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INVESTIGATION OF ANTIOXIDANT PROPERTIES OF RAPE PRESSING

Valeriy Mank Doctor of sciince, professor*
E-mail: vmank38@rambler.ru
Tamara Nosenko Ph.D, professor assistent*
E-mail: tnosenko@yahoo.com
Tetyana Voloschenko post graduate student*
E-mail: tanya.kot.90@list.ru
*Department of Fat, Perfume and cosmetic products Technology,
National University of Food Technologies, Volodymyrska, 68, Kyiv, Ukraine, 01601

Анотація. У роботі досліджено індукційний період окиснення пресових олій озимого та ярового гібридів рапсу, визначено вміст антиоксидантів та термін придатності олій до споживання. Концентрація антиоксидантів у перерахунку на токоферол в олії ярового ріпаку становить 50,3 мг %, в олії озимого ріпаку − 54 мг % Проведені дослідження свідчать, що ріпакова олія, одержана із насіння озимого та ярового гібриду, має тривалий термін придатності до споживання та високу антиоксидантну здатність. Стійкість ріпакової олії до окиснення визначається особливостями її жирнокислотного складу та вмісту токоферолів і їх синергістів. Антиоксидантна здатність олії з озимого ріпаку, одержаної методом холодного пресування, дещо вища в порівнянні з антиоксидантною стійкістю до окиснення олії з ярового ріпаку.
Ключові слова: пресова ріпакова олія, антиоксиданти, окиснення, пероксиди, індукційний період, термін придатності

Аннотация. В работе исследован индукционный период окисления прессовых масел озимого и ярового гибридов рапса, определены содержание антиоксидантов и срок годности масел к потреблению. Концентрация антиоксидантов в пересчете на токоферол в масле ярового рапса составляет 50,3 мг %, в масле озимого рапса –54 мг % Проведенные исследования показывают, что рапсовое масло, полученное из семян озимого и ярового гибрида, имеет длительный срок годности и высокой антиоксидантной способность. Устойчивость рапсового масла к окислению определяется особенностями ее жирнокислотного состава и содержания токоферолов и их синергистов. Антиоксидантная способность масла из озимого рапса, полученного методом холодного прессования, несколько выше по сравнению с антиоксидантной устойчивостью к окислению масла из ярового рапса.
Ключевые слова: прессовое рапсовое масло, антиоксиданты, окисление, пероксиды, индукционный период, срок хранения

Introduction

Rape is a one of the most important and perspective plant for oil world production. Nutritive and biological values of rape oil are caused by its composition, first of all by fatty acid composition. High oleic acid content in rape oils of modern varieties increases its oxidation stability that, in turn, gives possibility for oil

producers to guarantee the long shelf life of rape oil [1,5,6].

Problem formulation

Now the rape oil is a one of the most popular in Europe as edible oil. It is very valuable vegetable oil and has balanced composition of saturated, monounsaturated and polyunsaturated fatty acids. But rape oil has not a great demand in Ukrainian consumers due to some causes. First of all, traditional using of sunflower oil as vegetable oil in Ukraine. Secondly, there are not sufficient information and popularization of such kind of vegetable oil as rape oil between consumers in our country. And finally, rape oil is almost absent on our consumers' market.

Thus the purpose of our work was to investigate the properties of rape oil, that was obtained by cold pressing from seeds of spring and winter rape varieties.

Literature review

Wide using of edible rape oil had become possible since 1961 year, when new rape varieties, which did not contain erucic acid negatively influencing on human organism, were selected in Canada [2,7,9].

When compare with another vegetable oils rape oil contains lower saturated fatty acids, a lot of vitamin E, preserves transparency for a long time and undesirable smell of oil does not appear under oxygen influence [3,6].

Rape oil exhibits antioxidation properties and this can be used for prevention of cardio-vascular and oncological diseases. Content of ω-3 and ω-6 polyunsaturated fatty acids, which sufficiently higher comparing with another vegetable oils, determines very high nutritive value of this oil [13, 14]. Rape oil is a real leader for vitamins E content, this vitamin is a nature antioxidant, which protect living cells from free radicals. Additionally, rape oil contains vitamin K, that is very important for borne tissue health and provides normal blood coagulation. Rape oil can be used for frying, as salad dressing and also for baking [4,8-11].

It was shown also that high biological value of rape oil from seeds of modern rape varieties caused by such phenolic substances content as sinapic acid and its derivatives [12]. Very important sinapic acid derivative is canolol 4-vinil, 2,6-dimetoxyphenol. Canolol is a very strong antioxidant, has anticancerogenic properties, its antimutagenic property is higher relatively α-tocopherol and flavonoids. This substance was not detected in rape seeds but it was created during rape seeds processing due to decarboxylation of sinapic acid [13]. Thus this substance appears only in raw rape oil. Moreover the authors of this work have detected a new phenolic substances in rape oil and its deodistilate, mainly canolol dimers and threemers which have very high antioxidation capacity.

Main part

Rape seeds of spring and winter rape varieties were obtained from Lembke selection (Germany). In particular, hybrids Artus and Calibr were investigated. The rape oils were obtained by cold pressing. at 45 ºC i 75 ºC. The different perforation diameters of attachment (4 and 6 mm) for oil cake output were used during pressing.

Moisture and volatile compounds content were determined according to National and ISO Standard 662:2004, tocopherols content − according to National and ISO Standard 9936:2004. The peroxide values were determined according to National and ISO Standard 3960-2001, the acid values − according to National and ISO Standard 4350:2004, the color values − according to National and ISO Standard 4568:2006, iodine values − according to National and ISO Standard 3961:2004.

The investigated samples have been saving in a glass packings at 20±2 °C. The samples were withdrawing for analysis every 7 days. Peroxide value determinations were carried out until they reach 10 mMol½O/kg.

Induction period of initiated oxidation and determination of antioxidants concentrations were investigated according to [15], that means to measure the dependence the mass of oxygen absorbed by oil from time during initiated oxidation at 80 °C. This method gives possibility to determine the molar concentration antioxidants in fats (oils) in the range $(1–20)\cdot10^{-4}$ mol/l with confidence interval of relative variance (2–8) % at confidence probability 0,95.

At chain free radicals oxidation of organic substances in presence of inhibitors of third type (according to [18]), which breaking the chains reacting with free radicals the content of oxidation inhibitors are proportional to induction period on the curve of initiated oxidation of investigated substances in model conditions [16-18]. The antioxidants concentrations were calculated according to:

$$\tau = \frac{f[\mathrm{InH}]}{V_i}, \qquad (1)$$

whence it follows:

$$[\mathrm{InH}] = \frac{1\times[\mathrm{AIBH}]_0\times(1-e^{-K_p\times\tau})}{f} = \qquad (2)$$

$$= 0,48\times[\mathrm{AIBH}]_0\times(1-0,9999^{\tau}),$$

where τ – induction period, s; [InH] – molar concentration of inhibitors; Vj – rate of free radicals initiation by initiator, $[AIBH]_0$ – initial initiator concentration, mol/l, K_p – constant of initiator breaking rate at 80 °C equal $6\cdot10^{-5}$ c^{1}, 1/f = 0,48 (1 – radicals quantity from one initiator molecule, f – inhibition coefficient equal to quantity of chains breaking by one antioxidant molecule).

The physico-chemical values of rape oils obtained from spring and winter rape varieties by cold pressing are shown in Table 1. The data obtained have demonstrated that these values were much closed. But nevertheless acid

and especially peroxide values of winter rape seeds were lower relatively oil from spring variety. Such differences could be due to seeds quality and due to particularities of chemical composition of winter rape seeds too.

Table 1 – The physico-chemical properties of obtained rape oils

Value	Spring rape oil	Winter rape oil
Colour value, mg J_2/100 ml	45±0,05	50±0,03
Acid value, mg KOH/g	1,06±0,02	0,84±0,02
Peroxide value, mMol½O/kg	1,8±0,02	0,76±0,02
iodine value, g J_2/100 g	118±0,03	118±0,03
Moisture and volatile compounds content, %	0,2±0,01	0,2±0,01

Investigated oils had high content of β-tocopherol (67,4 – 73,1 % from common content of tocopherols), which had most prominent antioxidant properties preventing oxidation of polyunsaturated fatty acids. The content of α-tocopherol, which has the highest biological activity, was 26,9 – 32,6 % (from common content of tocopherols).

Peroxides accumulation in investigated oils were estimated as peroxide values increase during storage (fig. 1).

The dynamic peroxide values increase have shown that oil from seeds of spring rape had a little higher oxidation rate (especially during first 14 days) in comparison to oil from winter rape seeds. After 74 days storage of oil samples the peroxide values were 10, 3 mmol ½O/kg and 11,8 mmol ½O/kg for winter and spring rape oil respectively.

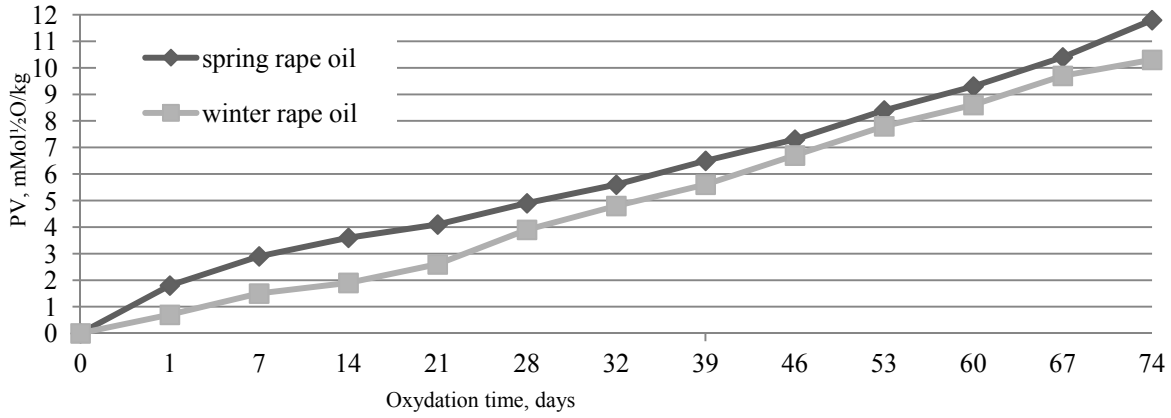

Fig. 1. Peroxide values changes of spring rape oils during storage

Approval of investigation data

Using of mathematic treatment of kinetics of oxidation degree changes we have got the next dependence of predicted peroxide value and shelf life from storage time for spring (3) and winter (4) rape oil:

$$Y = 0{,}889x - 1{,}3308 \quad (3)$$

$$Y = 0{,}9845x - 0{,}3308 \quad (4)$$

where x is a storage time, days.

The induction periods of oxidation were detected for the determination of antioxidant activities of investigated sample of rape oils (fig. 2). During induction period presented in oil antioxidants, have been connecting the free radicals of polyunsaturated fatty acids and thus preventing increase of their oxidation rate. Calculated induction periods were 27 and 29 min for spring and winter rape oil respectively.

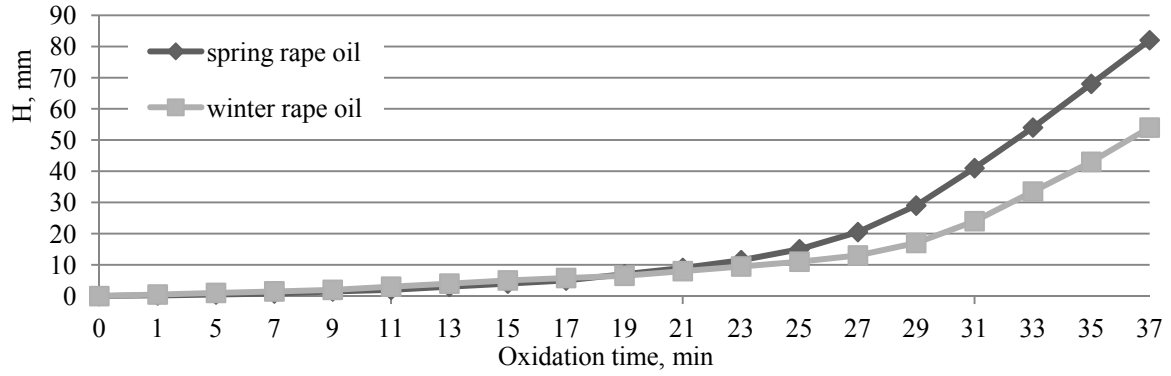

Fig.2. Initiated oxidation curves of cold press rape oil.

Using the values of induction periods of investigated oils we have calculated the antioxidants concentration. They were 50,3 mg % and 54 mg % (calculated to tocopherols) for spring and winter rape oil respectively.

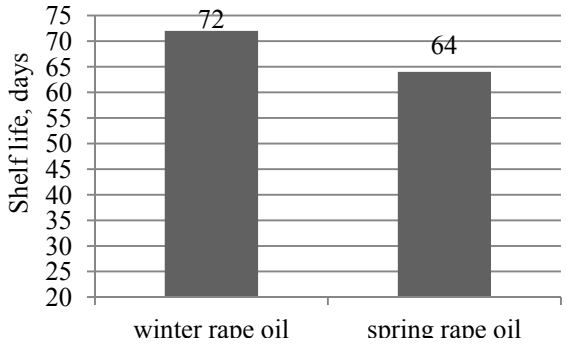

Fig. 3. Shelf life of press oils from spring and winter rape seed varieties.

The data obtained have shown that winter rape oil had longer induction period and it could be the result of higher antioxidants and their synergists content in winter rape oil than in spring rape oil.

Higher antioxidants content in winter rape oil, obtained by cold pressing, obviously results in longer shelf life which was 72 days at the presence of light and air (fig. 3). At the same time spring rape oil had also the high antioxidant stability during storage and its shelf life was 64 days.

Conclusions

Our data have demonstrated that oils of spring and winter rape varieties had long shelf life and high antioxidative capacity. Oxidation stability of rape oils depended from fatty acids composition, content of antioxidants and their synergists. Oxidation stabilities of oils from spring and winter rape varieties were very closed as well as the content of their native antioxidants.

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