

Supplementary Information

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Figure S6. Enhanced ion product mass spectra of partially identified aeruginosin **19** with [M + H] ion at m/z 603 (*N. spumigena* KAC66). The mass signals were assigned to the following fragments: 585 [M + H – H₂O], 429 [M + H – Arg], 342 [Choi-Arg + H], 325 [Choi-Arg + H – NH₂], 307 [Choi-Arg + H – H₂O – NH₃], 300 [Choi-Arg + H – CH₂N₂], 282 [Choi-Arg + H – H₂O – CH₂N₂], 175 [Arg + H], 140 Choi-immonium ion, 122 Choi-immonium – H₂O. 8

Figure S7. Enhanced ion product mass spectra of partially identified aeruginosin **22** with [M + H] ion at m/z 559 (*N. spumigena* Node2). The mass signals were assigned to the following fragments: 541 [M + H – H₂O], 298 [Choi-Agm + H], 281 [Choi-Agm + H – NH₂], 256 [Choi-Arg + H – CH₂N₂], 238 [Choi-Arg + H – H₂O – CH₂N₂], 210 [Choi-Arg + H – H₂O – CH₂N₂ – CO], 140 Choi-immonium ion, 122 Choi-immonium – H₂O, 114 [C₅H₁₂N₃] (Agm).

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Figure S8. Enhanced ion product mass spectra of anabaenopeptin **25** Phe-CO-[Lys-Val-Hty-MeHty-MetO] with [M + H] ion at m/z 934 (*N. spumigena* bloom sample, 3 July 2012). The mass signals were assigned to the following fragments: 916 [M + H – H₂O], 906 [M + H – CO], 888 [M + H – H₂O – CO], 870 [M + H – CH₃SOH (from MetO)], 787 [M + H – MetO], 769 [M + H – Phe – 2H], 757 [M + H – Hty], 705 [M + H – Phe – 2H – CH₃SOH (from MetO)], 677 [M + H – (CO-Phe) – 2H – CH₃SOH (from MetO)], 594 [Val-(Lys-CO)-MetO-MeHty + H], 511 [MeHty-MeO-(Lys-CO) + H], 447 [MeHty-MeO-(Lys-CO) + H – CH₃SOH (from MetO)], 403 [Lys-Val-Hty-H], 369 [MeHty-Hty + H], 339 [MetO-MeHty + H], 164 MeHty, 107 [CH₂PhOH], 84 Lys-immonium ion.

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Figure S9. Enhanced ion product mass spectra of anabaenopeptin **32** Ile-CO-[Lys-MetO-Hph-MeHty-MetO] with [M + H] ion at m/z 932 (*N. spumigena* CCNP1402). The mass signals were assigned to the following fragments: 914 [M + H – H₂O], 904 [M + H – CO], 886 [M + H – H₂O – CO], 868 [M + H – CH₃SOH (from MetO)], 801 [M + H – Ile – 2H], 737 [M + H – Ile – 2H – CH₃SOH (from MetO)], 511 [MeHty-MeO-(Lys-CO) + H], 447 [MeHty-MeO-(Lys-CO) + H – CH₃SOH (from MetO)], 436 [MeHy-Hph-MetO + H – CH₃SOH (from MetO)], 339 [MeHty-MetO + H], 164 MeHty, 107 [CH₂PhOH], 84 Lys-immonium ion.

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Figure S10. Enhanced ion product mass spectra of anabaenopeptin **39** Ile-CO-[Lys-Met-Hph-MeHph-AcSer] with [M + H] ion at m/z 882 (*N. spumigena* BY1). The mass signals were assigned to the following fragments: 864 [M + H – H₂O], 854 [M + H – CO], 822 [M + H – CH₃COOH (from AcSer)], 751 [M + H – Ile – 2H], 725 [M + H – (CO-Ile)], 723 [M + H – (CO-Ile) – 2H], 530 [Met-(Lys-CO-Ile)-Met + H – H₂O], 486 [Met-(Lys-CO-Ile)-(AcSer) + H – CH₃COOH (from AcSer)], 477 [MeHph-AcSer-(Lys-CO) + H], 468 [MeHph-Hph-Met + H], 337 [Hph-MeHph + H], 84 Lys-immonium ion.

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Figure S11. Enhanced ion product mass spectra of anabaenopeptin **41** Ile-CO-[Lys-Ile-Hph-MeHty-AcSer] with [M + H] ion at m/z 880 (*N. spumigena* Node2). The mass signals were assigned to the following fragments: 862 [M + H – H₂O], 852 [M + H – CO], 834 [M + H – H₂O – CO], 820 [M + H – CH₃COOH (from AcSer)], 767 [M + H – Ile], 749 [M + H – Ile – 2H], 723 [M + H – (CO + Ile)], 719 [M + H – Hph], 606 [MeHty-AcSer-(Lys-CO-Ile) + H], 493 [MeHty-AcSer-(Lys-CO) + H], 164 MeHty, 107 [CH₂PhOH], 84 Lys-immonium ion.

13

Figure S1. Total ion current chromatograms of *N. spumigena* strains: NSBL-06 (A), NSBR-02 (B), CCNP1401 (C) and BY1 (D).

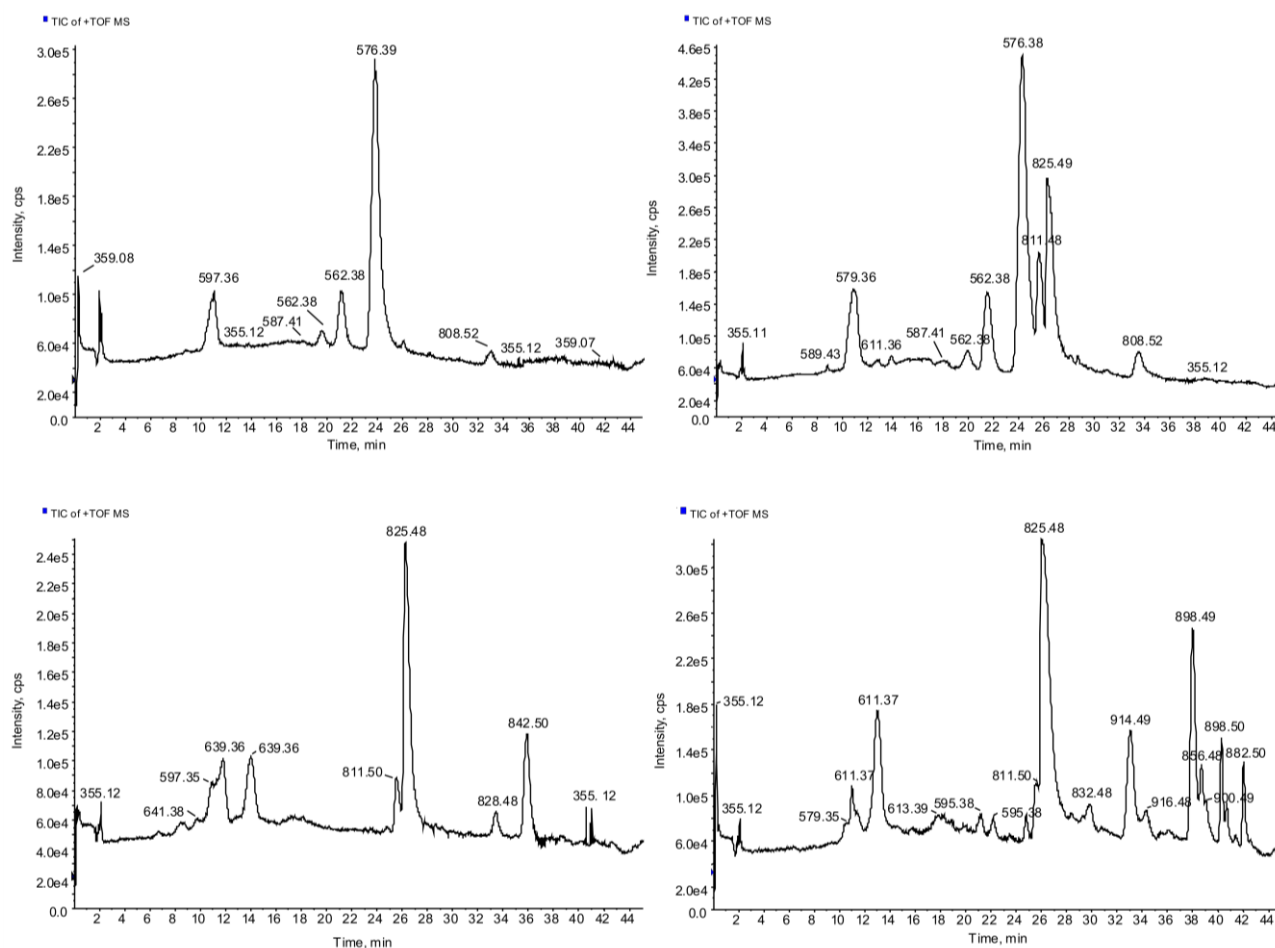


Figure S2. Enhanced ion product mass spectra of spumigin **12** Hpla-Tyr-Pro-Argal with $[M + H]$ ion at m/z 583 (*N. spumigena* 1403). The structure was elucidated mainly based on the mass signals at m/z : 565 $[M + H - H_2O]$, 523 $[M + H - H_2O - CH_2N_2]$, 425 $[Hpla-Tyr-Pro + H]$, 300 $[Hpla-Tyr + H - CO]$, 239 $[Pro-Argal + H - NH_2]$, 221 $[Pro-Argal + H - H_2O - NH_2]$, 142 $[Argal + H - NH_3]$, 136 Tyr-immonium ion, 100 $[C_4H_{10}N_3]$ Argal fragment, 70 Pro-immonium ion.

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Acq. Date: Friday, December 03, 2010

Polarity/Scan Type: Positive Enhanced Product Ion

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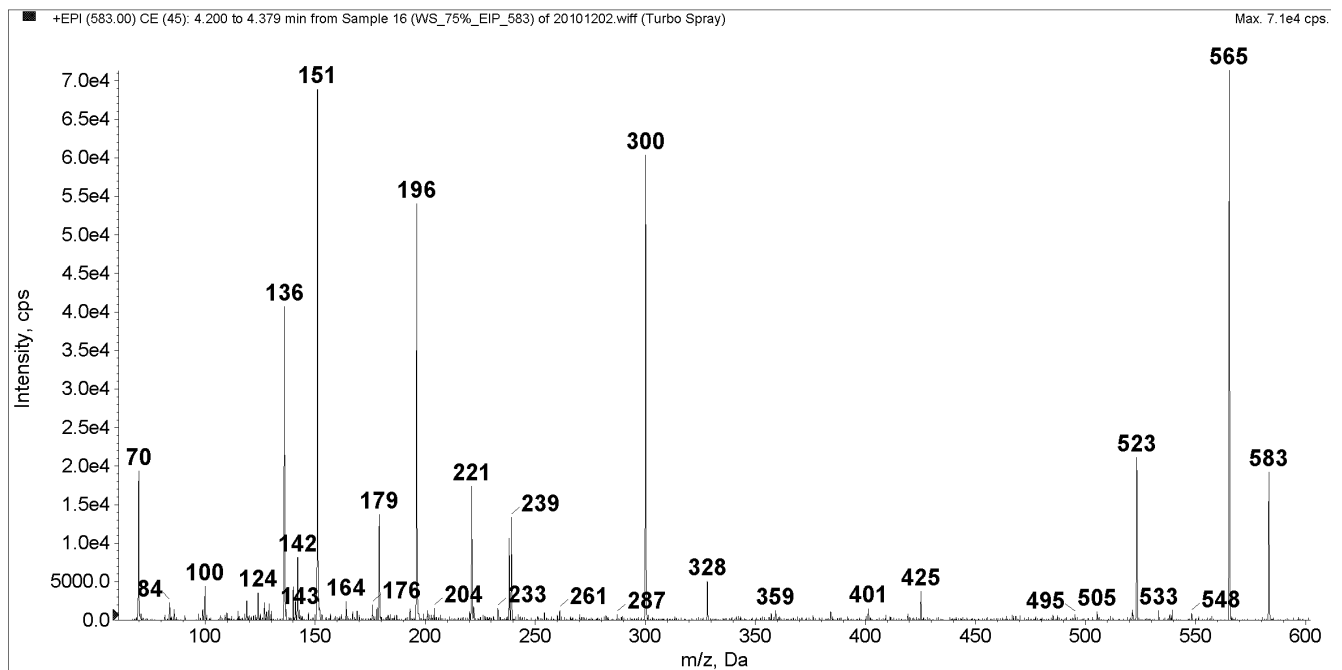


Figure S3. Enhanced ion product mass spectra of spumigin **13** Hpla-Hty-MePro-Agm with $[M + H]$ ion at m/z 583 (*N. spumigena* Nodh2). The structure was elucidated mainly based on the mass signals at m/z : 565 $[M + H - H_2O]$, 541 $[M + H - CH_2N_2]$, 523 $[M + H - H_2O - CH_2N_2]$, 453 $[Hpla-Hty-MePro + H]$, 342 $[Hpla-Hty + H]$, 314 $[Hpla-Htyr + H - CO]$, 225 $[MePro-Agm + H - NH_2]$, 208 $[HOCHCO-Hty + H - CO]$, 114 $[C_5H_{12}N_3]$ (Agm), 107 $[CH_2PhOH]$, 84 MePro-immonium ion.

Acq. Time: 13:29
Acq. Date: Friday, July 29, 2011

Polarity/Scan Type: Positive Enhanced Product Ion

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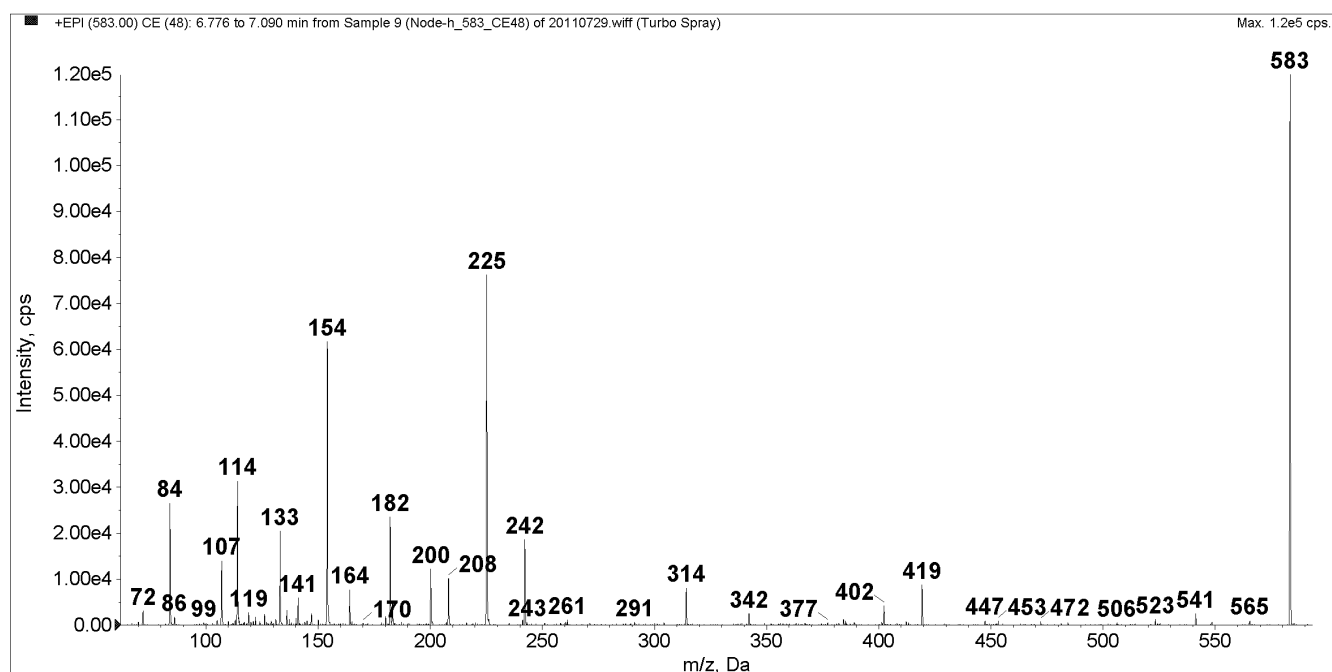


Figure S4. Enhanced ion product mass spectra of spumigin 15 (Hpla + 42)-Leu-Pro-Argal with $[M + H]$ ion at m/z 575 (*N. spumigena* B15a). The structure was elucidated mainly based on the mass signals at m/z : 557 $[M + H - H_2O]$, 515 $[M + H - H_2O - CH_2N_2]$ or/and $[M + H - CH_3COOH]$, 417 $[(Hpla + 42)\text{-Leu-Pro} + H]$, 320 $[(Hpla + 42)\text{-Leu} + H]$, 292 $[(Hpla + 42)\text{-Leu} + H - CO]$, 239 $[\text{Pro-Argal} + H - NH_2]$, 221 $[\text{Pro-Argal} + H - H_2O - NH_2]$, 142 $[\text{Argal} + H - NH_3]$, 100 $[C_4H_{10}N_3]$ Argal fragment, 86 Leu-immonium ion, 70 Pro-immonium ion.

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Acq. Date: Tuesday, March 09, 2010

Polarity/Scan Type: Positive Enhanced Product Ion

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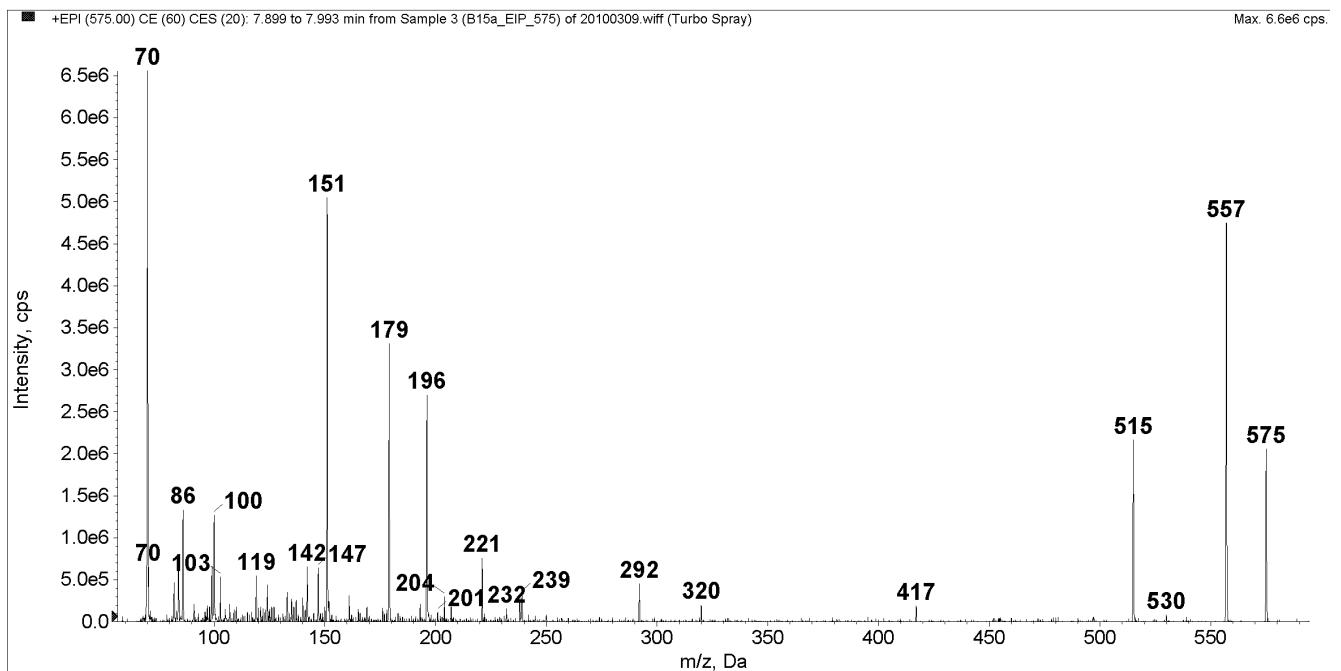


Figure S5. Enhanced ion product mass spectra of spumigin **18** Hpla-Hty-Pro-OH with $[M + H]$ ion at m/z 457 (*N. spumigena* CCNP1403). The structure was elucidated mainly based on the mass signals at m/z : 439 [Hpla-Hty-Pro + H], 342 [Hpla-Hty + H], 314 [Hpla-Hyr + H - CO], 208 [HOCHCO-Hty + H - CO], 107 [CH₂PhOH], 70 Pro-immonium ion.

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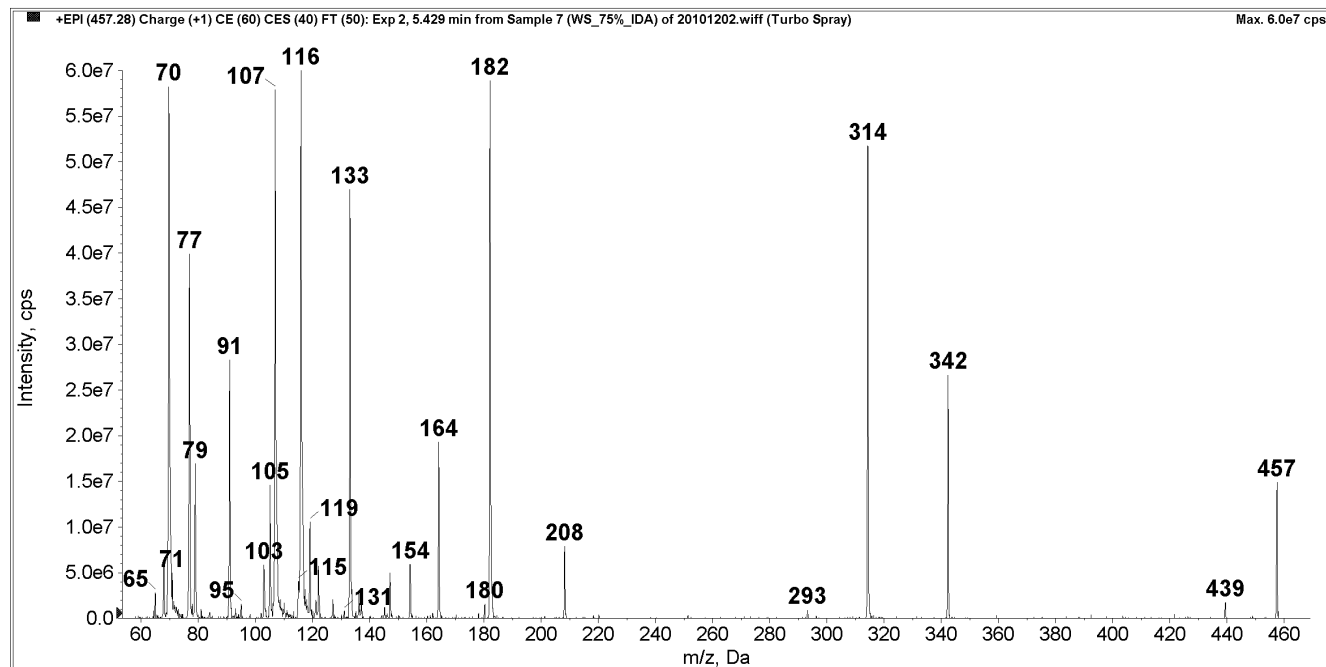


Figure S6. Enhanced ion product mass spectra of partially identified aeruginosin **19** with $[M + H]$ ion at m/z 603 (*N. spumigena* KAC66). The mass signals were assigned to the following fragments: 585 $[M + H - H_2O]$, 429 $[M + H - Arg]$, 342 $[Choi-Arg + H]$, 325 $[Choi-Arg + H - NH_2]$, 307 $[Choi-Arg + H - H_2O - NH_3]$, 300 $[Choi-Arg + H - CH_2N_2]$, 282 $[Choi-Arg + H - H_2O - CH_2N_2]$, 175 $[Arg + H]$, 140 Choi-immonium ion, 122 Choi-immonium $- H_2O$.

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Acq. Date: Friday, March 19, 2010

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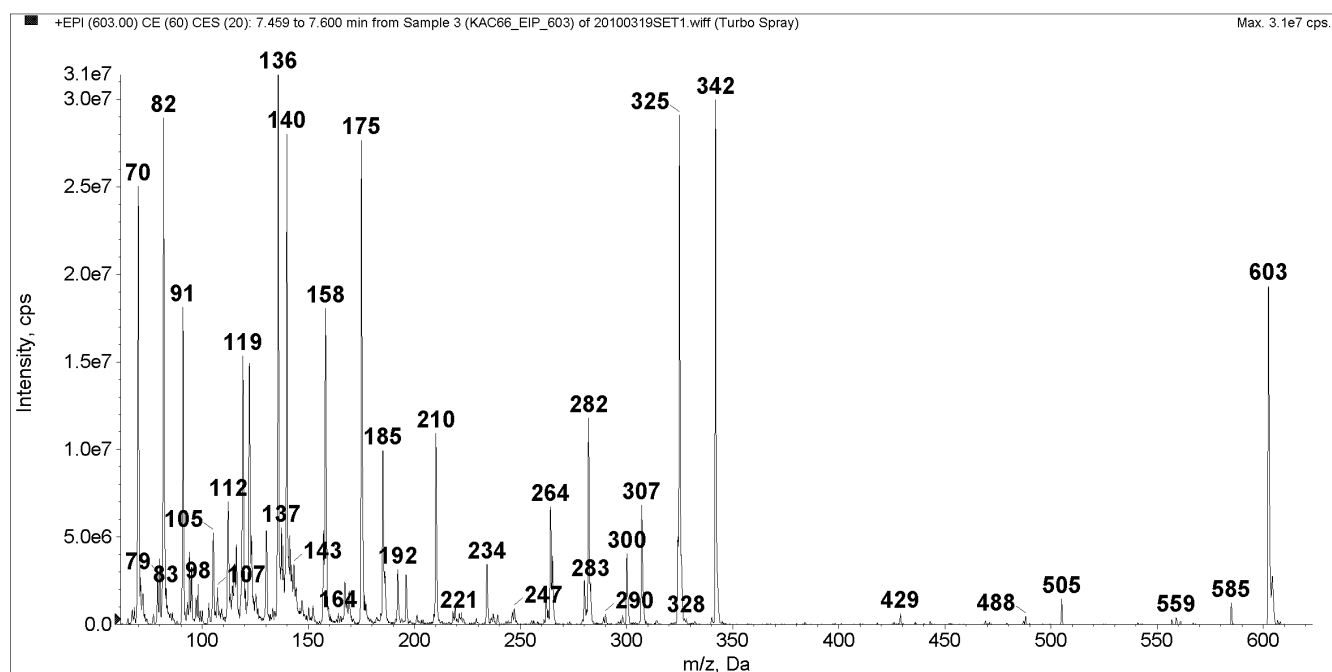


Figure S7. Enhanced ion product mass spectra of partially identified aeruginosin **22** with $[M + H]$ ion at m/z 559 (*N. spumigena* Node2). The mass signals were assigned to the following fragments: 541 $[M + H - H_2O]$, 298 [Choi-Agm + H], 281 [Choi-Agm + H - NH_2], 256 [Choi-Arg + H - CH_2N_2], 238 [Choi-Arg + H - $H_2O - CH_2N_2$], 210 [Choi-Arg + H - $H_2O - CH_2N_2 - CO$], 140 Choi-immonium ion, 122 Choi-immonium - H_2O , 114 $[C_5H_{12}N_3]$ (Agm).

Acq. Time: 11:10
Acq. Date: Monday, August 22, 2011

Polarity/Scan Type: Positive Enhanced Product Ion

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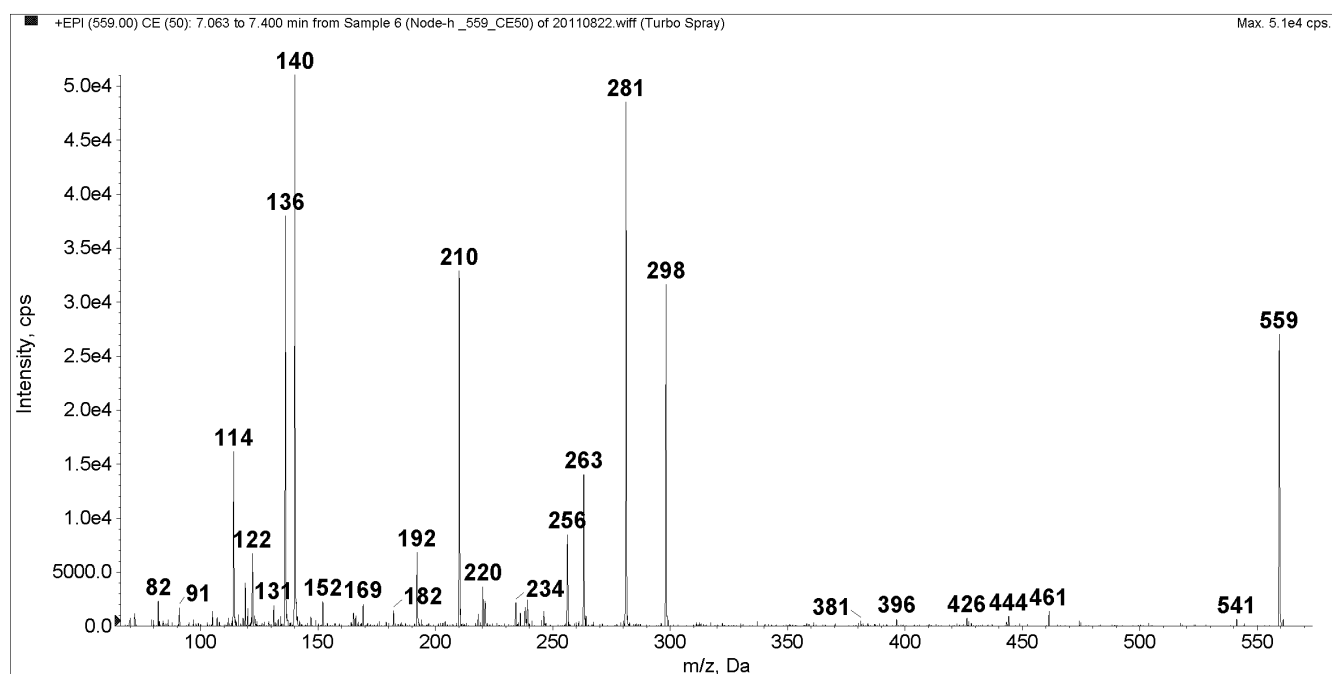


Figure S8. Enhanced ion product mass spectra of anabaenopeptin 25 Phe-CO-[Lys-Val-Hty-MeHty-MetO] with $[M + H]$ ion at m/z 934 (*N. spumigena* bloom sample, 3 July 2012). The mass signals were assigned to the following fragments: 916 $[M + H - H_2O]$, 906 $[M + H - CO]$, 888 $[M + H - H_2O - CO]$, 870 $[M + H - CH_3SOH$ (from MetO)], 787 $[M + H - MetO]$, 769 $[M + H - Phe - 2H]$, 757 $[M + H - Hty]$, 705 $[M + H - Phe - 2H - CH_3SOH$ (from MetO)], 677 $[M + H - (CO-Phe) - 2H - CH_3SOH$ (from MetO)], 594 $[Val-(Lys-CO)-MetO-MeHty + H]$, 511 $[MeHty-MeO-(Lys-CO) + H]$, 447 $[MeHty-MeO-(Lys-CO) + H - CH_3SOH$ (from MetO)], 403 $[Lys-Val-Hty-H]$, 369 $[MeHty-Hty + H]$, 339 $[MetO-MeHty + H]$, 164 MeHty, 107 $[CH_2PhOH]$, 84 Lys-immonium ion.

Acq. Time: 09:43
Acq. Date: Wednesday, July 11, 2012

Polarity/Scan Type: Positive Enhanced Product Ion

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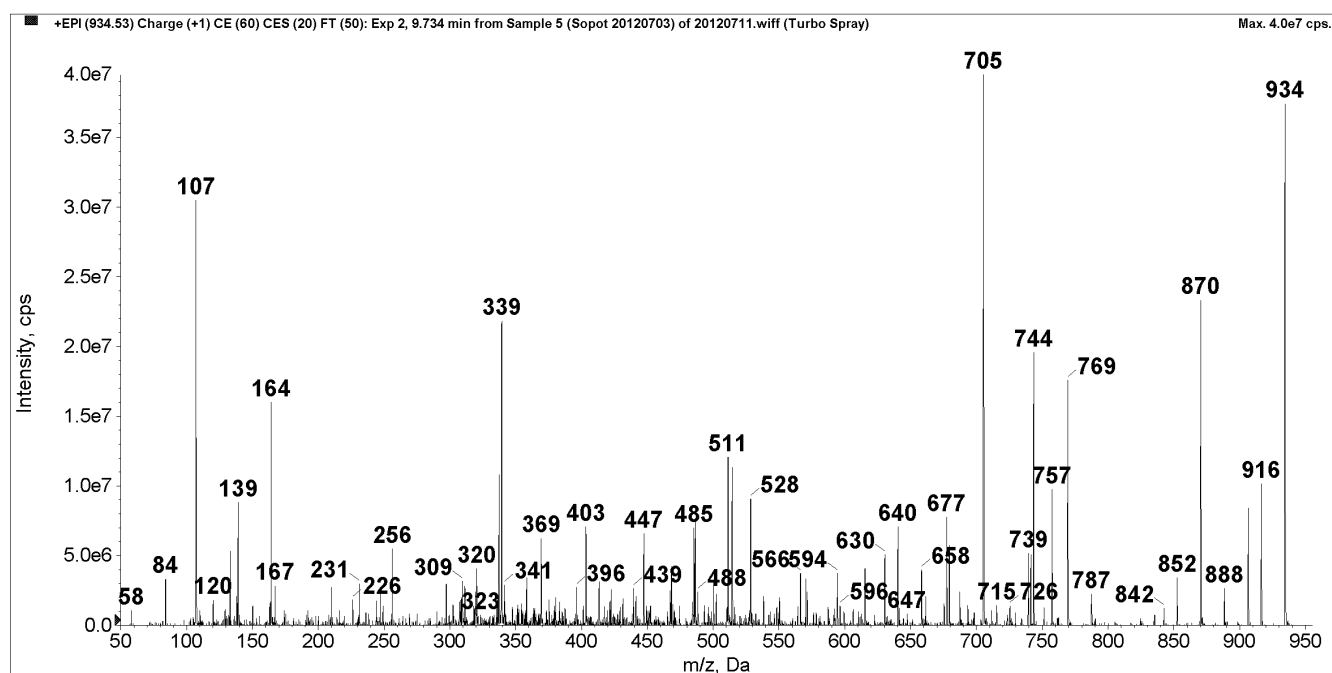
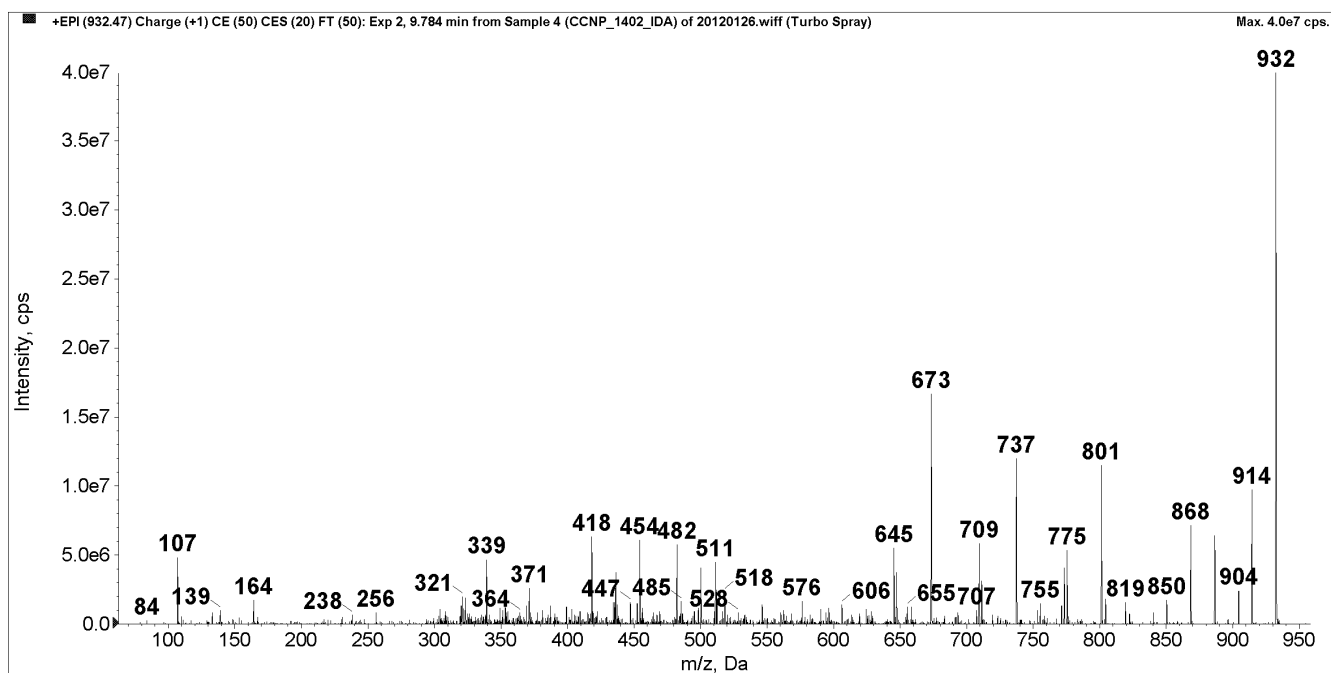


Figure S9. Enhanced ion product mass spectra of anabaenopeptin 32 Ile-CO-[Lys-MetO-Hph-MeHty-MetO] with $[M + H]$ ion at m/z 932 (*N. spumigena* CCNP1402). The mass signals were assigned to the following fragments: 914 $[M + H - H_2O]$, 904 $[M + H - CO]$, 886 $[M + H - H_2O - CO]$, 868 $[M + H - CH_3SOH$ (from MetO)], 801 $[M + H - Ile - 2H]$, 737 $[M + H - Ile - 2H - CH_3SOH$ (from MetO)], 511 $[MeHty-MeO-(Lys-CO) + H]$, 447 $[MeHty-MeO-(Lys-CO) + H - CH_3SOH$ (from MetO)], 436 $[MeHy-Hph-MetO + H - CH_3SOH$ (from MetO)], 339 $[MeHty-MetO + H]$, 164 MeHty, 107 $[CH_2PhOH]$, 84 Lys-immonium ion.

Acq. Time: 11:15
Acq. Date: Thursday, January 26, 2012

Polarity/Scan Type: Positive Enhanced Product Ion

Acq. File: 20120126.wiff



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Figure S10. Enhanced ion product mass spectra of anabaenopeptin **39** Ile-CO-[Lys-Met-Hph-MeHph-AcSer] with $[M + H]$ ion at m/z 882 (*N. spumigena* BY1). The mass signals were assigned to the following fragments: 864 $[M + H - H_2O]$, 854 $[M + H - CO]$, 822 $[M + H - CH_3COOH$ (from AcSer)], 751 $[M + H - Ile - 2H]$, 725 $[M + H - (CO-Ile)]$, 723 $[M + H - (CO-Ile) - 2H]$, 530 $[Met-(Lys-CO-Ile)-Met + H - H_2O]$, 486 $[Met-(Lys-CO-Ile)-(AcSer) + H - CH_3COOH$ (from AcSer)], 477 $[MeHph-AcSer-(Lys-CO) + H]$, 468 $[MeHph-Hph-Met + H]$, 337 $[Hph-MeHph + H]$, 84 Lys-immonium ion.

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Acq. Date: Wednesday, February 15, 2012

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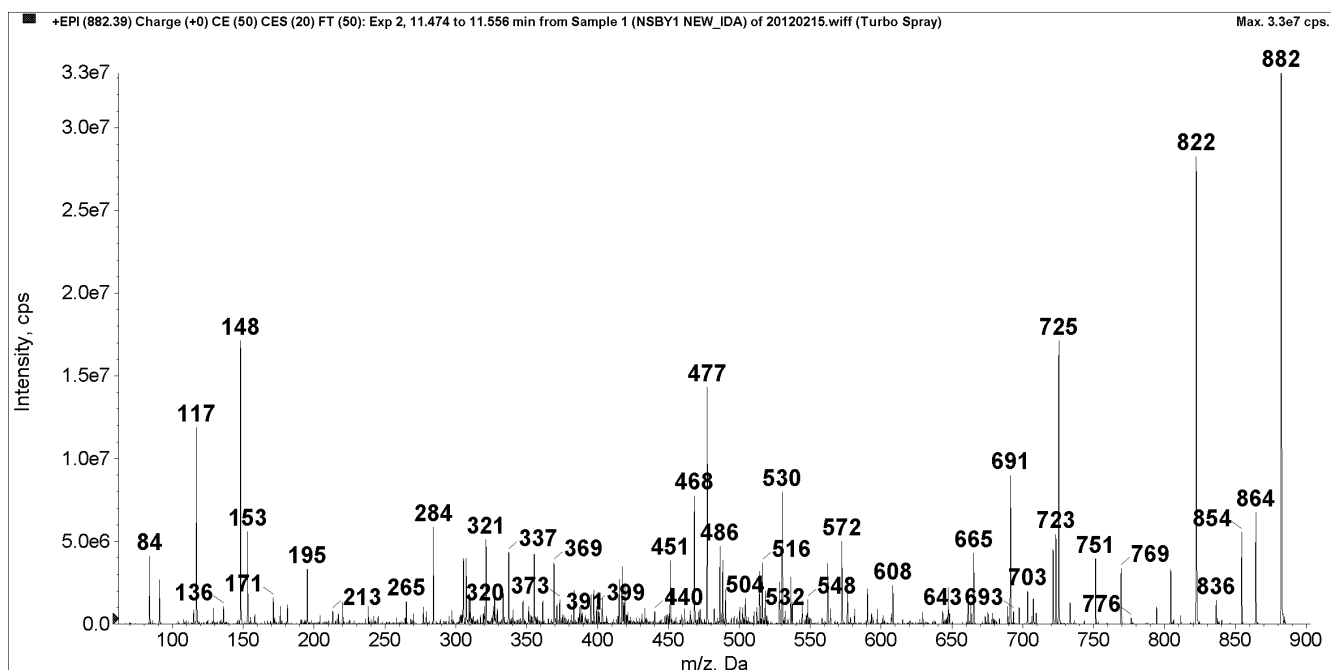


Figure S11. Enhanced ion product mass spectra of anabaenopeptin **41** Ile-CO-[Lys-Ile-Hph-MeHty-AcSer] with $[M + H]$ ion at m/z 880 (*N. spumigena* Node2). The mass signals were assigned to the following fragments: 862 $[M + H - H_2O]$, 852 $[M + H - CO]$, 834 $[M + H - H_2O - CO]$, 820 $[M + H - CH_3COOH$ (from AcSer)], 767 $[M + H - Ile]$, 749 $[M + H - Ile - 2H]$, 723 $[M + H - (CO + Ile)]$, 719 $[M + H - Hph]$, 606 $[MeHty-AcSer-(Lys-CO-Ile) + H]$, 493 $[MeHty-AcSer-(Lys-CO) + H]$, 164 MeHty, 107 $[CH_2PhOH]$, 84 Lys-immonium ion.

Acq. Time: 12:53
Acq. Date: Thursday, January 26, 2012

Polarity/Scan Type: Positive Enhanced Product Ion

Acq. File: 20120126.wiff

