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1 **Phenolic and polysaccharidic composition of applesauce is** 2 **close to that of apple flesh**

3
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25 1. Abstract.

26 Apple fruit is well known for its health properties, ascribed to its content in both
27 phenolics and fibres. As more and more apples are consumed after processing, there is a
28 need to understand the impact of the conventional process on the nutritional potential of
29 applesauce. We have investigated the variation in composition between fresh and
30 processed apples of 12 cultivars, focussing on polysaccharides and polyphenols. The
31 polysaccharide content estimated in the alcohol insoluble solid (AIS) of the apple flesh
32 varied from 17 (cv. Greensleeves, obtention TMR 7 A 82) to 25 (cv. Jolyne) mg/g fresh
33 weight. The AIS contents varied from 15 to 32 mg/g fresh weight in applesauce. The
34 applesauces were fractionated into serum, containing low concentrations (< 5 mg/g) of
35 soluble fibers, and particles concentrating the fibers (40-60 mg/g) and the cellulose (> 30%
36 of the AIS). Total phenolic concentrations varied in the flesh from 578 (cv. Golden
37 Delicious) to 1596 mg/kg fresh weight (cv. 3535), and in the peel from 1658 (cv.
38 Greensleeves) to 7658 mg/kg fresh weight (cv. Sinta). The applesauces contained
39 flavonols, coming from the skin, and slightly higher concentration of dihydrochalcones
40 coming from the pips than the flesh. A dihydrochalcone oxidation product was also
41 detected. The concentration of hydroxycinnamic acids and flavan-3-ols were decreased in
42 proportions depending on the cultivar. The flavan-3-ols were concentrated in the particles
43 of the applesauce. The composition of applesauce thus appeared to be very close to that of
44 apple flesh.

45

46 Keywords: *malus domestica*, polyphenols, fibers, fruit processing, procyanidins.

47

48 2. Introduction.

49 The health effects of apples, especially their cholesterol-lowering properties, are
50 ascribed to the combined fiber and polyphenol fractions. Aprikian et al., (2003) found that
51 apple pectin and polyphenol fractions are more effective together than are either apple
52 pectin alone or apple polyphenol alone for lowering plasma and liver cholesterol and
53 triglycerides. Thus the beneficial effect of apple on health may be better achieved in
54 products which are rich in fiber and phenolics. An example of this kind of product is
55 applesauce.

56 Both fiber and phenolic compositions of apple are fairly well known in terms of
57 structure (Renard, Voragen, Thibault, & Pilnik, 1990; Renard & Thibault, 1991; Nicolas,
58 Richard-Forget, Goupy, Amiot, & Aubert, 1994; Massiot, Baron & Drilleau, 1994; Massiot
59 & Renard, 1997; Guyot, Marnet, Laraba, Sanoner, & Drilleau 1998; Sanoner, Guyot,
60 Marnet, Molle, & Drilleau, 1999; Guyot, Le Bourvellec, Marnet, & Drilleau, 2002; van der
61 Sluis, Dekker, de Jager, & Jongen, 2001; Tsao, Yang, Young, Zhu, 2003; Vrhovsek, Rigo,
62 Tonon, & Mattivi, 2004; Renard, 2005a; Marks, Mullen, & Crozier, 2007; Khanizadeh,
63 Tsao, Rekika, Yang, Charles, & Rupasinghe, 2008). Five classes of phenolic compounds
64 are present in apple fruit : hydroxycinnamic acids derivatives, monomeric and oligomeric
65 flavan-3-ols named procyanidins, dihydrochalcones, flavonols and anthocyanins only
66 present in the peel of some red varieties (Nicolas et al., 1994; Guyot et al., 1998; Sanoner
67 et al., 1999; Guyot et al., 2002; van der Sluis et al., 2001; Tsao et al., 2003; Vrhovsek et
68 al., 2004; Marks et al., 2007; Khanizadeh et al., 2008). Apple cell wall is mainly composed
69 of cellulose, highly methylated pectins relatively rich in xylogalacturonans, the
70 hemicelluloses fucogalactoxyloglucan and mannan (Renard et al., 1990; Renard &
71 Thibault, 1991 ; Massiot et al., 1994; Massiot & Renard, 1997; Renard, 2005a). However,

72 the effects of the whole processing for production of apple applesauce on fiber and
73 phenolic are not well known.

74 In industrial apple applesauce production, the fruits are either crushed, refined and
75 cooked in a cold-break process or cooked then refined in a hot-break process. There are
76 thus three potential mechanisms for modification of the phenolic and fiber compositions:
77 oxidation, selectivity at refining, and heat treatment.

78 Oxidation can occur during crushing step, during which polyphenols, polyphenol
79 oxidase, oxygen and cell walls, initially segregated, come into contact and may react
80 (Nicolas et al., 1994, Renard, Baron, Guyot, & Drilleau, 2001). Effects of these reactions
81 are well known for apple juice: oxygenation of the juice or crushed apples during
82 processing result in a significant decrease of phenolic compounds variable depending on
83 the phenolic class and the variety (Guyot, Marnet, Sanoner, & Drilleau, 2003). Catechins
84 and procyanidins are particularly affected by oxidation, whereas 5'-caffeoylquinic acid is
85 partly preserved suggesting the involvement of a coupled oxidation mechanism (Cheynier
86 & Ricardo da Silva, 1991). As oxidation can lead to browning, it is usually palliated by
87 addition of ascorbic acid at crushing.

88 A major cause for loss of polyphenols and fibers is the refining step, which
89 eliminates the peel and pips. Concerning polyphenols, interest has been focused on
90 flavonols, concentrated in peels (Guyot et al., 1998; Sanoner et al., 1999; Guyot et al.,
91 2002; Tsao et al., 2003; Marks et al., 2007; Khanizadeh et al., 2008). Peel elimination is
92 thus a major cause of losses (Oszmianski & Wojdylo, 2008). Apple peel and carpels also
93 contain more cell walls, and thus more fibers, than apple flesh (Massiot et al., 1994;
94 Massiot & Renard, 1997). Moreover, apple flesh contains a higher content in pectic
95 components while carpels are richer in xyloglucans and glucans. Colin-Henrion,

96 Mehinajic, Renard, Richomme, & Jourjon (2009) thus recorded a highly significant
97 decrease in the insoluble fibre content of a hot-break applesauce after the refining step.

98 Last, heating may also be detrimental for polyphenol and polysaccharide content.
99 On pear, Renard (2005a) shows that after 1 hour of cooking, 65% of the original flavan-3-
100 ols and 40% of the original 5'-caffeoylquinic acid are still detectable in the pear tissue.
101 During cooking the pectic fractions are degraded becoming more soluble and of lower
102 molecular weight (Renard, 2005a, Colin-Henrion et al., 2009), while xylans and cellulose
103 are not affected (Renard, 2005a).

104 The objectives of the present study were to evaluate the impact of conventional
105 cold-break process production of apple applesauce on the nutritional properties. To reach
106 this aim polysaccharide and polyphenol profiles (qualitative and quantitative) of twelve
107 apple varieties were investigated focussing on their variation between fresh apples and
108 applesauce produced using a cold-break process.

109

110 3. Materials and methods

111 3.1. Standards and chemical

112 Chlorogenic acid, (+)-catechin, (-)-epicatechin were obtained from Sigma-Aldrich
113 (Deisenhofen, Germany). 4-coumaric acid and quercetin were obtained from Extrasynthese
114 (Lyon, France). Phloridzin was obtained from Fluka (Buchs, Switzerland). Sugar standards
115 were from Fluka (Buchs, Switzerland). d3-methanol was from Acros organics (Geel,
116 Belgium). NaBH₄, N-methyl imidazole, acetic anhydride, toluene- α -thiol were from
117 Sigma-Aldrich (Deisenhofen, Germany). Acetonitrile was analytical grade and from Fisher
118 Scientific (Fair Lawn, New Jersey, USA).

119 3.2. Plant material

120 Apple fruits (*Malus domestica* Borkh.) of the 2007 crops were obtained from the
121 experimental orchard of INRA in Angers (49, France) as part of an investigation of the
122 French Association of Fruit and Vegetables Processing (AFIDEM), into the potential of
123 various varieties for applesauce production. 12 cultivars were used: Baujade, Chanteline,
124 Freiberg, Golden Delicious, Greensleeves, Granny Smith, Jolyne, New Gold, Newton
125 Pippin, Sinta, TMR 7 A 82, 3535. Three triplicates of 10 apples were constituted. Each
126 apple was peeled and cored (**Figure 1a**) and then divided as follows: each apple was cut
127 vertically into 12 equal portions (**Figure 1b** and **Figure 1c**). Portions 2, 5, 8 and 11 were
128 discarded (**Figure 1d**). Each of the other 8 portions was cut in two vertically giving 16
129 pieces per apple (**Figure 1e**). The 16 portions were divided in two containers A and B in
130 such a way that container A received 2 left and 2 right quarters from portions 1, 4, 7 and 10
131 and container B received 2 left and 2 right quarters from portions 3, 6, 9 and 12 (**Figure**
132 **1f**). The two containers were freeze-dried but only container A was used.

133 3.3. Industrial processing and sample preparation

134 Applesauce processing was carried out by the Centre Technique de la Conservation
135 des Produits Agricoles (CTCPA), using a cold-break process. The process was composed
136 of several steps, summarized in **Figure 2**. The fruits were washed, and crushed. A solution
137 of ascorbic acid at 250 g/l was then added to the crushed apple (1 liter for 50 kg). Crushed
138 apples were refined (sieve opening 1.25 mm) before cooking (95°C, 2 min). A saccharose
139 syrup was then added in order to obtain a Brix degree of 16° +/- 0.5°. Applesauce was hot
140 conditioned and pasteurised (90°C, 5 min) then cooled (water at 20 °C, 20 min). For each
141 apple variety two cans of applesauce were collected.

142 Serum and particles were separated by centrifugation. 80 g of applesauce were
143 centrifuged at 13 600 g for 10 minutes. The supernatant was removed and filtered in a G3
144 sintered glass filter. Serum and particles were frozen and stored at -20°C before use.

145 3.4. Alcohol insoluble solid (AIS)

146 AIS were prepared according to Renard et al., (1990) and Renard (2005b).

147 Approximately 2 g of freeze-dried apple powder, in a 50 ml empty Sep-pack
148 column (Interchim, France) equipped with a sinter of porosity 20 µm, were suspended in
149 30 ml of boiling 96% ethanol and left 20 minutes. The supernatant was removed by
150 filtration. The material was resuspended in 70% ethanol and extracted at room temperature
151 still absence of sugars as shown by negative reaction in the phenol sulfuric test (Dubois et
152 al., 1956). Samples were then washed twice with acetone : water : acetic acid (v/v/v 60 : 39
153 : 1), then twice with acetone: water solution (v/v 80 : 20), then with pure acetone until
154 discolouration of the supernatant. The residue was dried at 40°C during 24 hours and
155 weighed (AIS). For each apple variety three replicates were performed.

156 For each apple variety AIS were prepared from each of the two cans for applesauce,
157 serum and particles. Approximately 20 g of fresh applesauce or fresh particles were
158 suspended in 80 ml of 96% ethanol and left 24 hours. The supernatant was removed by

159 filtration and a portion of 70% ethanol was added. The same washing and drying
160 procedures were used as for apple. For each apple variety AIS from applesauce were
161 performed on each of the two cans.

162 40 ml of serum were poured in 120 ml of 96% ethanol and left to stand at 4°C
163 during 24 hours. Samples were first centrifuged at 4200 g for 20 minutes, the supernatant
164 was removed and a portion of 70% ethanol was added. The samples were then centrifuged
165 at 8900 g for 10 min. The washings were continued till absence of sugars as shown by
166 negative reaction in the phenol sulfuric test (Dubois, Gilles, Hamilton, Rebers, & Smith,
167 1956). The same drying procedure was used as for apple.

168 3.5. Analytical

169 Polyphenols were measured by HPLC after thioacidolysis as described by Guyot et
170 al., 2001. The average degree of polymerisation was measured by calculating the molar
171 ratio of all the flavan-3-ol units (thioether adducts plus terminal units) to (-)-epicatechin
172 and (+)-catechin corresponding to terminal units. Polyphenols were separated in an Agilent
173 1050 separation system (Agilent Technologies) including a quaternary pump coupled to a
174 diode array detector and controlled by Chemstation A.10.02 software. Separations were
175 achieved using a (250 × 4mm i.d.) Licrospher PR-18 5 µm column (Merck, Darmstadt,
176 Germany) with a guard column (Licrospher PR-18 5 µm column, Merck, Darmstadt,
177 Germany) operated at 30 °C. The mobile phase consisted of water/acetic acid (97.5:2.5,
178 v/v) (eluent A) and acetonitrile (eluent B). The flow rate was 1 ml/min. The elution
179 programme was as follows: 3–9% B (0–5 min); 9–16% B (5–15 min); 16–50% B (15–
180 45 min); 50–90% B (45–48 min); 90–90% B (48–52 min); 90–3% B (52–55 min); 3–3% B
181 (55–60 min). For apple the three batches were analysed and for applesauce, serum and
182 particles each of the two cans were analysed. Samples were injected at a level of 20 µl. The

183 column effluent was monitored at 280, 320 and 350 nm. Quantification was achieved by
184 injection of standard solutions of known concentrations.

185 UPLC-MS analyses were performed on the Acquity Ultra performance LC™
186 (UPLC™) apparatus from Waters (Milford, MA, USA), equipped with an UV-visible
187 diode array detector and coupled with a Bruker Daltonics (Bremen, Germany) HCT ultra
188 ion trap mass spectrometer with a negative electrospray ionization mode. Separations were
189 achieved using a (150 × 2.1 mm i.d.) 1.7 µm Acquity UPLC HSS T3 column (Waters,
190 Milford, MA, USA) operated at 30 °C. The mobile phase consisted of water/formic acid
191 (99.95:0.05, v/v) (eluent A) and acetonitrile (eluent B). The flow rate was 0.6 ml/min. The
192 elution programme was as follows: 3–9% B (0–1.4 min); 9–16% B (1.4–4 min); 16–50% B
193 (4–15 min); 50–97% B (15–15.5 min); 97–97% B (15.5–18 min). Samples were injected at
194 a level of 2 µl. The column effluent was monitored at 280, 320 and 365 nm. The mass
195 spectra were generated in the Ultrascan mode in the m/z range 100–900. Nitrogen was used
196 as the nebulising gas. The ion source parameters were : nebuliser pressure, 40 psi; drying
197 gas flow, 10 L/min; drying gas temperature, 365°C; capillary voltage, 2 kV. Helium was
198 used as the damping gas. Data were collected and processed using Bruker Compass Data
199 Analysis software.

200 Neutral sugars, galacturonic acids and methanol were analysed as described by
201 Renard & Ginies (2009). Dry matter was estimated by the loss of weight recorded after
202 freeze-drying.

203 3.6. Statistical analysis

204 Results are presented as mean values, and the reproducibility of the results was
205 expressed as pooled standard deviation. Pooled standard deviations were calculated for
206 each series of replicates using the sum of individual variances pondered by the individual
207 degrees of freedom (Box, Hunter & Hunter, 1978). The variability of the composition

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208 between varieties was expressed calculating the average of the mean values for each
209 variety and the standard deviation of the mean.

210 Two-way analysis of variance (ANOVA) by Fisher 's test (F) was used to compare
211 the means and performed using the Excelstat package of Microsoft Excel. Differences
212 were considered to be significant at $P < 0.05$.

213

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214 4. Results and discussion

215 4.1. Cell wall characterisation

216 **Table 1** summarized the yields and compositions of the AIS of apple flesh. The
217 AIS content of apple flesh varied from 17 mg/g (cv Greensleeves) to 25 mg/g (cv Jolyne)
218 fresh weight (FW), which was consistent with previously published works (15-24 mg/g of
219 fresh weight) (Renard & Thibault, 1991; Massiot & Renard, 1997; Renard, 2005b; Colin-
220 Henrion et al., 2009). The sugar composition of the AIS of the different apple varieties
221 were very close (**Table 1**). They reflected the macromolecular composition of the apple
222 cell wall (Renard et al., 1990; Massiot et al., 1994; Massiot & Renard, 1997; Renard,
223 2005b): cellulose, highly methylated pectins relatively rich in xylogalacturonans,
224 fucogalactoxyloglucan and mannan. The two main sugars were glucose (from 233 mg/g
225 (cv. Freiberg) to 349 mg/g (cv. Golden Delicious)) and galacturonic acid (from 209 mg/g
226 (cv. Freiberg) to 273 mg/g (cv. Granny Smith and TMR 7 A 82)). Glucose came essentially
227 from cellulose (Renard et al., 1990). Pectic substances were present in high amount as
228 shown by the high galacturonic acid content, and were highly methylated (from 71% (cv.
229 Granny Smith, New Gold and Sinta) to 80% (cv. Jolyne)). In previous work (Voragen et
230 al., 1980; Renard et al., 1990; Renard, 2005b), degrees of esterification from 63 to 75%
231 were obtained in the AIS preparations from apple. Besides glucose and galacturonic acid,
232 the neutral sugars arabinose (from 68 mg/g (cv. Greensleeves) to 133 mg/g (cv. Sinta)),
233 xylose (from 50 mg/g (cv. Newton Pippin) to 66 mg/g (cv. New Gold)) and galactose
234 (from 45 mg/g (cv. Greensleeves) to 80 mg/g (cv. Freiberg)) dominated. Arabinose and
235 galactose enter in the composition of the side chains of the hairy region of the pectic
236 substances (de Vries, Rombouts, Voragen, & Pilnik, 1982), while xylose, together with
237 fucose (from 7 mg/g (cv. Newton Pippin) to 11 mg/g (cv. Golden Delicious)), part of the

238 galactose and glucose, constitute fucogalactoxyloglucan, which is the main hemicellulose
239 of apple cell wall (Renard et al., 1990, Renard, Voragen, Thibault, & Pilnik, 1991).
240 Mannose (from 10 mg/g (cv. new Gold) to 22 mg/g (cv. Sinta)) enter in the composition of
241 mannan (Renard et al., 1991).

242 The yields and the composition of the AIS of applesauces are summarised in **Table**
243 **2**. After processing into applesauce the AIS contents varied from 15 to 32 mg/g FW and
244 were either higher (Freiberg, Golden Delicious, Greensleeves, Jolyne, New Gold and
245 Sinta) or lower (Newton Pippin, Chanteline, Granny Smith, 3535, TMR 7 A 82) than for
246 the corresponding raw apple. Few studies report the polysaccharide content of applesauces,
247 yet values obtained here were slightly higher than those reported by Marlett & Wollendorf
248 (1994) (14 mg/g) or contained that reported by Colin-Henrion et al., (2009) (18 mg/g).

249 During processing into applesauce, four main mechanisms may affect the AIS content :

- 250 - a dilution during addition of sugar and ascorbic acid,
- 251 - the temperature applied (90°C) may have contributed to the solubilization by
252 depolymerisation of pectins (Ng & Waldron, 1997; Renard, 2005b; Colin-Henrion et al.,
253 2009) by acid hydrolysis and β -elimination (Sajjaanantakul, van Buren, & Dowling, 1989;
254 Fraeye, de Roeck, Duvetter, Verlent, Hendrickx, van Loey 2007),
- 255 - the presence of particles coming from skin and pips, both containing more AIS
256 material than parenchyma (Massiot et al., 1994; Massiot & Renard, 1997),
- 257 - co-precipitation of proteins and polyphenols from the apple fruit (Colin-Henrion
258 et al., 2009). Cutting and crushing could favour the formation of processing-induced
259 complexes between polyphenols, especially procyanidins, and cell wall polysaccharides
260 (Renard et al., 2001, Le Bourvellec, Guyot, & Renard, 2004). Renard (2005a) reported a
261 similar effect of cooking on AIS content of boiled pear wedges. As here the Brix chosen

262 for the puree was very close to that obtained for most of the apples, there was no dominant
263 dilution effect.

264 AIS from applesauce mainly contained less galacturonic acid and rhamnose and
265 more galactose than those of the apple flesh (**Table 2**). The applesauces were fractionated
266 into serum and particles. The serum contained low concentrations (< 5 mg/g FW) of
267 soluble fibers mainly containing galacturonic acid, rhamnose, arabinose and galactose, i.e.
268 primarily pectic polymers. Particles concentrated the fibers (40-60 mg/g FW) and the
269 major component was glucose coming from cellulose (> 30% of the AIS), but high
270 amounts of galacturonic acid were also detectable. Glucose and xylose content were higher
271 than in apple flesh, coming probably from carpel zone (Massiot et al., 1994; Massiot &
272 Renard, 1997). The same trends for AIS and soluble and insoluble fibres of applesauce has
273 also been reported by Colin-Henrion et al. (2009).

274 Two-ways ANOVAs (variety and “type of product” effects, with interactions) were
275 performed on apple flesh and applesauce AIS compositions. The variety effect was
276 significant ($P < 0.0001$) for all variables, except degree of methylation and the “type of
277 product” for all variables except degree of methylation, mannose and galacturonic acid
278 (**Table 3**). The variety effect was more important for arabinose, mannose, glucose, and
279 galacturonic acid whereas the 'type of product' effect was more important for rhamnose,
280 fucose, xylose, galactose and methanol.

281 **4.2. Polyphenol characterisation**

282 **Apple peel and flesh**

283 Composition and concentrations of the major phenolics found in the peel and in the
284 flesh of the 12 apple varieties are shown in **Table 4** and **5** respectively. Five major
285 phenolic groups with a total of fourteen identified individual compounds were quantified.
286 The sum of phenolics determined by HPLC ranged from 1658 mg/kg (cv. Greensleeves) to
287 7658 mg/kg FW (cv. Sinta) in the peel. For all varieties, in the flesh, the total polyphenols

288 were significantly lower than in the peel, ranging from 539 mg/kg (cv. Newton Pippin) to
289 1596 mg/kg FW (cv. 3535). In our study, total polyphenols in the flesh were slightly
290 higher, but in the range of previous works for dessert and cider apples (228-6999 mg/kg
291 FW)(Sanoner et al., 1999; van der Sluis et al., 2001; Guyot et al., 2002; Tsao et al., 2003;
292 Vrhovsek et al., 2004, Khanizadeh et al., 2008). The different varieties of apples studied
293 come from a collection of INRA Angers and are intended for different use and therefore
294 have significant biodiversity.

295 Among the five major groups, procyanidins were the predominant class in both the
296 skin (73%) and the flesh (69%) (**Table 4** and **5**). These data are in agreement with other
297 authors (Guyot et al., 1998; Sanoner et al., 1999; Guyot et al., 2002; Tsao et al., 2003;
298 Vrhovsek et al., 2004; Khanizadeh et al., 2008). For all varieties, in the flesh, the
299 procyanidins' average degrees of polymerisation ($\overline{DP}n$) were significantly lower than
300 those of the peel, ranging respectively from 2.9 (cv. Baujade) to 3.8 (cv. Chanteline) and
301 from 1.4 (cv. Sinta) to 5.6 (cv. Granny Smith) as observed in previous work (Sanoner et
302 al., 1999; Guyot et al., 2002). However, $\overline{DP}n$ in the flesh were slightly lower than the
303 $\overline{DP}n$ observed by Sanoner et al., (1999) and Guyot et al., (2002) in the flesh of dessert
304 variety with $\overline{DP}n$ from 5.7 to 6.0. The flavan-3-ols monomers were detected as (-)-
305 epicatechin and (+)-catechin, the former being highly preponderant and the later sometimes
306 only in traces amounts (**Table 4** and **5**).

307 Hydroxycinnamic acids accounted for only 4% of the total polyphenols in the peel
308 while they constituted the second polyphenol class in the flesh where they accounted for
309 circa 20% of the total polyphenols. Hydroxycinnamic acids were lowest in Granny Smith
310 and particularly concentrated in the peel and flesh of TMR 7 A 82with about half a g per
311 kg FW. The main hydroxycinnamic acid was always 5'-caffeoylquinic acid. The highest
312 concentrations of *p*-Coumaroylquinic acid were only circa 50 mg/kg FW (**Table 4** and **5**).

313 For all varieties, dihydrochalcones were a minor group which accounted for an
314 average of 3% and 1.5% of the total polyphenols in the peel and in the flesh, respectively
315 (**Table 4** and **5**). Higher concentration were found in the peel, up to about 300 mg/kg FW,
316 than in the flesh (up to 40 mg/kg FW). Phloridzin and phloretin-2-xyloglucoside were the
317 major constituent of this class, and in all the cultivar tested here, phloridzin was
318 preponderant.

319 For all variety no compounds of the flavonol class could be detected in the flesh.
320 Flavonols represented the second highest class in apple peel with 14% of the total
321 polyphenols (**Table 5**). Six quercetin glycosides were found and quantified in quercetin
322 equivalent : quercetin 3-galactoside > quercetin 3-arabinopyranoside > quercetin 3-
323 rhamnoside > quercetin 3-glucoside > quercetin 3-xyloside > quercetin 3-rutinoside.
324 Depending on the variety, total flavonols ranged from 300 mg/kg (cv. Golden Delicious) to
325 901 mg/kg FW (cv. TMR 7 A 82) in the peel.

326 All these concentrations and relative composition of each class are consistent with
327 previous works. Previous studies have also shown a wide variation in the phenolic content
328 of different cultivars (Guyot et al., 1998; Sanoner et al., 1999; Guyot et al., 2002; Tsao et
329 al., 2003; Vrhovsek et al., 2004; Marks et al., 2007; Khanizadeh et al., 2008). These
330 different works deal with the characterization of phenolic profiles of dessert apples (Guyot
331 et al., 2002; Tsao et al., 2003; Vrhovsek et al., 2004), of selected apple genotypes for
332 processing with high polyphenol content (Khanizadeh et al., 2008) while having, however,
333 less extreme concentrations than those achieved by cider apple (Guyot et al., 1998;
334 Sanoner et al., 1999; Marks et al., 2007).

335 Applesauces

336 Composition and concentrations of the major phenolics found in the apple
337 applesauces are shown in **Table 6**. The composition and concentrations of phenolics

338 compounds in the applesauce were closely related to their contents in the raw material
339 (Oszmianski, Wolniak, Wojdylo, & Wawer, 2008; Oszmianski & Wojdylo, 2008). The
340 total phenolics ranged from 182 mg/kg (cv. Greensleeves) to 1334 mg/kg FW (cv. 3535)
341 and were significantly lower than in the flesh as previously shown by Dragovic-Uzelac,
342 Pospisil, Levaj, & Delonga (2005). Total native polyphenols in the applesauce accounted
343 for 37% (cv. New Gold) to 94% (cv. Golden Delicious) of those in the initial flesh. The
344 applesauce polyphenol retention was mainly related to those of flavan-3-ols. As in apple
345 flesh, most of the flavan-3-ols of the applesauce were procyanidins (**Table 6**). The total
346 procyanidins ranged from 72 mg/kg (cv. Greensleeves) to 814 mg/kg FW (cv. Granny
347 Smith). They represented from 18% (cv. New Gold) to 90% (cv. Granny Smith) of the
348 procyanidins initially present in the flesh. \overline{DP}_n of the procyanidins essentially did not
349 change from apple to applesauce, ranging respectively from 2.3 (cv. Newton Pippin) to 3.7
350 (cv. Jolyne). (-)-Epicatechin was the preponderant flavan-3-ol monomer, but also the least
351 stable. (-)-Epicatechin retention ranged from 27% (cv. Greensleeves) to 90% (cv. Granny
352 Smith) and applesauce concentrations ranged from 12 mg/kg (cv. Greensleeves) to 93
353 mg/kg FW (cv. Granny Smith). (+)-Catechin retention ranged from 41% (Baujade) to 78%
354 (cv. Jolyne) and applesauce concentrations ranged from traces (cv. Freiberg, Golden
355 Delicious, Greensleeves, New Gold, Newton Pippin) to 93 mg/kg FW (cv. Granny Smith).

356 Total hydroxycinnamic acids content of applesauces decreased, compared to that of
357 the flesh, only by a small amount for most varieties except for cultivars Freiberg, Golden
358 Delicious and Granny Smith where total hydroxycinnamic acids content increased.
359 Concentrations ranged from 45 mg/kg (cv. Greensleeves) to 433 mg/kg FW (cv. 3535)
360 (**Table 6**). The increase in hydroxycinnamic acids content may be due to facilitating the
361 diffusion of phenolic compounds favored by cooking. As in apple flesh, among
362 hydroxycinnamic acids, the main compound in applesauce was always 5'-caffeoylquinic

363 acid, the retention of which ranged from 53% (cv. Greensleeves) to 125% (cv. Granny
364 Smith) .*p*-Coumaroylquinic acid concentrations represented from 33% (cv. New Gold) to
365 108% (cv. 3535) of those in the flesh (**Table 6**).

366 Total dihydrochalcones content of applesauces increased compared to that of the
367 flesh, with concentration ranging from 9 mg/kg (cv. Granny Smith) to 57 mg/kg FW (cv.
368 TMR 7 A 82) and representing from 98% (cv. New Gold) to 844% (cv. Chanteline) of
369 those in the flesh (**Table 6**). The increase observed was mainly due to an increased
370 phloridzin content. During applesauce processing dihydrochalcones, abundant in peel and
371 seeds (Sanoner et al., 1999; Guyot et al., 2002), may have diffused before refining.
372 Oszmianski & Wojdylo (2008) have shown that applesauce prepared from peeled apple
373 slices devoid of seeds had lower content of phloretin derivatives than applesauce prepared
374 from non-peeled apples. The main dihydrochalcone in applesauce was always phloridzin
375 which retention ranged from 98% (cv. Granny Smith) to 192% (cv. Jolyne) of those in the
376 flesh.. Phloretin-2-xyloglucoside retention ranged from 64% (cv. New Gold) to 168% (cv.
377 Greensleeves)) of those in the flesh. (**Table 6**).

378 Quercetin derivatives were detected in applesauce (**Table 6**) whereas they were not
379 present in apple flesh. Quercetin derivatives, abundant in peel (Sanoner et al., 1999; Guyot
380 et al., 2002), may have diffused during applesauce processing and before refining or could
381 be trapped within small peel particles. Like in apple peel six quercetin glycosides were
382 found in applesauce and quantified in quercetin equivalent. The same order of importance
383 was observed : quercetin 3-galactoside > quercetin 3-arabinopyranoside > quercetin 3-
384 rhamnoside > quercetin 3-glucoside > quercetin 3-xyloside > quercetin 3-rutinoside.
385 Depending on the variety, total flavonols ranged from 9 mg/kg (cv. 3535) to 35 mg/kg FW
386 (cv. TMR 7 A 82). The concentrations of flavonols in applesauce were not directly
387 correlated to those in the flesh of the corresponding apples. This phenomenon might be

388 explained by differences in the skin of apples, and notably different structures, mechanical
389 resistance and cuticle thickness.

390 Two-ways ANOVAs (variety and “type of product” effects, with interactions) were
391 performed on apple flesh and applesauce phenolic compositions. The variety and type of
392 product effect were always highly significant ($P < 0.0001$) (**Table 7**) except for phloretin-2-
393 xyloglucoside for which the type of product effect was not significant ($F = 0.38$ and $P =$
394 0.54). There was more variability with variety for hydroxycinnamic acids (5'-
395 caffeoylquinic acid and *p*-coumaroylquinic acid) whereas for other phenolic classes and
396 total phenolics the variability was more important with "type of product". This
397 phenomenon might be explained by the decrease in flavan-3-ols between apple flesh and
398 applesauce and by the increase in dihydrochalcones coming from the peel and seeds and
399 flavanols coming from the peel.

400 At the beginning of the applesauce chromatograms (**Figure 4**) the onset of a new
401 compound was observed. This component was assigned to the dihydrochalcone group
402 because of its UV-spectra, which maximum absorbance was 292 nm. This compound was
403 further analysed by HPLC-DAD/ESI-MS. It had a deprotonated molecular ion $[M-H]^-$ at
404 $m/z = 467$ which fragmented upon MS^2 to yield a major ion at $m/z = 305$. The loss of 162
405 mass units on MS^2 experiment correspond to the glucose moiety. The MS^3 fragmentation
406 of the 305 aglycon ion showed a main fragment at $m/z = 261$ that corresponded to the loss
407 of the carbonyl group (44 mass units). This compound was identified as the colourless
408 compound resulting from the oxidation of phloridzin named POPi (colourless phloridzin
409 oxidation product) (Guyot, Serrand, Le Quéré, Sanoner, & Renard, 2007; Le Guernevé,
410 Sanoner, Drilleau, & Guyot, 2004). Its amount was expressed in phloridzin equivalent and
411 its concentration ranged from 13 mg/kg (cv. Freiberg) to 30 mg/kg FW (cv. Baujade) in
412 applesauce. presence of POPi and absence of further compounds in the oxidation chain of

413 phloridzin, i.e. primarily POPj, the coloured compounds (Guyot et al., 2007; Le Guernevé
414 et al., 2004) indicated that a limited enzymatic oxidation had occurred during processing.

415 The decrease in phenolic content was probably a result of the processing
416 technology and more specifically of oxidation of polyphenols by polyphenoloxidase. Thus,
417 the phenolic composition of apple applesauce depends first on the initial composition of
418 the fruit and second on the processing conditions of the applesauce and the response of
419 each variety to the technology used. Oxidation of polyphenols during applesauce
420 processing, despite the addition of ascorbic acid, led to the formation of new phenolic
421 compounds not, one of which (POPi) was identified on the chromatogram.

422 A linear relationship was obtained (**Figure 3**) between hydroxycinnamic acids
423 retention and procyanidin retention in applesauces. The more hydroxycinnamic acids were
424 consumed by oxidation, the more procyanidins were also. Two groups were observed: a
425 group relatively protected from oxidation with procyanidin concentration in the applesauce
426 ranging from 71% (cv. Jolyne) to 90% (cv. Granny Smith) of those in the flesh and one
427 other without protection where this ratio applesauce to flesh ranged from 29% (cv.
428 Greensleeves) to 57% (cv. Baujade). Only New Gold variety did not follow this trend with
429 a an applesauce to flesh ratio for hydroxycinnamic acids of 90% and of 18% for
430 procyanidins. This close relationship between the concentrations of the hydroxycinnamic
431 acids and procyanidins in apple flesh and apple sauce is probably related to secondary
432 oxidation reactions. In apple, the main substrate of PPO is caffeoylquinic acid (Janovitz-
433 Klapp, Richard, & Nicolas, 1989). It is first enzymatically oxidised to its highly reactive *o*-
434 quinones, with the simultaneous consumption of oxygen, the second substrate of PPO
435 (Mayer & Harel 1979; Mayer, 1987). Then, *o*-quinones react following different pathways
436 according to their electrophilic and/or oxidant character with nucleophilic compounds
437 present in the medium such as polyphenols - or proteins, to produce secondary products by

438 covalent interactions (Jervis & Pierpoint 1989). Procyanidins are not substrates of PPO
439 (Goodenough & Lea 1979), but they can be converted into corresponding *o*-quinones by
440 coupled oxidation/reduction involving primary *o*-quinones formed by PPO catalysis.
441 During this reaction the primary *o*-quinones are reduced back to their *o*-diphenol form
442 (Cheynier & Ricardo da Silva, 1991). During applesauce processing the *o*-quinone of 5'-
443 caffeoylquinic acid may react with an *o*-diphenol like 5'-caffeoylquinic acid or flavan-3-ol
444 monomers to yield a condensation product by a mechanism analogous to a Michael 1,4
445 nucleophilic addition (Oszmianski & Lee, 1990) or with a procyanidin by a coupled
446 oxidation/reduction (Cheynier & Ricardo da Silva, 1991). This mechanism may explain the
447 correlation between 5'-caffeoylquinic acid and procyanidins consumption. The existence of
448 two groups, one protected from oxidation and the other not may be due to a higher PPO
449 activity in the second group.

450 **Particles and serums**

451 The polyphenols were not equally distributed between particles and serum, they
452 were mainly concentrated in the solid part of the applesauce (**Table 8 and 9**) with different
453 proportions between the different classes. Total phenolics in the particles ranged from 228
454 mg/kg (cv. Greensleeves) to 2690 mg/kg FW (cv. 3535) and in the serum from 123 mg/kg
455 (cv. Greensleeves) to 863 mg/kg FW (cv. 3535). Flavan-ols in particular were concentrated
456 in the particles of the applesauce (**Table 9**). This could be explained as particles
457 concentrate the fibers (4-6 mg/g FW) (**Table 2**), which are able to absorb selectively
458 procyanidins (Renard et al., 2001; Le Bourvellec et al., 2004). A selective partition of the
459 procyanidins between the particles and the serum was observed both in concentration and
460 in degree of polymerisation. The concentration of of procyanidins in the particles ranged
461 from 1757 mg/kg FW (3535) to 99 mg/kg FW (Newgold), and those in the serum from 366
462 mg/kg FW (Granny Smith) to 19 mg/kg FW (Newgold). The \overline{DP}_n of the procyanidins of

463 the particles (**Table 8**) ranged from 2.4 to 3.8 and were for each individual variety higher
464 than those of the procyanidins of the serum (**Table 9**), ranging from 2.3 to 3.1. By studying
465 the adsorption of procyanidins on cell wall material, Renard et al., (2001) and Le
466 Bourvellec et al., (2004) have also shown a selective partition of procyanidins between the
467 soluble phase and the insoluble material: the \overline{DP}_n of the bound procyanidins were higher
468 than those of the initial fraction and of the free procyanidins. Unlike procyanidins, which
469 were selectively distributed between particles and serum, flavan-3-ols monomers were
470 distributed equally over particles and serum (**Table 8** and **9**). The same was observed for
471 hydroxycinnamic acids, flavonols and dihydrochalcones. For example, (-)-epicatechin
472 concentrations ranged from 11 mg/kg (cv. Greensleeves) to 95 mg/kg FW (cv. Granny
473 Smith) in the particles and from 4 mg/kg (cv. Greensleeves) to 82 mg/kg FW (cv. Sinta) in
474 the serum.

475 Like the other polyphenol classes flavanols were distributed equally between
476 particles and serum (**Table 8** and **9**). Flavonols concentrations ranged from 9 mg/kg (cv.
477 3535) to 42 mg/kg FW (cv. Baujade) in the particles and from trace mg/kg (cv. 3535) to 24
478 mg/kg FW (cv. Baujade) in the serum.

479

480 5. Conclusions

481 We have investigated here the polysaccharidic and phenolic composition of 12
482 apple varieties and their applesauces. Fiber composition varied little between apple
483 cultivars and processing to applesauce induced little modification, with however a
484 solubilisation of pectins in the serum. The polyphenol compositions were much more
485 variable, so that variety was the main determinant of phenolic composition in applesauces.
486 Though applesauce phenolic compositions were still very close to those of apple flesh,
487 there were significant increases in dihydrochalcones and flavonols. In spite of added
488 ascorbic acid during processing, there could be marked losses in hydroxycinnamic acids
489 and procyanidins between the fresh apple and the applesauce. Further in the applesauce the
490 procyanidins were concentrated in the particles while the smaller molecules were more
491 equally distributed between serum and particles.

492 The phenolic compound concentrations in applesauce were results of their content
493 of raw materials and the diffusion and enzymatic oxidation reactions which phenolics
494 undergo during applesauce processing. On average concentration of phenolics in the
495 applesauce represented 70% of those in the flesh. Processing of apples into applesauces
496 caused limited changes in phenolic content compared to processing into juices where only
497 42% of fruit total phenolics were found in juices (Guyot et al., 2003). The nutritional
498 properties of applesauce can therefore be expected to be close to those of apple flesh.

499

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505 qualities".

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508

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1 **Figure Captions**

2 Figure 1 : Scheme of fractionation of apples into twelve sample, with a systematic
3 repartition of right and left faces.

4 Figure 2 : Applesauce processing

5 Figure 3 : Comparison of the relative variations in the concentrations of 5'-
6 caffeoylquinic acid and procyanidins between the fruit and the applesauce.

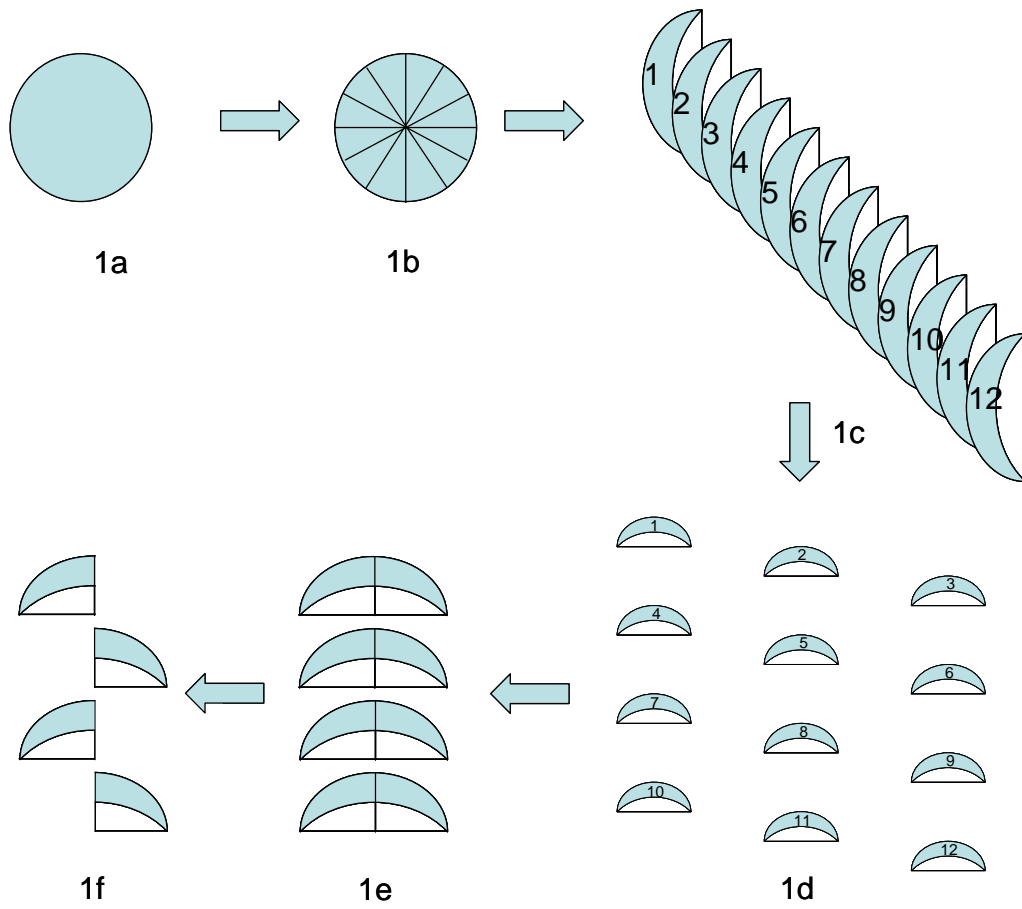
7 Figure 4 : Typical RP-18 chromatograms at 280 nm of apple flesh (Var. 3535, A) and
8 applesauce (Var. 3535, B). Peak identification : 1, POPI; 2, (+)-catechin; 3, 5'-caffeoylquinic
9 acid; 4, procyanidin B2; 5, (-)-epicatechin, 6, para-coumaroylquinic acid; 7, phloretin-2-
10 xyloglucoside; 8, phloridzin.

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13 Le Bourvellec et al.,

14 Fig 1

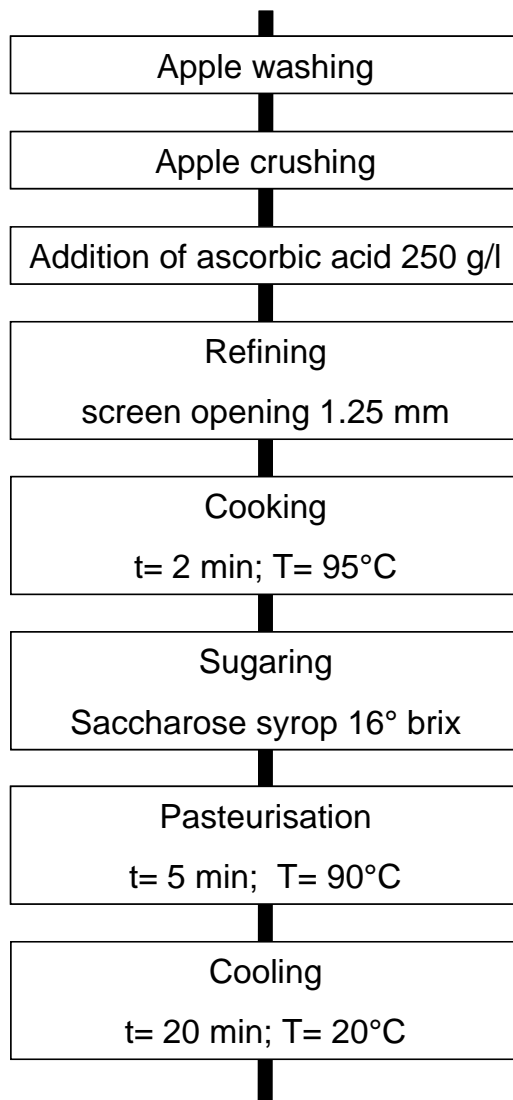


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18 Fig 2

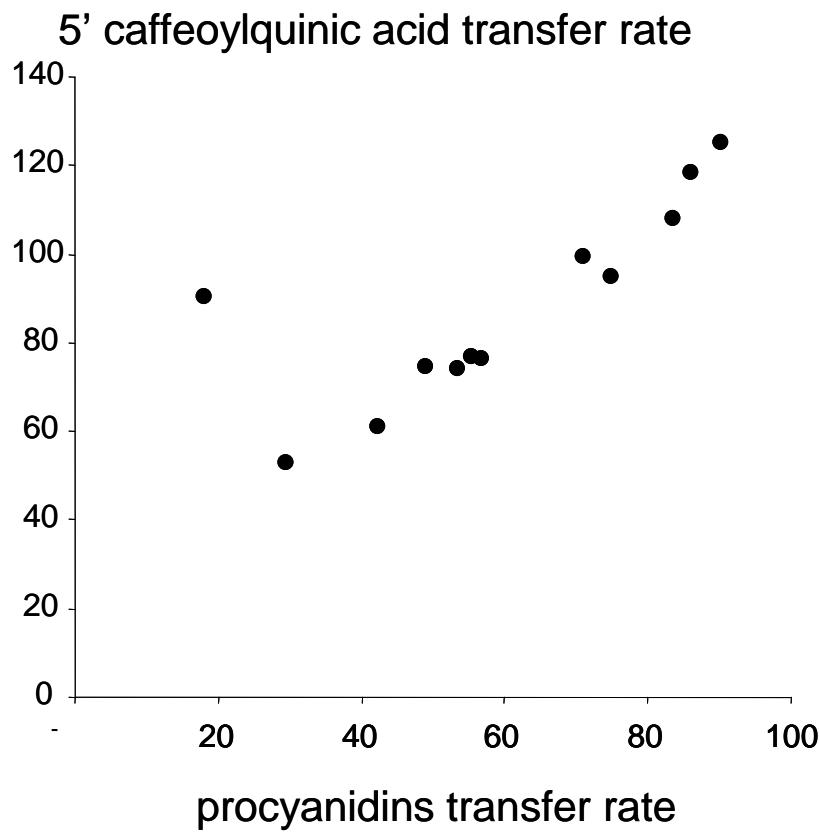


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22 Fig 3

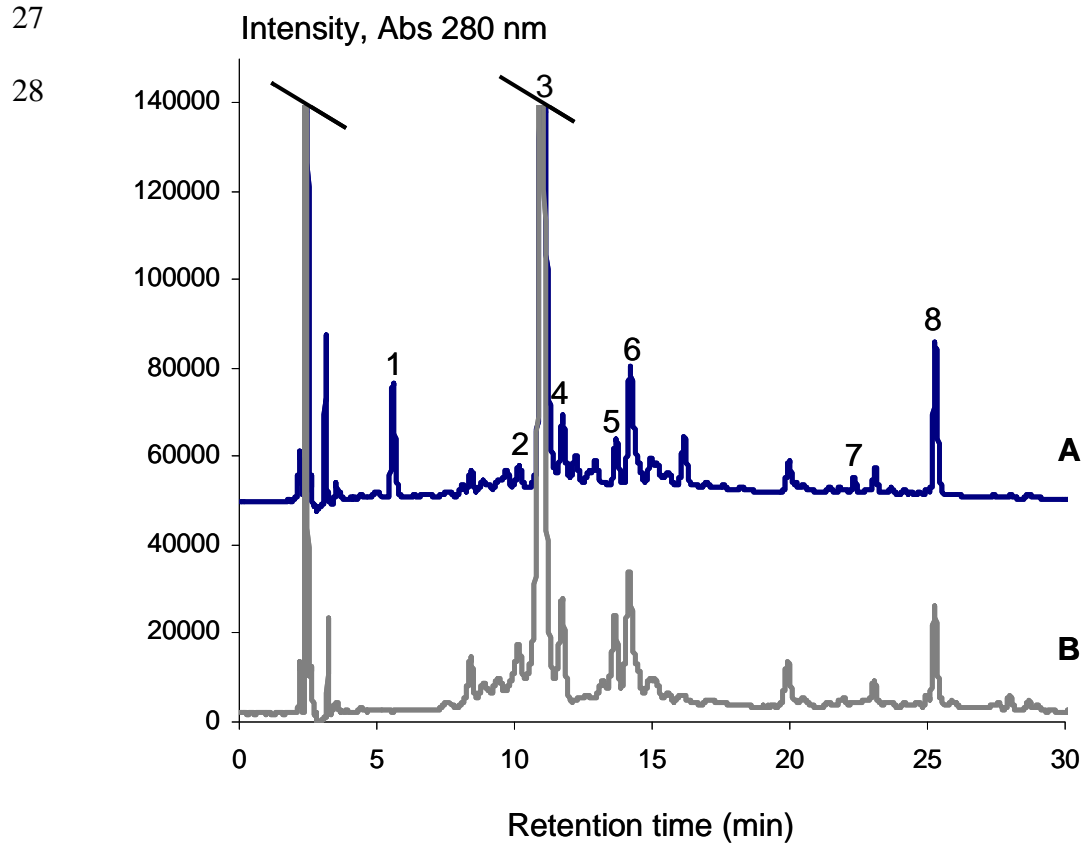


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25 Le Bourvellec et al.,

26 Fig 4



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1 Tables

2 Le Bourvellec et al.,

3 **Table 1** : Yields from fresh weight (mg/g fresh weight) and compositions (mg/g
4 dry matter) of the different apple flesh AIS.

Variety	Yields	Rha	Fuc	Ara	Xyl	Man	Gal	Glc	Gal A	MeOH (DM)
Baujade	19.3	9	8	124	52	14	51	286	247	33 (79)
Chanteline	18.8	9	8	101	62	16	53	338	238	33 (75)
Freiberg	27.0	10	8	88	52	14	80	233	209	28 (73)
Golden D.	22.0	11	11	104	63	21	58	349	255	33 (72)
Granny Smith	24.5	9	8	126	51	19	59	301	273	36 (71)
Greensleeves	17.4	10	8	68	53	11	45	258	236	32 (74)
Jolyne	25.2	11	9	117	52	18	50	320	255	37 (80)
New Gold	22.3	11	9	98	66	10	65	310	256	33 (71)
Newton Pippin	23.0	8	7	118	50	16	71	246	237	32 (75)
Sinta	22.9	11	9	133	60	22	77	319	236	31 (71)
TMR 7 A 82	17.2	10	8	104	54	20	54	285	273	33 (72)
3535	18.4	9	9	119	59	17	62	308	230	31 (74)
SDM	0.07	0.1	0.1	1.1	0.5	0.2	0.5	2.6	2.6	0.1 (0.8)

5 AIS, alcool insoluble solid. Rha, rhamnose. Fuc, Fucose. Ara, arabinose. Xyl, xylose. Man, mannose. Gal,
6 galactose. Glc, glucose. Gal A, galacturonic acid. MeOH, methanol. DM, degree of methylation. SDM,
7 standard deviation of the mean n= 72, except for the yields n = 24.

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3 **Table 2** : Yields from fresh weight (mg/g fresh weight) and compositions (mg/g

4 dry matter) of the AIS of applesauces, particles and serum.

Variety	P.	Yields	Rha	Fuc	Ara	Xyl	Man	Gal	Glc	Gal A	MeOH (DM)
Baujade	AS	22 2	6 0.2	7 0.3	91 1.8	38 1.8	14 0.5	62 1.8	243 10.3	311 5.3	33 0.2 (59 2)
	Pl	45 2	8 0.2	11 0.2	138 2.4	60 1.2	23 0.4	90 1.4	385 7.9	326 5.0	28 0.2 (47 3)
	S	4 0.3	7 0.2	2 0.1	81 1.8	6 0.2	0 0.0	79 1.7	0 0.0	502 10.8	70 0.4 (77 2)
Chanteline	AS	29 2	6 0.2	7 0.3	99 1.8	56 1.8	15 0.5	67 1.8	310 10.3	250 5.3	28 0.2 (64 2)
	Pl	53 2	7 0.2	7 0.2	85 2.4	48 1.2	15 0.4	62 1.4	292 7.9	183 5.0	25 0.2 (75 3)
	S	3 0.3	17 0.2	4 0.1	147 1.8	16 0.2	0 0.0	113 1.7	0 0.0	456 10.8	77 0.4 (94 2)
Freiberg	AS	21 2	8 0.2	6 0.3	78 1.8	41 1.8	14 0.5	77 1.8	229 10.3	178 5.3	27 0.2 (85 2)
	Pl	57 0.2	9 0.2	7 0.2	88 2.4	49 1.2	17 0.4	89 1.4	290 7.9	199 5.0	25 0.2 (70 3)
	S	1 0.3	6 0.2	1 0.1	43 1.8	4 0.2	0 0.0	46 1.7	0 0.0	407 10.8	55 0.4 (75 2)
Golden D.	AS	20.2	9 0.2	8 0.3	88 1.8	48 1.8	18 0.5	51 1.8	296 10.3	205 5.3	32 0.2 (86 2)
	Pl	42 2	10 0.2	9 0.2	93 2.4	52 1.2	20 0.4	53 1.4	332 7.9	216 5.0	28 0.2 (72 3)
	S	3 0.3	6 0.2	2 0.1	52 1.8	6 0.2	2 0.0	41 1.7	0 0.0	356 10.8	64 0.4 (100 2)
Greensleeves	AS	31 2	6 0.2	6 0.3	83 1.8	32 1.8	15 0.5	101 1.8	253 10.3	170 5.3	22 0.2 (73 2)
	Pl	59 2	5 0.2	6 0.2	96 2.4	38 1.2	17 0.4	116 1.4	307 7.9	76 5.0	20 0.2 (100 3)
	S	4 0.3	3 0.2	1 0.1	41 1.8	6 0.2	0 0.0	45 1.7	0 0.0	505 10.8	77 0.4 (85 2)
Granny	AS	15 2	10 0.2	5 0.3	76 1.8	41 1.8	12 0.5	39 1.8	217 10.3	237 5.3	30 0.2 (70 2)
	Pl	49 2	8 0.2	6 0.2	59 2.4	43 1.2	12 0.4	38 1.4	258 7.9	171 5.0	27 0.2 (88 3)
	S	2 0.3	11 0.2	2 0.1	73 1.8	8 0.2	0 0.0	76 1.7	0 0.0	271 10.8	67 0.4 (100 2)
Jolyne	AS	24 2	9 0.2	9 0.3	139 1.8	56 1.8	21 0.5	71 1.8	340 10.3	245 5.3	33 0.2 (74 2)
	Pl	53 2	7 0.2	6 0.2	97 2.4	45 1.2	16 0.2	51 1.4	259 7.9	233 5.0	28 0.2 (67 3)
	S	5 0.3	5 0.2	2 0.1	50 1.8	9 0.2	0 0.0	35 1.7	0 0.0	465 10.8	67 0.4 (80 2)
New Gold	AS	18 2	10 0.2	9 0.3	114 1.8	61 1.8	12 0.5	80 1.8	349 10.3	215 5.3	31 0.2 (79 2)
	Pl	47 2	11 0.2	10 0.2	118 2.4	65 1.2	12 0.2	78 1.4	367 7.9	133 5.0	28 0.2 (100 3)
	S	3 0.3	4 0.2	1 0.1	27 1.8	2 0.2	0 0.0	29 1.7	0 0.0	421 10.8	60 0.4 (80 2)
Newton	AS	32 .2	6 0.2	5 0.3	73 1.8	28 1.8	12 0.5	65 1.8	198 10.3	292 5.3	26 0.2 (49 2)
	Pl	59 2	8 0.2	8 0.2	112 2.4	45 1.2	20 0.4	97 1.4	359 7.9	137 5.0	22 0.2 (91 3)
	S	5 0.3	4 0.2	1 0.1	39 1.8	6 0.2	0 0.0	37 1.7	0 0.0	334 10.8	59 0.4 (75 2)
Sinta	AS	21 2	11 0.2	9 0.3	140 1.8	58 1.8	26 0.5	102 1.8	352 10.3	225 5.3	29 0.2 (71 2)

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	PI	53 2	10 0.2	8 0.2	118 2.4	53 1.2	23 0.4	84 1.4	320 7.9	199 5.0	23 0.2 (63 3)
	S	5 0.3	6 0.2	1 0.1	76 1.8	5 0.2	0 0.0	53 1.7	0 0.0	521 10.8	76 0.4 (80 2)
TMR 7 A 82	AS	18 2	11 0.2	8 0.3	113 1.8	54 1.8	25 0.5	62 1.8	333 10.3	215 5.3	30 0.2 (79 2)
	PI	51 2	6 0.2	6 0.2	78 2.4	41 1.2	19 0.4	41 1.4	256 7.9	195 5.0	23 0.2 (66 3)
	S	4 0.3	6 0.2	1 0.1	60 1.8	4 0.2	0 0.0	38 1.7	0 0.0	421 10.8	67 0.4 (88 2)
3535	AS	22 2	9 0.2	11 0.3	132 1.8	69 1.8	21 0.5	89 1.8	374 10.3	222 5.3	31 0.2 (77 2)
	Pl.	54 2	8 0.2	10 0.2	120 2.4	67 1.2	21 0.4	79 1.4	380 7.9	186 5.0	25 0.2 (80 3)
	S	3 0.3	2 0.2	1 0.1	27 1.8	4 0.2	0 0.0	25 1.7	0 0.0	560 10.8	71 0.4 (72 2)

- 1 AIS, alcool insoluble solid. P. : Product. AS. : Applesauce. Pl. : Particles. S : Serum. Rha, rhamnose. Fuc,
- 2 Fucose. Ara, arabinose. Xyl, xylose. Man, mannose. Gal, galactose. Glc, glucose. Gal A, galacturonic acid.
- 3 MeOH, methanol. DM, degree of methylation. Values in italic correspond to the standard deviation of the
- 4 mean n= 24, except for the yields n = 12.

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2 **Table 3** : Fishers' F-values and *p*-values associated with two-way ANOVAs (type
3 of product and variety effects, with interactions) performed on apple flesh and applesauce
4 AIS compositions (mg/g dry matter).

Variable	Variety effect		Type of product effect		Variety x type of product effect	
	F	P	F	P	F	P
Rha	16.9	<0.0001	40.9	<0.0001	3.03	<0.0001
Fuc	13.0	<0.0001	30.9	<0.0001	4.6	<0.0001
Ara	14.5	<0.0001	8.38	<0.0001	6.5	<0.0001
Xyl	11.2	<0.0001	41.0	<0.0001	5.2	<0.0001
Man	39.7	<0.0001	1.04	0.311	5.4	<0.0001
Gal	20.1	<0.0001	45.47	<0.0001	9.4	<0.0001
Glc	11.0	<0.0001	1.35	<0.0001	3.9	<0.0001
Gal A	5.8	<0.0001	3.16	0.078	7.1	<0.0001
MeOH	12.1	<0.0001	44.4	<0.0001	7.4	<0.0001
DM	1.5	0.154	2.4	0.121	5.146	<0.0001

5 AIS, alcool insoluble solide. Rha, rhamnose. Fuc, Fucose. Ara, arabinose. Xyl, xylose. Man,
6 mannose. Gal, galactose. Glc, glucose. Gal A, galacturonic acid. MeOH, méthanol. DM, degré of
7 methylation.

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2 **Table 4** : Polyphenol composition and concentrations (mg/kg of fresh weight) and \overline{DP}_n in the peel of the twelve apple varieties.

Variety	CAT	EC	PCA	\overline{DP}_n	XPL ^a	PLZ	TotalFI ^b	CQA	pCoQA ^c	Total
Baujade	24	363	3279	3.9	17	52	616	187	5	4542
Chanteline	24	173	2879	5.3	6	47	331	90	5	3555
Freiberg	t	198	1966	3.4	91	222	799	162	9	3447
Golden Delicious	t	250	2397	4.0	17	75	300	100	6	3146
Granny Smith	t	171	3337	5.6	18	21	763	10	t	4321
Greensleeves	24	94	1021	3.7	15	47	373	81	3	1658
Jolyne	26	424	3154	4.1	24	51	704	46	12	4440
New Gold	T	244	1816	5.0	14	43	500	78	3	2698
Newton Pippin	20	165	1333	3.8	t	32	381	103	2	2037
Sinta	29	265	6080	1.4	6	33	426	20	t	7658
TMR 7 A 82	45	359	3228	3.5	32	230	901	517	7	5315
3535	55	301	3558	4.2	t	98	481	400	47	4942
Pooled SD	0.8	5.7	112.2	0.8	0.5	3.0	9.6	1.4	0.1	117.1
mean	20	251	2904	4.0	20	79	548	150	8	3980
%	1	6	73		1	2	14	4	0.2	100
SDM	17.5	97.2	1509.5	1.1	24.4	71.5	202.6	154.9	12.7	1619.4

3 CAT : (+)catechin, EC : (-)-epicatechin, PCA : procyanidins, \overline{DP}_n : average degree of polymerisation of flavanols (catechins + procyanidins), XPL : phloretin-2-
 4 xyloglucoside, PLZ : phloridzin, TotalFI : total flavonols, CQA : 5'-caffeoylquinic acid, pCoQA : para-coumaroylquinic acid, Total : total polyphenols, SD : standard
 5 deviation, n= 24, SDM : standard deviation of the mean, n = 12, t = traces. a : quantified as phloridzin, b : quantified as quercetin c : quantified as p-coumaric acid. ..

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2 **Table 5** : Polyphenol composition and concentrations (mg/kg of fresh weight) and \overline{DP}_n in the flesh of the twelve apple varieties.

Variety	CAT	EC	PCA	\overline{DP}_n	XPL ^a	PLZ	CQA	pCoQA ^b	Total
Baujade	35	162	926	2.9	8	t	336	15	1482
Chanteline	39	98	1128	3.8	2	t	169	19	1456
Freiberg	t	82	474	3.1	6	t	47	11	620
Golden Delicious	t	54	414	3.6	3	t	98	8	578
Granny Smith	42	103	902	3.5	4	5	44	1	1101
Greensleeves	t	43	244	3.2	4	9	86	2	637
Jolyne	19	76	910	3.6	8	13	86	47	1159
New Gold	t	52	355	3.1	12	16	77	27	539
Newton Pippin	23	97	501	3.6	2	16	230	6	874
Sinta	28	175	1075	2.6	3	13	64	6	1364
TMR 7 A 82	15	102	679	3.3	6	32	519	6	1358
3535	43	71	1006	3.5	3	20	430	23	1596
Pooled SD	0.6	1.8	14.0	0.05	0.2	0.5	5.1	0.4	21.4
mean	20	93	718	3.3	5	10	182	14	1043
%	2	9	69	-	0.5	1	17	1	100
SDM	17.3	40.9	308.8	0.4	3.0	9.9	162.0	13.3	426.0

3 CAT : (+)catechin, EC : (-)-epicatechin, PCA : procyanidins, \overline{DP}_n : average degree of polymerisation of flavanols (catechins + procyanidins), XPL : phloretin-2-
 4 xyloglucoside, PLZ : phloridzin, CQA : 5'-caffeoylquinic acid, pCoQA : para-coumaroylquinic acid, Total : total polyphenols, SD : standard deviation, n = 24, SDM :
 5 standard deviation of the mean, n=12, t : traces. a : quantified as phloridzin, b : quantified as *p*-coumaric acid.

1 **Table 6** : Polyphenol composition and concentrations (mg/kg of fresh weight) and \overline{DP}_n in the applesauce of the twelve apple varieties.

Variety	CAT	EC	PCA	\overline{DP}_n	XPL ^a	PLZ	POPi ^a	TotalFl ^b	CQA	pCoQA ^c	Total
Baujade	14	73	527	2.8	11	36	30	32	256	13	991
Chanteline	16	45	554	3.5	2	17	18	26	126	16	871
Freiberg	t	62	408	3.4	5	18	13	32	55	9	603
Golden Delicious	t	37	346	3.3	4	24	18	20	106	8	562
Granny Smith	31	93	814	3.2	4	5	21	18	55	t	1042
Greensleeves	t	12	72	3.2	7	16	17	14	45	t	182
Jolyne	15	50	647	3.7	9	24	27	32	85	39	930
New Gold	t	16	65	2.6	8	19	15	13	70	9	214
Newton Pippin	t	38	212	2.3	2	23	21	15	140	3	452
Sinta	15	89	595	3.1	2	20	19	20	49	3	812
TMR 7 A 82	9	59	364	3.0	8	49	18	35	384	4	929
3535	27	50	755	3.5	3	33	25	9	408	25	1334
Pooled SD	0.7	1.3	15.2	0.7	0.7	1.0	0.5	1.9	3.7	0.5	17.3
mean	11	52	446	3.1	5	24	20	22	148	11	743
%	1	7	60	-	1	3	3	3	20	1	100
SDM	11.0	25.3	246.8	0.4	3.2	11.3	5.1	9.0	129.5	11.6	346.8

- 2 CAT : (+)-catechin, EC : (-)-epicatechin, PCA : procyanidins, \overline{DP}_n : average degree of polymerisation of flavanols (catechins + procyanidins), XPL : phloretin-2-
- 3 xyloglucoside, PLZ : phloridzin, POPi : colourless phloridzin oxidation product, TotalFl : total flavonols, CQA : 5'-caffeoylquinic acid, pCoQA : para-coumaroylquinic acid, ,
- 4 Total : total polyphenols, SD: standard deviation, n = 24, SDM : standard deviation of the mean, n=12, t : traces. a : quantified as phloridzin.. b : . quantified as quercetin. c :
- 5 quantified as *p*-coumaric acid.

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2 **Table 7** : Fishers' F-values and *p*-values associated with two-way ANOVAs (type
3 of product and variety effects, with interactions) performed on apple flesh and applesauce
4 phenolic compositions (mg/kg of fresh weight).

Variable	Variety effect		Type of product effect		Variety x type of product effect	
	F	P	F	P	F	P
(+)-Catechin	154.5	<0.0001	201.3	<0.0001	15.3	<0.0001
(-)-Epicatechin	98.9	<0.0001	434.5	<0.0001	15.0	<0.0001
Procyanidin	73.2	<0.0001	203.9	<0.0001	5.4	0.0004
\overline{DP}_n	11.6	<0.0001	26.0	<0.0001	2.5	0.015
Phloretin-2-xyloglucoside	27.9	<0.0001	0.40	0.54	2.9	0.0008
Phloridzin	63.1	<0.0001	388.8	<0.0001	17.2	<0.0001
5'-caffeoylquinic acid	250.3	<0.0001	37.8	<0.0001	5.8	<0.0001
Para-coumaroylquinic acid	313.8	<0.0001	77.3	<0.0001	12.8	<0.0001
Total polyphenols	92.6	<0.0001	162.20	<0.0001	6.1	<0.0001

5 \overline{DP}_n : average degree of polymerisation of flavanols (catechins + procyanidins).

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2 **Table 8** : Polyphenol composition and concentrations (mg/kg of fresh weight) and \overline{DP}_n in the particles of the twelve apple varieties.

Variety	CAT	EC	PCA	\overline{DP}_n	XPL ^a	PLZ	POPi ^a	TotalFl ^b	CQA	pCoQA ^c	Total
Baujade	16	80	792	3.1	12	43	25	42	275	13	1298
Chanteline	18	48	660	3.5	2	19	15	28	128	17	936
Freiberg	10	65	517	3.5	5	19	11	37	49	8	721
Golden Delicious	t	35	505	3.7	4	25	16	20	96	8	709
Granny Smith	34	95	1029	3.4	4	11	19	14	55	1	1262
Greensleeves	t	11	108	3.3	3	17	17	26	46	t	228
Jolyne	9	53	772	3.9	8	25	26	20	83	38	1035
New Gold	t	16	99	2.4	8	23	13	28	72	10	270
Newton Pippin	11	47	262	2.4	1	27	20	17	152	5	541
Sinta	11	87	756	3.3	2	22	17	40	49	4	988
TMR 7 A 82	t	68	1103	3.4	61	20	30	32	698	9	2020
3535	39	69	1757	3.8	31	46	28	9	659	42	2690
Pooled SD	2.2	2.2	13.7	0.7	0.4	0.4	0.7	2.1	3.5	0.3	13.3
mean	12	56	697	3.3	12	25	21	26	197	13	1058
%	1	5	66		1	2	2	2	19	1	100
SDM	13.0	26.4	465.4	0.5	17.5	10.1	7.7	10.4	234.1	13	708.4

3 CAT : (+)-catechin, EC : (-)-epicatechin, PCA : procyanidins, \overline{DP}_n : average degree of polymerisation of flavanols (catechins + procyanidins), XPL : phloretin-2-
 4 xyloglucoside, PLZ : phloridzin, POPi : colourless phloridzin oxidation product, TotalFl : total flavonols, CQA : 5'-caffeoylquinic acid, pCoQA : para-coumaroylquinic acid,
 5 Total : total polyphenols, SD: standard deviation, n = 24, SDM : standard deviation of the mean, n=12, t : traces. a : quantified as phloridzin.. b : quantified as quercetin. c :
 6 quantified as *p*-coumaric acid.

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2 **Table 9** : Polyphenol composition and concentrations (mg/kg of fresh weight) and \overline{DP}_n in the serum of the twelve apple varieties.

Variety	CAT	EC	PCA	\overline{DP}_n	XPL ^a	PLZ	POPi ^a	TotalFl ^b	CQA	pCoQA ^c	Total
Baujade	12	58	269	2.4	10	31	31	24	237	12	684
Chanteline	14	37	303	2.8	2	15	15	21	122	16	546
Freiberg	t	50	215	2.6	5	14	11	19	51	8	372
Golden Delicious	t	27	189	2.9	3	19	16	10	92	8	364
Granny Smith	22	68	366	2.5	4	8	18	10	42	t	537
Greensleeves	t	4	45	3.0	2	12	16	5	39	t	123
Jolyne	t	43	359	3.0	7	20	24	21	79	37	590
New Gold	t	43	19	3.1	7	17	14	20	70	7	198
Newton Pippin	t	13	224	2.3	8	43	17	7	365	3	679
Sinta	12	82	354	2.6	2	18	18	10	47	3	545
TMR 7 A 82	t	23	156	2.3	t	19	20	5	127	3	343
3535	15	33	399	3.0	2	27	21	t	344	22	863
Pooled SD	0.3	1.9	4.7	0.7	0.1	0.2	0.3	1.5	0.8	0.1	4
mean	6	40	241	2.7	4	20	18	13	134	10	469
%	1	8	50		1	4	4	3	28	2	100
SDM	8.1	22.3	124.5	0.3	3.0	9.3	5.2	7.9	116.5	10.7	213

3 CAT : (+)-catechin, EC : (-)-epicatechin, PCA : procyanidins, \overline{DP}_n : average degree of polymerisation of flavanols (catechins + procyanidins), XPL : phloretin-2-
4 xyloglucoside, PLZ : phloridzin, POPi : colourless phloridzin oxidation product, TotalFl : total flavonols, CQA : 5'-caffeoylquinic acid, pCoQA : para-coumaroylquinic acid,
5 Total : total polyphenols, SD: standard deviation, n = 24, SDM : standard deviation of the mean, n=12, t : traces. a : quantified as phloridzin. b : quantified as quercetin. c :
6 quantified as *p*-coumaric acid.