

**Table S1.** The content of volatile compounds identified in unfermented (UFC) and fermented (FC) coffee brew with four grinding size coffee beans by HS-SPME-GC-MS

No.	Compound Name	Molecular formula	RT (min)	LRI	LRI (NIST)	Conc. (ng/mL)									
						UFC1	UFC2	UFC3	UFC4	UFC5	FC1	FC2	FC3	FC4	FC5
Size 1 (250 μm)															
Pyridines															
1	Pyridine	C <sub>5</sub> H <sub>5</sub> N	10.49	1170	1169	0.36	0.72	0.48	0.99	0.78	0.48	0.61	0.38	0.72	0.29
Pyrazines															
2	2-Methylpyrazine	C <sub>5</sub> H <sub>6</sub> N <sub>2</sub>	13.01	1250	1252	1.98	1.43	1.59	1.64	2.15	2.40	2.24	2.21	2.05	1.61
3	2,5-Dimethylpyrazine	C <sub>5</sub> H <sub>6</sub> N <sub>2</sub>	14.73	1305	1316	0.79	0.65	0.66	0.84	1.06	1.01	0.97	0.93	0.99	0.67
4	2,6-Dimethylpyrazine	C <sub>6</sub> H <sub>8</sub> N <sub>2</sub>	14.92	1311	1314	1.12	0.96	1.05	1.16	1.44	1.50	1.46	1.38	1.38	1.07
5	2-Ethylpyrazine	C <sub>6</sub> H <sub>8</sub> N <sub>2</sub>	15.05	1316	1325	0.83	0.67	0.67	0.84	0.93	0.93	1.00	0.91	0.91	0.70
6	2-Ethyl-6-methylpyrazine	C <sub>7</sub> H <sub>10</sub> N <sub>2</sub>	16.55	1368	1375	0.93	0.84	0.77	1.10	1.43	1.09	1.28	1.08	1.26	0.89
7	2-Ethyl-5-methylpyrazine	C <sub>7</sub> H <sub>10</sub> N <sub>2</sub>	16.72	1374	1380	0.90	0.73	0.67	1.03	1.22	1.06	1.07	0.99	1.13	0.83
Acids															
8	Acetic acid	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	18.34	1432	1432	0.98	0.83	0.77	0.88	0.89	0.75	0.84	0.75	0.76	0.78
Furan and Furanic compounds															
9	Furfural	C <sub>5</sub> H <sub>4</sub> O <sub>2</sub>	18.54	1440	1443	6.09	10.53	8.02	10.26	12.03	7.67	10.32	7.29	9.29	5.89
10	2-Furanmethanol	C <sub>5</sub> H <sub>6</sub> O <sub>2</sub>	23.62	1646	1658	2.99	3.69	3.37	3.46	4.10	3.15	3.64	3.14	3.84	2.65
11	5-Methylfurfural	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	21.37	1551	1555	3.72	7.10	5.07	6.52	8.03	4.07	7.36	3.94	6.49	4.07
12	Furfuryl acetate	C <sub>7</sub> H <sub>8</sub> O <sub>3</sub>	20.52	1516	1523	2.00	3.12	1.93	2.84	3.16	1.49	5.00	1.67	2.99	2.22
Ketones															
13	2-Acetylfuran	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	19.64	1481	1484	1.47	2.47	2.06	2.09	2.26	1.57	2.30	1.57	2.05	1.45
Phenols															
14	2-Methoxy-4-vinylphenol	C <sub>9</sub> H <sub>10</sub> O <sub>2</sub>	34.77	2168	2172	0.34	0.36	0.40	0.35	0.36	0.40	0.36	0.40	0.35	0.37
Average content of overall detected VOC						30.73 ± 0.02					29.14 ± 0.01				

Table S1 (Continued)

Size 2 (350 µm)															
Pyridines															
1	Pyridine	C <sub>5</sub> H <sub>5</sub> N	10.49	1170	1169	0.42	0.83	0.65	0.84	1.00	0.49	0.47	0.34	0.57	0.32
Pyrazines															
2	2-Methylpyrazine	C <sub>5</sub> H <sub>6</sub> N <sub>2</sub>	13.01	1250	1252	1.90	1.17	1.75	1.87	2.04	2.63	1.85	2.37	1.61	1.71
3	2,5-Dimethylpyrazine	C <sub>5</sub> H <sub>6</sub> N <sub>2</sub>	14.74	1305	1316	0.67	0.48	0.74	0.97	0.89	1.17	0.70	0.97	0.65	0.59
4	2,6-Dimethylpyrazine	C <sub>6</sub> H <sub>8</sub> N <sub>2</sub>	14.92	1311	1314	1.02	0.74	1.15	1.27	1.32	1.61	1.13	1.44	1.06	1.09
5	2-Ethylpyrazine	C <sub>6</sub> H <sub>8</sub> N <sub>2</sub>	15.05	1316	1325	0.71	0.47	0.73	0.89	0.87	1.06	0.77	0.93	0.72	0.63
6	2-Ethyl-6-methylpyrazine	C <sub>7</sub> H <sub>10</sub> N <sub>2</sub>	16.56	1368	1375	0.77	0.60	0.91	1.21	1.20	1.30	0.99	1.04	0.92	0.88
7	2-Ethyl-5-methylpyrazine	C <sub>7</sub> H <sub>10</sub> N <sub>2</sub>	16.73	1374	1380	0.68	0.49	0.82	1.09	1.04	1.19	0.78	1.04	0.78	0.72
Acids															
8	Acetic acid	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	18.34	1432	1432	0.80	0.64	0.65	0.78	0.55	0.70	0.72	0.57	0.68	0.46
Furan and Furanic compounds															
9	Furfural	C <sub>5</sub> H <sub>4</sub> O <sub>2</sub>	18.54	1440	1443	5.71	10.32	8.75	13.08	11.34	8.66	9.05	6.56	7.55	5.65
10	2-Furanmethanol	C <sub>5</sub> H <sub>6</sub> O <sub>2</sub>	23.62	1646	1658	2.83	3.39	3.40	4.29	3.72	3.46	4.14	2.97	2.83	2.83
11	5-Methylfurfural	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	21.37	1551	1555	3.10	6.38	5.61	8.71	7.04	4.70	6.17	3.15	4.68	3.75
12	Furfuryl acetate	C <sub>7</sub> H <sub>8</sub> O <sub>3</sub>	20.52	1516	1523	1.48	2.64	2.20	3.30	2.85	2.04	4.76	1.34	2.28	2.15
Ketones															
13	2-Acetylfuran	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	19.64	1481	1484	1.33	2.36	2.10	2.67	2.00	1.86	1.97	1.41	1.54	1.43
Phenols															
14	2-Methoxy-4-vinylphenol	C <sub>9</sub> H <sub>10</sub> O <sub>2</sub>	34.77	2168	2172	0.33	0.35	0.35	0.43	0.34	0.53	0.42	0.44	0.42	0.39
Average content of overall detected VOC								32.05 ± 0.04				27.76 ± 0.04			

Table S1 (Continued)

Size 3 (550 µm)															
Pyridines															
1	Pyridine	C <sub>5</sub> H <sub>5</sub> N	10.49	1170	1169	0.46	0.68	0.53	0.94	0.85	0.39	0.48	0.42	0.58	0.34
Pyrazines															
2	2-Methylpyrazine	C <sub>5</sub> H <sub>6</sub> N <sub>2</sub>	13.01	1250	1252	2.03	1.03	1.71	1.81	2.01	2.32	1.64	2.22	1.48	1.87
3	2,5-Dimethylpyrazine	C <sub>5</sub> H <sub>6</sub> N <sub>2</sub>	14.73	1305	1316	0.74	0.37	0.65	0.86	0.95	0.88	0.54	0.88	0.52	0.67
4	2,6-Dimethylpyrazine	C <sub>6</sub> H <sub>8</sub> N <sub>2</sub>	14.91	1311	1314	1.17	0.61	0.98	1.23	1.30	1.33	0.96	1.32	0.87	1.14
5	2-Ethylpyrazine	C <sub>6</sub> H <sub>8</sub> N <sub>2</sub>	15.04	1316	1325	0.73	0.43	0.63	0.85	0.85	0.79	0.67	0.85	0.57	0.87
6	2-Ethyl-6-methylpyrazine	C <sub>7</sub> H <sub>10</sub> N <sub>2</sub>	16.55	1368	1375	0.82	0.46	0.71	1.03	1.22	0.90	0.74	0.89	0.72	0.94
7	2-Ethyl-5-methylpyrazine	C <sub>7</sub> H <sub>10</sub> N <sub>2</sub>	16.72	1374	1380	0.78	0.42	0.62	1.03	1.08	0.86	0.60	0.89	0.62	0.81
Acids															
8	Acetic acid	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	18.33	1432	1432	0.85	0.43	0.77	0.59	0.81	0.73	0.37	0.70	0.67	0.83
Furan and Furanic compounds															
9	Furfural	C <sub>5</sub> H <sub>4</sub> O <sub>2</sub>	18.54	1440	1443	5.65	9.10	7.59	10.46	10.88	8.25	7.91	7.11	6.99	5.68
10	2-Furanmethanol	C <sub>5</sub> H <sub>6</sub> O <sub>2</sub>	23.61	1646	1658	2.91	2.72	3.48	3.36	3.65	3.20	3.40	2.98	2.64	2.51
11	5-Methylfurfural	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	21.37	1551	1555	3.20	5.04	4.71	6.33	6.86	3.87	4.89	3.22	4.08	3.63
12	Furfuryl acetate	C <sub>7</sub> H <sub>8</sub> O <sub>3</sub>	20.51	1516	1523	1.83	2.31	1.79	2.76	2.94	1.60	4.04	1.22	2.01	2.20
Ketones															
13	2-Acetylfuran	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	19.63	1481	1484	1.41	2.05	1.97	2.12	2.12	1.61	1.80	1.54	1.42	1.45
Phenols															
14	2-Methoxy-4-vinylphenol	C <sub>9</sub> H <sub>10</sub> O <sub>2</sub>	34.76	2168	2172	0.37	0.25	0.43	0.35	0.39	0.46	0.37	0.39	0.37	0.40
Average content of overall detected VOC								29.01 ± 0.03				25.42 ± 0.01			

Table S1 (Continued)

Size 4 (750 µm)															
<b>Pyridines</b>															
1	Pyridine	C <sub>5</sub> H <sub>5</sub> N	10.48	1170	1169	0.35	0.74	0.45	0.66	0.53	0.37	0.47	0.35	0.66	0.36
<b>Pyrazines</b>															
2	2-Methylpyrazine	C <sub>5</sub> H <sub>6</sub> N <sub>2</sub>	13.00	1250	1252	1.98	1.09	1.32	1.20	1.18	2.21	1.59	1.63	1.46	1.66
3	2,5-Dimethylpyrazine	C <sub>5</sub> H <sub>6</sub> N <sub>2</sub>	14.72	1305	1316	0.91	0.42	0.41	0.50	0.47	0.79	0.53	0.55	0.54	0.64
4	2,6-Dimethylpyrazine	C <sub>6</sub> H <sub>8</sub> N <sub>2</sub>	14.90	1311	1314	1.25	0.64	0.66	0.77	0.70	1.19	0.93	0.83	0.88	1.05
5	2-Ethylpyrazine	C <sub>6</sub> H <sub>8</sub> N <sub>2</sub>	15.03	1316	1325	0.74	0.44	0.54	0.56	0.55	0.82	0.61	0.58	0.59	0.70
6	2-Ethyl-6-methylpyrazine	C <sub>7</sub> H <sub>10</sub> N <sub>2</sub>	16.54	1368	1375	1.06	0.49	0.47	0.61	0.59	0.78	0.71	0.59	0.69	0.84
7	2-Ethyl-5-methylpyrazine	C <sub>7</sub> H <sub>10</sub> N <sub>2</sub>	16.71	1374	1380	0.96	0.47	0.43	0.58	0.58	0.75	0.58	0.59	0.64	0.74
<b>Acids</b>															
8	Acetic acid	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	18.33	1432	1432	0.89	0.58	0.52	0.52	0.46	0.70	0.47	0.46	0.60	0.39
<b>Furan and Furanic compounds</b>															
9	Furfural	C <sub>5</sub> H <sub>4</sub> O <sub>2</sub>	18.53	1440	1443	7.13	9.86	5.83	8.99	7.24	7.63	7.93	5.09	6.79	5.65
10	2-Furanmethanol	C <sub>5</sub> H <sub>6</sub> O <sub>2</sub>	23.60	1646	1658	2.74	3.14	2.48	2.71	2.62	3.01	3.55	2.18	2.93	2.52
11	5-Methylfurfural	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	21.365	1551	1555	5.08	5.75	3.04	4.88	3.96	3.43	4.84	2.17	3.92	3.72
12	Furfuryl acetate	C <sub>7</sub> H <sub>8</sub> O <sub>3</sub>	20.51	1516	1523	1.97	2.35	1.30	2.21	1.93	1.61	3.82	0.87	2.04	1.88
<b>Ketones</b>															
13	2-Acetylfuran	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	19.63	1481	1484	1.52	2.19	1.44	1.73	1.15	1.47	1.63	0.91	1.33	1.41
<b>Phenols</b>															
14	2-Methoxy-4-vinylphenol	C <sub>9</sub> H <sub>10</sub> O <sub>2</sub>	34.75	2168	2172	0.78	0.36	0.33	0.31	0.36	0.45	0.47	0.08	0.40	0.38
Average content of overall detected VOC								24.73 ± 0.02				23.13 ± 0.03			

RT is short for retention time. LRI is short for linear retention index. All values represented the average of three replicates from unfermented (UFC) and fermented coffee samples (FC) with five different brands.