Accelerated storage conditions effect on ginger- and turmeric-enriched soybean oils with comparing a synthetic antioxidant BHT

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Journal Pre-proof

1	Accelerated storage conditions effect on ginger- and turmeric-enriched soybean oils
2	with comparing a synthetic antioxidant BHT
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11	

12 Abstract

Commercial and freeze-dried powders of ginger and turmeric rhizomes were incorporated 13 in the soybean oil at the concentration of 10% (w/w) to develop a food seasoning 14 containing natural antioxidants to improve lipid stability. The phenolic composition, 15 antioxidant activity, and oxidative stability of ginger- and turmeric-enriched soybean oils 16 were evaluated during storage at 62 °C for 28 days. The phenolic characterization was 17 performed by detecting total polyphenols through Folin-Ciocalteu assay and HPLC 18 analyzing 6-gingerol and curcumin, respectively. The antioxidant activity was 19 spectrophotometrically measured through 2,2-di(4-tertoctylphenyl)-1-picrylhydrazyl 20 (DPPH) radical scavenging capacity and ferric ion reducing antioxidant power (FRAP) 21 22 assays. The peroxide value (PV) and induction period (IP) have been determined through spectrophotometric and Rancimat methods thus monitoring the primary and secondary 23 phases of lipid oxidation, respectively. The addition of freeze-dried powders derived 24 especially from turmeric rhizome contributed to enhanced antioxidant activity and 25 oxidative stability of soybean oil under accelerated storage conditions thanks to its 26 enrichment in bioactive compounds highly resistant to thermal degradation. Hence, ginger 27 28 and turmeric powders can be valorized as functional ingredients to be incorporated in vegetable oils for preventing their lipid structure against to oxidation, and simultaneously 29 providing health benefits to consumers. 30

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32 *Keywords*: Oil stability; Rancimat; Natural antioxidants; 6-Gingerol; Curcumin.

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35 1. Introduction

Soybean oil, which is widely used in the formulation and manufacture of foods, has a high content of polyunsaturated fatty acids susceptible to the oxidation reactions contributing to its reduced oxidative stability during storage and heat treatments such as cooking and frying (Banerjee et al., 2015; Yang et al., 2016; Freitas, Cattelan, Rodrigues, Luzia, & Jorge, 2017; Tinello et al., 2018). In fact, the lipid oxidation is one of the most critical factors affecting not only the shelf-life but also the quality attributes of oil as a consequence of the formation of volatile and non-volatile decomposition products (Choe & Min, 2007).

The addition of antioxidants can effectively counteract the lipid oxidation by giving their hydrogen to free radicals formed during initial stages of autoxidation or by stalling the propagation phase (Laguerre, Lecomte, & Villeneuve, 2007). However, the food application of synthetic antioxidants has been regulated in most countries to ensure safety and avoid any hazardous effects on human health (Carocho, Morales, & Ferreira, 2018).

Currently, the research is moving towards replacing synthetic additives such as BHA 48 (butylated hydroxyanisole) and BHT (butylated hydroxytoluene) with natural substances 49 50 that have more antioxidant activity and thermal stability in different edible oils and meet the increased attention of consumers to health (Taghvaei & Jafari, 2015). Agro-food 51 products, by-products, and wastes contain several bioactive compounds (Tinello & Lante, 52 2018) that can be used for developing functional products (Tinello, Mihaylova, & Lante, 53 2018). In this regard, soybean oil has been previously enriched with plant extracts derived 54 from olive leaf (Taghvaei et al., 2014), aromatic plants (Saoudi et al., 2016), rosemary 55 (Yang et al., 2016), grape seed (Freitas et al., 2017), coffee husk (Ribeiro & Jorge, 2017), 56

peanut skin (Franco et al., 2018), and goji berry (Pedro et al., 2018) to improve oxidative
stability.

The Zingiberaceae family includes ginger (Zingiber officinale) and turmeric (Curcuma 59 longa) rhizomes, which are mainly used as spices and are widely recognized for their intake 60 of phenolic antioxidants (Chen et al., 2008). Ginger rhizome is rich in gingerols and 61 shogaols belonging to the class of hydroxycinnamic or phenylpropanoic acids consisting of 62 a phenolic ring bound to a chain of three carbon atoms (Hu et al., 2011). These phenolic 63 compounds contributed to the antioxidant, anti-inflammatory, anticancer, antidiabetic, and 64 anti-obesity effects of ginger (Shukla & Singh, 2007). Turmeric rhizome mainly contains 65 curcuminoids consisting of a diarylphotanoic structure bound to two phenolic rings, also 66 67 called aryls, by a chain of seven carbon atoms (Osorio-Tobón et al., 2016). Curcumin is the major yellow curcuminoid, which brings several health benefits to humans thanks to its 68 antioxidant potential (Rauf, Imran, Orhan, & Bawazeer, 2018). 69

Several studies have demonstrated the strong antioxidant properties of ginger and turmeric 70 rhizomes and peels (Singh et al., 2010; Pawar, Pai, Nimbalkar, & Dixit, 2011; Li, Hong, 71 Han, Wang, & Xia, 2016; Tinello & Lante, 2019), but none has added them to soybean oil 72 73 for investigating their effects on its lipid stability. Hence, in the present study soybean oil has been added with different ginger and turmeric powders at the concentration of 10% 74 75 (w/w), which is generally used to prepare a homemade aromatic oil for human consumption, with the aim of valorizing a food seasoning rich in natural antioxidants to 76 prevent lipid oxidation during thermal storage. 77

78 2. Materials and methods

79 2.1 Materials and chemicals

80 Soybean oil, fresh rhizomes, as well as commercial spices of ginger and turmeric, were

81 purchased by a local supplier. All of the reagents and HPLC standards were purchased from

82 Sigma-Aldrich (St. Louis, MO, USA).

83 2.2 Preparation of ginger- and turmeric-enriched soybean oils

The fresh rhizomes were manually peeled, cut into small pieces, freeze-dried at -40 °C, and 84 grounded in a water-cooled laboratory miller (IKA Werke M20, Germany) to particles sizes 85 of 1 mm. The dry matter, which was measured after drying samples in a stove at 103 °C for 86 24h (AOAC, 2000a), was 90.8% and 96.3% for commercial and freeze-dried powders of 87 ginger while it was 90.0% and 91.2% for commercial and freeze-dried powders of turmeric, 88 respectively. The ginger- and turmeric-enriched soybean oils have been prepared by 89 90 following the traditional procedure of a homemade aromatic oil. In details, the ginger and turmeric powders were dissolved in soybean oil at 10% (w/w) concentration. The soybean 91 oils containing ginger and turmeric powders were then subjected to the mixing of 10 92 minutes through an ULTRA-TURRAX® disperser tool, which corresponded to a 93 maceration of 1 week as observed in a preliminary study. After centrifuging for 10 minutes 94 at 5,000 rpm and 4 °C, the oily supernatant was recovered. The soybean oils with 95 96 commercial and freeze-dried powders of ginger (GC and GR, respectively) and turmeric (TC and TR, respectively) were placed in amber bottles, flushed with nitrogen, and stored 97 at -18 °C until analysis. 98

99 2.3 Schaal oven test

Schaal oven test, which is aimed at evaluating the accelerated storage conditions effect on
the oxidative stability of oils, has been performed as described by Yang et al. (2016) on
soybean oils without any addition (C), with ginger (GC and GR,) and turmeric (TC and TR)

103 powders, and with butylated hydroxyl toluene (BHT) as a synthetic antioxidant at the 104 0.02% (w/w) concentration corresponding to the maximum level set by Codex Alimentarius 105 (2019). In detail, the oil samples were accurately weighed (40 g \pm 0.01 g) into amber 106 bottles without headspace and stored in an oven at a constant temperature of 62 \pm 1 °C for 107 28 days. Every 7 days the samples were taken and subjected to the following analysis.

108 *2.4 Determination of the oxidative stability of soybean oil samples*

109 The oxidative stability was evaluated by peroxide value (PV) and Rancimat test for110 monitoring the primary and secondary phases of lipid oxidation, respectively.

111 2.4.1 PV

The PV was determined using AOAC (2000b) method. The oil sample (0.5 g) was dissolved in 25 mL mixture of acetic acid-chloroform (3:2 v/v) and then 0.5 mL saturated KI solution was added. The reaction solution was shaken and kept at room temperature under dark condition for 5 min. After adding 75 mL distilled water and 1mL starch indicator, the reaction solution was titrated with 0.01 N until reaching the endpoint of colorless. The PV was calculated as follows:

118 PV (meq O/kg oil) = $(V \times N \times 1000)/m$

where V is the volume of sodium thiosulfate added to the oil sample (mL); N is thenormality of sodium thiosulfate; m is the mass of oil sample (g).

121 2.4.2 Rancimat test

122 The Rancimat test was performed in a fixed amount of oil sample (3 g) using a Rancimat 123 apparatus (Metrohm, model 743, Herisau, Switzerland) and measuring over time the water 124 conductivity at 110 °C temperature and 20 L h^{-1} air flow (Tinello et al., 2017). The 125 oxidative stability was expressed as the induction period (IP) corresponding to the time (h) at the intersection point between the horizontal (conductivity, $\mu S \min^{-1}$) and vertical (time, h) tangents of the fitted exponential oxidation curves. At this break point, the water conductivity increased over time because of the production of lipid oxidation-related compounds.

130 2.5 Analysis on the phenolic extracts of soybean oil samples

131 2.5.1 Phenolic extraction

Before detecting the antioxidant activity and the contents of bioactive compounds, the 132 phenolic extraction has been performed by following the slightly modified procedure of 133 Capannesi, Palchetti, Mascini, & Parenti (2000). An amount equal to 5 g of oil sample was 134 extracted three times with 5 mL mixture of MeOH and 10% v/v Tween 80 (80:20 v/v) by 135 using an orbital shaker for 5 min. After centrifuging for 20 minutes at 5,000 rpm and 10 °C, 136 all of the supernatants were collected and stored under refrigerated and dark conditions 137 until use. The phenolic extracts of soybean oil samples were subjected to the following 138 139 analysis.

140 2.5.2 Determination of antioxidant activity

141 The antioxidant activity was spectrophotometrically detected through 2,2-di(4-142 tertoctylphenyl)-1-picrylhydrazyl (DPPH) radical scavenging capacity and ferric ion 143 reducing antioxidant power (FRAP) assays according to Tinello & Lante (2019). The 144 antioxidant activity was expressed as Trolox equivalents per gram of oil (mg TE/g).

145 2.5.3 Measurement of the total phenolic content

146 The total phenolic content was detected through the Folin-Ciocalteu colorimetric method

147 according to Tinello & Lante (2019). The total phenolic content was expressed as gallic

acid equivalents per gram of oil (mg GAE/g).

149 2.5.4 HPLC analysis of 6-gingerol and curcumin

The 6-gingerol and curcumin contents were determined in the phenolic extracts of 150 respectively ginger- and turmeric-enriched soybean oils by HPLC using a Thermo Finnigan 151 SpectraSystem UV6000LP HPLC system (Thermo Finnigan, San Jose, CA, USA) with 152 diode-array detection and a Supelcosil LC-18 column (Sigma-Aldrich). Before their 153 injection into the column, samples were filtered through 0.22 µm Millipore cellulose 154 acetate filters (Merck Millipore, Billerica, MA, USA). Regarding 6-gingerol, the HPLC 155 operating parameters were according to the slightly modified method of Hu et al. (2011): 156 mobile phase consisting of distilled water (solvent A) and acetonitrile (solvent B) at 157 different gradient elution (0-8 min, 50% B; 8-17 min, 50-55% B; 17-32 min, 55-100% B; 158 32-38 min, 100% B; 38-40 min, 100-45% B; 40-50 min, 45% B; 50-60 min, 45-50% B); 159 0.2 mL/min flow rate; 10 µL injection volume; 30 °C column temperature; 60 min 160 chromatographic run time. Regarding curcumin, the HPLC operating parameters were 161 according to the slightly modified method of Osorio-Tobón et al. (2016): mobile phase 162 consisting of acetonitrile/0.1% v/v acetic acid (solvent A) and distilled water/0.1% acetic 163 acid (solvent B) at different gradient elution (0-6 min, 45-35% B; 6-21 min, 35-10% B; 164 21-27 min, 10% B; 27-30 min, 10-25% B; 30-39 min, 25% B; 39-51 min, 25-45% B; 165 51-70 min, 45% B); 1.2 mL/min flow rate; 10 µL injection volume; 55 °C column 166 temperature; 70 min chromatographic run time. The 6-gingerol and curcumin contents were 167 expressed as milligrams per gram of oil (mg/g). 168

169 2.6 Statistical analysis

170 All of the data obtained from three replicates were analyzed by one-way analysis of 171 variance (ANOVA), after verifying the normal distribution and homogeneity of variance, 172 using the PROC GLM of SAS[®] 9.3 software package. Differences among means with $P \le$ 173 0.05 were accepted as representing statistically significant differences according to the 174 Bonferroni test.

175 **3. Results and discussion**

176 *3.1 Phenolic characterization*

The phenolic content of soybean oil, which was zero as confirmed also by Lee, Lee, & 177 Choe (2007), increased after adding ginger and turmeric powders. The concentration of 178 total polyphenols detected by Folin-Ciocalteu assay statistically differed ($P \le 0.05$) among 179 soybean oil samples at each thermal storage day depending on the powder type and 180 following this order: TR > GR > TC > GC (Fig. 1). At day 0, their corresponding amounts 181 (4,133, 1,398, 1,272, and 1,211 mg GAE/kg oil, respectively) were higher than those found 182 by Saoudi et al. (2016) in soybean oils macerated in the darkness for 7 days with 6% (w/w) 183 dried leaves of thyme and rosemary (926 and 37 mg GAE/kg oil, respectively) and 184 subjected to a similar phenolic extraction. A lower total phenolic content was also achieved 185 by Yang et al. (2016) in soybean oil stirred for 10 min at room temperature with 4% (w/w) 186 commercial rosemary extract containing 70% (w/v) carnosic acid (approximately 400 187 mg/kg oil). After 28 days of storage at 62 °C, the total phenolic content of TR (3,947 mg 188 GAE/kg oil) was 3 times higher than that of GR (1,297 mg GAE/kg oil) and 4 times higher 189 than that of TC (1,102 mg GAE/kg oil) and GC (1,002 mg GAE/kg oil). Generally, 190 phenolic antioxidants undergo degradation during high-temperature storage of oils and fats 191 thus forming several oxidation products (Shahidi & Ambigaipalan, 2015). However, they 192 have more thermal stability than synthetic additives in edible oils during heat processing 193 194 (Taghvaei & Jafari, 2015). In fact, Fig. 1 showed that the phenolic reduction was very slow

with increasing storage days and was approximately 3 times lower in soybean oils containing freeze-dried rhizomes (GR = -7% and TR = -4%) compared with those containing commercial powders (GC = -17% and TC = -13%).

The phenolic antioxidants containing in ginger and turmeric such as respectively 6-gingerol 198 and curcumin are hydrophobic compounds highly soluble in oil (Eshghi et al., 2014; 199 200 Banerjee et al., 2015; Zou et al., 2015; Xu et al., 2016; Si, Chen, Zhang, Chen, & Chung, 2018). Comparing 6-gingerol and curcumin contents of oil samples at day 0 (GC = 361201 mg/kg oil, GR = 763 mg/kg oil, TC = 1669 mg/kg oil, and TR = 5694 mg/kg oil; Fig. 2) 202 with those of the corresponding powders analyzed in our previous study (Tinello & Lante, 203 2019), their oil solubility for ginger and turmeric commercial powders (60% and 65%, 204 205 respectively) was lower than that for freeze-dried ones (100% and 90%, respectively). In 206 this regard, several studies confirmed that the bioaccessibility and bioavailability of phytonutrients were affected by the food matrix, processing, and preservation techniques 207 (Ribas-Agustí, Martín-Belloso, Soliva-Fortuny, & Elez-Martínez 2018; Thakur et al., 208 2020). Moreover, the 6-ginger and curcumin contents of soybean oils added with 209 respectively ginger (Fig. 2A) and turmeric (Fig. 2B) powders were almost unchanged 210 211 during thermal storage. Only a slight decrease in curcumin content up to 4% was observed in TC oil (Fig. 2B). 212

213 *3.2 Evaluation of antioxidant activity*

The antioxidant of soybean oil, which was zero as confirmed by DPPH and FRAP data, increased after adding ginger and turmeric powders. The DPPH (Fig. 3A) and FRAP (Fig. 3B) assays gave essentially the same antioxidant curves and results by using different oxidants that captured an electron from the antioxidant causing specific color and

218	absorbance changes (Huang et al. 2005). The averaged values of Trolox equivalents
219	corresponding to the percentage of the DPPH remaining and the Fe(III) ion reducing
220	capability significantly differed (P \leq 0.05) among soybean oils at each thermal storage day
221	depending on powder type as follows: $TR > GR > TC > GC$ (Fig. 3A and Fig. 3B,
222	respectively). At 0 day, the DPPH and FRAP values of TR (2,847 and 4,008 mg TE/kg oil)
223	were 2 times higher than that of GR (1,505 and 1,984 mg TE/kg oil), 4 times higher than
224	that of GC (846 and 1,124 mg TE/kg oil), and 9 times higher than that of TC (384 and 582
225	mg TE/kg oil). After 28 days of storage at 62 °C, the DPPH and FRAP values of TR (2,024
226	and 2,960 mg TE/kg oil) were 2 times higher than that of GR (990 and 1,390 mg TE/kg
227	oil), 4 times higher than that of GC (540 and 760 mg TE/kg oil), and 9 times higher than
228	that of TC (220 and 370 mg TE/kg oil). The antioxidant activity of all ginger- and turmeric-
229	enriched soybean oils decreased over storage time as confirmed by DPPH and FRAP assays
230	(Fig. 3A and Fig. 3B, respectively). However, the antioxidant reduction after 28 storage
231	days was lower in soybean oils containing freeze-dried rhizomes (DPPH: $GR = -34\%$ and
232	TR = - 29%; FRAP: GR = - 30% and TR = - 26%) compared with commercial powders
233	(DPPH: GC = -36% and TC = -43% ; FRAP: GC = -32% and TC = -36%). This could be
234	related to the highest yields of total polyphenols (Fig. 1) as well as curcumin (Fig. 2A) and
235	6-gingerol (Fig. 2B) in soybean oils enriched with freeze-dried rhizomes. In fact, the
236	correlation between the antioxidant activity and the phenolic composition of agro-food
237	products and wastes has been widely demonstrated (Tinello et al., 2018; Tinello & Lante,
238	2019). Several authors confirmed also the strong antioxidant properties of 6-gingerol
239	(Pawar et al., 2011; Gan et al., 2016; Li et al., 2016) and curcumin (Ak & Gulcin, 2008).

3.3 Evaluation of oxidative stability

241 Hydroperoxides are the primary products of lipid oxidation without undesirable flavor, whereas their decomposed products are mostly responsible for rancid off-flavor (Choe & 242 Min, 2007). The peroxide value (PV) and induction period (IP) have been selected as 243 reference oxidative parameters for respectively the primary and secondary phases of lipid 244 oxidation with the aim of evaluating the oxidative stability of soybean oil samples 245 246 with/without antioxidants during storage at 62 °C for 28 days. The increasing trend in PV of soybean oil samples was slow at the first 14 days while a sharp increment was observed 247 until the end of thermal storage (Fig. 4A). The PV increasing trend was previously 248 observed in soybean oil samples heated at 55 °C for 20 days (Taghvaei et al., 2014), 60 °C 249 for 20 days (Ribeiro & Jorge, 2017), 62 °C for 24 days (Yang et al., 2016), 180 °C for 20 h 250 251 (Freitas et., 2017), and 180-190 °C for 24 h (Banerjee, Ghosh, & Ghosh, 2015). The PV 252 significantly differed ($P \le 0.05$) among soybean oils at each storage day. After 21 storage days at 62 °C, the PV of oil samples with turmeric powders (TC = 42.6 meq O_2/kg oil and 253 TR = 36.1 meq O_2/kg oil) was lower than that of control oil (C= 46.4 meq O_2/kg oil) and oil 254 samples with synthetic antioxidant (BHT = $36.2 \text{ meq } O_2/\text{kg oil}$) and ginger powders (GC = 255 61.0 meq O_2/kg oil oil and GR = 52.7 meq O_2/kg oil). The PV of ginger- and turmeric-256 257 enriched soybean oils was lower than that of soybean oil added with 200 mg/kg of coffee husk extract (74.1 meq O₂/kg oil) and a mixture of 100 mg/kg of coffee husk extract and 258 100 mg/kg of BHA and (87.5 meq O_2 /kg oil) but higher than that of soybean containing a 259 mixture of 100 mg/kg of coffee husk extract and 100 mg/kg of TBHQ (3.51 meq O₂/kg oil) 260 after 20 heating days at 60 °C (Ribeiro & Jorge, 2017). Their PV data was approximately 2 261 times lower than that of soybean oil containing 1,000 mg/kg of peanut skin extracts (92.4 262 263 meq O₂/kg oil) after 16 storage days at 60 °C (Franco et al., 2018). Moreover, the PV

264 inhibition of TR and BHT (22% compared to C sample) was greater than that found by Taghvaei et al. (2014) in soybean oils added with protein hydrolysates isolate from Crucian 265 carp (Carassius carassius) fish (2.5, 14.2 and 17.6% for 200, 500 and 1,000 mg/kg oil, 266 respectively) and from cow's intestine (5.9 and 13.6% for 200 and 500 mg/kg oil, 267 respectively) after 20 days storage at 55 °C. After 28 storage days at 62 °C, the C sample 268 achieved the highest PV of 70.9 meq O₂/kg oil, which was similar to that found by 269 Taghvaei et al. (2014) after 20 days of storage in an oven at 55 °C with forced air 270 circulation. Instead, the PV results of TR (61.3 meq O₂/kg) and BHT (57.1 meq O₂/kg oil) 271 samples were significantly lower than those of TC, GC, and GR samples (71.7, 95.0, and 272 90.4 meq O₂/kg, respectively). The IP increment of TR (+ 76%) and BHT (+ 80%) samples 273 274 after 28 storage days was lower than that of C oil (+ 85%) and other enriched soybean oils 275 (+ 90%). Moreover, TR, as well as BHT, had the highest PV inhibition rate (19% and 14% compared to C sample, respectively). In this regard, Banerjee et al. (2015) showed that the 276 marination of potato chips with turmeric powder before frying was useful to lower PV of 277 soybean oil at 180–190 °C for 24 h (8 h daily for 3 consecutive days). 278

Contrariwise, the IP value detected by the Rancimat test in soybean oil samples linearly 279 280 decreased with increasing storage days at 62 °C (Fig. 4B). This IP decreasing trend was previously found in soybean oil samples heated at 60 °C for 20 days (Ribeiro & Jorge, 281 2017) and 180 °C for 24 h (Saoudi et al., 2016). The IP value significantly differed (P \leq 282 0.05) among soybean oils at each storage day depending on the sample type. At 0 day, the 283 IP value of soybean oil containing freeze-dried powders (TR = 10.7 h and GR = 9.1 h) was 284 higher than that of control oil (C = 5.8 h) and oil samples with synthetic antioxidant (BHT 285 = 6.1 h) and commercial spice (TC = 6.7 h and GC = 6.9 h). The IP values of TR and GR 286

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287 samples were higher than those showed by Freitas et al. (2017) in soybean oils containing 100 mg/kg of grape seed extract (7.5 h) and 50 mg/kg of both BHT and extract (7.2 h). 288 Moreover, their IP values were much lower than those of soybean oils added to coffe husk 289 extract alone and with BHA (approximately 6 hours) but similar when compared to that of 290 soybean oil containing a mixture of coffe husk extract and TBHQ (approximately 10 hours) 291 292 (Ribeiro & Jorge, 2017). The IP increments after adding antioxidants to soybean oil were as follows: TR (+4.9 h) > GR (+3.3 h) > GC (+1.1 h) > TC (+0.9 h) > BHT (+0.3 h). The 293 IP increments of TR and GR samples were much greater than those observed by Taghvaei 294 et al. (2014) in soybean oils containing 1,000 mg/kg protein hydrolysates isolate from 295 cow's intestine or 1,823 mg/kg olive leaf extract encapsulated by arabic gum (+ 2.2 h and + 296 297 0.4 h, respectively). Moreover, they were greater than that found by Yang et al. (2016) in soybean oil added with 400 mg/kg of rosemary extract (+ 3.4 h) and by Freitas et al. (2017) 298 in soybean oil containing grape seed extract alone and with BHT (+ 0.7 h and + 0.4 h, 299 respectively). After 28 storage days, TR sample had an IP value (5.5 h) approximately 2 300 times higher than that of control oil (C = 3.5 h) and soybean oils with synthetic antioxidant 301 (BHT = 3.9 h), commercial spices (TC = 3.2 h and GC = 2.5 h), and ginger freeze-dried 302 303 powder (GR = 3.0 h). The IP reduction of TR (- 49%) after 28 storage days was lower than that of soybean oils with turmeric commercial spice (TC = -52%) and ginger powders (GC 304 = - 64% and GR = - 67%). Moreover, its IP reduction was lower than that achieved in 305 soybean added to coffee husk extract alone and with BHA (approximately - 70%) after 20 306 storage days at 60 °C (Ribeiro & Jorge, 2017). Hence, TR achieved the best PV and IP 307 results because its enrichment with turmeric freeze-dried powder was effective in 308

309 significantly decreasing lipid oxidation and enhancing stability during thermal storage (Fig.310 4).

Several authors associated the oxidative stability of plant extracts-enriched soybean oils 311 with their phenolic composition and antioxidant activity (Taghvaei et al., 2014; Saoudi et 312 al., 2016; Yang et al., 2016; Franco et al., 2018; Pedro et al., 2018). Thus, the best oxidative 313 stability of TR sample could be due not only to its higher phenolic yields (Fig. 1) and 314 antioxidant performance in DPPH and FRAP assays (Fig. 3A and Fig. 3B, respectively) but 315 also to the stability of curcumin during storage under accelerated oxidation conditions (Fig. 316 2B). In this regard, the thermal resistance of curcuminoids has been demonstrated by 317 Prathapan, Lukhman, Arumughan, Sundaresan, & Raghu (2009) evaluating the effect of 318 319 heat treatment at different temperatures (60–100 °C) for di erent durations (10–60 min) in 320 fresh turmeric rhizome. Park et al. (2019), studying the effects of extraction temperature (60-90 °C) and time (15-180 min) on curcuminoids of aqueous turmeric extracts, showed 321 that the contents of curcumin, demethoxycurcumin, and bisdemethoxycurcumin increased 322 until achieving the maximum extraction at 90 °C for 60 min but decreased under prolonged 323 324 heating. Nevertheless, Eshghi et al. (2014) confirmed that turmeric-derived curcumin was 325 significantly effective in decreasing the oxidation rate of soybean oil at 55 °C based on peroxide, acid, and iodine values. 326

327 4. Conclusions

The oxidative stability of soybean oil under accelerated storage conditions was significantly improved after adding freeze-dried powders derived especially from turmeric rhizome. The greatest antioxidant properties of GR and TR oils have been attributed to their strong enrichment in phenolic antioxidants such as respectively 6-gingerol and curcumin, which 332 showed high solubility in oil and resistance to thermal degradation. Hence, the freeze-dried 333 powders of ginger and turmeric rhizomes can be proposed not only as eco-friendly 334 alternatives to synthetic additives for preventing the lipid oxidation in oil- and fat-335 containing products but also as functional food ingredients.

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Fig. 1. The total phenolic content of soybean oil samples enriched with ginger commercial powder (GC), ginger freeze-dried rhizome powder (GR), turmeric commercial powder (TC), and turmeric freeze-dried rhizome powder (TR) during 28 days storage at 62 °C.

Fig. 2. The 6-gingerol (A) and curcumin (B) contents of soybean oil samples enriched with respectively ginger commercial powder (GC), ginger freeze-dried rhizome powder (GR), turmeric commercial powder (TC), and turmeric freeze-dried rhizome powder (TR) during 28 days storage at $62 \,^{\circ}$ C.

Fig. 3. The antioxidant activity performed by DPPH (A) and FRAP (B) assays in soybean oil samples containing ginger commercial powder (GC), ginger freeze-dried rhizome powder (GR), turmeric commercial powder (TC), and turmeric freeze-dried rhizome powder (TR) during 28 days storage at 62 °C.

Fig. 4. The PV (A) and IP (B) values of soybean oil samples without any additives (C) and with 0.02% w/w butylated hydroxyl toluene (BHT), ginger commercial powder (GC), ginger freezedried rhizome powder (GR), turmeric commercial powder (TC), and turmeric freeze-dried rhizome powder (TR) during 28 days storage at 62 °C.

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- The oxidative stability of soybean oil was improved after adding antioxidants.
- GR and TR oils showed the best antioxidant properties during thermal storage.
- 6-gingerol and curcumin were found as heat-resistant phenolic compounds.
- Ginger and tumeric freeze-dried powders can replace synthetic antioxidants in oils.

Journal Prevention



UNIVERSITÀ DEGLI STUDI DI PADOVA

Legnaro, 28th February 2020

Dear Editor

We are submitting our manuscript entitled "Evaluation of the phenolic composition, antioxidant activity and oxidative stability in ginger- and turmeric-enriched soybean oils under accelerated storage conditions" by Federica Tinello and Anna Lante, for consideration by your referees.

THE AUTHORS DECLARE NO CONFLICT OF INTEREST, FINANCIAL OR OTHERWISE.

We hope that you will consider the paper of interest for the Journal *LWT*.

We look forward to hear from you.

Sincerely yours,

Anna Lante (on behalf of my co-author)

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