

Supporting information

Ionic liquid based dynamic supercritical carbon dioxide extraction of six different cannabinoids from *Cannabis sativa* L.

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Table S1 Extraction parameters for IL-SFE.

Exp.	IL	t _{Pre} / min	T _{Pre} / °C	m _{IL} / g	m _{H₂O} / g	P _{SFE} / MPa	T _{SFE} / °C
1	[C ₂ mim][OAc]	60	25	3	6	20	70
2	[C ₂ mim][OAc]	60	70	3	6	20	70
3	[C ₂ mim][OAc]	15	25	3	6	20	70
4	[C ₂ mim][OAc]	15	70	3	6	20	70
5	[C ₂ mim][OAc]	15	70	3	3	20	70
6	[C ₂ mim][OAc]	15	70	3	9	20	70
7	[C ₂ mim][OAc]	15	70	3	-	20	70
8	[C ₂ mim][OAc]	15	70	-	9	20	70
9	-	-	-	-	-	20	70
10	[C ₂ mim][OAc]	15	70	3	9	10	70
11	[C ₂ mim][OAc]	15	70	3	9	15	70
12	[C ₂ mim][OAc]	15	70	3	9	30	70
13	[C ₂ mim][OAc]	15	70	3	9	20	35
14	[C ₂ mim][OAc]	15	70	3	9	10	35
15	[Ch][OAc]	15	70	3	9	20	70
16	[C ₂ mim][DMP]	15	70	3	9	20	70

Pre: IL pre-treatment before SFE

Exp. Number corresponds to the main article

Table S2. Extracted cannabinoids by IL-SFE and conventional extraction, (n = 3 ± SD).

Exp.	Yield CBD / (mg/g)	Yield CBDA / (mg/g)	Yield Δ ⁹ -THC / (mg/g)	Yield THCA / (mg/g)	Yield CBG / (mg/g)	Yield CBGA / (mg/g)
IL-SFE						
1	4.29 ± 0.24 ^f	8.8 ± 1.0 ^{cd}	0.159 ± 0.004 ^{de}	0.306 ± 0.008 ^{def}	0.137 ± 0.007 ^d	0.092 ± 0.019 ^{fg}
2	6.58 ± 0.24 ^c	6.3 ± 0.6 ^{fg}	0.164 ± 0.008 ^{cde}	0.307 ± 0.013 ^{cdef}	0.186 ± 0.003 ^c	0.058 ± 0.017 ^g
3	5.0 ± 0.3 ^{de}	7.9 ± 0.6 ^{de}	0.169 ± 0.008 ^{cd}	0.308 ± 0.023 ^{cdef}	0.154 ± 0.008 ^d	0.067 ± 0.012 ^{fg}
4	5.29 ± 0.27 ^d	8.3 ± 0.4 ^{cde}	0.174 ± 0.004 ^{cd}	0.339 ± 0.013 ^{abcd}	0.164 ± 0.007 ^{cd}	0.082 ± 0.012 ^{fg}
5	7.45 ± 0.05 ^b	1.09 ± 0.17 ^h	0.1807 ± 0.0007 ^c	0.150 ± 0.014 ⁱ	0.226 ± 0.007 ^b	n.d.
6	4.6 ± 0.3e ^f	10.9 ± 0.4 ^{ab}	0.177 ± 0.007 ^{cd}	0.365 ± 0.011 ^{ab}	0.157 ± 0.016 ^{cd}	0.178 ± 0.003 ^{cd}
7	0.150 ± 0.021 ⁱ	0.1727 ± 0.0025 ^h	0.023 ± 0.007 ⁱ	0.0099 ± 0.0020 ^k	n.d.	n.d.
8	2.24 ± 0.12 ^h	9.8 ± 0.5 ^{bc}	0.114 ± 0.003 ^g	0.260 ± 0.019 ^g	0.0641 ± 0.0015 ^f	0.196 ± 0.007 ^{bc}
9	3.01 ± 0.04 ^g	7.1 ± 0.5 ^{ef}	0.165 ± 0.003 ^{cde}	0.190 ± 0.012 ^h	0.101 ± 0.012 ^e	0.095 ± 0.007 ^{fg}
10	3.388 ± 0.012 ^g	0.27 ± 0.06 ^h	0.0793 ± 0.0010 ^h	0.0092 ± 0.0019 ^k	0.045 ± 0.008 ^{fg}	n.d.
11	4.44 ± 0.03 ^{ef}	8.56 ± 0.18 ^{cde}	0.1596 ± 0.0015 ^{de}	0.297 ± 0.004 ^{efg}	0.158 ± 0.005 ^{cd}	0.100 ± 0.005 ^f
12	4.1 ± 0.4 ^f	10.68 ± 0.28 ^{ab}	0.163 ± 0.013 ^{cde}	0.338 ± 0.011 ^{abcd}	0.142 ± 0.028 ^d	0.213 ± 0.009 ^{bc}
13	3.29 ± 0.20 ^g	11.6 ± 0.5 ^a	0.148 ± 0.006 ^{ef}	0.345 ± 0.007 ^{abc}	0.105 ± 0.005 ^e	0.219 ± 0.013 ^b
14	3.01 ± 0.17 ^g	10.6 ± 0.6 ^{ab}	0.137 ± 0.006 ^f	0.330 ± 0.013 ^{bcde}	0.103 ± 0.007 ^e	0.145 ± 0.009 ^{be}
15	4.04 ± 0.22 ^f	11.4 ± 0.3 ^a	0.161 ± 0.005 ^{de}	0.374 ± 0.007 ^a	0.144 ± 0.011 ^d	0.258 ± 0.013 ^a
16	3.255 ± 0.028 ^g	8.6 ± 0.9 ^{cde}	0.171 ± 0.006 ^{cd}	0.278 ± 0.019 ^{fg}	0.106 ± 0.006 ^e	0.19 ± 0.03 ^{bc}
Conventional extraction (70 °C)						
17 ¹	4.24 ± 0.09 ^f	11.2 ± 0.4 ^{ab}	0.225 ± 0.006 ^b	0.274 ± 0.018 ^{fg}	0.158 ± 0.006 ^{cd}	0.294 ± 0.018 ^a
18 ²	9.50 ± 0.19 ^a	5.34 ± 0.14 ^g	0.351 ± 0.004 ^a	0.096 ± 0.005 ^j	0.300 ± 0.005 ^a	0.1396 ± 0.0023 ^e
19 ³	0.70 ± 0.18 ⁱ	0.86 ± 0.15 ^h	0.036 ± 0.009 ⁱ	0.020 ± 0.004 ^k	0.017 ± 0.004 ^g	0.015 ± 0.003 ^h

Mean values with different letters (a, b, c, etc.) within the same column are statistically different (p < 0.05)

¹2 h in EtOH; ²24 h in EtOH; ³2 h in H₂O

Exp. Number corresponds to the main article

Figure S1. General structures of investigated ionic liquids.

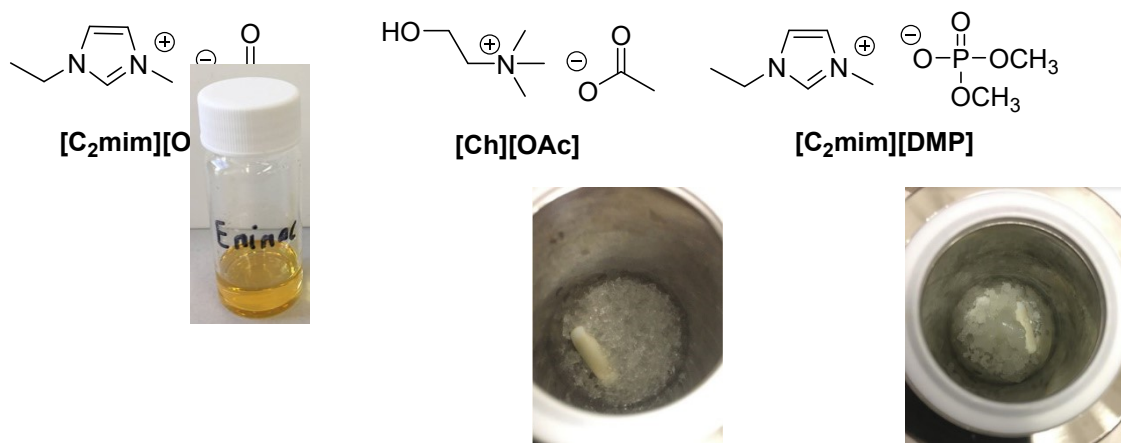


Figure S2. Extracts of different IL-SFE. Left: Extract with [C₂min][OAc]; Middle: Extract with [Ch][OAc]; Right: Extract with [C₂min][DMP].

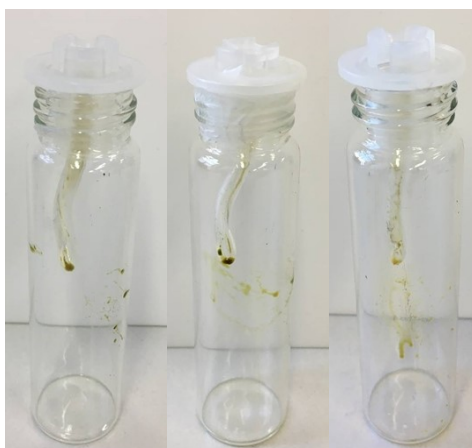


Figure S3. Residues after extraction of different IL-SFE. Left: Extract with [C₂min][OAc]; Middle: Extract with [C₂min][DMP].

Extract with [Ch][OAc]; Right:



Figure S4. ILS after purification. Left: Extract with [C₂min][OAc]; Middle: Extract with [Ch][OAc]; Right: Extract with [C₂min][DMP].

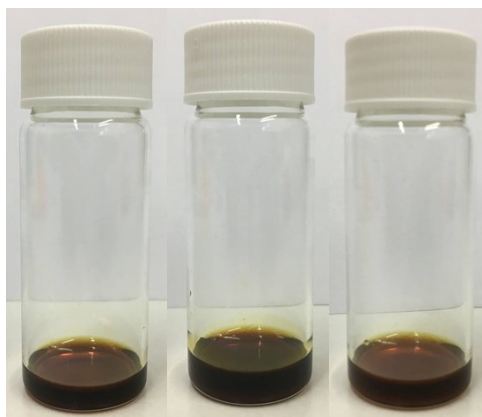


Table S3. Cannabinoid yields of supercritical CO₂ extraction with EtOH as a modifier and conventional ethanolic extraction of another batch of industrial hemp, (n = 3 ± SD). SFE was performed at various temperatures, pressures and vol% EtOH. Total flow: 1 mL/min; Static extraction 30 min; Dynamic extraction 120 min. Conventional extraction was performed at various temperatures and a hemp:EtOH ratio of 1:10.

No.	EtOH/ vol%	T _{Pre} / °C	Σ(CBD)/ (mg/g)	Σ(THC)/ (mg/g)	Σ(CBG)/ (mg/g)
SFE					
1	1	35	4.1 ± 0.4 ^c	0.086 ± 0.010 ^b	0.045 ± 0.006 ^c
2	10	35	9.48 ± 0.18 ^b	0.222 ± 0.012 ^a	0.177 ± 0.003 ^b
3	20	35	9.55 ± 0.20 ^b	0.243 ± 0.022 ^a	0.178 ± 0.005 ^b
4	20	80	0.36 ± 0.10 ^d	0.00492 ± 0.00021 ^c	n.d.
Conventional extraction					
5	-	35	10.29 ± 0.07 ^a	0.233 ± 0.006 ^a	0.2173 ± 0.0017 ^a
6	-	60	10.9 ± 0.4 ^a	0.249 ± 0.015 ^a	0.229 ± 0.010 ^a
7	-	80	10.9 ± 0.3 ^a	0.250 ± 0.012 ^a	0.231 ± 0.009 ^a

Mean values with different letters (a, b, c, etc.) within the same column are statistically different ($p < 0.05$)
n.d.: not detected

Table S4. NMR spectroscopic data of purified [C₂min][OAc], [Ch][OAc] and [C₂min][DMP] recorded in chloroform-*d*₄. All ¹H-NMR chemical shifts [ppm] are listed together with relative integral, multiplicity as well as coupling constants [Hz].

IL	δH (J in Hz)
[C ₂ min][OAc]	11.59 (s), 7.19 (d, 2.0, 1H), 7.17 (d, 2.0, 1H), 4.33 (q, 7.4, 2H), 4.02 (s, 3H), 1.96 (s, 3H), 1.52 (t, 7.4, 3H)
[Ch][OAc] ^b	4.13 (m, 2H), 3.75 (m, 2H), 3.37 (s, 9H), 1.94 (s, 3H)
[C ₂ min][DMP]	10.70 (s, 1H), 7.31 (m, 1H), 7.28 (1H, m), 4.33 (q, 7.4, 2H), 4.03 (s, 3H), 3.57 (d, 10.5, 6H), 1.53 (t, 7.4, 3H)

Figure S5. $^1\text{H-NMR}$ of purified $[\text{C}_2\text{min}][\text{OAc}]$ in chloroform- d_4 .

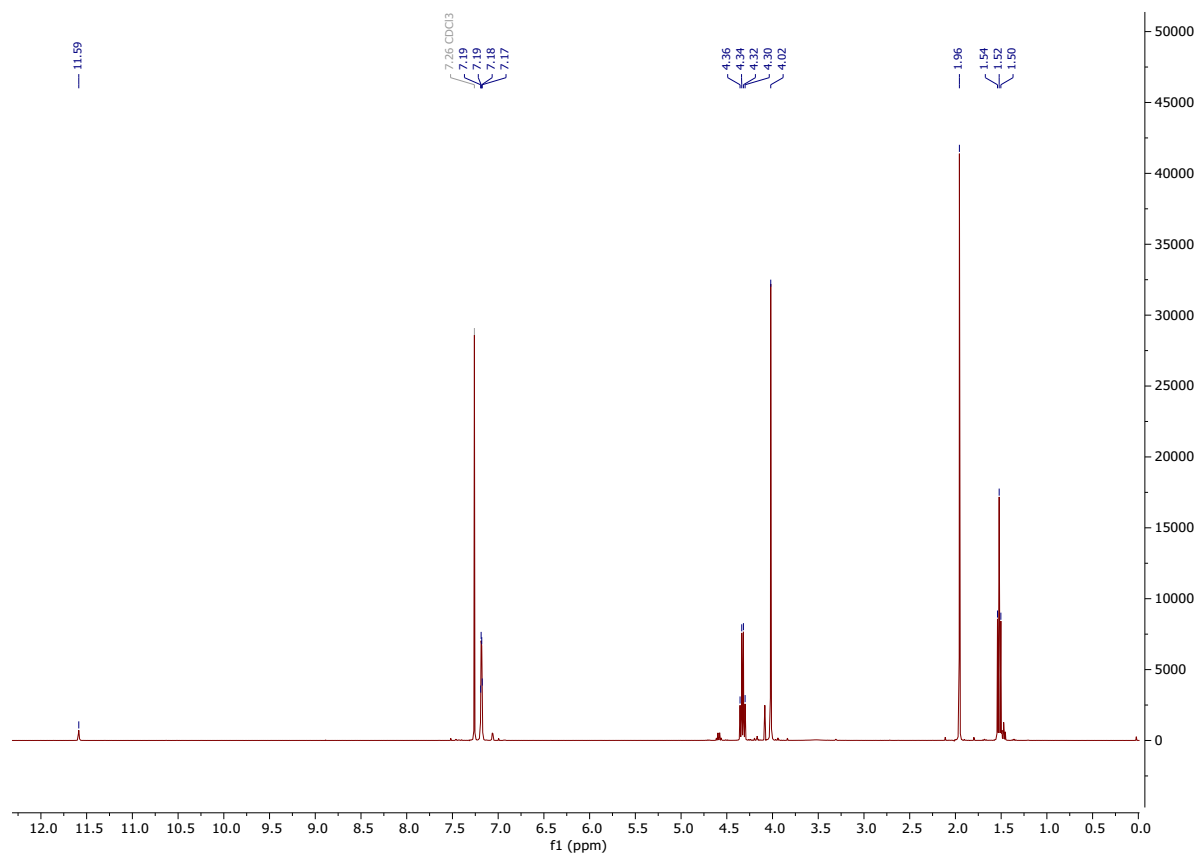


Figure S6. $^1\text{H-NMR}$ of purified $[\text{Ch}][\text{OAc}]$ in chloroform- d_4 .

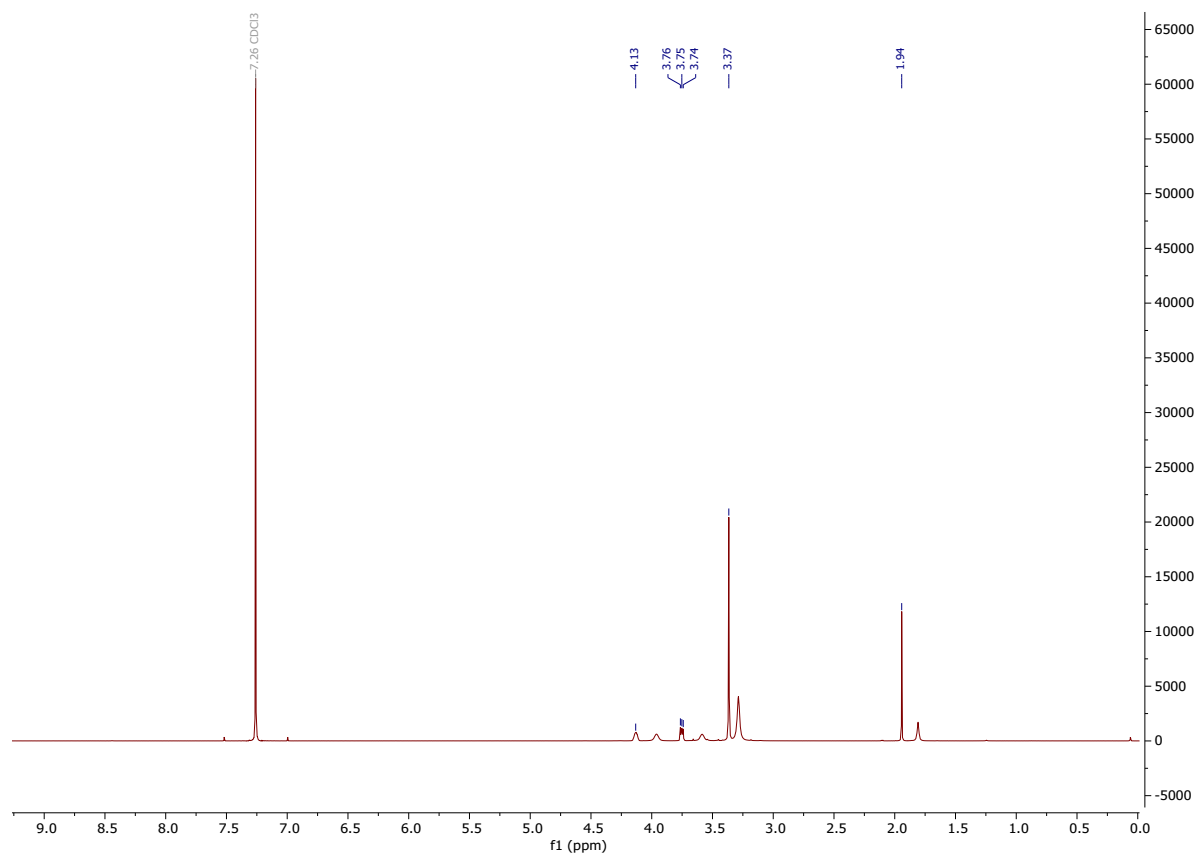


Figure S7. $^1\text{H-NMR}$ of purified $[\text{C}_2\text{min}][\text{DMP}]$ in chloroform- d_4 .

