Food Chemistry 45 (1992) 41–43

Kinetics of galactose and tagatose formation during heat-treatment of milk

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(Received 11 September 1991; revised version received and accepted 21 October 1991)

The kinetics of the formation of galactose and tagatose during the heating of milk at various temperatures (115–135°C) was studied. A first-order kinetic model was satisfactorily used to describe the formation of both carbohydrates. The Arrhenius plot enabled calculation of the activation energies to be made (113 kJ/mol for galactose and 115 kJ/mol for tagatose). The formation of tagatose in appreciable amounts takes place only under sterilization conditions, and its presence in commercial milks may be an indication of the severity of the heat-treatment.

INTRODUCTION

In order to clarify the nature of heat-induced chemical changes in milk carbohydrates, many studies have been carried out, mostly based on whey proteins and the disaccharide fraction of this product (Fox, 1989). Thus, it has been established that lactose undergoes two types of reaction during the heating of milk: isomerization (Lobry de Bruyn–Alberda van Ekenstein rearrangement) and amino-sugar condensation (Maillard reaction).

The aldose–ketose isomerization has been intensively studied, and the formation of lactulose (Adachi, 1958; Adachi & Patton, 1961; Martínez-Castro & Olano, 1978), epilactose (Martínez-Castro & Olano, 1980), galactose (Olano & Martínez-Castro, 1981; Calvo & Olano, 1989) and tagatose (Adachi, 1958; Richards, 1963) has been reported.

Lactulose, epilactose and galactose have been used as indicators of the heat-treatment conditions to which milk has been subjected. Tagatose is formed from galactose, and its concentration in milk increases with the severity of heat-treatment. Therefore, the presence of tagatose in milk can be of considerable interest when the severity of heat-treatments are being monitored or when retrospective assessments of the heat-treatments given to milk are required. A study of galactose and tagatose formation during the heating of milk is reported in this paper.

Food Chemistry 0308-8146/92/$05.00

MATERIALS AND METHODS

Heat-treatments of milk samples

Milk samples (10 ml) were heated at 115, 120, 130 and 135°C for 5, 10, 15, 20, 25, 30, 45, 60, 75, 90 and 105 min in tightly stoppered Pyrex glass (16 × 162 mm) tubes in a silicone oil-bath.

Preparation of milk samples

Milk (1 ml) was mixed with 1 ml of 0·005% methyl-α-D-galactopyranoside, and the mixture was diluted to 10 ml with methanol, kept 1 h at room temperature and filtered; 2 ml of the filtrate was evaporated under vacuum at room temperature. Trimethylsilyl derivatives were obtained by the addition of 0·1 ml of pyridine and 0·1 ml of *N*-trimethylsilyl-imidazole : trimethylchlorosilane (2:1). Then, hexane (0·1 ml) and water (0·2 ml) were added, and 1 μl of the upper layer was taken for injection.

Gas chromatography

Gas-chromatographic analyses were performed on a HP-8290 gas-chromatograph equipped with a fused silica capillary column (18 m × 0·22 mm) coated with AT-1000. The temperature of the injector and detector were 275 and 250°C, respectively; the analysis was performed using temperature programming from 180 to 210°C at a heating rate of 15°C with an initial holding at 180°C for 22 min.

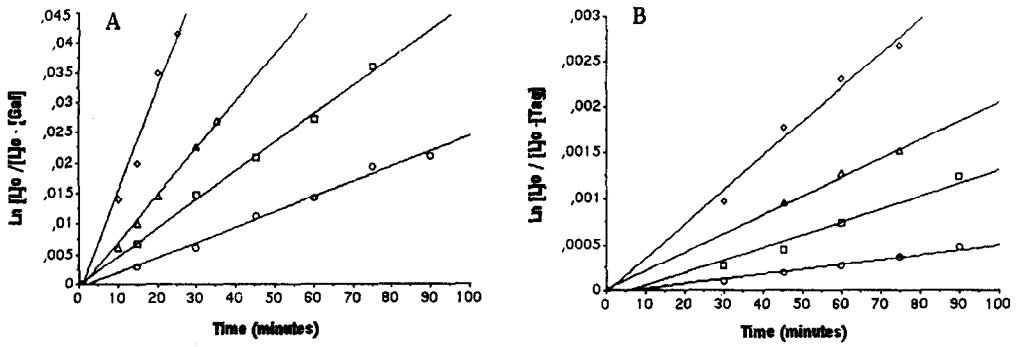

Fig. 1. The formation of galactose (A) and tagatose (B), plotted according to a first-order reaction: 115°C (○), 120°C (□), 130°C (Δ) and 135°C (◇).

RESULTS AND DISCUSSION

Previous studies have shown that the formation of lactulose, epilactose and galactose in heated milk proceed according to first-order reaction kinetics (Olano & Calvo, 1989). Thus, the rate at which the monosaccharides are formed may be expressed by the following equation:

$$\ln \frac{[Lac]_0}{[Lac]_0 - [X]_t} = K_t$$

in which $[Lac]_0$ is the lactose concentration at time zero and $[X]_t$ is the galactose or tagatose concentration at time t.

Figure 1 shows the application of the equation to fit the data of the formation of galactose and tagatose. The kinetic model fitted the data well, the coefficient of correlation never being lower than 0·99.

The rate coefficients for galactose and tagatose conform well with the Arrhenius relationship (see Fig. 2), and the activation energies were calculated from the plot of ln K versus $1/T$.

There are few data reported that are similar to those presented here. For the formation of galactose, the activation energy calculated by Olano and Calvo (1989) was 139·4 ± 3·92 kJ/mol, which compares reasonably well with the present values.

With respect to tagatose, Adachi (1958) reported the presence of this carbohydrate in strongly heated milk (autoclaved at 120°C for 10 h), and Richards (1963) studied the formation of tagatose in dried milk during storage. However, no data are available on the kinetics of tagatose formation to compare with the present results.

According to these results, the formation of tagatose in appreciable amounts takes place only under sterilization conditions, and its presence in commercial milks may be an indication of the severity of the heat-treatment. Other parameters, such as storage conditions and milk composition, can affect the formation of tagatose in milk. A detailed study of these parameters should be carried out in order to provide a clear understanding of the presence of tagatose in processed milks.

ACKNOWLEDGEMENT

The authors wish to acknowledge the financial support for the research project ALI-158/88 provided by the Comisión Interministerial de Ciencia y Tecnología.

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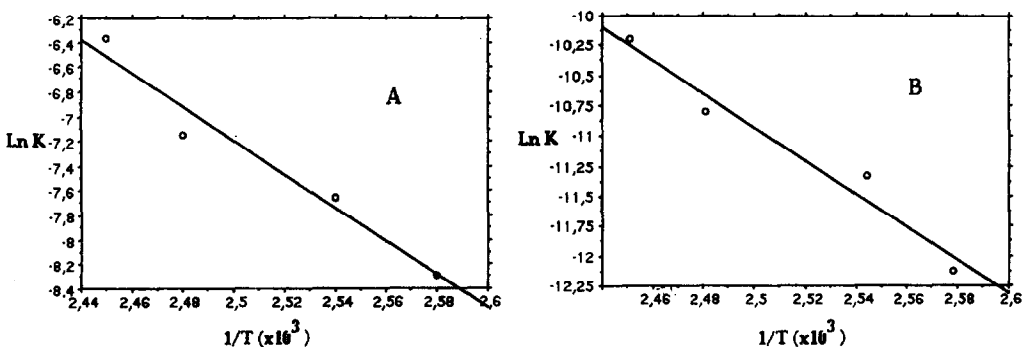

Fig. 2. Arrhenhuis plots for the formation of galactose (A) and tagatose (B) in milk: activation energies—113 ± 1·96 and 115 ± 1·98 kJ/mol, respectively.

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