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Assessment of Initial Stages of Maillard Reaction in Dehydrated Onion and Garlic Samples

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The initial steps of the Maillard reaction in freshly laboratory-freeze-dried and commercial dehydrated onion and garlic samples have been assessed by quantitative determination of 2-furoylmethylamino acids, obtained after acid hydrolysis of the corresponding Amadori compound. In freshly prepared samples, hardly any presence of 2-furoylmethylamino acids was detected, whereas in commercial samples, onion contained much more important levels of 2-furoylmethylamino acids as compared to garlic species. 2-Furoylmethyl-γ-aminobutyric acid (**1**), 2-furoylmethyl-lysine (furosine; **2**), and 2-furoylmethylarginine (**3**) were identified in all commercial dehydrated onion samples, with compound **3** being the most abundant. All garlic samples presented slightly higher levels of **2** than **3** with no presence of **1**. The observed differences between onion and garlic commercial samples may be due to their very different content of reducing sugars. Moreover, some variations found in 2-furoylmethyl derivatives within both onion and garlic species could be also attributed to different processing and storage conditions during the manufacture of these products. The findings of this study show the first evidence of important levels of Amadori compounds in dehydrated garlic and onion samples, as well as the usefulness of 2-furoylmethyl derivatives as quality indicators for the early detection of the Maillard reaction in onion and garlic products.

KEYWORDS: Amadori compounds; Maillard reaction; 2-furoylmethylamino acids; onion; garlic

INTRODUCTION

Onion (*Allium cepa* L.) and garlic (*Allium sativum* L.) are well-known ingredients that can be widely used for the elaboration of different types of foodstuffs such as ketchup, sauces, soups, potato chips, meat products, and crackers (*1*, *2*). Moreover, these vegetables have been reported to possess important health benefits related to their antimicrobial, antioxidant, procirculatory, and antithrombic properties (*3*−*7*).

With the aim of having shelf-stable products, onion and garlic are usually subjected to a drying process, which may cause serious damage to the quality of the product (*8*). During the drying operation and storage of dried vegetables chemical modifications such as the Maillard reaction can take place. This reaction, favored at high temperatures and low water activities within the range 0.3−0.7 (*9*), is responsible for losses of essential amino acids and important organoleptic changes (*10*, *11*). In fact, Adam et al. (*12*) claimed that drying temperatures in onion above 60 °C should be avoided to retard flavor losses and undesirable color changes.

During the initial steps of the Maillard reaction a condensation among the free amino groups of an amino acid, peptide, or protein and the carbonyl groups of reducing sugars leads to the formation of Amadori compounds. These first stable products of the reaction are precursors of numerous compounds important in the formation of characteristic flavors, aromas, and brown polymers. Amadori compounds are originated before the occurrence of sensory changes; therefore, their determination provides a very sensitive indicator for early detection of quality changes caused by the Maillard reaction (*13*).

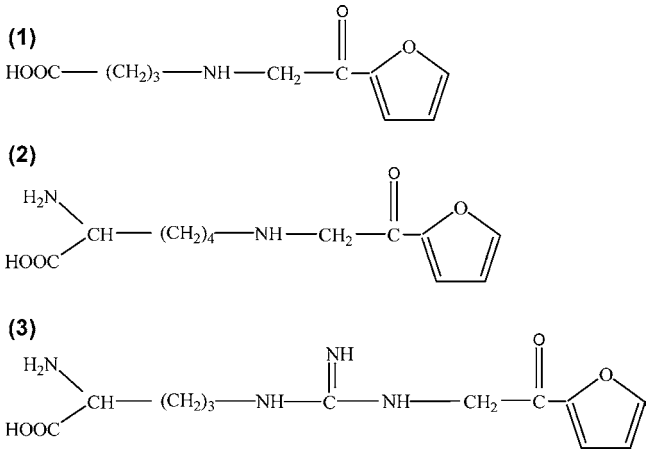

Figure 1. Molecular structures of (**1**) 2-furoylmethyl-γ-aminobutyric acid, (**2**) 2-furoylmethyl-lysine, and (3) 2-furoylmethylarginine.

To date, one of the most sensitive methods for evaluating the early steps of the Maillard reaction is the determination of 2-furoylmethylamino acids, generated during the acid hydrolysis of the corresponding Amadori compound (*14*). 2-Furoylmethyl

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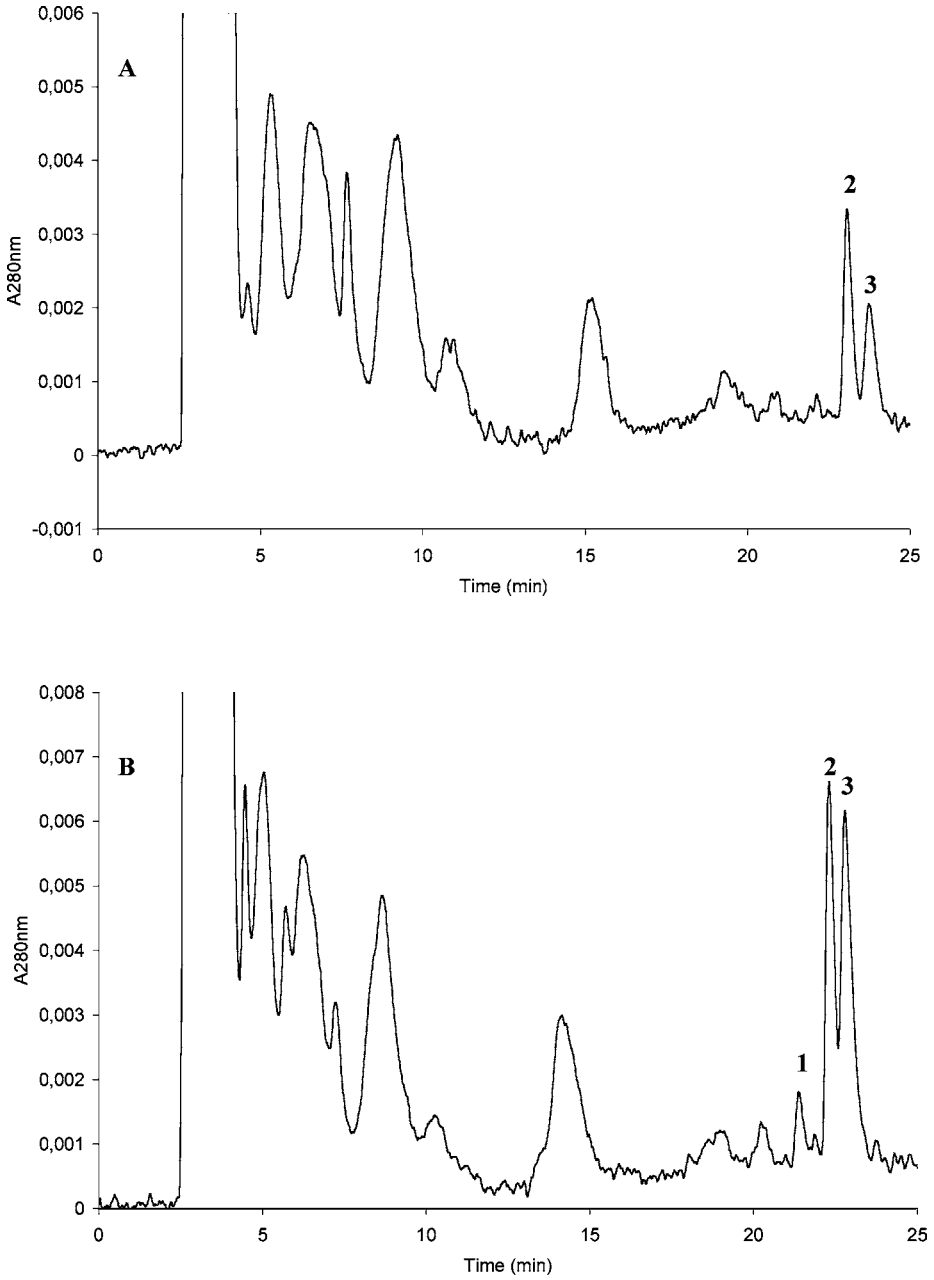

Figure 2. HPLC chromatogram of 2-furoylmethylamino acids in acid hydrolysates of commercial samples of garlic (**A**) and onion (**B**). Compounds are numbered as in **Figure 1**.

derivatives have been detected in several products of vegetal origin such as orange juice (*15*), tomato products (*16*), dehydrated fruits (*17*), jams and fruit-based infant foods (*18*), potato, carrot, and rice (*19*), and cereal-based foods (*20*, *21*).

In onion and garlic, a number of studies on the influence of temperature and water activity on browning development during drying and storage of these products have been performed (*1*, *2*, *12*, *22*−*25*). However, to our knowledge, no data are available in the literature on the assessment of the initial steps of the Maillard reaction in onion and garlic by measurements of 2-furoylmethyl derivatives. Because these vegetables may contain considerable amounts of reducing sugars and amino acids (*26*−*28*), the formation of Amadori compounds could be expected. In fact, fructosylarginine has been identified in an aged garlic extract (AGE) (*29*, *30*). In this paper, the presence of Amadori compounds, through the detection of their corresponding 2-furoylmethyl derivatives, has been investigated in dehydrated onion and garlic commercial samples with the aim of evaluating the usefulness of these compounds as quality indicators for the early detection of the Maillard reaction.

MATERIALS AND METHODS

Samples. Eleven samples of dehydrated vegetables, four onion (*A. cepa* L.) and seven garlic (*A. sativum* L.) samples, were purchased at different local markets in Spain. Additionally, two freshly laboratory-freeze-dried samples, one of garlic and another of onion, were also analyzed. All samples were ground prior to analyses.

Storage Assays. One batch of commercial powder onion was stored under vacuum in a desiccator at 50 °C for 6 days and a water activity of 0.44 achieved with a saturated K_2CO_3 solution. Samples were taken in duplicate at 0, 2, 4, and 6 days of storage for further analysis.

Analytical Determinations for the Characterization of Samples. Water activity (a_w) was determined at 25 °C using a Novasina a_w Sprint TH-500 (Pfäffikon, Switzerland) previously calibrated with saturated solutions of different salts. Total nitrogen (TN) was determined by means of the Kjeldahl method (*31*), and the protein level was calculated

Table 1. Water Activity (a_w) and Protein, 2-Furoylmethyl Amino Acids, and Mono- and Disaccharide Contents in Freshly Laboratory-Freeze-Dried (I) and Commercial Dehydrated Onion (II–V) and Garlic (II–VIII) Samples ($n = 2$)

sample	a_w	protein (g/100 g of product)	compd **1**[a] (mg/100 g of protein)	compd **2**[a] (mg/100 g of protein)	compd **3**[a] (mg/100 g of protein)[a]	glucose (g/100 g of product)	fructose (g/100 g of product)	sucrose (g/100 g of product)	total reducing sugars (g/100 g of product)
onion I	0.29 ± 0.003	10.36 ± 0.02	nd[b]	trace	nd	25.4 ± 1.6	22.7 ± 3.3	4.9 ± 0.01	48.1
onion II	0.26 ± 0.001	10.11 ± 0.46	94.7 ± 8.5	576.1 ± 26.6	1035.0 ± 61.1	14.9 ± 0.9	5.1 ± 0.2	8.2 ± 0.4	20
onion III	0.20 ± 0.01	9.31 ± 0.34	139.1 ± 11.6	886.2 ± 39.2	2113.9 ± 185.3	9.5 ± 0.2	4.4 ± 0.1	8.4 ± 0.5	13.9
onion IV	0.26 ± 0.00	8.95 ± 0.41	108.5 ± 7.9	588.6 ± 37.9	938.2 ± 124.1	17.3 ± 0.8	5.7 ± 0.2	10.5 ± 0.2	23
onion V	0.27 ± 0.00	10.84 ± 0.20	99.7 ± 3.2	761.2 ± 7.5	1230.8 ± 78.5	10.8 ± 0.5	6.9 ± 0.3	12.8 ± 0.6	17.7
garlic I	0.15 ± 0.00	18.83 ± 0.92	nd	nd	nd	0.08 ± 0.002	0.2 ± 0.03	2.0 ± 0.07	0.28
garlic II	0.18 ± 0.001	18.09 ± 0.21	nd	25.0 ± 1.8	17.8 ± 1.2	0.06 ± 0.01	1.0 ± 0.1	2.5 ± 0.3	1.06
garlic III	0.33 ± 0.00	19.56 ± 1.00	nd	33.5 ± 1.2	27.1 ± 1.5	0.40 ± 0.01	2.4 ± 0.08	3.2 ± 0.3	2.8
garlic IV	0.20 ± 0.01	18.67 ± 1.38	nd	18.0 ± 0.2	9.2 ± 0.5	0.08 ± 0.01	1.1 ± 0.1	1.8 ± 0.1	1.18
garlic V	0.26 ± 0.005	20.27 ± 0.76	nd	12.2 ± 0.2	6.7 ± 0.6	0.03 ± 0.002	0.4 ± 0.04	2.1 ± 0.04	0.43
garlic VI	0.18 ± 0.01	17.68 ± 0.70	nd	20.0 ± 0.0	17.2 ± 0.3	0.06 ± 0.01	1.1 ± 0.04	2.9 ± 0.2	1.16
garlic VII	0.21 ± 0.001	18.10 ± 0.20	nd	16.0 ± 1.0	9.6 ± 0.6	0.02 ± 0.002	0.6 ± 0.01	2.3 ± 0.1	0.62
garlic VIII	0.32 ± 0.02	15.13 ± 0.10	nd	3.8 ± 0.0	1.5 ± 0.1	0.03 ± 0.003	0.5 ± 0.03	2.5 ± 0.1	0.53

[a] See structures in **Figure 1**. [b] Not detected.

using 6.25 as conversion factor (TN × 6.25) (*32*). The pH of samples was measured in a MP 225 pH-meter with a glass electrode (Mettler-Toledo GmbH, Schwerzenbach, Switzenbach, Switzerland) after their extraction with Milli-Q water (0.5 g/5 mL) during 10 min at room temperature (25 °C) and centrifugation at 7000*g* for 15 min at 25 °C. All determinations were carried out in duplicate, and the results are expressed as mean values.

2-Furoylmethylamino Acids Determination. Determination of 2-furoylmethylamino acids was carried out by ion-pair RP-HPLC (*33*) analysis using a C_8 column (250 mm × 4.6 mm i.d.) (Alltech furosine dedicated) thermostated at 37 °C, with a linear binary gradient and a variable-wavelength detector at 280 nm (LCD Analytical SM 4000). Samples (0.5 g) were hydrolyzed under inert conditions (helium) with 8 mL of 8 N HCl at 110 °C for 23 h in a screw-capped Pyrex vial with PTFE-faced septa. The hydrolysate was filtered with a medium-grade paper filter (Whatman no. 40); 0.5 mL of the filtrate was applied to a Sep-Pack C_{18} cartridge (Millipore) prewetted with 5 mL of methanol and 10 mL of water and then eluted with 3 mL of 3 N HCl, and 50 μL was injected.

Quantitation was performed by the external standard method, using a commercial standard of pure 2-furoylmethyl-lysine (furosine, **2** in **Figure 1**) (Neosystem Laboratoire, Strasbourg, France). All analyses were done in duplicate, and the data are the mean values expressed as milligrams per 100 g of protein. Syntheses of 2-furoylmethyl-γ-aminobutyric acid (**1** in **Figure 1**) and 2-furoylmethylarginine (**3** in **Figure 1**) were carried out following the method described by Sanz et al. (*17*).

The identity of 2-furoylmethyl derivatives in commercial onion and garlic samples was confirmed by HPLC-MS by comparison of their retention times and mass spectrometry data with those of the synthesized reference compounds. Analyses were performed at ambient temperature on a Hewlett-Packard 1100 liquid chromatograph working in electrospray ionization mode, under atmospheric pressure and positive polarity (API-ES positive). Chromatographic and spectrometric conditions were as previously reported by del Castillo et al. (*34*).

Carbohydrate Determination. The chromatographic determination of mono- and disaccharides was performed following the method described by García-Baños et al. (*35*) in a Hewlett-Packard 6890 (Avondale, PA) gas chromatograph equipped with a flame ionization detector and a fused silica capillary column (25 m × 0.25 mm) coated with methyl silicone. The temperatures of the injector and detector were 280 and 300 °C, respectively. The oven temperature was programmed from 180 °C at 2 °C/min to 280 °C (1 min) and finally at 10 °C/min to 290 °C (15 min). Nitrogen was used as a carrier gas (0.5 mL/min), and injections were made in the split mode (1:40). Chromatographic peaks were measured using a HPChem acquisition system from Hewlett-Packard. Data are expressed as grams per 100 g of product. Samples of 0.1 g were weighed into a volumetric flask, followed by the addition of 5 mL of Milli-Q water and 20 min of stirring for 20 min at room temperature; finally, the volume was completed to 25 mL with pure ethanol, obtaining 80% as final concentration of ethanol. Then, samples were centrifuged at 9600*g* and 10 °C for 10 min. In the precipitates, a second extraction with 80% ethanol was performed to obtain recovery values of the carbohydrates close to 100%. Half a milliliter of supernatants was mixed with 1 mL of a solution of β-phenyl-glucoside (0.01%), as internal standard. The mixture was evaporated under vacuum, and the sugars were converted to their corresponding oxime for chromatographic analysis (*36*).

Determination of Browning Development. Formation of browning pigments was determined by means of the official method (*37*). A sample of 0.3 g was extracted with 15 mL of 10% NaCl solution by stirring for 1 h at room temperature. The crude extract was filtered through a Whatman filter paper no. 40, and the absorbance was measured at 420 nm using a Beckman DU-70 spectrophotometer UV−vis (190−800 nm; Beckman Coulter).

RESULTS

RP-HPLC-UV profiles of the acid hydrolysate of a dehydrated garlic sample (**Figure 2A**) revealed the presence of two peaks susceptible to correspond to 2-furoylmethylamino acids, whereas three main peaks were detected in the acid hydrolysate of onion (**Figure 2B**). Analysis by HPLC-ESI-MS showed the presence of the ions $(M + H)^+$ at 212, 255, and 283 in peaks 1, 2, and 3, respectively, which allowed the identification of the compounds **1**, **2**, and **3** (structures in **Figure 1**) (*17*, *34*).

Prior to quantification of the 2-furoylmethylamino acids in dehydrated onion and garlic samples, the suitability of the method was evaluated. The repeatability of the entire method (including acid hydrolysis, sample preparation, and HPLC analysis) was determined by analyzing the same sample ($n = 3$) on different days. The relative standard deviation (RSD) was 4.6%. To evaluate the accuracy of the method, a known amount of standard **2** was added to the acid hydrolysates of two different garlic samples, obtaining a recovery of 95.2%.

Table 1 shows water activity (a_w) values and protein, 2-furoylmethylamino acid, and carbohydrate contents in dehydrated commercial and freshly prepared onion and garlic samples. a_w values were similar for both dehydrated vegetables, whereas garlic samples had a higher protein content ranging from 15.13 to 20.27% and onion samples contained between 8.95 and 10.84%, values that are in very good agreement with those found in the literature (*38*, *39*). Both vegetables had pH values slightly above 5 in aqueous solutions.

With regard to 2-furoylmethylamino acids, noticeable quantitative differences were found between both species. Thus, onion samples contained much higher amounts of 2-furoylmethyl derivatives, with **3** having the greatest abundance, followed by **2** and **1**. All garlic samples presented slightly higher levels of **2** than **3** with no presence of **1**. Freshly prepared samples were also analyzed; **2** was found in trace amount in

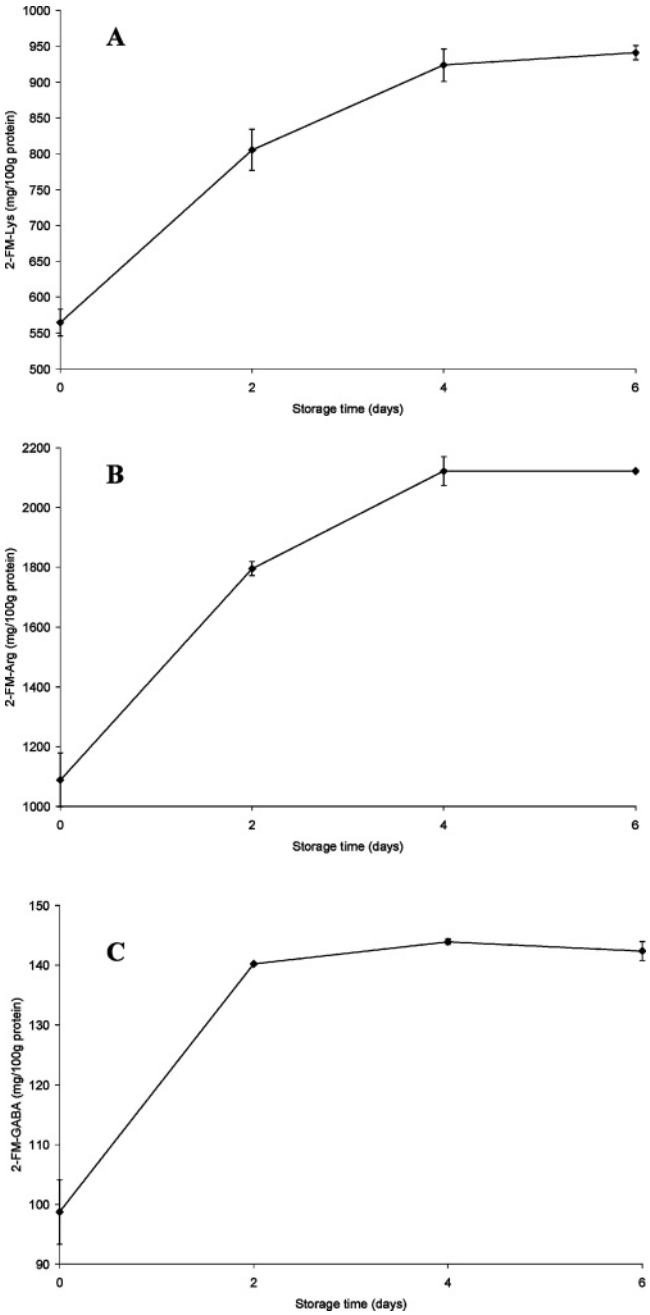

Figure 3. Evolution of **2** (**A**), **3** (**B**), and **1** (**C**) content during storage at 50 °C and 0.44 a_w of commercial dehydrated onion sample II. Vertical bars represent standard deviation values ($n = 2$).

onion, whereas no presence of 2-furoylmethylamino acids was detected in fresh garlic samples.

As far as carbohydrate content is concerned, onion had a much higher content of carbohydrates as compared to garlic. With the exception of fresh onion sample I, the concentration of glucose was found to be considerably higher than that of fructose in onion samples; conversely, fructose was the main reducing sugar in garlic samples. Previous studies have shown a similar trend in the content of carbohydrates in onion (*38*, *40*) and garlic samples (*41*, *42*).

To evaluate the effect of storage under inappropriate conditions on the Amadori compound formation in dehydrated vegetables, a sample of powder onion (onion sample II) was stored at 50 °C and 0.44 a_w for various periods (0, 2, 4, and 6 days). **Figure 3** illustrates the evolution of 2-furoylmethylamino acids during this storage. A considerable increase of all 2-furoylmethylamino acids was found during the first 2 days of incubation, although the formation then slowed, and from the fourth day of incubation the contents of 2-furoylmethyl derivatives remained constant. Browning at 420 nm increased gradually as storage proceeded, being more pronounced from the second day of storage. Thus, the absorbance at 0 days increased from 0.07 ± 0.01 to 0.12 ± 0.006 after 2 days of incubation, whereas at 4 and 6 days of storage it reached values of 0.21 ± 0.004 and 0.32 ± 0.008, respectively. Overall, these results indicated that the formation of Amadori compounds proceeded at a relatively fast rate at the beginning of storage, although this increase gradually diminished with incubation time, suggesting that from the fourth day of storage the progress of advanced stages of the Maillard reaction led to a partial degradation of the Amadori compounds (*43*).

DISCUSSION

The Amadori compound fructosylarginine was previously identified in AGE, a concentrate product obtained after >10 months of storage at room temperature, but not in raw and heated garlic juice, probably due to the low content of glucose in garlic (*29*, *30*). However, we have detected the presence of Amadori compounds (by 2-furoylmethylamino acids determination) in all dehydrated commercial garlic and onion products. This can be explained by the fact that the Maillard reaction is strongly promoted by the combined effect of prolonged heating and low water activity obtained during the dehydration process (*44*).

As mentioned above, important differences in the development of the initial steps of the Maillard reaction were found among dehydrated onion and garlic samples. Lysine and arginine have been previously reported to be found in similar concentrations in garlic and onion (*39*). This fact, together with the similar obtained data of a_w and pH in both species, indicates that the higher amounts of 2-furoylmethylamino acids detected in onion samples compared to garlic species may be explained by their high content of fructose and, especially, glucose. In addition, substantial variations in 2-furoylmethylamino acids content found within both onion and garlic species can be attributed not only to the different reducing sugar contents but also to the different processing and/or storage conditions used during the manufacture of these products.

In conclusion, findings presented in this work show, to our best knowledge, the first evidence of Amadori compounds in dehydrated commercial onion and garlic samples and the usefulness of the 2-furoylmethyl derivatives as quality indicators for the early detection of the Maillard reaction in these products. These results seem to indicate that changes in the formation of 2-furoylmethylamino acids may be a suitable indicator to characterize the storage conditions of onion and garlic dehydrated products before color change becomes more significant. Such information is crucial for preventing quality deterioration in dehydrated vegetables.

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