

Supplementary Material: *Nostoc edaphicum* CCNP1411 from the Baltic Sea – a new producer of nostocyclopeptides

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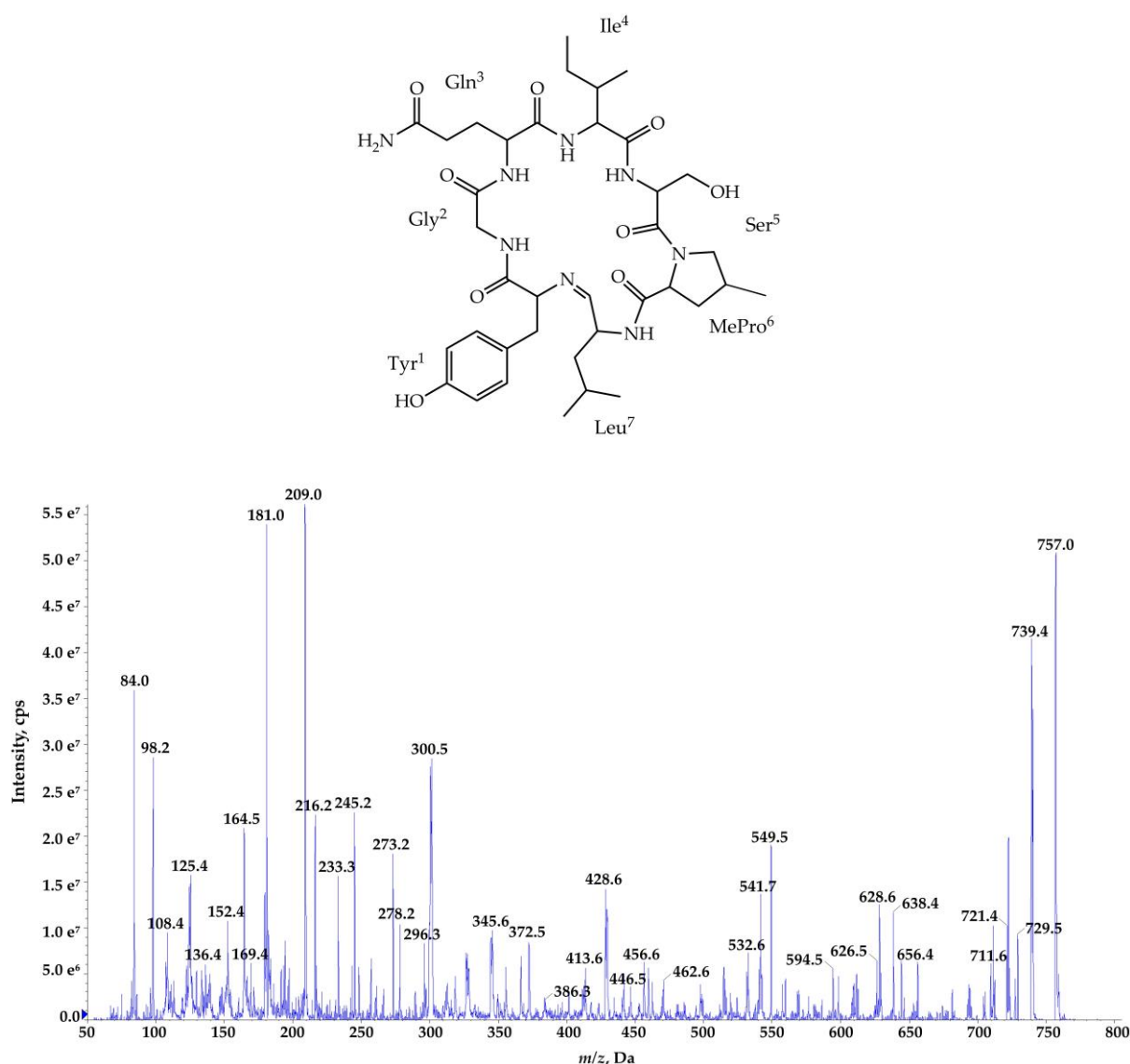


Figure S1: Structure and enhanced product ion mass spectrum of the cyclic nostocyclopeptide **Ncp-A1** cyclo[Tyr+Gly+Gln+Ile+Ser+MePro+Leu] identified based on the following fragment ions: m/z 757 [M+H]; 739 [M+H – H₂O]; 729 [M+H – CO]; 721 [M+H – 2H₂O]; 628 [M+H – MePro – H₂O], 626 [M+H – Ile – H₂O]; 594 [M+H – Tyr]; 549 [Tyr+Gly+Gln+Ile+Ser+H]; 541 [M+H – (Ser+MePro) – H₂O], 446 [M+H – (Ile+Ser+MePro)]; 428 [M+H – (Ile+Ser+MePro) – H₂O]; 386 [Gly+Gln+Ile+Ser+H]; 372 [MePro+Leu+Tyr+H]; 300 [Leu+Tyr+Gly+H – H₂O]; 209 [MePro+Leu+H]; 181 [MePro+Leu+H – CO]; 86 – Ile/Leu immonium; 84 MePro immonium.

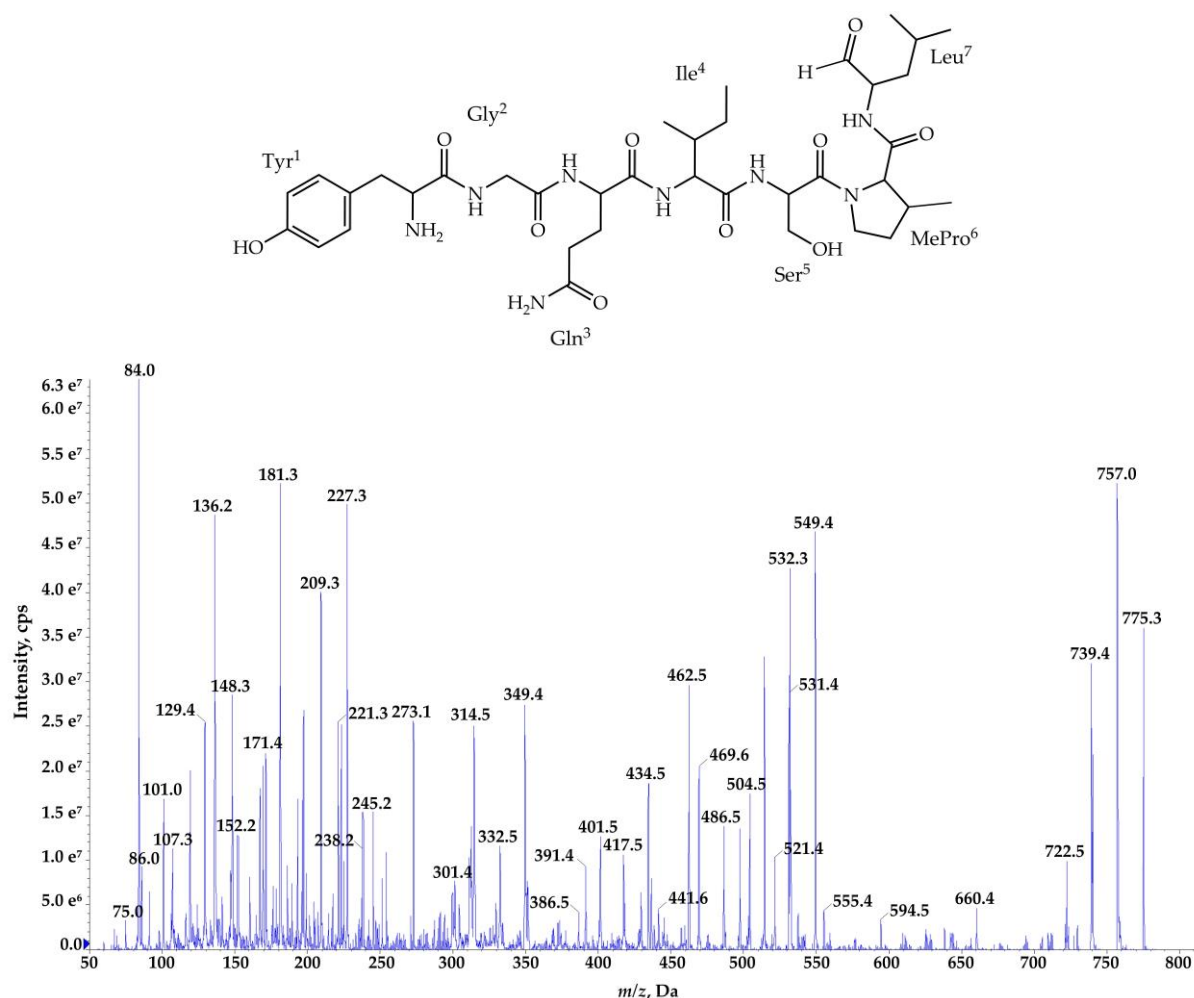


Figure S2: Structure and enhanced product ion mass spectrum of the linear peptide aldehyde **Ncp-A1-L** (linear aldehyde of **Ncp-A1**) Tyr+Gly+Gln+Ile+Ser+MePro+Leu identified based on the following fragment ions: m/z 775 [M+H]; 757 [M+H – H₂O]; 739 [M+H – 2H₂O]; 660 [M+H – Leu]; 549 [Tyr+Gly+Gln+Ile+Ser+H]; 531 [Tyr+Gly+Gln+Ile+Ser+H – H₂O]; 521 [Tyr+Gly+Gln+Ile+Ser+H – CO]; 532 [M+H – (MePro+Leu) – H₂O]; 462 [Tyr+Gly+Gln+Ile+H]; 434 [Tyr+Gly+Gln+Ile+H – CO]; 386 [Gly+Gln+Ile+Ser+H]; 349 [Tyr+Gly+Gln+H]; 301 [Gln+Ile+Ser+H – CO]; 227 [MePro+Leu+H]; 221 [Tyr+Gly+H]; 209 [MePro+Leu+H – H₂O]; 181 [MePro+Ile+H – H₂O – CO]; 148 [Tyr – NH₂]; 136 Tyr immonium; 86 – Ile/Leu immonium; 84, 101 (immonium), 129 Gln; 84 MePro immonium.

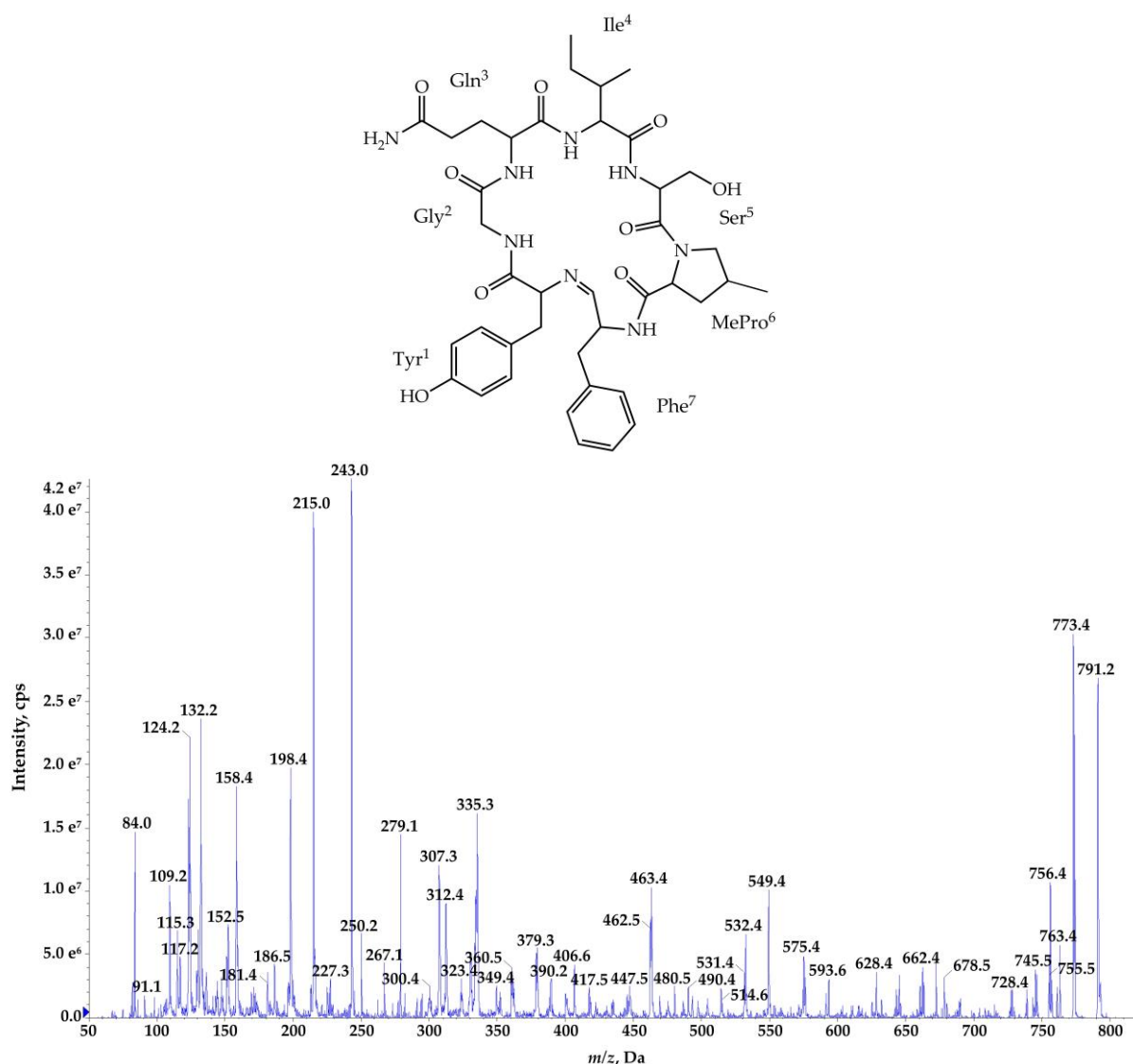


Figure S3: Structure and enhanced product ion mass spectrum of the cyclic nostocyclopeptide **Ncp-A2** cyclo[Tyr+Gly+Gln+Ile+Ser+MePro+Phe] identified based on the following fragment ions: m/z 791 [M+H]; 773 [M+H – H₂O]; 763 [M+H – CO]; 755 [M+H – 2H₂O]; 745 [M+H – CO – H₂O]; 678 [M+H – Ile]; 628 [M+H – Tyr]; 593 [M+H – (Ser+MePro)]; 549 [Tyr+Gly+Gln+Ile+Ser+H]; 531 [Tyr+Gly+Gln+Ile+Ser+H – H₂O]; 480 [M+H – (Ile+Ser+MePro)]; 462 [Tyr+Gly+Gln+Ile+H]; 406 [MePro+Phe+Tyr+H]; 379 [MePro+Phe+Tyr+H – CO]; 349 [Tyr+Gly+Gln+H]; 335 [Phe+Tyr+Gly+H – H₂O]; 312 [Ile+Ser+MePro+H]; 307 [Phe+Tyr+Gly+H – H₂O – CO]; 243 [MePro+Phe+H]; 215 [MePro+Phe+H – CO]; 158 [Gly+Gln+H – CO]; 132 Phe; 84 MePro immonium.

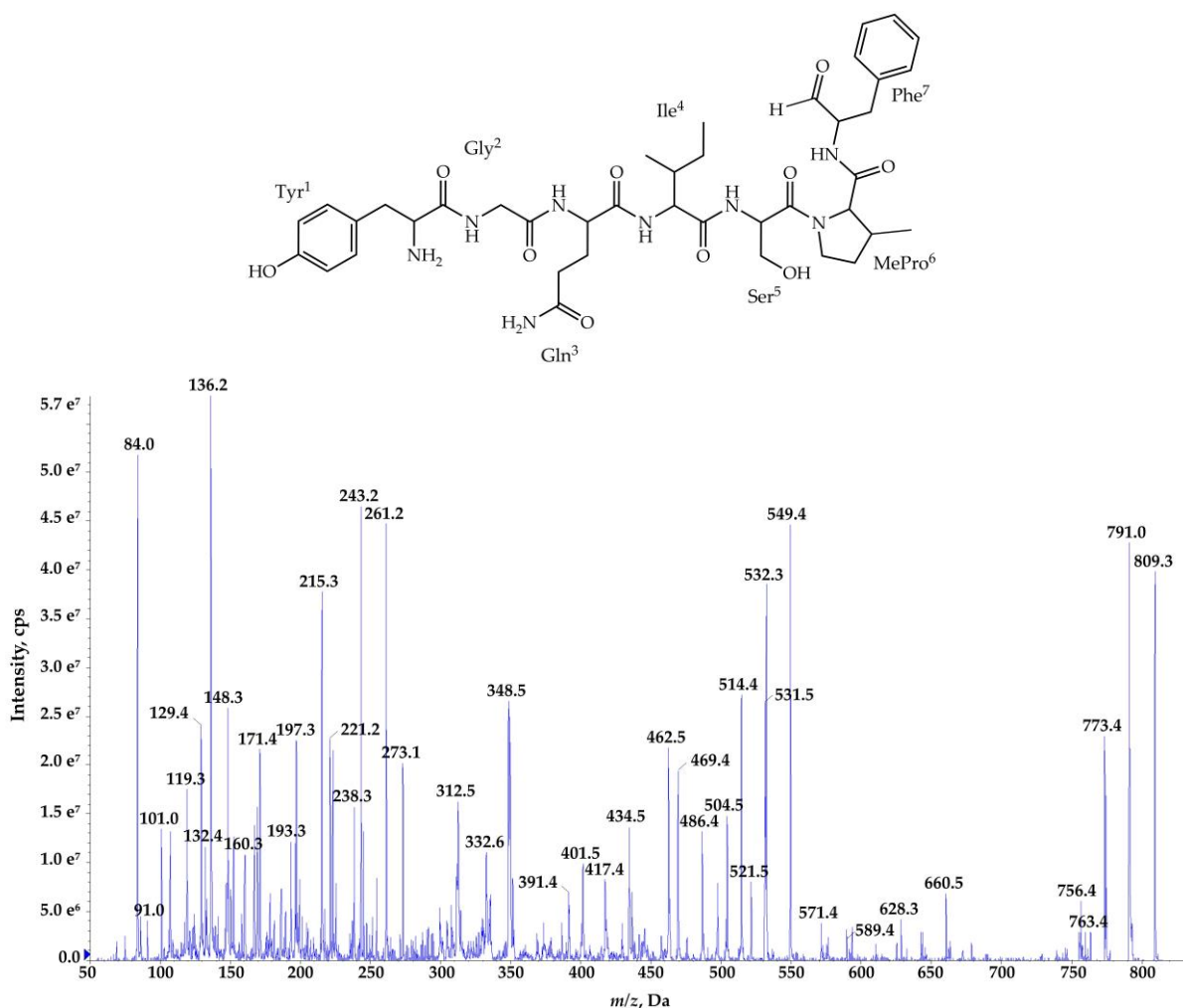


Figure S4: Structure and enhanced product ion mass spectrum of the linear nostocyclopeptide aldehyde **Ncp-A2-L** (linear aldehyde of **Ncp-A2**) Tyr+Gly+Gln+Ile+Ser+MePro+Phe identified based on the following fragment ions: m/z 809 [M+H]; 791 [M+H – H₂O]; 773 [M+H – 2H₂O]; 763 [M+H – CO – H₂O]; 660 [M+H – Phe]; 628 [M+H – Tyr – H₂O]; 549 [Tyr+Gly+Gln+Ile+Ser+H]; 531 [M+H – (MePro+Phe) – H₂O]; 462 [Tyr+Gly+Gln+Ile+H]; 434 [Tyr+Gly+Gln+Ile+H – CO]; 312 [Ile+Ser+MePro+H]; 261 [MePro+Phe+H]; 243 [MePro+Phe+H – H₂O]; 221 [Tyr+Gly+H], 193 [Tyr+Gly+H – CO]; 148 [Tyr – NH₂]; 136 Tyr immonium; 84, 101 (immonium), 129 Gln; 84 MePro immonium.

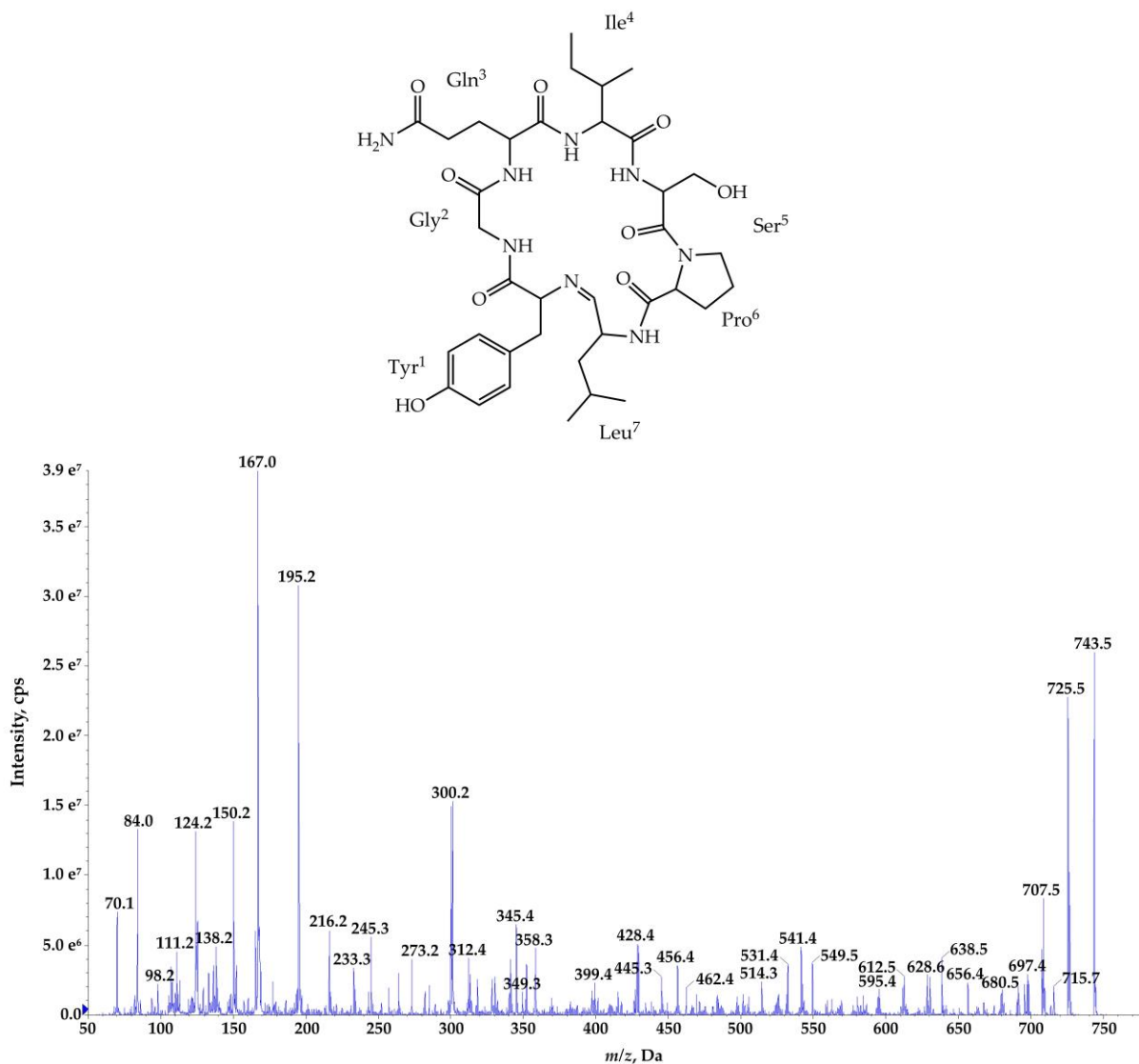


Figure S5: Proposed structure and enhanced product ion mass spectrum of cyclic nostocyclopeptide **Ncp-E2** cyclo[Tyr+Gly+Gln+Ile+Ser+Pro+Leu] characterized based on the following fragment ions: m/z 743 [M+H]; 725 [M+H - H₂O]; 715 [M+H - CO]; 707 [M+H - 2H₂O]; 697 [M+H - H₂O - CO]; 656 [M+H - Ser]; 638 [M+H - Ser - H₂O]; 628 [M+H - Ser - CO]; 612 [M+H - Ile - H₂O]; 549 [Tyr+Gly+Gln+Ile+Ser+H]; 541 [M+H - (Ser+Pro) - H₂O]; 531 [Tyr+Gly+Gln+Ile+Ser+H - H₂O]; 428 [M+H - (Ile+Ser+Pro) - H₂O]; 349 [Tyr+Gly+Gln+H]; 300 [Leu+Tyr+Gly+H - H₂O]; 195 [Pro+Leu+H]; 167 [Pro+Leu+H - CO]; 84 Gln; 70 Pro immonium.

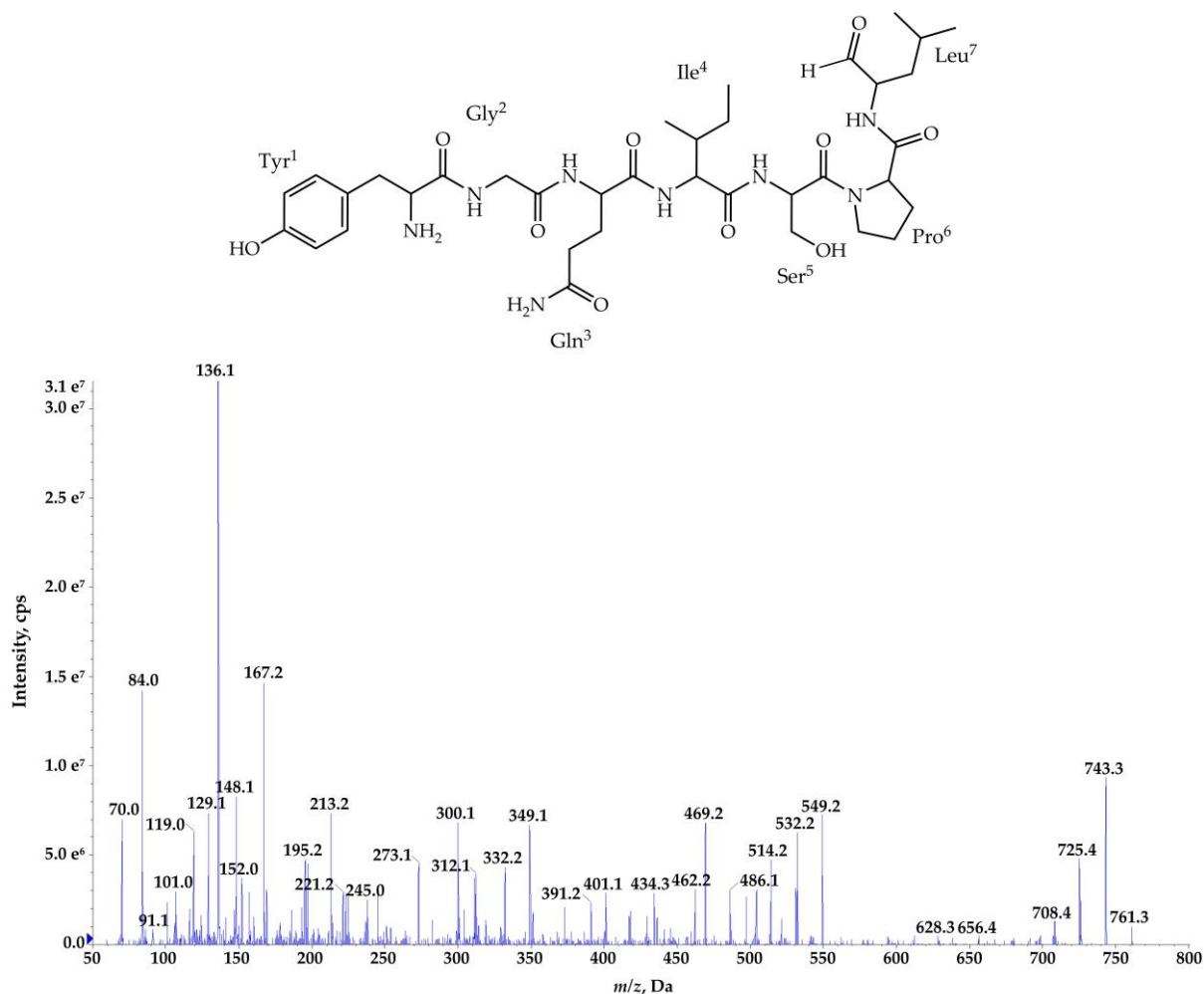


Figure S6: Proposed structure and enhanced product ion mass spectrum of the linear nostocyclopeptide aldehyde **Ncp-E2-L** (linear aldehyde of **Ncp-E2**) with general structure Tyr+Gly+Gln+Ile+Ser+Pro+Leu characterized based on the following fragment ions: *m/z* 761 [M+H]; 743 [M+H - H₂O]; 725 [M+H - 2H₂O]; 549 [Tyr+Gly+Gln+Ile+Ser+H]; 532 [Tyr+Gly+Gln+Ile+Ser+H - H₂O]; 462 [Tyr+Gly+Gln+Ile+H]; 349 [Tyr+Gly+Gln+H]; 434 [Tyr+Gly+Gln+Ile+H - CO]; 300 [Ser+Pro+Leu+H]; 221 [Tyr+Gly+H]; 213 [Pro+Leu+H]; 195 [Pro+Leu+H - H₂O]; 148 [Tyr - NH₂]; 136 Tyr immonium; 84, 101 (immonium), 129 Gln; 70 Pro immonium.

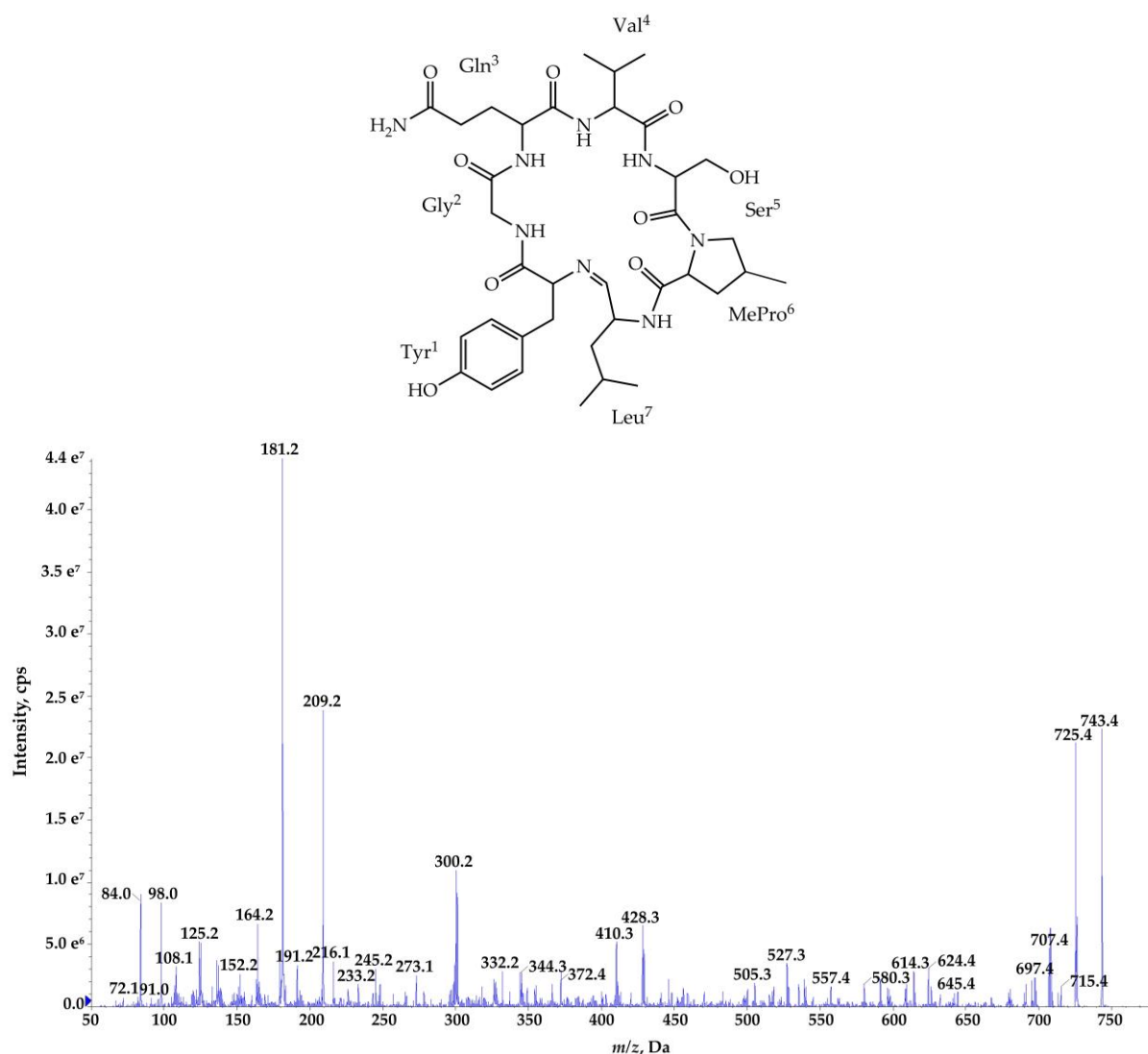


Figure S7: Proposed structure and enhanced product ion mass spectrum of cyclic nostocyclopeptide **Ncp-E3** cyclo[Tyr+Gly+Gln+Val+Ser+MePro+Leu] characterized based on the following fragment ions: m/z 743 [M+H]; 725 [M+H – H₂O]; 715 [M+H – CO]; 707 [M+H – 2H₂O]; 697 [M+H – H₂O – CO]; 645 [M+H – Val]; 580 [M+H – Tyr]; 527 [M+H – (Ser+MePro) – H₂O]; 428 [M+H – (Val+Ser+MePro) – H₂O]; 410 [M+H – (Val+Ser+MePro) – 2H₂O]; 372 [Gly+Gln+Val+Ser+H] ; 344 [Gly+Gln+Val+Ser+H – CO]; 300 [Leu+Tyr+Gly+H – H₂O]; 233 [Leu+Tyr+H – CO]; 209 [MePro+Leu+H]; 181 [MePro – Leu+H – CO]; 84 MePro immonium; 72 Val immonium.

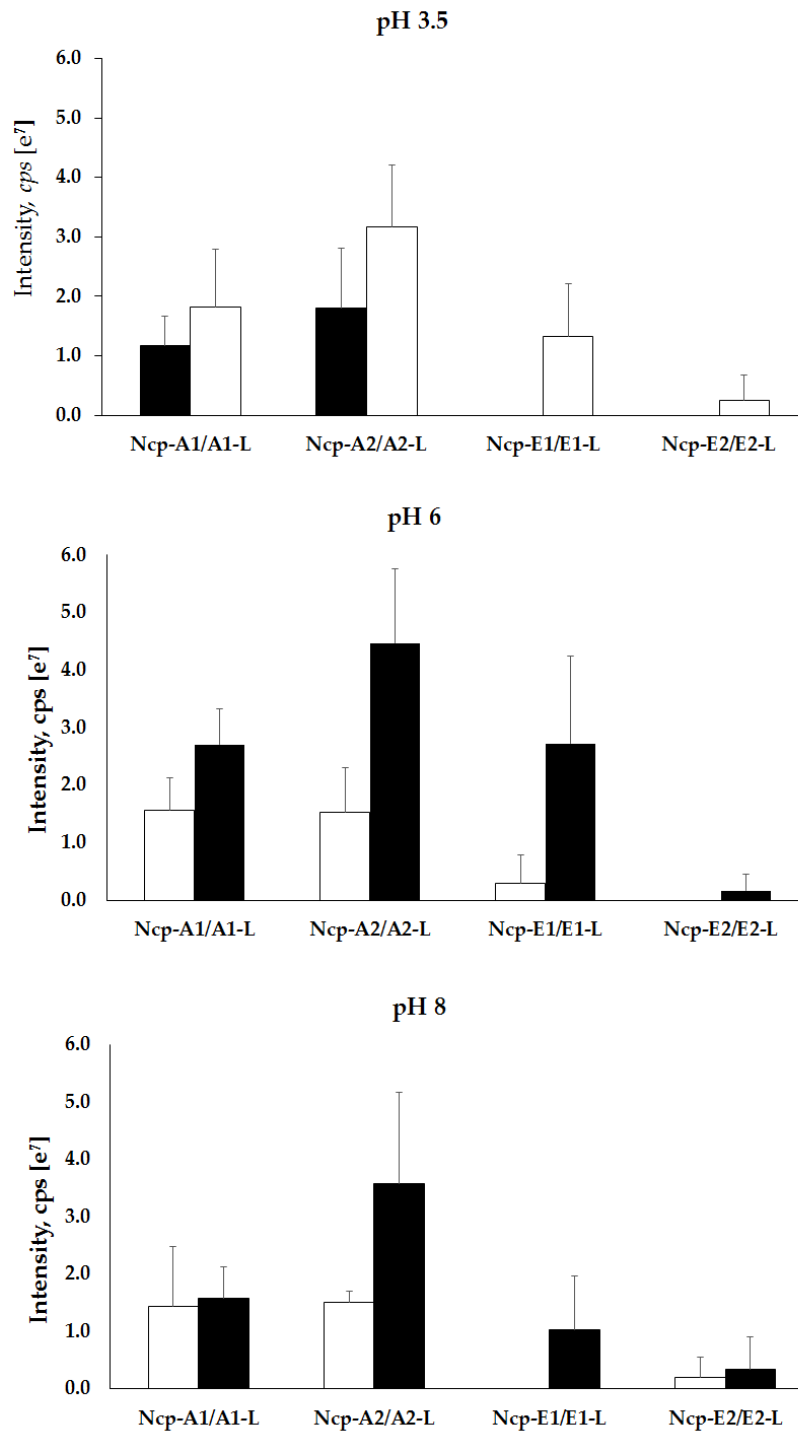


Figure S8: Relative cell contents of nostocyclopeptides extracted from 10 mg of lyophilized biomass of *N. edaphicum* CCNP1411 with 20% MeOH in different pH (3.5, 6 and 8).