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Oxidative properties of interesterified mixtures of milk fat, rapeseed oil and n-3 fatty acids

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In this paper, the oxidative stability of an interesterified mixture of milk fat, rapeseed oil and n-3 fatty acids in the form of their concentrates was studied. The peroxide value as well as the oxidative induction time were investigated. Interesterified fats were characterized by a shorter induction time and a higher peroxide value than the starting mixture.

Key words: interesterification, oxidative stability, peroxide value

Introduction

Milk fat is one of the main sources of dietary fats. It has been less and less well perceived due to its poor spreadability when refrigerated and its high content of saturated fatty acids regarded as promoters of coronary heart diseases. Milk fat occupies an important place in human nutrition. It is probably the most complex of all natural fats, being a mixture of more than 100 000 different triacylglycerols with a melting range from -40 to 40 °C. The decreasing consumption of high fat milk and dairy products is driving the dairy industry to seek other uses for increasing surplus of milk fat [1]. One of the option to reach milk fat is enzymatic interesterification. Unlike hydrogenation, it leaves the fatty acid composition unchanged and only alters the distribution of the fatty acids over the triacylglycerols [2, 3]. Enzymatic interesterification gives rise to new products with the original triacylglycerol structure and consequently modified physical properties [3].

The interesterification of fats is thought to prolong the resistance of fats to oxidation. Oxidation reactions consist of the initiation, propagation, and termination stages. Oxidative stability is one of the most important factors determining the quality of edible oils and fats as well as foodstuffs [4]. One of the most frequently used analytical instruments to measure the oxidation parameters is the differential scanning calorimeter DSC [5]. The DSC experiments are performed with a linear increase of temperature (dynamic conditions) or at a constant temperature (isothermal conditions). The oxidation medium (oxygen or air) can be maintained at a normal (atmospheric) or at an increased pressure (PDSC or HPDSC) [6]. The oxidation induction time as a function of temperature can be used as a parameter to assess the oxidative stability of fats.

The aim of this paper was to assess the oxidative properties of an interesterified mixture of milk fat (MF), rapeseed oil (RSO), and n-3 fatty acids.

Materials and methods

Materials

The mixtures of MF, RSO and n-3 fatty acids in the form of their concentrates (ROPUFA), in proportions 4 : 5 : 1 were used in our investigations. Anhydrous milk fat and rapeseed oil were provided by an industrial plant. ROPUFA 30 n-3 FOOD Oil (min. 30 % omega-3) was purchased in the DSM Nutritional Products company. The properties were as follows: peroxide value = 0.6 mekv/kg for MF, 1.0 mekv/kg, for RSO and 1.30 mekv/kg for ROPUFA; the value of induction time was 72 min for MF, 51 min for RSO, and 17.1 min for ROPUFA.

Catalyst of enzymatic interesterification

Flasks containing the initial mixtures were prepared and positioned in a thermostated mineral-oil bath shaker. After the thermal equilibration of fat + oils blend at 50 °C, 8 % of Lipozyme RM IM containing 4 % of water was added. The interesterifications were performed with a continuous shaking. After a predetermined time (2, 4, 8 h) of interesterification, filtering off the catalyst stopped the reaction.

DSC measurements

The differential scanning calorimeter (TA Instruments Q 200) equipped with a pressure cell (PDSC) was used. The instrument was calibrated using high purity indium as a standard. Samples of fats (3–4 mg) were placed in open aluminum pans; the reference pan identical to the pan with the sample was left empty. Experiments were performed at 120 °C under 1400 kPa pressure of oxygen. From the resulting PDSC exotherm, the time for reaching its maximum was determined.

Peroxide value (PV) determination

A modified method proposed by Hornero-Mendez et al. [7] was used for the determination of PV. Absorbance at a wavelength of 500 nm was measured. Spectrophotometer readings were set to zero using a blank

sample. The concentration of lipid hydroperoxides was expressed as PV.

Results and discussion

The results of PDSC measurements, expressed as the oxidation induction times, are shown in Fig. 1. The PDSC tests performed for interesterified fats showed that their induction times were reduced as compared with the starting mixture. The induction times obtained for the analyzed fats can be used as primary parameters for assessing the resistance of the test fats to their oxidative decomposition. Generally, samples with a higher induction time are more stable than those for which the induction time obtained at the same temperature is lower [8].

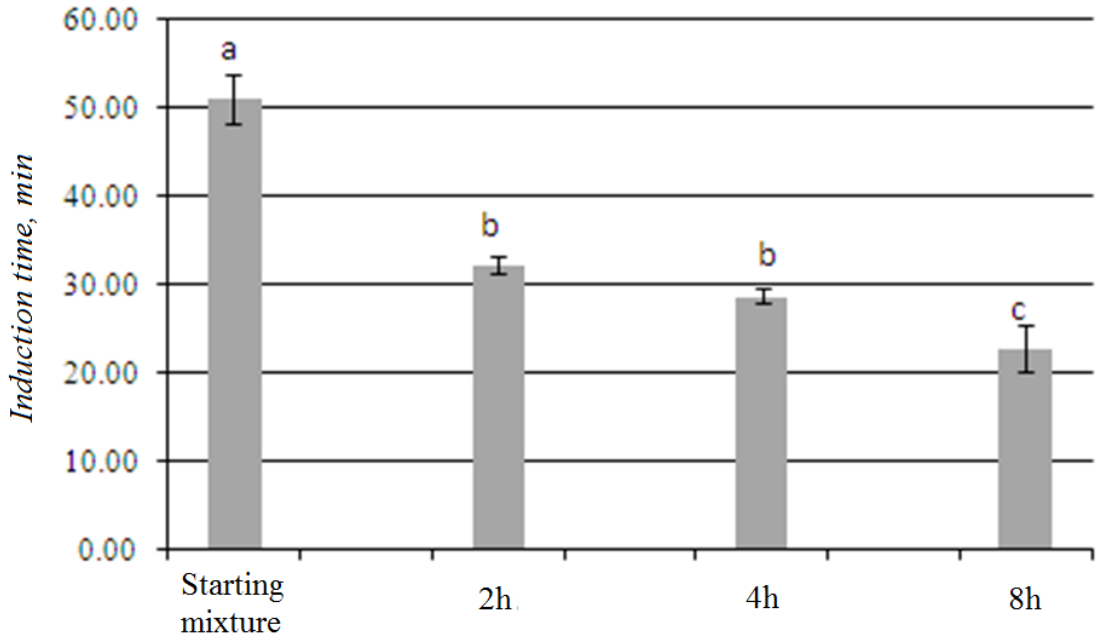

Fig. 1. Oxidation induction time of interesterified fats and starting mixture. Different letters indicate that the samples are significantly different at $p < 0.05$

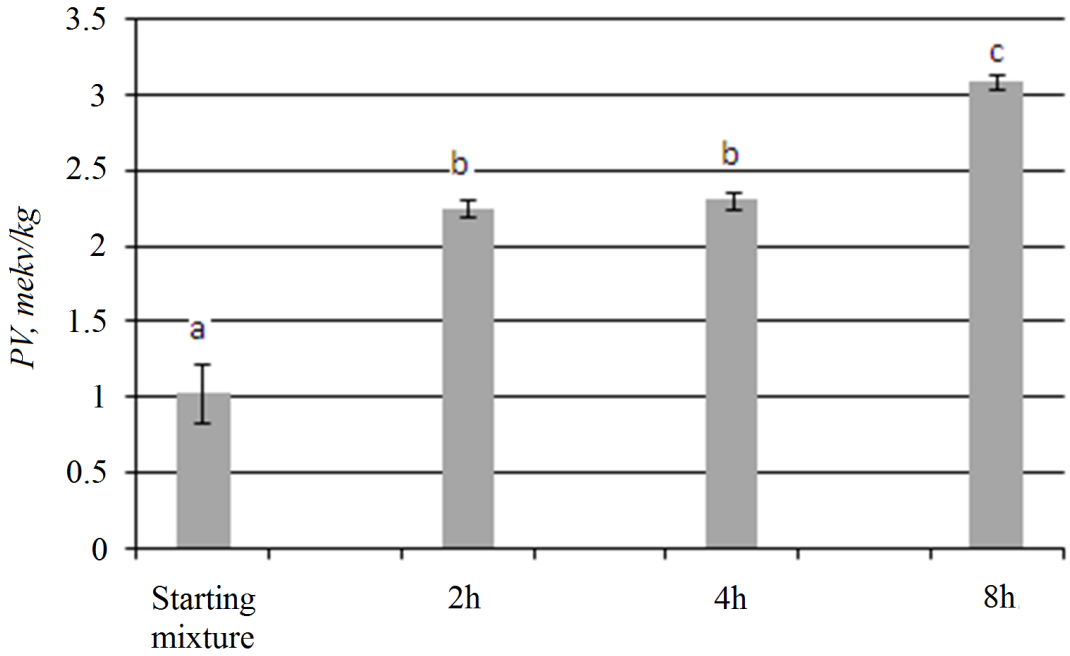

Fig. 2. Peroxide value of interesterified fats and starting mixture. Different letters indicate that the samples are significantly different at $p < 0.05$

The natural function of lipases is to catalyze fats hydrolysis. They catalyze the hydrolysis of fats to give free fatty acids (FFA), partial acylglycerols (monoacylglycerols – MAG, diacylglycerols – DAG) and glycerol. The reaction is reversible, and the enzymes can be shown to catalyze the formation of acylglycerols from glycerol and free fatty acids under certain conditions. If the water level is reduced, however, some lipases will continue to catalyze reactions, and at a certain level interesterification begins to dominate over hydrolysis [5]. An increased content of FFA and (DAG + MAG) in the interesterified fatty product can reduce its resistance to oxidation [8].

Similarly, for the peroxide values, the following rule can be applied: the higher peroxide value, the less stable is the fat. Interesterification causes an increase in the peroxide value (Fig. 2). A mixture interesterified for 8 hours was characterized by the highest peroxide value.

In general, most studies have reported a decrease in the oxidative stability of interesterified fats as compared with the initial mixture [3, 9, 10]. Among different reasons for explaining the worse oxidative stability of interesterified fats, the removal of endogenous antioxidants of interesterified fats has been pointed out as one of the main reasons for this phenomenon [4]. The oxidative stability of fats is influenced by the degree of polyunsaturation. The fats that are more unsaturated are oxidized more quickly than those less unsaturated [2]. Among all fatty acids, polyunsaturated fatty acids are highly labile molecules and susceptible to oxidation processes giving rise to free radicals, hydroperoxides and polymers, which might lead to a loss of technological and healthy qualities of the interesterified fats [4].

Conclusions

The results of the present research show that interesterification influences the reduction of induction time and increases the peroxide value.

The oxidation induction time obtained in this study can help to predict the oxidative stability of interesterified fat-based products.

PDSC is a method that can be used to assess the oxidation parameters of interesterified mixtures of milk fat, rapeseed oil and n-3 fatty acids.

Acknowledgements

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PIENO RIEBALŲ, RAPSŲ ALIEJAUS IR N-3 RIEBALŲ RŪGŠČIŲ PERESTERINTŲ MIŠINIŲ OKSIDACINĖS SAVYBĖS

S a n t r a u k a

Buvo tirtas peresterinto pieno riebalų, rapsų aliejaus ir n-3 riebalų rūgščių mišinio oksidacinis stabilumas. Peresterintų riebalų, palyginti su peresterinti naudojamo mišinio, indukcijos periodas buvo trumpesnis, o peroksidų vertė didesnė.