Quinoa bitterness: causes and solutions for improving product acceptability

Running title: Quinoa bitterness: causes and solutions

Diego Suárez-Estrella[1], Luisa Torri[2], Maria Ambrogina Pagani[1], Alessandra Marti[1*]

[1] Department of Food, Environmental and Nutritional Sciences (DeFENS), Università degli Studi di Milano, Via G. Celoria 2, Milan 20133, Italy

[2] University of Gastronomic Sciences, Piazza Vittorio Emanuele 9, 12060 Bra, CN, Italy

*corresponding author:

alessandra.marti@unimi.it

Abstract

Awareness of the several agronomic, environmental, and health benefits of quinoa has led to a constant increase in its production and consumption not only in South America - where it is a native crop – but also in Europe and the United States. However, producing wheat or gluten-free based products enriched with quinoa alters some quality characteristics, including sensory acceptance. Several anti-nutritional factors such as saponins are concentrated in the grain pericarp. These bitter and astringent substances may interfere with the digestion and absorption of various nutrients. Developing processes to decrease or modify the bitterness of quinoa can enhance palatability and thus consumption of quinoa. In addition to the production of sweet varieties of quinoa, other processes have been proposed. Some of them (i.e. washing, pearling and the combination of the two) have a direct effect on saponins, either by solubilisation and/or the mechanical removal of seed layers. Others, such as fermentation or germination, are able to mask the bitterness with aroma compounds and/or sugar formation. This review presents the major sources of the undesirable sensory attributes of quinoa, included bitterness, and various ways of counteracting the negative characteristics of quinoa.

Keywords Quinoa; bitterness; saponins; washing; pearling

INTRODUCTION

Quinoa (*Chenopodium quinoa* Willd.) is a dicotyledonous plant belonging to the *Chenopodiaceae* family and is widespread in Latin America, particularly in South America where the crop had its origin 5000 years ago,[1] on the present Peruvian and Bolivian border near Titicaca lake. In ancient times, native South American populations used this grain in their daily diet as their main food. In 1989, the National Academy of Sciences of the United States includes quinoa as one of the best sources of protein in the vegetal kingdom.[2] Moreover, in the last few years, there has been a global re-evaluation of this crop, in light of numerous traits that make quinoa a sustainable and healthy grain. In fact, the 66th session of the General Assembly to the United Nations declared 2013 as the International Year of Quinoa, citing the potentially significant contribution of quinoa in the fight against hunger and malnutrition. Indeed, quinoa is one of the best alternatives to the global need to increase the dietary intake of plant proteins with high nutritional value for greater sustainability, safety and nutritional benefits.[3]

Awareness of the health benefits of quinoa, reflected in the growing number of gluten-free and vegetarian/vegan dieters, might account for the on-going global expansion of quinoa production, that increased by 60% from 2013 to 2014 (FAO; www.fao.org). Moreover, the last few years have been characterized by a proliferation of research on quinoa from various perspectives (e.g. agriculture, environmental impact, nutrition, food production, etc.). A systematic review of the scientific literature of the last 10 years using “quinoa” as a search term resulted in the identification of about 930 scientific papers (Figure 1A). It is worth mentioning that the number of contributions has doubled in the last five years, highlighting the growing interest in this topic. Almost 50% of the contributions (Figure 1B) fall into the “food science/chemistry/nutrition” categories of research, with about 40% of them dealing with agricultural and agronomic aspects of quinoa. Fourteen of the articles are reviews containing “quinoa” in their titles, and a summarized in Table 1. Most concern agronomic and nutritional aspects of the “golden grain”, while, others are dedicated to the development of food products, including bread, pasta, snacks and cookies, enriched with quinoa to improve their nutritional properties. However, in South America it’s the whole seed of quinoa that is mainly used and generally cooked like rice to be used in soups, salads, and stews.[4]

Producing quinoa-enriched wheat- or gluten-free based products alters several quality attributes according to Wang and Zhu.[17] Among these, sensory acceptance is the most critical factor in ensuring the consumption of quinoa and its successful use in food products. In this context, the presence of bitter compounds in quinoa limits its consumption, despite its numerous nutritional benefits. Developing processes to decrease or modify the bitterness of quinoa serve to enhance palatability. Such processing involves washing, pearling, and biotechnological treatments. This review presents the major sources of the undesirable sensory attributes of quinoa; the various approaches for counteracting the negative perception of quinoa consumption are also discussed.

AGRONOMIC, COMPOSITIONAL AND NUTRITIONAL BENEFITS

From a botanical and agronomic standpoint, quinoa can be characterized using the terms “biodiversity” and “sustainability”, two keywords of the 21st century denoting qualities that make this crop one of the best alternative and resistant grain with respect to current climate change. Its environmental adaptability and efficient water utilization make it an excellent substitute for traditional cereals, especially in marginal areas.[5,19,20] Despite its mountain origin, research indicates it can be grown from sea level to altitudes over 4000 meters with large yield ranges (from 0.32 to 9.83 t ha $^{-1}$).[21] Moreover, the quinoa plant is able to grow under stress conditions of temperature (from -5 °C to 38 °C, with optimal temperatures ranging from 15 °C to 20 °C), relative humidity (40% - 88%), drought and water availability (from 50 mm up to 2000 mm year^{-}

diversity, its exceptional tolerance to drought and salinity, and the crop's ecological advantages have been extensively reviewed by Ruiz *et al*.[9]

Concerning biodiversity, quinoa presents a wide genetic variability in terms of forms, size, color and grain composition. Originally quinoa classification was made according to the color of the plant and fruits, in fact seed color can range from white to grey and black, but varieties exhibiting a yellow, rose, red, purple or violet color are also found; sometimes, with several of them present on the same panicule. Betalains are the most relevant phytochemicals present in quinoa grains and are responsible for their color. They are classified into yellow betaxanthins and violet betacyanins; the joint presence of both types of pigments makes the orange and red shades that coexist in nature with the pure yellow and violet colors. The presence of betalains is correlated with high antioxidant and free radical scavenging activities.[23,24] Violet, red and yellow quinoa grain extracts show remarkable antioxidant activity in comparison with the white and black one. The highest activity was observed in the red-violet varieties containing both betacyanins and betaxanthins, with remarkable activity also in the yellow varieties, where dopaxanthin is a significant constituent.[23]

The potential health benefits of quinoa have been extensively reviewed in recent years (Table 1). It was reported that one serving of quinoa (about 40 g) meets an important part of daily requirements for essential nutrients and health-improving compounds.[16] In particular, the high amount of lysine - the limiting amino acid in all cereals - makes quinoa unique among grains.[13,25] It can be used not only as a highly nutritious source of proteins but also as source of minerals and antioxidants, such as phenolic compounds. High dietary fiber and stable polyunsaturated fatty acids increase its potential to treat obesity, hypercholesterolemia and cardiovascular disorders.[11,12] Quinoa is tolerable and acceptable to people with celiac disease and/or gluten intolerance. Indeed, although several varieties (Ayacuchana, Pasankalla, LP-4B and Witulla) have celiacconsiderably lower than the level required for gluten-free products (20 mg kg^{-1}).[27] Finally, it has been suggested that quinoa could contain a significant amount of rapidly digestible starch fraction,[28] likely due to smaller starch granules (1.2 to 2.66 μm), indicating that careful formulation and processing of quinoa products would be needed for glycemic index management. However, to the best of our knowledge, the available information on enzymatic susceptibility of quinoa starch refers to pure starch or to uncooked samples, neglecting the role of other components and/or cooking processes on starch hydrolysis kinetics. *In-vivo* studies showed that about one cup of cooked quinoa (or 150 g) has a glycemic index score of 53, which is considered low.[29] *In-vitro* studies on gluten-free bread demonstrated that quinoa-enriched products had a significantly lower glycemic index than white wheat bread due to its lower content of total available carbohydrates.[30] However, gluten-free bread made with quinoa indicated higher starch digestibility compared to bread from other gluten-free grains (i.e. buckwheat, sorghum and teff),[30] although these findings need to be confirmed by *in vivo* studies.

SENSORY PROPERTIES AND ACCEPTABILITY OF QUINOA FOOD PRODUCTS

As already mentioned, the boom in gluten-free, vegan and vegetarian diets reflects the increase in quinoa consumption even outside producer countries. In the Occident, quinoa seeds are mainly used in salads, whereas quinoa flour is mixed with other gluten-free grains for making bread, pasta, and cookies.[17] The following section will summarize consumer perception of its sensory attributes and consumer acceptance of quinoa-containing foods in the past 10 years.

Grains

We know of only one study dealing with the sensory analysis of quinoa grains.[31] The results of this study showed a wide range of sensorial characteristics. For example, a whereas attributes such as pasty, sticky and cohesive were negative. Preference seemed to be influenced not only by the sensory properties of the grain but also by the consumer's familiarity with quinoa. Those whose diets consisted of 750 g kg^{-1} to 1000 g kg^{-1} of organic foods scored significantly higher for all quinoa varieties than those who consumed 0 to 250 g kg^{-1}.[31]

Bread

Quinoa has been used in bread-making as a partial substitute for wheat or rice flour in varying amounts. Quinoa-enriched bread has typically been prepared using whole quinoa seeds, flakes or flour.

Despite a slightly bitter taste, wheat-based bread with up to 200 g kg^{-1} of dehulled and washed quinoa seeds were judged to be fully acceptable to the taste, with a very pleasant aroma and flavour.[32] These positive results were subsequently confirmed for bread with higher levels (300 and 400 g kg^{-1}) of similarly treated quinoa seeds.[33]

Using quinoa flakes in bread-making has also been investigated and no significant differences were revealed for appearance, colour, texture, flavour, taste, porosity and overall acceptability when up to 200 g kg^{-1} of quinoa had been added.[34]

Although the positive results found using quinoa seeds and flakes as bread ingredients, using quinoa flour often opposed sensory problems.

The 60 g kg^{-1} substitution of wheat flour with quinoa flour for bread was considered acceptable.[35] Adding texturing ingredients, such as whey, was efficacious in guaranteeing the acceptability of wheat bread fortified with 150 g kg^{-1} quinoa flour. On the contrary, adding 200 g kg^{-1} of quinoa made the bread less acceptable, due to its slight bitterness.[36] Another study demonstrated that acceptability significantly decreased for samples with 500 and 1000 g kg^{-1} of quinoa flour, even if the quinoa kg^{-1} quinoa flour induced the perception of a strong pea-like odour and of cooked potato and mould aromas, mainly responsible for moderate overall disliking.[38] Using sourdough fermented with *Lactobacillus plantarum*[39] or *Weissella cibaria*[40] did not improve the sensory characteristics of quinoa bread, while with *Lactobacillus plantarum* T6B10 and *Lactobacillus rossiae* T0A16 a wheat bread with improved crust and crumb colour, saltiness, acid flavour and taste, and overall positive taste attributes was made[41]. Good palatability and overall acceptable taste were obtained with sourdough fermentation of quinoa flour, also when blended with flours from other pseudo-cereals (i.e. amaranth and buckwheat) and pulses (i.e. chickpea).[42]

Quinoa flour can also replace rice flour in gluten-free formulations. Substitution levels in the range of 300 – 1000 g kg^{-1} increased acceptability in terms of crust and crumb color and appearance, in comparison with acceptance scores for 1000 g kg^{-1} rice flour reference bread.[43] Overall, a substitution level equal to 300 g kg $^{-1}$ of quinoa flour was considered suitable to avoid negative aroma and taste and guarantee an overall acceptability comparable to that obtained for the control rice bread.[43,44] Conversely, other studies showed that 500 g kg^{-1} quinoa flour increased crumb softness and cohesiveness of rice-based breads, without adversely affecting sensory properties.[45] As expected, the removal of bran components largely decreased bitterness and off-flavour in white quinoa breads, compared to whole quinoa samples.[46] Indeed, as mentioned elsewhere, saponins – which are responsible for quinoa bitterness – are mainly located in the bran. Therefore, only addition of 100 g kg^{-1} of quinoa bran to rice and corn bran resulted in improved appearance, and reduced crumb firmness, without compromising taste, whereas higher quantities (200, 300 and 400 g kg^{-1}) increased bitterness and off-flavours.[47]

Pasta

Information regarding the effect of quinoa on the sensory properties of pasta products that 70% of consumers declared they would probably or certainly buy the product.[48] A similar quinoa enrichment resulted in a product with lower firmness but similar adhesiveness and bulkiness than the control (1000 g kg^{-1} amaranth).[49] A higher percentage of quinoa (250 g kg^{-1}) in a gluten-free formulation received lower liking scores than wheat noodles, for the attributes evaluated before (i.e. surface smoothness, appearance, and colour) or after (i.e. taste, odour, colour and overall acceptability) cooking.[50] However, the acceptability of the quinoa-based product was high when containing chick-pea or soy flour compared to other gluten-free formulations.[51]

Cookies

Several studies reported the impact of quinoa on cookie acceptability, however with contrasting results, whether for wheat-based or gluten-free products. As expected, low quinoa enrichment levels (< 100 g kg^{-1}) did not affect the sensory acceptability of cookies made primarily from wheat flour, but a slightly higher substitution level (150 g kg^{-1}) reduced flavour, taste and overall acceptability.[52] However, quinoa cookies were still acceptable, and similar results were observed by Pagamunici *et al*.[53] In gluten-free formulations, the presence of quinoa positively affected overall acceptance and purchase intention.[54]

BITTER COMPOUNDS IN QUINOA

Various compounds with diverse structures (i.e. amino acids and peptides, esters and lactones, phenols and polyphenols, flavonoids and terpenes) are responsible for bitterness in foods and multiple mechanisms have been described for the perception of bitterness.[55] The most common bitter compounds in quinoa and the key mechanisms leading to bitterness are summarized in Table 2 and described in the following section. The bitterness of quinoa has always been associated with the presence of saponins in the threshold for human perception of bitterness. Very little work has focused on the role of polyphenols and other compounds on the bitter taste or aftertaste of quinoa seeds and its products.

Saponins

Saponins are a class of natural compounds produced by some plants for protection against harmful microorganisms, birds and insects.[66] Saponins are present in legumes (such as soybeans, broad beans, chickpeas, peas, etc.)[67,68] and some vegetables (as spinach, lettuce, cauliflower, mustard, asparagus).[69,70] Regarding grains, only oats[67] and quinoa exhibit detectable amounts of saponins.[71] In quinoa, these compounds are mainly located in the husk and the quantity therein – which is greatly influenced by the environment, climate conditions and genotype[5,72,73] - varies from 0.1 mg g^{-1} to about 50 mg g^{-1}.[74] Indeed, "bitter" varieties (with a saponin content higher than 1.1 mg g^{-1}), are more resistant to pests than "sweet" varieties.[5,75] As will be extensively discussed later on in this paper, the bitter taste is recognizable in samples having an amount of saponin greater than 1.1 mg g^{-1}.[56]

Saponin molecules are characterized by the presence of a non-polar aglycone (or sapogenin), bonded to one or more carbohydrate chains.[58,76] Quinoa contains only triterpene saponins,[77-79] which can be classified according to the number of carbohydrate chains linked to aglycone.[58] The saccharide chains of saponins assure high hydrophilic properties, whereas the sapogenins (formed only by the triterpene fraction) exhibit lipophilic traits. Hence, the amphiphilic properties of saponins assure high solubility both in polar and non-polar solvents.

Detailed information about the chemical and structural characteristics of quinoa saponins are presented in comprehensive reviews.[58,76,80]

Although the majority of studies report around 20 saponins in quinoa,[78,79] Madl *et al.*[78] refer to 87 triterpene saponins. More recently, Jarvis *et al.*[73] identified 43 different saponins in a variety used as a reference.

Several studies have focused on the chemical and biological properties of saponins,[58,76,81] highlighting their complexity and controversial biological role. Indeed, quinoa extracts containing saponins have been exploited in numerous traditional and industrial applications for their foaming and bioactive properties but, usually, saponins in foods have traditionally been considered as anti-nutritional factors, as stated by Güçlü-Ustündağ and Mazza.[76] However, the consequences of long term consumption of saponins for human health are still unknown.[82]

The anti-nutritional properties of saponins have been investigated in several studies.[14,83,] The main negative effects associated with consumption of foods rich in saponins are the decrease in mineral and vitamin bioavailability,[84-86] the damage to small intestine mucous cells due to the alteration of their membrane permeability, and the decrease in food conversion efficiency.[82] The chemical structure of quinoa saponins strictly influences their biological activities,[58] e.g. the carbohydrate chain attached at C3 of the terpenic fraction is usually critical for both membrane permeabilization and antifungal properties[58,79] and their toxicity depends on the saponin type and on the sensitivity of the recipient organism, [83]

Nowadays, saponins are considered bioactive, health-promoting compounds, with many interesting nutritional characteristics as a result of their hypocholesterolemic, analgesic, antiallergic and antioxidant activities.[76,79] In any case, as already mentioned, the bitter taste associated with saponins greatly limits the use of quinoa as food.

Phenolic compounds

Phenolic compounds constitute a group of important components to bitterness in cereal products.[60] Free phenolic compounds are the most flavour-active because they adhere to taste receptors.[60] However, studies on bread and crackers suggest that the bound fraction of phenolic acids may also contribute to taste and flavour properties of wholegrain products.[59] In this context, the authors hypothesized that during mastication with taste receptors and other compounds inside the mouth.[59] Moreover, it has been shown that lower-molecular-weight phenolic compounds tend to be bitter, whereas higher-molecular-weight polymers are more likely to be responsible for food astringency.[87] In addition, the impact of free phenolic compounds on flavour is greater than that of bound compounds.[57]

Phenolic compounds are mainly located in the outer layers of the grain, and therefore highly found in wholegrain and bran content.[88-90] Various strategies have been proposed to increase the bioaccessibility and bioavailability of phenolic compounds, in baked products because of the health benefits associated with them.[91-93] A comprehensive review of phytochemicals in quinoa grains and their potential health benefits have been proposed by Tang and Tsao.[11] Quinoa contained lower levels of phenolic acids compared with common cereals like wheat and rye, but they were of the same magnitude (250–600 mg kg $^{-1}$) as in other cereals.[94,95] The majority of phenolic compounds found in quinoa were phenolic acids consisting of vanillic acid, ferulic acid and their derivatives (303-597 mg kg^{-1}), along with flavonoids quercetin, kaempferol and their glycosides (36.2-72.6 mg kg^{-1});[95] also tannins have been reported with concentrations of up to 5.3 g kg^{-1}.[41,96]

The perceived bitterness of rye results from pinoresinol and syringic acid in particular,[60] whereas ferulic acid was identified as the most abundant phenolic acid in wheat bread crust and crumb.[97] On the contrary, phenolic compounds responsible for bitter taste have not been adequately determined in whole grain foods.[98] To the best of our knowledge, no information is available regarding quinoa seeds. Thus, further efforts should be directed to identifying the major phenolic compounds responsible for the bitterness of quinoa seeds.

Peptides

Bitter peptides occur to a varying extent after protein hydrolysis.[64] Although small molecular weight peptides are deemed responsible for the bitter taste in rye,[65] the amino acid composition of peptides has been considered to be a more important determinant of bitterness than peptide size.[99] The role of peptides and amino acids in the perceived flavour of cereal products, including quinoa, remains, however, largely unknown.[57]

APPROACHES TO DECREASE BITTERNESS IN QUINOA

Attempts to introduce quinoa as an ingredient in food products all over the world have proved difficult because of the presence of saponins which are responsible for lowering product acceptability due to their bitter taste and/or aftertaste. To this end, several strategies have been proposed to remove saponins or to hide their bitterness. The effects of the main processing together with their advantages and disadvantages are summarized in Table 3 and discussed in the following sections.

Washing

Washing is the most common way to remove saponins from the seeds at the household level, due to the high water solubility of these compounds. American pre-Hispanic populations, such as the Incas, Cañaris and others used to wash quinoa in rivers and lakes.[100] Traditionally, in rural areas, washing is done by hand in water - placed in rudimentary tanks[101,102] - which sometimes could be alkaline to enhance saponin extraction[4,102] or in river water.[102] The large amount of water used and contaminated with saponins constitutes a health hazard for cold-blooded animals[103] and creates economic and ecological concerns. Moreover, wet seeds need to be dried immediately to inhibit their high germinating power[72,104] as well as mold growth.[105]

Washing is also used on a commercial scale by using tanks equipped with rotating blades for turbulence washing.[106] Heat treatment in a tunnel completes the drying

Quispe-Fuentes *et al*.[101] have proposed an efficient, industrial scale mathematical model to reduce cost, energy waste and optimize water flow rate when leaching saponins from quinoa seeds by means of a continuous washing process. Saponins leach out very rapidly at the beginning of the washing process and the total concentration of saponins inside quinoa seeds tend to have an asymptotic value. High temperatures accelerate saponin leaching, in fact leaching at 70 °C was more effective than at 20 °C.[101] However, since starch gelatinization begins at 50 ºC for most quinoa varieties,[28] this treatment could cause the quinoa perisperm to swell, thus facilitating embryo separation.

Another consideration is that valuable nutrients including vitamins and minerals may also be lost during these washing procedures.[85]

Pearling

Dry polishing techniques (i.e. pearling) apply abrasion to separate the external layers and allow the intact seeds to be recovered and processed in successive stages. Pearling is a well-established technology in the processing of covered cereals, such as rice and barley.[107] Nowadays, pearling is also used on wheat to reduce microbial contamination, as most of the microorganisms present can be found on the surface of the kernel.[108] More recently, pearling has proven to be an effective way to recover the phenolic compounds in the external layers of grains.[93]

As regards quinoa seeds, the pearling process has been successfully used to decrease the amount of saponins, located in the external layers of the seed.[100,109] An abrasion degree of 30% reduced saponin levels by more than 70%, compared with the initial content in whole quinoa, reaching a level below 1.1 mg g^{-1} for several varieties, which is the threshold for the detection of bitterness and astringency in quinoa based products.[56]

Pearling is a more environmental-friendly process compared to washing because no water is needed, no thermal treatment to dry the seeds is required, and no environmental contamination is produced.[109] Other advantages of the abrasion process include the reduction of time and energy consumption. Pearled by-products – which comprise from 8% to 12% of the grain weight and contain from 200 to 300 g kg^{-1} of saponins[74] – can be used for medical purposes, detergents, and pesticides.

On the other hand, as the degree of abrasion increases, the content of fiber and phenolic compounds decreases.[32,109] However, the loss of phenolic compounds in quinoa after pearling is lower than in cereals. Gómez-Caravaca *et al*.[109] found that after intense pearling (30%) in order to obtain a sweet product, the quantity of freed and bound phenolic compounds decreased by 35%. Fiber and mineral content, especially calcium, sodium, potassium and manganese, also decreased after pearling.[34,96,110]

Pearling and washing can be performed separately or combined to enhance the effects on saponin removal, and lower the negative impact of each individual process (Table 3).

Other methods

Other methods have been proposed such as the combination of washing and heat treatments in different conditions (i.e. toasting, cooking at atmospheric pressure, cooking under pressure).[111] However, none of them resulted in a higher loss of saponin content than just washing.[111]

Bioprocessing

Sourdough fermentation is a biotechnological process that transforms complex molecules into simpler ones through the enzymatic activity of microorganisms, such as yeasts and lactic acid bacteria. The positive effects of grain fermentation include the bioactive and/or antifungal compounds.[112,113] Moreover, sourdough fermentation improves the sensory quality of products, due to the production of organic acids and the development of new aromatic compounds.[113] In particular, adding quinoa sourdough to wheat enhances the sensory traits of wheat bread, resulting in higher acidity, a salty taste and less sweetness.[41] However, it is not clear if this new sensory profile masks the bitterness of quinoa.

Sprouting (or germination) is a natural process that decreases the anti-nutrient compounds in cereals, pseudocereals and pulses while substantially increasing micronutrient bioavailability and improving sensory properties.[114,115] Germinated grains are characterized by a sweet taste, due to the formation of simple sugars, that may mask the bitter taste in whole wheat bread.[116] However, no information about the effect of germination on quinoa saponins and, consequently, on its bitter taste or aftertaste has been reported. Nevertheless, the effectiveness of germination in decreasing saponin content in bitter quinoa varieties might be a hoped-for result, given the precedent of the positive results observed in sprouted chickpeas[117] and huazontle[118] (*Chenopodium berlandieri spp.)*, closely related to quinoa.

Breeding

Several bio-technological approaches have been proposed to decrease the amount of saponins. Although effective, they are costly and impact negatively on the environment. Therefore, the possibility of selecting “sweet” genotypes with low saponin content for direct consumption without any grain pre-treatments are being explored: this approach would facilitate the expansion of quinoa production and utilization, above all, beyond the Andean regions.[119]

Quinoa, in fact, is still an under-utilized crop and breeding efforts to improve its agronomic traits (length of growing season; crop yield) are required to expand its production worldwide, especially at higher latitudes where some lines are characterized with little or no saponin is one of the most important breeding objectives for the future,[121,122] not only to improve crops in South American countries but also in Mediterranean environments.[123] However, breeding this trait into quinoa varieties is still a challenge due to the difficulty of measuring saponin levels prior to anthesis and fixing appropriate alleles.[124] Jarvis *et al*.[73] recently sequenced the genome of a Chilean coastal variety of quinoa along with the genomes of additional *Chenopodium* species to characterize the genetic diversity of quinoa. They also proposed the pathway for saponin biosynthesis, indicating the enzymes involved in each step and the genes encoding each enzyme. Interestingly, these scientists discovered that only one key gene is implicated in the regulation of saponin production. The authors suggest using the identified genetic markers to develop non-bitter or sweet commercial quinoa varieties with lower saponin levels by means of the marker assisted selection. These findings would provide the scientific bases for accelerating the genetic improvement of quinoa, to enhance global food security for a growing world population.

CONCLUSIONS

The presence of bitter compounds - mainly saponins - highly affect sensory acceptance of quinoa; consequently, the consumption of this pseudocereal as whole grain and/or as a valuable nutritive ingredient in composite flours for wheat or gluten-free products has to carefully consider this aspect. Presently, decreasing or modifying the bitterness of quinoa is achieved applying washing and/or mechanical pearling. Although they are widely used, these processes present critical aspects, namely low environment-sustainability, energy and specific equipment requirements, that force researchers to find other approaches. Besides the breeding studies that might select new “sweet” varieties with low or no saponin content and with high adaptability to different climatic environments, bio-technological and not-expensive processes have to be developed. Indeed, germination could not only enhance important nutritional traits of grains, but also represent a valid tool for decreasing bitterness in quinoa, due to sugar formation.

ACKNOWLEDGEMENTS

Diego Suárez is grateful recipient of a PhD fellowship from Secretaría de Educación Superior, Ciencia, Tecnología e Innovación (SENESCYT), Ecuador.

REFERENCES

1. González JA, Eisa SSS, Hussin SAES and Prado FE, Quinoa: an Incan crop to face global changes in agriculture, in *Quinoa: Improvement and Sustainable Production, Variety Improvement, and Nutritive Value in Agroecological Systems*, ed. by Murphy K, Matanguihan J, New York, pp. 1–18. (2015).

2. National Research Council (NRC), *Lost Crops of the Incas: Little-Known Plants of the Andes with Promise for Worldwide Cultivation*. National Academy Press, Washington, DC, pp. 149-161 (1989).

3. Scanlin L and Lewis KA, Quinoa as a sustainable protein source: production, nutrition, and processing, in *Sustainable Protein Sources*, ed. by Nadathur SR, Wanasundara JPD and Scanlin L, Chennai, pp. 223–238 (2017).

4. Valencia-Chamorro SA, Quinoa: Overview, in *Encyclopedia of Food Grains*, ed. by Wringley C, Corke H, Seetharaman K, Faubion J, Waltham, pp. 341–348 (2016).

5. Zurita-Silva A, Fuentes F, Zamora P, Jacobsen SE and Schwember AR, Breeding quinoa (*Chenopodium quinoa* Willd.): potential and perspectives. *Mol Breed* **34:** 13–30 (2014).

6. Burrieza HP, López-Fernández MP and Maldonado S, Analogous reserve distribution and tissue characteristics in quinoa and grass seeds suggest

7. Bazile D, Pulvento C, Verniau A, Al-Nusairi MS, Ba D, Breidy J, Hassan L, Mohammed M, Mambetov O, Otambekova M, Sepahvand NA, Shams A, Souici D, Miri K and Padulosi S, Worldwide evaluations of quinoa: preliminary results from post international year of quinoa FAO projects in nine countries. *Front Plant Sci* **7:** 1–18 (2016).

8. Choukr-Allah R, Rao NK, Hirich A, Shahid M, Alshankiti A, Toderich K, Gill S and Butt UR, Quinoa for marginal environments; toward future food and nutritional security in MENA and Central Asia regions. *Front Plant Sci* **7:** 1–11 (2016).

9. Ruiz KB, Biondi S, Oses R, Acuña-Rodríguez IS, Antognoni F, Martinez-Mosqueira EA, Coulibaly A, Canahua-Murillo A, Pinto M, Zurita-Silva A, Bazile D, Jacobsen SE and Molina-Montenegro MA, Quinoa biodiversity and sustainability for food security under climate change. A review. *Agron Sustain Dev* **34:** 349–59 (2014).

10. Simnadis TG, Tapsell LC and Beck EJ, Physiological effects associated with quinoa consumption and implications for research involving humans: a review. *Plant Foods Hum Nutr* **70:** 238–249 (2015).

11. Tang Y and Tsao R, Phytochemicals in quinoa and amaranth grains and their antioxidant, anti-inflammatory, and potential health beneficial effects: a review. *Mol Nutr Food Res* **61:** 1–16 (2017).

12. Navruz-Varli S and Sanlier N, Nutritional and health benefits of quinoa (*Chenopodium quinoa* Willd.). *J Cereal Sci* **69:** 371–376 (2016).

13. Maradini Filho AM, iMedPub Journals Quinoa: nutritional aspects. *J Nutraceuticals Food Sci* **2:** 1–5 (2017).

14. Vega-Gálvez A, Miranda M, Vergara J, Uribe E, Puente L and Martínez EA, Nutrition facts and functional potential of quinoa (*Chenopodium quinoa* Willd.), an ancient Andean grain: a review. *J Sci Food Agric* **90:** 2541–2547 (2010).

15. Jancurová M, Minarovičová L and Dandár A, Quinoa – a review. *Czech J Food Sci* **27:** 71–9 (2009).

16. Graf BL, Rojas-Silva P, Rojo LE, Delatorre-Herrera J, Baldeón ME and Raskin I, Innovations in health value and functional food development of quinoa (*Chenopodium quinoa* Willd.). *Compr Rev Food Sci Food Saf* **14:** 431–445 (2015).

17. Wang S and Zhu F, Formulation and quality attributes of quinoa food products. *Food Bioprocess Technol* **9:** 49–68 (2016).

18. Janssen F, Pauly A, Rombouts I, Jansens KJA, Deleu LJ and Delcour JA, Proteins of amaranth (*Amaranthus spp*.), buckwheat (*Fagopyrum spp*.), and quinoa (*Chenopodium spp*.): a food science and technology perspective. *Compr Rev Food Sci Food Saf* **16:** 39–58 (2017).

19. Algosaibi AM, Badran AE, Almadini AM and El-Garawany MM, The effect of irrigation intervals on the growth and yield of quinoa crop and its components. *J Agric Sci* **9:** 182–91 (2017).

20. Martínez EA, Quinoa: Nutritional aspects of the rice of the Incas, in *State of the Art. Report of Quinoa in the World in 2013*, ed. by Bazile D, Bertero HD, Nieto C, Rome, pp. 278–285 (2015).

21. Bhargava A, Shukla S and Ohri D, Genetic variability and interrelationship among various morphological and quality traits in quinoa (*Chenopodium quinoa* Willd.). *F Crop Res* **101:** 104–116 (2007).

22. Jacobsen SE, Mujica A and Jensen CR, The resistance of quinoa (*Chenopodium quinoa* Willd.) to adverse abiotic factors. *Food Rev. Int* **19:** 99-109 (2003).

23. Escribano J, Cabanes J, Jiménez-Atiénzar M, Ibañez-Tremolada M, Gómez-Pando LR, García-Carmona F and Gandía-Herrero F, Characterization of betalains, saponins and antioxidant power in differently colored quinoa (*Chenopodium quinoa*) varieties. *Food Chem* **234:** 285–294 (2017).

24. Abderrahim F, Huanatico E, Segura R, Arribas S, Gonzalez MC and Condezo-Hoyos L, Physical features, phenolic compounds, betalains and total antioxidant capacity of coloured quinoa seeds (*Chenopodium quinoa* Willd.) from Peruvian Altiplano. *Food Chem* **183:** 83–90 (2015).

25. Mota C, Santos M, Mauro R, Samman N, Matos AS, Torres D and Castanheira I, Protein content and amino acids profile of pseudocereals. *Food Chem* **193:** 55–61 (2016).

26. Zevallos VF, Ellis HJ, Herencia LI and Ciclitira PJ, Variable activation of immune response by quinoa (*Chenopodium quinoa* Willd.) prolamins in celiac disease 1 – 3. *Am J Clin Nutr* **96:** 337–344 (2012).

27. The European Commission, Commission implementing regulation (EU) No 828/2014 of 30 July 2014. *Off J Eur Union* 2014.

28. Li G, Wang S and Zhu F, Physicochemical properties of quinoa starch. *Carbohydr Polym* **137:** 328–338 (2016).

29. Singh S, Singh R and Singh KV, Quinoa (*Chenopodium quinoa* Willd), functional superfood for today’s world: a review. *World Sci News* **58:** 84-96 (2016).

30. Wolter A, Hager AS, Zannini E and Arendt EK, Influence of sourdough on in vitro starch digestibility and predicted glycemic indices of gluten-free breads. *Food*

31. Wu G, Ross CF, Morris CF and Murphy KM, Lexicon development, consumer acceptance, and drivers of liking of quinoa varieties. *J Food Sci* **82:** 993–1005 (2017).

32. Stikic R, Glamoclija D, Demin M, Vucelic-Radovic B, Jovanovic Z, Milojkovic-Opsenica D, Jacobsen SE and Milovanovic M, Agronomical and nutritional evaluation of quinoa seeds (*Chenopodium quinoa* Willd.) as an ingredient in bread formulations. *J Cereal Sci* **55:** 132–138 (2012).

33. Demin MA, Vucelić-Radović B V, Banjac NR, Tipsina NN and Milovanović MM, Buckwheat and quinoa seeds as supplements in wheat bread production. *Hem Ind* **67:**115–121 (2013).

34. Gewehr MF, Danelli D, De Melo LM, Flöres SH and De Jong EV, Nutritional and technological evaluation of bread made with quinoa flakes (*Chenopodium quinoa* Willd). *J Food Process Preserv* **41:** 1-8 (2017).

35. Calderelli VAS, Benassi M de T, Visentainer JV and Matioli G, Quinoa and flaxseed: potential ingredients in the production of bread with functional quality. *Brazilian Arch Biol Technol* **53:** 981–986 (2010).

36. Salazar DM, Naranjo M, Pérez LV, Valencia AF, Acurio LP, Gallegos LM, Alvarez FC, Amancha PI, Valencia MP, Rodriguez CA and Arancibia MY, Development of newly enriched bread with quinoa flour and whey. *IOP Conf Ser Earth Environ Sci* **77:** 1-7 (2017).

37. Rosell CM, Cortez G and Repo-Carrasco R, Breadmaking use of Andean crops quinoa, kañiwa, kiwicha, and tarwi. *Cereal Chem* **86:** 386–392 (2009).

38. Hager AS, Wolter A, Czerny M, Bez J, Zannini E, Arendt EK and Czerny M, Investigation of product quality, sensory profile and ultrastructure of breads made

from a range of commercial gluten-free flours compared to their wheat counterparts. *Eur Food Res Technol* **235:** 333–344 (2012).

39. Wolter A, Hager AS, Zannini E, Czerny M and Arendt EK, Impact of sourdough fermented with lactobacillus plantarum FST 1.7 on baking and sensory properties of gluten-free breads. *Eur Food Res Technol* **239:** 1–12 (2014).

40. Wolter A, Hager AS, Zannini E, Czerny M and, Arendt EK, Influence of dextran-producing *Weissella cibaria* on baking properties and sensory profile of gluten-free and wheat breads. *Int J Food Microbiol* **172:** 83-91 (2014).

41. Rizzello CG, Lorusso A, Montemurro M and Gobbetti M, Use of sourdough made with quinoa (*Chenopodium quinoa*) flour and autochthonous selected lactic acid bacteria for enhancing the nutritional, textural and sensory features of white bread. *Food Microbiol* **56:** 1–13 (2016).

42. Coda R, Rizzello CG and Gobbetti M, Use of sourdough fermentation and pseudo-cereals and leguminous flours for the making of a functional bread enriched of γ-aminobutyric acid (GABA). *Int J Food Microbiol* **137:** 236–245 (2010).

43. Burešová I, Tokár M, Mareček J, Hřivna L, Faměra O and Šottníková V, The comparison of the effect of added amaranth, buckwheat, chickpea, corn, millet and quinoa flour on rice dough rheological characteristics, textural and sensory quality of bread. *J Cereal Sci* **75:** 158–164 (2017).

44. Turkut GM, Cakmak H, Kumcuoglu S and Tavman S, Effect of quinoa flour on gluten-free bread batter rheology and bread quality. *J Cereal Sci* **69:** 174–181 (2016).

45. Alvarez Jubete L, Auty M, Arendt EK and Gallagher E, Baking properties and microstructure of pseudocereal flours in gluten-free bread formulations. *Eur Food Res Technol* **230:** 437–445 (2010).

46. Elgeti D, Nordlohne SD, Föste M, Besl M, Linden MH, Heinz V, Jekle M and Becker T, Volume and texture improvement of gluten-free bread using quinoa white flour. *J Cereal Sci* **59:** 41–47 (2014).

47. Föste M, Nordlohne SD, Elgeti D, Linden MH, Heinz V, Jekle M and Becker T, Impact of quinoa bran on gluten-free dough and bread characteristics. *Eur Food Res Technol* **239:** 767–775 (2014).

48. Caperuto L, Amaya-Farfan J and Camargo CRO, Performance of quinoa (*Chenopodium quinoa* Willd) flour in the manufacture of gluten free spaghetti. *J Sci Food Agric* **81:** 95–101 (2000).

49. Chillo S, Laverse J, Falcone PM and Del Nobile MA, Quality of spaghetti in base amaranthus wholemeal flour added with quinoa, broad bean and chick pea. *J Food Eng* **84:** 101–7 (2008).

50. Bilgiçli N, Some chemical and sensory properties of gluten-free noodle prepared with different legume, pseudocereal and cereal flour blends. *J Food Nutr Res* **52:** 251–255 (2013).

51. Mastromatteo M, Chillo S, Civica V, Iannetti M, Suriano N and Del Nobile MA, A multistep optimization approach for the production of healthful pasta based on nonconventional flours. *J Food Process Eng* **35:** 601–621 (2012).

52. Watanabe K, Kawanishi-Asaoka M, Myojin C, Awata S, Ofusa K and Kodama K, Amino acid composition, oxidative stability, and consumer acceptance of cookies made with quinoa flour. *Food Sci Technol Res* **20:** 687–691 (2014).

53. Pagamunici LM, Gohara AK, Souza AHP, Bittencourt PRS, Torquato AS, Batiston WP, Gomes STM, Souza NE, Visentainer JV and Masushita M, Using chemometric techniques to characterize gluten-free cookies containing the whole flour of a new quinoa cultivar. *J Braz Chem Soc* **25:** 219–228 (2014).

54. Brito IL, de Souza EL, Felex SSS, Madruga MS, Yamashita F and Magnani M, Nutritional and sensory characteristics of gluten-free quinoa (*Chenopodium quinoa* Willd)-based cookies development using an experimental mixture design. *J Food Sci Technol* **52:** 5866–5873 (2015).

55. Drewnowski A, The science and complexity of bitter taste. *Nutr Rev* **59:** 163–169 (2001).

56. Koziol MJ, Afrosimetric estimation of threshold saponin concentration for bitterness in quinoa (*Chenopodium quinoa* Willd). *J Sci Food Agric* **54:** 211–219 (1991).

57. Heiniö RL, Noort MWJ, Katina K, Alam SA, Sozer N, de Kock HL, Hersleth M and Poutanen K, Sensory characteristics of wholegrain and bran-rich cereal foods - a review. *Trends Food Sci Technol* **47:** 25–38 (2016).

58. Kuljanabhagavad T and Wink M, Biological activities and chemistry of saponins from *Chenopodium quinoa* Willd. *Phytochem Rev* **8:** 473–490 (2009).

59. Challacombe CA, Abdel-Aal ESM, Seetharaman K and Duizer LM, Influence of phenolic acid content on sensory perception of bread and crackers made from red or white wheat. *J Cereal Sci* **56:** 181–188 (2012).

60. Heiniö RL, Liukkonen KH, Myllymäki O, Pihlava JM, Adlercreutz H, Heinonen SM and Poutanen K, Quantities of phenolic compounds and their impacts on the perceived flavour attributes of rye grain. *J Cereal Sci* **47:** 566–575 (2008).

61. Kobue Lekalake RI, Taylor JRN and De Kock HL, Effects of phenolics in sorghum grain on its bitterness, astringency and other sensory properties. *J Sci Food Agric* **87:** 1940–1948 (2007).

62. Soares S, Kohl S, Thalmann S, Mateus N, Meyerhof W and De Freitas V, Different phenolic compounds activate distinct human bitter taste receptors. *J Agric Food Chem* **61:** 1525–1533 (2013).

63. Jiang Deshou and Peterson DG, Identification of bitter compounds in whole wheat bread. *Food Chem* **141:** 1345–1353 (2013).

64. Brijs K, Bleukx W and Delcour JA, Proteolytic activities in dormant rye (*Secale cereale* L.) grain. *J Agric Food Chem* **47:** 3572–3578 (1999).

65. Heiniö RL, Nordlund E, Poutanen K and Buchert J, Use of enzymes to elucidate the factors contributing to bitterness in rye flavour. *Food Res Int* **45:** 31–38 (2012).

66. Singh B and Kaur A, Control of insect pests in crop plants and stored food grains using plant saponins: A review. *J Food Sci Technol* ***87:*** 93-101 (2018).

67. Osbourn AE, Saponins in cereals. *Phytochemistry* **62:**1–4 (2003).

68. Shi J, Arunasalam K, Yeung D, Kakuda Y, Mittal G and Jiang Y, Saponins from edible legumes: chemistry , processing , and health benefits. *J Med Food* **7:** 67–78 (2004).

69. Negi JS, Joshi GP, Rawat MS, Bisht VK and Singh P, Chemical constituents of *Asparagus*. *Pharmacogn Rev* **4:** 215–221 (2004).

70. Gupta K and Wagle DS, Nutritional and antinutritional factors of green leafy vegetables. *J Agric Food Chem* **36:** 472–474 (1988).

71. Taylor JRN and Parker ML, Quinoa, in *Pseudocereals and Less Common Cereals*, ed. by Belton PS and Taylor JRN, Berlin, pp. 93-122 (2002).

72. De Santis G, Maddaluno C, D'Ambrosio T, Rascio A, Rinaldi M and Troisi J, Characterization of quinoa (*Chenopodium quinoa* Willd.) accessions for the saponin content in Mediterranean environment. *Ital J Agron* **11:** 277–81 (2016).

73. Jarvis DE, Ho YS, Lightfoot DJ, Schmöckel SM, Li B, Borm TJA, Ohyanagi H, Mineta K, Michell CT, Saber N, Kharbatia NM, Rupper RR, Sharp AR, Dally N, Boughton BA, Woo YH, Gao G, Schijlen EGWM, Guo X, Momin AA, Negrão S, Al-Babili S, Gehring C, Roessner U, Jung C, Murphy K, Arold ST, Gojobori T, Van der Linden CG, van Loo EN, Jellen EN, Maughan PJ and Tester M, The genome of *Chenopodium quinoa*. *Nature*, **542:** 307–312 (2017).

74. Stuardo M and San Martín R, Antifungal properties of quinoa (*Chenopodium quinoa* Willd) alkali treated saponins against *Botrytis cinerea*. *Ind Crops Prod* **27:** 296–302 (2008).

75. San Martín R, Ndjoko K and Hostettmann K, Novel molluscicide against *Pomacea canaliculata* based on quinoa (*Chenopodium quinoa*) saponins. *Crop Prot* **27:** 310–319 (2008).

76. Güçlü-Ustündağ Ö and Mazza G, Saponins: properties, applications and processing. *Crit Rev Food Sci Nutr* **47:** 231–258 (2007).

77. Woldemichael GM and Wink M, Identification and biological activities of triterpenoid saponins from *Chenopodium quinoa*. *J Agric Food Chem* **49:** 2327–2332 (2001).

78. Madl T, Sterk H, Mittelbach M and Rechberger GN, Tandem mass spectrometric analysis of a complex triterpene saponin mixture of *Chenopodium quinoa*. *J Am Soc Mass Spectrom* **17:** 795–806 (2006).

79. Kuljanabhagavad T, Thongphasuk P, Chamulitrat W and Wink M, Triterpene saponins from *Chenopodium quinoa* Willd. *Phytochemistry* **69:** 1919–1926 (2008).

80. Troisi J, Di Fiore R, Pulvento C, D'Andria R, Vega-Gálvez A, Miranda M, Martínez EA and Lavini A, Saponins, in *State of the Art. Report of Quinoa in the World in 2013*, ed. by Bazile D, Bertero HD, Nieto C, Rome, pp. 267–277 (2015).

81. Singh B, Singh JP, Singh N and Kaur A, Saponins in pulses and their health promoting activities: a review. *Food Chem* **233:**540–549 (2017).

82. Gee JM, Price KR, Ridout CL, Wortley GM, Hurrell RF and Johnson IT, Saponins of quinoa (*Chenopodium quinoa*): effects of processing on their abundance in quinoa products and their biological effects on intestinal mucosal tissue. *J Sci Food Agric* **63:** 201–209 (1993).

83. Maradini Filho AM, Pirozi MR, Da Silva Borges JT, Pinheiro Sant'Ana HM, Paes Chaves JB and Dos Reis Coimbra JS, Quinoa: nutritional, functional and antinutritional aspects. *Crit Rev Food Sci Nutr* **57:** 1618–1630 (2017).

84. Southon S, Wright AJA, Price KR, Fairweather-Tait SJ and Fenwick GR, The effect of three types of saponin on iron and zinc absorption from a single meal in the rat. *Br J Nutr* **59:** 389–396 (1988).

85. Ruales J and Nair BM, Content of fat, vitamins and minerals in quinoa (*Chenopodium quinoa* Willd) seeds. *Food Chem* **48:** 131–136 (1993).

86. Cheeke PR, Actual and potential applications of *Yucca schidigera* and *Quillaja saponaria* saponins in human and animal nutrition. *J Anim Sci* **77:** 1–10 (2000).

87. Noble AC, Bitterness in wine. *Physiol Behav* **56:** 1251–1255 (1994).

88. Heiniö RL, Liukkonen KH, Katina K, Myllymäki O and Poutanen K, Milling fractionation of rye produces different sensory profiles of both flour and bread. *J Food Sci Technol* **36:** 577–583 (2003).

89. Hemalatha P, Bomzan DP, Rao BVS and Sreerama YN, Distribution of phenolic antioxidants in whole and milled fractions of quinoa and their inhibitory effects on α-amylase and α-glucosidase activities. *Food Chem* **199:** 330–338 (2016).

90. Rocchetti G, Chiodelli G, Giuberti G, Masoero F, Trevisan M and Lucini L, Evaluation of phenolic profile and antioxidant capacity in gluten-free flours. *Food Chem* **228:** 367–373 (2017).

91. Gordillo-Bastidas E, Díaz-Rizzolo D, Roura E, Massanés T and Gomis R, Quinoa (*Chenopodium quinoa* Willd), from nutritional value to potential health benefits: an integrative review. *J Nutr Food Sci* **6:** 1–10 (2016).

92. Asao M and Watanabe K, Functional and bioactive properties of quinoa and amaranth. *Food Sci Technol Res* **16:** 163–8 (2010).

93. Angelino D, Cossu M, Marti A, Zanoletti M, Chiavaroli L, Brighenti F, Del Rio D and Martini D, Bioaccessibility and bioavailability of phenolic compounds in bread: a review. *Food Funct* **8:** 2368–2393 (2017).

94. Mattila P, Pihlava JM and Hellström J, Contents of phenolic acids, alkyl- and alkenylresorcinols, and avenanthramides in commercial grain products. *J Agric Food Chem* **53:** 8290–8295 (2005).

95. Repo-Carrasco-Valencia R, Hellström JK, Pihlava JM and Mattila PH, Flavonoids and other phenolic compounds in Andean indigenous grains: quinoa (*Chenopodium quinoa*), kañiwa (*Chenopodium pallidicaule*) and kiwicha (*Amaranthus caudatus*). *Food Chem* **120:** 128–133 (2010).

96. Chauhan GS, Eskin NAM and Tkachuk R, Nutrients and antinutrients in quinoa seed. *Cereal Chem* **69:** 85–8 (1992).

97. Jensen S, Oestdal H, Skibsted LH, Larsen E and Thybo AK, Chemical changes in wheat pan bread during storage and how it affects the sensory perception of aroma, flavour, and taste. *J Cereal Sci* **53:** 259–268 (2011).

98. Bin Q and Peterson DG, Identification of bitter compounds in whole wheat bread crumb. *Food Chem* **203:** 8–15 (2016).

99. Lemieux L and Simard RE, Bitter flavour in dairy products. II. A review of bitter peptides from caseins: their formation, isolation and identification, structure masking and inhibition. *Lait* **72:** 335–385 (1992).

100. Ridout CL, Price KR, DuPont MS, Parker ML and Fenwick GR, Quinoa saponins - analysis and preliminary investigations into the effects of reduction by processing. *J Sci Food Agric* **54:** 165–176 (1991).

101. Quispe-Fuentes I, Vega-Gálvez A, Miranda M, Lemus-Mondaca R, Lozano M and Ah-Hen K, A kinetic approach to saponin extraction during washing of quinoa (*Chenopodium quinoa* Willd.) seeds. *J Food Process Eng* **36:** 202–210 (2013).

102. Quiroga C, Escalera R, Aroni G, Bonifacio A, Gonzalez JA, Villca M, Saravia R and Ruiz A, Traditional processes and technological innovations in quinoa harvesting, processing and industrialization, in *State of the Art. Report of Quinoa in the World in 2013*, ed. by Bazile D, Bertero HD, Nieto C, Rome, pp. 218–249 (2015).

103. Ruales J and Nair BM, Saponins, phytic acid, tannins and protease inhibitors in quinoa (*Chenopodium quinoa* Willd) seeds. *Food Chem* **48:** 137–143 (1993).

104. Repo-Carrasco R, Espinoza C and Jacobsen SE, Nutritional value and use of the Andean crops quinoa (*Chenopodium quinoa*) and kañiwa (*Chenopodium pallidicaule*). *Food Rev Int* **19:** 179–189 (2003).

105. Pappier U, Fernández Pinto V, Larumbe G and Vaamonde G, Effect of processing for saponin removal on fungal contamination of quinoa seeds (*Chenopodium quinoa* Willd.). *Int J Food Microbiol* **125:** 153–157 (2008).

106. Scanlin LA and Burnett C, Quinoa grain processing and products, US Patent, US2010/0196569 A1 (2010).

107. Dexter JE and Wood PJ, Recent applications of debranning of wheat before milling. *Trends Food Sci Technol* **7:** 35–41 (1996).

108. Bottega G, Caramanico R, Lucisano M, Mariotti M, Franzetti L and Pagani MA, The debranning of common wheat (*Triticum aestivum* L.) with innovative abrasive rolls. *J Food Eng* **94:** 75–82 (2009).

109. Gomez-Caravaca AM, Iafelice G, Verardo V, Marconi E and Caboni MF, Influence of pearling process on phenolic and saponin content in quinoa (*Chenopodium quinoa* Willd). *Food Chem* **157:** 174–178 (2014).

110. Konishi Y, Hirano S, Tsuboi H and Wada M, Distribution of minerals in quinoa (*Chenopodium quinoa* Willd.) seeds. *Biosci Biotechnol Biochem* **68:** 231–234 (2004).

111. Nickel J, Spanier LP, Botelho FT, Gularte MA and Helbig E, Effect of different types of processing on the total phenolic compound content, antioxidant capacity, and saponin content of *Chenopodium quinoa* Willd grains. *Food Chem* **209:** 139–143 (2016).

112. Dallagnol AM, Pescuma M, Rollán G, Torino MI and De Valdez GF, Optimization of lactic ferment with quinoa flour as bio-preservative alternative for packed bread. *Appl Microbiol Biotechnol* **99:** 3839–3849 (2015).

113. Poutanen K, Flander L and Katina K, Sourdough and cereal fermentation in a nutritional perspective. *Food Microbiol* **26:** 693–699 (2009).

114. Omary MB, Fong C, Rothschild J and Finney P, Effects of germination on the nutritional profile of gluten-free cereals and pseudocereals: a review. *Cereal Chem* **89:** 1–14 (2012).

115. Marengo M, Carpen A, Bonomi F, Casiraghi MC, Meroni E, Quaglia L, Iametti S, Pagani MA and Marti A,. Macromolecular and micronutrient profiles of sprouted chickpeas to be used for integrating cereal-based food. *Cereal Chem* **94:** 82-88 (2016).

116. Richter K, Christiansen K and Guo G, Wheat sprouting enhances bread baking performance. *Cereal Foods World* **59:** 231–3 (2014).

117. El-Adawy TA, Nutritional composition and antinutritional factors of chickpeas (*Cicer arietinum* L.) undergoing different cooking methods and germination. *Plant Foods Hum Nutr* **57:** 83–97 (2002).

118. Lazo Vélez MA, Guajardo Flores D, Mata Ramírez D, Gutiérrez Uribe JA and Serna Saldivar SO. Characterization and quantitation of triterpenoid saponins in raw and sprouted *Chenopodium berlandieri spp*. (Huauzontle) grains subjected to germination with or without selenium stress conditions. *J Food Sci* **81:** 19–26 (2016).

119. Ward SM, Response to selection for reduced grain saponin content in quinoa (*Chenopodium quinoa* Willd.). *F Crop Res* **68:** 157–63 (2000).

120. Ward SM, A Recessive allele inhibiting saponin synthesis in two lines of Bolivian quinoa (*Chenopodium quinoa* Willd.). *J Hered* **92:** 83–86 (2001).

121. Bhargava A, Shukla S and Ohri D, Chenopodium quinoa - an Indian perspective. *Ind Crops Prod* **23:** 73–87 (2006).

122. Spehar CR and Rocha JES, Exploiting genotypic variability from low-altitude Brazilian savannah-adapted *Chenopodium quinoa*. *Euphytica* **175:** 13–21 (2010).

123. De Santis G, D'Ambrosio T, Rinaldi M and Rascio A, Heritabilities of morphological and quality traits and interrelationships with yield in quinoa (*Chenopodium quinoa* Willd.) genotypes in the Mediterranean environment. *J Cereal Sci* **70:** 177–185 (2016).

124. Masterbroek HD, Limburg H, Giles T and Marvin HJ, Ocurrence of sapogenins in leaves and seeds of quinoa (*Chenopodium quinoa* Willd). *J Sci Food Agric* **80:** 152–156 (2000).

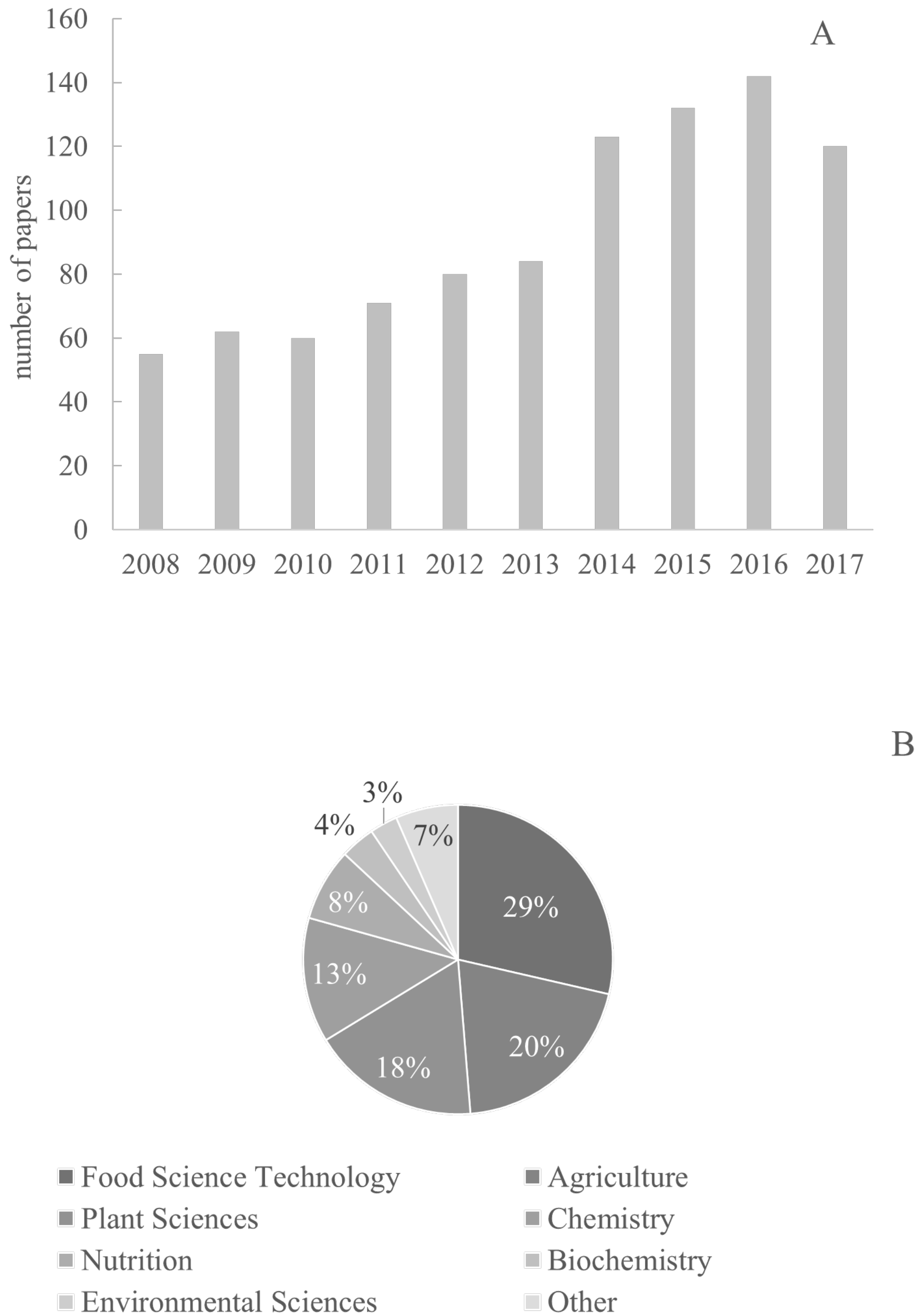

Figure 1. Papers on quinoa (A) and the related distribution in the main research areas (B) (source: Web of Science; 2008-2017; updated to August 31th, 2017).

Table 1. Topics of the main reviews published on quinoa (source: Web of Science; 2008-2017; updated to August 31th, 2017)

Research area	**Topic**	**References**
Agriculture/Agronomy	Breeding	Zurita-Silva *et al.*[5]
	Structure	Burrieza *et al.*[6]
	Cultivation	Bazile *et al.*[7]
	Sustainability	Choukr-Allah *et al.*[8] Ruiz *et al.*[9]
Nutrition/Health benefits	Weight gain	Simnadis *et al.*[10]
	Lipid profile	Simnadis *et al.*[10]
	Antioxidant activities	Simnadis *et al.*[10] Tang & Tsao[11]
	Anti-inflammatory activities	Tang & Tsao[11]
	Anti-obesity and anti-diabetic activities	Tang & Tsao[11] Navruz-Varli & Sanlier[12]
	Cardiovascular disease and other chronic diseases	Tang & Tsao[11] Navruz-Varli & Sanlier[12]
	Celiac disease safety	Tang & Tsao[11]
Food Science and Technology	Compositional, nutritional and functional aspects	Navruz-Varli & Sanlier[12] Maradini-Filho *et al.*[13] Vega-Galvez *et al.*[14] Jancurová *et al.*[15]
	Product development	Graf *et al.*[16] Wang & Zhu[17]
	Protein functionality	Janssen *et al.*[18]

Table 2. Hypothesis of key mechanisms leading to bitterness in quinoa (adapted from Heiniö *et al.*[57])

Compound	**Mechanism**	**References**
Saponins	Molecule properties	Kuljanabhagavad & Wink[58]
Phenolic compounds	Release of unbound flavour-active phenolic compounds	Challacombe *et al*.[59] Heiniö *et al*.[60] Kobue-Lekalake *et al*.[61] Soares *et al*.[62]
Peptides/aminoacids	Proteolysis of the albumins and proteolysis of globulins forming bitter peptides	Jiang & Peterson[63] Brijs *et al*.[64] Heiniö *et al*.[65]

Table 3. Approaches to decrease bitterness in quinoa

Approach	Type of effect	Advantages	Disadvantages
Washing	Direct effect: saponin solubilisation from the seed layers	Low investment Efficiency	Drying cost Water contamination Possibility of grain germination
Pearling	Direct effect: Mechanical removal of seed layers which contain saponins	No drying costs No water need and contamination	Limited efficiency Loss in bioactive compounds
Pearling and washing	Direct effect: Mechanical removal of seed layers which contain saponins and saponin solubilisation from the seed layers	Low washing and drying time cost Low water need Low amount of broken seeds High efficiency	Water contamination Loss in bioactive compounds
Fermentation	Indirect effect: masking of bitterness by aroma compounds and sugar formation	Widespread knowledge Side advantages (nutritional, technological and sensory characteristics) No/limited equipment costs	Refreshment required Time-consuming
Germination	Indirect effect: masking of bitterness by sugar formation	Widespread knowledge Side advantages (nutritional, technological and sensory characteristics) No/limited equipment costs	Standardization Possibility of mold growth
Breeding	Direct effect: Development of sweet cultivars	Low environmental impact	Limited number of varieties