

Supplementary material for:

***venoMS* – A Database for the Low Molecular Mass Compounds in Spider Venoms**

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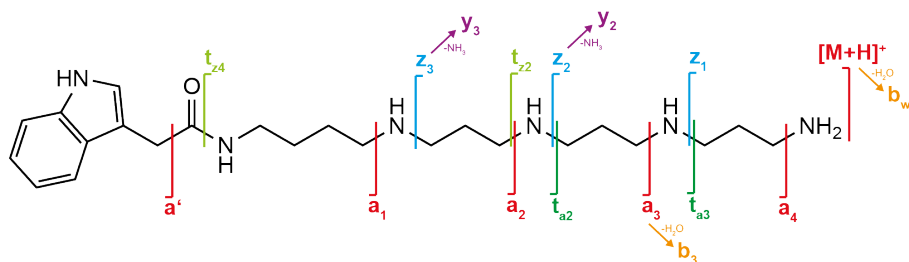
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Supplementary Figure 1: UHPLC-HR-ESI-MS(/MS) data acquired with the SAM2020 method and used for the characterization of IndAc4333 from the venom of *A. aperta*, and the comparison of this data with the values generated by FRIOC (full scan values before and after H/D exchange and MS/MS fragment ion masses).

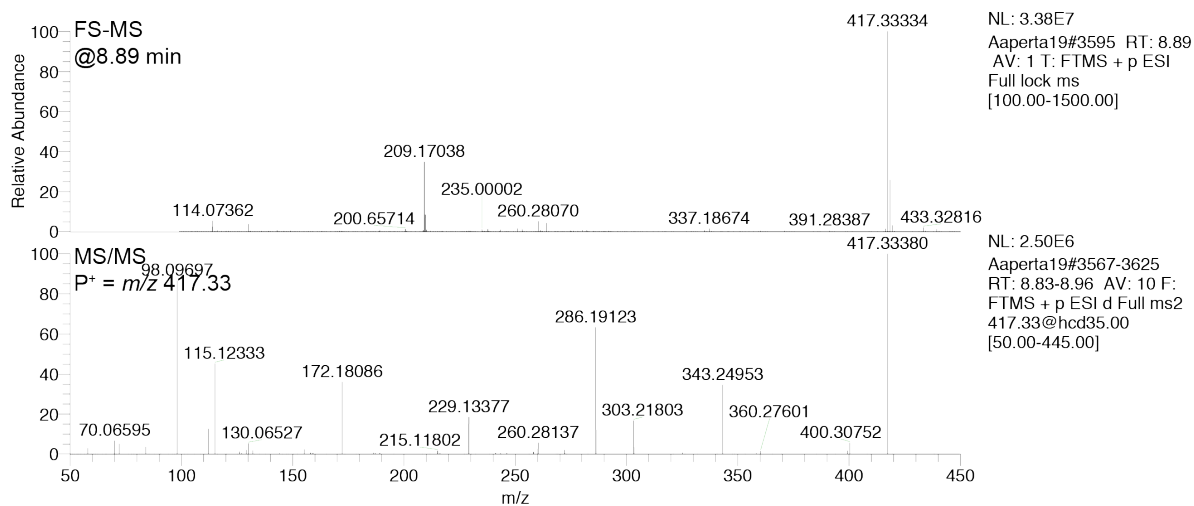
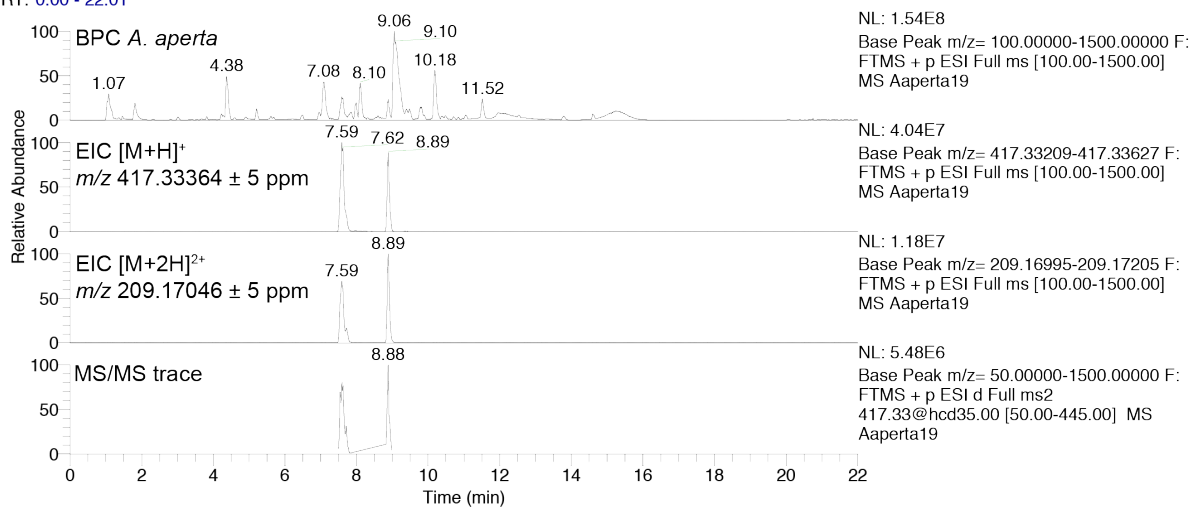
Supplementary Figure 2: UHPLC-HR-ESI-MS(/MS) data acquired with the SAM2020 method and used for the characterization of 4-OH-IndAc3(OH)335(NMe₃)⁺ from the venom of *A. aperta*, and the comparison of this data with the values generated by FRIOC (full scan values before and after H/D exchange and MS/MS fragment ion masses).

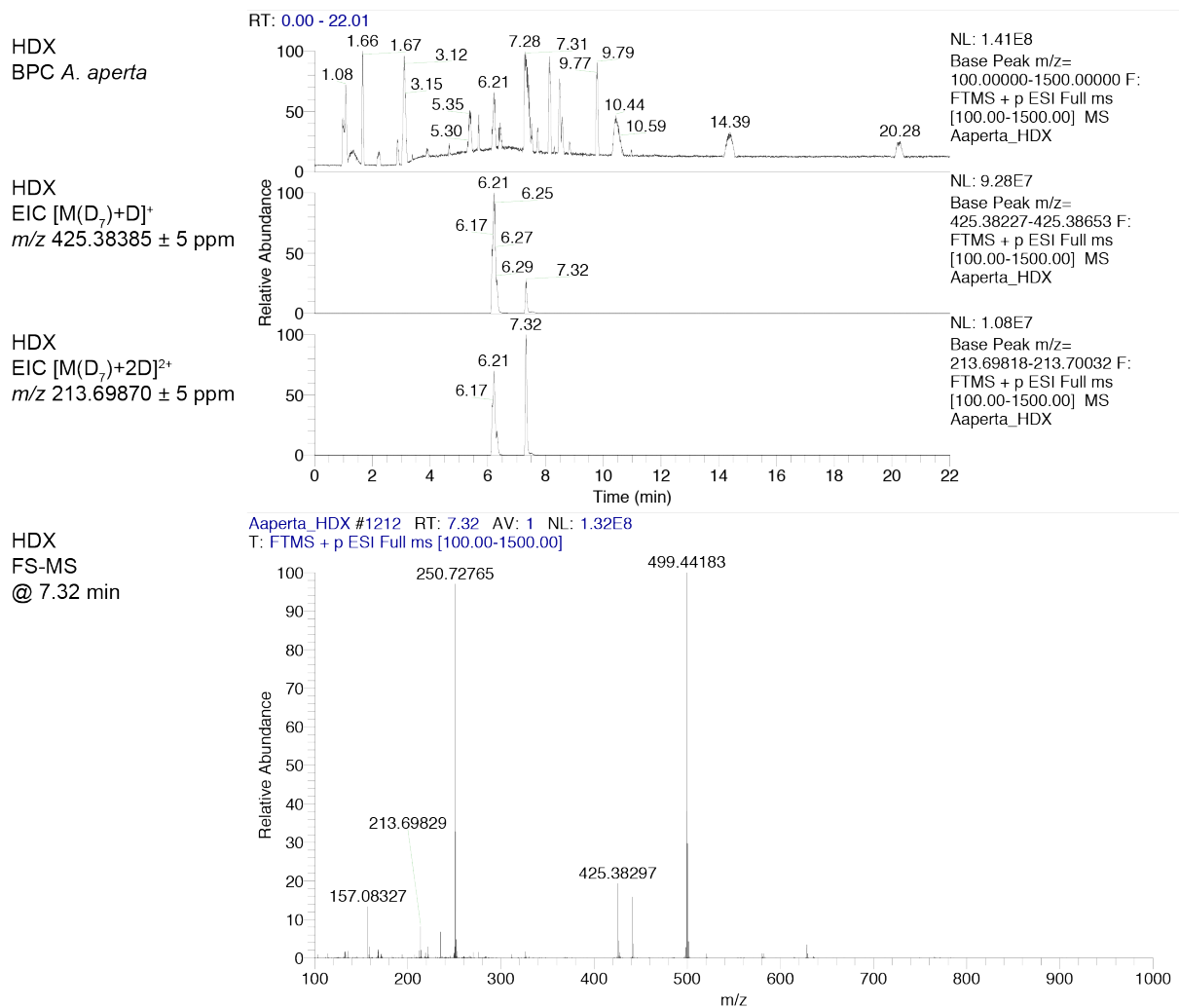
Supplementary Figure 3: UHPLC-HR-ESI-MS(/MS) data acquired with the SAM2020 method and used for the characterization of 4-OH-IndAc3(OH)335(NMe₂) from the venom of *A. aperta*, and the comparison of this data with the values generated by FRIOC (full scan values before and after H/D exchange and MS/MS fragment ion masses).

Supplementary Figure 1: IndAc4333 (*Agelenopsis aperta*)



RT: 0.00 - 22.01





FS-MS / FS-MS HDX

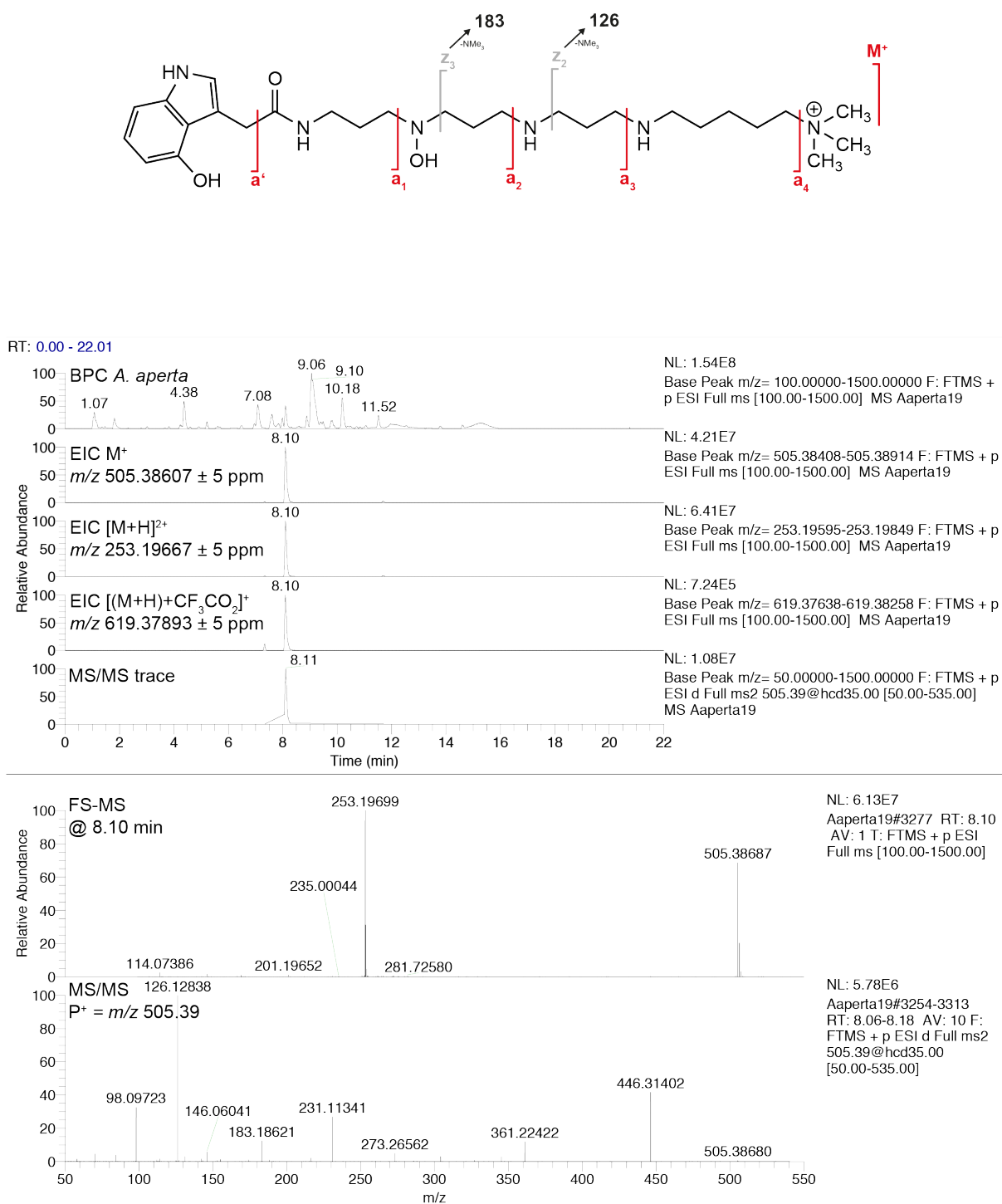
	<i>m/z</i> detected	<i>R</i> _t [min]	<i>m/z</i> FRIOC	Molecular formula	Δ [ppm]
[M+H] ⁺	417.33334	8.89	417.33364	C ₂₃ H ₄₁ N ₆ O ⁺	-0.72
[M(D ₇)+D] ⁺	425.38297	7.32	425.38385	C ₂₃ H ₃₃ D ₈ N ₆ O ⁺	-2.07

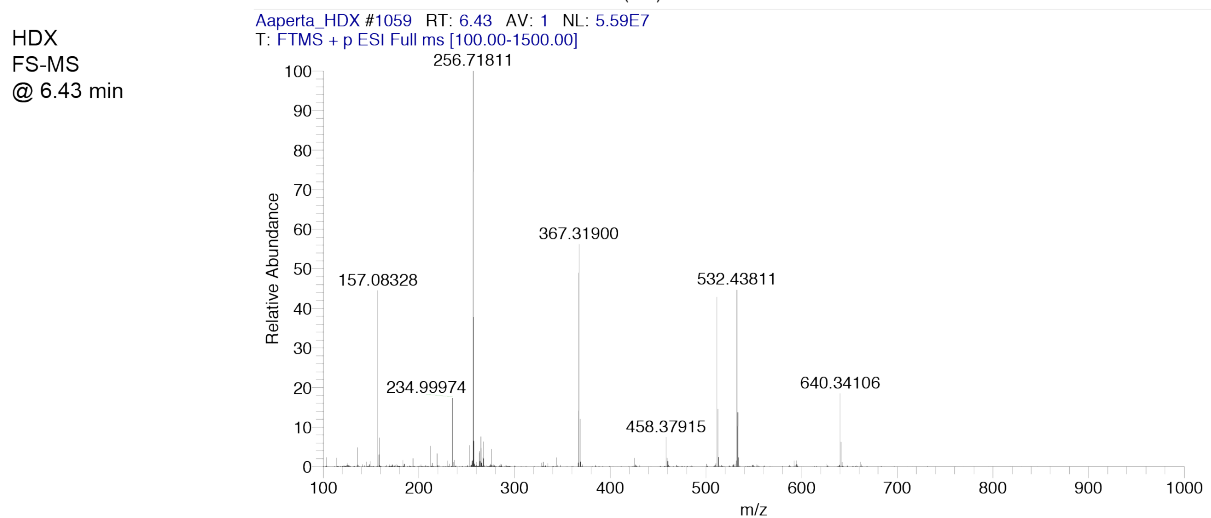
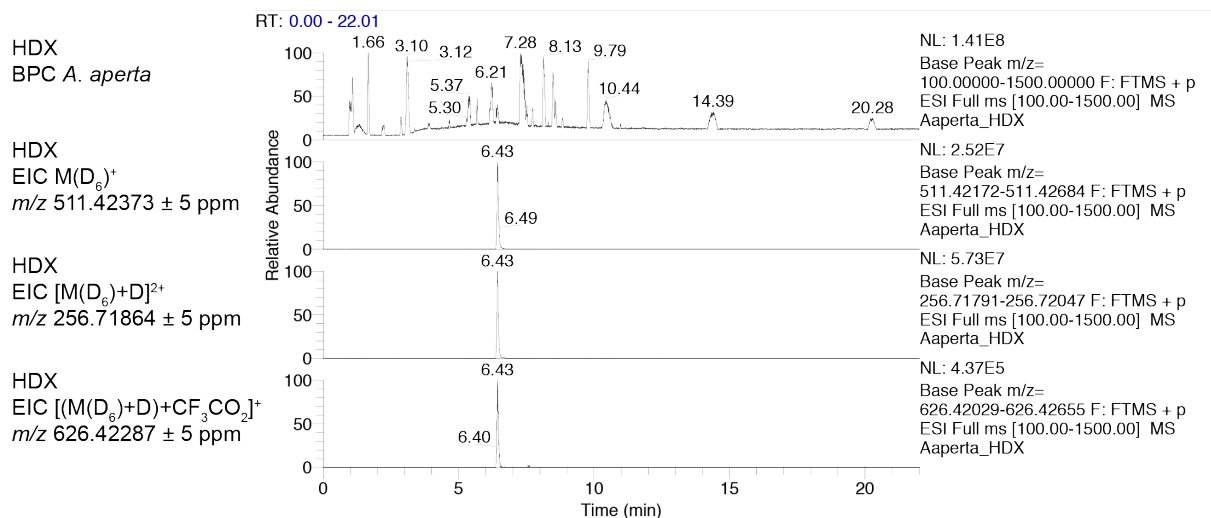
MS/MS fragment ions (P⁺ = *m/z* 417.33)

<i>m/z</i> detected	Rel. Int.	<i>m/z</i> FRIOC	Molecular formula	Δ [ppm]	Fragment type
58.06602	2.82	58.06513	C ₃ H ₈ N ⁺	15.33	z ₁
70.06595	6.68	–			
72.08155	5.08	–			
84.08158	3.45	–			
98.09697	86.36	98.09643	C ₆ H ₁₂ N ⁺	5.50	y ₂
112.11246	12.67	–	C ₇ H ₁₄ N ⁺	3.39	y ₂ ' *
115.12333	45.27	115.12297	C ₆ H ₁₅ N ₂ ⁺	3.13	z ₂
126.12816	1.44	–			
129.13899	1.93	–	C ₇ H ₁₇ N ₂ ⁺	2.79	z ₂ ' *
130.06528	5.26	–	C ₉ H ₈ N ⁺	1.15	a' *
132.14979	1.80	132.14952	C ₆ H ₁₈ N ₃ ⁺	2.04	tz ₂
155.15458	2.25	155.15428	C ₉ H ₁₉ N ₂ ⁺	1.93	y ₃
158.06061	0.61	–	C ₁₀ H ₈ NO ⁺	3.61	a ₀ *
159.09208	0.50	–			
172.18086	36.00	172.18082	C ₉ H ₂₂ N ₃ ⁺	0.23	z ₃
186.19689	0.64	–			
215.11799	1.66	–			
229.13377	18.62	229.13354	C ₁₄ H ₁₇ N ₂ O ⁺	1.00	a ₁
258.16048	1.06	–			
260.28134	5.73	260.28087	C ₁₃ H ₃₄ N ₅ ⁺	1.81	tz ₄
272.17614	2.02	–			
286.19123	64.04	286.19139	C ₁₇ H ₂₄ N ₃ O ⁺	-0.56	a ₂
303.21803	16.76	303.21793	C ₁₇ H ₂₇ N ₄ O ⁺	0.33	ta ₂
325.23977	0.68	325.23867	C ₂₀ H ₂₉ N ₄ ⁺	3.38	b ₃
343.24953	34.97	343.24924	C ₂₀ H ₃₁ N ₄ O ⁺	0.84	a ₃
360.27607	1.54	360.27579	C ₂₀ H ₃₄ N ₅ O ⁺	0.78	ta ₃
399.32389	1.61	–			
400.30750	5.57	400.30709	C ₂₃ H ₃₈ N ₅ O ⁺	1.02	a ₄
417.33380	100.00	417.33364	C ₂₃ H ₄₁ N ₆ O ⁺	0.38	[M+H] ⁺

* this fragment ion is not generated by FRIOC

Supplementary Figure 2: 4-OH-IndAc3(OH)335(NMe₃)⁺ (*Agelenopsis aperta*)





FS-MS / FS-MS HDX

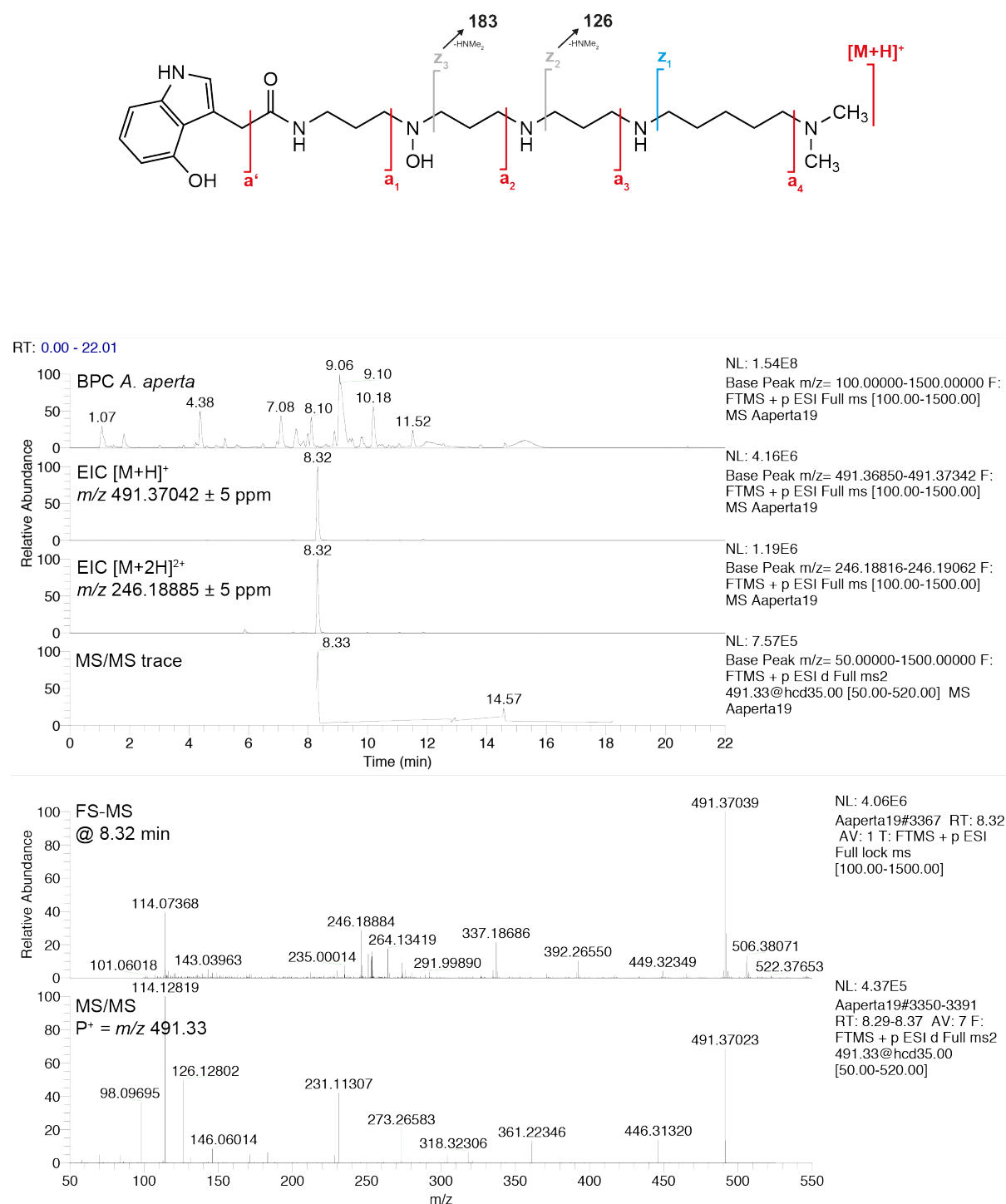
	m/z detected	R_t [min]	m/z FRIOC	Molecular formula	Δ [ppm]
M^+	505.38687	8.10	505.38607	$C_{27}H_{49}N_6O_3^+$	1.58
$M(D_6)^+$	511.42300	6.43	511.42373	$C_{27}H_{43}D_6N_6O_3^+$	-1.43

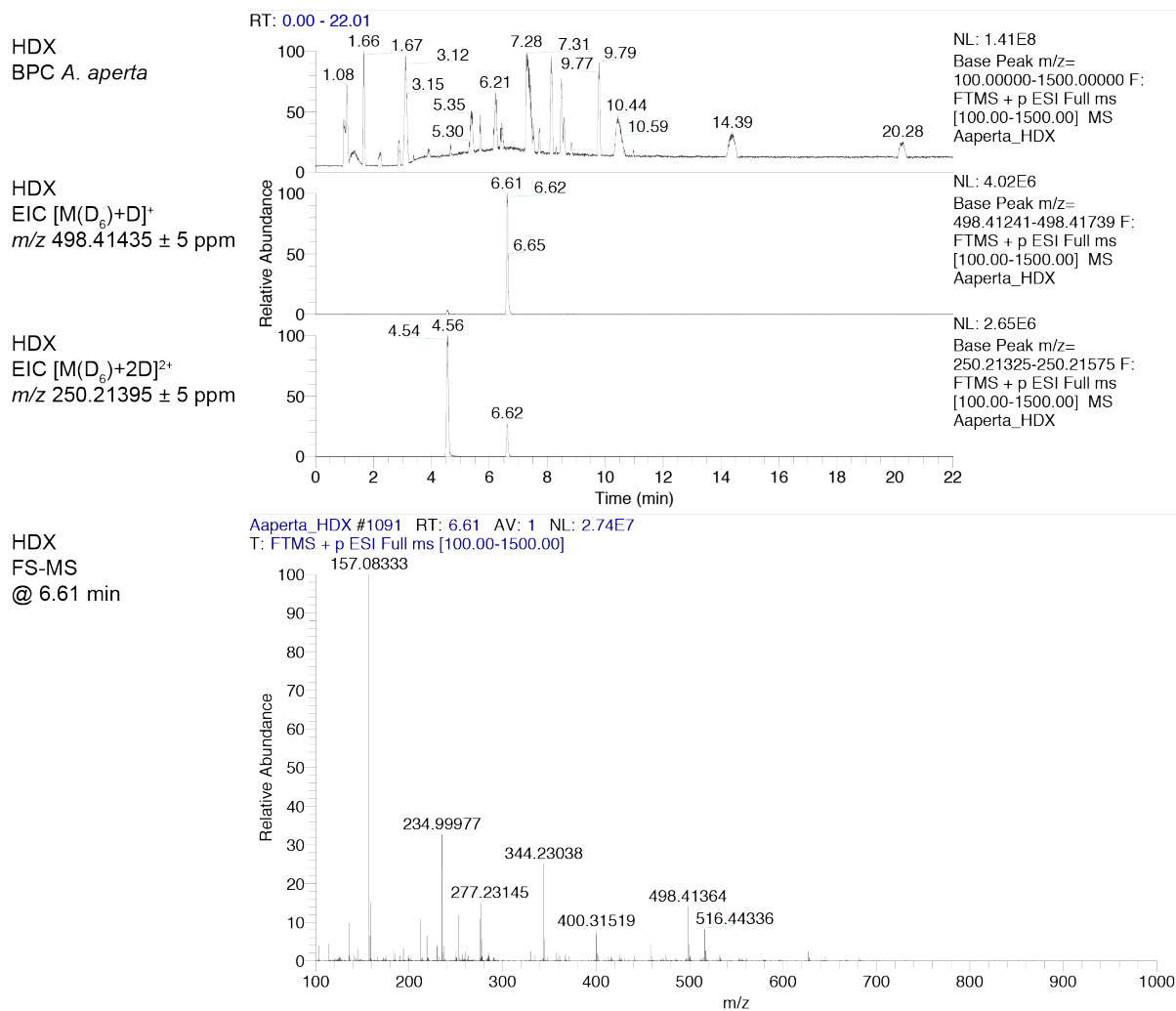
MS/MS ($P^+ = m/z$ 505.39)

m/z detected	Rel. Int.	m/z FRIOC	Molecular formula	Δ [ppm]	Fragment type
58.06612	1.51	–			
70.06610	4.55	–			
84.08169	3.83	–			
98.09723	32.66	–	$C_6H_{12}N^+$	8.16	$y_2'^*$
112.11267	1.12	–			
114.09202	1.64	–			
125.12059	0.63	–			
126.12838	100.00	–	$C_8H_{16}N^+$	5.15	$z_2 - NMe_3^*$
127.12353	0.61	–			
131.11855	3.05	–			
142.12307	1.60	–			
143.15498	0.78	–			
146.06041	5.73	–	$C_9H_8NO^+$	2.53	a'^*
153.13895	0.84	–			
155.15491	1.19	–			
174.05582	1.03	–	$C_{10}H_8NO_2^+$	5.00	a_0^*
183.18621	12.33	–	$C_{11}H_{23}N_2^+$	3.44	$z_3 - NMe_3^*$
188.17666	0.98	–			
216.20792	2.06	–	$C_{11}H_{26}N_3O^+$	4.02	$t_{z3} - NMe_3^*$
231.11341	27.40	231.11280	$C_{13}H_{15}N_2O_2^+$	2.64	a_1
273.26562	4.86	–	$C_{14}H_{33}N_4O^+$	2.67	$t_{z4} - NMe_3^*$
304.16639	3.14	304.16557	$C_{16}H_{22}N_3O_3^+$	2.70	a_2
327.21856	0.82	–			
345.22911	2.85	–			
361.22422	11.79	361.22342	$C_{19}H_{29}N_4O_3^+$	2.21	a_3
446.31402	42.64	446.31257	$C_{24}H_{40}N_5O_3^+$	3.25	a_4
505.38680	0.58	505.38606	$C_{27}H_{49}N_6O_3^+$	1.44	M^+

* this fragment ion is not generated by FRIOC

Supplementary Figure 3: 4-OH-IndAc3(OH)335(NMe₂) (*Agelenopsis aperta*)





FS-MS / FS-MS HDX

	<i>m/z</i> detected	<i>R</i> _t [min]	<i>m/z</i> FRIOC	Molecular formula	Δ [ppm]
[M+H] ⁺	491.37039	8.32	491.37042	C ₂₆ H ₄₇ N ₆ O ₃ ⁺	-0.06
[M(D ₆)+D] ⁺	498.41364	6.61	498.41435	C ₂₆ H ₄₀ D ₇ N ₆ O ₃ ⁺	-1.42

MS/MS ($P^+ = m/z$ 491.37)

m/z detected	Rel. Int.	m/z FRIOC	Molecular formula	Δ [ppm]	Fragment type
58.06600	1.78	–			
70.06584	4.91	–			
84.08144	4.66	–			
86.09706	0.89	–			
98.09695	37.91	–	$C_6H_{12}N^+$	5.30	$y_2'^*$
112.11271	1.31	–			
113.10795	1.12	–			
114.09179	2.65	–			
114.12819	100.00	114.12773	$C_7H_{16}N^+$	4.03	z_1
126.12802	49.78	–	$C_8H_{16}N^+$	2.30	$z_2 - NHMe_2^*$
131.11825	3.30	–			
143.15428	0.65	–			
146.06014	8.73	–	$C_9H_8NO^+$	0.68	a'^*
171.18599	5.02	–			
183.18580	6.61	–	$C_{11}H_{23}N_2^+$	1.20	$z_3 - NHMe_2^*$
228.24420	4.76	–			
231.11307	42.42	231.11280	$C_{13}H_{15}N_2O_2^+$	1.17	a_1
231.13557	0.62	–			
261.26518	0.54	–			
273.26583	1.55	–	$C_{14}H_{33}N_4O^+$	3.44	$t_{z4} - NHMe_2^*$
304.16583	4.64	304.16557	$C_{16}H_{22}N_3O_3^+$	0.85	a_2
318.32306	6.61	–			
321.19306	1.50	–			
361.22346	13.13	361.22342	$C_{19}H_{29}N_4O_3^+$	0.11	a_3
446.31320	13.94	446.31257	$C_{24}H_{40}N_5O_3^+$	1.41	a_4
491.37023	68.84	491.37042	$C_{26}H_{47}N_6O_3^+$	-0.39	$[M+H]^+$

* this fragment ion is not generated by FRIOC