Chapter 8

Phenolic Compounds in Maize Grains and Its Nixtamalized Products

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Abstract

Among the cereals most consumed by humans, maize grain is in the third position, surpassed only by rice and wheat. In several countries, maize grain is the main source of carbohydrates and proteins. Maize grain is ranked as one of the cereals with the highest content of phenolic compounds. The importance for human health of the consumption of phenolic compounds is due to their proved antioxidant activity. Diets with high amount of antioxidants have been associated with a reduced probability of suffering degenerative chronic diseases. In maize grain, the phenolic acids predominate, among which the main is ferulic acid, followed by p-coumaric acid, which are highly abundant in their bound forms. However, other phenolics such as anthocyanins, flavonols, and flavanols have been identified in colored maize grains. Additionally, the processing of maize grain into different products for human consumption incorporates changes both in quantity and quality of some phenolic compounds. In the present chapter, we present the most recent information available regarding phenolic compounds in maize grain and their nixtamalized products.

Keywords: *Zea mays* L., phenolic acids, flavonoids, nixtamalization, tortilla

1. Introduction

Phenolic compounds are widely distributed in plants as products of their secondary metabolism; they are produced during plant development and some are of vital importance for their adequate functioning and interaction with the environment while others are synthesized in response to stress conditions such as infections, injuries, ultraviolet radiation, among others [1, 2]. Furthermore, phenolic compounds serve as defense mechanisms since many of them display antifeedant and antipathogenic properties [3], which contribute to their adaptation to different environments. The presence of phenolic compounds in different plant foods contributes to their distinctive characteristics and to its flavor and color. They can be found in soluble/free and bound/insoluble form. In maize grain the highest amount of phenolics (98.9%) is present in the insoluble fraction, and the remainder in the soluble fraction [4]. However, it is the soluble fraction that shows the greater chemical diversity, which depends on the color of the grain. The goal of this document is to provide a review of the various phenolic compounds present in maize grains of different colors, and the changes that occur when the grain is subject to nixtamalization processing for the elaboration of tortillas and all the diversity of nixtamalized products consumed in Mexico and in many other parts of the world.

2. The phenolic compounds

The biosynthesis of these compounds occurs via the shikimate pathway, from the amino acids phenylalanine and tyrosine and the participation of the enzyme phenylalanine ammonia lyase (PAL) that catalyzes the removal of the ammonia residue of the amino acids phenylalanine and tyrosine to produce cinnamic acid and 4-coumaric acid, respectively [5]. Both compounds further enter the phenylpropanoid pathway and it is within the various branches of this pathway where the great diversity of phenolic compounds so far identified is synthesized.

Regarding their chemical structure, phenolic compounds possess at least one aromatic ring with one or more hydroxyl groups, including their functional derivatives [6]. The polyphenols are within the group of phenolic compounds, which according to Quideau et al. [7], the term "phenolics" should be used to define compounds derived exclusively from the shikimate/phenylpropanoid pathway and/or the route of polyketides, which include more than one phenolic unit (phenol). This restriction is necessary because substances from alternative metabolic pathways may also present more than one phenolic unit. In literature, the term polyphenols and phenolic compounds are often encountered, however, if the former term is used it would not include the phenolic acids, as their structure contains only one phenol. Therefore, throughout this work we will use the term "phenolic compounds" as we will be commenting on some flavonoids and phenolic acids.

The complexity of the phenolic compounds ranges from simple molecules as phenolic acids to highly polymerized compounds as tannins. Phenolic compounds are present in plants in conjugated form with one or more sugar residues bound to the hydroxyl groups, although in some cases direct connections between a sugar molecule and an aromatic carbon may occur. The most common way to find them in nature is as glycosides, conferring them solubility in water and in organic solvents. All phenolic compounds exhibit strong absorption in the UV spectral region, and some colorful phenolic compounds absorb in the visible region as well [8].

Phenolic compounds can be classified in various ways, one proposed by Harborne and Simmonds [9] considers the number of carbons contained in their molecule. According to this

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criterion a total of 20 different groups of phenolic compounds are considered, where simple phenols are the simplest and the phlobaphenes are the most complex group [10]. Another criterion is used by Shahidi and Naczk [6], which classifies groups of compounds based on their complexity. **Figure 1** illustrates this classification.

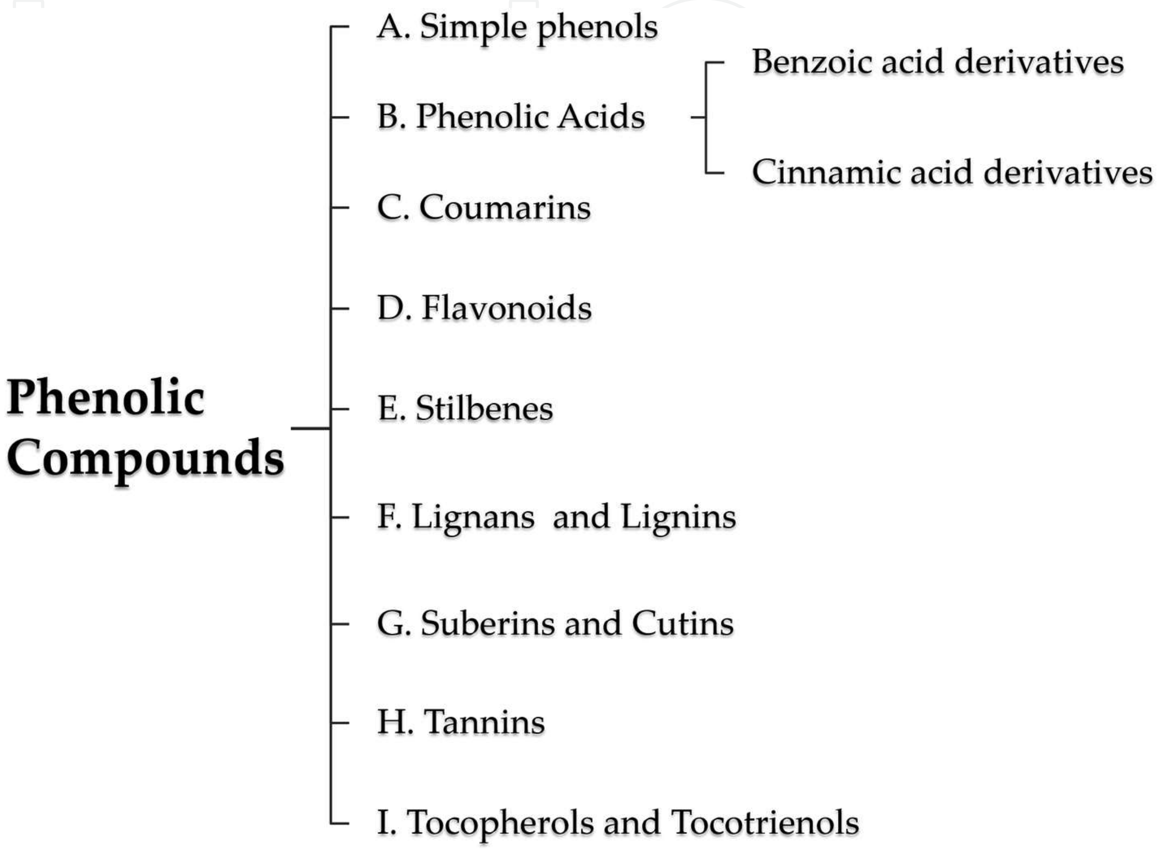

Figure 1. General classification of phenolic compounds (adapted from Shahidi and Nazck [6]).

3. Phenolic compounds in maize grain

Phenolic acids are the main phenolics in maize grain; however, other compounds like phenolic amines and some flavonoids have also been described [11]. The most abundant phenolic acids are ferulic and p-coumaric, which may be in their isomeric form cis or trans, the most common being the trans form. Both acids are present in soluble form or bound to cell wall components. Ferulic acid (3-methoxy-4-hydroxycinnamic acid) is the most abundant in the cell wall of monocots and is found in all fractions of the maize grain, but most abundantly in the pericarp and the aleurone layer. Chemically it is mostly ester-linked to plant cell wall components, hemicellulose chains, mainly in the arabinose residues, but it can also be polymerized in lignin by ether linkages [12]. When ferulic acid is oxidized, it forms dimers or trimers, which after being hydrolyzed, are capable of forming gels when linked to two pentosans or protein molecules.

Among the flavonoids present in maize grain are the flavonols, anthocyanins, and proanthocyanidins. Das and Singh [13] reported the presence of quercetin and kaempferol (flavonols) in the germ and pericarp of quality protein maize (QPM), popcorn and sweet corn. Meanwhile, Ramos et al. [14] reported the presence of kaempferol and morin in purple maize grains. The chemical structures of some phenolic compounds present in maize grain are shown in **Figure 2**.

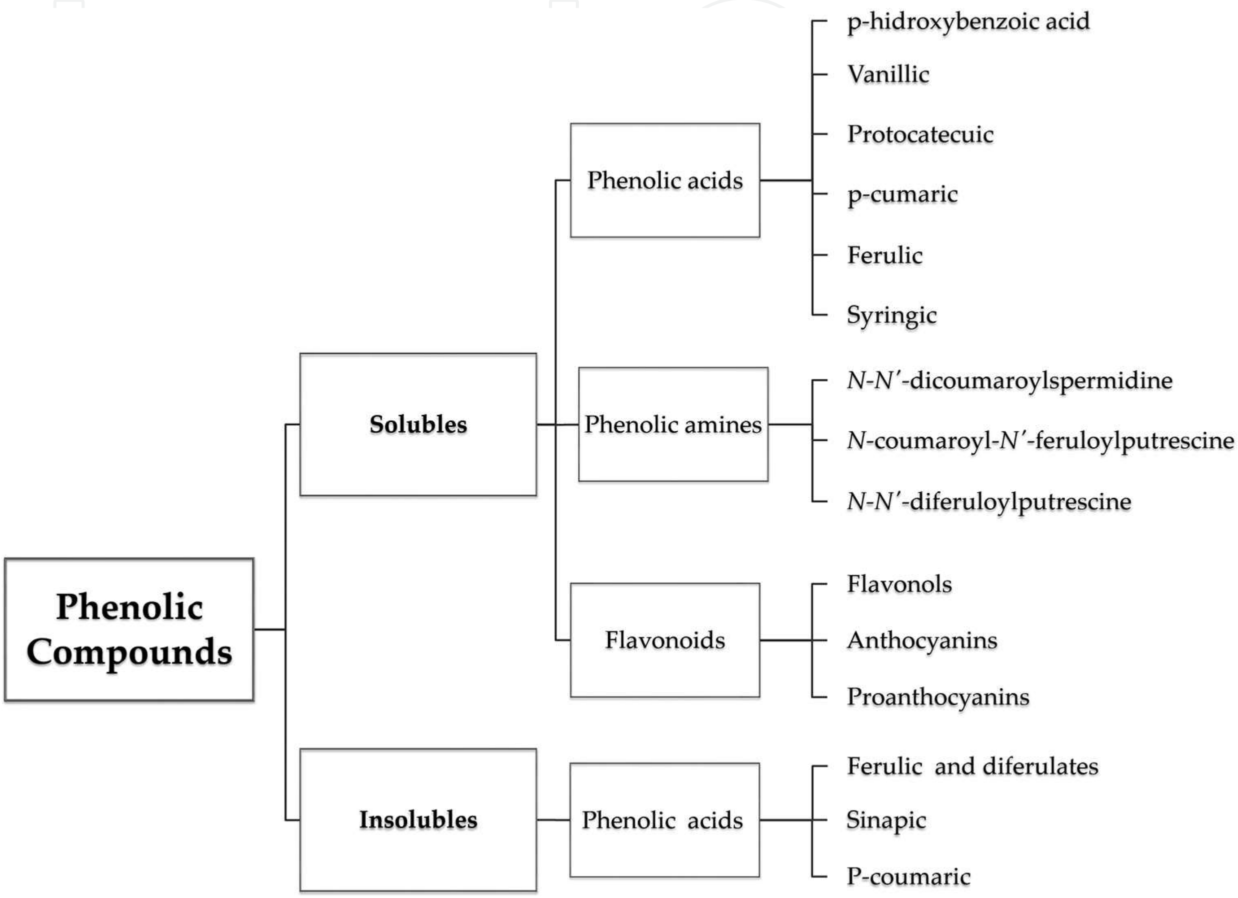

Figure 2. Phenolic compounds identified in white and pigmented maize grains.

Phenolic amines were initially identified in the pericarp of white maize grain by Sen et al. [15], who associated their presence with tolerance to storage pests; recently, Collison et al. [16] reported that the phenolic amines: N-N′-dicoumaroylspermidine, N-coumaroyl-N′-feruloylputrescine, and N-N′-diferuloylputrescine were the most abundant soluble phenolics in the methanolic extract of nixtamalized grains from red, blue, and purple maize grain. It is not known for sure what is the role of phenolic amines in maize grain.

3.1. Soluble phenolic compounds

These compounds correspond to those obtained by treating a given sample size of ground maize grain to extraction with an organic solvent, typically aqueous solutions of methanol or ethanol. Quantification is performed by the Folin-Ciocalteau method [17]. The identification of the different types of phenolic compounds is achieved by high-resolution liquid chromatography (HPLC) when standards are available or by means of mass spectrometry (MS). The

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position in which the different moieties of the molecule are attached is elucidated by nuclear magnetic resonance (NMR) techniques.

3.1.1. Phenolic acids

Phenolic acids can be found in maize grain in soluble and insoluble form. The soluble fraction is also known as free, although in a strict sense, in this fraction phenolic acids can be present in their free soluble forms, glycosylated or esterified. This fraction is very small compared to the insoluble or bound fraction. However, the fraction of soluble phenolic acids is more diverse than the insoluble, particularly in the grains containing anthocyanin-type pigments. Phenolic acids that occur in maize grain are derived from both benzoic acid and cinnamic acid. The chemical structures of the most common are shown in **Figure 3**.

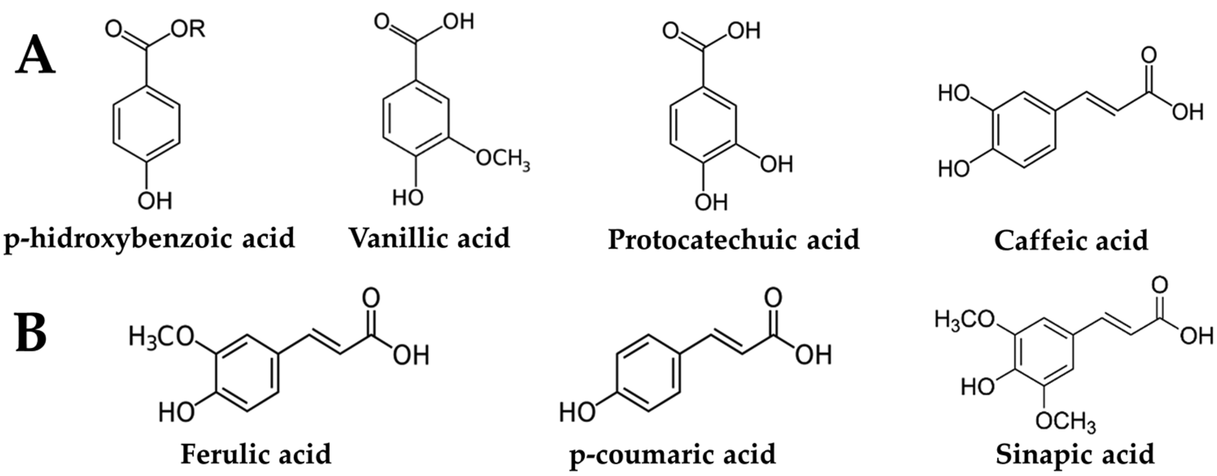

Figure 3. Phenolic acids in the maize grain. (A) Benzoic acid derivatives and (B) cinnamic acid derivatives.

Among the phenolic acids present as soluble form in the maize grain are p-hydroxybenzoic, vanillic, and protocatechuic, all derived from benzoic acid. The first two have been reported in the pericarp of popcorn and in the germ of QPM, as well as in baby corn, with greater abundance of p-hydroxybenzoic [18]. In the grain of purple maize the presence of protocatechuic, vanillic acid, and p-coumaric has been reported in amounts of 14.61 ± 0.08 and 8.46 ± 0.09 mg equivalents of ferulic acid/g sample for the former two acids, whereas the latter was found only in trace amounts [19]. Meanwhile, Sosulski et al. [20] identified in yellow maize flour, in addition to the previously mentioned acids, p-coumaric, ferulic, and syringic acids in the free phenolic fraction. This fraction was much smaller than the soluble esterified phenolic fraction, in which ferulic and syringic acids predominated. **Table 1** shows the reported concentrations of some phenolic acids in maize grain of different colors.

3.1.2. Flavonoids

They are phenolic compounds that form a very large group of which more than 5000 different members have been identified [21], many of which possess important biological activities such as antioxidant, antimutagenic, and microbicidal. Different types of flavonoids have been identified in colored maize grain with anthocyanin-type pigments. They can be found free

Concentration of phenolic acids (μg/g of dry sample)								
Maize grain color	***p*-Hydroxybenzoic**	**Vanillic**	**Caffeic**	**Syringic**	***p*-Coumaric**	**Ferulic**	**Protocatechuic**	**Reference**
White					34.4	4841.4	18.4	Del Pozo-Insfran et al. [27]
Yellow		2123.2	95.7		230.1	4543.2		Das and Singh [13]
Yellow	1.3	3.7	4.5	11.5	18.9	5.1		Sosulski et al. [20]
Red					319.90	2712.58		Zilic et al. [22]
Mexican blue					1.15	428.4		Del Pozo-Insfran et al. [27]
American blue					58.6	1237.5		Del Pozo-Insfran et al. [27]
Purple		8460			Traces		14610	Pedreschi and Cisneros [19]

Table 1. Concentrations of some phenolic acids in maize grain with different colors.

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or in conjugated forms [22]. These compounds are very susceptible to hydrolysis and some losses may occur during their analysis. The presence of these phenolic has been reported in maize grains with anthocyanin-type pigments and the flavonoids reported are anthocyanins, flavonols, and proanthocyanins (flavan 3-ols).

3.1.2.1. Anthocyanins

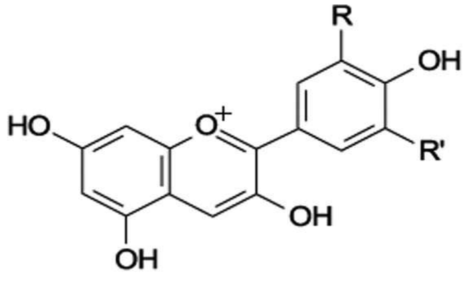
Anthocyanins are a class of water-soluble flavonoids that are visible to the naked eyes. They are glycosides of polyhydroxy and polymethoxy derivates of 2-phenylbenzopyrylium or flavylium salts and are responsible for the red, purple, and blue colors of many fruits, vegetables, and cereal grains [23]. In maize grain, they are located in the pericarp, the aleurone layer, or in both structures [24]. Anthocyanins have sugars attached to the B-ring at the 3′ and 5′-hydroxyl position. The two most important types of glucosides are 3-monoglycoside and 3-4-diglycoside. As a rule, the 3-hydroxyl always has a sugar, except in 3-desoxypelargonidin, 3-desoxycyanidin, and 3-desoxydelphinidin [25]. The basic structure of the anthocyanidins present in maize grain is shown in **Figure 4**.

3.1.2.2. Flavonols and proanthocyanidins

In the grain of blue maize, derivatives from quercetin have been reported [27], while in the grain of purple maize, in addition to these derivatives, morin and kaempferol have also been identified and quantified [14]. These flavonols have not been reported in white maize grain, whereas in yellow maize grain, quercetin and kaempferol have been reported to be present in trace amounts [13]. Within the group of proanthocyanidins, only catechin has been reported to be present in the blue maize grain of Mexican and American origins [27].

3.2. Insoluble or bounded phenolic compounds

Insoluble phenolics from maize grain are those obtained from alkaline hydrolysis of the sample residue once soluble phenolics have been removed. The pH of the hydrolyzed sample is adjusted to 2 and liquid-liquid extractions with ethyl acetate are used to recover them. The total content is quantified by the Folin-Ciocalteau assay. They can also be analyzed by HPLC-DAD techniques or HPLC/MS/MS for a complete identification of the different phenolics present in this fraction.



Aglicons	R1	R′
Pelargonidin	H	H
Malvidin	OCH3	OCH3
Cyanidin	OH	H
Peonidin	OCH3	H

Figure 4. Basic structure of the anthocyanidins (aglycons) present in maize grain (adapted from Rodríguez and Wrolstad [26]).

3.2.1. Ferulic acid and diferulates

Most of the phenolic acids in maize grain are found in the bound form and in this fraction, the ferulic acid (4-hydroxy-3-methoxycinnamate) predominates. It is found esterified to arabinoxylans from the hemicelluloses in the cell wall of the various structures of the maize kernel. Most of this acid in its free form is present in the germ, while its bound form is concentrated in the grain pericarp [18]. As noted above, the ferulic acid is mainly esterified to cell wall components. In the free form, it can be also found conjugated to different molecules, among which the most common are simple sugars and some amines [15, 16].

3.2.2. p-coumaric acid

After ferulic acid, the second most abundant phenolic compound in maize grain is p-coumaric acid. It is present in both forms, the soluble phenolic fraction and the insoluble, with greater presence in the latter. In the insoluble fraction it is mainly linked to lignin, and to a lesser extent to polysaccharides embedded in the cell wall [28]. In the soluble fraction of purple maize the value reported for this acid is 34.1 mg/100 g DW, and for the phenolic insoluble fraction is 573.4 mg/100 g DW. Surprisingly, ferulic acid values reported in the insoluble fraction of this maize were significantly lower (154.2 mg/100 g DW) compared to the amount of p-coumaric acid [29].

4. Phenolic compounds in maize by grain color

The content and type of phenolic compounds in the maize grain will vary depending on the color of the grain, the genetic origin, and the extraction method used. In the latter factor is determining if technologies such as ultrasound and microwave to favor extraction are used, in addition to the type of solvent used to extract them. **Table 2** contains information regarding the amount of free or bound soluble and insoluble phenolics found in maize grain. The data show very large differences in the reported values by different authors for the same maize grain color. This is undoubtedly due to the genetic variability of the biological material itself. Furthermore, in some works as that of Montilla et al. [29], the extraction of the insoluble phenolic was performed sequentially with three different hydrolysis methods and finally the phenolic compounds recovered from each were added. This method differs from what has been done, for example, by López-Martínez et al. [30], who performed alkaline hydrolysis and recovered the phenolics by liquid-liquid extraction with ethyl acetate, which is the most common method applied. Under this method, the authors reported very different values in four samples of purple grain of different genetic background.

4.1. White maize grain

In white maize grain, differences in total phenolic content (solubles + insolubles) due to grain hardness are present. These differences are supported by the role of ferulic acid to provide strength to the cell wall of different grain structures. But also, each botanical grain structure has a content and a particularly phenolic profile, which is associated with its functionality.

Maize grain color	(μg GAE/g DW) FP	SGP	SEP	IP	TP	References
Yellow	61.7 ± 0.3	163.5 ± 9.1	254.7 ± 44.2	2331.5 ± 103.3	2811.4 ±	Xu et al. [31]
Yellow	1040 ± 22.0			4470.0 ± 43	5510 ± 38	López-Martínez et al. [30]
White	334 ± 15			1360 ± 32	1700 ± 11	López-Martínez et al. [30]
White	347.0 ± 4.0			2260 ± 63	2607 ± 61	De la Parra et al. [48]
Purple	821.0			5296.0	6117.0	Montilla et al. [29]
Purple	837–6800			3810–27,200	4650–34,000	López-Martínez et al. [30]
Blue	455 ± 5			2207 ± 5	2662 ± 7	De la Parra et al. [48]

FP: free phenolics; SGP: soluble glycosylated phenolics; SEP: soluble esterified phenolics; IP: insoluble phenolics; TP: total phenolics; GAE: gallic acid equivalents; DW: dry weight.

Table 2. Contents of soluble and insoluble phenolic compounds in maize grain with different colors.

4.1.1. Differences by grain hardness

Few studies have studied the relationship between the hardness of the maize grain and its phenolic content. The hardness of the grain is a widely studied aspect, because of the importance that this feature has for the different processes to which maize grains are subject to obtain the myriad of products derived from it [32]. Among the literature on the matter, Cabrera-Soto et al. [33] analyzed the soluble and insoluble phenolic fractions in the grain of seven maize hybrids of different hardness. The authors observed a significant positive correlation between the values of soluble esterified phenolics in the three grain structures (pericarp, germ, and endosperm) and the grain hardness. In the study by Chiremba et al. [34] in maize and sorghum, a higher content of phenolic acids in grains of greater hardness was observed, however, the correlation between the content of these phenolics and hardness was higher in maize grains than in sorghum grains.

4.1.2. Differences by grain botanical structure

Phenolic compounds are distributed in all maize grain structures, however, their concentration and type varies among them. Several studies using fluorescent techniques have reported that the pericarp is the structure with the highest concentration of phenolics, followed by the germ and the endosperm [15].

Pericarp. The pericarp of maize grain is a rich source of phenolics, mainly in their bound form. However, a minor amount of phenolics can also be present in their free form. The main phenolic in the bound form is ferulic acid, followed by p-coumaric and sinapic acids. Several free phenolic acids reported in this structure are ferulic (in its conjugated form), vanillic, caffeic, p-coumaric, and p-hydroxybenzoic. However, the abundance of each one varied according to the maize type [18].

Most of the ferulic acid in the pericarp of the maize grain is linked by ester bonds to cell wall polysaccharides [35]. Nonetheless, they are also present in the form of dehydrodimers originating from the oxidative coupling of ferulate esters by means of the enzyme peroxidase. The diferulates that have been identified in maize grain are 8,5′-diferulic acid, 8,O,4′-diferulic acid, 8-8-diferulic acid, 4-O-5-diferulic acid, and 5.5′-diferulic acid [35], of which the most abundant is the first one [26]. The diferulates are linked to the arabinoxylans of the polymers that form the cell wall [36]. The resistance of the pericarp cells is attributed to the presence of these compounds and their abundance has been associated to resistance toward the development of fumonisins [37, 38] and tolerance to warehouse pests [15, 39]. The presence of ferulic acid dehydrotrimers was reported by Rouau et al. [40] in maize bran, which is a fraction that is composed of remnants of pericarp and aleurone layer. Until now, seven different ferulic acid dehydrotrimers have been identified [35]. The different ways in which ferulic acid is integrated into the cell wall components contributes to the formation of networks that support the resistance of this structure whose main function is to isolate and protect the grain from external agents.

The type of maize affects the values reported for total soluble phenolics in the grain pericarp. In dent maize grain, Cabrera-Soto et al. [33] reported a variation of 232.4–334.0 mg EAG/g DW in seven different maize varieties. In cornpop, Das and Singh [18] observed a value of 13.1 ± 0.66 μmol of FAE/g of DW, while the value for QPM maize was of 15.9 ± 0.28. Insoluble phenolic content (IPs) in this structure is between 18 and 21 times that of soluble phenolics (SPs). Das and Singh [13] reported values of SPs of 11.9 and 10.4 μmol of FAE/g of DW in the pericarp of dent and crystalline maize types, respectively: the values of IPs were 218.6 and 219.4 μmol of FAE/g of DW, for the same maize grains. In the SPs fraction, the phenolic acids presented were vanillic, caffeic, ferulic, and p-coumaric, with predominance of the latter; in IPs, ferulic acid represented between 40 and 50% of this fraction.

In maize grain with presence of anthocyanin pigments in the pericarp, the SPs content is commonly higher than the values observed in white maize grain. This is due to the presence of anthocyanins that occurred mainly in soluble form, because the amount of bounded anthocyanins reported is very low [29].

Germ. The germ concentrated the highest content of soluble phenolics of the maize grain structures. In seven varieties of white maize grain, Cabrera-Soto et al. [33] reported in the germ values of 499.1–689.2 μg GAE/g DW; in the pericarp, the values were of 232.4–334.1 μg GAE/g DW, while in the endosperm, they reported values of 124.1–194.0 μg GAE/g DW. Meanwhile, Das and Singh [13] reported 14.2 ± 0.3 for germ, 11.9 ± 1.1 for pericarp, and 0.4 ± 0.02 μmol of FAE/g of DW, in one sample of dent maize grain. In the germ, the phenolic acids: 3-hydroxybenzoic acid, caffeic, p-coumaric, ferulic in itsr cis and trans forms, and salicylic have been reported. Ferulic acid predominates in its esterified soluble form [41].

Endosperm. The concentration of phenolic compounds in this structure is very low. Cabrera-Soto et al. [33] reported values of 124.1–194.0 μg GAE/g DW. The amount of IPs is also marginal since it is less than 2% of that present in the pericarp and 3.56% of that contained in the

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germ. However, the endosperm represents 80–85% of the total weight of the grain, so its total contribution is close to that of the germ.

4.2. Pigmented maize grain

4.2.1. Blue/purple grain

The purple grain maize is the most studied with respect to the phenolic compounds because it is highly used for pigments extraction with application in foods [41–43]. In purple maize grain the phenolic acids have been reported: protocatechuic, vanillic, and p-coumaric acid, besides four hydroxycinnamic acid derivatives [19]. Additionally, Ramos et al. [14] found in purple maize grain the following phenolic acids: chlorogenic, caffeic, and ferulic. Of the flavonoids present in purple maize grain, the anthocyanins are the most abundant. Ramos et al. [14] reported values of 2.76 ± 0.05 g of cyanidin-3-glucoside (C3G)/kg DW, meanwhile for flavonols and flavanols the values observed were of 0.41 ± 0.02 g of rutin equivalents (RE)/kg of DW and 0.23 ± 0.01 g of catechin equivalents (CE)/kg of DW, respectively. Other flavonoids described in this maize grain color were rutin, morin, quercetin, naringenin, and kaempferol. Others phenolic compounds that have been identified in purple maize grain are those resulting from the condensation of flavanols (catechin or epicatechin) and anthocyanins. Some of these compounds are catechin-(4,8)-cyanidin-3-glucoside, catechin-(4,8)-peonidin-3-glucoside, catechin-(4,8)-pelargonidin-3-glucoside, and the corresponding derivatives in which the epicatechin is the flavonol attached [44].

4.2.2. Red grain

The red maize grain like the blue maize is especially high in phenolic compounds as compared to light colored maize genotypes. The average value of total phenolics for these grains is of 6056.9 mg/kg DW. The most abundant phenolic acids identified in red maize grain are ferulic and p-cumaric [22].

In **Table 3**, the total anthocyanins content (TAC) for different grain colors and the predominant anthocyanins in each sample are shown. It should be clarified that, within the same shade of grain color, different intensities may be present, which are evidenced by the different contents of total anthocyanins of grains of a similar shade.

Maize grain color	TAC*	Main anthocyanins	Reference
Red	85.2 ± 2.2	Cyanidin-3-glucoside Cyanidin-3,6-malonylglucoside	Zilic et al. [22] López-Martínez et al. [30]
Red	9.75 ± 0.44	Peonidin-3,6-EthylMalonylGlucoside Pelargonidin-3,6-Ethy-MalonylGlucoside	De La Parra et al. [48]
Blue	99.5 ± 1.8	Cyanidin-3-glucoside	López-Martínez et al. [30]
Blue	36.87 ± 0.71	Pelargonidin-3-glucoside Peonidin-3-glucoside	Pedreschi and Cisneros [19] De La Parra et al. [48]

* Concentration expressed in mg cyanidin-3-glucoside/100 g of sample.

Table 3. Anthocyanins content and main anthocyanins presented in the maize grain with different colors.

5. Changes of phenolic compounds during processing (nixtamalization) of maize grain

Nixtamalization results in multiple changes in the chemical components of the maize grain. Under the traditional process, the cooking water has high pH (~12) which hydrolyzes the ester bond by which ferulic acid is linked to cell wall components. The grain structure that is mostly affected by this process is the pericarp, which becomes partially or fully hydrolyzed [45, 46]. As the most abundant phenolic in the grain, the hydrolysis of the ester linkage between the ferulic acid and the cell wall components causes the soluble fraction to be higher in nixtamalized maize products relative to that found in the whole grain, white maize. However, in colored maize that contains anthocyanin pigments, the soluble fraction is reduced due to the significant loss of anthocyanins [47–49]. According to the information presented in **Table 4**, in white maize grain soluble phenolics increase by about 26% when the grains are processed into tortillas, while in red maize grain, they are reduced by 20%. The magnitude of the reduction varies according to the grain color and the origin of the genetic material. The cooking of the tortilla results in an additional loss of phenolic compounds, but much less significant that resulting from nixtamalization [47].

Phenolic compounds in maize grain	SP (mg GAE/100 g DW)	IP	TP	Ferulic (mg FAE/100 g DW)	References
WG					
Raw	34.7 ± 0.4	226.0 ± 6.3	260.7 ± 6.1	120.45	De la Parra et al. [48]
Tortilla	47.2 ± 1.8	119.0 ± 6.2	166.2 ± 6.2	85.16	
Raw			167.4	474.49	Mora-Rochin et al. [49]
Tortilla			85.4	101.66	
RG					
Raw	38.2 ± 0.4	205.6 ± 4.5	243.8 ± 4.6	130.3	De la Parra et al. [48]
Tortilla	30.5 ± 0.7	106.0 ± 3.6	136.5 ± 2.9	73.83	
Raw			149.2	532.16	Mora-Rochin et al. [49]
Tortilla			89.8	208.12	
BG					
Raw	45.5 ± 0.5	220.7 ± 0.5	266.2 ± 0.7	123.01	De la Parra et al. [47]
Tortilla	39.1 ± 1.5	122.7 ± 0.6	161.8 ± 2.1	101.36	
Raw			140.1	336.49	Mora-Rochin et al. [49]
Tortilla			86.3	187.79	

SP: soluble phenolics; IP: insoluble phenolics; TP: total phenolics; WG: white grain; RG: red grain; BG: blue grain.

Table 4. Phenolic compounds in raw grain and tortillas obtained by the traditional nixtamalization process, from maize grains with different colors.

When nixtamalization is performed by the extrusion method, total phenolic losses in maize grain are lower than those resulting from the traditional method [49]. The differences were

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attributed to the fact that the extrusion method does not produce losses from hydrolyzed pericarp, and there is no leaching of phenolics.

Of the phenolic acids present in maize grain, the changes in ferulic acid have been monitored, as the most abundant member of this group. In white maize grain, the losses of this acid in the process of going from grain to tortillas are between 20 and 30%; nevertheless, in red maize grain they are higher and account between 44 and 60%, while in the blue maize grain they represent 18–45%, according to the information shown in **Table 4**. It is probable that the high losses of ferulic acid observed in red or blue maize grain may be a result of the maize varieties used in the studies that have a floury grain, which is very likely to occur if the maize used were native of Mexico. Floury maize generally has a thinner pericarp as compared to that of hard grains, and thus during nixtamalization the grain is hydrated faster than hard grain. Thinner pericarps could favor the hydrolysis of the ester bond that keeps the ferulic acid linked to cell wall components, and thus the acid is leached to the cooking water, known as nejayote. There are no reports on contents of ferulic acid in the nejayote of maize of different grain hardness, processed under the same nixtamalization method. In addition, when cooking times are adjusted to achieve optimal nixtamalization for each type of maize, the values of ferulic acid found in nejayote relate more to the cooking length than with grain hardness [50] and have values of ferulic acid content greater than those found in the grain and the masa for tortillas.

6. Conclusions

Phenolic compounds are present in the maize grain in free or soluble and bound or insoluble form. The insoluble fraction is the most abundant, but the most chemically diverse is the soluble fraction. There exists greater diversity of phenolic compounds in the grain of maize with anthocyanin-type pigments than in the white maize grain. Phenolic acids are the most abundant phenolic compounds in maize grain, followed by flavonoids, particularly anthocyanins in the blue red and purple maize grain. Phenolic amines are present in the pericarp of white maize grain and grain containing anthocyanin pigments, being most abundant in the latter. Nixtamalization significantly reduces the content of phenolics present in maize grain, in white grain maize, they are lost mainly as ferulic acid, while in the maize grain that contains anthocyanin pigments, in addition to ferulic acid, anthocyanins are almost entirely lost.

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References

[1] Nicholson RL and Hammerschmid R. Phenolic compounds and their role in diseases resistance. Annual Review of Phytopathology. 1992; 30: 369–389. DOI: 10.1146/annurev.py.30.090192.002101

[2] Boudet AM. Evolution and current status of research in phenolic compounds. Phytochemistry. 2007; 68:2722–2735. DOI: 10.1016/j.phytochem.2007.06.012

[3] Lattanzio V, Kroon PA, Quideau S, and Treutter D. Plant phenolics – secondary metabolites with diverse functions. In: Daayf F, Lattanzio V, editors. Recent advances in polyphenols research, Singapore: Wiley; Vol I; 2011. Pp. 1–35. DOI: 10.1002/9781444302400

[4] Adom KK and Liu RH. Antioxidant activity of grains. Journal of Agriculture and Food Chemistry. 2002; 50: 6182-6187. DOI: 10.1021/jf0205099

[5] Shaw NM, Bolwell GP, and Smith C. Wound-induced phenylalanine ammonia-lyase in potato (*Solanum tuberosum*) tuber discs. Biochemical Journal. 1992; 267: 163–170. DOI: 10.1042/bj2670163

[6] Shahidi F and Naczk M. Biosynthesis, classification, and nomenclature of phenolics in food and nutraceuticals. In: Phenolics in food and nutraceuticals. CRC Press, Washington, DC; 2004. pp. 1–16.

[7] Quideau S, Deffieux D, Douat-Casassus C, and Pouységu L. Plant polyphenols: Chemical properties, biological, activities, and synthesis. Angewandte Chemie International Edition. 2011; 50: 586–621. DOI: 10.1002/anie.201000044

[8] Harborne, J. B. Plant phenolics. In: Encyclopedia of plant physiology, New Series, Vol. 8. (Pirson, A. & Zimmerman, M. H. (Eds), Springer-Verlag, Berlin, 239–402.

[9] Harborne JB and Simmonds NW. Biochemistry of Phenolic Compounds. Academic Press. London; 1964. p. 101.

[10] Vermerris W and Nicholson R. Families of phenolic compounds and means of classification. Phenolic compound biochemistry. Springer, Netherlands; 2008. pp. 1–34. DOI: 10.1007/978-1-4020-5164-7

[11] Choi SW, Sung KL, Eun OK, Ji HO, Kyung SY, Parris N, Hicks KB, and Moreau RA. Antioxidant and antimelanogenic activities of polyamine conjugate from corn bran and related hydroxicinnamic acids. Journal of Agricultural and Food Chemistry. 2007; 55: 3920–3925. DOI: 10.1021/jf0635154

[12] Liyama K, Lam TBT, and Stone BA. Covalent cross-links in the cell wall. Plant Physiology. 1994; 104: 315–320. DOI: 10.1104/pp.104.2.315

[13] Das AK and Singh V. Antioxidative free and bound phenolic constituents in pericarp, germ and endosperm of Indian dent (Zea mays var. indentata) and flint (Zea mays var. indurata) maize. Journal of Functional Foods. 2015; 13: 363–374. DOI: 10.1016/j.jff.2015.01.012

[14] Ramos FE, Muñóz AM, Alvarado OC, Alvarado A, and Yañéz JA. Purple corn (Zea mays L.) phenolic compounds profile and its assessment as an agent against oxidative stress in isolated mouse organs. Journal of Medicinal Foods. 2012; 15: 206–215. DOI: 10.1089/jmf.2010.0342

[15] Sen A, Bergvinson D, Miller SS, Atkinson J, Fulcher RG, and Arnason J. Distribution and microchemical detection of phenolic acids, flavonoids, and phenolic acid amides in maize kernels. Journal of Agricultural and Food Chemistry. 1994; 42: 1879–1883. DOI: 10.1021/jf00045a009

[16] Collison A, Yang L, Dykes L, Murray S, and Awika JM. Influence of genetic background on anthocyanin and copigment composition and behavior during thermoalkaline processing of maize. Journal of Agricultural and Food Chemistry. 2015; 63: 5528-5538. DOI: 10.1021/acs.jafc.5b00798

[17] Singleton VL and Rossi JA. Colorimetry of total phenolics with phosphomolybdic-502 phosphotungstic acid reagents. American Journal of Enology and Viticulture. 1965; 16: 144–158. DOI:

[18] Das AK and Singh V. Antioxidative free and bound phenolic constituents in botanical fractions of Indian specialty maize (*Zea mays* L.). Food Chemistry. 2016; 201: 298–306. DOI: 10.1021/jf100868b

[19] Pedreschi R and Cisneros L. Phenolic profiles of Andean purple corn (*Zea mays* L.). Food Chemistry. 2007; 100: 956–963. DOI: 10.1016/j.foodchem.2005.11.004

[20] Sosulski F, Krygier K, and Hogge L. Free, esterified, and insoluble-bound phenolic acids. 3. Composition of phenolic acids in cereal and potato flours. Journal of Agriculture and Food Chemistry. 1982; 30: 337–340.DOI: 10.1021/jf00110a030

[21] Prior RL, Wu H, and Gu L. Flavonoid metabolism and challenges to understanding mechanisms of health effects. Journal of the Science of Food and Agriculture. 2006; 86: 2487-2491. DOI: 10.1002/jsfa.261

[22] Zilic S, Serpen A, Akıllıoglu G, Gokmen V, and Vanc EJ. Phenolic compounds, carotenoids, anthocyanins, and antioxidant capacity of colored maize (*Zea mays* L.) Kernels Journal of Agricultural and Food Chemistry. 2012; 60: 1224-1231.DOI: 10.1021/jf204367z

[23] Giusti MM and Wrolstad RE. Acylated anthocyanins from edible sources and their applications in food systems. Biochemical Engineering Journal. 2003; 14: 217–225. DOI: 10.1016/S1369–703X(02)00221-8

[24] Salinas-Moreno Y, Soto-Hernández M, Martínez-Bustos F, González-Hernández V, and Ortega-Paczka R. Analysis of anthocyanins in blue and red maize grains of four races. Revista Fitotecnia Mexicana. 1999; 22: 161–174.

[25] Rodríguez SL and Wrolstad RE. Extraction, isolation and purification of anthocyanins. Current Protocols in Food Analytical Chemistry. John Wiley, New York; 2001. pp. 7–17. DOI: 10.1002/0471142913.faf0101s00

[26] Yoshitama K. An acylated delphinidin-3-rutinoside-5, 3′, 5′-triglucoside from Lobelia erinus. Phytochemistry. 1977; 16: 1857–1858. DOI: 10.1016/0031-9422(71)85123-3

[27] Del Pozo-Insfran D, Brenes CH, Serna-Saldivar SO, and Talcott ST. Polyphenolic and antioxidant content of white and blue corn (*Zea mays* L.) products. Food Research International. 2006; 39: 696–703. DOI: 10.1016/j.foodres.2006.01.014

[28] Ralph J, Quideau S, Grabber JH, and Hatfield RD. Identification and synthesis of new ferulic acid dehydrodimers present in grass cell walls. Journal of the Chemical Society, Perkin Transactions. 1994; 1: 3485–3498. DOI: 10.1039/P19940003485

[29] Montilla CE, Hillebrand S, Antezana A, and Winterhalter P. Soluble and bound phenolic compounds in different Bolivian purple corn (*Zea mays* L.) cultivars. Journal of Agriculture and Food Chemistry. 2011; 59: 7068– 7074. DOI: 10.1021/jf201061x

[30] López-Martínez LX, Oliart-Ros RM, Valerio-Alfaro G, Lee CH, Parkin KL, and García HS. Antioxidant activity, phenolic compounds and anthocyanins content of eighteen strains of Mexican maize. LWT—Food Science and Technology. 2009; 42: 1187–1192. DOI: 10.1016/j.lwt.2008.10.010

[31] Xu JG, Hu QP, Wang XD, Luo JY, Liu Y, and Tian CR. Changes in the main nutrients, phytochemicals, and antioxidant activity in yellow corn grain during maturation. Journal of Agriculture and Food Chemistry. 2010; 58: 5751–5756. DOI: 10.1021/jf100364k

[32] Blandino M, Mancini MC, Peila A, Rolle L, Vanara F, and Reyneri A. Determination of maize kernel hardness: comparison of different laboratory tests to predict dry-milling performance. Journal of the Science of Food and Agriculture. 2010; 90:1870–1878. DOI: 10.1002/jsfa.4027

[33] Chiremba C, John RN, Taylor , Rooney LW, and Trust B. Phenolic acid content of sorghum and maize cultivars varying in hardness. Food Chemistry. 2012; 134: 81–88. DOI: 10.1016/j.foodchem.2012.02.067

[34] Cabrera-Soto ML, Salinas-Moreno Y, Velázquez-Cardelas GA, and Espinosa-Trujillo E. Content of soluble and insoluble phenols in the structures of corn grain and their relationship with physical properties. Agrociencia. 2009; 43: 827–839.

[35] Bunzel M. Chemistry and occurrence of hydroxycinnamate oligomers. Phytochemical Reviews. 2010; 9: 47–64. DOI: 10.1007/s11101-009-9139-3

[36] Bunzel M, Allerdings E, Ralph J, and Steinhart H. Cross-linking of arabinoxylans via 8-8-coupled diferulates as demonstrated by isolation and identification of diarabinosyl 8-8(cyclic)-dehydrodiferulate from maize bran. Journal of Cereal Science. 2008; 47: 29–40. DOI: 10.1016/j.jcs.2006.12.005

[37] Bily AC, Reid LM, Taylor JH,Johnston D, Malouin C, Burt AJ, Bakan B, Regnault-Roger C, Pauls KP, Arnason JT, and Philogène BJR. Dehydrodimers of ferulic acid in maize grain pericarp and aleurone: resistance factors to Fusarium graminearum. Phytopathology. 2003; 93: 712–719. DOI: 10.1094/PHYTO.2003.93.6.712

[38] Sampietro DA, Fauguel CM, Vattuone MA, Presello DA, and Catalán CAN. Phenylpropanoids from maize pericarp: resistance factors to kernel infection and fumonisin accumulation by Fusarium verticillioides. European Journal of Plant Pathology. 2003; 135: 105–113. DOI: 10.1007/s10658-012-0069-3

[39] Arnason JT, Gale J, Conilh de Beyssac B, Sen A, Miller SS, Philogene BJR, Lambert JDH, Fulcher RG, Serratos A, and Mihm J. Role of phenolics in resistance of maize grain to the stored grain insects, Prostephanus truncatus (Horn) and Sitophilus zeamais (Motsch.). Journal of Stored Products Research. 1992; 28: 119–126. DOI: 10.1016/0022-474X(92)90019-M

[40] Rouaua X, Cheynier V, Surget A, Gloux D, Barron C, Meudec E, Monterod JL, and Criton M. A dehydrotrimer of ferulic acid from maize bran. Phytochemistry. 2003; 63: 899–903. DOI: 10.1016/S0031-9422(03)00297–8

[41] Bakan B, Bily AC, Melcion D, Cahagnier B, Regnault- Roger C, Philogene BJR, and Richard-Molard D. Possible role of plant phenolics in the production of trichothecenes by Fusarium graminearum strains on different fractions of maize kernels. Journal of Agriculture and Food Chemistry. 2003; 51: 2826–2831. DOI: 10.1021/jf020957g

[42] Aoki H, Kuze N, and Kato Y. Anthocyanins isolated from purple corn (*Zea mays* L.). Foods & Food Ingredients Journal of Japan. 2002; 199: 41–45.

[43] Cevallos-Casals BA and Cisneros-Zevallos L. Stability of anthocyanin-based aqueous extracts of Andean purple corn and red-fleshed sweet potato compared to synthetic and natural colorants. Food Chemistry. 2004; 86: 69–77. DOI: 10.1016/j.foodchem.2003.08.011

[44] González-Manzano S, Pérez-Alonso JJ, and Salinas-Moreno Y. Flavanol-anthocyanin pigments in corn: NMR characterisation purple corn phenolic profile and assessment 213 and presence in different purple corn varieties. Journal of Food Composition and Analysis. 2008; 21: 521–526. DOI: 10.1016/j.jfca.2008.05.009

[45] Martínez-Bustos F, Martínez-Flores HE, and Sanmartín-Martínez E. Effect of the components of maize on the quality of masa and tortillas during the traditional nixtamalization process. Journal of the Science of Food and Agriculture. 2001; 81: 1455–1462. DOI: 10.1016/j.jfca.2008.05.009

[46] González R, Reguera E, Mendoza L, Figueroa JM, and Sánchez F. Physicochemical changes in the hull of corn grains during their alkaline cooking. Journal of Agriculture and Food Chemistry. 2004; 52: 3831–3837. DOI: 10.1021/jf035175h

[47] Salinas-Moreno Y, Martínez-Bustos F, Soto-Hernández M, Ortega-Paczka R, and Arellano-Vázquez JL. Efecto de la nixtamalización sobre las antocianinas del grano de maíces pigmentados. Agrociencia. 2003; 37: 617–628.

[48] De la Parra C, Serna-Saldivar SO, and Hai L. Effect of processing on the phytochemical profiles and antioxidant activity of corn for production of masa, tortillas, and tortilla chips. Journal of Agriculture and Food Chemistry. 2007; 55: 4177–4183. DOI: 10.1021/jf063487p

[49] Mora-Rochin SR, Gutiérrez-Uribe JA, Serna-Saldivar SO, Sánchez-Peña P, Reyes-Moreno C, and Milán-Carrillo J. Phenolic content and antioxidant activity of tortillas produced from pigmented maize processed by conventional nixtamalization or extrusion cooking. Journal of Cereal Science. 2010; 52: 502–508. DOI: 10.1016/j.jcs.2010.08.010

[50] Gutiérrez-Uribe JA, Rojas-García C, García-Lara S, and Serna-Saldivar SO. Phytochemicals of wastewater (nejayote) obtained after lime-cooking of different types of maize kernel processed into masa for tortillas. Journal of Cereal Science. 2010; 52: 410–416. DOI: 10.1016/j.jcs.2010.07.003