Supplementary materials: Liquid Chromatography Coupled to High Resolution Mass Spectrometry for the Confirmation of Caribbean Ciguatoxin-1 as the Main Toxin Responsible for Ciguatera Poisoning Caused by Fish from European Atlantic Coasts

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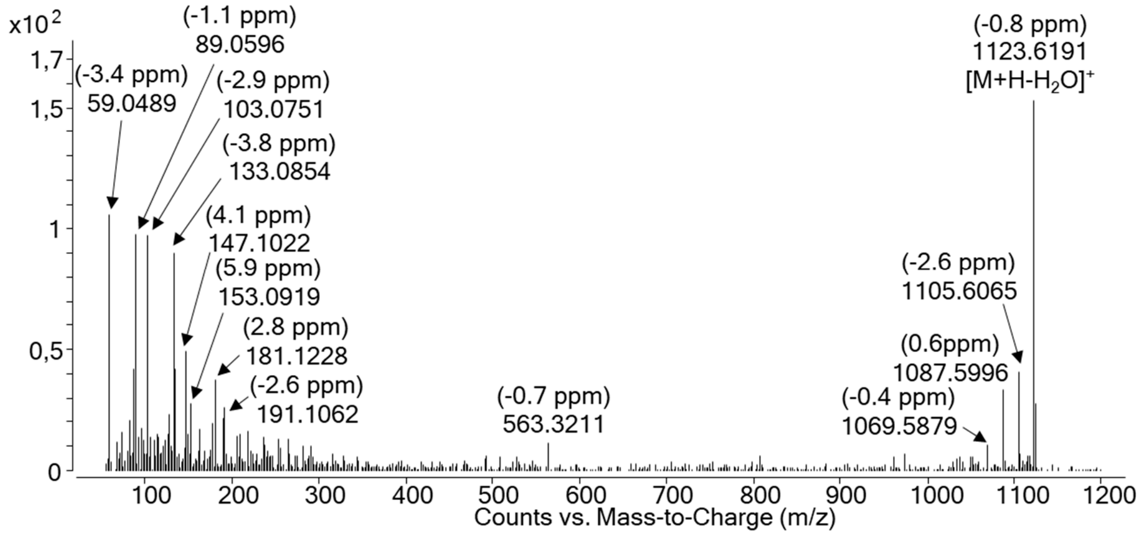

Figure S1. ESI+ Targeted MS/MS spectra of C-CTX1 LRM (123 ng/mL approx.) selecting C-CTX1 m/z 1123.6200 $[M+H-H_2O]^+$ at an average collision energy of 20, 40 and 60 eV.

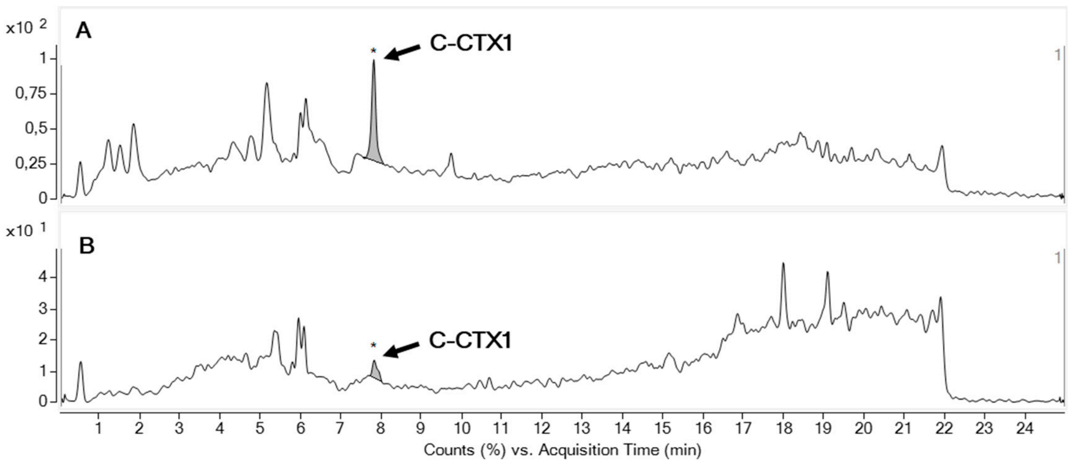

Figure S2. LC-HRMS chromatogram of **A**) C-CTX1 LRM (123 ng/mL approx.) at 7.8 min; **B**) C-CTX1 detected at 7.8 min in a naturally contaminated sample of barred hogfish (*Bodianus scrofa)* from Selvagens Islands (Portugal)

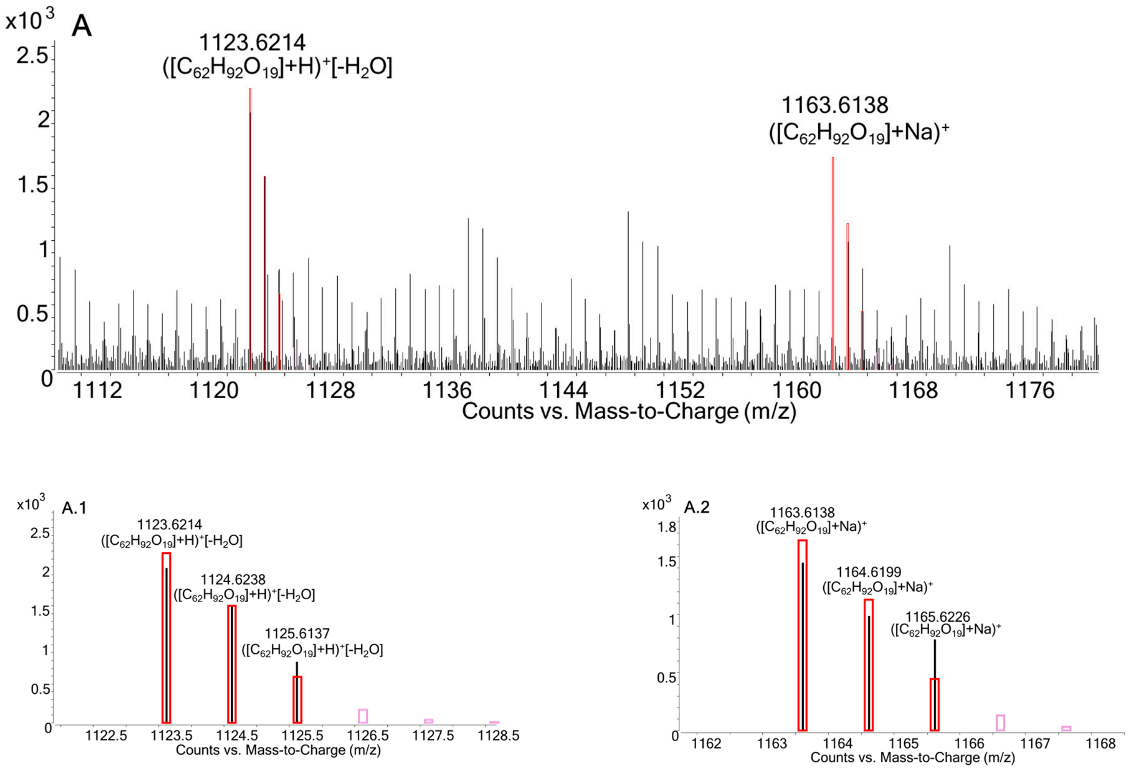

Figure S3. A) ESI+ Full scan MS spectra of Barred hogfish (*Bodianus scrofa)* from Selvagens Islands (Portugal); **A.1**) Zoom of C-CTX1 *m/z* 1123.6214 $[M+H-H_2O]^+$; **A.2**) Zoom of C-CTX1 *m/z* 1163.6138 $[M+Na]^+$.

Table S1. Accurate mono-isotopic masses (theoretical and measured) of C-CTX1 after ESI+ Targeted MS/MS analysis selecting $[M+H-(H_2O)]^+$ at *m/z* 1123.6200 with an averaged collision energy of 20, 40 and 60 eV (**A**) and 30, 50 and 70 eV (**B**).

Ion	Molecular Formula	Theoretical *m/z*	A		B	
			Measured *m/z*	Error (ppm)	Measured *m/z*	Error (ppm)
$[M+H-H_2O]^+$	$C_{62}H_{91}O_{18}^+$	1123.6200	1123.6191	−0.8	1123.6158	−3.7
$[M+H-2H_2O]^+$	$C_{62}H_{89}O_{17}^+$	1105.6094	1105.6065	−2.6	1105.6063	−2.8
$[M+H-3H_2O]^+$	$C_{62}H_{87}O_{16}^+$	1087.5989	1087.5996	0.6	1087.5933	−5.1
$[M+H-4H_2O]^+$	$C_{62}H_{85}O_{15}^+$	1069.5883	1069.5879	−0.4	1069.5865	−1.7
	$C_{31}H_{47}O_9^+$	563.3215	563.3211	−0.7	n.d.	n.d.
	$C_{31}H_{45}O_8^+$	545.3109	n.d.	n.d.	545.3072	−6.8
	$C_{31}H_{43}O_7^+$	527.3003	n.d.	n.d.	527.2953	−9.5
	$C_{31}H_{41}O_6^+$	509.2898	n.d.	n.d.	509.2873	−4.9
	$C_{14}H_{21}O_4^+$	253.1434	n.d.	n.d.	253.1431	−1.2
	$C_{14}H_{19}O_3^+$	235.1329	n.d.	n.d.	235.1334	2.1
	$C_{12}H_{17}O_3^+$	209.1172	n.d.	n.d.	209.1173	0.5
	$C_{12}H_{15}O_2^+$	191.1067	191.1062	−2.6	191.1066	−0.5
	$C_{11}H_{17}O_2^+$	181.1223	181.1228	2.8	181.1224	0.6
	$C_9H_{13}O_2^+$	153.0910	153.0919	5.9	n.d.	n.d.
	$C_7H_{15}O_3^+$	147.1016	147.1022	4.1	147.1011	−3.4
	$C_6H_{13}O_3^+$	133.0859	133.0854	−3.8	133.0856	−2.3
	$C_5H_{11}O_2^+$	103.0754	103.0751	−2.9	103.0751	−2.9
	$C_4H_9O_2^+$	89.0597	89.0596	−1.1	89.0595	−2.2
	$C_3H_7O^+$	59.0491	59.0489	−3.4	59.0487	−6.8