ANTIRADICAL ACTIVITY OF VEGETABLE OILS

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Abstract

This research presents the antiradical activity and fatty acids changes of vegetable oils. Natural antiradical activity and its changes during storage for one and two years of rapeseed, linseed and hemp oils were determined with 1.1-diphenyl-2-picrylhydrazyl (DPPH). Fresh hemp oil show the higher antiradical activity.

The content of fatty acids of fresh rapeseed, linseed and hemp oils and of the mixture of rapeseed (800 g kg^{-1}) and linseed (200 g kg^{-1}) oils was determined by the method of gas chromatography. After heating the mixture of rapeseed and linseed oils at the temperature of 160-180 °C, changes proportions in saturated and unsaturated fatty acids.

Key words: antiradical activity, fatty acids, vegetable oil, gas chromatography.

Introduction

The content of many widely used oils incompletely matches the needs of food scientists. Often these oils contain insufficient amount of essential polyunsaturated fatty acids (Bluka et al., 2004). During the last years, usage of polyunsaturated oils has increased due to prophylaxis of heart and blood vessel diseases. Therefore it is important to develop production of such oils as linseed, hemp, soy, mustard, corn, and peanut, because they are rich with essential fatty acids. Choise of oils in food market is, supplemented with oils produced in Latvia: linseed oil and hemp oil – oils previously used rarely. These oils contain a significant amount of essential fatty acids (Vucāne et al., 2004)

Polyunsaturated oils easily undergoe oxidation making hydroperoxide. Peroxidation of oils not only lowers the nutritional quality of food, but it is also associated with aging, membrane damage, heart diseases, stroke, emphysema and cancer in living organisms (Abulude et al., 2005). The addition of antioxidants is effective in retaining the oxidation of fats. It is impressive that many substances have been identified that prevent peroxidation of lipids. Some of these componds are synthetic antioxidants, and others occur as natural dietary constituents (Wagner et al., 2000).

Vegetable oils contain tocopheroles with various oxidative and vitamin activity. γ- and σ-tocopheroles have the highest antioxidative activity (Brand-Williams et al., 1995). For example, linseeds contain 0.45 mg kg^{-1} of σ-tocopherole and 29.70 mg kg^{-1} of γ-tocopherole. It means that vegetable oils have their own antioxidative activity. 1.2-diphenil-2-picrylhydrazyl (DPPH) can be used as a free radical to evaluate antioxidative activity of natural oils (Osakada et al., 2004; Tang et al., 2005).

The tasks of this investigation are:

- Compare antiradical activity of different vegetable oils;
- To clarify the content of fatty acids of different vegetable oils;
- Derive oil mixture from 80% rapseed and 20%

Table 1

Samples of vegetable oils (produced in 'Iecavnieks' Ltd)

Code of Vegetable oils	Vegetable oils	Type of oil
A	Hemp oil	cold pressed, fresh
B	Hemp oil	cold pressed, one-year-old
C	Hemp oil	cold pressed, two-year-old
D	Linsed oil	cold pressed, fresh
E	Linsed oil	cold pressed, one-year-old
F	Linsed oil	cold pressed, two-year-old
G	Rapeseed oil	cold pressed, fresh
H	Rapeseed oil	cold pressed, one-year-old
I	Mixture of rapeseed 80% and linseed 20% oil	cold pressed, fresh
J	Mixture of rapeseed 80% and linseed 20% oil	after 4 h heating
K	Mixture of rapeseed 80% and linseed 20% oil	after 8 h heating

linseed oils and determined by the method of gas chromatography fatty acids, too after heating at the temperature of 160-180 °C.

Materials and Methods

The obtained samples of vegetable oils are summarized in Table 1. The oil samples were stored at temperature 4±2 °C.

To increase the content of essential polyunsaturated fatty acids in rapeseed oil, a mixture of fresh rapeseed oil (80%) and fresh linseed oil (20%) was made.

Samples of this mixture were heated at the temperature of 160-180 °C for 4 and 8 hours.

1.1-diphenyl-2-picrylhydrazyl (DPPH) is a stable radical which reacts with hydrogen donors creating 1.1-diphenyl-2-picrylhydrazil. Absorption of about 517 nm is typical for DPPH radicals. Reducing maximum of DPPH the absorption decreases. The antiradical activity of plant oils will be defined after decrease of DPPH absorption in the specified time period.

To define the antiradical activity, the following solution is prepared, 0.00394 g ($1 \cdot 10^{-4}$ M).

DPPH dissolved in 100 mL of 96% ethanol solution, while stirring with magnetic mixer for 4 hours. 0.1 mL of vegetable oil were added to 2.9 mL $1 \cdot 10^{-4}$ M of DPPH ethanol solution. Solution was stirred and thermostated at the temperature of 37 °C. After 30 minutes, absorption was measured at 517 nm (Jenwey 6405 UV/Vis. Spectrophotometer). Then the control was established, namely, 0.1 mL of ethanol were added to 2.9 mL of DPPH ethanol solution and the absorption was read. The obtained measurements are used in calculation of antiradical activity.

Take 0.1 mL of vegetable oil with a pipette and pour into a test-glass, then add 2.9 mL DPPH solution.

The solution was stired and placed in a thermostat for 30 min. at the temperature of 37 °C; absorption was measured at 517 nm.

The antiradical activity of the vegetable oil sample was determined by decrease of DPPH absorption in the specified time period.

The antiradical activity (hereafter ARA) is expressed in percents, how DPPH reacted with vegetable oils:

$$ARA,\% = \frac{(A_{control} - A_{sample})}{(A_{control} - A_{background})} \cdot 100, \quad (1)$$

where

$A_{control}$ - DPPH with ethanol which has reacted in 30 min.;
A_{sample} - DPPH with ethanol which has reacted in 30 min.;
$A_{background}$ - constant 0.09.

Vegetable oils were researched with the method of gas chromatography by LVS EN ISO 5508:1995 in seminal of plants from Latvia flax, hemp, and rapeseed (ISO 5508, 1995).

The content of fatty acids was determined in oil samples by the method of gas chromatography (Shimadzu GC -17A, 2003) with flame ionization detector (FID), column AT-Wax, 50 m, internal diameter-0.25 mm, thickness of immobile phase-0.2 µm.

Each measuring was carried out several times and

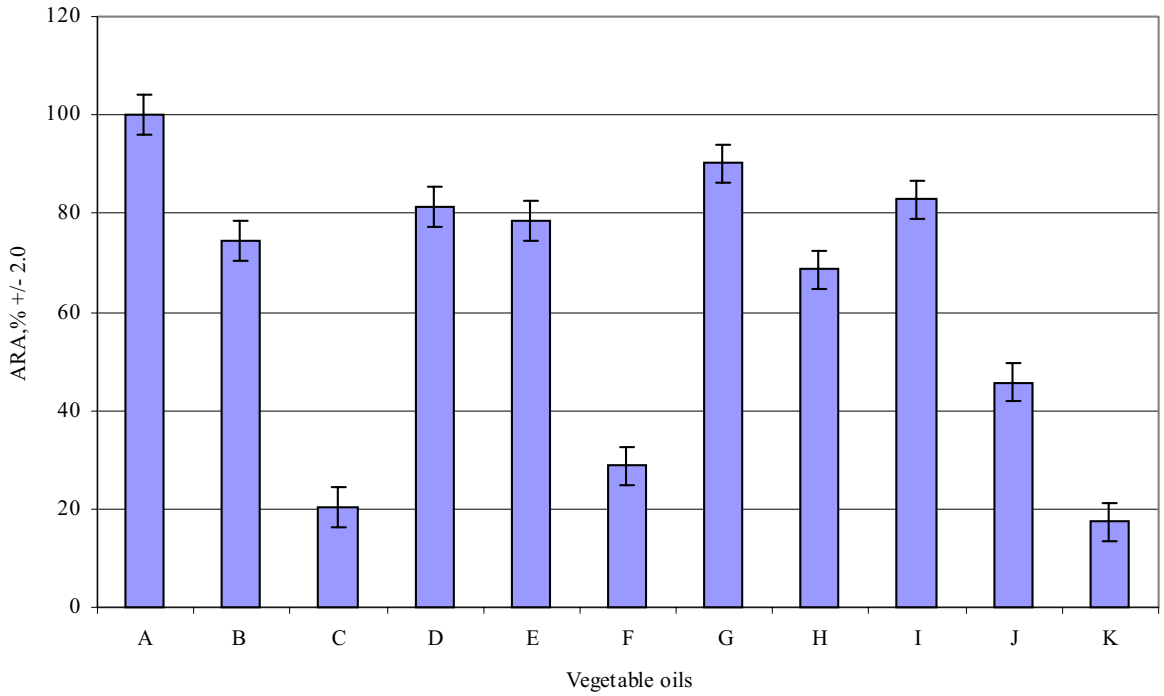

Figure 1. The antiradical activity of vegetable oils.

Table 2

The content of fatty acids in fresh vegetable oils

Fatty acids	Rapeseed oil, % ± 2.0	Linseed oil, % ± 2.0	Hemp oil, % ± 2.0
Myristic C 14:0	-	-	0.25
Palmitic C 16:0	3.84	4.41	10.58
Stearic C 18:0	1.87	3.02	2.30
Oleic C 18:1(9)	60.83	20.42	25.24
Linoleic C 18:2(9,12)	20.98	16.63	43.77
Linolenic C 18:3(9,12,15)	10.33	55.09	17.37
Arachidic C 20:0	0.59	0.14	0.25
Gondoic C 20:1	1.21	0.29	0.24
Behenic C 22:0	0.06	-	-
Erucic C 22:1(13)	0.07	-	-
Other fatty acids	0.12	-	-

then the simple average was calculated.

The data were analyzed statistically by using SPSS for Windows, MS Excel.

Results and Discussion

The results of antiradical activity are summarized in Figure 1.

During storage of oils at the temperature of 4±2 °C for one and two years, antiradical activity of hemp oil decreased correspondingly 1.3 and 4.9 times, of linseed oil-1.0 to 2.8 times, of rapeseed oil after one year storage-1.3 times.

Vegetable oils contain natural antioxidants, but in figure 1 can see that was been oxidative degradation (autooxidation). This autooxidation may be initiated by various agents, such as light, temperature, especially, air oxygen. At the presence of oxygen side products are formed which decreased the quality of oils.

Lipid peroxidation is a free-radical chain reaction process which occurs during autoxidation of unsaturated fatty acids of lipids.

By the method of gas chromatography, fatty acids of rapeseed, linseed, and hemp oil were identified, and their content is shown in Table 2.

The common content of unsaturated fatty acids in linseed oil is 92.43%, in hemp oil – 86.62%, but the content of

Table 3

The content of fatty acids in vegetable oils mixture before and after heating

Fatty acids	Mixture of oils before heating, % ± 2.0	Mixture of oil after 4 h heating, % ± 2.0	Mixture of oil after 8 h heating, % ± 2.0
Myristic C 14:0	-	0.05	-
Palmitic C 16:0	3.01	3.21	4.56
Stearic C 18:0	1.89	1.95	2.09
Oleic C 18:1(9)	52.74	52.51	49.32
Linoleic C 18:2(9,12)	20.22	20.19	18.68
Linolenic C 18:3(9,12,15)	20.51	20.27	20.19
Arachidic C 20:0	0.50	0.49	0.41
Gondoic C 20:1	1.02	1.06	4.75
Behenic C 22:0	0.04	0.27	-
Erucic C 22:1(13)	0.02	-	-
Other fatty acids	0.05	-	-

Table 4

Changes in the proportion of saturated and unsaturated fatty acids in rapeseed and linseed oils mixture after 4 hours and 8 hours of heating at the temperature of 160-180 °C

Vegetable oil samples	SFA : USFA *	USFA decrease , %
Mixture of oils before heating, %	1 : 17.24	-
Mixture of oils after 4 h heating, %	1 : 15.75	8.64
Mixture of oils after 8 h heating, %	1 : 13.16	16.44

**SFA – saturated fatty acid, USFA – unsatured fatty acid*

polyunsaturated fatty acids in linseed oil – 71.72%, in hemp oil – 61.14%. So both oils belong to polyunsaturated fats in contrast to rapeseed oils which belong to monounsaturated fats due to the high content of oleic acids – 60.90% accordingly.

Linseed oil is rich of linolenic acid 55.09% which is essential fatty acids for human being. The unsaturated fatty acids are very important for our immune system and help us regulate our blood pressure.

By the method of gas chromatography, fatty acids of rapeseed and linseed oils mixture were identified and their content is shown in Table 3.

In the mixture of rapeseed and linseed oils, the content of polyunsaturated fatty acids increased. For example, the content of linolenic acid increased 2 times compared to its content in rapeseed oil (Tables 2 and 3).

Using the obtained results, it was calculated how the proportion of saturated and unsaturated fatty acids in linseed oil was changing in the process of heating. The results of calculations are summarized in Table 4.

After heating the mixture of rapeseed and linseed oils at the temperature of 160-180 °C for 4 and 8 hours, the content of unsaturated fatty acids decrease. This indicates serious changes-cleavage processes-in the molecules of unsaturated fatty acids.

The greater the degree of unsaturation in a fatty acid (the more double bonds in the fatty acid), the more vulnerable it is to lipid peroxidation (rancidity).

Table 3 and 4 shows that unsaturated fatty acids of lipids during heating was been peroxidation, what decreased the quality of vegetable oil.

Conclusions

The obtained fresh rapeseed, hemp and linseed oils demonstrate the highest antiradical activity, so proving that they contain total natural antioxidants.

During storage of oils at the temperature of 4±2 °C for one and two years, antiradical activity of hemp oil decreases correspondingly 1.3 and 4.9 times, of linseed oil-1.0 to 2.8 times, of rapeseed oil after one year storage-1.3 times.

The common content of unsaturated fatty acids in linseed oil is 91.17%, in hemp oil – 86.62%, but the content of polyunsaturated fatty acids in linseed oil – 71.72%, in hemp oil – 61.14%.

After heating the mixture of rapeseed and linseed oils at the temperature of 160-180 °C for 4 and 8 hours, the content of unsaturated fatty acids decreases. This indicates serious changes-cleavage processes-in unsaturated fatty acids molecules.

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