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Determination of hydroxymethylfurfural in commercial jams and in fruit-based infant foods

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Abstract

Fifty six commercial samples, 38 jams with several fruit and sugar contents and 18 fruit-based infant foods, were analysed for pH, dry matter and hydroxymethylfurfural (HMF) content. Samples of jams had pH and dry matter values similar to those reported in the literature. Fruit-based infant foods presented higher values of pH and lower dry matter than jam samples. HMF was found in all samples of jams, regardless of the pH, sugar or dry matter, from traces to 7.17 mg/100 g product (mean value close to 1.35 mg/100 g product). Three samples of fruit-based infant foods did not show appreciable amounts of HMF and the average value for the rest of samples was 0.29 mg/100 g product. The difference between the values of HMF in jams and in fruit-based infant foods may be in part due to the lower fruit concentration in the latter. In general terms, the considerable variations of HMF content found in the analysed samples may be an indication of differences in the processing conditions.

Keywords: Hydroxymethylfurfural; Jams; Fruit-based infant foods

1. Introduction

Heat processing is the most common way of preserving food and making it edible. Under adequate conditions, foods retain their expected organoleptic and nutritional properties; however, overprocessing may cause damage of constituents and decrease in the nutritional value. Chemical indicators for assessing quality of heat-treated foods have proved to be useful for the control of processes, creating the possibility of optimizing manufacture conditions.

Hydroxymethylfurfural (HMF) is a recognised indicator of quality deterioration, as a result of excessive heating or storage in a wide range of foods containing carbohydrates. Its content is practically zero in fresh, untreated fruit juice (Askar, 1984) and HMF formation is judged to be the most useful method for assessing the effectiveness of heat treatment in destroying spoilage organisms in jams and fruit products (Steber & Klostermeyer, 1987). In vegetable products, such as tomato pastes, the extent of damage can be determined by the HMF content (Allen & Chin, 1980; Porretta, 1991). In apple sauce and grape jelly, the level of HMF has been used as indicator of long-term storage quality (Shaw, Roche, & Dunne, 1996).

During the manufacture of jams and infant foods, severe heat treatment can be applied; moreover, these products are usually stored for long periods of time (Belitz & Grosch, 1987; Camacho-Salas, Diez-Marques, & Cámara-Hurtado, 1999; Internal Document from Nestlé; Shi, Chiralt, Fito, Serra, Escoin, & Gasque, 1996). These processes may lead to Maillard reaction and caramelisation of carbohydrates in the acid medium of jams and fruit-based infant foods, and, consequently, variable amounts of HMF can be present in these products. Although there are some studies on the presence of HMF in jams (Corradini, Nicoletti, Cannarsa, Corradini, Pizzoferrato, & Vivanti, 1995; Simonyan, 1971; Steber & Klostermeyer, 1987), scarce data on its content in commercial samples are available in the literature and no studies on fruit-based infant foods have been reported. The quality of fruit-based infant foods is of considerable importance, since babies may be obtaining all their nutrients from a small number of foods; so overprocessed infant foods may affect the nutritional status of consumers.

In the present paper, we carry out a survey of the content of HMF in commercial samples of jams with several fruit and sugar contents and in fruit-based infant foods.

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2. Materials and methods

2.1. Samples

Twenty samples of jams from various types of fruits (orange, lemon, apple, apricot, mulberry, bilberry, fig, pineapple, plum, strawberry, banana, mixture of fruits and tropical fruits), with a shelf-life of 1–3 years, were collected at the Spanish market: 10 samples with a content of sugar $\geqslant 60\%$ (three standard and seven extra jams) and 10 samples with reduced sugar content (40–55%). Special attention was paid to peach jam and thus, 18 peach samples were also analysed: six extra jams ($\geqslant 60\%$ of sugar) and 12 reduced-sugar jams (31–55% of sugar). In addition, 18 commercial samples of fruit-based infant foods (different fruits and mixtures of them), were also studied. Prior to analytical determinations, all samples were homogenised using an Ultra-turrax (Janke & Kunkel Ika-Werk) tissue macerator. The pH of samples was measured in a pH meter, MP 225, with glass electrode (Mettler-Toledo GmbH, Schwerzenbach, Switzerland). The dry matter (DM) of the samples was determined following the AOAC method 920.15.

2.2. Determination of HMF

The analysis of HMF was carried out by HPLC. Samples (1 g) were placed in a 25-ml flask; 2 ml each of Carrez I and II reagents were added with stirring and the volume made up with Milli-Q water (Millipore, Bedford, MA, USA; Porretta & Sandei, 1991). After standing for 30 min, the supernatant was filtered through a filter of 0.45 μm (Waters) and then injected into the chromatograph.

Chromatographic determination was carried out, following the method of Viñas, Campillo, Hernández-Córdoba, and Candela (1992), using a Nova-Pak® C_{18} column (3.9×150 mm; Waters) at ambient temperature. The mobile phase consisted of methanol:water, using a linear gradient from methanol:water (5:95) to methanol: water (80:20) in 6 min. Isocratic elution was then continued for 6 min and, finally, initial conditions were re-established in 1 min and held for 10 min. The flow rate was 1 ml/min and injection volume 50 μl. The UV detector was set at 283 nm. Quantitation was carried out by the external standard method, using a commercial standard of HMF (Sigma, St. Louis, MO, USA). All

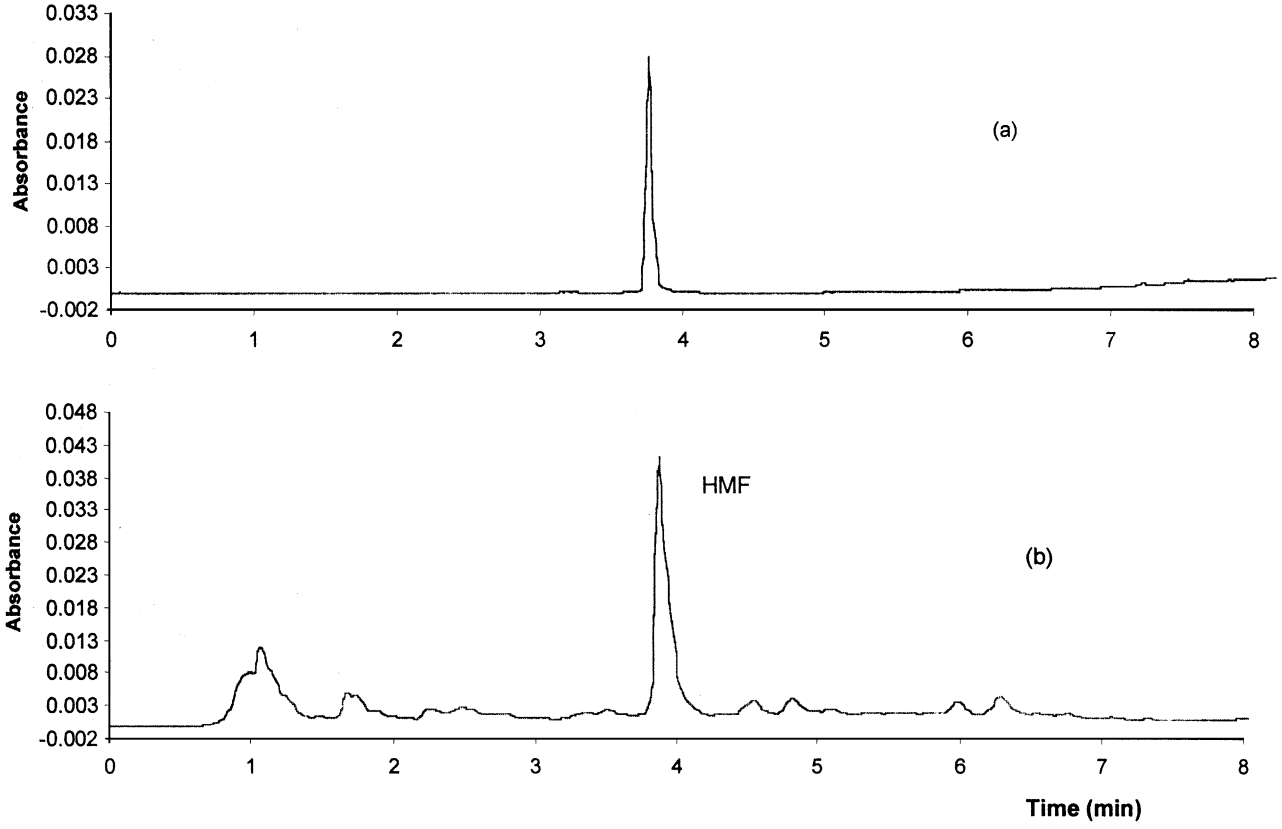

Fig. 1. (a) HPLC chromatogram of a standard of HMF and (b) a commercial sample of peach jam.

analyses were done in duplicate and the data were the mean values expressed as mg/100 g.

The identity of HMF was confirmed by HPLC–MS. The analyses were performed at ambient temperature on a Hewlett-Packard 1100 liquid chromatograph working in electrospray ionisation mode under atmospheric pressure and positive polarity (API-ES positive). With the exception of the flow rate, that was 0.7 ml/min, the chromatographic conditions were as previously mentioned for the quantitative analyses. The ion used for selective monitoring was m/z 127, corresponding to HMF $[M+H]^+$.

3. Results and discussion

The typical chromatograms of a standard of pure HMF (a) and a commercial sample of peach reduced-sugar jam (b) are shown in Fig. 1. HMF is eluted in less than 4 min. Peak identity was assigned by retention time and confirmed by HPLC–MS.

Since the analytical procedure for HMF determination was taken from methods previously used for tomato products (Porretta & Sandei, 1991) and honey (Viñas et al., 1992), a study on the suitability of the method was needed in the samples studied in the present paper. The HMF calibration curve was linear in the range from 0.00828 to 5 ng/μl, with a detection limit of 0.00432 ng/μl, calculated as the necessary amount to obtain a value of 3 for the signal/noise ratio. The repeatability of the method, assessed by performing 5 replicate measurements on a sample of reduced-sugar jam from peach, was lower than 2.1%, expressed as relative standard deviation (RSD). The accuracy of the method was tested by adding known amounts of HMF standard to a sample of reduced-sugar jam from peach and the average value was 97.9%, 1.05% being the RSD.

Tables 1 and 2 show the pH, sugar, DM and HMF contents in commercial jams. The pH of samples varied within the range 3.11–4.45, whereas the DM content was around 63–67% in extra and standard samples, and 34–60% in reduced-sugar samples. These data are in agreement with those previously reported in the literature (Carbonell, Costell, & Durán, 1991; Costell, Baidón, & Durán, 1988; Fernández-Salguero, Gómez & Carmona, 1993; Villarroel & Costell, 1989). The amount of HMF in samples varied from traces to 7.17 mg/100 g product, regardless of the pH, sugar or DM. The mean value of the 38 analysed samples was close to 1.35 mg HMF/100 g product, considerably lower than 8.85, 8.30 and 6.20 mg of HMF/100 g in samples of cherry, strawberry and plum jams, respectively, reported by Simonyan (1971), but close to 3.8 mg of HMF/100 g reported by Corradini et al. (1995) in commercial jams. According to the previous studies of Steber and

Table 1
Content of HMF (mg/100 g) and other parameters in commercial jams

Jams	Fruit (%)[a]	Sugar (%)[a]	pH	DM (%)	HMF (mg/100 g)
Standard					
Orange (sour)	35	63	3.31	66.6	0.55
Orange (sweet)	35	63	3.22	67.3	1.34
Lemon	35	63	3.30	67.7	1.67
Extra					
Apple	50	63	3.54	65.7	0.98
Apricot	50	60	3.34	67.6	1.18
Mulberry	50	60	3.18	63.8	2.42
Mixture of fruits	50	63	3.11	66.2	2.66
Bilberry A	50	60	3.22	66.2	3.77
Bilberry B	50	60	3.24	63.2	3.27
Fig	50	60	4.39	63.4	0.75
Reduced-sugar					
Pineapple A	60	40	3.60	40.9	0.33
Plum	45	54	3.40	56.8	0.30
Pineapple B	48	52	3.65	52.9	0.11
Orange (sweet)	45	53	3.31	56.2	0.35
Apricot	55	48	3.41	49.8	0.09
Strawberry	57	47	3.50	50.4	1.36
Mixture of fruits	57	47	3.54	49.1	1.23
Banana	60	–	4.45	37.0	0.05
Tropical	45	55	3.54	58.9	1.86
Lemon	40	50	3.24	51.4	0.90

DM, dry matter.
[a] Manufacturer-reported values.

Table 2
Content of HMF (mg/100 g) and other parameters in commercial peach jams

Jams	Fruit (%)[a]	Sugar (%)[a]	pH	DM (%)	HMF (mg/100 g)
Extra					
A	50	60	3.13	63.1	1.57
B	50	63	3.41	65.8	0.46
C	50	63	3.50	64.5	0.72
D	50	60	3.22	63.5	2.14
E	50	63	3.47	64.9	0.81
F	50	63	3.42	67.4	2.95
Reduced-sugar					
G	50	31	3.73	34.7	1.40
H	55	40	3.60	39.4	0.68
I	45	55	3.31	56.4	0.15
J	55	42	3.56	41.2	7.17
K	55	48	3.47	49.7	0.67
L	50	44	3.68	42.7	1.67
M	50	40	3.58	40.7	0.80
N	50	45	3.58	46.4	Traces
O	–	55	3.46	60.5	0.47
P	50	40	3.63	41.6	0.94
Q	57	47	3.97	49.8	0.81
R	50	44	3.64	43.3	Traces

DM, dry matter.
[a] Manufacturer-reported values.

Klostermeyer (1987) on the formation of HMF during jam processing, values lower than 5 mg/100 g product, result when samples are treated under adequate processing conditions. Therefore, it seems reasonable to suppose that the reported samples, manufactured in 1971, were submitted to severe heating or stored under inappropriate conditions.

Table 3 shows the pH, DM and HMF contents of 18 commercial fruit-based infant foods. Variations in pH and DM were lower than those found in jams and HMF content was lower than 0.80 mg/100 g in all samples. Three samples, manufactured with juice from citric fruits, did not show appreciable amounts of HMF and the average value for the remaining samples was 0.29 mg/100 g. The low HMF contents in fruit-based infant foods, compared with those found in jams, may in part be due to the lower fruit concentration in fruit-based infant foods. Presence of negligible amounts of HMF in some samples is an indication of application of moderate heat-treatment conditions during processing. The considerable variations of HMF content among fruit-based infant foods may be indicative of differences in the processing conditions.

Since compositions of fruit-based infant foods and jams are quite different, data on the formation of HMF during jam manufacture cannot be extrapolated to fruit-based infant foods. Further studies on the kinetic formation of HMF during elaboration of fruit-based infant foods, are necessary in order to establish limits of its content in commercial products.

Table 3
Content of HMF (mg/100 g) and other parameters in commercial fruit-based infant foods

Samples	pH	DM (%)	HMF (mg/100 g)
1	3.98	28.0	0.55
2	4.01	19.5	0.10
3	3.77	18.4	0.43
4	3.89	16.2	0.45
5	3.71	15.5	0.80
6	4.25	18.8	0.05
7	3.93	25.9	0.12
8[a]	4.03	21.6	0.09
9	3.97	20.7	0.22
10	4.04	15.7	0.39
11	3.90	25.7	0.17
12[a]	4.20	26.3	Not detectable
13[a]	4.01	21.2	Not detectable
14	3.98	26.6	0.03
15[a]	3.84	20.8	0.44
16	4.38	20.2	Not detectable
17[a]	4.05	18.2	0.48
18[a]	4.14	23.1	0.06

[a] Samples manufactured with juice from citric fruits.

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