SUPPLEMENTARY MATERIAL

SHS-GC-MS applied in *Coffea arabica* and *Coffea canephora* blends assessment

Marcos Valério Vieira Lyrio[a], Pedro Henrique Pereira da Cunha[a], Danieli Grancieri Debona[a], Bárbara Zani Agnoletti[a], Bruno Quirino Araújo[a], Roberta Quintino Frinhani[a], Paulo Roberto Filgueiras[a]*, Lucas Louzada Pereira[b], and Eustaquio Vinicius Ribeiro de Castro[a]

[a]Federal University of Espirito Santo/UFES, Department of Chemistry, Campus Goiabeiras, Avenida Fernando Ferrari, 514, CEP 29075-910 Vitoria, Espírito Santo, Brazil.
[b]Federal Institute of Espírito Santo, Department of Food Science and Technology, Avenida Elizabeth Minete Perim, S/N, Bairro São Rafael, CEP 29375-000 Venda Nova do Imigrante, Espírito Santo, Brazil.
*Corresponding author: filgueiras.pr@gmail.com

Number of figures and tables: **8**

Supplementary Materials Captions:

Fig. S1. Loading plot of PLS-DA model for samples data from (A) GC-MS TIC, (B) GC-MS EIC, and (C) FTIR. VIP Score of PLS-DA model for samples data from (D) GC-MS TIC, (E) GC-MS EIC, and (F) FTIR. The compounds are labeled according to elution order in Table 1S.

Fig. S2. VIP score for PLS models with data from (A) GC-MS TIC and (B) GC-MS EIC. The compounds are labeled according to elution order in **Table 1S**.

Fig. S3. VIP score for PLS model with FTIR data.

Fig. S4. Variable selection result for FTIR data with **(A)** siPLS and **(B)** UVE-PLS.

Fig. S5. Residuals plot for PLS models.

Table S1. Identified compounds for arabica and conilon coffee by gas chromatography-mass spectrometry.

Table S2. Confusion matrix for PLS-DA model.

Table S3. Performance parameters for training and prediction set of PLS-DA model.

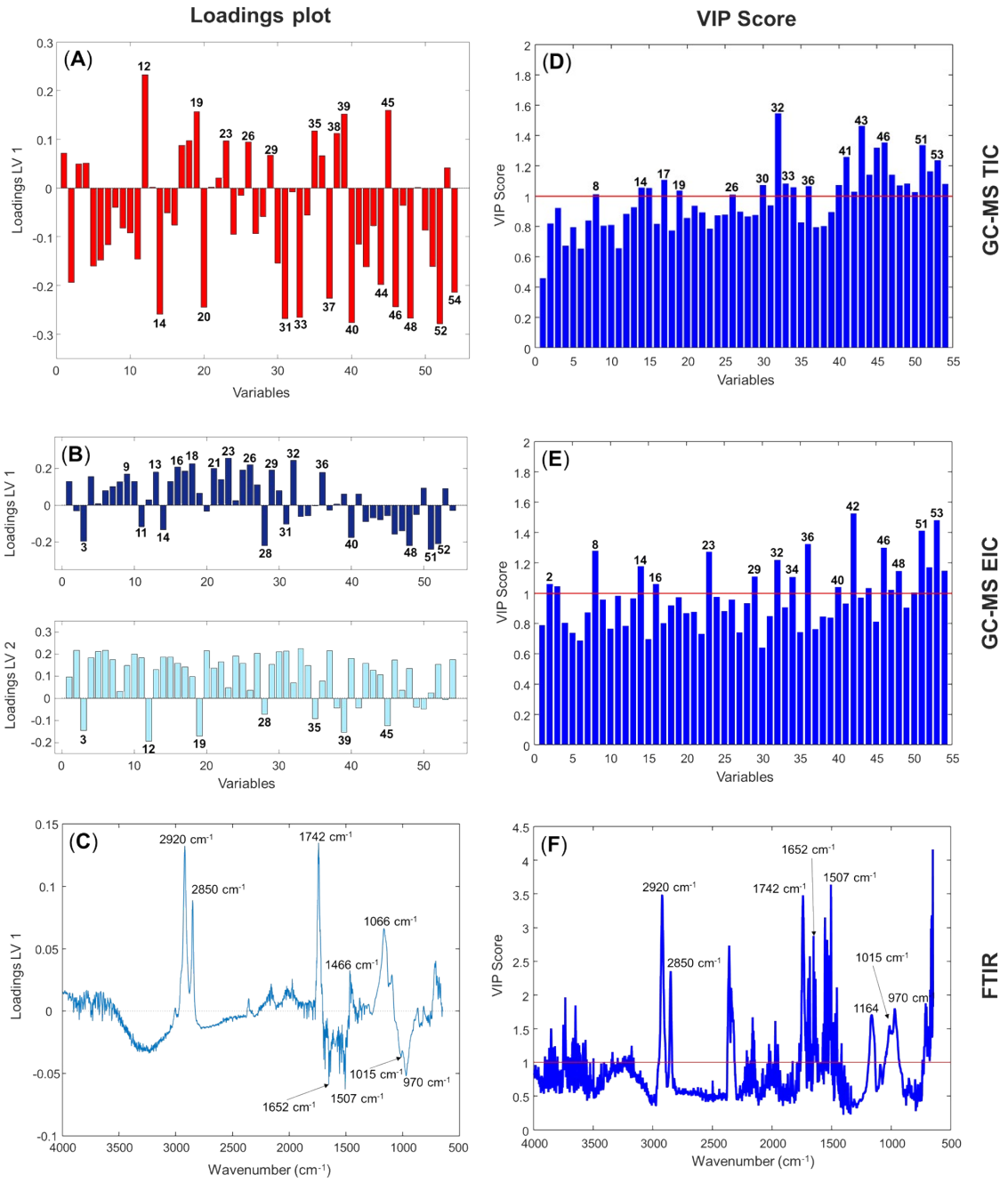

Fig. S1. Loading plot of PLS-DA model for samples data from **(A)** GC-MS TIC, **(B)** GC-MS EIC, and **(C)** FTIR. VIP Score of PLS-DA model for samples data from **(D)** GC-MS TIC, **(E)** GC-MS EIC, and **(F)** FTIR. The compounds are labeled according to elution order in **Table 1S**.

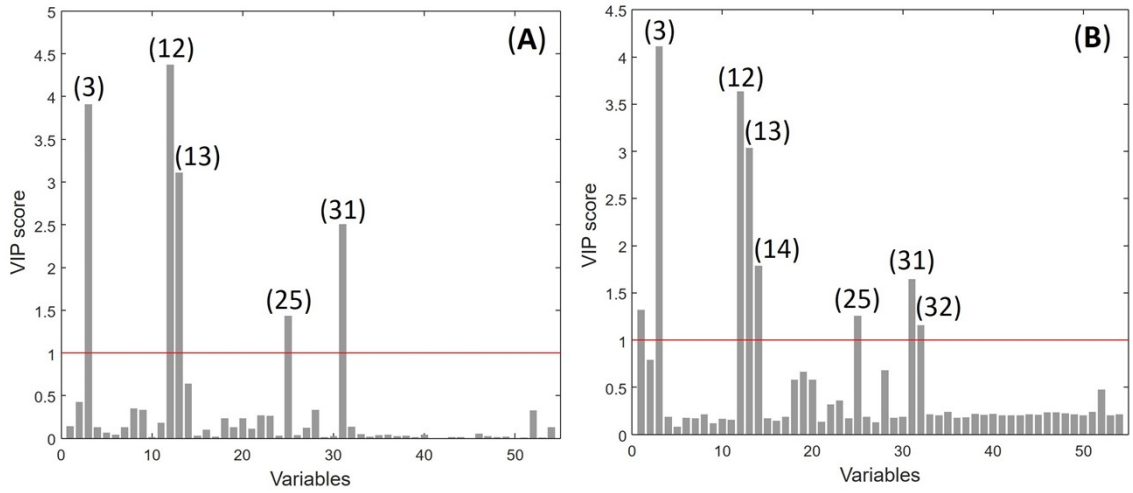

Fig. S2. VIP score for PLS models with data from (A) GC-MS TIC and (B) GC-MS EIC. The compounds are labeled according to elution order in **Table 1S**.

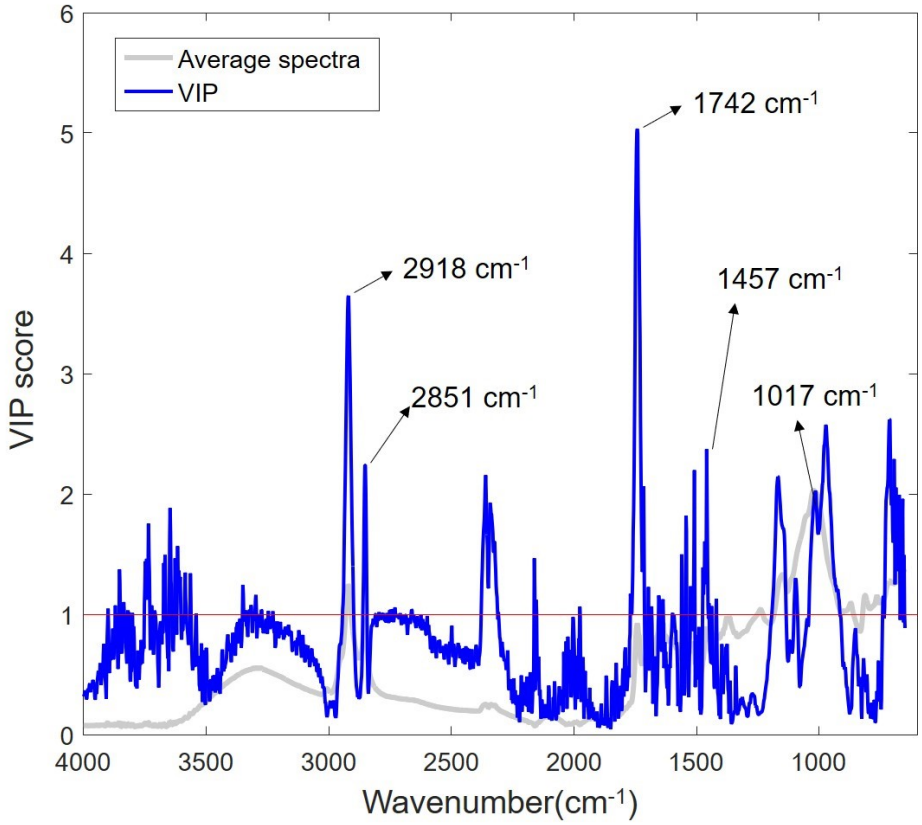

Fig. S3. VIP score for PLS model with FTIR data.

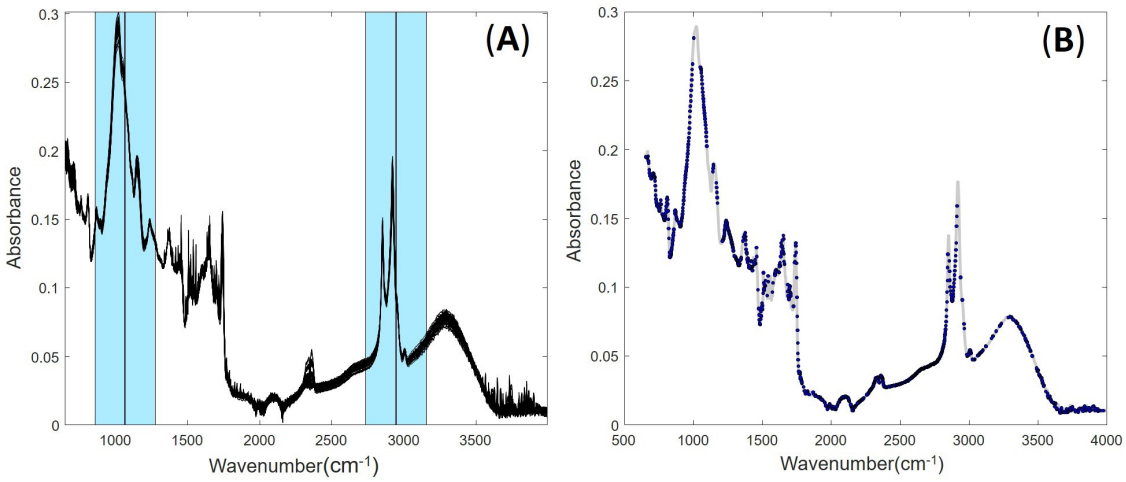

Fig. S4. Variable selection result for FTIR data with **(A)** siPLS and **(B)** UVE-PLS.

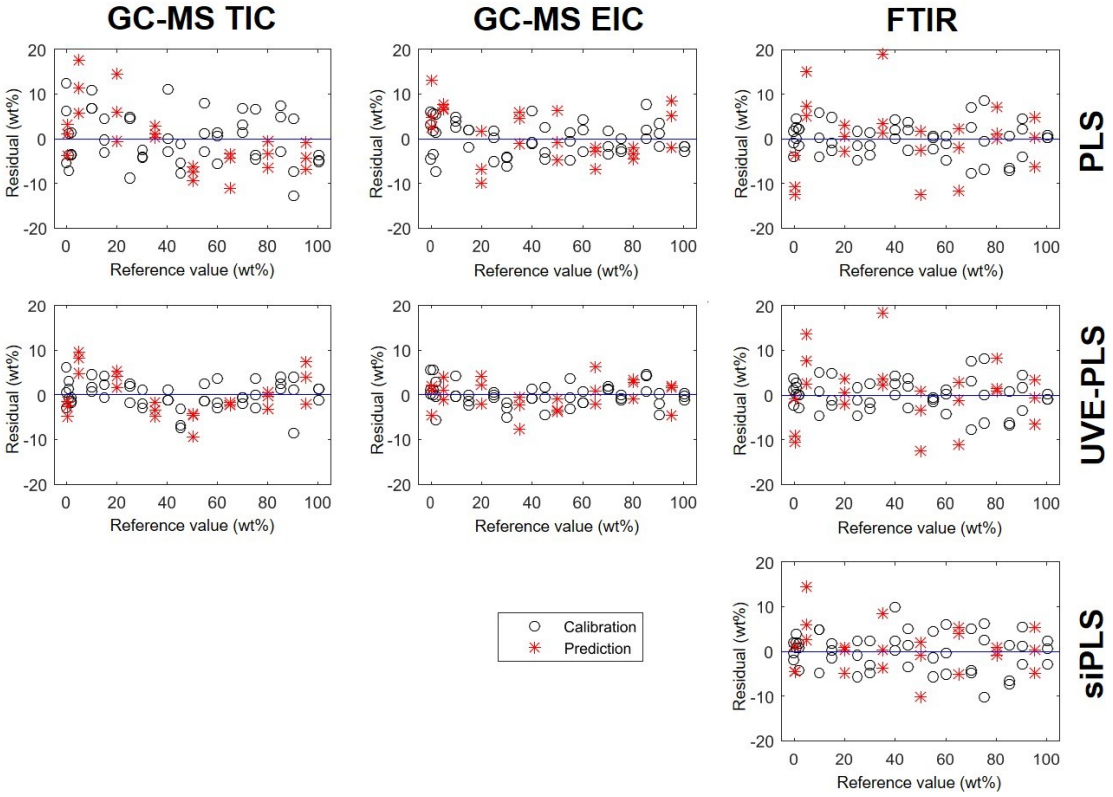

Fig. S5. Residuals plot for PLS models.

Table S1. Chemical compounds of arabica and conilon coffees identified by SHS-GC-MS.

Peak	tR (min)	Compounds	LRI	target (*m*/*z*)	Class
1	6.650	Dihydro-2-methyl-3(2H)-Furanone	1260	43	Furanone
2	7.309	Acetoin	1288	45	Ketone
3	7.741	1-Hydroxy-propan-2-one	1305	43	Ketone
4	8.649	2-Hydroxy-pentan-3-one	1339	59	Ketone
5	8.739	2,3-Dimethylpyrazine	1342	108	Pyrazine
6	8.917	1-Hydroxy-pentan-2-one	1349	82	Ketone
7	9.119	2-Methylpropyl 2-hydroxypropanoate	1356	45	Ester
8	9.603	1-Hydroxy-butan-2-one	1374	57	Ketone
9	10.487	2,5-Furandione	1406	54	Anhydride
10	11.222	Ethenylpyrazine	1432	106	Pyrazine
11	11.458	3-Ethyl-3,5-dimethylpyrazine	1440	135	Pyrazine
12	11.493	Acetic acid	1442	43	Carboxylic acid
13	12.079	Furfural	1462	96	Furan
14	12.377	1-(Acetyloxy)-propan-2-one	1473	43	Ester
15	12.608	3,5-Diethyl-2-methylpyrazine	1481	120	Pyrazine
16	12.993	2,5-Dimethyl-3(2H)-furanone	1494	112	Furanone
17	13.069	Furfuryl formate	1497	81	Furan
18	13.147	2-Acetylfuran	1500	95	Furan
19	13.379	Formic acid	1508	46	Carboxylic acid
20	13.455	Pyrrole	1511	67	Pyrrole
21	13.639	1-(2-Furyl)-propan-2-one	1517	81	Furan
22	14.177	2-Acetoxymethylfuran	1536	81	Furan
23	14.265	Propanoic acid	1540	74	Carboxylic acid
24	14.587	2-Methyl-1H-pyrrole	1551	80	Pyrrole
25	15.058	5-Methyl-2-furancarboxaldehyde	1568	110	Furan
26	15.318	Cyclopent-4-ene-1,3-dione	1577	68	Ketone
27	16.197	1-Methyl-1H-Pyrrole-2-carboxaldehyde	1610	108	Pyrrole
28	16.395	Butyrolactone	1618	42	Furanone
29	16.770	Butanoic acid	1634	60	Carboxylic acid
30	17.186	2-Acetyl-1-methylpyrrole	1652	108	Pyrrole
31	17.849	2-Furanmethanol	1680	98	Furan
32	17.884	3-Methylbutanoic acid	1682	60	Carboxylic acid
33	19.169	N-Acetyl-4(H)-pyridine	1733	80	Pyridine

to be continued

continuation

Peak	tR (min)	Compounds	LRI	target (*m*/*z*)	Class
34	19.518	5-Methyl-2-furanmethanol	1746	95	Furan
35	19.870	2(5H)-Furanone	1760	55	Furanone
36	21.093	3-Methyl-but-2-enoic acid	1809	100	Carboxylic acid
37	21.565	N-Furfurylpyrrole	1834	81	Furan
38	21.658	2-Hydroxy-3-methyl-Cyclopent-2-en-1-one	1838	112	Ketone
39	22.110	2,3-Dihydro-5-hydroxy-6-methyl-4H-pyran-4-one	1862	128	Pyranone
40	22.168	2-Methoxyphenol	1865	124	Phenol
41	22.718	3-Ethyl-2-hydroxy-Cyclopent-2-en-1-one	1893	126	Ketone
42	23.121	2-Phenylethanol	1921	91	Alcohol
43	23.507	2-Thiophenemethanol	1942	114	Thiophene
44	23.794	2-Acetylpyrrole	1968	109	Pyrrole
45	24.215	Methyl 2-furoate	2007	95	Furan
46	24.239	Phenol	2009	94	Phenol
47	24.421	1H-Pyrrole-2-carboxaldehyde	2026	95	Pyrrole
48	24.472	4-Ethylguaiacol	2031	137	Phenol
49	24.601	2,5-Dimethyl-4-hydroxy-3(2H)-furanone	2042	128	Furanone
50	24.915	5-Acetyldihydro-2(3H)-furanone	2071	85	Furanone
51	25.135	Triacetin	2091	43	Ester
52	26.232	4-Vinylguaiacol	2204	150	Phenol
53	28.932	5-Hydroxymethylfurfural	2531	97	Furan
54	35.639	Caffeine	3160	194	Xanthine

tR – retention time (minutes); LRI – Linear retention indices calculated for VB-WAX column. The calculated LRI were compared with reference values from literature data.[1-29]

Table S2. Confusion matrix for PLS-DA model

Training (n = 70)						
	Reference\predicted	**Class 1**	**Class 2**	**Class 3**	**Class 4**	**Not-assigned**
GC-MS TIC	Class 1	13	0	0	0	0
	Class 2	0	11	0	1	1
	Class 3	0	0	24	0	1
	Class 4	0	0	0	18	1
GC-MS EIC	Class 1	11	0	1	0	1
	Class 2	0	11	0	0	2
	Class 3	0	0	24	0	1
	Class 4	0	0	0	18	1
FTIR	Class 1	13	0	0	0	0
	Class 2	0	11	0	1	1
	Class 3	0	0	24	0	1
	Class 4	0	0	1	17	1

Prediction (n = 29)						
	Reference\predicted	**Class 1**	**Class 2**	**Class 3**	**Class 4**	**Not-assigned**
GC-MS TIC	Class 1	5	0	0	0	0
	Class 2	0	4	0	0	1
	Class 3	0	0	10	0	1
	Class 4	0	0	0	8	0
GC-MS EIC	Class 1	5	0	0	0	0
	Class 2	0	4	0	0	1
	Class 3	0	0	11	0	0
	Class 4	0	0	1	7	0
FTIR	Class 1	5	0	0	0	0
	Class 2	0	4	0	1	0
	Class 3	0	0	10	0	1
	Class 4	0	0	0	8	0

Table S3. Performance parameters for training and prediction set of PLS-DA model.

Model	Class	Sensitivity	Specificity	Accuracy	Error rate	Not-assigned
		(%)				
Training (n = 70)						
GC-MS TIC	Class 1	100	100	99	2	4
	Class 2	92	100			
	Class 3	100	100			
	Class 4	100	98			
GC-MS EIC	Class 1	92	100	98	2	7
	Class 2	100	100			
	Class 3	100	98			
	Class 4	100	100			
FTIR	Class 1	100	100	97	3	4
	Class 2	92	100			
	Class 3	100	98			
	Class 4	94	98			
Prediction (n = 29)						
GC-MS TIC	Class 1	100	100	100	0	7
	Class 2	100	100			
	Class 3	100	100			
	Class 4	100	100			
GC-MS EIC	Class 1	100	100	96	3	3
	Class 2	100	100			
	Class 3	100	94			
	Class 4	88	100			
FTIR	Class 1	100	100	96	5	3
	Class 2	80	100			
	Class 3	100	100			
	Class 4	100	95			

References

1 A. Amanpour and S. Selli, *J. Food Process. Preserv.*, 2016, **40**, 1116–1124.

2 M. Amrani-Hemaimi, C. Cerny and L. B. Fay, *J. Agric. Food Chem.*, 1995, **43**, 2818–2822.

3 S. Bi, A. Wang, F. Lao, Q. Shen, X. Liao, P. Zhang and J. Wu, *Food Chem.*, 2021, **339**, 127878.

4 S. Birtić, C. Ginies, M. Causse, C. M. G. C. Renard and D. Page, *J. Agric. Food Chem.*, 2009, **57**, 591–598.

5 M. Cardinal, M. Chaussy, C. Donnay-Moreno, J. Cornet, C. Rannou, C. Fillonneau, C. Prost, R. Baron and P. Courcoux, *Food Res. Int.*, 2020, **134**, 109254.

6 J. S. Elmore, J. K. Parker, N. G. Halford, N. Muttucumaru and D. S. Mottram, *J. Agric. Food Chem.*, 2008, **56**, 6173–6179.

7 W. Fan and M. C. Qian, *J. Agric. Food Chem.*, 2005, **53**, 7931–7938.

8 V. Ferreira, F. S. Juan, A. Escudero, L. Culleré, P. Fernández-Zurbano, M. P. Saenz-Navajas and J. Cacho, *J. Agric. Food Chem.*, 2009, **57**, 7490–7498.

9 O. Gonzalez-Rios, M. L. Suarez-Quiroz, R. Boulanger, M. Barel, B. Guyot, J. P. Guiraud and S. Schorr-Galindo, *J. Food Compos. Anal.*, 2007, **20**, 297–307.

10 A. Hallier, C. Prost and T. Serot, *J. Agric. Food Chem.*, 2005, **53**, 7204–7211.

11 M. Ishikawa, O. Ito, S. Ishizaki, Y. Kurobayashi and A. Fujita, *Flavour Fragr. J.*, 2004, **19**, 183–187.

12 A. Korkmaz, A. A. Hayaloglu and A. F. Atasoy, *LWT - Food Sci. Technol.*, 2017, **84**, 842–850.

13 U. Krings, K. Zelena, S. Wu and R. G. Berger, *Eur. Food Res. Technol.*, 2006, **223**, 675–681.

14 K. G. Lee, S. E. Lee, G. R. Takeoka, J. H. Kim and B. S. Park, *J. Sci. Food Agric.*, 2005, **85**, 1580–1586.

15 I. López-Galilea, N. Fournier, C. Cid and E. Guichard, *J. Agric. Food Chem.*, 2006, 8560–8566.

16 T. Luo, W. Fan and Y. Xu, *J. Inst. Brew.*, 2008, **114**, 172–179.

17 M. S. Madruga and D. S. Mottram, *J. Braz. Chem. Soc.*, 1998, **9**, 261–271.

18 H. Mayorga, H. Knapp, P. Winterhalter and C. Duque, *J. Agric. Food Chem.*, 2001, **49**, 1904–1908.

19 C. Osorio, M. Alarcon, C. Moreno, A. Bonilla, J. Barrios, C. Garzon and C. Duque, *J. Agric. Food Chem.*, 2006, **54**, 509–516.

20 M. A. Pozo-Bayon, A. Ruiz-Rodriguez, K. Pernin and N. Cayot, *J. Agric. Food Chem.*, 2007, **55**, 1418–1426.

21 B. S. Radovic, M. Careri, A. Mangia, M. Musci, M. Gerboles and E. Anklam, *Food Chem.*, 2001, **72**, 511–520.

22 S. Rochat, J. Egger and A. Chaintreau, *J. Chromatogr. A*, 2009, **1216**, 6424–6432.

23 I. Steen, S. S. Waehrens, M. A. Petersen, M. Münchow and W. L. P. Bredie, *Food Chem.*, 2017, **219**, 61–68.

24 K. Umano, Y. Hagi, K. Nakahara, A. Shyoji and T. Shibamoto, *J. Agric. Food Chem.*, 1995, **43**, 2212–2218.

25 J. E. Welke, V. Manfroi, M. Zanus, M. Lazarotto and C. Alcaraz Zini, *J. Chromatogr. A*, 2012, **1226**, 124–139.

26 X. Xu, M. Yu, J. Raza, H. Song, L. Gong and W. Pan, *Lwt*, 2021, **137**, 110371.

27 K. Yanagimoto, H. Ochi, K.-G. Lee and T. Shibamoto, *J. Agric. Food*

Chem., 2004, 592–596.

28 P. Yang, H. Song, L. Wang and H. Jing, *J. Agric. Food Chem.*, 2019, **67**, 7926–7934.

29 M. Yokoi and M. Shimoda, *J. Chromatogr. Sci.*, 2017, **55**, 373–377.