

# Supplementary Information

## Contents of Tables and Figures

### Tables

**Table S1.** Strains used to screen for antifungal compounds using disc diffusion assay.

**Table S2.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR data for modified 7-OMe-Scytonycin B (**2**, conformers A and B), unknown 7-OMe-Scytonycin B (C) and 7-OMe-Scytonycin B (**1**, conformers D and E) in [D6] DMSO. ( ) = weak signal, [ ] = split signal.

**Table S3.** Scytonycin variants (No and Name), retention times ( $R_t$ ), experimental (Exp) and calculated (Cal) ion masses ( $m/z$ ) of  $[\text{M} + \text{H} - \text{H}_2\text{O}]^+$ ,  $[\text{M} + \text{Na}]^+$  and  $[\text{h} - 4\text{H} + \text{Na}]^+$ , mass error ( $\Delta$ ) in ppm, molecular formula and frequency in strains HAN3/2 = *Scytonema* sp. HAN3/2, HAN11/1 = *Nostoc* sp. HAN11/1, HAN21/1 = *Anabaena* sp. HAN21/1 and PH133 = *Anabaena cf. cylindrica* PH133.

hk = product ion of the sodiated scytonycin, see Figure 2. Accurate mass measurements obtained with Q-TOF and others with ion trap.

**Table S4.** Previously published scytonycin variants, their monoisotopic masses (M), positions of the variable functional groups. 6-OH-7-OMe-scytonycin B = tolytoxin A. Carbon numbers in Figure 1.

**Table S5.** Sodiated ion  $[\text{M} + \text{Na}]^+$  mass ( $m/z$ ), product ions and their  $m/z$ , intensities and comments concerning the tentative structures of scytonycin variants No 1–33. Ion structures a–n are presented in Figure S8.

### Figures

**Figure S1.** Disc diffusion bioassay using cyanobacterial extracts against *Candida albicans* (A) and *Aspergillus flavus* (B). PH133 = *Anabaena cf. cylindrica* PH133; HAN3/2 = *Scytonema* sp. HAN3/2; HAN21/1 = *Anabaena* sp. HAN21/1; HAN11/1 = *Nostoc* sp. HAN11/1; HAN7/1 = *Anabaena* sp. HAN7/1; JV1 = *Anabaena* sp. BIR JV1; 219 = *Nostoc* sp. CENA 219; 6sf = *Nostoc calcicula* 6 sf Calc; 298 = *Fischerella* sp. CENA 298; N107 = *Nostoc* sp. N107.3; 7110 = *Scytonema hofmanni* PCC 7110; – is negative control with methanol and + is 0.1mg of nystatin (Sigma-Aldrich, St. Louis, MO, USA).

**Figure S2.** Nonlabeled ( $^{14}\text{N}$ ) and  $^{15}\text{N}$ -labeled sodiated and dehydrated protonated scytonycin ions from *Anabaena* sp. HAN21/1.

**Figure S3.** NMR spectra of scytonycin preparate containing mainly 7-OMe-scytonycin-B derivative (**2**, Figure 1) and as a minor component native 7-OMe-scytonycin-B (**1**, Figure 1).  $^1\text{H}$  NMR spectrum (A). Annotated  $^1\text{H}$ - $^1\text{H}$  COSY spectra (B and C).  $^1\text{H}$ - $^1\text{H}$  TOCSY spectrum (D). Annotated  $^{13}\text{C}$ -HSQC spectrum (E). Annotated  $^{13}\text{C}$  HMBC spectrum (F, G and H).  $\circ$  = signal intensity too low to be seen in  $^{13}\text{C}$ -HSQC spectrum.

**Figure S4.** Structure of photoreacted 7-OMe-scytonycin B (**2**, Figure 1) with  $^1\text{H}$ - $^1\text{H}$  DQF-COSY (bold lines) and  $^{13}\text{C}$  HMBC (arrows) correlations.

**Figure S5.** Product ion spectrum from sodiated 7-OMe-scytonycin-B ( $m/z$  856.5) produced by *Anabaena* sp. HAN21/1.

**Figure S6.** Product ion spectrum from dehydrated protonated 7-OMe-scytonycin-B from *Anabaena* sp. HAN21/1.

**Figure S7.** Nonlabeled ( $^{14}\text{N}$ ) and  $^{15}\text{N}$ -labeled product ion spectrum from sodiated 7-OMe-scytophycin-B (1, Figure 1 and No 30, Table 2) of *Anabaena* sp. HAN21/1.

**Figure S8.** Structure of scytophycin-B (No 25 in Tables 2, S2 and S4) showing the product ions (a, b, c, dk, ek, fk, gk, hk, ik, jk, lhk, l, mhk, m and n) studied from the sodiated ion  $[\text{M} + \text{Na}]^+$ .

**Figure S9.** Mass spectra of *Nostoc* sp. CENA 219 hassallidins 1, 2, 3, 5 and 7.

**Figure S10.** Mass spectra of *Nostoc* sp. CENA 219 hassallidins 8, 11, 15, 22, 26 and 27.

**Figure S11.** Mass spectra of *Nostoc* sp. CENA 219 hassallidins 10, 17 and 24.

**Figure S12.** Mass spectra of *Nostoc* sp. 6 sf Calc hassallidins 12, 14, 19 and 25.

**Figure S13.** Mass spectra of *Anabaena* sp. HAN7/1 hassallidins 18, 20, 21 and 23.

**Figure S14.** Mass spectra of *Anabaena cylindrica* BIR JV1 hassallidins 4, 6, and 9.

**Figure S15.** Mass spectra of *Anabaena cylindrica* BIR JV1 hassallidins 13, 16, and 21.

**Table S1.** Strains used to screen for antifungal compounds using disc diffusion assay.

Genera	Growth Media #	Strain	City/State or State	place of Sampling	Year of Isolation	Identification Based on 16S rRNA Sequences
<i>Strains from Brazil</i>						
<i>Nostoc</i> sp.*	AA/Z8x	CENA219	Morro Branco/CE	water accumulated	2009	+
<i>Phormidium</i> sp.	BG50/Z8	CENA270	Paulista/PA	water in the pond	2009	JQ771627
<i>Fischerella</i> sp.*	ASM	CENA298	Paraíba	soil	2009	
<i>Cyanospira</i> *	AA	CENA215	Morro Branco/CE	water accumulated	2009	+
<i>Limnothrix</i>	BG50	CENA217	Morro Branco/CE	water accumulated	2009	
<i>Nostoc</i> *	AA	CENA221	Morro Branco/CE	water accumulated	2009	
<i>Synechococcus</i>	BG50	CENA222	Morro Branco/CE	water accumulated	2009	
<i>Aphanocapsa</i>	BG50	CENA223	Morro Branco/CE	water accumulated	2009	
<i>Geitlerinema</i>	BG50	CENA224	Morro Branco/CE	water accumulated	2009	
<i>Nostoc</i> *	AA	CENA227	Açude São Mateus/CE	water used by population (lake)	2009	
<i>Geitlerinema</i>	BG50	CENA228	Açude São Mateus/CE	water used by population (lake)	2009	
<i>Leptolyngbya</i>	BG50	CENA229	Açude São Mateus/CE	water used by population (lake)	2009	
<i>Synechococcus</i>	BG50	CENA232	Açude São Mateus/CE	water used by population (lake)	2009	
<i>Synechococcus</i>	BG50	CENA233	Açude São Mateus/CE	water used by population (lake)	2009	
<i>Nostoc</i> *	AA	CENA234	Açude São Mateus/CE	water used by population (lake)	2009	
<i>Pseudanabaena</i>	BG50	CENA235	Povoado Novo Aurora/CE	water in the pond	2009	
<i>Planktothrix</i>	BG50	CENA236	Povoado Novo Aurora/CE	water in the pond	2009	
<i>Nostoc</i> *	AA	CENA237	Lagoa Povoado Nova Aurora/CE	water pond used by cattle	2009	
<i>Nostoc</i> *	AA	CENA238	Lagoa Povoado Nova Aurora/CE	water pond used by cattle	2009	
<i>Nostoc</i> *	AA	CENA239	Lagoa Povoado Nova Aurora/CE	water pond used by cattle	2009	
<i>Myxosarcina</i>	BG50	CENA240	Cisterna/Canindé/CE	water in the cistern	2009	
<i>Myxosarcina</i>	BG50	CENA241	Cisterna/Canindé/CE	water in the cistern	2009	+
<i>Myxosarcina</i>	BG50	CENA242	Cisterna/Canindé/CE	water in the cistern	2009	
<i>Myxosarcina</i>	BG50	CENA244	Cisterna/Canindé/CE	water in the cistern	2009	
<i>Anabaena</i> *	BG0	CENA247	Rio Camarão/CE	river water	2009	

Table S1. Cont.

<i>Synechococcus</i>	BG50	CENA249	Rio Camarão/CE	river water	2009	
<i>Gloeotrichia</i> *	AA	CENA250	Rio Camarão/CE	river water	2009	
<i>Microchaete</i> *	BG50	CENA251	Rio Camarão/CE	river water	2009	
<i>Geitlerinema</i>	BG50	CENA252	Sodrelândia/BA	water in the pond	2009	
<i>Synechococcus</i>	BG50	CENA253	Sodrelândia/BA	water in the pond	2009	
<i>Leptolyngbya</i>	BG50	CENA254	Sodrelândia/BA	water in the pond	2009	
<i>Leptolyngbya</i>	BG50	CENA256	Sodrelândia/BA	water in the pond	2009	
<i>Nostoc</i> *	AA	CENA257	Sodrelândia/BA	water in the pond	2009	
<i>Nostoc</i> *	AA	CENA258	Sodrelândia/BA	water in the pond	2009	
<i>Nostoc</i> *	BG50	CENA259	Sodrelândia/BA	water in the pond	2009	
<i>Nostoc</i> *	AA	CENA261	Sodrelândia/BA	water in the pond	2009	
Chroococcales	BG0	CENA263	Baixão dos Bois/BA	water accumulated	2009	
<i>Merismopedia</i>	BG50	CENA264	Icó/CE	water accumulated	2009	+
<i>Pseudanabaena</i>	ASM	CENA266	Paulista/PA	water in the pond	2009	
<i>Pseudanabaena</i>	BG50	CENA267	Paulista/PA	water in the pond	2009	
<i>Scytonema</i> *	BG50	CENA268	Paulista/PA	water in the pond	2009	
<i>Nostoc</i> *	ASM	CENA269	Paulista/PA	water in the pond	2009	
<i>Nostoc</i> *	ASM	CENA271	Paulista/PA	water in the pond	2009	
<i>Gloeotrichia</i> *	BG50	CENA272	Paulista/PA	water in the pond	2009	
<i>Nostoc</i> *	ASM	CENA274	Bahia	soil	2009	
<i>Nostoc</i> *	ASM	CENA275	Bahia	soil	2009	
Chroococcales	AA	CENA276	Bahia	soil	2009	
<i>Nostoc</i> *	AA	CENA277	Bahia	soil	2009	
<i>Nostoc</i> *	BG0	CENA278	Bahia	soil	2009	
<i>Lyngbya</i>	BG50	CENA281	Piauí	soil	2009	
<i>Leptolyngbya</i>	ASM	CENA282	Piauí	soil	2009	

Table S1. Cont.

<i>Calothrix</i> *	ASM	CENA283	Piau í	soil	2009	
<i>Gloeotrichia</i> *	ASM	CENA285	Piau í	soil	2009	
<i>Pseudanabaena</i>	BG11	CENA287	Piau í	soil	2009	
<i>Gloeotrichia</i> *	AA	CENA288	Cear á	soil	2009	
<i>Stigonema</i> *	BG50	CENA291	Cear á	soil	2009	
<i>Leptolyngbya</i>	BG50	CENA292	Cear á	soil	2009	
<i>Nostoc</i> *	BG50	CENA293	Cear á	soil	2009	
Nostocales *	ASM	CENA294	Cear á	soil	2009	
<i>Stigonema</i> *	BG50	CENA295	Cear á	soil	2009	
<i>Nostoc</i> *	ASM	CENA296	Cear á	soil	2009	
<i>Leptolyngbya</i>	BG11	CENA299	Rio Grande do Norte	soil	2009	
<b>Strains from Finland</b>						
<i>Unknown</i> *	Z8x	HAN3/1	Kobben, Hanko	green biofilm in the pond	2012	
<i>Scytonema</i> sp.*	Z8x	HAN3/2	Kobben, Hanko	green biofilm in the pond	2012	
<i>Unknown</i> *	Z8x	HAN6/1	Kobben, Hanko	Growth on rock waterline	2012	
<i>Calothrix</i> sp.*	Z8x	HAN6/3	Kobben, Hanko	Growth on rock waterline	2012	+
<i>Calothrix</i> sp. *	Z8x	HAN6/4	Kobben, Hanko	Growth on rock waterline	2012	+
<i>Unknown</i> *	Z8x	HAN7/1	Kobben, Hanko	small stones in the water	2012	
<i>Calothrix</i> sp. *	Z8x	HAN8/2	Kobben, Hanko	Growth on rock waterline	2012	+
<i>Nostoc</i> sp. *	Z8x	HAN10/1	Kobben, Hanko	small pond on a rock	2012	+
<i>Nostoc</i> sp. *	Z8x	HAN11/1	Kobben, Hanko	small pond on a rock	2012	+
<i>Calothrix</i> sp. *	Z8x	HAN12/2	Kobben, Hanko	black spots film, benthic	2012	+
<i>Anabaena</i> sp. *	Z8x	HAN15/2	Kobben, Hanko	Gastropod from waterline	2012	+
<i>Unknown</i> *	Z8x	HAN15/3	Kobben, Hanko	Gastropod from waterline	2012	
<i>Calothrix</i> sp. *	Z8x	HAN16/2	Kobben, Hanko	Waterplant from shallow water	2012	+

Table S1. Cont.

<i>Calothrix</i> sp. *	Z8x	HAN17/1	Kobben, Hanko	Red biofilm	2012	+
<i>Calothrix</i> sp. *	Z8x	HAN19/2	Kobben, Hanko	black/green biofilm from waterline	2012	+
<i>Unknown</i> *	Z8x	HAN19/3	Kobben, Hanko	black/green biofilm from waterline	2012	
<i>Unknown</i> *	Z8x	HAN20/1	Kobben, Hanko	sediments 10 cm under water	2012	
<i>Calothrix</i> sp. *	Z8x	HAN20/3	Kobben, Hanko	sediments 10 cm under water	2012	+
<i>Anabaena</i> sp. *	Z8x	HAN21/1	Kobben, Hanko	Gastropod 10 cm under water	2012	+
<i>Unknown</i> *	Z8x	HAN21/2	Kobben, Hanko	Gastropod 10 cm under water	2012	
<i>Calothrix</i> sp. *	Z8x	HAN21/3	Kobben, Hanko	Gastropod 10 cm under water	2012	+
<i>Calothrix</i> sp. *	Z8x	HAN21/4	Kobben, Hanko	Gastropod 10 cm under water	2012	+
<i>Calothrix</i> sp. *	Z8x	HAN21/5	Kobben, Hanko	Gastropod 10 cm under water	2012	+
<i>Nostoc</i> sp. *	Z8x	HAN22	Kobben, Hanko	biofilm growth on rock waterline	2012	+
<i>Calothrix</i> sp. *	Z8x	HAN22/1	Kobben, Hanko	Black biofilm	2012	+
<i>Unknown</i> *	Z8x	HAN22/2	Kobben, Hanko	Black biofilm	2012	
<i>Nostoc</i> sp. *	Z8x	HAN24/1	Kobben, Hanko	epilithic	2012	+
<i>Tolypothrix</i> sp. *	Z8x	HAN25/1	Kobben, Hanko	epilithic	2012	+
<i>Tolypothrix</i> sp. *	Z8x	HAN26/2	Hanko Casino sea shore, Hanko	Black biofilm	2012	+
<i>Nostoc</i> sp. *	Z8x	HAN27	Hanko Casino sea shore, Hanko	small rock pond	2012	+
<i>Unknown</i> *	Z8x	HAN29/3	Hanko Casino sea shore, Hanko	green biofilm on the rock	2012	
<i>Calothrix</i> sp. *	Z8x	HAN30/2	Hanko Casino sea shore, Hanko	Green biofilm and Gastropod	2012	+
<i>Calothrix</i> sp. *	Z8x	HAN30/3	Hanko Casino sea shore, Hanko	Green biofilm and Gastropod	2012	+
<i>Unknown</i> *	Z8x	HAN31/a	Hanko	biofilm	2012	
<i>Unknown</i> *	Z8x	HAN32/2	Hanko Casino sea shore, Hanko	epilithic	2012	
<i>Calothrix</i> sp. *	Z8x	HAN33/1	Hanko Casino sea shore, Hanko	brown biofilm on the rock	2012	+
<i>Calothrix</i> sp. *	Z8x	HAN33/2	Hanko Casino sea shore, Hanko	Brown/yellow biofilm	2012	+
<i>Calothrix</i> sp. *	Z8x	HAN36/2	Hanko Casino sea shore, Hanko	Biofilm	2012	+

Table S1. Cont.

<i>Anabaena</i> sp. *	Z8x	HAN37/1	Hanko Casino sea shore, Hanko	green biofilm	2012	+
<i>Calothrix</i> sp. *	Z8x	HAN37/2	Hanko Casino sea shore, Hanko	green biofilm	2012	+
<i>Calothrix</i> sp. *	Z8x	HAN37/3	Hanko Casino sea shore, Hanko	Green biofilm	2012	+
<i>Calothrix</i> sp. *	Z8x	HAN38/2	Hanko Casino sea shore, Hanko	Red biofilm	2012	+
<i>Unknown</i> *	Z8x	HAN40/1	Hanko Casino sea shore, Hanko	epilithic	2012	
<i>Cyanobium</i> sp.	Z8	HIID A3A	Hiidenvesi, Kirkkoj ärvi	sediment	1999	
<i>Pseudanabaena</i> sp.	Z8	HIID A13A	Hiidenvesi, Kirkkoj ärvi	sediment	1999	
<i>Leptolyngbya</i> sp.	Z8	HIID A16A	Hiidenvesi, Kirkkoj ärvi	sediment	1999	
<i>Leptolyngbya</i> sp.	Z8	HIID A19B	Hiidenvesi, Kirkkoj ärvi	sediment	1999	
<i>Leptolyngbya</i> sp.	Z8	HIID A25A	Hiidenvesi, Kirkkoj ärvi	sediment	1999	
<i>Trichormus</i> sp. *	Z8x	HIID B6A	Hiidenvesi, Mustionselk ä	sediment	1999	
<i>Synechocystis</i> sp.	Z8	HIID B11B	Hiidenvesi, Mustionselk ä	sediment	1999	
<i>Leptolyngbya</i> sp.	Z8	HIID B15A	Hiidenvesi, Mustionselk ä	sediment	1999	
<i>Pseudanabaena</i> sp.	Z8	HIID B19	Hiidenvesi, Mustionselk ä	sediment	1999	
<i>Phormidium</i> sp.	Z8	HIID B22B	Hiidenvesi, Mustionselk ä	sediment	1999	
<i>Pseudanabaena</i> sp.	Z8	HIID C15A	Hiidenvesi, Nummelanselk ä	sediment	1999	
<i>Nostoc</i> sp. *	Z8x	HIID C18A	Hiidenvesi, Nummelanselk ä	sediment	1999	
<i>Leptolyngbya</i> sp.	Z8	HIID D2A	Hiidenvesi, Kiihkelyksenselk ä	sediment	1999	
<i>Trichormus</i> sp. *	Z8x	HIID D3	Hiidenvesi, Kiihkelyksenselk ä	sediment	1999	
<i>Anabaena</i> sp. *	Z8x	HIID D7A	Hiidenvesi, Kiihkelyksenselk ä	sediment	1999	
<i>Nostoc</i> sp. *	Z8x	XHIID A1	Hiidenvesi, Kirkkoj ärvi	sediment	1999	
<i>Nostoc</i> sp. *	Z8x	XHIID A6	Hiidenvesi, Mustionselk ä	sediment	1999	
<i>Anabaena</i> sp. *	Z8x	XHIID B2A	Hiidenvesi, Mustionselk ä	sediment	1999	+
<i>Anabaena</i> sp. *	Z8x	XHIID B6	Hiidenvesi, Mustionselk ä	sediment	1999	+
<i>Nostoc</i> sp. *	Z8x	XHIID C1	Hiidenvesi, Nummelanselk ä	sediment	1999	

Table S1. Cont.

<i>Nostoc</i> sp. *	Z8x	XHIID C2	Hiidenvesi, Nummelanselkä	sediment	1999
<i>Nostoc</i> sp. *	Z8x	XHIID C3	Hiidenvesi, Nummelanselkä	sediment	1999
<i>Nostoc</i> sp. *	Z8x	XHIID C4	Hiidenvesi, Nummelanselkä	sediment	1999
<i>Nostoc</i> sp. *	Z8x	XHIID C5A	Hiidenvesi, Nummelanselkä	sediment	1999
<i>Nostoc</i> sp. *	Z8x	XHIID C5B	Hiidenvesi, Nummelanselkä	sediment	1999
<i>Cylindrospermum</i> sp.*	Z8x	XHIID C12	Hiidenvesi, Nummelanselkä	sediment	1999
<i>Aphanothece</i> sp.	Z8x	XHIID D1	Hiidenvesi, Kiihkelyksenselkä	sediment	1999
<i>Nostoc</i> sp. *	Z8x	XHIID D7	Hiidenvesi, Kiihkelyksenselkä	sediment	1999
<i>Nostoc</i> sp. *	Z8x	XHIID D8	Hiidenvesi, Kiihkelyksenselkä	sediment	1999
<i>Nostoc</i> sp. *	Z8x	XHIID D12	Hiidenvesi, Kiihkelyksenselkä	sediment	1999
<i>Nostoc</i> sp. *	Z8x	XHIID D13	Hiidenvesi, Kiihkelyksenselkä	sediment	1999
<i>Nostoc</i> sp. *	Z8x	XHIID D14	Hiidenvesi, Kiihkelyksenselkä	sediment	1999
<i>Nostoc</i> sp. *	Z8x	116.7.5		lichen	
<i>Nostoc</i> sp. *	Z8x	116.6.23		lichen	
<i>Nostoc</i> sp. *	Z8x	N135.9.1		lichen	
<i>Nostoc</i> sp. *	Z8x	N990622III		lichen	
		Ilona			
<i>Tolypothrix</i> sp. *	Z8xS	BIR MGR4	The Gulf of Finland		
<i>Nostoc</i> sp. *	Z8x	N122.4.B		lichen	
<i>Nostoc</i> sp. *	Z8x	N124.3.B		lichen	
<i>Nostoc</i> sp. *	Z8x	N122.4B		lichen	
<i>Nostoc</i> sp. *	Z8x	UK4	Itä-Pakila, Helsinki, Finland	lichen <i>Peltigera spuria</i>	
<i>Nostoc</i> sp. *	Z8x	UK18AIII	Autti, Finland	lichen <i>Peltigera leucophlebia</i>	
<i>Nostoc</i> sp. *	Z8x	N115.3.2		lichen	
<i>Nostoc</i> sp. *	Z8x	UK1	Oulunkylä Helsinki, Finland	lichen <i>Peltigera</i> sp.	



Table S1. Cont.

<i>Nostoc</i> sp. *	Z8x	N990653.17		lichen		
<i>Nostoc</i> sp. *	Z8x	102I		lichen		
<i>Nostoc</i> sp. *	Z8x	N123.4		lichen		
<i>Nostoc</i> sp. *	Z8x	N107.3		lichen		
<i>Nostoc</i> sp. *	Z8xS	BIR L1S7	The Gulf of Finland			
<i>Anabaena cylindrica</i> *	Z8x	BIR JV1	The Gulf of Finland			+
<i>Calothrix</i> sp. *	Z8x	UHCC 0022				
<i>Nostoc</i> sp. *	Z8x	N138		lichen		
<i>Nostoc</i> sp. *	Z8x	UK7BIIIm	It äPakila, Helsinki, Finland	Lichen <i>Peltigera canina</i> ?		
<i>Nostoc</i> sp. *	Z8x	UK35		lichen		
<i>Nostoc</i> sp. *	Z8x	UK18AIV	Autti, Finland	Lichen <i>Peltigera leucophlebia</i>		
<i>Nostoc</i> sp. *	Z8x	UK18AI	Autti, Finland	Lichen <i>Peltigera leucophlebia</i>	2006	+
<i>Nostoc</i> sp. *	Z8x	UK18BI	Autti, Finland	Lichen <i>Peltigera leucophlebia</i>		
<i>Nostoc</i> sp. *	Z8x	UK18BIV	Autti, Finland	Lichen <i>Peltigera leucophlebia</i>		
<i>Nostoc</i> sp. *	Z8x	UK18BIII	Autti, Finland	Lichen <i>Peltigera leucophlebia</i>		
<i>Nostoc</i> sp. *	Z8x	UK2aImI	Oulunkyl ä Helsinki, Finland	Lichen <i>Peltigera praetextata</i>		+
<i>Nostoc</i> sp. *	Z8x	UK18BII	Autti, Finland	Lichen <i>Peltigera leucophlebia</i>		
<i>Nostoc</i> sp. *	Z8x	XPORK5A	Porkkala cape	epiphytic	1999	+
<i>Anabaena</i> sp. *	Z8x	XPORK6B	Porkkala cape	sediment		
<i>Tolypothrix</i> sp. *	Z8x	XPORK34B	Porkkala cape			
<i>Nostoc</i> sp. *	Z8x	Nostoc 152	Lake S ääksj ärvi, Finland			AJ133161
<i>Calothrix</i> sp. *	Z8x	Cal 336/2	Vihti, En äj ärvi Laukilanlahti			
<i>Nostoc</i> sp. *	Z8x	N159	Lake Haukkaj ärvi, Finland			
<i>Tolypothrix</i> sp. *	Z8x	Tol 328	Kuopio, Finland	greenhouse soil	1999	
<i>Calothrix</i> sp. *	Z8x	Cal 336/3	Lake En äj ärvi, Finland	Lake water	1999	

Table S1. Cont.

<i>Other strains</i>						
<i>Anabaena cf.</i>	Z8x	PH133	Lake Arres ø DK		1993	AJ293110
<i>Cylindrica</i> *						
<i>Scytonema sp.</i> *	Z8x	PCC7110	Bermuda	Limestone	1971	
<i>Tolypothrix sp.</i> *	Z8x	PCC7415	Stockholm, Sweden	greenhouse soil	1972	
<i>Calothrix sp.</i> *	Z8x	PCC7103	United States	Herbarium specimen of <i>Anacystis montana</i>		
<i>Calothrix sp.</i> *	Z8x	PCC7102	Antofagasta, Chile	sand	1958	
<i>Tolypothrix sp.</i> *	Z8x	PCC7101	Borneo	soil	1950	
<i>Tolypothrix sp.</i> *	Z8x	PCC7504	Stockholm, Sweden	aquarium	1972	
<i>Anabaena cylindrica</i> *	Z8x	PCC7122	Cambridge, UK	water, most likely pond	1939	AF091150
<i>Anabaena sp.</i> *	Z8x	PCC7108	Moss Beach, California USA	intertidal zone	1970	AJ133162
<i>Anabaena variabilis</i> *	Z8x	ATCC29413	Mississippi, USA	Freshwater	1964	NR_074300
<i>Calothrix sp.</i> *	Z8x	PCC7103	unknown	herbarium specimen of <i>Anacystis montana</i>		AM230700
<i>Calothrix sp.</i> *	Z8x	PCC7507	near Kastanienbaum, Vierwaldst ätersee, Switzerland	sphagnum bog	1972	NR_102891
<i>Cylindrospermopsis raciborskii</i> *	Z8	CS-505	Queensland, Australia	waterbodies Solomon Dam	1996	EU552055
<i>Cylindrospermum stagnale</i> *	Z8x	PCC7417	Stockholm, Sweden	soil, greenhouse	1972	NR_114701
<i>Nostoc punctiforme</i> *	Z8x	PCC73102	Australia	root section, <i>Macrozamia sp.</i>	1973	AF027655
<i>Nostoc sp.</i> *	Z8x	PCC7120	unknown	unknown	unknown	NR_074310
<i>Fischerella sp.</i> *	Z8x	PCC9339	unknown	unknown	unknown	AB075984
<i>Anabaena sp.</i> *	Z8x	6 sf Calc	Dobre Pole	unknown	1998	

# Culture medium containing nitrogen: Z8, BG50, BG11, AA, ASM; Culture medium without nitrogen: Z8x, Z8xS (Z8 without nitrogen plus salt), BG0. \* Nostocales or Stigonematales Order which are able to produce heterocyst. + Cyanobacterial strains classified based on 16S rRNA sequences not available in the NCBI database.

**Table S2.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR data for modified 7-OMe-Scytophycin B (**2**, conformers A and B), unknown 7-OMe-Scytophycin B (C) and 7-OMe-Scytophycin B (**1**, conformers D and E) in  $[\text{D}_6]$  DMSO. ( ) = weak signal, [ ] = split signal.

No	$\delta_{\text{C}}$	$\delta_{\text{H}}$	mult., $J$ (Hz)	COSY	HMBC (H→C)
1	165.3	-		-	
2	116.8	5.68	d 15.8	3	1, [2], 3, 4, 5
3	147.4	7.31	d 15.8	2	1, 2, [3], 4, 4-CH <sub>3</sub> , 5
4	133.9	-		-	
4-CH <sub>3</sub>	11.7	1.75	s	-	3, 4, [4-CH <sub>3</sub> ], 5, 6
5	136.3	5.80		6, 6'	3, 4, 4-CH <sub>3</sub> , 6, 7
6	31.9	2.17		5, 6'	(3), 4, 5, 7, 8
6'		2.69		5, 6	(4, 5, 7, 8)
7	77.6	3.45		6, 6', 8, 8'	7-OCH <sub>3</sub> , (5, 8, 9)
7-OCH <sub>3</sub>	55.8	3.32	s	-	7, [7-OCH <sub>3</sub> ]
8	38.3	1.31		7, 8', 9	6, 7, (9), 10
8'		1.59		(7), 8, 9	6, 7-OCH <sub>3</sub> , 9, 10
9	69.6	4.30		8, 8', 10, 11	(8), 10, 11, (13)
10	129.9	5.63		9, 11, 12'	9, [10], 11, 12
11	124.0	5.77		9, 11, 12	9, 10, [11], 12, 13
12	30.3	1.84		11, 13	10, 11, 13
12'		1.87		10, 13	10, 11, 13
13	65.3	3.31		12', 14'	9, 11, (14), 15
14	34.8	1.42		14', 15	12, 13, 15, 16
14'		1.50		13, 14, 15	12, 13, 15, 16
15	77.7	3.67	dd 4.4, 6.2	14, 14'	13, 14, 15-OCH <sub>3</sub> , 16, 16-CH <sub>2</sub> , 17
15-OCH <sub>3</sub>	56.8	3.31	s	-	15, [15-OCH <sub>3</sub> ]
16	60.1	-		-	
16-CH <sub>2</sub>	45.0	2.56		16'-CH <sub>2</sub>	15, 16, [16-CH <sub>2</sub> ], 17
16'-CH <sub>2</sub>		2.65		16-CH <sub>2</sub>	15, 16, [16-CH <sub>2</sub> ], 17
17	75.1	3.53		18, 18'	15, 16, 16-CH <sub>2</sub> , 17-OCH <sub>3</sub> , 18, 19
17-OCH <sub>3</sub>	53.4	3.14	s	-	17, [17-OCH <sub>3</sub> ]
18	28.2	1.37		17, 18', 19	16, 17, 19, 20
18'		1.73		17, 18, 19	16, 17, 19, 20
19	75.8	3.07		18, 18'	(17), 18, 19-OCH <sub>3</sub> , 20, 20-CH <sub>3</sub> , 21
19-OCH <sub>3</sub>	56.6	3.10	s	-	19, [19-OCH <sub>3</sub> ]
20	37.8	1.87		21, 20-CH <sub>3</sub>	(18), 20-CH <sub>3</sub> , 21
20-CH <sub>3</sub>	9.2	0.79		20	19, 20, [20-CH <sub>3</sub> ], 21
21A	71.9	5.28		20	1, 19, 20, 20-CH <sub>3</sub>
21B	72.1	5.07	9.5, 19.1	20, 22	1, 19, 20, 22, 22-CH <sub>3</sub> , 23
22	34.3	2.03		21B, 22-CH <sub>3</sub> , 23	20, 22-CH <sub>3</sub> , 23
22-CH <sub>3</sub>	11.3	0.99		22	21, 22, [24-CH <sub>3</sub> ], 23
23	79.2	2.97		22, 24	21, 22, 22-CH <sub>3</sub> , 24, 24-CH <sub>3</sub> , 27
24	30.3	1.87		24-CH <sub>3</sub>	24-CH <sub>3</sub> , 25
24-CH <sub>3</sub>	17.3	0.76		24	23, 24, [24-CH <sub>3</sub> ]
25	30.3	1.60			23, 24, 24-CH <sub>3</sub> , 26, 27ABC
26	27.8	1.27			25, 27

Table S2. Cont.

26'		1.49			27, 28, 31AB
27A	84.5	-			
27B	84.3	-			
27C	84.0	-			
27D,E	213.4	-			
28A	48.0	1.62		29A, 28-CH <sub>3</sub> A	26, 27A, 28-CH <sub>3</sub> A, 29A
28B	48.0	1.68		29B, 28-CH <sub>3</sub> B	26, 27B, 28-CH <sub>3</sub> B, 29B, (30B)
28CDE	48.0	1.68			
28-CH <sub>3</sub> A	7.8	0.76		28A	27A, 28A, [28-CH <sub>3</sub> A], 29A
28-CH <sub>3</sub> B	7.8	0.77		28B	27B, 28B, [28-CH <sub>3</sub> B], 29B
28-CH <sub>3</sub> DE	12.9	0.86			[28DE], 29DE
29A	86.0	3.35		28A, 30A	27A,B; (28, 28-CH <sub>3</sub> ), 29-OCH <sub>3</sub> , 30-CH <sub>3</sub> , 31A,B
29B	86.1	3.33		28B, 30B	27B, (28, 28-CH <sub>3</sub> ), 29-OCH <sub>3</sub> , 30-CH <sub>3</sub> , 31B
29C	84.0	3.31			27C, 30-CH <sub>3</sub> C, 31C
29D,E	85.7	3.03			30-CH <sub>3</sub> DE, 31D
29-OCH <sub>3</sub>	59.7	3.15	s	-	29, [29-CH <sub>3</sub> ]
30A	35.6	2.46		29A, 30-CH <sub>3</sub> A, 31A	31A, 30-CH <sub>3</sub> A, 32A
30B	36.2	2.40		29B, 30-CH <sub>3</sub> B, 31B	27B, (28B), 29B, 31B, 30-CH <sub>3</sub> , 32B
30D	36.3	2.40			(31D)
30E	36.5	2.40			(31E)
30-CH <sub>3</sub> A	15.8	0.97		30A	29AB, 30AB, [30-CH <sub>3</sub> AB], 31AB
30-CH <sub>3</sub> B	15.8	0.96		30B	29AB, 30AB, [30-CH <sub>3</sub> AB], 31AB
30-CH <sub>3</sub> C	15.0	0.90			27C, 29C, [30-CH <sub>3</sub> C], 31C
30-CH <sub>3</sub> DE	19.4	1.06			29DE, 30DE, [30-CH <sub>3</sub> DE], 31DE
31A	52.9	2.01		30A, 32A	27A, 28, 29A, 30A, 32A
31B	52.9	2.04		30B, 32B	27B, 28, (28-CH <sub>3</sub> ), 29B, 30B, 30-CH <sub>3</sub> , 32B
31C	52.1	2.17		32C	27C, 28, 29C, 30-CH <sub>3</sub> C, 32C, 33-NCH <sub>3</sub> C
31D	110.6	4.97, 5.00		32D, 2.37	30-CH <sub>3</sub> D,E , 32D
31E	112.7	5.07, 5.10		32E, 2.4	-
32A	83.2	5.19	d 2.6	31A	27A, 30A, 31A, 33-NCH <sub>3</sub> A, 34A
32B	89.4	4.50	d 4.0	31B	27B, 30B, 31B, [32B], 33-NCH <sub>3</sub> B, 34B
32C	90.3	4.25	d 9.9	31C	27C, 31C, 33-NCH <sub>3</sub> C, 34C
32D	128.5	6.72, 6.76	d 14.3	31D	30D, 31D, 33-NCH <sub>3</sub> D, 34D
32E	123.7	6.95, 7.01	d	31E	30E, 31E, [32E], 33-NCH <sub>3</sub> E
33-NCH <sub>3</sub> A	28.6	2.86	s	-	32A, [33-NCH <sub>3</sub> A], 34A
33-NCH <sub>3</sub> B	25.7	2.72	s	-	32B, [33-NCH <sub>3</sub> B], 34B
33-NCH <sub>3</sub> C	24.3	2.61	s	-	32C, [33-NCH <sub>3</sub> C], 34C
33-NCH <sub>3</sub> D	26.5	2.86	s	-	32D, [33-NCH <sub>3</sub> D], 34D
33-NCH <sub>3</sub> E	32.3	2.98	s	-	32E, [33-NCH <sub>3</sub> E], 34E
34A	163.7	8.18	s	-	32A, 33-NCH <sub>3</sub> A, [34A]
34B	162.2	8.26	s	-	32B, 33-NCH <sub>3</sub> B, [34B]
34C	163.2	8.22	s	-	32C, 33-NCH <sub>3</sub> C, [34C]
34D	162.3	8.34	s	-	32D, 33-NCH <sub>3</sub> D, [34D]
34E	161.1	8.07	s	-	32E, 33-NCH <sub>3</sub> E, [34E]

**Table S3.** Scytophycin variants (No and Name), retention times ( $R_t$ ), experimental (Exp) and calculated (Cal) ion masses ( $m/z$ ) of  $[M + H - H_2O]^+$ ,  $[M + Na]^+$  and  $[hk - 4H + Na]^+$ , mass error ( $\Delta$ ) in ppm, molecular formula and frequency in strains HAN3/2 = *Scytonema* sp. HAN3/2, HAN11/1 = *Nostoc* sp. HAN11/1, HAN21/1 = *Anabaena* sp. HAN21/1 and PH133 = *Anabaena cf. cylindrica* PH133. hk = product ion of the sodiated scytophycin, see Figure S8. Accurate mass measurements obtained with Q-TOF and others with ion trap.

No	Variant Name (Sc = scytophycin)	$R_t$ (min)	$(m/z)$			$\Delta$ (ppm)	Formula	$(m/z)$			$\Delta$ (ppm)	Formula	Strain			
			$[M + H - H_2O]^+$ Exp	$[M + Na]^+$ Cal	$\Delta$			$[hk - 4H + Na]^+$ Exp	$\Delta$	Formula			HAN3/2	HAN11/1	HAN21/1	PH133
1	6-OH-7-OMe-Sc	18.1	848.5	888.5				620.4133				-	+	-	-	
2	6-OH-7-OMe-17-OH-Sc-D/E	18.9	820.5	860.5				608.4133				-	+	-	-	
3	6-OH-7-OMe-Sc	18.9	864.5	904.5				652.4031				-	+	-	-	
4	Sc	19.3	774.5	814.5								+	-	-	-	
5	6-OH-Sc-D/E	19.3	820.5	860.5				622.4289				-	+	-	-	
6	6-OH-Sc-B	19.4	818.5	858.4951	858.4974	-2.69	$C_{45}H_{73}NO_{13}$	620.4133				+	-	-	+	
7	Sc	19.4	834.5	874.5								+	-	-	-	
8	6-OH-7-OMe-Sc-D/E	19.5	850.5	890.5				638.4239				-	+	-	-	
9	Sc	19.8	818.5	858.5				636.4082				-	-	-	+	
10	6-OH-7-OMe-15-O-deMe-Sc-B	19.9	818.5	858.5				606.4340				-	++	-	-	
11	Sc	20.0	774.5	814.5								+	-	-	+	
12	Sc	20.0	804.5	844.5				606.3976				+	+	-	-	
13		20.0	834.5	874.5								+	-	-	-	
14	29-OH-Sc-B	20.1	788.5	828.5				606.3976				+	-	-	-	
15	6-OH-7-OMe-Sc-D/E	20.1	834.5	874.5				622.4289				-	++	-	-	
16	X-OH-Sc-D/E (not 6-OH)	20.3	820.5	860.5116	860.5131	-1.70	$C_{45}H_{75}NO_{13}$	638.4239				++	-	+	++	
17	Sc	20.4	834.5	874.5				652.4395				+	-	-	+	
18	Sc-D/E	20.6	804.5	844.5157	844.5181	-2.90	$C_{45}H_{75}NO_{12}$	622.3926	622.3926	0.08	$C_{32}H_{57}NO_9$	++	-	+	++	
19	Sc	20.6	814.5	-								-	++	-	-	
20	6-OH-7-OMe-Sc-B	20.6	832.5	872.5				620.4133				-	+++	+	-	
21	Sc	20.8	788.5	828.4861	828.4868	-0.90	$C_{44}H_{71}NO_{12}$	606.3602	606.3613	-1.74	$C_{31}H_{53}NO_9$	+	-	+	+	
22	Sc	20.9	802.5	842.5								++	-	+	-	

Table S3. Cont.

23	Sc	21.0	804.5	844.5				622.4289				+	+	+	+
24	Sc	21.2	774.5	814.5063	814.5076	-1.58	C <sub>44</sub> H <sub>73</sub> NO <sub>11</sub>	592.3782	592.3820	-6.40	C <sub>31</sub> H <sub>55</sub> NO <sub>8</sub>	+	+	+	-
25	Sc-B	21.3	802.5	842.5022	842.5025	-0.35	C <sub>45</sub> H <sub>73</sub> NO <sub>12</sub>	620.3766	620.3769	-0.49	C <sub>32</sub> H <sub>55</sub> NO <sub>9</sub>	+++	++	++	+++
26	Sc	21.9	786.5	826.5062	826.5076	-1.67	C <sub>45</sub> H <sub>73</sub> NO <sub>11</sub>	604.3822	604.3820	0.35	C <sub>32</sub> H <sub>55</sub> NO <sub>8</sub>	++	+	+	++
27	Sc-C	22.4	788.5	828.5221	828.5232	-1.37	C <sub>45</sub> H <sub>75</sub> NO <sub>11</sub>	606.3971	606.3976	-0.89	C <sub>32</sub> H <sub>57</sub> NO <sub>8</sub>	++	++	+	++
28	7-OMe-Sc	22.5	834.5	874.5								-	-	+	-
29	7-OMe-29-OAc-Sc-B	22.6	844.5	884.5129	884.5131	-0.18	C <sub>47</sub> H <sub>75</sub> NO <sub>13</sub>	648.3705	648.3718	-2.03	C <sub>33</sub> H <sub>55</sub> NO <sub>10</sub>	-	-	++	-
30	7-OMe-Sc-B (1)	23.5	816.5	856.5	856.5181				620.4133			+	+	+++	+++
31	7-OMe-Sc	24.0	800.5	840.5	840.4868				604.3820			-	+	++	+
32	Sc	24.8	743.5	783.5	783.4654				561.3762			+	-	-	+
33	7-OMe-Sc-C	24.9	802.5	842.5	842.5389				606.4340			-	+	+	+

**Table S4.** Previously published scytophycin variants, their monoisotopic masses (M), positions of the variable functional groups. 6-OH-7-OMe-scytophycin B = tolytoxin A. Carbon numbers in Figure S8.

No	Name	M	C-6	C-7	C-16	C-19	C-23	C-27	Reference
1	Scytophycin A	821.5	-H	-OH	-epoxy	-OMe	-OH	-OH	[1]
2	Scytophycin B	819.5	-H	-OH	-epoxy	-OMe	-OH	=O	[1]
3	Scytophycin C	805.5	-H	-OH	-Me	-OMe	-OH	=O	[2]
4	Scytophycin D	821.5	-H	-OH	-(OH)CH <sub>3</sub>	-OMe	-OH	=O	[2]
5	Scytophycin E	821.5	-H	-OH	-CH <sub>2</sub> OH	-OMe	-OH	=O	[2]
6	6-OH-7-OMe-scytophycin B	849.5	-OH	-OMe	-epoxy	-OMe	-OH	=O	[3]
7	23-Ac-tolytoxin A	891.5	-OH	-OMe	-epoxy	-OMe	-OAc	=O	[4]
8	6-OH-scytophycin B	835.5	-OH	-OH	-epoxy	-OMe	-OH	=O	[3]
9	7-Ac-scytophycin B	861.5	-H	-OAc	-epoxy	-OMe	-OH	=O	[1]
10	7-OMe-scytophycin B	833.5	-H	-OMe	-epoxy	-OMe	-OH	=O	[5]

Table S4. Cont.

11	19-O-deMe-scytophycin C	791.5	-H	-OH	-Me	-OH	-OH	=O	[3]
12	6-OH-7-OMe-scytophycin E	851.5	-OH	-OMe	-CH <sub>2</sub> OH	-OMe	-OH	=O	[3]
13	6-OH-scytophycin D/E	837.5	-OH	-OH	-(OH)CH <sub>3</sub> /-CH <sub>2</sub> OH	-OMe	-OH	=O	[5]
14	7-OMe-19-deMe-scytophycin D/E	821.5	-H	-OMe	-(OH)CH <sub>3</sub> /-CH <sub>2</sub> OH	-OH	-OH	=O	[5]

**Table S5.** Sodiated ion  $[M + Na]^+$  mass ( $m/z$ ), product ions and their  $m/z$ , intensities and comments concerning the tentative structures of scytophycin variants No 1–33. Ion structures a–n are presented in Figure S8.

No	$[M+Na]^+$ ( $m/z$ )	Diagnostic Product Ions (x if Same As in the Column Header) and Intensities (Superscripts) from $[M + Na]^+$ ( $m/z$ )															Comment (+ and – Compared to Sc No25)	
		a-2H 262	b-2H 320	c-H <sub>2</sub> O 332	dk-2H 390	ek-4H 460	fk-4H 490	gk-(2H + H <sub>2</sub> O) 560	hk-4H 620	ik-4H 686	jk-2H 718	l 545 1545	lhk-4H 323	m 687 687	mhk-4H 465	n 731 731		
1	888.5	x <sup>3</sup>	x <sup>26</sup>	x <sup>1</sup>	x <sup>9</sup>	x <sup>6</sup>	x <sup>7</sup>	x <sup>6</sup>	x <sup>100</sup>	660 <sup>30</sup>	732 <sup>3</sup>	591 <sup>13</sup>	x <sup>2</sup>	733 <sup>3</sup>	x <sup>1</sup>	777 <sup>1</sup>	-	
2	860.5	x <sup>1</sup>	x <sup>19</sup>	x <sup>1</sup>	x <sup>6</sup>	446 <sup>1</sup>	476 <sup>14</sup>	548 <sup>2</sup>	608 <sup>100</sup>	720 <sup>8</sup>	734 <sup>1</sup>	563 <sup>5</sup>	x <sup>-</sup>	705 <sup>1</sup>	453 <sup>1</sup>	749 <sup>&lt;1</sup>	-	
3	904.5	x <sup>1</sup>	x <sup>18</sup>	x <sup>3</sup>	x <sup>7</sup>	x <sup>5</sup>	x <sup>14</sup>	x <sup>-</sup>	652 <sup>100</sup>	718 <sup>1</sup>	764 <sup>1</sup>	x <sup>-</sup>	x <sup>2</sup>	749 <sup>2</sup>	497 <sup>1</sup>	793 <sup>1</sup>	-	+2 x O in C13–34
4	814.5	x <sup>2</sup>	x <sup>25</sup>	x <sup>2</sup>	x <sup>15</sup>	x <sup>-</sup>	-	532 <sup>1</sup>	592 <sup>100</sup>	658 <sup>1</sup>	736 <sup>3</sup>	517 <sup>2</sup>	295 <sup>1</sup>	673 <sup>100</sup>	-	703 <sup>-</sup>	-	-28 Da
5	860.5	x <sup>2</sup>	x <sup>15</sup>	x <sup>1</sup>	x <sup>5</sup>	x <sup>2</sup>	x <sup>3</sup>	562 <sup>1</sup>	622 <sup>100</sup>	688 <sup>5</sup>	x <sup>1</sup>	563 <sup>7</sup>	325 <sup>3</sup>	705 <sup>2</sup>	467 <sup>1</sup>	749 <sup>&lt;1</sup>	-	
6	858.5	x <sup>7</sup>	x <sup>42</sup>	x <sup>1</sup>	x <sup>8</sup>	x <sup>6</sup>	x <sup>11</sup>	x <sup>4</sup>	x <sup>100</sup>	686 <sup>4</sup>	x <sup>1</sup>	561 <sup>13</sup>	x <sup>4</sup>	703 <sup>7</sup>	x <sup>1</sup>	747 <sup>&lt;1</sup>	-	
7	874.5	x <sup>1</sup>	x <sup>5</sup>	x <sup>-</sup>	x <sup>2</sup>	x <sup>1</sup>	x <sup>1</sup>	592 <sup>2</sup>	652 <sup>100</sup>	718 <sup>2</sup>	x <sup>2</sup>	577 <sup>4</sup>	355 <sup>3</sup>	719 <sup>1</sup>	497 <sup>&lt;1</sup>	763 <sup>&lt;1</sup>	-	+32 Da (2O) in ion lhk
8	890.5	x <sup>&lt;1</sup>	x <sup>9</sup>	x <sup>-</sup>	x <sup>4</sup>	x <sup>1</sup>	x <sup>2</sup>	578 <sup>2</sup>	638 <sup>100</sup>	704 <sup>-</sup>	750 <sup>1</sup>	593 <sup>3</sup>	341 <sup>2</sup>	735 <sup>3</sup>	483 <sup>1</sup>	779 <sup>-</sup>	ek-4H: 476 <sup>2</sup>	+16 Da (O) in ion lhk
9	858.5	x <sup>2</sup>	x <sup>12</sup>	x <sup>2</sup>	x <sup>4</sup>	x <sup>7</sup>	x <sup>9</sup>	576 <sup>2</sup>	636 <sup>100</sup>	702 <sup>3</sup>	734 <sup>-</sup>	561 <sup>5</sup>	339 <sup>1</sup>	703 <sup>-</sup>	481 <sup>1</sup>	747 <sup>-</sup>	-	+16 Da (O)
10	858.5	x <sup>2</sup>	x <sup>12</sup>	x <sup>4</sup>	x <sup>6</sup>	x <sup>2</sup>	x <sup>3</sup>	546 <sup>4</sup>	606 <sup>100</sup>	672 <sup>-</sup>	718 <sup>&lt;1</sup>	561 <sup>5</sup>	309 <sup>2</sup>	703 <sup>3</sup>	451 <sup>-</sup>	747 <sup>1</sup>	-	16-CH <sub>3</sub>
11	814.5	x <sup>9</sup>	x <sup>21</sup>	x <sup>2</sup>	x <sup>9</sup>	432 <sup>2</sup>	462 <sup>2</sup>	532 <sup>1</sup>	592 <sup>100</sup>	658 <sup>2</sup>	690 <sup>-</sup>	517 <sup>3</sup>	295 <sup>2</sup>	659 <sup>5</sup>	437 <sup>1</sup>	703 <sup>-</sup>	-	-28 Da in ion lhk

Table S5. Cont.

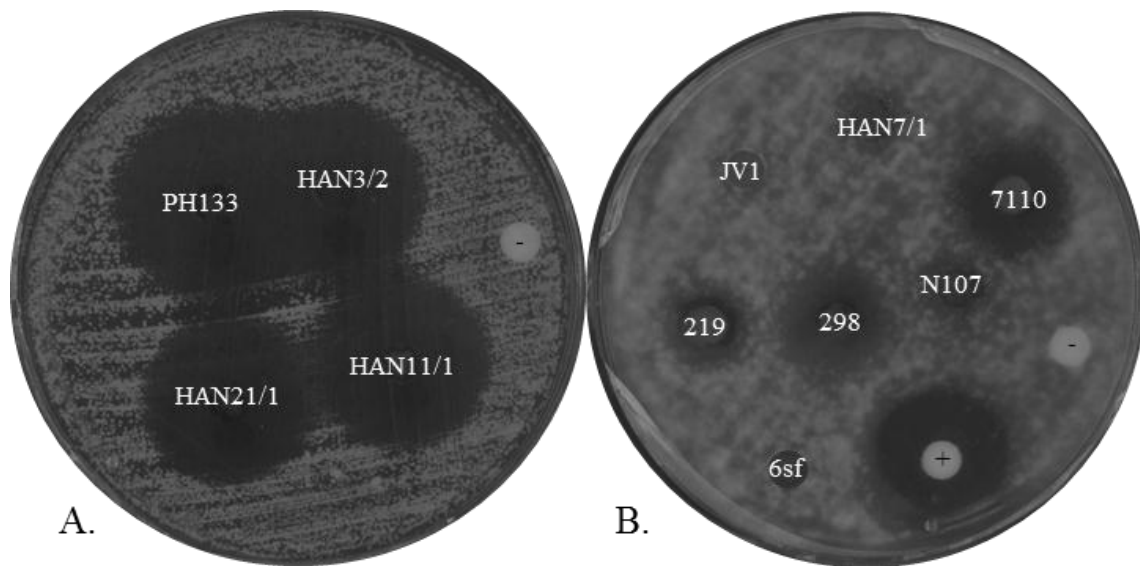
12	844.5	x <sup>9</sup>	x <sup>51</sup>	x <sup>2</sup>	x <sup>16</sup>	444 <sup>1</sup>	476 <sup>3</sup>	546 <sup>3</sup>	606 <sup>100</sup>	688 <sup>7</sup>	704 <sup>OP</sup>	547 <sup>11</sup>	309 <sup>1</sup>	689 <sup>5</sup>	451 <sup>2</sup>	733 <sup>&lt;1</sup>	416 <sup>5</sup> , 587 <sup>10</sup> , 703 <sup>20</sup>	Detailed structure not identifiable
13	874.5	x <sup>3</sup>	x <sup>15</sup>	x <sup>&lt;1</sup>	x <sup>3</sup>	x <sup>7</sup>	x <sup>5</sup>	x <sup>1</sup>	x <sup>100</sup>	x <sup>2</sup>	x <sup>5</sup>	577 <sup>3</sup>	x <sup>1</sup>	719 <sup>-</sup>	x <sup>&lt;1</sup>	763 <sup>-</sup>		+32 in C1-12
14	828.5	x <sup>&lt;1</sup>	x <sup>13</sup>	x <sup>1</sup>	x <sup>3</sup>	x <sup>&lt;1</sup>	x <sup>3</sup>	546 <sup>5</sup>	606 <sup>59</sup>	671 <sup>2</sup>	704 <sup>1</sup>	x <sup>OP</sup>	x <sup>1</sup>	687 <sup>100</sup>	x <sup>29</sup>	717 <sup>-</sup>	306 <sup>2</sup> , 546 <sup>5</sup> , 564 <sup>25</sup>	Spectrum contaminated from ion m/z 830.5
15	874.5	x <sup>3</sup>	x <sup>11</sup>	x <sup>3</sup>	x <sup>5</sup>	x <sup>1</sup>	x <sup>3</sup>	562 <sup>2</sup>	622 <sup>100</sup>	688 <sup>&lt;1</sup>	734 <sup>2</sup>	577 <sup>5</sup>	325 <sup>2</sup>	719 <sup>1</sup>	467 <sup>1</sup>	763 <sup>OP</sup>		
16	860.5	x <sup>1</sup>	x <sup>9</sup>	-	x <sup>4</sup>	x <sup>&lt;1</sup>	x <sup>2</sup>	578 <sup>1</sup>	638 <sup>100</sup>	704 <sup>2</sup>	736 <sup>-</sup>	563 <sup>4</sup>	341 <sup>2</sup>	705 <sup>1</sup>	483 <sup>1</sup>	749 <sup>1</sup>		+18 Da (2H, O) in ion lhc
17	874.5	x <sup>1</sup>	x <sup>5</sup>	-	x <sup>2</sup>	x <sup>1</sup>	x <sup>1</sup>	592 <sup>2</sup>	652 <sup>100</sup>	718 <sup>2</sup>	750 <sup>-</sup>	577 <sup>4</sup>	355 <sup>3</sup>	719 <sup>1</sup>	497 <sup>&lt;1</sup>	763 <sup>-</sup>		+32 Da (2O) in ion lhc
18	844.5	x <sup>1</sup>	x <sup>14</sup>	x <sup>&lt;1</sup>	x <sup>4</sup>	x <sup>1</sup>	x <sup>3</sup>	562 <sup>2</sup>	622 <sup>100</sup>	688 <sup>2</sup>	720 <sup>-</sup>	547 <sup>3</sup>	325 <sup>2</sup>	689 <sup>2</sup>	467 <sup>3</sup>	733 <sup>-</sup>		
20	872.5	x <sup>2</sup>	x <sup>24</sup>	x <sup>2</sup>	x <sup>7</sup>	x <sup>4</sup>	x <sup>3</sup>	x <sup>1</sup>	x <sup>100</sup>	x <sup>OP</sup>	732 <sup>&lt;1</sup>	575 <sup>6</sup>	x <sup>1</sup>	717 <sup>3</sup>	x <sup>&lt;1</sup>	761 <sup>-</sup>	jk-4H:730 <sup>3</sup>	
21	828.5	x <sup>3</sup>	x <sup>25</sup>	x <sup>&lt;1</sup>	x <sup>9</sup>	x <sup>3</sup>	x <sup>5</sup>	546 <sup>3</sup>	606 <sup>100</sup>	672 <sup>2</sup>	704 <sup>-</sup>	531 <sup>5</sup>	309 <sup>2</sup>	673 <sup>3</sup>	451 <sup>1</sup>	717 <sup>-</sup>	562 <sup>65</sup>	-CH <sub>2</sub> from ion lhc
22	842.5	x <sup>1</sup>	x <sup>1</sup>	x <sup>7</sup>	-	x <sup>1</sup>	x <sup>4</sup>	x <sup>2</sup>	x <sup>100</sup>	x <sup>1</sup>	x <sup>-</sup>	x <sup>-</sup>	x <sup>-</sup>	x <sup>OP</sup>	x <sup>1</sup>	x <sup>-</sup>		Detailed structure not identifiable
23	844.5	x <sup>2</sup>	x <sup>19</sup>	x <sup>1</sup>	x <sup>5</sup>	x <sup>&lt;1</sup>	x <sup>2</sup>	562 <sup>3</sup>	622 <sup>100</sup>	688 <sup>&lt;1</sup>	720 <sup>-</sup>	547 <sup>4</sup>	325 <sup>2</sup>	689 <sup>1</sup>	467 <sup>&lt;1</sup>	733 <sup>-</sup>		Detailed structure not identifiable
24	814.5	x <sup>2</sup>	x <sup>25</sup>	x <sup>2</sup>	x <sup>15</sup>	x <sup>1</sup>	x <sup>-</sup>	532 <sup>1</sup>	592 <sup>100</sup>	658 <sup>1</sup>	690 <sup>-</sup>	517 <sup>2</sup>	295 <sup>&lt;1</sup>	659 <sup>2</sup>	437 <sup>&lt;1</sup>	703 <sup>1</sup>		-28 Da (C and O)
25	842.5	x <sup>3</sup>	x <sup>15</sup>	x <sup>&lt;1</sup>	x <sup>4</sup>	x <sup>4</sup>	x <sup>4</sup>	x <sup>3</sup>	x <sup>100</sup>	x <sup>1</sup>	x <sup>1</sup>	x <sup>3</sup>	x <sup>2</sup>	x <sup>1</sup>	x <sup>&lt;1</sup>	x <sup>&lt;1</sup>		
26	826.5	x <sup>3</sup>	x <sup>30</sup>	x <sup>2</sup>	x <sup>6</sup>	-	-	544 <sup>4</sup>	604 <sup>100</sup>	670 <sup>1</sup>	x <sup>1</sup>	529 <sup>3</sup>	307 <sup>1</sup>	671 <sup>1</sup>	449 <sup>&lt;1</sup>	715 <sup>&lt;1</sup>		-16 (O) from C15/16/17/19
27	828.5	x <sup>3</sup>	x <sup>22</sup>	x <sup>1</sup>	x <sup>6</sup>	x <sup>2</sup>	x <sup>1</sup>	546 <sup>1</sup>	606 <sup>100</sup>	672 <sup>2</sup>	704 <sup>-</sup>	531 <sup>2</sup>	309 <sup>1</sup>	673 <sup>OP</sup>	451 <sup>2</sup>	717 <sup>-</sup>		



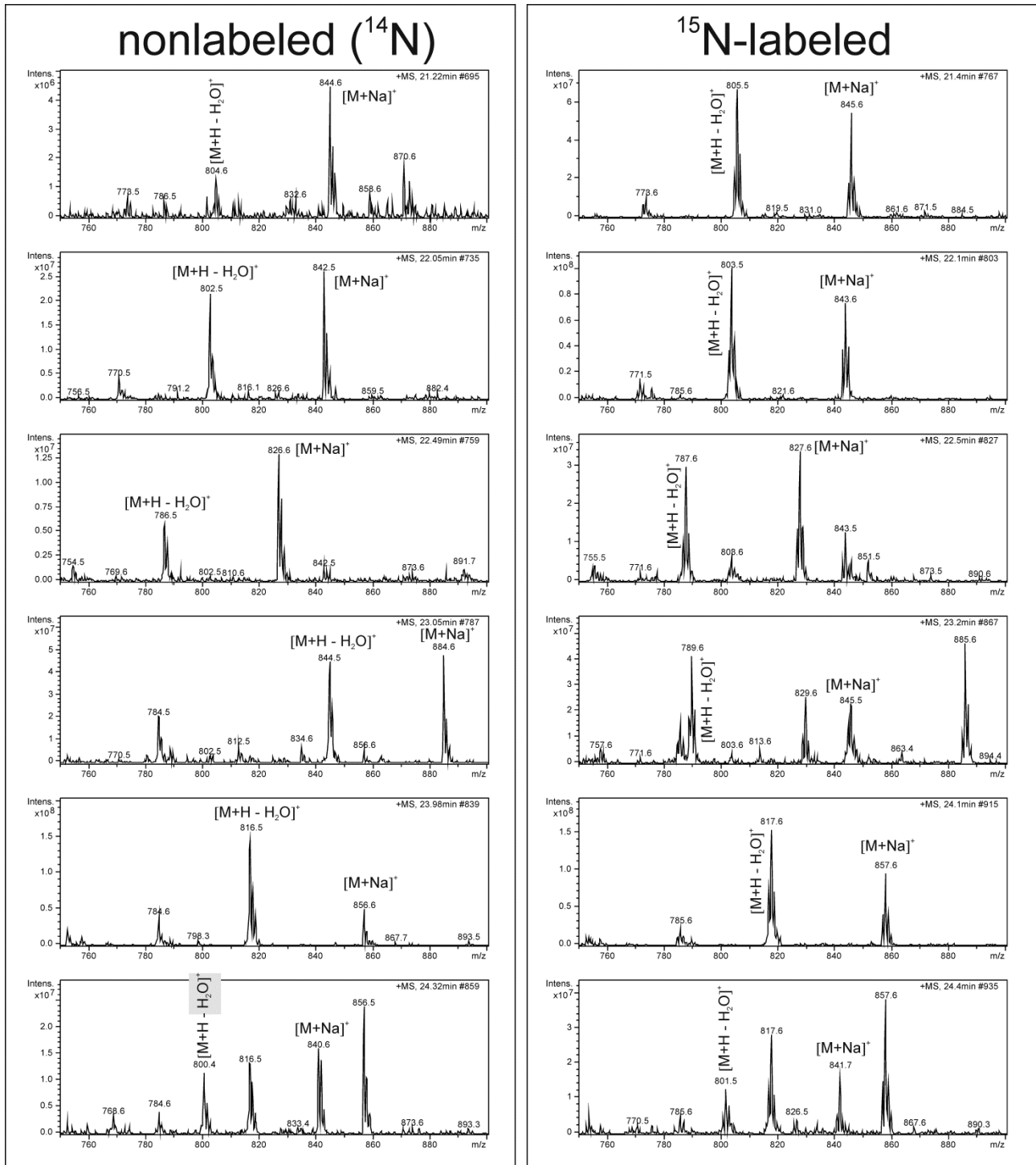
Table S5. Cont.

28	874.5	x <sup>&lt;1</sup>	x <sup>7</sup>	x <sup>&lt;1</sup>	x <sup>3</sup>	x <sup>2</sup>	x <sup>4</sup>	578 <sup>3</sup>	638 <sup>100</sup>	704 <sup>op</sup>	750 <sup>·</sup>	577 <sup>2</sup>	341 <sup>4</sup>	719 <sup>1</sup>	483 <sup>1</sup>	763 <sup>·</sup>	+18 Da (2H, O) in ion lhk	
29	884.5	290 <sup>·</sup>	348 <sup>7</sup>	360 <sup>&lt;1</sup>	418 <sup>3</sup>	488 <sup>·</sup>	458 <sup>2</sup>	588 <sup>op</sup>	648 <sup>55</sup>	714 <sup>1</sup>	732 <sup>·</sup>	559 <sup>7</sup>	x <sup>7</sup>	701 <sup>5</sup>	x <sup>5</sup>	759 <sup>·</sup>	288 <sup>6</sup> , 528 <sup>17</sup> , 588 <sup>100</sup>	-OAc cleave as HAc (60 Da)
30	856.5	x <sup>2</sup>	x <sup>20</sup>	x <sup>2</sup>	x <sup>4</sup>	x <sup>5</sup>	x <sup>5</sup>	x <sup>3</sup>	x <sup>100</sup>	686 <sup>·</sup>	732 <sup>·</sup>	559 <sup>5</sup>	x <sup>5</sup>	701 <sup>1</sup>	x <sup>2</sup>	745 <sup>·</sup>		
31	840.5	x <sup>5</sup>	x <sup>27</sup>	x <sup>&lt;1</sup>	x <sup>4</sup>	x <sup>&lt;1</sup>	x <sup>&lt;1</sup>	544 <sup>4</sup>	604 <sup>100</sup>	670 <sup>·</sup>	716 <sup>&lt;1</sup>	543 <sup>5</sup>	207 <sup>1</sup>	685 <sup>1</sup>	449 <sup>1</sup>	x <sup>&lt;1</sup>	-16 Da (O) from C15/16/17	
32	783.5	203 <sup>·</sup>	261 <sup>·</sup>	273 <sup>&lt;1</sup>	331 <sup>2</sup>	401 <sup>6</sup>	431 <sup>7</sup>	501 <sup>1</sup>	561 <sup>100</sup>	627 <sup>2</sup>	659 <sup>1</sup>	x <sup>·</sup>	x <sup>1</sup>	x <sup>&lt;1</sup>	x <sup>&lt;1</sup>	x <sup>·</sup>	-59 Da (H <sub>3</sub> CNHCHO)	
33	842.5	x <sup>1</sup>	x <sup>37</sup>	x <sup>3</sup>	x <sup>5</sup>	-	x <sup>2</sup>	546 <sup>op</sup>	606 <sup>100</sup>	672 <sup>&lt;1</sup>	x <sup>1</sup>	x <sup>2</sup>	309 <sup>1</sup>	687 <sup>1</sup>	451 <sup>&lt;1</sup>	x <sup>·</sup>		

<sup>op</sup> = Overlapping peaks.



**Figure S1.** Disc diffusion bioassay using cyanobacterial extracts against *Candida albicans* (A) and *Aspergillus flavus* (B). PH133 = *Anabaena cf. cylindrica* PH133; HAN3/2 = *Scytonema* sp. HAN3/2; HAN21/1 = *Anabaena* sp. HAN21/1; HAN11/1 = *Nostoc* sp. HAN11/1; HAN7/1 = *Anabaena* sp. HAN7/1; JV 1 = *Anabaena* sp. BIR JV1; 219 = *Nostoc* sp. CENA 219; 6sf = *Nostoc calcicula* 6 sf Calc; 298 = *Fischerella* sp. CENA 298; N107 = *Nostoc* sp. N107.3; 7110 = *Scytonema hofmanni* PCC 7110; – is negative control with methanol and + is 0.1 mg of nystatin (Sigma-Aldrich, St. Louis, MO, USA).



**Figure S2.** Nonlabeled ( $^{14}\text{N}$ ) and  $^{15}\text{N}$ -labeled sodiated and dehydrated protonated scytopycin ions from *Anabaena* sp. HAN21/1.



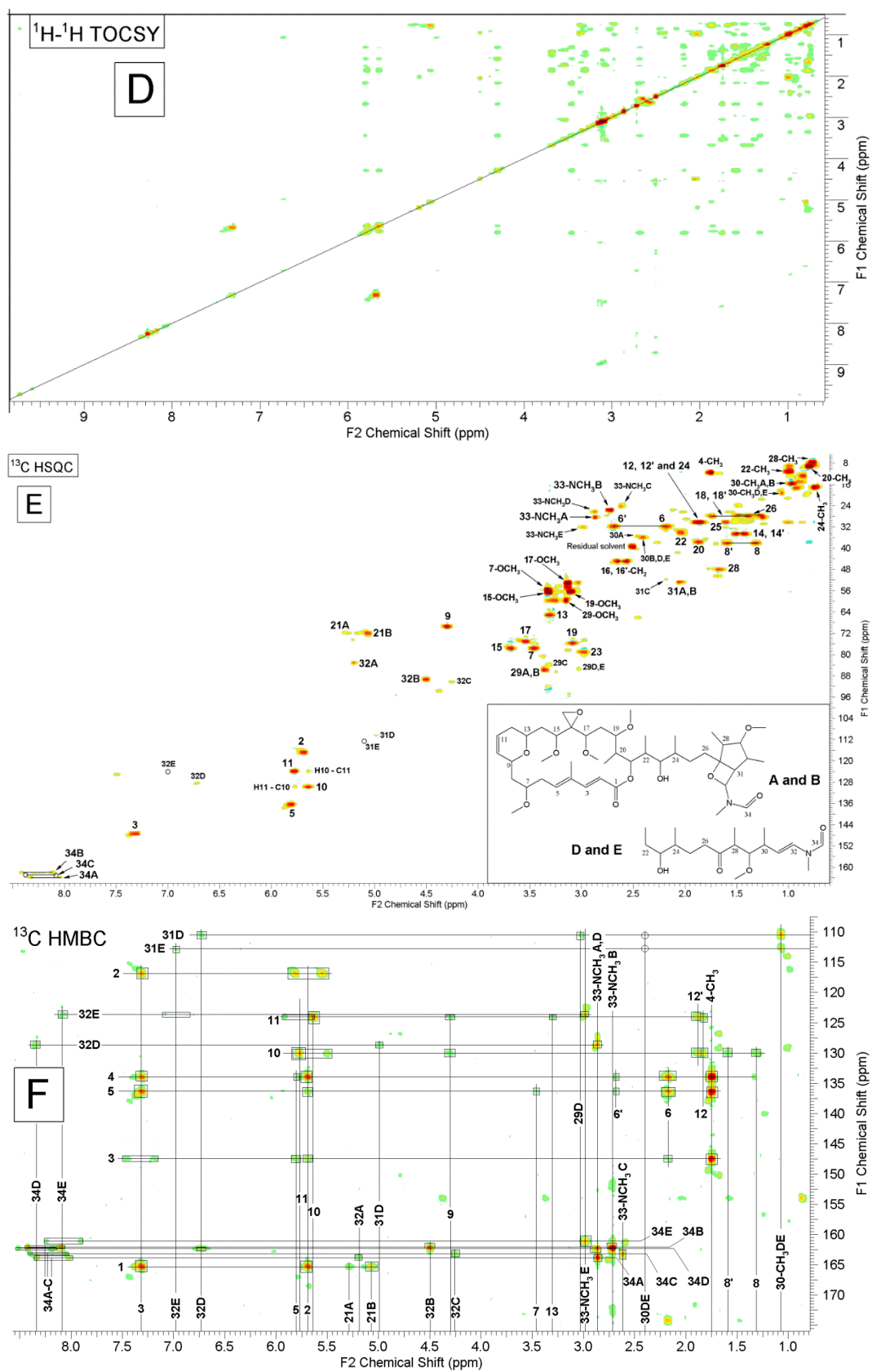
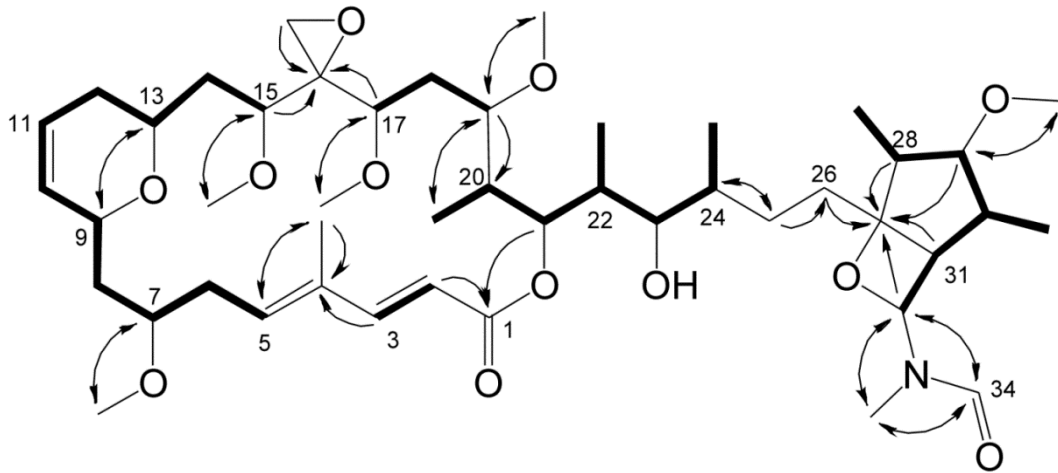
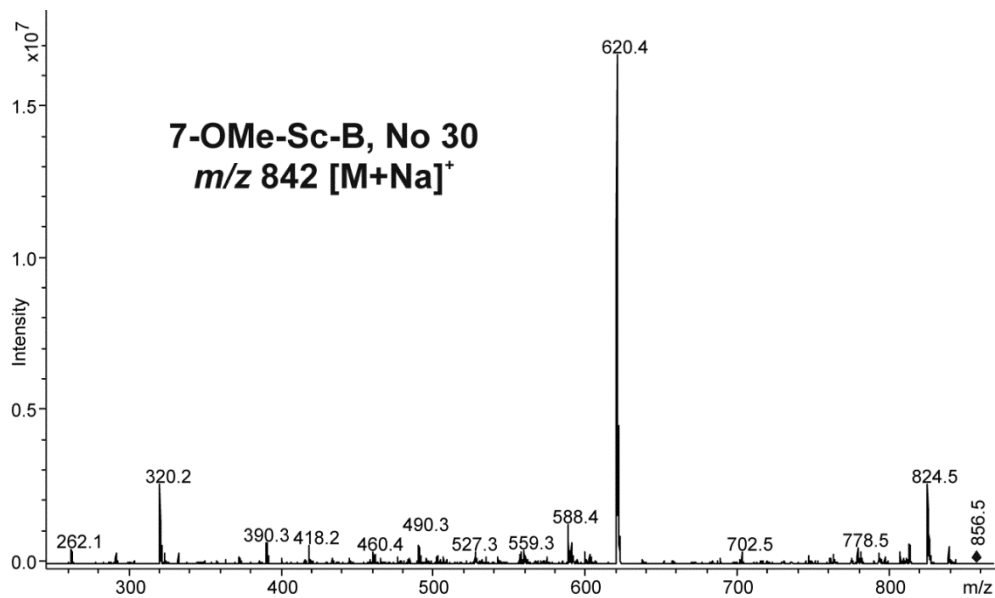


Figure S3. Cont.

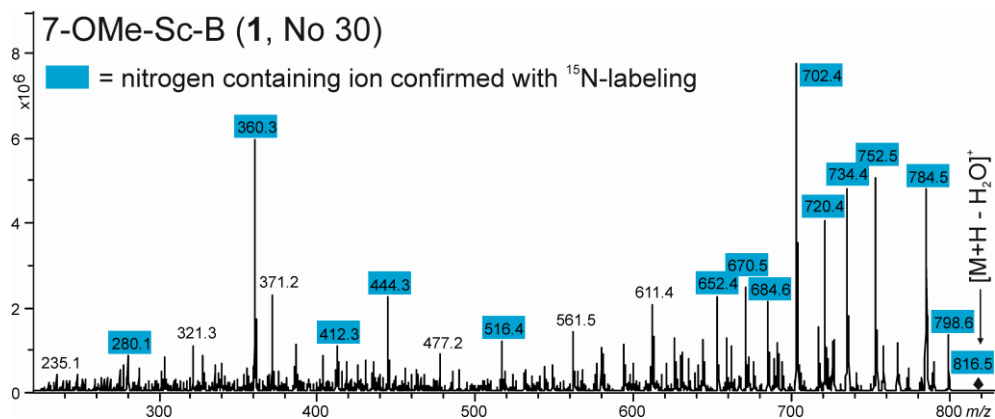




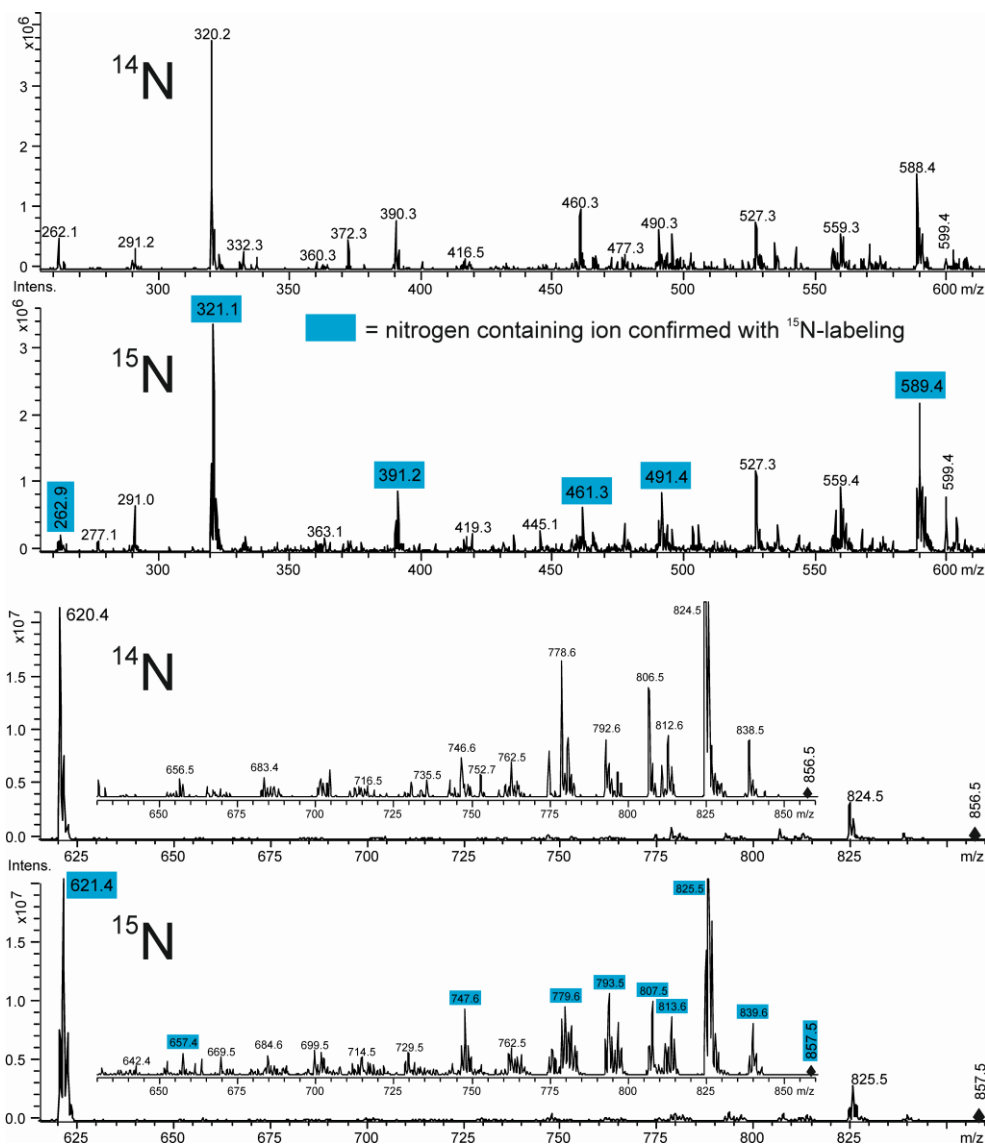
**Figure S4.** Structure of photoreacted 7-OMe-scytophycin B (2, Figure 1) with  $^1\text{H}$ - $^1\text{H}$  DQF-COSY (bold lines) and  $^{13}\text{C}$  HMBC (arrows) correlations.



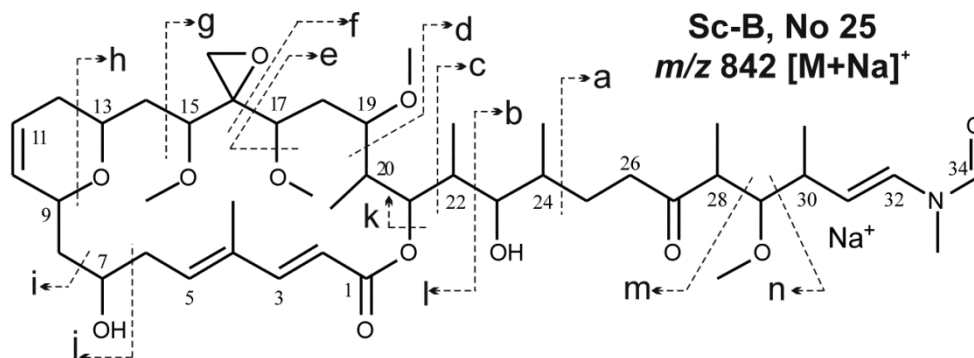
**Figure S5.** Product ion spectrum from sodiated 7-OMe-scytophycin-B ( $m/z$  856.5) produced by *Anabaena* sp. HAN21/1.



**Figure S6.** Product ion spectrum from dehydrated protonated 7-OMe-scytophycin-B from *Anabaena* sp. HAN21/1.



**Figure S7.** Nonlabeled ( $^{14}\text{N}$ ) and  $^{15}\text{N}$ -labeled product ion spectrum from sodiated 7-Ome-scytophycin-B (**1**, Figure 1 and No 30, Table 2) of *Anabaena* sp. HAN21/1.



**Figure S8.** Structure of scytophycin-B (No 25 in Table 2 and Tables S2 and S4) showing the product ions (a, b, c, dk, ek, fk, gk, hk, ik, jk, lhk, l, m, hk, m and n) studied from the sodiated ion [M + Na]<sup>+</sup>.



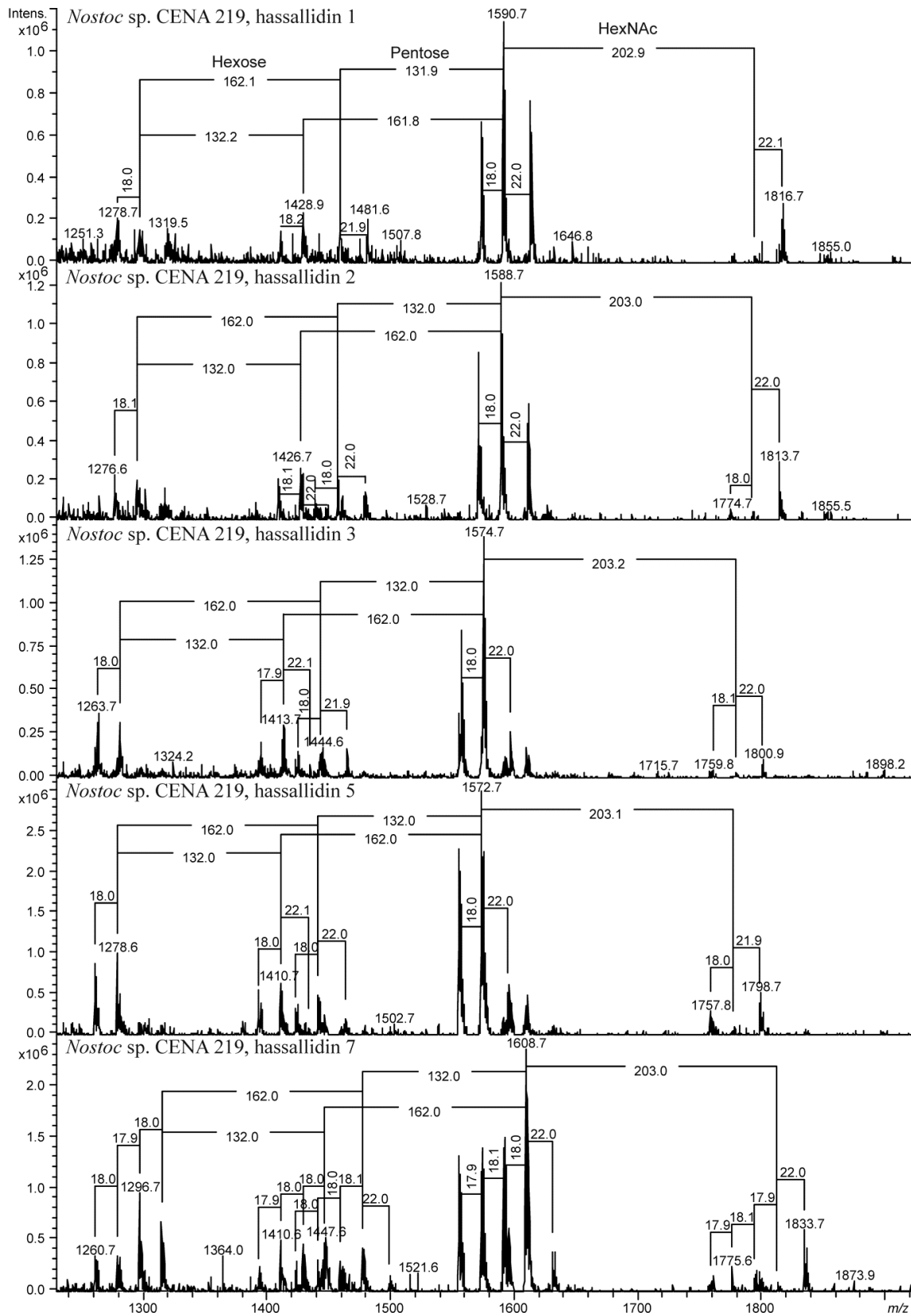


Figure S9. Mass spectra of *Nostoc* sp. CENA 219 hassallidins 1, 2, 3, 5 and 7.

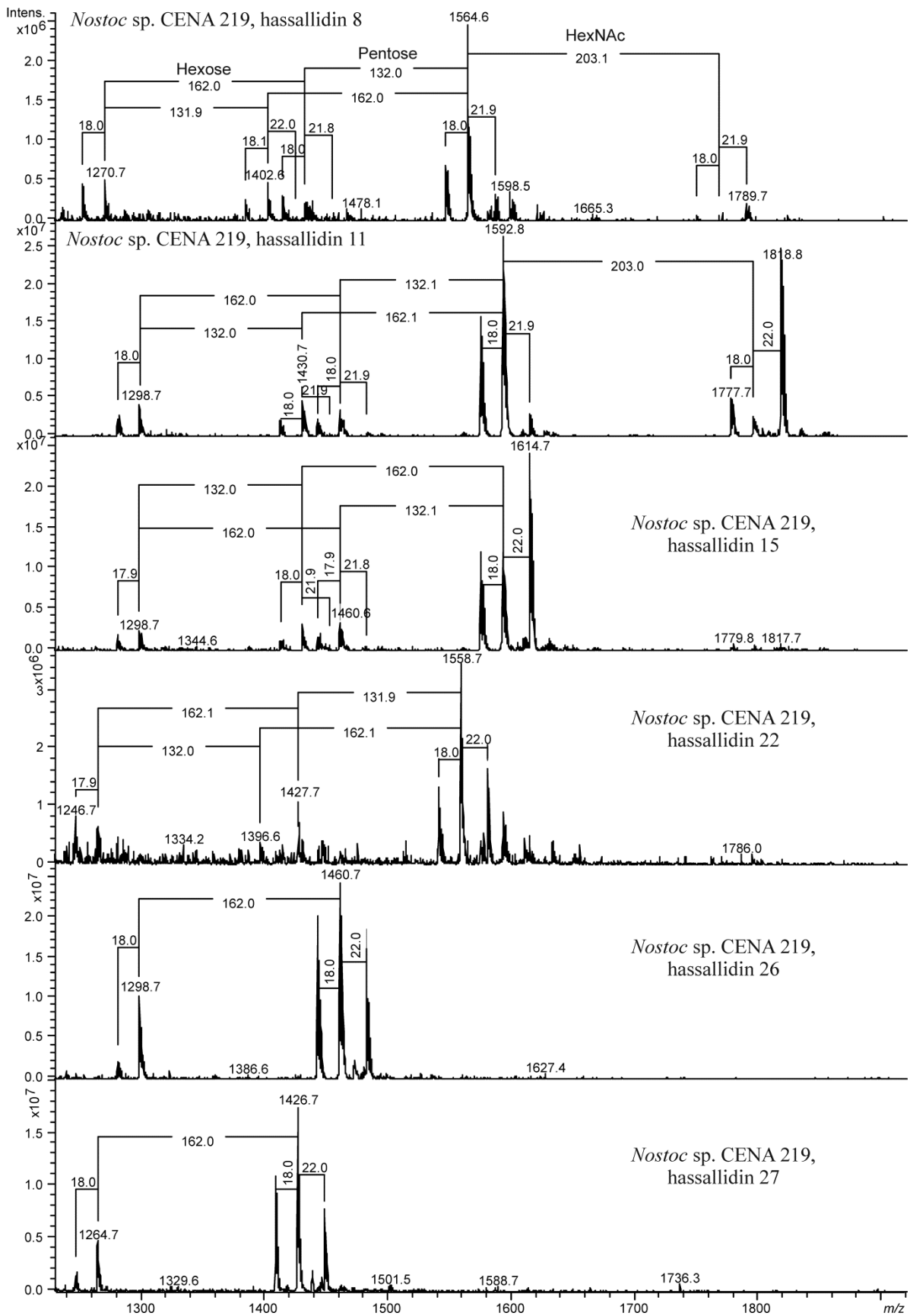


Figure S10. Mass spectra of *Nostoc* sp. CENA 219 hassallidins 8, 11, 15, 22, 26 and 27.

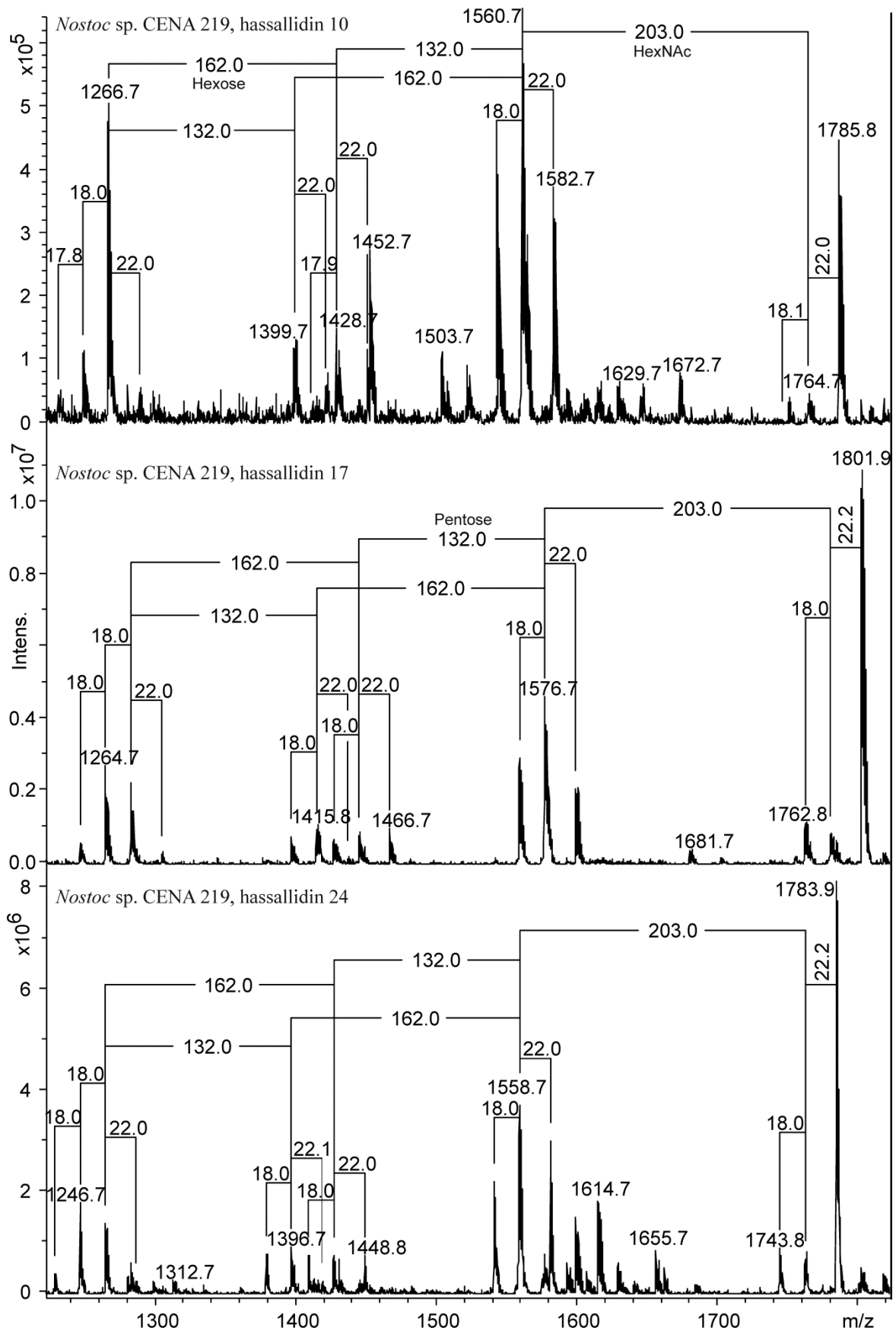


Figure S11. Mass spectra of *Nostoc* sp. CENA 219 hassallidins 10, 17 and 24.

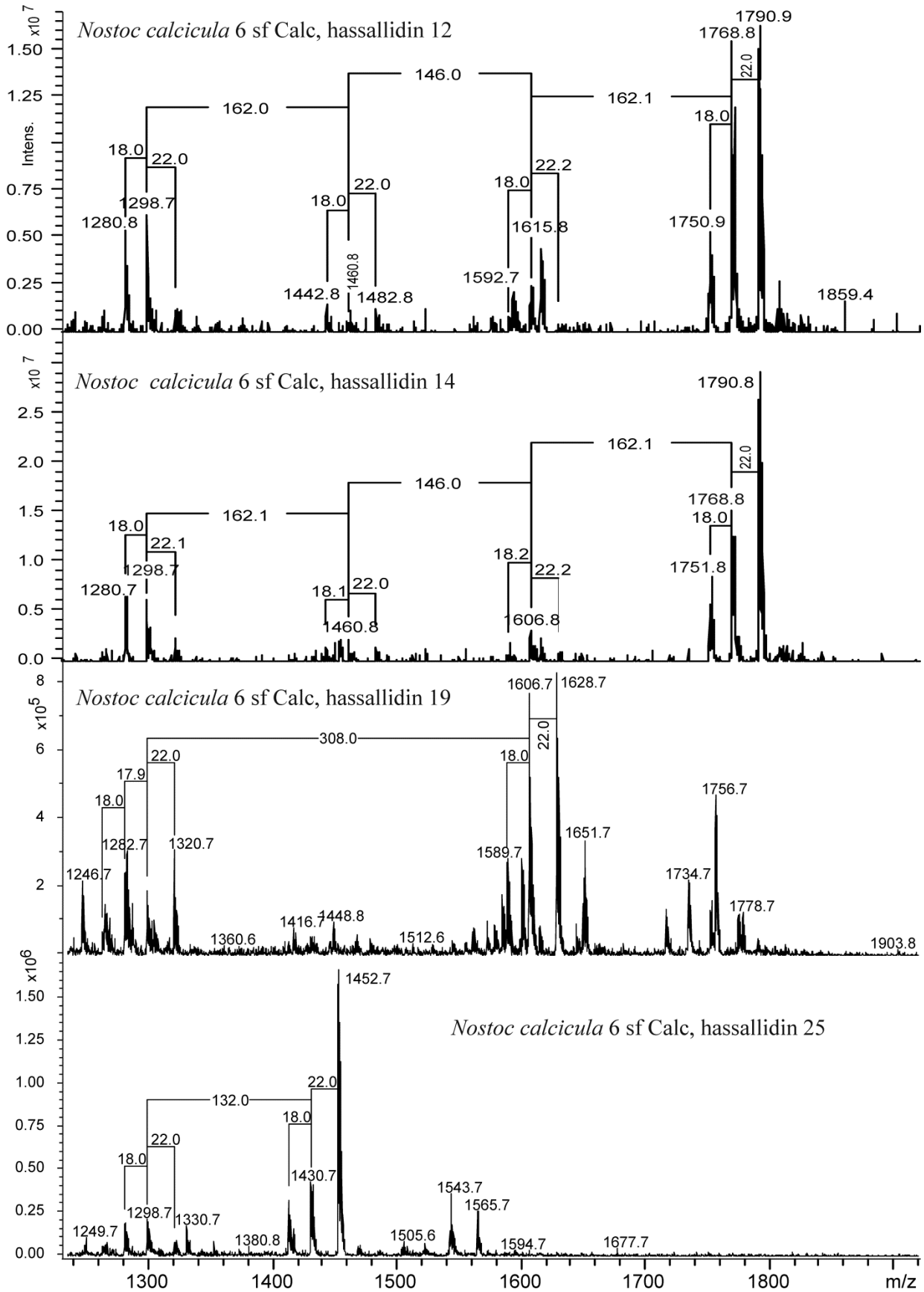


Figure S12. Mass spectra of *Nostoc* sp. 6 sf Calc hassallidins 12, 14, 19 and 25.

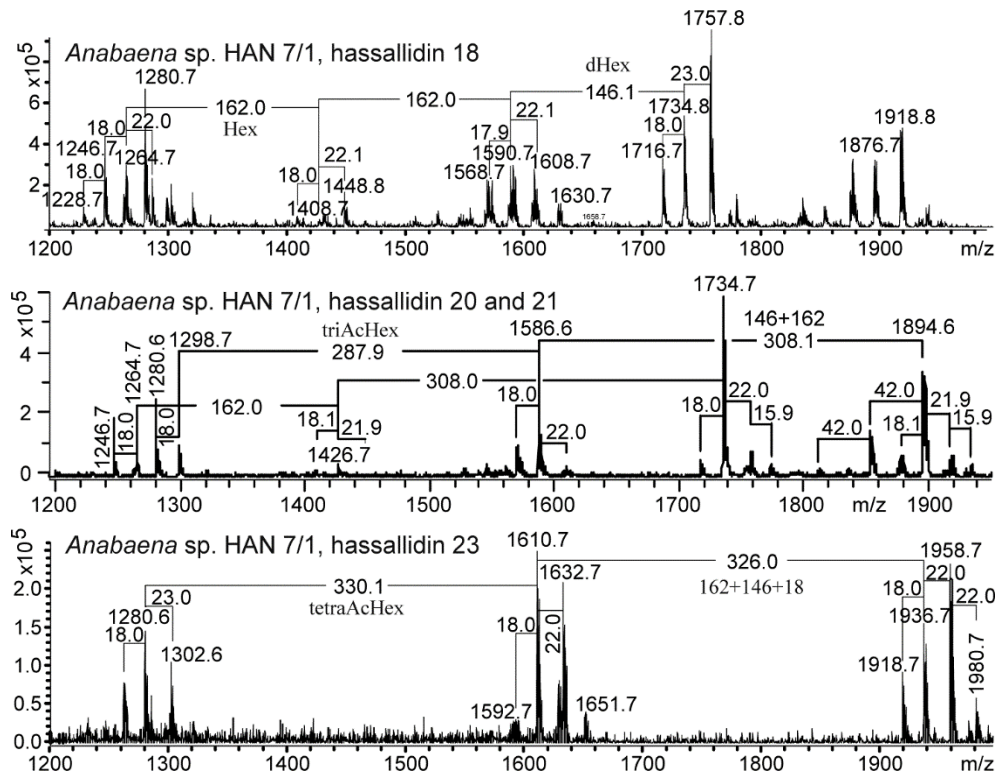


Figure S13. Mass spectra of *Anabaena* sp. HAN7/1 hassallidins 18, 20, 21 and 23.

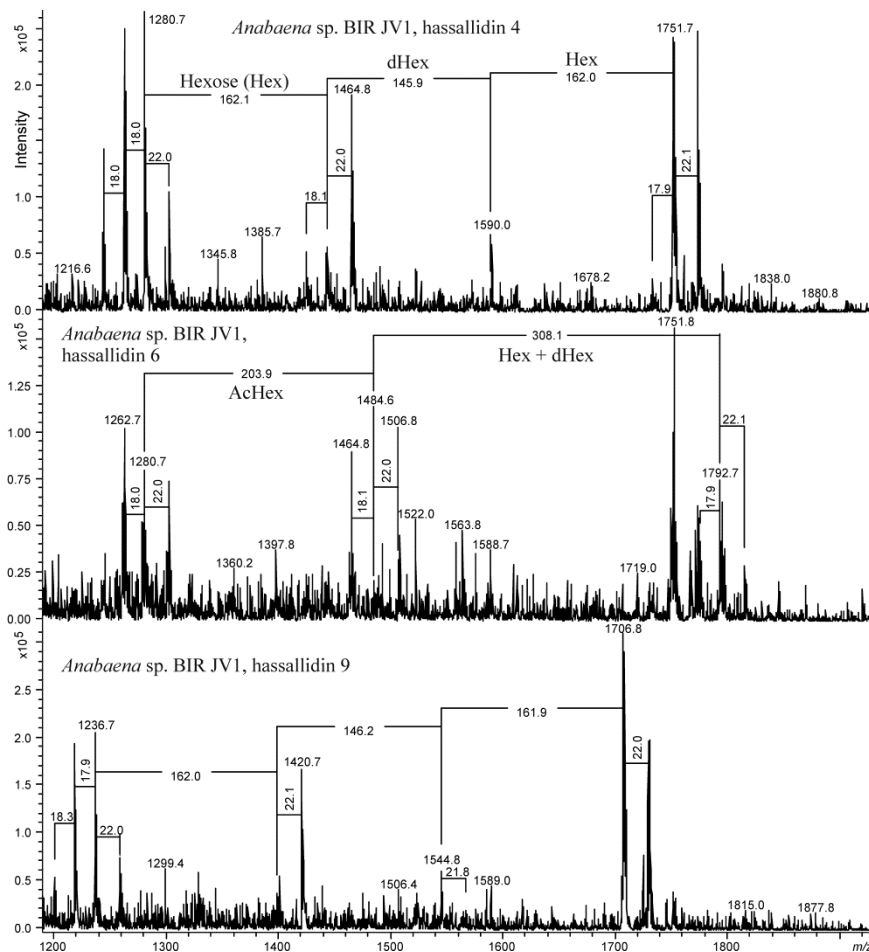
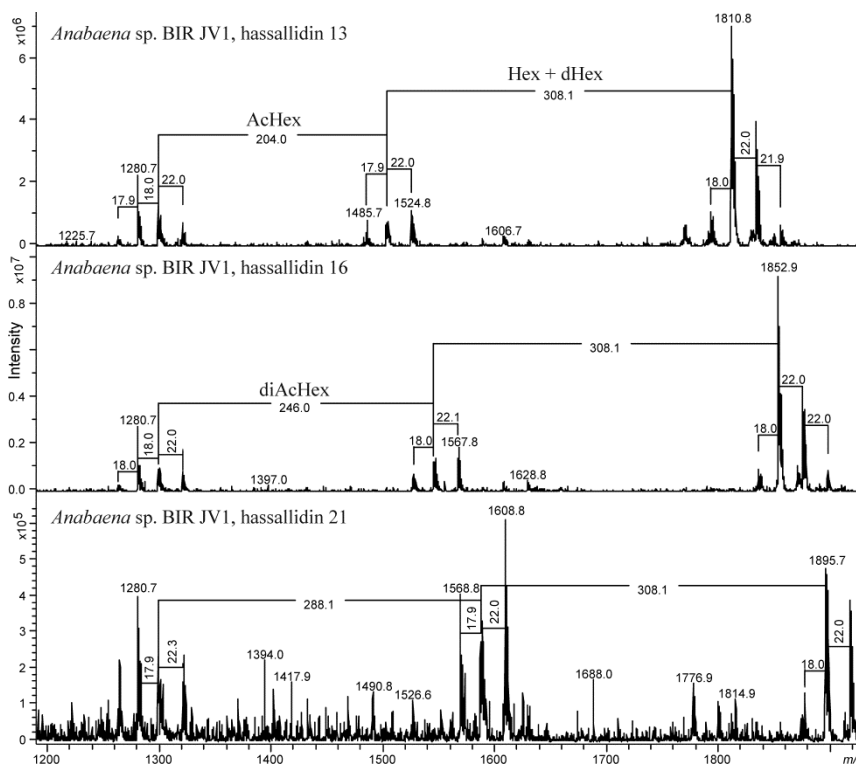


Figure S14. Mass spectra of *Anabaena cylindrica* BIR JV1 hassallidins 4, 6, and 9.



**Figure S15.** Mass spectra of *Anabaena cylindrica* BIR JV1 hassallidins 13, 16, and 21.

## References

1. Moore, R.E.; Patterson, G.M.L.; Mynderse, J.S.; Barchi Jr., J.; Norton, T.R.; Furusawa, E.; Furusawa, S. Toxins from cyanophytes belonging to the scytonemataceae. *Pure Appl. Chem.* **1986**, *58*, 263–271.
2. Ishibashi, M.; Moore, R.E.; Patterson, G.M.L. Scytophycins, Cytotoxic and antimycotic agents from the cyanophyte *Scytonema pseudohofmanni*. *J. Org. Chem.* **1986**, *51*, 5300–5306.
3. Carmeli, S.; Moore, R.E.; Patterson, G.M.L. Tolytoxin and new scytophycins from three species of *Scytonema*. *J. Nat. Prod.* **1990**, *53*, 1533–1542.
4. Nakao, Y.; Yoshida, W.Y.; Szabo, C.M.; Baker, B.J.; Scheuer, P.J. More Peptides and Other Diverse Constituents of the Marine Mollusk *Philineopsis speciosa*. *J. Org. Chem.* **1998**, *63*, 3272–3280.
5. Tomsickova, J.; Ondrej, M.; Cerny, J.; Hrouzek, P.; Kopecky, J. Analysis and detection of scytophycin variants by HPLC-ESI-MS. *Chem. Nat. Compd.* **2014**, *49*, 1170–1171.

© 2015 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).