Supporting Information

Quantitation of select terpenes/terpenoids and nicotine using gas chromatography–mass spectrometry with high-temperature headspace sampling

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Table S1. Molecular ions used for selected ion monitoring (SIM) analysis of terpenes/terpenoids and nicotine in headspace GC-MS.

ID	Compound	Retention time (min)	Quantitation (*m/z*)	Qualifiers (*m/z*)
1	α-pinene	4.45	93	77, 91
2	camphene	4.76	79	93, 121
3	β-myrcene	5.07	93	69, 91
4	(–)-β-pinene	5.20	93	69, 92
5	δ-3-carene	5.60	91	79, 93
6	α-terpinene	5.76	136	93, 121
7	*cis*-β-ocimene	5.84	79	91, 93
8	(+)-limonene	5.95	67	69, 107
9	*p*-cymene	6.02	117	119, 134
10	*trans*-β-ocimene	6.10	93	79, 91
11	8-cineole (eucalyptol)	6.22	81	139, 154
12	γ-terpinene	6.46	91	93, 136
13	terpinolene	7.06	121	93, 136
14	*cis*-linalool oxide	7.26	111	59, 94
15	*trans*-linalool oxide	7.55	111	59, 94
–	(±)-linalool-d_3	7.63	96	55, 69, 74
16	linalool	7.64	121	71, 93
17	(–)-isopulegol	8.61	67	55, 121
18	α-terpineol	9.20	121	59, 93
19	citronellol	9.45	95	55, 81
20	nerol	9.50	93	67, 69
21	geraniol	9.74	93	68, 69
22	β-damascenone	11.09	121	69, 105
23	β-caryophyllene	11.29	161	133, 189
24	β-damascone	11.34	177	69, 192
25	α-humulene	11.56	80	93, 147
26	*cis*-nerolidol	11.97	69	93, 107
27	*trans*-nerolidol	12.18	107	69, 136
28	(–)-guaiol	12.62	161	59, 204
29	(–)-caryophyllene oxide	12.71	93	79, 121
30	(–)-α-bisabolol	13.04	119	69, 105
31	nicotine	10.86	162	84, 133

Table S2. Molecular precursor and product ions used for selected reaction monitoring (SRM) analysis of terpenes/terpenoids in GC-MS/MS cross-validation.

ID	Compound	Retention time (min)	Quantitation (*m/z*)	Qualifiers (*m/z*)
1	α-pinene	4.74	93 → 77 (12)	93 → 91 (6)
2	camphene	5.07	93 → 77 (10)	121 → 93 (5)
3	β-myrcene	5.43	93 → 77 (10)	93 → 91 (6)
4	(–)-β-pinene	5.53	93 → 77 (10)	93 → 91 (6)
5	δ-3-carene	5.96	93 → 77 (10)	105 → 79 (5)
6	α-terpinene	6.13	93 → 77 (12)	105 → 79 (5)
7	*cis*-β-ocimene	6.22	93 → 77 (10)	121 → 93 (5)
8	(+)-limonene	6.33	107 → 91 (10)	93 → 97 (12)
9	*p*-cymene	6.39	134 → 119 (6)	119 → 117 (8)
10	*trans*-β-ocimene	6.51	93 → 77 (10)	121 → 93 (5)
11	8-cineole (eucalyptol)	6.60	108 → 93 (6)	108 → 77 (20)
12	γ-terpinene	6.85	136 → 93 (8)	136 → 121 (6)
13	terpinolene	7.42	136 → 121 (8)	121 → 93 (6)
14	*cis*-linalool oxide	7.62	94 → 79 (6)	94 → 77 (20
15	*trans*-linalool oxide	7.90	94 → 79 (6)	94 → 77 (20
–	(±)-linalool-d_3	7.95	74 → 43 (8)	96 → 79 (10)
16	linalool	7.99	93 → 77 (12)	93 → 91 (6)
17	(–)-isopulegol	8.89	121 → 93 (10)	111 → 55 (10)
18	α-terpineol	9.45	59 → 31 (8)	59 → 43 (22)
19	citronellol	9.70	138 → 95 (6)	95 → 67 (8)
20	nerol	9.75	93 → 77 (12)	93 → 91 (6)
21	geraniol	9.98	69 → 41 (6)	69 → 39 (14)
22	β-damascenone	11.32	121 → 105 (8)	121 → 79 (14)
23	β-caryophyllene	11.50	93 → 77 (12)	133 → 105 (8)
24	β-damascone	11.57	177 → 121 (12)	177 → 149 (8)
25	α-humulene	11.78	93 → 77 (12)	93 → 91 (6)
26	*cis*-nerolidol	12.19	93 → 77 (12)	136 → 121 (5)
27	*trans*-nerolidol	12.36	93 → 77 (12)	136 → 121 (5)
28	(–)-guaiol	12.71	161 → 105 (8)	161 → 119 (8)
29	(–)-caryophyllene oxide	12.78	121 → 93 (5)	161 → 105 (5)
30	(–)-α-bisabolol	13.02	109 → 67 (5)	93 → 77 (12)

Collision energies (V) are included in parentheses following each SRM transition.

Table S3. Calibration scheme for validating the terpenoid quantitation method for plant tissue using HS GC-MS.

Calibration level	Concentration (ng/mL)	Source stock concentration (µg/mL)
Cal 9	4000	800
Cal 8	3000	600
Cal 7	2000	400
Cal 6	1000	200
Cal 5	500	100
Cal 4	200	40
Cal 3	100	20
Cal 2	50	10
Cal 1	25	5

Each calibration curve sample includes 25 µL source stock, 25 µL 400 µg/mL (±)-linalool-*d3* (internal standard), and 5000 µL glycerol.

Table S4. Calibration scheme for validating the terpenoid and nicotine quantitation method for vaping liquids using HS GC-MS.

Calibration level	Concentration		Source stock concentration	
	Terpenoid (ng/mL)	Nicotine (µg/mL)	Terpenoid (ng/mL)	Nicotine (mg/mL)
Cal 9	3000	300	600	60
Cal 8	2000	200	400	40
Cal 7	1000	100	200	20
Cal 6	500	50	100	10
Cal 5	200	20	40	4
Cal 4	100	10	20	2
Cal 3	50	5	10	1
Cal 2	25	2.5	5	0.5
Cal 1	10	1	2	0.2

Each calibration curve sample includes 25 µL source stock, 25 µL 400 µg/mL (±)-linalool-*d3* (internal standard), and 5000 µL glycerol.

Table S5. Method validation using stinging nettle as the blank matrix for quantitating terpenoids in plant materials by GC-MS/MS analysis with direct injection of liquid extracts.

ID	Analyte	Limit (ppm)		Recovery (%)			RSD (%)	
		MDL	MRL	low (200 ppm)	mid (500 ppm)	high (2000 ppm)	Intraday	Interday
1	α-pinene	44.1	200	73.3	87.2	81.1	3.09	22.6
2	camphene	51.2	200	73.2	81.2	82.9	3.09	28.7
3	β-myrcene	52.0	200	75.2	85.8	83.8	3.55	26.4
4	(–)-β-pinene	53.3	200	74.3	84.7	83.5	3.26	27.3
5	δ-3-carene	57.3	200	73.2	84.4	82.1	3.19	27.9
6	α-terpinene	46.4	200	77.2	85.6	84.9	3.37	26.8
7	*cis*-β-ocimene	51.4	200	74.6	85.1	84.2	3.41	27.0
8	(+)-limonene	38.1	200	73.3	87.2	83.1	3.66	25.9
9	*p*-cymene	47.4	200	73.6	84.5	82.9	3.88	24.9
10	*trans*-β-ocimene	45.0	200	75.1	87.4	83.8	3.64	26.1
11	8-cineole (eucalyptol)	46.8	200	77.5	86.6	83.3	3.21	24.9
12	γ-terpinene	45.2	200	75.1	87.0	84.0	3.40	23.3
13	terpinolene	48.4	200	74.8	86.8	84.7	3.56	24.3
14	*cis*-linalool oxide	49.6	200	96.6	94.9	101	3.67	22.1
15	*trans*-linalool oxide	56.2	200	97.5	94.9	100	3.30	22.2
16	linalool	38.5	200	78.1	90.5	85.2	3.39	22.0
17	(–)-isopulegol	60.0	200	82.4	87.9	85.9	3.99	29.1
18	α-terpineol	53.3	200	95.9	94.1	102	3.97	20.6
19	citronellol	48.4	200	94.2	87.5	98.0	4.84	27.5
20	nerol	48.4	200	90.5	85.4	97.0	3.34	23.5
21	geraniol	50.8	200	70.4	79.3	85.6	4.70	21.3
22	β-damascenone	53.2	200	93.3	94.4	96.1	5.10	24.1
23	β-caryophyllene	56.7	200	80.9	86.3	87.4	5.56	29.0
24	β-damascone	58.6	200	81.2	94.2	83.5	5.53	27.8
25	α-humulene	56.4	200	81.5	86.8	87.1	5.90	28.4
26	*cis*-nerolidol	63.1	200	82.1	90.3	87.4	6.95	27.2
27	*trans*-nerolidol	49.7	200	81.5	86.4	86.8	7.97	29.0
28	(–)-guaiol	59.6	200	85.5	87.3	88.8	7.71	28.3
29	(–)-caryophyllene oxide	34.7	200	85.8	78.5	86.6	10.5	28.0
30	(–)-α-bisabolol	66.3	200	87.0	86.7	88.4	11.2	30.0

Concentrations are presented based on plant weight. MDL: method detection limit. MRL: method reporting limit. The calibration ranges were from 400 to 10,000 ppm.

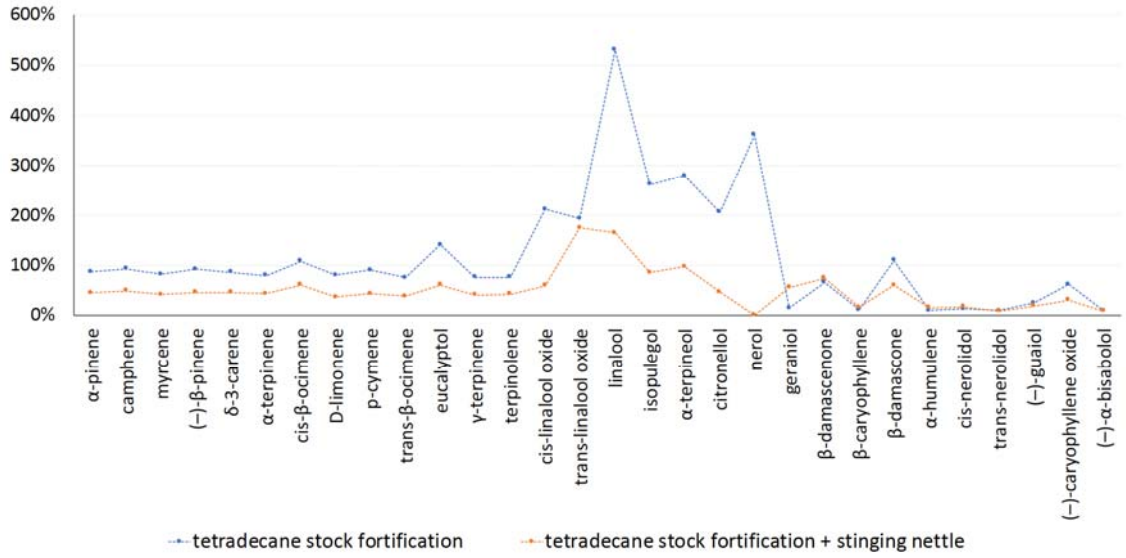

Figure S1. Relative recoveries ($n = 3$) of select terpenes/terpenoids in different headspace liquids: brine incubated at 85 °C compared to glycerol incubated at 180 °C. Data are response ratios of analytes in brine:glycerol. Blue line represents analysis of headspace solvents fortified with terpenes/terpenoids in tetradecane stocks. Organe line represents analysis of stinging nettle (as matrix surrogate) fortified with terpenes/terpenoids in tetradecane stocks.

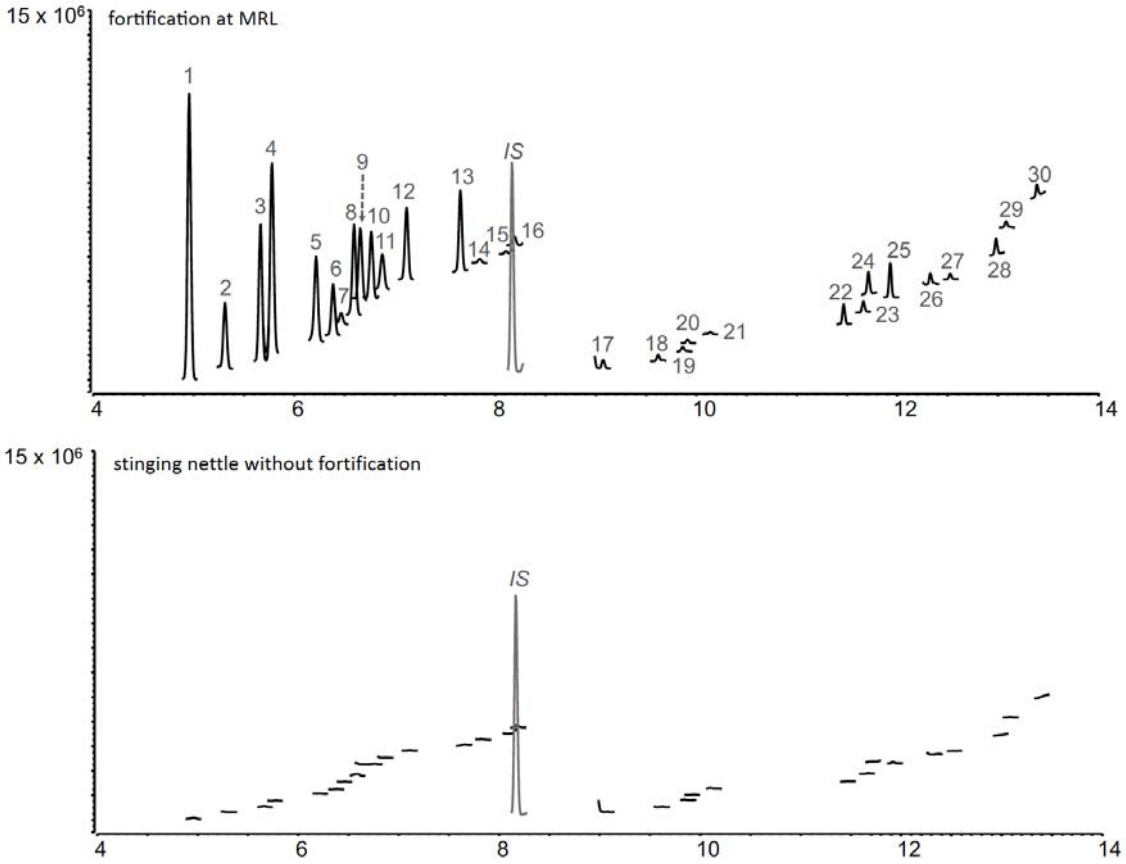

Figure S2. Sample SIM chromatogram for the 30 terpenoids under investigation in the surrogate matrix, dry stinging nettle tissue (bottom), compared to that of standards at method reporting limit concentrations (top). Names and structures of the terpenoids are depicted in Figure 1. *IS* is internal standard, (±)-linalool-*d3*.