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Chemical changes during microwave treatment of milk

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Raw milk was heated in a microwave oven at 2450 MHz in order to study the effect on the main chemical changes taking place during heating processes: lactose isomerization, Maillard reaction and protein denaturation. Lactulose, epilactose, furosine and undenaturated whey proteins were measured as indicators of the heat damage in milk. Comparison with control samples treated by conventional heating showed a rate enhancement of the studied reactions during microwave treatment. These differences are supposed to be due, at least to some extent, to uneven heating of the milk in the microwave oven. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Since the first reported study on the use of a microwave system for pasteurization of milk (Hamid *et al.*, 1969), several works on microwave milk treatment, mainly conducted on microbiological aspects, have been reported (Jaynes, 1975; Merin & Rosenthal, 1984; Knutson *et al.*, 1988; Thompson & Thompson, 1990). Although the enhancement of chemical reactions by microwave irradiation is known, few studies have been performed on chemical changes produced during microwave heating of milk. Lubec *et al.* (1989) stated that microwave-treated milk might be a public health hazard because of its increased D-amino acids levels. Subsequent research showed no significant differences between isomerization in conventionally- and microwave-heated milk (Dehne *et al.*, 1992; Marchelli *et al.*, 1992).

As microwave heating of milk is becoming increasingly common, detailed studies on chemical changes have to be performed to ascertain nutritional value and safety of microwave heat-treated milk. Lactulose, furosine and undenatured β-lactoglobulin are useful indicators of the heat-treatment intensity undergone by milk (Erbersdobler *et al.*, 1987; Olano & Calvo, 1989; Resmini *et al.*, 1989*b*), so their determination in microwave-treated milk could afford information on the behaviour of lactose and whey proteins during microwave treatment.

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The purpose of this work was to study the effect of heat-treatment intensity on lactose isomerization, whey protein denaturation and Maillard reaction using microwave heating and to compare these results with those obtained using conventional heating.

MATERIALS AND METHODS

Milk samples

Raw milk from healthy cows was obtained from a local farm. Skim milk was obtained by centrifugation at 3800*g* for 15 min.

Thermal treatments

Microwave irradiation was carried out in quadruplicate at 2450 MHz in an oven MDS-2000 (CEM Corporation, Buckingham, UK), 600 W full power. A microwave transparent fibre-optic temperature probe was inserted into the thermowell of the sample vessel and connected to a temperature control mounted on the system CPU board. The temperature sensor consists of a phosphor which emits fluorescent light after excitation transmitted down the fibre-optic. The decay rate of fluorescence emission is temperature-dependent, allowing an accurate and precise determination of temperature. Samples of 25 ml were placed in closed Teflon vessels with inside dimensions of 3.6×10.5 cm. The times to attain the desired temperature were in all cases less than 50 s.

Temperature was continuously monitored during the experiment using a Citizen Swift 9 printer. The oscillation was ±2.5°C every 15 s.

Comparative experiments using conventional heating were performed in duplicate using a silicone oil bath with stirring and thermostatic control (±1°C). Samples were heated in closed stainless steel tubes (3 m×2.16 mm ID) which allowed the desired temperature to be attained in very short times, as shown by Pagliarini *et al.* (1990). Thus, the heating-up times were considered negligible in treatments lasting 10 min or more.

Both microwave and conventional treatments were performed under the desired conditions on portions of the same raw milk sample. After treatment, samples were immediately cooled for 10 min in an ice–water bath.

Analytical determinations

Lactulose and epilactose were determined as their trimethylsilyl ethers by gas chromatography, with phenyl-β-D-glucoside as internal standard (Olano *et al.*, 1986).

Furosine was determined by ion-pair reverse-phase high-pressure liquid chromatography (HPLC) (Delgado *et al.*, 1992). Calibrations curves were constructed using an authentic sample of furosine obtained by acid hydrolysis of ε-*N*-(1-deoxy-D-fructosyl)-L-lysine according to the procedure of Finot *et al.* (1968).

Undenatured whey proteins were analysed by reverse-phase HPLC (Resmini *et al.*, 1989*a*). Calibrations were made using an external standard method. Standard curves of α-lactalbumin, bovine serum albumin (BSA) and β-lactoglobulin were linear at the same concentration range and chromatographic conditions at which the milk samples were run.

RESULTS AND DISCUSSION

The most striking feature of microwave treatment was the difficulty in reproducing their effect on milk composition. Although the irradiation power was modulated according to the temperature reached inside the sample, and the containers were continuously rotated during treatment, the corresponding analytical determinations showed variation coefficients markedly higher than those obtained with conventionally heated samples (Table 1).

Denaturation of whey proteins

Denaturation of whey proteins was observed when milk was heated at 70°C for 10, 20 and 30 min, being higher after microwave treatment than after conventional heating of samples. Figure 1 shows the α-lactalbumin, β-lactoglobulin and BSA contents. Both microwave and conventional heating of milk at higher temperatures (100, 110 and 120°C for 10, 20 and 30 min) resulted in almost complete denaturation of whey proteins.

Table 1. Average variation coefficients (%) obtained for lactulose, furosine and undenatured whey protein determinations, carried out on several series of milk samples submitted to conventional ($n = 18$) and microwave heat treatments ($n = 36$)

Treatment	Lactulose	Furosine	Whey proteins
Conventional	8.7	3.0	2.7
Microwave	22.3	10.0	28.6

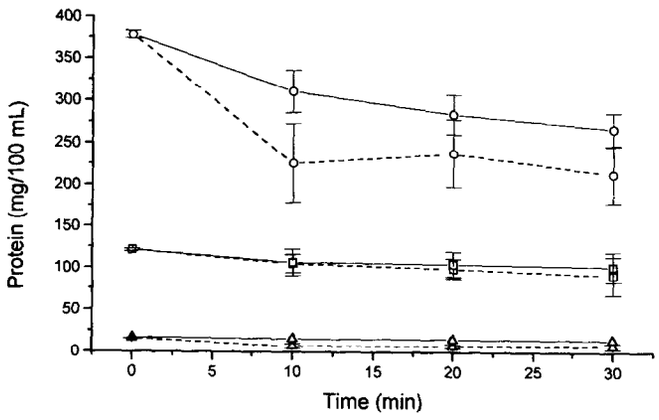

Fig. 1. Variation of α-lactalbumin (□), BSA (Δ) and β-lactoglobulins (B + A) (○) content during microwave (– – – –) and conventional (———) heating of skim milk samples at 70°C.

Formation of lactulose

Heat treatment at 70°C for 30 min gave rise to the formation of lactulose in amounts lower than 5 mg/100 ml for both microwave and conventional heating. For treatments at 100–120°C, lactulose levels found in microwave treated samples were higher than those in conventionally heated samples (Fig. 2). Epilactose was formed in all samples, and it was higher during microwave treatments (Fig. 3). The lactulose/epilactose ratio was very similar for both types of treatments.

Furosine

The formation of furosine during treatments at 100–120°C increased with temperature and time, the levels found in the microwave-treated samples being higher

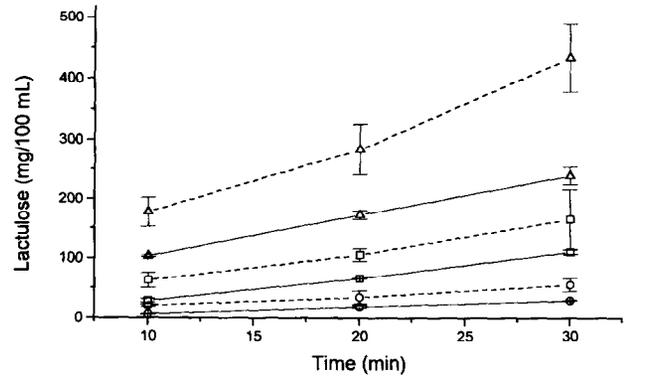

Fig. 2. Formation of lactulose during microwave (– – – –) and conventional (———) treatments of milk samples at 100°C (○), 110°C (□) and 120°C (Δ).

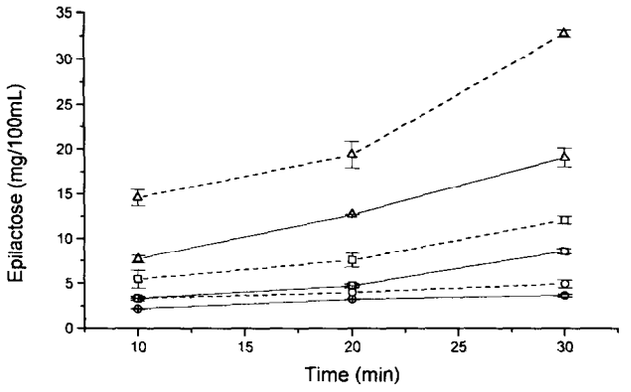

Fig. 3. Formation of epilactose during microwave (– – – –) and conventional (———) treatment of milk samples at 100°C (○), 110°C (□) and 120°C (△).

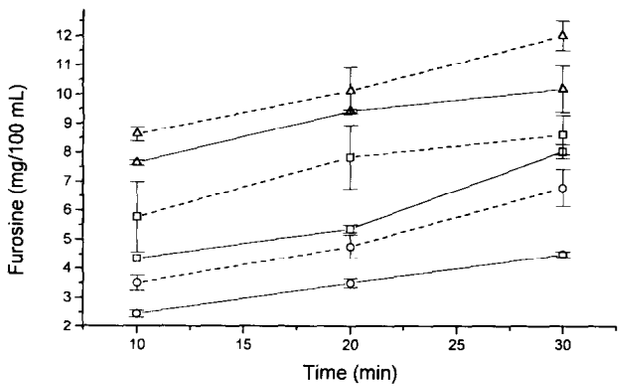

Fig. 4. Formation of furosine during microwave (– – – –) and conventional (———) treatment of milk samples at 100°C (○), 110°C (□) and 120°C (△).

than those in the conventionally-heated samples. As for lactulose and epilactose formation, the trends observed for both types of heating were similar (Fig. 4).

According to these results, chemical modifications of lactose and whey proteins in milk samples were the same under microwave and conventional treatment. From the three parameters measured, it can be concluded that the irradiated milk samples exhibited isomerization of lactose, Maillard reaction and protein denaturation as observed in conventionally-heated milks, but in a higher proportion as a result of an extra accelerating effect of the microwave treatment. This effect could be due to the previously reported non-uniform temperature distribution during microwave treatment (Mudgett, 1986; Jahngen *et al.*, 1990; Vasavada, 1990; Giese, 1992; Heddleson *et al.*, 1994). The temperature distribution varies with the size and shape of the food, and, in the case of foods of cylindrical geometry as in the present work, there is a pronounced concentration of heating at the central axis (Ohlsson & Risman, 1978). This may give rise to the observed acceleration of the chemical reactions. Moreover, the low-temperature control stability during microwave treatment allowed samples to reach temperatures 2.5°C beyond the set-point which could contribute to the differences observed between microwave and conventional heating. The development of new processing equipment with variable continuous power and an improved feedback temperature controller for batch and continuous heating of foods would overcome the problem of non-uniform temperature distribution, and, consequently, the chemical changes in microwave-processed foods would be reduced.

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