DYNAMICS OF PEROXIDE VALUE IN FLAVOURED RAPESEED OIL

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Abstract

Spices are used to season food products. Investigations were carried out to determine dynamics of primary oxidation products in flavoured rapeseed oil depending on used spice, its concentration, storage duration, and sample preparing method. The oil was flavoured with winter savoury *Satureja Montana* L., hyssop *Hyssopus officinalis* L., and marjoram *Oreganum vulgare* L. Results showed that dynamics of peroxide value in flavoured oils were influenced significantly ($p<0.05$) by all investigated factors – used spice, its concentration, storage duration, sample preparing method, and interaction of these factors, too. Heating of oil in particular cases caused unusual, hard explainable dynamics of peroxide value. It is necessary to investigate optimal conditions of flavouring of oils and components of spices which can influence oxidation of flavoured oils.
Key words: aromatised oil, winter savoury, marjoram, hyssop, peroxide value.

Introduction

Vegetable oils are beneficial due to their nutritional value, content of fatty acids, and cholesterol lowering effect in blood. Variety of oil products could be expanded by flavouring oils with spices. Spices could enhance the flavour of oil and also work as antioxidants or prooxidants.

Comprehensive investigations are completed about spices from the family *Lamiaceae (Labiateae)*, a family composed of species with exploitable antioxidant activity (Jayasinhe et al., 2003; Jose del Bano et al., 2003). Oils were flavoured with three spices from plant family *Lamiaceae L.* – winter savoury, marjoram, hyssop. *Satureja Montana* L., or winter savoury, is perennial. Essential oil of winter savoury includes the phenols carvacrol and thymol, as well as p-cymene, linalool, terpineol and various organic acids (Sefidkon et al., 2004). Marjoram is perennial, and contains 0.12–1.2% of essential oils. Major components of essential oil are thymol (up to 50%) and carvacrol (Indriksons E., 1992). Among the herbal or aromatic plants, the hyssop (Hyssopus officinalis L.) is a plant that has not been studied very much. According to some bibliography sources, the hyssop contains more than 1% of volatile oil with maximum content at the offset of flowering stage (Jankovsky et al., 2002). The oils of hyssop could be categorised depending upon their percentage composition of β-pinene, limonene, pinocamphone, and isopinocamphone. The oils were rich in isopinocamphone (5–50%), pinocamhone (3–50%) or contained beta-pinene and limonene (1–60%) as major components (Jankovsky et al., 2002).

There are two methods of oil flavouring – extraction of aromatic compounds with heating and without heating. Extraction without heating means that oil with spices is hold 5-6 weeks at temperature of 4 °C. The similar sensory properties oil obtains after 6 hours, if the spices in oil are heated (Žukauska I., 1997).

Fats and oils undergo pronounced oxidative changes during storage. It is necessary to detect oxidation processes in flavoured oil. The rate of oxidation process can be described by peroxide value, which characterises primary products of autoxidation, mainly hydroperoxides (Matiseks et al., 1998).

The aim of research was to determine dynamics of primary oxidation products in flavoured oils depending on used spice, its concentration (by mass) in oil, storage duration, and sample preparing method.

Materials and methods

The investigations were performed in the laboratory of the Department of Chemistry at the Faculty of Food Technology. Studies were carried out on unrefined (the fraction of phospholipids was separated) rapeseed oil, with initial peroxide value (POV) 1.73 mmol kg^{-1}. As a control was used unheated oil with POV 1.73 mmol kg^{-1} and heated oil with POV 4.22 mmol kg^{-1}.

The oil was flavoured with dried winter savoury *Satureja Montana* L., hyssop *Hyssopus officinalis* L., and marjoram *Oreganum vulgare* L. which were grown in test fields of the Department of Gardening, Faculty of Agriculture of Latvia University of Agriculture.

Flavoured rapeseed oil samples were made using two methods:

- Extraction of spices in oil, holding it for 5 weeks at temperature of 4 °C (extraction without heating), temperature was chosen the same as in home refrigerator. Unflavoured oil was used as control.
- Extraction of spices in oil, heating for 20 minutes at 80 °C, then holding at temperature of 4 °C (extraction with heating). Heated unflavoured oil was used as control.

Concentrations of spices in oil – 10 g kg^{-1} and 100 g kg^{-1}.

The degree of oxidation is described with the peroxide value. The peroxide value in flavoured and unflavoured rapeseed oil was determined by Wheeler method (Matiseks et al., 1998) after 24 hours, 2 and 5 weeks. The results in this work are the average of three measurements. Multiple analysis of variance was performed using SPSS 8.0 for Windows. Significant differences between means were determined by Tukey's test at a level of $p<0.05$.

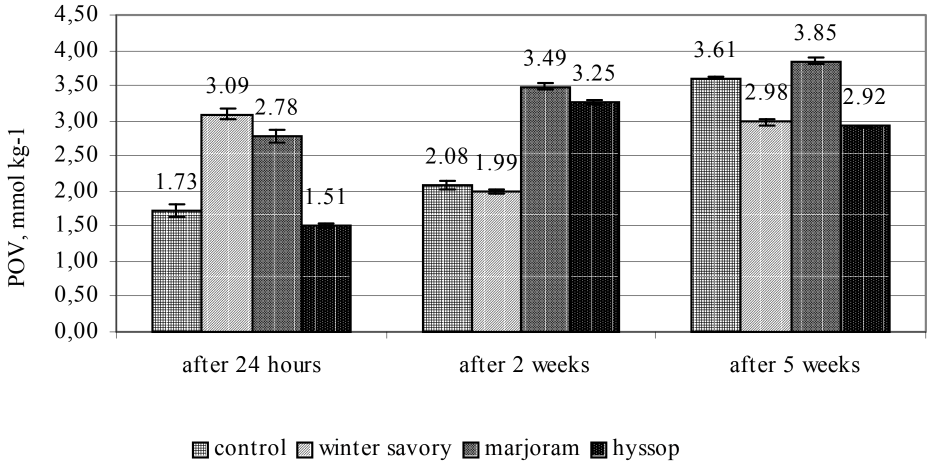

Fig. 1. Changes in POV in oil (held at 4 °C) with 10 g kg^{-1} of spices.

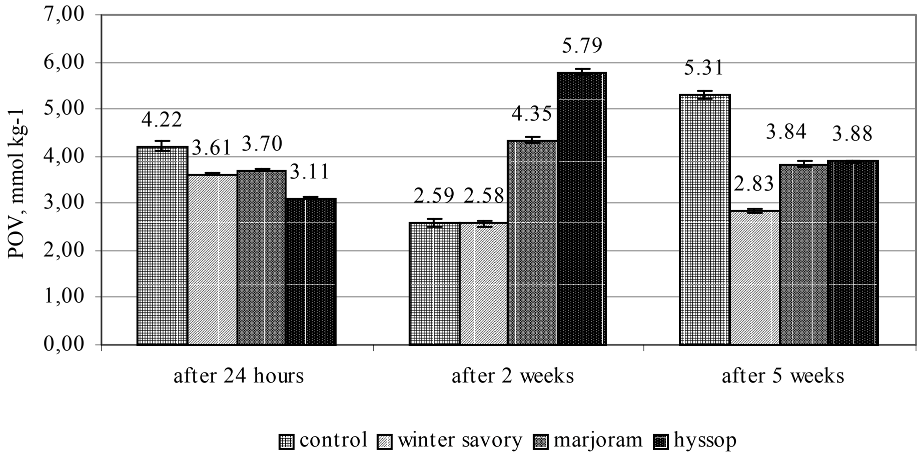

Fig. 2. Changes in POV in heated (20 minutes at 80 °C) oil with 10 g kg^{-1} of spices.

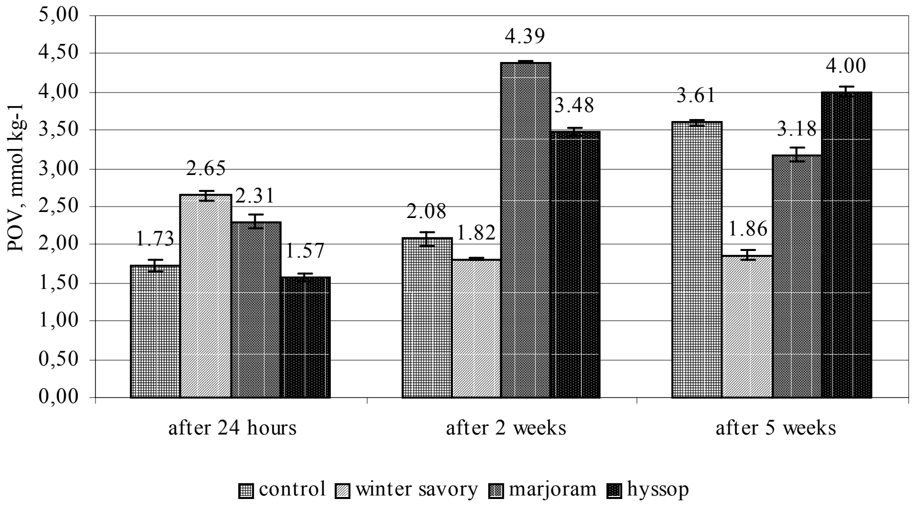

Fig. 3. Changes in POV in oil (held at 4 °C) with 100 g kg^{-1} of spices.

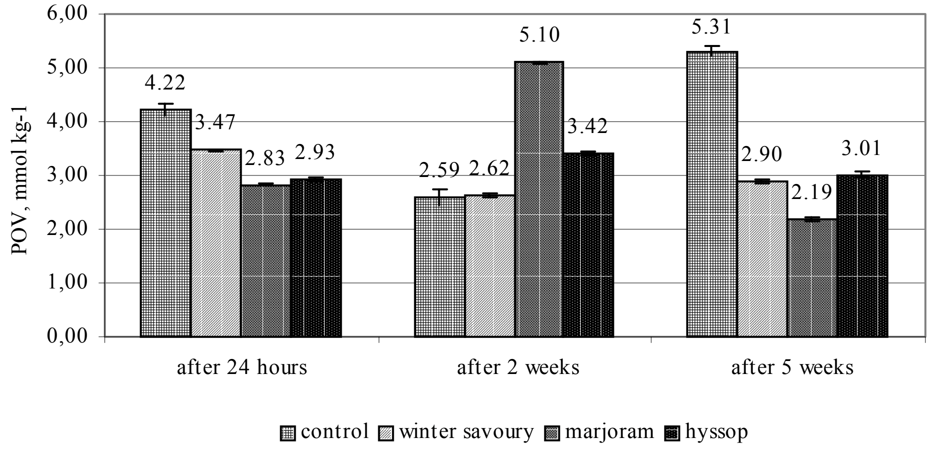

Fig. 4. Changes of POV in heated (20 minutes 80 °C) oil with 100 g kg^{-1} of spices.

Results and discussion

The results are presented in Figures 1–4.

Four factors and their interaction which could influence oxidation of flavoured oils was nominated: used spice, concentration of spices in oil, storage duration and sample preparing method. Results of multiple analysis of variation showed that all factors (method, spice, its concentration, storage duration) and their interaction had significant ($p<0.05$) influence on dynamics of peroxide value in flavoured oils.

Sample preparing method influenced changes in peroxide value in oil. In unflavoured heated oil after 24 hours, POV increased for 150%, and during all period of investigation it was higher than in unheated oil (Figs. 1 and 2).

After 24 hours in all flavoured oil samples which were obtained with heating, POV were increased for 17–106% compared with unheated oil. Increasing of POV depended on spice and its concentration in oil.

After 5 weeks it is possible to see interaction of three factors – method, spice, and concentration of spices in oil. Different tendencies of dynamics of POV between flavoured oils preparing by both methods were observed:

- Analyses of flavoured oil with 10 g kg^{-1} of winter savoury and with 10 g kg^{-1} of marjoram obtained by both methods showed that POV in these oils did not differ significantly depending on preparation (Figs. 1 and 2).
- In flavoured oils with 10 g kg^{-1} of hyssop and with 100 g kg^{-1} of winter savoury (Figs. 2 and 4), POV was higher in flavoured oils which was obtained with heating, compared with flavoured oils obtained without heating.
- Analysing oils with 100 g kg^{-1} of marjoram and with 100 g kg^{-1} of hyssop, POV was lower in flavoured oils obtained with heating, compared with oils obtained without heating.

The changes in peroxide value in all samples were significant. It is possible to state different trends of the changes in the amount of peroxides:

- During 5 weeks, the peroxide value increases (more or less equable), which could be explained by rapid formation of primary oxidation products (hydrogenperoxides). The rate of primary oxidation products formation is larger than the rate of secondary products. The following increase of peroxide value could be observed in unheated unflavoured oil with 10 g kg^{-1} of marjoram and 100 g kg^{-1} of hyssop (Fig.1 and 3).
- The peroxide value increases after 2 weeks, but decreases after 5 weeks. During the oxidation, peroxide value increases and then declines, because primary products of autoxidation are unstable and they break down to secondary products, forming ketons and aldehydes (Matiseks et al., 1998) The above described distribution could be observed in oils flavoured with marjoram and hyssop, exceptions are unheated oil with 10 g kg^{-1} of marjoram and 100 g kg^{-1} of hyssop.
- The peroxide value decreases after 2 weeks, but increases after 5 weeks. Such trend of distribution can be observed in heated unaromatised oil and in all oils flavoured with winter savoury. Obtained results are very hard to explain only with formation of primary oxidation products.

Dynamics of peroxide value in flavoured oil with winter savoury could be explained with properties of spice phenols. Recent experiments indicate that processing and storage conditions are expected to strongly affect the content and biological activity of phenol molecules (Pinelo et al., 2004). The antioxidant capacity of phenol-containing foods is expected to greatly change during processing as a function of the technological conditions adapted. Plant food contains numerous phenolic substances whose oxidation concomitantly occurs, potentially contributing to unexpected changes in antioxidant activity. Certainly, the ability of phenols to resist oxidative cleavage and polymerise, leading into improvement in the overall antioxidant activity of plant foods, is highly associated with their structure (Pinelo et al., 2004). The peculiar evaluation of the antioxidant activity during phenol oxidation has been attributed to the formation of partially polymerized phenols, which exhibit higher antioxidant activity than non-oxidised phenols or tannins formed in advanced steps of the reaction. In fact, it is beyond a certain level of molecular complexity (more than four monomer residues), the antioxidant activity of poliphenols would decrease as a consequence of steric hindrance (Lu Y et al., 2000; Saint-Cricq de Gaulejac N.,1999). It could be explained that after 24 hours phenols can not work so efficiently, but during period until 2 weeks, phenols start to polymerise, and can attach peroxides. Polymerisation is in progress and capability of phenols to attach peroxides decreases.

Conclusions

1. Changes in peroxide value in flavoured oil were influenced by all investigated factors – used spice, its concentration, storage duration, and sample preparation method.

2. Multiple analysis of variance showed that interaction of investigated factors was significant therefore it is not possible to determine which factor dominates.

3. In particular cases flavouring caused unusual, hard explainable dynamics of peroxide value. It is very difficult to explain the processes in flavoured oils by investigating only dynamics of primary products of oxidation, therefore it is necessary to study the components of spices which move to oil and could promote or inhibit oxidation of flavoured oils.

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