

Determination of Furan Precursors and Some Thermal Damage Markers in Baby Foods: Ascorbic Acid, Dehydroascorbic Acid, Hydroxymethylfurfural and Furfural

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The presence of ascorbic acid (AA), vitamin C (AA + dehydroascorbic acid (DHAA)) and furfural as potential precursors of furan in commercial fruit and vegetable jarred baby food was studied. Hydroxymethylfurfural (HMF) was also determined and used, together with furfural levels, as markers of thermal damage. AA, calculated DHAA and vitamin C values ranged between 22.4 and 103, 2.9 and 13.8, and 32.1 and 113.2 mg/100 g, respectively, in fruit-based baby food. However, no trace of AA was found in the vegetable-based baby food samples tested, probably because these samples are not enriched in vitamin C and the content of this vitamin in fresh vegetables is destroyed during processing. Furfural values ranged from not detected to 236 $\mu\text{g}/100\text{ g}$, being higher in vegetable samples than in fruit samples possibly because of greater AA degradation favored by a higher pH in the vegetable samples. HMF values (range: not detected–959 $\mu\text{g}/100\text{ g}$), however, were higher in the fruit samples, probably due to greater carbohydrate content degradation and as a consequence of the Maillard reaction, favored by a lower pH in these samples. According to these results, HMF would be the optimum indicator of thermal treatment for fruits, and furfural for vegetables. The higher furfural content of vegetable baby food could be considered an index of greater AA degradation and, therefore, the furan content might be higher in this kind of sample than in fruit-based baby food.

KEYWORDS: Ascorbic acid; dehydroascorbic acid; HMF; furfural; furan; HPLC

INTRODUCTION

Vitamin C is a water-soluble vitamin, which cannot be stored by the body except in insignificant amounts. The body requires it to form and maintain bones, blood vessels, and skin, thus, it must be replenished daily. Most of the vitamin C in human diets comes from fruits and vegetables; moreover, its intake may be considerable, as ascorbic acid is added to some processed foods for its antioxidant properties. This vitamin has two active forms: ascorbic acid (AA) and its oxidized derivative, dehydroascorbic acid (DHAA), but the vitamin activity is essentially the same for both acids (1). It is assumed that vitamin C is the sum of the content of AA and DHAA (2).

Vitamin C oxidation and loss during processing and cooking is a matter of great concern for nutritionists and consumers. This vitamin is used as an index of the health-related quality of fruits, since, compared to other beneficial compounds, it is more sensitive to degradation by processing and storage. Vitamin C is particularly prone to degradation during processing because of its high susceptibility to oxidation in the presence of oxygen and metal ions, and to degradation during heat treatment (3),

generating different compounds, especially furan. Furan is a very volatile compound which can be generated from carbohydrates, amino acids, vitamins, polyunsaturated fatty acids and carotenoids (4), with ascorbic acid and its derivatives being among the major precursors of furan formed by thermal decomposition (5). The latter authors showed that DHAA generates approximately 10 times more furan than does ascorbic acid. During the reaction, different compounds, precursors of furan, such as furfural, are derived from ascorbic acid. Furfural is formed in processed food from ascorbic acid during thermal treatment or storage but also from the degradation of sugars (6) and is a useful indicator for assessing the extent of the Maillard reaction (7). Another compound used as an indicator of the Maillard reaction is hydroxymethylfurfural (HMF), which is formed as an intermediate in this reaction and, also, from the degradation of sugars. In a wide range of foods containing carbohydrates, it is recognized as an indicator of quality deterioration as a result of excessive heating or storage (8, 9).

It is known that during the manufacture of products such as infant foods, severe treatment may be applied and, moreover, these products are usually stored for long periods of time (10). On the one hand, these processes may lead to the Maillard reaction, and, consequently, variable amounts of HMF and furfural can be

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present in these products. On the other hand, ascorbic acid can degrade and generate furfural, and both of these compounds are precursors of furan formation (5).

In recent years, the presence of furan in foods has been the object of special attention by organizations such as the US Food and Drug Administration (FDA) and the European Food Safety Authority (EFSA), because this compound is considered possibly carcinogenic to humans (11, 12). The long-term effects of furan on children's health is unknown, but its presence in baby foods is a matter of concern because of infants' high sensitivity to carcinogens, as well as the larger amounts (relative to body weight) of certain foods (such as fruit juices) that are consumed. Moreover, baby foods often comprise an important part of the diet for most infants. Baby foods are often fortified with vitamin C prior to thermal processing, which would increase furan formation (13). Furthermore, food intended for consumption by babies may have been heated at high temperatures to ensure that the product is microbiologically safe, which again increases furan formation. In consequence, various studies have identified furan in canned and jarred baby foods (14, 15).

Fruits and vegetables are known to be a good source of ascorbic acid, and, consequently, furan and its derivatives may be formed in the thermal treatment of these products. Therefore, the objective of the present study was to determine AA, DHAA, furfural and HMF levels in fruit- and vegetable-based jarred baby foods. With this purpose, HPLC methods were adequately developed. AA, DHAA and furfural were studied as potential precursors of furan in different commercial presentations of these products. HMF and furfural were analyzed as thermal damage markers.

MATERIALS AND METHODS

Chemicals. AA (Sigma-Aldrich, St. Louis, MO), DHAA (Sigma-Aldrich), furfural (Merck, Darmstadt, Germany) and HMF (Sigma-Aldrich) were used to prepare the standard solutions. Analytical reagent-grade metaphosphoric acid (Panreac, Barcelona, Spain), dithiothreitol (DTT) (Sigma-Aldrich) and K_2HPO_4 (Panreac) were used to determine AA and vitamin C levels. 95–98% sulfuric acid (Panreac) was employed to adjust the pH of the mobile phase. For furfural and HMF determination, 15% potassium ferrocyanide (w/v) (Merck) (Carrez I) and 30% zinc acetate (w/v) (Merck) (Carrez II) were prepared as the clarified solution; trichloromethane (Panreac) was used for purification and acetonitrile (J. T. Baker) for the mobile phase. All solutions were prepared with demineralized water obtained by filtering distilled water through a Milli-Q Ultrapure Water System (Millipore, Bedford, MA).

Samples. A total of 17 different fruit-based and 9 vegetable-based jarred baby foods were purchased in a local supermarket and used for the analysis. The ingredients of the different baby foods are shown in **Tables 1** and **2** (data provided by the manufacturer). Throughout the sample preparation process, amber glass material was used, to avoid direct light falling on the food.

Ascorbic Acid. AA extraction was based on a procedure proposed by Giménez et al. (16) with some modifications. Portions of 0.5 g of homogenized sample were mixed with 2.5 mL of a 10% (w/v) metaphosphoric acid solution, and then diluted to a final volume of 25 mL in a glass volumetric flask with demineralized water. The mixture was homogenized and centrifuged at 9000 rpm for 15 min (room temperature) (Centrifuge Universal 32, Hettich, Tuttlingen, Germany). The supernatant was filtered through 0.20 μ m Millex filters (Millipore, Bedford, MA), and the samples were then ready to be injected into the HPLC system.

Vitamin C. In order to assess the total content of vitamin C (DHAA + AA) present in the samples, the prior reduction of DHAA to AA must be occluded. A solution of dithiothreitol (DTT) (1 mg/mL diluted in 45% K_2HPO_4) was prepared as reductant agent, and an aliquot of 0.2 mL was added to 1 mL of the filtered sample, obtained in AA analysis, following the method proposed by Odriozola-Serrano et al. (17) with some modifications. The mixtures were kept in darkness for 30 min at room temperature, and then the reduction was stopped by the addition of 0.2 mL of H_3PO_4 2 M and the samples were injected into the HPLC system.

Table 1. Ingredients of Fruit-Based Jarred Baby Foods^a

samples	composition
F 1	apple and pear with milk
F 2	pineapple and banana with milk
F 3	apple, peach and banana with milk
F 4	apple and peach
F 5	apple, pineapple, banana and cereals
F 6	pineapple, apple, pear and cereals
F 7	apple compote
F 8	apple, banana, mango, orange, grape and cereals
F 9	orange and banana with cereals
F 10	fresh cheese with fruits (apple, peach, banana, tangerine)
F 11	fresh cheese with pear
F 12	fresh cheese with banana and apple
F 13	apple, banana and pineapple
F 14	peach, apple, banana, apricot, orange and grape
F 15	banana, tangerine, pear
F 16	pineapple, pear, peach
F 17	peach, banana

^a All of the samples were enriched with vitamin C.

Table 2. Ingredients of Vegetable-Based Jarred Baby Foods

samples	composition
V 1	vegetable purée with pasta (beans, peas, carrots, onion, pasta, rice)
V 2	chickpeas (milk, beans, peas, carrots, onion, pasta, rice, cream, olive oil)
V 3	lentils (lentils, potatoes, veal, carrots, tomatoes, onion, olive oil)
V 4	vegetables (potatoes, beans, tomatoes, carrot, peas, celery, onion)
V 5	beans with potatoes (beans, milk, potatoes, onion, olive oil)
V 6	zucchini cream (zucchini, milk, potatoes, rice flour, onion, milk cream, peas, olive oil)
V 7	7 vegetables (beans, peas, potatoes, carrots, zucchini, onion, spinach)
V 8	spinach cream (spinach, milk, potatoes, rice flour, onion, milk cream, olive oil)
V 9	vegetables with rice (milk, carrots, rice, peas, zucchini, onion)

DHAA content was calculated by the difference between the vitamin C (after DHAA reduction) and initial AA (prior to reduction) (2). Both determinations (AA and vitamin C) were performed in triplicate.

Furfural and HMF. Extraction, purification and concentration were carried out as described by Rufian-Henares et al. (18). One gram of sample was mixed with 150 μ L each of Carrez I and II solutions and 3 mL of demineralized water. The resulting mixture was centrifuged at 9000 rpm for 10 min (room temperature) (Centrifuge, Universal 32, Hettich). The same procedure was followed twice again, adding 3 mL of demineralized water to the pellet and shaking vigorously for 2 min. The supernatants were combined, and the solution was brought to 10 mL. Both HMF and furfural were studied in this extraction procedure. Purification was necessary for HMF determination, because several compounds present in the sample may interfere with the quantification process; however, no differences were found between the results obtained after purification of furfural compared with those without purification, and so this compound was determined directly after the extraction procedure. It should be noted that **Figure 2** presents chromatograms **b** and **c** on different scales, thus, the furfural peak is observed in a different way.

- HMF: 10 mL of the aqueous extract described above was added to 10 mL of trichloromethane and shaken vigorously for 2 min. The organic fraction was separated, and the same procedure was followed 9 more times. Three milliliters of demineralized water was added to 100 mL of trichloromethane extract and evaporated under vacuum. The water fraction was filtered through a 0.2 μ m disk filter before injection.
- Furfural: The aqueous extract was filtered, without purification, through a 0.2 μ m disk filter before injection. Both determinations (HMF and furfural) were performed in triplicate.

pH and Moisture. The pH of samples was determined with a pH meter (Basic 20, Crison, Barcelona, Spain). Moisture was determined by gravimetric method.

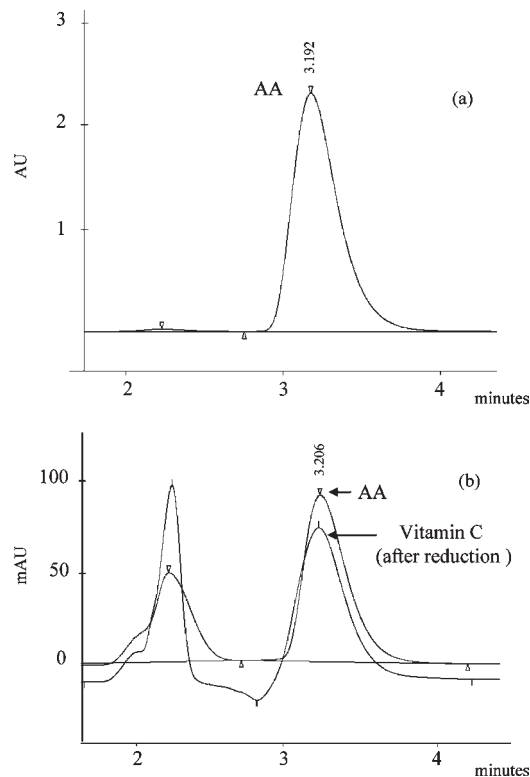


Figure 1. HPLC chromatogram (a) of a standard of ascorbic acid (AA) and (b) of a commercial sample of jarred baby food. Vitamin C in the sample is obtained after reduction with DTT.

HPLC Conditions. The HPLC system used in this study was equipped with a Varian Prostar model 230 pump, a Varian Prostar autosampler injector model 410 and a Varian Prostar model 325 ultraviolet detector. Samples were introduced into the column through an automatic injector equipped with a sample loop (20 μ L). The different mobile phases were filtered through 47 mm Nylon 0.45 μ m paper filters (Waters), before their introduction into the chromatographic system. Separations were performed on a Nova-pak 4 μ m C18 (250 \times 4.6 mm) Waters column for all the compounds.

AA and vitamin C were analyzed using the HPLC method described by Giménez et al. (16). The measurement was performed under isocratic conditions, using demineralized water acidified with sulfuric acid to pH 2.2 as the mobile phase at a flow rate of 0.6 mL/min, with a wavelength of 245 nm. **Figure 1** shows a chromatogram in the optimized conditions. It should be noted that the difference between peaks originated from the dilution of the samples, since vitamin C is measured in a more diluted sample and, thus, the area for vitamin C is lower than that for AA.

Furfural and HMF determination was carried out as described by Guerra Hernández et al. (7) with some modifications. The mobile phase was acetonitrile:water (5:95), flow rate 1 mL/min and a wavelength of 280 nm. **Figure 2** shows a typical chromatogram.

Statistical Analysis. Evaluation of the relationships between the different parameters analyzed and pH or carbohydrate composition was carried out by computing the relevant correlation coefficient (Pearson linear correlation) at the $p < 0.05$ confidence level. SPSS for Windows, version 13.0 (SPSS Inc., 1999–2004, Chicago, IL), was used to support the statistical analyses.

RESULTS AND DISCUSSION

Validation of the Methods. The chromatograph was calibrated by means of three curves, established by measuring ascorbic acid, furfural and HMF peak areas over a 5-fold concentration range. The linear regression equations used for AA, HMF and furfural determination were $Y = (4 \times 10^6)X + 10^6$ ($r^2 = 0.9998$); $Y = (6 \times 10^6)X + 131143$ ($r^2 = 0.9999$); and $Y = (7 \times 10^6)X + 166428$ ($r^2 = 0.9999$), respectively. In the equations, Y is the peak area

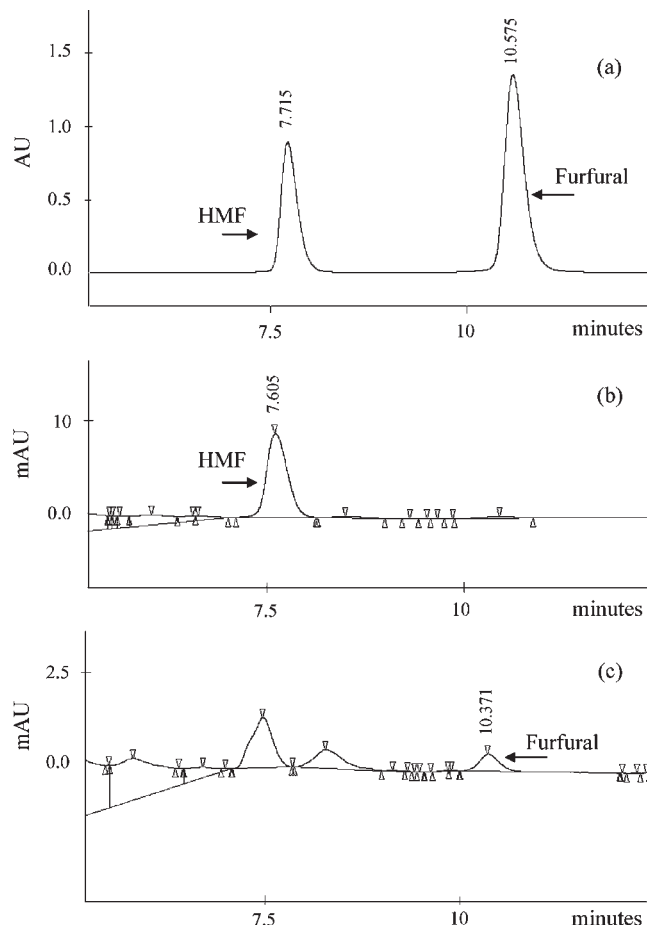


Figure 2. HPLC chromatogram (a) of a standard of HMF and furfural and of a commercial sample of jarred baby food with (b) (V-3) and without (c) purification (V-1).

Table 3. Analytical Parameters of AA, Vitamin C, HMF and Furfural Determination

analytical parameter	AA	vitamin C	HMF	furfural
detection limit	2.5 mg/100 g		0.8 μ g/100 g	0.35 μ g/100 g
quantification limit	8.5 mg/100 g		2.7 μ g/100 g	1.16 μ g/100 g
repeatability ^a	38.5 \pm 0.81	41.3 \pm 1.37	73.8 \pm 3.10	14.9 \pm 0.56
reproducibility ^a	39.4 \pm 1.61	54.7 \pm 2.47	138 \pm 5.38	106 \pm 3.61
recovery ^a (%)	99.4 \pm 3.04	76.4 \pm 5.68	80.2 \pm 2.87	90.0 \pm 5.61

^a Values are expressed as mean \pm standard deviation ($n = 6$).

and X is AA, HMF or furfural concentration. The AA concentration range was 4–100 mg/L, corresponding to 20–500 mg/100 g in the sample. For HMF determination, the concentration range was 0.008–1 mg/L, corresponding to 8–1000 μ g/100 g in the sample, and for furfural the range was 0.014–0.30 mg/L, corresponding to 14–300 μ g/100 g in the sample.

Detection limits (three times the signal-to-noise ratio), quantification limits (ten times the signal-to-noise ratio), precision and recovery percentages from the compounds are shown in **Table 3**. Recovery was tested by the addition of known quantities of a standard of AA, DHA, furfural and HMF, respectively, to a sample of fruit or vegetable-based jarred baby food.

The precision of the instrumental technique was evaluated by analyzing different samples of baby foods (F 13 for AA analysis; F 7 and F 11 for furfural; F 3 and F 5 for HMF), on the same day (repeatability) and on different days (reproducibility).

Ascorbic Acid and Vitamin C. To determine AA, different sample weights were assayed (0.5, 1, and 2.5 g) and diluted to a

Table 4. AA, DHAA and Vitamin C Content of Analyzed Fruit-Based Jarred Baby Food^a

samples	content (mg/100 g)		
	AA	DHAA	vitamin C
F 1	73.4 ± 0.15	9.7 ± 2.11	83.1 ± 2.15
F 2	66.4 ± 0.08	10.5 ± 1.22	76.9 ± 1.22
F 3	84.3 ± 0.87	13.8 ± 2.51	98.4 ± 1.71
F 4	90.2 ± 0.56	6.8 ± 0.21	97.1 ± 0.51
F 5	103 ± 0.10	10.1 ± 0.49	113.2 ± 0.42
F 6	22.4 ± 1.86	9.6 ± 5.34	32.1 ± 3.72
F 7	65.0 ± 0.21	7.1 ± 0.92	72.7 ± 1.36
F 8	60.1 ± 0.42	6.1 ± 0.27	66.2 ± 0.64
F 9	55.2 ± 0.35	8.6 ± 0.76	63.8 ± 1.04
F 10	56.5 ± 1.50	8.5 ± 1.27	64.2 ± 0.12
F 11	47.4 ± 2.18	6.3 ± 2.08	53.7 ± 1.06
F 12	54.1 ± 0.09	5.9 ± 1.79	60.0 ± 1.78
F 13	37.3 ± 0.56	8.6 ± 0.22	45.9 ± 0.39
F 14	57.0 ± 0.02	7.5 ± 0.55	64.5 ± 0.54
F 15	54.7 ± 0.56	8.3 ± 0.27	63.0 ± 0.65
F 16	49.9 ± 0.06	10.8 ± 0.67	60.7 ± 0.70
F 17	43.5 ± 0.51	2.9 ± 1.17	46.4 ± 0.74

^a Values are expressed as mean ± standard deviation ($n = 3$). Results are expressed as fresh matter.

final volume of 25 or 50 mL. Similar results were obtained with the different tests, and so a ratio of 0.5 g/25 mL was chosen. All determinations were performed immediately after opening the packing, since previous results showed that, in only two days, considerable losses of the nutrient can occur, whether the sample remains capped and refrigerated (8%) or uncovered and at room temperature (17%) (unpublished data). Similar results have been obtained regarding the ascorbic acid content of commercial fruit juices (19).

Homocysteine and DTT were assayed in this study in order to convert DHAA into its reduced form and stabilize AA, following the method described by Brause et al. (20) and Sánchez-Mata et al. (2), but as no results were obtained with the first of these compounds, DTT was selected as the reductant agent.

The reduction of DHAA to AA depends on the pH, temperature and reaction time. We carried out this reduction under both acidic and basic conditions and found that the best reduction (80% higher) was observed at basic pH. Takayanagi et al. (21), however, reported that the maximum reaction is obtained at pH conditions of around 7. Under the chromatographic conditions used in the present study, the injection of neutral samples into the acidic mobile phase caused a deformation of the peaks, similar to that observed by Sánchez-Mata et al. (2), and for this reason, it was necessary to add sulfuric acid prior to injection, as found also by Vázquez and Vazquez-Blanco (22). Sánchez-Mata et al. (2) reported that a pH equal to or lower than 5 is necessary in the mobile phase to maintain the stability of vitamin C during the analysis. Again, however, a deformation of the peaks similar to the previous one was observed when the pH of the mobile phase was 3 or higher; this deformation was not observed at a pH of 2.2, and so this condition was selected, in accordance with Vázquez and Vazquez-Blanco (22) and Giménez et al. (16).

Different DTT concentrations were also tested, and a final concentration of 1 mg/mL was selected because this produced the highest percentage of recovery (55% higher recovery than that observed with 0.2% DTT concentration), as shown too by Gökmen et al. (1). Another parameter studied was the reaction time, which can vary from 10 (23) to 120 min (17). We assayed 10, 20, 30, 60, 90, and 120 min of reaction time. The recovery with 10 and 20 min was 90% of that obtained with 30, 60, 90 or 120, which

Table 5. Furfural and HMF Content and pH of Analyzed Fruit and Vegetable-Based Jarred Baby Food^a

samples	content ($\mu\text{g}/100\text{ g}$)		pH
	furfural	HMF	
F 1	61.4 ± 4.16	403 ± 2.65	3.44
F 2	182 ± 25.14	97.6 ± 5.83	3.72
F 3	68.1 ± 0.24	80.7 ± 3.80	3.72
F 4	23.9 ± 1.10	959 ± 29.17	3.83
F 5	27.7 ± 1.10	144 ± 19.45	3.74
F 6	89.9 ± 9.04	87.3 ± 8.49	3.64
F 7	104 ± 4.73	822 ± 2.65	3.88
F 8	157 ± 14.30	764 ± 16.97	3.84
F 9	60.2 ± 7.23	308 ± 1.77	3.84
F 10	nd ^b	21.9 ± 0.18	4.18
F 11	16.4 ± 0.16	16.1 ± 0.27	4.12
F 12	nd	14.1 ± 0.18	4.34
F 13	25.9 ± 5.19	45.0 ± 3.54	4.02
F 14	70.6 ± 0.71	326 ± 10.61	4.03
F 15	39.0 ± 1.41	329 ± 0.88	3.98
F 16	119 ± 2.28	544 ± 26.52	3.95
F 17	32.5 ± 2.91	261 ± 5.30	3.96
V 1	172 ± 8.64	24.1 ± 0.09	5.80
V 2	152 ± 7.07	92.5 ± 1.77	5.81
V 3	236 ± 35.36	288 ± 17.68	5.59
V 4	123 ± 18.86	136 ± 0.88	5.05
V 5	57.8 ± 7.86	15.0 ± 1.77	5.73
V 6	116 ± 2.36	19.9 ± 3.36	5.94
V 7	287 ± 3.93	14.9 ± 1.97	5.71
V 8	126 ± 4.71	nd	6.04
V 9	151 ± 3.93	nd	5.92

^a Values are expressed as mean ± standard deviation ($n = 3$). Results are expressed as fresh matter. ^b Not detectable.

were similar, and so 30 min was considered suitable for the reaction.

Table 4 shows the AA, DHAA and vitamin C content in fruit-based baby food as fresh matter. The AA values ranged from 22.4 to 103 mg/100 g; DHAA values from 2.9 to 13.8 mg/100 g and vitamin C values from 32.1 to 113.2 mg/100 g. This latter range was greater than that observed by Cizková et al. (24) in an analysis of 10 samples of commercial fruit-based baby foods (18.6–55.0 mg/100 g).

It is known that losses of vitamin C occur during processing and storage and, moreover, that these losses may be used as an indicator of the aggression to nutritional value suffered in the industrial or culinary process (25). AA losses have been described in foods such as fruits and vegetables; for example, Uckiah et al. (26) reported vitamin C losses of 46.8% during the processing of pineapple jam and additional losses of 44.7% during storage for 60 days at room temperature, therefore, in a further 80 days, all vitamin C content will have been lost. Due to such losses, it might be thought that AA is detected in higher content in processed foods which have been enriched in vitamin C. These observations coincide with the findings of Cizková et al. (24), who indicated that the AA content in commercial baby foods was, for the most part, artificially added and declared as an antioxidant. We did not find any trace of AA in the vegetable-based baby food samples tested, probably because these samples are not enriched in vitamin C and the content of this vitamin in fresh vegetables is destroyed during processing. In this respect, McErlain et al. (27) reported that the cooking methods and the time and temperatures employed during thermal food processing may have a detrimental effect on the ascorbic acid content of vegetables. Moreover, ascorbic acid degradation could be favored by the higher pH of these samples (**Table 5**) since it is known that the rate of ascorbic acid oxidation increases as pH increases from 3 to 6 (28).

In fruit-based baby foods, no correlation was observed between DHAA and pH ($p = 0.0765$), probably because the low variation in pH of these products is not significant as regards accelerating AA oxidation.

Furfural and HMF. Furfural content in the samples ranged between not detected and $236 \mu\text{g}/100 \text{ g}$ (Table 5), with the mean value being $71.8 \mu\text{g}/100 \text{ g}$ in fruit-based jarred baby food and $158 \mu\text{g}/100 \text{ g}$ in vegetables. The higher values found in vegetables compared to those in fruits is probably the result of greater natural ascorbic acid decomposition during vegetable chopping, since the pH of these samples is optimum for increasing ascorbate oxidase activity, as has been observed in green beans by Sánchez-Mata et al. (2). Moreover, the later warming favors the decomposition of the ascorbic acid. Little has been reported about furfural content in jarred baby food; Cizkova et al. (24) recently observed a mean furfural content of $253 \mu\text{g}/100 \text{ g}$ in fruit-based baby food (range $210\text{--}330 \mu\text{g}/100 \text{ g}$), these values being higher than those found in our study.

Neither samples met the maximum HMF concentration allowed in fruit juices and purees ($2000 \mu\text{g}/100 \text{ g}$) according to the AIJN Code of Practice (29). The content ranged between not detected and $959 \mu\text{g}/100 \text{ g}$, with a mean value of $307.2 \mu\text{g}/100 \text{ g}$. These results were lower than those observed by Cizkova et al. (24) in fruit-based baby food ($1454 \mu\text{g}/100 \text{ g}$) and similar to the range obtained by Rada-Mendoza (10) ($30\text{--}800 \mu\text{g}/100 \text{ g}$) in fruit-based infant foods. HMF content in fruits was much higher than that observed in vegetables, probably due to the higher content of carbohydrates in the former (14.7%) compared to the latter (2.7%) (data provided by the manufacturer) and to the higher rate of sugar degradation in these samples, which is favored by the lower pH of the fruits (Table 5). In accordance with the above, a negative correlation was observed between pH and HMF ($r = -0.7144$, $p < 0.001$), while a positive one was found between carbohydrates and HMF ($r = 0.6855$, $p < 0.001$). The mean moisture content in both types of samples was similar (79.87% in fruits and 82.91% in vegetables) (data not shown).

According to these results, the ideal indicator of thermal treatment for fruits would be HMF, and furfural for vegetables, in the first case due to the degradation of carbohydrates and in the second one due to the decomposition of the ascorbic acid.

Relation with Furan Formation. Furan levels of over $100 \mu\text{g}/\text{kg}$ have been found in three major food groups: coffee, baby food, and sauces and soups. Furan has been detected in 262 of the 273 baby food samples reported by FDA (12) and EFSA (11) with an average level of $28 \mu\text{g}/\text{kg}$, and in 70 of 71 infant foods at similar levels. Different concentrations in foods have been detected and quantified depending both on the matrix and on the cooking technique. Bianchi et al. (30) analyzed different baby foods, reporting that all the processed baby foods examined showed higher furan levels than did the homemade products. This was concluded to be due to the fact that commercial processed foods are submitted to heat treatments in closed pots, whereas homemade baby food is cooked in open containers, and in these conditions furan is more easily released because of its high volatility.

On the other hand, several authors have shown that furan results in AA and DHAA depend on pH conditions (31, 32). Moreover, furfural formation depends on AA degradation. Therefore, we believe the higher furfural content of vegetable-based baby food is an index of greater AA degradation and, therefore, the furan content could be higher in this kind of food and lower in fruit-based samples, in accordance with the findings of Jestoi et al. (15), who observed higher furan content in vegetable-based baby food than in fruit-based samples.

Due to the well-known toxicity of furan, it would be interesting to know whether, from the levels of its precursors, it is possible to predict the content of furan in baby food. Thus, future studies will be aimed at verifying the relation between AA, DHAA, and furfural with furan content and between furan with furfural and HMF as indicators of thermal treatment.

In summary, vitamin C was present in fruit-based baby food, but not in vegetable foods, because the content of this vitamin in fresh products is destroyed during the treatment of the foods, and only the fruit samples were enriched in vitamin C. Moreover, ascorbic acid is less prone to degradation at the lower pH of the fruit samples. In fruit-based baby food, the ideal indicator of thermal treatment would be HMF, due to the degradation of its higher carbohydrate content and to the fact that sugar degradation is favored by the lower pH of these samples. However, in vegetable-based baby food, the ideal indicator would be furfural due to the greater ascorbic acid decomposition favored by the higher pH. Since ascorbic acid and furfural are considered to be potential precursors of furan formation, furan content could be higher in vegetable-based and lower in fruit-based baby food.

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