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PII: S0023-6438(20)30217-6

DOI: https://doi.org/10.1016/j.lwt.2020.109229

Reference: YFSTL 109229

To appear in: *LWT - Food Science and Technology*

Received Date: 22 July 2019

Revised Date: 1 March 2020

Accepted Date: 3 March 2020

Please cite this article as: Jiménez, D., Lobo, M., Irigaray, B., Grompone, Marí.Antonia., Sammán, N., Oxidative stability of baby dehydrated purees formulated with different oils and germinated grain flours of quinoa and amaranth, *LWT - Food Science and Technology* (2020), doi: https://doi.org/10.1016/j.lwt.2020.109229.

Author Contributions Section

Dolores Jiménez: Conceptualization, Investigation, Formal analysis, Writing-Original Draft; **Manuel Lobo:** Resources, Validation, Writing-Review & Editing; **Bruno Irigaray:** Resources, Validation, Writing-Original Draft; **María Antonia Grompone:** Resources, Supervision, Visualization; **Norma Samman:** Resources, Writing-Review & Editing, Supervision. Responsible for ensuring that the descriptions are accurate and agreed by all authors.

Oxidative stability of baby dehydrated purees formulated with different oils and germinated grain flours of quinoa and amaranth

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Abstract

Fat oxidative stability (OS) is an important food parameter because it causes sensory deterioration and rejection. The aim of this work was to evaluate the OS of the lipid fraction of baby dehydrated purees. Purees (6) were formulated with Andean potato, pumpkin, non-germinated and germinated quinoa and amaranth flours, and different oils: soybean-sunflower (SSO), canola (CO) and sunflower-chia (SChO). Purees were dehydrated by forced air circulation oven. The fat from the purees and the grain flours was extracted by Soxhlet method. Lipid profile, tocopherol contents and OS were analyzed in oils and lipid fractions. Changes of free fatty acids (FFA) during germination were studied. Tertiary-butyl hydroquinone (TBHQ) was determined in the oils used in formulations. During germination, FFA increased in both grains; tocopherols decreased in quinoa and increased in amaranth. Purees with germinated grain flours had lower OS than those made with non-germinated grain flours. SSO had the best OS due to the high content of TBHQ. However, purees made with SSO had OS like those formulated with CO. Purees with SChO had the lowest OS due to its great ω3

content and low antioxidant contents. Germinated grain flours and CO were the best ingredients to formulate baby purees.

Key words

Andean grains; Germination; Fat; Tocopherols; Fat oxidative stability

1. Introduction

The consumption of polyunsaturated fatty acids (PUFA) is essential in human nutrition, particularly during pregnancy and for infants (FAO/WHO, 2010). Fats have structural and regulatory functions, so their deficiency can cause metabolic alterations. Fats are involved in the transport of fat-soluble vitamins and their absorption; they stimulate the release of gastrointestinal hormones, etc. (Haque et al., 2016; Shen et al., 2018).

The linoleic (ω6) and linolenic acids (ω3) must be provided by the diet. Vegetable oils such as olive, flaxseed, soybeans, sunflower are rich in ω6. The main sources of ω3 are marine animals, such as tuna or salmon, and in less proportion some vegetable oils such as peanut, linseed, soybean, canola and chia (Bañares et al., 2019). Currently, ω3 consumption is deficient; so, the food industry is incorporating ω3 into formulated food (Simopoulos, 2016; Haque et al., 2016; Shen et al., 2018). Moreover, fats and oils can have a positive effect on the organoleptic and texture properties of food formulations; but they can also have a negative effect when oxidized, particularly PUFAs (Osuna et al., 2018).

Tocopherols and tocotrienols are synthesized exclusively by photosynthetic organisms. They are necessary to prevent fat oxidation, improving shelf-life of foods. Besides, they have hypocholesterolemic, anticancer and neuroprotective properties (Santos et al., 2012; Lushchak & Semchuk, 2012; Osuna et al., 2018).

The intake of gluten-free cereals such as rice, corn, sorghum, millet, buckwheat and Andean grains is being increasingly promoted, especially in infant feeding to avoid food

allergies such as celiac disease. Quinoa and amaranth are particularly characterized by their excellent protein and lipid profile, and they contain bioactive compounds such as polyphenols, tocopherols, squalene, carotenoids, among others (Valcárcel-Yamani et al., 2012; Tang et al., 2016).

Germination causes enzymatic hydrolysis of reserve molecules; thereby improving the nutrient availability (Hager, Mäkinen, & Arent, 2014; Aphalo, Martinez, & Añon, 2015). During germination, a decrease in the antinutrients, an increase in some antioxidant compounds (Jan, Saxena, & Singh, 2016) and changes in the fatty acid profile were observed, with an increase in PUFA (Gamel et al., 2007; Jan, Saxena, & Singh, 2018). Besides, changes in the tocopherol contents in different grains and legumes were observed (Tang et al., 2016; Suryanti, Maliyana, & Putri, 2016). It is important to consider these changes if germinated grains are to be used to formulate foods, because the kind of fatty acids and the lipophilic antioxidant contents influence the fat oxidative stability of the products (Pardauil et al., 2011).

Fat oxidation causes food rejection in consumers, because it causes unpleasant odors that worsen progressively. Resistance to oxidation of an oil or fat is known as oxidative stability. The oxidation is an exothermal reaction; so, enthalpic changes of this reaction can be measured by differential scanning calorimetry (DSC) to determine the oxidative stability of foods. This method is precise and requires a small amount of sample. The rate of fat oxidation depends on the fatty acids profile, their exposure to air, light and temperature, and their natural or synthetic antioxidants contents (Pardauil et al., 2011; Guimarães-Inácio et al., 2017; Osuna et al., 2018).

Antioxidants are used to increase the oxidation induction period or to decrease the rate of oxidation. In addition to the natural antioxidants, synthetic antioxidants are used in

food industry to prevent fat oxidation. Some synthetic antioxidants decompose thermally; while the natural antioxidants are heat resistant (Santos et al., 2012).

It is important to ensure that sensory attributes of foods are maintained throughout the shelf life; so, the analysis of the oxidative stability of a formulated food is a factor to be considered during the process (Pardauil et al., 2011).

The aim of this work was to study the changes on the fat oxidative stability of both quinoa and amaranth germinated grain flours and their influence on the oxidative stability of baby purees elaborated with those grain flours and different types of oils.

2. Materials and methods

2.1. Quinoa and amaranth

Quinoa (*Chenopodium quinoa*, Cica variety) and amaranth (*Amaranthus*, Mantegazzianus variety) were obtained from "Centro de Investigación y Desarrollo Tecnológico para la Agricultura Familiar" (CIPAF, Hornillos - Jujuy, Argentina). The grains were washed and the saponin of quinoa was removed by successive washes with tap water.

2.2. Quinoa and amaranth germination

The washed grains were soaked both in boiled and cooled tap water (1:5 w/v) for 6 h at room temperature, and then were germinated in controlled conditions (22-24ºC, 80-90% RH), in darkness; quinoa for 24 h and amaranth for 48 h, according to the speed of emergence of each radicle (Hager et al., 2014; Aphalo et al., 2015).

2.3. Grain flours

The grains (non-germinated and germinated) were dried in a forced air circulation oven with electric heating (Memmert Radiant Warmer Model A52200-35_Vac 230, Germany) at 45ºC, until constant weight, and then milled in a centrifugal mill

(CHINCAN model FW 100, China). The flours were vacuum-packed in polyethylene bags and stored at room temperature for further analysis and preparation of purees.

2.4. Potato and pumpkin

The Andean potato (*Collareja* variety) was obtained from CIPAF; regional producers provided the pumpkin. They were both washed, cooked in boiling water (20 min), peeled and processed with a commercial food processor to prepare the purees.

2.5. Other ingredients

Sugar, xanthan gum, citric acid, ascorbic acid, soybean-sunflower refined oil (19:1) (SSO), canola cold-pressed oil (CO), sunflower refined oil and chia cold-pressed oil, were obtained from local stores.

Sunflower-chia oil (SChO) was obtained by mixing the commercial oils in volumetric ratio 2:1.

2.6. Dehydrated purees formulation

The formulated purees (PA1, PA2, PB1, PB2, PC1 and PC2) were elaborated according to Table 1.

The raw materials were mixed and cooked for 20 min. The oil was added and mixed. Purees were dehydrated in an air forced circulation oven (45ºC), as well as milled and vacuum-packed in polyethylene bags, and stored at room temperature.

2.7. Lipid contents

Lipids were extracted from non-germinated and germinated grain flours, and dehydrated purees by the Soxhlet method with petroleum ether 35-60°C (AOAC 963.15, 2018). Extracted oil was stored in sealed vials at -18°C under nitrogen atmosphere for further analysis.

2.8. Fatty acids profile

Fatty acid methyl esters (FAMEs) were prepared according to IUPAC 2.301 (1987). Samples (50 mg) were mixed with 1.5 mL of methanolic solution of potassium hydroxide (0.5 N) in a dry bath (100ºC, 10 min) and then cooled. Boron fluoride methanolic solution (14%, 2 mL) was added and heated in a dry bath (5 min). Then, petroleum ether (35-60ºC) was added and the samples were centrifuged (6000 rpm, 5 min). The fatty acids were quantified in a GC-2014 gas chromatograph (Shimadzu, Japan) equipped with SP-2560 GC column (100 m x 0.25 mm). A mixture of FAME (Supelco FAME Mix C4-C24 18919) was employed as standard.

2.9. Contents of antioxidants in lipid extracts and oils

Tocopherols were determined from the lipid extracts of the formulated purees and from the raw materials used for the formulations. Tert-butylhydroquinone content (TBHQ) was determined from the oils used in the formulations.

Isopropanol (1 mL) was added to the oil sample (30 mL). Tocopherols and TBHQ were analyzed in the extracts (3 μL) according to Tang et al. (2016) using a high-performance liquid chromatography system (Shimadzu model 20, Japan) with a Phenomenex silica column C18 (250×4.6 mm, 5.0 μm) (Macherey-Nagel) with a fluorescence detector (λexcitation=290 nm and λemission=330 nm). The mobile phase was acetonitrile, methanol, water with phosphoric acid and isopropanol (flow rate was kept constant at 1.0 mL/min). The isomers of tocopherol (alpha, beta and gamma, and delta tocopherols) and TBHQ were identified using standards (Sigma Aldrich).

2.10. Separation and identification of lipid fractions

Fats of the quinoa and amaranth oils (non-germinated and germinated) were separated according to Fuchs et al. (2011) on thin layer chromatography (TLC) plates coated with silica gel (TLC PET-foils, 17 μm) using hexane-diethyl ether-acetic acid (90:9:1, v/v/v) as mobile phase. The spots on the TLC plate were visualized with iodine vapors. A

mixture 1:1 of high oleic sunflower oil and oleic acid (J.T. Baker Chemical Co., Philipsburg, N.J.) was used as reference sample.

2.11. Oxidative stability of fat extracts and oils

The inherent oxidation was calculated multiplying the percentage contents of oleic (ω9), linoleic (ω6) and linolenic (ω3) acids by their respective relative oxidation rate (1, 12 and 25, respectively)(Woo, Kim, & Lee, 2019).

The oxidative stability of fat extracts was determined by the non-isothermal differential scanning calorimetry method (Shimadzu DSC-60, Japan) according to Cabral et al. (2018). Oil samples (15±0.5 mg) were weighed in open aluminum pans. The scanning was between 40-250ºC, and programmed for three different ramps (5, 10 and 15ºC/min); and purified oxygen (99%) passed through the sample enclosure at 50 mL/min. The induction point (T0) of the oxidative reaction corresponded closely to the intersection of the extrapolated baseline and the tangent line of the flow curve versus the temperature obtained. With these three temperatures obtained with each ramp, a plot Log(ramp) versus 1/T (K) was done. The coefficients "a" and "b" (Y = aX + b) were determined according to the line obtained. The kinetic constants of the Arrhenius equation (Ea, A and k) were calculated with the following equations: Ea= -2.19Ra; $A=\frac{R}{Ea}10^{(b+2.31)}$; k (383K)=A$2.72^{-Ea/(RT)}$.Where "Ea" is the activation energy (kJ/mol), "R" is the universal gas constant $8.31x10^{-3}$ kJ($mol^{-1}K^{-1}$), "A" is the pre-exponential factor or frequency factor (min^{-1}) and "k" is the rate coefficient (min^{-1}).

2.12. Statistical analysis

Results were expressed as mean. One-way analysis of variance (ANOVA) with $p<0.05$. Comparison of means was performed using Tukey's multiple comparison test. Statistical analyses were performed with XL-Stat 2017 software (Addinsoft™, Paris, France).

3. Results and discussions

3.1. Lipid contents

Lipid content did not change significantly with the germination of quinoa and amaranth grains (Table 2), so the lipid content of formulated purees did not show significant differences (Table 3). These results agreed with the ones informed by Omary et al. (2012). Nevertheless, other researches informed a reduction of the lipid content with germination, possibly either because fats were used as an energy source or due to an increase in the lipolytic activity which resulted in the conversion of fat into fatty acids and glycerol (Gamel et al., 2007; Devi, Kushwaha, & Kuwar, 2015; Jan et al., 2016). On the other hand, contrasting effects have been reported with an increase in lipid contents in some seeds and legumes; according to Khalil et al. (2007). The increases in nutrients would be apparent possibly due to the loss of dry matter, mainly in the form of carbohydrates, caused by respiration during germination.

Therefore, the changes originated during germination depend on the type of crops, genotype, conditions and time of germination.

3.2. Fatty acids profile

Table 2 shows the fatty acids profile of quinoa and amaranth grain oils, and oils used in the formulation of purees; and, Table 3 shows the fatty acids profile of the elaborated purees.

Fatty acids profile for non-germinated quinoa and amaranth agreed with those informed by Tang et al. (2016). The decrease in saturated fatty acids (SFA) of both grains, caused by the reduction of palmitic and behenic acids, was possibly due to the lipolytic activity and the decomposition of triglycerides and polar lipids into simpler compounds during germination. These results agreed with those reported by Gamel et al. (2007), Kim et al. (2012) and Jan et al. (2018) for amaranth, rice and *Chenopodium* during germination, respectively.

The increase in monounsaturated fatty acids (MUFA) and PUFA was possibly an apparent increase due to the reduction in SFA. These results agreed with those informed by Gamel et al. (2007) for the germination of amaranth grains. Ozturk et al. (2012) also observed these changes for the germination of wheat. Mainly, during the first days of germination, palmitic acid synthesis occurred in developing seeds and to the end of germination, the synthesis of PUFA from free fatty acids would be intensified (Zhukov, 2015). The changes of fatty acids profile depend on the time and conditions of germination (Tang et al., 2014; Zhukov, 2015).

The contents of raw materials (grain flours and oils) used in the puree formulation had influence in the fatty acids profile of the products. SChO had the highest PUFA content, mainly ω3; this could have a negative effect on the oxidative stability of this oil and of the purees formulated with this oil due to their high degree of unsaturation (Osuna et al., 2018; Shen et al., 2018). On the other hand, the ω6/ω3 ratios of all samples were less than 10. Therefore, they complied with Simopoulos' (2016) recommendation. This ω6/ω3 ratio favors the cardiovascular health and prevents the formation of Eicosanoids from the Araquidonic acid, preventing inflammatory processes.

Germinated grain flours with CO or SChO would be the best options for the formulation of purees, because PUFA/SFA ratio increased with germination, and the CO and SChO had the recommended ω6/ω3 ratio. However, it is important to evaluate the impact of the high content of PUFA, mainly ω3, on the oxidative stability of the purees elaborated with these oils.

3.3. Separation and identification of lipid fractions

Figure 1 shows the separation of the lipid fractions of quinoa and amaranth flours by TLC before and after germination.

Triglycerides showed the highest percentage among lipid fractions of non-germinated and germinated grain oils. Similar results were shown by Qian et al. (2009) and Kamal et al. (2012), who found that principal non-polar lipid fraction in the oils from barley bran and barley is triacylglycerol.

An increase in free fatty acids, phospholipids, diacylglycerols and sterols was observed during germination of quinoa and amaranth grains. These changes in lipids fractions might be due to the breakdown of triglycerides and polar lipids components into simpler compounds, such as free fatty acids because of the action of lipases (Jan et al., 2018). An increase in the amount of free lipids was also found by Kamal et al. (2012) and Hung, Maeda & Morita (2015) during germination of barley and wheat, respectively. These results could suggest that glycerol and free fatty acids were rapidly released by hydrolytic degradation during germination (Hung, Maeda & Morita, 2015).

The amount of free fatty acids can be considered a quality index for oils and foods, because several studies had shown that free fatty acids autoxidize faster than their respective methyl esters. Therefore, the increase in free fatty acids during germination could negatively influence the fat oxidative stability during processing and storage of foods elaborated with germinated grains (Paradiso et al., 2010).

3.4. Contents of antioxidants in lipid extracts and oils

Table 4 shows tocopherol contents of raw materials and purees, and TBHQ contents of used oils in the formulations.

Quinoa and amaranth grains had different behaviors on the tocopherols with germination. The total tocopherols decreased significantly during quinoa germination, with a decrease in β-γ-, despite the increase in α-tocopherol. On the other hand, the total tocopherols increased with the germination of amaranth due to the significant increase in α- and β-γ-tocopherols, despite the decrease in δ-tocopherol. The results obtained

were like those informed by Tang et al. (2016) about α-, β-γ- and δ-tocopherols of different cultivars of quinoa and amaranth. The changes of the tocopherol contents were possibly due to the activation of metabolic pathways during germination. The tocopherols are synthesized from the precursors which derived from these metabolic pathways: cytosolic shikimate and plastid methylerythritol phosphate pathways. Besides, the biosynthesis and the increase or decrease in tocopherols depend on the stress conditions. Lushchak & Semchuk (2012) explained that in dicots (like soybean, quinoa and amaranth) the α-tocopherol levels initially increased during germination and then they decreased. Ozturk et al. (2012) and Suryanti et al. (2016) observed an increase in α-tocopherol during the germination of wheat and *Leucaena leucocephala*, respectively. Kim et al. (2012) informed that α-, β-γ- and δ-tocopherols increased distinctively in different parts of rice during germination. Therefore, the variation of the tocopherol levels depends on the crops, the conditions and time of germination.

The tocopherols of the oils were significantly different and therefore the tocopherol contents in purees elaborated with them were also different. Purees elaborated with germinated grain flours had higher total tocopherols, with higher α-tocopherol and less β-γ-tocopherol contents with respect to those made with non-germinated grain flours. The increase in total tocopherols in purees elaborated with germinated grain flours should improve the oxidative stability of their lipids. Antioxidants, like tocopherols, can interrupt fat oxidation by interfering either the chain propagation or the decomposition process during storage, reducing the rancidity (Lushchak & Semchuk, 2012; Osuna et al., 2018).

On the other hand, all oils had TBHQ. CO and SChO had contents below the limit allowed by the Argentine Food Code on the addition of artificial antioxidants to oils (CAA, 2019), which is currently 200 ppm. SSO had a TBHQ content higher than 200

ppm, because when this study was carried out the allowed TBHQ values were 100-1000 ppm (CAA, 2016). TBHQ could protect the oils and the purees made with oils containing TBHQ from fat oxidation (Santos et al., 2012; Osuna et al., 2018).

3.5. Oxidative stability

Table 5 shows the kinetic constants of the Arrhenius equation and the inherent oxidation of the lipids. The oxidative stability of the lipids was analyzed considering the activation energy (Ea) and oxidation rate (k) obtained by DSC with non-isothermal method. Micić et al. (2015) explained that values of Ea and k should be considered to conclude which oil is more prone to oxidation. The Ea is the energy that the oil must reach (at a certain temperature) to start the oxidation reaction (Guimarães-Inácio et al., 2017), being the first step of the thermal decomposition of edible oils and it is the most important parameter to determine the oxidative stability, because the decomposition of unsaturated fatty acids begins in this step. On the other hand, k is the speed at which the chain reactions are carried out once oxidative deterioration has begun.

Germinated quinoa began its oxidative deterioration at a lower Ea and had higher k than native quinoa, probably due to the increase in PUFA and free fatty acids, and the decrease in tocopherols during germination. In contrast, the amaranth improved its oxidative stability after germination because its Ea is higher and its k lower than non-germinated amaranth, probably due to the increase in tocopherols, although an increase in PUFA and fatty acids was also observed.

The values of Ea and k for the oils used in the formulations were within the range reported by Bañares et al. (2019). SChO had the lowest value of Ea because chia oil is a PUFA-rich oil susceptible to degrade when heated in oxidizing atmospheres (Guimarães-Inácio et al., 2017). On the other hand, SSO showed the highest Ea with respect to CO and SChO, because SSO had higher content of SFA than the other used

oils (Bañares et al., 2019). In addition, SSO had the lowest k due to its higher content of total tocopherols and TBHQ, compared to the other oils. However, the purees made with SSO had oxidation rates like those formulated with CO, although CO had a higher k with respect to SSO. This behavior possibly happened because SSO lost TBHQ in the thermal treatment during the cooking and sterilization of purees, and therefore it remained more susceptible to oxidative deterioration (Santos et al., 2012). On the other hand, the SChO and purees made with this oil were the most unstable to oxidation (with the lowest Ea and the highest k) due to its high PUFA content, mainly ω3, and its lower amount of tocopherol and TBHQ than the other oils. These results agreed with Ghosh et al. (2018) who explained that oxidative stability decreases when the PUFA/SFA ratio increases.

Purees formulated with germinated grain flours had higher oxidative stability (higher Ea and lower k) than purees formulated with non-germinated grain flours. This behavior was observed in the purees with the different oils and it may be because germination increased tocopherol contents that protect fats from oxidation (Osuna et al., 2018). However, inherent oxidation expressed an oxidation stability was significantly different to that determined by oxidation rate coefficients (k) by DSC test. The germinated grain flours and the purees made with them had greater inherent oxidation with respect to the non-germinated grain flours and the purees elaborated with them, because PUFA/SFA ratio increased after germination (Ghosh et al., 2018), and the inherent oxidation equation does not consider the tocopherol and TBHQ contents of the samples. Therefore, the inherent oxidation equation should not be used to estimate the oxidative deterioration rate for the type of samples studied, because they have antioxidant compounds that influence the oxidative stability of the products.

4. Conclusions

Germination of quinoa and amaranth caused changes in the fatty acids profile of their flours. In both grains, a decrease in saturated fatty acids was observed and a relative increase in monounsaturated and polyunsaturated fatty acids was verified. Also, free fatty acids content increased due to lipolysis during germination. On the other hand, the total tocopherol content decreased after germination in quinoa. In contrast, an increase was determined in amaranth.

Baby purees with adequate ratios of PUFA/SFA, content of essential fatty acids and tocopherols, and stable to fat oxidation were formulated with different oils, and non-germinated and germinated Andean grain flours. Despite the relative increase in unsaturated and free fatty acids during germination, the fat oxidative stability increased in purees made with germinated grain flours; possibly, due to the increased content of tocopherol after germination. In addition, the oxidative stability of the purees has been influenced by the oil used in its formulation. Purees made with sunflower-chia oil had the highest oxidation rate due to the highest content of linolenic fatty acid (ω3) and the lowest content of antioxidants (tocopherols and TBHQ) with respect to soybean-sunflower and canola oils. However, the purees with canola oil had a better ratio of essential fatty acids.

Therefore, the puree formulated with flours of germinated grains and canola oil would have the best performance due to its proper ω6/ω3 ratio, good content of tocopherols and fat oxidative stability.

Acknowledgment

The authors would like to thank the National Council of Scientific and Technical Research (CONICET) and Secretariat of Science and Technology and Regional Studies (SECTER) of the National University of Jujuy (Argentina) by grant Ia ValSe-Food-CYTED (Ref. 119RT0567).

Declarations of interest: none.

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*The key references were selected from the research groups with many publications with high impact journals. These papers were used to understand and compare the results obtained on the study of fatty acids profile, free fatty acids, lipophilic antioxidants content (tocopherols and TBHQ) and fat oxidative stability (inherent and determinate by DCS) of the formulated purees and raw materials used for the formulations.

Figure captions

Figure 1: Lipid fractions

S: standard high oleic sunflower oil:oleic acid (1:1); Q: quinoa oil; GQ: germinated quinoa oil; A: amaranth oil; GA: germinated amaranth oil; 1: Triglycerides; 2: Free fatty acids; 3 and 4: Diacylglycerols and Sterols; 5: Phospholipids.

Table captions

Table 1. Formulations of the purees

Table 2: Total lipid content and fatty acids profile of the grains and oils

Table 3: Total lipid content and fatty acids profile of the purees

Table 4: Tocopherol and TBHQ contents of the grain flours, oils and dehydrated purees

Table 5: Fat oxidative stability of oils and lipid extracted of the grain flours purees

Table 1. Formulations of the purees

Raw material	PA1	PA2	PB1	PB2	PC1	PC2
Andean potato without skin (g)	40.00	40.00	40.00	40.00	40.00	40.00
Pumpkin without skin (g)	13.00	13.00	13.00	13.00	13.00	13.00
Quinoa flour (g)	7.00	-	7.00	-	7.00	-
Germinated quinoa flour (g)	-	7.00	-	7.00	-	7.000
Amaranth flour (g)	4.00	-	4.00	-	4.00	-
Germinated amaranth flour (g)	-	4.00	-	4.00	-	4.00
Sugar (g)	0.50	0.50	0.50	0.50	0.50	0.50
Xanthan gum (g)	0.10	0.10	0.10	0.10	0.10	0.10
Citric acid (g)	0.03	0.03	0.03	0.03	0.03	0.03
Ascorbic acid (g)	0.07	0.07	0.07	0.07	0.07	0.07
SSO (mL)	0.5	0.5	-	-	-	-

CO (mL)	-	-	0.5	0.5	-	-
SCHO (mL)	-	-	-	-	0.5	0.5
Distilled water (mL)	35.00	35.00	35.00	35.00	35.00	35.00

PA1, PB1, PC1: purees with non-germinated grain flours; PA2, PB2, PC2: purees with germinated grain flours; PA1, PA2: purees with soybean-sunflower oil; PB1, PB2: purees with canola oil; PC1, PC2: purees with sunflower-chia oil; SSO: soybean-sunflower oil; CO: canola oil; SChO: sunflower-chia oil.

Table 2. Total lipid content and fatty acids profile of the grains and oils

Sample	Q	GQ	A	GA	SSO	CO	SChO
Total fat content (g/100 g db)	7.48^{b}	6.52^{b}	7.00^{b}	6.66^{b}	100^{a}	100^{a}	100^{a}
Fatty acids (g methyl esters/100 g fat)							
Myristic (14:0)	0.12^{b}	0.12^{b}	0.22^{a}	0.23^{a}	0.05^{c}	-	-
Palmitic (16:0)	8.84^{c}	7.08^{d}	21.04^{a}	19.30^{b}	8.18^{cd}	3.99^{f}	5.93^{e}
Palmitoleic (16:1)	0.08^{b}	0.19^{a}	0.11^{b}	0.21^{a}	-	0.14^{ab}	-
Stearic (18:0)	0.44^{d}	0.46^{d}	3.32^{bc}	3.47^{b}	4.11^{a}	1.95^{c}	3.11^{bc}
Oleic (18:1 cis, ω9)	20.88^{f}	23.37^{e}	25.56^{d}	26.54^{d}	34.64^{b}	67.12^{a}	30.63^{c}
Linoleic (18:2 cis, ω6)	50.55^{a}	52.32^{a}	42.81^{ab}	45.84^{ab}	46.57^{ab}	14.75^{c}	37.47^{b}
Arachidonic (20:0)	0.42^{d}	0.46^{d}	1.01^{b}	1.15^{ab}	-	0.70^{c}	0.28^{e}
Gamma Linolenic (18:3, ω6)	0.05^{c}	0.05^{c}	0.22^{a}	0.23^{a}	0.22^{a}	0.03^{d}	0.07^{b}
Eicosenoic (20:1)	1.83^{a}	1.82^{a}	0.23^{c}	0.24^{c}	0.20^{c}	1.26^{b}	-
Linolenic (18:3, ω3)	9.65^{c}	11.49^{b}	0.63^{g}	1.14^{f}	2.69^{e}	6.49^{d}	20.23^{a}
Eicosadienoic (20:2 cis)	0.43^{a}	0.48^{a}	-	-	-	0.05^{b}	-

Behenic (22:0)	0.77[a]	0.46[c]	-	-	-	0.40[c]	0.64[b]
9-Docosenoic/Erucic acid (22:1 cis)	1.86[b]	2.24[a]	-	0.14[c]	-	-	-
Eicosenoic/Eicosatrienoic (20:3 cis)	0.21[a]	0.20[a]	-	-	-	-	-
Docosadienoic (22:2 cis)	0.24[b]	0.46[a]	-	0.13[c]	-	-	-
Tetracosanoic (24:0) y EPA (20:5)	0.40[b]	0.52[a]	0.26[c]	0.42[b]	-	-	-
Tetracosaenoic (24:1)	0.27[a]	0.25[a]	0.10[b]	0.10[b]	-	-	-
SFA	**10.58**[bc]	**8.59**[cd]	**25.69**[a]	**24.05**[a]	**12.41**[b]	**7.04**[d]	**9.95**[c]
MUFA	**23.09**[f]	**26.06**[de]	**25.77**[e]	**27.00**[d]	**34.64**[b]	**67.26**[a]	**30.69**[c]
PUFA	**61.53**[b]	**65.52**[a]	**43.12**[e]	**47.95**[d]	**49.48**[d]	**21.32**[f]	**57.77**[c]
PUFA/SFA	**5.81**	**7.62**	**1.67**	**1.99**	**3.98**	**3.02**	**5.80**
ω6/ω3	**5.24**	**4.55**	**67.95**	**40.21**	**17.31**	**2.27**	**1.85**

Data are the mean of 3 measurements. Significant difference ($P<0.05$) is marked by different letters in the row.

Q: quinoa; GQ: germinated quinoa; A: amaranth; GA: germinated amaranth; SSO: soybean-sunflower oil; CO: canola oil; SChO: sunflower-chia oil; SFA: saturated fatty acid; MUFA: monounsaturated fatty acid; PUFA: polyunsaturated fatty acid.

Table 3. Total lipid content and fatty acids profile of the purees

Sample	PA1	PA2	PB1	PB2	PC1	PC2
Total fat content (g/100 g db)	4.54^{a}	3.91^{a}	5.22^{a}	5.09^{a}	5.03^{a}	3.92^{a}
Fatty acids (g methyl esters/100 g fat)						
Myristic (14:0)	0.12^{a}	0.12^{a}	0.13^{a}	0.11^{a}	0.12^{a}	0.12^{a}
Palmitic (16:0)	11.33^{a}	10.65^{ab}	9.87^{bc}	8.58^{cd}	10.15^{abc}	8.24^{d}
Palmitoleic (16:1)	0.10^{ab}	0.08^{b}	0.12^{a}	0.12^{a}	0.09^{b}	0.10^{ab}
Stearic (18:0)	2.57^{ab}	2.77^{a}	1.81^{b}	1.79^{b}	0.20^{c}	0.29^{c}
Oleic (18:1 cis, ω9)	27.73^{cd}	28.32^{cd}	40.97^{b}	43.68^{a}	27.77^{cd}	29.45^{c}
Linoleic (18:2 cis, ω6)	48.04^{ab}	49.29^{a}	34.19^{c}	36.16^{c}	42.17^{b}	44.90^{b}
Arachidonic (20:0)	0.47^{c}	0.52^{b}	0.61^{a}	0.65^{a}	0.47^{c}	0.50^{bc}
Gamma Linolenic (18:3, ω6)	0.11^{a}	0.12^{a}	0.02^{c}	0.03^{bc}	0.04^{b}	0.05^{b}
Eicosenoic (20:1)	0.57^{b}	0.60^{b}	0.99^{a}	1.08^{a}	0.60^{b}	0.60^{b}
Linolenic (18:3, ω3)	4.78^{e}	6.04^{de}	6.57^{d}	8.05^{c}	12.20^{b}	14.84^{a}
Eicosadienoic (20:2 cis)	-	-	0.07^{a}	0.07^{a}	0.05^{b}	0.06^{b}

Behenic (22:0)	0.61^{b}	0.73^{a}	0.46^{c}	0.53^{bc}	0.67^{ab}	0.71^{a}
9-Docosenoic/Erucic acid (22:1 cis)	0.49^{a}	0.50^{a}	0.54^{a}	0.49^{a}	0.52^{a}	0.50^{a}
Eicosenoic/Eicosatrienoic (20:3 cis)	0.07^{a}	0.07^{a}	0.07^{a}	0.06^{a}	0.07^{a}	0.08^{a}
Docosadienoic (22:2 cis)	0.09^{a}	0.09^{a}	0.10^{a}	0.10^{a}	0.09^{a}	0.09^{a}
Tetracosanoic (24:0) y EPA (20:5)	0.29^{a}	0.38^{a}	0.24^{a}	0.30^{a}	0.28^{a}	0.40^{a}
Tetracosaenoic (24:1)	0.09^{a}	0.09^{a}	0.14^{a}	0.10^{a}	0.10^{a}	0.09^{a}
SFA	**15.10^{a}**	**14.80^{a}**	**14.39^{a}**	**11.67^{b}**	**13.03^{ab}**	**11.41^{b}**
MUFA	**28.31^{bc}**	**28.91^{b}**	**41.76^{a}**	**44.32^{a}**	**28.48^{bc}**	**30.14^{b}**
PUFA	**53.38^{b}**	**55.90^{b}**	**41.23^{d}**	**44.78^{c}**	**54.91^{b}**	**60.32^{a}**
PUFA/SFA	**3.53**	**3.77**	**2.86**	**3.83**	**4.21**	**5.28**
ω6/ω3	**10.05**	**8.16**	**5.20**	**4.49**	**3.46**	**3.03**

Data are the mean of 3 measurements. Significant difference ($P<0.05$) is marked by different letters in the row.

PA1, PB1, PC1: purees with non-germinated grain flours; PA2, PB2, PC2: purees with germinated grain flours; PA1, PA2: purees with soybean:sunflower oil; PB1, PB2: purees with canola oil; PC1, PC2: purees with sunflower:chia oil; SFA: saturated fatty acid; MUFA: monounsaturated fatty acid; PUFA: polyunsaturated fatty acid.

Table 4. Tocopherol and TBHQ contents of the grain flours, oils and dehydrated purees

Sample	α-tocopherol (μg/g)	β-γ-tocopherol (μg/g)	δ-tocopherol (μg/g)	Tocopherol total (μg/g)	TBHQ (μg/g)
Q	1049^{b}	3101^{a}	119^{c}	4265^{a}	-
GQ	1144^{a}	2815^{b}	93^{c}	4056^{b}	-
A	173^{d}	1829^{b}	581^{a}	2583^{d}	-
GA	275^{c}	2038^{a}	491^{b}	2803^{c}	-
SSO	438^{b}	1539^{b}	557^{a}	2532^{a}	681.00^{a}
CO	175^{c}	1442^{a}	38^{b}	1655^{b}	64.57^{c}
SChO	416^{a}	528^{c}	32^{b}	976^{c}	94.75^{b}
PA1	549^{cd}	1796^{d}	372^{a}	2717^{b}	-
PA2	736^{bc}	1971^{e}	397^{a}	3104^{a}	-
PB1	482^{d}	1908^{a}	185^{b}	2575^{d}	-
PB2	596^{cd}	1878^{b}	164^{b}	2638^{c}	-
PC1	571^{b}	1581^{c}	169^{b}	2321^{e}	-
PC2	742^{a}	1622^{e}	170^{b}	2534^{f}	-

Data are the mean of 3 measurements. Significant difference ($P<0.05$) is marked by different letters in the column. The grain flours, oils and purees were separately analyzed.

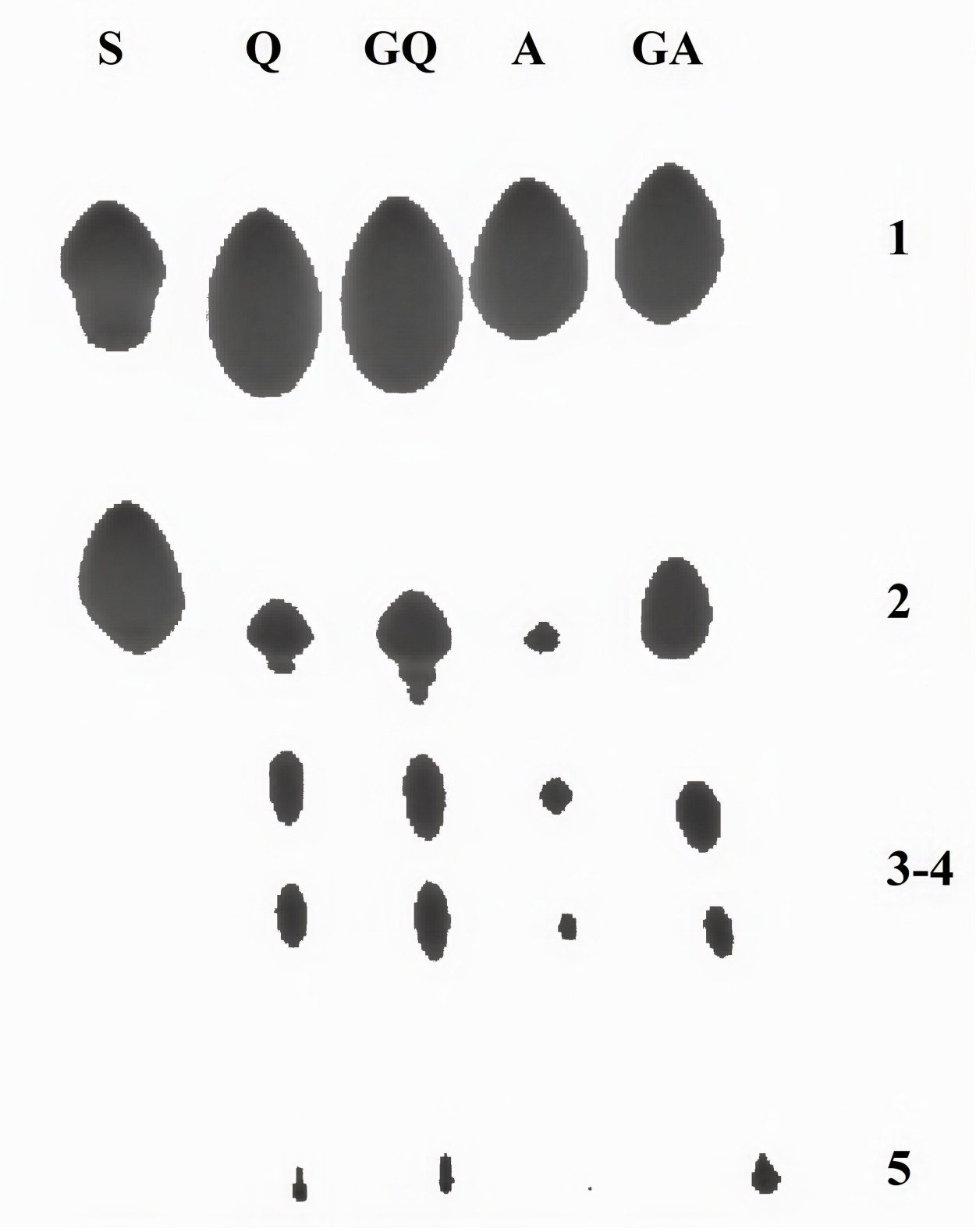
Q: quinoa; GQ: germinated quinoa; A: amaranth; GA: germinated amaranth; SSO: soybean-sunflower oil; CO: canola oil; SChO: sunflower-chia oil; PA1, PB1, PC1: purees with non-germinated grain flours; PA2, PB2, PC2: purees with germinated grain flours; PA1, PA2: purees with soybean-sunflower oil; PB1, PB2: purees with canola oil; PC1, PC2: purees with sunflower-chia oil.

Table 5. Fat oxidative stability of oils and lipid extracted of the grain flours purees

Sample	Estimated Arrhenius parameters on non-isothermal conditions				Inherent oxidation
	Ea	A	k (min^{-1})	R^2	
Q	109^{b}	$1.21x10^{12\ b}$	$1.62x10^{-3\ b}$	0.99	7.68^{b}
GQ	92^{c}	$1.42x10^{10\ d}$	$4.64x10^{-3\ a}$	0.99	8.34^{a}
A	107^{b}	$6.95x10^{11\ c}$	$1.95x10^{-3\ b}$	0.99	4.69^{d}
GA	114^{a}	$2.70x10^{12\ a}$	$8.40x10^{-4\ c}$	0.99	5.13^{c}
SSO	126^{a}	$1.50x10^{14\ a}$	$9.12x10^{-4\ c}$	0.99	5.68^{b}
CO	109^{b}	$4.75x10^{11\ b}$	$2.62x10^{-3\ b}$	0.99	3.77^{c}
SChO	101^{c}	$4.95x10^{11\ b}$	$9.37x10^{-3\ a}$	0.99	9.11^{a}
PA1	109^{b}	$1.06x10^{12\ b}$	$1.49x10^{-3\ c}$	0.99	6.28^{d}
PA2	114^{a}	$3.42x10^{12\ a}$	$9.92x10^{-4\ d}$	0.99	6.72^{c}
PB1	105^{b}	$2.94x10^{11\ e}$	$1.40x10^{-3\ c}$	0.99	5.47^{e}
PB2	113^{a}	$3.07x10^{11\ e}$	$1.01x10^{-3\ d}$	0.99	6.07^{d}
PC1	105^{b}	$6.83x10^{11\ c}$	$2.95x10^{-3\ a}$	0.99	7.54^{b}
PC2	109^{b}	$3.70x10^{11\ d}$	$2.46x10^{-3\ b}$	0.99	8.49^{a}

Data are the mean of 3 measurements. Significant difference ($P<0.05$) is marked by different letters in the column. The grain flours, oils and purees were separately analyzed.

Q: quinoa; GQ: germinated quinoa; A: amaranth; GA: germinated amaranth; SSO: soybean-sunflower oil; CO: canola oil; SChO: sunflower-chia oil; PA1, PB1, PC1: purees with non-germinated grain flours; PA2, PB2, PC2: purees with germinated grain flours; PA1, PA2: purees with soybean-sunflower oil; PB1, PB2: purees with canola oil; PC1, PC2: purees with sunflower-chia oil ; Ea: Activation energy; A: frequency factor; k: Rate coefficient.


S
Q
GQ
A
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1
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Highlights

Germination produced changes in fatty acids profile of quinoa and amaranth

Total tocopherols decreased in quinoa and increased in amaranth during germination

Purees made with germinated grain flours had more fat oxidative stability

Purees with canola oil had the better performance