

Supplementary Table

Table S1. Instrumental conditions of LC-MS/MS, results of quality assurance and quality control, LOD and LOQ for analysis of free MC variants (MC-LR, MC-RR, MC-LA, MC-YR, MC-LF, MC-LW, MC-LY, dmMC-LR, dmMC-RR) and of MMPB as oxidation product of total MC.

LC system	Nexera Shimadzu®		
Column	Phenomenex Kinetex XB-C18 100 x 2,1 mm (2,6 µm)		
Mobile phase A	Water + HCOONH ₄ 2 mM + HCOOH 50 mM		
Mobile phase B	Water /ACN 5/95 + HCOONH ₄ 2 mM + HCOOH 50 mM		
Separation	Gradient: B 30-80% (0-5 min) → B 80% (5-6 min) → B 80-30% (6-6.5 min) → B 30% (6.5-10.5 min)		
Flow rate	0.3 mL min ⁻¹		
Injection volume	5 µL		
MS/MS system	AB Sciex API 5500 QTRAP		
Source	ESI (electrospray ionization)		
Ion mode	Positive		
Ion Spray voltage	5.5 kV		
Dwell time	40 msec		
Curtain gas	25 psi		
Collision Gas	Medium		
Ion Source gas 1	30 psi		
Ion Source gas 2	70 psi		
Temperature	550 °C		
Transitions	Ion precursor (m/z)	Transition (m/z) quantification	Transition (m/z) identification
dmMC-RR	512.8	135.0	103.0
MC-RR	520.1	135.2	213.2
MC-YR	1045.6	213.2	375.2
MC-LR	995.6	213.2	374.5
dmMC-LR	981.4	103.0	135.2
MC-LA	910.7	375.2	135.2
MC-LY	1002.6	375.2	135.2
MC-LW	1025.6	375.2	135.2
MC-LF	986.6	375.2	135.2
MMPB	209	131.1	91.9
LOD/LOQ (ng/g of digestive gland, FW for mussels, ng/mL for phytoplankton samples)	<i>A. anatina</i> tissues	<i>M. edulis</i> tissues	phytoplankton
dmMC-RR	4 / 12	3 / 9	0.3 / 1.1
MC-RR	7 / 21	14 / 42	0.5 / 1.5
MC-YR	26 / 84	29 / 95	3.6 / 12
MC-LR	36 / 85	29 / 88	7.6 / 24.5
dmMC-LR	6 / 20	11 / 35	0.6 / 2.1
MC-LA	13 / 42	16 / 50	1.3 / 4.4
MC-LY	16 / 50	11 / 34	0.6 / 2.0
MC-LW	14 / 45	22 / 68	2.1 / 7.0
MC-LF	4 / 13	14 / 42	1.4 / 4.5

Supplementary Figures

Figure S1. Chromatograms of the nine MC variants (MC-LR, MC-RR, MC-LA, MC-YR, MC-LF, MC-LW, MC-LY, dmMC-LR, dmMC-RR).

