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Research Article

GINGER POWDER PROTECTS SOYBEAN OIL FROM OXIDATIVE DEGRADATIONS AND ESPECIALLY VITAMIN E DURING INTERMITTENT FRYING OF PLANTAIN CHIPS

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A B S T R A C T

This study aimed at evaluating the potential of ginger powder to improve the oxidative stability of soybean oil during intermittent frying of plantain chips. Plantain slices were fried in soybean oil with and without 15 g/l of ginger powder.The oils sampled during 5 days of intermittent frying were analyzed for total polar compounds, conjugated dienes, malondialdehyde, vitamin E and fatty acid composition. The results showed that the presence of ginger limited the oxidative deteriorations. Based on comparison of the results of the two types of frying, the formation of total polar compounds, conjugated dienes, malondialdehyde, were reduced respectively by 26.9%, 12.5% and 2.6%while up to 42.4% of vitamin E, and 39 % polyunsaturated fatty acids were preserved. So, the use of ginger powder during intermittent frying of plantain chips could be an alternative way to protect nutritional quality of soybean oils.

INTRODUCTION

Frying is widely used in the world for the cooking of a large number of raw foods such as meat, fish and tubers including for exampleplantains and potatoes. In Cameroon, plantain chips fried at small scale at home and sold directly on the market place is a great source of revenues for households. However, the chips are generally preparedwithout any control of the process or of the quality of the oils. Frying induces chemical modifications of the oils generating various products of oxidation among them cytotoxic and genotoxic compounds (Esterbauer, 1993; Dobarganes *et al.,* 2000). Researches on frying processes have thus been the subject of many investigations to improve the nutritional, chemical and sensory qualities of fried products (Kupongsak and Phimkaew, 2013; Taha *et al.,* 2014). The conditions to limit of the potential toxicological risks associated with the consumption of fried products have been also addressed (Boskou *et al.,*2006). In Cameroon, plantain chips are usually fried in palm olein but other oils can also be used. For example, the unsaturated soybean oil is sometimes used because the flavor of the plantain chips is appreciated by the consumers. In a previous study, we found that oxidation develops significantly when plantain chips were prepared with soybean oil, contrary to chips prepared with palm olein (Kansci *et al.,* 2016).That is why alternative and sustainable solutions, acceptable for consumers and easy to apply by producers for protecting the soybean oil during the frying process should be explored.

To slow down the oxidative degradation of oils during frying, several approaches have been investigated, including the control of process parameters and the use of protecting ingredients (Dobarganes *et al.,*2010; Warner and Gehring, 2009). Among them, the use of plant extracts and spices rich in antioxidants is increasingly recommended (Jorge and Andreo, 2013).To avoid the use of chemicals, natural extracts or powders of plants, could be an alternative to limit oil oxidation during frying as accordingly observed by Taha *et al.* (2014) with powder of thyme, rosemary and sage in rapeseed oil. Ginger (*Zingiber officinale Roscoe*) is among the most important sources of natural antioxidants (Dimitrios, 2006). Ginger extract scavenged up to 90.1% of 2, 2-diphenyl-1-picril hydrazyl (DPPH) radicals which made it more efficientthanbuty lated hydroxytoluene (BHT)(Stoilova *et al.,*2007). In frying conditions, ethanolic extract of ginger was able to slow down the thermoxidation of soybean oil (Jorge and Andreo, 2013). This protecting activity was mainly attributed to the very high antioxidant activity of 6-gingerol and of its derivatives. Notice that the degradation products of 6-gingerol are more stable than 6-gingerol at high temperature (Ok and Jeong, 2012; Chen *et al.,* 1986). However, to our knowledge, ginger powder has not yet been tested to protect oils during intermittent frying of plantain chips despite the easiness of its usage by producers.

This study aims at evaluating the effect of the direct addition of ginger powder during intermittent frying of plantain chips on the oxidative stability of soybean oil. Oxidative deterioration of the frying soybean oil was appreciated by quantitative measurements of tocopherols (vitamin E), total polar compounds, conjugated dienes, malondialdehyde and fatty acid composition.

MATERIALS AND METHODS

Preparation of ginger powder

Ginger rhizomes (*Zingiber officinale roscoe*) were bought in Yaoundé market Mfoundi. They were cleaned, peeled, ground with electric grinder (Masterchef 5000) and then dried in a convection oven (Memmert 100-800) at 50°C during 72 hours. Dried ginger powder was sieved, packaged in polyethylene bags, sealed under vacuum and stored at room temperature until use.

Experimental frying design

Frying was carried out using a deep-fryer (Profry Oléoclean, 2300 watts, Seb, France) according to the method described by Lemaire *et al.*(1996) and Cheand Tan (1999). 4 liters of soybean oil (Oleor) were first preheated to 60°C.Then 15 g of ginger powder per liter of oil was added. The mixture was stirred for 10 minutes to facilitate impregnation of ginger powder and dissolution of active molecules into the oil. Finally, the temperature was raised to 180°C and 200 g per batch of plantain slices poured into the hot oil. Each batch was fried for 3 min with 60 min intervals. The frying was conducted 4 hours per day for 5 days. After each frying day, the oil bath was cooled at room temperature. Aliquots (300 ml) of the oil were collected before frying (0 h) and at the end of each day of frying (4 h, 8 h, 12 h, 16 h and 20 h). At the beginning of each frying day, the oil was added to complete the oil level at 4L. Two experimental groups were carried out: frying process in the presence of ginger powder (FG) and in its absence (Control: FC). The oil samples were kept in opaque bottles and stored at 4°C.

Oil analyses

Quantification of total polar compounds

The total polar compounds contents were measured using the cooking oil tester Testo 270 (Mönchaltorf, Swizerland). The sensor is sensitive to the oil dielectric constant which increases proportionally with the amount of total polar compounds formed during frying. The electrode of the device was directly plunged into the hot oil bath at 0 h, 4 h, 8 h, 12 h, 16 h and 20 h until direct reading of the percentage (wt%) of total polar compounds in the oil. Each measurement was carried out ten times and means calculated.According to Chen *et al.* (2013) who observed that Testo 270 overestimates the content of total polar compounds in soybean oil by 10.5%, on each value obtained, 10.5% was subtracted.

Determination of conjugated dienes

The absorbance of a solution of the oil in hexane (5 µg/ml) was read at 233 nm. Conjugated dienes were expressed in nmol/g of oil using the molar extinction coefficient of conjugated dienes hydroperoxides (27000 L. M^{-1} cm^{-1}) (White, 1995). Each measurement was carried out twice and means calculated.

Quantification of malondialdehyde

Malondialdehyde formation in soybean oils was determined according to the method described by Kenmogne-Domguia *et al.* 2012. Malondialdehyde quantification was performed with an external calibration curve and the result was expressed in nmol/g. Each measurement was carried out twice and means calculated.

Quantification of Vitamin E

The tocopherols and tocotrienols were separated and detected without prior saponification step or extraction by high performance liquid chromatography with a system equipped with a fluorescence detector as described in (Kabri *et al.,* 2013). They were quantified using external calibration curves prepared with standards. The sum of tocopherols and tocotrienols, known as vitamin E, was expressed in µg/g of oil. Each measurement was carried out in duplicate and means calculated.

Determination of fatty acid composition of the oils

The fatty acid composition of the oil was determined using gas chromatography according to the method described by Kabri *et al.* 2013. To achieve this, the fatty chains were first derivatized in the form of volatile methyl esters by direct transesterification of the oil in the presence of trifluoroborohydrure/methanol according to the method described by Morrison and Smith (1964). A known amount of heptadecanoic acid was added as internal standard prior the reaction. A volume of 1 µl of methyl esters solubilized in n-hexane was injected using a syringe in the gas chromatograph (Clarus, Perkin Elmer) equipped with a polar capillary column (DB 225, length 30 m x internal diameter 0.25 µm, film thickness 0.25µm), and a flame ionization detector.The flow of the carrier gas (hydrogen) wat set at 2 ml/min. The chromatographic profiles were processed for integration of each peak and the fatty acids were identified by comparing their retention times with those of standards. The amounts of fatty acids were expressed in mg/g of oil.

Statistical analysis

The results are presented as mean ± standard deviation. The data were analyzed using IBM SPSS 20.0 (Statistical Package for Social Science) software for Windows by applying the independent-samples t-test. Means data were considered as significantly differentfor $p < 0.05$.

RESULTS

Effect of ginger powder on oxidative degradation of soybean oil

Total polar compounds formation was reduced by ginger powder

The evolution of amounts of polar compounds in the presence and absence of ginger is presented in Fig. 1. Before frying, soybean oil contained 1.5 ± 0.0% total polar compounds. During intermittent frying without ginger, this amount increased gradually from 4.3 ± 0.3% after 4 h to 13.5 ± 0.0 % after 20 hours of frying. In the presence of ginger, total polar compound concentration was significantly lower ($p<0.05$): 1.7 ± 0.2% after 4 hours and 10.3 ± 0.0% after 20 hours. Thus, in the presence of ginger the formation of total polar compounds was decreased by about 92.9 % and 26.9% after 4 h and 20 h of intermittent frying, respectively.

Table 1 Effect of ginger powder on fatty acid contentof soybean oil during intermittent frying of plantain chips

Fatty Acids (FA) (mg/g oil)	FC0h	FC 4h	FC8h	FC 12h	FC 16h	FC 20h	FG 4 h	FG 8h	FG 12h	FG 16h	FG 20h
Σ saturated FA	141.8	149.8	147.6	146.8	145.5	145.4	147.4	146.2	151.3	144.1	149.2
Σmonounsaturated FA	215.7	216.8	212.2	209.0	207.5	205.8	221.3	220.8	223.3	214.8	220.7
18 :2n-6	475.5	477.2	467.2	450.2	441.8	430.5	480.0	471.5	468.8	446.5	449.8
18 :3n-3	61.1	61.0	59.2	55.9	54.1	51.8	61.7	59.2	57.6	54.4	53.7
Σpolyunsaturated FA	536.6	538.2	526.4	506.1	495.9	482.2	541.7	530.7	526.5	501.0	503.4
Total fatty acids	894.1	904.8	886.2	861.9	848.8	833.5	910.4	897.8	901.1	859.9	873.3

FC: Frying Control, FG: Frying with ginger

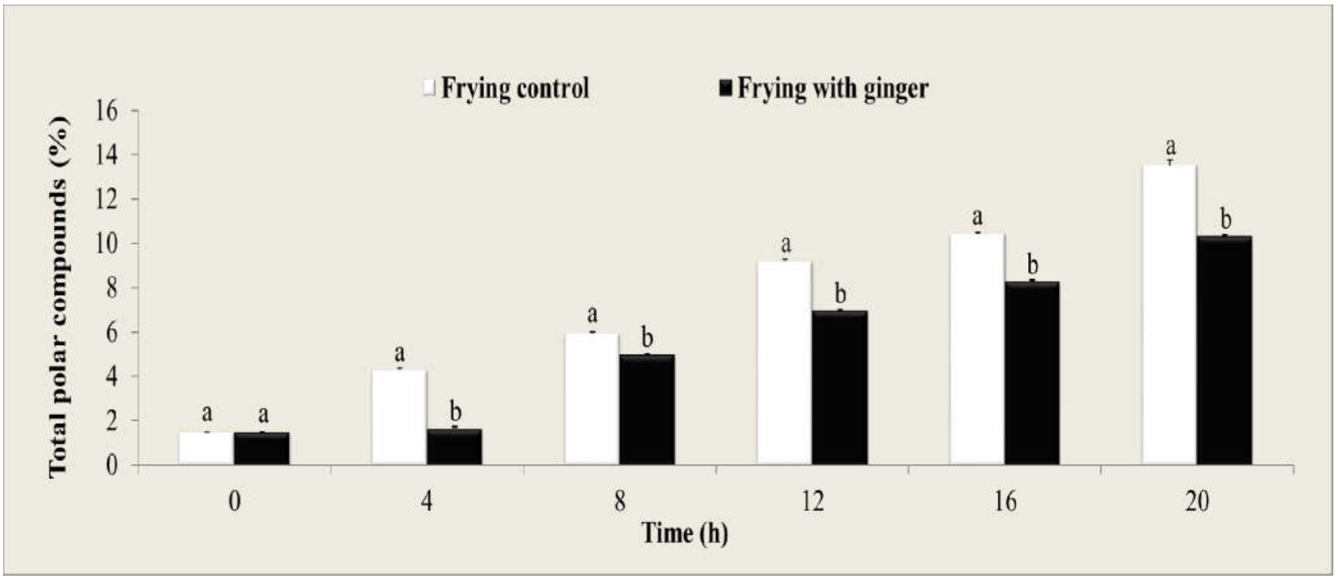

Figure 1 Effect of ginger powder on the amounts of total polar compounds in soybean oil during intermittent frying of banana/plantain. At each frying time, means with different letters are significantly different (p< 0. 05; n=10). Error bars represent standard error.

The content of these compounds in both systems after 20h of intermittent frying remained however very far from the 25% threshold recommended in some countries to discard frying oils (Dobarganes and Márquez-Ruiz, 1998).

Conjugated dienes formation was decreased by ginger powder

Fig. 2 shows the evolution of conjugated dienes in soybean oils collected during intermittent frying of plantain in the absence and presence of ginger.

The concentration of conjugated dienes of soybean oil before frying was 0.7 x 10^3 ± 0.1nmol/g. Without ginger (frying control), the concentration of conjugated dienes reached 1.7 x 10^3 ± 0.1nmol/g after 4h, and 4.7 x 10^3 ± 0.1nmol/g after 20h. In the presence of ginger, it reached 0.9 x 10^3 ± 0.02 nmol/g after 4 hours of frying and 4.2 x 10^3 ± 0.2 nmol/gafter 20h. The conjugated dienes concentration at 4h was significantly lower than that measured in the control, their formation being reduced by 80 %.

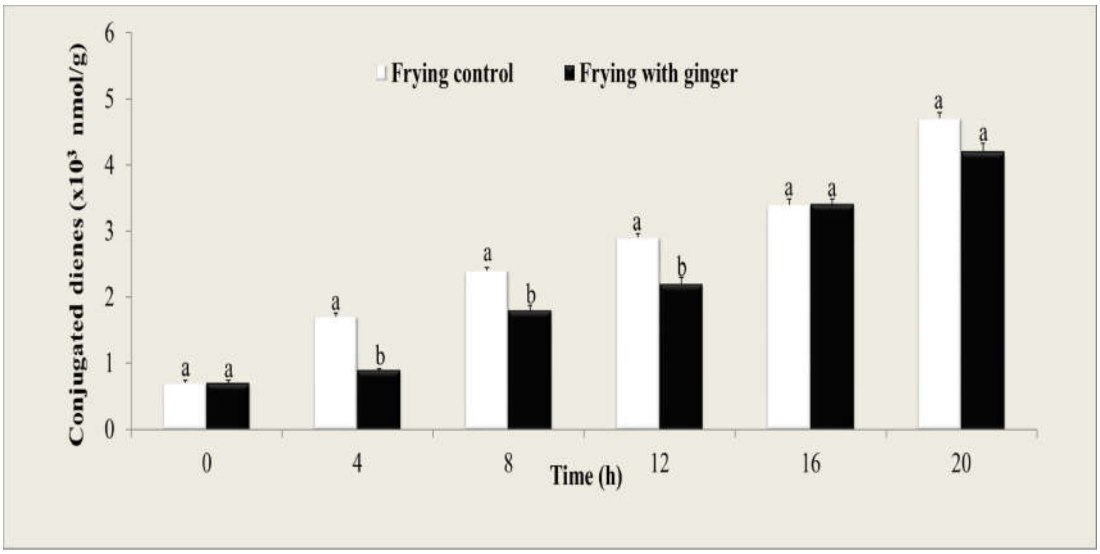

Figure 2 Effect of ginger powder on the amounts of conjugated dienes in soybean oil during intermittent frying of banana/plantain. At each frying time, means with different letters are significantly different (p< 0.05; n=2). Error bars represent standard error

The differences between control and ginger samples remained significant until 12h of frying. After 20h of intermittent frying the formation of conjugated dienes remained reduced by 12.5% as compared to control.

Ginger powder limited malondialdehyde formation the first hours of frying

Malondialdehyde concentration in fresh soybean oil was 3.3 ± 0.6 nmol/g (Fig. 3). After 4h of intermittent frying in absence of ginger, this concentration increased to 7.7 ± 0.4 nmol/g and reached 10.8±1.4 nmol/g after 20h of intermittent frying. In the presence of ginger, this concentration was significantly lower than in the control, 2.2 ± 1 nmol/g at 4h and reached 10.6 ± 0.6 nmol/g after 20h.

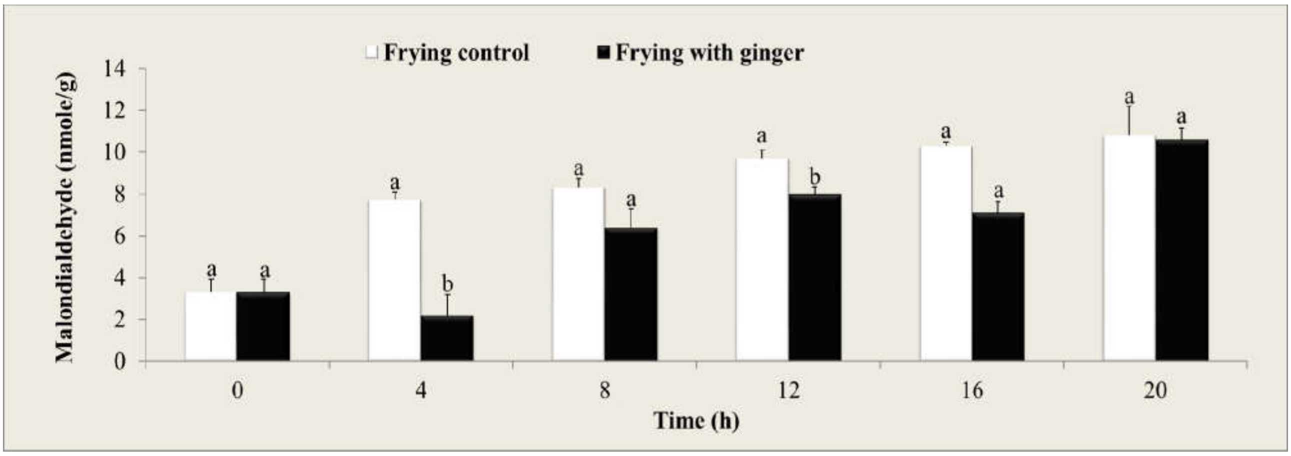

Figure 3 Effect of ginger powder on the amount of malondialdehydein soybean oil during intermittent frying of banana/plantain. At each frying time, means with different letters are significantly different ($p < 0.05$; n=2). Error bars represent standard error.

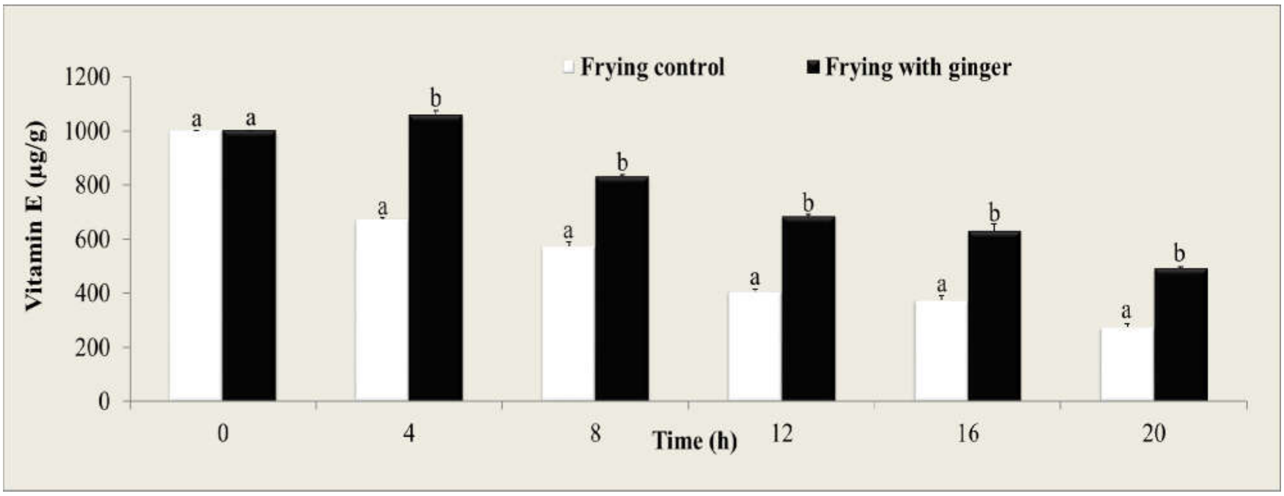

Figure 4 Effect of ginger powder on the amount of vitamin E in soybean oil during intermittent frying of banana/plantain. At each frying time, means with different letters are significantly different ($p < 0.05$; n=2). Error bars represent standard error.

Hence, ginger reduced by around 75% malondialdehyde formation after 4h of intermittent frying of plantain chips.

Protective effect of ginger on nutritional compounds of soybean oil

Fatty acids profiles

The fresh soybean oil contained around 142 mg/g of saturated fatty acids, 216 mg/g of monounsaturated fatty acids and 537mg/g of polyunsaturated fatty acids: namely the essential fatty acids linoleic acid (476 mg/g) and linolenic acid (61 mg/g) (Table 1). The amounts of saturated fatty acids remained stable during frying whatever the conditions (in presence or in absence of ginger powder). By contrast, the amounts of polyunsaturated fatty acids remained stable during the first four hours of frying but decreased slightly thereafter. During frying without ginger, the values ranged from 538 mg/gafter 4 h to 482 mg/g at the twentieth hour of intermittent frying. In presence of ginger, amounts of polyunsaturated fatty acids ranged from 542 mg/g (4h) to 503 mg/g (20h). Similar tendencies were found for linoleic and linolenic acids. These results evidence that ginger powder protects the unsaturated fatty acids during frying. However, the losses of polyunsaturated fatty acids remained low even after 4 days of intermittent frying (20h).

Vitamin E content

The effect of ginger powder on tocopherol amounts is showed in Fig. 4. The initial content of vitamin E was 1002.9 ± 0.2 µg/g before frying. After 4 h of intermittent frying in absence of ginger, vitamin E content plunged to 674.3 ± 6.0 µg/g. Then, it decreased gradually to attain 276.6 ± 12.9 µg/g after 20 h of frying. During frying with ginger, vitamin E content was significantly higher than in control; it decreased however to 492.8 ± 6.0 µg/g after 20 h. Thus, the level of protection of vitamin E during intermittent frying in the presence of ginger was 82.5% at 4 hours and 42.4% at 20 h.

DISCUSSION

In this work, the effect of the addition of ginger powder in the frying bath on the losses of several nutritional compounds, namely polyunsaturated fatty acids and vitamin E, and on the formation of oxidation products during intermittent frying of plantain chips in soybean oil have been studied.

The results show important losses of tocopherols during intermittent frying control and little degradation of polyunsaturated fatty acids. The oil degradation was also characterized by the formation of conjugated dienes, malondialdehyde and polar compounds showing that oxidation of the oil took place during frying. The formed compounds could be responsible of the rejection of oils (Choe and Min, 2007) and chips and the decrease of their nutritional quality. In the presence of the ginger powder vitamin E was partly preserved while polyunsaturated fatty acids losses and formation of degradation markers were significantly limited. We presume that these limited losses in essential fatty acids can hardly affect the nutritional qualities of the oil and the chips which have been prepared with, and the consumer's essential fatty acids dietary intakes. As complementary markers of oxidative degradations were measured, the possible mechanism involved in recorded protective effects can be discussed.

Ginger powder contains phenolic compounds with OH group on their aromatic ring. We can thus postulate that their antioxidant mechanism is similar to the mechanism of phenolic acids. By dissociation of O-H bond these moleculesgive a hydrogen tothe reactive oxygen compounds formed during oxidation (Choe and Min, 2009), breaking the oxidation chain reactions. Our results show that the active compounds are released at sufficient concentrations in the oil when the powder is directly added in the frying bath, to be active against the oxidative degradations at frying temperature. According to Réblová *et al.* (2012), phenolic acids (ferulic, gallic, protocatechic and sinapic; 600 mg/kg) were able toincrease two to four times the half-life of α-tocopherol in the soybean oil during heating. Also, ginger exhibited higher antioxidative activity than α-tocopherol (Brewer, 2011) and is probably able to regenerate α-tocopherol from the tocopheroxyl radical (Réblová *et al.*, 2012). During intermittent frying, phenolic compounds of ginger acted probably as synergist in the presence of tocopherol leading to 42.4% of vitamin E maintained at the end of frying with ginger.

Considering oxidation products, the use of ginger during frying was characterized by less production of primary and secondary oxidation compounds. The antioxidant efficacy of ginger (Zingiber officinale Roscoe) ethanol extract has been previously demonstrated by Jorge and Andreo (2013) in soybean oil subjected to thermal oxidation. Also, during frying of potatoes in refined palm olein, Jaswir *et al.* (2005) observed the preservation of unsaturated fatty acids by rosemary and sage. Submitted to frying temperature, oxidative and hydrolytic degradations of oil are promoted giving rise to number of degradation products among them total polar compounds are considered as a good marker of the evolution of the quality of the oil. The decrease of the amounts of conjugated dienes and the malondialdehyde are in the line of the decrease of amounts of total polar compounds in presence of ginger powder as compared to controls. Regarding conjugated dienes formation, the decrease of 12.5% in the presence of ginger powder shows that ginger acts against the oxidation of polyunsaturated fatty acids. Ramalho and Jorge (2008) also observed a decrease of the amounts conjugated dienes during thermooxidation of soybean oil in the presence of ethanol rosemary extract. The decrease of malondialdehyde formation in the presence of ginger the first hours of frying could be explained by the protection of linolenic and linoleic acids from oxidation. Linolenic acid is the main precursors of malondialdehyde in vegetable oils (Viau *et al.,* 2016). Basuny *et al.* (2013) previously obtained a reduction in malondialdehyde levels in sunflower oil in the presence of eggplant polyphenols during the intermittent frying of potatoes for 6 consecutive days. The phenolic compounds of ginger may act both as a regenerator of tocopherols and as a scavenger of free radicals of the fatty acids of the oil. The ability of ginger to limit the formation of malondialdehyde is reduced with time, partly because of the high temperature and the addition of new oil at the beginning of each frying day. Finally, the oxidative protection is not only attributed to phenolic compounds of ginger; vitamin E naturally present in the oil is also involved which explains that the amounts of vitamin E were severely reduced in the control.

CONCLUSION

During intermittent frying of plantain chips with soybean oils, the use of ginger powder presents a double interest. It preserves the oil against oxidative degradations and protects vitamin E from degradation probably to regenerating effects of active compounds transferred from the powder to the oil. We presume that the limited losses of polyunsaturated fatty acids can hardly affect the nutritional quality of the oil and the chips prepared with, and the consumer's essential fatty acids dietary intakes. Besides, being easily available for small-size producers, ginger powder confers the chips interesting and appreciated sensorial properties. It can therefore be considered as an effective alternative to reduce oxidative degradation of oil during intermittent frying.

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