SUPPLEMENTARY MATERIAL – SPME-GCMS ANALYSIS

Analytical conditions

VOCs were extracted using Solid Phase Microextraction (SPME) with 1-cm fibre coated with 50/30-µm divinyl benzene/carboxen/poly-dimethylsiloxane (DVB/CAR/PDMS). Three replicates of 0.5 grams of each sample were placed in a 20-ml screw-capped clear vial. The sample was incubated at 70°C for 20 minutes. The extraction time with SPME was set at 70°C for 40 minutes. After sampling, the fibre was immediately injected into the GC-MS injection port at 250°C for 5 minutes. VOCs were determined by gas chromatography/mass spectrometry (GC-MS). Analysis was carried out using Agilent Technologies 7820A/5977B Series MSD with Supelco SPB-624 (20 m x 0.18 mm ID x 1.0 µm film thickness). The oven temperature was initially set at 40°C for 5 minutes, then increased to 100°C at a 4°C/min rate, increased to 220°C at a 6°C/min rate and maintained for 20 minutes. Helium was used as carrier gas at a flow rate 0.8 ml/min and the ion source temperature was set to 230°C. The mass analyser operated in scan mode in the range 25 – 300 m/z.

Data processing

SPME-GCMS data processing was carried out using MS-DIAL software, which provides a complete workflow for mass spectral deconvolution, peak alignment, integration and annotation[1,2]. Peak annotation was performed against the NIST 14 mass spectral library. Matches with dot product/reverse dot product scores higher than 0.7 were retained.

Mass peak annotation

The samples analysed by SPME-GCMS analysis were a subset of those analysed by PTR-ToF-MS and included both softwood (n = 19) and hardwood (n = 16). Mass peak annotation was carried out according to the following procedure:

(1) Sum formula was estimated using measured exact mass from PTR-ToF-MS.
(2) Using SPME-GCMS data, a list of candidate compounds was compiled having a sum formula matching the reagent ion sum formula from step (1).
(3) Linear correlation was evaluated between PTR-ToF-MS mass peak and corresponding peak areas of candidate compound obtained from step (2).
(4) Whenever possible, matching references were sought in the literature on wood and TMW VOC analysis.

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[1] H. Tsugawa, T. Cajka, T. Kind, Y. Ma, B. Higgins, K. Ikeda, M. Kanazawa, J. VanderGheynst, O. Fiehn, M. Arita, MS-DIAL: data-independent MS/MS deconvolution for comprehensive metabolome analysis, Nat Methods. 12 (2015) 523–526. https://doi.org/10.1038/nmeth.3393.

[2] Z. Lai, H. Tsugawa, G. Wohlgemuth, S. Mehta, M. Mueller, Y. Zheng, A. Ogiwara, J. Meissen, M. Showalter, K. Takeuchi, T. Kind, P. Beal, M. Arita, O. Fiehn, Identifying metabolites by integrating metabolome databases with mass spectrometry cheminformatics, Nat Methods. 15 (2018) 53–56. https://doi.org/10.1038/nmeth.4512.

Table S1. List of PTR-ToF-MS mass peaks. A tentative identification is provided when possible.

Measured mass (Th)	Theoretical mass (Th)	Sum formula	Tentative identification	Reference*	r†	*p*-value‡	chemical class
31.018	31.018	CH_3O^+	Formaldehyde	A			carbonyls
34.037	34.037	$^{13}CH_5O^+$	Methanol	A			alcohols
41.038	41.039	$C_3H_5^+$	Fragment				fragments
42.010	not available	not available	Unknown				unknown
44.057	44.058	$^{13}CC_2H_7^+$	Fragment				fragments
46.036	46.037	$^{13}CCH_5O^+$	Acetaldehyde	A			carbonyls
47.012	47.013	$CH_3O_2^+$	formic acid	A	0.848	<0.001	acids
53.002	not available	not available	Unknown				unknown
53.039	53.039	$C_4H_5^+$	Fragment				fragments
55.054	55.054	$C_4H_7^+$	Fragment				fragments
57.033	57.033	$C_3H_5O^+$	Unknown				unknown
57.070	57.070	$C_4H_9^+$	Fragment				fragments
60.019	60.016	$^{13}CCH_3O_2^+$	Unknown				unknown
60.052	60.052	$^{13}CC_2H_7O^+$	acetone/propanal (^{13}C isotope)	A			carbonyls
62.032	62.032	$^{13}CCH_5O_2^+$	acetic acid (^{13}C isotope)	A,B,F,G	0.719	0.029	acids
65.037	65.039	$C_5H_5^+$	fragment				fragments
65.058	not available	not available	Unknown				unknown
67.023	not available	not available	Unknown				unknown
69.033	69.033	$C_4H_5O^+$	Furan	H	0.767	0.005	furans
69.069	69.070	$C_5H_9^+$	Fragment				unknown
71.048	71.049	$C_4H_7O^+$	Unknown				unknown
71.085	71.086	$C_5H_{11}^+$	Fragment				unknown
73.028	73.028	$C_3H_5O_2^+$	Unknown				unknown

73.064	73.065	$C_4H_9O^+$	Butanal	A			carbonyls
74.034	74.032	$^{13}CC_2H_5O_2^+$	Unknown				unknown
75.995	not available	not available	Unknown				unknown
76.047	76.047	$^{13}CC_2H_7O_2^+$	propanoic acid/methyl acetate (^{13}C isotope)	A,F			acids/esters
79.053	79.054	$C_6H_7^+$	Fragment				fragment
82.027	not available	not available	Unknown				unknown
83.045	83.049	$C_5H_7O^+$	Unknown				unknown
83.085	83.086	$C_6H_{11}^+$	Fragment				fragments
85.028	not available	not available	Unknown				unknown
85.064	85.065	$C_5H_9O^+$	Unknown				unknown
85.096	not available	not available	Unknown				unknown
87.043	87.044	$C_4H_7O_2^+$	Diacetyl	G			carbonyls
87.079	87.080	$C_5H_{11}O^+$	Pentanal	A	0.667	0.049	carbonyls
89.059	89.060	$C_4H_9O_2^+$	methyl-propionate	F,G	0.671	0.023	esters
95.020	not available	not available	unknown				unknown
95.044	95.049	$C_6H_7O^+$	phenol	A,E,F			phenols
98.031	98.032	$^{13}CC_4H_5O_2^+$	furfural	A,B,C,D,E,F	0.985	<0.001	furans
99.080	99.080	$C_6H_{11}O^+$	hexenal	A			carbonyls
101.057	101.060	$C_5H_9O_2^+$	2,3-Pentanedione	E,F			carbonyls
101.095	101.096	$C_6H_{13}O^+$	hexanal	A,B,F	0.691	0.039	carbonyls
103.036	103.039	$C_4H_7O_3^+$	dihydro-hydroxyfuranone	E,F			furans
103.075	103.075	$C_5H_{11}O_2^+$	pentanoic acid/ethyl-propanoate	B,G			acids/esters
105.067	105.070	$C_8H_9^+$	unknown				unknown
107.047	107.049	$C_7H_7O^+$	benzaldehyde	A,C,E,F	0.679	0.044	carbonyls
107.085	107.086	$C_8H_{11}^+$	ethylbenzene	F			aromatics
109.061	109.065	$C_7H_9O^+$	methyl-phenol	C			phenols
109.101	109.101	$C_8H_{13}^+$	unknown				unknown

111.043	111.044	$C_6H_7O_2^+$	methyl-furfural	E,F	0.965	<0.001	furans
111.075	not available	not available	unknown				unknown
111.115	111.117	$C_8H_{15}^+$	unknown				unknown
113.059	113.060	$C_6H_9O_2^+$	2-hydroxy-3-methyl-2-cyclopenten-1-one	F,G			carbonyls
113.097	113.096	$C_7H_{13}O^+$	2-heptenal, (z)-	G			carbonyls
115.039	115.039	$C_5H_7O_3^+$	4-hydroxy-5,6-dihydro-(2*H*)-pyran-2-one	E,F			carbonyls
115.076	115.075	$C_6H_{11}O_2^+$	2,5-hexanedione				carbonyls
115.112	115.112	$C_7H_{15}O^+$	2-heptanone	A	0.610	0.046	carbonyls
117.055	117.055	$C_5H_9O_3^+$	acetol acetate	E,F			carbonyls
117.091	117.091	$C_6H_{13}O_2^+$	hexanoic acid	A,B,F			acids
119.082	119.086	$C_9H_{11}^+$	unknown				unknown
121.049	121.050	$C_4H_9O_4^+$	methyl acetoxyacetate				esters
121.102	121.101	$C_9H_{13}^+$	unknown				unknown
123.044	123.044	$C_7H_7O_2^+$	Benzaldehyde, 2-hydroxy-	C			carbonyls
123.081	123.080	$C_8H_{11}O^+$	Phenol, 2,3-dimethyl-	C	0.829	0.005	phenols
123.117	123.117	$C_9H_{15}^+$	unknown				unknown
125.060	125.060	$C_7H_9O_2^+$	1-Propanone, 1-(2-furanyl)-/2-Acetyl-5-methylfuran	C,E,F	0.815	0.002	furans
125.097	125.096	$C_8H_{13}O^+$	4,5-dimethyl-2-ciclohexen-1-one	E,F			carbonyls
125.133	125.132	$C_9H_{17}^+$	unknown				unknown
127.040	127.039	$C_6H_7O_3$+	3-Furancarboxylic acid, methyl ester/Methyl 2-furoate/5-Hydroxymethylfurfural	E,F,G	0.770	0.005	furans
127.075	127.075	$C_7H_{11}O_2^+$	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	E,F	0.763	0.006	carbonyls
127.112	127.112	$C_8H_{15}O^+$	2-Octenal, (E)-	A,E,F,G	0.767	0.005	carbonyls
129.092	129.091	$C_7H_{13}O_2^+$	3,6-Heptanedione		0.615	0.043	carbonyls
129.128	129.127	$C_8H_{17}O^+$	Octanal	A			carbonyls
131.072	131.070	$C_6H_{11}O_3^+$	2-Butanone, 1-(acetyloxy)-	E,F	0.747	0.008	carbonyls
131.107	131.107	$C_7H_{15}O_2^+$	heptanoic acid	B			acids
135.053	not available	not available	unknown				unknown

135.117	135.117	$C_{10}H_{15}^+$	Bicyclo[3.1.0]hex-2-ene, 4-methylene-1-(1-methylethyl)- / p-Mentha-1,5,8-triene	A	0.895	0.001	terpenes
138.137	138.136	$^{13}CC_9H_{17}^+$	alpha- and beta-pinene, camphene, D-limonene and delta-carene	A	0.684	0.042	terpenes
139.114	139.112	$C_9H_{15}O^+$	furan, 2-pentyl-	A,G	0.816	0.002	furans
141.127	141.127	$C_9H_{17}O^+$	2-Nonenal, (E)-	A,E,F,G	0.815	0.022	carbonyls
143.106	143.107	$C_8H_{15}O_2^+$	unknown				unknown
143.143	143.143	$C_9H_{19}O^+$	Nonanal	A,B			carbonyls
145.120	145.122	$C_8H_{17}O_2^+$	Octanoic acid	B			acids
147.116	not available	not available	unknown				unknown
149.096	149.096	$C_{10}H_{13}O^+$	Anethole/2-Butanone, 4-phenyl-	A	0.959	<0.001	carbonyls
151.113	151.112	$C_{10}H_{15}O^+$	Bicyclo[3.1.1]hept-3-en-2-one, 4,6,6-trimethyl-, (1S)-/2-Cyclohexen-1-one, 3-methyl-6-(1-methylethylidene)-		0.872	0.002	terpenes
153.128	153.127	$C_{10}H_{17}O^+$	Camphenol, 6-/2-Cyclohexen-1-ol, 1-methyl-4-(1-methylethenyl)-, trans-/Carveol/cis-p-mentha-1(7),8-dien-2-ol	B,G	0.945	<0.001	terpenes
155.106	155.107	$C_9H_{15}O_2^+$	3,5-dimethyl-2-hydroxy-2-ciclopenten-1-one	E,F			carbonyls
155.143	155.143	$C_{10}H_{19}O^+$	Fenchol / Cyclohexanol,1-methyl-4-(1-methylethenyl)-/ Cyclopentanol, 1,2-dimethyl-3-(1-methylethenyl)- / Bicyclo[2.2.1]heptan-2-ol,2,3,3-trimethyl- / 3-Cyclohexen-1-ol, 4-methyl-1-(1-methylethyl)-,(R)- / alpha terpineol	A,B,G	0.928	<0.001	terpenes
157.089	157.086	$C_8H_{13}O_3^+$	unknown				unknown
159.138	159.138	$C_9H_{19}O_2^+$	Nonanoic acid	B			acids
161.129	161.132	$C_{12}H_{17}^+$	unknown				unknown
163.148	163.148	$C_{12}H_{19}^+$	unknown				unknown
175.147	not available	not available	unknown				unknown
179.145	179.143	$C_{12}H_{19}O^+$	5,5,8-Trimethyl-3,6,7-nonatrien-2-one				carbonyls
191.180	not available	not available					unknown
205.196	205.195	$C_{15}H_{25}^+$	alpha-muurolene, beta-isocaryophyllene and longifolene	A	0.856	0.003	terpenes
217.196	not available	not available					unknown

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[†] Pearson's correlation coefficient. When more than one candidate copound is available, correlation is computed using the sum of their peak areas.