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Effect of added rosemary extract on oxidative stability of *Camelina sativa* oil

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ABSTRACT

The protective effect of added rosemary extract (RE) on the oxidative stability of highly unsaturated *Camelina sativa* oil was followed by periodic determination of its peroxide value (*PV*) during storage in darkness at room temperature. In camelina oil containing RE, a peroxide value of 10 mmol O_2 / kg, the upper limit for unrefined oils, was not attained after 11 months' storage. Compared to unprotected camelina oil the formation of hydroperoxides in oil containing RE was reduced by more than 40 %. The effect of RE against oxidation of camelina oil was also measured by the Rancimat test. In fresh camelina oil treated with RE the induction period was extended by 60 % as compared to untreated oil. Also, RE was more effective in preventing oil from oxidation when the oil was stored in darkness than in daylight.

Key words: *Camelina sativa* oil, rosemary extract, antioxidants, omega-3 fatty acids, oxidative stability

IZVLEČEK

UČINEK ROŽMARINOVEGA EKSTRAKTA NA OKSIDATIVNO STABILNOST OLJA NAVADNEGA RIČKA (*Camelina sativa*)

Zaščitni učinek rožmarinovega ekstrakta (RE) na oksidativno stabilnost olja navadnega rička smo ugotavljali tako, da smo periodično določali peroksidno število (*PV*) olja, ki smo ga skladiščili v temi pri sobni temperaturi. Po enajstih mesecih skladiščenja vrednost peroksidnega števila v olju navadnega rička, ki je vsebovalo rožmarinov ekstrakt, ni dosegla najvišje dovoljene vrednosti za nerafinirana olja. Dodatek rožmarinovega ekstrakta je upočasnil tvorbo hidroperoksidov v olju za 40 %. Učinek rožmarinovega ekstrakta na odpornost olja do oksidacije smo določali tudi z Rancimat testom. Ugotovili smo, da rožmarinov ekstrakt v svežem olju za 60 % podaljša indukcijsko periodo. Rožmarinov ekstrakt je učinkoviteje zaščitil pred oksidacijo olje skladiščeno v temi kot olje skladiščeno na svetlobi.

Ključne besede: olje navadnega rička, *Camelina sativa*, rožmarinov ekstrakt, omega-3 maščobne kisline, oksidativna stabilnost

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1 INTRODUCTION

Camelina sativa, with the popular names false flax or gold of pleasure, is a cruciferous oilseed plant (Zubr, 1997). Oil extracted from *Camelina sativa* seeds contains a high level of α-linolenic acid (18:3ω3), making camelina oil a rich source of essential omega-3 fatty acids (Budin et al., 1995; Strasil, 1997; Zubr & Matthäus, 2002). Camelina oil has been shown to reduce serum triglycerides and cholesterol (Karvonen et al., 2002; Eidhin et al., 2003a). Because of its unique fatty acid composition camelina oil can be used for direct consumption or in omega-3 fatty acid - enriched preparations (Zubr, 1997). Because of its possible nutriceutical effects, the oil has potential promise for use in the production of health promoting foods.

Due to the high content of linolenic acid and other unsaturated fatty acids in camelina oil, its oxidative stability is an important factor. In some investigations (Eidhin et al., 2003b; Matthäus, 2004) camelina oil was found to be more stable towards oxidation than highly unsaturated linseed oil but less stable than rapeseed, olive, corn, sesame and sunflower oils.

Oxidation of lipids not only produces rancid odours, unpleasant flavours and discoloration, but can also decrease the nutritional quality and safety. Use of antioxidants is one of the methods that retard or prevent lipid oxidation, preserve the quality and extend the shelf-life of food products. To avoid the use of synthetic additives, in recent decades, interest in natural antioxidants increased, especially because of the belief that natural food ingredients are safer than synthetics. Among the plants reported to have antioxidative activity, rosemary in its ground form or as an extract is widely used in many food applications. A number of components have been identified that are responsible for the antioxidative properties of rosemary. The main antioxidative effect is attributed to three phenolic diterpenes: carnosic acid, carnosol and rosmarinic acid (Frankel et al., 1996).

The main parameters that determine the susceptibility of oil to oxidation are fatty acid composition and the presence of antioxidant compounds. We recently published data regarding the oxidative stability of camelina oil under different storage conditions (Abramovič and Abram, 2005). In the present investigation we tried to prepare a blend of camelina oil and rosemary extract that would be a safe and oxidatively stable combination of very important bioactive compounds such as essential omega-3 fatty acids and phenolics. The purpose of this current work was to describe the effect of added rosemary extract in the protection of *Camelina sativa* oil against the oxidation process.

2 MATERIALS AND METHODS

Materials

The camelina oil used in this study was produced from seeds of *Camelina sativa* plants grown in 2002 near Prevalje in the Koroška region, Slovenia. The camelina oil was obtained by the following procedure. Dried seeds were milled and mixed with water. The mixture obtained was roasted at temperatures ranging from 60 °C to 90 °C. After pressing, the oil thus obtained was filtered. According to the local oil producers, roasting of the seeds is necessary, as otherwise oil cannot be obtained from non -roasted milled seeds. This oil had an attractive yellow colour and distinctive mustard like odour. In our camelina oil the content of

polyunsaturated acids as a percentage of total fatty acids was 55.8 %, the free fatty acid content was 2.35 %, the iodine value amounted to 104.7 g I_2 / 100 g oil, the saponification number was 187.8 mg KOH / g oil and the peroxide value was 1.18 mmol O_2 / kg (Abramovič and Abram, 2005). Rosemary extract (RE) (ROS.oleo H clear) was obtained from Vitiva, Markovci, Slovenia. It contained 12 % of carnosic acid dissolved in sunflower oil. RE was added to camelina oil to 0.2 %. The concentration of carnosic acid, the component responsible for the antioxidative activity of RE in camelina oil, was 0.024 %.
All other chemicals and solvents were of analytical grade.

Determination of oxidative stability
Storage conditions
Oil samples were transferred to transparent glass bottles (400 mL of 12 cm in diameter). The bottles were closed and for 330 days subjected to different storage conditions:
1 - at room temperature with exposure to daylight,
2 - at room temperature in darkness,
3 - at 8 °C in darkness.

For each storage condition two bottles were used, one with oil without RE and one with added RE. Periodically from each bottle cca 40 ml of oil was withdrawn and subjected to the Rancimat test and for determination of the peroxide value.

In the summer months (June, July and August) the room temperature varied between 25 °C and 30 °C, while in the rest of the year the temperature was between 20 °C and 25 °C. The oil samples exposed to daylight were placed approximately 1.5 m from the window and were not exposed to direct sunlight. The intensity of light in the room depended on the weather conditions. These are shown on http://www.arso.gov.si for each month of the experiment as hours of bright sunshine duration in Ljubljana.

Peroxide value
Oxidation rate was followed by periodic determination of the peroxide value. This was determined according to AOAC Official Method 965.33 (AOAC, 1999). The determinations were carried out in triplicate. *PV* was expressed as mmol O_2 per kg of oil. The standard deviation for each *PV* determination was less than 2 %.

Rancimat test
The susceptibility of camelina oil to oxidation was also studied using the Rancimat test (Läubli and Bruttel, 1986). The test was performed on a Rancimat apparatus 679 (Methrom, Herisau, Switzerland) by measuring the induction period at 110 °C and an air flow rate of 20 dm^3/h. Determination of the induction period was based on the conductometric detection of volatile acids. The determination was carried out in duplicate. The induction time measurements were reproducible to within ± 2 %.

3 RESULTS AND DISCUSSION

The effect of RE on the formation of primary oxidation products, expressed as *PV*, in oil stored in darkness at room temperature versus time of storage is shown in Fig. 1. The data were compared to previously published data for *PV* of camelina oil without added RE (Abramovič and Abram, 2005). Fig. 1 illustrates that the presence of RE at 0.2 % (0.024 % of carnosic acid) in the investigated highly unsaturated oil reduces the peroxide value. During the first three months of storage, *PV* of the oil with added antioxidant increased to 2.53 mmol O_2 / kg. During the next eight months the oxidation process occurred more progressively and at the end of the experiment the *PV* value of this sample reached 9.21 mmol O_2 / kg. After that time the peroxide value in oil containing RE was more than 40 % lower than *PV* in the oil with no RE. A *PV*

of 10 meq O_2 / kg, which is the upper limit for unrefined oils according to the Regulations on Edible Oils, (1999), was not attained in oil treated with RE even after 11 months of storage. In oil stored in darkness at room temperature without added antioxidant the value 10 meq O_2 / kg was attained in 6.5 months.

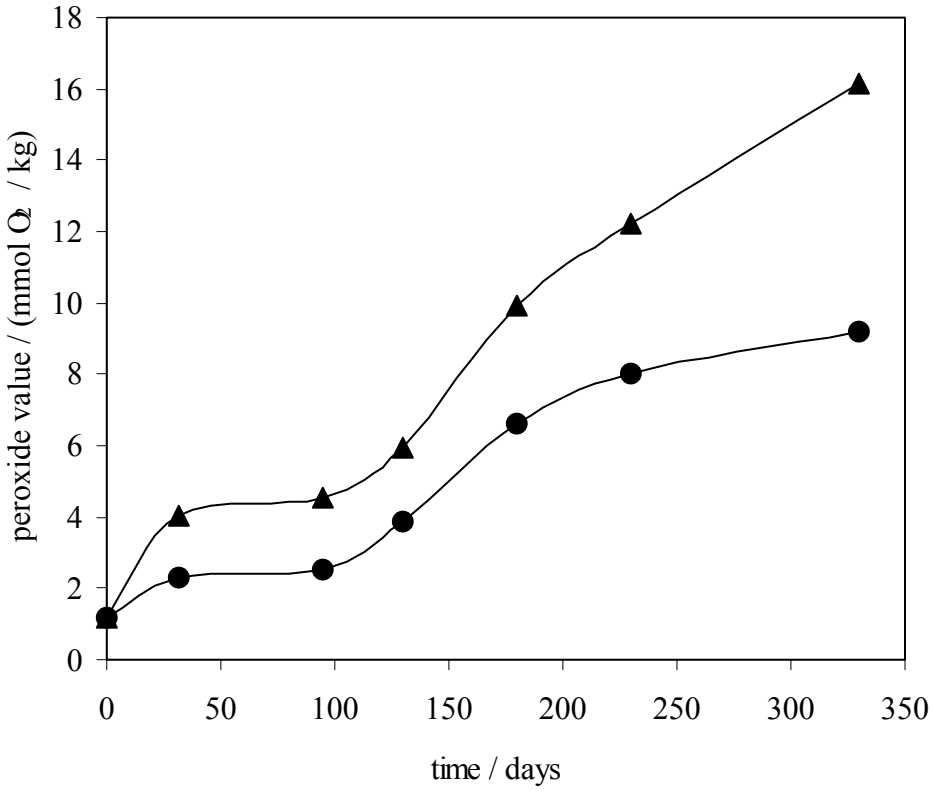

Fig. 1. Effects of added rosemary extract on the peroxide value of *Camelina sativa* oil during storage in darkness at room temperature (● – added rosemary extract; ▲– no rosemary extract).

The susceptibility of camelina oil to oxidation was also measured by the Rancimat test and expressed by the induction period. The induction period represents the time needed for decomposition of hydroperoxides produced by oil oxidation (Läubli and Bruttel, 1986). The Rancimat test was applied in our investigation because this technique allows the automatic determination of the oxidative stability of oils and fats without the need for expensive and environmentally hazardous chemicals and time consuming titrations. The Rancimat test is a commonly used procedure in the food industry to examine the oxidative stability of edible oils and predict their shelf life. It has been shown for rapeseed oil that an induction period of 1 h determined at 100 °C was equivalent to 2 days storage at 20 °C (Gordon and Mursi, 1994). Maszewska (2002) found that an induction period of 1 h at 120 °C was equal to 5 months storage at 12 °C.

Compared to an already published value for the induction period of 4.8 h (at 110 °C) in fresh camelina oil with no added antioxidant (Abramovič and Abram, 2005), the presence of RE extended the induction period to 7.6 h. Some investigators (Rudnik et al., 2001) of highly unsaturated linseed oil without antioxidant, with 0.02 % BHA or with 0.05 % of a blend containing α-tocopherol, ascorbyl palmitate, citric acid,

ascorbic acid and ethoxylated ethylene glycol obtained values for the induction period (at 100 °C) of 6.4 h, 7.2 h and 8.3 h, respectively.

The protective factor of RE on the susceptibility to oxidation of camelina oil expressed as percentage extension of the induction period, E_{RE}, was calculated as:

$$E_{RE} = \frac{IP_{RE} - IP}{IP} \times 100 \quad (1)$$

where IP_{RE} and IP mean the induction period with and without RE. In fresh camelina oil the presence of added antioxidant extended the induction period by 60 %. As the Rancimat test measures the time needed for decomposition of hydroperoxides, the extended induction period in the presence of RE may be due the protective effect of carnosic acid on the decomposition of these primary products of oxidation (Reblova et al., 1998). The results of the Rancimat test for camelina oil with added antioxidant stored under different conditions are given in Table 1. It is evident that the induction period decreases with time of storage.

Table 1. Values of induction period (IP_{RE}) (Rancimat test) for *Camelina sativa* oil with added rosemary extract (RE) and protective factor of RE expressed as percentage extension of induction period (E_{RE}) in relation to storage conditions and storage time.

Storage time / days	*65*		*155*		*280*	
	IP_{RE} / *hours*	E_{RE} / *%*	IP_{RE} / *hours*	E_{RE} / *%*	IP_{RE} / *hours*	E_{RE} / *%*
daylight, room temp.	*4.3*	*16.2*	*3.2*	*18.5*	*2.2*	*4.76*
dark, room temp.	*6.7*	*76.3*	*5.3*	*82.8*	*4.6*	*91.7*
dark, 8 °C	*6.8*	*65.8*	*nd*	-	*6.3*	*75.0*

nd - not determined

The antioxidative components either those naturally present or those added to camelina oil, depending on the storage conditions, were degraded with time, thus loosing their antioxidant properties (Gregory, 1996). A close correlation between total phenolics content and oil stability towards oxidation has been confirmed in many studies (Morello et al., 2004; Monteleone et al., 1998; Okogeri and Tasioula-Margari, 2002). In a study on virgin olive oil (Morello et al., 2004), after 12 months of storage in the darkness at ambient temperature, a decrease of the total phenolics content was established, while the induction period (by Rancimat test at 120 °C) was about 50 % of the initial (10 h) value.

In Table 1 we can also see that the susceptibility to oxidation is affected by the storage conditions. A higher temperature and the presence of light reduce the induction period considerably. This means that in oil stored in daylight at room

temperature a critical concentration of degradable volatile products under the Rancimat test conditions and the collapse of the system was reached faster. The effect of added antioxidant in preventing oxidation was more pronounced in oil stored in darkness than in daylight. In oil stored in darkness E_{RE} rose with time. The presence of RE in camelina oil stored in darkness at room temperature for 280 days extended the induction period by more than 90 %. When stored in darkness at 8 °C for 280 days camelina oil treated with RE still had a 6.3 h induction period which is appreciably higher than the value (4.8 h) for fresh oil without added RE. However, in oil exposed to daylight the protective effect of added antioxidant decreased and after 280 days of storage became minor.

In conclusion Camelina oil blended with RE seems to be oxidatively stable combination of very important health promoting compounds, such as essential omega-3 fatty acids and phenolics that are not only beneficial for their antioxidant activity in the lipid system but also show important biological activity *in vivo*.

5 ACKNOWLEDGEMENT

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