

Supplementary Materials

Table S1. Protocol use C18 SPE

PHASE	solvent	flow	action
conditioning	6 ml MeOH 6 ml H ₂ O mQ	5 ml/min	discharge
Load & collect	1 ml of crude extract	3 ml/min	collect
elute	2 ml H ₂ O MQ	5 ml/min	collect

Table S2. Protocol use COOH SPE

PHASE	solvent	flow	action	toxins
conditioning	10 ml Ammonium Acetate solution 0,01 M	3 ml/min	discharge	
Fraction1				
Load & collect	2 ml SPE C18 extract	3 ml/min	collect	
elute	4 ml H ₂ O MQ	5 ml/min	Collect_Fraction 1	C1,2-C3,4
Fraction2				
elute	4 ml NaCl 0,05 M	5 ml/min	Collect_Fraction 2	GTX1,3-GTX2,3-dcGTX2,3-GTX5-GTX6
Fraction3				
elute	5 ml NaCl 0,3 M	5 ml/min	Collect_Fraction 3	STX; NEO; dcNEO, dcSTX

Table S3. Instrument parameters used in the analytical method for LTs toxins with LC-MS/Ms under the multiple reaction monitoring

Toxin	ESI mode	Parent ion	Precursor ion m/z	Product ion m/z	DP(v)	CE(v)
OA	NEG	[M-H] ⁻	803.5	255.0	-25	-62
OA	NEG	[M-H] ⁻	803.5	113.0	-25	-98
DTX-2	NEG	[M-H] ⁻	803.4	255.0	-25	-62
DTX-2	NEG	[M-H] ⁻	803.4	113.0	-25	-98
DTX-1	NEG	[M-H] ⁻	817.5	255.0	-90	-62
DTX-1	NEG	[M-H] ⁻	817.5	113.0	-90	-100
YTX	NEG	[M-2H] ²⁻	570.4	467.2	-106	-42
YTX	NEG	[M-2H] ²⁻	570.4	396.1	-106	-44
45 OH-YTX	NEG	[M-2H] ²⁻	578.4	467.4	-106	-42
45 OH-YTX	NEG	[M-2H] ²⁻	578.4	396.4	-106	-44
HomoYTX	NEG	[M-2H] ²⁻	577.5	474.2	-118	-44
HomoYTX	NEG	[M-2H] ²⁻	577.5	403.2	-118	-45
45 OH-HomoYTX	NEG	[M-2H] ²⁻	578.4	474.4	-106	-42
45 OH-HomoYTX	NEG	[M-2H] ²⁻	578.4	403.4	-106	-44
AZA-1	POS	[M+H] ⁺	842.5	824.5	114	43

AZA-1	POS	[M+H] ⁺	842.5	806.5	114	56
AZA-2	POS	[M+H] ⁺	856.5	838.5	110	44
AZA-2	POS	[M+H] ⁺	856.5	820.5	110	56
AZA-3	POS	[M+H] ⁺	828.5	810.5	62	43
AZA-3	POS	[M+H] ⁺	828.5	792.5	62	56

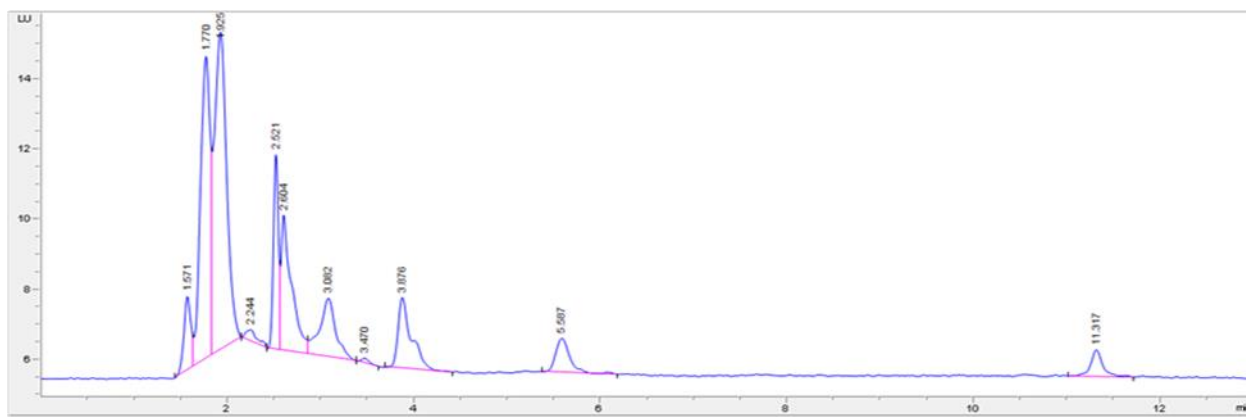


Figure S1. Chromatographic profile of the sample without oxidation for naturally fluorescence coextractives.

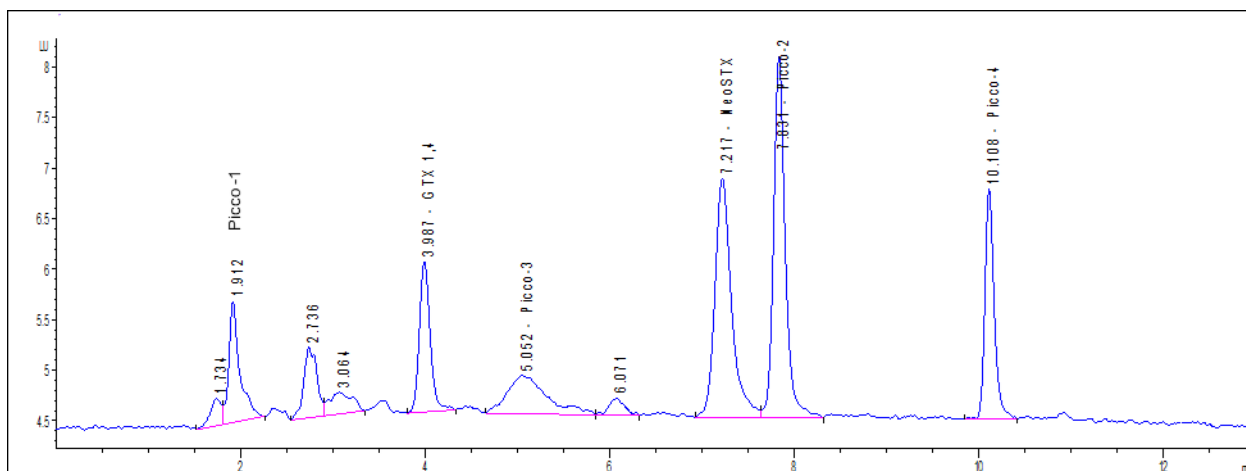


Figure S2. MIX I GTX1,4 and secondary oxidation products (peaks 1 and 2) NEO and secondary products (peaks 3 and 4) Oxidated with periodate.

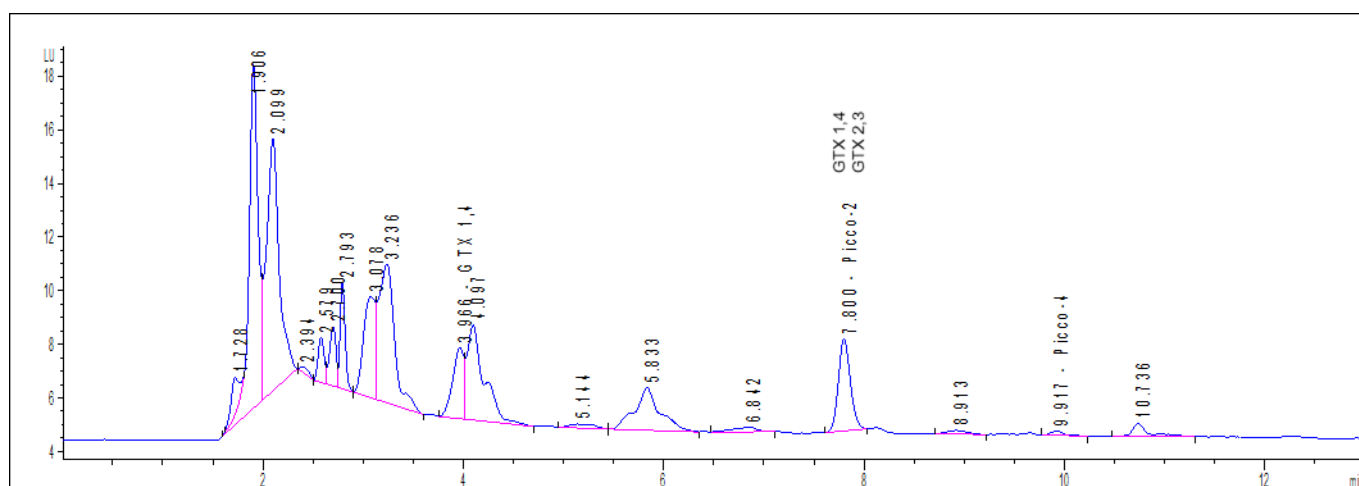


Figure S3. Sample after C18 Purification-Oxidated with periodate.

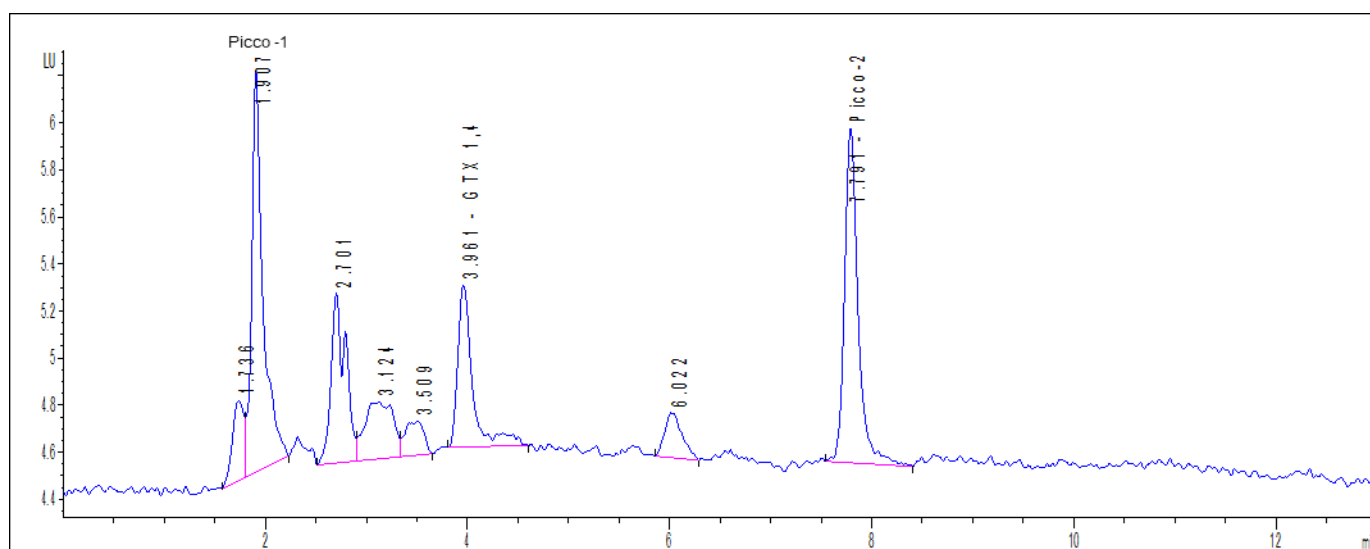


Figure S4. Sample after C18 and COOH Purification-Fraction 2-Oxidated with periodate.

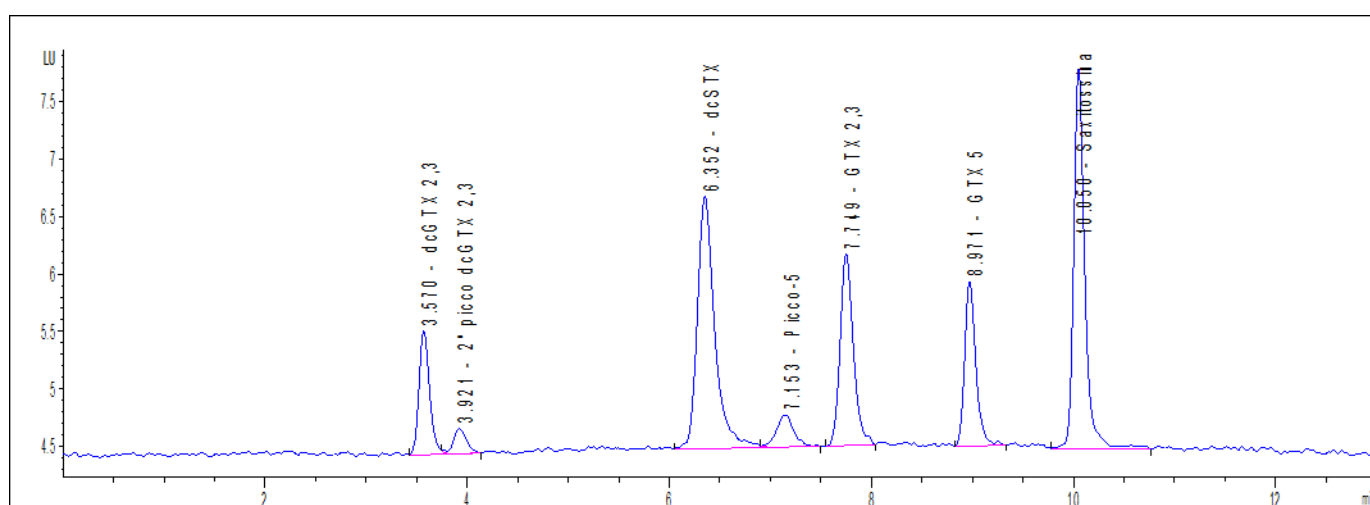


Figure S5. MIXII dcGTX2,3 and secondary product peak; dcSTX and secondary product peak 5; GTX2,3; GTX5; STX aNEO -Oxidated with peroxide.

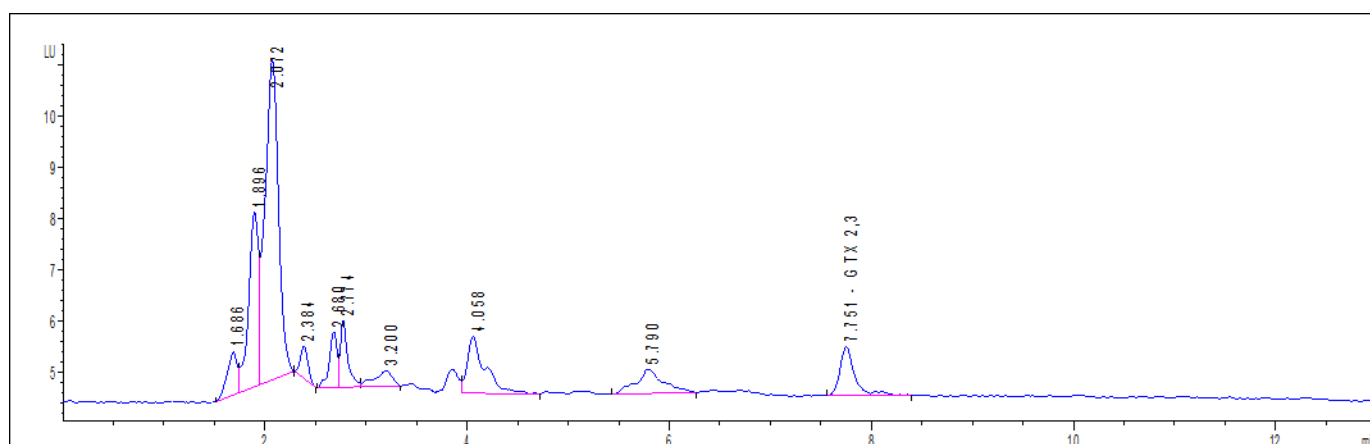


Figure S6. Sample after C18 Purification-Oxidated with peroxide.

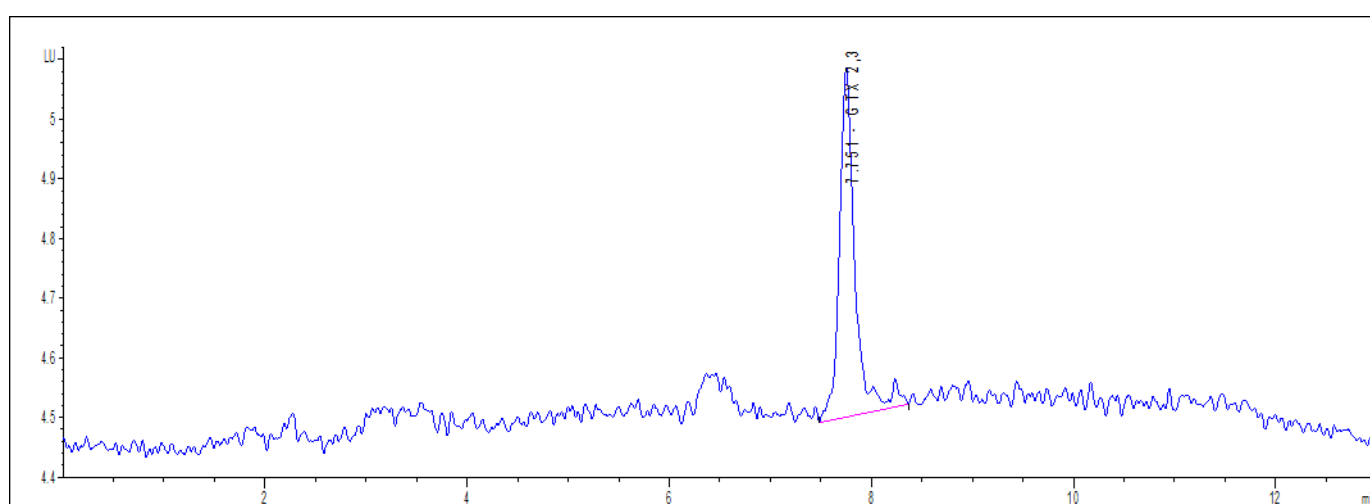


Figure S7. Sample after C18 and COOH Purification-Fraction 2-Oxidated with peroxide