

Supplemental Material

Seven New Microcystin Variants Discovered from a Native *Microcystis Aeruginosa* Strain – Unambiguous Assignment of Product Ions by Tandem Mass Spectrometry

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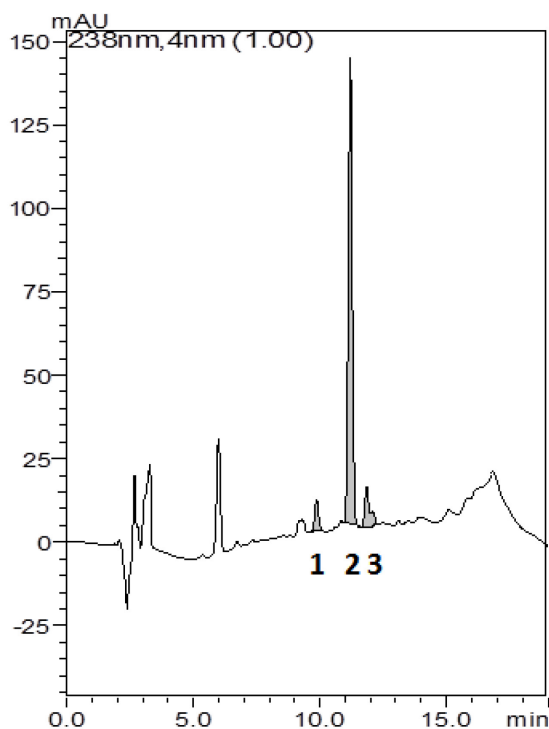


Figure S1. HPLC chromatogram of CAAT 2005-3 (238 nm). Peaks 1, 2, and 3 were collected for detailed further MS analysis.

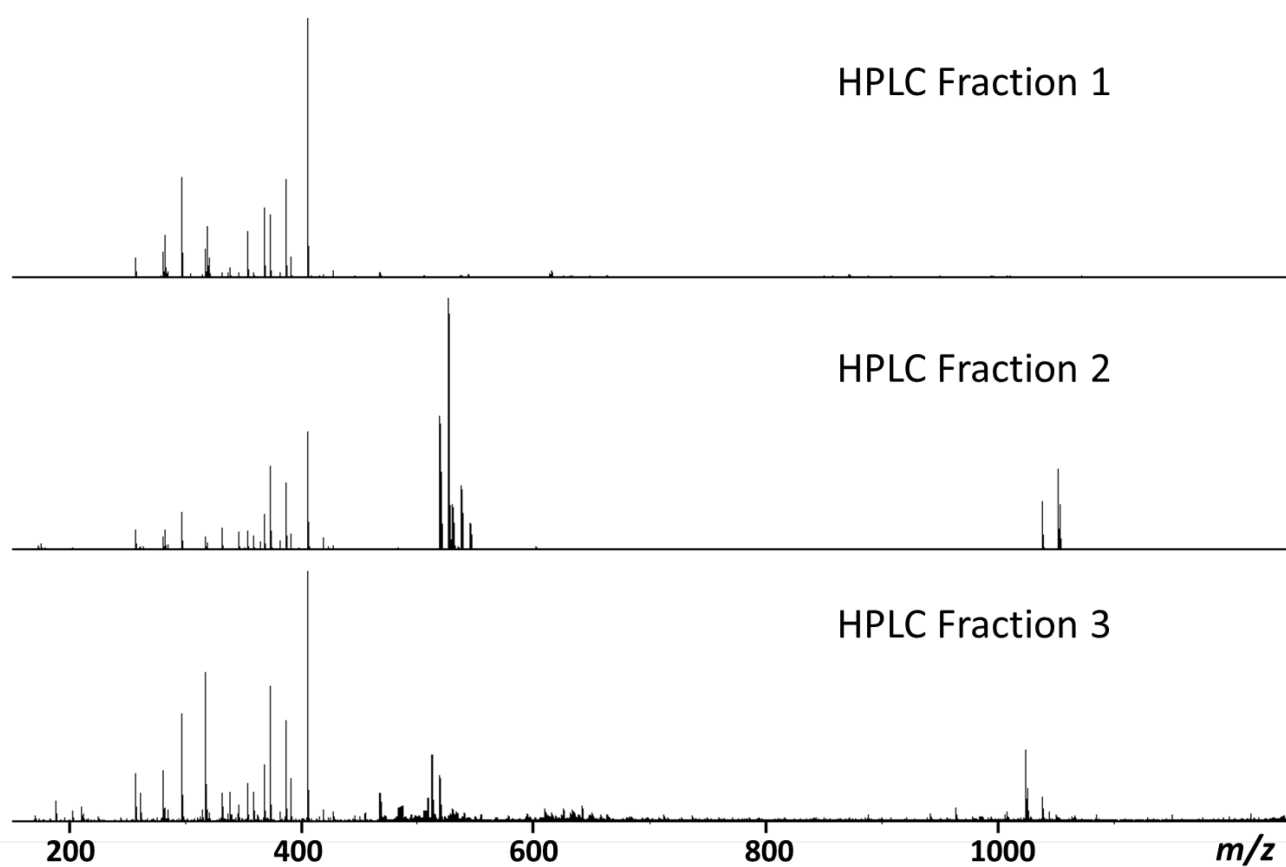


Figure S2. Full scan mass spectra of the three HPLC fractions separated from CAAT 2005-3.

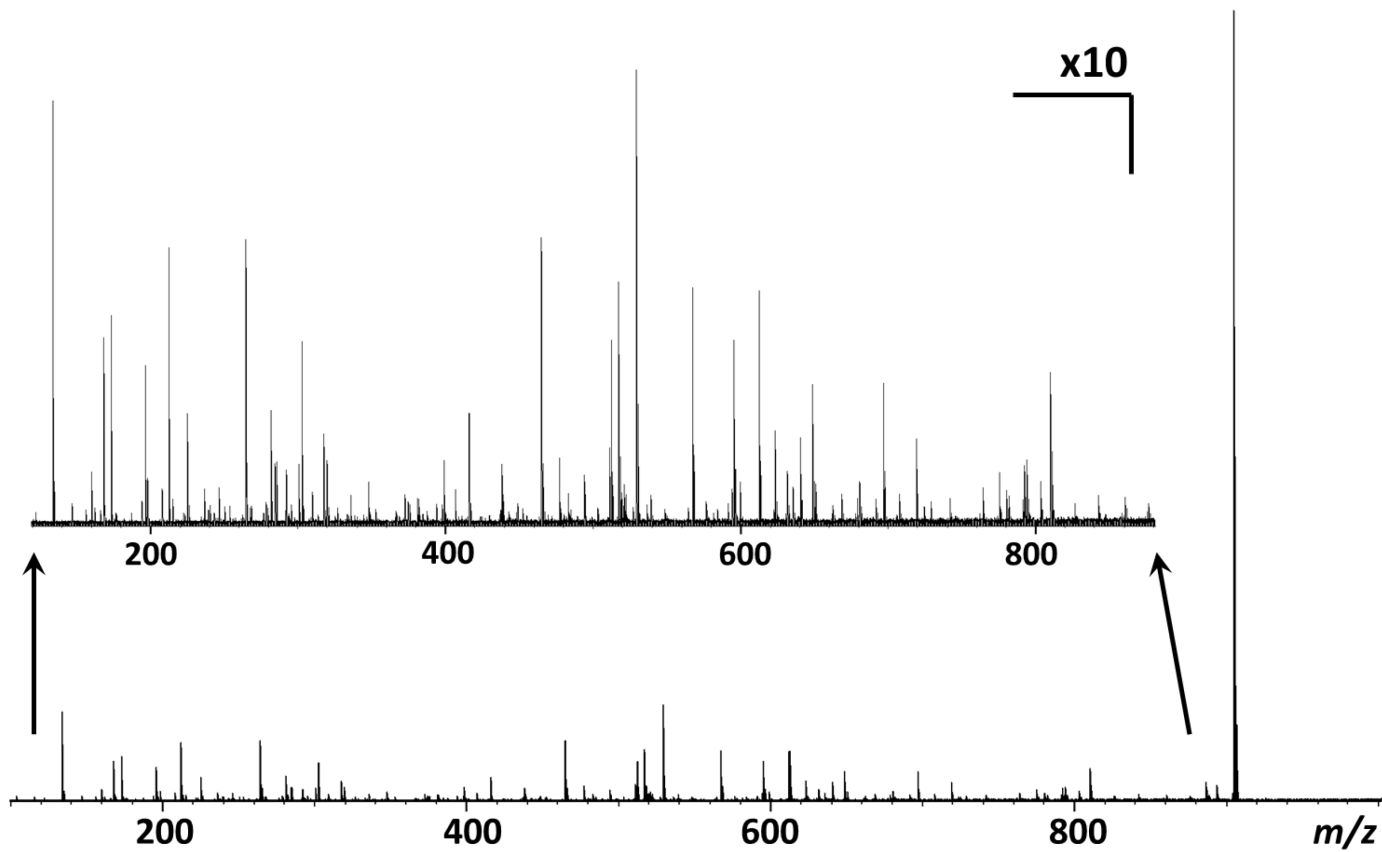


Figure S3. CID mass spectrum of doubly-charged [Leu¹]MC-LR ($[M+2H]^{2+}$, m/z 519.30514) from fraction 2. The inset shows the y-axis expansion of the product ions. The full peak list is available in Table S1.

Table S1. CID product ions of [Leu¹]MC-LR ([M+2H]²⁺ *m/z* 519.30514) from HPLC fraction 2

Formula	Theoretical <i>m/z</i>	Experimental <i>m/z</i>	Mass Error in ppm	Product Ion Assignment
C9H11O	135.08044	135.08044	0.00	Adda
C6H13N4O	157.10839	157.10840	0.06	4
C11H15O	163.11174	163.11170	-0.26	Adda+C2H4
C9H17N2O	169.13354	169.13353	-0.06	7 [~] 1-CO
C6H16N5O1	174.13494	174.13492	-0.11	4+NH2
C10H17N2O2	197.12845	197.12846	0.03	7 [~] 1
C9H13N2O4	213.08698	213.08698	0.00	6 [~] 7
C12H23N2O2	227.17540	227.17535	-0.22	1 [~] 2
C11H20N5O4	286.15098	286.15098	0.00	3 [~] 4
C11H23N6O4	303.17753	303.17755	0.07	3 [~] 4+NH2
C16H28N3O3	310.21252	310.21252	0.01	7 [~] 2
C17H30N5O2	336.23940	336.23943	0.09	4 [~] 5-134
C17H30N3O5	356.21800	356.21792	-0.22	1 [~] 3
C17H31N6O5	399.23505	399.23509	0.11	2 [~] 4
C17H34N7O5	416.26159	416.26162	0.07	2 [~] 4+NH2
C21H37N6O4	437.28708	437.28717	0.21	4 [~] 6-CO-134 or 3 [~] 5-CO-134
C21H35N4O6	439.25511	439.25501	-0.23	6 [~] 3
C22H37N6O5	465.28199	465.28202	0.06	4 [~] 6-134 or 3 [~] 5-134
C50H76O9N10	480.28929	480.28925	-0.08	[M-C2H6O3]2+
C50H78O10N10	489.29457	489.29459	0.04	[M-C2H4O2]2+
C51H76O10N10	494.28675	494.28672	-0.05	[M-CH4O-H2O]2+
C51H78O11N10	503.29203	503.29205	0.04	[M-CH4O]2+
C52H80O11N10	510.29985	510.29990	0.09	[M-H2O]2+
C23H42N7O6	512.31911	512.31914	0.06	1 [~] 4
C52H82O12N10	519.30514	519.30516	0.05	[M+H]2+
C23H45N8O6	529.34566	529.34565	-0.02	1 [~] 4+NH2
C26H42N7O6	548.31911	548.31915	0.07	4 [~] 7-134
C28H48N7O6	578.36606	578.36622	0.28	2 [~] 5-134
C27H44N7O8	594.32459	594.32465	0.10	3 [~] 6-134
C27H47N8O7	595.35622	595.35628	0.10	7 [~] 4
C31H47N6O6	599.35516	599.35526	0.17	3 [~] 5 or 4 [~] 6
C27H50N9O7	612.38277	612.38278	0.02	7 [~] 4+NH2
C28H50N9O8	640.37769	640.37773	0.06	CO+7 [~] 4+NH2
C32H53N8O7	661.40317	661.40321	0.06	4 [~] 7-134
C31H49N8O9	677.36170	677.36168	-0.03	3 [~] 7-134
C34H59N8O7	691.45012	691.45014	0.03	1 [~] 5-134
C33H55N8O9	707.40865	707.40854	-0.16	2 [~] 6-134
C32H54N9O10	724.39882	724.39895	0.19	6 [~] 4
C36H54N7O9	728.39775	728.39759	-0.22	3 [~] 6
C32H57N10O10	741.42536	741.42546	0.13	6 [~] 4+NH2
C37H59N6O10	747.42872	747.42876	0.05	5 [~] 3-134
C38H64N9O8	774.48724	774.48727	0.04	7 [~] 5-134

C37H60N9O10	790.44577	790.44586	0.11	2^{7-134} or 3^{1-134}
C39H64N9O9	802.48215	802.48208	-0.09	$C0+7^{5-134}$
C43H69N8O8	825.52329	825.52322	-0.08	1^5
C42H65N8O10	841.48182	841.48196	0.17	2^6
C43H71N10O11	903.52983	903.52963	-0.22	M-134
C46H70N9O11	924.51893	924.51882	-0.12	2^7 or 3^1

Table S2. CID product ions of MC-LR ($[M+2H]^{2+}$ m/z 498.28166) from HPLC fraction 1

Formula	Theoretical m/z	Experimental m/z	Mass Error in ppm	Product Ion Assignment
C9H11O	135.08044	135.08044	0.00	Adda
C11H15O	163.11174	163.11179	0.29	Adda+C2H4
C6H16N5O	174.13494	174.13488	-0.33	4+NH2
C9H19N2O2	187.14410	187.14417	0.37	1 [~] 2
C9H13N2O4	213.08698	213.08701	0.13	6 [~] 7
C10H11N2O5	239.06625	239.06633	0.34	6 [~] 7+C0
C13H22N3O3	268.16557	268.16557	0.01	7 [~] 2
C11H20N5O4	286.15098	286.15096	-0.07	3 [~] 4
C11H23N6O4	303.17753	303.17759	0.20	3 [~] 4+NH2
C16H27N2O4	311.19653	311.19655	0.06	5 [~] 6-134
C17H30N5O2	336.23940	336.23931	-0.27	4 [~] 5-134
C17H31N6O5	399.23505	399.23510	0.14	2 [~] 4
C17H34N7O5	416.26159	416.26144	-0.36	2 [~] 4+NH2
C22H37N6O5	465.28199	465.28204	0.11	3 [~] 5-134 or 4 [~] 6-134
C20H39N8O6	487.29871	487.29867	-0.08	1 [~] 4+NH2
C20H36N7O6	470.27216	470.27208	-0.17	1 [~] 4
C20H39N8O6	487.29871	487.29874	0.06	1 [~] 4+NH2
C47H70N10O9	459.26581	459.26616	0.76	$[M-C2H6O3]^{2+}$
C47H72N10O10	468.27110	468.27099	-0.23	$[M-C2H4O2]^{2+}$
C48H70N10O10	473.26327	473.26303	-0.51	$[M-CH4O-H2O]^{2+}$
C48H72N10O11	482.26855	482.26823	-0.66	$[M-CH4O]^{2+}$
C49H74N10O11	489.27638	489.27592	-0.94	$[M-H2O]^{2+}$
C49H76N10O12	498.28166	498.28150	-0.32	$[M+2H]^{2+}$
C24H41N8O7	553.30927	553.30921	-0.11	7 [~] 4
C24H44N9O7	570.33582	570.33581	-0.02	7 [~] 4+NH2
C32H46N4O7	598.33610	598.33678	-1.14	5 [~] 1
C31H47N6O6	599.35516	599.35563	0.78	3 [~] 5 or 4 [~] 6
C29H48N9O10	682.35187	682.35183	-0.05	6 [~] 4
C35H50N7O8	696.37154	696.37164	0.15	3 [~] 6-134
C29H51N10O10	699.37841	699.37800	-0.59	6 [~] 4+NH4
C39H59N8O7	751.45012	751.45005	-0.10	1 [~] 5-134
C42H60N9O10	850.44577	850.44555	-0.25	3 [~] 1-134
C40H65N10O11	861.48288	861.48292	0.05	M-134

Table S3. CID product ions of [Glu(OCH₃)⁶]MC-LR ([M+2H]²⁺ *m/z* 505.28949) from HPLC fraction 1

Formula	Theoretical <i>m/z</i>	Experimental <i>m/z</i>	Mass Error in ppm	Product Ion Assignment
C9H11O	135.08044	135.08045	0.07	Adda
C7H11N2O2	155.08150	155.08144	-0.39	7 [~] 1
C11H15O	163.11174	163.11167	-0.44	Adda
C6H16N5O	174.13494	174.13492	-0.10	4+NH ₂
C10H15N2O4	227.10263	227.10269	0.26	6 [~] 7
C13H22N3O3	268.16557	268.16559	0.08	7 [~] 2
C13H19N2O5	283.12885	283.12881	-0.14	6 [~] 1-NH ₂
C11H20N5O4	286.15098	286.15098	0.00	3 [~] 4
C11H23N6O4	303.17753	303.17750	-0.10	3 [~] 4+NH ₂
C17H33N6O2	353.26595	353.26615	0.57	4 [~] 5+NH ₂ -134
C17H31N6O5	399.23505	399.23512	0.19	2 [~] 4
C17H34N7O5	416.26159	416.26163	0.10	2 [~] 4+NH ₂
C22H37N6O5	465.28199	465.28198	-0.02	3 [~] 5-134
C20H39N8O6	487.29871	487.29867	-0.08	1 [~] 4+NH ₂
C20H36N7O6	470.27216	470.27222	0.13	1 [~] 4
C23H39N6O5	479.29764	479.29758	-0.13	4 [~] 6-134
C20H39N8O6	487.29871	487.29867	-0.08	1 [~] 4+NH ₂
C48H72N10O9	466.27364	466.27368	0.09	[M-C2H6O3] ²⁺
C48H74N10O10	475.27892	475.27906	0.29	[M-C2H4O2] ²⁺
C49H72N10O10	480.27110	480.27097	-0.26	[M-CH4O-H2O] ²⁺
C49H74N10O11	489.27638	489.27631	-0.14	[M-CH4O] ²⁺
C50H76N10O11	496.28420	496.28420	0.00	[M-H2O] ²⁺
C50H78N10O12	505.28949	505.28948	-0.01	[M+2H] ²⁺
C24H41N8O7	553.30927	553.30939	0.21	7 [~] 4
C24H44N9O7	570.33582	570.33591	0.16	7 [~] 4+NH ₂
C30H50N9O10	696.36752	696.36726	-0.37	6 [~] 4
C30H53N10O10	713.39406	713.39413	0.10	6 [~] 4+NH ₂
C39H59N8O7	751.45012	751.45001	-0.15	1 [~] 5-134
C35H56N9O10	762.41447	762.41379	-0.89	3 [~] 1-134
C41H67N10O11	875.49853	875.49817	-0.41	M-134

Table S4. CID product ions of [M(O)¹]MC-LR ([M+2H]²⁺ *m/z* 536.28080) from HPLC fraction 1

Formula	Theoretical <i>m/z</i>	Experimental <i>m/z</i>	Mass Error in ppm	Product Ion Assignment
C9H11O	135.08044	135.08044	0.00	Adda
C11H15O	163.11174	163.11172	-0.13	Adda+C2H4
C6H16N5O1	174.13494	174.13492	-0.11	4+NH2
C9H13N2O4	213.08698	213.08703	0.23	6 [~] 7
C9H15N2O3S	231.07979	231.07988	0.39	7 [~] 1
C11H21N2O3S	261.12674	261.12671	-0.11	1 [~] 2
C11H20N5O4	286.15098	286.15100	0.07	3 [~] 4
C11H23N6O4	303.17753	303.17750	-0.10	3 [~] 4+NH2
C15H26N3O4S	344.16385	344.16382	-0.09	7 [~] 2
C17H31N6O5	399.23504	399.23522	0.45	2 [~] 4
C17H34N7O5	416.26159	416.26163	0.10	2 [~] 4+NH2
C22H37N6O5	465.28199	465.28198	-0.02	3 [~] 5-134 or 4 [~] 6-134
C26H40N5O3	470.31257	470.31231	-0.55	4 [~] 5
C20H33N4O7S	473.20645	473.20653	0.17	6 [~] 2
C49H74N10O10S	497.26496	497.26498	0.04	[M-C2H6O3]2+
C49H76N10O11S	506.27024	506.27041	0.34	[M-C2H4O2]2+
C50H74N10O11S	511.26241	511.26249	0.16	[M-CH4O-H2O]2+
C50H76N10O12S	520.26770	520.26771	0.02	[M-CH4O]2+
C51H78N10O12S	527.27552	527.27567	0.28	[M-H2O]2+
C51H80N10O13S	536.28080	536.28074	-0.11	[M+2H]2+
C22H40N7O7S	546.27044	546.27035	-0.16	1 [~] 4
C26H42N7O6	548.31948	548.31931	-0.31	4 [~] 7-134
C22H43N8O7S	563.29699	563.29712	0.23	1 [~] 4+NH2
C27H44N7O8	594.32459	594.32470	0.19	3 [~] 6-134
C31H47N6O6	599.35516	599.35509	-0.12	3 [~] 5 or 4 [~] 6
C26H45N8O8S	629.30756	629.30746	-0.16	7 [~] 4
C26H48N9O8S	646.33411	646.33410	-0.02	7 [~] 4+NH2
C27H45N8O9S	657.30247	657.30246	-0.02	C0+7 [~] 4
C27H48N9O9S	674.32902	674.32886	-0.24	C0+7 [~] 4+NH2
C35H54N7O8	700.40284	700.40254	-0.43	3 [~] 6
C33H55N8O9	707.40865	707.40882	0.24	2 [~] 6-134
C33H57N8O8S	725.40146	725.40129	-0.23	1 [~] 5-134
C31H52N9O11S	758.35015	758.34987	-0.37	6 [~] 4
C31H55N10O11S	775.37670	775.37680	0.13	6 [~] 4+NH2
C37H62N9O9S	808.43857	808.43834	-0.28	4 [~] 2-134
C38H62N9O10S	836.43349	836.43370	0.25	C0+7 [~] 5-134
C42H67N8O9S	859.47462	859.47469	0.08	1 [~] 5
C42H69N10O12S	937.48117	937.48114	-0.03	M-134

Table S5. CID product ions of $[M(O)^1, Glu(OCH_3)^6]MC-LR$ ($[M+2H]^{2+}$ m/z 543.28863) from HPLC fraction 1

Formula	Theoretical m/z	Experimental m/z	Mass Error in ppm	Product Ion Assignment
C9H11O	135.08044	135.08044	0.00	Adda
C6H13N4O	157.10839	157.10838	-0.06	4
C11H15O	163.11174	163.11174	0.00	Adda+C2H4
C6H16N5O1	174.13494	174.13499	0.29	4+NH2
C10H15N2O4	227.10263	227.10264	0.04	6~7
C9H15N2O3S	231.07979	231.07979	0.00	7~1
C11H21N2O3S	261.12674	261.12676	0.08	1~2
C11H20N5O4	286.15098	286.15093	-0.17	3~4
C11H23N6O4	303.17753	303.17749	-0.13	3~4+NH2
C17H28N04	310.20128	310.20115	-0.42	5~6-NH2
C17H30N5O2	336.23940	336.23950	0.30	4~5-134
C15H26N3O4S	344.16385	344.16380	-0.15	7~2
C16H28N3O6S	390.16933	390.16925	-0.21	1~3
C17H31N6O5	399.23504	399.23508	0.10	2~4
C17H34N7O5	416.26159	416.26158	-0.02	1~4+NH2
C22H37N6O5	465.28199	465.28198	-0.02	3~5-134
C20H33N4O7S	473.20645	473.20633	-0.25	7~3
C23H39N6O5	479.29764	479.29766	0.04	4~6-134
C50H76N10O10S	504.27278	504.27267	-0.22	$[M-C2H6O3]^{2+}$
C50H78N10O11S	513.27806	513.27807	0.02	$[M-C2H4O2]^{2+}$
C51H76N10O11S	518.27024	518.27021	-0.06	$[M-CH4O-H2O]^{2+}$
C51H78N10O12S	527.27552	527.27538	-0.27	$[M-CH4O]^{2+}$
C52H80N10O12S	534.28335	534.28331	-0.07	$[M-H2O]^{2+}$
C52H82N10O13S	543.28863	543.28894	0.57	$[M+2H]^{2+}$
C27H44N7O6	562.33476	562.33469	-0.12	4~7-134
C22H43N8O7S	563.29699	563.29705	0.11	1~4+NH2
C28H48N7O6	578.36606	578.36630	0.41	2~5-134
C31H47N6O6	599.35516	599.35517	0.02	3~5
C28H46N7O8	608.34024	608.34033	0.15	3~8-134
C26H45N8O8S	629.30756	629.30761	0.08	7~4
C26H48N9O8S	646.33411	646.33420	0.14	7~4+NH2
C32H51N8O9	691.37735	691.37718	-0.25	3~7-134
C32H53N8O8S	709.37016	709.37020	0.06	4~1-134
C34H57N8O9	721.42430	721.42442	0.17	2~6-134
C32H54N9O11S	772.36580	772.36576	-0.05	6~4
C32H57N10O11S	789.39235	789.39247	0.15	6~4+NH2
C43H71N10O12S	951.49681	951.49650	-0.33	M-134

Table S6. CID product ions of [Leu¹,Glu(OCH₃)⁶]MC-LR ([M+2H]²⁺ *m/z* 526.31296) from HPLC fraction 2

Formula	Theoretical <i>m/z</i>	Experimental <i>m/z</i>	Mass Error in ppm	Product Ion Assignment
C9H11O	135.08044	135.08044	0.00	Adda
C6H10NO3	144.06552	144.06540	-0.83	6
C6H13N4O	157.10839	157.10840	0.08	4
C11H15O	163.11174	163.11175	0.05	Adda+C2H4
C9H17N2O	169.13354	169.13353	-0.06	7 [~] 1-CO
C10H17N2O2	197.12845	197.12846	0.03	7 [~] 1
C9H13N2O4	213.08698	213.08691	-0.33	6 [~] 7-NH2
C10H15N2O4	227.10263	227.10261	-0.10	6 [~] 7
C12H23N2O2	227.17540	227.17561	0.91	1 [~] 2
C11H20N5O4	286.15098	286.15097	-0.04	3 [~] 4
C11H23N6O4	303.17753	303.17751	-0.07	3 [~] 4+NH2
C16H28N3O3	310.21252	310.21252	0.00	7 [~] 2
C20H28N02	314.21146	314.21132	-0.43	5
C17H27N2O4	323.19653	323.19652	-0.04	5 [~] 6-134
C17H30N5O2	336.23940	336.23932	-0.24	4 [~] 5-134
C21H29N2O5	389.20710	389.20712	0.06	5 [~] 7
C17H31N6O5	399.23505	399.23508	0.09	2 [~] 4
C21H35N4O6	439.25511	439.25514	0.07	7 [~] 3
C22H37N6O5	465.28200	465.28204	0.10	4 [~] 6-134-NH2
C23H39N6O5	479.29765	479.29769	0.09	4 [~] 6-134
C51H78O9N10	487.29711	487.29715	0.08	[M-C2H6O3]2+
C51H80O10N10	496.30240	496.30236	-0.07	[M-C2H4O2]2+
C52H78O10N10	501.29457	501.29460	0.06	[M-CH4O-H2O]2+
C52H80O11N10	510.29985	510.29987	0.03	[M-CH4O]2+
C23H42N7O6	512.31911	512.31910	-0.02	1 [~] 4
C53H82O11N10	517.30768	517.30773	0.10	[M-H2O]2+
C53H84O12N10	526.31296	526.31295	-0.02	[M+H]2+
C27H44N7O6	562.33476	562.33487	0.20	4 [~] 7-134
C27H47N8O7	595.35622	595.35621	-0.02	7 [~] 4
C28H46N7O8	608.34024	608.34014	-0.16	3 [~] 6-134
C33H55N8O7	675.41882	675.41922	0.59	4 [~] 1-134
C32H51N8O9	691.37735	691.37716	-0.28	3 [~] 7-134
C34H57N8O9	721.42430	721.42422	-0.11	2 [~] 6-134
C33H56N9O10	738.41447	738.41449	0.03	6 [~] 4
C37H56N7O9	742.41340	742.41362	0.29	3 [~] 6
C38H61N6O10	761.44437	761.44438	0.01	5 [~] 3-134
C39H66N9O8	788.50289	788.50257	-0.40	4 [~] 2-134
C38H62N9O10	804.46142	804.46120	-0.27	2 [~] 7-134
C43H67N8O10	855.49747	855.49736	-0.13	2 [~] 6
C44H73O11N10	917.54548	917.54550	0.02	M-134

Table S7. CID product ions of [Leu¹,Ser⁷]MC-LR ([M+2H]²⁺ *m/z* 528.31042) from HPLC fraction 2

Formula	Theoretical <i>m/z</i>	Experimental <i>m/z</i>	Mass Error in ppm	Product Ion Assignment
C9H11O	135.08044	135.08044	0.00	Adda
C6H13N4O	157.10839	157.10833	-0.38	4
C11H15O	163.11174	163.11180	0.36	Adda+C2H4
C6H16N5O	174.13494	174.13498	0.23	4+NH2
C12H23N2O2	227.17540	227.17542	0.09	1 [~] 2
C11H19N2O4	243.13393	243.13392	-0.04	2 [~] 3
C11H20N5O4	286.15098	286.15090	-0.28	3 [~] 4
C11H23N6O4	303.17753	303.17748	-0.16	3 [~] 4+NH2
C16H25N2O4	309.18088	309.18087	-0.03	5 [~] 6-134
C17H30N5O2	336.23940	336.23934	-0.18	4 [~] 5-134
C17H30N3O5	356.21800	356.21794	-0.17	1 [~] 3 or C0+7 [~] 2
C17H31N6O5	399.23504	399.23507	0.08	2 [~] 4
C17H34N7O5	416.26159	416.26165	0.14	2 [~] 4+NH2
C21H37N6O4	437.28708	437.28717	0.21	3 [~] 5-CO-134 or 4 [~] 6-CO-134
C21H37N4O7	457.26568	457.26560	-0.17	6 [~] 2 or 7 [~] 3
C22H37N6O5	465.28199	465.28203	0.09	3 [~] 5-134 or 4 [~] 6-134
C37H61N6O11	465.43928	465.43918	-0.21	5 [~] 3-134
C26H40N5O3	470.31257	470.31254	-0.06	4 [~] 5
C50H78N10O10	489.29457	489.29470	0.27	[M-C2H6O3]2+
C51H78N10O11	503.29203	503.29202	-0.02	[M-CH4O-H2O]2+
C51H80N10O12	512.29731	512.29748	0.33	[M-CH4O]2+
C23H42N7O6	512.31911	512.31921	0.20	1 [~] 4
C52H82N10O12	519.30514	519.30518	0.08	[M-H2O]2+
C52H84N10O13	528.31042	528.31067	0.47	[M+2H]2+
C23H45N8O6	529.34566	529.34559	-0.13	1 [~] 4+NH2
C26H44N5O10	586.30827	586.30810	-0.29	6 [~] 3
C27H44N7O8	594.32459	594.32471	0.20	3 [~] 6-134
C31H47N6O6	599.35516	599.35570	0.90	3 [~] 5 or 4 [~] 6
C32H55N8O8	679.41374	679.41334	-0.59	4 [~] 1-134
C36H54N7O9	728.39775	728.39767	-0.11	3 [~] 6
C32H60N10O11	760.44375	760.44367	-0.11	6 [~] 4+NH2
C38H66N9O9	792.49780	792.49787	0.09	1 [~] 6-134-CO or 4 [~] 2-134 or 7 [~] 5-134
C39H66N9O10	820.49272	820.49289	0.21	1 [~] 6-134 or 7 [~] 5-134+CO
C43H73N10O12	921.54039	921.54034	-0.06	M-134

Table S8. CID product ions of [Leu¹,Glu(OCH₃)⁶,Ser⁷]MC-LR ([M+2H]²⁺ *m/z* 535.31824) from HPLC fraction 2

Formula	Theoretical <i>m/z</i>	Experimental <i>m/z</i>	Mass Error in ppm	Product Ion Assignment
C9H11O	135.08044	135.08042	-0.15	Adda
C6H13N4O	157.10839	157.10833	-0.38	4
C11H15O	163.11174	163.11168	-0.38	Adda+C2H4
C6H16N5O	174.13494	174.13495	0.06	4+NH ₂
C12H23N2O2	227.17540	227.17541	0.04	1 [~] 2
C11H19N2O4	243.13393	243.13380	-0.53	C0+7 [~] 1
C11H20N5O4	286.15098	286.15097	-0.03	3 [~] 4
C11H23N6O4	303.17753	303.17748	-0.16	3 [~] 4+NH ₂
C17H27N2O4	323.19653	323.19649	-0.12	5 [~] 6-134
C17H30N5O2	336.23940	336.23932	-0.24	4 [~] 5-134
C17H31N6O5	399.23504	399.23523	0.48	2 [~] 4
C21H34N2O6	410.24114	410.24126	0.29	5 [~] 7-134-NH ₂
C17H34N7O5	416.26159	416.26154	-0.12	2 [~] 4+NH ₂
C22H37N6O5	465.28199	465.28197	-0.04	3 [~] 5-134
C26H40N5O3	470.31257	470.31253	-0.09	4 [~] 5
C22H39N4O7	471.28133	471.28127	-0.13	6 [~] 2
C23H39N6O5	479.29764	479.29741	-0.48	4 [~] 6-134
C51H80O10N10	496.30240	496.30245	0.11	[M-C2H6O3]2+
C52H80O11N10	510.29985	510.29981	-0.08	[M-CH4O-H2O]2+
C23H42N7O6	512.31911	512.31914	0.06	1 [~] 4
C52H82O12N10	519.30514	519.30516	0.05	[M-CH4O]2+
C53H84O12N10	526.31296	526.31305	0.17	[M-H2O]2+
C23H45N8O6	529.34566	529.34567	0.02	1 [~] 4+NH ₂
C53H86O13N10	535.31824	535.31828	0.07	[M+H]2+
C31H47N6O6	599.35516	599.35549	0.55	3 [~] 5
C27H46N5O10	600.32392	600.32390	-0.03	6 [~] 3
C28H46N7O8	608.34024	608.34055	0.51	3 [~] 6-134
C36H56N7O8	714.41849	714.41902	0.74	4 [~] 7
C34H57N8O9	721.42430	721.42447	0.24	2 [~] 7-134
C37H56N7O9	742.41340	742.41329	-0.15	3 [~] 6
C39H68N9O9	806.51345	806.51367	0.27	4 [~] 2-134
C44H75O12N10	935.55604	935.55584	-0.22	M-134

Table S9. CID product ions of [Leu¹,Asp³]MC-LR ([M+2H]²⁺ *m/z* 512.29731) from HPLC fraction 3

Formula	Theoretical <i>m/z</i>	Experimental <i>m/z</i>	Mass Error in ppm	Product Ion Assignment
C9H11O	135.08044	135.08044	0.00	Adda
C11H15O	163.11174	163.11165	-0.56	Adda+C2H4
C10H17N2O2	197.12845	197.12852	0.33	7 [~] 1
C9H13N2O4	213.08698	213.08699	0.05	6 [~] 7
C10H18N5O4	272.13533	272.13526	-0.26	3 [~] 4
C10H21N6O4	289.16188	289.16179	-0.31	3 [~] 4+NH2
C16H28N3O3	310.21252	310.21251	-0.03	7 [~] 2
C17H30N5O2	336.23940	336.23927	-0.39	4 [~] 5-134
C20H27N2O5	375.19145	375.19143	-0.05	5 [~] 7-NH2-134
C16H29N6O5	385.21939	385.21926	-0.35	2 [~] 4
C16H32N7O5	402.24594	402.24579	-0.37	2 [~] 4+NH2
C21H37N6O4	437.28708	437.28691	-0.39	4 [~] 6-CO-134
C21H35N6O5	451.26634	451.26615	-0.42	3 [~] 5-134
C22H37N6O5	465.28200	465.28190	-0.20	4 [~] 6-134
C22H40N7O6	498.30346	498.30340	-0.12	1 [~] 4
C49H74N10O9	473.28146	473.28150	0.08	[M-C2H6O3]2+
C49H76N10O10	482.28675	482.28671	-0.07	[M-C2H4O2]2+
C50H74N10O10	487.27892	487.27891	-0.02	[M-CH4O-H2O]2+
C50H76N10O11	496.28420	496.28429	0.18	[M-CH4O]2+
C22H40N7O6	498.30346	498.30340	-0.12	1 [~] 4
C51H78N10O11	503.29203	503.29186	-0.33	[M-H2O]2+
C51H80N10O12	512.29731	512.29727	-0.08	[M+2H]2+
C22H43N8O6	515.33001	515.32996	-0.10	1 [~] 4+NH2
C26H42N7O8	580.30894	580.30914	0.35	3 [~] 6-134
C26H45N8O7	581.34057	581.34064	0.12	7 [~] 4
C26H48N9O7	598.36712	598.36722	0.17	7 [~] 4+NH2
C27H45N8O8	609.33549	609.33557	0.13	5 [~] 6
C27H48N9O8	626.36204	626.36208	0.06	CO+7 [~] 4+NH2
C33H57N8O7	677.43447	677.43460	0.19	1 [~] 5-134
C32H53N8O9	693.39300	693.39314	0.20	2 [~] 6-134
C31H52N9O10	710.38317	710.38315	-0.02	6 [~] 4
C35H52N7O9	714.38210	714.38266	0.78	3 [~] 6
C31H55N10O10	727.40971	727.40962	-0.12	6 [~] 4+NH2
C37H62N9O8	760.47159	760.47191	0.42	7 [~] 5-134
C38H64N9O8	774.48724	774.48701	-0.30	4 [~] 2-134
C36H58N9O10	776.43012	776.43057	0.58	2 [~] 7-134
C38H62N9O9	788.46650	788.46655	0.06	CO+7 [~] 5-134
C42H69N10O11	889.51418	889.51421	0.03	M-134

Table S10. CID product ions of [Leu¹,Glu(OCH₃)⁶]MC-HiLR ([M+2H]²⁺ *m/z* 533.32079) from HPLC fraction 3

Formula	Theoretical <i>m/z</i>	Experimental <i>m/z</i>	Mass Error in ppm	Product Ion Assignment
C9H11O	135.08044	135.08045	0.07	Adda
C11H15O	163.11174	163.11163	-0.69	Adda+C2H4
C6H16N5O1	174.13494	174.13486	-0.46	4+NH2
C10H17N2O2	197.12845	197.12844	-0.05	7 [~] 1
C10H15N2O4	227.10263	227.10259	-0.18	6 [~] 7
C13H25N2O2	241.19105	241.19107	0.08	1 [~] 2
C11H20N5O4	286.15098	286.15102	0.14	3 [~] 4
C11H23N6O4	303.17753	303.17759	0.20	3 [~] 4+NH2
C17H27N2O4	323.19653	323.19652	-0.03	5 [~] 6-134
C17H30N3O3	324.22817	324.22820	0.09	7 [~] 2
C18H33N6O5	413.25069	413.25076	0.17	2 [~] 4
C18H36N7O5	430.27724	430.27740	0.37	2 [~] 4+NH2
C23H39N6O5	479.29764	479.29758	-0.13	4 [~] 6-134
C52H80N10O9	494.30494	494.30500	0.12	[M-C2H6O3]2+
C52H82N10O10	503.31022	503.31026	0.08	[M-C2H4O2]2+
C53H80N10O10	508.30240	508.30246	0.12	[M-CH4O-H2O]2+
C53H82N10O11	517.30768	517.30775	0.14	[M-CH4O]2+
C54H84N10O11	524.31550	524.31564	0.27	[M-H2O]2+
C24H44N7O6	526.33476	526.33489	0.25	1 [~] 4
C54H86N10O12	533.32079	533.32078	-0.02	[M+2H]2+
C24H47N8O6	543.36131	543.36136	0.09	1 [~] 4+NH2
C31H47N6O6	599.35516	599.35539	0.38	3 [~] 5
C28H49N8O7	609.37187	609.37188	0.02	7 [~] 4
C32H49N6O6	613.37081	613.37114	0.54	4 [~] 6
C28H52N9O7	626.39842	626.39856	0.22	7 [~] 4+NH2
C32H51N8O9	691.37735	691.37752	0.25	3 [~] 7-134
C35H59N8O9	735.43995	735.43997	0.03	2 [~] 6-134
C34H58N9O10	752.43012	752.43033	0.28	6 [~] 4
C34H61N10O10	769.45666	769.45673	0.09	6 [~] 4+NH2
C39H63N6O10	775.46002	775.45953	-0.63	5 [~] 3-134
C40H68N9O8	802.51854	802.51895	0.51	4 [~] 2-134
C45H75O11N10	931.56113	931.56108	-0.05	M-134