Supporting Information

Non-Target Analysis and Stability Assessment of Reference Materials Using Liquid Chromatography–High-Resolution Mass Spectrometry

Elliott J. Wright, Daniel G. Beach*, Pearse McCarron

Biotoxin Metrology, National Research Council of Canada, 1411 Oxford Street, Halifax, Nova Scotia, B3H 3Z1, Canada

*corresponding author:
Tel +1 902-426-8274
Fax +1 902-426-5426;
Email: Daniel.Beach@nrc-cnrc.gc.ca

List of Tables

List of Figures

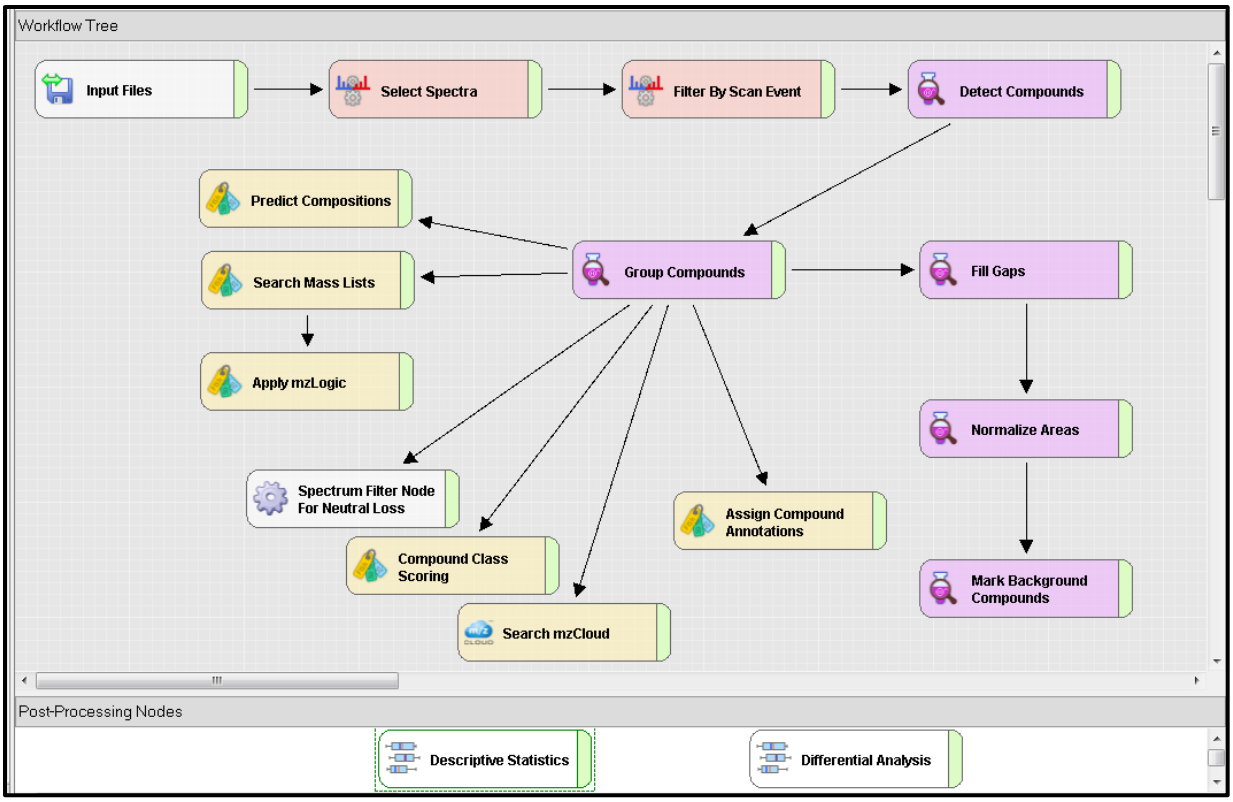

Fig. S1. Schematic of Compound Discoverer processing workflow for toxin profiling. Each box represents a "node" that performs specific data processing operations. Detailed settings for the workflow used are provided in Table S1.

Table S1. Compound Discoverer 3.0 settings used in this study.

Node	Settings
Input Files	N/A
Select Spectra	*General Settings* - Precursor Selection: Use MS1 Precursor - Use Isotope Pattern in Precursor Re-evaluation: True - Provide Profile Spectra: Automatic - Store Chromatograms: False *Spectrum Properties Filter* - Lower RT Limit: 6 - Upper RT Limit: 45 - First Scan: 0 - Last Scan: 0 - Ignore Specified Scans: (not specified) - Lowest Charge State: 0 - Highest Charge State: 0 - Min. Precursor Mass: 200 Da - Max. Precursor Mass: 1400 Da - Total Intensity Threshold: 0 - Minimum Peak Count: 1 *Scan Event Filters* - Mass Analyzer: Is FTMS - MS Order: Any - Activation Type: Is HCD - Min. Collision Energy: 0 - Max. Collision Energy: 1000 - Scan Type: Any - Polarity Mode: Is + or Is - *Peak Filters* - S/N Threshold (FT-only): 0 *Replacements for Unrecognized Properties* - Unrecognized Charge Replacements: 1 - Unrecognized Mass Analyzer Replacements: FTMS - Unrecognized MS Order Replacements: MS1 - Unrecognized Activation Type Replacements: HCD - Unrecognized Polarity Replacements: + or − - Unrecognized MS Resolution@200 Replacements: 60000 - Unrecognized MSn Resolution@200 Replacements: 30000
Filter By Scan Event	- Mass Analyzer: Is FTMS - MS Order: Is MS1; MS2 - Activation Type: Is HCD - Min. Collision Energy: 0 - Max. Collision Energy: 1000 - Scan Type: Any - Polarity Mode: Is + or Is −
Detect Compounds	*General Settings* - Mass Tolerance [ppm]: 5 ppm - Intensity Tolerance [%]: 50 - S/N Threshold: 3 - Min. Peak Intensity: 50 000 (*250 000 for positive stability analysis*)[a] - Ions: $[2M+K]^+$, $[2M+Na]^+$, $[M+H]^+$, $[M+H-H_2O]^+$, $[M+H-2H_2O]^+$ $[M+K]^+$, $[M+Na]^+$, $[M+NH_4]^+$ or $[M-2H]^{-2}$, $[M-2H+K]^-$, $[M-2H+Na]^-$, $[M-H]^-$, $[M-H-H_2O]^-$

	- Base Ions: $[M+H]^+$, $[M+NH_4]^+$ or $[M-H]^-$, $[M-2H]^{2-}$ - Min. Element Counts: C H - Max. Element Counts: C90 H190 N2 O80 P S2 *Peak Detection* - Filter Peaks: False - Max. Peak Width [min]: 1 - Remove Singlets: False - Min. # Scans per Peak: 6 - Min. # Isotopes: 3
Group Compounds	*Compound Consolidation* - Mass Tolerance: 5 ppm - RT Tolerance [min]: 0.5 *Fragment Data Selection* - Preferred Ions: $[M+H]^+$, $[M+NH_4]^+$ or $[M-H]^-$
Search Mass Lists	*Search Settings: Mass Lists* - Mass Tolerance: 5 ppm - Use Retention Time: False - RT Tolerance [min]: 0.5
Apply mzLogic	*Search Settings* - FT Fragment Mass Tolerance: 5 ppm - IT Fragment Mass Tolerance: 0.4 Da - Max. # Compounds: 0 - Max. # mzCloud Similarity Results to consider per Compound:10 - Match Factor Threshold: 30
Assign Compound Annotations	*General Settings* - Mass Tolerance: 4 ppm *Data Sources* - Data Source #1: MassList Search - Data Source #2: mzCloud Search - Data Source #3: Predicted Compositions - Data Source #4: (not specified) - Data Source #5: (not specified)
Predict Compositions	*Prediction Settings* - Mass Tolerance: 4 ppm - Min. Element Counts: C H - Max. Element Counts: C90 H190 N2 O80 P S2 - Min. RDBE: 5 - Max. RDBE: 40 - Min. H/C: 1 - Max. H/C: 2 - Max. # Candidates: 20 - Max. # Internal Candidates: 200 *Pattern Matching* - Intensity Tolerance [%]: 30 - Intensity Threshold [%]: 0.01 - S/N Threshold: 10 - Min. Spectral Fit [%]: 30 - Min. Pattern Cov. [%]: 90 - Use Dynamic Recalibration: False *Fragments Matching* - Use Fragments Matching: True - Mass Tolerance: 5 ppm - S/N Threshold: 10

Compound Class Scoring	*General Settings* - Compound Classes: shown in Table 1 - S/N Threshold: 0 - High Acc. Mass Tolerance: 5 ppm - Low Acc. Mass Tolerance: 0.5 Da - Allow AIF Scoring: False
Search mzCloud	*Search Settings* - Compound Classes: Natural Toxins - Match Ion Activation Type: True - Match Ion Activation Energy: Match with Tolerance - Ion Activation Energy Tolerance: 5 - Apply Intensity Threshold: True - Precursor Mass Tolerance: 5 ppm - FT Fragment Mass Tolerance: 5 ppm - IT Fragment Mass Tolerance: 0.4 Da - Identity Search: HighChem HighRes - Similarity Search: None - Library: Reference - Post Processing: Recalibrated - Match Factor Threshold: 60 - Max. # Results: 10
Spectrum Filter Node For Neutral Loss	- Intensity Threshold: 0 - Mass Loss Of Precursor: see Table 1 - Mass Tolerance (ppm): 110 for positive mode or 50 for negative mode
Mark Background Compounds	*General Settings* - Max. Sample/Blank: 5 - Max. Blank/Sample: 0 - Hide Background: False
Fill Gaps [b]	- Mass Tolerance: 5 ppm - S/N Threshold: 10 - Use Real Peak Detection: True
Normalize Areas [b]	- Regression Model: Linear - Min. QC Coverage (%): 100 - Max QC Area RSD (%): 30 - Max # Files Between QC: 15 - Area Normalization: Constant Mean - Exclude Blanks: True
Descriptive Statistics [b]	
Differential Analysis [b]	

[a] Intensity threshold was increased to 250 000 for combined profiling & stability study analysis.

[b] Only used for stability analysis.

Table S2. Suspected toxin analogues detected using non-target analysis methods for toxin profiling. Identities (ID) are tentative except those that are in bold type, which were confirmed previously [1].

Tentative ID	Formula	neutral exact mass	RT (min)	ESI mode	Area (counts)	Mass List Match [d]	Compound Class	MS/MS Ions Confirmed [e]	mzCloud Scoring
[a]	$C_{33}H_{53}NO_9$	607.3726	16.52	+	7.79×10^5		AZA	7	
[a]	$C_{33}H_{53}NO_{10}$	623.3671	14.63	+	5.04×10^5		AZA	5	
	$C_{33}H_{53}NO_{10}$	623.3671	14.50	+	1.65×10^5		AZA	2	
See fig S6	[b]	689.4513	22.01	+	7.99×10^5		AZA	8	
See fig S5	$C_{40}H_{63}NO_9$ [b]	701.4516	21.58	+	1.51×10^6		AZA	8	
AZA33 [a]	$C_{41}H_{65}NO_9$	715.4666	23.85	+	1.35×10^7		AZA	11	
	$C_{41}H_{65}NO_{10}$	731.4617	19.56	+	7.09×10^5		AZA	7	
	$C_{41}H_{65}NO_{10}$	731.4619	19.86	+	2.84×10^5		AZA	2	
AZA25 isomer [a]	$C_{46}H_{69}NO_{12}$ [b]	809.4720	20.79	+	4.58×10^5		AZA	7	74.7
AZA25 [a]	$C_{46}H_{69}NO_{12}$	809.4728	21.73	+	9.12×10^6		AZA	10	85.9
AZA39 [a]	$C_{45}H_{69}NO_{12}$ [b]	815.4826	19.85	+	3.82×10^5		AZA	4	
AZA26 [a]	$C_{46}H_{65}NO_{12}$	823.4507	16.78	+	5.33×10^5		AZA	5	
21,22-dehydroAZA6 [a]	$C_{47}H_{71}NO_{12}$ [c]	823.4883	23.53	+	1.74×10^6		AZA	7	86
21,22-dehydroAZA1 [a]	$C_{47}H_{71}NO_{12}$ [c]	823.4883	23.87	+	5.13×10^5		AZA	3	73.5
AZA48 [a]	$C_{46}H_{69}NO_{13}$	825.4671	17.84	+	2.34×10^6		AZA	9	86.1
21,22-dehydroAZA4	$C_{46}H_{69}NO_{13}$	825.4673	18.22	+	3.00×10^5		AZA	3	69.7
	$C_{46}H_{69}NO_{12}$	827.4825	15.76	+	2.49×10^5	✓	AZA	1	69.8
	$C_{46}H_{69}NO_{12}$	827.4825	15.53	+	4.03×10^5	✓	AZA	1	73.8
AZA3 isomer [a]	$C_{46}H_{69}NO_{12}$	827.4827	19.48	+	4.18×10^6	✓	AZA	11	87.6
AZA3 [a]	$C_{46}H_{69}NO_{12}$	827.4827	19.71	+	2.59×10^7	✓	AZA	11	89.1
AZA3 isomer [a]	$C_{46}H_{69}NO_{12}$	827.4828	23.83	+	1.77×10^6	✓	AZA	6	76.4
AZA3 isomer [a]	$C_{46}H_{69}NO_{12}$	827.4828	24.18	+	3.34×10^6	✓	AZA	11	88.1
AZA3 isomer [a]	$C_{46}H_{69}NO_{12}$	827.4828	25.20	+	2.50×10^7	✓	AZA	11	85.7
AZA3 isomer [a]	$C_{46}H_{69}NO_{12}$	827.4831	22.24	+	8.34×10^5	✓	AZA	5	84.4
	$C_{46}H_{71}NO_{12}$ [b]	829.4994	21.21	+	2.34×10^5		AZA	3	

Tentative ID	Formula	neutral exact mass	RT (min)	ESI mode	Area (counts)	Mass List Match [d]	Compound Class	MS/MS Ions Confirmed [e]	mzCloud Scoring
	$C_{46}H_{71}NO_{12}$ [b]	829.4997	21.66	+	4.69×10^{5}		AZA	3	
AZA6 [a]	$C_{47}H_{71}NO_{12}$	841.4985	20.68	+	1.32×10^{7}	✓	AZA	11	84
AZA1 [a]	$C_{47}H_{71}NO_{12}$	841.4985	21.42	+	2.49×10^{8}	✓	AZA	11	86.8
AZA1/6 isomer	$C_{47}H_{71}NO_{12}$ [c]	841.4983	16.46	+	4.57×10^{5}	✓	AZA	3	69.6
AZA1/6 isomer	$C_{47}H_{71}NO_{12}$ [c]	841.4983	16.92	+	4.16×10^{5}	✓	AZA	0	
AZA6 isomer [a]	$C_{47}H_{71}NO_{12}$ [c]	841.4985	20.32	+	9.33×10^{5}	✓	AZA	8	79.7
AZA1 isomer [a]	$C_{47}H_{71}NO_{12}$	841.4985	24.95	+	3.95×10^{5}	✓	AZA	5	85.8
AZA6 isomer [a]	$C_{47}H_{71}NO_{12}$	841.4985	26.82	+	7.45×10^{6}	✓	AZA	11	78.4
AZA6 isomer [a]	$C_{47}H_{71}NO_{12}$	841.4985	25.78	+	1.46×10^{6}	✓	AZA	12	82.3
AZA1/6 isomer	$C_{47}H_{71}NO_{12}$ [c]	841.4985	19.91	+	1.52×10^{5}	✓	AZA	1	70.3
	$C_{46}H_{69}NO_{13}$	843.4759	19.52	+	1.86×10^{5}	✓	AZA	3	63.7
AZA5 isomer [a]	$C_{46}H_{69}NO_{13}$ [c]	843.4751	17.21	+	1.14×10^{5}	✓	AZA	0	
	$C_{46}H_{69}NO_{13}$ [c]	843.4759	19.52	+	1.86×10^{5}	✓	AZA	3	63.7
	$C_{46}H_{69}NO_{13}$ [c]	843.4759	19.23	+	7.06×10^{4}	✓	AZA	1	62.1
	$C_{46}H_{69}NO_{13}$	843.4767	20.53	+	2.97×10^{6}	✓	AZA	10	79.8
AZA4 isomer [a]	$C_{46}H_{69}NO_{13}$	843.4767	20.61	+	4.33×10^{6}	✓	AZA	10	79.8
AZA4 isomer [a]	$C_{46}H_{69}NO_{13}$	843.4767	20.28	+	1.66×10^{6}	✓	AZA	9	81.8
	$C_{46}H_{69}NO_{13}$ [c]	843.4782	21.10	+	2.06×10^{5}	✓	AZA	0	
AZA5 [a]	$C_{46}H_{69}NO_{13}$	843.4769	17.63	+	3.48×10^{6}	✓	AZA	10	89.9
	$C_{46}H_{69}NO_{13}$	843.4771	15.69	+	2.19×10^{5}	✓	AZA	2	66.2
AZA4 isomer [a]	$C_{46}H_{69}NO_{13}$	843.4771	16.30	+	6.21×10^{5}	✓	AZA	4	82.1
AZA4 [a]	$C_{46}H_{69}NO_{13}$	843.4771	16.63	+	1.06×10^{7}	✓	AZA	12	86.4
	$C_{47}H_{73}NO_{12}$	843.5135	23.71	+	1.17×10^{6}		AZA	5	
AZA2 isomer [a]	$C_{48}H_{73}NO_{12}$	855.5138	27.51	+	1.74×10^{6}	✓	AZA	7	87.5
AZA2 isomer	$C_{48}H_{73}NO_{12}$ [c]	855.5138	28.17	+	2.13×10^{5}	✓	AZA		
AZA2 isomer [a]	$C_{48}H_{73}NO_{12}$	855.5138	23.81	+	3.87×10^{5}	✓	AZA	2	67.4
AZA2 [a]	$C_{48}H_{73}NO_{12}$	855.5140	22.70	+	1.18×10^{8}	✓	AZA	11	86.8
AZA9 isomer [a]	$C_{47}H_{71}NO_{13}$	857.4910	21.37	+	1.78×10^{5}	✓	AZA	2	74.6

Tentative ID	Formula	neutral exact mass	RT (min)	ESI mode	Area (counts)	Mass List Match [d]	Compound Class	MS/MS Ions Confirmed [e]	mzCloud Scoring
	$C_{47}H_{71}NO_{13}$ [c]	857.4915	20.54	+	1.99×10^{5}	✓	AZA		
	$C_{47}H_{71}NO_{13}$	857.4911	16.34	+	2.86×10^{4}	✓	AZA	0	
	$C_{47}H_{71}NO_{13}$	857.4915	20.77	+	2.98×10^{5}	✓	AZA	2	61.4
AZA9 isomer [a]	$C_{47}H_{71}NO_{13}$	857.4921	21.98	+	1.97×10^{6}	✓	AZA	10	83.1
AZA9 isomer [a]	$C_{47}H_{71}NO_{13}$	857.4929	16.91	+	2.51×10^{5}	✓	AZA	4	69.1
AZA9 [a]	$C_{47}H_{71}NO_{13}$	857.4933	17.34	+	2.53×10^{6}	✓	AZA	10	86.6
AZA7 [a]	$C_{47}H_{71}NO_{13}$	857.4933	17.86	+	2.93×10^{6}	✓	AZA	9	84.5
AZA8 [a]	$C_{47}H_{71}NO_{13}$	857.4933	18.24	+	4.55×10^{6}	✓	AZA	11	85.7
[a]	$C_{47}H_{71}NO_{13}$ [c]	857.4933	18.07	+	6.14×10^{5}	✓	AZA	5	76.7
AZA10 [a]	$C_{47}H_{71}NO_{13}$	857.4933	18.40	+	6.68×10^{5}	✓	AZA	10	88.2
AZA13 [a]	$C_{46}H_{69}NO_{14}$	859.4723	15.12	+	4.00×10^{5}	✓	AZA	4	
	$C_{46}H_{69}NO_{14}$ [b]	859.4726	13.63	+	3.41×10^{4}	✓	AZA	0	
AZA2 methyl ester	$C_{49}H_{75}NO_{12}$	869.5300	28.74	+	3.43×10^{5}	✓	AZA	3	
AZA2 methyl ester	$C_{49}H_{75}NO_{12}$	869.5302	25.47	+	6.25×10^{4}	✓	AZA	0	
[a]	$C_{47}H_{69}NO_{14}$	871.4729	14.84	+	1.20×10^{5}	✓	AZA	1	
[a]	$C_{47}H_{69}NO_{14}$	871.4725	15.81	+	7.09×104	✓	AZA	0	
AZA11 [a]	$C_{48}H_{73}NO_{13}$ [b]	871.5091	18.61	+	2.50×10^{5}	✓	AZA	1	
AZA12 [a]	$C_{48}H_{73}NO_{13}$ [c]	871.5110	19.07	+	1.14×10^{5}	✓	AZA	1	
AZA15 [a]	$C_{47}H_{71}NO_{14}$	873.4870	16.30	+	2.33×10^{5}	✓	AZA	2	
AZA14 [a]	$C_{47}H_{71}NO_{14}$ [b]	873.4889	15.62	+	6.10×10^{5}	✓	AZA	7	
	$C_{47}H_{71}NO_{14}$	873.4889	15.71	+	3.51×10^{5}	✓	AZA	3	
OA/DTX2 isomer [a]	$C_{44}H_{68}O_{13}$	804.4663	15.24	+	2.85×10^{4}	✓	OA	0	
				-	1.38×10^{5}	✓	OA	3	
19-*epi*-OA [a]	$C_{44}H_{68}O_{13}$ [b]	804.4663	14.95	+	4.42×10^{3}	✓	OA	0	
				-	7.65×10^{4}	✓	OA	2	
OA [a]	$C_{44}H_{68}O_{13}$	804.4663	15.88	+	2.04×10^{5}	✓	OA	0	
				-	3.64×10^{6}	✓	OA	8	
OA/DTX2 isomer [a]	$C_{44}H_{68}O_{13}$	804.4663	14.95	-	7.65×10^{4}	✓	OA	2	

Tentative ID	Formula	neutral exact mass	RT (min)	ESI mode	Area (counts)	Mass List Match [d]	Compound Class	MS/MS Ions Confirmed [e]	mzCloud Scoring
DTX2 [a]	$C_{44}H_{68}O_{13}$	804.4663	16.50	+	1.23×10^{7}	✓	OA	3	
				-	1.19×10^{7}	✓	OA	8	
OA/DTX2 isomer [a]	$C_{44}H_{68}O_{13}$	804.4663	17.03	-	2.78×10^{5}	✓	OA	5	
DTX1 [a]	$C_{45}H_{70}O_{13}$	818.4830	18.00	+	1.84×10^{6}	✓	OA	0	
				-	3.55×10^{6}	✓	OA	8	
19-*epi*-DTX1 [a]	$C_{45}H_{70}O_{13}$	818.4826	17.22	-	5.62×10^{4}	✓	OA	0	
OA 24-*O*-β-D-glucoside [a]	$C_{50}H_{78}O_{18}$	966.5203	12.10	-	1.01×10^{6}		OA	7	
DTX2 24-*O*-β-D-glucoside [a]	$C_{50}H_{78}O_{18}$ [b]	966.5203	12.41	-	7.46×10^{5}		OA	6	
DTX1 24-*O*-β-D-glucoside [a]	$C_{51}H_{80}O_{18}$ [b]	980.5359	13.84	-	4.58×10^{4}		OA	5	
7-*O*-acyl OA/DTX2 (12:0)	$C_{56}H_{90}O_{14}$	986.6302	25.31	-	3.65×10^{3}	✓	OA	0	
7-*O*-acyl OA/DTX2 (12:0)	$C_{56}H_{90}O_{14}$	986.6330	25.08	-	4.09×10^{3}	✓	OA	0	
7-*O*-acyl OA/DTX2 (14:0) [a]	$C_{58}H_{94}O_{14}$	1014.6637	26.29	-	2.69×10^{4}	✓	OA	0	
7-*O*-acyl OA/DTX2 (14:0) [a]	$C_{58}H_{94}O_{14}$	1014.6661	27.31	-	1.03×10^{6}	✓	OA	10	
				+	3.62×10^{5}	✓	OA	0	
7-*O*-acyl OA/DTX2 (14:0) [a]	$C_{58}H_{94}O_{14}$	1014.6661	27.02	-	6.06×10^{5}	✓	OA	6	
				+	4.54×10^{5}	✓	OA	0	
7-*O*-acyl OA/DTX2 (14:0) [a]	$C_{58}H_{94}O_{14}$	1014.6666	26.73	-	3.83×10^{4}	✓	OA	0	
7-*O*-acyl OA/DTX2 (14:0) [a]	$C_{58}H_{94}O_{14}$	1014.6661	27.56	-	2.72×10^{4}	✓	OA	0	
7-*O*-acyl OA/DTX2 (14:0) [a]	$C_{58}H_{94}O_{14}$	1014.6661	25.93	-	1.12×10^{4}	✓	OA	0	
7-*O*-acyl OA/DTX2 (15:0)	$C_{59}H_{96}O_{14}$	1028.6803	27.86	-	3.93×10^{4}	✓	OA	0	
7-*O*-acyl OA/DTX2 (15:0)	$C_{59}H_{96}O_{14}$	1028.6805	28.29	-	2.67×10^{5}	✓	OA	0	
				+	4.62×10^{4}	✓	OA	0	
7-*O*-acyl OA/DTX2 (15:0)	$C_{59}H_{96}O_{14}$	1028.6805	28.77	-	4.86×10^{4}	✓	OA	0	
7-*O*-acyl OA/DTX2 (15:0)	$C_{59}H_{96}O_{14}$	1028.6805	28.63	-	3.86×10^{4}	✓	OA	0	
7-*O*-acyl OA/DTX2 (16:4)	$C_{60}H_{90}O_{14}$	1034.6335	23.90	-	4.00×10^{4}	✓	OA	0	
7-*O*-acyl OA/DTX2 (16:4)	$C_{60}H_{90}O_{14}$	1034.6341	24.09	-	1.85×10^{4}	✓	OA	0	
7-*O*-acyl OA/DTX2 (16:1) [a]	$C_{60}H_{96}O_{14}$	1040.6810	27.12	-	6.05×10^{5}	✓	OA	8	
				+	3.23×10^{5}	✓	OA	0	

Tentative ID	Formula	neutral exact mass	RT (min)	ESI mode	Area (counts)	Mass List Match [d]	Compound Class	MS/MS Ions Confirmed [e]	mzCloud Scoring
7-*O*-acyl OA/DTX2 (16:1) [a]	$C_{60}H_{96}O_{14}$	1040.6810	27.42	-	3.82×10^{6}	✓	OA	9	
				+	7.08×10^{5}	✓	OA	0	
7-*O*-acyl OA/DTX2 (16:1) [a]	$C_{60}H_{96}O_{14}$	1040.6810	27.59	-	6.58×10^{5}	✓	OA	7	
7-*O*-acyl OA/DTX2 (16:1) [a]	$C_{60}H_{96}O_{14}$	1040.6810	27.90	+	1.01×10^{5}	✓	OA	0	
7-*O*-acyl OA/DTX2 (16:0) [a]	$C_{60}H_{98}O_{14}$	1042.6966	28.40	-	2.62×10^{5}	✓	OA	6	
7-*O*-acyl OA/DTX2 (16:0) [a]	$C_{60}H_{98}O_{14}$	1042.6966	28.07	-	2.16×10^{5}	✓	OA	3	
7-*O*-acyl OA/DTX2 (16:0) [a]	$C_{60}H_{98}O_{14}$	1042.6966	28.75	-	6.99×10^{4}	✓	OA	0	
				+	9.29×10^{4}	✓	OA	0	
7-*O*-acyl OA/DTX2 (16:0) [a]	$C_{60}H_{98}O_{14}$	1042.6966	29.32	-	8.45×10^{4}	✓	OA	0	
7-*O*-acyl OA/DTX2 (16:0) [a]	$C_{60}H_{98}O_{14}$	1042.6971	29.84	-	1.64×10^{6}	✓	OA	10	
				+	1.39×10^{6}	✓	OA	0	
7-*O*-acyl OA/DTX2 (16:0) [a]	$C_{60}H_{98}O_{14}$	1042.6971	30.29	-	9.36×10^{5}	✓	OA	9	
				+	1.12×10^{6}	✓	OA	1	
7-*O*-acyl OA/DTX2 (17:1)	$C_{61}H_{98}O_{14}$	1054.6944	29.32	-	9.02×10^{4}	✓	OA	0	
7-*O*-acyl OA/DTX2 (17:1)	$C_{61}H_{98}O_{14}$	1054.6959	28.38	-	1.57×10^{5}	✓	OA	0	
7-*O*-acyl OA/DTX2 (17:1)	$C_{61}H_{98}O_{14}$	1054.6983	28.76	-	9.52×10^{4}	✓	OA	0	
7-*O*-acyl OA/DTX2 (17:1)	$C_{61}H_{98}O_{14}$	1054.6983	28.96	-	1.10×10^{5}	✓	OA	0	
7-*O*-acyl OA/DTX2 (17:1)	$C_{61}H_{98}O_{14}$	1054.6983	29.15	-	3.13×10^{4}	✓	OA	0	
7-*O*-acyl OA/DTX2 (17:0)	$C_{61}H_{100}O_{14}$	1056.7120	31.17	-	9.70×10^{4}	✓	OA	1	
7-*O*-acyl OA/DTX2 (17:0)	$C_{61}H_{100}O_{14}$	1056.7120	31.74	-	1.63×10^{5}	✓	OA	2	
7-*O*-acyl OA/DTX2 (18:4) [a]	$C_{62}H_{94}O_{14}$	1062.6641	24.40	-	4.81×10^{3}	✓	OA	0	
7-*O*-acyl OA/DTX2 (18:4) [a]	$C_{62}H_{94}O_{14}$	1062.6646	24.80	-	2.77×10^{5}	✓	OA	8	
7-*O*-acyl OA/DTX2 (18:4) [a]	$C_{62}H_{94}O_{14}$	1062.6646	25.01	-	2.99×10^{5}	✓	OA	3	
				+	1.56×10^{5}	✓	OA	0	
7-*O*-acyl OA/DTX2 (18:3)	$C_{62}H_{96}O_{14}$	1064.6814	25.90	-	1.05×10^{5}	✓	OA	0	
7-*O*-acyl OA/DTX2 (18:3)	$C_{62}H_{96}O_{14}$	1064.6814	26.13	-	1.38×10^{5}	✓	OA	0	
7-*O*-acyl OA/DTX2 (18:3)	$C_{62}H_{96}O_{14}$	1064.6814	26.29	-	5.00×10^{4}	✓	OA	0	
7-*O*-acyl OA/DTX2 (18:2)	$C_{62}H_{98}O_{14}$	1066.6960	27.75	-	1.03×10^{5}	✓	OA	0	

Tentative ID	Formula	neutral exact mass	RT (min)	ESI mode	Area (counts)	Mass List Match [d]	Compound Class	MS/MS Ions Confirmed [e]	mzCloud Scoring
				+	1.22×10^5	✓	OA	0	
7-*O*-acyl OA/DTX2 (18:2)	$C_{62}H_{98}O_{14}$	1066.6927	28.18	-	2.37×10^4	✓	OA	0	
7-*O*-acyl OA/DTX2 (18:2)	$C_{62}H_{98}O_{14}$	1066.6960	27.44	-	6.42×10^5	✓	OA	9	
				+	4.01×10^4	✓	OA	0	
7-*O*-acyl OA/DTX2 (18:1)	$C_{62}H_{100}O_{14}$	1068.7100	30.73	-	7.52×10^4	✓	OA	0	
				+	1.39×10^5	✓	OA	0	
7-*O*-acyl OA/DTX2 (18:1)	$C_{62}H_{98}O_{14}$	1068.7126	31.19	-	7.31×10^4	✓	OA	9	
				+	4.53×10^4	✓	OA	0	
7-*O*-acyl OA/DTX2 (18:1)	$C_{62}H_{100}O_{14}$	1068.7126	29.94	-	3.13×10^5	✓	OA	5	
				+	3.93×10^4	✓	OA	0	
7-*O*-acyl OA/DTX2 (18:1)	$C_{62}H_{100}O_{14}$	1068.7126	30.35	-	1.94×10^5	✓	OA	2	
				+	5.19×10^4	✓	OA	0	
7-O-acyl OA/DTX2 (18:0)	C62H102O14	1070.7292	33.27	-	3.80×10^4	✓	OA	0	
7-*O*-acyl OA/DTX2 (18:0)	$C_{62}H_{102}O_{14}$	1070.7270	33.82	-	3.24×10^4	✓	OA	0	
				+	1.96×10^4	✓	OA	0	
7-*O*-acyl OA/DTX2 (18:0)	$C_{62}H_{102}O_{14}$	1070.7290	34.18	-	3.90×10^4	✓	OA	0	
				+	3.06×10^4	✓	OA	0	
7-*O*-acyl OA/DTX2 (18:0)	$C_{62}H_{102}O_{14}$	1070.7270	34.81	-	2.95×10^4	✓	OA	0	
				+	4.37×10^4	✓	OA	0	
7-*O*-acyl DTX1 (18:4) [a]	$C_{63}H_{96}O_{14}$	1076.6821	25.97	-	3.52×10^4	✓	OA	0	
7-*O*-acyl OA/DTX2 (20:5)	$C_{64}H_{96}O_{14}$	1088.6833	25.52	-	1.03×10^5	✓	OA	2	
7-*O*-acyl OA/DTX2 (22:6) [a]	$C_{66}H_{98}O_{14}$	1114.6977	25.86	-	4.46×10^4	✓	OA	0	
				+	1.13×10^4	✓	OA	0	
36R-PTX12 [a]	$C_{47}H_{68}O_{14}$	856.4619	18.16	+	3.28×10^5	✓	PTX	2	
PTX-i [a,g]	$C_{46}H_{73}NO_{14}$ [f]	863.5031	14.12	+	1.55×10^5		PTX	2	
PTX-i [a,g]	$C_{46}H_{73}NO_{14}$ [b,f]	863.5032	14.63	+	1.36×10^5		PTX	1	
PTX-i [a,g]	$C_{46}H_{73}NO_{14}$ [b,f]	863.5032	13.76	+	5.48×10^4		PTX	1	
	$C_{47}H_{73}NO_{15}$ [b]	874.4731	13.74	+	7.28×10^4	✓	PTX	0	

Tentative ID	Formula	neutral exact mass	RT (min)	ESI mode	Area (counts)	Mass List Match [d]	Compound Class	MS/MS Ions Confirmed [e]	mzCloud Scoring
	$C_{47}H_{73}NO_{15}$ [c]	874.4730	15.86	+	1.16×10^{4}	✓	PTX	0	
PTX2 isomer [a] (NH_4 adduct)	$C_{47}H_{73}NO_{14}$ [b]	875.5031	18.93	+	1.54×10^{5}		PTX	2	
PTX2 [a] (NH_4 adduct)	$C_{47}H_{73}NO_{14}$	875.5033	17.18	+	1.28×10^{6}		PTX	11	
PTX2sa isomer [a]	$C_{47}H_{72}O_{15}$	876.4886	15.31	+	1.65×10^{5}	✓	PTX	1	
				-	5.53×10^{4}	✓	PTX	0	
PTX2sa [a]	$C_{47}H_{72}O_{15}$	876.4886	15.63	+	5.41×10^{6}	✓	PTX	11	
				-	2.21×10^{5}	✓	PTX	2	
PTX2sa isomer [a]	$C_{47}H_{72}O_{15}$	876.4886	15.88	+	1.26×10^{6}	✓	PTX	11	
				-	1.63×10^{5}	✓	PTX	2	
PTX2sa isomer [a]	$C_{47}H_{72}O_{15}$	876.4876	16.04	+	4.74×10^{5}		PTX	3	
				-	2.15×10^{5}	✓	PTX	2	
PTX2sa isomer [a]	$C_{47}H_{72}O_{15}$	876.4865	16.31	+	9.38×10^{4}		PTX	2	
				-	8.19×10^{3}	✓	PTX	0	
7-*epi*-PTX2sa [a]	$C_{47}H_{75}NO_{15}$ [f]	893.5138	16.66	+	5.26×10^{6}		PTX	11	
				-	1.09×10^{6}	✓	PTX	3	
PTX2sa isomer [a]	$C_{47}H_{75}NO_{15}$ [f]	893.5138	16.89	+	7.15×10^{5}		PTX	10	
				-	1.19×10^{5}	✓	PTX	0	
Sulfonated PTX-i [g]	$C_{46}H_{70}O_{17}S$ [b]	926.4343	13.59	-	8.92×10^{4}		PTX	1	
Sulfonated PTX-i [g]	$C_{46}H_{70}O_{17}S$	926.4345	14.25	-	1.60×10^{5}		PTX	1	
Sulfonated PTX-i [a, g]	$C_{46}H_{70}O_{17}S$	926.4345	14.46	-	4.23×10^{5}		PTX	1	
Sulfonated PTX-i seco acid [g]	$C_{46}H_{72}O_{18}S$ [b]	944.4456	13.15	-	2.03×10^{5}		PTX	3	
Sulfonated PTX-i seco acid [g]	$C_{46}H_{72}O_{18}S$	944.4456	13.25	-	1.35×10^{5}		PTX	1	
	$C_{62}H_{100}O_{15}$	1084.7065	26.63	+	4.61×10^{5}		PTX	1	
	$C_{62}H_{100}O_{15}$	1084.7074	31.06	+	7.21×10^{5}		PTX	1	
O-acyl PTX2sa (14:0) [a]	$C_{61}H_{98}O_{16}$	1086.6866	23.76	+	1.28×10^{6}		PTX	4	
O-acyl PTX2sa (14:0) [a]	$C_{61}H_{98}O_{16}$	1086.6859	24.21	+	3.51×10^{6}		PTX	10	
				-	1.47×10^{5}		PTX	3	
O-acyl PTX2sa (14:0) [a]	$C_{61}H_{98}O_{16}$	1086.6862	24.48	+	3.69×10^{5}		PTX	2	

Tentative ID	Formula	neutral exact mass	RT (min)	ESI mode	Area (counts)	Mass List Match [d]	Compound Class	MS/MS Ions Confirmed [e]	mzCloud Scoring
O-acyl PTX2sa (14:0) [a]	$C_{61}H_{98}O_{16}$ [b]	1086.6862	25.05	+	1.25×10^5		PTX	5	
O-acyl PTX2sa (14:0) [a]	$C_{61}H_{98}O_{16}$	1086.6863	25.24	+	2.93×10^6		PTX	10	
				-	1.09×10^5		PTX	2	
O-acyl PTX2sa (14:0) [a]	$C_{61}H_{98}O_{16}$ [b]	1086.6864	25.44	+	1.42×10^6		PTX	12	
O-acyl PTX2sa (14:0) [a]	$C_{61}H_{98}O_{16}$ [b]	1086.6864	25.57	+	4.94×10^6		PTX	12	
			25.29	-	3.36×10^5		PTX	2	
O-acyl PTX2sa (15:1)	[c]	1098.6862	24.91	+	4.72×10^5		PTX	1	
O-acyl PTX2sa (14:0) [a]	$C_{61}H_{101}NO_{16}$ [b,f]	1103.7132	24.73	+	2.29×10^5		PTX	1	
O-acyl PTX2sa (14:0) [a]	$C_{61}H_{101}NO_{16}$ [f]	1103.7132	24.14	+	3.87×10^5		PTX	7	
O-acyl PTX2sa (16:1) [a]	$C_{63}H_{100}O_{16}$ [c]	1112.7021	26.14	+	7.06×10^5		PTX	3	
O-acyl PTX2sa (16:1) [a]	$C_{63}H_{100}O_{16}$ [b]	1112.7021	24.66	+	7.62×10^5		PTX	3	
O-acyl PTX2sa (16:1) [a]	$C_{63}H_{100}O_{16}$ [b]	1112.7022	24.38	+	2.45×10^6		PTX	8	
O-acyl PTX2sa (16:1) [a]	$C_{63}H_{100}O_{16}$ [c]	1112.7022	24.87	+	1.50×10^5		PTX	2	
O-acyl PTX2sa (16:1) [a]	$C_{63}H_{100}O_{16}$ [b]	1112.7022	24.91	+	9.13×10^5		PTX	3	
O-acyl PTX2sa (16:1) [a]	$C_{63}H_{100}O_{16}$ [b]	1112.7022	24.17	+	1.04×10^5		PTX	1	
O-acyl PTX2sa (16:0) [a]	$C_{63}H_{102}O_{16}$	1114.7179	25.17	+	1.42×10^6		PTX	9	
O-acyl PTX2sa (16:0) [a]	$C_{63}H_{102}O_{16}$ [b]	1114.7186	25.60	-	2.07×10^5		PTX	3	
O-acyl PTX2sa (16:0) [a]	$C_{63}H_{102}O_{16}$	1114.7183	25.70	+	6.85×10^6		PTX	12	
				-	3.73×10^5		PTX	3	
O-acyl PTX2sa (16:0) [a]	$C_{63}H_{102}O_{16}$	1114.7179	26.41	+	2.14×10^6		PTX	9	
				-	1.36×10^5		PTX	3	
O-acyl PTX2sa (16:0) [a]	$C_{63}H_{102}O_{16}$	1114.7183	26.60	+	2.32×10^5		PTX	9	
O-acyl PTX2sa (16:0) [a]	$C_{63}H_{102}O_{16}$	1114.7181	27.16	+	6.69×10^6		PTX	11	
				-	5.99×10^5		PTX	4	
O-acyl PTX2sa (16:0) [a]	$C_{63}H_{102}O_{16}$	1114.7177	27.37	-	2.67×10^5		PTX	3	
O-acyl PTX2sa (16:0) [a]	$C_{63}H_{102}O_{16}$	1114.7181	27.63	+	1.51×10^7		PTX	13	
				-	5.86×10^5		PTX	4	
O-acyl PTX2sa (15:1)	$C_{62}H_{101}NO_{16}$ [b,f]	1115.7123	25.23	+	5.58×10^5		PTX	5	

Tentative ID	Formula	neutral exact mass	RT (min)	ESI mode	Area (counts)	Mass List Match [d]	Compound Class	MS/MS Ions Confirmed [e]	mzCloud Scoring
O-acyl PTX2sa (15:1)	$C_{62}H_{101}NO_{16}$ [b,f]	1115.7133	24.00	+	1.98×10^5		PTX	4	
	$C_{63}H_{104}O_{16}$	1116.7331	27.90	+	6.85×10^5		PTX	6	
O-acyl PTX2sa (15:0)	$C_{62}H_{103}NO_{16}$ [c,f]	1117.7275	24.42	+	1.24×10^5		PTX	1	
O-acyl PTX2sa (15:0)	$C_{62}H_{103}NO_{16}$ [b,f]	1117.7287	26.12	+	5.09×10^5		PTX	6	
O-acyl PTX2sa (15:0)	$C_{62}H_{103}NO_{16}$ [b,f]	1117.7287	26.23	+	2.67×10^5		PTX	6	
O-acyl PTX2sa (15:0)	$C_{62}H_{103}NO_{16}$ [f]	1117.7287	26.51	+	8.04×10^5		PTX	6	
O-acyl PTX2sa (17:1)	$C_{64}H_{102}O_{16}$ [c]	1126.7172	26.69	+	1.32×10^6		PTX	7	
O-acyl PTX2sa (17:1)	$C_{64}H_{102}O_{16}$ [b]	1126.7173	25.05	+	3.82×10^5		PTX	2	
O-acyl PTX2sa (17:0)	$C_{64}H_{104}O_{16}$	1128.7331	26.37	+	4.22×10^5		PTX	2	
O-acyl PTX2sa (17:0)	$C_{64}H_{104}O_{16}$	1128.7330	26.64	+	7.09×10^5		PTX	5	
O-acyl PTX2sa (17:0)	$C_{64}H_{104}O_{16}$	1128.7330	28.07	+	4.69×10^5		PTX	3	
O-acyl PTX2sa (17:0)	$C_{64}H_{104}O_{16}$	1128.7330	29.04	+	6.96×10^5		PTX	3	
O-acyl PTX2sa (16:1) [a]	[c]	1129.7288	25.41	+	1.44×10^6		PTX	8	
O-acyl PTX2sa (16:1) [a]	[c]	1129.7288	25.57	+	4.32×10^5		PTX	7	
[a]	[c]	1130.7124	25.37	+	1.79×10^5		PTX	1	
O-acyl PTX2sa (16:0) [a]	$C_{63}H_{105}NO_{16}$ [f]	1131.7449	25.59	+	2.09×10^6		PTX	11	
O-acyl PTX2sa (16:0) [a]	$C_{63}H_{105}NO_{16}$ [f]	1131.7450	26.02	+	5.65×10^5		PTX	8	
O-acyl PTX2sa (16:0) [a]	$C_{63}H_{105}NO_{16}$ [b,f]	1131.7449	27.40	+	2.79×10^6		PTX	11	
O-acyl PTX2sa (16:0) [a]	$C_{63}H_{105}NO_{16}$ [b,f]	1131.7449	28.36	+	2.58×10^5		PTX	5	
O-acyl PTX2sa (18:4) [a]	$C_{65}H_{98}O_{16}$ [b]	1134.6863	23.16	+	5.05×10^5		PTX	4	
O-acyl PTX2sa (18:4) [a]	$C_{65}H_{98}O_{16}$ [b]	1134.6864	23.48	+	4.79×10^5		PTX	1	
O-acyl PTX2sa (18:4) [a]	$C_{65}H_{98}O_{16}$ [b]	1134.6864	23.97	+	5.82×10^5		PTX	2	
O-acyl PTX2sa (18:4) [a]	$C_{65}H_{98}O_{16}$ [b]	1134.6865	24.09	+	7.78×10^5		PTX	7	
O-acyl PTX2sa (18:1)	$C_{65}H_{104}O_{16}$	1140.7324	25.82	+	9.17×10^5		PTX	6	
O-acyl PTX2sa (18:1)	$C_{65}H_{104}O_{16}$ [c]	1140.7327	26.26	+	1.95×10^5		PTX	1	
O-acyl PTX2sa (18:1)	$C_{65}H_{104}O_{16}$ [c]	1140.7329	27.31	+	3.77×10^5		PTX	4	
O-acyl PTX2sa (18:1)	$C_{65}H_{104}O_{16}$ [c]	1140.7324	28.46	+	6.89×10^5		PTX	3	
O-acyl PTX2sa (18:0)	$C_{65}H_{106}O_{16}$ [c]	1142.7487	29.43	+	3.10×10^5		PTX	2	

Tentative ID	Formula	neutral exact mass	RT (min)	ESI mode	Area (counts)	Mass List Match [d]	Compound Class	MS/MS Ions Confirmed [e]	mzCloud Scoring
O-acyl PTX2sa (18:0)	$C_{65}H_{106}O_{16}$	1142.7486	30.78	+	9.41×10^5		PTX	5	
O-acyl PTX2sa (17:1)	$C_{64}H_{105}NO_{16}$ [f]	1143.7438	25.39	+	2.60×10^5		PTX	1	
O-acyl PTX2sa (17:1)	$C_{64}H_{105}NO_{16}$ [c]	1143.7438	27.17	+	5.05×10^5		PTX	6	
O-acyl PTX2sa (17:0)	$C_{64}H_{107}NO_{16,f}$	1145.7595	28.60	+	1.38×10^6		PTX	9	
O-acyl PTX2sa (18:2)	$C_{65}H_{105}NO_{16}$ [c,f]	1155.7444	26.04	+	1.92×10^5		PTX	1	
O-acyl PTX2sa (18:1)	$C_{65}H_{107}NO_{16}$ [c,f]	1157.7593	27.79	+	2.26×10^6		PTX	9	
O-acyl PTX2sa (18:1)	$C_{65}H_{107}NO_{16}$ [c,f]	1157.7593	28.13	+	4.58×10^5		PTX	4	
O-acyl PTX2sa (18:1)	$C_{65}H_{107}NO_{16}$ [c,f]	1157.7593	27.53	+	5.75×10^5		PTX	1	
O-acyl PTX2sa (18:1)	$C_{65}H_{107}NO_{16}$ [c,f]	1157.7593	26.16	+	2.74×10^4		PTX	1	
O-acyl PTX2sa (18:1)	$C_{65}H_{107}NO_{16}$ [f]	1157.7593	26.53	+	1.86×10^5		PTX	2	
O-acyl PTX2sa (18:0)	$C_{65}H_{109}NO_{16}$ [f]	1159.7715	27.36	+	4.95×10^5		PTX	6	
O-acyl PTX2sa (18:0)	$C_{65}H_{109}NO_{16}$ [b,f]	1159.7730	28.35	+	1.51×10^5		PTX	1	
O-acyl PTX2sa (18:0)	$C_{65}H_{109}NO_{16}$ [f]	1159.7752	29.78	+	1.54×10^5		PTX	1	
O-acyl PTX2sa (18:0)	$C_{65}H_{109}NO_{16}$ [f]	1159.7752	30.09	+	1.08×10^6		PTX	7	
O-acyl PTX2sa (18:0)	$C_{65}H_{109}NO_{16}$ [c]	1159.7752	30.54	+	1.70×10^5		PTX	5	
O-acyl PTX2sa (20:5) [a]	$C_{67}H_{100}O_{16}$ [b]	1160.7009	23.49	+	1.54×10^5		PTX	1	
O-acyl PTX2sa (20:5) [a]	$C_{67}H_{100}O_{16}$ [b]	1160.7009	24.23	+	5.81×10^5		PTX	4	
O-acyl PTX2sa (20:5) [a]	$C_{67}H_{100}O_{16}$ [b]	1160.7017	24.52	+	7.04×10^5		PTX	4	
Sulfonated PTX-i ester (16:0) [a]	$C_{62}H_{100}O_{18}S$	1164.6638	21.82	-	3.07×10^5		PTX	6	
Sulfonated PTX-i ester (16:0) [a, g]	$C_{62}H_{100}O_{18}S$ [b]	1164.6648	21.45	-	5.80×10^5		PTX	5	
Sulfonated PTX-i ester (16:0) [a, g]	$C_{62}H_{100}O_{18}S$ [b]	1164.6648	22.34	-	1.59×10^6		PTX	6	
Sulfonated PTX-i ester (16:0) [a, g]	$C_{62}H_{100}O_{18}S$ [b]	1164.6648	22.65	-	3.95×10^5		PTX	7	
O-acyl-PTX2sa (20:3)	$C_{67}H_{104}O_{16}$ [c]	1164.7344	26.67	+	2.25×10^5		PTX	2	
O-acyl-PTX2sa (20:2)	$C_{67}H_{106}O_{16}$ [b]	1166.7482	28.10	+	7.98×10^5		PTX	4	
O-acyl-PTX2sa (20:2)	$C_{67}H_{106}O_{16}$ [b]	1166.7482	28.69	+	8.67×10^5		PTX	6	
O-acyl PTX2sa (20:1)	$C_{67}H_{108}O_{16}$ [c]	1168.7065	24.98	+	1.17×10^5		PTX	1	
O-acyl PTX2sa (20:5) [a]	$C_{67}H_{103}NO_{16}$ [b,f]	1177.7289	23.49	+	1.93×10^5		PTX	1	
O-acyl PTX2sa (20:3)	$C_{67}H_{107}NO_{16}$ [f]	1181.7592	25.07	+	9.60×10^4		PTX	2	

Tentative ID	Formula	neutral exact mass	RT (min)	ESI mode	Area (counts)	Mass List Match [d]	Compound Class	MS/MS Ions Confirmed [e]	mzCloud Scoring
O-acyl PTX2sa (20:2)	$C_{67}H_{109}NO_{16}$ [f]	1183.7741	26.42	+	5.14×10^5		PTX	5	
O-acyl PTX2sa (20:1)	$C_{67}H_{111}NO_{16}$ [f]	1185.7898	27.85	+	3.55×10^5		PTX	3	
O-acyl PTX2sa (20:1)	$C_{67}H_{111}NO_{16}$ [f]	1185.7898	28.16	+	4.33×10^5		PTX	2	
O-acyl PTX2sa (20:1)	$C_{67}H_{111}NO_{16}$ [b,f]	1185.7902	30.85	+	5.16×10^5		PTX	4	
O-acyl PTX2sa (22:6) [a]	$C_{69}H_{102}O_{16}$	1186.7167	24.82	+	1.59×10^5		PTX	2	
O-acyl PTX2sa (22:6) [a]	$C_{69}H_{102}O_{16}$ [b]	1186.7167	24.70	+	1.15×10^6		PTX	6	
O-acyl PTX2sa (22:6) [a]	$C_{69}H_{102}O_{16}$	1186.7172	23.91	+	2.48×10^6		PTX	8	
O-acyl PTX2sa (22:6) [a]	$C_{69}H_{102}O_{16}$ [b]	1186.7173	24.25	+	2.14×10^5		PTX	2	
O-acyl PTX2sa (22:6) [a]	$C_{69}H_{102}O_{16}$ [b]	1186.7183	25.00	-	1.20×10^5		PTX	2	
[a]	$C_{34}H_{49}NO_4$	535.3664	11.44	+	1.44×10^5		SPX/PnTX	2	
[a]		597.4136	10.86	+	1.10×10^4		SPX/PnTX	1	
[a]	$C_{42}H_{61}NO_7$ [c]	691.4448	11.50	+	3.66×10^4	✓	SPX/PnTX	2	
13-desmethyl SPX C [a]	$C_{42}H_{61}NO_7$	691.4448	11.38	+	8.08×10^6	✓	SPX/PnTX	9	
13-desmethyl SPX D [a]	$C_{42}H_{63}NO_7$	693.4607	11.52	+	2.78×10^5	✓	SPX/PnTX	6	
PnTX-G [a]	$C_{42}H_{63}NO_7$	693.4615	12.64	+	8.87×10^5	✓	SPX/PnTX	7	
SPX C[a]	$C_{43}H_{63}NO_7$	705.4607	11.38	+	2.18×10^5	✓	SPX/PnTX	4	
[a]	$C_{43}H_{63}NO_7$	705.4611	13.45	+	6.07×10^4	✓	SPX/PnTX	2	
SPX "C3" [a]	$C_{43}H_{63}NO_7$	705.4617	12.28	+	4.15×10^5	✓	SPX/PnTX	7	
	$C_{43}H_{63}NO_7$	705.4620	11.82	+	6.03×10^4	✓	SPX/PnTX	1	
20-methyl SPX G [a]	$C_{43}H_{63}NO_7$	705.4620	11.92	+	1.23×10^5	✓	SPX/PnTX	5	
	$C_{42}H_{61}NO_8$	707.4395	10.23	+	2.06×10^5		SPX/PnTX	4	
	$C_{42}H_{61}NO_8$	707.4399	11.09	+	8.92×10^4		SPX/PnTX	3	
27-hydroxy-13-desmethyl SPX C [a]	$C_{42}H_{61}NO_8$	707.4399	11.25	+	3.64×10^6		SPX/PnTX	12	
SPX D [a]	$C_{43}H_{65}NO_7$	707.4750	11.71	+	6.19×10^3	✓	SPX/PnTX	0	
SPX "D3" [a]	$C_{43}H_{65}NO_7$	707.4772	12.60	+	5.75×10^4	✓	SPX/PnTX	2	
20-methyl SPX G (C2-C3 saturated) [a]	$C_{43}H_{65}NO_7$	707.4781	12.07	+	8.85×10^3	✓	SPX/PnTX	0	
[a]	$C_{42}H_{63}NO_8$	709.4562	10.77	+	3.21×10^4	✓	SPX/PnTX	1	
	$C_{42}H_{63}NO_8$	709.4572	12.66	+	2.36×10^4	✓	SPX/PnTX	0	

Tentative ID	Formula	neutral exact mass	RT (min)	ESI mode	Area (counts)	Mass List Match [d]	Compound Class	MS/MS Ions Confirmed [e]	mzCloud Scoring
	$C_{43}H_{63}NO_8$	721.4539	11.39	+	2.42×10^5		SPX/PnTX	7	
[a]	$C_{34}H_{49}NO_4$	535.3664	11.44	+	1.44×10^5		SPX/PnTX	2	
[a]	$C_{34}H_{49}NO_4$	535.3664	11.87	+	1.29×10^5		SPX/PnTX	1	
[a]	$C_{36}H_{55}NO_6$	597.4019	11.48	+	4.16×10^5		SPX/PnTX /AZA [h]	3	
[a]	$C_{36}H_{55}NO_6$	597.4019	11.59	+	2.46×10^5		SPX/PnTX /AZA [h]	4	
[a]	$C_{38}H_{53}NO_5$	603.3920	15.39	+	2.50×10^6		SPX/PnTX /AZA [h]	4	
	$C_{42}H_{61}NO_9$	723.4358	11.95	+	6.92×10^5		SPX/PnTX /AZA [h]	8	
	$C_{55}H_{84}O_{21}S$[c]	555.2952	13.16	-	1.17×10^4		YTX	2	
Desulfoyessotoxin [a]	$C_{55}H_{82}O_{18}S$	1062.5236	16.54	-	1.62×10^5	✓	YTX	5	
Desulfohydroxyyessotoxin [a]	$C_{55}H_{82}O_{19}S$[b]	1078.5167	14.25	-	1.44×10^5		YTX	4	
Desulfocarboxyyessotoxin [a]	$C_{55}H_{82}O_{20}S$	1094.5126	14.52	-	5.77×10^5		YTX	5	
Desulfocarboxyhydroxyyessotoxin [a]	$C_{55}H_{82}O_{21}S$[b]	1110.5080	13.62	-	1.01×10^5		YTX	2	
Desulfocarboxyhydroxyyessotoxin [a]	$C_{55}H_{82}O_{21}S$	1110.5085	13.18	-	2.44×10^5		YTX	2	
Desulfocarboxyhydroxyyessotoxin [a]	$C_{55}H_{82}O_{21}S$[b]	1110.5085	13.27	-	1.48×10^5		YTX	1	
Desulfocarboxyhydroxyyessotoxin [a]	$C_{55}H_{82}O_{21}S$[b]	1110.5085	13.54	-	3.67×10^4		YTX	1	
Yessotoxin [a]	$C_{55}H_{82}O_{21}S_2$	1142.4790	14.76	-	9.04×10^5	✓	YTX	6	
45-hydroxyyessotoxin [a]	$C_{55}H_{82}O_{22}S_2$	1158.4755	13.00	-	1.82×10^5	✓	YTX	5	
Carboxyyessotoxin [a]	$C_{55}H_{82}O_{23}S_2$	1174.4702	13.24	-	8.17×10^5	✓	YTX	6	
Dihydroxyyessotoxin [a]	$C_{55}H_{84}O_{23}S_2$	1176.4847	12.10	-	2.75×10^4	✓	YTX	0	
Carboxyhydroxyyessotoxin [a]	$C_{55}H_{82}O_{24}S_2$	1190.4646	12.17	-	5.98×10^5	✓	YTX	2	
Carboxyhydroxyyessotoxin [a]	$C_{55}H_{82}O_{24}S_2$[b]	1190.4647	11.92	-	8.78×10^4	✓	YTX	2	
Carboxyhydroxyyessotoxin [a]	$C_{55}H_{82}O_{24}S_2$[b]	1190.4650	12.58	-	1.25×10^5	✓	YTX	4	
Carboxyhydroxyyessotoxin [a]	$C_{55}H_{82}O_{24}S_2$[b]	1190.4652	12.76	-	1.22×10^4	✓	YTX	0	
Carboxyhydroxyyessotoxin [a]	$C_{55}H_{82}O_{24}S_2$[b]	1190.4652	12.07	-	8.63×10^3	✓	YTX	0	
[a]	$C_{55}H_{84}O_{24}S_2$	1192.4736	11.54	-	1.08×10^4	✓	YTX	0	

[a] toxin analogues reported in CRM-FDMT1[1]

[b] formula predicted by Compound Discoverer, but not automatically selected as the top candidate
[c] formula not predicted by Compound Discoverer
[d] Compound Discoverer mass list match using combined mass lists from Miles [2] and Gerssen [3].
[e] includes both neutral losses and product ions from Table 1
[f] formula predicted in Compound Discoverer includes additional ammonia from ammonium adduct when no $[M+H]^+$ was observed
[g] tentative ID given as previously described [4] [h] MS/MS spectra contained product ions from multiple compound classes.

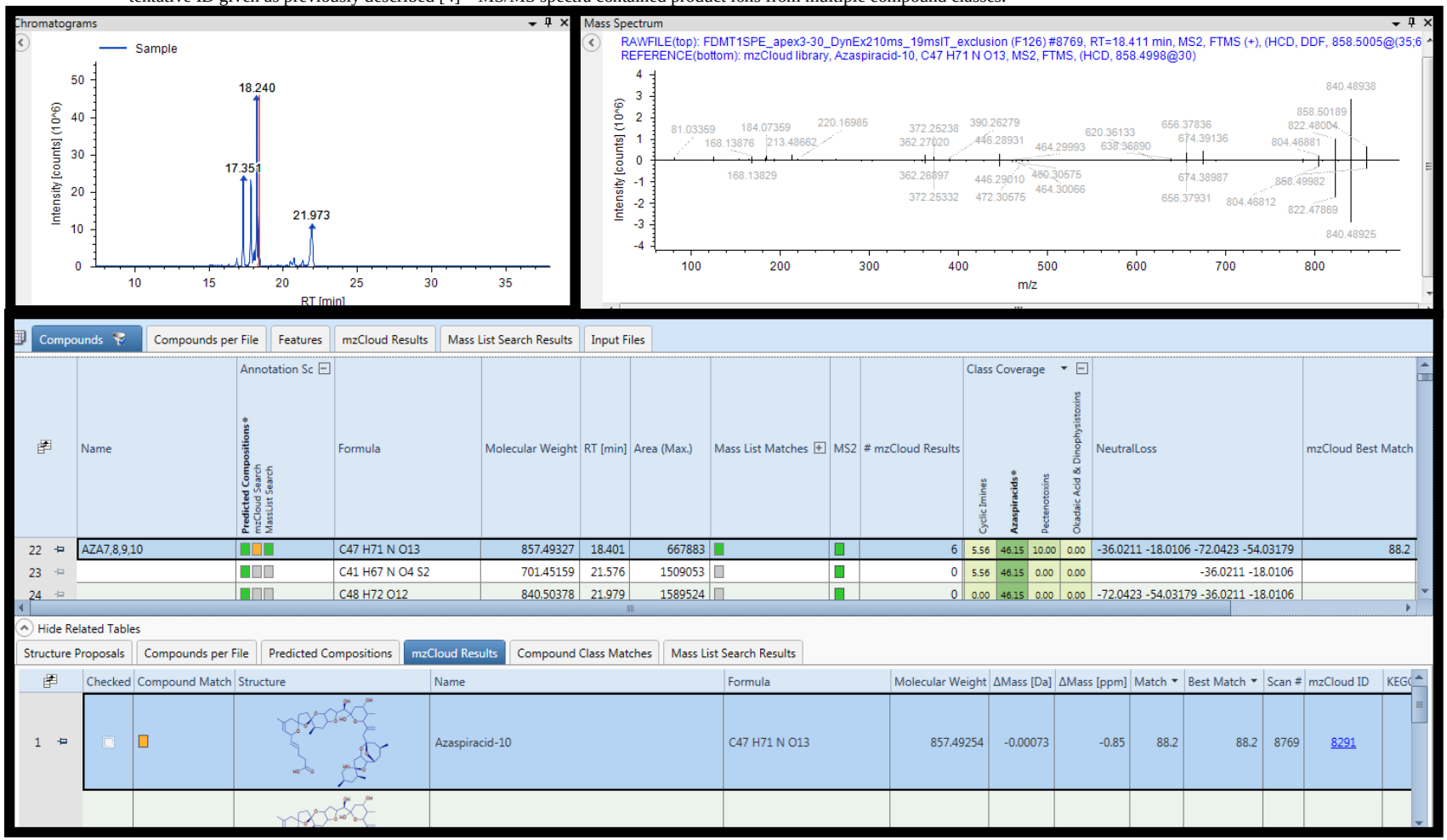

Fig. S2. mzCloud search for AZA10 in CRM-FDMT1 showing the sample chromatogram (top left) and comparison of the experimental MS/MS spectrum to the mzCloud database entry (top right) along with corresponding information for the database entry (bottom pane, row 22).

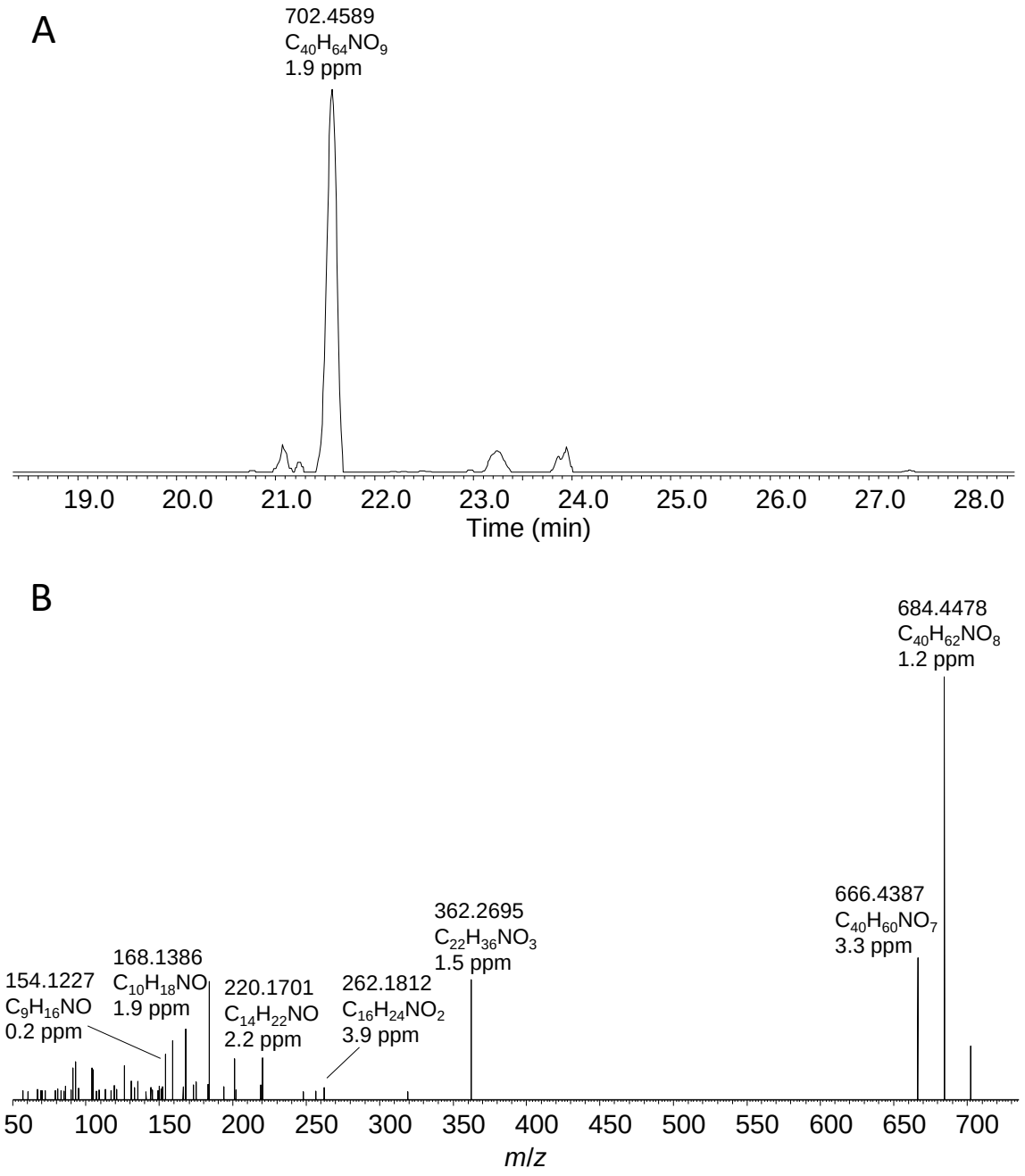

Fig. S3. Extracted ion chromatogram (±5 ppm) from positive mode full-scan data showing an AZA-like compound (A) and associated MS/MS spectrum (B) showing several product ions commonly observed among AZAs (Table 1) that indicate the structure from C-24 onward shown in Figure 1 is preserved [5], with significant structural differences to the left-hand side of the AZA structure.

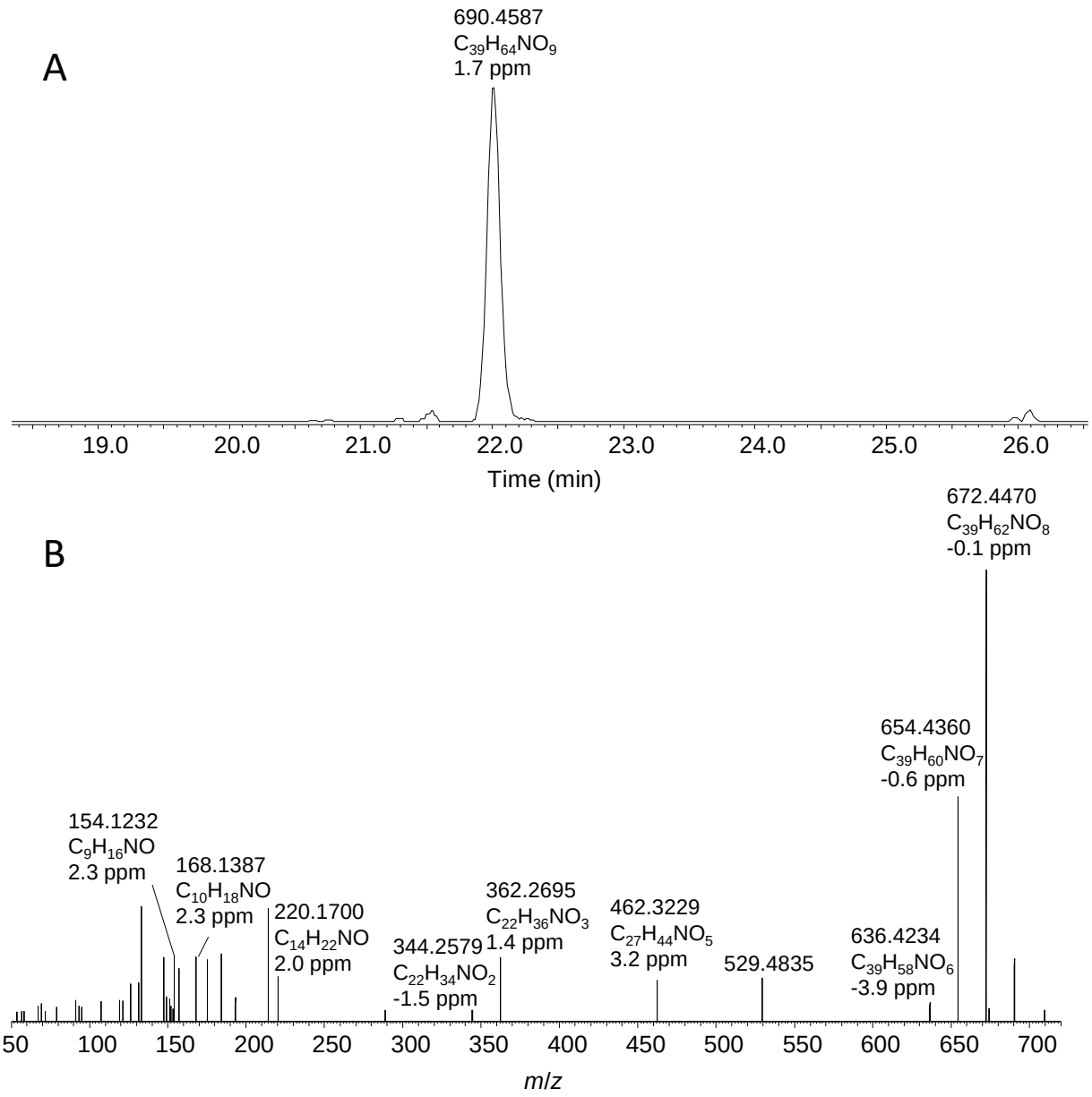

Fig. S4. Extracted ion chromatogram (±5 ppm) from positive mode full-scan data showing an AZA-like compound (A) and associated MS/MS spectrum (B), labelling several product ions commonly observed among AZAs (Table 1), suggesting the structure from C-20 onward shown in Figure 1 is preserved [5], with significant structural differences to the left-hand side of the AZA structure.

.

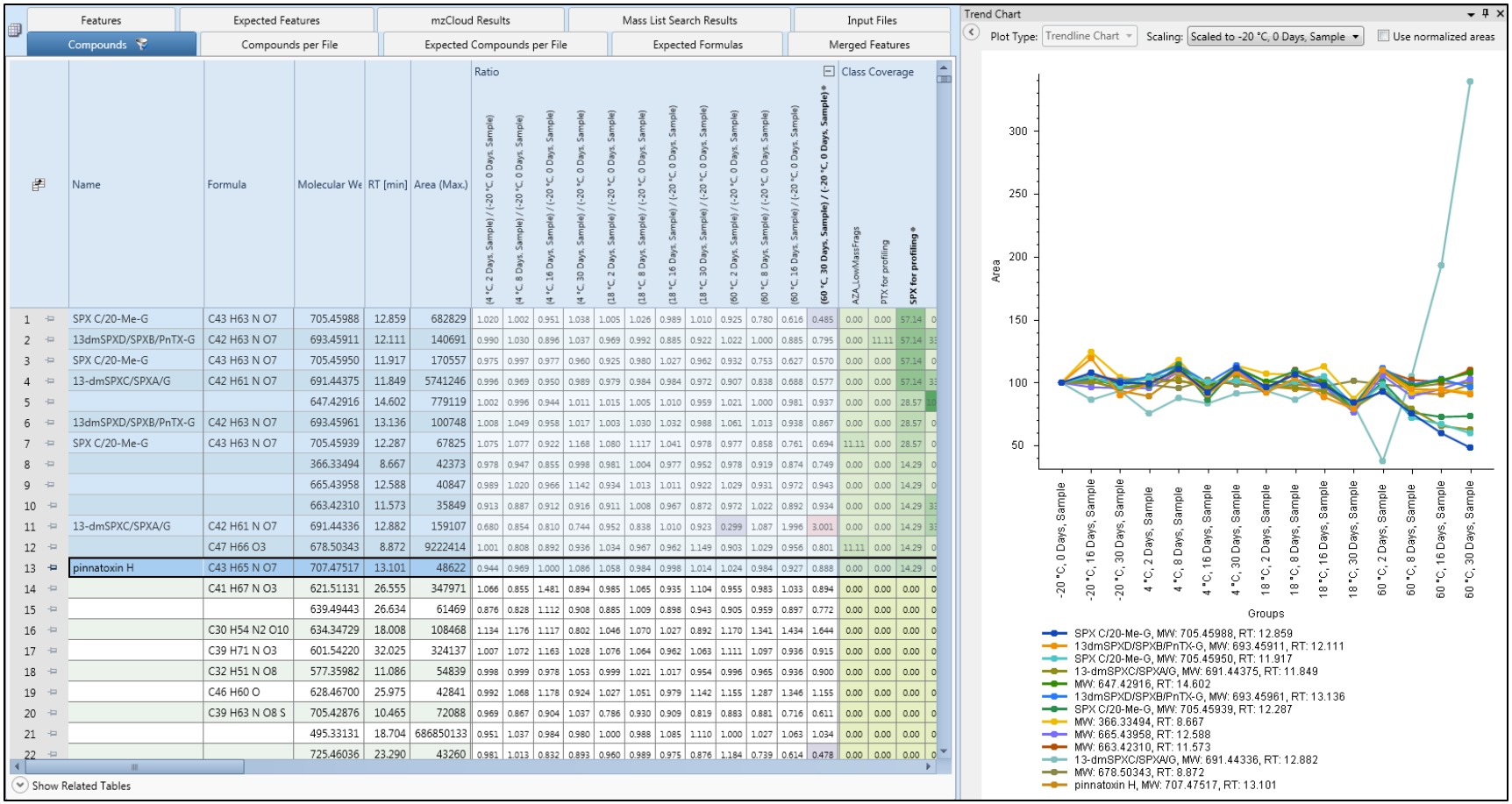

Fig. S5. Screen capture of a Compound Discoverer results table from analysis of short-term stability study samples of CRM-FDMT1. Entries are sorted by class coverage for the cyclic imine group, with the average peak area (n=3) normalized to −20°C day 0 of selected compounds plotted vs. temperature condition (right).

References

[1] E.J. Wright, P. McCarron, A mussel tissue certified reference material for multiple phycotoxins. Part 5: profiling by liquid chromatography–high-resolution mass spectrometry, Anal. Bioanal. Chem. 413 (2021) 2055–2069.
[2] C.O. Miles, D.J. Stirling, Toxin mass list, 2017. https://www.researchgate.net/profile/Christopher-Miles-2. (Accessed October 10 2019).
[3] A. Gerssen, P.P.J. Mulder, J. de Boer, Screening of lipophilic marine toxins in shellfish and algae: development of a library using liquid chromatography coupled to orbitrap mass spectrometry, Anal. Chim. Acta 685 (2011) 176–185.
[4] K. Knudsen, Mass spectral characterisation of three new groups of algal toxins, Chemistry, University of Waikato, New Zealand, 2009, p. 111.
[5] N. Rehmann, P. Hess, M.A. Quilliam, Discovery of new analogs of the marine biotoxin azaspiracid in blue mussels (Mytilus edulis) by ultra-performance liquid chromatography/tandem mass spectrometry, Rapid Commun. Mass Spectrom. 22 (2008) 549–558.