

Figure S1. Observed relative concentrations of GYM-A CRMs in the homogeneity assessment.

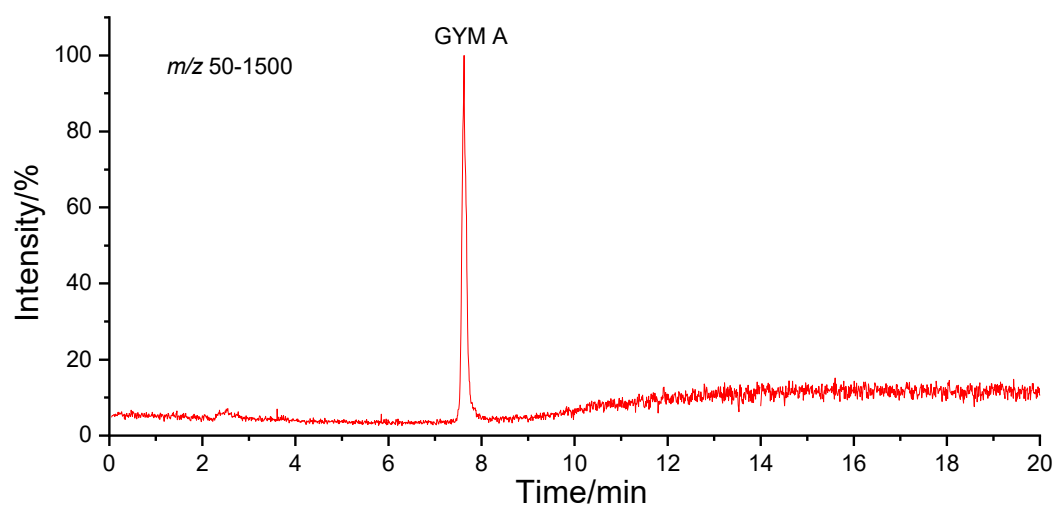


Figure S2. Full-scan chromatogram of the purified GYM-A CRMs (m/z 50-1500).

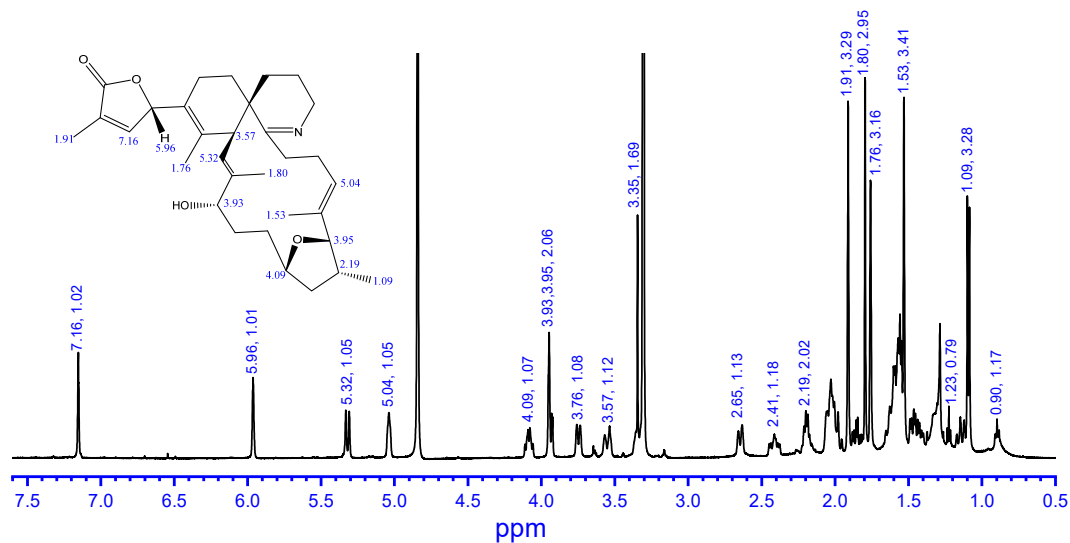


Figure S3. ^1H NMR spectrum (0.5–7.5 ppm) of GYM-A in CD_3OD .

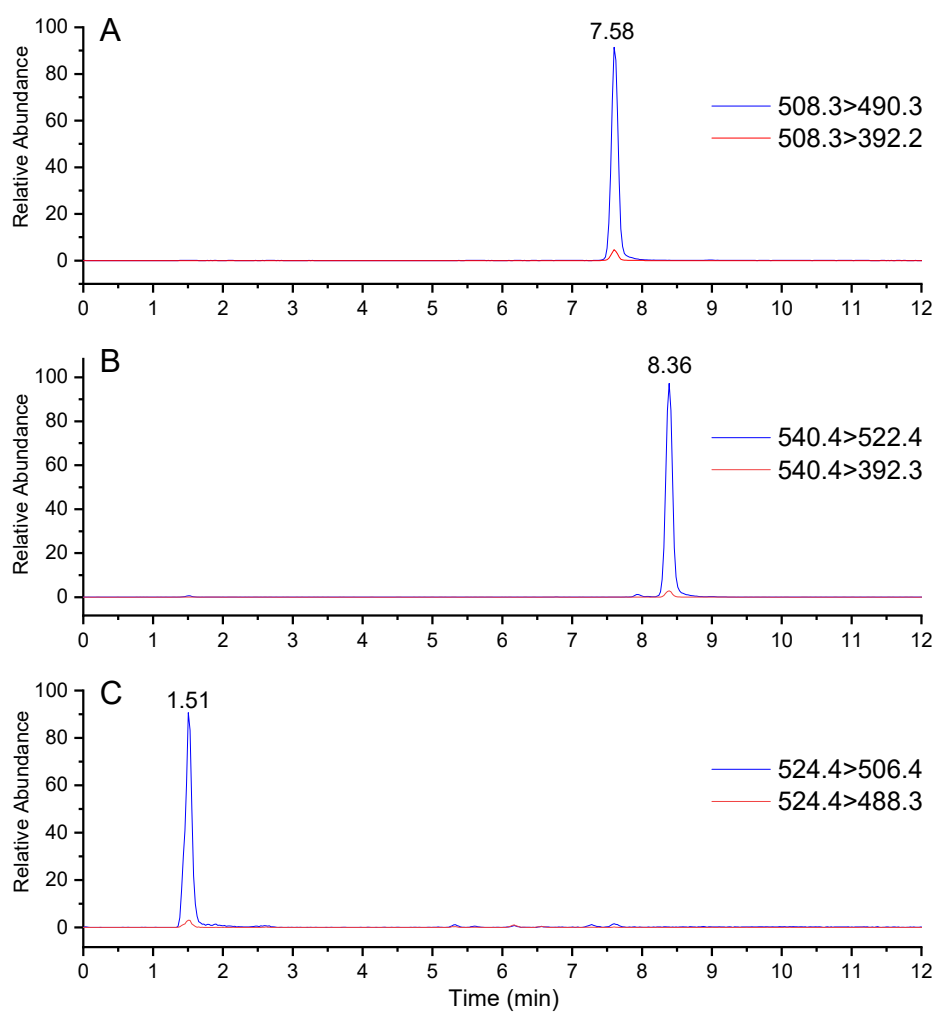


Figure S4. Extracted ion chromatograms (XIC) of GYM-A (**A**), GYM-K (m/z 540.4) (**B**), and GYM-L (m/z 524.3) (**C**).

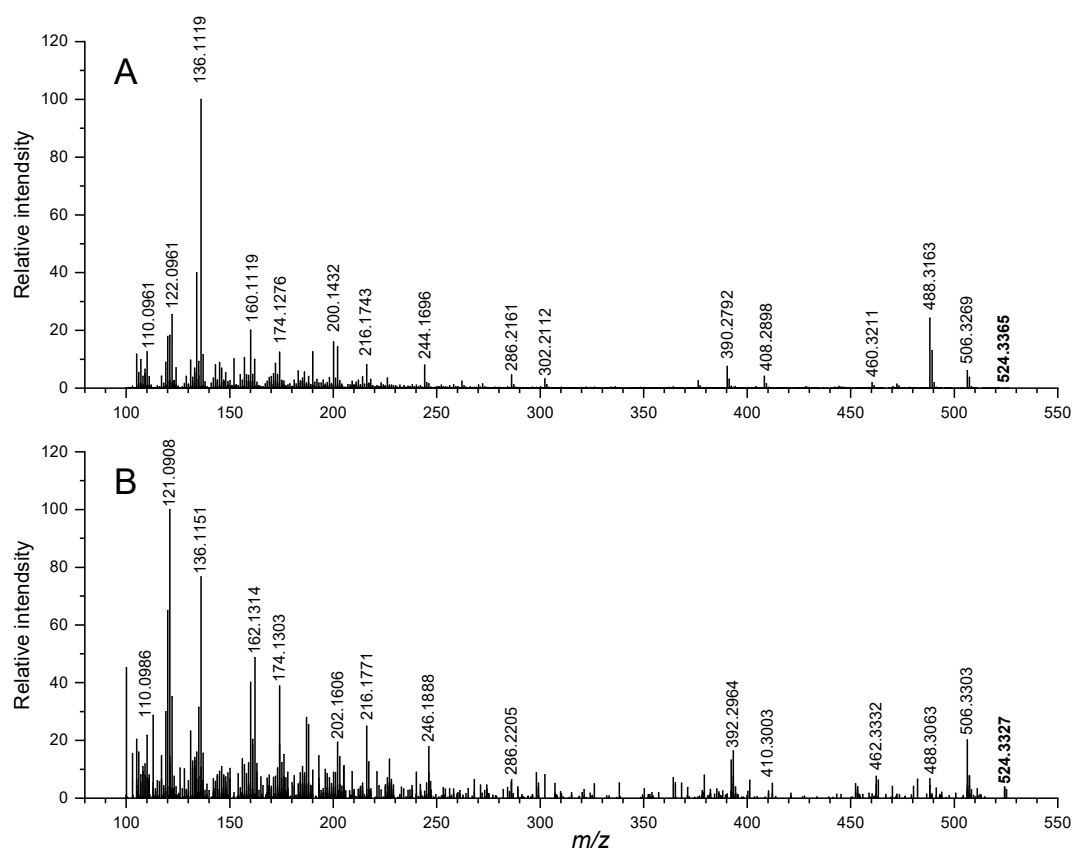


Figure S5. High-resolution product ion spectra of GYM-B at m/z 524.3365 (A) and GYM-L at m/z 524.3327 (B).

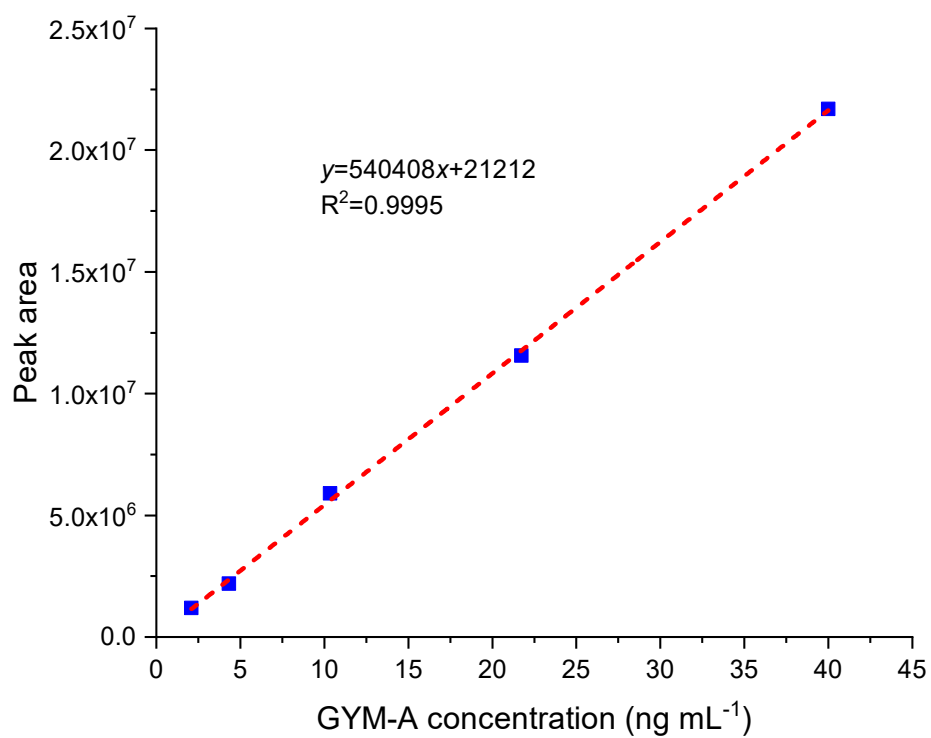


Figure S6. Calibration curve of GYM-A quantification by LC-MS/MS

Table S1. Measurement data of homogeneity assessment of GYM-A ($\mu\text{g mL}^{-1}$)

Bottle No.	Run 1	Run 2	Run 3	Mean	Standard error
1	0.569	0.544	0.604	0.572	0.017
2	0.538	0.592	0.569	0.566	0.016
3	0.565	0.589	0.575	0.577	0.007
4	0.548	0.604	0.579	0.577	0.016
5	0.608	0.649	0.653	0.637	0.014
6	0.567	0.624	0.632	0.608	0.020
7	0.566	0.633	0.610	0.603	0.020
8	0.595	0.617	0.632	0.615	0.011
9	0.565	0.622	0.587	0.591	0.017
10	0.574	0.569	0.634	0.592	0.021

Table S2. The ANOVA analysis of homogeneity assessment.

Source of variation	Sum of squares	Degree of freedom	Mean square
Between bottles	0.013	9	0.0014 (s_1^2)
Within bottles	0.016	20	0.0008 (s_2^2)
Total	0.029	29	

Table S3. The qNMR analysis results of GYM-A purity assessment.

Toxin	Weighing result (mg)	qNMR result (mg)	Purity (%)
GYM-A	1.954	1.868	95.6

Table S4. The solvent volume of GYM-A samples under different treatments after 4 months.

120 d	Temperature (°C)	Solvent volume (μL)			Mean	Standard error
		1	2	3		
pH 3	20	80.9	69.3	68.4	72.9	4.0
	4	90.7	91.6	85.4	89.2	2.0
	-20	87.1	82.7	83.6	84.5	1.4
pH 5	20	69.3	75.5	64.8	69.9	3.1
	4	92.5	94.3	93.4	93.4	0.5
	-20	92.5	93.4	90.7	92.2	0.8
pH 7	20	55.0	84.5	70.2	69.9	8.5
	4	91.6	88.9	85.4	88.6	1.8
	-20	87.1	89.8	84.5	87.1	1.5

Table S5. The solvent volume of GYM-A samples under different treatments after 6 months.

180 d	Temperature (°C)	Solvent volume (μL)			Mean	Standard error
		1	2	3		
pH 3	20	70.2	73.8	67.5	70.5	1.8
	4	81.8	85.4	79.1	82.1	1.8
	-20	84.5	87.1	80.9	84.2	1.8
pH 5	20	88.0	67.5	77.3	77.6	5.9
	4	88.0	91.6	93.4	91.0	1.6
	-20	99.6	83.6	86.3	89.8	5.0
pH 7	20	46.1	79.1	63.9	63.0	9.5
	4	69.3	92.5	89.8	83.9	7.3
	-20	89.8	80.9	95.2	88.6	4.2

Table S6. The solvent volume of GYM-A samples under different treatments after 8 months.

240 d	Temperature (°C)	solvent volume (μL)			Mean	Standard error
		1	2	3		
pH 3	20	75.0	67.0	43.8	61.9	9.4
	4	87.5	75.0	91.1	84.5	4.9
	-20	89.8	91.6	72.9	84.8	6.0
pH 5	20	85.7	84.8	42.0	70.8	14.4
	4	91.1	81.3	75.9	82.7	4.4
	-20	89.8	83.6	91.6	88.3	2.4
pH 7	20	70.5	72.3	38.4	60.4	11.0
	4	91.1	88.4	91.1	90.2	0.9
	-20	78.2	81.8	84.5	81.5	1.8

Table S7. List of the compounds corresponding to gymnodimines in this study. Mass differences (Δ ppm) were compared between measured and exact theoretical masses.

Compound	RT (min)	Molecular formula	[M+H] ⁺		Unsaturation	Putative identity
			theoretical <i>m/z</i>	Δ ppm		
Compound 1 524.3327	1.51	C ₃₂ H ₄₅ NO ₅	524.3371	-8.392	11	GYM-L
Compound 2 508.3405	7.58	C ₃₂ H ₄₅ NO ₄	508.3421	-3.147	11	GYM-A
Compound 3 540.3698	8.36	C ₃₃ H ₄₉ NO ₅	540.3684	2.591	10	GYM-K