Invited Review

NUTRITIONAL COMPOSITION AND BIOACTIVE COMPONENTS OF MASHUA (*Tropaeolum tuberosum* Ruiz and Pavón)[1]

[COMPOSICIÓN NUTRICIONAL Y COMPONENTES BIOACTIVOS DE LA MASHUA (*Tropaeolum tuberosum* Ruiz y Pavón)]

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SUMMARY

The objective of this revision is to collect information about the chemical and nutritional composition and the bioactive components of mashua; an economically important tuber in the Andean region. This tuber has a high content of bioactive compounds (total phenols, Flavin 3-ols, anthocyanins, proanthocyanins, carotenoids, triterpenes, steroids, flavones and leucoanthocyanidins) which confers it with therapeutic and medicinal properties that have allowed it to be used since pre-Hispanic times, which has elicited a peak in scientific interest in recent years. Recent studies have reported the efficient use of mashua in treating benign prostatic hyperplasia, cancer, as well as chelating properties in metallic ions to remove peroxyl radicals. However, other studies find evidence of negative effects caused by the tuber due to the presence of thiocyanates that when releasing hydrocyanic block oxygen transportation in red blood cells, whilst tannins diminish voluntary feeding of poly-gastric animals, reducing digestibility and productivity. On the other hand, the bioactive components and nutritional composition of the tuber are high in relation to various Andean tubers and certain fruit that have demonstrated an important scientific contribution in medicine and industry

Keywords: antioxidant capacity, *Tropaeolum tuberosum*, phenols, glucosinolates, anthocyanins, flavonoids.

RESUMEN

El objetivo de esta revisión es recopilar información sobre la composición química y nutricional y los componentes bioactivos de mashua; un tubérculo económicamente importante en la región andina. Este tubérculo tiene un alto contenido de compuestos bioactivos (fenoles totales, Flavin 3-oles, antocianinas, proantocianinas, carotenoides, triterpenos, esteroides, flavonas y leucoantocianidinas) que confiere con propiedades terapéuticas y medicinales que han permitido que sea utilizado desde la época pre-hispánica, y ha despertado un gran interés científico en los últimos años. Estudios recientes han reportado el uso eficiente de mashua en el tratamiento de la hiperplasia prostática benigna, cáncer, así como, las propiedades quelantes en iones metálicos para eliminar los radicales peroxilo. Sin embargo, otros estudios encuentran evidencia de efectos negativos causados por el tubérculo debido a la presencia de tiocianatos que cuando al liberar hidrocianato bloquean el transporte de oxígeno a los glóbulos rojos, mientras que los taninos disminuyen la alimentación voluntaria de los animales poligástricos, lo que reduce la digestibilidad y la productividad. Por otro lado, los componentes bioactivos y la composición nutricional del tubérculo son altos en relación con varios tubérculos andinos y ciertos frutos que han demostrado una importante contribución científica en medicina e industria.

Palabras clave: capacidad antioxidante, *Tropaeolum tuberosum*, fenoles, glucosinolatos, antocianinas, flavonoides

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INTRODUCTION

In the inter-Andean region the domestication of roots and tubers such as *Tropaeolum tuberosum* began in the Andes, and though the exact date is unknown it is estimated to be around 5500 AC (Flannery, 1973 as cited by King and Gershoff, 1987). The tuber originated in Peru and Bolivia (León, 1964), but its cultivation has extended to other countries of the plateau, such as Ecuador, Venezuela, Colombia, (Chirinos et al., 2007), the north of Argentina, and for many years regions of New Zealand, Canada (Manrique et al., 2013), United States and England (National Research Council, 1989). In Andean countries the tuber is sown at an altitude range of between 2400 and 4300 masl and at cool temperatures that vary between 8 and 11°C (Grau et al., 2003). It is a crop that adapts to poor soils that don't need fertilization, and being a rustic plant it is resistant to plagues, nematodes and insects (Manrique et al., 2013). In Ecuador and Cuzco mashua can yield over 70000 kg/ha in experimental plots (Arbizu and Tapia, 1992; Hermann, 1992 citado por Barrera et al., 2004) in Bolivia fields have yielded between 30 and 60 t/ha and in Peru values range between 4 and 7 t/ha (Cadima et al., 2003b citado por Cadima, 2006).

Of all Andean crops mashua has the least importance in Peru, Ecuador and Bolivia (Cadima, 2006). In Ecuador production of the tuber is decreasing, as well as its genetic variability as is the case of yellow and black mashua; the reasons for this being the low culinary status of the tuber (rusticity and poverty), nescience of the beneficial properties and methods of preparation, as well as the bitter and slightly spicy flavor (Barrera et al., 2004). On the other hand in Colombian markets mashua is one of the most commercial tubers sold in large quantities, while in Peru and Bolivia it is in low demand (Surco, 2004).

Mashua contains a significant value of bioactive compounds which has evidenced its role in the prevention of various diseases, these beneficial effects have been linked to the existence of certain metabolites like glucosinolates, polyphenols, anthocyanins, among others. The glucosinolates in the plant act as a natural defense against plagues and diseases; different studies have reported more than a hundred types of glucosinolates some of which have are beneficial to the health as anticarcinogens, but there are others that could act as antinutrients (Roca et al., 2005). These metabolites are popular in traditional medicine due to their antibiotic, nematicide and diuretic properties (Johns et al., 1982), some authors have linked their effect to kidney problems, liver pains, urinary disorders, anaphrodisiac properties(Hodge, 1951 as cited by Pissard et al., 2008) and anticarcinogen effects in cancerous cells of the colon and prostate (Norato et al., 2004 as cited by Roca et al., 2005). For this reason, the objective of this study is to analyze the scientific evidence available through literature regarding the role of the bioactive compounds of mashua in human health and to supply a contribution that enriches the current knowledge about the nutritional composition of the tuber.

Characterization and morphology of mashua

Mashua is a rustic tuber with a cultivation cycle of 6 to 9 months, it is an herbaceous plant with a glabrous that is 20-30 cm tall, the tuber is a schizocarp separated into three mericarps with a rugged surface; some Ecuadorian morphotypes have 2 to 5 mericarps when ripe. The form can be conic, lengthened conic and lengthened (Cardenas, 1989; Grau et al., 2003; Barrera et al., 2004; Cadima, 2006 as cited in Cadima 2006), with erect growth, that later varies to semi prostrate when ripe (Tapia and Fries, 2007), with leaves that are solitarily distributed along the branch separated by internodes that are 1-8 cm with a 2-30 cm long petiole (Cardenas, 1989). In mashua collections from Ecuador, Peru, and Bolivia pigmented nerves have been found on the underside of the leaves (Cadima, 2006). The flowers are solitary, zygomorphs that grow from the axils of the leaves (Tapia and Fries, 2007). The surface of the tuber has a variety of colors of which prevail a yellow orange, deep yellow, light yellow, yellow, yellowish white, brown, black, intense grayish red and a secondary surface of a purple, grayish purple, yellow, grayish red, deep grayish red, light red (pink), or predominantly orange yellow with orange or blackish eyes and bands or irregular spots on tuberizations (Manrique et al., 2013).

Nutritional Composition

Mashua is a food that is highly nutritional (Table 1), that is characterized by containing a high level of protein of an elevated biological value with an ideal balance of essential amino acids. To the proteins add a high level of energy content, fiber, vitamin B1 y B2. According to Barrera et al. (2004) his tuber stands out from the other Andean roots (miso, jicama, oca, white carrot, melloco and achira) because of its content of vitamin C and elevated quantity of provitamin A (equivalents of Retinol) especially in the varieties ECU-1128 y ECU-1089. Among the minerals, those of highest concentration are phosphorus and magnesium followed by zinc and iron. In addition, its low contribution in Na and high content in K makes this tuber ideal for hypertensive people. Mashua contains various metabolites, including phenolic compounds, antioxidants, anthocyanins, isothiocyanates, and glucosinolates (National Research Council, 1989; Barrera et al., 2004; Campos et al., 2006; Manrique et al., 2013)

Table 1. Nutritional Composition of mashua (*Tropaeolum tuberosum* Ruiz y Pavón)

Parameter	WBR	WBA	DBR	DBA	References
Humid (%)	n/i	n/i	78.3 – 92.4	84.5	Gross et al. (1989); King and Gershoff (1987)
Proteins (%)	n/i	n/i	6.9 – 15.7	7.7	Gross et al. (1989); King and Gershoff (1987)
Carbohydrates (%)	n/i	n/i	69.7 – 79.5	85.8	Gross et al. (1989); King and Gershoff (1987)
Fat material (%)	n/i	n/i	– 0.4	1.0	Gross et al. (1989); King and Gershoff (1987)
Raw fiber (%)	n/i	n/i	7.8 – 8.6	0.7	Gross et al. (1989); King and Gershoff (1987)
Ash (%)	n/i	n/i	4.0 – 6.5	4.8	Gross et al. (1989); King and Gershoff (1987)
Ca (%)	n/i	n/i	n/i	0.006	Espín et al. (2001)
P (%)	n/i	n/i	n/i	0.32	Espín et al. (2001)
Mg (%)	n/i	n/i	n/i	0.11	Espín et al. (2001)
Na (%)	n/i	n/i	n/i	0.044	Espín et al. (2001)
K (%)	n/i	n/i	n/i	1.99	Espín et al. (2001)
Cu (ppm)	n/i	n/i	n/i	9.0	Espín et al. (2001)
Fe (ppm)	n/i	n/i	n/i	42.0	Espín et al. (2001)
Mn (ppm)	n/i	n/i	n/i	7.0	Espín et al. (2001)
Zn (ppm)	n/i	n/i	n/i	48.0	Espín et al. (2001)
Energy (Kcal/g)	n/i	n/i	4.19 – 4.64	4.41	Espín et al. (2001)
Starches (%)	n/i	n/i	20.01 – 79.46[a]	48.31[a]	Espín et al. (2001)
Total Sugars (%)	n/i	n/i	6.77 – 55.23[b]	28.42[b]	Espín et al. (2001)
Reducing sugars (%)	n/i	n/i	6.41 – 45.29[b]	23.65[b]	Espín et al. (2001)
Vitamin A ß-carotene (µg/100 g)	n/i	10	n/i	n/i	Collazos et al. (1996) as cited by Grau et al. (2003)
Provitamine A (Eq. Retinol /100 g)	n/i	73.56	n/i	n/i	Espín et al. (2001)
Vitamine C (mg/100 g)	n/i	77.37	n/i	n/i	Espín et al. (2001)
Lysine (mg/g of protein)	35 – 69	n/i	n/i	n/i	Grau et al. (2003); King and Gershoff (1987)
Threonine (mg/g of protein)	22 – 46	n/i	n/i	n/i	Grau et al. (2003); King and Gershoff (1987)
Valine (mg/g of protein)	25 – 88	n/i	n/i	n/i	Grau et al. (2003); King and Gershoff (1987)
Isoleucine (mg/g of protein)	25 – 44	n/i	n/i	n/i	Grau et al. (2003); King and Gershoff (1987)
Leucine (mg/g of protein)	35 – 56	n/i	n/i	n/i	Grau et al. (2003); King and Gershoff (1987)
Tyrosine (mg/g of protein)	13 – 62	n/i	n/i	n/i	Grau et al. (2003); King and Gershoff (1987)
Tryptophan (mg/g of protein)	5 – 12	n/i	n/i	n/i	Gross et al. (1989); Grau et al. (2003)
Cysteine (mg/g of protein)	1.4 – 29	n/i	n/i	n/i	Gross et al. (1989); Grau et al. (2003)

[a] Sample free from sugars and pigments. [b] Values obtained from sugars such as % Glucose. n/i = no available information. WBR: Wet Base Range. WBA: Wet Base Average. DBR: Dry Base Range. DBA: Dry Base Average.

The fraction of carbohydrate consists mainly of starch, in the form of granules, whose components are amylose 27% and amylopectin 73%, and 85% digestible starch with a fraction of 15% that is not absorbed at the level of the gastrointestinal tract (Villacrés and Espín, 1999 cite by Barrera et al., 2004). The granules of starch are smaller than in other tubers such as oca and ulluco with oval, spherical, and truncated sizes between 4.39 and 16.29 μm in length and 4.07 and 13.09 μm in diameter (Valcárcel-Yamani et al., 2013). Composed of 2-3 grains that are not very similar (Surco, 2004); which are stable in heat but with the tendency of gelification, with a lower water solubility index 0.62 ± 0.05, higher water absorption index 1.95 ± 0.04 and low swelling power 1.95 ± 0.02 (Villacrés and Espín, 1999 as cited by Barrera et al., 2004).

Bioactive Components

Bioactive compounds or phytochemicals are very important components of plants due to their therapeutic contribution to health. Studies in Mashua have shown a high content of bioactive compounds when compared to other Andean crops (Campos et al., 2006). Researchers have identified total phenols, Flavin 3-ols, anthocyanins, proanthocyanins, carotenoids (Chirinos et al., 2007), triterpenes, steroids, flavones and leucoanthocyanidins as shown in Table 2 (Barrera et al., 2004).

Polyphenols

Phenolic compounds or polyphenols are part of the plant secondary metabolites or phytochemical. Its basic structure is a molecule of phenol linked to one or more hydroxyl groups and an aromatic ring. These compounds are widely distributed in different plants, for example fruits, vegetables, roots and cereals (Peñarrieta et al., 2014). Studies with Andean tubers such as mashua, native potato, oca and ulluco have shown significant differences in the content of these metabolites, of which Mashua has the highest phenolic content (Campos et al., 2006). Polyphenols accumulate in higher concentration in purple genotypes unlike yellow varieties. The genotype ARB-5241 is the most remarkable with a total value of 3.37 mg eq. chlorogenic acid/g fresh weight.

Another important subgroup are anthocyanins that are partly responsible for the organoleptic quality of food (Tomás-Barberán, 2003). According to Campos et al. (2006) the purple mashua (standing out the genotype DP-0224) has demonstrated a higher anthocyanin content with respect to tubers such as the native oca and potato. The anthocyanin content of the tuber ranges from 0.5 to 2.05 mg. eq. cyanidin3-glycoside/g fresh weight. A detailed study by Chirinos et al. (2006) identified in extracts of mashua in 11 sub fractions of anthocyanins. These metabolites are derivatives of delphinidin (delphinidin-3-glycoside-5-acetyl rhamnoside and delphinidin-3-sophoroside-5-acetyl rhamnoside, other pigments were delphinidin-3-glucoside-5-rhamnoside, delphinidin-3-sophoroside-5 -ramnoside, delphinidin-3-glycoside, cyanidin-3-sophoroside, cyanidin-3-sophoroside-5-rhamnoside, cyanidin-3-glycoside, cyanidin-3-rutinoside, pelargonidin 3-sophoroside and pelargonidin 3-sophoroside-5-rhamnoside).

Moreover, Chirinos et al. (2008 b) characterized non-anthocyanin phenolic compounds in purple mashua genotypes. The sub-fractions identified corresponded to Flavan-3ol (gallocatechin, epigallocatechin, epicatechin and its derivatives), procyanidin B2, hydroxycinnamic acids (derivatives of o-coumaric acid and p-coumaric acid) and p-hydroxybenzoic acid (derivatives of gallic acid, hydroxybenzoic acid and protocatequico), proanthocyanidins and anthocyanidins (delphinidin). Another important metabolite in the mashua tuber and with antioxidant properties are the carotenoids. The same study by the researchers Campos et al. (2006) shows a content that varies between 1 to 25 mg carotene/g in fresh weight in yellow genotypes (the varieties ARB-5576, M6COL2C and DP-0207 stand out). Total carotene values are higher than those registered in commercial potatoes, native potatoes and papaya, but lower compared to foods such as tomato, mango and carrot as shown in Table 3.

Glucosinolates

Eight types of glucosinolates have been identified in the Tropaeolaceae family such as glucotropaeoline, glucolepidiin, glucosinalbine, glucoconringiina, glucoaubrietina, glucoputranjivina, glucococleorina and glucorafenina all derived from amino acids (Fahey et al., 2001; Bayer and Appel, 2003 ; Ramallo et al., 2004).

The identification of the principle glucoaubrietin (4-methoxybenzyglucosinolate) in the Tropaeolum tuberosum species by Ruíz and Pavón. Later three other aromatic glucosinolates were identified by Ortega et al. (2006): 4-hydroxybenzyl glucosinolate (OHB, Glucosinalbine), benzyl glucosinolate (B, Glucotropaeoline), m-methoxybenzyl glucosinolate (MOB, Glucolimnatin). The glucosinolates are the precursors of the isothiocyanates distributed in sixteen families of dicotyledonous angiosperms and domestic species (Fahey et al., 2001).

The cultivated species *Tropaeolum tuberosum* sub-specie tuberosum (seeds tuber, leaves and flowers) present p-methoxybenzyl isothiocyanate and N, N-di (methoxy-4-benzyl) thiourea and in the wild species Tropaeolum tuberosum subspecies wild were identified benzyl-isothiocyanate, 2-propyl-isothiocyanate, 2-butyl-isothiocyanate and N, N- di (4-methoxybenzyl) thiourea (Johns and Neil, 1981). Numerous studies point out the medicinal properties of glucosinolates and their derivatives, among them Benzyl-isothiocyanate as responsible for acting against tumor cells and which is associated as an anticancer agent and p-methoxy-benzyl glucosinolate

Table 2. Bioactive components and reference values in dry and wet bases

Components	Units	Wet base	Dry base	References
Total Phenolics	mg eq. Chlorogenic acid/g		9 – 21[a]	Chirinos et al., (2007)
	mg eq. Chlorogenic acid/g	0.92 – 3.37[d]		Campos et al., (2006)
	mg eq. Gallic acid/100g	174.9 – 374.4[g]		Chirinos et al., (2006)
	mg eq. Gallic acid/100g	311– 343[h]		Aro and Tipacti (2016)
Flavan–3 oles	mg eq. catechin /g		0.2 – 5.3[a]	Chirinos et al., (2007)
Anthocyanins	mg. eq. Cyanidin3-glycoside/g		2.4-5.7[a]	Chirinos et al., (2007)
	mg. eq. Cyanidin3-glycoside/100g	45.5 – 131.9[g]		Chirinos et al., (2006)
	mg. eq. Cyanidin3-glycoside/g	0.5 – 2.05[c]		Campos et al., (2006)
Carotenoids	µg eq. β carotene/g		70-132[a]	Chirinos et al., (2007)
	µg eq. β carotene/g	1 – 25[b]		Campos et al., (2006)
Antioxidant Capacity	µmol equivalent of Trolox/g ABTS		80 – 378[a]	Chirinos et al., (2007)
	µmol equivalent of Trolox/g ABTS	16.2 – 45.7[g]		Chirinos et al., (2006)
	µmol equivalent of Trolox/g ABTS	35 – 92[h]		Calsin et al., (2016)
	µmol equivalent of Trolox/g ORAC)		59 – 389[a]	Chirinos et al., (2007)
Hydrophilic antioxidant capacity	µg equivalent of Trolox/g ABTS	955 – 9800[e]		Campos et al., (2006)
Lipophilic antioxidant capacity	µg equivalent of Trolox/g ABTS	93 – 279[f]		Campos et al., (2006)
Glucosinolates (antinutrient)	µmol/g		36.5 – 90.0[i]	Ramallo et al., (2004)
	µmol/g		0.27 – 50.74	Ortega et al., (2006)
Linolenic acid	%		48.70[j]	Ramallo (2004)
α-linolenic acid	%		22.13[j]	Ramallo (2004)
Palmitic acid	%		21.2[j]	Ramallo (2004)
Oleic acid	%		3.96[j]	Ramallo (2004)
Stearic acid	%		1.47[j]	Ramallo (2004)
Vacnic acid	%		1.30[j]	Ramallo (2004)

[a] Genotypes ARB 5241, DP 0224 y AGM 5109. [b] Genotypes ARB- 5576, M6COL2C y DP-0207 (highest values). [c] Genotypes colored. [d] Genotypes ARB-5241, DP-0224 y AGM-5109 (highest values). [e] Genotypes ARB-5241, DP- 0224 y ARV-5366 (highest values). [f] Genotypes M6COL2C, ARV-5366 y DP-02-03 (highest values). [g] Genotypes ARB-5241, DP-0224 y AGM-5109. [h] Genotypes ARB-5241, DP-5366 y AGM-0224. [i] Variety Kulli kisaño, Kellu anaranjado, Kellu cheschi, Kellu A, Zapallo, Kellu B. [j] Variety Kulli kisaño, Kellu anaranjado, Kellu cheschi, Kellu A, Zapallo, Kellu B.

which is related to reproductive function (Johns et al., 1982; Hasegawa et al., 1992; Pintao et al., 1995 cite by Quispe et al., 2015).

A recent study developed in male Holtzman rats demonstrated the efficacy of mashua with benign prostatic hyperplasia (BPH). The researchers used three doses of which the second dose (500mg/kg/rat) and third dose (800mg/kg/rat). Rats treated with the tuber obtained the best results in echo-graphic and histopathological studies, despite this, the effects of mashua was not superior to finasteride (antiandrogenic drug used for BPH); concluding that the two methods were efficient against BPH (Aire-Artezano et al., 2013).

Fatty Acids

Ramallo (2004) investigated fatty acids in the mashua flour via gas phase chromatography. The author pointed out a high content of polyunsaturated fatty acids (70.8%), among six varieties of mashua; highlighting the presence of linoleic acid n-6 (48.70%), α-linolenic n-3 (22.13%), palmitic (21.2%), and with less importance oleic acid n-9 (3.96%), stearic (1.47%) and Cis-vacénico (1.30%). The ratio between linoleic/α-linolenic acids for mashua was 2.2, compared with other vegetables such as rapeseed is 2.49; walnut is 4.64. It's value is optimal according to the nutritional recommendations that establishes a ratio less than 5. The study of polyunsaturated fatty acids of the series: n-3, n-6 and n-9 are of interest due to their therapeutic properties. Polyunsaturated fatty acids (PUFAs) n-3 and n-6 are necessary during pregnancy, specifically for the child's fetal and cognitive brain development (Rodríguez-Cruz et al., 2005). α-linolenic acid (n-3) acts in the prevention of coronary diseases, inhibiting angiogenesis, possessing cytotoxic activity on tumor cells and reducing blood cholesterol levels (Serrano et al., 2006). Linoleic acid (n-6) reduces cholesterol levels. Deficiencies of linoleic acid (n-6) involves inflammatory processes at the level of animal and human skin. Excessive consumption of n-6 PUFAs suggests a tendency to acquire some type of cancer, mitochondrial DNA damage and cardiac disorder (Rodríguez-Cruz et al., 2005; Urango et al., 2008).

Flavonoids

Chirinos et al. (2008) have shown that phenolic compounds such as anthocyanidins, Flavan monomers 3 oles, flavonols and proanthocyanins contribute to the antioxidant capacity of mashua, the latter metabolite being the most significant. The author and his collaborators have reported a range of 34.7 - 39.2% of the condensed tannin.

Proanthocyanins are complex structures derived from flavan-3-oles (Peñarrieta et al., 2014), and are important for their health benefits. These metabolites are attributed to have antioxidant, anti-carcinogenic, cardioprotective, antimicrobial and neuroprotective properties (Navarro et al., 2013). Studies in animals show an inhibitory effect against the oxidation of tissues and low density lipoproteins are preventing the formation of thrombi in the circulatory system, in addition they kidnap and neutralize free radicals (Vázquez- Flores et al., 2012).

The content of flavan-3-oles in the mashua tuber varies between 0.2 - 5.3 mg eq. catechin / g (Chirinos et al., 2007). Flavan-3-oles, flavanols or flavanols, are considered minor flavonoids chemically formed by a C ring and an OH group in the 3-position of the heterocyclic 2-phenylbenzopyran (Peñarrieta et al., 2014; Soriano, 2003). Studies on the benefits of flavan 3 oles mention its ability to regulate the synthesis of glutathione known for its antioxidant power and stabilizes or deactivates free radicals that attack cells and damages them (Moskaug et al., 2005). Regarding the anti-cancer activity, Torres et al. (2002) report that flavan-3-ols decrease the increase of cancer cells, especially those that come from the human colon. An unwanted effect due to the high intake of these flavonoids can lead to a leukemia in the case of infants. In addition to inhibiting certain enzymes such as topoisomerases responsible for acting on the DNA topology (Moskaug et al., 2005).
Other metabolites reported in mashua by Chirinos et al. (2006) are the anthocyanins that vary between 45.5-131.9 mg. eq. cyanidin3-glycoside / 100g. They are an extensive group of water soluble pigments responsible for a high range of colors and are present in the plant kingdom (Fenema, 1993 as cited by Ortíz et al., 2011).

Anthocyanins are considered a subclass of flavonoids. Approximately 300 anthocyanins have been identified, however, the most important are: Pelargonidin, delphinidin, cyanidin, petunidin, peonidin and malvidin known as anthocyanidins because of the combination of these with different sugars. Its coloration depends on factors such as: ph effect, union with other compounds and ions, effects of enzymes, acids, presence of oxygen, the increase of hydroxyl phenolic ring in its chemical composition generates blue color and an increase in methoxyl generates red color (Badui, 2006). The importance of anthocyanins lies mainly in the benefits for human health (De Pascual-Teresa and Sanchez-Ballesta, 2008) due to it's farmalogical and therapeutic conditions (Astrid, 2008).

The therapeutic relationship of anthocyanins is given by its antioxidant activity (Ghiselli et al., 1998). Investigations carried out live and in vitro demonstrate that cyanine extracted from red beans that are more rhamnose; Red soy which has glucose play an important role in immunological effects, especially in the suppression or prevention of tumors (Koide et al., 1997). Cyanidin presents greater antimutagenic activity than peonidin (Yoshimoto et al., 2001). The flavonoids present in some fruits and vegetables are important in the human diet (Yoshimoto et al., 2001). For example, the content of flavonoids present in strawberries and spinach, avoided effects of neural and cognitive aging (Joseph et al., 1998). According to varios studies, three types of pigments have been identified (antioxidants, flavonoids, anthocyanins and carotenoids) that help with the reduction of degenerative diseases in humans, such as cancer and coronary diseases (Badui, 2006).

Table 3. Bioactive components and referential values for different vegetables

Component	Units	Range	References
Antioxidant Capacity			
Sweet potato	(µg equivalent of Trolox/g Fresh weight DPPH)	12 409 ± 1024	Cevallos-Casals and Cisneros-Zevallos (2003)
Purple Corn	(µg equivalent of Trolox/g Fresh weight DPPH)	21 351 ± 121	Cevallos-Casals and Cisneros-Zevallos (2003)
Cranberries	(µg equivalent of Trolox/g Fresh weight DPPH)	5646 ± 389	Cevallos-Casals and Cisneros-Zevallos (2003)
Hydrophilic antioxidant capacity			
Native Potatoes	(µg equivalent of Trolox/g Fresh weight ABTS)	860 – 3780	Campos et al. (2006)
Oca	(µg equivalent of Trolox/g Fresh weight ABTS)	1637 – 4771	Campos et al. (2006)
Ulluco	(µg equivalent of Trolox/g Fresh weight ABTS)	483 – 1524	Campos et al. (2006)
Cranberry	(µg equivalent of Trolox/g Fresh weight ABTS)	6900 – 9572	Roca et al. (2007)
Lipophilic antioxidant capacity			
Native Potatoes	(µg equivalent of Trolox/g Fresh weight ABTS)	115 – 361	Campos et al. (2006)
Oca	(µg equivalent of Trolox/g Fresh weight ABTS)	69 – 320	Campos et al. (2006)
Total phenolics			
Ulluco	(mg eq. Chlorogenic acid/g Fresh weight)	0.41 – 0.77	Campos et al. (2006)
Oca	(mg eq. Chlorogenic acid/g Fresh weight)	0.71 – 1.32	Campos et al. (2006)
Potato	(mg eq. Chlorogenic acid/g Fresh weight)	0.64 – 2.32	Campos et al. (2006)
Blackberries	(mg eq. Gallic acid/100g Fresh weight)	226 ± 4.1	Wang Shiow and Lin (2000)
Black raspberries	(mg eq. Gallic acid/100g Fresh weight)	267 ± 4.3	Wang Shiow and Lin (2000)
Raspberries	(mg eq. Gallic acid/100g Fresh weight)	234 ± 5.1	Wang Shiow and Lin (2000)
Strawberry	(mg eq. Gallic acid/100g Fresh weight)	103 ± 2.0	Wang Shiow and Lin (2000)
Sweet potato	(mg eq. Chlorogenic acid/100g Fresh weight)	1756 ± 64	Cevallos-Casals and Cisneros-Zevallos (2003)
Purple corn	(mg eq. Chlorogenic acid/100g Fresh weight)	945 ± 82	Cevallos-Casals and Cisneros-Zevallos (2003)
Cranberries	(mg eq. Chlorogenic acid/100g Fresh weight)	574 ± 35	Cevallos-Casals and Cisneros-Zevallos (2003)
Anthocyanin			
Ulluco	(mg. eq. Cyanidin3-glycoside/g Fresh weight)	0.41 – 0.77	Campos et al. (2006)
Oca	(mg. eq. Cyanidin3-glycoside/g Fresh weight)	0.14 – 1.3	Campos et al. (2006)

Table 3. Continuation

Component	Units	Range	References
Potato	(mg. eq. Cyanidin3-glycoside/g Fresh weight)	0.08 – 0.8	Campos et al. (2006)
Blackberries	(mg. Eq. Cyanidin3-glycoside/100 g Fresh weight)	152.8 ± 8.0	Wang Shiow and Lin (2000)
Black raspberries	(mg. Eq. Cyanidin3-glycoside/100 g Fresh weight)	197.2 ± 8.5	Wang Shiow and Lin (2000)
Raspberries	(mg. Eq. Cyanidin3-glycoside/100 g Fresh weight)	68.0 ± 3.0	Wang Shiow and Lin (2000)
Strawberry	mg. Eq. Pelargonidin 3 glycoside/100g Fresh weight)	31.9 ± 4.1	Wang Shiow and Lin (2000)
Sweet potato	(mg. Eq. Cyanidin3-glycoside/100 g Fresh weight)	1642 ± 92	Cevallos-Casals and Cisneros-Zevallos (2003)
Purple corn	(mg. Eq. Cyanidin3-glycoside/100 g Fresh weight)	182 ± 2	Cevallos-Casals and Cisneros-Zevallos (2003)
Cranberries	(mg. Eq. Cyanidin3-glycoside/100 g Fresh weight)	276 ± 25	Cevallos-Casals and Cisneros-Zevallos (2003)
Carotenoids			
Oca	(µg eq. β-carotene/g Fresh weight)	2 – 25	Campos et al. (2006)
Tomato	(µg β-carotene/g Fresh weight)	56 – 210	Gross (1987)
Papaya	(µg β-carotene/g Fresh weight)	4.08	Gross (1987)
Mango	(µg β-carotene/g Fresh weight)	74.3	Gross (1987)

Tannins

In the plants there is a diversity of secondary compounds that when consumed create a toxic effect as a defensive response to attack by predators. Tannins and certain phenolic compounds constitute the chemical protection of the plant (Chaves, 1994; Sepúlveda et al., 2003). Different varieties of mashua contain condensed tannins at a value of 2210 mg.eq. catechin / 100 g (López, 2001 as cited by Urresta, 2010). Condensed tannins are derivatives of flavan-3-oles; they are found in leaves, fruits and barks (Peñarrieta et al., 2014). The negative biological effect of these metabolites on health is to precipitate salivary proteins, decrease the digestion and absorption of dietary protein. In addition to preventing the absorption of metals such as non-heme iron and carbohydrates, thus slowing the growth process. Studies in animals, show a dose of 0.5 to 2 g / kg / day (5% of the diet) without acute toxic effects, however it shows problems during growth (Vázquez-Flores et al., 2012).

On the other hand, tannins can have negative effects on the nutritional content of forages of ruminant feeders. At concentrations of 6-10% of the dry matter (DM) decreases the voluntary feeding of the animal, reducing digestibility and productivity. While at a moderate and low concentration, ie 2-4% of the DM, its effect is positive where digestion is not depressed there is greater absorption of essential amino acids etc. (Barry et al., 1986, Reed et al., 1990, Barry and MacNabb 1999, as cited by Otero e Hidalgo, 2004).

Anitoxidate Capacity of mashua

Several investigations relate the antioxidant potential of the bioactive compounds (polyphenols, flavan-3-oles anthocyanins and carotenoids) of the Mashua with respect to its hereditary characters and processes of plant development.From the available studies, a significant relationship of antioxidant activity and genetic variety is indicated. The study of Campos et al. (2006) affirms a high hydrophilic antioxidant capacity of the varieties ARB-5241, DP-02-24 and ARV-5366 compared with Andean crops such as the oca, native potatoes and ulluco. While the genotypes M6COL2C, ARV-5366 and DP-02-03 present a similar lipophilic antioxidant capacity among tubers (mashua, Native Potatoes and oca). The lipophilic fraction contributes between 2-19% of the total antioxidant capacity. On the other hand, in an analysis between genotypes, several researchers claim that purple mashua is eight to ten times richer in antioxidant activity than the yellow variety (Chirinos et al., 2007 as cited by Chirinos et al., 2008).

The maturation of the Mashua is associated with changes in its physical and chemical structure; in such a way, that the content of some bioactive components and the antioxidant capacity varies according to the stage of development. Chirinos et al. (2007) found in the genotypes ARB 5241, DP 0224 and AGM 5109 purple color, collected after 7.5 months of planting, a high antioxidant capacity (271-446 μmol equivalent of Trolox/g dry matter ORAC), a high content of phenols (14-24 mg eq. chlorogenic acid/g fresh weight) and an increase in anthocyanin content (3.7 - 8.7 mg eq cyanidin3-glycoside/100g fresh weight). While the carotenoids were only evidenced in yellow mashuas of the genotypes DP 0207, AVM 5562 and ARB 5576 with a range of 8.9 - 14.4 (μg eq. B Carotene/g Fresh weight). During the post harvest, the mashua appeared to increase their bioactive components with the exception of the carotenoids that remained stable. The genotypes DP 0224, ARB 5241 and AGM 5109 stand out as those with the highest phenolic content and antioxidant power (Chirinos et al., 2007).

Antioxidants prevent the oxidation of the cell membrane by forming stable complexes. (Goodam, 1998; Halliwell, 1990 as cited by Avello and Suwalsky, 2006). The interest of antioxidant capacity has intensified due to its pharmacological and therapeutic benefits. Some of the positive effects of antioxidant capacity are related in the treatment of strokes and neurodegenerative diseases (Castañeda et al., 2008). Studies in animals with metastatic lung cancer have shown inhibition of the tumor neovascularization process (Monte et al., 1994 as cited by Castañeda et al., 2008). An important aspect about the study of mashua is to know the contributions of the total antioxidant capacity of the tuber and its incidence in health. Studies with phenolic compounds (flavonoids, anthocyanins and phenols) and antioxidant capacity from purified mashua extracts have demonstrated the ability to prevent oxidative damage of LDL and inhibit erythrocyte hemolysis. These results suggest that mashua phenolic compounds have the capacity to chelate metal ions as well as eliminate peroxyl radicals (Chirinos et al., 2008).

Correlation between antioxidant properties and phenolic compounds

The measurement of the antioxidant capacity in food is considered as a relevant contribution in recent years, since the oxidation resistance of a product is determined (Zulueta et al., 2009). Antioxidant activity is evaluated by different methods either in vitro or live; several studies coincide with the use of chemical techniques (in vitro) such as DPPH (2.2-Diphenyl-1-picrilhydracil), ORAC (Absorption Capacity of Oxygen Radicals) and ABTS (2.2'-azino-bis (3-ethylbenzthiazoline- 6-sulfonic) of which the most commonly used methods are ABTS and DPPH.

The study done by Chirinos et al. (2007) found a high correlation between the ABTS and ORAC methods ($0.794 < r < 0.953$, $P < 0.01$) for eight mashua genotypes, both techniques describe the same oxidative mechanism. The researchers highlighted a significant association of the content of Flavan 3 oles (FA), anthocyanins (AT) and total phenols (FT) with respect to the ABTS antioxidant capacity with a coefficient of $r = 0.897$, $P < 0.01$; $r = 0.891$, $P < 0.05$; $r = 0.879$, $P < 0.01$, respectively. The genotypes analyzed were ARB 5241 (FA and AT) and the DP 0224 (FT) genotype. The study concludes a significant difference between genotypes.

Chirinos et al. (2006) determined a high correlation between the antioxidant capacity (ABTS) and the phenolic content with a positive coefficient (r= 0.9873). However, when the comparison between the antioxidant capacity (ABTS) and the fraction rich in anthocyanins is made, the coefficient decreases (r= 0.637). The researchers suggest that the phenolic compounds were directly responsible for antioxidant activity (ABTS).

Campos et al. (2006) agrees with the data obtained by Chirinos et al. (2006). Different phenolic profiles of mashua tubers influenced the correlation index between hydrophilic antioxidant capacity (ABTS), total anthocyanins and total phenol content. The researchers found a low correlation of anthocyanins (r2 = 0.48, P = 0.11) and a significant correlation with respect to the phenolic content (r2 = 0.84, P = 0.00). Similar results were evidenced when comparing the content of phenolic compounds and the ORAC antioxidant activity in four purified phenolic extracts of mashua (fractions I, II, III and IV); the correlation coefficients were positive (r = 0.9983, 0.9801, 0.9891 and 0.9976). The study deduces that the phenolic compounds were responsible for the antioxidant activity (ORAC) in the four fractions. (Chirinos et al., 2008b).

Nutritional Properties of mashua

In tradictional medicine, mashua is used as a digestive cleanser and cicatrizant. In Ecuador is taken as an infusion mixed with caballochupa (*Equisetum* sp.) and corn silk (*Zea mays*) to treat kidney problems. It is also cooked with brown sugar (panela) for prostatitis and gonorrhea (Cárdenas 1989; Espinoza et al., 1996 citado por Cadima, 2006). It can be used as a treatment of skin ulcers and to kill lice (Oblitas, 1969 as cited by Johns et al., 1982).

Around 600 carotenoids are distributed in the form of red, orange and yellow liposoluble pigments in fruits and vegetables, however, only 20 have been related to certain biological properties (García-Casal et al., 2013). The β Carotene is the most remarkable metabolite because of its potential health benefit. Like other components it has the capacity to become a source of vitamin A (α-carotene, β-carotene and β-cryptoxanthin) (Vitale et al., 2010; García-Casal et al., 2013). Carotenoids have been investigated for their possible preventive properties of diseases such as cancer, arteriosclerosis, cataracts, macular degeneration, premature aging among others (Sánchez et al., 1999). Studies with Andean crops such as mashua suggest that carotenoids and other phenolic compounds found in the tuber can be considered an important source of antioxidants for health. (Chirinos et al., 2007). The vitamin A content in the tuber corresponds to 10, expressed in β-carotene as shown in Table 1.

Liebler et al. (1997) have demonstrated the antioxidant capacity of β-carotene when incorporated in the carotenoid in liposomes. The result showed a correct inhibition of lipid peroxidation that was induced by AAPH, however, the effect was ineffective when the carotenoid was added to preformed liposomes. In the same way Nagler et al. (2003) as cited by Krinsky and Johnson (2005), stated that β-Carotene effectively inhibits the oxidation of linoleic acid, but not that of α-linoleic acid. In general, β-Carotene has been linked to its protective effect against photooxidation and radical-mediated peroxidation, reduction of precancerous lesions in the cervix and oral cavity, and, moreover, to prevent sunburn (Krinsky and Johnson, 2005; Taylor, 1996; Sánchez et al., 1999). Nonetheless, there exists disadvantages to the β-Carotene supplementation, it is that a high dose could inhibit the intestinal absorption of other nutrients which are relevant to the prevention of carcinogenic diseases (Mobarhan et al., 1994; Sánchez et al., 1999). Other studies suggestion that supplementation with beta carotene could cause a risk of cardiovascular disease and lung cancer (Taylor, 1996)

Table 4. Recommend daily intake reference values and bio-active components

Components	Units	Values	Intake	References
Total polyphenols	mg/day/person	2803	Spain	Saura-Calixto (2007)
	mg/day/person	2500 – 3000	Spain	Roldan and Carbajal (2012)
Flavonoids	mg/day/person	64	Japan	Martínez-Valverde et al. (2000)
	mg/day/person	6	Finlandia	Martínez-Valverde et al. (2000)
	mg/day/person	25	Spain	Roldan and Carbajal (2012)
Proanthocyanins	mg/day/person	240 – 450	Spain	García-Casal et al. (2013)
Anthocyanidins	mg/day/person	185 – 215	n/i	Wu et.al (2006) citado por Beas et al. (2011)
Carotenoids	mg/day/person	1–2 with reports of up to 10	United States and United Kingdom	(García-Casal et al., 2013)
	mg/day/person	3 – 4.3	Spain	Roldan and Carbajal (2012)
Antioxidant Capacity	µmol equivalent of Trolox/person/day.	3528	Spain	Saura-Calixto (2007)
Glucosinolate	mg/k of body mass (toxic dose in HCN)	1.5	n/i	Kermanshai et al. 200 as cited by (Rinc, 2014)
	mg/day	6.5	Spain	Roldan and Carbajal (2012)
Polyunsaturated fatty acids (AGPIs)	Proportion	n–6: n–3 of 5–10: 1/day.	FAO/ OMS	Rodríguez-Cruz et al., (2005)
	AGPIs n-3 (g/ day)	1.1 a 1.5	FAO/ OMS	Rodríguez-Cruz et al. (2005)

n/i= not available information

Bio-active compounds and recommended intake

In recent years, researchers have associated the consumption of foods rich in antioxidants as a source of benefits for health. For this reason, Medical and Traditional publications of the last decades have been examined, and the levels of intake per day/person of polyphenols, anthocyanins, carotenoids, antioxidant capacity and glucosinolates have been identified as shown in Table 4. This is prior to a comparison between the actual content of these metabolites and their comparison with other foods, these values are reported in Table 2 and Table 3 respectively.

The content of polyphenol in mashua oscillates in a range of 174.9-374 mg eq. gallic acid/100g higher than those reported for blackberry, black raspberry, red raspberry and strawberry (226, 267, 234, 103 mg eq. gallic acid/100g respectively). If this phytonutrient is analyzed in the context of the recommended daily intake (RDI) in Spain, 2500-3000 mg/day/person is required. The levels of anthocyanins reported in the tuber vary between 45.5-131.9 (mg. eq. cyanidin3-glycoside/100g) which is an inferior content when compared to the blackberry, black raspberry, sweet potato, purple corn and cranberries (152.8, 197.2, 1642, 182, 276 mg. eq. cyanidin3-glycoside/100g respectively). The daily intake requirements in values of mg/day/person of these metabolites is of 185-215, higher than those found in the tuber.

Other metabolites of importance are the carotenoids, in mashua a content of 1-25 µg eq. β-carotene/g, whose value is lower than the tomato and mango (56 – 210; 74.3 µg β-carotene/g fresh weight respectively) and equal to oca (2 – 25 µg eq. β-carotene/g) and higher than the papaya (4.08 µg eq. β Carotene/g) have been identified. Spain has established a recommended intake of 3-4.3 mg/day/person. The ABTS value found for the antioxidant capacity of the mashua is of 16.2-92 µmol equivalent to Trolox/g ABTS, which is inferior to those found in sweet potato, purple corn and cranberries (12409, 21351, 5646 µg equivalent to Trolox/g fresh weight DPPH respectively). Nevertheless, the daily requirement per person in Spain is higher, reporting a value of 3528 µmol equivalent to Trolox/person/day. The authors have indicated a content of 0.27-90.0 µmol/g glucosinolates in mashua. This metabolite is very controversial because of its properties have been recommended in Spain with an ingestion doses of 6.5 mg/day.

Secondary effects of the mashua on health

The Tropaeolum tuberosum like all other members of the Tropaeolaceae family have isothiocyanates such as glucosinolates. These metabolites could be responsible for suppressing of the sexual appetite and the lowering of the reproductive potential of the Incas during the military operations of the XVI century, according to popular belief (Johns et al., 1982). Taking into consideration this background Johns et al. (1982) demonstrated an anti-aphrodisiac action in the mashua (m-methoxybenzyl glucosinolates) in rats that were feed the tuber. The rats with the treatment and the control group had the same capacity to impregnate the females, however, the rats that were feed the tuber showed a lowering of 45% in the levels of testosterone/dihydrotestosterone in their blood. Current studies like that of Cárdenas-Valencia et al. (2008) demonstrated the effect of the mashua (benzyl-glucosinolates) in the reduction of the testicular function in a test done with male Holtzman rats for 42 days. The results indicated a reduction in sperm for 12 to 42 days of the treatment. Moreover, there was a delay in the transit of spermatozoids by the epididymis for 7 days and with an accelerated movement after day 12 up to day 21. The results did not find any significant differences between the levels of testosterone between the treatment rats and control group.

Vásquez et al. (2012) suggested that mashua lowers sperm parameters in the male reproductive system. The author and collaborators used an extract of a hydro-alcoholic Tropaeolum tuberosum in laboratory rats. The effect was a lowering of the sperm in transit and an increment of the number of spermatozoids after 21 days of the treatment. One of the disadvantages of consuming mashua is the presence of thiocyanates. The Ecuadorian genotypes of fresh mashua presents thiocyanates with values of 23-33 mg / 100 g (Dolores and Espín 1997; Grau et al., 2003; as cited by Grau et al., 2003). These metabolize upon being hydrolyzed liberate molecules hydrogen cyanide; the INIAP reported that the values fluctuate between 33.55 y 23.11 mg of cyanide per 100 g of the plant (INIAP, 1996 as cited by Urresta, 2010). These values are low when compared to other food like sorghum with 250 mg, Cassava leaves 104 mg and Cassava root 53 mg of cyanide per 100 g of the plant.

The process of cooking, washing and sifting, exposure to sunlight or in combination lowers the toxicity of the cyanide to values of 9.2 to 9.4 mg per hundred. Through exposure to light, cooking and fermentation with yeasts, the levels can be dropped to 0.36 mg which is below the limit of toxicity. The larger, yellow reddish varieties of Mashua have a higher content of cyanides (INIAP, 1996 as cited by Urresta, 2010). Cyanide block the transportation of oxygen to the red blood cells. The ingestion of 60 mg de cyanide (dry weight) for a person who weighs 60 kg is considered a fatal dose (relationship of 1 mg per kilo of body weight), which could be one of the possible causes of polyneuropathies (Zaninovic´, 2003).

CONCLUSION

In conclusion, the antioxidant capacity and the polyphenol content of the mashua are higher than that which is reported for many of the fruits and tubulars of high consumption in the Americas. The scientific investigation consolidates the preventive role that the bioactive components of the mashua have in the prevention of cardiovascular illness, cancer, and other neurodegenerative illnesses. Moreover, it contributes in the food industry by avoiding the lipid oxidation of vegetable oils and pork

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