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Table S1. Microcystin (MC) congeners produced by reported cyanobacterial strains [a].

Cyanobacterial Strain	Microcystins Identified	Number of MCs [b]	Position Two [c]	Position Four [d]	Other Modifications	Potential MCs [e]	Reference(s)
Anabaena 18B6	[Dha^7] MC-RR; [Asp^3, Dha^7] MC-RR; Unidentified MCs × 2	4	Arg	Arg	Position 3 × 2 Position 7 × 1	-	[1]
Anabaena 60	MC-LR; [Asp^3] MC-LR; MC-RR; [Asp^3] MC-RR	4	Leu Arg	Arg	Position 3 × 2	4	[2]
Anabaena 66	[Dha^7] MC-HphR; [Dha^7] MC-HtyR; [Ser^7] MC-HtyR; [Asp^3, Dha^7] MC-HtyR	4	Hph Hty	Arg	Position 3 × 2 Position 7 × 2	8	[2,3]
Anabaena 66A	[Dha^7] MC-LR; [Ser^7] MC-LR; [Asp^3, Ser^7] MC-LR; [Asp^3, Dha^7] MC-LR; [Dha^7] MC-FR; [Asp^3, Dha^7] MC-FR; [Dha^7] MC-HphR; [Asp^3, Dha^7] MC-HphR; MC-HtyR; [Dha^7] MC-HtyR; [Ser^7] MC-HtyR; [Asp^3, Dha^7] MC-HtyR; [Asp^3, Ser^7] MC-HtyR; Unidentified MCs × 20	33	Leu Phe Hph Hty	Arg	Position 3 × 2 Position 7 × 3	-	[1]
Anabaena 90	MC-LR; [Asp^3] MC-LR; [DMAdda^5] MC-LR; [Dha^7] MC-LR; [MeSer^7] MC-LR; [Asp^3, MeSer^7] MC-LR; MC-HilR; [Asp^3] MC-HilR; MC-RR; [Asp^3] MC-RR; [Dha^7] MC-RR	11	Leu Hil Arg	Arg	Position 3 × 2 Position 5 × 2 Position 7 × 3	36	[1,2,4,5]
Anabaena 141	MC-LR; [Asp^3] MC-LR; MC-RR; [Asp^3] MC-RR	4	Leu Arg	Arg	Position 3 × 2	4	[2]
Anabaena 186	[Dha^7] MC-E(OMe)E(OMe); [Ser^7] MC-E(OMe)E(OMe); [Asp^3, Dha^7] MC-E(Ome)E(OMe); [Asp^3, Ser^7] MC-E(OMe)E(OMe); [Dha^7] MC-EE(OMe); [Ser^7] MC-EE(OMe); [Asp^3, Dha^7] MC-EE(OMe)	7	Glu Glu(OMe)	Glu(OMe)	Position 3 × 2 Position 7 × 2	8	[6]
Anabaena 202 A1	[Dha^7] MC-LR; [Asp^3, Dha^7] MC-LR; [Ser^7] MC-LR; [Asp^3, Ser^7] MC-HilR; [Dha^7] MC-RR; [Asp^3, Dha^7] MC-RR; [Ser^7] MC-RR	7	Leu Hil Arg	Arg	Position 3 × 2 Position 7 × 2	12	[2,7]

Table S1. *Cont.*

Anabaena 202 A2	[Dha^7] MC-LR; [Asp^3, Dha^7] MC-LR; [Ser^7] MC-LR; [Dha^7] MC-RR; [Asp^3, Dha^7] MC-RR; [Ser^7] MC-RR	6	Leu Arg	Arg	Position 3 × 2 Position 7 × 2	8	[2,5,7]
Anabaena flos-aquae CYA83/1	MC-LR; [Asp^3] MC-LR; MC-RR; [Asp^3] MC-RR; [Glu(OMe)^6] MC-LR; [Asp^3, Glu(OMe)^6] MC-LR	6	Leu Arg	Arg	Position 3 × 2 Position 6 × 2	8	[8]
Anabaena flos-aquae NRC 525-17	MC-LR; [Asp^3] MC-LR; MC-HtyR; [Asp^3] MC-HtyR	4	Leu Hty	Arg	Position 3 × 2	4	[9]
Fischerella CENA161	MC-LR	1	Leu	Arg		1	[10]
Hapalosiphon hibernicus BZ-3-1	MC-VA; [Asp^3] MC-VA; MC-LA; [Asp^3] MC-LA; [Dha^7] MC-LA; [Asp^3, $DMAdda^5$] MC-LA; MC-LV; MC-LL; MC-RA; [Asp^3] MC-RA	10	Val Leu Arg	Ala Val Leu	Position 3 × 2 Position 5 × 2 Position 7 × 2	72	[1]
Microcystis CAWBG11	MC-LA; [Asp^3] MC-LA; MC-FA; [Asp^3] MC-FA; MC-YA; MC-WA; [Asp^3] MC-WA; MC-RA; [Asp^3] MC-RA; MC-RAba; [Asp^3] MC-RAba; MC-RL; MC-LAba; MC-FAba; MC-WAba; MC-LL; MC-FL; MC-WL; MC-LR; [Asp^3] MC-LR; MC-FR; [Asp^3] MC-FR; MC-YR; MC-WR; [Asp^3] MC-WR; MC-RR; [Asp^3] MC-RR	27	Leu Phe Tyr Trp Arg	Ala Aba Leu Arg	Position 3 × 2	40	This Study
Microcystis HUB 5-2-4	MC-LR; dmMC-LR; MC-RR; dmMC-RR; MC-YR	5	Leu Tyr Arg	Arg	DM × 2	6	[11]
Microcystis MB-K	MC-LR; dmMC-LR; MC-YR; dmMC-YR	4	Leu Tyr	Arg	DM × 2	4	[12]
Microcystis MG-K	MC-RR; dmMC-RR; MC-WR	3	Arg Trp	Arg	DM × 2	4	[12]

Table S1. *Cont.*

Microcystis PCC7806	MC-LR; [Asp^3] MC-LR; [Dha^7] MC-LR; [MeSer^7] MC-LR; [Asp^3, Dha^7] MC-LR; [Asp^3, MeSer^7] MC-LR; Unidentified MCs × 5	11	Leu	Arg	Position 3 × 2 Position 7 × 3	-	[1,13]
Microcystis PCC7813	MC-LR; [Asp^3] MC-LR	2	Leu	Arg	Position 3 × 2	2	[11]
Microcystis aeruginosa	MC-LR	1	Leu	Arg		1	[14]
Microcystis aeruginosa B2666	MC-LA; [Asp^3] MC-LA; MC-LAba; [Asp^3] MC-LAba; MC-LL; MC-LF; MC-LR; [MeSer^7] MC-LR	8	Leu	Ala Aba Leu Phe Arg	Position 3 × 2 Position 7 × 2	20	[15]
Microcystis aeruginosa CALU972	[Dha^7] MC-LR; [Asp^3, Dha^7] MC-LR; [Dha^7] MC-RR; [Asp^3, Dha^7] MC-RR; [Dha^7] MC-YR	5	Leu Tyr Arg	Arg	Position 3 × 2 Position 7 × 1	6	[16]
Microcystis aeruginosa K-139	[Dha^7] MC-LR; [Asp^3, Dha^7] MC-LR	2	Leu	Arg	Position 3 × 2 Position 7 × 1	2	[5]
Microcystis aeruginosa MK10.10	MC-VR; MC-LR; MC-HilR	3	Val Leu Hil	Arg		3	[17]
Microcystis aeruginosa NIES90	MC-LR; MC-YR; MC-RR	3	Leu Tyr Arg	Arg		3	[18]

Table S1. *Cont.*

Microcystis aeruginosa PCC7820	MC-LR; dmMC-LR; [Glu(OMe)^{6}] MC-LR; MC-LF; dmMC-LF; MC-LW; dmMC-LW; MC-LL; MC-LM; MC-LY	10	Leu	Arg Phe Leu Met Trp Tyr	DM × 2 Position 6 × 2	24	[19]
Microcystis aeruginosa TN-2	MC-LR; MC-FR; [Asp^{3}] MC-FR; MC-WR; [Asp^{3}] MC-WR; MC-RR; MC-RA	7	Leu Phe Trp Arg	Arg Ala	Position 3 × 2	16	[20]
Microcystis aeruginosa UAM1303	MC-LR; [Asp^{3}] MC-LR; [MeSer^{7}] MC-LR; MC-HilR; MC LY; MC-LF; MC-LW	7	Leu Hil	Arg Tyr Phe Trp	Position 3 × 2 Position 7 × 2	32	[21]
Microcystis aeruginosa UTEX2666	MC-LA; [Asp^{3}] MC-LA; MC-LAba; [Asp^{3}, Glu(OMe)^{6}] MC-LAba; MC-LR; [Asp^{3}] MC-LR; didmMC-LR	7	Leu	Ala Aba Arg	Position 3 × 2 Position 6 × 2	24	[21]
Microcystis aeruginosa UTEX2670	MC-YA; MC-YL; MC-YM; MC-YM(O); Unidentified MC	5	Tyr	Ala Leu Met Met(O)		-	[21]
Microcystis aeruginosa UV-006	MC-LA; MC-LAba; MC-LV; MC-LL; MC-LR; [Asp^{3}] MC-LR; Unidentified MCs × 2	8	Leu	Ala Aba Val Leu Arg	Position 3 × 2	≥10	[22]
Microcystis novacekii UAM250	MC-LR; MC-YR; MC-RR	3	Leu Tyr Arg	Arg		3	[23]

Table S1. *Cont.*

Microcystis viridis NIES102	[Asp^{3}] MC-LR; [Dha^{7}] MC-LR; [Ser^{1}, Asp^{3}, Dha^{7}] MC-LR; MC-HilR; MC-FR; MC-YR; [Asp^{3}] MC-YR; MC-HtyR; MC-WR; [Asp^{3}] MC WR; MC-RR; [Asp^{3}] MC-RR; Unidentified MCs ×35	47	Leu Hil Phe Tyr Hty Trp Arg	Arg	Position 1 ×2 Position 3 ×2 Position 7 ×2	-	[1]
Nostoc 152	[Asp^{3}, ADMAdda^{5}] MC-VR; [DMAdda^{5}] MC-LR; [ADMAdda^{5}] MC-LR; [Mdhb^{7}] MC-LR; [Ser^{1}, ADMAdda^{5}] MC-LR; [Ser^{1}, Asp^{3}, ADMAdda^{5}] MC LR; [Asp^{3}, DMAdda^{5}] MC-LR; [ADMAdda^{5}, MeSer^{7}] MC-LR; [ADMAdda^{5}, Dha^{7}] MC-LR; [Asp^{3}, ADMAdda^{5}, Dha^{7}] MC-LR; [ADMAdda^{5}] MC-LHar; [DMAdda^{5}] MC-LHar; [Asp^{3}, ADMAdda^{5}] MC-LHar; [ADMAdda^{5}] MC-HilR; [ADMAdda^{5}] MC-HilHar; [Asp^{3}, ADMAdda^{5}] MC-HilR; Unidentified MCs ×9	25	Val Leu Hil	Arg Har	Position 1 ×2 Position 3 ×2 Position 5 ×3 Position 7 ×3	≥216	[1,24–26]
Nostoc IO-102-I	[ADMAdda^{5}] MC-LR; [DMAdda^{5}] MC-LR; [Asp^{3}, ADMAdda^{5}] MC LR; [DMAdda^{5}] MC-HilR; [ADMAdda^{5}] MC-YR; Unidentified MCs ×15	20	Leu Hil Tyr	Arg	Position 3 ×2 Position 5 ×2	-	[1,27]
Nostoc species	[Asp^{3}, ADMAdda^{5}, Dhb^{7}] MC-LR; [Asp^{3}, ADMAdda^{5}, Dhb^{7}] MC HtyR; [Asp^{3}, ADMAdda^{5}, Dhb^{7}] MC-RR	3	Leu Hty Arg	Arg	Position 3 ×1 Position 5 ×1 Position 7 ×1	3	[28]
Planktothrix Max06	[Asp^{3}, DMAdda^{5}] MC-HtyR; [Asp^{3}] MC-YR; [Asp^{3}, MeSer^{7}] MC-HtyR; [Asp^{3}, MeSer^{7}] MC-LR; [Asp^{3}] MC-HtyR; [Asp^{3}] MC-LR; [Asp^{3}, Dha^{7}] MC-LR; [Asp^{3}] MC-HilR; [Asp^{3}, Glu(OMe)^{6}] MC-HtyR; [Asp^{3}] MC-HphR; [Asp^{3}, Glu(OMe)^{6}] MC-LR	11	Leu Hil Tyr Hty Hph	Arg	Position 3 ×1 Position 5 ×2 Position 6 ×2 Position 7 ×3	60	[29]

Table S1. *Cont.*

Planktothrix agardhii	[Asp^3] MC-LR; [Asp^3] MC-RR	2	Leu Arg	Arg	Position 3 × 1	2	[30]
Planktothrix agardhii 213	[Asp^3] MC-LR; [Asp^3, Dha^7] MC-LR; [Asp^3] MC-RR	3	Leu Arg	Arg	Position 3 × 1 Position 7 × 2	4	[1]
Planktothrix agardhii CYA 56/3	[Asp^3] MC-LY; [Asp^3] MC-LR; [Asp^3] MC-HtyR; [Asp^3] MC-RR; [Asp^3, Dha^7] MC-RR; [Asp^3] MC-RY; [Asp^3, Dha^7] MC-RY; [Asp^3, $DMAdda^5$] MC-RY; Unidentified MC	9	Leu Hty Arg	Tyr Arg	Position 3 × 1 Position 5 × 2 Position 7 × 2	≥24	[31]
Planktothrix agardhii CYA 137	[Asp^3] MC-LY; [Asp^3] MC-LR; [Asp^3] MC-HtyR; [Asp^3] MC-RR; [Asp^3, Dha^7] MC-RR; [Asp^3] MC-RY; [Asp^3, Dha^7] MC-RY; [Asp^3, $DMAdda^5$] MC-RY; Unidentified MC	9	Leu Hty Arg	Tyr Arg	Position 3 × 1 Position 5 × 2 Position 7 × 2	≥24	[31]
Planktothrix agardhii CYA 532	[Asp^3] MC-LY; [Asp^3] MC-LR; [Asp^3] MC-HtyR; [Asp^3] MC-RR; [Asp^3, Dha^7] MC-RR; [Asp^3] MC-RY; [Asp^3, Dha^7] MC-RY; [Asp^3, $DMAdda^5$] MC-RY; Unidentified MC	9	Leu Hty Arg	Tyr Arg	Position 3 × 1 Position 5 × 2 Position 7 × 2	≥24	[31]
Planktothrix agardhii CYA 537	[Asp^3] MC-LR; [Asp^3] MC-RR; [Asp^3, Dha^7] MC-RR; Unidentified MC	4	Leu Arg	Arg	Position 3 × 1 Position 7 × 2	≥4	[31]
Planktothrix agardhii CYA 544	[Asp^3] MC-LR; [Asp^3] MC-RR; [Asp^3, Dha^7] MC-RR; Unidentified MC	4	Leu Arg	Arg	Position 3 × 1 Position 7 × 2	≥4	[31]
Planktothrix agardhii NIVA 126/8	[Asp^3] MC-LR; [Asp^3] MC-RR; Unidentified MC	3	Leu Arg	Arg	Position 3 × 1	-	[1]
Planktothrix agardhii PH-123	[Asp^3] MC-LR; [Asp^3, $ADMAdda^5$] MC-LR; [Asp^3] MC-HtyR; [Asp^3, $ADMAdda^5$] MC-HtyR	4	Leu Hty	Arg	Position 3 × 1 Position 5 × 2	4	[32]
Planktothrix rubescens CYA 406	[Asp^3, Dhb^7] MC-LR; [Asp^3, Dhb^7] MC-HtyR; [Asp^3, Dhb^7] MC-RR; [Asp^3, Dha^7] MC-RR; Unidentified MC	5	Leu Hty Arg	Arg	Position 3 × 1 Position 7 × 2	≥6	[31]

Table S1. *Cont.*

Planktothrix rubescens CYA 408	[Asp^3, Dhb^7] MC-LR; [Asp^3, Dhb^7] MC-HtyR; [Asp^3, Dhb^7] MC-RR; [Asp^3, Dha^7] MC-RR; Unidentified MC	5	Leu Hty Arg	Arg	Position 3 × 1 Position 7 × 2	≥6	[31]
Planktothrix rubescens No80	[Asp^3, Dhb^7] MC-LY; [Asp^3, Dhb^7] MC-LW; [Asp^3, Dhb^7] MC-HtyY; [Asp^3, Dhb^7] MC-HtyHty; [Asp^3, Dhb^7] MC-HtyW	5	Leu Hty	Tyr Hty Trp	Position 3 × 1 Position 7 × 1	6	[33,34]

[a] An assessment of the microcystin diversity of 49 microcystin-producing strains reported in scientific journals; [b] Number of microcystins observed, including unidentified microcystins which the researchers noted during the studies; [c] Amino acids incorporated into position two of the microcystins reported to be produced by the cyanobacterial strain; [d] Amino acids incorporated into position four of the microcystins reported to be produced by the cyanobacterial strain; [e] Potential number of microcystins which could be produced by the cyanobacterial strain according to the information collected; In some cases this is omitted as the presence of unidentified microcystins makes this value difficult to estimate.

Table S2. Tandem mass spectrometry fragment assignments for the CAWBG11 -RR microcystin (MC) congeners observed by electrospray ionization collision-induced dissociation.

Fragment Assignment [a]	MC-RR		[Asp[3]] MC-RR	
	$[M + 2H]^{2+}$	**$[M + H]^{+}$**	**$[M + 2H]^{2+}$**	**$[M + H]^{+}$**
M	519.8	1038.6	512.8	1024.6
M − H_2O	510.7	1020.4[b]	503.7	1006.4[b]
M − Mdha − H_2O	469.2	937.4[b]	462.2	923.4[b]
M − Adda sidechain	452.8	904.4	445.7	890.3
M − Adda sidechain − H_2O	443.7	886.4	436.6	872.3
M − Adda	363.2	725.3	356.1	711.3
M − Adda − H_2O	354.2	707.3	347.1	693.3
Arg-Adda-Glu − NH_3		582.2		582.2
Arg-Adda − NH_3 + H		453.2		453.2
Arg-Adda-Glu − CO		571.3		571.2
(Me)Asp-Arg-Adda-Glu		728.3		714.2
(Me)Asp-Arg-Adda		599.3		585.2
Arg-Adda-Glu		599.3		599.2
Mdha-Ala-Arg-(Me)Asp-Arg	298.2	596.3	291.2	582.2
Mdha-Ala-Arg-(Me)Asp		440.2		426.1
Mdha-Ala-Arg		311.2		311.1
Mdha-Ala		155.1		155.0
Adda′-Glu-Mdha		375.2		375.1
Adda′		163.1		163.0
(Me)Asp-Arg		286.2		272.1
Arg		157.1		157.1

[a] Adda′ = Adda minus NH_2 and the sidechain ($C_9H_{11}O$); [b] $[M + H]^{+}$ ion was deconvoluted from the $[M + 2H]^{2+}$ ion.

Table S3. Tandem mass spectrometry fragment assignments for the CAWBG11 -XR microcystin (MC) congeners observed by matrix-assisted laser desorption/ionization post-source decay and electrospray ionization collision-induced dissociation.

Fragment Assignment [a]	**MC-LR** ***X* = 113 Da**	**[Asp³] MC-LR** ***X* = 113 Da**	**MC-FR** ***X* = 147 Da**	**[Asp³] MC-FR** ***X* = 147 Da**	**MC-YR** ***X* = 163 Da**	**MC-WR** ***X* = 186 Da**	**[Asp³] MC-WR** ***X* = 186 Da**
M + H	995	981	1029	1015	1045	1068	1054
M − Ala + H	924	910	958	944	974	997	
M − $CH_2NHCN_2H_3$ + H	923	909	957	943	973	996	
M − (Me)Asp + H	866	866	900	900	916	939	939
M − Glu + H	866	852	900	886	916	939	925
M − Adda sidechain + H	861	847	895	881	911	934	920
(Me)Asp-Arg-Adda-Glu + H	728	714	728	714	728	728	714
(Me)Asp-Arg-Adda + H	599	585	599	585	599	599	585
Arg-Adda-Glu + H	599	599	599	599	599	599	599
Arg-Adda + H	470	470	470	470	470	470	470
Mdha-Ala-*X*-(Me)Asp-Arg + NH_4	570	556	604	590	620	643	629
Ala-*X*-(Me)Asp-Arg + NH_4	487	473	521	507	537	560	546
Mdha-Ala-*X*-(Me)Asp-Arg + H	553	539	587	573	603	626	612
Ala-*X*-(Me)Asp-Arg + H	470	456	504	490	520	543	529
X-(Me)Asp-Arg + H	399		433	419	449		
Mdha-Ala-*X*-(Me)Asp + H	397	383	431		447	470	456
Mdha-Ala-*X* + H	268	268	302	302	318	341	341
Mdha-Ala + H	155	155	155	155	155	155	155
Adda′-Glu-Mdha-Ala + H	446	446	446	446	446	446	446
Adda′-Glu-Mdha + H	375	375	375	375	375	375	375
Adda′ + H	163	163	163	163	163	163	163
Glu-Mdha + H	213	213	213	213	213	213	213
Adda sidechain	135	135	135	135	135	135	135
Arg related ions	70/84/112/174	70/84/112/174	70/84/112/174	70/84/112/174	70/84/112/174	70/84/112/174	70/84/112/174
X immonium	86	86	120	120	136	159	159

[a] *X* = Position two amino acid; Adda′ = Adda minus NH_2 and the sidechain ($C_9H_{11}O$); $CH_2NHCN_2H_3$ is a fragment of the arginine sidechain; Fragment ions containing NH_3 and CO losses have been omitted.

Table S4. Tandem mass spectrometry fragment assignments for the CAWBG11 -RZ microcystin (MC) congeners observed by matrix-assisted laser desorption/ionization post-source decay and electrospray ionization collision-induced dissociation.

Fragment Assignment [a]	MC-RA Z = 71 Da	[Asp^3] MC-RA Z = 71 Da	MC-RAba Z = 85 Da	[Asp^3] MC-RAba Z = 85 Da	MC-RL Z = 113 Da
M + H	953	939	967	953	995
M − H_2O + H	935	921	949	935	977
M − COOH + H	908	894	922	908	950
M − Z + H	882	868	882	868	882
M − $CH_2NHCN_2H_3$ + H	881	867	895	881	923
M − Glu + H	824	810	838	824	866
M − (Me)Asp + H	824	824	838	838	866
M − Adda sidechain + H	819	787	833	819	861
Mdha-Ala-Arg-(Me)Asp-Z + NH_4	528	514	542	528	570
Mdha-Ala-Arg-(Me)Asp-Z − H_2O + NH_4	510	496	524	510	552
Mdha-Ala-Arg-(Me)Asp-Z + H	511	497	525	511	553
Mdha-Ala-Arg-(Me)Asp − $CH_2NHCN_2H_3$ + H	368	354	368	354	368
Mdha-Ala-Arg-(Me)Asp + H	440	426	440	426	440
Mdha-Ala-Arg + H	311	311	311	311	311
Mdha-Ala + H	155	155	155		
Arg-(Me)Asp-Z + H	357	343		357	
Glu-Mdha-Ala-Arg − COOH + H	395	395	395	395	395
Glu-Mdha-Ala-Arg − $CH_2NHCN_2H_3$ + H	368	368	368	368	368
Glu-Mdha-Ala-Arg + H	440	440	440	440	440
Glu-Mdha + H	213		213		
Adda′-Glu-Mdha + H	375	375	375	375	375
Adda′ + H	163	163	163		

[a] Z = Position four amino acid; Adda′ = Adda minus NH_2 and the sidechain ($C_9H_{11}O$); $CH_2NHCN_2H_3$ is a fragment of the arginine sidechain.

Table S5. Tandem mass spectrometry fragment assignments for the CAWBG11 -XA microcystin (MC) congeners observed by electrospray ionization collision-induced dissociation.

Fragment Assignment [a]	**MC-LA** *X* **= 113 Da**	**[Asp^3] MC-LA** *X* **= 113 Da**	**MC-FA** *X* **= 147 Da**	**[Asp^3] MC-FA** *X* **= 147 Da**	**MC-YA** *X* **= 163 Da**	**MC-WA** *X* **= 186 Da**	**[Asp^3] MC-WA** *X* **= 186 Da**
M + H	910	896	944	930	960	983	969
M − H_2O + H	892	878	926	912	942	965	951
M − Mdha − H_2O + H	809	795	843	829		882	868
M − Adda sidechain + H	776	762	810	796	826	849	835
M − Adda sidechain − H_2O + H	758	744	792	778	808	831	817
M − Adda + H	597	583	631	617	647	670	656
M − Adda − H_2O + H	579	565	613	599	629	652	
Adda-Glu-Mdha-Ala-*X*-(Me)Asp − NH_3 + H	822	808	856	842	872	895	881
Adda-Glu-Mdha-Ala-*X* − NH_3 + H	693	693	727	727	743	766	766
Adda-Glu-Mdha-Ala − NH_3 + H	580	580	580	580	580	580	580
Adda-Glu-Mdha − NH_3 + H	509	509	509	509	509	509	509
Adda′-Glu-Mdha-Ala-*X* + H	559	559	593	593	609	632	632
Adda′-Glu-Mdha-Ala + H	446	446	446	446	446	446	446
Adda′-Glu-Mdha + H	375	375	375	375	375	375	375
Mdha-Ala-*X*-(Me)Asp-Ala + NH_4	485	471	519	505	535	558	
Ala-*X*-(Me)Asp-Ala + NH_4	402	388	436	422	452	475	461
X-(Me)Asp-Ala + NH_4	331	317	365	351	381	404	390
Mdha-Ala-*X*-(Me)Asp-Ala + H	468	454	502	334	518	541	527
Ala-*X*-(Me)Asp-Ala + H	385	371	419	405	435	458	444
X-(Me)Asp-Ala + H	314	300	348	488	364	387	373

[a] *X* = Position two amino acid; Adda′ = Adda minus NH_2 and the sidechain ($C_9H_{11}O$).

Table S6. Tandem mass spectrometry fragment assignments for the CAWBG11 -XAba microcystin (MC) congeners observed by electrospray ionization collision-induced dissociation.

Fragment Assignment [a]	**MC-LAba** *X* **= 113 Da**	**MC-FAba** *X* **= 147 Da**	**MC-WAba** *X* **= 186 Da**
M + H	924	958	997
M − H_2O + H	906	940	979
M − Mdha − H_2O + H	823	857	896
M − Adda sidechain + H	790	824	863
M − Adda sidechain − H_2O + H	772	806	845
M − Adda + H	611	645	684
M − Adda − H_2O + H	593	627	666
Adda-Glu-Mdha-Ala-*X*-Masp − NH_3 + H		856	895
Adda-Glu-Mdha-Ala-*X* − NH_3 + H	693	727	766
Adda-Glu-Mdha-Ala − NH_3 + H	580	580	580
Adda-Glu-Mdha − NH_3 + H	509	509	509
Adda′-Glu-Mdha-Ala-*X* + H	559	593	632
Adda′-Glu-Mdha-Ala + H	446	446	446
Adda′-Glu-Mdha + H	375	375	375
Mdha-Ala-*X*-Masp-Aba + NH_4	499	533	572
Ala-*X*-Masp-Aba + NH_4	416	450	489
X-Masp-Aba + NH_4	345	379	418
Mdha-Ala-*X*-Masp-Aba + H	482	516	555
Ala-*X*-Masp-Aba + H	399	433	472
X-Masp-Aba + H	328	362	401

[a] *X* = Position two amino acid; Adda′ = Adda minus NH_2 and the sidechain ($C_9H_{11}O$).

Table S7. Tandem mass spectrometry fragment assignments for the CAWBG11 -XL microcystin (MC) congeners observed by electrospray ionization collision-induced dissociation.

Fragment Assignment [a]	**MC-LL** ***X*** **= 113 Da**	**MC-FL** ***X*** **= 147 Da**	**MC-WL** ***X*** **= 186 Da**
M + H	952	986	1025
M − NH_3 + H	935	969	1008
M − H_2O + H	934	968	1007
M − Mdha − H_2O + H	851	885	924
M − Adda sidechain + H	818	852	891
M − Adda sidechain − H_2O + H	800	834	873
M − Adda + H	639	673	712
M − Adda − H_2O + H	621	655	694
Adda-Glu-Mdha-Ala-*X*-Masp − NH_3 + H		856	895
Adda-Glu-Mdha-Ala-*X* − NH_3 + H	693	727	766
Adda-Glu-Mdha-Ala − NH_3 + H	580	580	580
Adda-Glu-Mdha − NH_3 + H	509	509	509
Glu-Mdha-Ala-*X* + H	397	431	470
Adda′-Glu-Mdha-Ala-*X* + H	559	593	632
Adda′-Glu-Mdha-Ala + H	446	446	446
Adda′-Glu-Mdha + H	375	375	375
Mdha-Ala-*X*-Masp-Leu + NH_4		561	600
Ala-*X*-Masp-Leu + NH_4		478	517
X-Masp-Leu + NH_4		407	446
Unidentified fragment ion	440	474	513
Unidentified fragment ion	535	535	535
Mdha-Ala-*X*-Masp-Leu + H	509	544	583
Ala-*X*-Masp-Leu + H	426	461	500
X-Masp-Leu + H	355	390	429

[a] *X* = Position two amino acid; Adda′ = Adda minus NH_2 and the sidechain ($C_9H_{11}O$).

Table S8. Electrospray high-resolution mass spectrometry data for microcystins (MC) present in sufficient quantities in *Microcystis* CAWBG11.

Microcystin	**Measured *m/z***		**Proposed Formula**	**Expected *m/z***	**Deviation**
MC-LR (**1**)	995.5560	$[M + H]^+$	$C_{49}H_{75}N_{10}O_{12}$	995.5560	+0.1 ppm
MC-RR (**3**)	519.7884	$[M + 2H]^{2+}$	$C_{49}H_{77}N_{13}O_{12}$	519.7902	−3.4 ppm
MC-YR (**4**)	1045.5364	$[M + H]^+$	$C_{52}H_{73}N_{10}O_{13}$	1045.5353	+1.1 ppm
[Asp^3] MC-LR (**5**)	981.5369	$[M + H]^+$	$C_{48}H_{73}N_{10}O_{12}$	981.5404	−3.6 ppm
[Asp^3] MC-FR (**6**)	1015.5207	$[M + H]^+$	$C_{51}H_{71}N_{10}O_{12}$	1015.5247	−4.0 ppm
MC-FR (**7**)	1029.5411	$[M + H]^+$	$C_{52}H_{72}N_{10}O_{12}$	1029.5404	+0.6 ppm
[Asp^3] MC-WR (**8**)	1054.5398	$[M + H]^+$	$C_{53}H_{72}N_{11}O_{12}$	1054.5356	+3.9 ppm
MC-WR (**9**)	1068.5465	$[M + H]^+$	$C_{54}H_{74}N_{11}O_{12}$	1068.5513	−4.5 ppm
MC-RA (**11**)	953.5122	$[M + H]^+$	$C_{46}H_{69}N_{10}O_{12}$	953.5091	+3.3 ppm
MC-RAba (**13**)	967.5259	$[M + H]^+$	$C_{47}H_{71}N_{10}O_{12}$	967.5247	+1.1 ppm
[Asp^3] MC-LA (**16**)	918.4592	$[M + Na]^+$	$C_{45}H_{67}N_7O_{12}Na$	918.4583	+1.0 ppm
MC-LA (**17**)	910.4936	$[M + H]^+$	$C_{46}H_{68}N_7O_{12}$	910.4920	+1.7 ppm
MC-FA (**19**)	966.4550	$[M + Na]^+$	$C_{49}H_{65}N_7O_{12}Na$	966.4583	−3.3 ppm
MC-WA (**21**)	1005.4650	$[M + Na]^+$	$C_{51}H_{66}N_8O_{12}Na$	1005.4692	−4.3 ppm
MC-LAba (**22**)	946.4912	$[M + Na]^+$	$C_{47}H_{69}N_7O_{12}Na$	946.4896	+1.7 ppm
MC-FAba (**23**)	980.4744	$[M + Na]^+$	$C_{50}H_{67}N_7O_{12}Na$	980.4740	+0.4 ppm
MC-WAba (**24**)	1019.4836	$[M + Na]^+$	$C_{52}H_{68}N_8O_{12}Na$	1019.4849	−1.3 ppm

Figure S1. Advanced Marfey's amino acid analysis of MC-RA; extracted ion chromatograms of hydrolyzed MC-RA derivatized with L-FDLA.

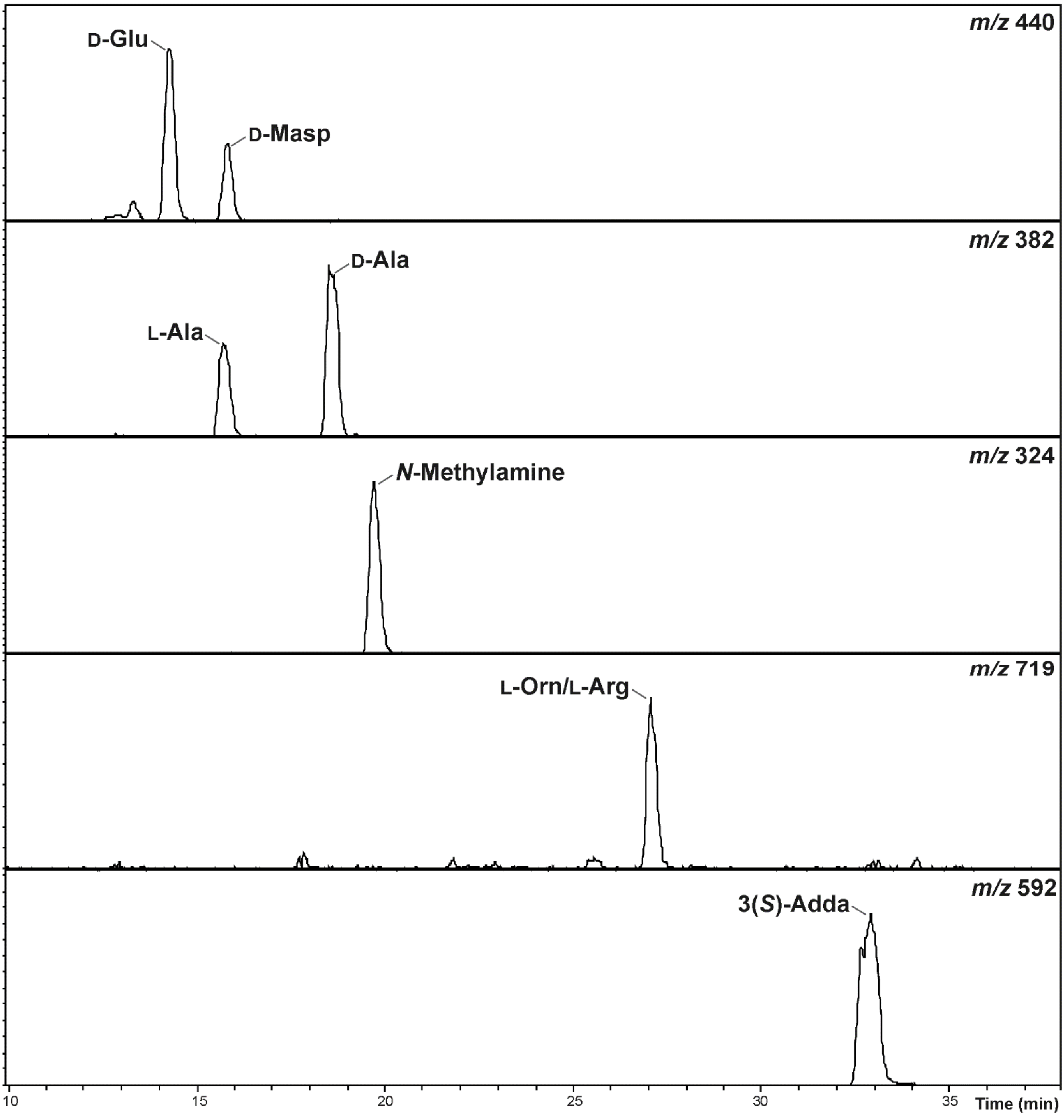


Figure S2. Advanced Marfey's amino acid analysis of MC-RAba; extracted ion chromatograms of hydrolyzed MC-RAba derivatized with L-FDLA.

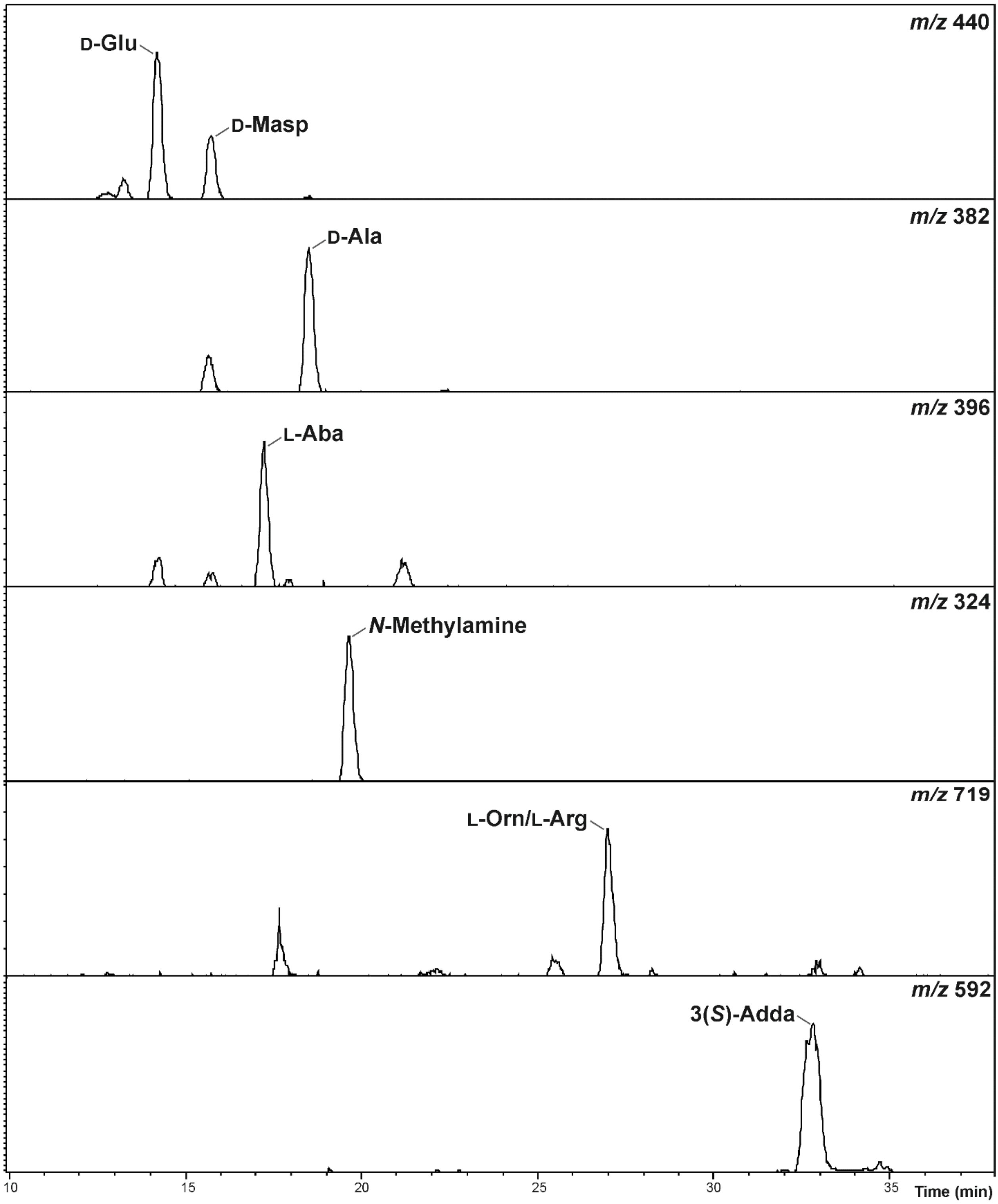


Figure S3. Box plots representing the spread in the number of microcystin congeners produced by reported cyanobacterial strains. Plots depict the number of microcystin congeners identified; 49 strains (**a**); the number of microcystin congeners observed; 49 strains (**b**) and the potential number of congeners which could be produced according to the reported data; 33 strains (**c**).

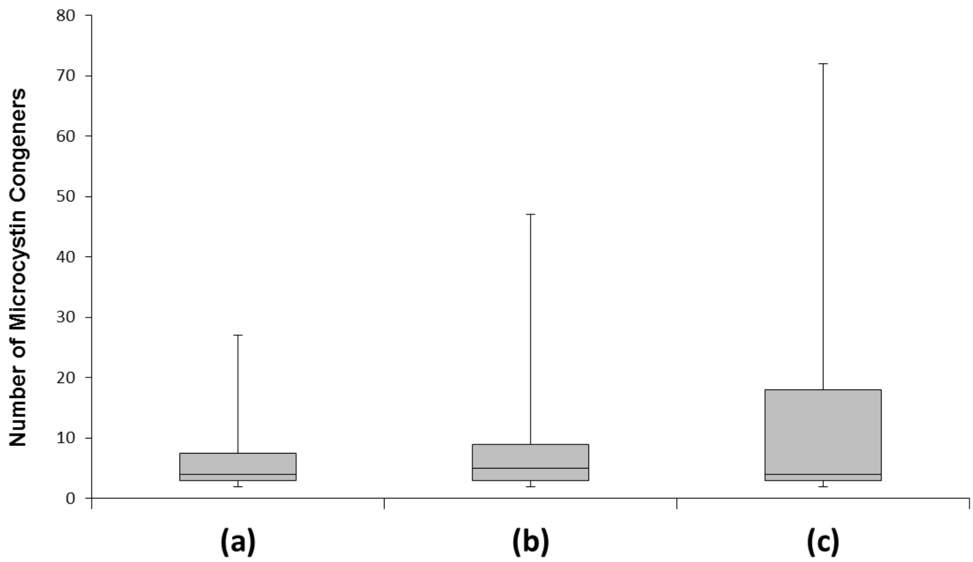


Figure S4. Microscopic images of *Microcystis* CAWBG11 acquired on an Olympus IX70 inverted microscope at 100 × magnification (**a**) and at 1000 × magnification (**b**).

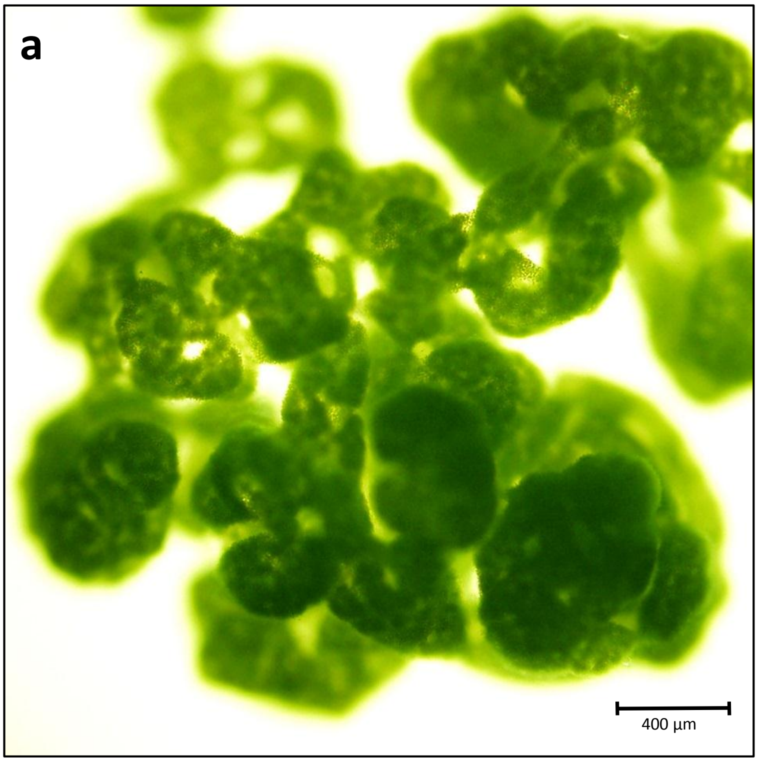
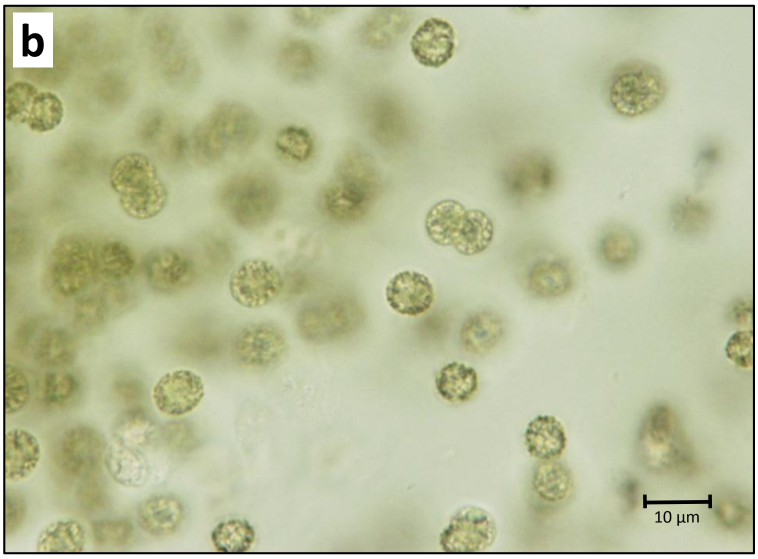


Figure S4. *Cont.*



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