# Wild Harenna Coffee: Flavour Profiling from the Bean to the Cup

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**Abstract (MAX 150 WORDS)**

As one of the last places where coffee grows spontaneously, the Harenna forest (Ethiopia) is the origin of the coffee analysed in the present study. The analysis of the volatile emission of each processing phase evaluates the chemical fingerprint of the reactions taking place at each stage, leading to the final aroma.

The green beans mainly emit non-terpene esters and alkanes. Once the roasting begins, monoterpenes are the main class until 160°C: at this point, 2,6-dimethylpyrazine prevails in the headspaces, as main product of the Maillard reactions. This compound, with its sweet and nut-like aroma, is also detected in the brewed coffee. The shed silverskins are rich in methyl chavicol and retain the monoterpenes from the beans: as these compounds are important aroma contributors, the removal of the silverskins prior to roasting seems non-advisable. The grinding of the samples breaks the matrices and leads to drastic changes in the volatile emissions.

**Keywords**: Coffee Aroma; Food Analysis; Gas Chromatography-Mass Spectrometry; Processing Chain; Pyrazines; Volatile Organic Compounds

**Main cited chemical compounds**: 1,3-Butanediol (PubChem CID: 7896); 2,3-Butanediol (PubChem CID: 262); Limonene (PubChem CID: 440917); 2,6-Diethylpyrazine (PubChem CID: 83101); 2,6-Dimethylpyrazine (PubChem CID: 7938); 2-Ethyl-5-methylpyrazine (PubChem CID: 25915); 2-Ethyl-6-methylpyrazine (PubChem CID: 26332); 2-Methylpyrazine (PubChem CID: 7976); 2,3,5-Trimethylpyrazine (PubChem CID: 26808).

## 1. Introduction

Second only to crude oil, coffee is the world's second most traded commodity (Goldschein, 2011): it is one of the most beloved beverages, with 151.3 million estimated 60 kg bags consumed in 2015/2016 over a 148 million produced bags (International Coffee Organization, 2016). Its global market (both import and export) is constantly growing, with an average annual increase of 1.3% (International Coffee Organization, 2016). *Coffea arabica* L. belongs to the Rubiaceae family, of which it is the most economically relevant member: its seeds represent over 60% of the global coffee production, followed by those of *Coffea canephora* Pierre ex A.Froehner (the 'robusta' variety) and, for less than 1%, *Coffea liberica* Hiern (Preedy & Abramovic, 2015). From October 2015 to October 2016, over a total of 9.13 million 60 kg bags, 71.93 million were of 'arabica' coffee (International Coffee Organization, 2016).

The coffee analysed in this study is produced in Ethiopia, where it grows spontaneously in the Harenna forest: it has been bestowed the Slow Food Presidium in 2012 and it is grown by around a hundred producers, united in two cooperatives, which export their coffee (mainly to Italy) through the Oromia Union ("Ethiopia – The Coffee of the Forest," 2015). It belongs to the species *C. arabica* L. variety 'typica': it is very susceptible to diseases, but it has excellent cup quality (Winston, Op de Laak, Marsh, Lempke, & Chapman, 2005). The presence of coffee in Ethiopia reaches as far as thousand years ago, when it was domesticated in its plains: its consumption still represents a traditional community ritual, in a ceremony which lasts almost an hour ("Caffè selvatico della foresta di Harenna," 2016; "Ethiopia – The Coffee of the Forest," 2015). The wild growing coffee plants represent 20% of the total Ethiopian coffee production: the species analysed in this study spontaneously grows in the thicket of the Harenna forest, located in the Bale Mountains National Park of the Oromia region ("Caffè selvatico della foresta di Harenna," 2016; "Ethiopia – The Coffee of the Forest," 2015). The forest provides the optimal growing conditions for coffee in terms of temperature, humidity, soil (which is moisture-retaining) and pollinators presence (mostly bees) (Davis, 2017).

Coffee grows well in mild temperatures and high elevation, originally belonging to the forest understorey: its production is located in all the countries lying in the tropical and sub-tropical belt and, more recently, in the Yunnan highlands in China (Oestreich-Janzen, 2010; Winston et al., 2005). Nowadays, though, the climate changes forced the producers either to plant coffee crops at lower altitudes than its natural range, or to move to higher ones: this lead to the development of less sustainable alternatives, mainly forcing the deforestation of areas normally not involved in coffee growth (Baker, 2017). This situation is even more challenging for developing countries, as they are the major coffee producers and their economies frequently rely on the coffee exports: coffee farms, indeed, represent the only economic livelihood for over 25 million people in the world (Goldschein, 2011). In Ethiopia alone, for instance, 90% of coffee comes from small-scale producers ("Ethiopia – The Coffee of the Forest," 2015). Of this, 25% comes from Ethiopian forests and it represents the only livelihood income for 15 million Ethiopian people: the preservation of these forests, though, is of major importance for this country (Davis, 2017). Climate change, indeed, is threatening the survival of this wild habitat, both directly and indirectly, as it forces farmers to convert their production to different crops (like corn), for which they require a changing of the land-use. This would not only lead to a loss in biodiversity, but also in all the products that the locals can harvest from the forest: not only coffee, but also honey, spices, etc. (Davis, 2017). The preservation of these forest reserves, though, is of major importance: the harvested coffee, with its high value in terms of quality, could be the answer, as its revenues can cover the cost of the wildlife reserves maintenance (Davis, 2017).

In the present work, we analysed the spontaneous volatile emissions of each phase of the processing chain of this coffee, from the dried green beans to a brewed cup, by means of headspace solid-phase micro extraction (HS-SPME) coupled with GC-MS. The aim was to assess the development of the aroma compounds in each stage of the manufacturing of this product, which took place in the artisanal Trinci Factory, where all the samples were prepared. The sensory experience of a cup of coffee, indeed, is dominated by the perception of its typical volatile aroma compounds: their pattern depends on the starting material, but they are also transformed and developed during the processing stages. Each processing phase is characterised by a peculiar volatile composition that testifies the chemical reactions occurring at that

stage: in a recent published study, it has been demonstrated that, not only each stage, but also the peculiar used species of coffee, is recognizable by means of headspace analysis (Colzi et al., 2017). The volatile fingerprint of each processing stage, as well as of the starting and final product, can be used as a quality authentication method if studied in a very large number of samples: these data needs to be made sense of coupling it with chemometric analyses, to develop reliable pattern recognition models (Bressanello et al., 2017). For this reason, the evaluation of the changes in the spontaneous volatile emission during the Harenna coffee production chain have been analysed by means of multivariate statistical analysis to evidence the emerging patterns.

## 2. Materials and methods

### *2.1. Analysed samples*

All the analysed samples come from the Trinci Factory (Attiva sas, Via Olanda 18, 56032 - Cascine di Buti, Pisa, Italy). The green beans (green Arabica quality, dry processing method) have been exported by the Oromia Coffee Farmers Cooperative Union (Addis Ababa, Ethiopia). The roasting process took place in the Trinci Factory in a batch-operated spouted bed roaster for 15 minutes (final roasting temperature: 204°C). 30 g of material have been collected in each analysed phase of production and put in sealed glass containers until analysis. 15 g of each sample were ground in a kitchen grinder and immediately put in a sealed glass vial and analysed.

### *2.2. Headspace Solid Phase Micro-Extraction (HS-SPME)*

All samples were individually put in 4 mL glass vials (up to 1/3 of their total volume), which were then covered with aluminium foil and left to equilibrate at room temperature for 30 min. Supelco SPME (Solid Phase Micro-Extraction) devices coated with polydimethylsiloxane (PDMS, 100 µm) were used to sampling the headspace of the samples. SPME sampling was performed using the same new fibre, preconditioned according to the manufacturer instructions, for all the analyses. Sampling was accomplished in an air-conditioned room (22±1°C) to guarantee a stable temperature. After 30 minutes of equilibration time, the fibre was exposed to the headspace for 20 minutes at room temperature. Once sampling was finished, the

fibre was withdrawn into the needle and transferred to the injection port of the GC-MS system. The desorption conditions were identical for all the samples (Paragraph 2.3). Furthermore, blanks were performed before each first SPME extraction and randomly repeated during each series. Quantitative comparisons of relative peaks areas were performed between the same chemicals in the different samples. Triplicates were performed for each analysis.

### *2.3. Gas Chromatography – Mass Spectrometry Analyses and Peaks Identification*

The GC/EI-MS analyses were performed with a Varian CP-3800 apparatus equipped with a DB-5 capillary column (30 m X 0.25 mm i.d., film thickness 0.25 µm) and a Varian Saturn 2000 ion-trap mass detector. The oven temperature was programmed rising from 60° C to 240° C at 3° C/min; injector temperature, 220°C; transfer-line temperature, 240° C; carrier gas, He (1 mL/min). The acquisition parameters were as follows: full scan; scan range: 35-300 m/z; scan time: 1.0 sec; threshold: 1 count.

The identification of the constituents was based on the comparison of their retention times ($t_R$) with those of pure reference samples and their linear retention indices (LRIs) determined relatively to the $t_R$ of a series of *n*-alkanes. The mass spectra were compared with those listed in the commercial libraries NIST 14 and ADAMS and in a home-made mass-spectral library, built up from pure substances and components of known oils, and MS literature data (R. P. Adams, Zanoni, Lara, Barrero, & Cool, 1997; Robert P. Adams, 1995; Davies, 1990; Jennings & Shibamoto, 1982; Masada, 1976; Swigar & Silverstein, 1981).

### *2.4. Statistical analyses*

The multivariate statistical analyses were carried out with the JMP software package (SAS Institute, Cary, NC, USA). For the statistical evaluation of the volatile composition, the covariance data matrix was a 269 x 16 matrix (269 individual compounds x 16 samples = 4304 data). The principal component analysis (PCA) was performed selecting the two highest principal components (PCs) obtained by the linear regressions operated on mean-centred, unscaled data; as an unsupervised method, this analysis aimed at reducing the dimensionality of the multivariate data of the matrix, whilst preserving most of the variance (Choi et al., 2004). The chosen PC1 and PC2 cover 43.52 and 17.56% of the variance, respectively, for a total explained

variance of 61.08%. The hierarchical cluster analysis (HCA) was performed using the Ward's method. Both the HCA and the PCA methods can be applied to observe groups of samples even when there are no reference samples that can be used as a training set to establish the model.

## 3. Results and discussion

### *3.1. The Harvesting and Processing: Producing the Green Beans*

Coffee harvesting should start when the unripe cherries show a minimum (5%) presence (Bee et al., 2005). This process can be performed i) stripping the beans onto the ground, sometimes onto sheets; ii) by mechanical means; iii) selectively handpicking the fruits (Bee et al., 2005). The latter is the method used by the Harenna forest coffee farmers: here coffee plants are spread out in the undergrowth, where the farmers move, collecting the fruits in wicker baskets they carry attached to their sides ("Ethiopia – The Coffee of the Forest," 2015). As only the ripe cherries are picked in this harvesting method, the fruits must be taken to the processing facility in the very same day, to avoid the triggering of undesirable fermentation processes (Bee et al., 2005). The Harenna cherries are not washed after the picking, and the processing phase immediately follows the harvesting.

The beans processing phase can be performed with the wet or dry method: they confer to the product different aroma properties, favouring the biosynthesis of some compounds over others. This is also due to the effect on the resident microbiota: dry-processed fruits showed a higher diversity of *Pichia* and non-*Pichia* yeasts, as well as acetic acid bacteria, whilst wet-processed ones exhibited a shift towards more acid-tolerant bacteria (De Vuyst et al., 2017). The metabolites produced by these bacteria are also accumulated differently, based on the processing method: in the wet processing method, they are stored in the pulp, whilst in the dry method they migrate towards the outer layers (De Vuyst et al., 2017). For the Harenna coffee, the processing is performed by means of the natural drying method: the beans are naturally sun-dried on suspended net-beds and, to ensure even drying and prevent spoilage, they are spread in thin layers of 2-3 cm of height (Bee et al., 2005). They must be raked and turned several (15-17) times a day, in both directions: this ensures the fast evaporation of the external water content and facilitates the

identification of fermented or moulded fruits, which must be eliminated to avoid cross-contamination (Bee et al., 2005). They are covered at night or in the event of rain. It takes 2-3 weeks of good, dry weather to dry the cherries thoroughly. Other than producing a tasty and peculiar aromatic coffee, the natural drying process is completely environmental-friendly: it does not require the use of water and does not produce solid nor liquid residues, rich in organic substances, which are instead produced by the wet processing method (Bee et al., 2005). The natural drying process of the fruits lasts longer, as the soluble solids loss is lower than in the wet process (Bee et al., 2005). This is also the reason of the increased 'body' of the dry-processed beans compared to the wet ones. The sugars of the pulp, which represent the precursor of the aroma active compound developed in the later processing phases, have more time to migrate from the pulp to the bean, as, in absence of water, there is far less solubilisation and elimination of both these sugars and the fruit pulp (of which up to 60% is lost during the washing) (Ascrizzi, Flamini, Tessieri, & Pistelli, 2017; Bee et al., 2005). Once dried, the fruits are hulled by hand: for the coffee analysed in the present study, the husks are removed, but the silverskin is left on the bean. After manual sorting, the coffee is stored in jute bags: they must be kept in a dry (moisture level below 12%) and dark place, with mild temperatures before being shipped for export.

These green raw beans represented the first analysed sample in this study, both in their whole and ground forms: the complete compositions of their headspaces are reported in Table 1.

Non-terpene derivatives were the most represented class of compounds in both the samples, accounting for up to 35.63 and 65.82% in whole and ground green beans, respectively, but with different qualitative profiles. The whole beans were richer in esters and alkanes: among the former, 2-(1,1-dimethylethyl)-cyclohexanol acetate was the most abundant. Alcohols and acids, instead, were the main non-terpene derivatives detected in the ground beans. 2,3- and 1,3-butanediol were the most abundant non-terpene alcohols, followed by isoamyl alcohol and 4,7-dimethyl-4-octanol. Among the non-terpene acids, isovaleric and 2-methylbutanoic acid were the most represented: no compound of this chemical class was detected in the whole green beans. The reason for this different emission is probably due to the thermal effect of

178 grinding: heat triggers the esters hydrolysis, developing the volatile acids and alcohols that are detected in
179 the ground beans. In addition, the activation of enzymes must be taken into account.

180 The oxygenated monoterpenes were the second most abundant class of volatile compounds in both the
181 samples, accounting for 35.12 and 18.57% in the whole and ground beans, respectively. In this case, the
182 qualitative profile was not so different: tetrahydrolinalool was the most relevant compound of this class in
183 the whole beans, whilst in the ground ones (*E*)-linalool oxide (furanoid) was the most abundantly detected
184 one.

185 The other detected chemical classes of compounds greatly differed in these samples. Phenylpropanoids
186 and sesquiterpene hydrocarbons accounted for up to 10.89 and 4.94%, respectively, in the whole beans,
187 while they were completely undetected in the ground ones. Conversely, pyrazines represented 7.90% of
188 the total emission profile of the ground sample, whilst being completely absent in the whole one. As
189 pyrazines are key aroma active compounds in coffee, their behaviour and development during the
190 processing chain is of great interest: they are responsible for the toasted and nutty notes in foods
191 processed under high temperature and low humidity conditions (Ascrizzi et al., 2017; Yu & Zhang, 2010).
192 Since Harenna coffee beans do not undergo a fermentation phase, these compounds were not detected in
193 very significant relative abundances before the roasting takes place, whilst in products like the fermented
194 cocoa beans they are already present before the roasting phase.

195 The quality of this starting raw material is of utmost importance, as green beans contain all the precursors
196 of aroma volatiles, which will be developed during the subsequent roasting phase (Bhumiratana, Adhikari,
197 & Chambers, 2011).

198 *3.2. The Roasting Process: Phases and Involved Reactions*

199 An enjoyable coffee comes from a top quality starting material, but it also is an optimally roasted one: the
200 roasting phase, indeed, is critical for the development of a pleasant final product. It is not just an
201 application of heat to the green beans; it is a complicate process in which the generation and control of the
202 operating temperatures must be checked carefully until the full development of the desired aroma and a

203 homogeneous colour throughout the whole bean. To avoid uneven roasting of the beans, the temperature
204 gradient must be small: fast roasting, indeed, causes an overlapping in the evaporation and roasting steps,
205 thus leading to an inhomogeneous profile (Bonnlander, Eggers, Engelhardt, & Maier, 2005). The analysed
206 Harenna coffee beans are roasted for 15 minutes in a batch-operated spouted bed roaster: the forced
207 convective flow of hot air passes through the moving bed of coffee beans. The heat is generated by the
208 pyrolysis of acacia wood, whose choice is environmentally friendly: this species is invasive, so there is large
209 availability of it, and, once burnt, its woods do not produce ashes.

210 A large number of compounds is involved in the roasting phase: carbohydrates, fragments of proteins, acids
211 with low molecular weight, caffeine, trigonelline, lipids, a wide range of melanoidins and over 900 volatile
212 compounds (Wei & Tanokura, 2015). Coffee oil constitutes up to 10% of the roasted beans: it carries most
213 of the coffee aroma, which is determined by a complex bouquet of volatile compounds (Buffo & Cardelli-
214 Freire, 2004). Conversely, the non-volatile compounds are responsible for the sour, bitter and astringent
215 attributes of coffee (Roy Teranishi, Wick, & Hornstein, 1999). The reactions involved in the development of
216 coffee aroma are numerous and complex, with overlapping pathways. The Maillard reaction, though, is the
217 most important one: it is responsible for the biosynthesis of alkylpyrazines, as well as aminoaldoses and
218 aminoketones through the condensation between nitrogen-containing compounds and reducing sugars
219 (Buffo & Cardelli-Freire, 2004). Intermediate compounds of this biosynthetic pathway are also able to react
220 with the breakdown products of proline and hydroxyproline: pyridines and pyrroles derive from the former,
221 whilst the latter produces alkyl-, acyl- and furfurylpyrroles (Buffo & Cardelli-Freire, 2004). Nitrogen
222 heterocyclic compounds and oxazoles, instead, are synthesized through the Strecker degradation pathway
223 (Buffo & Cardelli-Freire, 2004).

224 The roasting process consists of four stages, characterised by different thermal profiles: in the present
225 study, samples from each phase have been collected and analysed.

226 *3.2.1. The Warm Up: The First Endothermic Phase*

227 Most of the moisture is eliminated during this phase, in which the beans loose up to 20% of their weight.
228 The surface of the bean is heated, and, when the evaporation temperature is reached, the front of
229 evaporation starts moving towards the centre of the bean. As the bean walls are still relatively firm and
230 drier, they are more resistant to heat transfer: this causes a pressure build up in the centre of the bean,
231 which induces volume expansion (Bonnlander et al., 2005). The colour of the beans turns to yellow and
232 their smell changes from the pea-like of the raw form to bread-like (Buffo & Cardelli-Freire, 2004). The first
233 roasted sample in the present study has been collected at this stage, at 100°C: both the whole and the
234 ground 100°C roasted samples headspaces have been analysed, and their complete compositions are
235 reported in Table 2.

236 The whole 100°C roasted beans headspace was rich in monoterpene hydrocarbons, of which limonene is
237 the most abundant, as well as the most relevant compound in the entire volatile profile: it accounted for up
238 to 33.53% over 38.93% of its chemical class. In the ground sample, instead, monoterpene hydrocarbons
239 were the second most represented chemical class, with limonene as the major contributor among them, as
240 well.

241 The grinding of this sample caused significant changes in the headspaces composition. Moreover,
242 silverskins, which normally are shed further on along the roasting process, are forced to fall off the bean for
243 the mechanical action of the grinding: this causes the evaporation of volatiles that would otherwise be
244 retained for a longer time in the roasting process.

245 Non-terpene derivatives, indeed, showed the highest relative abundance in the ground 100°C roasted
246 beans, of which they represented over 68% of the total emission profile. Among this chemical class,
247 alcohols were the major contributors: 2,3- and 1,3-butanediol showed the most relevant presence,
248 representing 17.39 and 14.36% of the total headspace, respectively. The former exhibited a significant,
249 even though much lower (4.49%), relative abundance in the whole beans, whereas the latter was not
250 detected. For the whole 100°C roasted beans, the non-terpene derivatives contribution followed the
251 monoterpene hydrocarbons one, with nonanal and 2,3-butanediol as the most important ones.

252 The oxygenated monoterpenes showed an almost doubled relative presence in the whole beans: dihydro
253 myrcenol and tetrahydro linalool were significantly present, as they accounted for up to 7.57 and 6.41%,
254 respectively. In the ground beans, conversely, whilst the latter represented less than 1% of the total
255 emission, the former was not detected: *trans*- and *cis*- linalool oxides (furanoid) were, instead, the most
256 important compounds of this class.

257 The pyrazines synthesis by means of the Maillard reaction was visibly triggered at this point: their presence
258 was more evident in the ground beans, as they are more easily volatilised once the silverskins have been
259 mechanically shed by the grinding process. 2,3,5-Trimethyl pyrazine, 2,6-diethyl pyrazine and 2-methoxy-3-
260 (2-methylpropyl) pyrazine were the most relevant ones in the ground sample, whilst 2-methyl pyrazine and
261 2,6-dimethyl pyrazine are the only detected compounds for this chemical group in the whole beans.

262 *3.2.2. The First Crack: The First Exothermic Phase*

263 Once the mechanical and thermal stresses overcome the tensile strength of the outer layers of the bean, a
264 first crack takes place (Bonnlander et al., 2005). The pyrolytic reactions are now triggered, leading to the
265 release of copious amounts of carbon dioxide and many compounds (e.g. pyrazines) associated with coffee
266 aroma (Buffo & Cardelli-Freire, 2004). At this point, the majority of the silverskins have been shed and
267 beans are twice the size and their surface appears dry, with no visible oil; their colour has now turned to
268 brown. The headspace of the 160°C sample, collected during this phase, has been analysed, in both its
269 whole and ground forms: the complete compositions are reported in Table 2.

270 As the temperature rises, the Maillard reaction products increase and become more diversified. Pyrazines,
271 indeed, represented the most abundant class of compounds in both the whole and the ground 160°C
272 roasted beans, accounting for up to 39.19 and 72.26% of the total emission profiles, respectively. Some
273 compounds of this class are produced during this phase and begin to be detectable, and some of them in
274 relevant relative quantity, as well. 2,6-Dimethyl pyrazine accounted for up to 16.74 and 26.44% in the
275 whole and ground samples, respectively: in both cases, it also represented the most abundant compound in
276 the emission profile. 2-Ethyl-5-methyl pyrazine followed as the second most relevant pyrazine in terms of

277 relative quantity: it was not detected in the previous samples, so its development is triggered by
278 temperatures higher than 100°C. In the 160°C roasted beans, it represented 7.79 and 17.26% in the whole
279 and ground samples, respectively. 2-Methyl pyrazine, detected only in very low relative concentrations in
280 the previous samples, showed a significant increment: it accounted for 6.20 and 7.29% in the whole and
281 ground samples, respectively. 2,6-Diethyl pyrazine, 2,3-dimethyl and 2-ethyl-6-methyl pyrazines were also
282 detected in significant relative amounts in both the headspaces. 2-Ethyl-3,5-dimethyl pyrazine was only
283 detected in the ground sample, in which the disruption of the matrix caused by the grinding process most
284 probably triggered its volatilization.

285 In the whole sample, monoterpene hydrocarbons still exhibited a significant presence: limonene was again
286 the most represented constituent of this class, as it accounted for up to 15.11% over a total of 19.93% of its
287 chemical group. Their relevant decrement in the ground beans confirms the evaporation-triggering effect
288 of grinding, as well as the effect on the silverskins shedding. The oxygenated monoterpenes were also
289 important contributors to the whole beans volatile profile: α-terpinyl acetate and tetrahydrolinalool, both
290 undetected in the ground beans, contributed for up to 6.07 and 4.48%, respectively.

291 The non-terpene derivatives were the second most abundant chemical class of compounds in the ground
292 sample, and they showed a significant relative quantity in the whole beans as well. Unlike the green and
293 100°C roasted beans, though, these samples volatile profiles exhibited a relevant presence of aldehydes: 2-
294 methylbutanal, not detected in the whole sample, accounted for up to 8.32% in the ground sample, whilst
295 nonanal had a 2.00% relative quantity in the whole beans. In the latter sample, esters were significantly
296 present: among them, *cis*-2-tert-but-cyclohexanol acetate contributed for up to 4.48%.

297 *3.2.3. The Recovery: The Second Endothermic Phase*

298 Once the temperature reaches 180°C, the pyrolytic reactions are at their maximum peak, and the process
299 becomes endothermic again, with the release of volatile compounds (Buffo & Cardelli-Freire, 2004). As the
300 caramelisation of the sugars is still ongoing, this phase must be rapid to avoid baking: thus, the transition to
301 the next phase temperature must be performed quickly. For the present study, the analysis involved the

sample collected at 180°C, in both its whole and ground form: the complete compositions are reported in Table 2.

Pyrazines constituted most of the headspaces of both these samples, as they accounted for over 70% of the ground beans and over 45% of the whole ones, and the three most represented compounds of this class were common to both the samples. 2,6-Dimethyl pyrazine was the most abundant compound in both cases, followed by 2-methyl pyrazine in the whole beans and 2-ethyl-5-methyl pyrazine in the ground ones. Other than pyrazines, other nitrogen derivatives started to show a relevant presence in the headspaces: pyridine was the most abundant one in both cases, accounting for 0.74 and 4.78% in the whole and ground beans, respectively; in the latter sample, pyrimidine was also detected, with a relative presence of 0.64%.

Both samples shared relevant (and quite similar) relative amounts of non-terpene derivatives, representing 21.45% of the whole beans headspace and 16.46% for the ground sample. Among these compounds, esters showed a higher impact on the overall beans headspace: the most important ones, in terms of relative presence, were *cis*- and *trans*-tert-butyl-cyclohexanol acetate, and ethyl acetate. Aldehydes, instead, were more represented in the ground beans headspaces: 2-methylbutanal and furfural accounted for up to 3.32 and 2.14%, respectively.

The strong impact of grinding on the monoterpene fraction was confirmed in these headspaces: both the oxygenated and the hydrocarbon ones, indeed, whilst representing up to 15.08 and 11.57% in the whole beans, respectively, were detected only in very low amounts in the ground sample. As in the previous whole sample, limonene, dihydro myrcenol and tetrahydro linalool were the most abundant compounds of these classes, accounting for up to 10.24, 5.66 and 4.12%, respectively: the last two were not even detected in the ground sample, whereas the first one was almost trace-detected.

#### *3.2.4. The Second Crack (Second Exothermic Phase) and The Rapid Cooling*

Over 200°C, the process becomes exothermal again. The final temperature depends on the starting material and on the desired degree of roasting: for the analysed coffee, the final roasting temperature is 204°C. Once the material has reached the desired final roasting temperature, the beans must be cooled

down rapidly: a flow of cold air is forced through the beans, in order to stop further changes in colour, flavour and volume (Bonnlander et al., 2005). A typical feature of the analysed Harenna coffee is that the roasted beans show different shades of brown: some beans remain lighter, some others darker. The collected samples are analysed, in both their whole and ground forms, mixed as well as separately (darker and lighter coloured beans): the complete compositions are reported in Table 3.

The headspaces of both the whole and ground mixed beans were mainly rich in pyrazines, which accounted for up to 66.5 and 48.30%, respectively. The most abundant compound of this class was 2,6-dimethyl pyrazine in both the samples, and for the whole beans it also represented the main compound in the emission profile. 2,3,5-Trimethyl, 2-methyl and 2,6-diethyl pyrazines followed. The non-terpene derivatives were the second most relevant chemical group of volatiles in both the samples, contributing for up to 15.60 and 33.02% in the whole and ground samples, respectively. 2-Methylbutanal, undetected in the whole sample, reached 4.67% in the ground beans headspace, whilst ketones were far more relevant in the ground sample: 2-butanone, 1-acetyloxy-2-propanone and 2,3-pentanedione showed similar relative presence in this sample, despite being undetected in the whole beans. Furan derivatives showed relevant relative concentrations in both the samples: 2-furan methanol was the most represented one, followed by 5-methyl furfural and furfuryl acetate. Other than pyrazines, other nitrogen derivatives exhibited important presence in these samples headspaces: among these compounds, pyridine was the most abundant, accounting for up to 8.29% over a total of 9.40% in the whole beans, and as much as 12.62% over 15.23% in the other sample.

To assess the contribution of the darker and the lighter beans to the mix, the analyses of their individual headspaces have been performed, in both their whole and ground forms.

Pyrazines were the most represented compounds in all the headspaces: they accounted for over 40% of the volatile profiles of both the whole and ground samples. The grinding process, though, is responsible for the loss of these constituents with a more significant extent in the darker beans sample: grinding, indeed, caused a decrement in pyrazines relative abundance from 69.61 to 43.03%. In the lighter sample, instead,

352 the pyrazine relative concentration incremented after the grinding process. 2,6-Dimethyl pyrazine was the
353 most abundant constituent of this class and, apart from the darker ground beans, it was also the compound
354 with the highest relative abundance in all the headspaces. 2,3,5-Trimethyl, 2-methyl, 2,6-diethyl and 2,3-
355 dimethyl pyrazines followed, showing the same trend of the entire class: the ground darker beans were the
356 sample in which their decrement was more significant. 2-Ethyl pyrazine is the only compound in this
357 chemical group that did not show a decrement in the ground dark sample.

358 Non-terpene derivatives were the second most abundant chemical class of compounds, with the highest
359 relative abundance in the darker ground beans, where they accounted for up to 34.11%. Whilst 2-
360 methylbutanal and 1-acetyloxy-2-propanone were detected only in the ground samples, furan derivatives
361 were detected in both, even though their presence was more relevant for the ground samples. 2-Furan
362 methanol, 5-methyl furfural and furfuryl acetate were the most represented compounds of this class: this
363 pattern was the same as the mixed beans samples. Nitrogen-derivatives (other than pyrazines) exhibited
364 significant presence in all the samples, with a more marked abundance in the ground beans of both the
365 darker and the lighter samples. As in the mixed beans headspaces, pyridine was the most abundant
366 compound of this chemical group in all the samples, with the exception of the lighter ground one. For the
367 darker beans, it accounted for up to 9.51% over a total of 10.08% in the whole ones, and 10.32% over a
368 total of 14.02% in the ground ones; in the lighter whole sample headspaces, it reached up to 8.55% and it
369 was the only detected non-terpene nitrogen-derivative.

370 The oxygenated monoterpenes were still significantly represented in this phase, in both the mixed and the
371 individual samples. Overall, the headspace where more oxygenated monoterpenes were detected is the
372 dark ground ones, where they accounted for up to 5.86%. Qualitatively, linalool and its derivatives were the
373 most represented ones: (*E*)-linalool oxide was the most abundant.

374 *3.3. The Silverskins*

375 The silverskin is a thin tegument that acts as a seed coat. Some authors report the removal of all of part of
376 the silverskins right after the drying: this reduces the drying time (Steiman, 2013) and, according to some

377 home-roasters, the “grassy” aroma of coffee. For the coffee of the present study, the silverskins have been
378 kept until the roasting. During the roasting, they become chaff and are shed from the beans, from which
379 they are separated by the airflow. The dry-processing method used after the harvesting produces more
380 silverskins compared to the wet one (Narita & Inouye, 2014).

381 The headspace of the silverskins analysed in the present study is reported in Table 4. It was mainly rich in
382 monoterpenes, both hydrocarbons and oxygenated ones. Among the former, limonene and β-pinene were
383 the most abundant ones, as they accounted for 23.26 and 5.04%, respectively, over a total relative
384 presence of 38.95% for this chemical class. 1,8-Cineole was the most represented oxygenated
385 monoterpene. The most abundant compound in the headspace, though, was methyl chavicol: this
386 accounted for 32.53% and was the only detected phenylpropanoid. The only detected pyrazines were 2,5-
387 dimethyl and 2-methyl pyrazine, at as low as 0.30 and 0.18%, respectively.

388 Comparing these results with the whole and ground green beans head spaces, it emerges that both methyl
389 chavicol and 1,8-cineole are constitutively present in the silverskins. The former, indeed, accounted for
390 8.74% in the whole green beans, whilst it was not detected after the grinding process: the shedding of the
391 silverskins caused the disappearance of this compound in the headspace. 1,8-Cineole, whilst representing
392 up to 5.33% in the whole green beans, was undetectable in the ground sample: it was lost with the
393 shedding of the silverskins. Conversely, limonene seemed to be mostly retained in the silverskins from the
394 beans, as it was detected with a higher relative abundance in the ground green beans rather than the
395 whole ones.

396 *3.4. The Brewed Coffee*

397 The composition of the headspace of a freshly brewed filtered cup of Harenna coffee is reported in Table 4.
398 Non-terpene derivatives represented 48.10% of the total emission profile, with *n*-heptane as the most
399 abundant. C1-C7 alkanes like the latter are lipid peroxidation products generated during the roasting phase:
400 the fat content of the beans, indeed, drops after the roasting phase, as the lipids undergo oxidation, which
401 produces other compounds (Shibamoto, 2015). Among non-terpene derivatives, two aldehydes were

402 detected in relevant relative abundances: nonanal and decanal accounted for up to 6.69 and 4.13%,
403 respectively. They both confer a citrus-like, floral and sweet aroma to the brew (Burdock, 2010; Mosciano,
404 2001). Furan derivatives are heterocyclic compounds largely reported in coffee headspaces; some
405 compounds of this class, i.e. 2-alkylfurans, can derive from the lipid peroxidative pathway, whereas others
406 are produced by the Maillard reaction (Shibamoto, 2015). Furans, indeed, are the main metabolites formed
407 by the decomposition of D-glucose and sugar polymers of coffee during the roasting process (Heyns, Stute,
408 & Paulsen, 1966). 2-Furanmethanol acetate is a 2-alkylfuran reported in this sample headspace, where it
409 accounted for up to 4.82%: its aroma contribution to the brew is defined as a pleasant floral and fruity
410 note, typical of the Harenna brew (Burdock, 2010). Secondary aroma compounds, originated from the first
411 degradation metabolites (like reactive aldehydes) of less volatile constituents (like lipids and
412 carbohydrates), are synthesized in the Maillard reaction, in which the carbonyl group of a sugar reacts with
413 an amino group of an amino acid (Shibamoto, 2015). Furans like 5-methyl furfural, detected with a relative
414 content of 2.38%, originate from this pathway (Martins, Jongen, & Van Boekel, 2001; van Boekel, 2006).
415 This compound aroma profile is defined as spicy, sweet and caramel-like (Arctander, 1969; Burdock, 2010).

416 Among the products deriving from further interactions of the Maillard products, pyrazines have a
417 fundamental role in coffee flavour, followed by pyridines and pyrroles (Flament & Bessière-Thomas, 2002).
418 Dimethyl pyrazines are, indeed, involved in the typical coffee flavour, as well as the that of the roasted
419 peanuts (Mason, Johnson, & Hamming, 1966); among these compounds, 2,6-dimethyl pyrazine was the
420 most abundant in the analysed brewed coffee sample, where it accounted for 4.98%. Its aroma
421 contribution is described as cocoa- and nutty-like, and sweet (Burdock, 2010; Flament & Bessière-Thomas,
422 2002). 2-Ethyl-5-methyl and 2-ethyl-6-methyl pyrazines followed, with a relative content of 3.2 and 2.05%,
423 respectively: both share a roasted aroma, coupled with a nutty note for the former (Burdock, 2010;
424 Flament & Bessière-Thomas, 2002), whilst the latter has a “green” odour, with cocoa- and hazelnut-like
425 notes (Afoakwa, 2010; US3917872 A, 1974). Roasted and hazelnut-like notes are also conferred to the
426 sample by 2,6-diethyl pyrazine (López-Galilea, Fournier, Cid, & Guichard, 2006) and 2,3,5-trimethyl pyrazine
427 (Bonvehí, 2005; Frauendorfer & Schieberle, 2006, 2008).

Other detected aroma-relevant nitrogen derivatives were pyridine and 1-furfuryl pyrrole: they accounted for 6.39 and 2.33%, respectively. The former originates from the decomposition of trigonelline, which takes place during the roasting phase (Hughes & Smith, 1946); even though its aroma is generally considered as disturbing, in extreme dilution, like in a coffee brew, it confers a warm and smoked aroma (Arctander, 1969).

An interesting detected compound is (*E*)-anethole, the only phenylpropanoid in the headspace composition, whose aroma contribution is reported as sweet, spicy and anise-like (Burdock, 2010).

### *3.5. Multivariate statistical analysis*

The complete compositions of the headspaces of all the samples have been analysed by means of multivariate statistical analysis, with both the hierarchical cluster and principal component methods.

The dendrogram of the hierarchical cluster analysis (HCA) is shown in Figure 1. The samples were distributed in two macro-clusters (A and B), further divided in two clusters each (A1 and A2, B1 and B2).

The cluster A1 comprised the green and the 100°C roasted beans, both in their whole and ground forms. The green beans are the raw starting material, and the roasted beans still have not undergone the pyrolysis reactions, as at this point they are in the warming-up phase, in which they mainly lose their water content.

The silverskins headspace was clustered by itself in A2: this headspace was quite different from the other samples, as it was richer in monoterpenes and phenylpropanoids.

The B macro-cluster comprised all samples that have undergone higher roasting temperatures, in which new sets of compounds are synthesized. The B1 cluster comprised the whole and ground samples from the second and third phase of the roasting process, namely the first crack and the recovery phase. The two whole samples were clustered closer, and so were the ground ones: the grinding induced more statistically relevant differences in these samples compared to the two different roasting temperatures.

The B2 cluster comprised all the other samples: the 204°C roasted beans (mixed, darker and lighter) in both their whole and ground forms, and the brewed coffee. As in the B2 cluster, the grinding caused more

statistically relevant differences in the headspace compositions compared to the different combination of the differently coloured beans. The brewed coffee was placed a little apart from the 204°C roasted beans samples: this placement could indicate that it retains most of the aroma compounds of the powder used for its preparation.

This statistical distribution was confirmed by the score plot of the principal component analysis (PCA) shown in Figure 2.

All the samples of the HCA macro-cluster A were plotted in the right quadrants (positive PC1) of the plot. The silverskins sample was plotted by itself in the lower right quadrant (positive PC1, negative PC2): its limonene, 1,8-cineole and methyl chavicol contents sharply distinguished it from the other samples. All the samples from cluster A1 were plotted in the upper right quadrant (positive PC1 and PC2), except for the 100°C roasted whole sample: the latter, though, was plotted very close to the upper quadrant. Its position was due to its still relevant limonene relative abundance, but it also showed significant contents of nonanal, dihydromyrcenol and tetrahydrolinalool, whose vectors were responsible for its position in the plot. The whole green beans sample was plotted slightly upper, but still quite close to the 100°C roasted whole beans sample, as its methyl chavicol content was still relevant. The ground green and 100°C roasted samples were very close, being both grouped in the upper right quadrant: 1,3- and 2,3-butanediol, isovaleric acid and 2-methylbutanoic acid vectors were the reason for their positions in the score plot.

All the samples from the macro-cluster B were plotted in the left quadrants (negative PC1), except for the 160°C roasted whole beans sample, whose position was, though, very close to the left quadrants od the plot. The latter was plotted towards the leftmost area of the lower right quadrant (positive PC1, negative PC2) for its very significant relative abundance of limonene compared to other samples of the same roasting phase. The 180°C roasted whole sample was in the closest position to the previous, as its limonene content was still relevant. The ground samples, instead, were plotted towards the bottom left of this quadrant (negative PC1 and PC2): 2, methyl butanal, 2,6- and 2,3-dimethyl pyrazines, together with 2-ethyl-5-methyl pyrazine vectors plotted these samples close to each other in this position.

The B2 macro-cluster samples were plotted between the upper and the lower left quadrants. In the positive PC2 left quadrant, the brewed coffee was plotted in the rightmost position: the decanal and (*E*)-anethole vectors were responsible for the positioning towards the right, still, though, in the left quadrants section for the pyridine vector. All the ground samples from the 204°C roasting temperature were also plotted in the upper left quadrant (negative PC1, positive PC2), but their positions were very close to the lower one. 2-Methyl pyrazine, pyridine and 2-methyl butanal vectors were responsible for their lower positioning compared to the brewed sample; their relative abundances of 1-methyl-2-formyl pyrrole, 2-furan methanol and 3-aminopyridine, though, were more relevant than those of the whole samples, compared to which the ground ones were plotted in a higher position. All the 204°C roasted whole samples were in the lower left quadrant (negative PC1 and PC2): 2-methyl, 2,6-dimethyl and 2,3-dimethyl pyrazines, as well as pyridine and 2-furan methanol vectors caused their positioning in this area.

## 4. Conclusion

The aroma of coffee is undoubtedly the most important characteristic of this beverage, and its key feature for consumers' success. The volatile compounds are responsible for the final product aroma notes. The volatile bouquet depends on the quality of the starting material, where the pool of precursors is biosynthesized, but the subsequent processing phases are fundamental for the reactions leading to the formation of aromatic notes from these precursors.

As emerges from the results, the silverskins are responsible for the preservation of volatile compounds involved in the aroma of the final product: their removal prior to roasting seems to be unadvisable, particularly for strongly aromatic coffees like the Harenna variety.

The grinding process in each phase of the production of the Harenna coffee in the present study was performed to evaluate the effect of the mechanical disruption of the matrices, with the subsequent increment of the areas exposed to air oxidation and of the volatiles release, with an increase in their detectability. Its effect is more evident in the early (green and 100°C roasted beans) and intermediate (160 and 180°C roasted beans) phases: the forced removal of the silverskins through the grinding has been

hypothesized to be responsible for the statistically evident changes in the volatile profiles. The last phases of the roasting (204°C roasted beans) are less affected by the grinding.

The headspaces analysis of each phase of the processing chain of coffee is a fast and reliable method to evaluate the development of these aromatic compounds, from the raw beans to the final product. It is a valuable aid to the definition of an ideal temperature program, as well as a method to evaluate the quality of the starting material, thus helping in the definition of the best botanic varieties to use, as well as the best pre-processing practices.

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631 **Tables**

632 **Table 1.** Identified volatiles in the HS-SPME analysis of the whole and ground green beans samples.

| Constituents | l.r.i.[a] | Relative abundance (%) | |
|---|---|---|---|
| | | Whole green beans | Ground green beans |
| pentanal | 695 | -[b] | 0.69±0.03 |
| *n*-heptane | 700 | - | 1.20±0.03 |
| isoamyl alcohol | 736 | - | 7.66±0.18 |
| 1,3-butanediol | 785 | - | 8.03±0.51 |
| 2,3-butanediol | 799 | 1.35±0.46 | 9.86±1.22 |
| isovaleric acid | 834 | - | 5.07±0.33 |
| 2-methylbutanoic acid | 860 | - | 4.03±0.31 |
| ethylbenzene | 869 | - | 0.80±0.03 |
| 1-hexanol | 871 | 0.44±0.62 | 4.46±0.18 |
| 2,6-dimethyl pyridine | 884 | - | 1.16±0.06 |
| styrene | 890 | - | 1.52±0.49 |
| 4-methyldihydro-2(3H)-furanone | 914 | - | 1.98±0.06 |
| α-pinene | 941 | 1.67±0.04 | - |
| (*Z*)-2-heptenal | 963 | - | 0.33±0.47 |
| hexanoic acid | 986 | - | 1.95±0.18 |
| myrcene | 993 | 0.40±0.56 | - |
| octanal | 1001 | 0.53±0.74 | - |
| 2,3,5-trimethyl pyrazine | 1005 | - | 3.47±1.05 |
| benzyl alcohol | 1026 | - | 1.78±0.06 |
| limonene | 1032 | 7.51±0.16 | 6.59±0.23 |
| 1,8-cineole | 1034 | 5.33±0.09 | - |
| (*E*)-β-ocimene | 1052 | 0.37±0.52 | - |
| 4,7-dimethyl-4-octanol | 1065 | - | 6.15±0.30 |
| *trans*-arbusculone | 1066 | - | 1.31±0.01 |
| dihydro myrcenol | 1074 | 9.03±0.03 | - |
| *trans*-linalool oxide (furanoid) | 1076 | - | 9.56±0.16 |
| 2,6-diethyl pyrazine | 1080 | - | 3.44±0.14 |
| *cis*-linalool oxide (furanoid) | 1090 | 0.48±0.68 | 4.11±0.32 |
| tetrahydro linalool | 1098 | 9.54±0.25 | 2.44±0.21 |
| linalool | 1101 | - | 0.98±0.08 |
| nonanal | 1102 | 4.45±0.09 | 2.92±0.13 |
| isopentyl isovalerate | 1105 | - | 0.36±0.50 |
| phenylethyl alcohol | 1110 | - | 2.12±0.69 |
| (*Z*)-2-undecene | 1115 | 0.35±0.49 | - |
| camphor | 1143 | 1.73±0.01 | - |
| menthol | 1173 | 0.49±0.69 | - |
| *trans*-linalool oxide (pyranoid) | 1177 | - | 0.74±0.05 |
| isomenthol | 1179 | 0.44±0.62 | - |
| 2-methoxy-3-(2-methylpropyl) pyrazine | 1179 | - | 0.99±0.14 |
| methyl chavicol | 1197 | 8.74±0.38 | - |
| decanal | 1204 | 2.11±0.07 | 0.35±0.49 |
| carvone | 1244 | 5.07±0.19 | 0.77±0.18 |
| (*E*)-anethole | 1283 | 2.15±0.13 | - |
| isobornyl acetate | 1285 | 1.68±0.17 | - |
| *cis*-2-tert-butyl-cyclohexanol acetate | 1293 | 17.69±2.07 | 2.43±0.30 |

| | | | |
|---|---|---|---|
| *n*-tridecane | 1300 | 1.43±0.51 | - |
| undecanal | 1306 | 0.38±0.54 | - |
| *trans*-2-tert-butyl-cyclohexanol acetate | 1312 | 3.05±0.13 | - |
| α-terpinyl acetate | 1352 | 0.37±0.52 | - |
| neryl acetate | 1366 | 0.99±0.04 | - |
| *n*-tetradecane | 1400 | 2.78±0.42 | 0.85±0.03 |
| β-caryophyllene | 1420 | 1.06±0.04 | - |
| (*E*)-geranyl acetone | 1455 | 0.37±0.52 | - |
| (*E*)-β-farnesene | 1460 | 1.03±0.04 | - |
| *ar*-curcumene | 1483 | 1.95±0.19 | - |
| *n*-pentadecane | 1500 | 1.09±0.04 | - |
| β-bisabolene | 1509 | 0.91±0.05 | - |
| | | | |
| Monoterpene hydrocarbons | | 9.94±0.88 | 6.59±0.23 |
| Oxygenated monoterpenes | | 35.12±0.95 | 18.57±0.66 |
| Sesquiterpene hydrocarbons | | 4.94±0.33 | - |
| Apocarotenoids | | 0.37±0.52 | - |
| Pyrazines | | - | 7.90±0.77 |
| Other nitrogen compounds | | - | 1.16±0.06 |
| Phenylpropanoids | | 10.89±0.51 | - |
| Other non-terpene derivatives | | 35.63±0.39 | 65.82±0.41 |
| Total identified (%) | | 96.88±0.08 | 100.00±0.01 |

[a] Linear retention indices on a DB5 column. [b] Not detected.

633

634 **Table 2.** Identified volatiles in the HS-SPME analysis of the whole and ground beans samples at three intermediate roasting temperatures (100°C, 160°C and

635 180°C).

| Constituents | l.r.i.[a] | Relative abundance (%) | | | | | |
|---|---|---|---|---|---|---|---|
| | | 100 °C whole | 100 °C ground | 160 °C whole | 160 °C ground | 180 °C whole | 180 °C ground |
| ethyl acetate | 616 | -[b] | - | - | - | 0.9±0.07 | - |
| 2-methyl butanal | 662 | - | - | - | 8.32±0.02 | - | 3.32±0.01 |
| pentanal | 695 | - | 0.39±0.54 | 1.4±0.01 | - | - | - |
| *n*-heptane | 700 | - | 0.46±0.64 | - | - | - | - |
| isoamyl alcohol | 736 | - | 4.87±0.01 | - | 0.82±0 | - | - |
| pyrimidine | 736 | - | - | - | - | - | 0.64±0 |
| pyridine | 740 | - | - | 2.04±0.17 | 2.2±0 | 0.74±0.06 | 4.78±0.25 |
| 1,3-butanediol | 785 | 3.01±0.37 | 14.36±0.74 | - | 0.5±0.01 | - | 0.25±0.03 |
| 2,3-butanediol | 799 | 4.49±0.46 | 17.39±0.91 | - | 0.4±0.01 | - | - |
| *n*-hexanal | 802 | - | - | 0.67±0.32 | 0.8±0 | - | - |
| 2-methyltetrahydrofuran-3-one | 809 | - | - | - | - | - | 1.11±0.01 |
| 2-methyl pyrazine | 833 | 0.76±0.05 | - | 6.2±0.06 | 7.29±0.01 | 9.18±0.59 | 10.28±0.05 |
| isovaleric acid | 834 | - | 2.77±0.13 | - | 2.44±0 | - | 1.64±0.01 |
| furfural | 839 | 1.19±0.21 | - | - | - | 1.71±0.02 | 2.14±0.01 |
| 2-furan methanol | 859 | - | - | - | 1.92±0.01 | - | 3.78±0.01 |
| 2-methylbutanoic acid | 860 | - | 2.22±0.11 | - | 1.05±0.01 | - | 0.81±0 |
| ethylbenzene | 869 | - | 0.86±0.01 | - | - | - | - |
| 1-hexanol | 871 | - | 4.21±0.21 | - | 1.17±0.01 | - | - |
| furfuryl alcohol | 872 | - | - | - | - | 1.53±0.06 | - |
| 2,6-dimethyl pyridine | 884 | 0.16±0.22 | 0.9±0.08 | - | - | - | - |
| styrene | 890 | - | 1.18±0.07 | - | - | - | - |
| 2-heptanone | 891 | 1.74±0.38 | - | 2.33±0.09 | - | 3.3±0.22 | - |
| *o*-xylene | 897 | 0.15±0.21 | - | - | - | - | - |
| 2-butoxy ethanol | 905 | 0.6±0.06 | - | 0.57±0.01 | - | 0.55±0 | - |
| (*Z*)-2-methyl-2-butenoic acid | 908 | - | - | - | 0.3±0.01 | - | - |
| 2,6-dimethyl pyrazine | 910 | 0.19±0.26 | 0.83±0.18 | 16.74±1.22 | 26.44±0.11 | 19.34±1.41 | 21.17±0.13 |
| 4-methyldihydro-2(3H)-furanone | 914 | - | 2.09±0.34 | - | - | - | - |
| 2-ethyl pyrazine | 925 | - | - | - | - | - | 4.84±0.04 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 2,3-dimethyl pyrazine | 930 | - | - | 2.85±0.01 | 4.61±0.42 | 2.97±0.15 | 5.16±0.11 |
| α-pinene | 941 | 0.2±0.28 | - | 0.68±0.15 | - | 0.24±0.34 | - |
| 2-methyl cyclohexanone | 953 | - | - | - | 0.11±0.15 | - | 0.54±0.01 |
| benzaldehyde | 963 | 0.23±0.33 | 0.29±0.41 | 0.24±0.33 | 0.24±0 | - | - |
| 5-methyl furfural | 965 | - | - | - | - | 0.78±0.1 | 1.38±0.03 |
| 3-methyl-2-cyclopenten-1-one | 972 | 0.33±0.46 | - | - | - | - | - |
| sabinene | 976 | - | - | 0.19±0.27 | - | - | - |
| β-pinene | 982 | - | - | 0.45±0.05 | - | - | - |
| 6-methyl-5-hepten-2-one | 985 | 0.51±0.11 | - | 0.25±0.35 | - | - | - |
| myrcene | 993 | 0.84±0.06 | - | 0.92±0.14 | - | 0.56±0.04 | 0.45±0 |
| 2-pentyl furan | 993 | - | 1.11±0.16 | - | 0.56±0 | - | - |
| 2-furanmethanol acetate | 995 | - | - | - | - | - | 0.46±0 |
| octanal | 1001 | 0.98±0.05 | - | - | - | - | - |
| 2-ethyl-6-methyl pyrazine | 1001 | - | - | 1.53±0.01 | 3.56±0.11 | 2.64±0.16 | 5.45±0.03 |
| 2-ethyl-5-methyl pyrazine | 1004 | - | - | 7.79±0.23 | 17.26±0.85 | 8.73±0.54 | 14.83±0.47 |
| 2,3,5-trimethyl pyrazine | 1005 | - | 2.23±0.78 | - | - | - | - |
| δ-3-carene | 1011 | 0.84±0.04 | - | 0.76±0.18 | - | 0.53±0.07 | - |
| 1,4-cineole | 1016 | 1.5±0.04 | - | - | - | - | - |
| 1-*p*-menthene | 1026 | - | - | 0.21±0.29 | - | - | - |
| *p*-cymene | 1027 | 1.12±0.19 | - | 0.19±0.26 | - | - | - |
| 2-ethenyl-6-methyl pyrazine | 1031 | - | - | - | 0.88±0 | - | 1.07±0.38 |
| limonene | 1032 | 33.53±2.82 | 6.67±0.42 | 15.11±0.13 | 0.82±0.16 | 10.24±0.06 | 0.58±0.11 |
| γ-terpinene | 1062 | 1.23±0.11 | - | 0.22±0.3 | - | - | - |
| 2-acetyl pyrrole | 1062 | - | - | - | 0.24±0.04 | - | - |
| 4,7-dimethyl-4-octanol | 1065 | - | 5.91±0.09 | - | - | - | - |
| *trans*-arbusculone | 1066 | - | 1.08±0.01 | - | - | - | - |
| dihydro myrcenol | 1074 | 7.57±0.18 | - | 4.23±0.3 | - | 5.66±0.31 | - |
| *trans*-linalool oxide (furanoid) | 1076 | - | 7.82±0.29 | - | 0.96±0.08 | - | 0.53±0.01 |
| 2,6-diethyl pyrazine | 1080 | - | 2.76±0.11 | 4.08±0.21 | 8.06±0.08 | 3.83±0.08 | 6.02±0.01 |
| 2-ethyl-3,5-dimethyl pyrazine | 1085 | - | - | - | 2.02±0.01 | 0.26±0.37 | 1.89±0.03 |
| *p*-mentha-2,4(8)-diene | 1087 | 0.21±0.3 | - | - | - | - | - |
| terpinolene | 1088 | 0.99±0.43 | - | 1.24±0.09 | - | - | - |
| *cis*-linalool oxide (furanoid) | 1090 | - | 5.46±0.14 | - | - | 1.61±0.29 | - |
| 2,5-diethyl pyrazine | 1091 | - | - | - | 0.26±0.04 | - | - |
| tetrahydro linalool | 1098 | 6.41±0.21 | 0.99±0.24 | 4.48±0.13 | - | 4.12±0.01 | - |
| linalool | 1101 | 1.38±0.08 | 1.51±0.05 | - | 0.8±0.03 | - | 0.31±0.01 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| nonanal | 1102 | 7.82±0.36 | 2.9±0.21 | 2±0.14 | 0.6±0.04 | 1.64±0.23 | - |
| (*E*)-2-methyl-6-(1-propenyl) pyrazine | 1107 | - | - | - | - | - | 0.25±0.01 |
| phenylethyl alcohol | 1110 | - | 1.84±0.11 | - | - | - | - |
| *cis*-*p*-mentha-2,8-dien-1-ol | 1122 | - | - | 0.21±0.29 | - | 0.24±0.33 | - |
| 1-terpineol | 1138 | 1.15±0.15 | - | - | - | - | - |
| 5H-5-methyl-6,5-dihydrocyclopentapyrazine | 1142 | - | - | - | 0.13±0.18 | - | 0.35±0.02 |
| camphor | 1143 | - | - | 1.29±0.11 | - | 0.95±0.02 | - |
| 2,3-diethyl-5-methyl pyrazine | 1153 | - | - | - | 0.49±0.03 | - | 0.35±0.06 |
| 3,5-diethyl-2-methyl pyrazine | 1156 | - | - | - | 0.75±0.01 | - | 0.95±0.21 |
| *trans*-β-terpineol | 1159 | 0.15±0.21 | - | - | - | - | - |
| (*E*)-2-nonenal | 1164 | - | - | - | 0.58±0.03 | - | - |
| 2-acetyl-3-ethyl pyrazine | 1167 | - | - | - | - | 0.24±0.34 | - |
| menthol | 1173 | 0.52±0.03 | - | - | - | 0.19±0.27 | - |
| *cis*-linalool oxide (pyranoid) | 1174 | - | 0.25±0.35 | - | - | - | - |
| 4-terpineol | 1178 | 1.35±0.01 | - | 0.25±0.35 | - | - | - |
| 2-methoxy-3-(2-methylpropyl) pyrazine | 1179 | - | 1.13±0.13 | - | - | - | - |
| naphthalene | 1181 | 0.15±0.21 | - | - | - | - | - |
| (*Z*)-2-methyl-5-(1-propenyl) pyrazine | 1190 | - | - | - | 0.53±0.01 | - | 0.62±0.03 |
| 1-phenylethyl acetate | 1190 | - | - | 0.76±0.04 | - | 0.58±0.04 | - |
| α-terpineol | 1191 | - | 0.69±0.03 | - | 0.15±0.21 | - | - |
| γ-terpineol | 1195 | 4.8±0.49 | - | 0.44±0.01 | - | - | - |
| *n*-dodecane | 1200 | 1.97±0.22 | - | 0.95±0.05 | - | 0.62±0.03 | - |
| decanal | 1204 | 1.09±0.13 | 0.35±0.49 | 0.88±0.05 | 0.38±0.11 | 0.91±0.08 | - |
| *cis*-sabinene hydrate acetate | 1221 | 0.38±0.04 | - | - | - | - | - |
| carvone | 1244 | - | - | - | - | 1.57±0.19 | - |
| 2-phenylethyl-2-butenal | 1271 | - | - | - | 0.15±0.21 | - | - |
| (*E*)-anethole | 1283 | 1.65±0.21 | - | - | - | 0.84±0.06 | - |
| bornyl acetate | 1287 | 1.18±0.16 | - | 0.99±0.08 | - | 0.76±0.04 | - |
| *cis*-2-tert-butyl-cyclohexanol acetate | 1293 | 2.63±0.33 | 0.55±0.03 | 4.64±0.37 | - | 5.6±0.45 | - |
| *n*-tridecane | 1300 | 0.8±0.1 | - | 0.78±0.06 | - | 0.78±0.06 | - |
| *trans*-2-tert-butyl-cyclohexanol acetate | 1312 | 1.45±1.33 | - | 0.9±0.06 | - | 1.03±0.09 | - |
| 2-methoxy-4-vinylphenol | 1317 | - | - | - | - | - | 1.05±0 |
| α-terpinyl acetate | 1352 | - | - | 6.07±0.26 | - | - | - |
| α-copaene | 1376 | - | - | 0.59±0.04 | - | 0.56±0.06 | - |
| allyl nonanoate | 1376 | - | 0.72±0.01 | - | - | - | - |
| *n*-tetradecane | 1400 | 0.97±0.13 | 1±0.01 | 1.14±0.03 | - | 1.22±0.03 | - |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| β-caryophyllene | 1420 | 0.42±0 | - | 2.44±0.06 | - | - | - |
| *ar*-curcumene | 1483 | - | - | - | - | 0.78±0.31 | - |
| *n*-pentadecane | 1500 | - | - | - | - | 0.33±0.47 | - |
| cadalene | 1674 | - | - | - | - | 0.59±0.12 | - |
| 2-ethylhexyl octanoate | 1688 | - | 2.06±0.02 | - | - | - | - |
| Monoterpene hydrocarbons | | 38.93±1.64 | 6.67±0.42 | 19.93±1.6 | 0.82±0.16 | 11.57±0.39 | 1.03±0.11 |
| Oxygenated monoterpenes | | 26.37±0.67 | 16.71±0.46 | 17.94±0 | 1.9±0.31 | 15.08±0.72 | 0.83±0 |
| Sesquiterpene hydrocarbons | | 0.42±0 | - | 3.03±0.1 | - | 1.93±0.37 | - |
| Pyrazines | | 0.94±0.21 | 6.95±0.72 | 39.19±1.72 | 72.26±0.93 | 47.18±1.93 | 73.2±0.54 |
| Other nitrogen compounds | | 0.16±0.22 | 0.9±0.08 | 2.04±0.17 | 2.44±0.04 | 0.74±0.06 | 5.42±0.25 |
| Phenylpropanoids | | 1.65±0.21 | - | - | - | 0.84±0.06 | - |
| Other non-terpene derivatives | | 30.06±0.7 | 68.55±0.41 | 17.47±0.23 | 20.3±0.21 | 21.45±0.5 | 16.46±0.04 |
| Total identified (%) | | 98.52±1.39 | 99.78±0.36 | 99.6±0.62 | 97.71±0.2 | 98.77±1.07 | 96.93±0.71 |

[a] Linear retention indices on a DB5 columns. [b] Not detected.

636

637 **Table 3.** Identified volatiles in the HS-SPME analysis of the whole and ground samples at the final roasting temperature (204°C) as lighter, darker and mixed

638 beans.

| Constituents | l.r.i.[a] | Relative abundance (%) | | | | | |
|---|---|---|---|---|---|---|---|
| | | 204 °C light whole | 204 °C light ground | 204 °C dark whole | 204 °C dark ground | 204 °C mix whole | 204 °C mix ground |
| 2-methyl propanal | 552 | -[b] | - | - | - | - | 0.33±0.01 |
| 2-butanone | 598 | - | - | - | - | - | 1.64±0.04 |
| 2-methyl butanal | 662 | - | - | - | 1.51±0.01 | - | 4.67±0.09 |
| 2,3-pentanedione | 698 | - | - | - | - | - | 2.21±0.04 |
| 2,5-dimethylfuran | 707 | - | - | - | - | - | 0.33±0.01 |
| pyrimidine | 736 | - | - | - | 0.65±0.03 | - | - |
| pyridine | 740 | 8.55±0.01 | - | 9.51±0 | 10.32±0.15 | 8.29±0.04 | 12.62±0.25 |
| dihydro-2-methyl-3-furanone | 805 | 0.79±0.01 | - | 1.22±0 | 2.14±0.01 | 1.25±0 | 3.21±0.06 |
| 2-methyl pyrazine | 833 | 8.64±0 | - | 9.7±0 | 7±0.07 | 10.52±0.08 | 7.76±0.16 |
| isovaleric acid | 834 | - | - | - | 1.3±0.01 | - | 0.44±0.01 |
| 2,3-dimethyl-1-butanol | 835 | - | 0.86±0.11 | - | 0.92±0.01 | - | 0.48±0.01 |
| furfural | 839 | 1.93±0.01 | - | 2.04±0.01 | 2.19±0.02 | 1.92±0.03 | 2.96±0.06 |
| trimethyloxazole | 851 | 0.39±0.01 | - | - | - | 0.13±0.18 | - |
| 2-furan methanol | 859 | 4.46±0.03 | - | 2.31±0 | 7.96±0.07 | 1.82±0.06 | 4.65±0.09 |
| 1-acetyloxy-2-propanone | 870 | - | - | - | 3.26±0.03 | - | 2.87±0.06 |
| furfuryl formate | 902 | 0.39±0 | - | - | - | 0.47±0.01 | - |
| 2,6-dimethyl pyrazine | 910 | 18.34±0.02 | 21.42±0.16 | 18.36±0 | 11.2±0.11 | 16.74±0.13 | 12.08±0.25 |
| (*E*,*E*)-2,4-hexadienal | 911 | - | - | - | 0.73±0.01 | - | 0.59±0.01 |
| 2,5-dimethyl pyridine | 922 | - | 0.17±0.23 | - | 0.2±0.28 | - | - |
| 2-ethyl pyrazine | 925 | 4.8±0.01 | 8.16±0.05 | 4.64±0 | 4.92±0.04 | 5.48±0.04 | 3.42±0.07 |
| 2,3-dimethyl pyrazine | 930 | 4.15±0 | 5.92±0.04 | 4.52±0.42 | 2.97±0.03 | 4.3±0.04 | 3.5±0.07 |
| 3-methyl-2,5-furandione | 949 | - | 0.43±0 | - | 0.87±0 | - | 0.83±0 |
| 3-ethyl pyridine | 959 | - | 0.47±0.03 | - | - | - | 0.51±0.08 |
| 4-ethylpyridine | 960 | - | - | 0.57±0 | - | 0.39±0.01 | - |
| 5-methyl furfural | 965 | 2.28±0.01 | 0.75±0.01 | 3.42±0.09 | 5.28±0.01 | 2.99±0.01 | 3.38±0.4 |
| furfuryl acetate | 991 | 2.67±0.01 | - | 2.9±0 | - | 2.89±0.02 | - |
| myrcene | 993 | 0.39±0 | - | 0.44±0 | 0.61±0.01 | 0.39±0.01 | 0.45±0.07 |
| 2-furanmethanol acetate | 995 | - | 1.38±0.02 | - | 4.47±0.03 | - | 3.4±0.03 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 2-ethyl-6-methyl pyrazine | 1001 | 6.36±0.01 | 8.92±0.08 | 6.21±0 | 4±0.04 | 5.08±0.04 | 3.87±0.04 |
| 2-ethyl-5-methyl pyrazine | 1004 | - | - | - | - | 1.55±0.06 | - |
| 2,3,5-trimethyl pyrazine | 1005 | 13.87±0.02 | 19.98±0.21 | 13.06±0.01 | 7.66±0.05 | 12.2±0.09 | 9.25±2.22 |
| 2-ethyl-3-methyl pyrazine | 1014 | 2.54±0.58 | - | 1.85±0 | - | - | - |
| 1-methyl-2-formyl pyrrole | 1016 | - | - | - | - | - | 0.68±0.95 |
| 2-formyl-1-methyl pyrrole | 1016 | - | 3.4±0.08 | - | 1.83±0.01 | - | - |
| 2-ethenyl-6-methyl pyrazine | 1031 | - | 0.11±0.16 | - | - | - | 0.19±0.27 |
| limonene | 1032 | 0.95±0 | 0.5±0.31 | 1.02±0 | 0.79±0.03 | 0.57±0 | 0.58±0.06 |
| 2-acetyl pyrazine | 1033 | 0.58±0.28 | 0.74±0.2 | 0.76±0.01 | 1.24±0.03 | 0.36±0 | 0.61±0.06 |
| 1,8-cineole | 1034 | 0.43±0 | - | 0.56±0.01 | - | - | - |
| 2,3-dimethyl-2-cyclopenten-1-one | 1040 | - | - | - | 0.62±0.03 | - | 0.41±0.03 |
| (*E*)-β-ocimene | 1052 | 0.15±0.21 | 0.11±0.16 | 0.27±0.01 | 0.2±0.28 | - | - |
| 2-methyl-5-(1-methylethyl) pyrazine | 1059 | - | 0.25±0 | - | - | - | - |
| 2-acetyl pyrrole | 1062 | - | - | - | 0.5±0.05 | - | - |
| trans-linalool oxide (furanoid) | 1076 | 1.7±0.01 | 1.89±0.01 | 1.66±0 | 1.01±0.02 | 1.52±0 | 0.55±0.2 |
| 2,6-diethyl pyrazine | 1080 | 6.85±0.01 | 9.51±0.06 | 6.28±0.01 | 4.06±0.05 | 5.99±0 | 4.26±1.97 |
| 2-acetyl-1-methylpyrrole | 1083 | - | 0.58±0 | - | 0.59±0.02 | 0.39±0.01 | 0.19±0.27 |
| 2-ethyl-3,5-dimethyl pyrazine | 1085 | 2.74±0 | 1.72±0 | 2.7±0.01 | - | 2.67±0.01 | 0.62±0.19 |
| *o*-guaiacol | 1088 | 0.48±0 | - | 0.49±0.01 | - | 0.64±0.03 | - |
| *cis*-linalool oxide (furanoid) | 1090 | - | - | - | 2.11±0.04 | - | - |
| 2,5-diethyl pyrazine | 1091 | - | - | - | - | - | 1.53±0.24 |
| 2-methyl-3-propyl pyrazine | 1091 | - | 1.01±0.13 | - | - | - | - |
| 3-ethyl-2-hydroxy-2-cyclopenten-1-one | 1092 | - | - | - | - | - | 0.51±0.15 |
| α-pinene oxide | 1095 | - | - | - | 0.81±0.04 | - | - |
| tetrahydro linalool | 1098 | 0.6±0 | - | 0.61±0 | - | 0.83±0.04 | - |
| 3-ethyl-2,5-dimethyl pyrazine | 1099 | - | 4.53±0 | - | - | - | - |
| linalool | 1101 | 0.3±0 | 0.47±0 | 0.33±0 | 0.54±0.05 | 0.45±0.02 | 0.2±0.28 |
| nonanal | 1102 | - | - | - | - | 0.49±0.04 | - |
| 3-amino pyridine | 1105 | - | 0.23±0.32 | - | 1.34±0.15 | - | 0.85±0.04 |
| 6-camphenol | 1114 | - | - | - | 1.21±0.13 | - | - |
| *trans*-limonene oxide | 1141 | - | - | - | - | - | 0.63±0.04 |
| 5H-5-methyl-6,5-dihydrocyclopentapyrazine | 1142 | 0.44±0.01 | 0.82±0.06 | 0.36±0 | - | 0.47±0.12 | 0.36±0.01 |
| 1,2,3,4-tetramethylbenzene | 1146 | - | - | - | 0.21±0.29 | - | - |
| 2,3-diethyl-5-methyl pyrazine | 1153 | 0.57±0.01 | 0.62±0.01 | - | - | - | - |
| 3,5-diethyl-2-methyl pyrazine | 1156 | 1.42±0.01 | 1.33±0.01 | 0.62±0 | - | 0.66±0.01 | 0.36±0.01 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 2,3,5-trimethyl-6-ethyl pyrazine | 1163 | - | 0.99±0.01 | 0.57±0 | - | 0.65±0 | - |
| 2-acetyl-3-ethyl pyrazine | 1167 | - | 0.27±0 | - | - | - | - |
| 1-furfuryl pyrrole | 1185 | - | - | - | - | 0.34±0 | - |
| 1-(2-furanylmethyl)-1H-pyrrole | 1187 | - | 0.29±0 | - | 0.45±0.06 | - | 0.39±0.04 |
| (Z)-2-methyl-5-(1-propenyl) pyrazine | 1190 | - | - | - | - | - | 0.52±0.05 |
| methyl salicylate | 1192 | - | - | - | 0.84±0.13 | 0.92±0.01 | - |
| methyl chavicol | 1197 | - | - | - | - | 0.67±0.01 | - |
| decanal | 1204 | - | - | - | - | 0.41±0.05 | - |
| verbenone | 1205 | - | - | - | - | 0.39±0 | - |
| 2,4-nonadienal | 1213 | - | - | - | - | - | 0.17±0.24 |
| D-verbenone | 1228 | - | 0.41±0.01 | - | - | - | - |
| nerol | 1230 | - | - | - | 0.2±0.28 | - | - |
| carvone | 1244 | - | - | - | - | 0.35±0.01 | - |
| 2-isoamyl-6-methyl pyrazine | 1250 | - | 0.37±0.01 | - | - | - | - |
| 4-ethyl-2-methoxyphenol | 1282 | - | 0.3±0.08 | - | - | - | - |
| *cis*-2-tert-butyl-cyclohexanol acetate | 1293 | 0.38±0.01 | - | 0.64±0 | - | 0.98±0.01 | - |
| 4-vinyl guaiacol | 1315 | - | 0.24±0 | - | - | - | - |
| 4-hydroxy-3-methylacetophenone | 1323 | - | - | - | - | 0.71±0 | - |
| Monoterpene hydrocarbons | | 1.49±0.21 | 0.61±0.47 | 1.73±0.01 | 1.59±0.31 | 0.96±0.01 | 1.03±0.13 |
| Oxygenated monoterpenes | | 3.03±0.01 | 2.76±0.01 | 3.16±0.01 | 5.86±0.01 | 3.53±0.06 | 1.38±0.52 |
| Pyrazines | | 71.26±0.37 | 86.63±0.8 | 69.61±0.42 | 43.03±0.25 | 66.65±0.35 | 48.3±2.77 |
| Other nitrogen compounds | | 8.55±0.01 | 1.73±0.52 | 10.08±0 | 14.02±0.24 | 9.4±0.04 | 15.23±1.48 |
| Phenylpropanoids | | - | - | - | - | 0.67±0.01 | - |
| Other non-terpene derivatives | | 14.15±0.6 | 7.35±0.1 | 13.01±0.08 | 34.11±0.01 | 15.6±0.15 | 33.02±0.52 |
| Total identified (%) | | 98.47±0 | 99.08±0.66 | 97.58±0.5 | 98.61±0.16 | 96.79±0.42 | 98.95±0.12 |

[a] Linear retention indices on a DB5 column. [b] Not detected.

639 **Table 4.** Identified volatiles in the HS-SPME analyses of the silverskins and of the brewed coffee.

| Constituents | l.r.i.[a] | Relative abundance (%) | |
|---|---|---|---|
| | | Silverskins | Brewed coffee |
| pyrrolidine | 680 | -[b] | 2.04±0.05 |
| *n*-heptane | 700 | - | 6.77±0.13 |
| pyridine | 740 | - | 6.39±0.42 |
| *n*-hexanal | 802 | 0.8±0.1 | - |
| 2-methyl pyrazine | 833 | 0.18±0.25 | 1.94±0.18 |
| furfural | 839 | - | 1.85±0.28 |
| 2-furan methanol | 859 | - | 3.46±0.27 |
| 3-methylcyclopentyl acetate | 905 | 1.92±0.04 | - |
| 2,6-dimethyl pyrazine | 910 | - | 4.98±0.19 |
| 2,5-dimethyl pyrazine | 920 | 0.3±0.42 | 1.35±0.58 |
| α-pinene | 941 | 2.87±0.15 | - |
| (*Z*)-2-heptenal | 963 | 0.73±0.23 | - |
| 5-methyl furfural | 965 | - | 2.38±0.51 |
| sabinene | 976 | 0.77±0.55 | - |
| β-pinene | 982 | 5.04±0.14 | - |
| 6-methyl-5-hepten-2-one | 985 | 0.92±0.21 | - |
| myrcene | 993 | 1.29±0.16 | - |
| 2-furanmethanol acetate | 995 | - | 4.82±0.18 |
| octanal | 1001 | 0.96±0.57 | - |
| 2-ethyl-6-methyl pyrazine | 1001 | - | 2.05±0 |
| 2-ethyl-5-methyl pyrazine | 1004 | - | 3.2±1.39 |
| 2,3,5-trimethyl pyrazine | 1005 | - | 0.98±1.39 |
| *n*-hexyl acetate | 1010 | - | 0.43±0.61 |
| 2-formyl-1-methyl pyrrole | 1016 | - | 1.13±0.18 |
| *p*-cymene | 1027 | 1.76±0.01 | - |
| limonene | 1032 | 23.26±2.75 | - |
| 1,8-cineole | 1034 | 11.34±0.85 | - |
| (*E*)-β-ocimene | 1052 | 0.82±0.2 | - |
| γ-terpinene | 1062 | 2.8±0.14 | - |
| artemisia ketone | 1063 | - | 0.46±0.64 |
| dihydro myrcenol | 1074 | 0.76±0.19 | - |
| 2,6-diethyl pyrazine | 1080 | - | 2.04±0.12 |
| *p*-mentha-2,4(8)-diene | 1087 | 0.36±0.51 | - |
| 2-furfurylfuran | 1088 | - | 2.04±0.13 |
| 2,3-diethyl pyrazine | 1089 | - | 1.7±0.25 |
| (*Z*)-6-nonenal | 1097 | - | 0.38±0.54 |
| tetrahydro linalool | 1098 | 0.29±0.4 | - |
| ethyl heptanoate | 1099 | - | 1.41±0.23 |
| linalool | 1101 | 0.2±0.28 | 0.39±0.55 |
| nonanal | 1102 | 2.97±0.12 | 6.69±0.57 |
| *cis*-rose oxide | 1111 | 0.8±0.17 | - |
| camphor | 1143 | 0.69±0.06 | 0.38±0.54 |
| menthone | 1154 | 0.7±0.03 | - |
| menthofuran | 1164 | - | 0.41±0.58 |
| benzyl acetate | 1165 | - | 1.12±0.42 |
| 4-terpineol | 1178 | 0.63±0.08 | - |
| 1-furfuryl pyrrole | 1185 | - | 2.33±0.15 |
| α-terpineol | 1191 | 0.27±0.37 | - |
| methyl salicylate | 1192 | - | 0.95±0.21 |

| | | | |
|---|---|---|---|
| ethyl maltol | 1196 | - | 2.58±0.67 |
| methyl chavicol | 1197 | 32.53±3.03 | - |
| decanal | 1204 | - | 4.13±0.55 |
| (*E*,*E*)-2,4-nonadienal | 1216 | - | 0.4±0.56 |
| *endo*-fenchol acetate | 1223 | 0.21±0.29 | - |
| furfuryl-3-methyl butanoate | 1224 | - | 0.55±0.77 |
| (*E*)-2-decenal | 1260 | 0.19±0.27 | - |
| (*E*)-anethole | 1283 | - | 6.24±0.75 |
| isobornyl acetate | 1285 | 0.47±0.04 | - |
| *cis*-2-tert-butyl-cyclohexanol acetate | 1293 | 1.11±0.94 | - |
| *n*-tridecane | 1300 | 0.42±0.05 | - |
| undecanal | 1306 | - | 0.47±0.66 |
| 2-acetyl-4-methylphenol | 1316 | - | 1.21±1.7 |
| neryl acetate | 1366 | - | 0.42±0.59 |
| linalool isobutyrate | 1373 | - | 1.95±0.18 |
| 7-*epi*-sesquithujene | 1391 | - | 1.1±0.21 |
| β-caryophyllene | 1420 | - | 0.88±0.14 |
| (*E*,*E*)-2,4-undecadienal | 1428 | - | 0.5±0.7 |
| (*E*)-geranyl acetone | 1455 | - | 0.97±0.11 |
| α-humulene | 1456 | - | 0.61±0.86 |
| (*E*)-β-farnesene | 1460 | - | 1±0.23 |
| γ-muurolene | 1477 | - | 1.25±0.21 |
| valencene | 1492 | - | 0.4±0.56 |
| cubebol | 1516 | - | 0.43±0.61 |
| ledol | 1566 | - | 0.41±0.58 |
| *epi*-cedrol | 1597 | - | 1.67±0.11 |
| valerianol | 1656 | - | 0.98±0.02 |
| octyl octanoate | 1779 | - | 1.45±0.07 |
| Monoterpene hydrocarbons | | 38.95±1.75 | - |
| Oxygenated monoterpenes | | 16.33±0.78 | 4.01±1.53 |
| Sesquiterpene hydrocarbons | | - | 5.22±2.19 |
| Oxygenated sesquiterpenes | | - | 3.48±1.27 |
| Apocarotenoids | | - | 0.97±0.11 |
| Pyrazines | | 0.48±0.67 | 18.22±0.23 |
| Other nitrogen compounds | | - | 10.75±0.52 |
| Phenylpropanoids | | 32.53±3.03 | 6.24±0.75 |
| Other non-terpene derivatives | | 9.99±2.26 | 48.1±0.48 |
| Total identified (%) | | 98.27±1.07 | 96.99±1.48 |

[a] Linear retention indices on a DB5 column. [b] Not detected.

640

641

642 **Figure captions**

643 **Figure 1.** Dendrogram of the HCA for the samples headspaces. (G: ground; W: whole; 100, 160, 180,
644 204: roasting temperatures in °C; SKINS: silverskins; DARK: darker roasted beans; LIGHT: lighter roasted
645 beans; MIX: mixed darker and lighter beans; GREEN: raw green beans; BREW: brewed coffee)

646

647 **Figure 2.** a) Total score plot of the PCA; b) Expanded area of the PCA score plot (G: ground; W: whole;
648 100, 160, 180, 204: roasting temperatures in °C; SKINS: silverskins; DARK: darker roasted beans; LIGHT:
649 lighter roasted beans; MIX: mixed darker and lighter beans; GREEN: raw green beans; BREW: brewed
650 coffee)