NOTE ON BEHAVIOR OF 1-AMINO-1-DEOXY-2-KETOSE DERIVATIVES DURING COOKING WHEN ADDED TO STARCH-BASED FOODSTUFFS

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Cereal Chem. 55(6): 1056-1059

As part of investigations into the possibility of using Maillard reaction products in foodstuffs (1-3), we wanted to determine their heat stability because no experimental data were available on their behavior during cooking either alone or when added to foodstuffs. This article reports the results of tests conducted on samples of bread, biscuits, cakes, and polenta prepared in the laboratory, with addition of some 1-amino-1-deoxyketoses obtained from the reaction of essential amino acids with hexoses (glucose and galactose) and pentoses (ribose and arabinose). These products were baked in traditional, microwave, and infrared ovens.

MATERIALS AND METHODS

Preparation of Breads

To 50 g of wheat flour were added 25 ml of water and 1.25 g of undried yeast. The dough was allowed to rise for 1 hr at 35° C. Breads were baked in a muffle oven at 220° C for 30 min, in an infrared oven (Heraeus, model H420) at 220° C for 40 min, or in a microwave oven (Raytheon, model 500N) for 3 min.

Preparation of Biscuits

To 50 g of wheat flour were added 20 ml of water, 5 g of sucrose, 2 g of shortening, and 1 g of yeast. Biscuits were baked in a muffle oven at 240° C for 20 min, in an infrared oven (Heraeus, model H420) at 240° C for 30 min, or in a microwave oven (Raytheon, model 500N) for 1 min.

Preparation of Polenta

To 25 g of cornmeal were added 350 ml of water and 0.5 g of sodium chloride. The polenta was cooked over a direct fire for 45 min and stirred continually.

Each product was prepared in the following ways: 1) without additive, 2) with 2% of derivative (dry matter), 3) with the corresponding percentage of the sugar of origin, 4) with the corresponding percentage of the amino acid of origin, and 5) with the corresponding percentage of the sugar and amino acid of origin (to a total of 2%).

The following determinations were done on samples of the products.

Free Amino Acids and Amino Ketose Compounds

A water extract was prepared for determination of soluble nitrogen; 100-µl aliquots were subjected to circular paper chromatography (4).

Sugars

The water extract, $200 \mu l$, was subjected to circular paper chromatography (5).

Thermogravimetric Analysis

The thermal behavior of the derivatives was determined by thermogravimetry in an Adamel TH 59 thermoanalyzer (6,7).

RESULTS AND DISCUSSION

Free amino acids were stable under the different cooking methods employed; 95–96% of the amounts added were recovered. On the contrary, the added sugars were recovered in only small amounts (data not reported here), but it is well known that caramelization takes place during heating.

Addition of an amino acid and sugar together gives results that depend on the products and the manner of cooking. In bread baked in the traditional oven and in the infrared oven, concurrent addition led to the formation of small amounts of 1-amino-1-deoxy-2-ketose derivatives in only a few cases. In bread baked in the microwave oven, large amounts of 1-amino-1-deoxyketoses were obtained with a corresponding decrease of the original amino acid (70-75%) (Table I).

In the wheat flour biscuits, small amounts of 1-amino-1-deoxyketoses were formed on baking in the traditional oven, while in the biscuits baked in the microwave oven, large amounts were formed (Table II).

In the polenta of cornmeal, no derivative was formed; the original amino acid was recovered unchanged (results not reported for brevity).

Direct addition of 1-amino-1-deoxyketoses to the unbaked products revealed a high stability in the breads baked in the traditional and infrared ovens (more than 80% recovered on the average); however, a high degree of degradation with

TABLE I
Behavior of Amino Acids, Sugars, and Corresponding
Amino-Ketose Compounds When Added to Bread

Added Substances	Amounts Added (g% dry matter)	Determined Substances (g% Dry Matter)						
		Traditional Oven		Microwave Oven		Infrared Oven		
		Amino Acid	Derivative	Amino Acid	Derivative	Amino Acid	Derivative	
Leucine	1.03	1.00		0.89		0.98		
Leucine + glucose	1.03 + 1.25	0.97	0.10	0.19	0.82	0.96	0.20	
Leucine – fructose	2.28	Trace	1.97	0.68	0.06	0.09	1.96	
Valine	0.96	0.90	•••	0.93		0.92		
Valine + glucose	0.96 + 1.32	0.90		0.31	1.28	0.90		
Valine – fructose	2.28	0.19	1.79	0.90	0.09	0.21	1.71	
Valine	0.93	0.92	•••					
Valine + arabinose	0.93 + 1.35	0.92						
Valine – ribulose	2.28	•••	2.29					
Lysine	0.68	0.70						
Lysine + glucose	0.68 + 1.60	0.66	•••					
Lysine – fructose	2.28	0.12	1.68					

concomitant regeneration of the original amino acid in corresponding amounts was observed after heating in the microwave oven. Also, large amounts of the original amino acid in biscuits were regenerated from the 1-amino-1-

TABLE II
Behavior of Amino Acids, Sugars, and Corresponding Amino-Ketose
Compounds When Added to Wheatmeal Biscuits

Added Substances	Amounts Added (g% dry matter)	Determined Substances (g% Dry Matter)						
		Traditional Oven		Microwave Oven		Infrared Oven		
		Amino Acid	Derivative	Amino Acid	Derivative	Amino Acid	Derivative	
Leucine	1.03	0.84		0.88	+	0.86		
Leucine + glucose	1.03 + 1.25	0.77	0.04	0.49	0.89	0.79	0.05	
Leucine – fructose	2.28	0.72	0.19	0.83	0.16	0.68	0.20	
Valine	0.96	0.88		0.93		0.91		
Valine + glucose	0.96 + 1.32	0.82	0.082	0.39	1.08	0.85	0.09	
Valine – fructose	2.28	0.77	0.45	0.85	0.27	0.66	0.47	
Leucine	1.01	0.77						
Leucine + arabinose	1.01 + 1.27	0.67	Trace					
Leucine - ribulose	2.28	0.62	0.34					
Lysine	0.68	0.60						
Lysine + glucose	0.68 + 1.60	0.58						
Lysine – fructose	2.28	0.36	0.72					

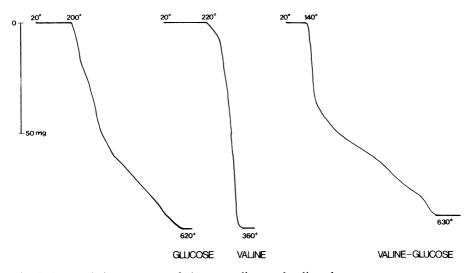


Fig. 1. Thermobalance curves of glucose, valine, and valine-glucose.

deoxyketose in high percentages in the traditional and infrared ovens (70–80%) and in higher percentages in the microwave oven (90%) (Table II). In the polenta of cornmeal, the 1-amino-1-deoxyketoses were stable.

From these results, we can conclude that formation of the 1-amino-1-deoxyketose derivatives when the amino acid and the sugar were added together was determined by the temperature and the type of cooking. The polenta was cooked at 100° C, and no compound was formed. The bread was baked at 220° C, and only traces were formed. The biscuits were baked at 240° C, and large amounts were formed.

Large amounts of 1-amino-1-deoxyketoses were also formed from sugars and amino acids when the bread or biscuits were baked in a microwave oven, but the temperature under these conditions was unknown. Why this is so is indicated from experiments in which 1-amino-1-deoxyketoses were added before heating. The compounds were unstable at 240°C and in the microwave oven, but they were stable in polenta boiled at 100°C. Breakdown reforms the amino acid.

The thermal stability of the 1-amino-1-deoxyketoses was much higher in foodstuffs such as those prepared with cereal flours than in those prepared in a thermobalance where they are heated directly and are stable only to 120–130° C (Fig. 1). Also, the extent of transformation from amino acid plus sugar to 1-amino-1-deoxyketose and from 1-amino-1-deoxyketose to amino acid were high (about 80–90%)—much higher than the yields obtained when the amino acid and sugar were reacted in methanolic solution (15–20%) (2).

Literature Cited

- CIUSA, W., MAZZARACCHIO, P., and BARBIROLI, G. Considerazioni sulle reazioni fra amminoacidi e zuccheri. Rass. Chim. 3: 136 (1974).
- CIUSA, W., BARBIROLI, G., and MAZZARACCHIO, P. Ricerche sistematiche sulla reattivita di 20 amminoacidi con mono e disaccaridi e sui rendimenti di N-ammino-deossi-cheto derivati. Rass. Chim. 2: 94 (1975).
- 3. CIUSA, W., BARBIROLI, G., an MAZZARACCHIO, P. Reazioni fra amminoacidi e zuccheri:
 Ricerche sulla formazione dei prodotti primari. Rass. Chim. 4: 176 (1975).
- 4. BARBIROLI, G. Papierchromatographische Trennung und Bestimmung von 22 Aminosauren. Mikrochim. Acta 4: 653 (1965).
- 5. BARBIROLI, G. Separazione e dosaggio di miscele di zuccheri mediante cromatografia circolare su carta. Rass. Chim. 2: 62 (1964).
- 6. BARBIROLI, G. Die Identifizierung von Plastomerem, der Zellulose und ihrer Derivative mittels thermogravimetrischer Messungen. Mikrochim. Acta 1: 41 (1967).
- 7. BARBIROLI, G. Kohlenanalyse mit der Thermowaage. Mikrochim. Acta 1: 26 (1968).

[Received November 30, 1977. Accepted May 16, 1978]