Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Electronic Supplementary Material

Ionic liquids. ultra-sounds and microwaves: an effective combination for a sustainable extraction with higher yields.

The cumin essential oil case.

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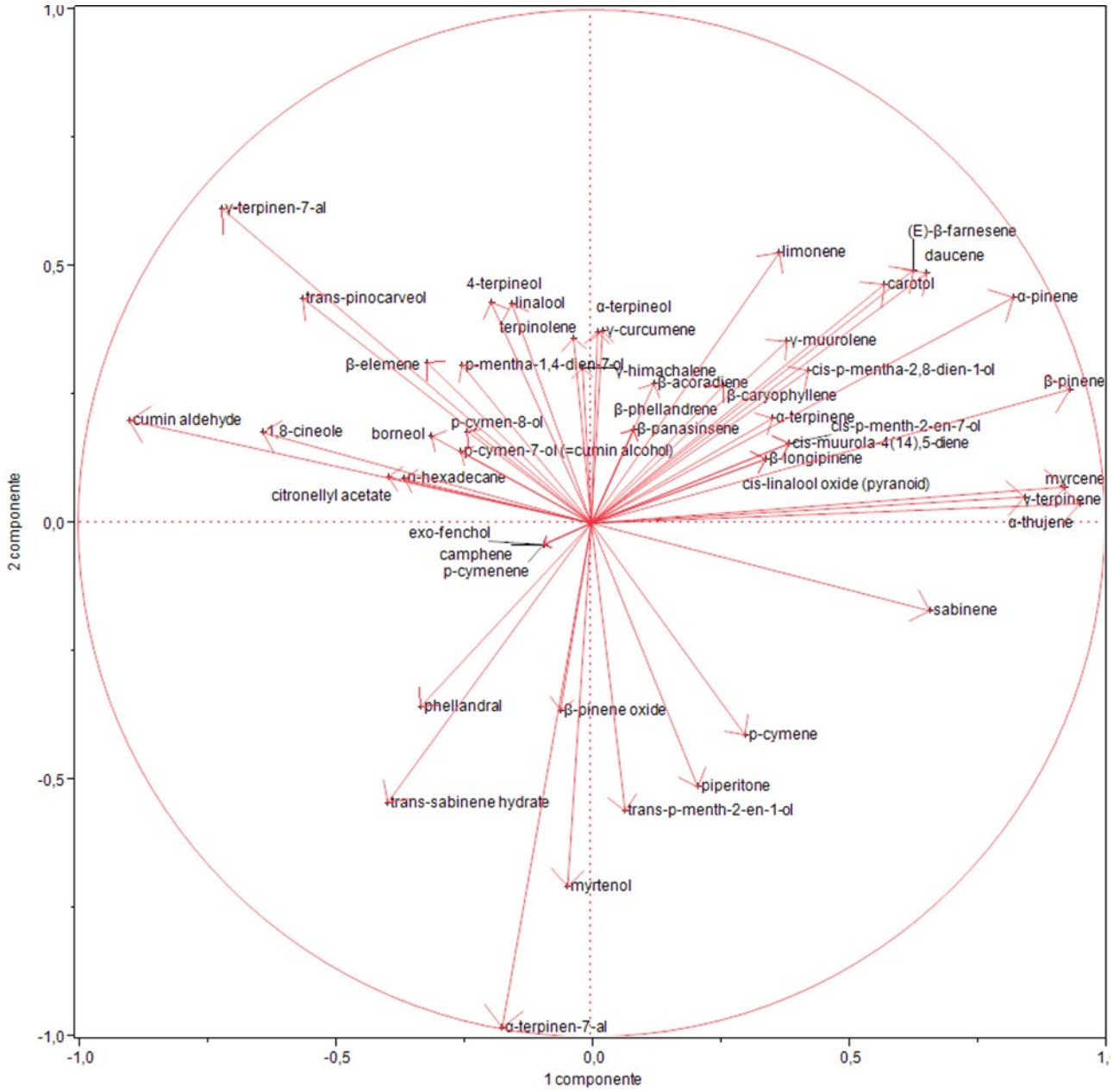

Figure S1. PCA loading plot for the total composition of the EOs based on the method of extraction.

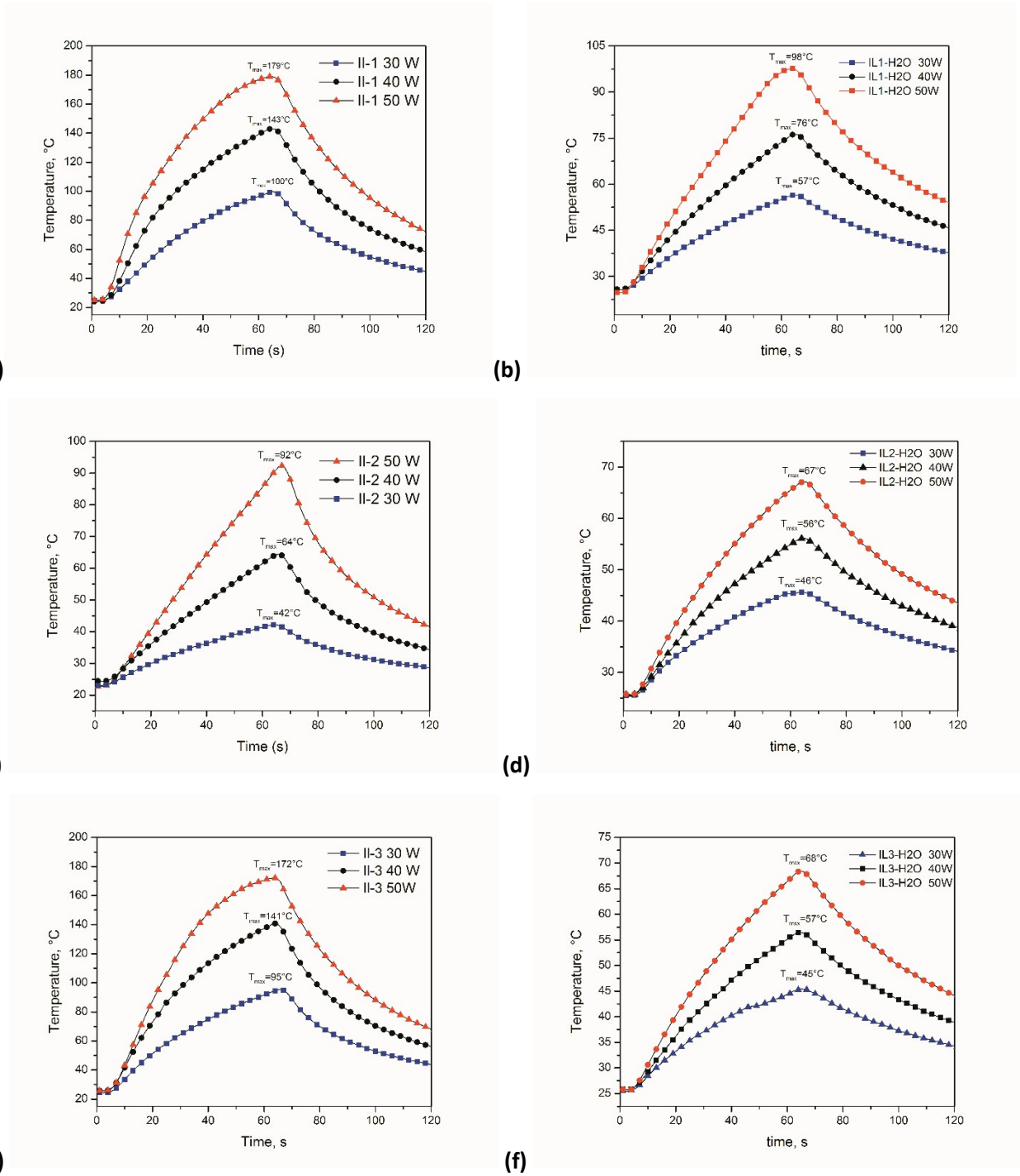

Figure S2. Temperature profiles of pure ILs (a, c, e) and ILs/water mixtures (b, d, f) at different MW powers.

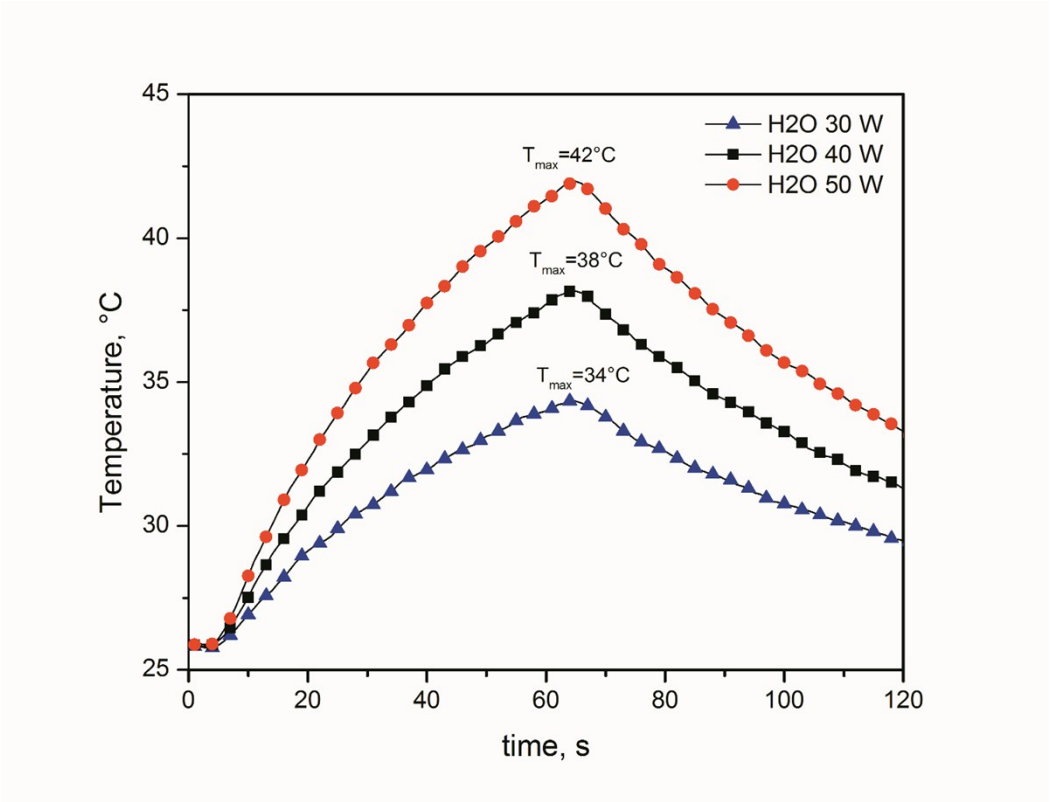

Figure S3. Temperature profile of water at different MW powers.

Table S1. Cumin EO extraction yields for all the extraction processes

Liquid medium	HD			MWHD			US-MWHD		
	Extraction yield	CI		Extraction yield	CI		Extraction yield	CI	
		<95%	>95%		<95%	>95%		<95%	>95%
water	$1.78 \pm 0.14^{G;\ a}$	0.02	0.02	$2.18 \pm 0.05^{E,F;\ b}$	0.02	0.03	$2.66 \pm 0.05^{B,C,D;\ c}$	0.03	0.03
IL1/water	$2.07 \pm 0.19^{E,F,G;\ a}$	0.02	0.03	$2.40 \pm 0.05^{C,D,E;\ a}$	0.03	0.03	$3.06 \pm 0.14^{A,B;\ a,b}$	0.03	0.03
IL2/water	$1.98 \pm 0.07^{F,G;\ a}$	0.02	0.03	$2.30 \pm 0.07^{D,E,F;\ a,b}$	0.03	0.03	$2.72 \pm 0.22^{A,B,C;\ b,c}$	0.03	0.03
IL3/water	$2.18 \pm 0.24^{E,F;\ a}$	0.02	0.03	$2.39 \pm 0.05^{C,D,E;\ a}$	0.03	0.03	$3.12 \pm 0.09^{A;\ a}$	0.03	0.03

Mean yields (% w/w) from three replications ± standard deviation. Confidence intervals (CI) at 95%. Different superscript uppercase letters (A,B,C,D,E,F,G) indicate significant differences ($P < 0.05$) among all the different distillation methods. Different superscript lowercase letters (a,b,c) indicate significant differences ($P < 0.05$) among the same distillation technology (among the same column).

Table S2. Literature data (raw material, extraction approach, extraction time, EO yield and EO composition) of cumin seeds EO extractions

Raw material		**Extraction conditions**			**EO**	**Ref.**
f.Dry seeds	**Origin**	**Approach**	**Yield (% w/w)**	**Extraction time (min)**	**Main compounds**	
Ground seeds	Turkey	SD[a]	1.4-2.8 (based on particle size)	180	1. cuminaldehyde (27.60%)	[1]
					2. γ-terpinene (17.25%)	
					3. α-terpinen-7-al (as p-mentha-1,3-dien-7-al, 15.18%)	
					4. β-pinene (10.22%)	
					5. γ-terpinen-7-al (as p-mentha-1,4-dien-7-al, 9.48%)	
Whole seeds	n.r.	SFME[b]	0.63	60	1. cuminaldehyde (37.4%)	[2]
					2. α-terpinen-7-al (29.1%)	
					3. γ -terpinene (12.9%)	
					4. *p*-cymene (12.1%)	
					5. β-pinene (5.9%)	
		HD[c]	1.4	480	1. cuminaldehyde (22.8%)	
					2. γ -terpinene (22.3%)	
					3. *p*-cymene (18.4%)	
					4. β-pinene (16.2%)	
					5. α-terpinen-7-al (14.4%)	
Ground seeds	China	SD	3.8	120	1. cuminaldehyde (36.3%)	[3]
					2. cumin alcohol (16.9%)	
					3. γ -terpinene (11.1%)	
					4. safranal (10.9%)	
Whole seeds	Bulgaria	HD	5.4	n.r.	1. cuminaldehyde (36.0%)	[4]
					2. β-pinene (19.3%)	

					3. *p*-cymene (18.4%)	
					4. γ -terpinene (15.3%)	
Ground seeds	Tunisia	HD	1.62	120	1. γ -terpinene (25.58%)	[5]
					2. 1-phenyl-1,2-ethanediol (23.16%)	
					3. cuminaldheyde (15.31%)	
					4. β-pinene (15.16%)	
					5. *p*-cymene (9.05%)	
	India		1.21		1. cuminaldheyde (22.29%)	
					2. γ -terpinene (20.20%)	
					3. *p*-cymene (18.99%)	
					4. β-pinene (15.73%)	
					5. 1-phenyl-1,2-ethanediol (13.58%)	
	Tunisia	HD	1.64	120	1. γ-terpinene (25.58%)	[6]
					2. 1-phenyl-1,2 ethanediol (23.16%)	
					3. cuminaldehyde (15.31%)	
					4. β-pinene (15.16%)	
					5. *p*-cymene (9.05%)	
	Different regions of NE Iran	HD	1.36-2.20	180	1. safranal (16.82-28.97%)	[7]
					2. cuminaldehyde (17.54-22.29%)	
					3. γ-terpinene (14.07-19.59%)	
					4. γ-terpinen-7-al (13.52-25.47%)	
					5. β-pinene (6.79-10.39%)	
Whole seeds	India	SD	2.3	480	1. cuminaldehyde (50.0%)	[8]
					2. α-terpinen-7-al (15.1%)	
					3. β-terpinen-7-al (11.6%)	

					4. β-pinene (8.9%)	
					5. γ-cymene (6,6%)	
	Iran	HD	2.7	300	1. γ-terpinene (24.30%)	[9]
					2. cuminaldehyde (21.07%)	
					3. *p*-cymene (16.56%)	
					4. β-pinene (13.74%)	
					5. safranal (12.95%)	

[a] Steam distillation; [b] Solvent Free Microwave Extraction; [c] Hydrodistillation

Table S3. Energy consumption involved in the EO extraction processes

Extraction approach	Induction period			Extraction period~		$E_{consumed, tot/g EO}$ (kWh/g)	Carbon footprint[b] ($kgCO_2$/g OE)
	t_{ind} (s)	Effective power* (W)	$E_{consumed, ind}$ (kWh)	Effective Power* (W)	$E_{consumed, extract}$ (kWh)		
IL1-CH	900	500	0.125	380	0.76	1.43	0.75
IL2-CH	900	500	0.125	380	0.76	1.49	0.79
IL1-MWHD	660	350	0.11	200	0.67	1.08	0.57
IL2-MWHD	660	350	0.11	200	0.67	1.13	0.60
IL1-USMWHD	600	MW 350	0.10	200	0.918	1.19	0.63
		US[a]	0.01	US[a]	0.06		
IL2-USMWHD	600	MW 350	0.10	200	0.621	0.97	0.51
		US[a]	0.01	US[a]	0.06		

*Effective power consumed (≈70% of nominal power); ~ extraction time: 120 min; [a] experimental value; [b] emission factor 0.527 kg / kWh[10], including an allowance for the 7.5% of losses on the national grid

Table S4 Total compositions of cumin EO extracted with all the studied extraction methods.

	Constituents	l.r.i.	BLANK	NaCl	IL1	IL2	IL3	MW	IL1-MW	IL2-MW	IL3-MW	US	IL1-US-MW	IL2-US-MW	IL3-US-MW
1	α-thujene	931	0.21±0.05	0.17	0.30±0.15	0.14±0.14	0.08±0.07	0.13±0.03	0.16±0.03	0.19±0.05	0.10±0.17	0.29±0.07	0.35±0.01	0.30±0.02	0.28±0.02
2	α-pinene	941	0.30±0.07	0.26	0.50±0.26	0.34±0.12	0.34±0.16	0.2±0.05	0.25±0.06	0.30±0.09	0.44±0.39	0.75±0.19	0.89±0.05	0.73±0.05	0.90±0.07
3	camphene	954	-	-	-	0.06±0.11	-	-	-	-	-	-	-	-	-
4	sabinene	976	0.54±0.13	0.36	0.71±0.33	0.26±0.23	-	0.29±0.07	0.4±0.06	0.36±0.10	0.10±0.18	0.68±0.15	0.80±0.04	0.57±0.06	0.32±0.02
5	β-pinene	982	7.37±1.54	5.94	10.88±5.30	6.01±3.92	5.89±2.79	4.65±1.10	5.96±1.25	7.27±2.16	6.08±4.48	12.57±3.39	12.27±0.2	10.36±0.59	13.13±1.10
6	myrcene	993	0.69±0.12	0.53	0.85±0.40	0.63±0.18	0.65±0.24	0.34±0.06	0.47±0.08	0.55±0.15	0.57±0.23	0.74±0.13	0.87±0.03	0.76±0.03	0.83±0.05
7	α-terpinene	1018	-	-	-	0.14±0.14	0.11±0.10	-	-	0.08±0.07	0.13±0.02	-	1.82±3.15	0.12±0.01	0.20±0.01
8	*p*-cymene	1027	6.75±1.16	5.20	7.49±3.18	5.91±1.00	5.55±1.91	3.73±0.59	5.14±0.69	5.93±1.40	4.62±0.92	5.50±0.50	3.51±3.09	4.95±0.13	5.63±0.26
9	β-phellandrene	1031	-	-	-	-	-	-	-	-	-	-	-	0.26±0.45	-
10	limonene	1032	0.20±0.07	0.11	0.32±0.20	0.43±0.39	0.81±0.22	0.12±0.02	0.18±0.02	0.20±0.06	0.69±0.31	0.22±0.19	0.74±0.25	0.56±0.49	0.94±0.06
11	1,8-cineole	1034	0.13±0.11	-	0.04±0.07	0.17±0.17	0.24±0.23	0.15±0.02	0.15±0.03	0.18±0.04	0.14±0.12	0.08±0.07	-	-	-
12	γ-terpinene	1062	8.58±1.18	6.80	10.76±4.77	8.46±1.86	8.25±3.65	4.69±0.73	6.44±1.03	7.32±1.59	6.51±2.51	9.85±1.75	10.13±0.16	8.70±0.39	10.66±0.68
13	terpinolene	1088	-	-	-	0.28±0.48	0.36±0.08	-	-	-	0.30±0.01	-	-	-	0.34±0.02
14	*p*-cymenene	1089	-	-	-	0.10±0.17	-	-	-	-	-	-	-	-	-
15	*trans*-sabinene hydrate	1095	0.21±0.02	0.20	0.07±0.06	-	-	0.22±0.08	0.23±0.06	-	-	0.04±0.08	-	0.08±0.07	-
16	linalool	1101	-	-	-	-	0.04±0.06	0.04±0.06	0.03±0.06	0.17±0.05	0.04±0.06	0.04±0.07	0.11±0.10	0.04±0.08	-
17	*exo*-fenchol	1120	-	-	-	0.05±0.09	-	-	-	-	-	-	-	-	-
18	*cis-p*-mentha-2,8-dien-1-ol	1122	-	-	-	-	-	-	-	-	-	-	-	-	0.03±0.06
19	*trans*-pinocarveol	1139	0.04±0.06	-	0.04±0.07	0.04±0.07	0.05±0.09	0.12±0.02	0.04±0.08	0.11±0.02	0.14±0.02	0.04±0.08	-	0.12±0.01	-
20	*trans-p*-menth-2-en-1-ol	1143	-	0.11	-	-	-	-	-	-	-	-	0.07±0.06	-	-
21	β-pinene oxide	1158	0.16±0.01	0.13	0.14±0.03	0.03±0.06	-	0.16±0.01	0.17±0.01	0.14±0.01	-	0.14±0.03	0.11±0.09	0.14±0.01	-
22	borneol	1167	-	-	-	0.11±0.19	0.08±0.07	-	-	-	0.08±0.07	-	-	-	-
23	*cis*-linalool oxide (pyranoid)	1174	-	-	-	-	-	-	-	-	-	-	0.05±0.09	-	-
24	4-terpineol	1178	0.19±0.01	0.23	0.23±0.03	0.53±0.27	0.88±0.01	0.24±0.05	0.20±0.02	0.37±0.03	0.82±0.09	0.19±0.06	0.22±0.02	0.41±0.02	0.59±0.08
25	*p*-cymen-8-ol	1183	-	-	-	-	0.09±0.08	-	-	-	0.04±0.07	-	-	-	-
26	α-terpineol	1191	-	-	-	2.14±3.71	3.04±2.70	-	-	-	2.42±2.12	-	-	-	3.26±0.28
27	myrtenol	1193	3.20±0.23	3.09	2.74±0.35	2.02±1.75	1.54±2.67	2.08±0.23	2.14±0.42	1.97±0.31	1.19±2.06	2.11±0.46	2.55±0.14	2.59±0.08	-

28	cuminaldehyde	1241	35.88±0.90	38.34	33.91±8.57	37.05±2.92	37.49±6.91	39.69±1.41	42.75±1.45	41.52±2.13	41.94±4.29	33.16±3.32	35.43±2.60	39.06±0.73	34.31±0.9
29	piperitone	1252	0.06±0.10	0.35	0.06±0.10	0.05±0.09	-	-	-	-	-	-	-	-	-
30	*cis*-*p*-menth-2-en-7-ol	1270	-	-	-	-	-	-	-	-	-	0.11±0.11	-	-	-
31	phellandral	1272	0.21±0.04	0.27	0.17±0.05	0.15±0.01	0.21±0.05	0.26±0.05	0.21±0.06	0.14±0.04	0.22±0.03	0.22±0.05	0.19±0.01	0.19±0.01	0.17±0.04
32	γ-terpinen-7-al	1275	21.85±2.12	20.37	19.69±7.43	25.31±5.47	25.35±2.59	26.45±4.09	25.83±0.77	25.80±2.05	26.41±3.92	23.26±3.59	21.68±2.68	22.68±0.88	22.66±0.80
33	α-terpinen-7-al	1284	13.21±0.70	17.55	11±2.48	9.55±5.08	8.52±1.91	8.53±0.37	8.55±0.32	7.29±1.01	5.88±0.86	6.40±0.85	6.65±0.41	6.13±0.25	5.05±0.35
34	cumin alcohol	1289	-	-	-	-	-	6.02±5.24	-	-	-	2.09±3.61	-	-	-
35	*p*-mentha-1,4-dien-7-ol	1333	-	-	-	-	0.32±0.29	1.66±1.01	0.22±0.22	0.11±0.19	0.41±0.10	0.95±0.61	0.24±0.21	-	0.10±0.17
36	piperitone	1345	0.23±0.26	-	0.10±0.17	-	-	-	-	-	-	-	-	-	-
37	citronellyl acetate	1380	-	-	-	-	-	0.05±0.09	-	-	-	-	-	-	-
38	daucene	1380	-	-	-	-	-	-	-	-	0.06±0.11	0.17±0.03	0.23±0.01	0.18±0.02	0.17±0.03
39	β-panasinsene	1383	-	-	-	-	-	-	-	-	-	-	-	0.08±0.07	-
40	β-elemene	1392	-	-	-	-	-	-	-	-	0.16±0.03	-	-	-	-
41	β-longipinene	1398	-	-	-	-	-	-	-	-	-	-	0.04±0.07	-	-
42	β-caryophyllene	1420	-	-	-	-	-	-	-	-	0.04±0.06	-	0.13±0	0.04±0.06	-
43	(*E*)-β-farnesene	1460	-	-	-	-	-	-	-	-	0.09±0.16	0.19±0.05	0.30±0.01	0.23±0.02	0.21±0.05
44	*cis*-muurola-4(14),5-diene	1462	-	-	-	-	-	-	-	-	-	0.03±0.06	-	-	-
45	β-acoradiene	1471	-	-	-	0.04±0.06	0.08±0.07	-	0.03±0.06	-	-	-	-	-	0.09±0.08
46	γ-himachalene	1475	-	-	-	-	-	0.07±0.06	0.04±0.06	-	-	0.08±0.07	-	0.11±0.10	-
47	γ-muurolene	1477	-	-	-	-	-	-	-	-	0.04±0.07	-	0.13±0.01	0.04±0.06	0.04±0.07
48	γ-curcumene	1480	-	-	-	-	-	-	-	-	0.17±0.02	-	0.16±0.01	0.06±0.11	-
49	carotol	1594	-	-	-	-	-	-	-	-	0.06±0.1	0.10±0.09	0.21±0.01	0.16±0.02	0.11±0.09
50	*n*-hexadecane	1600	-	-	-	-	-	-	0.39±0.68	-	-	-	-	-	-
	Monoterpene hydrocarbons		24.65±4.20	19.37	31.81±14.45	22.77±6.29	22.06±9.08	14.14±2.63	19.01±3.18	22.2±5.63	19.56±9.22	30.59±6.28	31.38±0.46	27.31±1.08	33.21±2.17
	Oxygenated monoterpenes		75.36±4.19	80.64	68.19±14.44	77.2±6.29	77.86±9.01	85.69±2.53	80.53±3.23	77.81±5.64	79.73±9.79	68.84±6.13	67.31±0.70	71.45±1.16	66.17±1.91
	Sesquiterpene hydrocarbons		-	-	-	0.04±0.06	0.08±0.07	0.07±0.06	0.07±0.06	-	0.56±0.4	0.47±0.18	1±0.06	0.74±0.19	0.51±0.21
	Oxygenated		-	-	-	-	-	-	-	-	0.06±0.1	0.1±0.09	0.21±0.01	0.16±0.02	0.11±0.09

sesquiterpenes													
Non-terpene derivatives	-	-	-	-	-	-	0.39±0.68	-	-	-	-	-	-
Total identified (%):	100	100	99.8	100	100	99.7	100	100	100	100	99.7	99.6	100

[a] Linear retention indices on a DB5 column. [b] Not detected.

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