Supplementary Material

Structure and Activity of Anabaenopeptins Produced by Baltic Sea Cyanobacteria

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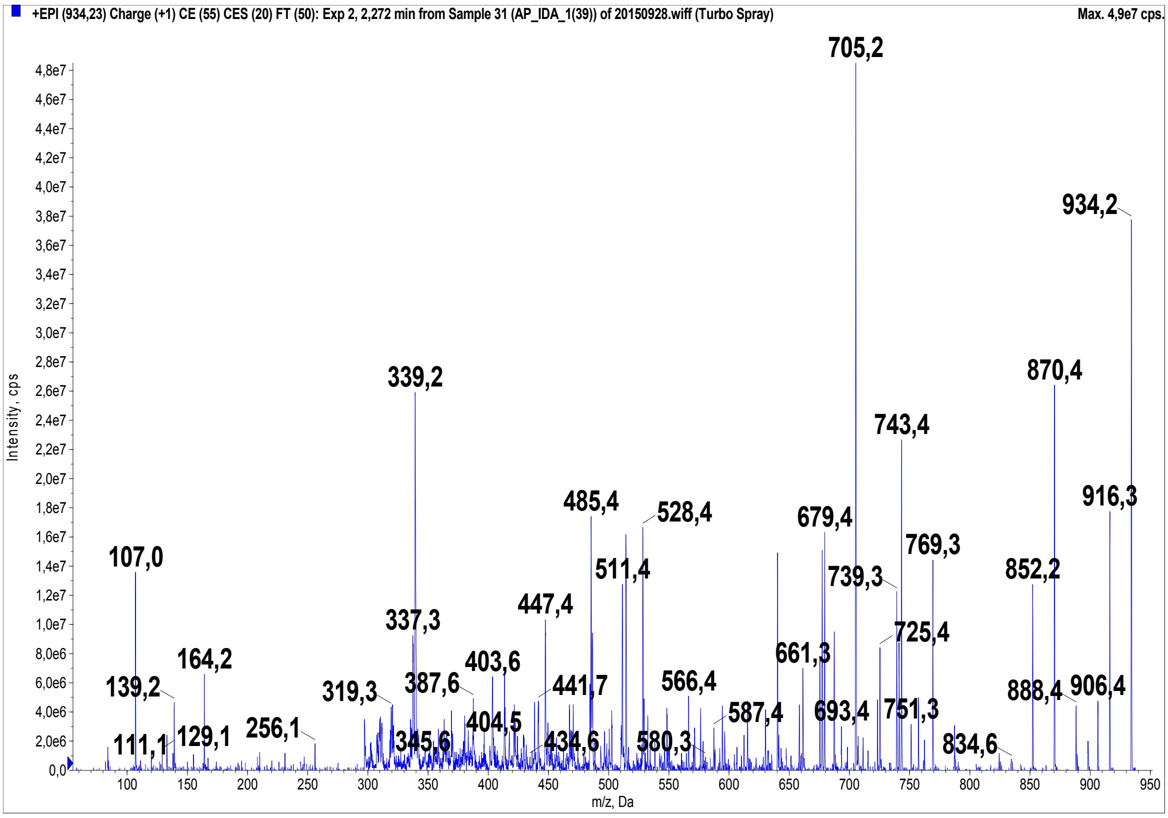

Figure S1. Mass fragmentation spectrum of anabaenopeptin with *m/z* of $[M + H]^+$ at 934 and structure Phe + CO + [Lys + Val + Hty + MeHty + MetO] elucidated on the basis of following fragments: 916 [M + H − H_2O], 906 [M + H − CO], 888 [M + H − H_2O − CO], 870 [M + H − CH_3SOH (from MetO)], 852 [M + H − CH_3SOH − H_2O], 769 [M + H − Phe − H_2O], 743 [M + H − (CO + Phe)], 705 [M + H − Phe − CH_3SOH − H_2O], 679 [M + H − (CO + Phe) − CH_3SOH], 661 [M + H − (CO + Phe) − CH_3SOH − H_2O], 566 [M + H − (Hty + MHty)], 528 [M + H − Phe − Hty − CH_3SOH − H_2O], 511 [M + H − Phe − (Hty + Val)], 447 [M + H − Phe − (Hty + Val) − CH_3SOH], 403 [MetO + Lys(CO) + Val + H], 339 [MetO + MeHty + H],164 MeHty, 107 [CH_2PhOH], 84 Lys–immonium ion.

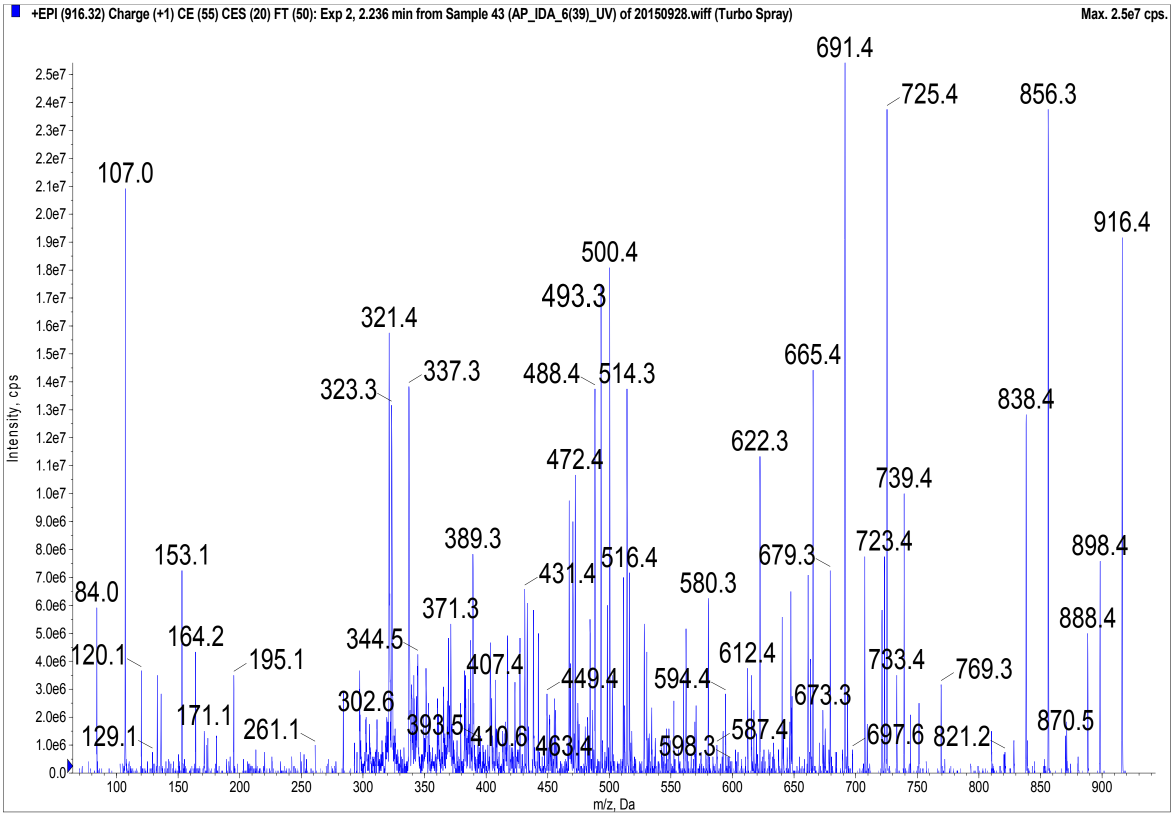

Figure S2. Mass fragmentation spectrum of anabaenopeptin with *m*/*z* of $[M + H]^+$ at 916 and structure Phe + CO + [Lys + Val + Hty + N − MeHty + AcSer] elucidated on the basis of following fragments: 898 $[M + H − H_2O]$, 888 [M + H − CO], 870 $[M + H − CO − H_2O]$, 856 $[M + H − CH_3COOH$ (from AcSer)], 769 [M + H − Phe], 739 [M + H − Hty], 725 [M + H − MHty] or [M + H − (CO + Phe)], 665 $[M + H − (CO + Phe) − CH_3COOH]$, 640 [M + H − (Val + Hty)], 622 $[M + H − (Val + Hty) − H_2O]$, 612 [M + H − (Val + Hty) − CO], 594 $[M + H − (Val + Hty) − CO − H_2O]$, 493 [M + H − Phe − (Hty + Val)], 488 $[Val + Lys + AcSer + MeHty − CH_3COOH + H]$, 389 $[Lys + (AcSer − CH_3COOH) + MeHty + H]$, 321 [MeHty + AcSer + H], 164 MeHty, 120 Phe immonium ion, 107 $[CH_2PhOH]$, 84 Lys–immonium ion.

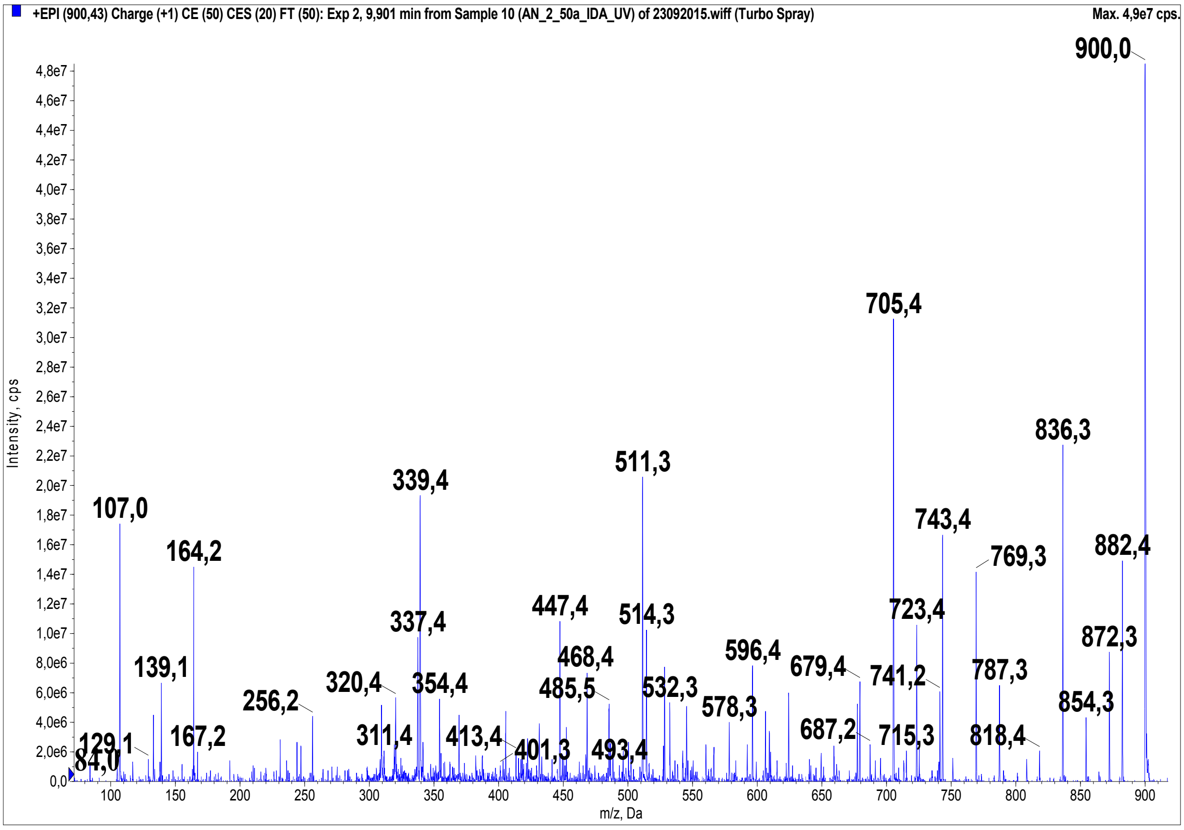

Figure S3. Mass fragmentation spectrum of anabaenopeptin with *m*/*z* of $[M + H]^+$ at 900 and structure Ile + CO + [Lys + Val + Hty + MeHty + MetO] elucidated on the basis of following fragments: 882 [M + H − H_2O], 872 [M + H − CO], 854 [M + H − H_2O − CO], 836 [M + H − CH_3SOH (from MetO)], 818 [M + H − CH_3SOH − H_2O], 787 [M + H − Ile], 769 [M + H − Ile − H_2O], 743 [M + H − (CO + Ile)], 705 [M + H − Ile − CH_3SOH − H_2O], 679 [M + H − (CO + Ile) − CH_3SOH], 528 [M + H − Ile − Hty − CH_3SOH − H_2O], 511 [M + H − Ile − (Hty + Val)], 468 [MeHty + Hty + Val + H], 447 [M + H − Ile − (Hty + Val) − CH_3SOH], 339 [MetO + MeHty + H],164 MeHty, 107 [CH_2PhOH], 84 Lys–immonium ion.

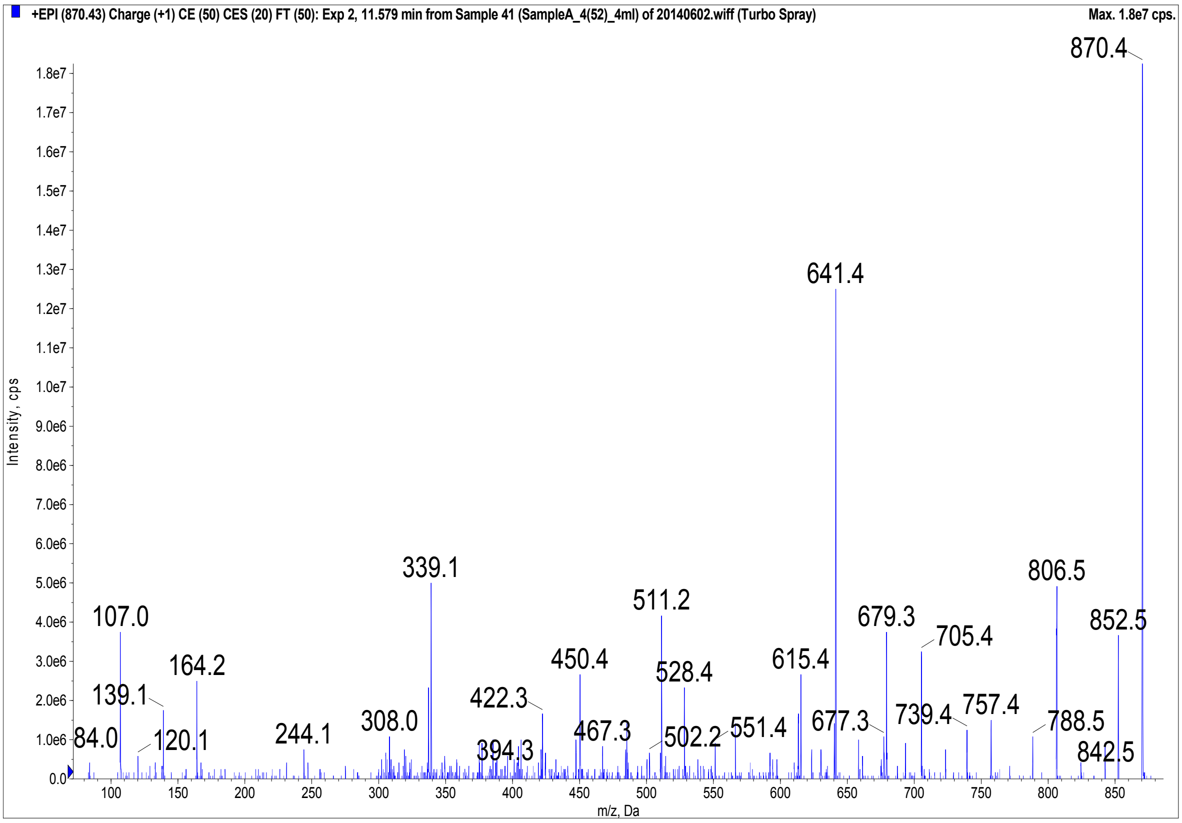

Figure S4. Mass fragmentation spectrum of anabaenopeptin with *m*/*z* of $[M + H]^+$ at 870 and structure [Phe + CO[Lys + Val + Leu + MeHty + MetO] elucidated on the basis of following fragments: 852[M + H − H_2O], 842 [M + H − CO], 806 [M + H − CH_3SOH (from MetO)], 788 [M + H − CH_3SOH − H_2O), 757 [M + H − Ile], 739 [M + H − Ile − H_2O], 705 [M + H − Phe − H_2O], 679 [M − MHty + H], 615 [M − Mhty + H − CH_3SOH], 641 [M + H − Phe − CH_3SOH − H_2O], 528 [M + H − Phe − Leu − CH_3SOH − H_2O], 511 [M + H − Phe − (Leu + Val)], 339 [MetO + MeHty + H], 164 MeHty, 120 Phe–immonium ion, 107 [CH_2PhOH], 84 Lys–immonium ion.

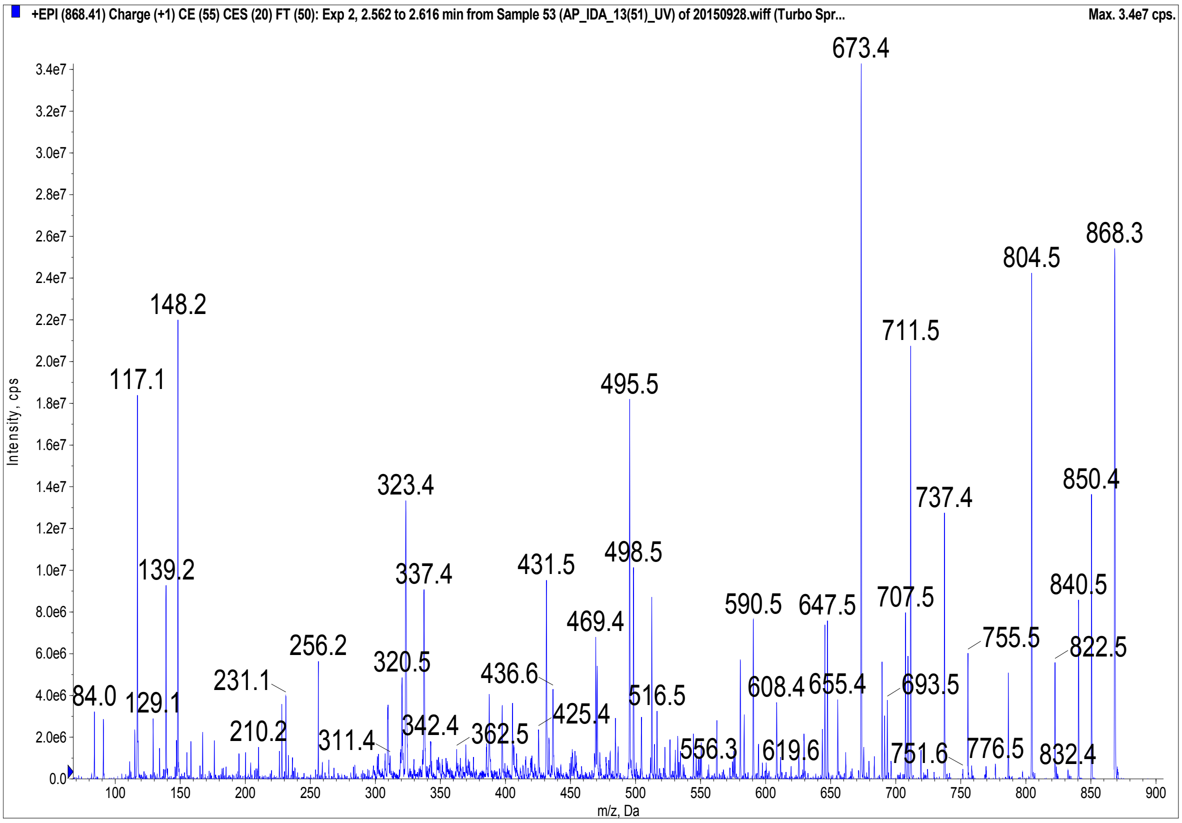

Figure S5. Mass fragmentation spectrum of anabaenopeptin with *m*/*z* of [M + H]⁺ at 868 and structure Ile + CO[Lys + Val + Hph + MeHty + Met] elucidated on the basis of following fragments: 850[M + H − H_2O], 840 [M + H − CO], 822 [M + H − CO − H_2O], 755 [M + H − Ile], 737 [M + H − Ile − H_2O], 711 [M + H − (Ile + CO)], 707 [M + H − Hph], 693 [M + H − (Ile + CO) − H_2O], 608 [M + H − (Hph + Val)], 590 [M + H − (Hph + Val) − H_2O], 580 [M + H − (Hph + Val) − CO], 495 [M + H − Ile − (Hph + Val)], 323 [MeHty + Met + H], 84 Lys–immonium ion.

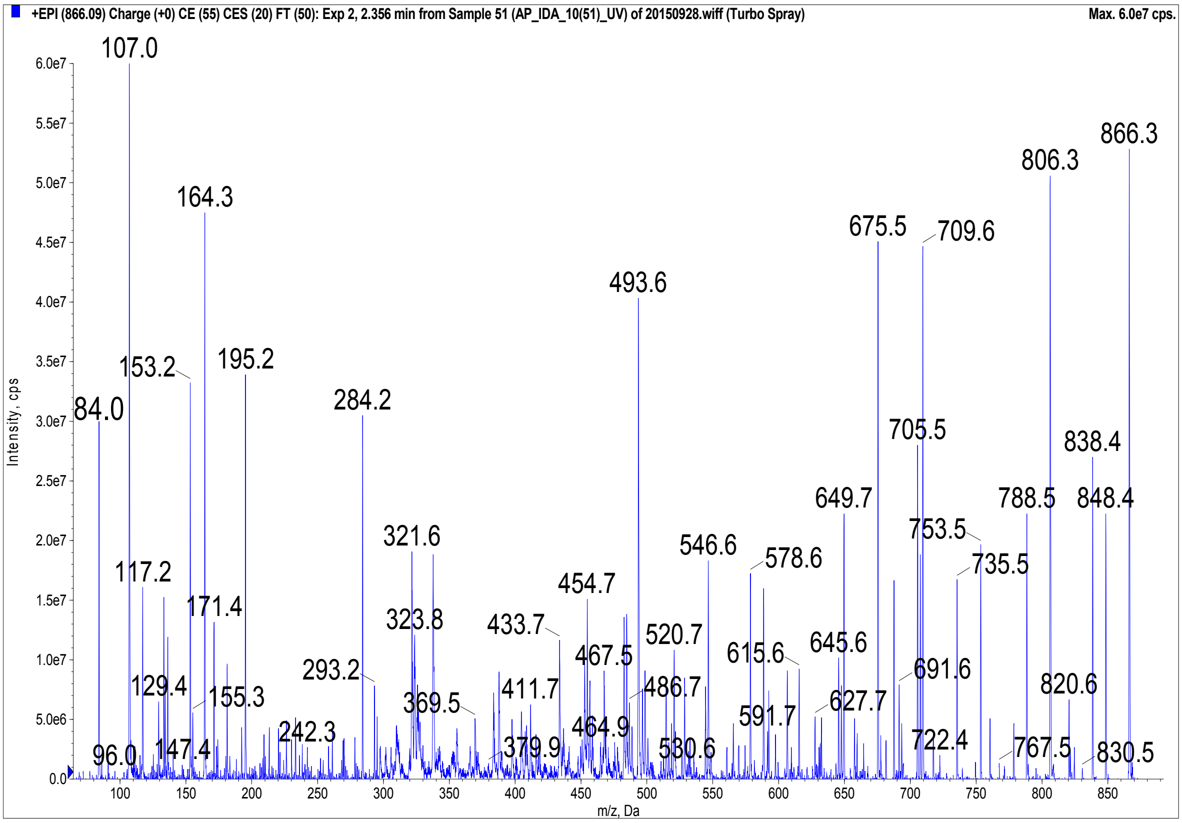

Figure S6. Mass fragmentation spectrum of anabaenopeptin with *m*/*z* of $[M + H]^+$ at **866** and structure Ile + CO[Lys + Val + Hph + MeHty + AcSer] elucidated on the basis of following fragments: 848 [M + H − H_2O], 838 [M + H − CO], 820 [M + H − CO − H_2O], 806 [M + H − CH_3COOH (from AcSer)], 753 [M + H − Ile], 735 [M + H − Ile − H_2O], 675 [M + H − Ile − CH_3COOH − H_2O], 709 [M + H − (CO + Ile)], 705 [M + H − Hph], 675 [M + H − MeHty], 649 [M + H − (CO + Ile) − CH_3COOH], 493 [M + H − Ile − (Hph + Val)], 337 [M + H − Ile − (Hph + MeHty) − CH_3COOH], 321 [MeHty + AcSer + H],164 MeHty, 107 [CH_2PhOH], 84 Lys–immonium ion.

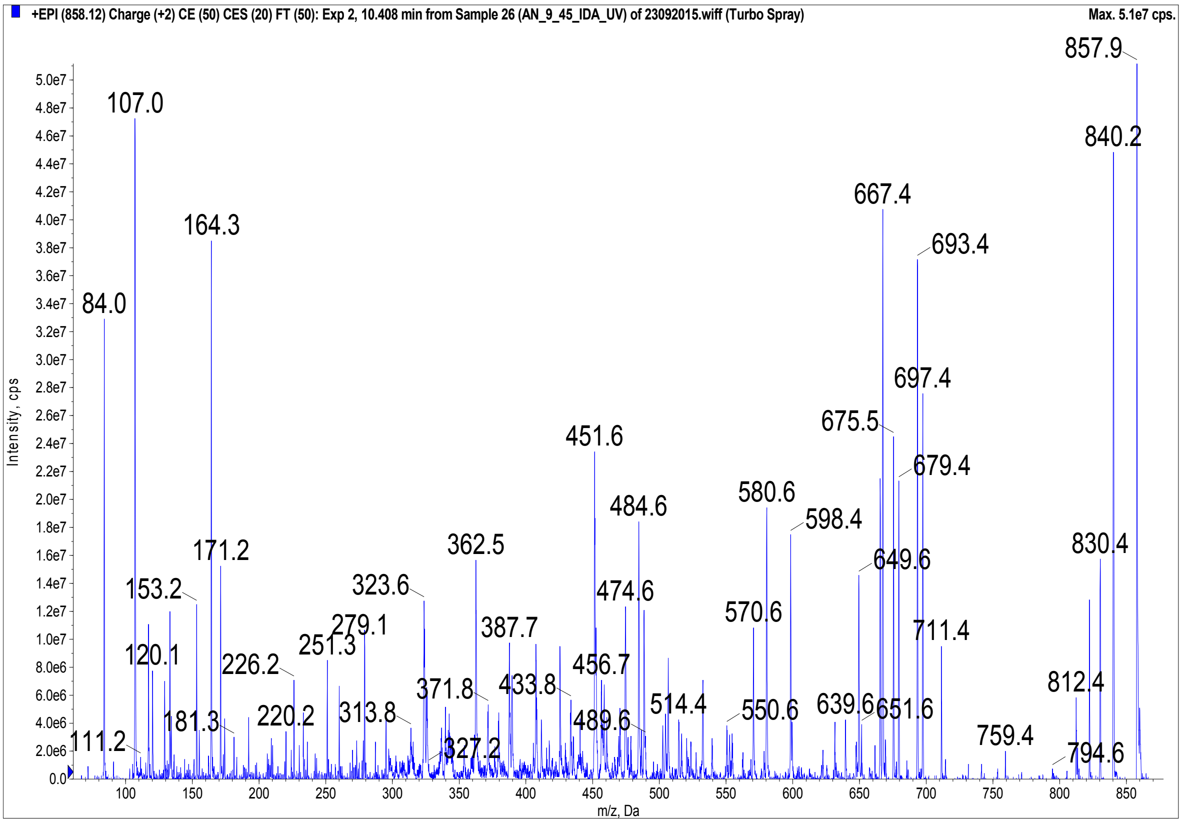

Figure S7. Mass fragmentation spectrum of anabaenopeptin with *m*/*z* of $[M + H]^+$ at **858** and structure Phe + CO[Lys + Val + Hph + MeHty + Ser] elucidated on the basis of following fragments: 840 [M + H − H_2O], 830 [M + H − CO], 812 [M + H − CO − H_2O], 711 [M + H − Phe], 697 [M + H − Hph], 667 [M + H − MeHty] and [M + H − (CO + Phe)], 649 [M + H − MeHty − H_2O], 639 [M + H − MeHty − CO], 598 [M + H − (Hph + Val)], 580 [M + H − (Hph + Val) − H_2O], 570 [M + H − (Hph + Val) − H_2O], 451 [M + H − Phe − (Hph + Val)], 279 [MeHty + Ser + H], 164 MeHty, 120 Phe–immonium ion, 107 [CH_2PhOH], 84 Lys–immonium ion.

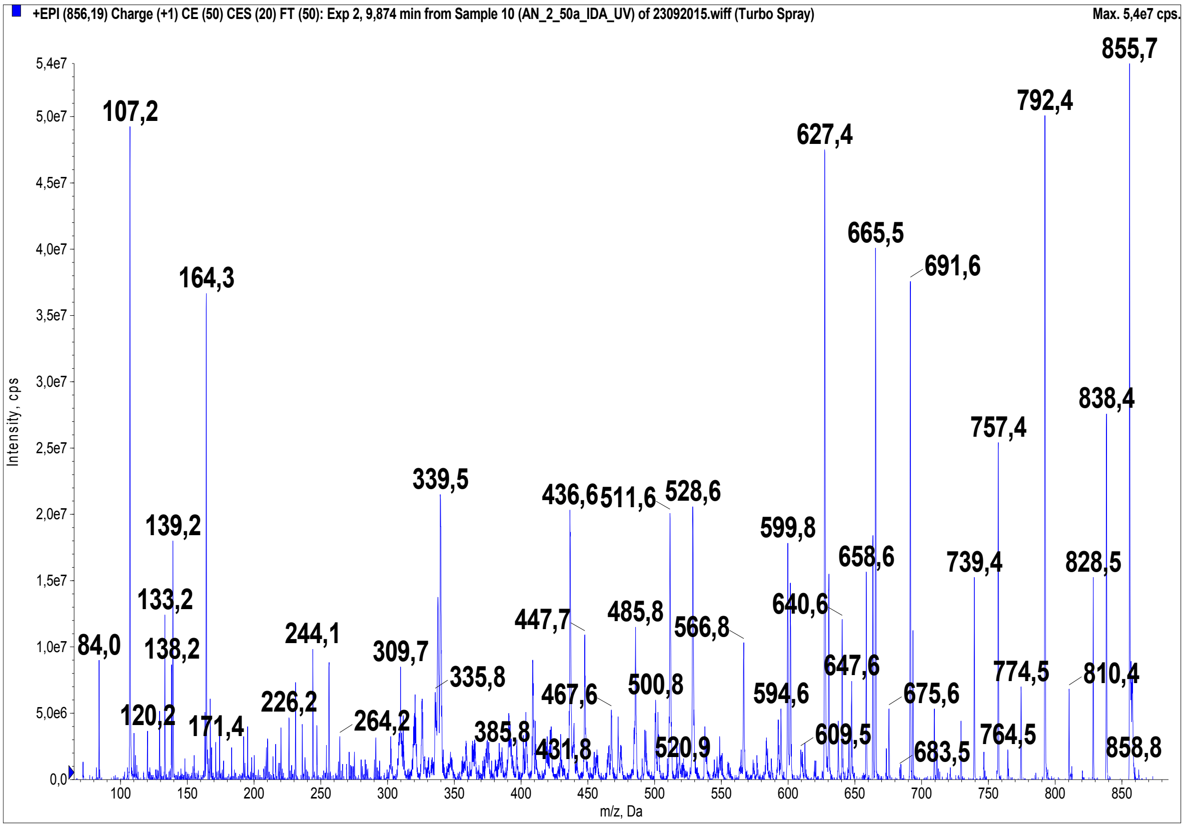

Figure S8. Mass fragmentation spectrum of anabaenopeptin with *m/z* of [M + H]$^+$ at 856 and structure Phe + CO + [Lys + Val + Val + MeHty + MetO] elucidated on the basis of following fragments 838 [M + H − H_2O], 828 [M + H − CO], 810 [M + H − CO − H_2O], 792 [M + H − CH_3SOH (from MetO)], 757 [M + H − Val], 739 [M + H − Val − H_2O], 691 [M + H − Phe − H_2O], 658 [M + H − (Val + Val)], 647 [M + H − MeHty − H_2O], 627 [M + H − Phe − CH_3SOH − H_2O], 566 [M + H − (Val + MeHty], 511 [M + H − Phe − (Val + Val)], 658 [M + H − (Val + Val], 447 [M + H − Phe − (Val + Val) − CH_3SOH], 339 [MetO − MeHty + H],164 MeHty, 120 Phe–immonium ion, 107 [CH_2PhOH], 84 Lys–immonium ion.

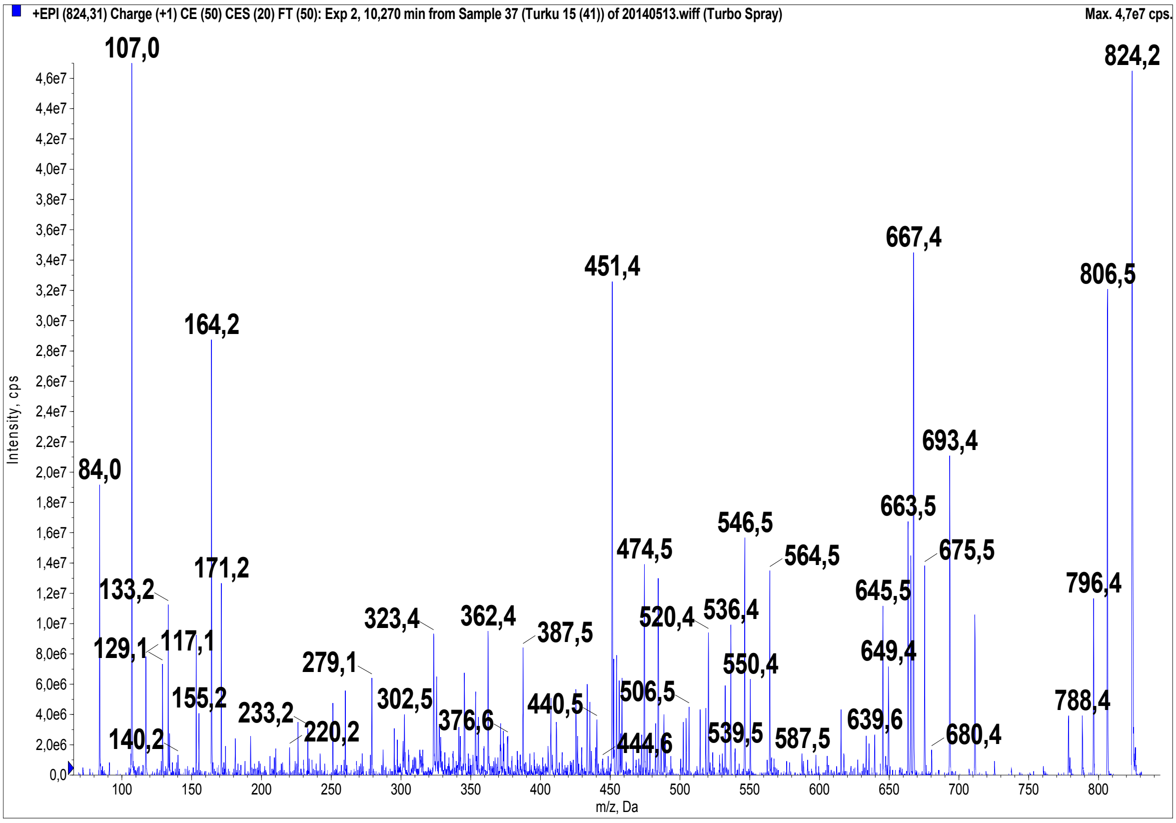

Figure S9. Mass fragmentation spectrum of anabaenopeptin with *m*/*z* of [M + H]$^+$ at 824 and structure Ile + CO + [Lys + Val + Hph + MeHty + Ser] elucidated on the basis of following fragments 806 [M + H − H_2O], 796 [M + H − CO], 778 [M + H − CO − H_2O], 711 [M + H − Ile], 693 [M + H − Ile − H_2O], 667 [M + H − (CO + Ile)], 663 [M + H − Hph], 645 [M + H − Hph − H_2O], 615 [M + H − MeHty − H_2O], 564 [M + H − (Hph + Val)], 546 [Hph + Val + Lys + CO + Ile + H], 520 [M + H − Ile − MeHty], 451 [M + H − (MeHty + Val) − Ile], 353 [Hph + MeHty + H], 279 [MeHty + Ser + H], 260 [MeHty + Ser + H − H_2O], 164 MeHty, 107 [CH_2PhOH], 84 Lys–immonium ion.

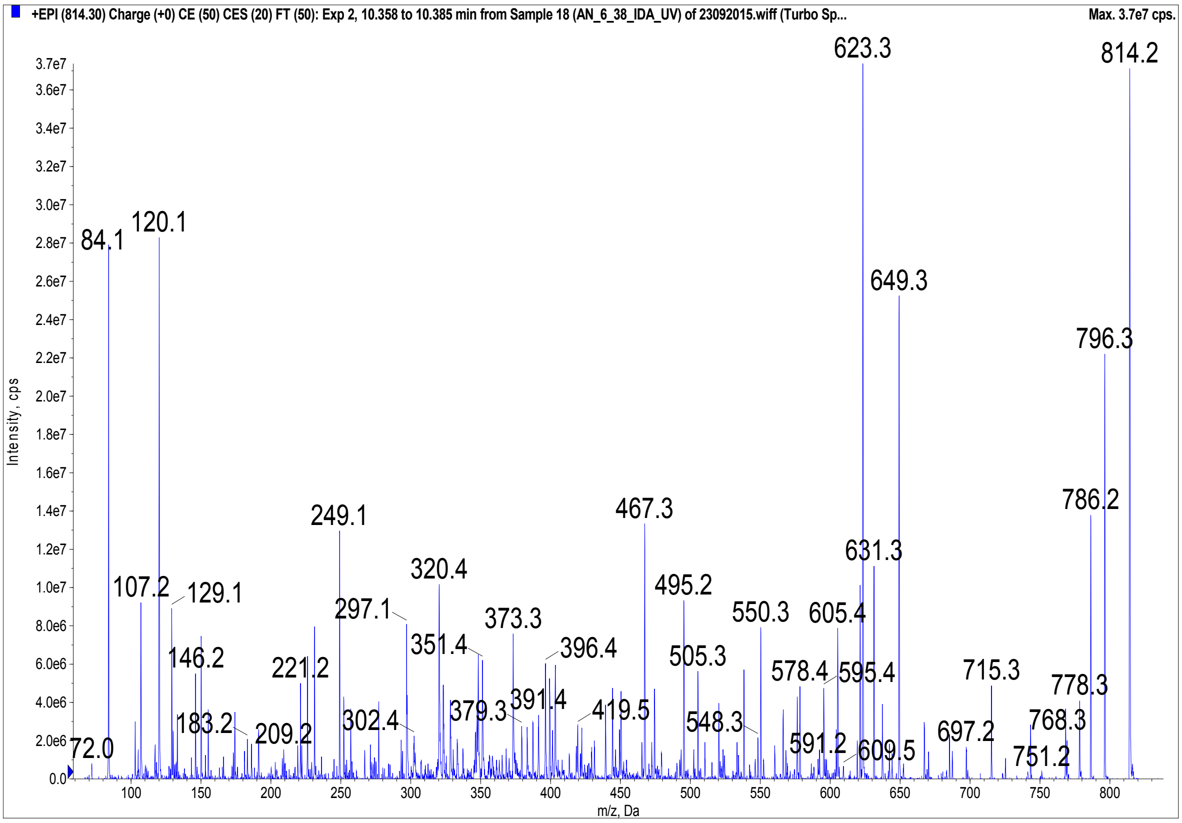

Figure S10. Mass fragmentation spectrum of anabaenopeptin with *m*/*z* of $[M + H]^+$ at **814** and structure Phe + CO[Lys + Val + Hty + MeGly + Phe] elucidated on the basis of following fragments: 796 [M + H − H_2O], 786 [M + H − CO], 768 [M + H − CO − H_2O], 715 [M + H − Val], 649 [M + H − Phe − H_2O], 623 [M + H − (CO + Phe)], 605 [M + H − (CO + Phe) − H_2O], 495 [Phe + MeGly + Hty + Val + H], 467 [Phe + Lys + CO + Phe + H], 396 [Hty + MeGly + Phe + H], 373 [M + H − Phe − (Hty + Val) − H_2O], 320 [M + H − Phe − (Val + Hty + MeGly + Phe)], 277 [Hty + Val + H], 249 [Hty + MeGly + H], 120 Phe immonium ion, 107 [CH_2PhOH], 84 Lys–immonium ion.

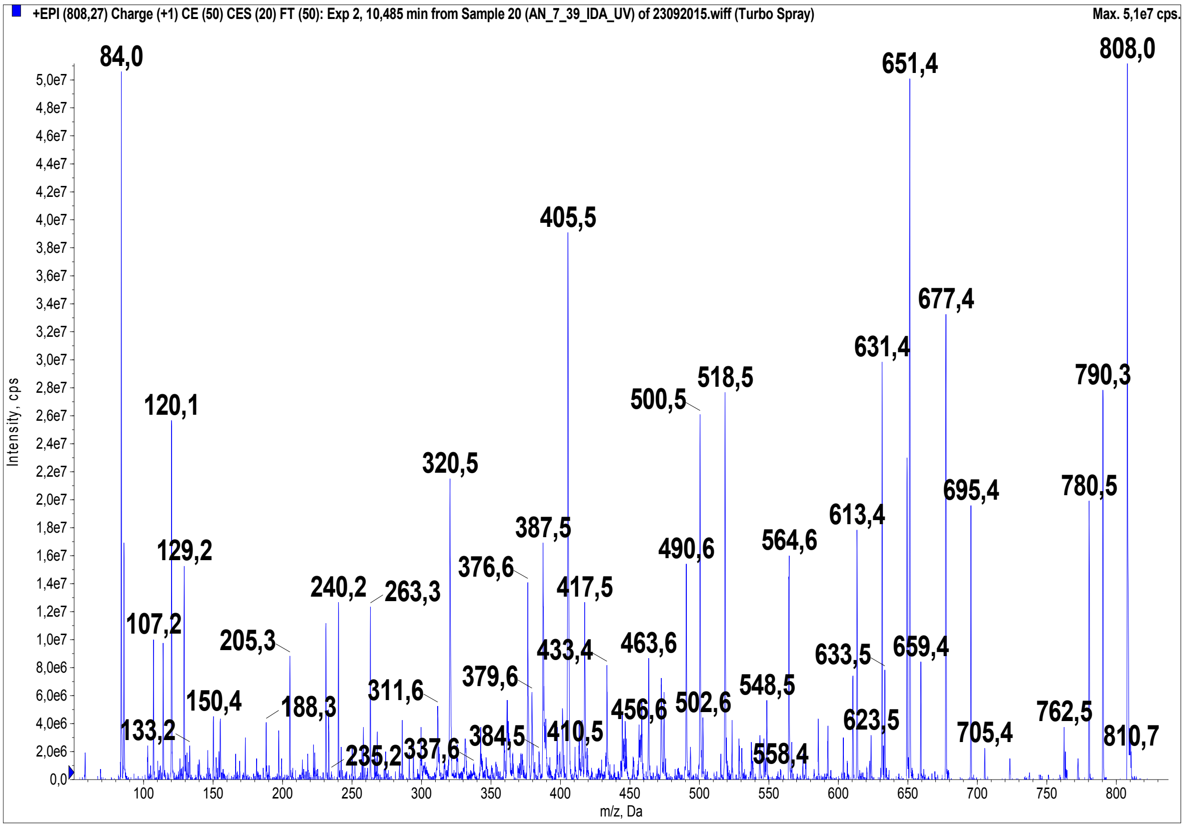

Figure S11. Mass fragmentation spectrum of anabaenopeptin with *m*/*z* of $[M + H]^+$ at 808 and structure Ile + CO + [Lys + Ile + Hty + MeAla + Phe] elucidated on the basis of following fragments: 790 [M + H − H_2O], 780 [M + H − CO], 762 [M + H − CO − H_2O], 695 [M + H − Ile], 677 [M + H − Ile − H_2O], 651 [M + H − (CO + Ile)], 631 [M + H − Hty], 613 [M + H − Hty − H_2O], 518 [M + H − Ile − Hty], 500 [M + H − Ile − Hty − H_2O], 490 [M + H − Ile − Hty − CO], 463 [M + H − (MeAla + Phe)], 405 [M + H − (Hty + Ile^3) − Ile^1], 387 [M + H − (Hty + Ile^3) − Ile^1 − H_2O], 320 [M + H − (MeAla + HTy + Ile^3) − Ile^1], 263 [MeAla + Hty + H], 120 Phe–immonium ion, 84 Lys–immonium ion.

Table S1. Published anabaenopeptin variants.

	m/*z*	**AA_1 (exo)**	**Ureido Linkage**	**AA_2 (D if Not Otherwise Indicated)**	**AA_3**	**AA_4**	**AA_5**	**AA_6**	**Source**	**Activity**	**Reference**
Arg in exocyclic position 1											
AP 820, [Hph[4]] AP F	821	Arg	CO	Lys	Val	Hph	*N*MeAla	Phe	*Microcystis* sp.	Not determined	Welker *et al*. 2006, *Peptides* 27, 2090–2103.
Anabaenopeptin B	837	Arg	CO	Lys	Val	Hty	*N*MeAla	Phe	*Anabaena flos-aquae* NRC 525-17 *Anabaena*, Strain 90 *Oscillatoria agardii* NIES-204 AP B *Planktothrix rubescence* bloom	rNEc, no PP1i TRYi No protease inh. PP1i ELAi, no TRY, no CHY, cytotoxicity No CPAi	Harada 1995 *Tetraheddon Letters* 36, 1511–1514. Repka *et al*. 2004 *Appl. Env. Microbiol*. 70, 4551–4560. Murakami *et al*. 1997, *Phytochemistry* 44, 449–452 Gkelis *et al*. 2006, *Aquatic toxicology* 78, 32–41. Bubik *et al*. 2008, *Biol. Chem*. 389, 1339–1346. Murakami *et al*. 2000, *J. Nat. Prod*. 63, (9) 1280–1282.
Anabaenopeptin B1	851	HArg	CO	Lys	Val	Hty	*N*MeAla	Phe	*P. rubescence*	Not determined	Ferranti *et al*. 2011, *Rapid Commun. Mass Spectrom*. 25, 1173–1183.

AP MM850	851	Arg(OMe)	CO	Lys	Val	Hty	*N*MeAla	Phe	*Microcystis* sp. bloom	CHYi, ELAi, TRYi, no THROi	Zafir-Ilan and Carmeli 2010, *Tetrahedron* 66, 9194–9202.
Anabaenopeptin E	851	Arg	CO	Lys	Val	MeHty	*N*MeAla	Phe	*Oscillatoria agardhii* NIES-204 *Planktothrix agardhii* HUB 011	Not determined Not determined no CPAi	Shin *et al*. 1997, *J. Nat. Prod*. 60, 139–141. Erhard *et al*. 1999, *Rapid Commun. Mass Spectrom*. 13, 337–343. Murakami *et al*. 2000, *J. Nat. Prod*. 63, (9) 1280–1282.
Anabaenopeptin F, APDA850	851	Arg	CO	Lys	Ile/*allo-*	Hty	*N*MeAla	Phe	*Oscillatoria agardhii* NIES-204 *Planktothrix rubescens* NIES-610 *Oscillatoria agardhii* Strain 97 *P. rubescence*, bloom *Microcystis aeruginosa*, bloom	Not determined PP1i, PP2i Not determined ELAi, no THROi, no CHYi, cytotoxicity No TRYi, no THROi	Shin *et al*. 1997, *J. Nat. Prod*. 60, 139–141. Sano *et al*. 2001, *J. Nat. Prod*. 64, 1052–1055. Fujii etal. 2000, *Tetrahedron* 56, 725–733. Bubik *et al*. 2008, *Biol. Chem. 389,* 1339–1346. Adiv *et al*. 2013, *J. Nat. Prod*. 76, 2307–2315.
Anabaenopeptin F1, AP KT864	865	HArg	CO	Lys	Ile	Hty	NMeAla	Phe	*Planktothrix rubescence* *Microcystis* sp. MB-K	Not determined No TRYi, no CHYi	Ferranti *et al*. 2011, *Rapid Commun. Mass Spectrom*. 25, 1173–1183. Beresovsky *et al*. 2006, *Isr. J. Chem* 46, 79–87.

Oscillamide B	869	Arg	CO	Lys	Met	Hty	NMeAla	Phe	*P. agardhii* CCAP 1459/11A	PP1i, PP2i	Sano *et al*. 2001, *J. Nat Prod*. 64, 1052–1055.
AP 877	878	Arg	CO	Lys	Ile	Hph	*N*MeAla	Phe	*Desmonostoc* sp.	Not determined	Sanz *et al*. 2015, *Marine Drugs* 13, 3892–3919
AP HU892	893	Arg	CO	Lys	Val	Hph	NMeHty	Ile	*Microcystis aeruginosa* bloom	Not determined	Gesner-Apter and Carmeli 2009, *J. Nat. Prod*. 72, 1429–1436.
AP KB906	907	Arg	CO	Lys	Ile	Hph	NMeHty	Ile	*Microcystis* spp. bloom	No TRYi, no CHYi	Elkobi-Peer and Carmeli 2015 *Marine Drugs* 13, 2347–2375.
AP 908	909	Arg	CO	Lys	Val	Hty	*N*MeHty	Ile	*P. agardhii*, CYA 126/8	CPAi, no TRYi no CHYi	Okumura *et al*. 2009, *J. Nat. Prod*. 72, 172–176.
Anabaenopeptin H	923	Arg	CO	Lys	Ile	Hty	NMeHty	Ile	*Oscillatoria agardhii* NIES-595	CPAi	Itou *et al*. 1999, *Bioorganic & Medical Chem. Lett*. 9, 1243–1246.
Oscillamide C	957	Arg	CO	Lys	Ile	Hty	NMeHty	Phe	*P. rubescens* CCAP 1459/14	PP1i, PP2i	Sano *et al*. 2001, *J. Nat Prod*. 64, 1052–1055.
AP 891	892	Arg	CO	Lys	Ile	MeHph	*N*MeAsn	Phe	*Desmonostoc* sp.	Not determined	Sanz *et al*. 2015, *Marine Drugs* 13, 3892–3919.
AP 905	906	Arg	CO	Lys	Ile	EtHph	*N*MeAsn	Phe	*Desmonostoc* sp.	Not determined	Sanz *et al*. 2015, *Marine Drugs* 13, 3892–3919.
Paltolide A	812	Arg	CO	Lys	Ala	Leu	Leu	Trp	*Theonella swinhoei*	No cytotoxicity	Plaza *et al*. 2010, *J. Nat. Prod*. 73, 485–488.
Paltolide B	842	Arg	CO	Lys	Ala	Leu	*N*MeLeu	L-5'-hydroxyTrp	*Theonella swinhoei*	No cytotoxicity	Plaza *et al*. 2010, *J. Nat. Prod*. 73, 485–488.

Paltolide C	904	Arg	CO	Lys	Ala	Leu	*N*MeLeu	L-6'-BrTrp	*Theonella swinhoei*	No cytotxicity	Plaza *et al.* 2010, *J. Nat. Prod.* 73, 485–488.
AP 906 (putative)	907	Arg	CO	Lys	Ile	MeHty	*N*MeLeu	Phe	*Microcystis* sp.	Not determined	Puddick *et al.* 2008, *Chemistry in New Zealand* 72, 25–28.
Anabaenopeptin G	909	Arg	CO	Lys	Ile	Hty	*N*MeLeu	Tyr	*Planktothrix agardhii* HUB 011	Not determined	Erhard *et al.* 1999, *Rapid Commun. Mass Spectrom.* 13, 337–343.
Glu(OMe) in exocyclic position											
AP MM822	823	Glu(OMe)	CO	Lys	Val	Hty	*N*MeAla	Phe	*Microcystis* sp.	CHYi, ELAi, no THROi, no TRYi	Zafir-Ilan and Carmeli 2010, *Tetrahedron* 66, 9194–9202.
Ile in exocyclic position 1											
Anabenopeptin I	760	Ile	CO	Lys	Val	Hty	*N*MeAla	Leu	*Aphanizomenon flos-aquae* NIES-81	CPAi	Murakami *et al.* 2000, *J. Nat. Prod.* 63, 1280–1282.
Scizopeptin 791	792	Ile	CO	Lys	Ile	Hph	*N*MeAla	Phe	Terrestial *Schizothrix* sp.	TRYi, no CHYi	Reshef and Carmeli 2002, *J. Natural Products* 65, 1187–1189.
Anabenopeptin J	794	Ile	CO	Lys	Val	Hty	*N*MeAla	Phe	*Aphanizomenon flos-aquae* NIES-81	CPAi	Murakami *et al.* 2000, *J. Nat. Prod.* 63, 1280–1282.
AP 807	808	Ile	CO	Lys	Ile	Hty	*N*MeAla	Phe	*Nodularia spumigena*, Australian strains Baltic Sea bloom	Not determined CPAi, PP1i	Mazur-Marzec *et al.* 2013, *Marine Drugs* 11, 1–19. This study
NP 823	824	Ile	CO	Lys	Val	Hph	*N*MeHty	Ser	Baltic Sea bloom	Not determined	This study
Nodulapeptin 855	856	Ile	CO	Lys	Met	Hph	*N*MeHty	Ser	*Nodularia spumigena* CCNP1402	Not determined	Mazur-Marzec *et al.* 2013, *Marine Drugs* 11, 1–19.

Anabaenopeptin T	866	Ile	CO	Lys	Val	Hty	*N*MeHty	Ile	Bloom material, lake Teganuma, Japan	CPAi	Kodani *et al*. 1999, *FEMS Microbiol. Lett*. 178, 343–348.
NP 865	866	Ile	CO	Lys	Val	Hph	*N*MeHty	AcSer	Baltic sea bloom	CPAi, PP1i	This study
NP 867	868	Ile	CO	Lys	Val	Hph	*N*MeHty	Met	Baltic sea bloom	CPAi, PP1i	This study
NP 879	880	Ile	CO	Lys	Ile	Hph	*N*MeHty	AcSer	*Nodularia spumigena* CCNP 1402, BY1,Node2, Nodg3, Nodh2	Not determined	Mazur-Marzec *et al*. 2013, *Marine Drugs* 11, 1–19.
Nodulapeptin 881	882	Ile	CO	Lys	Ile	Hph	*N*MeHty	Met	*Nodularia spumigena* CCNP 1402	Not determined	Mazur-Marzec *et al*. 2013, *Marine Drugs* 11, 1–19.
NP 883	884	Ile	CO	Lys	Val	Hph	*N*MeHty	Met(O)	Baltic sea bloom	CPAi, PP1i	This study
Nodulapeptin C	898	Ile	CO	Lys	Met	Hph	*N*MeHty	AcSer	*Nodularia spumigena* CCY9414	Not determined	Rouhiainen *et al*. 2010, *Chemistry & Biology* 17, 265–273.
NP 899	900	Ile	CO	Lys	Val	Hty	*N*MeHty	Me(O)	Baltic Sea bloom	PP1i, CPAi	This study
[Met][6] Nodulapeptin C	900	Ile	CO	Lys	Met	Hph	*N*MeHty	Met	*Nodularia spumigena* CCY9414	Not determined	Rouhiainen *et al*. 2010, *Chemistry & Biology* 17, 265–273.
Nodulapeptin B	914	Ile	CO	Lys	Met(O)	Hph	*N*MeHty	AcSer	*Nodularia spumigena* AV1	Not determined	Fujii *et al*. 1997, *Tetrahedron Letters* 31, 5525–5528.
NP 915	916	Ile	CO	Lys	Ile	Hph	*N*MeHty	Met	*Nodularia spumigena* , CCNP 1402, BY1, Node2, Nodg3, Nodh2	Not determined	Mazur-Marzec *et al*. 2013, *Marine Drugs* 11, 1–19.
Nodulapeptin A	930	Ile	CO	Lys	Met(O_2)	Hph	*N*MeHty	AcSer	*Nodularia spumigena* AV1	Not determined	Fujii *et al*. 1997, *Tetrahedron Letters* 31, 5525–5528.
NP931	932	Ile	CO	Lys	Met(O)	Hph	*N*MeHty	Met(O)	*Nodularia spumigena* CCNP1402, BY1	Not determined	Mazur-Marzec *et al*. 2013, *Marine Drugs* 11, 1–19.
Nodulapeptin 855	856	Ile	CO	Lys	MetO	Hph	*N*MeHph	Ser	*Nodularia spumigena* Baltic Sea and turkish strains	Not determined	Mazur-Marzec *et al*. 2013, *Marine Drugs* 11, 1–19.

[Ser][6] Nodulapeptin B	872	Ile	CO	Lys	MetO	Hph	*N*MeHph	Ser	*Nodularia spumigena* CCY9414	Not determined	Rouhiainen *et al.* 2010, *Chemistry & Biology* 17, 265–273.
Nodulapeptin 881	882	Ile	CO	Lys	Met	Hph	*N*MeHph	AcSer	*Nodularia spumigena* CCNP 1402, BY1	Not determined	Mazur-Marzec *et al.* 2013, *Mar. Drugs* 11, 1–19
Nodulapeptin 883	884	Ile	CO	Lys	MetO	Hph	*N*MeHph	Met	*Nodularia spumigena* CCNP 1402	Not determined	Mazur-Marzec *et al.* 2013, *Mar. Drugs* 11, 1–19.
[MHph][5] Nodulapeptin B	898	Ile	CO	Lys	MetO	Hph	*N*MeHph	AcSer	*Nodularia spumigena* CCY9414	not determined	Rouhiainen *et al.* 2010, *Chemistry & Biology* 17, 265–273.
Brunsvicamide A	845	Ile	CO	L-Lys D-Lys	Val	Leu	*N*Me-L-5'-hydroxyTrp	Phe	*Tychonema*	PPi (MptpB, weak) No PPi, CPAi and CPBi	Müller *et al.* 2006, *J. Med. Chem.* 49, 4871–4878. Walther *et al.* 2009, *ChemBioChem* 10, 1153–1162.
Brunsvicamide B	859	Ile/*allo*-Ile	CO	L-Lys	Ile	Leu	*N*Me-L-5'-hydroxyTrp	Phe	*Tychonema*	PPi (MptpB)	Muller *et al.* 2006, *J. Med Chem.* 49, 4871–4878.
Mozamide A	861	L-*allo*-Ile	CO	L-Lys	D-Val	Leu	*N*Me-L-5'-hydroxyTrp	Phe	*Theonella*, sponge	No anti-microbial activity	Schmidt *et al.* 1997, *J. Nat. Prod* 60, 779–782.
Mozamide B	875	L-*allo*-Ile	CO	L-Lys	D-Ile	Leu	*N*Me-L-5'-hydroxyTrp	Phe	*Theonella*, sponge	No anti-microbial activity	Schmidt *et al.* 1997, *J. Nat. Prod* 60, 779–782.
Brunsvicamide C	877	Ile/*allo*-Ile	CO	L-Lys	Val	Leu	*N*Me-L-*N*'-formyl-D-kynurenine	Phe	*Tychonema*	PPi (MptpB)	Muller *et al.* 2006, *J. Med Chem.* 49, 4871–4878.
(−)-Psymbamide	937	Ile	CO	Lys	Leu	Leu	*N*Me-L-5'-BrTrp	Phe	Sponge *Psammocinia* aff. *bulbosa*	Not determined	Robinson *et al.* 2007, *J. Nat. Prod.* 70, 1002–1009.
Pompanopeptin B	958	Ile	CO	Lys	Val	Hty	*N*MeAhpha	Htyr	*Lyngbya confervoides*, bloom	Not determined	Matthew *et al.* 2008, *Tetrahedron* 64, 4081–4089.

Leu in exocyclic position 1											
AP 848	849	Leu	CO	Lys	Ile	MeHph	*N*MeAsn	Phe	*Desmonostoc* sp.	Not determined	Sanz *et al*. 2015, *Marine Drugs* 13, 3892–3919.
AP 862	863	Leu	CO	Lys	Ile	EtHph	*N*MeAsn	Phe	*Desmonostoc* sp.	Not determined	Sanz *et al*. 2015, *Marine Drugs 13, 3892–3919.*
Konbamide	877	Leu	CO	L-Lys	Ala	Leu	*N*MeLeu	BhTrp	*Theonella*, sponge	CAM-PDE inhibition	Kobayashi *et al.* 1991, *J. Chem. Soc. Chem. Commun*. 1050–1052 Schmidt and Weinbrenner 1996, *Angew. Chem. Int. Ed. Engl*. 35(12) 1336–1338
Lys in exocyclic position 1											
Anabaenopeptin C	809	Lys	CO	Lys	Val	Hty	*N*MeAla	Phe	*Anabaena* sp. 90	Not determined	Fujii *et al.* 1996, In *Harmful and Toxic Algal Blooms* 559–562.
AP 849	850	Lys	CO	Lys	Ile	Hph	*N*MeAsn	Phe	*Desmonostoc* sp.	Not determined	Sanz *et al*. 2015, *Marine Drugs* 13, 3892–3919.
AP 863	864	Lys	CO	Lys	Ile	MeHph	*N*MeAsn	Phe	*Desmonostoc* sp.	Not determined	Sanz *et al*. 2015, *Marine Drugs* 13, 3892–3919.
AP 877	878	Lys	CO	Lys	Ile	EtHph	*N*MeAsn	Phe	*Desmonostoc* sp.	Not determined	Sanz *et al*. 2015, *Marine Drugs* 13, 3892–3919.
Phe in exocyclic position 1											
AP 813	814	Phe	CO	Lys	Val	Hty	*N*MeGly	Phe	Baltic Sea bloom	PP1i, CPAi	This study

Anabaenopeptin D	828	Phe	CO	Lys	Val	Hty	*N*MeAla	Phe	*Anabaena* sp. 202 A2/41 (*A. lemmermannii*), Baltic Sea bloom	not determined PP1i, CPAi	Fujii *et al*. 1996, In *Harmful and Toxic Algal Blooms* 559–562. This study
AP 841	842	Phe	CO	Lys	Ile	Hty	*N*MeAla	Phe	*Nodularia spumigena* CCNP 1401,1403, B15a	not determined	Mazur-Marzec *et al*. 2013, *Mar. Drugs* 11, 1–19
AP 841	842	Phe	CO	Lys	Val	Hph	*N*MeAla	Hty	*Desmonostoc* sp.	not determined	Sanz *et al*. 2015, *Marine Drugs* 13, 3892–3919.
Lyngbyaureidamide B	842	D-Phe	CO	Lys	Ile	Hty	*N*MeAla	Phe	*Lyngbya* sp. SAG 36.91	No CHY-like inh.	Zi *et al*. 2012, *Phytochemistry* 74, 173–177.
Lyngbyaureidamide A	856	D-Phe	CO	Lys	Ile	Hty	*N*MeAla	Hph	*Lyngbya* sp. SAG 36.91	No CHY-like inh.	Zi *et al*. 2012, *Phytochemistry* 74, 173–177.
AP 855	856	Phe	CO	Lys	Ile	Hph	*N*MeAla	Hty	*Nostoc* sp.	Not determined	Sanz *et al*. 2015, *Marine Drugs* 13, 3892–3919.
AP 855	856	Phe	CO	Lys	Val	Val	*N*MeHty	Met(O)	Baltic Sea bloom	PP1i, CPAi	This study
AP 857	858	Phe	CO	Lys	Val	Hty	*N*MeAla	Hty	*Nostoc* sp.	Not determined	Sanz *et al*. 2015, *Marine Drugs* 13, 3892–3919.
AP 857	858	Phe	CO	Lys	Val	Hph	*N*MeHty	Ser	Baltic Sea bloom	PP1i, CPAi	This study
NP 869	870	Phe	CO	Lys	Val	Leu	*N*MeHty	Met(O)	Baltic Sea bloom	PP1i	This study
AP 871	872	Phe	CO	Lys	Ile	Hty	*N*MeHty	Hty	*Nostoc* sp.	Not determined	Sanz *et al*. 2015, *Marine Drugs* 13, 3892–3919.
NP 899	900	Phe	CO	Lys	Val	Hph	*N*MeHty	AcSer	*Nodularia spumigena* KAC 66 Baltic Sea bloom	Not determined PP1i, CPAi	Schumacher *et al.* 2012, *Tetrahedron* 68, 1622–1628. This study
NP 901	902	Phe	CO	Lys	Val	Hph	*N*MeHty	Met	*Nodularia spumigena* KAC 66	Not determined	Schumacher *et al.* 2012, *Tetrahedron* 68, 1622–1628.

NP 915	916	Phe	CO	Lys	Val	Hty	*N*MeHty	AcSer	*Nodularia spumigena* KAC66, CCNP 1423, CCNP 1424, CCNP 1425 Baltic Sea bloom	PP1i, CPAi	Mazur-Marzec *et al.* 2013, *Marine Drugs* 11, 1–19. This study
NP 917	918	Phe	CO	Lys	Val	Hph	*N*MeHty	Met(O)	*Nodularia spumigena* KAC 66 Baltic Sea bloom	Not determined PP1i, CPAi	Schumacher *et al.* 2012, *Tetrahedron* 68, 1622–1628. This study
NP 933	934	Phe	CO	Lys	Val	Hty	*N*MeHty	Met(O)	*Nodularia spumigena* CCNP 1423, CCNP 1424, CCNP 1425 Baltic Sea bloom	PP1i, CPAi	Mazur-Marzec *et al.* 2013, *Marine Drugs* 11, 1–19. This study
NP 883	884	Phe	CO	Lys	Val	Hph	NMeHph	AcSer	*Nodularia spumigena* KAC66, CCNP 1423, CCNP 1424, CCNP 1425	not determined	Mazur-Marzec *et al.* 2013, *Marine Drugs* 11, 1–19.
AP 813	814	Phe	CO	Lys	Val	Hty	*N*MeGly	Phe	Baltic Sea bloom	PP1i, CPAi	This study
AP NZ825	826	Phe	CO	Lys	Ile	Hph	*N*MeGly	Hph	*Anabaena* sp. TAU strain NZ-3-1	No activity towards serine proteaser	Grach-Progrebinsky and Carmeli 2008, *Tetrahedron* 64, 10233–10238.
AP NZ841	842	Phe	CO	Lys	Ile	Hty	*N*MeGly	Hph	*Anabaena* sp. TAU strain NZ-3-1	No activity towards serine proteaser	Grach-Progrebinsky and Carmeli 2008, *Tetrahedron* 64, 10233–10238.
Nostamide A	842	Phe	CO	Lys	Ile	Hph	*N*MeGly	Hty	*Nostoc punctiforme* PCC73102	Not determined	Rouhiainen *et al.* 2010, *Chemistry & Biology* 17, 265–267.
AP NZ857	858	Phe	CO	Lys	Ile	L-Hty	*N*MeGly	Hty	*Anabaena* sp. TAU strain NZ-3-1 *Nostoc punctiforme* PCC73102	No activity towards serine proteaser	Grach-Progrebinsky and Carmeli 2008, *Tetrahedron* 64, 10233–10238. Rouhiainen *et al.*

											2010, *Chemistry & Biology* 17, 265–273.
AP 882	883	Phe	CO	Lys	Ile	MeHph	*N*MeAsn	Phe	*Nostoc* sp.	Not determined	Sanz *et al*. 2015, *Marine Drugs* 13, 3892–3919.
AP 896	897	Phe	CO	Lys	Ile	EtHph	*N*MeAsn	Phe	*Nostoc* sp.	Not determined	Sanz *et al*. 2015, *Marine Drugs* 13, 3892–3919.
Keramamide A	943	Phe	CO	L-Lys	Leu	Leu	*N*MeCht	Phe	*Theonella*, sponge	No cytotoxicity, SERCA inhibition	Kobyashi *et al.* 1991, *J. Chem. Soc. Perin. Trans.* 1, 2609–2611.
Keramamide L	927	Phe	CO	L-Lys	Leu	Leu	*N*MeCTrp	Phe	*Theonella*, sponge	Cytotoxicity	Uemoto *et al.* 1999, *Tetrahedron* 55, 12543–12548.
Trp in exocyclic position 1											
Ferintoic acid A	867	Trp	CO	Lys	Val	Htyr	*N*MeAla	Phe	*Microcystis aeruginosa* bloom	No CHYi	Williams *et al.* 1996, *J. Nat. Prod.* 59, 570–575.
Ferintoic acid B	881	Trp	CO	Lys	*allo*-Ile	Htyr	*N*MeAla	Phe	*Microcystis aeruginosa* bloom	No CHYi	Williams *et al.* 1996, *J. Nat. Prod.* 59, 570–575.
Tyr in exocyclic position 1											
Anabaenopeptin A	844	Tyr	CO	Lys	Val	Hty	*N*MeAla	Phe	*Anabaena flos-aquae* NRC 525-17 Baltic Sea bloom	rNEc, no Ppi PP1i PP1i, CPAi	Harada *et al.* 1995, *Tetraheddon Letters* 36, 1511–1514. Gkelis *et al.* 2006, *Aquatic Toxicology* 78, 32–41. This study
Oscillamide Y	858	Tyr	CO	Lys	Ile	Hty	*N*MeAla	Phe	*Oscillatoria agardhii*= *P. rubescense* NIES-610 Synthetic and	CHYi No CHYi PP1i, CPAi	Sano and Kaya 1995, *Tetrahedron lett.* 36, 5933–5936. Marsh *et al.* 1997, *J. Org. Chem.* 62,

									natural Baltic Sea bloom		6199–6203. This study
AP KB899	900	Tyr	CO	Lys	Val	Hph	*N*MeHty	Ile	*Microcystis* spp. bloom	No TRYi, no CHYi	Elkobi-Peer and Carmeli 2015, *Mar. Drugs* 13, 2347–2375.
AP MM913	914	Tyr	CO	Lys	Ile	Hph	*N*MeHty	Ile	*Microcystis* sp., bloom	No endoprotease inhibition	Zafir-Ilan and Carmeli 2010, *Tetrahedron* 66, 9194–9202.
AP 915	916	Tyr	CO	Lys	Ile	Hty	*N*MeHty	Ile	*P. agardhii*, CYA 126/8	No TRYi, no CHYi	Okumura *et al*. 2009, *J. Natural Products* 72, 172–176.
Anabaenopeptin G *	930	Tyr	CO	Lys	Ile	Hty	*N*MeHty	Ile	*Oscillatoria agardhii* NIES-595	CPAi	Itou *et al*. 1999, *Bioorganic & Medical Chem. Lett*. 9, 1243–1246.
Oscillamide H	930	Tyr	CO	Lys	*N*MeIle	Ile	*N*MeHty	Ile	*Planktothrix agardhii*, NIES-595	Not determined	Sano *et al*. 1996, *Tennen Yuki Kagobatsu Toronkai Koen Yoshishu* 38, 433–438. Dr T. Sano, personal communication
Val in exocyclic position 1											
AP 802	803	Val	CO	Lys	Ile	Trp	*N*MeAla	Phe	*Brasilonema* spp.	Not determined	Sanz *et al*. 2015, *Marine Drugs* 13, 3892–3919.

Abbreviations: BhTrp, 2-bromo-5-hydroxytryptophan. CAM-PDE, calmodulin -activated brain phosphodiesterase. CHY, chymotrypsin. CPA, carboxypeptidase A. ELA, elastase. i, inhibition. MeCht, 6-chloro-5-hydroxy-*N*-methyltryptophan. MptpB, *Mycobacterium tuberculosis* protein tyrosine phophatase B. PP, protein phosphatase. rNec, norepinephrin induced contraction. SERCA, sarcoplasmic reticulum Ca^{2+}-ATPase. TRY, trypsin. THRO, thrombin.