Electronic supplementary information for

## Dammarane-type Triterpenoids as 11β-HSD1 Inhibitors from

## Homonoia riparia

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**Table S1.** Preliminary assay results of tested compounds against human 11 $\beta$ -HSD1 at 10  $\mu$ M. **Table S2.** Preliminary assay results of tested compounds against mouse 11 $\beta$ -HSD1 at 10  $\mu$ M. **Table S3.** X-ray crystallographic data for horipenoid E (5).

- Figure S1. <sup>1</sup>H NMR spectrum of horipenoid A (1) in C<sub>5</sub>D<sub>5</sub>N
- Figure S2. <sup>13</sup>C NMR spectrum of horipenoid A (1) in  $C_5D_5N$

**Figure S3.** <sup>1</sup>H-<sup>1</sup>H COSY spectrum of horipenoid A (1) in  $C_5D_5N$ 

Figure S4. HSQC spectrum of horipenoid A (1) in C<sub>5</sub>D<sub>5</sub>N

Figure S5. HMBC spectrum of horipenoid A (1) in  $C_5D_5N$ 

Figure S6. ROESY spectrum of horipenoid A (1) in C<sub>5</sub>D<sub>5</sub>N

Figure S7. ESI(+)MS spectrum of horipenoid A (1)

**Figure S8.** HRESI(–)MS spectrum of horipenoid A (1)

Figure S9. IR spectrum of horipenoid A (1)

Figure S10. <sup>1</sup>H NMR spectrum of horipenoid B (2) in CD<sub>3</sub>OD

Figure S11. <sup>13</sup>C NMR spectrum of horipenoid B (2) in CD<sub>3</sub>OD

Figure S12. HSQC spectrum of horipenoid B (2) in CD<sub>3</sub>OD

Figure S13. HMBC spectrum of horipenoid B (2) in CD<sub>3</sub>OD

Figure S14. ROESY spectrum of horipenoid B (2) in CD<sub>3</sub>OD

Figure S15. EIMS spectrum of horipenoid B (2)

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Figure S17. IR spectrum of horipenoid B (2)

Figure S18. <sup>1</sup>H NMR spectrum of horipenoid C (3) in CDCl<sub>3</sub>

**Figure S19.** <sup>13</sup>C NMR spectrum of horipenoid C (**3**) in CDCl<sub>3</sub>

Figure S20. <sup>1</sup>H-<sup>1</sup>HCOSY spectrum of horipenoid C (3) in CDCl<sub>3</sub>

Figure S21. HSQC spectrum of horipenoid C (3) in CDCl<sub>3</sub>

Figure S22. HMBC spectrum of horipenoid C (3) in CDCl<sub>3</sub>

Figure S23. ROESY spectrum of horipenoid C (3) in CDCl<sub>3</sub>

Figure S24. ESI(+)MS spectrum of horipenoid C (3)

Figure S25. ESI(-)MS spectrum of horipenoid C (3) Figure S26. HRESI(-)MS spectrum of horipenoid C (3) Figure S27. IR spectrum of horipenoid A (3)

Figure S28. <sup>1</sup>H NMR spectrum of horipenoid D (4) in CDCl<sub>3</sub> Figure S29. <sup>13</sup>C NMR spectrum of horipenoid D (4) in CDCl<sub>3</sub> Figure S30. HSQC spectrum of horipenoid D (4) in CDCl<sub>3</sub> Figure S31. HMBC spectrum of horipenoid D (4) in CDCl<sub>3</sub> Figure S32. ESI(+)MS spectrum of horipenoid D (4) Figure S33. HRESI(-)MS spectrum of horipenoid D (4) Figure S34. IR spectrum of horipenoid D (4)

Figure S35. <sup>1</sup>H NMR spectrum of horipenoid E (5) in  $C_5D_5N$ Figure S36. <sup>13</sup>C NMR spectrum of horipenoid E (5) in  $C_5D_5N$ Figure S37. <sup>1</sup>H-<sup>1</sup>HCOSY spectrum of horipenoid E (5) in  $C_5D_5N$ Figure S38. HSQC spectrum of horipenoid E (5) in  $C_5D_5N$ Figure S39. HMBC spectrum of horipenoid E (5) in  $C_5D_5N$ Figure S40. ROESY spectrum of horipenoid E (5) in  $C_5D_5N$ Figure S41. ESI(+)MS spectrum of horipenoid E (5) Figure S42. ESI(-)MS spectrum of horipenoid E (5) Figure S43. HRESI(-)MS spectrum of horipenoid E (5) Figure S44. IR spectrum of horipenoid E (5)

Figure S45. <sup>1</sup>H NMR spectrum of horipenoid F (6) in  $C_5D_5N$ Figure S46. <sup>13</sup>C NMR spectrum of horipenoid F (6) in  $C_5D_5N$ Figure S47. HSQC spectrum of horipenoid F (6) in  $C_5D_5N$ Figure S48. HMBC spectrum of horipenoid F (6) in  $C_5D_5N$ Figure S49. ROESY spectrum of horipenoid F (6) in  $C_5D_5N$ Figure S50. ESI(+)MS spectrum of horipenoid F (6) Figure S51. ESI(-)MS spectrum of horipenoid F (6) Figure S52. HRESI(-)MS spectrum of horipenoid F (6)

Figure S53. IR spectrum of horipenoid F (6)

Figure S54. <sup>1</sup>H NMR spectrum of horipenoid G (7) in  $C_5D_5N$ Figure S55. <sup>13</sup>C NMR spectrum of horipenoid G (7) in  $C_5D_5N$ Figure S56. HSQC spectrum of horipenoid G (7) in  $C_5D_5N$ Figure S57. HMBC spectrum of horipenoid G (7) in  $C_5D_5N$ Figure S58. ROESY spectrum of horipenoid G (7) in  $C_5D_5N$ Figure S59. ESI(+)MS spectrum of horipenoid G (7) Figure S60. ESI(-)MS spectrum of horipenoid G (7) Figure S61. HRESI(-)MS spectrum of horipenoid G (7) Figure S62. IR spectrum of horipenoid G (7)

**Figure S63.** <sup>1</sup>H NMR spectrum of horipenoid H (8) in C<sub>5</sub>D<sub>5</sub>N

Figure S64. <sup>13</sup>C NMR spectrum of horipenoid H (8) in C<sub>5</sub>D<sub>5</sub>N
Figure S65. HSQC spectrum of horipenoid H (8) in C<sub>5</sub>D<sub>5</sub>N
Figure S66. HMBC spectrum of horipenoid H (8) in C<sub>5</sub>D<sub>5</sub>N
Figure S67. ROESY spectrum of horipenoid H (8) in C<sub>5</sub>D<sub>5</sub>N
Figure S68. ESI(+)MS spectrum of horipenoid H (8)
Figure S69. ESI(-)MS spectrum of horipenoid H (8)
Figure S70. HRESI(-)MS spectrum of horipenoid H (8)
Figure S71. IR spectrum of horipenoid H (8)

Compds no.	Expt.1	Expt.2	Expt.3	Average	SD
1	61.07%	60.88%	57.17%	59.70%	2.20%
3	44.06%	45.04%	40.13%	43.08%	2.60%
4	59.28%	52.93%	58.92%	57.04%	3.57%
5	72.12%	74.49%	77.83%	74.81%	2.87%
6	75.86%	80.61%	72.67%	76.38%	4.00%
7	58.39%	55.57%	50.80%	54.92%	3.84%
8	71.06%	65.30%	67.13%	67.83%	2.94%
9	40.59%	37.70%	40.68%	39.66%	1.69%
Glycyrrhetinic acid 1 nM	14.83%	11.14%	11.62%	12.53%	2.00%
Glycyrrhetinic acid 10 nM	44.66%	45.00%	45.18%	44.94%	0.26%
Glycyrrhetinic acid 100 nM	95.15%	99.83%	91.85%	95.61%	4.01%

Table S1. Preliminary assay results of tested compounds against human 11 $\beta$ -HSD1 at 10  $\mu$ M.

**Table S2.** Preliminary assay results of tested compounds against mouse  $11\beta$ -HSD1 at 10  $\mu$ M.

Compds no.	Expt.1	Expt.2	Expt.3	Average	SD
1	33.05%	36.23%	30.55%	33.28%	2.85%
3	91.72%	85.55%	90.98%	89.42%	3.36%
4	64.36%	61.30%	53.63%	59.76%	5.53%
5	78.62%	89.05%	80.36%	82.68%	5.58%
6	77.18%	79.88%	71.84%	76.30%	4.09%
7	56.67%	57.78%	48.83%	54.43%	4.88%
8	70.88%	71.75%	65.67%	69.44%	3.29%
9	43.89%	43.26%	39.64%	42.26%	2.30%
Glycyrrhetinic acid 1 nM	16.88%	15.73%	19.69%	17.43%	2.04%
Glycyrrhetinic acid 10 nM	54.05%	55.13%	60.39%	56.53%	3.39%
Glycyrrhetinic acid 100 nM	89.37%	90.45%	92.69%	90.83%	1.69%

Empirical formula	$C_{30}H_{52}O_4{\cdot}H_2O$					
Formula weight	494.73					
Temperature	296(2) K					
Wavelength	1.54178 Å					
Crystal system	Orthorhombic					
Space group	P 2(1)2(1)2(1)					
Unit cell dimensions	$a = 10.5637(3) \text{ Å} \qquad \alpha = 90^{\circ}$					
	$b = 13.2734(3) \text{ Å} \qquad \beta = 90^{\circ}$					
	$c = 20.6274(5) \text{ Å} \qquad \gamma = 90^{\circ}$					
Volume	$2892.30(13) \text{ Å}^3$					
Z	4					
Density (calculated)	1.136 Mg/m <sup>3</sup>					
Absorption coefficient	0.588 mm <sup>-1</sup>					
F(000)	1096					
Crystal size	$0.300\times0.200\times0.150~\text{mm}^3$					
Theta range for data collection	3.960 to 69.482°.					
Index ranges	-12<=h<=12, -16<=k<=15, -24<=l<=24					
Reflections collected	21688					
Independent reflections	5337 [R(int) = 0.0630]					
Completeness to theta = $67.679^{\circ}$	99.6 %					
Absorption correction	Semi-empirical from equivalents					
Max. and min. transmission	0.7532 and 0.4678					
Refinement method	Full-matrix least-squares on F2					
Data / restraints / parameters	5337 / 0 / 328					
Goodness-of-fit on F <sup>2</sup>	1.037					
Final R indices [I>2sigma(I)]	R1 = 0.0606, wR2 = 0.1672					
R indices (all data)	R1 = 0.0674, $wR2 = 0.1746$					
Absolute structure parameter	-0.08(13)					
Extinction coefficient	n/a					
Largest diff. peak and hole	0.415 and -0.215 e.Å <sup>-3</sup>					
<sup><i>a</i></sup> Colorless crystals of <b>5</b> were obtained in methanol with trace of water.						

 Table S3. X-ray crystallographic data for horipenoid E (5).



Figure S1. <sup>1</sup>H NMR spectrum of horipenoid A (1) in C<sub>5</sub>D<sub>5</sub>N



Figure S2.  $^{13}$ C NMR spectrum of horipenoid A (1) in C<sub>5</sub>D<sub>5</sub>N

Figure S3.  ${}^{1}$ H- ${}^{1}$ HCOSY spectrum of horipenoid A (1) in C<sub>5</sub>D<sub>5</sub>N



8



f1 (ppm)

9



Figure S5. HMBC spectrum of horipenoid A (1) in  $C_5D_5N$ 

f**1** (ppm)



Figure S6. ROESY spectrum of horipenoid A (1) in  $C_5D_5N$ 

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### Figure S7. ESI(+)MS spectrum of horipenoid A (1)



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# Figure S8. HRESI(–)MS spectrum of horipenoid A (1)

Elemental Composition Report Page 1									
Single Mass Analysis Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0 Element prediction: Off Number of isotope peaks used for i-FIT = 3									
Monoisotopic 64 formula(e Elements Us C: 10-50 I EHC2-121	: Mass, Even Ele ) evaluated with ed: H: 1-80 O: 0-	ectron lons 1 results within li 30	mits (up to	50 best is LCT PXE	otopic matches KE324	for each ma	iss)		09-Mar-2012
EHC2-121_20	120309 14 (0.301)	AM2 (Ar,11500.0,	0.00,0.70); A	<b>BS; Cm (14</b>	4:34)			1:	13:37:10 TOF MS ES-
100		47	5.2556						1.93e+004
%- - - 271.1 0- <sup>1044-147-1414</sup>	363.2 345.2424 546	409.2593 528 448.305	i9 476.2587 495.31	144 544.966	691.49 2 594.9694	709.5060	27.5167 ,774.524	<sup>9</sup> 831.4939	924.6970
250	300 350	400 450	500	550	600 650	<b>70</b> 0 7	50 800	850	900
Minimum: Maximum:		5.0	5.0	-1.5 50.0					
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT	(Norm) Form	nula	
363.2528	363.2535	-0.7	-1.9	5.5	196.2	0.0	C22	н35 о	4

Figure S9. IR spectrum of horipenoid A (1)





Figure S10. <sup>1</sup>H NMR spectrum of horipenoid B (2) in CD<sub>3</sub>OD



Figure S11. <sup>13</sup>C NMR spectrum of horipenoid B (2) in CD<sub>3</sub>OD



Figure S12. HSQC spectrum of horipenoid B (2) in CD<sub>3</sub>OD

![](_page_17_Figure_0.jpeg)

Figure S13. HMBC spectrum of horipenoid B (2) in CD<sub>3</sub>OD

![](_page_18_Figure_0.jpeg)

![](_page_18_Figure_1.jpeg)

![](_page_19_Figure_0.jpeg)

Figure S15. EIMS spectrum of horipenoid B (2)

LIST: h120743-c1 25-Sep-12 05:36.9 Elapse: 27 Samp: EC2-131 16:36:31 28 Start : Finnigan/MAT95//70eV/Tsou:220c/R:10000 EI +VE +LMR BSCAN (EXP) UP HR NRM WANG\_J@SIMM.CAS Comm: Mode: Study : S/N: PT200712-01-01 Oper: Inlet : ( 0) ( 441) C23.H100.O4 1000.00 mmu R+1 CMASS : converted Limt: Peak: R+D: -2.0 > 60.0Data: 202125 (mmu) Mass Intensity 71.04881 \* 242531 8RA %RIC Delta R+D Composition 9.62 0.49 0.9 1.5 C4.H7.0 \* 77.03811 205891 8.16 16.58 0.42 1.0 4.5 C6.H5 79.05358 \* 418283 0.85 1.2 3.5 2.5 C6.H7 81.06792 \* 805305 31.93 1.64 C6.H9 C5.H7.O 83.04740 \* 217947 8.64 0.44 2.3 2.5 85.06372 205477 8.15 0.42 1.6 C5.H9.O 1.5 91.05422 \* 418874 С7.H7 С7.H9 16.61 0.85 0.6 4.5 93.07084 \* 619743 24.57 1.26 -0.4 3.5 94.07702 \* 95.08595 \* 215938 8.56 3.0 0.44 1.2 C7.H10 652423 0.1 25.87 1.33 2.5 C7.H11 96.09263 219306 \* 8.69 0.45 1.3 2.0 C7.H12 97.06484 \* 273143 10.83 0.56 0.5 2.5 C6.H9.O 105.0675 \* 107.0833 \* 421829 16.72 0.86 2.9 2.8 4.5 C8.H9 908074 36.00 1.85 3.5 C8.H11 108.0899 \* 294595 11.68 0.60 109.0626 399904 15.85 0.81 2.7 3.5 C7.H9.0 109.0988 \* 723693 1.47 1.73 0.56 2.5 28.69 C8.H13 C7.H10.0 2.9 110.0707 \* 848978 33.66 2.5 111.0779 \* 276275 10.95 113.0585 \* 238985 9.47 0.49 1.7 2.5 C6.H9.O2 119.0855 \* 484649 19.21 0.99 0.6 4.5 C9.H11 121.1013 \* 562006 22.28 1.14 0.4 3.5 C9.H13 464438 122.1087 \* 18.41 0.94 0.8 3.0 C9.H14 123.0805 \* 619152 24.55 1.26 0.4 0.5 3.5 2.5 C8.H11.O C9.H15 123.1169 \* 2522350 100.00 5.13 124.1199 \* 231657 9.18 0.47 \* 126.0675 351386 13.93 0.71 0.6 3.0 C7.H10.02 133.1009 \* 471943 18.71 0.96 0.8 4.5 C10.H13 134.1075 \* 210087 8.33 0.43 C10.H14 C9.H11.O 2.1 4.0 135.0806 \* 135.1167 \* 265697 10.53 0.54 0.4 4.5 396477 15.720.81 0.7 3.5 C10.H15 137.0954 259964 10.31 0.53 1.3 3.5 C9.H13.O 138.0675 \* 525839 20.85 1.07 4.0 0.6 C8.H10.O2 139.0750 \* 480571 19.05 0.98 0.9 3.5 5.5 C8.H11.O2 145.1010 \* 290931 11.53 0.59 C11.H13 147.1165 315751 12.52 9.30 0.64 0.9 C11.H15 4.5 149.1323 234671 0.48 0.7 3.5 C11.H17 151.1124 \* 550423 21.82 1.12 -0.1 3.5 C10.H15.O 159.1176 259019 10.27 0.53 5.5 -0.2C12.H15 C12.H17 161.1331 \* 215819 8.56 0.44 0.0 4.5 163.1127 288744 11.45 0.59 -0.4 4.5 C11.H15.0 173.1334 218183 8.65 0.44 -0.4 5.5 C13.H17 175.1485 \* 209082 8.29 0.43 0.1 4.5 C13.H19 187.1487 1029694 2.09 40.82 0.0 5.5 C14.H19 188.1539 \* 290754 0.59 5.0 11.53 2.6 C14.H20 189.1643 338622 13.42 0.69 0.0 4.5 C14.H21 190.1709 242176 9.60 0.49 1.3 4.0 C14.H22 196.1464 24.51 16.25 618147 1.26 0.0 3.0 C12.H20.O2 409833 205.1599 0.83 -0.74.5 4.0 C14.H21.O 206.1671 \* 314865 12.48 0.64 0.0 C14.H22.O 207.1756 2245838 89.04 4.57 3.5 -0.7 C14.H23.O 208.1805 454096 2.2 18.00 0.92 3.0 C14.H24.0 224.1406 559819 22.19 1.14 4.0 C13.H20.O3 310196 313.2204 \* 12.30 0.63 328.2400 \* 367520 14.57 0.75 0.3 7.0 C22.H32.O2 346.2512 253346 10.04 0.52 -0.4 6.0 C22.H34.O3

![](_page_21_Figure_0.jpeg)

![](_page_21_Figure_1.jpeg)

![](_page_22_Figure_0.jpeg)

Figure S18. <sup>1</sup>H NMR spectrum of horipenoid C (3) in CDCl<sub>3</sub>

![](_page_23_Figure_0.jpeg)

**Figure S19.** <sup>13</sup>C NMR spectrum of horipenoid C (3) in  $CDCl_3$ 

**Figure S20.** <sup>1</sup>H-<sup>1</sup>HCOSY spectrum of horipenoid C (**3**) in CDCl<sub>3</sub>

![](_page_24_Figure_1.jpeg)

25

![](_page_25_Figure_0.jpeg)

Figure S21. HSQC spectrum of horipenoid C (3) in CDCl<sub>3</sub>

![](_page_26_Figure_0.jpeg)

Figure S22. HMBC spectrum of horipenoid C (3) in CDCl<sub>3</sub>

![](_page_27_Figure_1.jpeg)

#### Figure S24. ESI(+)MS spectrum of horipenoid C (3)

![](_page_28_Figure_1.jpeg)

![](_page_29_Figure_0.jpeg)

#### Figure S25. ESI(-)MS spectrum of horipenoid C (3)

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## Figure S26. HRESI(–)MS spectrum of horipenoid C (3)

#### **Elemental Composition Report**

Single Mass Analysis Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0 Element prediction: Off Number of isotope peaks used for i-FIT = 3

#### Monoisotopic Mass, Even Electron lons 76 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass) Elements Used: C: 10-50 H: 1-80 O: 0-30 EHC2-52 LCT PXE KE324

CHOZ-OL	COTTAL REGES	
EHC2-52_20120309	10 (0.212) AM2 (Ar,10000.0,0.00,1.00); ABS; Cm (5:20)	

393.2635

100- - %-				204 2676						
0-+	124.9899	311.3	2216 357.2268	423.2745	567.3918	659.4894 657.4739	731.5034	771.5428	869.6525	919.1322
Minimu Maximu	200 m:: m::	300	5.0	5.0	-1.5 50.0	000	700	800	900	1000
Mass	Calc. 1	Mass	mDa	PPM	DBE	i-FIT	i-FIT	(Norm)	Formula	
393.26	35 393.26	41	-0.6	-1.5	5.5	165.7	0.0		с23 н37	05

Page 1

09-Mar-2012 14:18:02 1: TOF MS ES-3.18e+004

![](_page_31_Figure_0.jpeg)

![](_page_31_Figure_1.jpeg)

![](_page_32_Figure_0.jpeg)

Figure S28. <sup>1</sup>H NMR spectrum of horipenoid D (4) in CDCl<sub>3</sub>

![](_page_33_Figure_0.jpeg)

Figure S29. <sup>13</sup>C NMR spectrum of horipenoid D (4) in CDCl<sub>3</sub>

![](_page_34_Figure_0.jpeg)

Figure S30. HSQC spectrum of horipenoid D (4) in CDCl<sub>3</sub>

![](_page_35_Figure_0.jpeg)

Figure S31. HMBC spectrum of horipenoid D (4) in CDCl<sub>3</sub>
### Figure S32. ESI(+)MS spectrum of horipenoid D (4)



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Figure S33. HRESI(-)MS spectrum of horipenoid D (4)

**Elemental Composition Report** Page 1 Single Mass Analysis Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0 Element prediction: Off Number of isotope peaks used for i-FIT = 3 Monoisotopic Mass, Even Electron Ions 109 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass) Elements Used: C: 10-80 H: 1-110 O: 0-30 EHC2-523 09-Mar-2012 15:28:04 1: TOF MS ES-1.35e+004 LCT PXE KE324 EHC2-523\_20120309 31 (0.671) AM2 (Ar,10000.0,0.00,1.00); ABS; Cm (25:48) 477.2853 100-435.2742 % 493.2811 925.5712 431.2793 494,2801 863.5729 530.2518 577.2449 377.1944 757.4738 857.5314 669.4650 719.1790 0 - m/z 350 400 450 550 500 600 650 700 750 800 850 900 Minimum: -1.5 50.0 Maximum: 5.0 10.0 Mass Calc. Mass mDa PPM DBE i-FIT i-FIT (Norm) Formula 477.2853 477.2852 0.1 0.2 7.5 125.8 0.0 C27 H41 07











**Figure S36.** <sup>13</sup>C NMR spectrum of horipenoid E (5) in  $C_5D_5N$ 

**Figure S37.**  $^{1}$ H- $^{1}$ HCOSY spectrum of horipenoid E (**5**) in C<sub>5</sub>D<sub>5</sub>N





Figure S38. HSQC spectrum of horipenoid E(5) in  $C_5D_5N$ 





Figure S39. HMBC spectrum of horipenoid E (5) in  $C_5D_5N$ 



Figure S40. ROESY spectrum of horipenoid E (5) in  $C_5D_5N$ 

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#### Figure S41. ESI(+)MS spectrum of horipenoid E (5)



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**Figure S42.** ESI(–)MS spectrum of horipenoid E (5)

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#### Figure S43. HRESI(-)MS spectrum of horipenoid E (5)

#### **Elemental Composition Report**

Single Mass Analysis Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0 Element prediction: Off Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions 126 formuta(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass) Elements Used: C: 10-50 H: 1-80 O: 0-30 EHC2-73 LCT PXE KE324

LCT PXE KE324 EHC2-73\_20120309 24 (0.512) AM2 (Ar,10000.0,0.00,1.00); ABS; Cm (6:25)

EHC2-7	3					09-Mar-2012				
EHC2-7	3_201	120309 24 (	(0.512) AN	12 (Ar,100	00.0,0.00,1.00	); ABS; Cm (6:2	5)		14:11 1: TOF MS E	:59 ES-
100			2.01e+( 997.778	004 80						
%- <u> </u>				511.	3546	560 3033			987.7488	
0	· • • • • • •	346.1438	417.28	17.2850 <sup>509.3383</sup>		620.4227	3.4224	773.6282.793.6018	893.6740 951.7681	
	300	350	400	450	500 550	600 6	50 700	750 800 850	րուներին հետուրում 900 950 1000	n/z
Minimu Maximu	m: m:			5.0	5.0	-1.5 50.0				
Mass		Calc.	Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula	
521.38	43	521.38	42	0.1	0.2	5.5	135.3	0.0	C31 H53 06	

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Figure S45. <sup>1</sup>H NMR spectrum of horipenoid F (6) in C<sub>5</sub>D<sub>5</sub>N



Figure S46.  $^{13}$ C NMR spectrum of horipenoid F (6) in C<sub>5</sub>D<sub>5</sub>N



Figure S47. HSQC spectrum of horipenoid F (6) in  $C_5D_5N$ 



f1 (ppm)



Figure S49. ROESY spectrum of horipenoid F (6) in  $C_5D_5N$ 

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#### Figure S50 ESI(+)MS spectrum of horipenoid F (6)



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## Figure S51. ESI(–)MS spectrum of horipenoid F (6)



#### Figure S52. HRESI(-)MS spectrum of horipenoid F (6)

#### **Elemental Composition Report** Page 1 Single Mass Analysis Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0 Element prediction: Off Number of isotope peaks used for i-FIT = 3 Monoisotopic Mass, Even Electron Ions 121 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass) Elements Used: C: 10-50 H: 1-80 O: 0-30 EHC2-7223 09-Mar-2012 14:24:20 1: TOF MS ES-1.34e+004 LCT PXE KE324 EHC2-7223\_20120309 6 (0.124) AM2 (Ar, 10000.0,0.00,1.00); ABS; Cm (5:19) 565.3739 100 519.3687 509.3392 993.7458 983.7173 % 566.3775 618.4051 645.4249 647.4249 731.5021 785 5697 393.2623 967.6959 465.2251 311.2207 . 867.6381 0 ŧŦŦ 850 900 m/z 300 600 700 350 400 450 500 550 650 750 800 950 1000 Minimum: Maximum: -1.5 5.0 50.0 5.0 Mass Calc. Mass DBE mDa PPM i-FIT i-FIT (Norm) Formula 519.3687 519.3686 0.1 0.2 6.5 95.7 0.0 C31 H51 06







Figure S54.  ${}^{1}H$  NMR spectrum of horipenoid G (7) in C<sub>5</sub>D<sub>5</sub>N



**Figure S55.** <sup>13</sup>C NMR spectrum of horipenoid G (7) in  $C_5D_5N$ 



Figure S56. HSQC spectrum of horipenoid G (7) in  $C_5D_5N$ 







Figure S58. ROESY spectrum of horipenoid G (7) in  $C_5D_5N$ 

#### Figure S59. ESI(+)MS spectrum of horipenoid G (7)



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### Figure S60. ESI(-)MS spectrum of horipenoid G (7)



# Figure S61. HRESI(–)MS spectrum of horipenoid G (7)

Elementa	al Compositi	on Report	:						Page 1
<b>Single M</b> Tolerance Element p Number of	ass Analysis = 5.0 PPM / rediction: Off f isotope peaks	BBE: min =	= -1.5, max = 5 FIT = 3	0.0					
Monoisotop 121 formula Elements U C: 10-80 EHC2-7211	ic Mass, Even E a(e) evaluated w sed: H: 1-110 O;	lectron lons ith 1 results v 0-30	vithin limits (up t	o 50 best	isotopic matches	for each r	nass)		
EHC2-7211	EHC1 7011 20120200 46 (2 24) http:// 10000 0.000 http:// 14:49:14								09-Mar-2012 14:49:14
	20120309 10 (0.5	10) AMZ (Ar, IL	000.0,0.00,1.00);	ABS; Cm (	8:33)				1: TOF MS ES- 4 73e+004
100 %- 311	I.2213 339.1983 -	157 2265	509.33	536.359 571.3	3 300		7	85 5849 813	.5732
- 311. 0	1660	399.1938	505.3063	المنابع المنابع	572.3329623.4473	677.4453	767.5470		5.5771 879.5962
250	300 350	400	450 500	550	600 650	700	750	800	850 m/z
Minimum: Maximum:		5.0	5.0	-1.5 50.0					
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT	(Norm)	Formula	
519.3689	519.3686	0.3	0.6	6.5	172.7	0.0		С31 Н51	06







Figure S63. <sup>1</sup>H NMR spectrum of horipenoid H (8) in C<sub>5</sub>D<sub>5</sub>N



Figure S64. <sup>13</sup>C NMR spectrum of horipenoid H (8) in  $C_5D_5N$ 



Figure S65. HSQC spectrum of horipenoid H (8) in  $C_5D_5N$ 



f1 (ppm)

Figure S67 ROESY spectrum of horipenoid H (8) in  $C_5D_5N$ 


# Figure S68. ESI(+)MS spectrum of horipenoid H (8)



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## Figure S69. ESI(-)MS spectrum of horipenoid H (8)



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## Figure S70. HRESI(-)MS spectrum of horipenoid H (8)

#### Elemental Composition Report

#### **Single Mass Analysis**

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0 Element prediction: Off Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions 121 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass) Elements Used: C: 10-80 H: 1-110 O: 0-30 EHC2-7221 LCT PXE KE324

09-Mar-2012 14:56:45 1: TOF MS ES-EHC2-7221\_20120309 8 (0.158) AM2 (Ar,10000.0,0.00,1.00); ABS; Cm (5:29) 4.01e+004 100 551.3592 541.3293 571.3305 509.3343 % 525.3347 552.3622 603.3217 587.3267 493.3162 519.3679 568.3517 463.2653 481.2197 494.3196 572.3336 604.3253 588 3298 ╶┲╾╍╺┯┹┍┫╢┙╉ 0-444 450 - m/z 460 470 480 490 500 510 520 530 540 550 570 560 580 590 600 Minimum: -1.5 Maximum: 5.0 5.0 50.0 Mass Calc. Mass mDa PPM DBE i - FITi-FIT (Norm) Formula 519.3679 519.3686 -0.7 ,7 -1.3 6.5 108.8 0.0 C31 H51 O6



