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COMPARATIVE STUDY OF OXIDATIVE STABILITY FOR DIFFERENT TYPES OF VEGETABLE OILS

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Abstract: *Use of oils in the diet requires their protection against oxidation under conditions of high temperature and light. The expiration date is different depending on the type of oil. The presence of light and heat affects its quality: acid value, peroxide value and antioxidant capacity due to the presence of natural oils, antioxidants such as tocopherols, polyphenols, vitamin C, and so on, or artificial, added during the technological processes of obtaining them. Changes in acid value and peroxide may be linked to the antioxidant content assessed by measuring antioxidant activity by DPPH method. Oxidative stability of sunflower oil, corn oil, extra virgin olive oil, grape seed oil and nut oil was studied before and after keeping them in oven for 5 days at 50 º C. Under these conditions of accelerated oxidation, oxidative stability was evaluated by measuring peroxide value, antioxidant activity of free acidity. From analyzes it came out that coconut oil has the highest antioxidant capacity and the lowest variation of peroxide value and free acidity in mentioned conditions.*

Keywords: *vegetable oils, antioxidant activity, peroxide value, free acidity,*

1. Introduction

Free radicals are atoms or molecules that have an unpaired electron with a high chemical instability and aggression, able to react with other molecular structures.
Their presence was associated with a lot of diseases such as cancer, autoimmune cardiovascular, pulmonary, rheumatic diseases, and nervous system disorders, [1].Therefore, eating non-oxidized food and antioxidants consumption play an important role in protecting against these degenerative processes.
Extra-virgin olive oil produced by the application of mechanical pressure on the fruit Olea europea L., the high proportion of monounsaturated fatty acids, for example oleic acid, and the modest presence of polyunsaturated fatty acids contain natural antioxidants such as tocopherols, carotenoids, sterols, and phenolic compounds [1]. The effects of polyphenols and tocopherols on oxidative stability during oil storage and the processes of heating have been extensively evaluated in different studies [1].
Oil walnut (Juglans regia L.), by the content of essential fatty acids is a good source of monounsaturated fatty acids (oleic acid mainly) and polyunsaturated fatty acids (linoleic and alpha-linolenic acid) [3].
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(oleic acid mainly) and polyunsaturated fatty acids (linoleic and alpha-linolenic acid) [3]. According to the study of Simopoulos (2002) walnut oil has a perfect balance of n-6: n-3 polyunsaturated acids, a 4:1 ratio, which has been shown to reduce the incidence of cardiovascular risk [3]. Sunflower oil has about 70% linoleic acid [2] and is very sensitive to lipid oxidation [2]. Polyunsaturated acids, are exposed to environmental factors such as air, light and temperature oxidation reactions produce undesirable flavors, odors and rancid, discoloration and other forms of deterioration. Primary autoxidation products are hydroperoxides, having no taste or flavor, but their degradation products (aldehydes, ketones) have very strong taste and aroma are changed [2].

Besides their chemical composition, the susceptibility to oxidation of oils depends on the processing, packaging and storage conditions. In a recent paper [2] it was established that, in general, oils are highly susceptible to degradation in the presence of light.

Oils stored in transparent bottles, exposed to fluorescent light (1100 lux) and ambient temperature, without addition of any antioxidant, could maintain acceptable quality for up to two months of storage, a very short shelf life. Although synthetic antioxidants are widely used as food additives, their safety has been questioned [4] the boost search of natural resources, of compounds with antioxidant properties has taken a large amplitude. Free radicals concentration and the amount of antioxidants in lipids are important factors for predicting oil stability.

DPPH method for estimating the stability of edible oils can be applied to determine the antioxidant activity of fat-soluble compounds. The objective of this study is to compare the thermal oxidative stability of sunflower oil, corn oil, grape seed oil, extra virgin olive oil and coconut oil.

2. Experimental

The oils used in this study were purchased commercially (Kaufland store Suceava) and herbal pharmacies inside this store: Sunflower oil from "Unisol" valid until 11.07.2013, corn oil for frying, valid until 07.25.2013, extra virgin olive oil obtained by cold pressing from "Solaris" valid until 10.16.2014, grape seed oil, packed in sleeves, available until March 2014, walnut Oil packed in Manic, validity until March 2014.

The reagents used for chemical determinations were analytically pure reagents and laboratory equipment used belongs to the Faculty of Food Engineering Suceava: oven spectrophotometer Ocean Optics fiber optic, laboratory utensils.

The oils were stored in an oven for 5 days at a temperature of 50 ° C, in the presence of light and atmospheric oxygen. The methods used to determine their stability was: Titrimetric method (peroxide index, acidity) and spectrophotometric methods (antioxidant capacity, DPPH method).

2.1. Determination of antioxidant activity of oils by spectrophotometric method DPPH (2,2-diphenyl-1-picrilhidrazil)

DPPH is one of the most stable organic radicals and commercially available and has a maximum absorption of 515 nm in the VIS. When the solution is discolored and reduced forward, the reaction is monitored spectrophotometrically (spectrophotometer Ocean Optics). In this way we can evaluate the antioxidant capacity of a system.

Inhibition % = 100 - [(A_{t5}/ A_{t0}) * 100

In which:

A_{t0} - DPPH is the absorbance at t = 0 min.

A_{t5} - is the absorbance of DPPH + oil sample after t = 5 min.

Titration methods for the determination of peroxide value and acidity were compliant with the standards in force.

2.2. Determination of peroxide-standard SR EN ISO 3960/2009

Reagents and tools required: -Bottles of 250 ml dry glass stopper, Chloroform, Glacial aceticmacid,KI, saturated ,$Na_2S_2O_3$ solution, 0.1 N

Starch 1% solution Mode: More than ~ 5 g of an oil, weighing analytical balance, was added 12 ml of chloroform, 18 ml of glacial acetic acid and 1 ml of KI, saturated. Close the bottle, shake 1 minute, allow to stand 15 minutes, then add 30 ml distilled water.

In parallel is prepared the blank. Titrate the liberated I_2 with sodium thiosulfate solution, 0.1 N, in the presence of starch as an indicator. Calculations and interpretation of results:

$$I.P= \frac{(V_1 - V_2)\cdot n}{m} \cdot 1000 \text{ (meq/kg)}$$

m-mass of the sample (g)

V_1- volume $Na_2S_2O_3$ (sample)

V_2- volume $Na_2S_2O_3$ (blank)

2.3. Determination of acidity oil according to NF ISO 660-1999

Mode: Over ~ 5g sample plus solvent is titrated with KOH solution in the presence of phenolphthalein as indicator.

Principle of the method: free fatty acids contained in a known volume of oil are titrated with alcoholic KOH solution of known concentration, using phenolphthalein as an indicator. 56.11 - the number of mg of KOH contained in one milliliter of solution of KOH,0,1n.

n-normality of the KOH V, the amount of KOH 0.1 N used in the titration The amount of oil to be taken of the sample, g in which:n- normality of $Na_2S_2O_3$ solution

Method of calculation:

$$\text{acidity index} = 56{,}11 * n/m$$

[mgKOH / g sample]

Titratable acidity: 0.1% -0.4% admitted values expressed as oleic acid. Acid value is twice acidity.

Table 1. Results from initial samples

Type of oil	Acidity (%)	RDS (%)	Peroxid value (meq/kg)	RDS (%)	Antioxidant activity (%)	RDS (%)
Sunflower oil	0.165	1.365	3.51	1.986	20	1.876
Corn oil	1.94	1.895	2.38	2.132	42	1.753
Extra virgin olive oil	0.61	1.257	11.34	1.587	24	2.233
Grape Seed Oil	0.28	2.008	10.24	1.180	10	1.540
Coconut Oil	18.5	1.789	19.1	1.711	49	1.999

Table 2. Results before the storage oven 5 days, 50 ° C

Type of oil	Acidity (%)	RDS (%)	Peroxid value (meq/kg)	RDS (%)	Antioxidant activity (%)	RDS (%)
Sunflower oil	0.24	1.664	8.15	1.956	10	1.567
Corn oil	2.05	1.887	3.062	1.833	12	1.775
Extra virgin olive oil	0.64	1.341	12.06	2.090	6	1.980
Grape Seed Oil	0.5	2.213	11.9	1.893	4	1.342
Coconut Oil	19.2	1.891	20.3	1.333	15	2.099

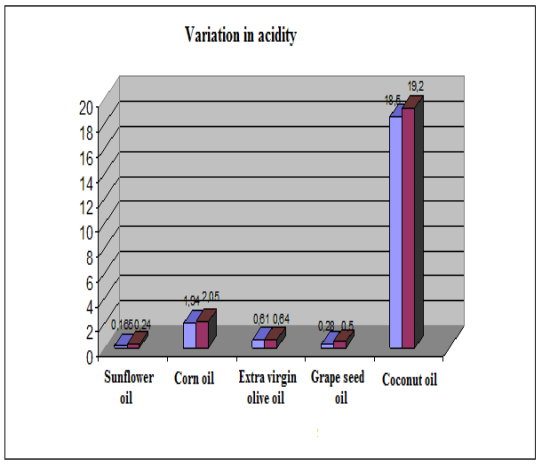

Fig. 1. Variation in acidity

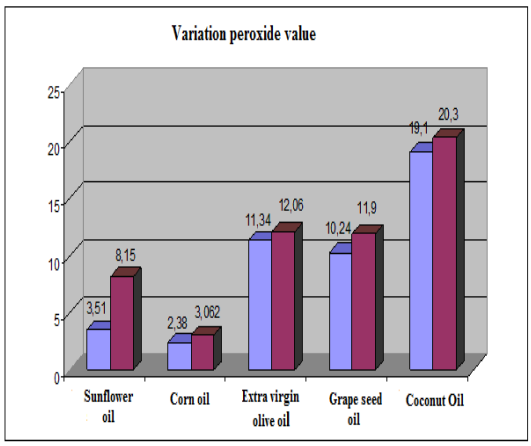

Fig. 2. Variation peroxide value

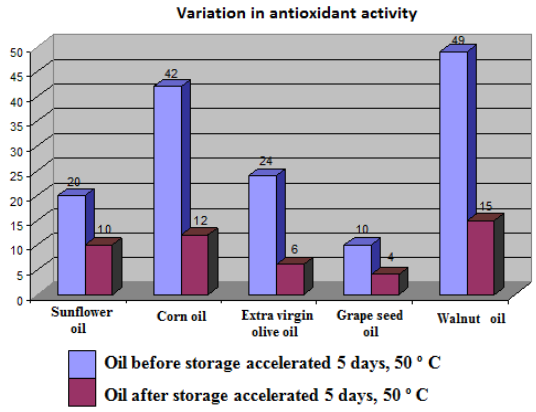

Fig. 3. Variation in antioxidant activity

3. Results and Discussion

The presence of natural antioxidant (polyphenols, tocopherols, vitamin C) in vegetable oils like sunflower oil, corn oil, olive oil, grape seed oil and walnut, influenced changes in the Peroxide and thus free acidity. Table 1 and Table 2 contain the results of peroxide value, free acidity and antioxidant activity of the oils, before and after accelerated storage for 5 days at 50 º C in an oven.

For the sunflower oil the peroxide value increased after accelerated storage by 132% from 3.51 eq / kg 8.15 eq / kg, titratable acidity rose with 45.45% from 0.165% to 0.24 %, and the antioxidant activity decreased due to the influence of light and heat by 50%, from 20% to 10%. Corn oil and peroxide changed to 41.26% from 2.38 eq / kg 3062 eq / kg, a free acidity increased by 5.67% from 1.94% to 2.05%, and the antioxidant activity decreased by 71.42%, from 42% to 12%.

Extra virgin olive oil has modified peroxide value with 6.34% from 11.34 meq / kg 12.06 meq / kg, free acidity increased with 4.91% from 0.61% to 0, 64%, and the antioxidant activity decreased by 75%, from 24% to 6%.

Grape seed oil has modified peroxide value with 16.21% from 10.24 meq / kg to 11.9 meq / kg, free acidity increased with 78.57% from 0.28% to 0,5%, and the antioxidant activity decreased by 60% from 10% to 4%.

Coconut oil has modified peroxide value with 6.28% from 19.1 meq / kg to 20.3 meq / kg, free acidity increased from 3.78% to 18.5% at 19 2% and the antioxidant activity decreased by 69.38% from 49% to 15%.

4. Conclusion

Deterioration resulting from oxidative processes that take place in the seed, in the course of manufacturing steps, as well as during storage, reduces the nutritional value of the oil and results in additional losses relating to the need for their reconditioning. Edible oils with higher content of unsaturated fatty acids, especially polyunsaturated fatty acids are more susceptible to oxidation. Lipid oxidation of oils can produce not only rancid odors, flavors and color changes, but it can also reduce the quality of nutritional values and safety due to the degradation of the products, with harmful effects on human health.

As a result of the oxidative degradation appears the taste of "rancid" due to the presence of secondary compounds found in very small amounts, usually less than 0.1% and sometimes up to 1%.

Of the oils analyzed, the walnut oil has the highest antioxidant capacity and the best chemical stability. It follow olive oil, grape seed oil, corn oil, sunflower oil, order that reflects their chemical composition and they recommended to be used.

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