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Formation of hydroxymethylfurfural and furosine during the storage of jams and fruit-based infant foods

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Abstract

Simultaneous formation of hydroxymethylfurfural (HMF) and furosine (Fu) during the storage of three batches of jam samples (one commercial and two laboratory prepared) and one of fruit-based infant food (commercial), at 20 and 35 °C during 12 months, was investigated to evaluate the reliability of the combination of both parameters as quality indicators. In general, the concentration of both indicators increased with time and temperature of storage, formation of furosine being less temperature dependent than that of HMF. HMF was proved to be a good indicator of the severity of heating during manufacture and/or inadequate temperature during prolonged storage, whereas furosine may be a useful indicator of the storage conditions. The combination of both indicators can afford important information on the quality of jams and fruit-based infant foods during processing and storage.

Keywords: Storage; Hydroxymethylfurfural; Furosine; Jams; Fruit-based infant food

1. Introduction

During manufacture and storage of jams and fruit-based infant foods, important chemical modifications involving carbohydrates can take place. In the acid medium of these products, dehydration of carbohydrates leads to the formation of hydroxymethylfurfural (HMF). Moreover, the Maillard reaction can also take place, giving rise to Amadori compounds during the first steps of the reaction, and HMF as a consequence of further reactions. These changes contribute, in some degree, to the typical sensorial characteristics of jams. However, in the case of fruit-based infant foods, processing conditions should ensure not only adequate sensory attributes, but also an appropriate nutritional value, because of the limited number of foods that babies can consume. Therefore, the control of manufacture and storage by chemical indicators plays an important role in the quality of these products.

HMF has been found to be a well-known indicator of heat processing and/or storage of several vegetable products, such as apricot and peach purees (Trifirò, 1962), tomato derivatives (Allen & Chin, 1980; Porretta, 1991), and apple sauce and grape jelly (Shaw, Roche, & Dunne, 1996). Some data have been reported on the presence of this indicator in jams (Trifirò & Landi, 1962; Simonyan, 1971; Steber & Klostermeyer, 1987; Corradini et al.,1995). Recently, a survey of the content of HMF in commercial jams and fruit-based infant foods noted the wide variations of HMF concentration, indicating differences in the processing conditions (Rada-Mendoza, Olano, & Villamiel, 2002a).

Furosine (2-furoylmethyl-lysine), generated during acid hydrolysis of an Amadori compound, is a recognized indicator of the degree of damage during the initial steps of the Maillard reaction in a number of vegetable foods, such as soybeans, barley and malt (Molnár-Perl, Pinter-Szakacs, Wittman, Reutter, & Eichner, 1986), potatoes, rice and carrots (Resmini & Pellegrino, 1992), infant cereals (Guerra-Hernández, Corzo, & Garcia-Villanova, 1999), tomato products (Hidalgo, Pompei, & Zambuto, 1998; Sanz, del Castillo, Corzo, & Olano, 2000) and dehydrated fruits (Sanz, del Castillo, Corzo, & Olano, 2001). In jams and fruit-based

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infant foods, the presence of furosine has recently been investigated and this compound has been proposed as quality indicator (Rada-Mendoza, Olano, & Villamiel, 2002b).

Simultaneous formation of HMF and furosine has been reported in tomato products (Hidalgo & Pompei, 2000) and bread (Ramirez-Jimenez, Guerra-Hernandez, & Garcia-Villanova, 2000; Ramirez-Jimenez, Garcia-Villanova, & Guerra-Hernandez, 2001; Guerra-Hernandez, Ramirez-Jimenez, & Garcia-Villanova, 2002). Recently, Sanz, del Castillo, Corzo, and Olano (2003) in a study on honey quality, recommended the use of both, HMF and furosine, to detect excessive heat treatment or prolonged storage of honey samples. However, to the best of our knowledge, no data are available, in the literature, on the usefulness of the combination of HMF and furosine in both, jams and fruit-based infant foods. The aim of the present paper was to study the evolution of HMF and furosine during the storage of jams and fruit-based infant foods, in order to assess the reliability of these parameters as quality indicators in this kind of product.

2. Materials and methods

2.1. Samples

One batch of peach jam ($\geqslant$60% of sugar) and one of fruit-based infant food (pear and banana) were purchased from local markets. Both commercial products had similar expected shelf-lives, as measured by the "best-before" date. In addition, two batches of peach jam were prepared in the laboratory, according to a traditional procedure, by boiling in an open kettle, with manual stirring, 900 g of fresh peaches (Calanda) with 1110 g of sugar, pectin (0.4%) and citric acid (0.1%) for 30 (laboratory prepared jam 1) or 40 min (laboratory prepared jam 2). The water added was equivalent to that evaporated from the fruit during boiling. Samples were cooked to about 66°Brix (laboratory prepared jam 1) and 64°Brix (laboratory prepared jam 2), as determined on a Atago Brix refractometer model 500 (Atago Co., Ltd, Japan). Then, the jam was poured into glass jars with screw caps and sterilised at 100 °C for 5 min. When samples were cooled to room temperature, they were stored under different conditions.

Prior to analytical determinations, all samples were homogenised using an Ultra-turrax macerator (Janke & Kunkel Ika-Werk).

2.2. Storage assays

The three batches of peach jam (one commercial and two laboratory prepared jams) and one of fruit-based infant food (pear and banana) were stored at room temperature (20 °C) and at 35 °C during 12 months. Samples were taken in duplicate at 0, 2, 5, 9 and 12 months of storage.

2.3. Analytical determinations

Formation of browning pigments was determined by measuring the absorbance at 420 nm using a Beckman DU®-70 spectrophotometer UV-Vis (190-800 NM; Beckman Coulter).

The pH of samples was measured in a pH meter MP 225 with glass electrode (Mettler-Toledo GmbH, Schwerzenbach, Switzerland). Water activity was determined at 25 °C using a Novasina a_w Sprint TH-500 instrument (Pfäffikon, Switzerland) previously calibrated with saturated solutions of different salts. Total

Table 1
Initial pH values, water activities (a_w) and protein contents (g/100 g) in the stored samples of jams and fruit-based infant food

Sample	pH	a_w	Protein (g/100 g)
Commercial jam	3.51	0.825	0.337
Laboratory-prepared jam 1	3.92	0.838	0.263
Laboratory-prepared jam 2	3.78	0.828	0.275
Commercial fruit-based infant food	3.96	0.828	0.678

Table 2
Colour development ($A_{420\ nm}$) in commercial and laboratory-prepared jams and commercial fruit-based infant food samples stored during 12 months at 20 and 35 °C ($n=2$)

Sample	Storage temperature (°C)	Storage time (months)	
		0	12
Commercial jam	20	0.187	0.211
	35	0.187	0.354
Laboratory-prepared jam 1	20	0.188	0.235
	35	0.188	0.258
Laboratory-prepared jam 2	20	0.198	0.231
	35	0.198	0.263
Commercial fruit-based infant food	20	0.119	0.123
	35	0.119	0.182

Table 3
Evolution of hydroxymethylfurfural (HMF) (mg/100 g product) and furosine (Fu) (mg/100 g protein) contents in jams and commercial fruit-based infant food stored during 12 months at 20 and 35 °C ($n = 2$)

Storage temperature (°C)	Storage time (months)	HMF (mg/100 g product)				Fu (mg/100 g protein)			
		Commercial jam	Laboratory-prepared jam 1	Laboratory-prepared jam 2	Commercial fruit-based infant food	Commercial jam	Laboratory-prepared jam 1	Laboratory-prepared jam 2	Commercial fruit-based infant food
20	0	0.6	0.1	3.4	0.1	264	38.0	120	75.2
	2	0.9	0.2	3.9	0.3	288	145	135	44.2
	5	1.0	0.3	3.9	0.3	478	194	142	63.4
	9	2.1	0.5	4.5	0.3	570	202	196	66.4
	12	2.5	0.4	4.9	0.6	404	198	240	111
35	0	0.6	0.1	3.4	0.1	264	38.0	120	75.2
	2	2.8	1.0	5.3	0.7	463	312	229	84.1
	5	12.4	3.0	9.0	1.8	769	464	531	179
	9	23.6	9.2	16.6	3.9	985	719	444	199
	12	35.2	16.2	18.0	6.5	813	799	476	384

nitrogen (TN) content was determined by the Kjeldahl method (AOAC. Method 920.152) and protein level was calculated using 6.25 as conversion factor (TN×6.25).

The analysis of HMF was carried out by HPLC using a Nova-Pak®C_{18} column (3.9×150 mm; Waters) at ambient temperature and a linear gradient with methanol and water. The UV detector was set at 283 nm (Viñas, Campillo, Hernández-Córdoba, & Candela, 1992). Sample preparation was performed according to the method of Porretta and Sandei (1991). Quantitation was carried out by the external standard method using a commercial standard of HMF (Sigma, St. Louis, MO, USA). Data were the mean values of duplicate expressed as mg/100 g of product.

The quantitation of furosine was performed by HPLC analysis, using a Spherisorb ODS(2) 5 μm column (250 mm×4.6 mm; Phenomenex, Torrance) at 25 °C. The mobile phase consisted of a solution of 5 mM sodium heptane sulphonate with 20% acetonitrile and 0.2% formic acid. The elution was isocratic and the UV detector was set at 280 nm (Delgado, Corzo, Santa-María, Jimeno, & Olano, 1992). The preparation of samples was carried out using the method described by Rada-Mendoza et al. (2002a). Quantitation was performed by the external standard method, using a commercial standard of pure furosine (Neosystem Laboratoire, Strasbourg, France). Data were the mean values of duplicates expressed as mg/100 g protein.

3. Results and discussion

Table 1 shows the pH, a_w and protein contents (g/100 g) in the studied samples of jams and fruit-based infant food. All the data were very similar to those previously reported by Rada-Mendoza et al. (2002b). During storage, no change was detected in the pH values of the samples analyzed.

Browning, measured at 420 nm, is shown in Table 2. The initial values were very similar in the commercial jam and in the laboratory prepared jam 1. Laboratory-prepared jam 2 had a slightly higher browning than the other laboratory prepared jam, probably due to the more severe heating process applied during manufacture. Fruit-based infant food underwent less browning than jam samples. As expected, a slight colour development was observed after 12 months at 20 °C in the stored samples, this being more noticeable when samples were stored at 35 °C.

Table 3 shows the evolution of HMF and furosine values during the storage of samples at 20 and 35 °C for 12 months. The initial values of HMF and furosine in commercial samples were within the ranges previously reported by Rada-Mendoza et al. (2002a, 2002b). As expected, laboratory-prepared jam 2, that was

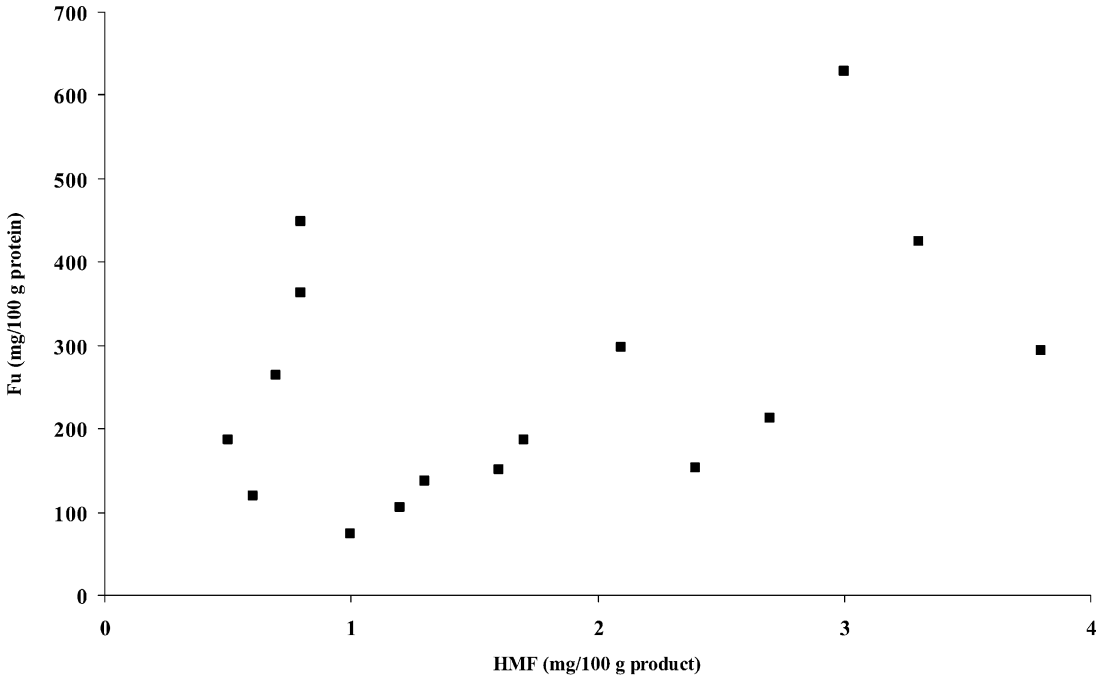

Fig. 1. Contents of hydroxymethylfurfural (HMF) (mg/100 g product) versus furosine (Fu) (mg/100 g protein) in commercial jams (data taken from Rada-Mendoza et al., 2002a, 2002b).

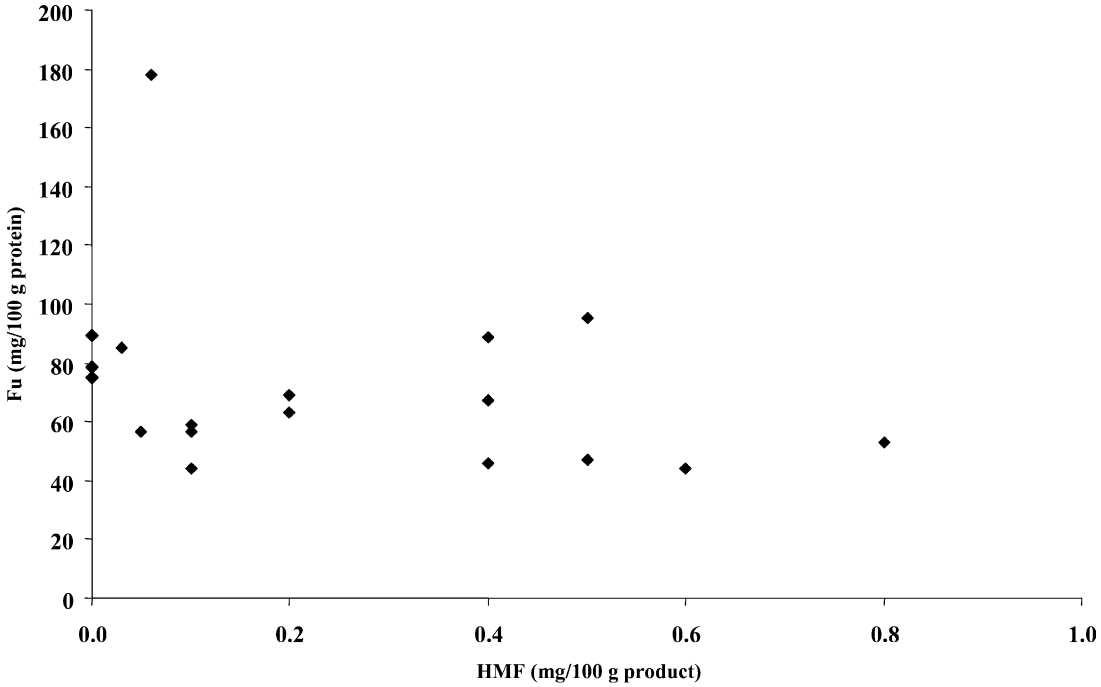

Fig. 2. Contents of hydroxymethylfurfural (HMF) (mg/100 g product) versus furosine (Fu) (mg/100 g protein) in commercial fruit-based infant foods (data taken from Rada-Mendoza et al., 2002a, 2002b).

submitted to a more severe heating than laboratory-prepared jam 1, was found to have higher HMF and furosine contents than laboratory-prepared jam 1.

With respect to the evolution of HMF and furosine contents during storage, small formation of HMF was observed during storage at 20 °C in all studied samples but a great increase in HMF during storage at 35 °C was observed, which indicates a large dependence of the formation of HMF on time and temperature of storage. Furosine increased considerably during storage at both temperatures. Although higher amounts of furosine were observed during storage at 35 °C, its formation was less temperature-dependent than that of HMF.

Published investigations on the formation of HMF in jams are scarce. Trifirò and Landi (1962) found an increase in HMF content, from 0.25 mg/100 g product to 29.8 mg/100 g product, after the storage of an apricot jam at 45 °C during 2 months. No data have been previously reported on the evolution of furosine concentration during the storage of these products.

These results seem to show that furosine is less sensitive to increase in temperature than HMF. Therefore the occurrence of high values of HMF could indicate that samples have been submitted to severe processing conditions during manufacture or elevated temperature during storage. Low values of furosine, together with high levels of HMF, could eliminate prolonged storage under inappropriate conditions. However, when furosine is also high, overheating of the sample might be suspected during the elaboration procedure.

Previous studies on commercial jams and fruit-based infant foods have shown the presence of furosine (Rada-Mendoza et al., 2002a) and HMF (Rada-Mendoza et al., 2002b) in these products, but no combination of both indicators has been considered. As can be observed in Figs. 1 and 2, commercial samples present a wide range of HMF and furosine contents. Low values of both furosine and HMF indicate that samples have been manufactured and stored under appropriate conditions. However, low values of HMF and high values of furosine may be due to prolonged storage under appropriate conditions and high values of HMF and low values of furosine may indicate severe heat treatment during manufacture.

The results obtained in the present paper underline the usefulness of simultaneous determination of HMF and furosine to assess the quality of jams and fruit-based infant foods during processing and storage.

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