

The biosynthesis of rare homo-amino acid containing variants of microcystin by a benthic cyanobacterium

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Figures

Figure S1. Relative amounts (%) of microcystin variants in *Phormidium* sp. LP904c (yellow) and DVL1003c (green). Peak areas of the extracted ion chromatograms of the protonated microcystins was used in calculations.

Figure S2. Ultraviolet (UV), total ion current (TICC) and extracted ion (EIC) chromatograms obtained with HPLC-ITMS of protonated microcystins found from *Phormidium* sp. LP904c. Mass/charge values of protonated microcystins are marked to the EIC traces.

Figure S3. Ultraviolet (UV), total ion current (TICC) and extracted ion (EIC) chromatograms obtained with HPLC-ITMS of protonated microcystins found from *Phormidium* sp. DVL1003c. Mass/charge values of protonated microcystins are marked to the EIC traces.

Figure S4. Product ion spectra of protonated microcystins from *Phormidium* sp. LP904c obtained with HPLC-ITMS. Mass/charge values of protonated microcystins and their retention times (min) are marked to the spectra.

Figure S5. Coding for the product ions generated from the protonated and sodiated microcystins. Variable methyl groups 1-3 are marked with a gray shade.

Figure S6. Product ion spectra of sodiated non Arg microcystins from *Phormidium* sp. LP904c obtained with HPLC-ITMS. Mass/charge values of protonated microcystins and their retention times (min) are marked to the spectra.

Figure S7. Effect of polar surface areas (PSA) to the retention times (R_t , min) of *Phormidium* sp. DVL1003c microcystins calculated with a topological polar surface area (TPSA) method (Ertl et al., 2000). High correlation ($R^2 = 0,937$) shows that the proposed microcystin structures fit well to the measured retention times.

Figure S8. Microcystin variants produced by studied *Phormidium* strains and relative amount produced.

Figure S9. Concatenated phylogenetic tree of the McyD and McyE sequences constructed using neighbor-joining with 1000 bootstrap replications. *Phormidium* sp. LP904c is indicated in bold.

Figure S10. Phylogenetic tree constructed using condensation (A) and adenylation (B) domains from McyB1 (blue) and McyC (pink) amino acid sequences. Neighbor-joining method with 1000 bootstrap replications. *Phormidium* sp. LP904c is indicated in bold.

Tables

Table S1. Assignments, ion masses (m/z) and intensities (%) of the protonated non Arg microcystins of the most important product ions. Red No = Ion structure confirmed by Diehnelt et al. 2006 with high resolution fourier transform ion cyclotron resonance mass spectrometer. CI = Code for ion structure presented in Figure S5.

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Table S4. Sequence similarity of the microcystin gene cluster from *Phormidium* sp. LP904c obtained by BLASTp.

Table S5. Microcystins variants detected in the strains from table 2 and 3. The homoamino acids detected are highlighted.

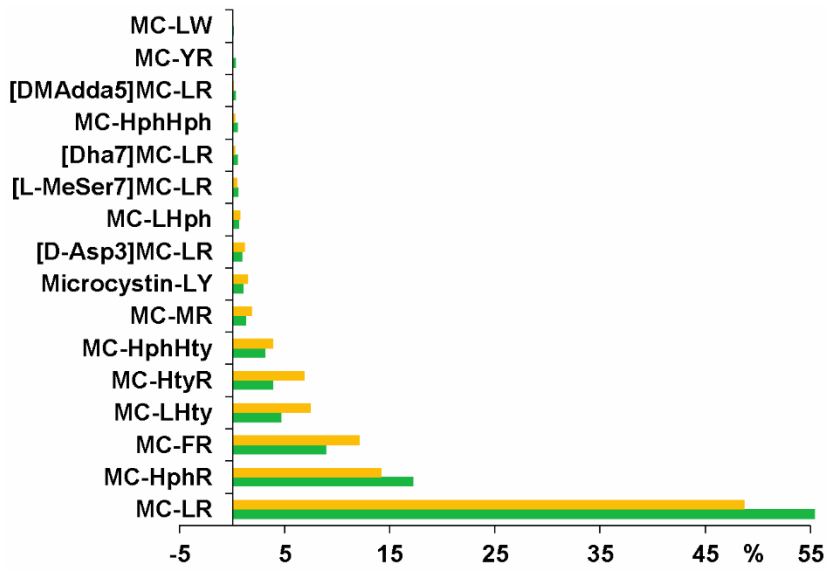


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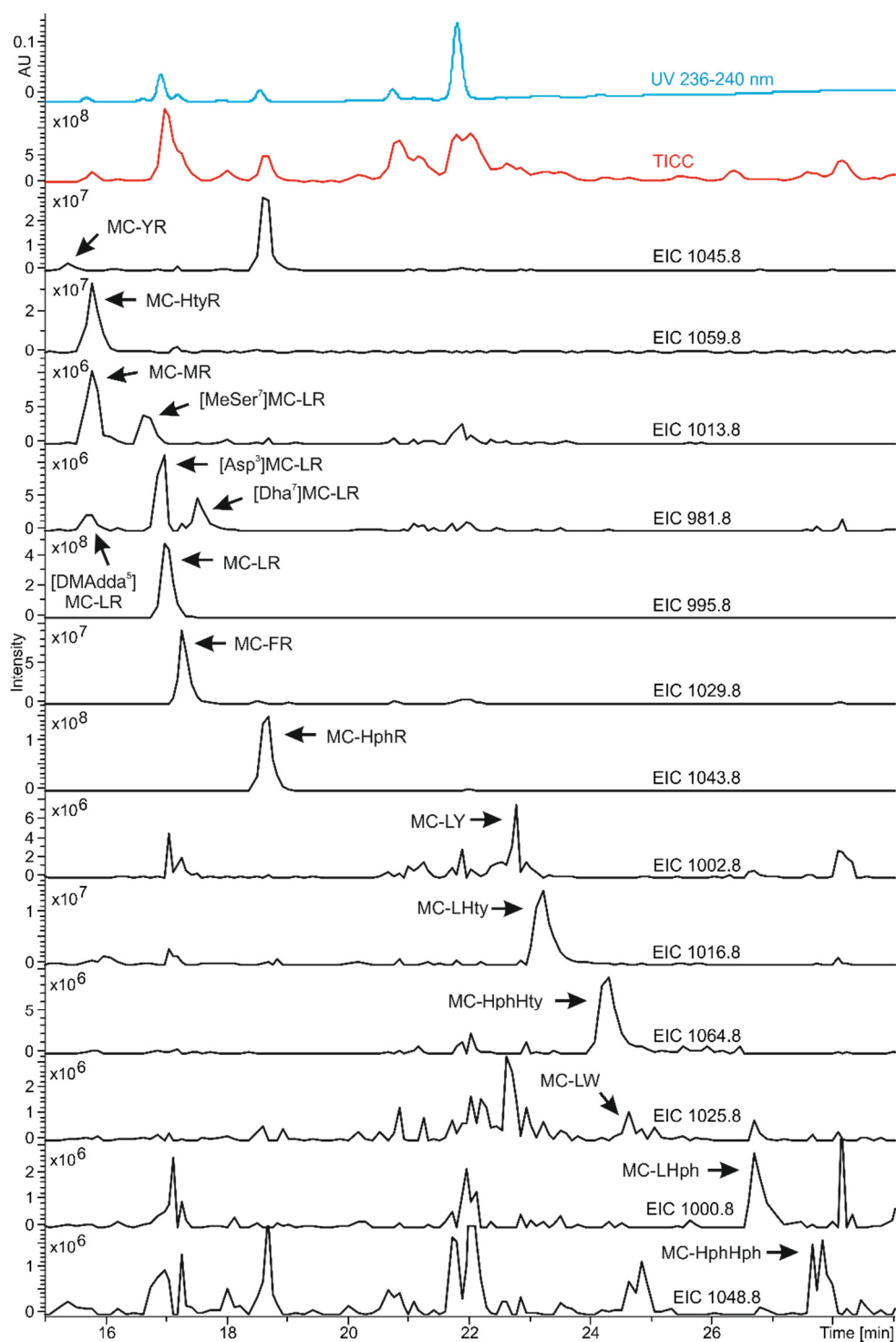


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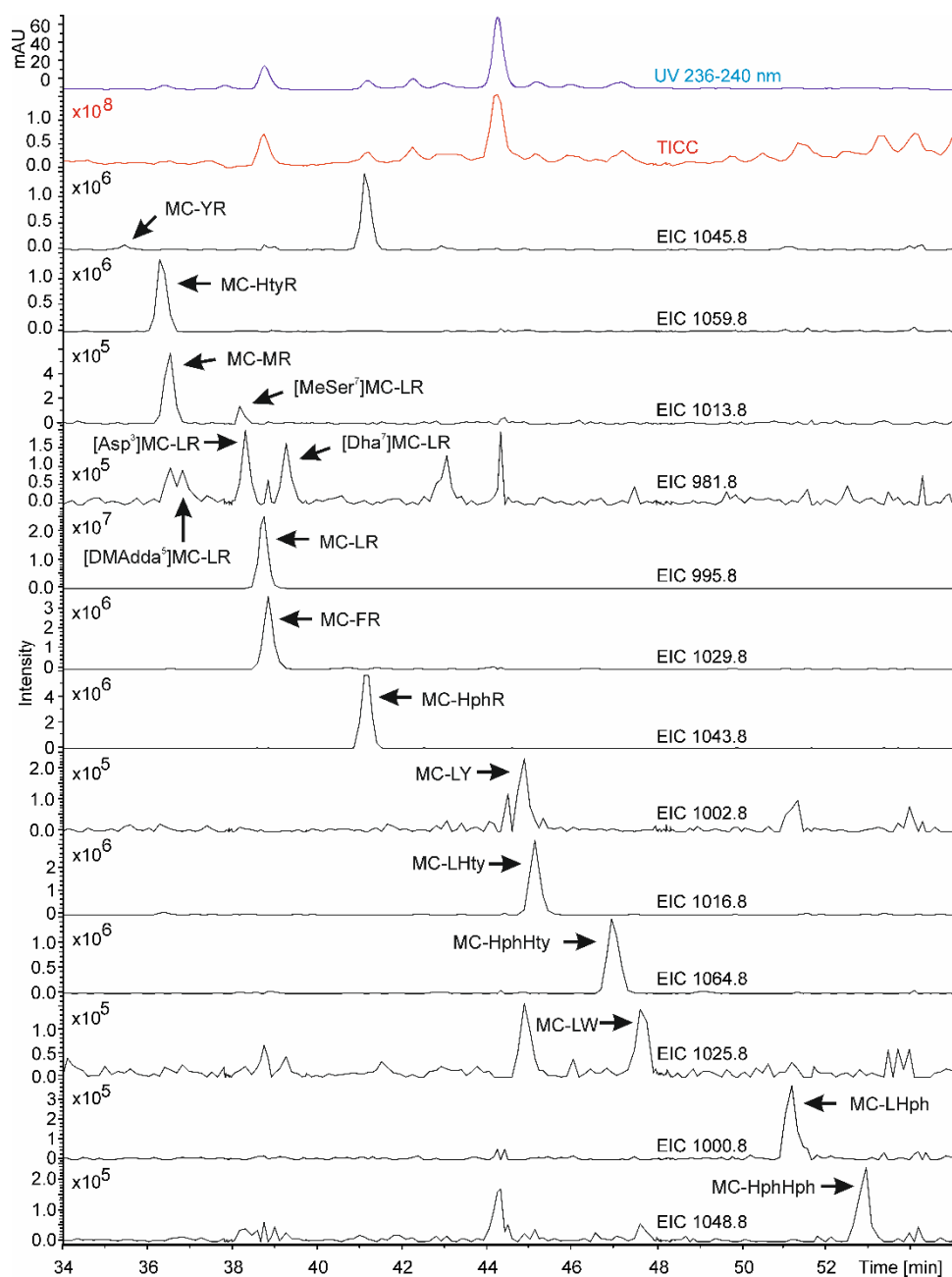


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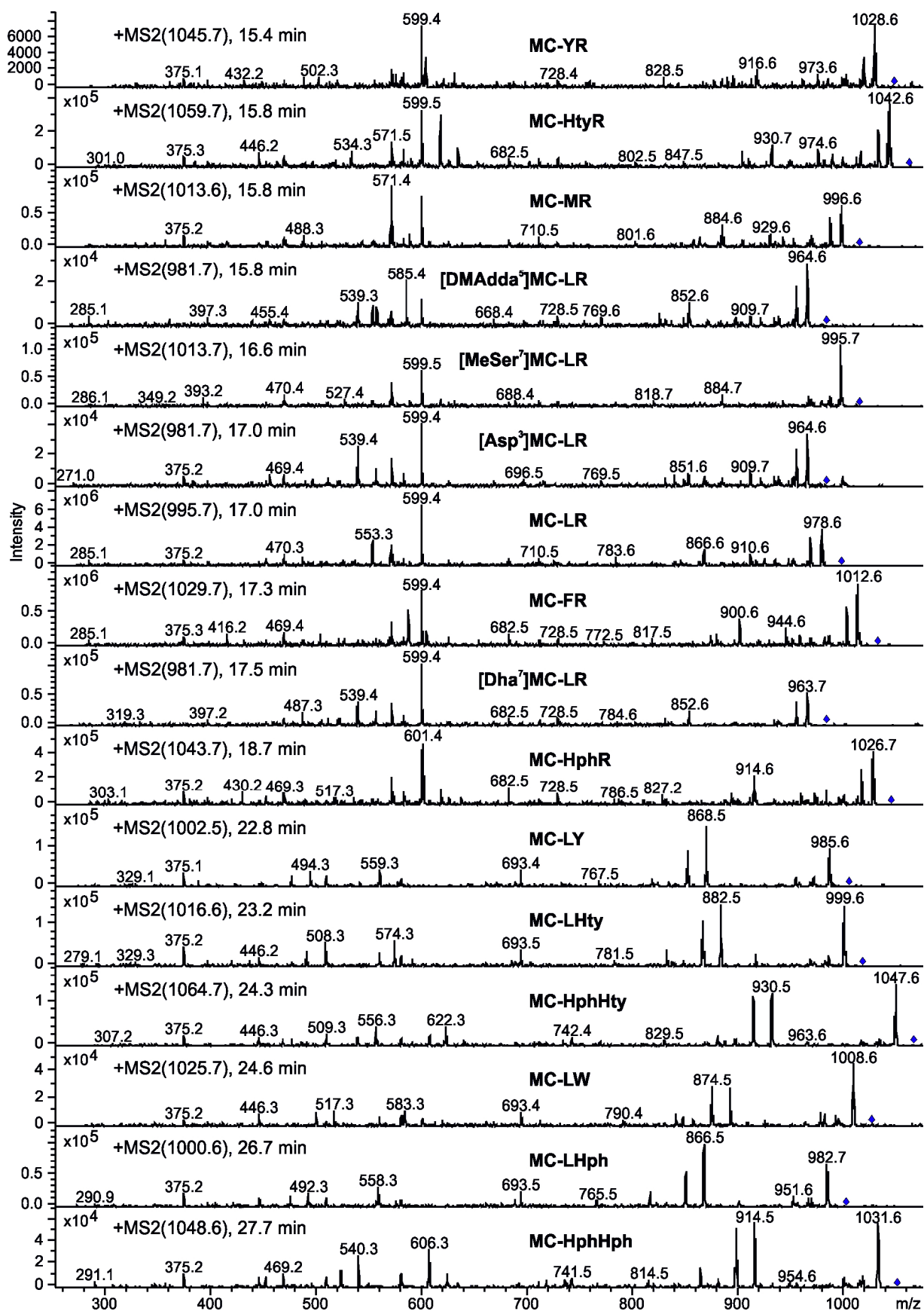


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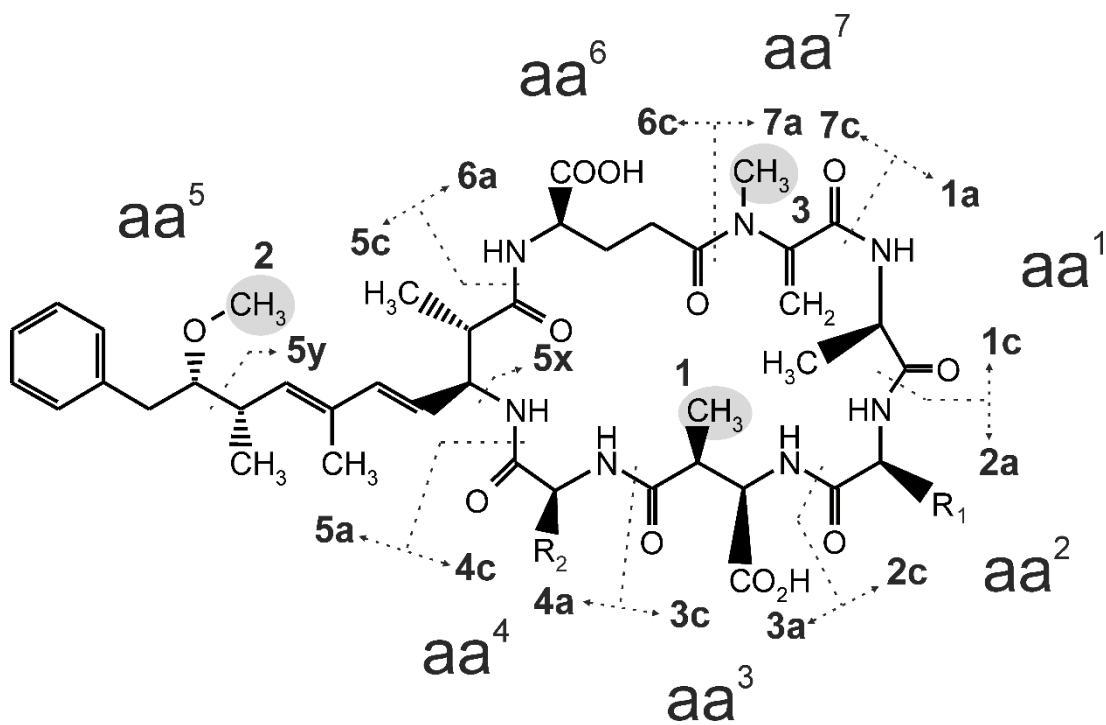


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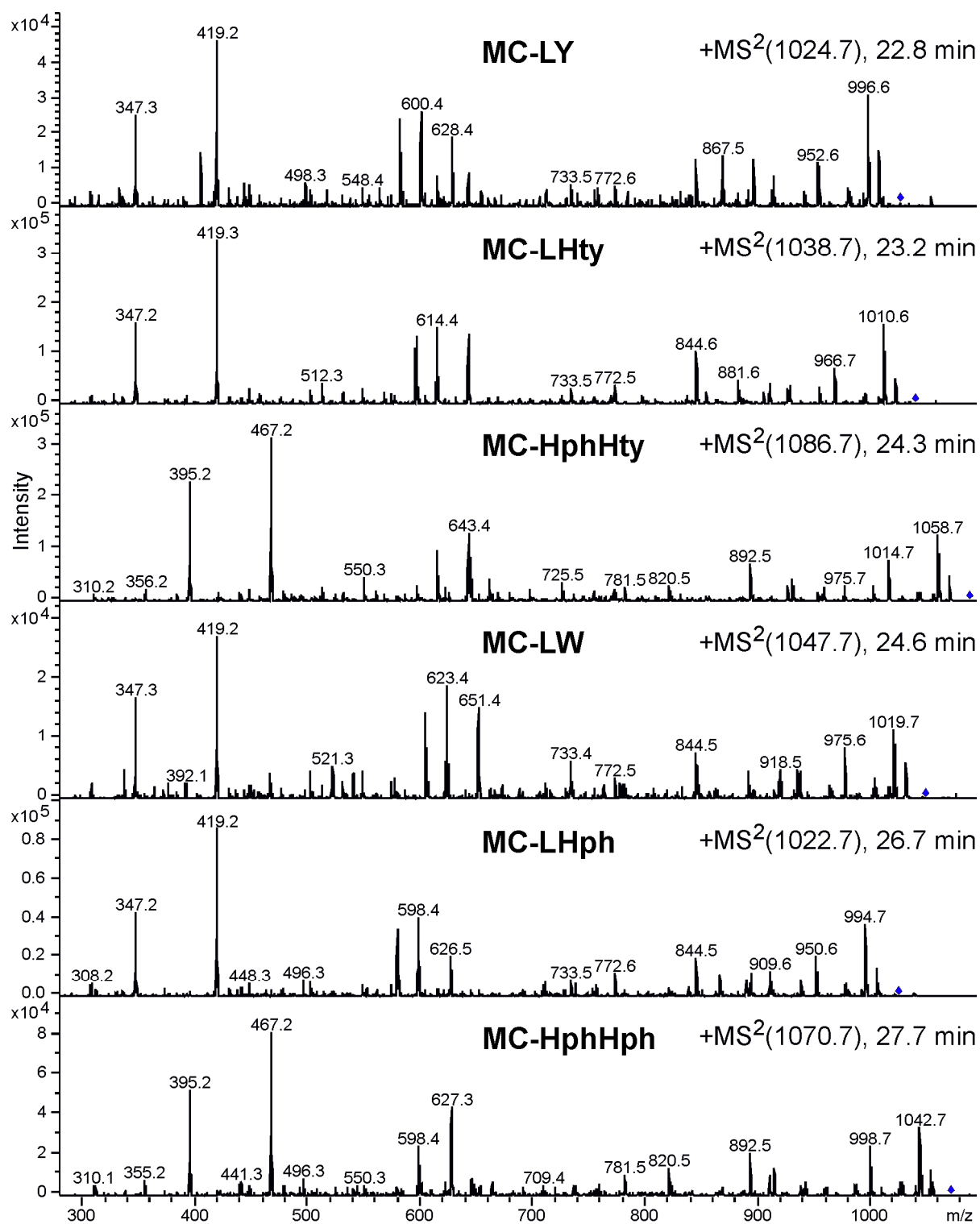


Figure S6. Product ion spectra of sodiated non Arg microcystins from *Phormidium* sp. LP904c obtained with HPLC-ITMS. Mass/charge values of protonated microcystins and their retention times (min) are marked to the spectra.

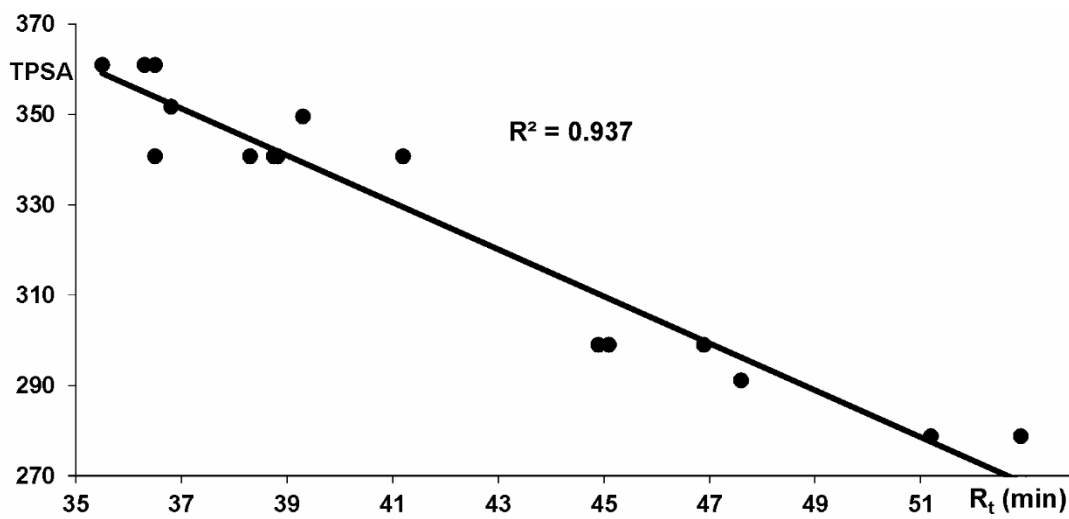


Figure S7. Effect of polar surface areas (PSA) to the retention times (R_t , min) of *Phormidium* sp. DVL1003c microcystins calculated with a topological polar surface area (TPSA) method (Ertl et al., 2000). High correlation ($R^2 = 0,937$) shows that the proposed microcystin structures fit well to the measured retention times.

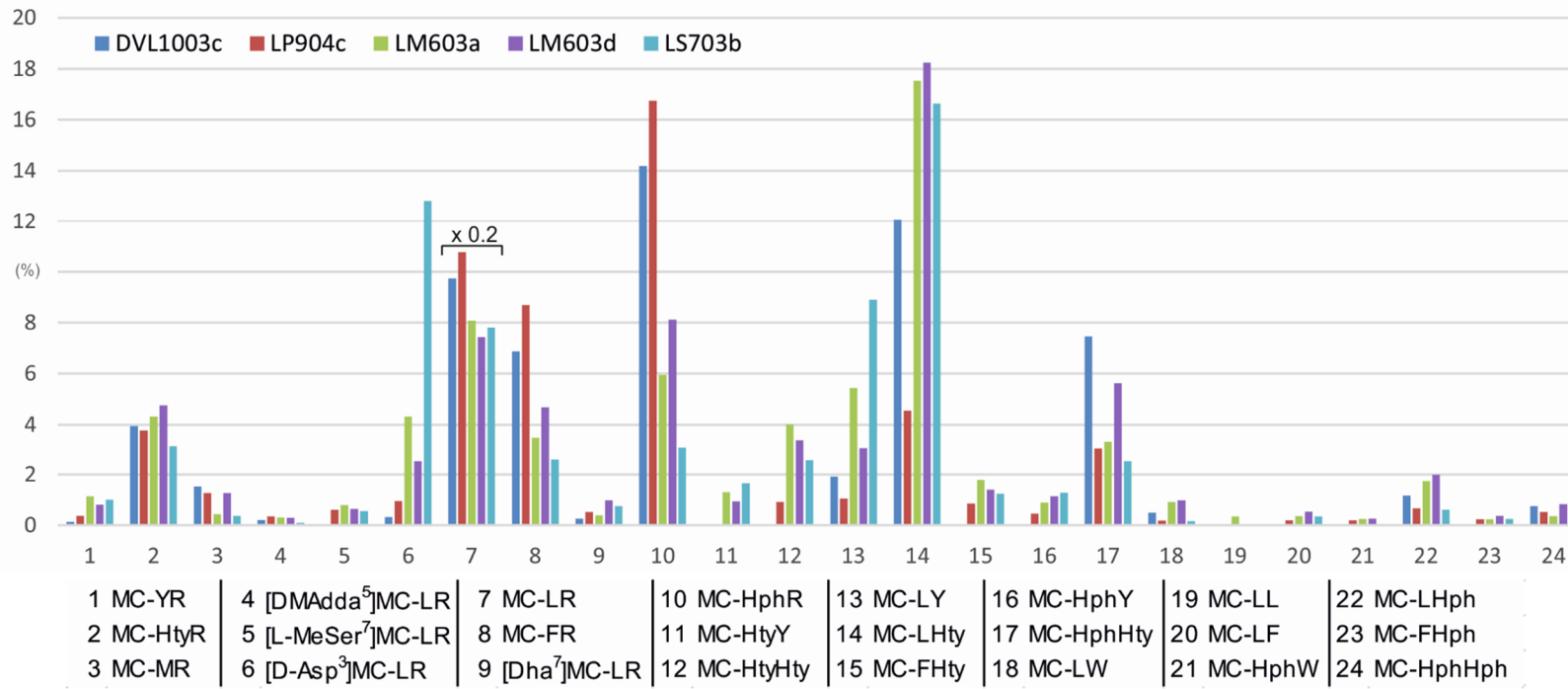


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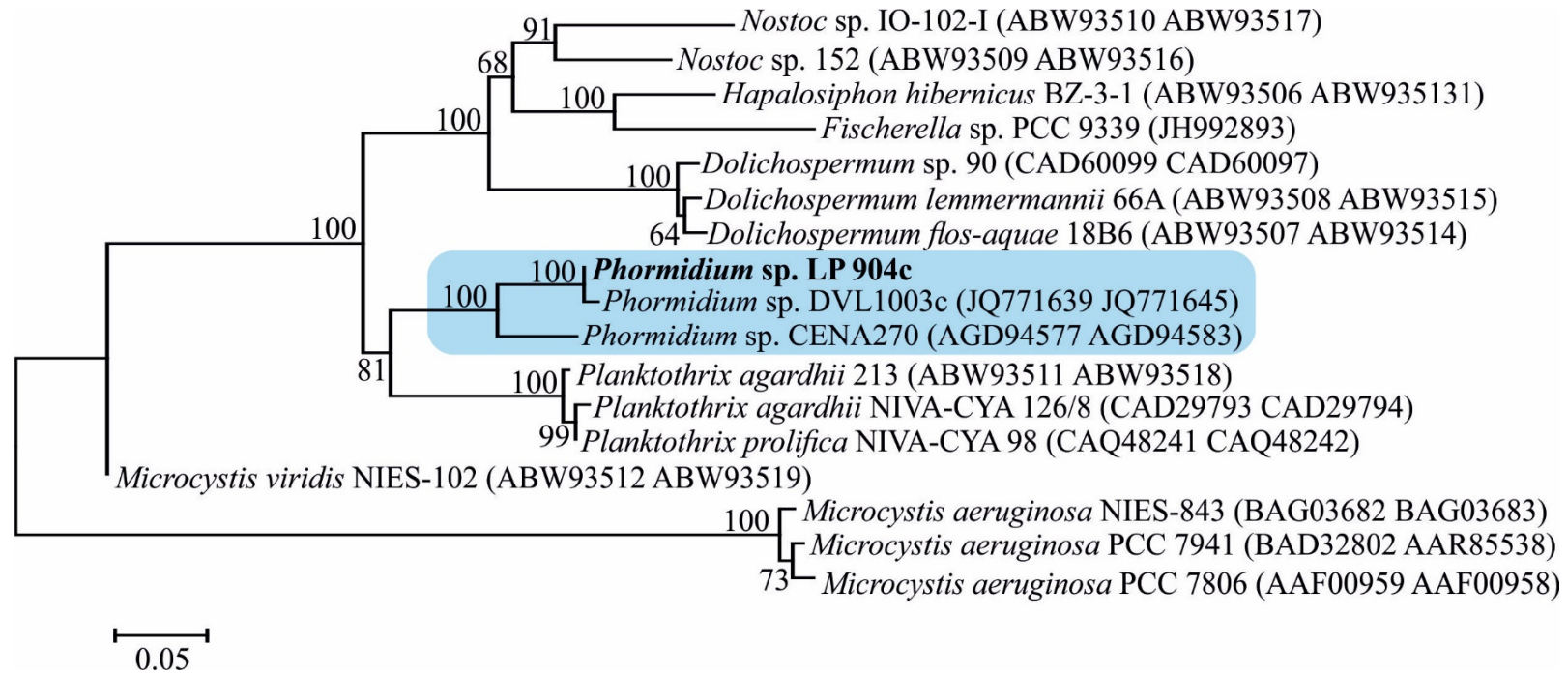


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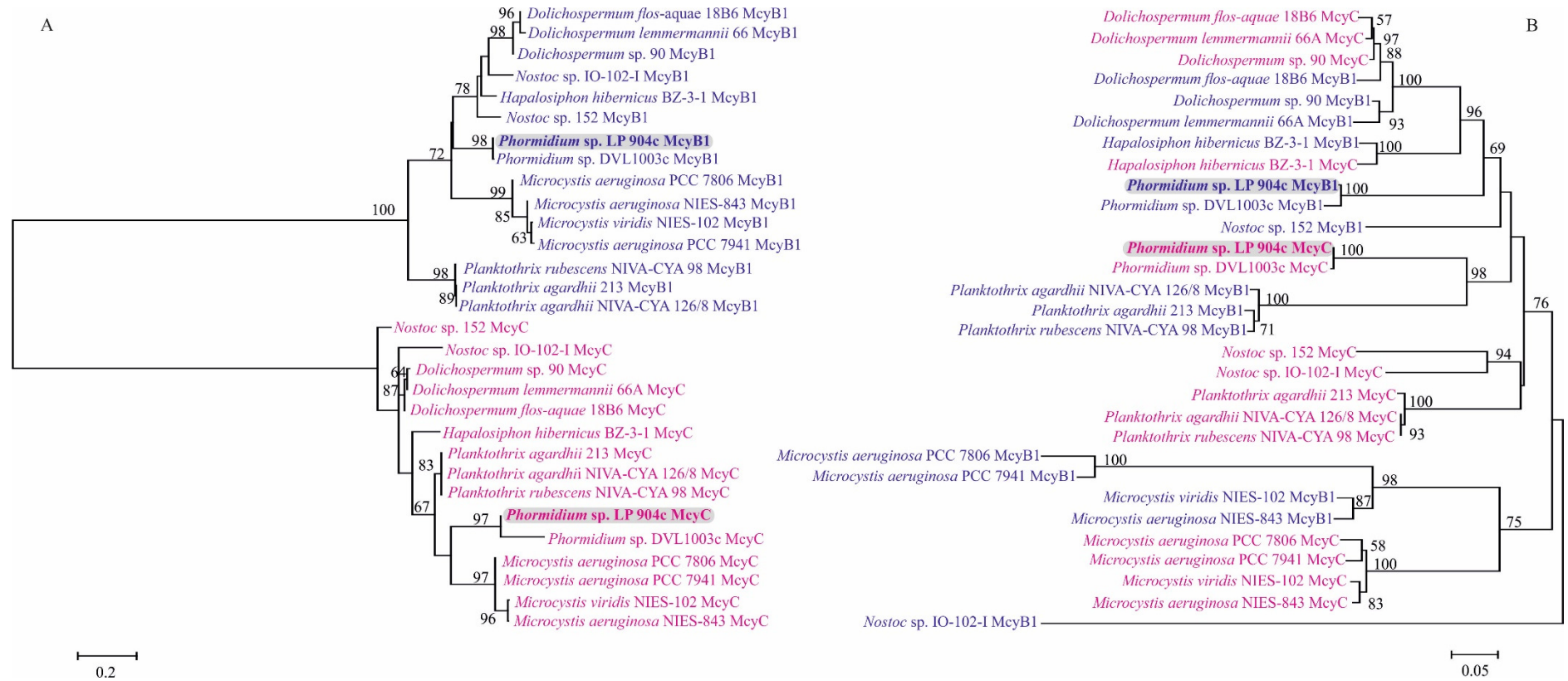


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No	CI	Protonated product ion structures		MC-LTyr		MC-LHty		MC-HphHty		MC-LW		MC-LHph		MC-HphHph	
		[peptide + H] ⁺	-Neutral	m/z	Intensity	m/z	Intensity	m/z	Intensity	m/z	Intensity	m/z	Intensity	m/z	Intensity
1	1a-7c	Ala-Aa2-Asp-Aa4-Adda-Glu-Mdha + H		1 002		1 016		1 064		1 025		1 000		1 048	
2	1a-7c	Ala-Aa2-Asp-Aa4-Adda-Glu-Mdha + H	NH ₃	985	100	999	100	1 047	85	1 008	100	983	92	1 031	100
3	1a-7c	Ala-Aa2-Asp-Aa4-Adda-Glu-Mdha + H	H ₂ O	984	80	998	38	1 046	35	1 007	53	982	70	1 030	62
4	1a-7c	Ala-Aa2-Asp-Aa4-Adda-Glu-Mdha + H	CH ₃ OH	970	9	984	6	1 032	6	993	8	968	10	1 016	14
5	1a-7c	Ala-Aa2-Asp-Aa4-Adda-Glu-Mdha + H	H ₂ O, NH ₃	967	16	981	9	1 029	11	990	15	965	14	1 013	10
6	1a-7c	Ala-Aa2-Asp-Aa4-Adda-Glu-Mdha + H	CH ₃ OH, NH ₃	953	14	967	11	1 015	10	976	16	951	13	999	11
7	1a-7c	Ala-Aa2-Asp-Aa4-Adda-Glu-Mdha + H	CH ₃ OH, H ₂ O	952	20	966	4	1 014	5	976	16	950	9	998	6
8	1a-6c	Ala-Aa2-Asp-Aa4-Adda-Glu + H	NH ₃	902	10	916	11	964	8	925	9	900	5	948	7
9	1a-6c	Ala-Aa2-Asp-Aa4-Adda-Glu + H	H ₂ O	901	9	915	5	963	3	924	4	899	5	947	4
10	1a-4c	Ala-Aa2-Asp-Aa4 + H		477	24	491	20	539	22	500	30	475	20	523	25
11	2a-4c	Aa2-Asp-Aa4 + H		406	5	420	6	468	7	429	4	404	8	452	6
12	3a-7c	MeAsp-Aa4-Adda-Glu-Mdha + H		818	13	832	21	832	0	841	10	816	12	816	0
13	3a-7c	MeAsp-Aa4 + H		293	6	307	2	307	2	316	6	291	3	291	1
14	4a-7c	Aa4-Adda-Glu-Mdha + H		689	8	703	6	703	0	712	4	687	12	687	0
15	4a-5c	Aa4-Adda + H		477	24	491	20	491	2	500	30	475	20	475	0
16	5y	C ₁₁ H ₁₇ NO-Glu-Mdha-Ala-Aa2-Asp-Aa4 + H		868	8	882	56	930	60	891	48	866	100	914	84
17	5y-5x-4c	C ₁₁ H ₁₄ O-Glu-Mdha-Ala-Aa2-Asp-Aa4 + H		851	77	865	72	913	77	874	48	849	84	897	76
18	5a-5y-4c	C ₁₁ H ₁₇ NO-Glu-Mdha-Ala-Aa2-Asp-Aa4 + H	H ₂ O	850	63	864	31	912	36	873	31	848	69	896	38
19	5a-2c	Adda-Glu-Mdha-Ala-Aa2 + H	NH ₃	693	35	693	15	741	12	693	23	693	29	741	14
20	5y-5x-3c	C ₁₁ H ₁₄ O-Glu-Mdha-Ala-Aa2-Asp + H		688	5	688	3	736	4	688	3	688	6	736	7
21	5a-1c	Adda-Glu-Mdha-Ala + H	NH ₃	580	20	580	12	580	16	580	12	580	22	580	12
22	5y-5x-2c	C ₁₁ H ₁₄ O-Glu-Mdha-Ala-Aa2 + H		559	28	559	16	607	20	559	15	559	44	607	30
23	5a-7c	Adda-Glu-Mdha + H	NH ₃	509	33	509	38	509	17	509	17	509	30	509	17
24	5y-5x-1c	C ₁₁ H ₁₄ O-Glu-Mdha-Ala + H		446	15	446	18	446	20	446	22	446	21	446	23
25	5y-5x-7c	C ₁₁ H ₁₄ O-Glu-Mdha + H		375	27	375	20	375	19	375	10	375	36	375	16
26	6a-4c	Glu-Mdha-Ala-Aa2-Asp-Aa4 + H		689	8	703	6	751	6	712	4	687	12	735	13
27	6a-3c	Glu-Mdha-Ala-Aa2-Asp + H	NH ₃	509	33	509	38	557	22	509	17	509	30	557	1
28	6a-3c	Glu-Mdha-Ala-Aa2-Asp + H	H ₂ O	508	12	508	33	556	41	508	5	508	7	556	4
29	6a-2c	Glu-Mdha-Ala-Aa2 + H		397	6	397	5	445	7	397	5	397	8	445	4
30	7a-4c	Mdha-Ala-Aa2-Asp-Aa4 + H		560	51	574	44	622	40	583	42	558	58	606	48
31	7a-3c	Mdha-Ala-Aa2-Asp + H		397	6	397	5	445	7	397	5	397	8	445	4

Table S2. Assignments, ion masses (m/z) and intensities (%) of the sodiated non Arg microcystins of the most important product ions. CI = Code for ion structure

No	CI	Sodiated product ion structures		MC-LTyr		MC-LHty		MC-HphHty		MC-LW		MC-LHph		MC-HphHph	
		[peptide + Na] ⁺	- Neutral	m/z	Intensity	m/z	Intensity	m/z	Intensity	m/z	Intensity	m/z	Intensity	m/z	Intensity
1	1a-7c	Ala-Aa2-MeAsp-Aa4-Adda-Glu-Mdha		1 024		1 038		1 086		1 047		1 022		1 070	
2	1a-7c	Ala-Aa2-MeAsp-Aa4-Adda-Glu-Mdha	NH ₃	1 007 ₉		1 021 ₁₁		1 069 ₁₁		1 030 ₁₇		1 005 ₁₁		1 053 ₇	
3	1a-7c	Ala-Aa2-MeAsp-Aa4-Adda-Glu-Mdha	H ₂ O	1 006 ₁₄		1 020 ₁₂		1 068 ₁₆		1 029 ₁₆		1 004 ₁₃		1 052 ₁₆	
4	1a-7c	Ala-Aa2-MeAsp-Aa4-Adda-Glu-Mdha	CO	996 ₅₇		1 010 ₅₂		1 058 ₅₉		1 019 ₄₆		994 ₄₈		1 042 ₄₇	
5	1a-7c	Ala-Aa2-MeAsp-Aa4-Adda-Glu-Mdha	CO ₂	980 ₇		994 ₁₀		1 042 ₁₁		1 003 ₆		978 ₈		1 026 ₉	
6	1a-7c	Ala-Aa2-MeAsp-Aa4-Adda-Glu-Mdha	CO, H ₂ O	978 ₉		992 ₄		1 040 ₉		1 001 ₇		960 ₂		1 008 ₂	
7	1a-7c	Ala-Aa2-MeAsp-Aa4-Adda-Glu-Mdha	CO ₂ , CO	952 ₃₇		966 ₂₈		1 014 ₂₉		975 ₂₆		950 ₂₃		998 ₂₈	
8	1a-4c	Ala-Aa2-MeAsp-Aa4		499 ₆		513 ₆		561 ₃		522 ₁₁		497 ₃		545 ₆	
9	1a-3c	Ala-Aa2-MeAsp	CO	308 ₅		308 ₄		356 ₈		308 ₂		308 ₆		356 ₁₈	
10	2a-7c	Aa2-MeAsp-Aa4-Adda-Glu-Mdha		953 ₁₈		967 ₂₁		1 015 ₁₈		976 ₁₀		951 ₂₀		999 ₂₀	
11	3a-1c	MeAsp-Aa4-Adda-Glu-Mdha-Ala		911 ₁₂		925 ₁₀		925 ₁₄		934 ₂₀		909 ₂₀		909 ₁₈	
12	3a-6c	MeAsp-Aa4-Adda-Glu		757 ₁₁		771 ₁₀		771 ₉		780 ₅		755 ₄		755 ₆	
13	3a-6c	MeAsp-Aa4-Adda-Glu	H ₂ O	739 ₅		753 ₈		753 ₈		762 ₁₃		737 ₈		737 ₅	
14	3a-6c	MeAsp-Aa4-Adda-Glu	CO, H ₂ O	711 ₁₅		725 ₁₁		725 ₉		734 ₁₄		709 ₇		709 ₁₁	
15	3a-5c	MeAsp-Aa4-Adda		628 ₄₂		642 ₃₉		642 ₃₄		651 ₄₆		626 ₄₆		626 ₄₆	
16	3a-5c	MeAsp-Aa4-Adda	CO	600 ₅₃		614 ₅₉		614 ₄₃		623 ₅₃		598 ₄₂		598 ₃₇	
17	4a-2c	Aa4-Adda-Glu-Mdha-Ala-Aa2		895 ₁₅		909 ₁₆		957 ₁₇		918 ₂₄		893 ₁₉		941 ₁₁	
18	4a-2c	Aa4-Adda-Glu-Mdha-Ala-Aa2	CO	867 ₂₀		881 ₁₇		929 ₂₃		890 ₇		865 ₂₅		913 ₁₈	
19	4a-7c	Aa4-Adda-Glu-Mdha		711 ₁₅		725 ₁₁		725 ₉		734 ₁₄		709 ₇		709 ₁₁	
20	4a-6c	Aa4-Adda-Glu		628 ₄₂		642 ₃₉		642 ₃₄		651 ₄₆		626 ₄₆		626 ₄₆	
21	4a-6c	Aa4-Adda-Glu	CO	600 ₅₃		614 ₅₉		614 ₄₃		623 ₅₃		598 ₄₂		598 ₃₇	
22	4a-6c	Aa4-Adda-Glu	CO, H ₂ O	582 ₃₂		596 ₃₄		596 ₁₁		605 ₂₃		580 ₃₀		580 ₂	
23	4a-5c	Aa4-Adda		499 ₆		513 ₆		513 ₆		522 ₁₁		497 ₃		497 ₂	
24	5a-3c	Adda-Glu-Mdha-Ala-Aa2-MeAsp	NH ₃	844 ₃₆		844 ₃₀		892 ₃₃		844 ₂₆		844 ₄₄		892 ₄₆	
25	5a-7c	Adda-Glu-Mdha		548 ₇		548 ₉		548 _{<1}		548 ₁₃		548 ₈		548 _{<1}	
26	6a-4c	Glu-Mdha-Ala-Aa2-MeAsp-Aa4		711 ₁₅		725 ₁₁		773 ₄		734 ₁₄		709 ₇		757 ₄	
27	6a-3c	Glu-Mdha-Ala-Aa2-MeAsp		548 ₇		548 ₉		596 ₁₁		548 ₁₃		548 ₈		596 ₃	
28	6a-3c	Glu-Mdha-Ala-Aa2-MeAsp	CO, H ₂ O	502 ₁₄		502 ₁₀		550 ₁₂		502 ₁₄		502 ₁₅		550 ₁₃	
29	6a-2c	Glu-Mdha-Ala-Aa2		419 ₁₀₀		419 ₁₀₀		467 ₁₀₀		419 ₁₀₀		419 ₁₀₀		467 ₁₀₀	
30	7a-5c	Mdha-Ala-Aa2-MeAsp-Aa4-Adda		895 ₁₅		909 ₁₆		957 ₁₇		918 ₂₄		893 ₁₉		941 ₁₁	
31	7a-5c	Mdha-Ala-Aa2-MeAsp-Aa4-Adda	CO	867 ₂₀		881 ₁₇		929 ₂₃		890 ₇		865 ₂₅		913 ₂₁	
32	7a-4c	Mdha-Ala-Aa2-MeAsp-Aa4		582 ₃₂		596 ₃₄		644 ₃₈		605 ₂₃		580 ₃₀		628 ₃₄	
33	7a-3c	Mdha-Ala-Aa2-MeAsp		419 ₁₀₀		419 ₁₀₀		467 ₁₀₀		419 ₁₀₀		419 ₁₀₀		467 ₁₀₀	
34	7a-3c	Mdha-Ala-Aa2-MeAsp	CO ₂ , CO	347 ₅₇		347 ₅₅		395 ₆₄		347 ₃₈		347 ₄₈		395 ₇₃	

Table S3. Microcystin variants, retention times (R_t), relative amounts (RA) and small diagnostic ions (from protonated MC's) with corresponding amino acids from *Phormidium* sp. LP904c by HPLC-ITMS and UPLC-QTOF. RA's were calculated from the sum of the peak areas of the extracted ion chromatograms of different ion species (H, Na, K and 2H) of microcystins. Hty = homotyrosine, Hph = homophenylalanine. Diagnostic ions of MC's No 14-16 were analyzed from sodiated MC's and additionally MC No 15 ions masses were corrected with the mass of sodiated MC No 15 exact mass.

No	Microcystin	Aa in pos		Rt (min)	RA (%)	Diagnostic ions (m/z) in MS ²				
		X	Z			Aa ²	Aa ⁴	Mdha ⁷	Glu ⁶ - Mdha ⁷	
1	MC-YR	Y	R	35,5	<1					
2	MC-HtyR	Hty	R	36,3	4	150,0913	Hty	70,0649	R	56,0489 213,0868
3	MC-MR	M	R	36,5	1					
4	[DMAdda ⁵]MC-LR	L	R	36,8	<1					
5	[MeSer ⁷]MC-LR	L	R	38,2	<1					
6	[Asp ³]MC-LR	L	R	38,3	<1					
7	MC-LR	L	R	38,8	55	86,0959	L	70,0649	R	56,0492 213,0867
8	MC-FR	F	R	38,8	9	120,0809	F	70,0653	R	56,0499 213,0864
9	[Dha ⁷]MC-LR	L	R	39,3	<1					
10	MC-HphR	Hph	R	41,2	17	134,0959	Hph	70,0645	R	56,0483 213,0869
11	MC-LY	L	Y	44,9	1					
12	MC-LHty	L	Hty	45,1	5	86,0957	L	150,0909	Hty	56,0489 213,0859
13	MC-HphHty	Hph	Hty	46,9	3	134,0959	Hph	150,0911	Hty	56,0487 213,0864
14	MC-LW	L	W	47,6	<1	86,0970	L	159,0873	W	56,0503 213,0877
15	MC-LHph	L	Hph	51,2	<1	86,0979	L	134,0950	Hph	- 213,0856
16	MC-HphHph	Hph	Hph	52,9	<1	-	-	-	-	56,0471 213,0870

Table S4. Sequence similarity of the microcystin gene cluster from *Phormidium* sp. LP904c obtained by BLASTp or Blastx.

Amino acid sequence from <i>Phormidium</i> sp. LP904c	Query length (amino acids)	Predicted function	Organism	Coverage/Identity	Accession number
McyA	2783	NRPS	<i>Fischerella</i> sp. PCC 9339	99/75	WP_017308558.1
			<i>Dolichospermum/Anabaena</i> sp. 90	100/75	WP_041458258.1
McyB	2130	NRPS	<i>Fischerella</i> sp. PCC 9339	99/76	WP_017308559.1
			<i>Dolichospermum/Anabaena</i> sp. 90	99/76	WP_015078940.1
McyC	1296	NRPS	MULTISPECIES: <i>Planktothrix</i>	99/80	WP_026787621.1
			<i>Planktothrix agardhii</i>	99/80	WP_042154169.1
McyD	3907	PKS	<i>Planktothrix prolifica</i> NIVA-CYA98	100/78	WP_026796481.1
			<i>Planktothrix agardhii</i> NIVA-CYA126/8	100/78	WP_042154180.1
McyE	3489	NRPS-PKS	<i>Planktothrix agardhii</i> NIVA-CYA56/3	100/82	WP_027255262.1
			MULTISPECIES: <i>Planktothrix</i>	100/82	WP_026795534.1
McyF	238	Aspartate racemase	<i>Microcystis aeruginosa</i> PCC9807	97/83	WP_002768078.1
			<i>Microcystis aeruginosa</i> PCC7941	97/83	WP_002776433.1
McyG	2644	NRPS-PKS	<i>Planktothrix prolifica</i> NIVA/CYA98	100/82	WP_026796479.1
			<i>Planktothrix agardhii</i> NIVA/CYA126/8	100/82	WP_042154175.1
McyH	584	ABC transporter	<i>Planktothrix agardhii</i>	99/82	WP_027250110.1
			MULTISPECIES: <i>Planktothrix</i>	99/81	WP_026787624.1
McyI	336	Dehydrogenase	<i>Microcystis aeruginosa</i> NIES88	99/77	WP_061431771.1
			<i>Microcystis aeruginosa</i> PCC9808	99/76	WP_044034182.1
McyJ	316	Methyltransferase	MULTISPECIES: <i>Planktothrix</i>	97/87	WP_026795539.1
			<i>Planktothrix agardhii</i> NIVA-CYA56/3	97/86	WP_027255267.1

Table S5. Microcystins variants detected in the strains from table 2 and 3. In highlight are the homoamino acids detected.

Genera	Strain	Microcystin variants	Amino acids in microcystin structure correspondent to the A domain		% MC*	Ref. ^a
			McyB ₁ (X)	McyC (Y)		
			<i>Phormidium</i> sp.	DVL1003c		
		MC-HphR	Hph	-	14	
		MC-LHty	-	-	12	
		MC-HphHty	Hph	Hty	7	
		MC-FR	Phe	-	7	
		MC-HtyR	Hty	-	4	
		[MeSer ⁷]MC-LR	-	-	2	
		[D-Asp ³]MC-LHty	-	Hty	2	
		MC-LHph	-	Hph	1	
		MC-HphHph	Hph	Hph	<1	
		MC-LW	-	Trp	<1	
		[D-Asp ³]MC-LR	-	-	<1	
		[Dha ⁷]MC-LR	-	-	<1	
		[DMAdda ⁵]MC-LR	-	-	<1	
		MC-YR	Tyr	-	<1	
<i>Planktothrix agardhii</i>	CYA 126/8	[D-Asp ³]MC-RR	Arg	-	92	3
		[D-Asp ³]MC-LR	-	-	7	
<i>Planktothrix agardhii</i>	213	[D-Asp ³]MC-RR	Arg	-	84	4
		[D-Asp ³]MC-LR	-	-	15	
		[Asp ³ , Dha ⁷]MC-LR	-	-	<1	
<i>Planktothrix agardhii</i>	NIVA-CYA56/3	Dm-MC-LR	-	-	Ni	5
		Dm-MC-RR	Arg	-	Ni	
		Dm-MC-YR	Tyr	-	Ni	
<i>Planktothrix prolifica</i>	NIVA-CYA 98	[Dha ⁷]MC-LR	-	-	Ni	6
		[Dha ⁷]MC-RR	Arg	-	Ni	
<i>Planktothrix rubescens</i>	NIVA-CYA 407	Dm-MC-LR	-	-	Ni	5

		Dm-MC-RR	Arg	-	Ni	
		Dm-MC-HtyR	Hty	-	Ni	
<i>Dolichospermum</i> sp.	90	MC-LR	-	-	55	4
		[D-Asp ³]MC-LR	-	-	34	
		MC-RR	Arg	-	5	
		[D-Asp ³]MC-RR	Arg	-	2	
		MC-HilR	Hil	-	1.5	
		[D-Asp ³]MC-HilR	Hil	-	<1	
		[MeSer ⁷]MC-LR	-	-	<1	
		[DMAdda ⁵]MC-LR	-	-	<1	
		[D-Asp ³ , MeSer ⁷]MC-LR	-	-	<1	
		[Dha ⁷]MC-LR	-	-	<1	
<i>Dolichospermum flos-aquae</i>	18B6	[D-Asp ³ , Dha ⁷]MC-RR	Arg	-	79	4
		Demethyl- MC-RR	Arg	-	20	
		[X]MC-RR	Arg	-	1	
		MC-XR	X	-	<1	
<i>Dolichospermum lemmermannii</i>	66 A	[Dha ⁷]MC-HtyR	Hty	-	56	4
		[D-Asp ³ , Dha ⁷]MC-XR	X	-	29	
		[L-Ser ⁷]MC-HtyR	Hty	-	4	
		[D-Asp ³ , L-Ser ⁷]MC-HtyR	Hty	-	2	
		[Dha ⁷]MC-LR	-	-	2	
		[Dha ⁷]MC-HphR	Hph	-	2	
		[D-Asp ³ , Dha ⁷]MC-LR	-	-	1	
		[DMAdda ⁵ , (M)dha ⁷]MC-(H)tyR	Hty/Ty	-	<1	
			r			
		[D-Asp ³ , Dha ⁷]MC-XR	X	-	<1	
		[X]MC-HtyR	Hty	-	<1	
		[D-Asp ³]MC-XR	X	-	<1	
		[X]MC-(H)tyR	Hty/Ty	-	<1	
			r			
		MC-XR	X	-	<1	
		[X]MC-X/HtyR	X/Hty	-	<1	
		[X]MC-(H)tyR	Hty/Ty	-	<1	
			r			
		MC-HtyR	Hty	-	<1	

		[X, L-Ser ⁷]MC-LR	-	-	<1	
		[D-Asp ³]MC-XR	X	-	<1	
		Demethyl-[L-Ser ⁷]MC-LR	-	-	<1	
		[L-Ser ⁷]MC-LR	-	-	<1	
		[Dha ⁷]MC-FR	Phe	-	<1	
		[D-Asp ³ , Dha ⁷]MC-FR	Phe	-	<1	
		[X]MC-LR	-	-	<1	
		[D-Asp ³ , Dha ⁷]MC-HphR	Hph	-	<1	
<i>Nostoc</i> sp.	152	[ADMAdda ⁵]MC-LR	-	-	44	4, 7
		[ADMAdda ⁵]MC-LHar	-	Har	40	
		[ADMAdda ⁵]MC-HilR	Hil	-	1.7	
		[ADMAdda ⁵]MC-HilHar	Hil	Har	1	
		[ADMAdda ⁵ , Dha ⁷]MC-LR	-	-	<1	
		[Ser ¹ , D-Asp ³ , ADMAdda ⁵]MC-LR	-	-	<1	
		[D-Asp ³ , ADMAdda ⁵ , Dha ⁷]MC-LR	-	-	<1	
		[DMAdda ⁵]MC-LR	-	-	<1	
		[DMAdda ⁵]MC-LHar	-	Har	<1	
		[D-Asp ³ , DMAdda ⁵]MC-LR	-	-	<1	
		[ADMAdda ⁵]MC-XR	X	-	<1	
		[D-Asp ³ , ADMAdda ⁵]MC-VR	Val	-	<1	
		[D-Asp ³ , ADMAdda ⁵ , Dha ⁷]MC-HilR	Hil	-	<1	
<i>Nostoc</i> sp.	IO-102-I	[ADMAdda ⁵]MC-LR	-	-	82	4, 8
		[ADMAdda ⁵]MC-XR	X	-	4	
		[D-Asp ³ , ADMAdda ⁵]MC-LR	-	-	3	
		[DMAdda ⁵]MC-LR	-	-	2	
		MC-XR	X	-	1	
		MC-XR	X	-	1	
		[(X), ADMAdda ⁵]MC-(F)R	Phe	-	1	
		MC-XR	X	-	1	
		[(X), DMAdda ⁵]MC-(Hil)R	Hil	-	1	
		[DMAdda ⁵]MC-HilR	Hil	-	<1	
		[ADMAdda ⁵]MC-XR	X	-	<1	
		[ADMAdda ⁵]MC-XR	X	-	<1	
		[ADMAdda ⁵]MC-YR	Tyr	-	<1	
		[ADMAdda ⁵]MC-XR	X	-	<1	
		[X]MC-LR	-	-	<1	
		MC-XR	X	-	<1	

		[X]MC-LR	-	-	<1	
		MC-XR	X	-	<1	
<i>Fischerella</i> sp.	PCC9339	MC-LR	-	-	Ni	9
<i>Hapalosiphon hibernicus</i>	BZ-3-1	MC-LA	-	Ala	70	4
		[D-Asp ³]MC-LA	-	Ala	16	
		MC-RA	Arg	Ala	7	
		[D-Asp ³]MC-RA	Arg	Ala	2	
		MC-VA	Val	Ala	1	
		[D-Asp ³ , DMAdda ⁵]MC-LA	-	Ala	1	
		[Dha ⁷]MC-LA	-	Ala	1	
		MC-LL	-	Leu	<1	
		[D-Asp ³]MC-VA	Val	Ala	<1	
		[D-Asp ³]MC-LV	-	Val	<1	
		MC-LV	-	Val	<1	
<i>Microcystis aeruginosa</i>	PCC 7806	[D-Asp ³]MC-LR	-	-	52	4
		MC-LR	-	-	46	
		[MeSer ⁷]MC-LR	-	-	<1	
		[D-Asp ³ , Dha ⁷]MC-LR	-	-	<1	
		[Dha ⁷]-MC-LR	-	-	<1	
		[D-Asp ³ , MeSer ⁷]MC-LR	-	-	<1	
<i>Microcystis aeruginosa</i>	FCY-28	Ni	Ni	Ni	Ni	10
<i>Microcystis aeruginosa</i>	FCY-26	Ni	Ni	Ni	Ni	10
<i>Microcystis aeruginosa</i>	UV027	MC-RR	Arg	-	100	11
<i>Microcystis aeruginosa</i>	K139	[Dha ⁷]MC-LR	-	-	76	12
		[Asp ³ , Dha ⁷]MC-LR	-	-	24	
<i>Microcystis aeruginosa</i>	DIANCHI905	Ni	Ni	Ni	Ni	13
<i>Microcystis aeruginosa</i>	PCC 9807	Ni	Ni	Ni	Ni	14
<i>Microcystis aeruginosa</i>	PCC 7941	Ni	Ni	Ni	Ni	14

MC-XR	X	-	<1
MC-XR	X	-	<1
MC-XR	X	-	<1
MC-XR	X	-	<1
MC-XR	X	-	<1
MC-XR	X	-	<1
MC-XR	X	-	<1
MC-XR	X	-	<1
MC-XR	X	-	<1
MC-XR	X	-	<1
MC-XR	X	-	<1
MC-XR	X	-	<1
MC-XR	X	-	<1
MC-XR	X	-	<1
MC-XR	X	-	<1
MC-XR	X	-	<1
MC-XR	X	-	<1

X. MC contains an unknown amino acid or the overall amino acid content is not known. * % MC. Amounts of microcystin detected. Ni. No information.

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