

Electronic Supplementary Material

Extraction and recovery processes for cynaropicrin from *Cynara cardunculus L.* using aqueous solutions of surface-active ionic liquids

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Table S1. Weight fraction percentage of cynaropicrin extracted from the leaves of *Cynara cardunculus* L. with several ILs at different concentrations and other fixed conditions (S/L ratio = 1:10, T = 25°C and t = 60 min).

Ionic Liquid/Concentration	Cynaropicrin (wt%)		
	100 mM	500 mM	1000 mM
[C ₂ mim]Cl	ND	0.175 ± 0.009	ND
[C ₄ mim]Cl	0.833 ± 0.001	0.974 ± 0.001	1.186 ± 0.003
[C ₄ mim](N(CN) ₂)	ND	1.512 ± 0.000	ND
[C ₈ C ₁ im]Cl	ND	1.669 ± 0.005	ND
[C ₁₀ C ₁ im]Cl	ND	2.050 ± 0.004	ND
[C ₁₂ C ₁ im]Cl	ND	2.867 ± 0.004	ND
[C ₁₄ C ₁ im]Cl	1.820 ± 0.002	3.182 ± 0.001	0.544 ± 0.005
[Ch][C CO ₂]	ND	0.155 ± 0.001	ND
[Ch][C ₁₀ CO ₂]	ND	0.174 ± 0.002	ND
[Ch][C ₁₂ CO ₂]	ND	0.122 ± 0.002	ND

*ND – Not determined.

Table S2. CMC values of the studied surface-active ILs at 30°C.

[Ionic Liquids]	CMC (mM) $\pm \sigma$ (measured in this work)	Literature
[C ₈ C ₁ im]Cl	233.0 \pm 1.4	238.0 ¹
[C ₁₀ C ₁ im]Cl	58.7 \pm 0.8	57.2 ² ; 55.0 ³
[C ₁₂ C ₁ im]Cl	15.2 \pm 0.9	15.1 ³ ; 13.5 ⁴
[C ₁₄ C ₁ im]Cl	3.9 \pm 0.1	3.8 ⁵ ; 3.6 ⁴
[Ch][C ₈ CO ₂]	300.3 \pm 0.9	383.0 ⁶
[Ch][C ₁₀ CO ₂]	104.3 \pm 0.7	103.3 ⁶
[Ch][C ₁₂ CO ₂]	25.8 \pm 0.3	ND

*ND – Not available in the literature.

Table S3. Optimization of the weight fraction percentage of cynaropicrin extracted from the leaves of *Cynara cardunculus L.* with aqueous solutions of [C₁₄mim]Cl at different concentrations and other fixed conditions (S/L ratio = 1:10, T = 25° and t = 60 min).

Ionic Liquid/ Concentration	Cynaropicrin (wt%)							
	0 mM	5 mM	10 mM	50 mM	100 mM	350 mM	500 mM	1000 mM
[C ₁₄ mim]Cl	0.676 \pm 0.004	0.691 \pm 0.002	0.957 \pm 0.006	1.175 \pm 0.005	1.820 \pm 0.002	2.079 \pm 0.002	3.132 \pm 0.006	0.544 \pm 0.005

Table S4. Optimization of the weight fraction percentage of cynaropicrin extracted from the leaves of *Cynara cardunculus L.* with aqueous solutions of [C₁₄mim]Cl at different temperatures and other fixed conditions (S/L ratio = 1:10, [IL] = 500 mM and t = 60 min).

Ionic Liquid/Temperature	Cynaropicrin (wt%)		
	25°C	35°C	45°C
[C ₁₄ mim]Cl	3.132 \pm 0.006	1.826 \pm 0.003	1.307 \pm 0.001

Table S5. Optimization of the weight fraction percentage of cynaropicrin extracted from the leaves of *Cynara cardunculus L.* with aqueous solutions of [C₁₄mim]Cl using different extraction times and other fixed conditions (S/L ratio = 1:10, [IL] = 500 mM and T = 25°C).

Ionic Liquid/ Extraction time	Cynaropicrin (wt%)							
	30 min	40 min	50 min	60 min	120 min	180 min	300 min	1440 min
[C ₁₄ mim]Cl	0.948 ± 0.002	2.760 ± 0.026	3.024 ± 0.001	3.132 ± 0.005	2.897 ± 0.006	2.557 ± 0.005	1.923 ± 0.006	1.581 ± 0.001

Table S6. Optimization of the weight fraction percentage of cynaropicrin extracted from the leaves of *Cynara cardunculus L.* with aqueous solutions of [C₁₄mim]Cl in different solid-liquid ratio and other fixed conditions ([IL] = 500 mM, T = 25°C and t = 60 min).

Ionic Liquid/Solid-liquid ratio	Cynaropicrin (wt%)			
	1:10	1:20	1:30	1:40
[C ₁₄ mim]Cl	3.132 ± 0.006	3.727 ± 0.006	4.001 ± 0.001	4.093 ± 0.003

Table S7. Weight fraction percentage of cynaropicrin extracted from the leaves of *Cynara cardunculus L.* with conventional surfactants and [C₁₄mim]Cl in different concentrations and other fixed conditions (S/L ratio = 1:20, t = 60 min, T = 25°C).

Ionic Liquid and Conventional Surfactant/ Concentration	Cynaropicrin (wt%)			
	10 mM	50 mM	100 mM	500 mM
[C ₁₄ mim]Cl	0.957 ± 0.006	1.175 ± 0.005	1.820 ± 0.002	3.727 ± 0.006
CTAB	0.627 ± 0.009	0.946 ± 0.007	1.346 ± 0.018	ND
CTAC	0.658 ± 0.006	1.420 ± 0.000	1.019 ± 0.005	0.403 ± 0.012
CPC	0.650 ± 0.009	0.890 ± 0.000	1.417 ± 0.001	2.033 ± 0.000
SDS	0.745 ± 0.001	0.818 ± 0.001	0.962 ± 0.012	ND
SDBS	1.082 ± 0.001	1.106 ± 0.006	1.629 ± 0.008	1.518 ± 0.001
Genapol	0.998 ± 0.009	1.151 ± 0.001	1.329 ± 0.026	ND

*ND – Not determined.

Table S8. Weight fraction percentage of cynaropicrin extracted from the leaves of *Cynara cardunculus L.* with several solvents and [C₁₄mim]Cl at the following fixed conditions: S/L ratio = 1:20, t = 60 min, T = 25°C (IL at 500 mM).

Solvent	Cynaropicrin (wt%)
[C ₁₄ mim]Cl	3.727 ± 0.006
<i>n</i> -hexane	0.037 ± 0.001
Acetone	0.346 ± 0.002
H ₂ O	0.676 ± 0.004
Dichloromethane	4.529 ± 0.027
Soxhlet	8.652 ± 0.041

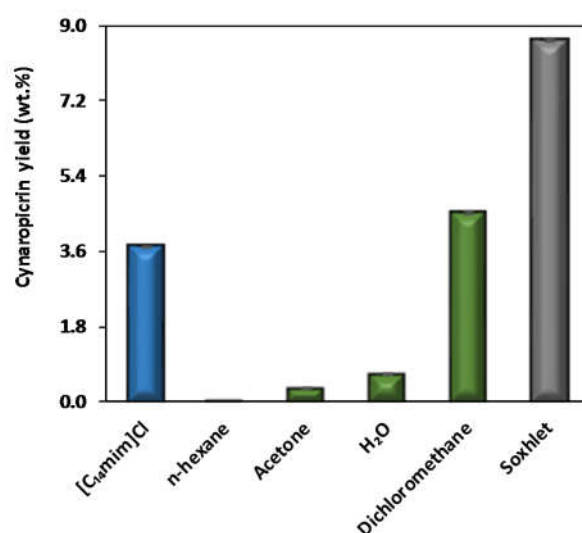


Figure S1. Weight fraction percentage of cynaropicrin extracted from the leaves of *C. cardunculus L.* with several solvents at the following fixed conditions: S/L ratio = 1:20, t = 60 min, T = 25°C ([C₁₄mim]Cl at 500 mM).

Table S9. Weight fraction percentage of cynaropicrin extracted from the leaves of *Cynara cardunculus L.* with several solvents and [C₁₄mim]Cl after 3 cycles of extraction using the same biomass. The fixed conditions are S/L ratio = 1:20, t = 60 min, T = 25°C and IL at 500 mM.

Solvent	Cynaropicrin (wt%)
[C ₁₄ mim]Cl (3cycles)	6.326 ± 0.006
Dichlorometane	4.529 ± 0.003
Soxhlet	8.652 ± 0.004

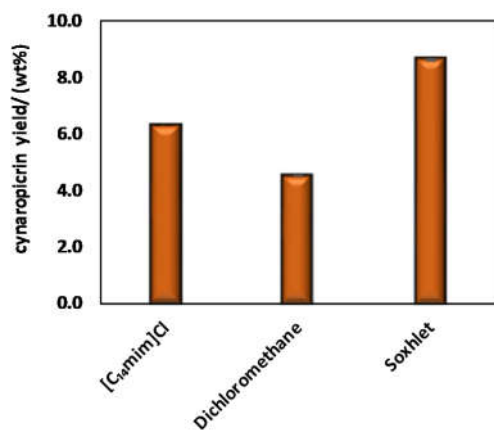


Figure S2. Weight fraction percentage of cynaropicrin extracted from the leaves of *Cynara cardunculus L.* with several solvents and [C₁₄mim]Cl after 3 cycles of extraction using the same biomass. The fixed conditions are S/L ratio = 1:20, t = 60 min, T = 25°C and IL at 500 mM.

Table S10. Weight fraction percentage of cynaropicrin extracted from the leaves of *Cynara cardunculus L.* using the surface-active IL solution and fresh biomass samples, at the following fixed conditions: S/L ratio = 1:20, t = 60 min, T = 25°C and [C₁₄mim]Cl at 500 mM.

Recycle	Cynaropicrin (wt%)
1 st	3.727 ± 0.006
2 nd	3.816 ± 0.004
3 th	4.142 ± 0.008
4 th	4.160 ± 0.002

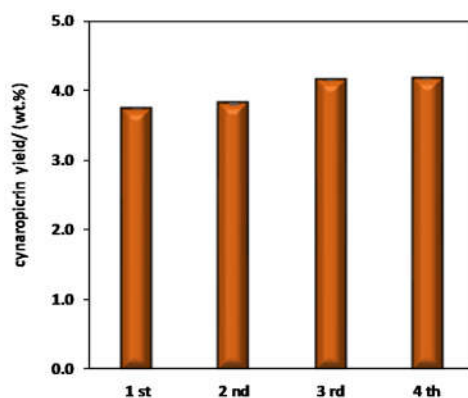


Figure S3. Weight fraction percentage of cynaropicrin extracted from the leaves of *Cynara cardunculus L.* using the surface-active IL solution and fresh biomass samples, at the following fixed conditions: S/L ratio = 1:20, t = 60 min, T = 25°C and [C₁₄mim]Cl at 500 mM.

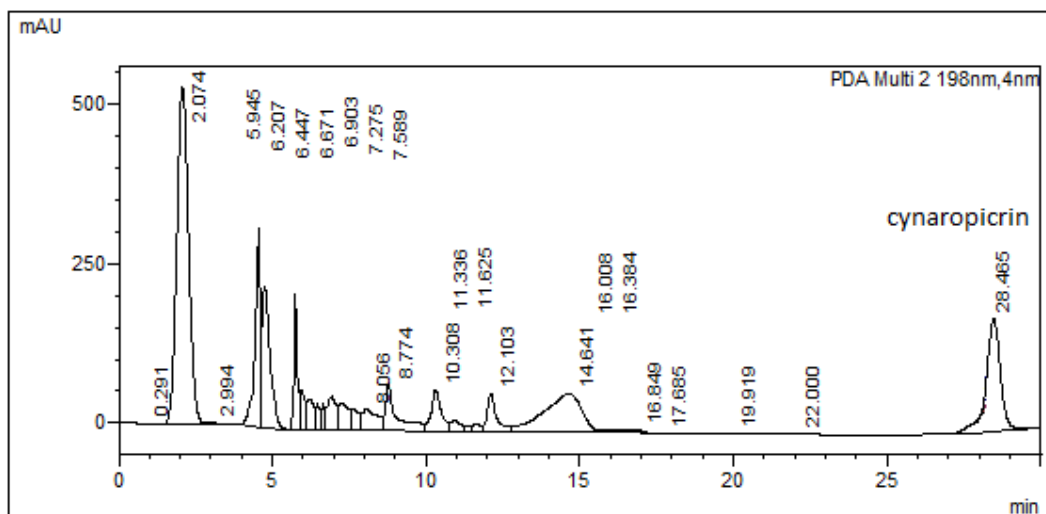


Figure S4. DAD-HPLC chromatogram of the extracted recovered from the leaves of *Cynara cardunculus* L. using the surface-active IL solution.

References

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