Supplementary Material

Chemical Profile of Robusta and Arabica Coffee by ESI(-)FT-ICR MS and ATR-FTIR: a Quantitative Approach

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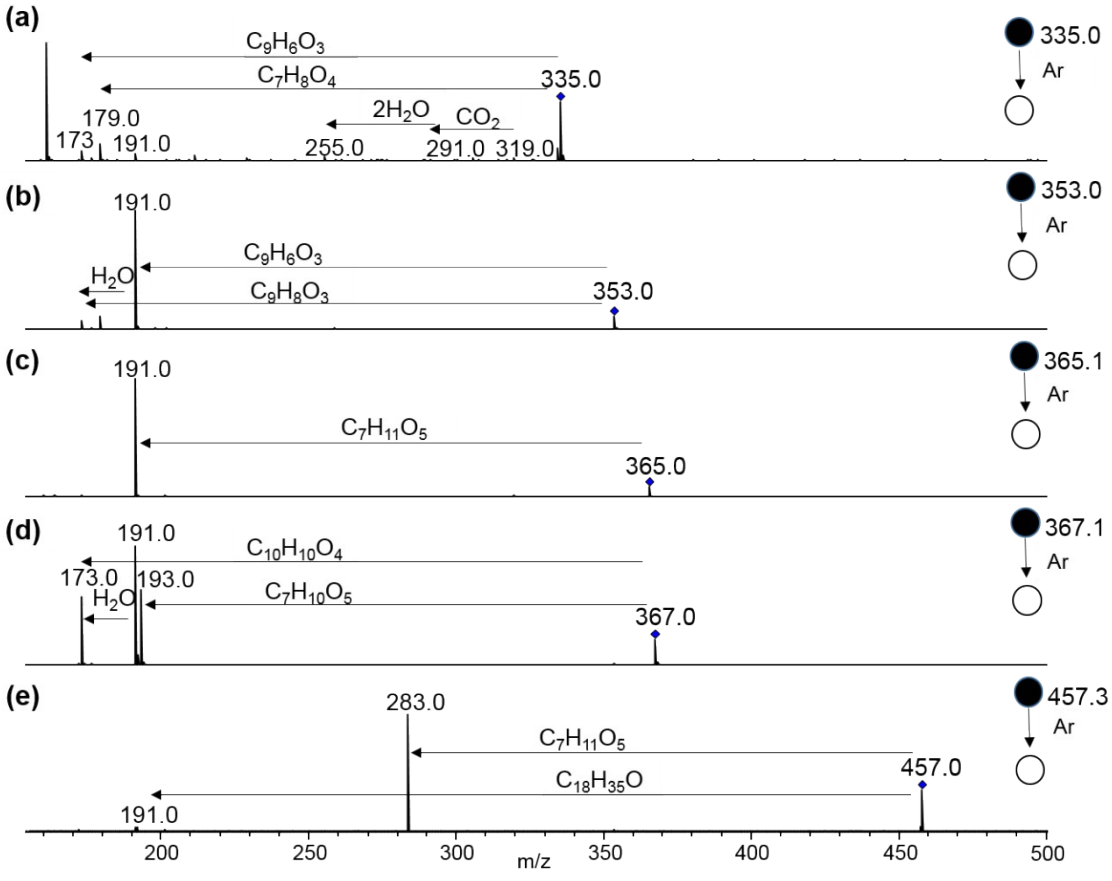
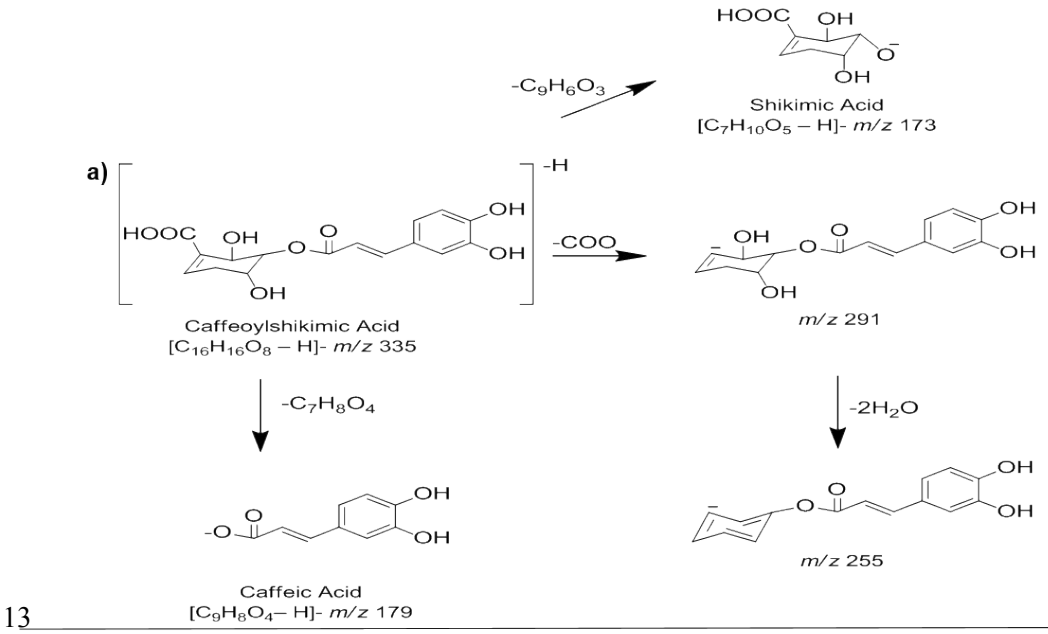


Figure 1S. ESI(-)MS/MS mass spectra for the most abundant species found in coffee blends: **(a)** Caffeoylshikimic acid, **(b)** Caffeoylquinic acid, **(c)** Dimer of Quinic Acid, **(d)** Ferulolquinic acid, and **(e)** ion of *m/z* 457.


a)
-H
-C9H6O3
Shikimic Acid
[C7H10O5 – H]- m/z 173
-COO
Caffeoylshikimic Acid
[C16H16O8 – H]- m/z 335
m/z 291
-C7H8O4
-2H2O
Caffeic Acid
[C9H8O4– H]- m/z 179
m/z 255

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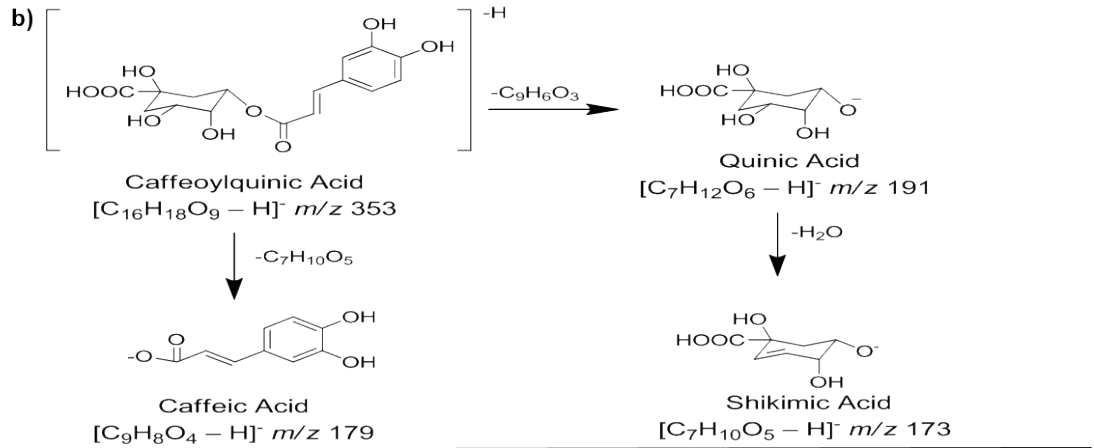
b)
-H
-C9H6O3
Caffeoylquinic Acid
[C16H18O9 – H]- m/z 353
Quinic Acid
[C7H12O6 – H]- m/z 191
-C7H10O5
-H2O
Caffeic Acid
[C9H8O4 – H]- m/z 179
Shikimic Acid
[C7H10O5 – H]- m/z 173

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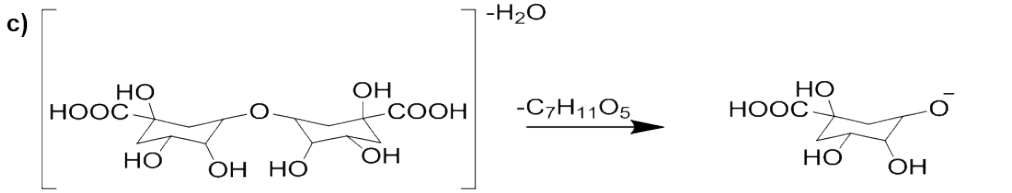
c)
-H2O
-C7H11O5
Dimer Quinic acid
[C14H22O11 – H2O]- m/z 365
Quinic Acid
[C7H12O6 – H]- m/z 191

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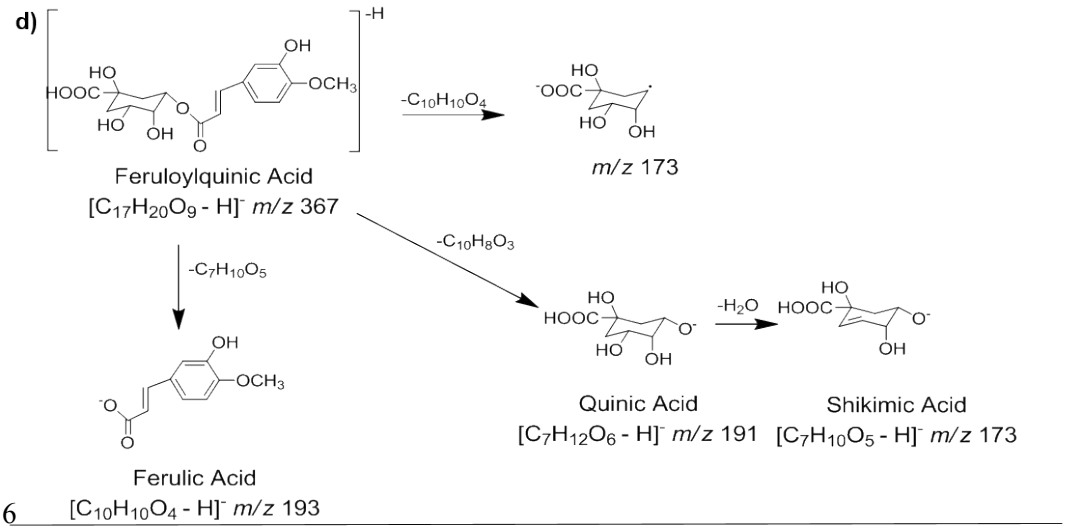

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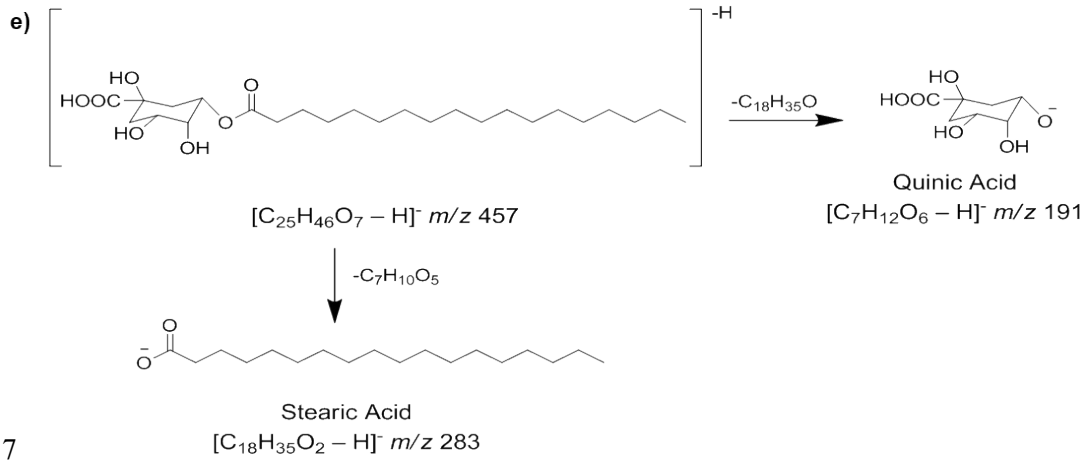

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18 **Figure 2S.** Fragmentation pathways proposed for the chemical species: (a)
19 caffeoylshikimic acid, *m/z* 335, (b) caffeoylquinic acid, *m/z* 353, (c) dimer quinic
20 acid , (d) feruloylquinic acid, *m/z* 367, and (e) the $[C_{25}H_{46}O_7 - H]^-$ ion, *m/z* 457.

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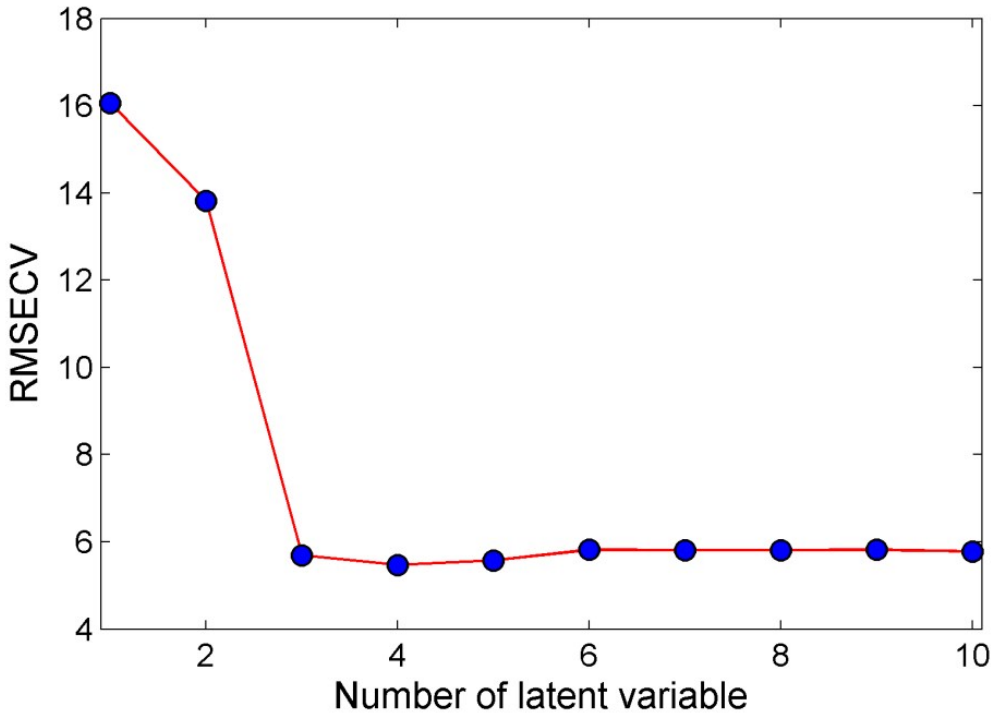

Figure 3S. Graphic of root mean square error of cross validation (RMSECV) against number of latent variables used in the PLS model.

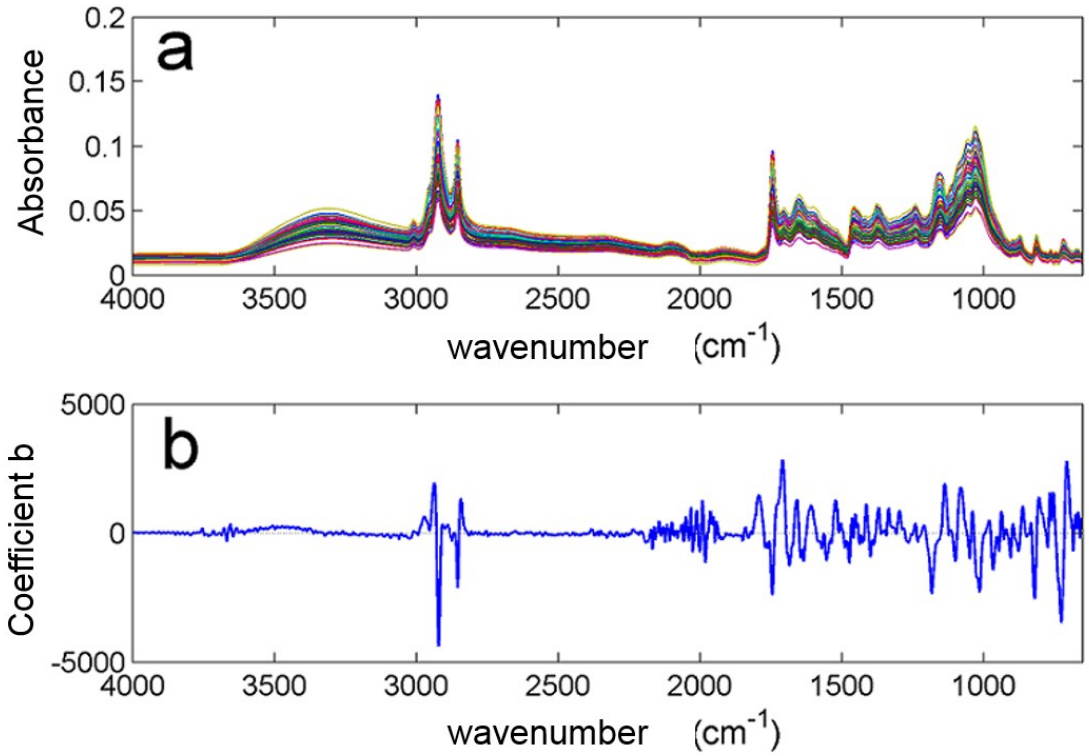

Figure 4S. (a) FTIR spectra of the coffee blends (after processing the data) and **(b)** graphic of the regression model coefficients.

Table 1S. Values used to calculate repeatability from ESI(-)FT-ICR MS data (ratios of the sums of the relative intensities of the signals at *m/z* 365 and 367 by signal at *m/z* 353).

Analysis	Triplicates			Averages
1º	0.330	0.339	0.338	0.3357
2º	0.361	0.355	0.360	0.3587
3º	0.370	0.372	0.372	0.3713
4º	0.360	0.360	0.360	0.3600
5º	0.376	0.374	0.378	0.3760

Tabela 2S. Values used to calculate intermediate precision by ESI(-)FT-ICR MS technique (ratios of the sums of the relative intensities of the signals at *m/z* 365 and 367 by signal at *m/z* 353).

Days	Analysis (9)									Average
1º	0.360	0.360	0.360	0.376	0.374	0.378	0.370	0.372	0.372	0.3661
2º	0.368	0.367	0.370	0.364	0.367	0.377	0.453	0.365	0.351	0.3691
3º	0.276	0.341	0.342	0.345	0.341	0.356	0.302	0.294	0.487	0.3246
4º	0.335	0.336	0.346	0.350	0.346	0.353	0.342	0.356	0.342	0.3451
5º	0.333	0.350	0.349	0.353	0.351	0.352	0.356	0.350	0.354	0.3496

Table 3S. Attributions of the main bands observed in ATR-FTIR spectra for Arabica and Robusta coffee samples.

#	Bands (cm^{-1})	Attribution
1	3308	O-H stretching
2	2923	Asymmetric stretching of aliphatic C-H
3	2853	Symmetric stretching of aliphatic C-H
4	1743	Axial deformation of C=O bond of esters
5	1652	Stretching of C=C bond of aromatic compounds
6	1464	Asymmetric deformation of aliphatic C-H bond
7	1374	C-O stretching
8	1026	C-O deformation