

Table S1. Pigments identified by HPLC-PDA-ESI/APCI(+) -Qq-TOF in the species analysed in the study.

Peak	Carotenoid	t_R (min)	UV-Vis maxima (nm)	[M+H] ⁺ (m/z)
1	5,8-furanoid-2'-3'-didehydro α -cryptoxanthin	5.6	400, 416, 440	567.4207
2	<i>cis</i> -violaxanthin	5.9	412, 434, 464	599.4125 ^a
3	<i>cis</i> -neoxanthin	6.3	412, 434, 462	599.4114 ^a
4	<i>cis</i> -mutatoxanthin	8.0	418, 438, 465	585.4298
5	<i>cis</i> -luteoxanthin	8.6	405, 422, 474	567.4374 ^b
6	diadinoxanthin	10.0	426, 448, 478	567.4217 ^c
7	<i>all-trans</i> -diatoxanthin	11.4	430, 453, 480	567.4194
8	<i>cis</i> -antheraxanthin	12.0	425, 446, 474	585.4306
9	<i>all-trans</i> -lutein	14.5	420, 444, 472	551.4152 ^b
10	<i>cis</i> -lutein	15.9	424, 446, 474	551.4149 ^b
11	chlorophyll <i>b</i>	16.1	466, 650	907.52.16
12	<i>cis</i> -zeaxanthin	16.6	425, 450, 476	569.4369
13	<i>all-trans</i> -zeaxanthin	17.2	425, 450, 476	569.4370
14	13 ² -hydroxy-chlorophyll <i>a</i>	18.5	432, 666	909.5372
15	chlorophyll <i>a</i>	19.9	432, 666	893.5491
16	5,6-epoxy- β -cryptoxyanthin	20.0	420, 444, 470	569.4375
17	chlorophyll <i>a'</i>	22.0	432, 666	893.5407
18	2-dehydrodeoxymyroxol	23.6	446, 472, 504	567.4172 ¹
19	<i>all-trans</i> -zeinoxanthin	26.0	420, 448, 472	553.4386
20	2'-linolenoyl-myroxol ester	26.5	446, 470, 502	829.6507 ²
21	<i>all-trans</i> -echinenone	27.7	461	551.4255
22	<i>cis</i> -5,8-furanoid- β -cryptoxyanthin	28.3	402, 426, 450	569.4326
23	<i>cis</i> -echinenone	29.4	455	551.4236
24	myristoyl- β -zeinoxanthin ester	31.2	420, 448, 472	763.6386
25	myristoyl- β -cryptoxyanthin ester	32.1	424, 450, 472	763.6390
26	9- <i>cis</i> - α -carotene	32.3	330, 420, 444, 472	537.4442
27	pheophytin <i>a</i>	33.2	410, 666	871.5822
28	<i>all-trans</i> - β -carotene	36.6	424, 451, 477	537.4434
29	9- <i>cis</i> - β -carotene	38.0	340, 420, 446, 472	537.4457

^aprotonated ion arising from the M^{•+} radical ion. ^b[M+H-18]⁺. ^c[M+H-16]⁺.

Table S2. Characterization by HPLC-PDA-APCI(+) -Qq-TOF-MS in bbCID mode of unusual and unknown carotenoids in microalgal extracts (peaks number as in Table 1).

peak	carotenoid	t_R (min)	Molecular formula	$[M+H]^+$ (m/z)	mass error (ppm)	mSigma
1		5.6	C ₄₀ H ₅₄ O ₂	567.4207	1.9	26.3
16	5,6-epoxy- β -cryptoxanthin	21.5	C ₄₀ H ₅₆ O ₂	569.4373	3.5	32.1
18	2'-dehydروdeoxymyxol	23.6	C ₄₀ H ₅₄ O ₂	567.4172	4.3	13.5
22	cis-5,8-furanoid- β -cryptoxanthin	28.3	C ₄₀ H ₅₆ O ₂	569.4325	4.9	32.1

Figure S1: Diagram of the holistic analytical methodology proposed to accurately identify lipophilic pigments in microalgae and cyanobacteria. Peak numbers in the HPLC trace at 450 nm in A (*Aphanotece* extract) and D (*Desertifilum* extract) correspond to Table 1. In both HPLC traces c means chlorophyll pigment.

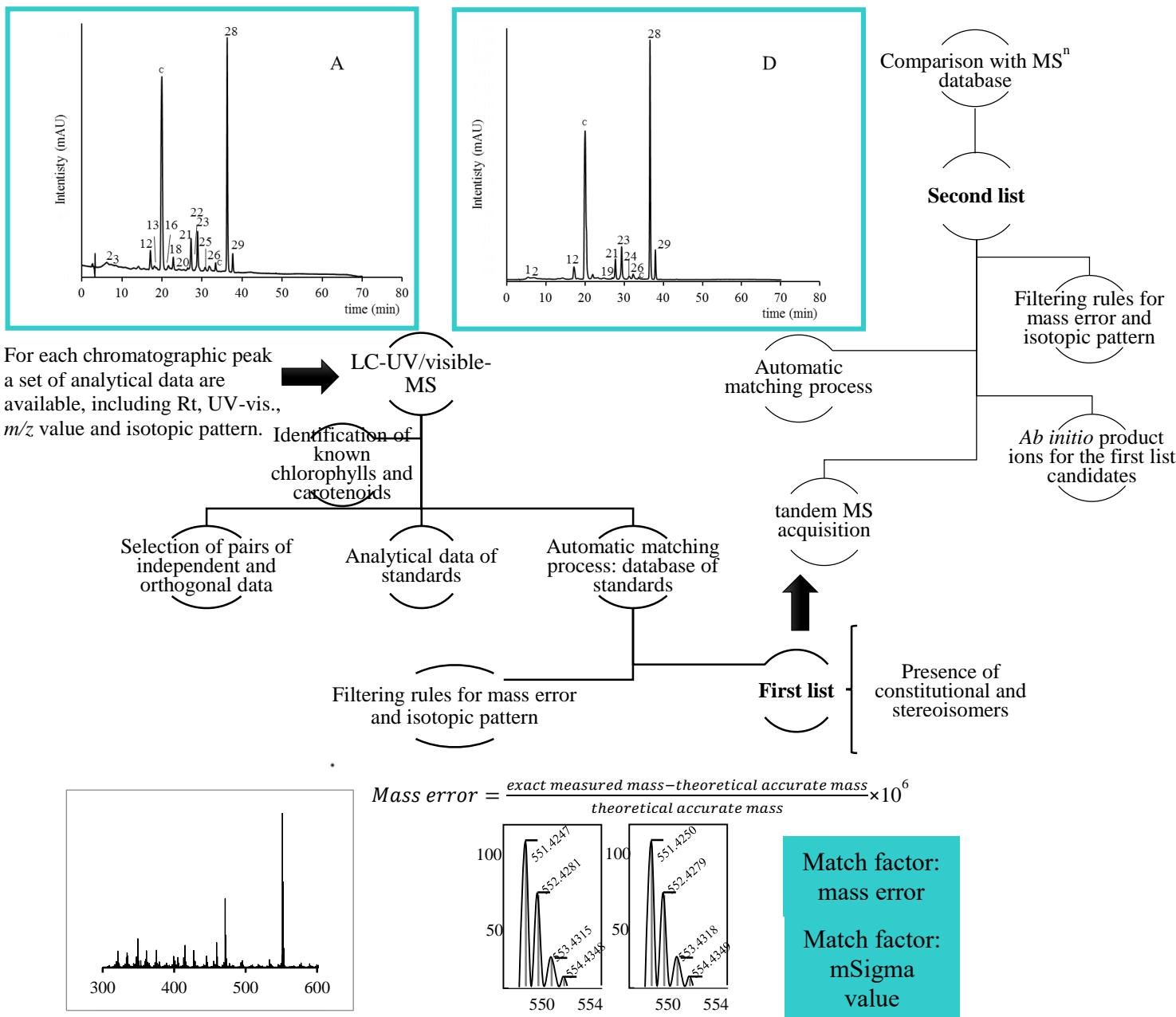


Figure S2: Proposed fragmentation scheme showing the location of the protonation processes in the parent compound that yield the corresponding product ions of 5,6-epoxy- β -cryptoxanthin (Table 2). The fragmentation pathway is similar for 5,8-furanoid- β -cryptoxanthin

