Browning Reactions between Oxidized Vegetable Oils and Amino Acids

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Abstract: Browning of stored food products, not exposed to heat treatment, is generally considered as a negative process. The formation of brown pigments at a temperature close to storage temperatures was followed in mixtures of either free fatty acids or vegetable oils with amino acids, deposited on cellulose fibres. The mixtures were studied at 50°C at free access of oxygen, and the browning process was monitored by reading the absorbance of brown products at 430 nm. Mixtures of free fatty acids and amino acids were turning brown in relation to their unsaturation degree. Mixtures of vegetable oils deposited on cellulose fibres were less coloured than if they were oxidized in presence of amino acids. The rate of browning increased with the degree of unsaturation in case of vegetable oils similarly as in case of free fatty acids. The browning degree was nearly the same in mixtures of oxidized fatty acids or vegetable oils with alanine, valine, lysine, serine or cystine, the browning was intermediate in mixtures with cysteine or methionine, but it was substantially more intensive in mixtures with proline or tryptophan. No significant difference was observed among different oils, but the discolouration was less rapid in case of low unsaturated peanut oil and more rapid in case of highly unsaturated linseed oil. The browning rate increased to a substantial degree with increasing cupric ion content, but decreased after addition of both synthetic and natural antioxidants, which decrease the oxidation rate.

Keywords: amino acids; browning reactions; lipids; Maillard reaction; oils; vegetable; oxidation

INTRODUCTION

Oxidized lipids react with amino acids and proteins under conditions of food production, food storage and culinary operations [1]. Hydroperoxides, free peroxy radicals or carbonylic secondary oxidation products form imines by reaction with amine groups [2]. Unsaturated imines polymerize forming insoluble brown coloured macromolecular melanoidins [3]. The browning intensity increases with increasing degree of lipid unsaturation [4]. Uematsu and Ishii [5] studied the browning reaction in model systems of linoleic acid or peanut oil and free amino acids on a cellulose support. In this paper, we present our results on the effect of prooxidants and antioxidants on the browning rate of lipids of different unsaturation degree under the conditions specified by the above authors [5].

EXPERIMENTAL

Material. All fatty acids and amino acids used in the experiments were products of Sigma-Aldrich (St. Louis, MO, USA). Soybean oil (iodine value of 127.4), zero-erucic winter rapeseed oil (iodine value of 101.4) and linseed oil (iodine value of 164.2) were plant-scale refined oils. Virginia peanuts were produced in China, and peanut oil was obtained by hexane extraction (linoleic acid content of 30.0%, iodine value of 106.0). SunOleic peanuts, developed in Florida and recultivated in Southern Japan were extracted with hexane, and oil had the linoleic acid content of 3.0% and an iodine value of 81.1. Cupric acetate monohydrate (Lach-Ner, Neratovice, CZ) was added as a catalyst in some experiments. Synthetic antioxidants tert. butylhydroxyanisole (BHA) and di-tert.-butyl hydroxytoluene (BHT) were obtained from Merck, Darmstadt, Germany.

Dried sweet grass (*Hierochloe odorata* L., family *Poaceae*) leaves and oregano (*Origanum vulgare* L., family *Lamiaceae*) leaves were obtained from Prof. R. Venskutonis (Kaunas, Lithuania), and were extracted with acetone.

Analytical methods. The course of oxidation was determined by measuring the absorbance at 430 nm, in agreement with the wavelength measurements used by Uematsu and Ishii [5].

Procedure. Hexane solutions of lipidic substances (antioxidants were added to the solution in some experiments) were applied on an ash-free filter paper impregnated with amino acids in the ratio previously applied [5], and the sample was kept at 50°C in the dark. The filter paper was then extracted with methanol, the solution was filled up to 25 ml, and the absorbance was measured.

RESULTS AND DISCUSSION

The effect of lipid unsaturation on the browning rate reported earlier [3, 4] was confirmed under our experimental conditions (Table 1) in case of free fatty acids. Similar results were obtained in experiments with vegetable oils, heated with different amino acids (Table 2). High-oleic SunOleic peanut oil was more resistant to browning than the conventional peanut virginia oil. The browning of samples containing rapeseed oil was about the same as in case of conventional peanut oil, which can be explained by similar iodine values of the two oils. The browning of samples containing soybean oil was only moderate in comparison with mixtures containing the substantially more unsaturated linseed oil. Mixtures of oils with cysteine and methionine were more intensively coloured than mixtures with alanine, valine, lysine, serine and cystine, and the most intensive browning was observed in mixtures with proline and tryptophan. Differences were observed between our results and those of former experiments [5], which can be explained by differences in the composition of lipids and other material used.

The browning of lipid-amino acid mixtures was due to oxidation reactions, which has been

Table 1. Effect of unsaturation of fatty acids on the relative browning rate in course of heating with amino acids

Fatty acid	Alanine	Cysteine
Lauric	1.0	1.0
Oleic	2.3	4.5
Linoleic	3.4	5.7
Linolenic	5.8	6.9

Table 2. Effect of vegetable oils on the relative browning rate during the heating with amino acids (the number of + signs is proportional to the relative rate of browning)

Vegetable oil	Alanine, valine, lysine, serine, cystine	Cysteine, methionine	Proline, tryptophan
SunOleic peanut oil	+	+	++
Virginia peanut oil	++	+++	++++
Rapeseed oil	++	+++	++++
Soybean oil	++	+++	++++
Linseed oil	+++	++++	++++++

Table 3. Effect of copper ions on the relative browning rate of a mixture of vegetable oils with proline

Vegetable oil	Browning rate		
	No copper salt added	Copper salt (5 mg)	Copper salt (15 mg)
SunOleic peanut oil	1.0	5.8	42
Virginia peanut oil	1.0	5.8	46
Rapeseed oil	1.0	8.5	62
Soybean oil	1.0	3.5	22

Table 4. Effect of antioxidants on the relative browning rate of mixtures of vegetable oils and cysteine

Antioxidant	Rapeseed oil	Soybean oil
Blank	1.0	1.0
BHA (0.02%)	0.3	0.3
BHT (0.02%)	0.4	0.5
Sweet grass extract (0.10%)	0.3	0.3
Oregano extract (0.10%)	0.5	0.5

confirmed by other experiments. An addition of prooxidative cupric ions enhanced the browning (Table 3). On the contrary, browning was inhibited by addition of both synthetic and natural antioxidants (Table 4).

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