

NUTRITIONAL ANALYSIS OF *LLUTEÑO* MAIZE AND FATTY ACIDS CHARACTERIZATION IN MODERN AND ANCIENT SAMPLES FROM NORTHERN CHILE

Juan Pablo Ogalde, Bernardo Arriaza and Mauricio Cuellar

SUMMARY

We present a food quality evaluation of *Zea mays L. amyloperla* from Lluta Valley, northern Chile, a species with important nutritional qualities for historic and current populations in the area. Studies were made of proximal analyses, antioxidant activity, and characterization of the fatty acids fraction. Also, the fatty acids fraction of six ancient maize samples were studied, searching for possible archaeometric markers. The results of the proximal analysis show that the modern Lluteño maize has a high carbohydrates and protein content, low moisture, high ash residue and low antioxidant activity (free radical scavenging).

The oleic and linoleic fatty acids show the highest concentrations in Lluteño maize. The presence of omega-6 and omega-9 present in the maize could provide health benefits against diseases such as type II diabetes and cardiovascular diseases. Finally, the fatty acid distribution of the ancient maize samples cluster in two categories, one of which was similar to the modern Lluteño maize. Thus, the fatty acid fraction can be considered in the future to investigate the antiquity and evolution of Lluteño maize, and his influence on the health of the local populations.

Introduction

Zea mays (maize or corn) is one of the most important food worldwide; its global production is surpassed only by wheat and rice. Since its discovery and initial consumption in antiquity, maize has been an important New World food staple. The early use and diffusion of *Zea mays* in the Americas produced diverse adaptations and varieties of this species. Special cases include the Michoacan 21 variety of Mexico, which has a latent stage with slow metabolism under water stress, and the Chococoño variety grown in the Pacific area of Colombia, which germinates when the fields are flooded (Bedoya, 2013). Management of salinity, hydration, and climate were essential for the domestication and systematic production of this species, as well as the food quality of maize: amounts of carbohydrates, proteins, lipids, fiber,

etc. (see, for example, Staller and Thompson, 2000; Otahola *et al.*, 2002; Ortíz, 2004; Bedoya, 2013). The nutritional potential of the *Lluteño* maize (*Zea mays L.* type *amyloperla*), found in northern Chile (Figure 1a, b), is of economic importance to this area, due mostly to the crop's ability to adapt to salty soils (Bastías, 2004, 2011, 2013; Chávez *et al.*, 2004; Beyoda, 2013). Thus, we want study the quality of maize to evaluate this unique species of northern Chile.

The basic study of food quality begins with the proximal analyses. In this sense, the carbohydrate content provides 60-65% of total energy intake in the diet of the population of Chile, according to INTA's report to the Health Department (Olivares and Zacarias, 2013). The concentration of this nutritional component in maize depends on the grain's degree of maturation (White and Jonson,

2003; Ortíz, 2006; Lafiandra, 2014). These compounds (starch, dextrin, sugars, and any carbohydrate-free or complex-form residue) have antibacterial, immunological, and anti-diabetic bioactive properties, and may also help in cancer prevention (see Gibson, 2005; Ortíz, 2006; Olivares and Zacarias, 2013; Lafiandra, 2014). Maize protein content of 12% or higher is considered nutritionally balanced (DRI, 2002-2005; Olivares and Zacarias, 2013; Han *et al.*, 2015); however, the greatest limitation of maize is the lack of essential amino acids such as tryptophan and lysine. Therefore, it is necessary to balance a maize diet with other lysine-rich foods, such as milk, eggs, beans, or meat (Olivares and Zacarias, 2013). In addition, the maize fiber fraction contribution to diet is 19 to 38g/day, according to the dietary recommended intake (DRI) set forth

in the report of the Panel on the Definition of Dietary Fiber and the Standing Committee on the Scientific Evaluation of DRI (Olivares and Zacarias, 2013).

The lipid fraction usually represents 90% of the edible fats in plants, providing 20-35% of the total energy in the human diet (DRI, 2002-2005; Olivares and Zacarias, 2013). Edible fats include all lipids in plant tissues, namely: monoacylglycerols, diacylglycerols, triglycerides, phospholipids, eicosanoids, resolvins, docosanoids, sterols, sterol esters, hydrocarbons and waxy esters, fatty alcohols, and fatty acids. This fraction is the second most important source of energy behind carbohydrates and contributes to better absorption of carotenoids and fat-soluble vitamins (A, D, E, and K; Coronado *et al.*, 2006; Orhun and Korkut, 2011; Olivares and Zacarias, 2013). The amounts

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ANÁLISIS NUTRICIONAL DEL MAÍZ LLUTEÑO Y CARACTERIZACIÓN DE LOS ÁCIDOS GRASOS EN MUESTRAS ANTIGUAS Y MODERNAS DEL NORTE DE CHILE

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RESUMEN

Presentamos una evaluación de la calidad alimentaria de *Zea mays L. amyloperla* del Valle de Lluta, norte de Chile, una especie con importantes cualidades nutricionales para las poblaciones históricas y actuales de la zona. Se realizaron estudios de análisis proximales, actividad antioxidante y caracterización de la fracción de ácidos grasos. Además, se estudió la fracción de ácidos grasos de seis maíces arqueológicos para la búsqueda de posibles marcadores arqueométricos. Los resultados de los análisis proximales muestran que el maíz Lluteño moderno tiene un alto contenido de carbohidratos y proteínas, baja humedad, alto residuo de cenizas y baja acti-

vidad antioxidante (captación de radicales libres). Los ácidos grasos oleico y linoleico que presentan las mayores concentraciones en el maíz Lluteño. La presencia de omega-6 y omega-9 brindaría protección frente a enfermedades como la diabetes tipo II y enfermedades cardiovasculares. Finalmente, la distribución de ácidos grasos de las muestras de maíz antiguo se agrupó en dos categorías, y una de ellas resultó similar al maíz Lluteño moderno. Así, se puede considerar a la fracción de ácidos grasos para investigar en el futuro la antigüedad y evolución del maíz Lluteño y su influencia en la salud de la población local.

ANÁLISE NUTRICIONAL DO MILHO DO VALE DO LLUTA E CARACTERIZAÇÃO DOS ÁCIDOS GRAXOS EM AMOSTRAS ANTIGAS E MODERNAS DO NORTE DO CHILE

Juan Pablo Ogalde, Bernardo Arriaza e Mauricio Cuellar

RESUMO

Apresentamos uma avaliação da qualidade alimentar de *Zea mays L. amyloperla* do Vale do Lluta, no norte do Chile, uma espécie com importantes qualidades nutricionais para as populações históricas e atuais da região. Foram realizados estudos de análise proximal, atividade antioxidante e caracterização da fração de ácidos graxos. Além disso, foi estudada a fração de ácidos graxos de seis amostras de milho arqueológico em busca por possíveis marcadores arqueométricos. Os resultados das análises proximais mostram que o milho moderno do Vale do Lluta tem alto conteúdo de carboidratos e proteínas, baixa umidade, alto teor de cinzas e baixa ati-

vidade antioxidante (captação de radicais livres). Ácidos graxos oleico e linoleico apresentam as maiores concentrações no milho do Vale do Lluta. A presença de omega-6 e omega-9 proporcionaria proteção diante de doenças como diabetes tipo II e doenças cardiovasculares. Finalmente, a distribuição de ácidos graxos das amostras de milho antigo foi agrupada em duas categorias, e uma delas resultou semelhante ao milho moderno do Vale do Lluta. Assim, a fração de ácidos graxos pode ser considerada no futuro para pesquisar a idade e evolução do milho do Vale do Lluta e sua influência na saúde da população local.

of omega-6 or omega-9 along with palmitic acid concentrations present in maize are important, for example, in understanding the grain's quality and implications for human health. Thus, the fatty acids (FA) fraction of maize has a great influence on health and therefore will be studied with gas chromatography.

Lluteño maize

The plant of *Lluteño* maize (*Zea mays L.* type *amyloperla*) reaches a height of ~4m; it has short conical or cylindrical corncobs and variably colored rounded or pointed grains in 14-18 rows. Particularly, the *Lluteño* maize contains concentrations of sodium and boron

up to six times greater than the reference values described for other maize crops (Bastías, 2004, 2011, 2013; Chávez *et al.*, 2004). This species is of interest because it has adapted to the Lluta Valley's high levels of salinity and excess boron in the soil (Bastías, 2004, 2011, 2013; Chávez *et al.*, 2004; Beyoda, 2013).

In Chile, the area planted with maize in 2009 was of 11,457.58ha, which represented 13.6% of the total cultivated land of Chile (INE-ODEPA, 2010). Most of this area (92%) is found in the Atacama and Biobío Regions, while the Arica y Parinacota region in northern Chile has 3.7% of the country's maize production. Currently this variety occupies

more than 50% of the agricultural soil of the extreme north of Chile in 2010, while the annual and permanent crops subtotal in 2019 was 10,891 (INE-ODEPA, 2010; ODEPA 2019). This latter area has year-round production and supplies the central Chilean zone during its low harvesting season. *Lluteño* maize has demonstrated its productive potential in marginal soils with poor quality irrigation water (Bastías, 2004, 2011, 2013; Chávez *et al.*, 2004; Beyoda, 2013). Due the economic and dietary relevance of *Lluteño* maize for local populations, it is important to evaluate the plant's nutritional component. Thus, we performed proximal analyses,

antioxidant activity and characterized the fatty acid fraction in *Lluteño* maize.

The adaptation of *Lluteño* maize to the saline soils of northern Chile may have begun in pre-Hispanic times, as suggested by the similarity of the modern variety in terms of morphology, texture, and color to archeological samples dated about 2000 B.C. (Erices, 1975; Muñoz, 2001, 2004; Díaz and García, 2014). In order to understand its significance, and his local influence in human health, it is appropriate to undertake instrumental analyses to follow the history of *Lluteño* maize.

To evaluate the fatty acids potential as archaeometric markers and nutraceutical

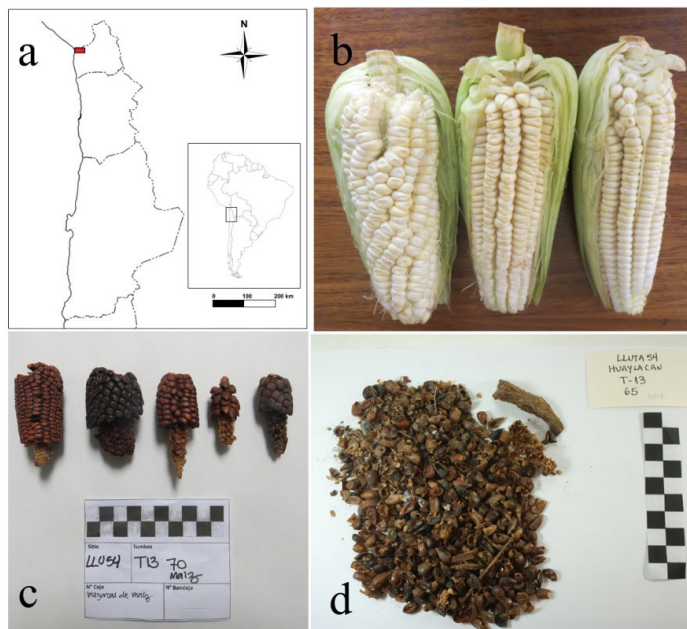


Figure 1. a) Location of the Lluta Valley (shown in red), b) *Lluteño* maize (*Zea mays* L. type *amylacea*), c) Corn cobs of *Zea mays* ordered by sequential order (1-5) from left to right and, d) loose maize kernels from Lluta 54 archeological cemetery.

factors, six archaeological *Zea mays* samples from the Lluta valley of northern Chile were studied. These samples probably were parts of local production of maize during the Inca State (ca. 1450-1530 A.D.). A comparison between ancient and modern maize samples of Lluta valley could provide tools to identify ancient species and/or nutraceutical aspects of the local diet. Thus, we characterized the fatty acid (FA) profile in six archeological samples of *Zea mays*: five archeological corncobs (Figure 1c) and loose corn kernels (Figure 1d).

Materials and Methods

Collection of modern samples

Lluteño maize (*Zea mays* L. type *amylacea*) samples were collected from current crops in the Lluta Valley, Chile, at 18°26'46.81"S and 70°5'28.63"W.

Collection of ancient samples

Six archeological maize samples were obtained from the Museo Arqueológico San Miguel de Azapa (MASMA), Arica, Chile. The six

pre-Hispanic samples of maize, including five corncobs (with kernels) and one sample of loose kernels of maize in an offering bowl were associated with the Lluta-54 site, burial 13. This archeological cemetery is contiguous to the *Huaylacan* site, which has a large set of *colqas* (underground deposits) for storage and management of local maize production during the Inca Horizon Period (1400-1536 A.D.).

Proximal analysis in modern samples

The fresh corn kernels of *Lluteño* maize were washed with deionized water to remove any foreign material and dried them to constant weight at 45°C. Subsequently, the dried corn kernels were ground to a fine powder using an electrical grinder. The samples were powdered to 300µm by mesh and stored them in polyethylene bags. Chemical characterization was then performed following the methods in AOAC (2005). In brief, the moisture content was study gravimetrically by drying 4

±0.0001g of fresh sample for 24h in a forced draft oven at 105°C until it reached constant weight. The crude protein percent was determined using the Kjeldahl method and a conversion factor of 6.25, and the total lipid content was found gravimetrically following the Soxhlet extraction method with hexane. The ash content was quantified by incineration in an oven furnace at 550°C. The carbohydrate content was calculated as the percentage difference compared to all the other constituents.

Determination of antioxidant activity

The 2,2-diphenyl-1-picryl-hydrazyl-hydrate (DPPH) free radical assay (Brand-Williams *et al.*, 1995) was used to determine antioxidant activity. Upon reduction of DPPH free radical by an antioxidant (as gallic acid) or a radical species, the spectroscopic absorbance disappears. This reduction of DPPH radical was spectroscopically followed at 500nm after 100min of reaction, using a Thermo Fisher Scientific Genesys 6 UV-ViS spectrophotometer. According to Mensor *et al.* (2001) the Trolox standard (0-1000µg in methanol) was used to calculate the scavenging activity percentage (AA%) according the formula $AA(\%) = 100 - ((Abs \text{ sample} - Abs \text{ blank}) \times 100) / Abs \text{ control}$.

Statistical analysis

All measurements were performed in quintuplicate. The Graph Pad Prism 6.0 (GraphPad Software Inc., La Jolla CA, USA) software was used to perform statistical analysis. Correlations were considered statistically significant at $p < 0.05$.

Extraction of fatty acids in modern samples

About 30g of powder (300µm) from ground dried corn kernels were macerated with hexane for 72h; then the solvent was evaporated with a rotary evaporator.

Extraction of fatty acids in ancient samples

About 19g of powder (300µm) from ground dried corn kernels were macerated with hexane for 72h; then the solvent was evaporated with a rotary evaporator.

Analysis of fatty acids

The fatty acid (FA) fraction composition was analyzed in a Perkin Elmer (USA) gas chromatography unit (model AutoSystem XL) equipped with a flame ionization detector and a SPTM-2560 fused silica capillary column (10m length, 0.25m film, 0.25mm internal diameter; Supelco). The flow rates of the carrier gas (nitrogen) were 5ml·min⁻¹ and 30ml·min⁻¹ at the makeup point; the injector and detector temperatures were 250 and 280°C, respectively. The oven temperature program was as follows: the initial temperature was 100°C; then the oven was heated at a rate of 4°C/min from 100 to 180°C, held for 10min, and heated at a rate of 2°C/min from 180 to 220°C. To integrate peaks, Total Chrom 6.3.1 software was used. Concentrations were expressed as a percentage of total FA.

Results

Table I summarizes previous studies reported in the literature. It also presents the proximal analyses of *Lluteño* maize, showing the amounts of carbohydrate (67.5%), protein (12%), crude fiber (6.8%) humidity (5.7%), and ash (3.8%). Also, the table shows a normal lipid fraction (4.2%), where the main FA components, as shown in Table II, are linoleic acid (48.55%) and oleic acid (29.49%). In addition, the free radical scavenging activity ranged between 6.7 ±4.9SD and 25.4 ±2.9SD (concentration at 1000 µg). The determination of free radical scavenging was significantly lower ($p=0.001$) in Trolox analyses.

Table II shows the FA levels found in *Lluteño* maize and in the six archeological samples

TABLE I
PROXIMAL ANALYSES (%) OF *LLUTEÑO* MAIZE AND OTHER STUDIES AND VALUES REPORTED IN THE LITERATURE

Humidity	Ash	Carbohydrates	Proteins	Fiber	Lipids	Reference
5.7	3.8	67.5	12	6.8	4.2	This study
10.76	2.08	74.42	7.56	1.97	3.45	Adeoti <i>et al.</i> (2013)
8.9-8.58	1.52-1.63		9.04		4.91-5.36	Castañeda-Sanchez <i>et al.</i> (2011)
9.7-10.2	1.23-1.58		9.4-13.0		3.32-4.70	Egesel <i>et al.</i> (2011)
6.93-10.66	0.85-1.71		8.21-12.02	1.87	1.91-7.13	Ortiz (2006)
	1.1-1.7					Méndez-Montalvo <i>et al.</i> (2005)
			8.10-1.50		3.9-5.8	White and Jonson (2003)
			7.9-9.6		2.8-4.0	Fox <i>et al.</i> (1992)
			6.8-7.51		2.6-3.3	Jeggins <i>et al.</i> (2002)

analyzed. The corn cobs are grouped according to the similarity of their FA profiles in two groups. The first group is ears 1 and 2, while the second group is ears 3, 4 and 5. The FA profile of the loose corn kernels does not resemble any of these groups. Table II includes other studies for comparison. Figure 2a shows the chromatograms with the FA profile of *Lluteño* maize, including six identified fatty acids and 1.5% unidentified substances. The chromatogram with the FA profile of archeological grains of maize (for example, Figure 2b) indicates nine identified fatty acids and 5.17% unidentified substances. This sample has the highest number of signals among the chromatograms.

Discussion

The high content of ash in the grain of *Lluteño* maize could be related to its high protein content. However, its ash content (3.8%) is much higher than that reported in varieties grown under normal salinity conditions. This high proportion of inorganic material is probably correlated to the crop's adaptive metabolic capacities in the valley's salty soils. Then, consideration of elemental analyses is important, particularly in mining areas such as those in northern Chile. Ecotoxic minerals (arsenic, boron, etc.) or pollutant sources (manganese, lead, mercury, tellurium, etc.) could alter the plants' nutrient and toxicity

levels. In the Lluta valley, the levels of arsenic and boron in the water are far above the norm, being 20-100 times the norm for arsenic (DGA, 2010; Niemeyer, 1981) and 2-184 times for boron (DGA, 2010; Figueroa y Cornejo, 2001; Niemeyer, 1980), values that which affects the quality of the plants.

The humidity of modern *Lluteño* maize (5.7%) was found to be low with respect to the other studies listed in Table I. The saline conditions of the Lluta Valley and the maize's adaptive response may explain the low moisture content in this maize variety. Humidity levels are influenced by grain type as well as by climatic conditions, such as temperature and precipitation (Méndez-Montalvo *et al.*, 2005; Ortiz, 2006). Given that fungi appear in storage conditions when the humidity is above 15.5%, the low moisture content of *Lluteño* maize allows for long-term storage in low-cost containers (Pomeranz and Meloan, 1994; Méndez-Montalvo *et al.*, 2005; Ortiz, 2006).

The good food quality of *Lluteño* maize results from its relatively high carbohydrate content (67.5%) and balanced protein content (12%). Also, its high crude fiber content (6.8%) is a nutritional advantage and a potential preventive factor for diseases such as colon cancer, diabetes, obesity, and digestive disorders (Pomeranz and Meloan, 1994; Trumbo *et al.*, 2002; Olivares and Zacarias, 2013; García *et al.*, 2014). The

lipid fraction of *Lluteño* maize (4.2%) presents linoleic and oleic acids as the main FA components.

These good food properties of *Lluteño* maize could be synergic with low antioxidant

activity shown in analyses with DPPH. While antioxidant activity of the *Lluteño* maize protects the principal molecules against radical activity, the presence of polyphenols could play an important role in the conservation and maintenance of FA fractions.

Earlier studies have shown that hexane extraction is optimal but that different extraction methodologies produce minor differences in the relative proportions of FA (Ariza *et al.*, 2011; Lafont *et al.*, 2011). The higher profiles obtained are qualitatively and semi-quantitatively comparable to other studies using similar experimental conditions. The content of linoleic acid (48.55%), an omega-6 polyunsaturated essential FA quantified in *Lluteño* maize, is

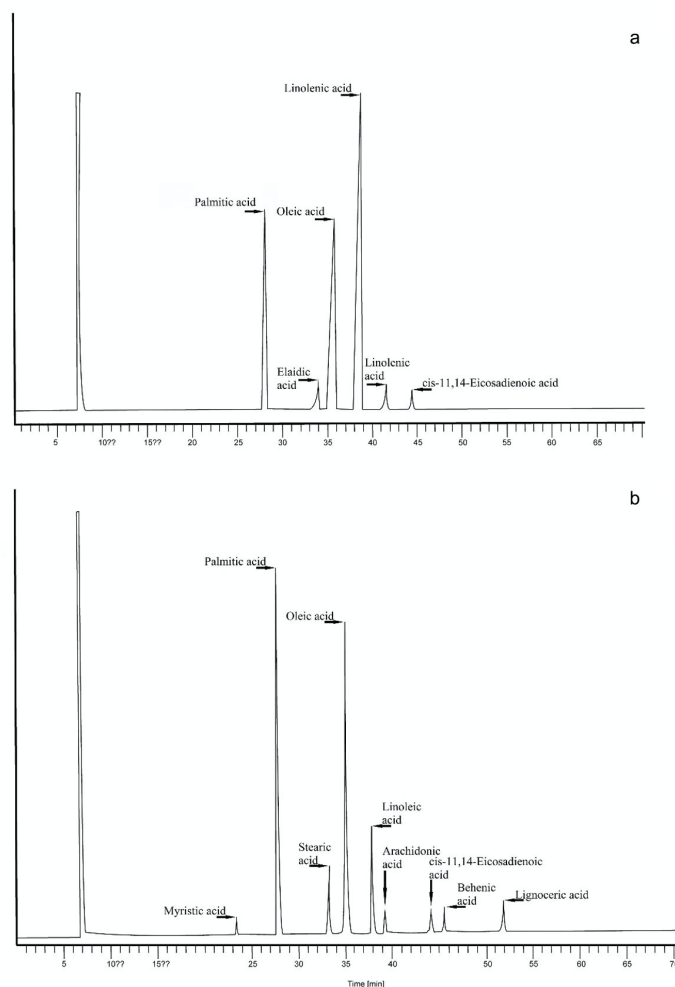


Figure 2. Profile of fatty acids detected in chromatograms of a) modern sample and b) archaeological loose maize kernels.

TABLE II
SUMMARY OF FATTY ACIDS PERCENTAGES IN *LLUTEÑO* MAIZE AND IN ARCHAEOLOGICAL SAMPLES, AND VALUES FROM OTHER STUDIES REPORTED IN THE LITERATURE

Fatty Acids (%)	Current <i>Lluteño</i>	Corn y cob 1	Corn cob 2	Corn cob 3	Corn cob 4	Corn cob 5	Grains	Alezones <i>et al.</i> (2010)	Egesel <i>et al.</i> (2011)	Adeoti <i>et al.</i> (2013)
Saturated fatty acids										
Palmitic	15.86	26.05	30.32	30.56	35.1	31.4	33.84	14.5-13.4	9.2-12.7	16.3
Stearic		3.0		5.86	9.1	9.2	6.85	2.4-3.3	1.5-2.1	15.06
Behenic							1.81		0.1-0.2	1.53
Lignoceric							3.46			
Myristic							0.84			
Arachidic		0.76	0.91					0.6-0.8	0.4-0.6	
Monounsaturated fatty acids										
Oleic	29.49	37.97	37.17				36.45	30.7-35.8	23.3-31.8	14.8
Elaidic	1.74									
Palmitoleic								0.2-0.3		
Gadoleic								0.3-0.6		
cis-11-Eicosenoic		1.03	1.20		2.12	3.13				
cis-11-Octadecenoic		0.99	1.14	49.66	48.32	51.24		0.3-0.6		
Erucic		0.75	0.85					0.3-0.6		
Polyunsaturated fatty acids										
Linoleic	48.55	27.57	22.30	13.93	5.38	5.03	8.62	45.1-50.2	50.8-62.4	12.4
Linolenic	1.72							0.9-1.9	0.8-1.4	15.7
cis-11,14-Eicosadienoic	1.14						1.48			
EPA		0.53	0.73							
Arachidonic							1.48		0.3-0.5	
Others	1.5						5.17			
Total number of FA	6	9	8	4	5	5	9	8	8	6

relatively high compared to other varieties listed in Table II. Precisely, linoleic and linolenic (1.72%) acids are omega-6 FAs that help maintain the integrity of the skin, cell membranes, and the immunological system; these compounds also support eicosanoid synthesis, which is required for cardiovascular and kidney function. Moreover, when these FAs intervene in the oxidative metabolism of glucose, they may serve as protection against type II diabetes mellitus and arterial hypertension, improving sensitivity to insulin and preventing protein modification (Coronado *et al.*, 2006; Olivares and Zacarías, 2013). Oleic acid (29.49%) is an omega-9 that may be synthesized from saturated stearic acid, and thus is not an essential FA. The omega-9 FAs help reduce blood levels of low-density lipoprotein, the elevation of which is an established risk factor for cardiovascular diseases. However, FAs such as

palmitic acid (15.86%) tend to increase blood levels of low-density lipoprotein (Otahola *et al.*, 2002; Coronado *et al.*, 2006; Orhun and Korkut, 2011; Olivares and Zacarías, 2013).

In brief, *Lluteño* maize has good nutritional properties (high amounts of carbohydrates, proteins, and fiber), as well as nutraceutical elements (high in omega-6 and presence of omega-9, and low but significant antioxidant activity). Thus, this maize variety is a good quality food, adapted to salty soils. These adaptative characteristics of modern *Lluteño* maize were already present in pre-Hispanic times and are important to understand health-related issues on local populations. The analysis of FAs could be useful to identify the *Lluteño* maize variety as well as to evaluate the related nutraceutical characteristics. In this sense, the five samples of corncobs fall into two groups according the FA

distribution. The first group (cobs 1 and 2) has an oleic acid content slightly higher than that of modern varieties, as shown in Table II. The profiles of palmitic, linoleic and oleic acids of cobs 1 and 2 is more similar to the FA distribution of the *Lluteño* maize and the modern varieties listed in Table II. The second group (cobs 3, 4, and 5) differs from the first group in that no oleic acid was detected in these samples. These results suggest that the FA fraction is useful to cluster these ancient samples, and to identify ancestors of modern *Lluteño* maize.

The ancient loose corn kernels showed more variation. The oleic acid is one of the most abundant FAs (36.45%), with palmitic acid (33.84%) being the main element. These values are similar to the FA profile of the first group of corncobs (1 and 2) and current varieties of maize listed in Table II. However, the low percentage of linoleic acid (8.62%)

in this sample is similar to the second group of corncobs (3, 4, and 5). It should be noted that oleic and palmitic acids are particularly abundant in meat, milk fat, and some vegetable oils such as coconut or palm oil. In addition, the archeological sample's polyunsaturated FA makeup included arachidonic acid (1.48%), an omega-6 that is mostly formed in the liver by the desaturation and elongation of linoleic acid, implying an animal origin (eggs, lean meats, viscera, and fish; (Coronado *et al.*, 2006; Olivares and Zacarías, 2013). Thus, we think that contamination of this archeological sample may be responsible for the high presence of FAs, the variable percentage of each acid, and occurrence of arachidonic acid identified in our analyses. Despite this argument, Egesel *et al.* (2011) also found arachidonic acid (0.26-0.52%) in *Zea mays* from Turkey.

It is certainly possible that this phenomenon be due to the

degradation of oleic acid over time; however, corncoobs 1 and 2 show even higher concentrations of FA than those found in the current varieties listed in Table II. The highest concentration of cis-11-octadecenoic in the second group of corncoobs shows another strong difference with respect to the first group of corncoobs and modern varieties reviewed in this paper. This unusual FA profile in the second group could be the expression of a natural variation in the lipid fraction for these corncoobs. Alternatively, this FA content suggests different processes of degradation for these samples; in this case, it still seems that the differentiated degradation processes have their origin in a lipid matrix that is different between the samples. Thus, in the study of the FA fraction as an archaeometric marker it is important to consider that the nutritional components degrade over time, especially certain FAs that are easily oxidizable. However, the work on the FA fraction, as an archaeometric marker, can be useful to evaluate the nutraceutical factors of the ancient maize consumption in the north of Chile

Concluding Remarks

The *Lluteño* maize presents a good nutritional profile and the consumption of this variety provides health benefits. Its omega-6 level is elevated compared to other varieties but is not out of the normal range. The FA content adds to the nutritional benefits of *Lluteño* maize, but its higher palmitic acid content detracts from these qualities. Moreover, the maize productivity rate throughout the entire year is important for Chile's national economy, and the cultivation and consumption of maize are relevant to large-scale economic and nutritional policies, which are beginning to incorporate functional or nutraceutical (health-related) elements. Unsaturated fatty acids, therefore, are an open door for pharmacological and nutraceutical research. Chile has no specific

legislation to publicize information regarding the content of FAs or the supposed benefits of consuming them; if made public, such information should help increase the consumption of long chain omega-3 polyunsaturated FAs and decrease that of saturated FAs.

The results reported showed similarities and differences between *Lluteño* maize and the archeological samples. The latter was probably contaminated; but even so, we know several maize varieties existed in ancient times in both the Lluta valley and in other parts of northern Chile. Thus, analysis of FA profiles in ancient maize samples (or other types of natural products) could prove a powerful analytical tool for testing the nutritional quality of food in antiquity.

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