

SUPPLEMENTARY INFORMATION

Table SI-1. Tentative identification of the separated compounds of *Cystoseira abies-marina* by HILIC x RP-DAD-MS/MS analysis.

Peak	tr 2D (s)	Total tr (min)	[M-H]-	Main MS/MS fragments	Relative peak area (%)	Identification
1	32.00	21.33	373.7	247, 125	2.20	Phlorotannin-3 PGU
2	30.05	25.20	329.8	249, 205, 163	0.19	NI
3	30.35	29.11	497.8	479, 372, 339, 249, 229	0.57	Phlorotannin-4 PGU
4	28.85	31.68	497.7	479, 453, 373, 249	0.53	Phlorotannin-4 PGU
5	35.10	31.79	497.9	479, 413, 373, 339, 245, 229	0.72	Phlorotannin-4 PGU
6	31.60	36.93	621.8	603, 559, 479, 247, 229	0.25	Phlorotannin-5 PGU
7	31.35	38.22	621.4	603, 479, 373, 247, 229	8.03	Phlorotannin-5 PGU
8	28.95	39.48	621.5	603, 479, 371, 247, 229	0.50	Phlorotannin-5 PGU
9	31.60	39.53	621.4	603, 495, 371, 263, 229	0.21	Phlorotannin-5 PGU
10	37.80	39.63	621.4	603, 495, 479, 371, 229	1.23	Phlorotannin-5 PGU
11	30.20	40.80	745.9	727, 621, 495, 479, 245, 229	0.23	Phlorotannin-6 PGU
12	34.10	40.87	745.5	727, 601, 479, 339, 229	2.62	Phlorotannin-6 PGU
13	35.70	40.90	745.5	727, 709, 229	0.42	Phlorotannin-6 PGU
14	28.60	42.08	745.7	728, 711, 586, 479, 355, 229	0.70	Phlorotannin-6 PGU
15	35.15	43.49	869.7	772, 712, 634, 621, 497, 245	17.53	Phlorotannin-7 PGU
16	36.70	43.51	869.6	854, 713, 620, 550, 447, 245	39.52	Phlorotannin-7 PGU
17	39.60	46.16	993.9	975, 869, 849, 745, 621, 495	3.44	Phlorotannin-8 PGU
18	36.65	47.41	993.3	975, 957, 932, 620	0.95	Phlorotannin-8 PGU
19	41.75	47.50	1117.6	1099, 993, 869, 849, 745, 619	2.12	Phlorotannin-9 PGU
20	31.55	47.33	893.3	875, 785, 727, 661, 497	0.53	NI
21	33.55	48.66	999.6	981, 963, 909, 891, 749, 601	0.58	NI
22	36.45	48.71	1241.6	1223, 1205, 993, 975, 851, 620	0.45	Phlorotannin-10 PGU
23	38.20	48.74	1242.3	1223, 1205, 993, 973, 867, 725	1.88	Phlorotannin-10 PGU
24	43.45	48.83	1241.6	1223, 1205, 993, 975, 851, 743	0.57	Phlorotannin-10 PGU
25	33.80	49.96	1017.3	999, 979, 927, 909, 851, 619	1.46	NI
26	35.20	49.99	1017.7	999, 981, 909, 869, 851, 619	1.78	NI
27	40.90	50.08	1017.9	999, 909, 851, 769, 663	0.52	NI
28	45.45	50.16	1365.4	1117, 993, 975, 867, 849, 727, 479	1.78	Phlorotannin-11 PGU
29	40.95	51.38	745.3*	1241, 1223, 1100, 993,	0.51	Phlorotannin-12 PGU

30	42.40	51.41	745.5*	726, 229 1241, 1223, 991, 867, 726, 619, 229	0.87	Phlorotannin-12 PGU
31	44.45	52.74	744.6*	1224, 1118, 995, 939, 614, 339, 228	0.35	Phlorotannin-12 PGU
32	48.55	52.81	806.7*	1365, 1224, 993, 867, 745, 619, 351, 229	1.12	Phlorotannin-13 PGU
33	45.75	54.06	869.3*		1.03	Phlorotannin-14 PGU
34	48.80	55.41	869.1*		0.86	Phlorotannin-14 PGU
35	51.15	55.45	930.7*		0.46	Phlorotannin-15 PGU

NI, Not identified; *, ions detected as $[M-2H]^{2-}$.

Each identified phlorotannin can belong to the phloretol, fucol or fucophlorethol type.

Table SI-2. Optimal theoretical volume fractions (Φ) for the mixture of ethanol, water and ethyl lactate and their Ra value for heptaphloretol and heptafucol.

<i>Heptaphloretol</i>									
Temperature (°C)	Mix1			Mix2			Mix3		
	Φ_{Ethanol}	Φ_{water}	Ra	$\Phi_{\text{Ethyl lactate}}$	Φ_{water}	Ra	$\Phi_{\text{Ethyl lactate}}$	Φ_{Ethanol}	Ra
25	0.80	0.20	19.44	0.63	0.37	19.28	0	1.0	20.01
100	0.53	0.47	23.56	0.47	0.53	22.94	0	1.0	25.65
150	0.30	0.70	25.41	0.34	0.66	24.76	0	1.0	29.16

<i>Heptafucol</i>									
Temperature (°C)	Mix1			Mix2			Mix3		
	Φ_{Ethanol}	Φ_{water}	Ra	$\Phi_{\text{Ethyl lactate}}$	Φ_{water}	Ra	$\Phi_{\text{Ethyl lactate}}$	Φ_{Ethanol}	Ra
25	0.60	0.40	24.81	0.47	0.53	24.70	0	1.0	26.571
100	0.29	0.71	28.28	0.28	0.72	27.94	0	1.0	32.201
150	0.02	0.98	29.65	0.12	0.88	29.49	0	1.0	35.693

Figure SI-1. Teas ternary plot. The position of the phlorotannins analyzed is shown with a star icon (★) and the solvent studied with a filled circle (●). The corresponding numbers are listed in the table on the right top of the figure.

