel (200-300 mesh; Qingdao Haiyang Chemical Group Co. of China), Silica gel 60 (0.015-0.040 mm, Merck), MCI gel (75-150 μ m, Mitsubishi) and RP-18 silica gel (Prepex 40-63 μ m, Phenomenex), and column fractions were monitored via thin-layer chromatography (TLC) over silica gel 60H (Qingdao Haiyang Chemical Group Co. of China) precoated plates. Semi-preparative HPLC for isolation was carried out using a Perkin Elmer Series 200 HPLC system (Lichrocart RP-C₁₈ column, 10 $\times$ 250 mm, 5 μ m). Solvents were distilled prior to use, and spectral grade solvents were used for spectroscopic measurements.

Plant material. Leaves and barks of *Cipadessa cinerascens* were collected in May 2004 at panzhihua city, Sichuan Province of China, and identified by Prof. Zuo-Cheng Zhao at Chengdu Institute of Biology, the Chinese Academy of Sciences. A voucher specimen (No. A-186) was deposited in the Department for Natural Products Research at Chengdu Institute of Biology, the Chinese Academy of Sciences.

Isolation. The air-dried and powdered aerial parts (4.8 kg) were extracted with 95% EtOH (40 L $\times$ 2, each 7 days) at room temperature. After evaporating the solvents in vacuo at 50 °C, a residue (310 g) was obtained. This residue was dissolved in H₂O (1 L) and extracted with CHCl₃ (1 L $\times$ 3). The CHCl₃ extract (75 g) was partitioned between 95% aqueous MeOH and petroleum ether (60-90 °C) to yield the MeOH solubles (45 g), which was then subjected to silica gel column chromatography (ϕ 8 $\times$ L 25 cm $\square$ 800 g) and eluted with CHCl₃ - EtOAc - MeOH (25 : 5 : 1) to give fractions A - C (A, 1.3 g; B, 12.2 g; C, 2.5g).

Fraction B was subjected to MCI gel column chromatography (ϕ 5 × L 12 cm □ 150 g) and eluted with aqueous EtOH (50% → 70% → 90% → 100%, each 2 L) to give fractions BA - BD. The fraction BB (2.7 g) was subjected to silica gel column chromatography (ϕ 5 × L 20 cm □ 300 g) and eluted with CHCl₃ - EtOAc - MeOH (50 : 5 : 1) to give fractions BBA - BBD. The fraction BBA (1.50 g) was further chromatographed over Silica gel 60 (ϕ 3.5 × L 15 cm □ 80 g) using petroleum ether (60-90 °C)-acetone (4:1) to give fractions BBAA and BBAB. The fraction BBAA was subjected to RP-18 silica gel (ϕ 2 × L 20 cm □ 40 g) and eluted with water-methanol (2 : 3) to give white powder (160 mg). The white powder was divided into subfractions 1-3 by reversed phase HPLC (56% aqueous MeOH, 3 mL/min, 227 nm). **1** (16 mg) was isolated from subfraction 3 (38 mg) by reversed phase HPLC (42% aqueous CH₃CN, 3 mL/min, 227 nm). **2** (12 mg) was obtained from subfraction 2 after evaporating the solvents in vacuo. **3** (4 mg) was obtained from BBAB (40 mg) by reversed phase HPLC (45% aqueous CH₃CN, 4 mL/min, 214 nm).

Cipadesin A (1): colorless needles (MeOH); mp 205.4-206.7 °C; $[\alpha]_D^{25}$ -33.1, $[\alpha]_{578}^{25}$ -34.3, $[\alpha]_{546}^{25}$ -40.0, $[\alpha]_{436}^{25}$ -57.3, $[\alpha]_{365}^{25}$ -56.2 (*c* 0.18, CHCl₃); UV $\lambda_{\max}^{CHCl_3}$ nm (log ϵ) 240 (3.41); IR $\nu_{\max}^{KBr}$: 3447, 2951, 1744, 1632, 1371, 1253, 1227, 1090, 1053, 877, 606 cm⁻¹; ¹H NMR data see Table 3.1; ¹³C NMR data see Table 3.2; HRESIMS (positive ion) *m/z* 669.2517 (calcd for C₃₃H₄₂Na₁O₁₃ [M+Na]⁺, 667.2518).

Cipadesin B (2): white powder; $[\alpha]_D^{25}$ -44.9°, $[\alpha]_{578}^{25}$ -48.7°, $[\alpha]_{546}^{25}$ -53.8°, $[\alpha]_{436}^{25}$ -81.6°, $[\alpha]_{365}^{25}$ -100.6° (*c* 0.16, CHCl₃); UV $\lambda_{\max}^{CHCl_3}$ nm (log ϵ) 240 (2.48), 310 (2.57); IR $\nu_{\max}^{KBr}$: 3439, 2981, 1739, 1634, 1370, 1254, 1091, 1025, 876, 603 cm⁻¹; ¹H NMR data see Table 3.1; ¹³C NMR data see Table 3.2; HRESIMS (positive ion) *m/z* 611.2469 (calcd for

C₃₁H₄₀Na₁O₁₁ [M+Na]⁺, 611.2463).

Cipadesin C (3): white powder; $[\alpha]_D^{25}$ -40.7°, $[\alpha]_{578}^{25}$ -42.2°, $[\alpha]_{546}^{25}$ -48.6°, $[\alpha]_{436}^{25}$ -90.5°, $[\alpha]_{365}^{25}$ -183.3° (*c* 0.73, CHCl₃); UV $\lambda_{\max}^{CHCl_3}$ nm (log ϵ) 314 (3.81); IR $\nu_{\max}^{KBr}$: 3437, 2923, 1740, 1655, 1372, 1243, 1112, 1050, 875, 604 cm⁻¹; ¹H NMR data see Table 3.1; ¹³C NMR data see Table 3.2; ESI-MS (positive mode) *m/z* 587 [M+H]⁺ (81), 609 [M+Na]⁺ (100); HRESIMS (positive ion) *m/z* 609.2311 (calcd for C₃₁H₃₈Na₁O₁₁ [M+Na]⁺, 609.2306).

X-ray Crystallographic Analysis of 1.

There was a hydrogen bond between CH₃OH and C-7 ester carbonyl group of **1** in the crystal. Crystal data: C₃₄H₄₆O₁₄; MW = 678.71; dimensions 0.56 × 0.46 × 0.26 mm; monoclinic system, space group *P*2₁2₁2₁, *a* = 9.745 (4) Å, *b* = 15.562 (6) Å, *c* = 11.779 (4) Å, $\alpha = \beta = \gamma = 90^\circ$, *V* = 1717.4 (13) Å³, *Z* = 2, *d* = 1.312 g/cm⁻³, $\lambda = 0.71073$ Å, μ (Mo KR) = 0.102 mm⁻¹, *F* (000) = 724, *T* = 298 (2) K. Of the 4300 reflections collected, 3894 was unique (*R*_{int} = 0.0315). The structure was solved by direct method with SHELX 97 (Sheldrick, G. M., University of Göttingen, Göttingen, Germany, 1997.) and refined by fullmatrix least-squares on *F*². Final refinement: data/restraints/parameters = 3894/1/445; *R*1 = 0.0827 (all data), *wR*2 = 0.0966 (all data); the Flack absolute structure parameter = 0 (10), and GOF = 0.984. The H coordinates were determined by calculated geometry. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.202 and -0.260 e⁻/Å³, respectively. CCDC 278634 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1223 336033.

ORTEP diagram of 1.

Detailed View of Crystal Packing of **1**.

Table 1. Atomic parameters for 1.

	x	y	z	U(eq)
O(1)	5692(3)	4535(2)	1138(2)	32(1)
O(2)	5360(3)	6480(2)	847(2)	47(1)
O(3)	6244(5)	8296(2)	3322(3)	80(1)
O(4)	9690(4)	4759(2)	6573(3)	67(1)
O(5)	8893(4)	5603(2)	5001(3)	58(1)
O(6)	8556(3)	4908(2)	1341(2)	40(1)
O(7)	9986(4)	4881(2)	149(3)	68(1)
O(8)	7033(3)	3676(2)	-186(2)	40(1)
O(9)	8585(4)	2676(2)	-438(3)	67(1)
O(10)	3335(3)	3058(2)	2830(3)	51(1)
O(11)	4373(5)	6435(3)	-1037(3)	94(1)
O(12)	4252(3)	5161(2)	4157(2)	38(1)
O(13)	6074(4)	5107(2)	5786(3)	65(1)
C(1)	6214(4)	3700(2)	1561(3)	31(1)
C(2)	7476(4)	3512(3)	1072(3)	33(1)
C(3)	8809(4)	4008(3)	1627(3)	36(1)
C(4)	9295(4)	3893(3)	2980(4)	37(1)
C(5)	8014(4)	4121(3)	3482(3)	29(1)
C(6)	8438(4)	4085(3)	4838(3)	36(1)
C(7)	9036(5)	4901(3)	5451(4)	44(1)
C(8)	3313(4)	4126(3)	1380(3)	37(1)
C(9)	3925(4)	3665(3)	2541(4)	36(1)
C(10)	6611(4)	3642(2)	2915(3)	29(1)
C(11)	5319(4)	4022(3)	3321(3)	32(1)
C(12)	5206(4)	5017(2)	3414(3)	30(1)
C(13)	4575(4)	5498(3)	2232(3)	31(1)
C(14)	4315(4)	4833(3)	1194(3)	31(1)
C(15)	3726(4)	5296(3)	36(4)	45(1)
C(16)	4500(5)	6094(3)	-101(4)	52(1)
C(17)	5713(4)	6123(3)	2037(3)	34(1)
C(18)	3221(4)	6012(3)	2214(4)	43(1)
C(19)	6667(4)	2681(3)	3265(4)	38(1)
C(20)	5986(5)	6912(3)	2810(4)	40(1)
C(21)	5918(6)	7722(3)	2406(4)	70(2)
C(22)	6338(5)	6996(3)	4059(4)	54(1)
C(23)	6494(6)	7819(4)	4310(5)	61(1)
C(28)	10542(4)	4496(3)	3495(4)	48(1)
C(29)	9888(4)	2964(3)	3226(4)	47(1)
C(30)	2687(5)	3495(3)	342(4)	50(1)
C(31)	10212(8)	5510(4)	7292(5)	111(3)
C(32)	7767(5)	3240(3)	-839(4)	48(1)
C(33)	7437(6)	3572(4)	-2055(4)	75(2)

C(34)	9163(5)	5247(3)	541(4)	47(1)
C(35)	8629(6)	6125(3)	197(5)	73(2)
C(36)	4838(5)	5216(3)	5336(4)	43(1)
C(37)	3733(5)	5416(3)	5955(4)	61(1)
O(14)	9392(9)	1922(5)	5803(7)	184(3)
C(24)	10141(12)	2155(8)	6981(8)	202(6)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 2. Bond lengths [Å] and angles [deg] for 1.

O(1)-C(1)	1.433(5)	O(5)-C(7)-O(4)	123.9(4)
O(1)-C(14)	1.439(4)	O(5)-C(7)-C(6)	125.0(4)
O(2)-C(16)	1.341(5)	O(4)-C(7)-C(6)	111.0(4)
O(2)-C(17)	1.458(4)	C(9)-C(8)-C(14)	111.3(3)
O(3)-C(23)	1.345(6)	C(9)-C(8)-C(30)	112.4(4)
O(3)-C(21)	1.369(6)	C(14)-C(8)-C(30)	118.1(3)
O(4)-C(7)	1.318(5)	C(9)-C(8)-H(8)	104.5
O(4)-C(31)	1.451(6)	C(14)-C(8)-H(8)	104.5
O(5)-C(7)	1.206(5)	C(30)-C(8)-H(8)	104.5
O(6)-C(34)	1.349(5)	O(10)-C(9)-C(8)	121.9(4)
O(6)-C(3)	1.447(5)	O(10)-C(9)-C(11)	122.3(4)
O(7)-C(34)	1.177(5)	C(8)-C(9)-C(11)	115.8(3)
O(8)-C(32)	1.366(5)	C(1)-C(10)-C(5)	111.2(3)
O(8)-C(2)	1.448(4)	C(1)-C(10)-C(19)	108.3(3)
O(9)-C(32)	1.193(5)	C(5)-C(10)-C(19)	112.9(3)
O(10)-C(9)	1.201(4)	C(1)-C(10)-C(11)	107.3(3)
O(11)-C(16)	1.199(5)	C(5)-C(10)-C(11)	112.0(3)
O(12)-C(36)	1.350(5)	C(19)-C(10)-C(11)	104.7(3)
O(12)-C(12)	1.459(4)	C(9)-C(11)-C(12)	109.7(3)
O(13)-C(36)	1.187(5)	C(9)-C(11)-C(10)	109.5(3)
C(1)-C(2)	1.523(5)	C(12)-C(11)-C(10)	118.2(3)
C(1)-C(10)	1.537(5)	C(9)-C(11)-H(11)	106.2
C(1)-H(1)	0.9800	C(12)-C(11)-H(11)	106.2
C(2)-C(3)	1.497(5)	C(10)-C(11)-H(11)	106.2
C(2)-H(2)	0.9800	O(12)-C(12)-C(13)	107.7(3)
C(3)-C(4)	1.542(5)	O(12)-C(12)-C(11)	105.3(3)
C(3)-H(3)	0.9800	C(13)-C(12)-C(11)	115.8(3)
C(4)-C(28)	1.523(6)	O(12)-C(12)-H(12)	109.3
C(4)-C(29)	1.555(6)	C(13)-C(12)-H(12)	109.3
C(4)-C(5)	1.562(5)	C(11)-C(12)-H(12)	109.3
C(5)-C(6)	1.537(5)	C(18)-C(13)-C(17)	108.7(3)
C(5)-C(10)	1.539(5)	C(18)-C(13)-C(12)	113.0(3)
C(5)-H(5)	0.9800	C(17)-C(13)-C(12)	108.4(3)
C(6)-C(7)	1.497(6)	C(18)-C(13)-C(14)	112.2(3)
C(6)-H(6A)	0.9700	C(17)-C(13)-C(14)	105.6(3)
C(6)-H(6B)	0.9700	C(12)-C(13)-C(14)	108.7(3)

C(8)-C(9)	1.515(5)	O(1)-C(14)-C(15)	103.9(3)
C(8)-C(14)	1.525(5)	O(1)-C(14)-C(8)	114.6(3)
C(8)-C(30)	1.556(5)	C(15)-C(14)-C(8)	112.0(3)
C(8)-H(8)	0.9800	O(1)-C(14)-C(13)	107.2(3)
C(9)-C(11)	1.521(6)	C(15)-C(14)-C(13)	109.2(3)
C(10)-C(19)	1.547(5)	C(8)-C(14)-C(13)	109.7(3)
C(10)-C(11)	1.579(5)	C(16)-C(15)-C(14)	114.8(4)
C(11)-C(12)	1.557(5)	C(16)-C(15)-H(15A)	108.6
C(11)-H(11)	0.9800	C(14)-C(15)-H(15A)	108.6
C(12)-C(13)	1.552(5)	C(16)-C(15)-H(15B)	108.6
C(12)-H(12)	0.9800	C(14)-C(15)-H(15B)	108.6
C(13)-C(18)	1.539(5)	H(15A)-C(15)-H(15B)	107.5
C(13)-C(17)	1.539(5)	O(11)-C(16)-O(2)	116.8(5)
C(13)-C(14)	1.568(5)	O(11)-C(16)-C(15)	122.9(5)
C(14)-C(15)	1.510(5)	O(2)-C(16)-C(15)	120.3(4)
C(15)-C(16)	1.484(6)	O(2)-C(17)-C(20)	103.1(3)
C(15)-H(15A)	0.9700	O(2)-C(17)-C(13)	113.3(3)
C(15)-H(15B)	0.9700	C(20)-C(17)-C(13)	116.0(3)
C(17)-C(20)	1.508(6)	O(2)-C(17)-H(17)	108.0
C(17)-H(17)	0.9800	C(20)-C(17)-H(17)	108.0
C(18)-H(18A)	0.9600	C(13)-C(17)-H(17)	108.0
C(18)-H(18B)	0.9600	C(13)-C(18)-H(18A)	109.5
C(18)-H(18C)	0.9600	C(13)-C(18)-H(18B)	109.5
C(19)-H(19A)	0.9600	H(18A)-C(18)-H(18B)	109.5
C(19)-H(19B)	0.9600	C(13)-C(18)-H(18C)	109.5
C(19)-H(19C)	0.9600	H(18A)-C(18)-H(18C)	109.5
C(20)-C(21)	1.343(6)	H(18B)-C(18)-H(18C)	109.5
C(20)-C(22)	1.422(6)	C(10)-C(19)-H(19A)	109.5
C(21)-H(21)	0.9300	C(10)-C(19)-H(19B)	109.5
C(22)-C(23)	1.314(7)	H(19A)-C(19)-H(19B)	109.5
C(22)-H(22)	0.9300	C(10)-C(19)-H(19C)	109.5
C(23)-H(23)	0.9300	H(19A)-C(19)-H(19C)	109.5
C(28)-H(28A)	0.9600	H(19B)-C(19)-H(19C)	109.5
C(28)-H(28B)	0.9600	C(21)-C(20)-C(22)	104.8(4)
C(28)-H(28C)	0.9600	C(21)-C(20)-C(17)	124.5(4)
C(29)-H(29A)	0.9600	C(22)-C(20)-C(17)	130.7(4)
C(29)-H(29B)	0.9600	C(20)-C(21)-O(3)	110.8(4)
C(29)-H(29C)	0.9600	C(20)-C(21)-H(21)	124.6
C(30)-H(30A)	0.9600	O(3)-C(21)-H(21)	124.6
C(30)-H(30B)	0.9600	C(23)-C(22)-C(20)	107.6(5)
C(30)-H(30C)	0.9600	C(23)-C(22)-H(22)	126.2
C(31)-H(31A)	0.9600	C(20)-C(22)-H(22)	126.2
C(31)-H(31B)	0.9600	C(22)-C(23)-O(3)	111.2(5)
C(31)-H(31C)	0.9600	C(22)-C(23)-H(23)	124.4
C(32)-C(33)	1.472(6)	O(3)-C(23)-H(23)	124.4
C(33)-H(33A)	0.9600	C(4)-C(28)-H(28A)	109.5

C(33)-H(33B)	0.9600	C(4)-C(28)-H(28B)	109.5
C(33)-H(33C)	0.9600	H(28A)-C(28)-H(28B)	109.5
C(34)-C(35)	1.479(6)	C(4)-C(28)-H(28C)	109.5
C(35)-H(35A)	0.9600	H(28A)-C(28)-H(28C)	109.5
C(35)-H(35B)	0.9600	H(28B)-C(28)-H(28C)	109.5
C(35)-H(35C)	0.9600	C(4)-C(29)-H(29A)	109.5
C(36)-C(37)	1.491(6)	C(4)-C(29)-H(29B)	109.5
C(37)-H(37A)	0.9600	H(29A)-C(29)-H(29B)	109.5
C(37)-H(37B)	0.9600	C(4)-C(29)-H(29C)	109.5
C(37)-H(37C)	0.9600	H(29A)-C(29)-H(29C)	109.5
O(14)-C(24)	1.426(10)	H(29B)-C(29)-H(29C)	109.5
O(14)-H(14)	0.8200	C(8)-C(30)-H(30A)	109.5
C(24)-H(24A)	0.9600	C(8)-C(30)-H(30B)	109.5
C(24)-H(24B)	0.9600	H(30A)-C(30)-H(30B)	109.5
C(24)-H(24C)	0.9600	C(8)-C(30)-H(30C)	109.5
C(1)-O(1)-C(14)	121.5(3)	H(30A)-C(30)-H(30C)	109.5
C(16)-O(2)-C(17)	123.9(3)	H(30B)-C(30)-H(30C)	109.5
C(23)-O(3)-C(21)	105.7(4)	O(4)-C(31)-H(31A)	109.5
C(7)-O(4)-C(31)	116.5(4)	O(4)-C(31)-H(31B)	109.5
C(34)-O(6)-C(3)	117.5(3)	H(31A)-C(31)-H(31B)	109.5
C(32)-O(8)-C(2)	115.7(3)	O(4)-C(31)-H(31C)	109.5
C(36)-O(12)-C(12)	117.9(3)	H(31A)-C(31)-H(31C)	109.5
O(1)-C(1)-C(2)	106.8(3)	H(31B)-C(31)-H(31C)	109.5
O(1)-C(1)-C(10)	112.2(3)	O(9)-C(32)-O(8)	122.6(4)
C(2)-C(1)-C(10)	112.4(3)	O(9)-C(32)-C(33)	125.9(4)
O(1)-C(1)-H(1)	108.4	O(8)-C(32)-C(33)	111.5(4)
C(2)-C(1)-H(1)	108.4	C(32)-C(33)-H(33A)	109.5
C(10)-C(1)-H(1)	108.4	C(32)-C(33)-H(33B)	109.5
O(8)-C(2)-C(3)	109.6(3)	H(33A)-C(33)-H(33B)	109.5
O(8)-C(2)-C(1)	107.9(3)	C(32)-C(33)-H(33C)	109.5
C(3)-C(2)-C(1)	115.5(3)	H(33A)-C(33)-H(33C)	109.5
O(8)-C(2)-H(2)	107.9	H(33B)-C(33)-H(33C)	109.5
C(3)-C(2)-H(2)	107.9	O(7)-C(34)-O(6)	124.2(4)
C(1)-C(2)-H(2)	107.9	O(7)-C(34)-C(35)	124.4(4)
O(6)-C(3)-C(2)	109.0(3)	O(6)-C(34)-C(35)	111.3(4)
O(6)-C(3)-C(4)	109.7(3)	C(34)-C(35)-H(35A)	109.5
C(2)-C(3)-C(4)	112.0(3)	C(34)-C(35)-H(35B)	109.5
O(6)-C(3)-H(3)	108.7	H(35A)-C(35)-H(35B)	109.5
C(2)-C(3)-H(3)	108.7	C(34)-C(35)-H(35C)	109.5
C(4)-C(3)-H(3)	108.7	H(35A)-C(35)-H(35C)	109.5
C(28)-C(4)-C(3)	109.0(3)	H(35B)-C(35)-H(35C)	109.5
C(28)-C(4)-C(29)	106.5(3)	O(13)-C(36)-O(12)	122.7(4)
C(3)-C(4)-C(29)	107.0(3)	O(13)-C(36)-C(37)	126.3(4)
C(28)-C(4)-C(5)	110.0(3)	O(12)-C(36)-C(37)	111.0(4)
C(3)-C(4)-C(5)	108.3(3)	C(36)-C(37)-H(37A)	109.5
C(29)-C(4)-C(5)	115.8(3)	C(36)-C(37)-H(37B)	109.5

C(6)-C(5)-C(10)	112.7(3)	H(37A)-C(37)-H(37B)	109.5
C(6)-C(5)-C(4)	111.8(3)	C(36)-C(37)-H(37C)	109.5
C(10)-C(5)-C(4)	115.7(3)	H(37A)-C(37)-H(37C)	109.5
C(6)-C(5)-H(5)	105.2	H(37B)-C(37)-H(37C)	109.5
C(10)-C(5)-H(5)	105.2	C(24)-O(14)-H(14)	109.5
C(4)-C(5)-H(5)	105.2	O(14)-C(24)-H(24A)	109.5
C(7)-C(6)-C(5)	115.4(3)	O(14)-C(24)-H(24B)	109.5
C(7)-C(6)-H(6A)	108.4	H(24A)-C(24)-H(24B)	109.5
C(5)-C(6)-H(6A)	108.4	O(14)-C(24)-H(24C)	109.5
C(7)-C(6)-H(6B)	108.4	H(24A)-C(24)-H(24C)	109.5
C(5)-C(6)-H(6B)	108.4	H(24B)-C(24)-H(24C)	109.5
H(6A)-C(6)-H(6B)	107.5		

HRESIMS spectrum of Cipadesin A (1)

Mass Spectrum Molecular Formular Report

Analysis Info

Analysis Name D:\Bruker\data\msdata\YL-16A\2.d
Method 1pass_pos_low.tofpar
Sample Name YL-16A
Comment ESI Source

Acquisition Date 4/20/2005 4:28:33 PM

Operator operator name
Instrument BioTOF Q

Acquisition Parameter

Capillary End Plate -4000 V
EndP -3500 V

Capillary Exit 160 V
Collision energy 0 eV

detbias 2 V
Number of Averages 100

Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	rdb	N Rule	e ⁻
C ₃₃ H ₄₂ NaO ₁₃	0.01	669.2518	0.14	-1.59	12.50	ok	even

¹H NMR spectrum of Cipadessin A (1)

Chemical shifts (ppm) listed on the right side of the spectrum:

- 8.0967
- 7.4464
- 7.4439
- 7.4410
- 7.2718
- 6.6053
- 6.6037
- 6.5336
- 6.5336
- 5.5249
- 5.5233
- 5.5233
- 5.5107
- 5.1046
- 5.0985
- 5.0670
- 5.0619
- 4.1290
- 4.1172
- 3.7712
- 3.7001
- 3.6909
- 3.6842
- 2.8615
- 2.8456
- 2.7755
- 2.7634
- 2.7516
- 2.7395
- 2.7350
- 2.7060
- 2.6968
- 2.6678
- 2.5668
- 2.5378
- 2.4527
- 2.4448
- 2.4282
- 2.4158
- 2.3992
- 2.1781
- 2.1118
- 2.0522
- 1.8808
- 1.6533
- 1.2777
- 1.2656
- 1.2624
- 1.2503
- 1.1368
- 1.0119
- 0.9696
- 0.8676
- 0.0003

Integration values (from left to right):

- 0.9958
- 1.0123
- 1.0080
- 1.0000
- 1.0007
- 1.0269
- 1.0040
- 3.0349
- 1.0383
- 1.0189
- 1.1758
- 1.7433
- 1.0202
- 2.0221
- 3.1331
- 3.3843
- 3.0056
- 3.5648
- 3.1391
- 3.0676
- 3.0532
- 3.1629

Chemical shifts (ppm) for integration regions (from left to right):

- 7.44
- 6.60
- 6.56
- 6.52
- 5.52
- 5.12
- 5.08
- 5.04
- 3.80
- 3.70

¹³C NMR spectrum of Cipadesin A (1)

HSQC spectrum of Cipadesin A (1)

Bruker Avance 60
probe: 13C-1H DUL

mple: YL16A
ent: CDCL3
trum: HSQC

HMBC spectrum of Cipadesin A (1)

Bruker
ce 600
pbe: 13C-1H
DUL
je: YL16A
solvent:
3
trum: HMBC

NOESY spectrum of Cipadesin A (1)

Bruker Avance 600
probe: 13C-1H DUL
sample: YL16A
solvent: CDCL3
spectrum: NOESY

HRESIMS spectrum of Cipadesin B (2)

Mass Spectrum Molecular Formular Report

Analysis Info

Analysis Name D:\Bruker\data\msdata\YL-15\2.d
Method 1pass_pos_low.tofpar
Sample Name YL-15
Comment ESI Source

Acquisition Date 4/20/2005 3:57:12 PM

Operator operator name
Instrument BioTOF Q

Acquisition Parameter

Capillary End Plate -4000 V
EndP -3500 V

Capillary Exit 160 V
Collision energy 0 eV

detbias 2 V
Number of Averages 100

Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	rdB	N Rule	e ⁻
C ₃₁ H ₄₀ NaO ₁₁	0.02	611.2463	-1.08	-5.28	11.50	ok	even

¹H NMR spectrum of Cipadesin B (2)

¹³C NMR spectrum of Cipadesin B (2)

HMQC spectrum of Cipadesin B (2)

HMBC spectrum of Cipadesin B (2)

NOESY spectrum of Cipadesin B (2)

HRESIMS spectrum of Cipadesin C (3)

Mass Spectrum Molecular Formular Report

Analysis Info

Analysis Name D:\Bruker\data\msdata\YL-20\1.d
Method 1pass_pos_low.tofpar
Sample Name YL-20
Comment ESI Source

Acquisition Date 5/18/2005 3:49:48 PM

Operator operator name
Instrument BioTOF Q

Acquisition Parameter

Capillary End Plate -4000 V
EndP -3500 V

Capillary Exit 120 V
Collision energy 0 eV

detbias 2 V
Number of Averages 100

Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	rdb	N Rule	e ⁻
C 31 H 38 Na 1 O 11	0.01	609.2306	-0.69	-1.49	12.50	ok	even

¹H NMR spectrum of Cipadesin C (3)

¹³C NMR spectrum of Cipadesin C (3)

HSQC spectrum of Cipadesin C (3)

Bruker Avance 60
probe: 13C-1H QNP
sample: YL20
solvent: CDCL3
pulse: HSGC

HMBC spectrum of Cipadesin C (3)

Bruker
nce 600
robe: 13C-1H
DUL
ple: YL20
solvent:
.3
trum: HMBC

NOESY spectrum of Cipadesin C (3)

Bruker Avance 600
probe: 13C-1H DUL
sample: YL20
solvent: CDCL3
spectrum: NOESY