Supporting Information

Production of amphidinols and other bioproducts of interest by the marine dinoflagellate microalga *Amphidinium carterae* unraveled by NMR metabolomics approach coupled to multivariate data analysis

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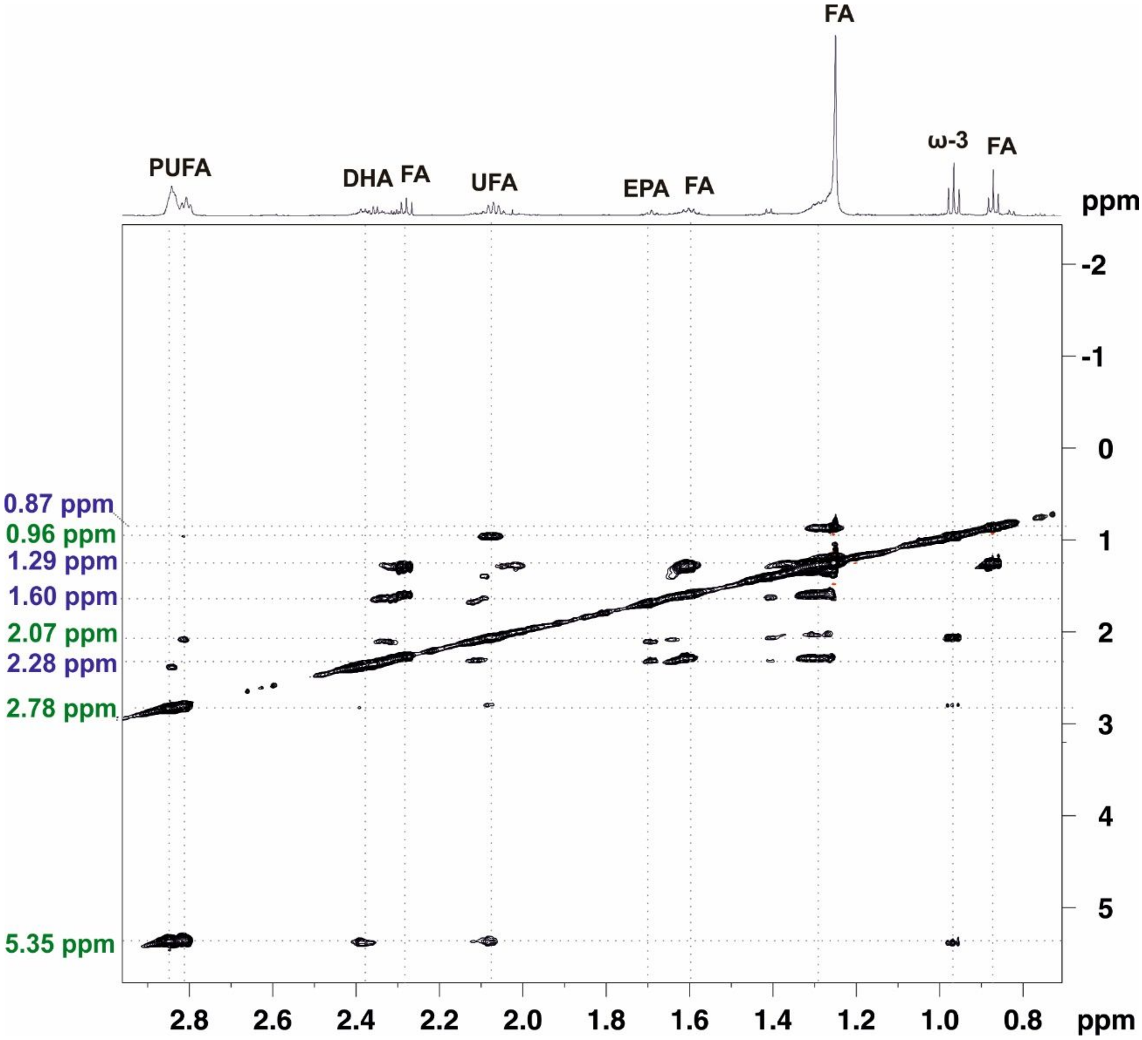


Figure S1. TOCSY experiment made for the characterization of fatty acids on a $CDCl_3$:CD_3OD (80:20, v/v) extract of *Amphidinium carterae* biomass (set 5).

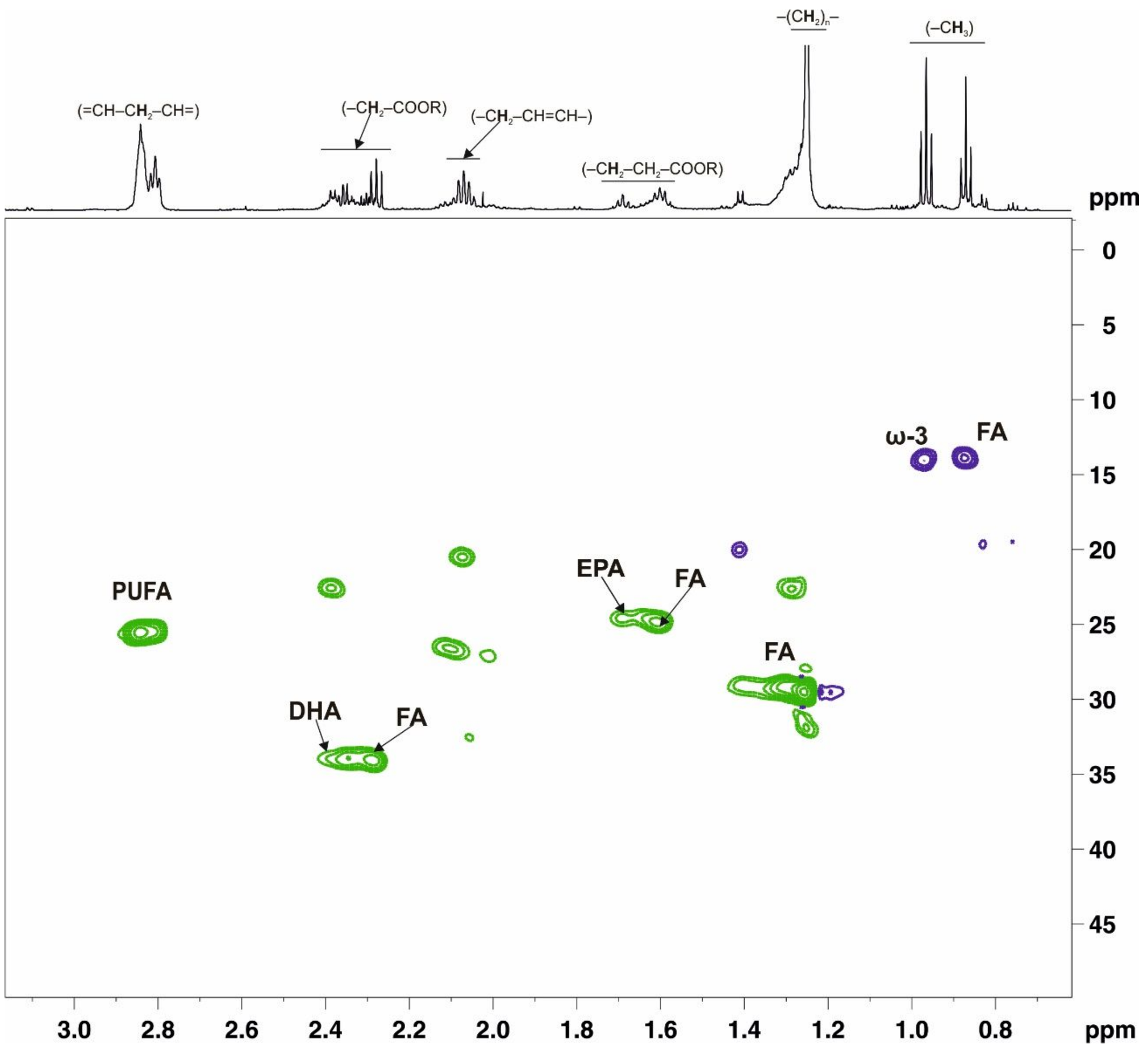


Figure S2. HSQC experiment made for the characterization of fatty acids on a $CDCl_3$:CD_3OD (80:20, v/v) extract of *Amphidinium carterae* biomass (set 5).

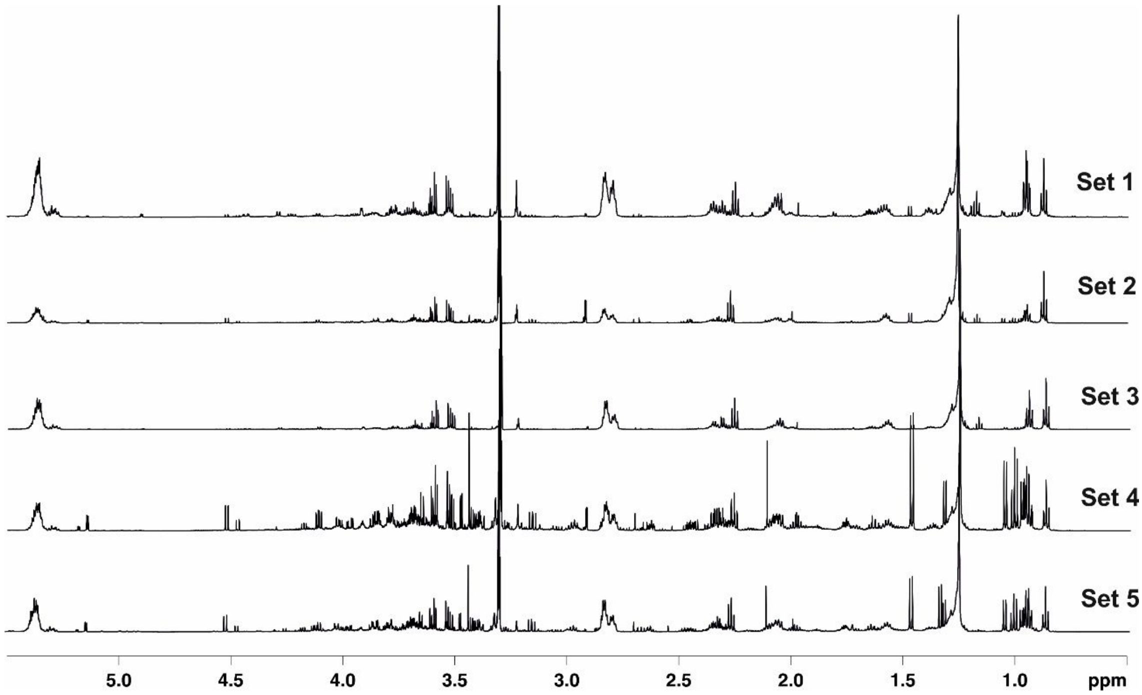
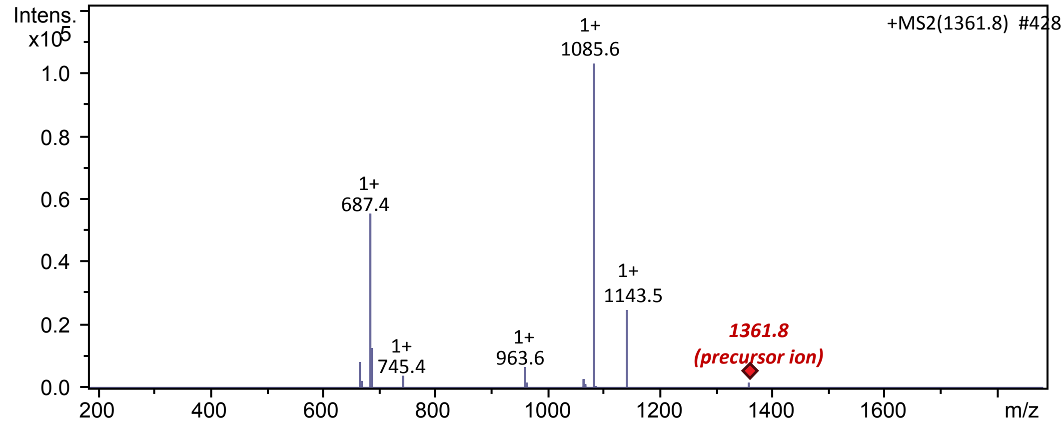


Figure S3. [1]H NMR (600 MHz) spectra of the CD_3OD: D_2O KH_2PO_4 buffer (80:20, v/v) extracts of *Amphidinium carterae* biomass from the five experimental sets.

a)



b)

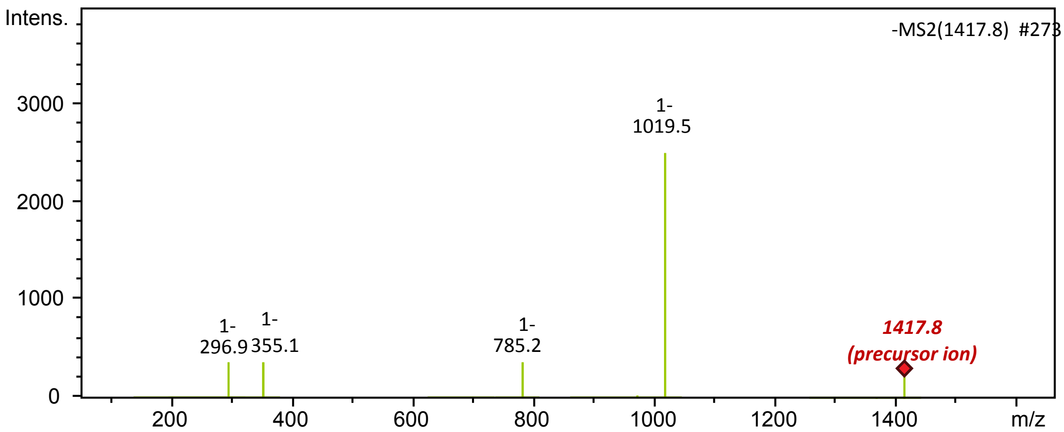


Figure S4. ESI-IT MS/MS spectra of the $CH_3OH:H_2O$ (80:20, v/v) extract in a) positive mode and b) negative mode, considering as precursor ions the *m/z* signals of 1361.8 and 1417.8, respectively. As stated within the text, the molecular ions found in both ionization modes (in HR-MS) demonstrated that the found APDs in the extract are Amphidinol A (positive mode) and Amphidinol B (negative mode).

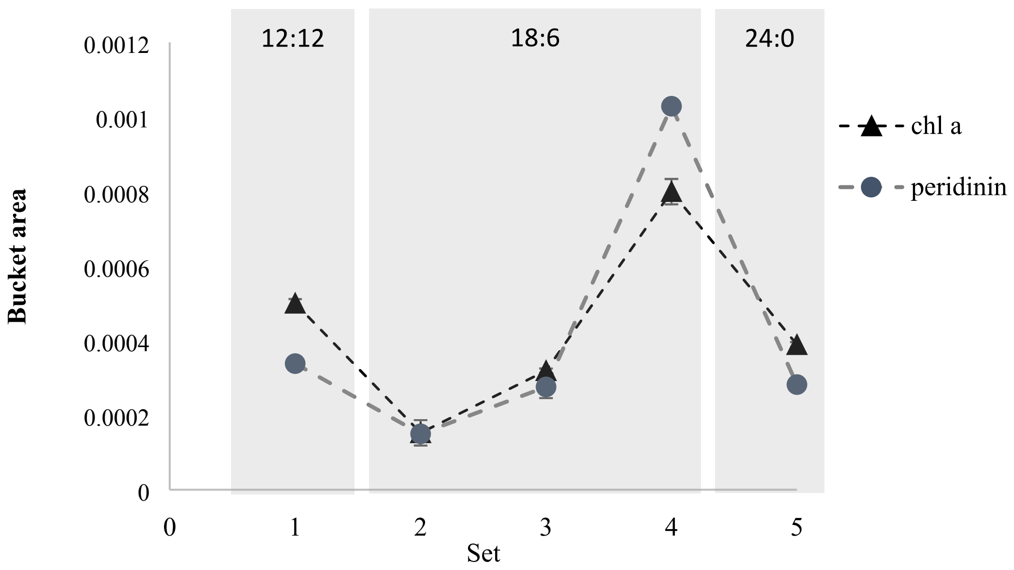
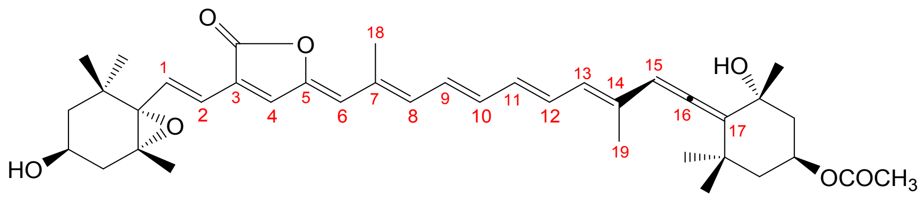


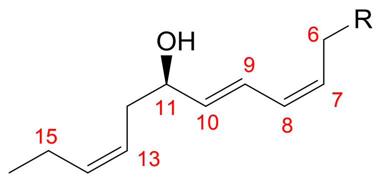
Figure S5. Content on the major pigments on A. carterae biomass (chlorophyll a and peridinin) along the 5 experimental sets with different light/dark illumination regimes (12:12, 18:6 or 24:0). The area values of the buckets containing peaks assigned to chlorophyll a (δ_H 9.50 ppm) and peridinin (δ_H 6.62 ppm) are given.

Table S1. Peak assignment and chemical structure of peridinin identified on *A. carterae* lipophilic extracts



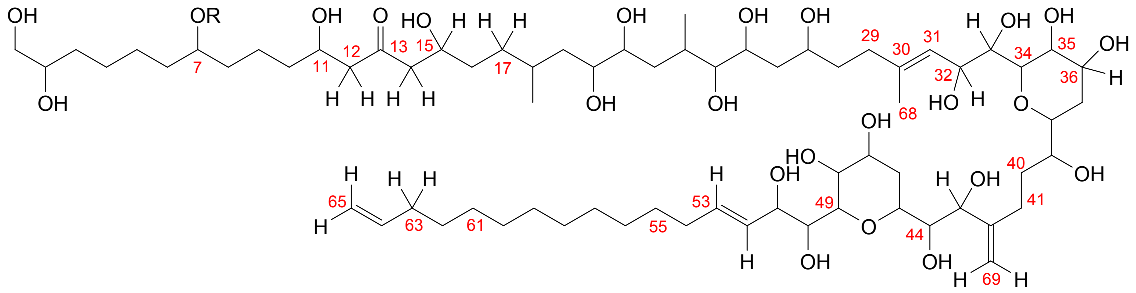
Position	δ_H (ppm)	δ_C (ppm)	Position	δ_H (ppm)	δ_C (ppm)
H8	6.02	133.9	H7’	7.13	133.5
H10	6.13	130.6	H8’	6.37	121.5
H11	6.63	130.1	H10’	7.05	136.6
H12	6.40	133.9	H12’	5.79	119.7
H15	6.59	130.8	H14’	6.44	134.7
			H15’	6.52	137.9

Table S2. Peak assignment and chemical structure of an oxylipin-type compound found on *A. carterae* aqueous extracts.



Position	δ_H (ppm)	δ_C (ppm)
1		
2 (R substituent)	2.33	35.2
3 (R substituent)	2.46	26.3
4		
5		
6	2.95	-
7	5.39	131.8
8	5.99	128
9	6.51	125.2
10	5.68	136.5
11	4.14	75.1
12		
13		
14		
15	2.07	-

Table S3. Peak assignment and chemical structure of amphidinol identified on *A. carterae* aqueous extracts.



Position	δ_H (ppm)	δ_C (ppm)
13	-	211.5
14	2.64	50.5
15	4.09	68.0
17	1.19	32.8
29	2.18	35.2
30	-	138.5
31		124.0
32	4.56	66.4
34		77.7
40	1.56, 1.98	
41	2.07, 2.41	26.1
42	-	149.5
43	4.20	75.2
44	3.38	73.3
51	4.37	72.3
52	5.58	126.4
53	5.79	135.2
54	2.06	32.1
55	2.07	32.3
63	2.03	33.4
64	5.81	138.9
65	4.92, 4.97	113.6
68	1.77	16.1
69	4.99, 5.07	112.3