The nutraceutical value of maize (*Zea mays* L.) landraces and the determinants of its variability: A review

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A R T I C L E   I N F O

A B S T R A C T

Maize is one of the major staple cereals in the world. The species has evolved for centuries into hundreds of landraces, adapting to different agroecological niches under careful farmer selection. This genotype diversity and heterogeneity are related to unique phytochemical or secondary metabolite profiles. Research has been dedicated to studying the variety in phytochemicals and the health benefits associated with the consumption of grains from these varieties, particularly in terms of antioxidant activity and the prevention of chronic diseases. These topics and the pre-harvest variability in phytochemicals that is generated due to the interaction of genotype, selection and adaptation, with agroecological determinants (planting environment and agricultural management) are reviewed and analyzed in the context of conservation and revalorization of landrace genetic diversity.

1. Introduction

Maize (*Zea mays* L.) has its center of origin in the Mexican highlands, where it was domesticated about 9000 years ago, then distributed across the American continent, and later disseminated to Europe, Asia and Africa in the years following the discovery of the New World (Prasanna, 2012). Centuries of continuous cultivation and adaptation to new regions led to a great diversity in this plant, observable in hundreds of landraces distributed all over the World (Gálvez Ranilla, 2020); maize landraces, unlike hybrids, are heterogeneous, meaning that each landrace population is a mixture of genotypes, and they are continuously selected by farmers due to different characteristics: resistance to pests and diseases, prolificacy, flowering dynamics, plant architecture, and their reliable productivity, for example (Guzzon et al., 2021; Prasanna, 2012). Each landrace can be differentiated and sometimes named by farmers according to color, texture, grain shape, ear shape, vegetative cycle or intended use (Burt et al., 2019; Camacho Villa et al., 2005), an example of this can be seen in Fig. 1.

Although the maize plant has other uses, the main historical reason

for its cultivation has been the production of food, and so the grains have been incorporated in the diets of people around the World. Nowadays, maize and their derivatives are staples for many human populations, since they constitute a significant part of the caloric and nutrient provision of 4.5 billion people globally, particularly in rural areas of Latin America and Africa (CONABIO, 2017; Palacios-Rojas et al., 2020). Maize diversity is relevant for food security, not only in nutritional terms, but also due to the content of phytochemicals or secondary metabolites such as carotenoids and phenolic compounds (Guzmán et al., 2021; Palacios-Rojas et al., 2020). On the one hand, the consumption of a diet rich in phytochemicals is associated with lower risk of chronic diseases such as cancer or diabetes, which are common problems in modern societies, so maize landraces can benefit human health in this way (Siyuan et al., 2018). Because of this, in the last decades there has been a growing interest in characterizing and studying the diversity of phytochemical profiles of existing maize landraces as well as the benefits of their consumption, particularly with regards to pigmented varieties (see for example, Gálvez Ranilla, 2020 or Colombo et al., 2021). On the other, secondary metabolites are also important for grain production, since they constitute one of the reasons why landraces can tolerate the stresses

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Abbreviations

ABTS	2,2′-Azinobis-(3-ethylbenzothiazoline-6-sulfonic acid
BP	Bound phenolics
C3GE	Cyanidin-3-Glucoside equivalents
CAA	Cellular antioxidant capacity assay
CE	Catechin equivalents
CUPRAC	Cupric Reducing Antioxidant Capacity
DPPH	2,2-di (4-tert-octylphenyl)-1-picrylhydrazyl)
FP	Free phenolics
FRAP	Ferric Reducing Antioxidant Power
HCAA	Hydroxycinnamic acid amides
masl	meters above sea level
ORAC	Oxygen Radical Absorbance Capacity
P1	Pericarp color1
QE	Quercetin equivalents
TAC	Total anthocyanin contents
TCC	Total carotenoid contents
TEAC	Trolox Equivalent Antioxidant Capacity
TFC	Total flavonoid contents
TPC	Total phenolic contents

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of the local environment, which confers them the ability to produce moderate but stable yields under low-input peasant approaches (CON-ABIO 2017). The study of the phytochemical diversity of landraces is important to identify the specific compounds that offer protection against biotic and abiotic stresses as the plant develops (Bernardi et al., 2018; Naikoo et al., 2019). The generation of such knowledge regarding landraces has been primarily used in participatory breeding programs for the development of new maize varieties with increased contents of secondary metabolites (Uarrota et al., 2011; Logrieco et al., 2021; Puglisi et al., 2018), but it can also be used for the development of additional marketing channels and information campaigns that increase the demand and value/market prices of the landraces cultivated by traditional farmers, promoting diversity preservation (Guzzon et al., 2021).

In this context, the present paper builds on the available evidence through a literature review on the nutraceutical potential of maize landraces. Focusing on the bioactive compounds contained in grains and their activities, and in the analysis of the agroecological factors that may contribute to the reported variability and diversity. Additionally, the authors of this paper hope to bring about additional recognition to maize farmers for their role as stewards of maize agrodiversity conservation.

2. Grain bioactives in landrace genotypes

2.1. Landraces, diversity, and nutraceutical studies

To assess the literature, the following working definition for landrace will be used: A dynamic population or variety, which possesses a historical origin, distinct identity and has not been improved through conventional breeding, which means it has high genetic heterogeneity (Camacho Villa et al., 2005). Several terms have been used to refer to maize landraces, reflecting the level of farmer involvement, the type of seed supply or management, and even the cultural heritage they represent (Camacho Villa et al., 2005). For example, the literature uses heirloom, ancient, traditional variety to name landraces that have been maintained by farmers for centuries (Nankar et al., 2016; Puglisi et al., 2018); other terms, such as farmer, creole, folk, or local varieties, refer to landraces that are preserved at a small scale and actively selected by farmers due to the specific uses they give them (Camacho Villa et al., 2005). Other synonyms include maize race, ecotype, or native maize variety, which are often used for related landraces or landrace groups.

Finally, the word "accession" is used in the reviewed literature mainly for genotypes conserved and catalogued in gene/germplasm banks (*e.g.* Trehan et al., 2018), but sometimes the literature uses it to denote landrace populations collected or obtained from a particular area (*e.g.* Mendoza-Mendoza et al., 2021). To provide a wide perspective on the maize landrace literature, studies explicitly using these terms were included in this review but the pertinence of each synonym to name a specific variety will not be discussed. Further details on the literature review process, the inclusion and exclusion criteria, as well as the included papers can be found in the Supplementary material.

As mentioned, the World's maize landrace genetic diversity is high but, according to our review, only a fraction of it has been studied in terms of grain phytochemicals. It can be said, nonetheless, that the selected studies are representative in terms of the different regions where maize is cultivated (Supplementary material, Table S1). Mexican and other American ancient and modern landraces have been studied for the last 20 years and, although the nutraceutical potential of diverse grain pigmentations have been analyzed, blue, red, and purple varieties have been of the greatest interest, so an important part of the information refers to them (Fig. S1b). European, and particularly pigmented Italian ancient landraces have been characterized since the 2010's as part of conservation and breeding efforts to generate phytochemically rich varieties (Capocchi et al., 2017; Puglisi et al., 2018). For Asian racial groups, phytochemical studies have dealt mainly with waxy or glutinous pigmented maize landraces of the Southeast parts of the continent (Harakotr et al., 2014), but a few examples from India were found (Trehan et al., 2018). Also, while studies on raw kernels of African landraces were scarce, the available information still gives an indication of the predominant types of maize cultivated by smallholder farmers due to their own food preferences, in terms of color and texture (Hwang et al., 2016).

Research on maize landraces has focused on a few phytochemical groups, predominantly carotenoids and phenolic compounds. In these studies, the content of bioactives has been measured with standard spectrophotometric quantification techniques (e.g. Folin-Ciocalteu method for phenolics) while specific profiles are determined via chromatographic techniques (HPLC, UPLC, UHPLC, etc.). Several factors preclude a direct comparison of the results for different landraces, for example: samples had a multitude of origins (*e.g.* field collection, market purchase, germplasm bank), preparation and storage conditions (*e.g.* air dried, freeze dried, frozen, refrigerated, etc.), and were subjected to different extraction or separation methods to prepare them for analysis. Additionally, studies often fail to state the sample size, the names of the landraces, their racial groups or give details on the agroecosystem where the grains originated, the prevalent growing conditions or even how they were sampled.

Regardless of the mentioned limitations, genotype remains the core source for the variability of secondary metabolites in the raw kernel (Uarrota et al., 2014) and we expect the general values and trends reported in this review can be useful to visualize the richness in phytochemical composition of landrace populations.

2.2. Phenolic compounds

These compounds are some of the most abundant secondary metabolites in plant tissues. For mature maize grains, the majority of phenolic compounds (anthocyanins, phenolic acids and flavanols, for example) are located in the outer layers of the kernel, *i.e.* the pericarp, aleurone and seed coat (Cassani et al., 2017), but some phenolic derivatives have been found in the germ of maize grains (Burt et al., 2019). They are categorized as flavonoids, phenolic acids, stilbenes, coumarins and tannins, and within these compounds, phenolic acids and flavonoids are the major groups, constituting over 70% of the TPC. For example, in Italian landraces, Bernardi et al. (2018) identified close to 300 different phenolics with the most detected classes being, in descending order: flavonoids, phenolic acids, tyrosols, alkylphenols, other phenolics; they

also observed that the diversity of phenolic classes tended to disappear as pigmentation increased. In the studied varieties, flavonoids (anthocyanins) were predominantly found in a purple-black landrace, while a deep orange one had more phenolic acids (hydroxycinnamic acids).

TPC in groups of maize landraces show great variability across countries, with dark-colored varieties (particularly deep purple or red ones) presenting the higher values in each group (Fig. 2). In raw kernels, most studies have reported the majority of phenolic compounds are not found in their free form, but rather bound to the cell walls of maize, in some cases, such as in the *Pisankalla* or *Morocho* Chilean landraces, less than 10% of the TPC is present in extractable forms (González-Muñoz et al., 2013). However, some pigmented landraces have been found to have higher FP contents, such as the Peruvian *Morado Canteño*, whose FP fraction amounts to 80% of the TPC (Gálvez Ranilla et al., 2021).

2.2.1. Phenolic acids

In relation to simple phenolic acids, hydroxycinnamic acids like ferulic, coumaric and sinapic acids are the most detected types in maize landraces, followed by hydroxybenzoic acid derivatives such as protocatechuic, vanillic and syringic acid. Although regional and genotypic variability is observed in terms of specific profiles and isomeric forms, the abundance of the main types of phenolic acids tends to remain constant in landraces (Cuevas Montilla et al., 2011; Gálvez Ranilla et al., 2019). HPLC analysis of different Indian accessions of yellow, purple-red, and white varieties showed that the levels of ferulic and sinapic acids were in the range of 1860–6275 and 1466–1532 mg/100 g (Trehan et al., 2018). Some Mexican genotypes showed levels of total ferulic acid ranging from 82.27 to 168 mg/100 g, while p-coumaric acid was below 30 mg/100 g (Gaxiola-Cuevas et al., 2017). South American landraces contents of ferulic acid ranged from 72.3 to 156.3 mg/100 g for Peruvian and 126.1–268.5 mg/100 g for Chilean; while in Bolivian landraces, the main phenolic acids were 251.8–607.5 mg/100 g for p-coumaric acid and 132.9–298.4 mg/100 g for ferulic acid (Cuevas Montilla et al., 2011; Gálvez Ranilla et al., 2019; González-Muñoz et al., 2013).

Regarding more complex forms of phenolic acids, studies on Portuguese landraces have found they have larger diversity than wheat or rye in terms of ferulic acid dehydrodimers, trimers and tetramers such as dehydrodiferulic, dehydrotriferulic and dehydrotetraferulic acids which are cross-linked with cell wall components and therefore are insoluble (Bento-Silva et al., 2020). Additionally, maize landraces have diverse profiles of soluble and insoluble hydroxycinnamic acid amides (HCAA), from ferulic, coumaric and caffeic acids dimers and trimers, and compounds that were not found in wheat and rye flours such as dehydrodiferulic and dehydrotriferulic acid putrescines (Bento-Silva et al., 2020).
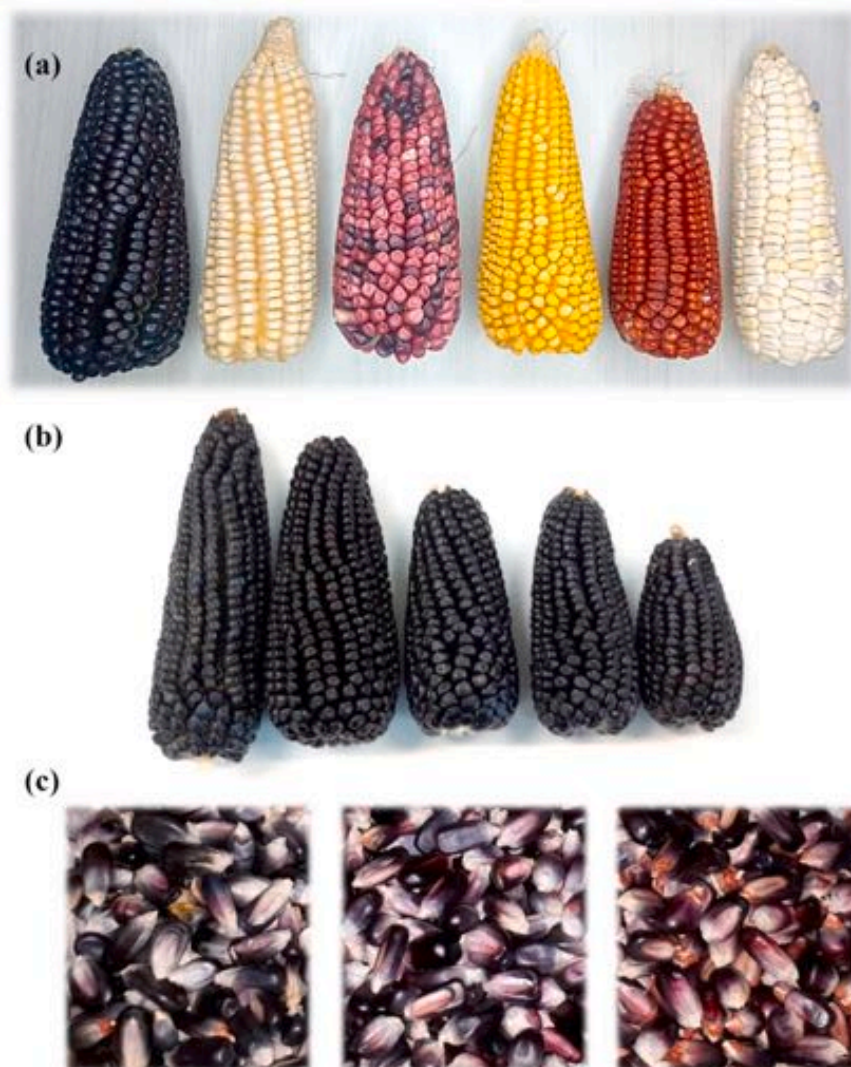
Fig. 1. A small example of the different levels of diversity collected in a farm located in the municipality of Ahuazotepec, in the state of Puebla, Mexico. (a) Maize cobs from some *Cónico* landraces planted and named by a local producer, from left to right: Black *Elote Cónico*, White *Palomo*, Purple-pink *Xucuyul*, Yellow *Cónico*, Red *Ladrillo* and White *Cacahuacintle* or Pozolero. (b) Variability in cob sizes within the *Elotes Cónicos* population. (c) Pigmentations within the same population, from dark blue to purple-red. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)
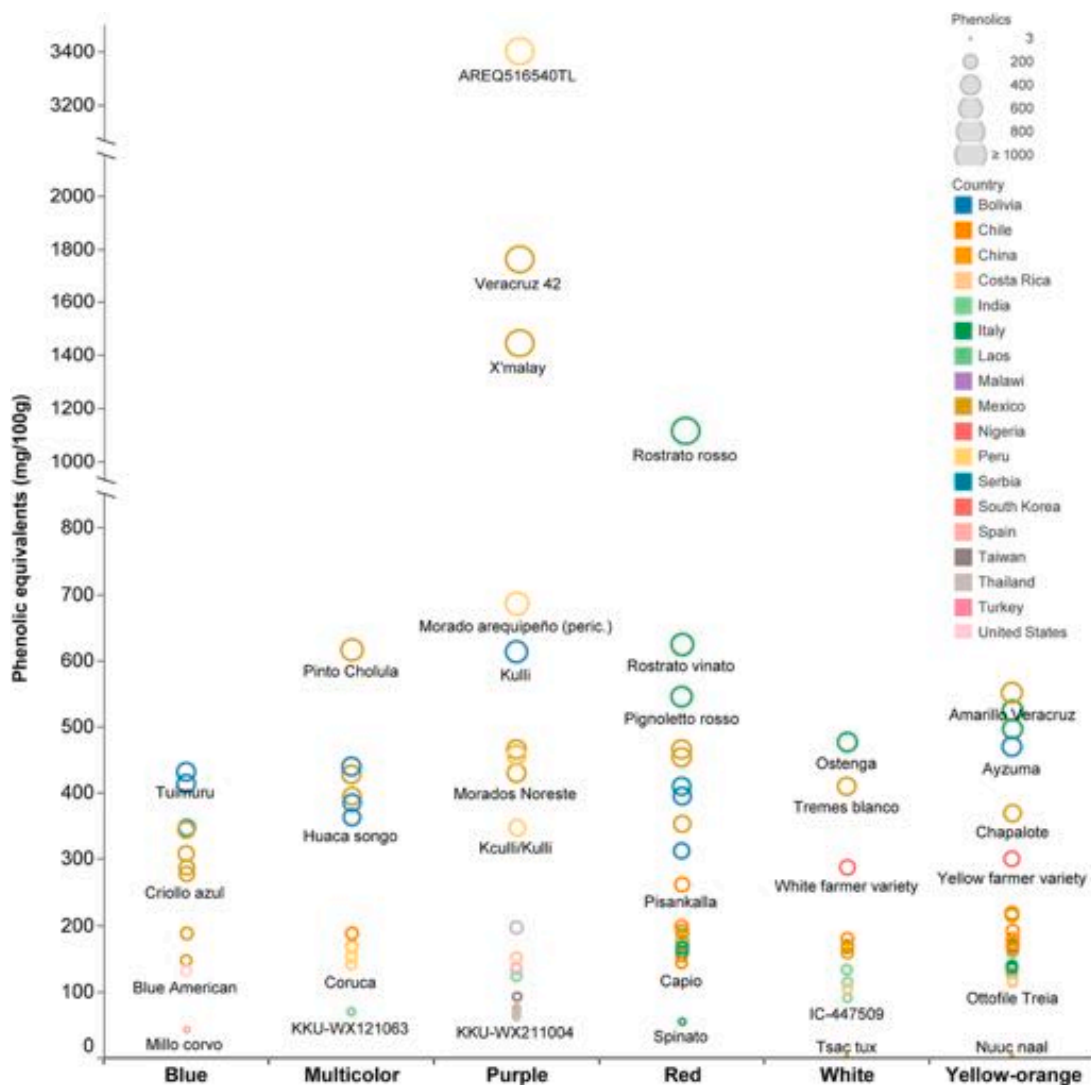
Fig. 2. Total phenolic contents of accessions of maize grain landraces from different countries, grouped by the dominant pigmentation of the kernel. Size of the circles gives an indication of the phenolic content of a landrace in relation to the overall range observed (3.9–3400 mg/100 g).

2.2.2. Flavonoids

Flavonoids in maize landraces are a large class of phenolics, containing anthocyanins, flavones, flavans, flavanols, flavonols, iso-flavonoids, etc. (Bernardi et al., 2018). The specific non-anthocyanin flavonoids in maize grains depend greatly on genotype and they show inter landrace variability, depending on accession/collection site (Chatham et al., 2018).

Researchers have identified the major non anthocyanin compounds of this group to be kaempferol derivatives and naringenin, but quercetin, catechin and rutin derivatives have also been detected (Trehan et al., 2018; Zhang et al., 2019). TFC of differently pigmented maize landraces have been measured in a few studies. Rodríguez-Salinas et al. (2020) characterized Mexican landraces from the North of Mexico, showing great variability in TFC per 100 g grain, depending on the pigmentation, from 24 mg_{CE} for white to 105.75 mg_{CE} for dark red, with purple and pinto (multicolored) varieties having intermediate flavonoid contents: between 39.7 and 96 mg_{CE}/100 g. Lower TFC values were found in red and blue maize samples from the center of Mexico, which ranged from 0.32 to 2.31 and 5.55–12.19 mg_{CE}/100 g, respectively (Loarca-Piña et al., 2019). This variability was also observed in yellow, orange, and red Italian landraces, whose TFC ranged from approximately 40.6 to

53.6 mg_{CE}/100 g, with higher levels corresponding to increasing redness levels (Capocchi et al., 2017). The highest reported total flavonoid values correspond to Peruvian *Kulli* or *Morado*, a purple variety (Gálvez Ranilla et al., 2021).

2.2.2.1. Anthocyanins. These compounds contribute to the reddish-pink, blue, purple, and black hues observed in maize, in Fig. 1a and c, the *Elotes Cónicos* and *Xucuyul* landraces exhibit colorations originated from anthocyanins. As can be seen in Fig. 3, TAC in maize landraces show genotype variations which correlate with the dominant pigmentation. The varieties showing the highest TAC are Peruvian *Morados* (purple), with accessions having up to 850 $mg_{Cyanidin-3-Glucoside\ Equivalents\ (C3GE)}$/100 g, the lowest anthocyanin contents correspond to white landraces with less than 1 mg_{C3GE}/100 g. These compounds also have been of great interest to research both for their bioactivity and for their prospective use as a natural coloring agent (see for example: Chatham et al. (2018) or Paulsmeyer et al. (2017)). An important number of reviews covering different topics on these compounds in maize and other grains, including detailed classifications, forms, occurrences, synthesis, interactions with nutrients, extraction, etcetera, are available and therefore this section of the review will mainly focus on diversity aspects
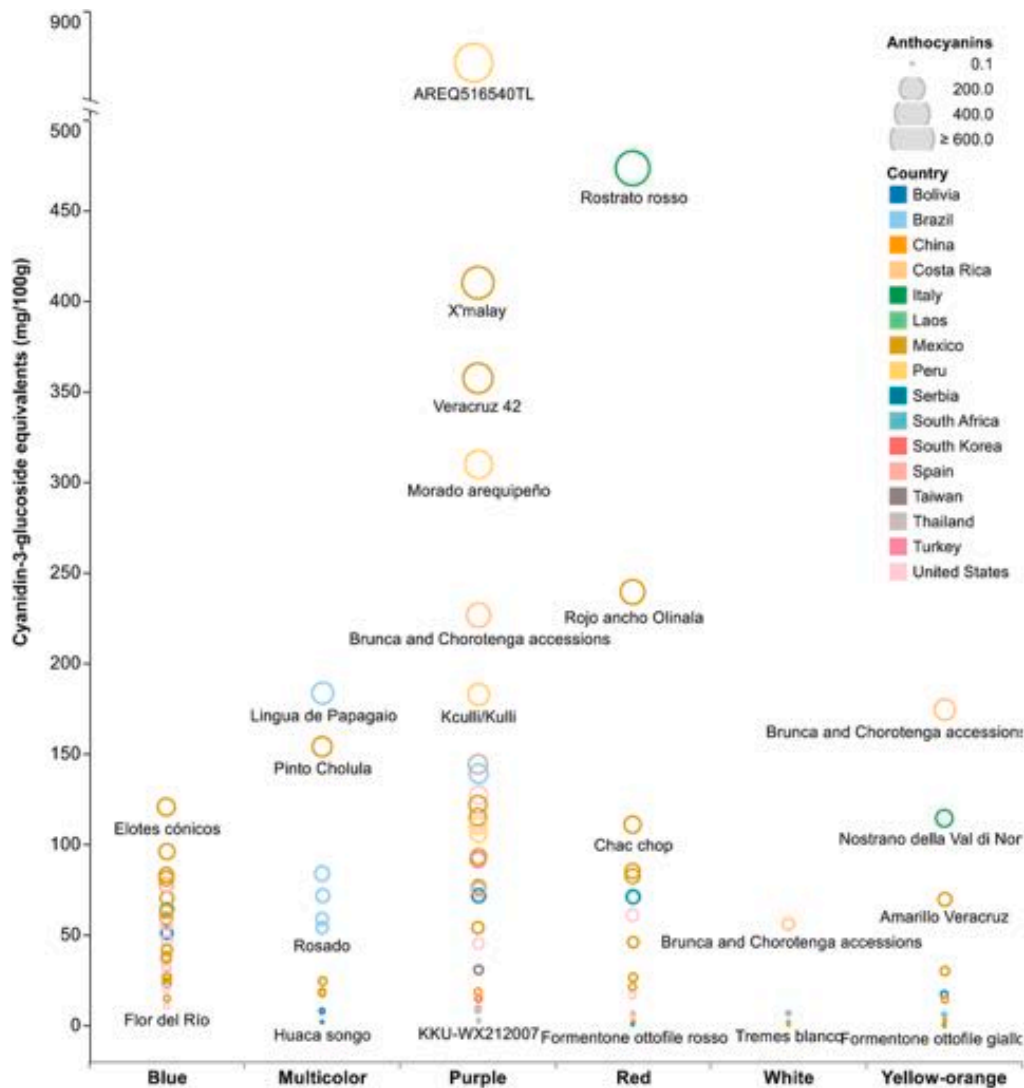
Fig. 3. Total anthocyanin contents of accessions of maize grain landraces from different countries, grouped by the dominant pigmentation of the kernel. Size of the circles gives an indication of the anthocyanin content of a landrace relative to the overall range observed (0.1–850 mg/100 g).

regarding maize landraces.

The most common anthocyanins identified in raw maize grains are glucosides from cyanidin, peonidin, pelargonidin (cyanidin-3-glucoside, peonidin-3-glucoside, and pelargonidin-3-glucoside), and in some cases delphinidin and malvidin (Ramírez et al., 2018; Salinas-Moreno et al., 2012). These can be further acylated with one or more moieties of pyruvic, acetic, succinic, or malonic acid, making them more stable. Paulsmeyer et al. (2017) performed a survey of 398 accessions of pigmented maize landraces and estimated the average percentage of acylated anthocyanins to be 58.9% of the TAC, but they also found a small subset characterized precisely by the extremely low concentration of acylated forms and the overall dominance of cyanidin-3-glucosides due to a reduced functionality of the enzyme in charge of acylation (anthocyanin acyltransferase).

Even when the profile is similar, the specific concentration of certain anthocyanins, the primary site of accumulation (pericarp or aleurone), as well as the pH of the matrix, determine the observed color in maize grains or products (Doria, 2015; Salinas Moreno et al., 2005). Cyanidin derivatives constitute the major anthocyanins in maize landraces, with levels between 70 and 87% of TAC in purple maize varieties from Mexico and Peru (Salinas Moreno et al., 2005) and 65.9% in the dark

blue *Millo corvo* (Lago et al., 2015); while malvidin derivatives are also common in blue maize varieties. Purple and blue varieties can be differentiated because anthocyanins in the first group accumulate in the aleurone or outermost endosperm layer and have higher diversity in pigment profile, while in the latter, the pigment is in the pericarp, at high concentrations, but contain fewer anthocyanin types (Paulsmeyer et al., 2017). Other anthocyanins become more prominent in pink or red landraces so, for instance cyanidin and peonidin had closer levels in deep red *Spinato* (48.5% and 42.1% of TAC, respectively), peonidin derivatives were the most abundant type in grains of pink *Elotes Occidentales* grains (Ramírez et al., 2018). Anthocyanins like delphinidin and malvidin derivatives have also been recently detected in European races such as *Millo corvo, Spinato* (Lago et al., 2015) and *Rostrato rosso* (Bernardi et al., 2018), with the latter containing characteristic delphinidin-3-O-xyloside and malvidin-3-O-(6-acetyl-galactoside).

2.2.2.2. Condensed forms. Flavanol-anthocyanin dimers have been identified and characterized as pigments in some pericarp-colored in maize landraces using chromatographic methods (HPLC, LC-MS/MS) (Chatham et al., 2018; Paulsmeyer et al., 2017). These condensed forms, also termed proanthocyanidins, are present independently of the

profile of monomeric and/or free anthocyanins and provide a coloration that is more heat and pH stable than other flavonoid pigments (Capocchi et al., 2017). According to Paulsmeyer et al. (2017), condensed forms in maize landrace accessions are present in a wide range of levels, correlating with genetic diversity, from 3.8 to 32.8% of TAC.

The major known condensed form in maize landraces is catechin-(4,8)-cyanidin-3,5-diglucoside, but other forms are present in *Arrocillo, Peruano* and *Purépecha* races, such as catechin-(4,8)-cyanidin-3-malonylglucoside or malonyl-5-glucoside, and catechin-(4,8)-peonidin-3-glucoside (González-Manzano et al., 2008). *Apache* red has been identified as a landrace that can produce pericarp-pigmented lines rich in pelargonidin based condensed forms, namely: (epi)catechin-(4, 8)-pelargonidin 3,5-diglucoside and (epi)afzelechin-(4,8)-pelargonidin 3,5-diglucoside (Chatham et al., 2018; Paulsmeyer et al., 2017). These *Apache* red lines also presented pigments derived from malonylated cyanidin and peonidin condensed with (epi)catechin, as well as the presence of flavones like *C*-hexosyl-*C*-pentosyl apigenin, which could form co-pigments with anthocyanins, increasing pigment stability or enhance the observed color (Chatham et al., 2018).

2.2.2.3. Phlobaphenes. These flavonoids are water insoluble polymerized flavan-4-ols that provide pigmentations ranging from orange to dark red in kernels and are located in the pericarp and can be sometimes confused with or masked by anthocyanin pigments (Paulsmeyer et al., 2017). These pigments were the most common flavonoid after anthocyanins in American landraces, with 166 (out of 398) accessions

presenting detectable levels and deep red colorations, while 11 showed bronze pigments to the naked eye that could not be detected chromatographically (Paulsmeyer et al., 2017). The production of phlobaphene pigments depends on the presence and activity of the *Pericarp color1 (P1)* gene, regardless of the activity of genes and enzymes in charge of regulating the synthesis of anthocyanins (*Booster1, Colorless1 Purple aleurone1,* and *O*-methyltransferase, for example). In Fig. 1a, the landrace *Ladrillo* takes its name from the kernel's brick red coloration, which is probably caused by phlobaphenes. Landoni et al. (2020) studied an ancient Italian landrace, *Nero Spinoso*, which is characterized by its dark red pigmentation and hard grains (flint type), the authors found a that the expression of the *P1* gene increased phlobaphene levels in the seeds and was associated with increased thickness of the pericarp.

Determination and quantification of phlobaphenes in maize has been done spectrophotometrically in Italian landraces and is based on the absorbance of these compounds and their precursors (flavan-4-ols) at 510 and 550 nm. Dark red and red landraces *Nero* and *Formentone ottofile rosso* (dark red and red) had the highest amounts of phlobaphenes or flavan-4-ols, followed by *Nostrato del Palazzaccio*, while yellow and orange landraces like *Ottofile giallo* and *Nano di Verni* contained lower levels or traces (Capocchi et al., 2017; Cassani et al., 2017; Landoni et al., 2020). Flavan-4-ol precursors have been tentatively identified as luteoforol and apiforol, which are also present in *Nostrano della Val di Non* and *Rostrato rosso* landraces, indicating the possibility of phlobaphene accumulation (Bernardi et al., 2018).
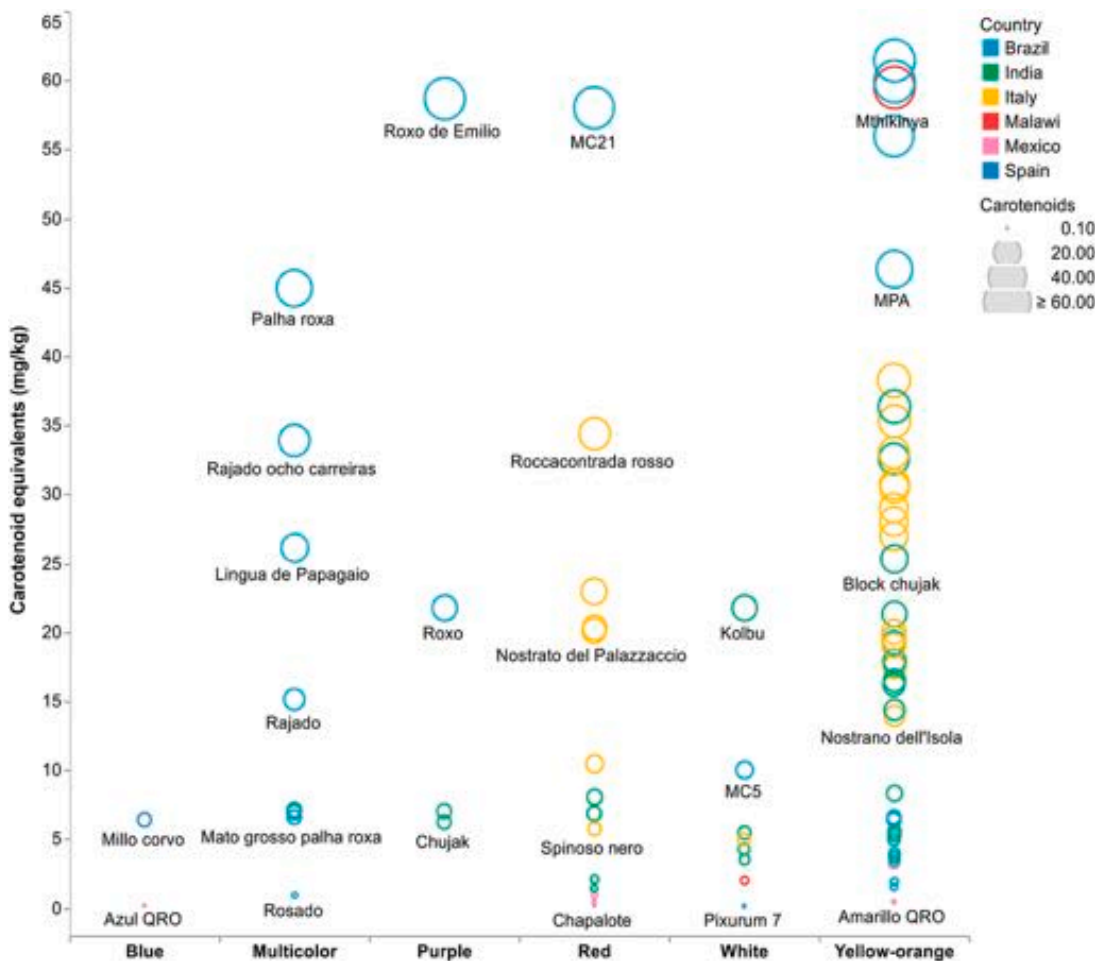

Fig. 4. Carotenoid contents of accessions of maize grain landraces from different countries, grouped by the dominant pigmentation of the kernel. Size of the circles gives an indication of the carotenoid content of a landrace relative to the overall range observed (0.1–61.5 mg/100 g).

2.3. Carotenoids

These compounds are tetraterpenoids which predominantly accumulate in the endosperm of maize grains producing yellow and orange colorations (Prasanna et al., 2020). According to our review, carotenoid contents have been quantified in all pigmentation landrace groups, however, these compounds have not been studied to the same extent as phenolic compounds and so, only few regions are represented in Fig. 4. The range of TCC corresponds with the intensity of the perceived color of the endosperm, so landraces with white endosperm had the lowest concentrations of carotenoids, often below 10 mg/kg, regardless of the pericarp color, while creamy-white/pale yellow ones had intermediate TCC values (*e.g.* 14.4–21.8 mg/kg) and orange landraces had the highest values (Fig. 4).

This wide variation can also be observed in Brazilian genotypes which have reported TCC between 0.1 and 61.5 mg/kg (Fig. 4), corresponding to white and yellow-to-orange varieties, respectively (Kuhnen et al., 2011; Messias et al., 2014). In some red, blue, and purple pigmentation groups, such as the Brazilian *Roxos* and the red accession *MC21* (Kuhnen et al., 2011; Messias et al., 2014), carotenoids are present in appreciable levels (TCC above 20 mg/kg) but may not be visible since the color of the outer layers masks the carotenoid pigmented endosperm (Fig. 4). Some red, purple or blue flint type landraces have the capacity to accumulate significant levels of phenolic pigments (anthocyanins/phlobaphenes) and carotenoids (10–58.75 mg/kg, Fig. 4), making them interesting sources of genetic material to obtain cultivars with more diverse nutraceutical profiles (Puglisi et al., 2018). Accordingly, a study of 17 landraces (48 accessions) from the borderland between Mexico and the USA found that, on average, floury endosperm varieties tended to have lower TCC than popping or flint types (mean values of 2.9 and 4.9–6 mg/kg, respectively), while anthocyanin levels tended to show a certain degree of independence from hardness, since floury and flint kernel types both showed high values (Ryu et al., 2013).

Although there are hundreds of carotenoids, the main types studied in the grains of maize landraces are xanthophylls, largely lutein and zeaxanthin, followed by pro-vitamin A (PVA) carotenoids, namely carotenes (α and β) and the xanthophyl β-cryptoxanthin (Messias et al., 2014). However, it has been noted that each landrace can present large TCC and compositional variations (Kuhnen et al., 2011; Uarrota et al., 2014). In Malawian *Mthikinya* orange maize lutein, zeaxanthin and carotenes amounted to 74.4% of the TCC, but lutein (21.2 mg/kg) and zeaxanthin (10.7 mg/kg) were detected at higher levels than pro-vitamin A ones (12.4 mg/kg) (Hwang et al., 2016). Lutein (levels between 0.05 and 11.0 mg/kg) was also the most abundant carotenoid in Mexican white, red, and yellow genotypes, (De La Parra et al., 2007; Lozano-Alejo et al., 2007). In contrast, Capocchi et al. (2017) noted the major carotenoid in yellow to red landraces was zeaxanthin, representing ≥55% of the TCC, while lutein only amounted to ≤30%.

PVA carotenoids are nutritionally important since they can be converted into retinol by intestinal enzymes, so some of the reviewed landraces have been studied to establish if they can be used to fight vitamin A deficiencies. Messias et al. (2014) estimated the contents of α- and ß-carotenes (0–14 mg/kg) and α- and ß-cryptoxanthins (0.55–5.85 and 0.30–13.8 mg/kg) in Brazilian landraces showed larger variations than those of lutein and zeaxanthin. In other studies, Lozano-Alejo et al. (2007) reported PVA ranges between 0.18 and 4.4 mg/kg in whole grain, for yellow Mexican genotypes. In some landraces, higher levels of PVA accumulation are correlated with lower lutein or zeaxanthin contents, for example, the Mexican *Tuxpeño* landrace tended to accumulate up to 3 times more ß-carotene than zeaxanthin, while a blue creole type had a carotenoid content in the order of ß-carotene > zeaxanthin > lutein > ß-cryptoxanthin (De La Parra et al., 2007). Similar results were found for Italian and Spanish landraces that tended to accumulate higher levels of zeaxanthin and PVA carotenoids than of lutein, so the latter accounted for less than 15% of quantified carotenoids while PVA

accounted for 30% (Bacchetti et al., 2013). The identification and molecular characterization of landraces with potential for synthesizing and accumulating larger proportions of carotenes and cryptoxanthins in their carotenoid pool, is one of the first steps in breeding programs aimed to develop maize varieties that can fulfill the targets of biofortification (above 15 mg of ß-carotene equivalents per kg of grain) needed to improve human health (Prasanna et al., 2020).

3. Landrace phytochemicals and their relation to bioactivity

The genotypic diversity of maize landraces is closely linked to their phytochemical profiles, which in turn reflects on their bioactivity or nutraceutical properties. Research has found evidence to support the conclusion that grains containing higher phytochemical levels have greater antioxidant activity, given that the effects of different chemical species seem to be additive (Beta and Hwang, 2018; Giordano et al., 2018b). The *in vitro* assays most used to evaluate antioxidant activity/capacity in maize grains are listed in Table 1. In general, the assays can be divided in two groups, according to the types of reactions they are based on. The first group, which includes the ORAC assay, measures a reaction where the food antioxidant and a fluorescent substrate compete for peroxyl radicals that are generated through the thermal decomposition of 2,2′-Azobis(2-methylpropionamidine) dihydrochloride (De La Parra et al., 2007). The second group, where the rest of the assays belong, measures the capacity of a sample to reduce or scavenge a cationic radical that acts as a chromophore (ABTS, NO•, Cu and Fe cations and DPPH), so the change in color is proportional to the content of antioxidants (Capocchi et al., 2017; Gaxiola-Cuevas et al., 2017; Rodríguez-Salinas et al., 2020).

Given this, antioxidant activity results are contingent on the type of determination, so most studies recommend the use multiple or redundant radical scavenging and metal reducing assays, and even solvents (lipophilic or hydrophilic), for the study of complex mixtures of bioactives. As seen in Table 1, several studies point out how the activities of different phytochemical species in the grain show more or less affinity with the employed radicals and thus correlate better with the results of certain assays (Amador-Rodríguez et al., 2019; Gaxiola-Cuevas et al., 2017; Rodríguez-Salinas et al., 2020).

In terms of specific compounds, the concentrations of monomeric anthocyanins (glucosides of cyanidin, pelargonidin and peonidin), flavonoids, condensed tannins, ferulic and coumaric acids (bound or conjugated) have been found to be positively correlated with antioxidant activity of maize grains (Capocchi et al., 2017; Harakotr et al., 2014; Rodríguez-Salinas et al., 2020). Pigmented landraces, which are often rich in a variety of compounds, have been found to have the largest potential and benefits (Gálvez Ranilla et al., 2019; Mendoza-Díaz et al., 2012). However, the antioxidant capacity levels (DPPH, ORAC hydrophilic or lipophilic, NO• scavenging activity) of white maize can compare favorably to pigmented landraces when TPC and bound phenolics are higher or equal, indicating that bound phenolic acids and other flavonoids have a large stake in the anti-free radical response of maize grains (Trehan et al., 2018). Reports have stated that raw maize has higher antioxidant activity than other cereals like common rice or wheat (Siyuan et al., 2018). Compared to other plant families, phenolics from maize contain more active hydroxyl groups than, for instance, blueberries (Cevallos-Casals and Cisneros-Zevallos, 2003), which allows them to interact with the radicals used in the different assays more efficiently and thus have a faster response in kinetic assays like DPPH or ORAC. This potential has also been observed in studies that compare commercial hybrids or even inbred lines to landraces of similar pigmentation or processing characteristics, since the latter often contain larger variety of phenolic acids and carotenoids (Chatham et al., 2018; Kuhnen et al., 2011; Messias et al., 2014).

Besides the direct effect of protection against oxidative damage, maize phenolics have been associated with cancer chemoprevention *in vitro* via different mechanisms. A study on different Mexican landraces

Table 1

A selection of studies on antioxidant activity and its relation to landrace phytochemicals, as measured by different assays.

Maize landraces/accessions	Country	Color	Activity measures and results		Reference
Morados Noreste Pintos Noreste Rojo Refugio de Cedillo Tremes blanco	Mexico	Purple Multicolor White	DPPH TEAC-ABTS FRAP ORAC	• All maize genotypes showed antioxidant activity in free and bound extracts. • Anthocyanin pigments (darker colorations) were correlated with antioxidant capacity. • ORAC detected higher activity in free extracts, while other methods were more efficient identifying differences in bound antioxidant activity	Rodríguez-Salinas et al. (2020)
Northern landraces	Mexico	Blue White	DPPH ABTS	• Anthocyanin rich blue maize recorded higher antioxidant activity. • DPPH activity was higher in blue varieties, but ABTS method showed bigger differences	Amador-Rodríguez et al. (2019)
Elotero Sinaloa and Chapalote	Mexico	Blue White	TEAC-ABTS ORAC Cellular antioxidant capacity (CAA)	• The use of different methods permitted the detection of differences in capacity of bound and free phenolics. • CAA was highest in blue variety. • The contribution of bound phenolics to CAA is important because they get released in the colon, where they exert health promoting effects.	Gaxiola-Cuevas et al. (2017)
Formentone ottofile giallo Formentone ottofile rosso Nano di Verni Nostrato del Palazzaccio	Italy	Orange-yellow Dark red Orange-red Red	CUPRAC FRAP DPPH	• High antioxidant capacities were correlated to soluble phenols and flavonoids of red varieties. • A correlation was also found between ascorbic acid content and flours antioxidant power.	Capocchi et al. (2017)
Criollos de Querétaro	Mexico	Yellow Red Blue	FRAP TEAC-ABTS	• Positive correlations between and TPC and anthocyanin contents in red and purple maize.	Loarca-Piña et al. (2019)
N.S.	USA	Red Blue	ORAC Lipophilic and hydrophilic	• Ferulic acid (bound, conjugated) contributed to hydrophilic ORAC. • Carotenoid contents corresponded to lipophilic ORAC. • Landraces with a balanced composition, rich in water and fat soluble bioactives, have the best antioxidant potential.	De La Parra et al. (2007)
14 native accessions	Chile	White Multicolored Red Yellow Orange Deep red	DPPH TEAC-ABTS	• Bound fractions highly contributed to the total antioxidant activity. • A significant negative correlation was found between lighter landrace color and TPC and ABTS activity.	González-Muñoz et al. (2013)
Mthikinya	Malawi	White Orange	DPPH ORAC	• TCC and most carotenoids were negligible in white variety. Antioxidant capacity was only slightly higher in orange maize, and it was more dependent in location than grain color. • Other compounds (phenolics, protein-carotenoid complexes) are responsible for most of the measured antioxidant activity.	Hwang et al. (2016) and Beta and Hwang (2018)
Tuxpeño, Tabloncillo Chapalote	Mexico	Red Yellow	ORAC-lipophilic	• Higher TCC were associated with antioxidant capacity. • Landraces high in lutein, zeaxanthin and ß-carotene tended to have higher activity. Red landraces only contained lutein.	Corrales-Bañuelos et al. (2016)
Spinato Millo corvo	Italy	Dark red Blue-black	DPPH	• Antiradical activity in *Spinato* was higher than *Millo corvo*. • Both landraces had high polyphenol and anthocyanin contents (cyanidin, pelargonidin and peonidin) than inbred lines, but lower carotenoids (lutein, zeaxanthin) • High DPPH activity in pigmented varieties could be attributable to other compounds than polyphenols.	Doria (2015)
Rostrato rosso Nostrano della Val di Non	Italy	Red Orange	DPPH FRAP	• Antioxidant activity of the kernels was highest in *Rostrato* followed by *Val di Non*. • Low molecular weight secondary metabolites such as flavonoid pigments contribute to this effect, so they are important for breeding and development of functional foods.	Bernardi et al. (2018)

ORAC Assay (Oxygen Radical Absorbance Capacity); TEAC (Trolox Equivalent Antioxidant Capacity); FRAP (Ferric Reducing Antioxidant Power); ABTS assay [2,2′-Azinobis-(3-ethylbenzothiazoline-6-sulfonic acid]; DPPH [2,2-di (4-tert-octylphenyl)-1-picrylhydrazyl)] free radical scavenging assay; CUPRAC (Cupric Reducing Antioxidant Capacity).

studied the capacity of antioxidants to induce quinone reductase activity, which plays an important anticarcinogenic role by detoxifying harmful quinones and inhibiting the growth of cancer cells *in vitro* (Lopez-Martinez et al., 2011). The purple accession *Veracruz 42*, high in phenolic compounds (flavonols, phenolic acids, anthocyanins, etc.) was especially effective in the activation of this enzyme in murine hepatic cells, while blue creole maize caused the greatest losses in cell viability. These two responses showed how specific polyphenol and anthocyanin profiles cause different, but additive effects. In this context, blue *Mixteco* maize (raw and in tortilla form) had antiproliferative activity on liver, lung, cervix, breast, and prostate human cancer cell lines (Herrera-Sotero et al., 2017). This effect was related to the presence of more complex anthocyanin forms (acylated and proanthocyanidins) in maize, which have been suggested to promote higher antioxidant activity but also interfere with cancer cell signaling. Maize phenolics can also function as dietary antimutagens, preventing DNA changes associated with cancer malignancies. A study using aqueous and ethyl-acetate extracts from Andean purple maize showed antimutagenic properties attributable to anthocyanins and phenolic acids + flavonols, respectively (Pedreschi and Cisneros-Zevallos, 2006). The authors determined the dominant mechanism of action of polyphenol fractions (phenolics and anthocyanins) involved the inhibition of different enzyme systems involved in mutagen activation, but quercetin derivative fractions also had the capacity of scavenging mutagenic electrophiles, hence the

importance of considering all phenolic fractions in the study of bioactivity (Pedreschi and Cisneros-Zevallos, 2006). Accordingly, a recent study found antimutagenic capacity in blue and red maize landraces, but the effect was higher in blue maize accessions due to both flavonoid and anthocyanin content, even at intermediate TPC (Loarca-Piña et al., 2019).

Phenolics can also interact with metabolic enzymes and blood components and produce helpful effects against non-communicable diseases like obesity (lipase, fatty acid synthase), dyslipidemia, and hyperglycemia (such as α-amylase and α-glucosidase, which could lead to type-2 diabetes mellitus). Some compounds can affect the digestibility of starch and the postprandial response of glucose by interfering with α-amylase and α-glucosidase activity, for example, in a study by Gálvez Ranilla et al. (2019) comparing several Peruvian landraces collected *in situ*, the purple *Kculli* or *Kulli*, followed by red *Granada*, both had moderate α-amylase activity (26.8% and ~15%) but highest *in vitro* α-glucosidase inhibition (76.1% and 64.8%, respectively, with 25 mg dose), which was correlated to TAC in free extracts and antioxidant capacity. However, other *in vitro* studies have failed to obtain significant correlations between free or conjugated phenolic acids or even anthocyanins and anti-glucosidase activity, even if free extracts of maize landraces such as Chilean *Curagua* and *Polulo*, show inhibition towards yeast glucosidase enzyme (71.7–72.5%, at 25 mg) at doses of 0.67 mg/mL (González-Muñoz et al., 2013). For example, Zhang et al. (2019) correlated flavonoids like rutin and luteolin to antidiabetic activity of *Apache* red maize extracts in terms of glucose uptake, generation of reactive oxygen species and inhibition of postprandial plasma glucose. Different *in vitro* anti-obesogenic effects have been studied in landraces; for instance, anthocyanin-rich extracts from *Apache red* pericarp were able to halt adipocyte differentiation thus potentially reducing the size of adipose tissue in humans but also help in preventing obesity complications such as inflammatory processes and insulin resistance (Luna-Vital et al., 2017). Regarding anti-lipase action (a desirable aid to reduce digestion and absorption of triglycerides) both *Kculli* maize accessions and *Apache* red extracts effectively reduced activity (92.1% at 12.5 mg, and 23.1 μg/mL IC$_{50}$, respectively), and inactivation was attributed to interactions between anthocyanins (glucosides of cyanidin, pelargonidin and peonidin) and the amino acid residues in the catalytic pocket of the enzyme (Gálvez Ranilla et al., 2019; Luna-Vital et al., 2017). Finally, phenolic antioxidants from *Apache* red and Italian landraces (which also contained carotenoids) have been found to directly delay lipid peroxidation, a type of oxidative stress that can lead to dyslipidemia (Bacchetti et al., 2013), but it is also related to changes associated with the onset of obesity, insulin resistance and inflammation (Luna-Vital et al., 2017). These effects could be attributed to major anthocyanins in each type of maize (*e.g.* cyanidin-3-glucoside, peonidin-3-glucoside and acylated derivatives), but further studies have shown that condensed forms like catechin-cyanidin-3,5-diglucoside and other tannins, as well as other phenolics (quercetin, luteolin, rutin, and naringenin; vanillic acid and protocatechuic acid) could act in an additive or synergistic way to elicit a wide range of anti-obesity or inflammation biological activities (Zhang et al., 2019).

Notably, the evidence regarding carotenoid contribution to antioxidant activity in maize landraces is inconclusive. While TCC, lutein and zeaxanthin content can correlate to overall antioxidant activity, their contributions to measures like FRAP, ORAC- hydrophilic, DPPH and ABTS assays are not as important, or clear, as those of phenolic compounds (Beta and Hwang, 2018; Hwang et al., 2016). One reason for these results is that most antioxidant activity assays are suitable for water soluble antioxidants, and thus cannot take into consideration the contribution of the lipid soluble fractions, such as carotenoids. This is why studies measuring lipophilic antioxidant capacity (ORAC-L) tended to find higher values in carotenoid rich yellow maize varieties, than in white, red, or blue ones (Corrales-Bañuelos et al., 2016; De La Parra et al., 2007). Additional mechanisms have been reported for landrace carotenoids. Kuhnen et al. (2009) studied the potential of carotenoid

rich maize (MPA1, creole variety) to inhibit angiogenesis *in vivo*, using chicken yolk sac membrane (YSM) assay and chorioallantoic membrane (CAM) assays. Inhibition of primordial vasculogenesis in YSM ranged from 12 to 50%, while CAM also showed inhibition of angiogenic activity in up to 52% at 10μM$_{Zeaxanthin\ equivalents}$, without toxicity to the embryos. This bioactivity potential could be important since uncontrolled neo-vascularization is a process that occurs in several malignancies, such as macular degeneration or tumor growth, but it also seemed to indicate that the positive effect of maize xanthophylls in the retina could be related to the prevention of degenerative diseases by means beyond antioxidant action. The authors suggested that lutein and zeaxanthin participate in the regulation of blood vessel remodeling, but further investigations are needed to confirm this hypothesis.

The results of these *in vitro* studies show the nutraceutical potential of landraces and their diverse bioactives, however, further studies are needed to establish with certainty the levels of grain consumption that can exert an effect on human health (*i.e.* the recommended dose). For purple maize extracts, it has been proposed that doses around 18 mg/d/person of anthocyanins, and 45 mg/d/person of phenolics could have beneficial effects in terms of cancer, hypertension, diabetes, obesity and antioxidant activity (Lao et al., 2017). According to our review, such levels could be obtained with the average yearly intake of maize in countries such as Mexico (above 100kg/person), where this grain is a staple (Palacios-Rojas et al., 2020). The beneficial dosages proposed by Lao et al. (2017) can also be achieved by consuming maize after processing, for example in the following traditional foods: 120 mL/person of *chicha de guiñapo* made with *Kculli* maize, ~65 g/person of blue maize tortilla or 100 g/person of boiled tender waxy maize kernels (Harakotr et al., 2014; Herrera-Sotero et al., 2017; Vargas-Yana et al., 2020).

4. Agroecological determinants for bioactive variability

4.1. Selection and adaptation

Maize landraces have successfully adapted to different environments, from sea level to high altitudes (4000 masl), soils with pH between 4 and 8, areas with annual rainfall between 400 and 2500 mm, and latitudes between 42° S and up to 58° N (Prasanna, 2012). In this wide range of conditions, the capacity of landraces to synthesize and accumulate bioactive compounds could be considered a consequence of adaptation and selection to thrive in a particular environment. In a study of 32 Mexican landraces, Burt et al. (2019) found high variability in HCAA across genotypes and agroecological zones, from the temperate high-altitude regions to low-altitude, more tropical conditions. The studied Mexican landraces belonged to a diverse group, and results showed that "ancient indigenous races", such as *Chapalote, Nal-Tel* or *Palomero Toluqueño*, contained the highest amounts of HCAA (such as diferuloyl putrescine), while "new/incipient races" (e.g. *Mushito*, *Zamorano*, *Onaveño*) contained the lowest. It also became apparent that races adapted to low altitudes with tropical climates had increased HCAA content, and that, as adaptation altitude increased (more temperate climate), the concentration of these compounds lowered.

These findings were attributed to the effects of farmer selection to obtain varieties with higher potential for accumulating secondary metabolites and its benefits for productivity. According to the literature, higher phenolic contents are associated with higher antioxidant activity in the plant and with harder genotypes (flint types such as *Chapalote* or the Italian landraces mentioned in previous sections), both of which contribute to protection against free-radicals and resistance to microbial and fungal infections in the grain (Landoni et al., 2020). In agreement, Burt et al. (2019) mentioned that higher HCAA's in low altitude races could provide resistance to pest and disease pressures and would make them better adapted to humid and rainy areas, where these biotic stresses are higher than in dryer environments. Besides, HCAA's and phenolic acids, other phenolic compounds contribute to these protective functions that are advantageous in humid conditions. For example,

landraces containing large quantities of phlobaphenes in their pericarp (Landoni et al., 2020) have been found to be less susceptible to *Fusarium* infections in the cob (Bernardi et al., 2018). Finally, condensed forms of flavanol-anthocyanins such as *C*-glucosyl flavones like vitexin (apigenin 8-C-glucoside) are precursors of apimaysin, which is associated with the resistance of maize landraces to insect pests(Chatham et al., 2018). Hwang et al. (2016) also mentioned that harder grain types have the additional benefit of better flour yield and are resistant to storage pests, which has made them attractive food sources with extended shelf life in traditional peasant systems in Africa. Thanks to these characteristics, derived from their phenolic content, landraces are recognized as a valuable resource in breeding approaches aimed to prevent and mitigate fungal infections and harvest loss through the development of new maize cultivars with improved resistance and grain safety and storability (Logrieco et al., 2021; Palacios-Rojas et al., 2020).

The presence of a diverse content and profile of secondary metabolites also offers protection against abiotic stress. In plants, carotenoids play a role in the stabilization of photosynthesis, but they also provide photoprotection and are precursors of apocarotenoids (such as abscisic acid) which improve tolerance to heat or water stress and help in plant signaling (Messias et al., 2014). In a review by Naikoo et al. (2019), phenolic compounds were shown to be implicated in the response of several crops, including maize, to a wide array of stresses such as salinity, phosphorus deficiency, heavy metals, frost, and radiation, as well as drought and excess moisture. These stresses are common in environments in which landraces with a potential for flavonoid synthesis and accumulation have been selected and preserved by smallholder farmers. For example, *Kculli* maize is adapted to the extreme radiation and cold present at the high altitudes of the Andean region, while the *Morado de Ixtenco* is strongly adapted to the sandy soils, scarce and scattered rainfall and frosts that prevail in the rainfed production systems in Tlaxcala, Mexico.

As showed in Fig. 1, traditional farmers rarely keep a single variety in their fields. Ryu et al. (2013) associated the high variation in pigments (anthocyanins and carotenoids) found in Northern Mexico and Southwestern USA dent, floury, pop and flint landraces to selection pressure by the farmers to add diversity to a heavily maize-based diet, so different foods can be prepared with them, for example snacks, breads, beverages, and porridges. The selection for a particular combination of color, taste, texture, traits in maize is related to their use in the making certain traditional foods, and this could, in turn affect the presence or absence of certain bioactives in the grains. One example of this are blue Mexican and American landraces which are characterized by the presence of acylated anthocyanins, such as cyanidin-3-malonylglucoside and acylated malvidins in blue *Arrocillo*, *Cónico* and *Purépecha* maize (Herrera-Sotero et al., 2017; Salinas-Moreno et al., 2012) or cyanidin-3-disuccinylglucoside in heirloom blue Southwestern USA varieties (Nankar et al., 2016), that are mainly located in the aleurone layer and can exert high antioxidant activity, even after nixtamalization. These landraces produce tortillas with an attractive blue color that are highly regarded by consumers, so it is not surprising that farmers selected for such pigmentation traits. Likewise, the Peruvian *Kculli* or *Morado Andino* maize has a deep purple color and possesses a high content of anthocyanins that are readily soluble in water, so it is appreciated as a natural coloring agent in the preparation of Andean foods and desserts such as *chicha* and *mazamorra morada* (Vargas-Yana et al., 2020). *Chicha* drinks made with Peruvian purple maize have been found to possess high antioxidant and even antidiabetic properties.

4.2. Growing location and environment

Due to the high contents and diverse profile of secondary metabolites, many blue and purple maize landraces have been promoted as a functional food and as options to develop new products to enrich the human diet with powerful antioxidants (Colombo et al., 2021). As their use is broadened beyond their places in origin, it is important to consider the effects of changing environmental conditions on the content of the secondary metabolites of interest. Studies reported variations in the phenolic compounds of landraces planted in locations with different environmental conditions. For example, the landrace *Morado* from the Arequipa region of Peru showed variable levels of TAC when planted in different latitude and altitude conditions: in a Peruvian study where maize was grown at 1600 masl, the accession AREQ-084 had 310 mg/100 g total anthocyanins, while the accession AREQUIPA 204 had a TAC of 110 mg/100 g when produced in the USA Corn Belt which is located about 500 masl (Fig. 3). Gálvez Ranilla et al. (2021), found no differences in the flavonoid profiles of the *Morado Canteño* landrace when grown in lower (1712–2249 masl) and higher (2759–2896 masl) locations within the Arequipa region. However, they found high altitude locations produced significantly higher contents of bound ferulic acid and TPC (mainly in the bound fraction) in the grains. The study also reported not significant changes in the profiles, such as increases in the flavonoid and anthocyanin contents, quercetin and ferulic acid derivatives, as well as lower p-coumaric acid concentrations.

Uarrota et al. (2014) stated that, although genetic variability was the main correlate with phytochemical content, TPC and anthocyanin levels in Brazilian landraces tended to decrease in planting sites with lower mean temperature and precipitation as well as different soil types (from predominantly clay to sandy ones). Variations due to edaphoclimatic factors were also reported by Martínez-Martínez et al. (2019), who studied the effect of plot location on phenolic compounds of pigmented Mexican landrace accessions, finding significant differences in TPC, anthocyanins, and antioxidant activity of red and blue maize. In this study, soil characteristics such as low pH and high electrical conductivity, paired with high levels of organic matter, phosphorus, magnesium, and copper promoted the synthesis of anthocyanins and TPC (Martínez-Martínez et al., 2019).

These observations reflect how final the levels of accumulation of bioactive compounds are caused by the interaction between the plant and the edaphoclimatic factors prevalent in different planting sites. Changes in latitude and altitude, as well as season, can cause the plant to receive different amounts of radiation, which has been shown to affect anthocyanin contents. This related to the enhancing effect of sunlight intensity on the phenylpropanoid and flavonoid synthetic paths and accumulation of anthocyanin pigments in maize grains (Hu et al., 2020). The effects of soil properties on the synthesis of secondary metabolites can be explained by the C:N balance hypothesis and the regulatory role played by nitrogen, whereby high organic matter (an indicator of organic carbon accumulation) and intermediate nitrogen levels can promote carbon allocation to secondary metabolism and synthesis of flavonoids and other phenolics (Hsu et al., 2009). The effect of soil type is related to the nutrient levels and availability in the soil and those provided by fertilization, as well as their interaction with aspects such as rainfall levels and temperature; however, the underlying mechanisms are not well understood so further experiments are needed to understand said effect in maize landraces.

Even if anthocyanin and phenolic content are not decreased significantly, other negative effects of a change in planting environment should be considered. Paulsmeyer et al. (2017) stated that most of the phenotypic variability of TAC was controlled by genetic factors rather than environmental ones, however, the same survey study reported entire maize crops lost to disease pressure and maladaptation when cultivating anthocyanin-rich landraces such as *Morado Andino* in the Corn Belt. In a study by Ryu et al. (2013) comparing the performance of borderland races in planting sites in Arizona and Ohio, and while TAC showed little variations, agronomic traits were affected by the differences in the sites. In Arizona, too high temperatures caused sensitive genotypes to have diminished plant height and poorly filled grains, while in Ohio, longer day lengths completely hindered the reproductive stage and thus no grain was obtained for landraces like *Chapalote, Onaveño, Reventador* and *Cochito pop*. Problems like these could make it financially unfeasible to adopt some of the most phytochemically rich

landraces, hence the importance of studying, preserving, and characterizing maize germplasm in search of high nutraceutical potential and better adaptability to local conditions. Using this type of knowledge, Guzzon et al. (2021) mentioned how breeding programs based in Latin American landraces are in place to develop open pollinated varieties that are rich in anthocyanins and can grow in different agroecological zones with no productivity loss.

Regarding carotenoids, Ryu et al. (2013) reported that although accession was the main determinant of carotenoid content, there was an interaction with location, and the negative environmental conditions that decreased grain yield components in the Arizona planting site, also reduced carotenoid contents of Borderland races. In another study, Uarrota et al. (2014) found carotenoids to remain largely unchanged in Brazilian landraces cultivated using similar agricultural practices, even when the planting sites presented distinct climate and soil conditions. In agreement, Hwang et al. (2016) observed highly significant differences in the carotenoid profile and antioxidant activity of white and orange Malawian maize varieties, while the location of the planting site only affected the levels of zeaxanthin and ß-cryptoxanthin of the white variety. These results indicate that landrace genotype plays a larger effect on carotenoids than location, but also the final levels of accumulation of these pigments are affected by similar factors than grain filling. Such observations have been made during improvement studies, where desirable carotenoid profiles and contents, as well as yields, can be obtained independently of environmental conditions, if agricultural practices are adequate (Prasanna et al., 2020).

4.3. Agronomic practices

Agricultural management is known to influence grain yield, weight, and fill, but it can also affect other grain quality parameters. Unfortunately, only a couple of studies have addressed the latter topic in maize landraces (Giordano et al., 2018a, 2018b), specifically regarding the effects of sowing date and nitrogen fertilization on pigmented landraces (dark-red, red, orange, yellow and white).

Changing sowing dates is a management strategy that aims to increase biomass and grain yield by establishing the crop cycle in the best season (regarding temperature, radiation, and rainfall conditions) available in the planting location. According to Giordano et al. (2018a), dark red varieties were sensitive to early sowing, which increased DPPH antioxidant activity and cell wall bound phenolics. In contrast, yellow varieties from all other genotypes showed reductions in bound phenolics and lutein but not ß-carotene or ß-cryptoxanthin during early sowing and during warmer cycles. It was seen that early sowing influenced the accumulation of some bioactive compounds due to the prevalent weather during the period of grain development, such as rainfall and temperature, particularly in warm years. Finally, the authors stated that for the landraces studied, the conditions that favor phenolic acid accumulation (warmer temperatures and lower rainfall) are different from those promoting anthocyanin and carotenoid contents (cooler and higher rainfall). Similar assertions were made by Uarrota et al. (2014) and Landoni et al. (2020) regarding the effect of season on anthocyanins and carotenoids on Brazilian genotypes and phlobaphenes on Italian ones. The seasonal effect on anthocyanins could be even more complex depending on the type of maize, for example, Peruvian purple maize cobs tends to have higher anthocyanin contents at lower mean temperatures (14 and 16 °C), while sweet maize required temperatures above 20 and 26 °C to have the same effect (Hu and Xu, 2011). In the production conditions of low-input farmers, selecting the wrong season increase the amount of radiation, the daylength and the temperature, thus affecting the final levels of flavonoids and other phenolics.

In terms of nitrogen fertilization, Giordano et al. (2018b) compared two urea treatments of low and high nitrogen levels (170 and 300 kg_N/ha, respectively, applied at the end of vegetative growth) observed that higher nitrogen rates increased lutein and zeaxanthin in the grains, as well as the total amount of cell bound phenolics. But no change was recorded in the phenolic profiles, anthocyanins, antioxidant capacity or pro-vitamin A (ß-carotene or ß-cryptoxanthin) levels. These results suggested that high nitrogen availability increased grain yield, and accumulation of phenolic acids ad carotenoids in maize, and that cultivation of pigmented landraces was recommended in fertile areas. Organic matter and little to no nitrogen application have been related to anthocyanin and flavonoid accumulation in purple maize (Martínez-Martínez et al., 2019). These findings, rather than promote the application of indiscriminate amounts of synthetic fertilizers, seemed to point towards the nutraceutical benefits of agroecological practices that maintain soil quality, organic matter, and fertility (such as intercropping, crop rotation, manure-amendments, and mulching) and are characteristic of traditional maize agroecosystems. Although fertilization levels seem to have little or no effect on most phenolics, future evaluations should consider other nutrients, since low-input maize agroecosystems tend to use organic fertilizers derived from manure, crop residues and composts, which contain microminerals and organic matter, in addition to phosphorus and potassium, as well as a lower proportion of nitrogen. Such organic fertilization regimens have been found to promote the accumulation of anthocyanins in purple cabbage, for example (Hsu et al., 2009).

More landrace field experiments could also integrate the evaluation of agronomic performance traits with the study of promising bioactives, to find if it's possible to improve them simultaneously or what tradeoffs can be expected. It is essential to understand the individual effect and the interaction of edaphoclimatic and management factors on both primary and secondary metabolite production. For example, landrace production in low-input systems is characterized by rainfed conditions, single dose fertilization and the use of low planting density (~60,000 plants/ha), which limit grain yield. Increasing planting density and providing irrigation can improve grain production, but also increase nutrient competition and reduce water stress during grain filling, which, depending on the genotype, could affect final levels of secondary metabolites such as flavonoids in the grain. On the other hand, split fertilization is also known to improve grain yields, but it should be timed in such a way that nutrient availability is high during the grain development stage and not only during vegetative growth, so grain filling is adequate and carotenoid and BP accumulation optimal. Other factors that could be explored in the production conditions of low-input farmers include the effects of climate change and increased pest or disease pressure, as well as adverse climatic events such as drought, which can increase the synthesis of protective bioactives but also affect the plants to the point where no grain can be harvested.

Finally, if the aim is to generate new varieties with improved nutraceutical, further studies are needed to find whether there's a correlation between the desirable characteristics (organoleptic and processing) the producers often use to select seeds and the bioactives they contain (CONABIO, 2017; Gálvez Ranilla, 2020; Guzzon et al., 2021). Also, it is important to understand how improving specific nutraceutical aspects could affect the plant's response to biotic and abiotic stresses, as well as the nutrients contained in grains and their acceptability for habitual consumers. Given these conditions, the integration of research in the fields of genetics, agronomy and even food science is required to fully understand the role of maize landraces in achieving sustainable development of local agriculture, reducing the use of external inputs such as synthetic fertilizers and pesticides, while at the same time ensuring grain safety and high nutraceutical value in maize products.

5. Conclusions

Maize landraces have a diverse array of secondary metabolites or phytochemicals, and although their whole profiles have not been elucidated, they should be considered as highly valuable functional foods, particularly the ones with pigmented grains. These varieties could be introduced or promoted easily, since maize is already amply

consumed in many parts of the world, as a dietary source to increase the amount of bioactives but also as a source of genetic material to create improved cultivars with better nutraceutical profiles.

The studies presented in the review also show evidence of how traditional maize farmers have continuously selected seeds from plants with different secondary metabolites to protect the plants from the specific stressors of their niche and provide a stable yield to satisfy their food needs, causing differences among maize populations, even in relatively small areas. And in this context, there is a need for further studies characterizing maize landraces and addressing the topic of phytochemical variability caused by pre-harvest factors, not only to maximize their contents in the grain, but also to understand the evolution and adaptation of landraces as humans expanded cultivation to different agroecological zones. Research is also needed to find the optimal conditions for different bioactive compounds, particularly phenolics, and establish whether their improvement is always associated with lower grain yields or if it is possible to enhance both traits simultaneously.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcs.2021.103399.

References

Amador-Rodríguez, K.Y., Silos-Espino, H., Valera-Montero, L.L., Perales-Segovia, C., Flores-Benítez, S., Martínez-Bustos, F., 2019. Physico-chemical, thermal, and rheological properties of nixtamalized creole corn flours produced by high-energy milling. Food Chem. 283, 481–488. https://doi.org/10.1016/j.foodchem.2019.01.044.

Bacchetti, T., Masciangelo, S., Micheletti, A., Ferretti, G., 2013. Carotenoids, phenolic compounds and antioxidant capacity of five local Italian corn (Zea mays L.) kernels. J. Nutr. Food Sci. https://doi.org/10.4172/2155-9600.1000237, 03.

Bento-Silva, A., Duarte, N., Mecha, E., Belo, M., Vaz Patto, M.C., do Rosário Bronze, M., 2020. Hydroxycinnamic acids and their derivatives in broa, a traditional ethnic maize bread. Foods 9. https://doi.org/10.3390/foods9101471.

Bernardi, J., Stagnati, L., Lucini, L., Rocchetti, G., Lanubile, A., Cortellini, C., De Poli, G., Busconi, M., Marocco, A., 2018. Phenolic profile and susceptibility to fusarium infection of pigmented maize cultivars. Front. Plant Sci. 9 https://doi.org/10.3389/fpls.2018.01189.

Beta, T., Hwang, T., 2018. Influence of heat and moisture treatment on carotenoids, phenolic content, and antioxidant capacity of orange maize flour. Food Chem. 246, 58–64. https://doi.org/10.1016/j.foodchem.2017.10.150.

Burt, A.J., Arnason, J.T., García-Lara, S., 2019. Natural variation of hydroxycinnamic acid amides in maize landraces. J. Cereal. Sci. 88, 145–149. https://doi.org/10.1016/j.jcs.2019.06.002.

Camacho Villa, T.C., Maxted, N., Scholten, M., Ford-Lloyd, B., 2005. Defining and identifying crop landraces. Plant Genet. Resour. 3, 373–384. https://doi.org/10.1079/pgr200591.

Capocchi, A., Bottega, S., Spanò, C., Fontanini, D., 2017. Phytochemicals and antioxidant capacity in four Italian traditional maize (Zea mays L.) varieties. Int. J. Food Sci. Nutr. 68, 515–524. https://doi.org/10.1080/09637486.2016.1261809.

Cassani, E., Puglisi, D., Cantaluppi, E., Landoni, M., Giupponi, L., Giorgi, A., Pilu, R., 2017. Genetic studies regarding the control of seed pigmentation of an ancient European pointed maize (Zea mays L.) rich in phlobaphenes: the "Nero Spinoso" from the Camonica valley. Genet. Resour. Crop Evol. 64, 761–773. https://doi.org/10.1007/s10722-016-0399-7.

Cevallos-Casals, B.A., Cisneros-Zevallos, L., 2003. Stoichiometric and kinetic studies of phenolic antioxidants from Andean purple corn and red-fleshed sweetpotato. J. Agric. Food Chem. 51, 3313–3319. https://doi.org/10.1021/jf034109c.

Chatham, L.A., West, L., Berhow, M.A., Vermillion, K.E., Juvik, J.A., 2018. Unique flavanol-anthocyanin condensed forms in Apache red purple corn. J. Agric. Food Chem. 66, 10844–10854. https://doi.org/10.1021/acs.jafc.8b04723.

Colombo, R., Ferron, L., Papetti, A., 2021. Colored corn: an up-date on metabolites extraction, health implication, and potential use. Molecules 26, 199. https://doi.org/10.3390/molecules26010199.

CONABIO, 2017. Ecosystems and Agro-Biodiversity across Small and Large-Scale Maize Production Systems. TEEB Agriculture and Food, UNEP, Geneva.

Corrales-Bañuelos, A.B., Cuevas-Rodríguez, E.O., Gutiérrez-Uribe, J.A., Milán-Noris, E. M., Reyes-Moreno, C., Milán-Carrillo, J., Mora-Rochín, S., 2016. Carotenoid composition and antioxidant activity of tortillas elaborated from pigmented maize landrace by traditional nixtamalization or lime cooking extrusion process. J. Cereal. Sci. 69, 64–70. https://doi.org/10.1016/j.jcs.2016.02.009.

Cuevas Montilla, E., Hillebrand, S., Antezana, A., Winterhalter, P., 2011. Soluble and bound phenolic compounds in different Bolivian purple corn (Zea mays L.) cultivars. J. Agric. Food Chem. 59, 7068–7074. https://doi.org/10.1021/jf201061x.

De La Parra, C., Serna Saldivar, S.O., Liu, R.H., 2007. Effect of processing on the phytochemical profiles and antioxidant activity of corn for production of masa, tortillas, and tortilla chips. J. Agric. Food Chem. 55, 4177–4183. https://doi.org/10.1021/jf063487p.

Doria, E., 2015. Preliminary analysis and biochemical characterization related to health implications for African populations in some maize cultivars. A special look at the South African environment. Food Sci. Nutr. 1, 1–7. https://doi.org/10.24966/fsn-1076/100005.

Gálvez Ranilla, L., 2020. The application of metabolomics for the study of cereal corn (Zea mays L.). Metabolites 10, 1–24. https://doi.org/10.3390/metabo10080300.

Gálvez Ranilla, L., Huamán-Alvino, C., Flores-Báez, O., Aquino-Méndez, E.M., Chirinos, R., Campos, D., Sevilla, R., Fuentealba, C., Pedreschi, R., Sarkar, D., Shetty, K., 2019. Evaluation of phenolic antioxidant-linked in vitro bioactivity of Peruvian corn (Zea mays L.) diversity targeting for potential management of hyperglycemia and obesity. J. Food Sci. Technol. 56, 2909–2924. https://doi.org/10.1007/s13197-019-03748-z.

Gálvez Ranilla, L., Rios-Gonzales, B.A., Ramírez-Pinto, M.F., Fuentealba, C., Pedreschi, R., Shetty, K., 2021. Primary and phenolic metabolites analyses, in vitro health-relevant bioactivity and physical characteristics of purple corn (Zea mays L.) grown at two andean geographical locations. Metabolites 11, 722. https://doi.org/10.3390/metabo11110722.

Gaxiola-Cuevas, N., Mora-Rochín, S., Cuevas-Rodriguez, E.O., León-López, L., Reyes-Moreno, C., Montoya-Rodríguez, A., Milán-Carrillo, J., 2017. Phenolic acids profiles and cellular antioxidant activity in tortillas produced from Mexican maize landrace processed by nixtamalization and lime extrusion cooking. Plant Foods Hum. Nutr. 72, 314–320. https://doi.org/10.1007/s11130-017-0624-3.

Giordano, D., Beta, T., Gagliardi, F., Blandino, M., 2018a. Influence of agricultural management on phytochemicals of colored corn genotypes (Zea mays L.). Part 2: sowing time. J. Agric. Food Chem. 66, 4309–4318. https://doi.org/10.1021/acs.jafc.8b00326.

Giordano, D., Beta, T., Vanara, F., Blandino, M., 2018b. Influence of agricultural management on phytochemicals of colored corn genotypes (Zea mays L.). Part 1: nitrogen fertilization. J. Agric. Food Chem. 66, 4300–4308. https://doi.org/10.1021/acs.jafc.8b00325.

González-Manzano, S., Pérez-Alonso, J.J., Salinas-Moreno, Y., Mateus, N., Silva, A.M.S., de Freitas, V., Santos-Buelga, C., 2008. Flavanol-anthocyanin pigments in corn: NMR characterisation and presence in different purple corn varieties. J. Food Compos. Anal. 21, 521–526. https://doi.org/10.1016/j.jfca.2008.05.009.

González-Muñoz, A., Quesille-Villalobos, A.M.A.M., Fuentealba, C., Shetty, K., Gálvez Ranilla, L., 2013. Potential of Chilean native corn (Zea mays L.) accessions as natural sources of phenolic antioxidants and in vitro bioactivity for hyperglycemia and hypertension management. J. Agric. Food Chem. 61, 10995–11007. https://doi.org/10.1021/jf403237p.

Guzzon, F., Arandia Rios, L.W., Caviedes Cepeda, G.M., Céspedes Polo, M., Chavez Cabrera, A., Muriel Figueroa, J., Medina Hoyos, A.E., Jara Calvo, T.W., Molnar, T.L., Narro León, L.A., Narro León, T.P., Mejía Kerguelén, S.L., Ospina Rojas, J.G., Vázquez, G., Preciado-Ortiz, R.E., Zambrano, J.L., Palacios Rojas, N., Pixley, K.V., 2021. Conservation and use of Latin American maize diversity: pillar of nutrition security and cultural heritage of humanity. Agronomy 11, 172. https://doi.org/10.3390/agronomy11010172.

Harakotr, B., Suriharn, B., Tangwongchai, R., Scott, M.P., Lertrat, K., 2014. Anthocyanin, phenolics and antioxidant activity changes in purple waxy corn as affected by traditional cooking. Food Chem. 164, 510–517. https://doi.org/10.1016/j.foodchem.2014.05.069.

Herrera-Sotero, M.Y., Cruz-Hernández, C.D., Trujillo-Carretero, C., Rodríguez-Dorantes, M., García-Galindo, H.S., Chávez-Servia, J.L., Oliart-Ros, R.M., Guzmán-Gerónimo, R.I., 2017. Antioxidant and antiproliferative activity of blue corn and tortilla from native maize. Chem. Cent. J. 11, 110. https://doi.org/10.1186/s13065-017-0341-x.

Hsu, Y.T., Shen, T.C., Hwang, S.Y., 2009. Soil fertility management and pest responses: a comparison of organic and synthetic fertilization. J. Econ. Entomol. 102, 160–169. https://doi.org/10.1603/029.102.0123.

Hu, X., Liu, J., Li, W., Wen, J., Li, T., Guo, X.B., Liu, R.H., 2020. Anthocyanin accumulation, biosynthesis and antioxidant capacity of black sweet corn (Zea mays L.) during kernel development over two growing seasons. J. Cereal Sci. 95, 103065. https://doi.org/10.1016/j.jcs.2020.103065.

Hu, Q.P., Xu, J.G., 2011. Profiles of carotenoids, anthocyanins, phenolics, and antioxidant activity of selected color waxy corn grains during maturation. J. Agric. Food Chem. 59, 2026–2033. https://doi.org/10.1021/jf104149q.

Hwang, T., Ndolo, V.U., Katundu, M., Nyirenda, B., Bezner-Kerr, R., Arntfield, S., Beta, T., 2016. Provitamin A potential of landrace orange maize variety (Zea mays L.) grown in different geographical locations of central Malawi. Food Chem. 196, 1315–1324. https://doi.org/10.1016/j.foodchem.2015.10.067.

Kuhnen, S., Lemos, P.M.M., Campestrini, L.H., Ogliari, J.B., Dias, P.F., Maraschin, M., 2009. Antiangiogenic properties of carotenoids: a potential role of maize as functional food. J. Funct.Foods 1, 284–290. https://doi.org/10.1016/j.jff.2009.04.001.

Kuhnen, S., Menel Lemos, P.M., Campestrini, L.H., Ogliari, J.B., Dias, P.F., Maraschin, M., 2011. Carotenoid and anthocyanin contents of grains of Brazilian maize landraces. J. Sci. Food Agric. 91, 1548–1553. https://doi.org/10.1002/jsfa.4346.

Lago, C., Landoni, M., Cassani, E., Doria, E., Landoni, M., et al., 2015. Study and characterization of an ancient European flint white maize rich in anthocyanins: Millo Corvo from Galicia. PloS one 10, 1–16. https://doi.org/10.1371/journal.pone.0126521.

Landoni, M., Puglisi, D., Cassani, E., Borlini, G., Brunoldi, G., Comaschi, C., Pilu, R., 2020. Phlobaphenes modify pericarp thickness in maize and accumulation of the fumonisin mycotoxins. Sci. Rep. 10, 1–9. https://doi.org/10.1038/s41598-020-58341-8.

Lao, F., Sigurdson, G.T., Giusti, M.M., 2017. Health benefits of purple corn (Zea mays L.) phenolic compounds. Compr. Rev. Food Sci. Food Saf. 16, 234–246. https://doi.org/10.1111/1541-4337.12249.

Loarca-Piña, G., Neri, M., Figueroa, J., de, D.J.D., Castaño-Tostado, E., Ramos-Gómez, M., Reynoso, R., Mendoza, S., 2019. Chemical characterization, antioxidant and antimutagenic evaluations of pigmented corn. J. Food Sci. Technol. 56, 3177–3184. https://doi.org/10.1007/s13197-019-03671-3.

Logrieco, A., Battilani, P., Leggieri, M.C., Jiang, Y., Haesaert, G., Lanubile, A., Mahuku, G., Mesterhazy, A., Ortega-Beltran, A., Pasti, M., Smeu, I., Torres, A., Xu, J., Munkvold, G., 2021. Perspectives on global mycotoxin issues and management from the mycokey maize working group. Plant Dis. 105, 525–537. https://doi.org/10.1094/PDIS-06-20-1322-FE.

Lopez-Martinez, L.X., Parkin, K.L., Garcia, H.S., 2011. Phase II-inducing, polyphenols content and antioxidant capacity of corn (Zea mays L.) from phenotypes of white, blue, red and purple colors processed into masa and tortillas. Plant Foods Hum. Nutr. 66, 41–47. https://doi.org/10.1007/s11130-011-0210-z.

Lozano-Alejo, N., Carrillo, G.V., Pixley, K., Palacios-Rojas, N., 2007. Physical properties and carotenoid content of maize kernels and its nixtamalized snacks. Innovat. Food Sci. Emerg. Technol. 8, 385–389. https://doi.org/10.1016/j.ifset.2007.03.015.

Luna-Vital, D., Weiss, M., Gonzalez de Mejia, E., 2017. Anthocyanins from purple corn ameliorated tumor necrosis factor-α-induced inflammation and insulin resistance in 3T3-L1 adipocytes via activation of insulin signaling and enhanced GLUT4 translocation. Mol. Nutr. Food Res. 61, 1–41. https://doi.org/10.1002/mnfr.201700362.

Martínez-Martínez, R., Vera-Guzmán, A.M., Chávez-Servia, J.L., Bolaños, E.N.A., Carrillo-Rodríguez, J.C., Pérez-Herrera, A., 2019. Bioactive compounds and antioxidant activities in pigmented maize landraces. Interciencia 44, 549–556.

Mendoza-Díaz, S., Ortiz-Valerio, M., del, C., Castaño-Tostado, E., Figueroa-Cárdenas, J. de D., Reynoso-Camacho, R., Ramos-Gómez, M., Campos-Vega, R., Loarca-Piña, G., 2012. Antioxidant capacity and antimutagenic activity of anthocyanin and carotenoid extracts from nixtamalized pigmented creole maize races (Zea mays L.). Plant Foods Hum. Nutr. 67, 442–449. https://doi.org/10.1007/s11130-012-0326-9.

Mendoza-Mendoza, C.G., Mendoza-Castillo, M.D.C., Delgado-Alvarado, A., Sánchez-Ramírez, F.J., Kato-Yamakake, T.Á., 2021. Anthocyanins content in the kernel and corncob of Mexican purple corn populations. Maydica 65, 1–10.

Messias, R. da S., Galli, V., e Silva, S.D., dos, A., Rombaldi, C.V., 2014. Carotenoid biosynthetic and catabolic pathways: gene expression and carotenoid content in grains of maize landraces. Nutrients 6, 546–563. https://doi.org/10.3390/nu6020546.

Naikoo, M.I., Dar, M.I., Raghib, F., Jaleel, H., Ahmad, B., Raina, A., Khan, F.A., Naushin, F., 2019. Role and regulation of plants phenolics in abiotic stress tolerance:
an overview. Plant Signal. Mol. Role Regul. Stress. Environ. 157–168. https://doi.org/10.1016/B978-0-12-816451-8.00009-5.

Nankar, A., Grant, L., Scott, P., Pratt, R.C., 2016. Agronomic and kernel compositional traits of blue maize landraces from the southwestern United States. Crop Sci. 56, 2663–2674. https://doi.org/10.2135/cropsci2015.12.0773.

Palacios-Rojas, N., McCulley, L., Kaeppler, M., Titcomb, T.J., Gunaratna, N.S., Lopez-Ridaura, S., Tanumihardjo, S.A., 2020. Mining maize diversity and improving its nutritional aspects within agro-food systems. Compr. Rev. Food Sci. Food Saf. 19, 1809–1834. https://doi.org/10.1111/1541-4337.12552.

Paulsmeyer, M., Chatham, L., Becker, T., West, M., West, L., Juvik, J., 2017. Survey of anthocyanin composition and concentration in diverse maize germplasms. J. Agric. Food Chem. 65, 4341–4350. https://doi.org/10.1021/acs.jafc.7b00771.

Pedreschi, R., Cisneros-Zevallos, L., 2006. Antimutagenic and antioxidant properties of phenolic fractions from Andean purple corn (Zea mays L.). J. Agric. Food Chem. 54, 4557–4567. https://doi.org/10.1021/jf0531050.

Prasanna, B.M., 2012. Diversity in global maize germplasm: characterization and utilization. J. Biosci. 37, 843–855. https://doi.org/10.1007/s12038-012-9227-1.

Prasanna, B.M., Palacios-Rojas, N., Hossain, F., Muthusamy, V., Menkir, A., Dhliwayo, T., Ndhlela, T., San Vicente, F., Nair, S.K., Vivek, B.S., Zhang, X., Olsen, M., Fan, X., 2020. Molecular breeding for nutritionally enriched maize: status and prospects. Front. Genet. 10, 1–16. https://doi.org/10.3389/fgene.2019.01392.

Puglisi, D., Landoni, M., Cassani, E., Toschi, I., Lucchini, G., Cesari, V., Borlini, G., Scapin, A., Pilu, R., 2018. Traditional farmers' varieties: a valuable source of genetic variability for biofortification programs. Maydica 63, 1–10.

Ramírez, L.B., Salcedo, H.E.R., Aulis, M.F.F., López, M.A.R., Ocaña, A.N., Radillo, J.J.V., 2018. Anthocyanins from rose maize (Zea mays L.) grains. Interciencia 43, 188–192.

Rodríguez-Salinas, P.A.P.A., Zavala-García, F., Urías-Orona, V., Muy-Rangel, D., Heredia, J.B.J.B., Niño-Medina, G., 2020. Chromatic, nutritional and nutraceutical properties of pigmented native maize (Zea mays L.) genotypes from the northeast of Mexico. Arabian J. Sci. Eng. 45, 95–112. https://doi.org/10.1007/s13369-019-04086-0.

Ryu, S.H., Werth, L., Nelson, S., Scheerens, J.C., Pratt, R.C., 2013. Variation of kernel anthocyanin and carotenoid pigment content in USA/Mexico borderland land races of maize. Econ. Bot. 67, 98–109. https://doi.org/10.1007/s12231-013-9232-9.

Salinas-Moreno, Y., Pérez-Alonso, J.J., Vázquez-Carrillo, G., Aragón-Cuevas, F., Velázquez-Cardelas, G.A., 2012. Antocianinas Y actividad antioxidante en maíces (Zea mays L.) de las razas chalqueño, Elotes Cónicos y Bolita. Agrociencia 46, 693–706.

Salinas Moreno, Y., Sánchez, G.S., Hernández, D.R., Lobato, N.R., 2005. Characterization of anthocyanin extracts from maize kernels. J. Chromatogr. Sci. 43, 483–487.

Siyuan, S., Tong, L., Liu, R.H., 2018. Corn phytochemicals and their health benefits. Food Sci. Hum. Wellness 7, 185–195. https://doi.org/10.1016/j.fshw.2018.09.003.

Trehan, S., Singh, N., Kaur, A., 2018. Characteristics of white, yellow, purple corn accessions: phenolic profile, textural, rheological properties and muffin making potential. J. Food Sci. Technol. 55, 2334–2343. https://doi.org/10.1007/s13197-018-3171-5.

Uarrota, V.G., Severino, R.B., Malinowsky, C., de Oliveira, S.K., Kuhnen, S., Yunes, R.A., Maraschin, M., 2014. Biochemical profile of leaf, silk and grain samples of eight maize landraces (Zea Mays L.) cultivated in two low-input agricultural systems. J. Food Biochem. 38, 551–562. https://doi.org/10.1111/jfbc.12087.

Uarrota, V.G., Severino, R.B., Maraschin, M., 2011. Maize landraces (Zea mays L.): A new prospective source for secondary metabolite production. Int. J. Agri. Res. 6 (3), 218–226. https://doi.org/10.3923/ijar.2011.218.226.

Vargas-Yana, D., Aguilar-Morón, B., Pezo-Torres, N., Shetty, K., Ranilla, L.G., 2020. Ancestral Peruvian ethnic fermented beverage "chicha" based on purple corn (Zea mays L.): unraveling the health-relevant functional benefits. J. Ethn. Foods 7. https://doi.org/10.1186/s42779-020-00063-3.

Zhang, Q., Gonzalez de Mejia, E., Luna-Vital, D., Tao, T., Chandrasekaran, S., Chatham, L., Juvik, J., Singh, V., Kumar, D., 2019. Relationship of phenolic composition of selected purple maize (Zea mays L.) genotypes with their anti-inflammatory, anti-adipogenic and anti-diabetic potential. Food Chem. 289, 739–750. https://doi.org/10.1016/j.foodchem.2019.03.116.