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1 **Chemical modifications of Tonda Gentile Trilobata hazelnut and derived**
2 **processing products under different IR and hot-air roasting conditions**
3 **– a combined analytical study**

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24 **BACKGROUND**

25 For the processing industry, it is crucial to know what effect the roasting process and conditions have
26 on hazelnut quality. The present study investigates, for the first time, on the effects of hot-air and
27 infrared (IR) roasting at different time-temperature combinations on Tonda Gentile Trilobata
28 hazelnut: whole kernels and derived processing products (paste and oil).

29 **RESULTS**

30 Nutritional and physical characteristics of hazelnuts and processing products were determined to
31 study the influence of the different roasting conditions as a function of the intended use. The
32 antioxidant profile (DPPH, ORAC and total phenolic content) were analyzed on roasted hazelnut and
33 paste extracts. For a comprehensive understanding of the complex bio-chemical phenomena
34 occurring during roasting, E-nose and near-infrared spectroscopy were also applied. All analytical
35 data were processed using univariate (ANOVA) and multivariate data analyses (PCA) .

36 Hazelnuts derived from IR roasting at higher temperatures (195°C) showed a richer antioxidant
37 profile and a more intense flavour. On the other hand, the yield associated to the oil extraction under
38 the same conditions was unsatisfactory making this process completely inadequate for oil production.
39 Oil obtained by hot-air roasting and IR roasting at lower temperature (135°C) resulted to be of good
40 quality, showing rather similar acidity grade, peroxide number and acidic composition. In particular,
41 a slightly but significantly lower acidity was related to lower roasting temperatures (0.21-0.22% vs
42 0.27 % for higher temperatures).

43 All roasting conditions tested, allow to quantitatively obtain homogeneous hazelnut paste and from a
44 rheological point of view, higher roasting temperatures gave pastes characterised by higher density
45 and viscosity values.

46

47 **CONCLUSION**

48 IR proved to be a promising alternative method for hazelnut roasting, thanks to its capability in
49 preserving nutritional values and enhancing organoleptic quality.

50 Keywords: Tonda Gentile Trilobata (TGT) hazelnut, Infrared (IR) roasting, hot-air roasting, Near
51 Infrared (NIR) spectroscopy, E-nose, Principal Component Analysis (PCA)

52

53 **Introduction**

54 From an economic point of view, the European hazelnut (*Corylus avellana* L.) is the most important
55 nut species in the *Betulaceae* family. There is general agreement on the fact that hazelnuts from
56 Piedmont (Italy) are among the most renowned, and the “Tonda Gentile Trilobata” (TGT) variety (as
57 covered by IGP designation) is particularly prized. Due to the intensity of its sweetness, the cooked-
58 bread aroma and the low intensity of the burnt aroma, TGT is widely recognised as the best-suited
59 hazelnut for industrial processing into roasted kernels¹.

60 Although hazelnuts can be consumed raw, the characteristics of the roasted nuts are more desirable
61 in terms of both taste and texture²⁻³.

62 Roasting can be defined as the dry heat treatment of seeds and nuts which not only brings about
63 dehydration but also leads to the development of the flavour, colour and crunchy texture⁴. A number
64 of chemical modifications and non-enzymatic browning lead to the peculiar characteristics
65 responsible for the pleasantness of roasted hazelnuts⁵⁻⁶. Roasting allows to reduce moisture content
66 in shelled hazelnuts, up to values ranging from 3.0-4.5% to 1.0-2.5%, contributing to the reduction
67 of possible microbial contaminations and of the activity of enzymes involved in lipid peroxidation.

68 It is crucial for the processing industry to know what effect the roasting process and conditions (e.g.
69 time and temperature) will have on hazelnut quality. The various roasting methods available have
70 been found to yield significant differences in phenolic and antioxidant activities⁷, humidity, protein
71 concentration as well as other nutritional and technological values⁸⁻¹⁰.

72 A common method for nut roasting is the convective heat transfer process, performed in hot-air
73 roasters working either in continuous or in batch systems¹¹. The conventional roasting of hazelnuts is
74 currently carried out in commercial electrical ovens at 100-180°C for 10-60 min, according to shell
75 thickness. It is well known that temperature modulation is an important parameter as it significantly
76 affects hazelnut product quality¹². However, long processing times, high energy consumption and
77 low heating efficiency are its main disadvantages¹³. Other alternative roasting methods have been

78 proposed: for example, Rakesh Kumar Raigar *et al.*¹⁴ compared the microwave roasting of peanuts
79 with conventional drum roasting. FTIR, SEM and E-nose results showed that the microwave roasting
80 can be effectively controlled by selecting an appropriate combination of time and microwave power
81 levels.

82 IR (infrared) heating has successfully been used for the dry-roasting and pasteurization of almonds¹⁵.
83 By contrast to conventional heating mechanisms, in which heat is usually transferred from the surface
84 to the interior, the main advantage of IR treatment is that roasting proceeds from the inside of the
85 hazelnut outwards without ventilation, meaning that the loss of aroma is minimised. However, the
86 effects of IR roasting on hazelnuts have only recently been investigated and, then, only partially
87 studied. Belvisio *et al.*¹⁶ monitored the changes in two different hazelnut cultivars caused by both hot
88 air and infrared roasting over nine months of storage.

89 In the present study, the effects of hot-air and IR roasting methods on TGT from Piedmont on the
90 hazelnut processing products (paste and oil) have been investigated for the first time. In particular,
91 two different time and temperature combinations have been considered for each roasting method.

92 Chemical, nutritional (fatty acids, peroxide value, total phenolic content, antioxidant capacity) and
93 physical (viscosity, density) characteristics of hazelnuts and processing products (pastes and oils)
94 were determined to study the influence of the different roasting conditions as a function of the
95 intended use. For the antioxidant profile, hazelnut and paste extracts were considered. Moreover, for
96 a comprehensive understanding of the complex bio-chemical phenomena occurring during roasting,
97 E-nose and near-infrared spectroscopy were applied in order to provide rapid and non-destructive
98 fingerprinting analyses to characterise physico-chemical and sensory attributes. There are, in fact,
99 numerous studies that highlight the potential of using NIRS on fruit and vegetables and that promote
100 it as an analytical technique for determining internal and external qualitative characteristics¹⁷.
101 Furthermore, the E-nose has recently received considerable attention as an aroma-technology tool for
102 the chemical and sensory characterisation of odorant products^{3,18}. As an example, the stability of
103 shelled peanuts during storage was assessed using a hybrid electronic nose with 18 MOS sensors by

104 Rakesh Kumar Raigar *et al.*¹⁹: the predictability of storage time using the sensors data closely
105 matched with conventional rancidity indices advocating the applicability of E-nose as an eco-friendly
106 alternative for rapid, non-destructive, and global analysis of shelled peanuts during post-harvest
107 operations.

108

109 **Materials and methods**

110 *Material*

111 Hazelnuts TGT from organic farming were supplied by "Lurgo Flavio" (Corneliano d'Alba, Cuneo,
112 Italy), stocked at controlled temperature (4° C) and shelled at roasting time.

113 Solvents and reagents, used to determine extraction and antioxidant profiles, were purchased from
114 Sigma-Aldrich (Darmstadt, Germany), diethyl ether and phenolphthalein were acquired from Panreac
115 Quimica S.A.U. (Barcelona, Spain). Ethyl alcohol, sodium hydroxide 0.1 mol/l in aqueous solution,
116 acetic acid 100%, potassium iodide and sodium thiosulphate 0.01 mol/l in aqueous solution were
117 acquired from VWR (Milan, Italy), while chloroform RPE for analysis and soluble starch RPE were
118 acquired from CARLO ERBA reagents (Milan, Italy). *n*-heptane, potassium hydroxide and methanol
119 were acquired from Merck (Darmstadt, Germany).

120 *Hazelnut Roasting*

121 The hot-air and IR roasting processes were performed by DSC Srl (Bernezzo, Cuneo, Italy).

122 The hot-air roasting device is created by DSC and is equipped with an internal transport tape, which
123 can be adapted to processed dry fruits, and a number of roasting compartments to manage temperature
124 conditions and optimise the process over its three steps: drying, roasting and cooling. Two different
125 time and temperature conditions were chosen, on the basis of preliminary hazelnut browning tests.
126 To understand the influence of temperature and time on hazelnut quality, treatments at lower
127 temperatures and longer times were compared with treatments at higher temperature for shorter times.

128 For hot air (HA) roasting, time and temperature were set at:

- 129 • 45 minutes at 135°C (HA-Lot1);

130 • 27 minutes at 195°C (HA-Lot2).

131 IR roasting was carried out in an infrared roaster (RI/700LAB, DSC) equipped with a cooling bath.

132 Roasting takes place in a controlled and uniform manner thanks to the direct monitoring of

133 temperature via specific probes. For infrared (IR) roasting, time and temperature were set at:

134 • 40 minutes at 135°C (IR-Lot1);

135 • 20 minutes at 195°C (IR-Lot2).

136 Each roasting condition was applied to two batches (referred to as ‘a’ and ‘b’) of 25 kg of hazelnuts.

137 Roasted hazelnuts were stored at room temperature in vacuum packaging.

138 *Hazelnut paste*

139 A total of eight pastes were produced from roasted hazelnut batches (four conditions for two batches).

140 Hazelnut paste was produced in a ball mill refiner (Easy Cream, DSC) with a power of 3 kW working

141 at room temperature in continuous mode without the need for compressed air. Samples were obtained

142 in one step (10 min from the whole hazelnut to the final paste) without significant heating during the

143 process. The yield was around 100% for all hazelnut types tested and about 7 kg of paste, with a

144 particle size of about 20 µm, was produced for each batch.

145 *Hazelnut oil*

146 An IBC (Monforts, Oekotec) cold press, equipped with a screw and 4 loading hoppers, was used for

147 oil extraction.

148 The process starts with the loading of hazelnuts that move into an internal chamber where the

149 extraction starts. Rotation speed of the screw was 40 rpm and press head temperature was set at 70°C.

150 The outlet oil temperature did not exceed 45°C. Oil was collected in a duct, carried into a bin and

151 then stored in a dry place. Two oil samples (one for each batch, ‘a’ and ‘b’) were collected starting

152 from 5 kg of roasted hazelnuts; due to technical hurdles, for IR-Lot2, a low yield was achieved and,

153 therefore, only one replicate sample was produced.

154

155 *Antioxidant profile (whole hazelnut and paste)*

156 *Extraction of phenolic compounds*

157 5 g of roasted hazelnut kernels, finely ground and previously defatted with hexane (1:10 w/v), were
158 extracted with 50 mL of 80% acetone – 20% water at 50 °C for 30 min under magnetic stirring⁹. The
159 procedure was repeated three times for a total extraction time of 1.5 h and the three extracts were
160 collected, dried under vacuum and then lyophilized.

161 5 g of each hazelnut paste were extracted with 50 mL of 80% acetone – 20% water according to the
162 same protocol described for hazelnut kernels. Each sample of hazelnuts and pastes was extracted in
163 triplicate and the yields obtained are reported in Table 1.

164 *Antioxidant activity: DPPH and ORAC assays*

165 The radical scavenging properties of each extract were determined via reactivity with the stable 2,2-
166 diphenyl-1-picrylhydrazyl radical (DPPH)²⁰. The absorbance decay of ethanolic DPPH solutions,
167 after the addition of the various dimethyl sulfoxide (DMSO) extract solutions, was followed for 30
168 min. Percentages of residual DPPH concentrations were calculated and radical absorbance values
169 were interpolated with a DPPH standard curve and correlated *vs* extracts concentrations, giving an
170 exponential decay curve analysed with non-linear regression to obtain EC₅₀ values.

171 The Oxygen Radical Absorbance Capacity (ORAC) test was also performed, using a PerkinElmer
172 2030 Multilabel Reader with 96-well black plates according to the ORAC assay described by Zeppa
173 *et al.*²¹. The Trolox equivalent molar concentrations were calculated using a linear regression model
174 between Trolox concentration and the net area under the fluorescein decay curve (delta AUC). Data
175 are expressed as ORAC values, defined as micromole Trolox equivalents present in 1 g of dried
176 extract. Results are reported in Table 1 as a mean of at least three measures.

177 *Total phenols determination*

178 Total phenols were determined using Folin-Ciocalteu's phenol reagent. Extracts were dissolved in
179 ethanol and analyses were performed as described by Singleton²². The phenolic content was
180 calculated using a standard curve for catechin and results were expressed as mg of catechin
181 equivalents per g of dried extract. Results are reported in Table 1 as a mean of at least three measures.

182

183 ***Viscosity and density (paste)***

184 Paste viscosity was determined using a steady-stress rheometer (Brookfield DV-II, LV Viscometer,
185 Brookfield Engineering Laboratories, Middleboro, MA, USA) equipped with a SC4-18/13R small
186 sample adapter. All measurements were carried out at 25.0 ± 0.1 °C, ensured by means of a controlled
187 fluid bath unit and an external thermostatic bath. Samples were allowed to equilibrate for 300 s to
188 establish a baseline shear history. Flow experiments were performed over a 0.4–80 s⁻¹ range of shear
189 rates in duplicate. Viscosity was designated in units of Centipoise (Cp) (Table 2).

190 Density determinations were performed in a sealed boron-silicate glass pycnometer of approximately
191 10 mL capacity (Duran Group, model BlauBrand). Measurements were carried out at room
192 temperature. Density unit was g/mL. Results are reported in Table 2 as a mean of at least three
193 measures.

194

195 ***Oil analysis***

196 Oil was analysed according to Annex II of European Regulation 2568/1991²³, which refers to
197 characteristics modifications of olive oil and olive-residue oil and on the relevant methods of analysis.
198 Oil samples were analysed in triplicate and results are reported in Table 3.

199 ***Acidity***

200 Acidity, measured by acid-base titration with a standardised sodium hydroxide 0.1 mol/l aqueous
201 solution, was expressed as a percentage (weight/weight) of oleic acid (Table 3).

202 ***Peroxide value***

203 Peroxides were determined by iodometric titration in which the obtained triiodide ion solution is
204 titrated against a standard sodium thiosulfate solution 0.01 M in water. The peroxide values were
205 expressed in milliequivalents of active oxygen per kg (Table 3).

206 ***Acidic composition***

207 6 mL of heptane were mixed with 0.3 g of hazelnut oil and 0.6 mL of a methanolic solution of KOH
208 2 N for acidic composition determination and the mixture was shaken for 30 s and centrifuged for 5
209 min at 3500 rpm. The obtained heptane solution was directly analysed by gas chromatography carried
210 out on a HRGC 5300 Mega Series Carlo Erba equipped with a capillary column (Supelco Phase SPtm
211 2340, 60 m length and 0.25 mm internal diameter, d_f 0.20 μm) and with a flame ionization detector
212 (FID) EL 580. The carrier gas was hydrogen (1 mL/min) and the temperature program was from
213 160°C to 205°C, with a rate of 5°C/min.

214 Acid identification was performed using an external standard method while quantitative data were
215 reported as normalised percentages (Table 3).

216

217 *Fingerprinting techniques*

218 *Electronic nose*

219 An electronic olfactory system (EOS 507, Sacmi Imola S.C., Imola, Italy) equipped with a measuring
220 chamber with six metal oxide sensors was used. During the analyses, sensors were maintained in the
221 temperature range of 350–450 °C. The EOS 507 was controlled by an integrated Personal Digital
222 Assistant and was connected to an automatic sampling apparatus (Model HT500H). Samples were
223 located in a chamber equipped with a system that removes humidity from the surrounding
224 environment and incubated at 37 °C for 7 min before injection. Ambient air, filtered with activated
225 silica and charcoal, was used as the reference gas.

226 15 whole hazelnuts, for each lot, and 10 g, for each paste, and 20 mL, for each oil, were analysed in
227 duplicate.

228 *NIR spectroscopy*

229 NIR measurements were performed on an FT-NIR spectrometer (Buchi NIRFLEX N-500) in the
230 4000–10,000 cm^{-1} range at 8 cm^{-1} resolution and using 64 scans on whole hazelnuts, pastes and oils.
231 The diameter of the circular surface analysed was reduced to 3.0 mm using a specific adaptor for
232 whole hazelnut spectra acquisition; spectra were recorded in the reflectance mode.

233 A total of 368 whole hazelnuts were analysed by NIR spectroscopy producing 368 spectra; 64 from
234 HA-Lot1 and HA-Lot2, 120 from IR-Lot1 and IR-Lot2.

235 Considering the variability among hazelnut kernels from the same batch, the average spectrum of
236 four replicated signals was calculated, obtaining 92 mean spectra.

237 Analyses were performed in duplicate and oil spectra were recorded in the transmittance mode.

238

239 ***Data Processing***

240 *Univariate statistical analysis*

241 All measurements were done in triplicate and results were expressed as mean \pm standard deviation
242 (SD). One-way ANOVA²⁴ was performed to evaluate the significance of differences among different
243 roasting conditions. Differences were considered to be significant at $p \leq 0.05$. All analysis were
244 performed with GraphPad Prism 7.00 software (San Diego, CA, USA).

245 *Multivariate analysis*

246 In this study, Principal Component Analysis (PCA)²⁵ was performed on the NIR, E-nose, viscosity,
247 density and antioxidant activity data.

248 Before PCA, NIR data were pre-treated using the Standard Normal Variate (SNV) transformation²⁶
249 in order to eliminate unwanted variations, such as global intensity effects and baseline shifts.

250

251 **Results and discussion**

252 ***Hazelnuts***

253 Results relative to DPPH, ORAC and total phenolic compounds assays on roasted hazelnut extracts
254 are reported in Table 1. They underline as IR-Lot2 roasting conditions allow to better preserve the
255 antioxidant activity, data are always significantly different from ones belonging to other lots
256 (ANOVA, $p < 0.05$). Considering literature data, there are a lot of differences due to type of cultivar,
257 harvest period, roasting conditions and antioxidant performed assays, nevertheless our values

258 regarding air roasted hazelnut extracts are in general agreement^{27,10}. To our knowledge, studies about
259 hazelnuts roasted by IR are still limited in number. However our results are similar to those reported
260 by Belviso *et al.*¹⁶, who found that this method of roasting at 170°C for 20 min resulted in total
261 phenolic content higher than those obtained with hot air at 120°C for 40 min.

262 Results derived from PCA performed on the **antioxidant data** confirm that IR radiation is less
263 destructive for antioxidant phenols overall, when applied for shorter time, even at higher temperature.
264 Figure 1 shows the PC1-PC2 biplot of the autoscaled data which describe 94% of the total variance.
265 Sample pattern, explained by score distribution, displays that the antioxidant profile of IR-Lot2 is
266 very different to the others, while the variable pattern, shown by loading distribution, reveals that IR-
267 Lot2 is characterised by a richer antioxidant profile.

268 Regarding PCA performed on the **E-nose data**, the first PC principally explains the variation in the
269 data due to the day of analysis (*data not shown*). The score plot on PC2-PC3 (Figure 2a), which
270 explains 47% of the total variance, shows that hazelnuts differ according to the roasting method, while
271 slight differences are highlighted between time and temperature levels. In particular, samples roasted
272 with hot air are found at positive scores on PC2 while samples roasted with IR at negative scores.

273 These results might be ascribable to the fact that hazelnuts roasted with IR can be more appreciable
274 thanks to a more intense flavour due to a lower aroma loss.

275 Concerning PCA on **NIR data**, the score plot on PC1-PC2 (Figure 3a), explaining 87% of the total
276 variance, shows four different groups that correspond to the four different roasting conditions. In
277 particular, it is possible to see the influence of both roasting method and temperature. In fact, samples
278 treated by IR are mainly found towards the right-bottom corner, while samples treated by hot air are
279 towards the left-top corner. Focusing on the temperature effect, it is possible to notice that samples
280 treated at higher temperatures are mainly located towards the right-top corner, while samples treated
281 at lower temperatures are grouped in the opposite direction.

282 Furthermore, the average NIR reflectance spectra of the four different lots (HA-Lot1, HA-Lot2, IR-
283 Lot1, IR-Lot2) were compared (Figure 4) in order to understand the changes that occur in the NIR

284 region due to hot air and IR roasting. By a visual inspection, the spectral regions in which major
285 changes occur can be easily detected. Many compounds may have chemical bonds with absorptions
286 in such spectral regions, but only few of them can be related with chemical changes due to roasting.
287 The bands at 8200 cm^{-1} and 7200 cm^{-1} may be related to absorptions of fats: in particular, to C-H
288 stretching second overtone and a combination between C-H stretching and C-H bending, respectively.
289 Both the broad band around 6900 cm^{-1} (first overtone of O-H stretching) and the band at 5150 cm^{-1}
290 (O-H combination bands) are related to water, whose decrease is highly influenced by the roasting
291 process.

292 The region around $4250 - 4300\text{ cm}^{-1}$ may be ascribable to compounds formed in the Maillard
293 reaction²⁸ which naturally occurs during hazelnut roasting. Since hazelnuts contain high amounts of
294 oxidisable lipids, lipid oxidation may also occur, contributing to the formation of reactive carbonyl
295 compounds which may promote the Maillard reaction². Such chemical changes are reflected in
296 absorptions of C-H and C-O stretching combination bands, and C-H stretching and C-H deformation
297 modes.

298

299 *Paste*

300 The conditions used to produce hazelnut paste do not affect antioxidant profiles, as showed in Table
301 1. Results from the PCA performed on these data are very similar to those obtained from the whole
302 hazelnuts themselves; pastes from IR-Lot2 have a richer antioxidant profile, thanks to the shorter
303 treatment time.

304 The processing of **E-nose data** is reported in Figure 2b. PC1, which explains 84% of the total
305 variance, clearly separates pastes obtained from IR-Lot2 from the others, due to a more intense
306 flavour originated by the higher temperatures in combination with the IR technology.

307 Figure 3b shows that the PCA outcomes of **NIR data** explains the temperature effect. In fact,
308 temperatures at which pastes were roasted are positively correlated with PC1 scores: lower
309 temperatures are associated with negative score values, while higher temperatures are associated with

310 positive score values. Since the chemical composition of the pastes is similar to that of hazelnuts, a
311 comparison between the various NIR spectra profiles gave the same information as reported in the
312 previous session for hazelnuts **Viscosity and density data** of the eight pastes, whose values are
313 reported in Table 2, were analysed in triplicate, but one replicate of HA-Lot1 was eliminated as an
314 outlier due to the aberrant values measured. The score plot in Figure 5a shows that the pastes obtained
315 from hazelnuts roasted at higher temperature are characterised by higher density and viscosity, as
316 indicated by a joint examination of loadings (Figure 5b). The significant difference between
317 rheological parameter obtained with higher and lower roasting temperatures is also confirmed by
318 ANOVA test.

319

320 *Oil*

321 Oils derived from the cold pressing procedure still contain solid particles in suspension, which were
322 separated by natural decantation in order to determine the final yield of clear oil. The part named
323 “pressing lost” was formed by hazelnuts which remained on the press surface during the pressing
324 process. **Yields** are reported in Table 3 and results show that the best oil yields were obtained for HA-
325 Lot1 roasted hazelnuts for which, furthermore, **pressing lost** values are the lowest.

326 IR-Lot1 roasted hazelnuts yields are slightly lower than HA-Lot1 yields, while pressing lost values
327 are slightly larger. HA-Lot2 pressing presented many problems; oil yield was low and pressing lost
328 values very high. Moreover, roasting conditions for IR Lot-2 made hazelnuts too friable for the screw
329 oil press and it was not possible to effectively separate the oil phase from the solid particles in
330 suspension. Nevertheless, a sufficient amount of oil to perform E-nose and NIR analyses was
331 obtained; conversely, yield associated to such an extraction makes this process completely inadequate
332 from an industrial point of view.

333 Produced oils were stored in a cold and dry place and then analysed for the determination of **acidity**,
334 **peroxide number and acidic composition** (Table 3). Values, that are in according with those
335 previously reported in literature ^{27, 16}, resulted very similar across all samples, indeed there aren't

336 significant differences in peroxide number and acidic composition. It may be just noted that lower
337 roasting temperatures implicate slightly lower acidity, with a significant ANOVA difference.
338 Noteworthy, acidity and peroxide number of roasted hazelnut oils are lower than extra-virgin olive
339 oils ²⁹ this indicating their good quality.

340 **E-nose** data were analysed with PCA (Figure 2c): PC1, which explains 78% of the total variance,
341 seems to be associated to the temperature effect, while PC2 clearly differentiates oils obtained from
342 HA-Lot1 hazelnuts from all of the others. In more detail, oils obtained from hazelnuts roasted at
343 higher temperature (195°C) have positive scores lengthwise PC1.

344 The differences between the oil samples were highlighted by PCA applied to the **NIR spectra**, where
345 the score plot on PC1-PC2 (Figure 3c) explains 97% of the total variance. In particular, PC2 evidently
346 differentiates the roasting methods, IR and hot air.

347 Average NIR spectra of the four oils (HA-Lot1, HA-Lot2, IR-Lot1 and IR-Lot2) are reported in
348 Figure 6. Comparison of the spectral profiles reveals that the spectral region in which the most
349 noticeable changes in absorption intensity occur is 5600–5800 cm⁻¹, ascribable to the first overtone
350 of C-H stretching vibrations of methylene and ethylene groups, involved in degradation processes of
351 triglycerides. Triacylglycerols, in fact, account for 95-98% of hazelnut oils and their composition can
352 be considered as fingerprints of oils.

353

354 **Conclusions**

355 The analytical and chemometric investigations carried out in this work demonstrate that the roasting
356 method and the conditions used for the roasting process affect not only the physico-chemical and
357 sensory properties of hazelnuts but also their nutritional profile. Whole kernels, pastes and oils
358 derived from hazelnuts were analysed by E-nose, NIRS and conventional analytical methods,
359 highlighting interesting differences between the two roasting methods (IR and hot air) and also
360 between temperature and time combinations. The advantage of combining information from different
361 analytical sources – including non-selective fingerprinting methods – is reflected in the possibility to

362 provide a comprehensive evaluation of the complex bio-chemical phenomena that occur in the final
363 products depending on process parameters.

364 It is not possible to define the best roasting process in general terms, because a key factor is the
365 intended use of the raw kernels and of their derived processing products.

366 As for as the whole hazelnuts are concerned, both the roasting method and the time-temperature
367 combination strongly affect the kernel characteristics, with an interestingly preserved content of
368 antioxidant compounds for those treated with IR radiation.

369 Concerning pastes, hazelnuts treated with IR process at 195°C are considerably differentiated from
370 the others, also from a rheological point of view, being characterised by higher viscosity and density,
371 besides by a stronger aroma. A potential intended use of such pastes is the preparation of creams,
372 chocolate and ice cream – products in which availability of an ingredient with higher concentration
373 of aroma and better spreadability is convenient from an economical point of view.

374 Considering oil, the yield associated to an extraction under the same conditions (IR process at 195°C)
375 is unsatisfactory, making this roasting process completely inadequate from an industrial point of view.

376 As a conclusion, IR roasting proved to be a promising alternative method for hazelnut roasting,
377 considering its capability in preserving nutritional values.

378 Obviously, when designing a hazelnut roasting process, not only the effects of the different roasting
379 conditions on kernels, but also the final use of the roasted products should be considered.

380

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384

385

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472 **Figure Captions:**

473 Figure 1: PCA biplot of hazelnut antioxidant profile data. The scores are shown using 4 different
474 colors that correspond to the 4 different roasting conditions. Loadings are written in black italics.

475 Figure 2: PCA score plots of E-nose data of whole hazelnuts (a), hazelnut pastes (b) and hazelnut
476 oils (c). The scores are shown using 4 different colors that correspond to the 4 different roasting
477 conditions.

478 Figure 3: PCA score plots of NIR data of whole hazelnuts (a), hazelnut pastes (b) and hazelnut oils
479 (c). The scores are shown using 4 different colors that correspond to the 4 different roasting
480 conditions.

481 Figure 4: Profiles of the NIR data of whole hazelnuts. The 4 profiles are shown using 4 different
482 colors that correspond to the 4 different roasting conditions.

483 Figures 5: (a) PCA score plot of hazelnut paste viscosity and density data; the scores are shown
484 using 4 different colors that correspond to the 4 different roasting conditions. (b) PCA loading plot:
485 the 3 loadings represent the 3 original variables in the orthogonal space of the Principal
486 Components.

487 Figure 6: Profiles of the NIR data of hazelnut oils. The 4 profiles are shown using 4 different colors
488 that correspond to the 4 different roasting conditions.

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490 **Table 1**491 Yields and antioxidant profile of hazelnut kernel and paste extractions expressed as a mean \pm SD (n
492 = 3).493 * Values within each column followed by different letters are significantly different ($p \leq 0.05$)

roasting conditions	Yields % \pm SD		DPPH EC ₅₀ \pm SD (μ g/mL)		ORAC μ mol Trolox/g extract \pm SD		Total Phenols mg catechin/g extract \pm SD	
	kernel	paste	kernel	paste	kernel	paste	kernel	paste
HA-Lot1 (45 min 135 °C)	12.6 \pm 1.3*	7.3 \pm 1.7	657 \pm 16 ^a	525 \pm 28 ^a	168 \pm 19 ^a	182 \pm 20 ^a	6.2 \pm 0.7 ^a	4.2 \pm 1.1 ^a
HA-Lot2 (27 min 195 °C)	10.2 \pm 1.6	18.7 \pm 2.1	553 \pm 22 ^b	405 \pm 18 ^b	219 \pm 8 ^a	192 \pm 65 ^a	7.0 \pm 0.7 ^a	8.4 \pm 1.0 ^b
IR-Lot1 (40 min 135 °C)	6.3 \pm 1.0	5.3 \pm 1.4	620 \pm 19 ^a	471 \pm 14 ^c	208 \pm 9 ^a	192 \pm 20 ^a	6.5 \pm 0.6 ^a	6.8 \pm 0.9 ^a
IR-Lot2 (20 min 195 °C)	9.9 \pm 0.5	16.7 \pm 1.8	371 \pm 14 ^c	226 \pm 20 ^d	286 \pm 15 ^b	224 \pm 12 ^a	11.7 \pm 1.5 ^b	13.6 \pm 1.4 ^c

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499 **Table 2**

500 Rheological profile of hazelnut pastes expressed as a mean \pm SD (n = 3).

roasting conditions	Viscosity (Cp)	Density (g/mL)
HA-Lot1 (45 min 135 °C)	1615 \pm 48 ^a	1.029 \pm 0.004 ^a
HA-Lot2 (27 min 195 °C)	4467 \pm 51 ^b	1.076 \pm 0.003 ^b
IR-Lot1 (40 min 135 °C)	2271 \pm 14 ^a	1.027 \pm 0.005 ^a
IR-Lot2 (20 min 195 °C)	3657 \pm 10 ^b	1.063 \pm 0.002 ^c

501 * Values within each column followed by different letters are significantly different ($p \leq 0.05$)

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505 **Table 3**

506 Yields, pressing lost, acidity, peroxide number and acidic composition of roasted hazelnut oils (the
 507 quantity of oil obtained from IR_Lot2 was very low and it was used only for E-nose and NIR
 508 analyses). Values are reported as a mean of batch a and b analyses \pm SD (n = 3).
 509

Parameter	HA-Lot1 (45 min 135 °C)	HA-Lot2 (27 min 195 °C)	IR-Lot1 (40 min 135 °C)
Yield oil %	51.8 \pm 7.60	17.8 \pm 0.40	46.5 \pm 1.50
Pressing lost %	6.6 \pm 1.80	19.8 \pm 1.80	11.8 \pm 0.40
Acidity (% of oleic acid)	0.2 \pm 0.01 ^a	0.3 \pm 0.01 ^b	0.2 \pm 0.05 ^a
peroxide number (millieq. O₂ /kg)	1.5 \pm 0.02 ^a	1.5 \pm 0.20 ^a	1.5 \pm 0.10 ^a
miristic acid %	N.D.**	N.D.	N.D.
palmitic acid %	6.2 \pm 0.20 ^a	6.2 \pm 0.10 ^a	6.1 \pm 0.20 ^a
palmitoleic acid %	0.2 \pm 0.04 ^a	0.2 \pm 0.06 ^a	0.3 \pm 0.03 ^a
stearic acid %	2.8 \pm 0.10 ^a	2.8 \pm 0.10 ^a	2.8 \pm 0.10 ^a
oleic acid %	83.7 \pm 0.30 ^a	83.5 \pm 0.70 ^a	83.5 \pm 0.80 ^a
linoleic acid %	6.8 \pm 0.20 ^a	7.0 \pm 0.40 ^a	7.0 \pm 0.20 ^a
linolenic acid %	0.1 \pm 0.02 ^a	0.1 \pm 0.02 ^a	0.1 \pm 0.03 ^a
arachidic acid %	0.1 \pm 0.01 ^a	0.1 \pm 0.01 ^a	0.1 \pm 0.02 ^a
eicosenoic acid %	0.1 \pm 0.02 ^a	0.1 \pm 0.03 ^a	0.1 \pm 0.01 ^a
behenic acid %	N.D.	N.D.	N.D.

510 *Values within each row followed by different letters are significantly different ($p \leq 0.05$).

511 ** N.D.: not detected.

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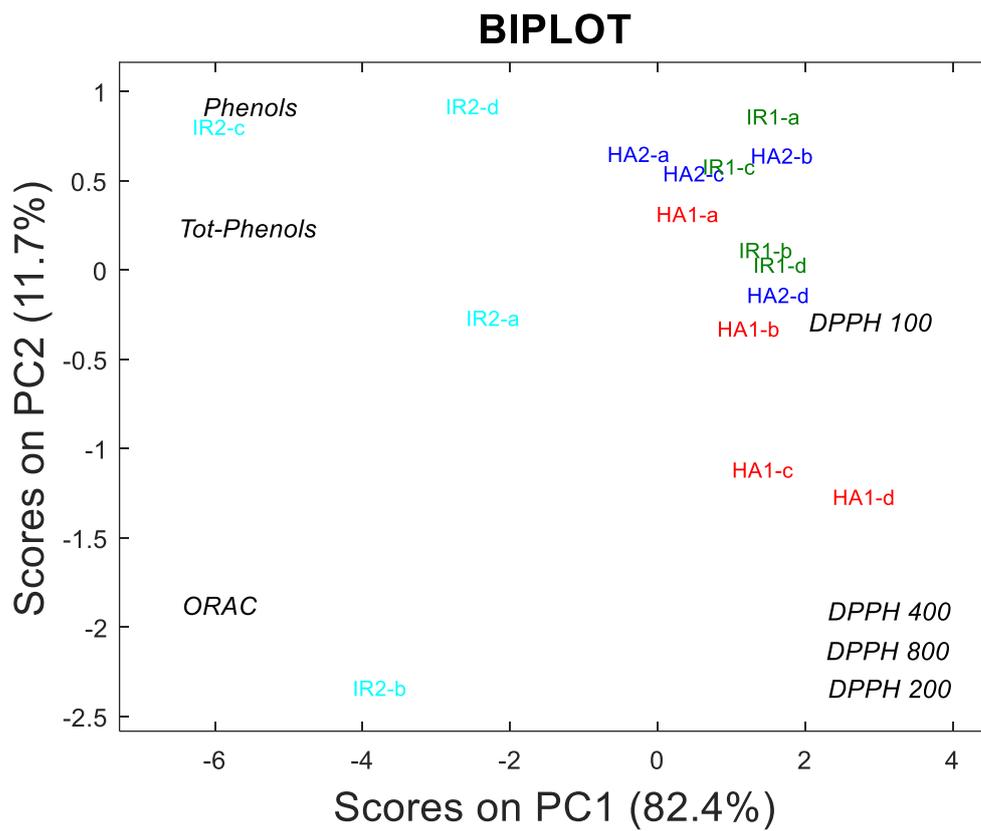


Figure 1

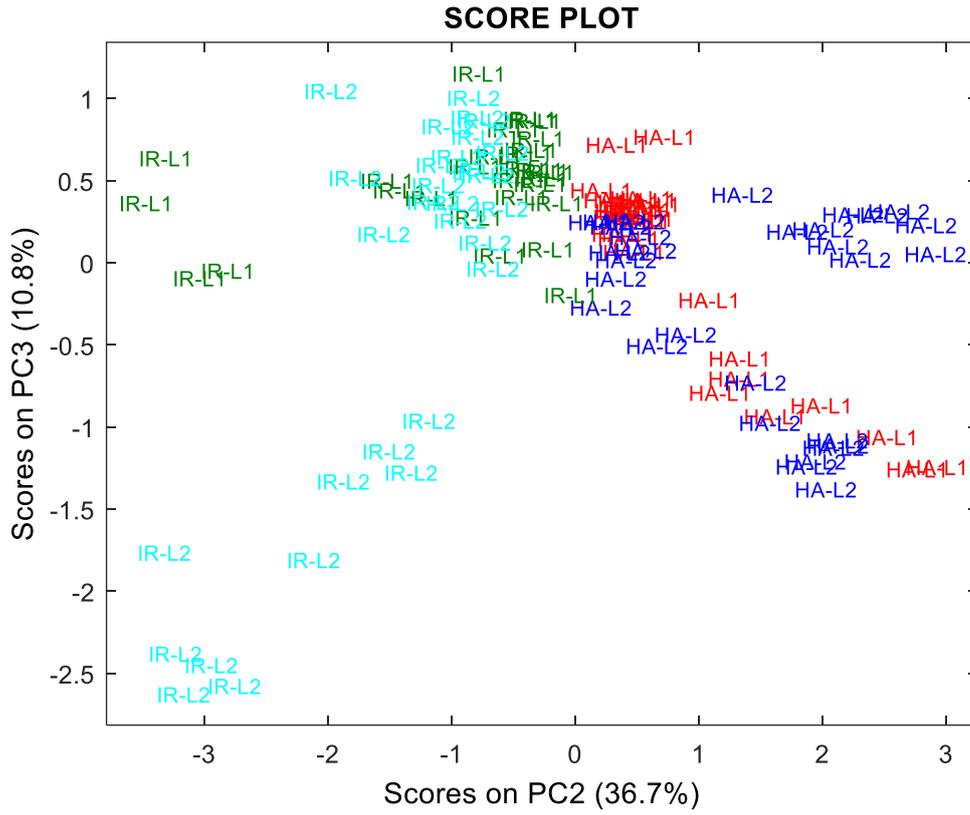
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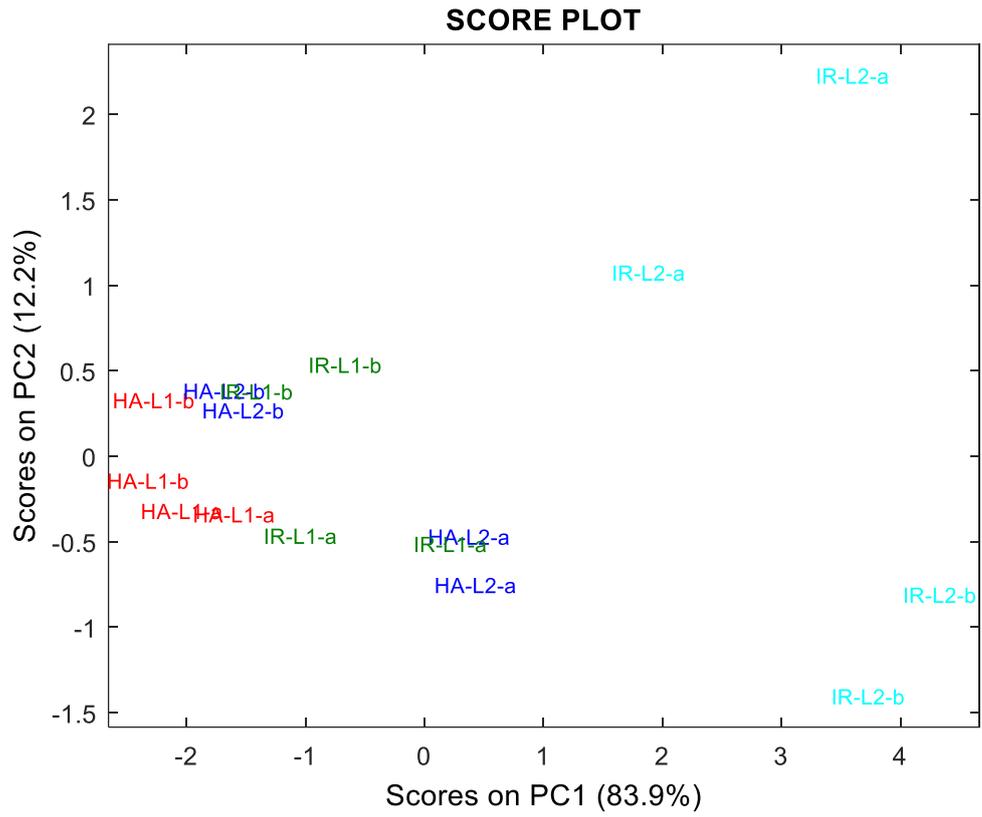
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Figure 2a



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Figure 2 b

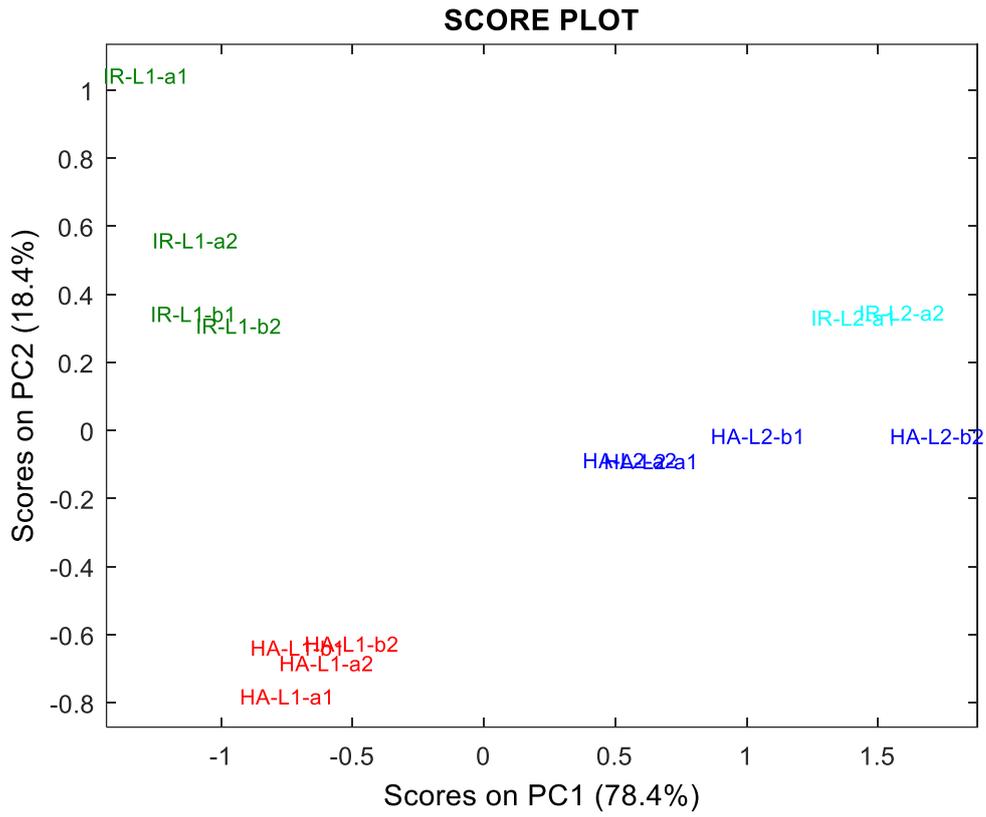


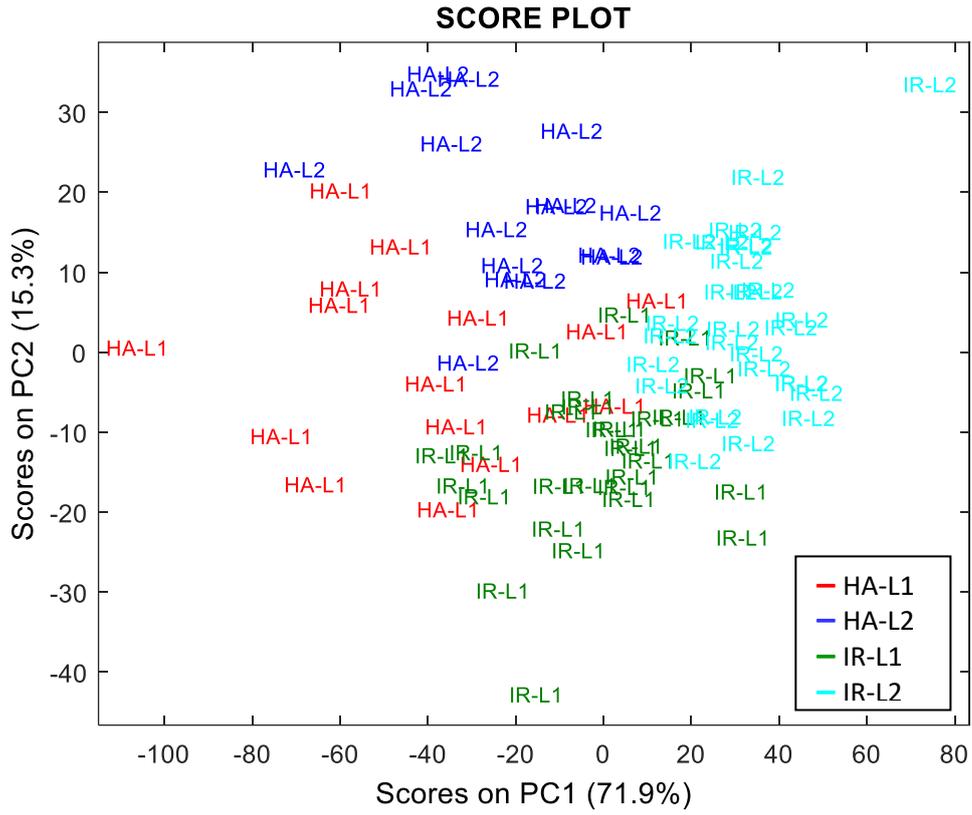
Figure 2c

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Figure 3a

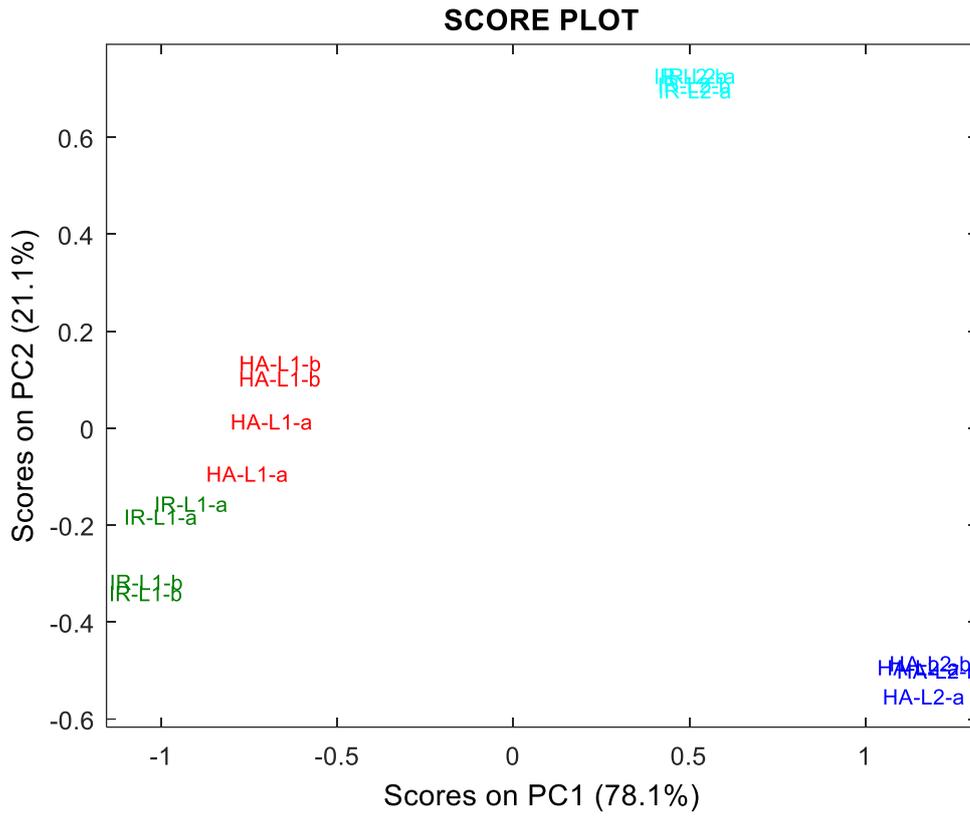


Figure 3b

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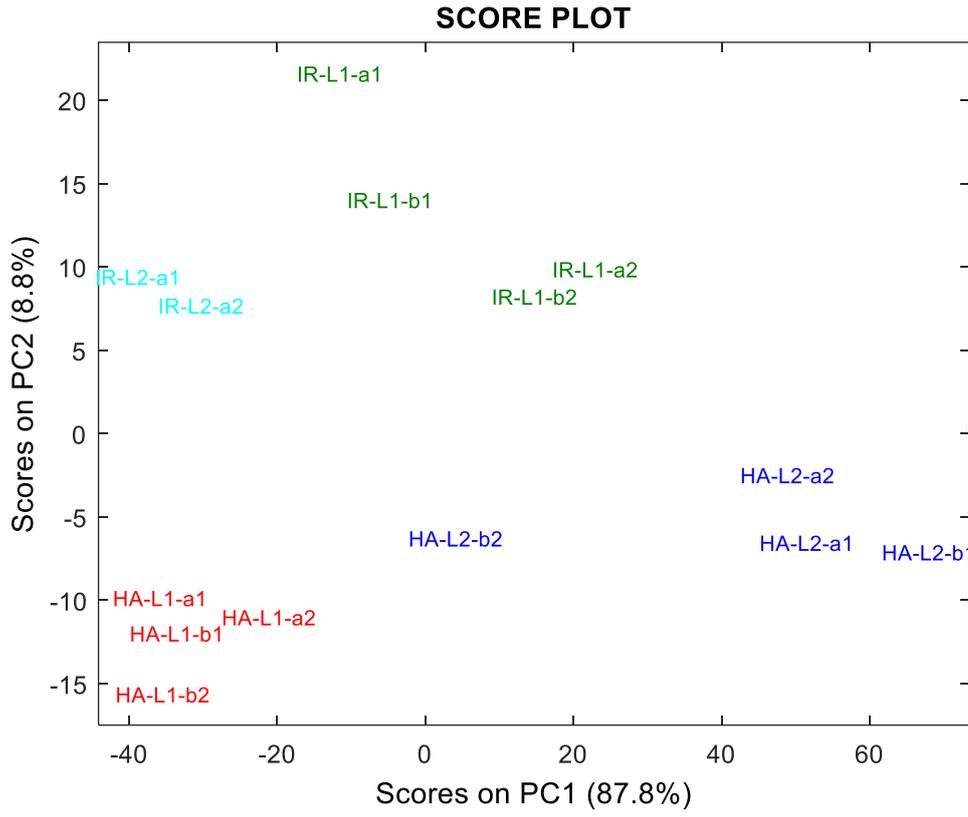


Figure 3c

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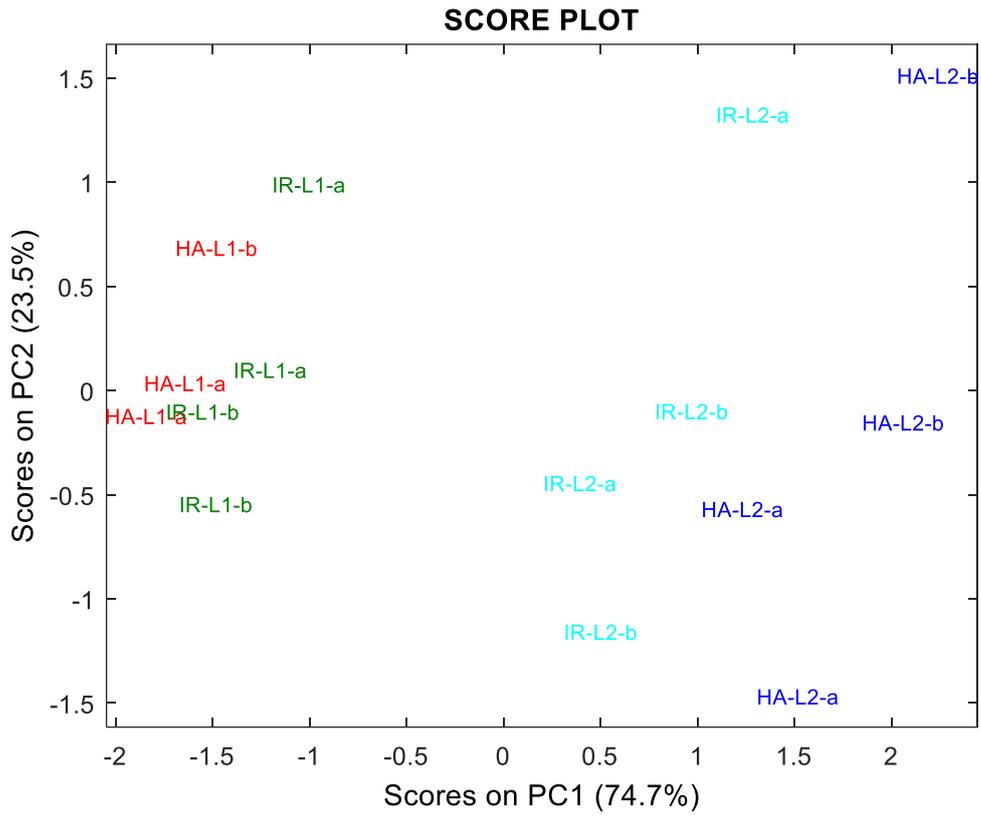


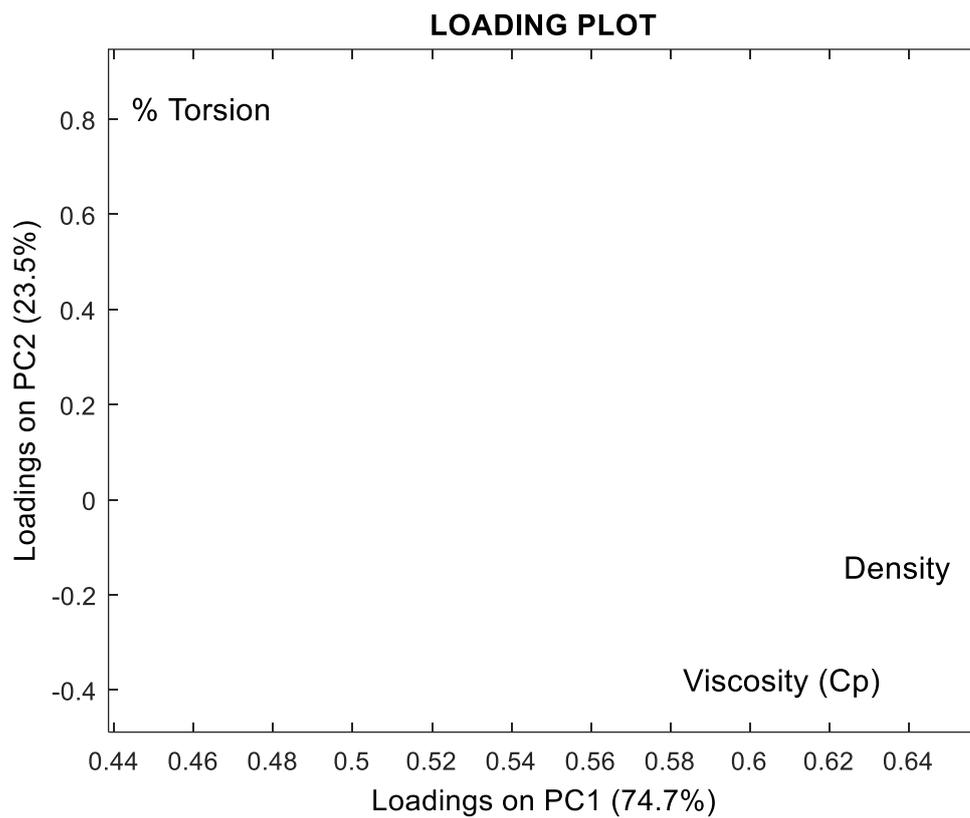
Figure 5a

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Figure 5b