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EFFECT OF LIGHT ON THE KINETICS OF OXIDATION REACTIONS IN VEGETABLE OILS

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Abstract. The article deals with the effect the lighting conditions of storage have on the oxidation stability of vegetable oils of various unsaturation degrees and made by different technologies (raw-pressed and unrefined sunflower oil and flaxseed oil) according to the main oxidation parameters: peroxide value (PV), acid value (AV), and colour value. It has been experimentally established that in natural lighting, at the end of the shelf life, the PV of flaxseed oil increased most significantly, from $0.55 \cdot 10^{-3}$ to $11.2 \cdot 10^{-3}$ mmolO_2/kg (20 times). The PV of sunflower oils varied less: in unrefined oil, it changed from $0.48 \cdot 10^{-3}$ to $4.5 \cdot 10^{-3}$ mmolO_2/kg (9 times), in raw-pressed, from $0.3 \cdot 10^{-3}$ to $4.4 \cdot 10^{-3}$ mmolO_2/kg (14.7 times). Under artificial UV radiation, the PV of sunflower oil increased from 0.3 to 0.55 mmol O_2/kg after 2 hours of the experiment, and remained practically unchanged. In the case of flaxseed oil, after a slight increase from 0.55 to 0.7 mmol O_2/kg, within the same period of time, there was then a decrease in the PV to 0.45 mmol O_2/kg, which may indicate a relative instability of hydroperoxides that, due to their degradation, converted into more stable secondary compounds. The analysis of the oil oxidation kinetics by the PV has shown that the average rates of peroxide compounds accumulation in unrefined, raw-pressed, and flaxseed oils was $47 \cdot 10^{-4}$, $48 \cdot 10^{-4}$, $127 \cdot 10^{-4}$ mmol ½O/kg·hour, respectively. At the same time, under natural light, the true rate of change of the AV in the oils studied was uneven over time. At the beginning of the experiment, it increased (especially noticeably in the case of flaxseed oil), at the end of the shelf life (the 5th week), it was slowed down significantly, decreasing to negative values, and in flaxseed oil, it had zero value, which indicates a constant value of AV in the experimental setting.

Key words: vegetable oils, sunflower unrefined oil, sunflower raw-pressed oil, flaxseed oil, kinetics of oxidation reactions.

Introduction. Formulation of the problem

Vegetable oils are a valuable source of high-calorie fats and essential fatty acids, phospholipids, carotenoids, natural antioxidants, and other physiologically active substances presented in different qualitative and quantitative proportions, depending on the type of oil and on the production technology.

The main value in creating such products is to study the processes of oils oxidation, which will minimize the oxidation process itself and develop adequate criteria for quality control, storage conditions, shelf life.

Analysis of recent research and publications

The current concept of healthy nutrition involves a reduced proportion of saturated fats and fried food in the diet, and making up for the deficit of omega-3 acids by consuming sea fish, nuts, and flaxseed oil. However, the prevalence of valuable polyunsaturated fatty acids in flaxseed oil leads to its rapid oxidation. Creation of mixtures of oxystable vegetable oils (olive, sunflower) with flaxseed oil can significantly increase the consumer properties and shelf life of this product. In addition, the development of oxygen-stable mixtures of vegetable oils is a promising way of producing safe and wholesome food products [1-4].

The process of oxidation of vegetable oils is influenced by many factors at the same time. So far, the well-studied mechanisms are those of auto-oxidation and photosensitized oxidation of vegetable oils [5-12], and chemical mechanisms of thermal oxidation [13-15]. A number of studies describe how oil oxidation depends on fatty acid composition [16-19], the conditions of production [20-24], transition metals [25,26], phospholipids, chlorophylls [27-31]. Besides, the mechanism of action of antioxidants has been described [32-38].

However, there remains an important problem of studying high oxidation susceptibility of the linolenic group of oils, of researching the oxidation kinetics in vegetable oils with various unsaturation degrees, and of establishing the dependence of the oil oxidation rate on a number of factors in the course of manufacturing oil and storing the final product.

In this regard, in our research, we find it practical to pay more attention to determining the kinetic parameters of the oxidation reactions induced by the lighting conditions of production and conservation of vegetable oils.

The purpose of this paper is to study the effect of lighting conditions of storage on the oxidation stability of vegetable oils with various degrees of unsaturation and made by different technologies.

Tasks of the research.

1. To study the patterns of oxidation of vegetable oils with various degrees of unsaturation and made by different technologies (raw-pressed and unrefined sunflower oil, and flaxseed oil), according to the main parameters of oxidation: peroxide value (PV), acid value (AV), colour value.
2. To study the kinetics of model oxidation in vegetable oils with various degrees of unsaturation and made by different technologies (raw-pressed and unrefined sunflower oil, and flaxseed oil), according to the main parameters of oxidation: peroxide value (PV), acid value (AV), colour value.
3. To establish the dependence of the oxidation rate of oil on sunlight and develop the recommendations for the storage conditions.
4. To evaluate the changes in the nutritional properties of the oils in the process of oxidation and develop the requirements for the terms and conditions of their storage.

Research materials and methods

The research was done using unrefined, winterized, pressed sunflower oil “Oleina” produced by “Dnipropetrovsk Oil Extraction Plant” PJSC, 2018; unrefined, raw-pressed sunflower oil of the first cold pressing by the Private Production Enterprise “Alex Trade Oil” in the Dnipropetrovsk region, 2018; unfiltered flaxseed oil of the first cold pressing by LLC “TK EKOOIL,” Kyiv, 2018.

The fatty acid composition of sunflower and linseed oil is given in Table 1.

Table 1 – Fatty acid composition of vegetable oils and their vitamin E content

The main fatty acids and vitamin E	**% to the amount of fatty acids**	
	Flaxseed oil	Traditional sunflower oil
Palmitic	5.0	6.1
Stearic	3.0	3.9
Oleic	17.3	25.6
Linolic	24.4	63.0
Linoleic	49.8	-
Vitamin E	mg/100 g	
Total amount of tocopherols	23	40–70

An organoleptic analysis of the nutritional quality of the oils was carried out by their transparency, taste, and aroma (DSTU 4492:2005. Oliya sonyashnikova. Tehnichni umovi; DSTU ISO 150-2002.Oliia lliana syra, rafinovana).

The physicochemical quality parameters of the oils under study were characterized by the determined indicators of the colour (DSTU 4492:2005. Oliya sonyashnikova. Tehnichni umovi; DSTU ISO 150-2002.Oliia lliana syra, rafinovana) peroxide (DSTU 4570:2006. Zhyry roslynni ta olii. Metod vyznachennia peroksydnoho chysla) and acid (DSTU 4350:2004. Olii. Metody vyznachennia kyslotnoho chysla) values.

To study the regularities of the kinetics of oil oxidation under the influence of light at room temperature, experiments were conducted in which the oil samples were irradiated with artificial UV light (the duration of the experiment was 4 hours), as well as in the conditions of natural lighting, and in its absence (the duration of the experiment was 5 weeks).

Experiments to study the kinetics of oxidation under artificial UV light were performed in the following way: 30 cm^3 of the oil sample in a glass without a lid was placed in a sealed light-proof chamber and irradiated from above with an LED matrix *Foton UF-LED* with a wavelength of 310 nm. Samples for analysis were taken after one hour.

Experiments to study the kinetics of oxidation in natural lighting and in its absence were carried out as follows: the oil samples were placed in 200 cm^3 glass jars and stored at room temperature in direct sunlight (or in its absence); samples for analysis were taken at the end of each week.

The kinetic parameters of the oxidation reactions were characterized by changes in the peroxide and acid values during the experiment, and by the average and true reaction rates calculated using these values.

The rate of oxidation reactions of the oils under study by the peroxide and acid values (fat value) was calculated as follows:

1. The average oxidation rate during the whole experiment (V_{av})

$$V_{av} = C_{beg} - C_{end}./t_{exp}, \quad (1)$$

where C_{beg} is the fat value at the beginning of the experiment;

C_{end} is the fat value at the end of the experiment;

t_{exp} is the time of the experiment, one hour.

2. The true oxidation rate (V_{tr}) was calculated according to the changes in the fat value between two adjacent points (n_1, n_2) per one unit of time (t)

$$V_{tr} = Cn_1 - Cn_2/t \quad (2)$$

where Cn_1 is the value of the parameter at the sampling point;

Cn_2 is the value of the parameter at the previous sampling point;

t is the interval between the samplings at the points n1 and n2, one hour.

Results of the research and their discussion

Organoleptic characteristics of the food quality of vegetable oils. To assess the main food quality parameters of the oil (transparency, taste, and aroma), 6 descriptors were selected, by which the organoleptic profiles of the studied oils were created at the beginning and at the end of their storage in the conditions of natural lighting and without it.

At the beginning of the experiment, all the oils complied with the quality characteristics of quality oils (Fig. 1). They were transparent enough, with a characteristic rich taste and aroma of a fresh product. At the end of the experiment (5 weeks), all the oils had a strong rancid taste, reduced transparency, and the smell of old fat appeared (Fig. 2).

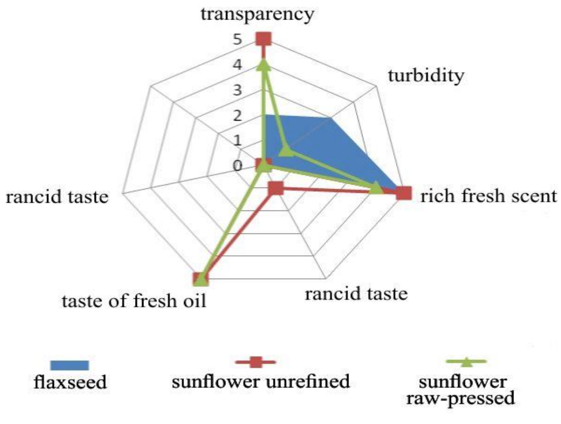

Fig. 1. Organoleptic profile of the oils at the beginning of the experiment

The organoleptic characteristics of the studied oils stored throughout the experiment without the access of light (5 weeks) showed an unchanged taste and the aroma of a fresh product.

To assess the effect of the lighting on the quality of vegetable oils, the colour value was chosen as the physical parameter.

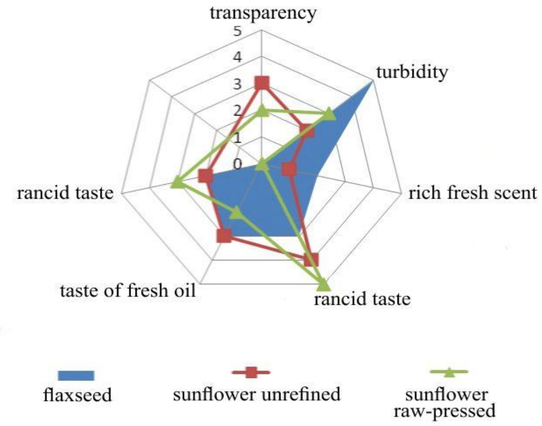

Fig. 2. Organoleptic profile of the oils at the end of the experiment

Dynamics of changes in the physical characteristic of quality during the experiment. Pigments contained in the seeds and fruits of oilseeds give different colours to vegetable oils. Red and yellow shades in the colour of oils are determined by the presence of carotenoids (a red tint is due to carotene, a yellow one due to xanthophyllum) [33].

Chlorophylls and products of their decomposition, pheophytins and pheophorbids, act as sensitizers forming $^1O_2$ in the presence of light and atmospheric oxygen and, thus, accelerate the oxidation of oil. Pheophytins have a higher sensitizing activity than chlorophylls, but lower than pheophorbids [39,40].

And although chlorophylls are strong prooxidants in the presence of light. They act as sensitizers in the process of generating singlet oxygen. In the dark, they exhibit antioxidant properties, possibly due to the transfer of hydrogen to free radicals [41, 42].

In conditions of natural lighting, the colour values presented in Table 2 increased: in the raw-pressed sunflower oil it increased 1.3 times, in the unrefined oil, 1.3 times, in the flaxseed oil, 1.2 times. Reduction in the colour value is due to oxidation of carotenoids by light. When the oil was stored with no light, this parameter did not change.

Table 2 – Dynamics of change in the colour value of oils during the experiment

Kind of oil	Colour value, mg I/100cm³			
	Natural light		No access of light	
	I week	V week	I week	V week
Unrefined sunflower oil	15	12	15	15
Raw-pressed sunflower oil	20	15	20	20
Flaxseed oil	12	10	12	12

Chemical parameters of oil quality. To assess the effect of the lighting conditions on the oxidation stability of the studied vegetable oils, experiments were carried out during which the oil samples were irradiated with light of different wavelengths. The oils were observed in artificial UV light (wavelength 310 nm), in natural lighting, and in its absence. The kinetic parameters of oxidation reactions were characterized by changes in the peroxide and acid values during the experiment.

During the storage of vegetable oils in natural light, their peroxide value (PV) was monotonously increasing for 3 weeks of storage, and then there was a sharp increase in this parameter until as late as the 5th week of the experiment (Fig. 3).

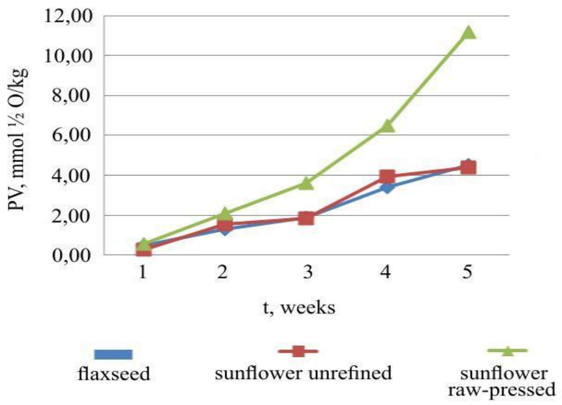

Fig. 3. Changes in the PV of the oils during their storage in natural lighting

In the flaxseed oil, the PV increased the most significantly, from 0.55 to 11.2 mmol ½ O/kg (20 times). The PV of the sunflower oil varied less: in the unrefined oil, it changed from 0.48 to 4.5 mmol ½ O/kg (9 times), in the raw-pressed oil, from 0.3 to 4.4 mmol ½ O/kg (14.7 times). At the same time, storage of all the studied oils without access of light led to a slight decrease in the PV, as shown in Table 3. It can be assumed that a slight decrease in PV in these conditions is explained by the action of natural antioxidants in oils and chlorophyll that also shows its antioxidant properties in the dark. The nature of the accumulation of peroxides in the first hours of exposure to artificial UV was different in the oils studied (Fig. 4).

Thus, in the sunflower oil, the PV increased by an average of 3 to 5.5 mmol ½ O/kg in 2 hours of the experiment and remained practically unchanged. With the flaxseed oil, after a slight increase from 0.55 to 0.7 mmol ½ O/kg within the same time, there was a further decrease in the PV up to 0.45 mmol ½ O/kg. This may indicate a relative instability of hydroperoxides that converted into more stable secondary compounds due to destruction. Within the same time (during the first 4 hours of the experiment) of being under natural light, the PV of all the oils tested remained practically unchanged. The results obtained confirm a more significant effect of shortwave (UV) radiation on the oxidative processes, compared to that of longwave radiation.

The (true) rate of accumulation of peroxides was uneven over time, and during the storage, there were a series of maxima and minima (Fig. 5). The presence of maxima at the beginning of oxidation (the 1st week of the experiment) indicates the free-radical nature of oil oxidation. The highest rate of accumulation of peroxides was observed for the flaxseed oil.

Table 3 – Dynamics of changes in the PV of the oils during storage without access of light

Kind of oil	Parameter PV, mmol ½ O/kg	
	1st week	5th week
Unrefined sunflower oil	0.48±0.07	0.25±0.06
Raw-pressed sunflower oil	0.30±0.03	0.20±0.05
Flaxseed oil	0.55±0.12	0.50±0.06

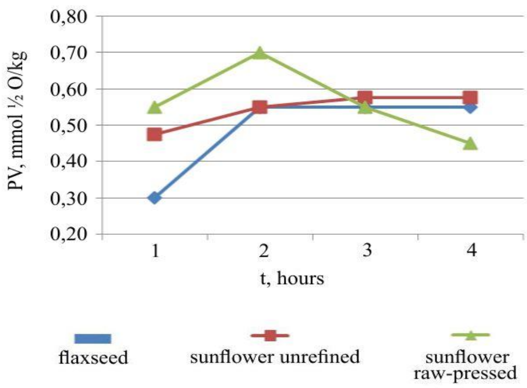

Fig. 4. Changes in the PV during artificial UV irradiation

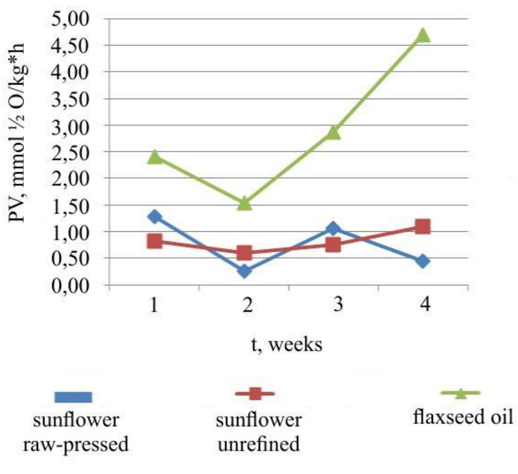

Fig. 5. The rate of changes in the PV during storage of the oil in sunlight

To calculate the true rate of changes in the PV in the fifth week of the experiment, it is necessary to have data for the sixth week (see the formula for calculating the true rate in the section *Research materials and methods*); however, the duration of our experiment was 5 weeks, so in the figure, the results of the true rate of changes in the PV can be presented only for four weeks.

Peroxides, being unstable primary products of fat oxidation, easily form new radicals or stable secondary products of oxidation. The rate of these processes is determined by the type of fatty acids or acylglycerols and is higher the more unsaturated fatty acids are included in the oil. Analysis of the kinetics of oil oxidation by the average rates of PV changes has shown that by the end of the experiment (5 weeks), the average rates of accumulation of peroxide compounds in the unrefined, raw-pressed, and flaxseed oils was, respectively, $47*10^{-4}$, $48*10^{-4}$, $127*10^{-4}$ mmol ½O/kg*hour. The highest rate of accumulation of peroxide compounds in the flaxseed oil may be explained by a traditionally high content of unsaturated fatty acids.

The acid value in the studied sunflower oils in natural lighting increased in the first 3 weeks of storage, growing 1.6 times on average; and then this index decreased, falling, on average, 1.3 times in the fifth week of the experiment (Table 4). Under these conditions, the acid value of the flaxseed oil increased 2.8 times and remained stable during the fourth and fifth weeks of the experiment. Storage of vegetable oils in a dark room resulted in almost no change in their AVs which are presented in Table 5. The (true) rate of accumulation of free fatty acids in the studied oils in natural lighting was uneven over time (Table 6).

Table 4 – AV of the oils stored in natural lighting, mgKOH/g

Kind of oil	AV, mgKOH/g				
	1st week	2nd week	3rd week	4th week	5th week
Unrefined sunflower oil	0.71± 0.087	0.95± 0.16	2.0± 0.18	2.0± 0.19	1.37± 0.08
Raw-pressed sunflower oil	1.29± 0.3	1.61± 0.13	2.27± 0.2	2.3± 0.2	1.82± 0.17
Flaxseed oil	0.94± 0.1	1.5±0.1 2	2.6±0. 2	2.7±0. 2	2.7±0. 2

Table 5 – AV of the oils stored without access of light, mg KOH/g

Kind of oil	AV, мg KOH/g	
	1st week	5th week
Unrefined sunflower oil	0.71± 0.10	0.66±0.09
Raw-pressed sunflower oil	1.29±0.5	1.31±0.7
Flaxseed oil	0.94±0.1	0.94±0.1

At the beginning of the experiment, it grew especially noticeably in the flaxseed oil. Thus, in the first week, the true rate of free fatty acid accumulation in the unrefined, raw-pressed, and flaxseed oils was 13.9, 19.34, 33.3, respectively.

At the end of the storage period (5th week), after storage in natural lighting, the true rate of changes in the AV in the sunflower oils was significantly inhibited, decreasing to negative values, and in the linseed oil, it was zero, which indicates the constant AV in the experimental conditions.

The AV in the studied oils remained practically unchanged during the artificial UV irradiation (Fig. 6). The largest AV increase (1.2 times) was in the linseed oil.

Table 6 – True rates (V_{tr}) of AV changes when storing the oils in natural lighting, мgKOH/g*hour

Kind of oil	$V_{tr.}*10^{-4}$ on the 1st week of storing, мgKOH/g*hour	$V_{tr.}*10^{-4}$ on the 5th week of storing, мgKOH/g*hour
Unrefined sunflower oil	13.99±3.78	-37.31±2.46
Raw-pressed sunflower oil	19.34±4.2	-27.98±2.46
Flaxseed oil	33.34± 4.7	0.00

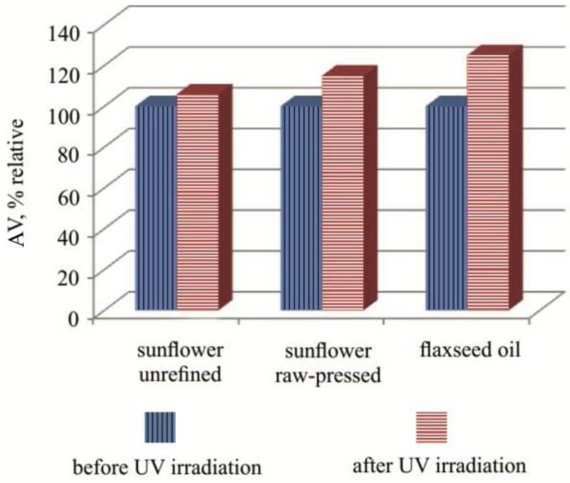

Fig. 6. AV (%, relative) during artificial UV irradiation

Thus, the results obtained indicate that vegetable oils oxidation depends both on their chemical composition and on the technology of their production as well as on the conditions of their storage. The most informative parameter of the oxidation degree of vegetable oils was the peroxide value compared with the acid value. In natural lighting, the oxidation of traditional high-linoleic sunflower oil was accompanied by accumulation and stabilization of peroxides.

The oxidation of high-linolenic flaxseed oil took place under the same lighting conditions at a much higher speed. The oxidation of oils under shortwave optical radiation has confirmed this mechanism and shown the instability of peroxides of flaxseed oil, which quickly decayed over time with formation of secondary oxidation products which can be assumed to be more stable.

It is known that the presence of antioxidants significantly increases the oxidation stability of oils. Tocopherols are natural antioxidants. Their action manifests itself in lengthening of the induction period and a decrease in the oxidation rate. This action is better performed by the isomer *a*–tocopherol which is a more active antioxidant and stabilizer of hydroperoxides. It has been found that the effect of tocopherols as antioxidants depends both on the fatty acid composition of the oils and on the isomeric composition of tocopherols. Due to a significantly higher content (by approximately 3 times) of tocopherol in sunflower oil compared to that in flaxseed oil, it can be assumed that the processes of oxidation in sunflower oil are directed towards the stabilization of hydroperoxides, whereas in linseed oil, they are directed towards the increase in their concentration. This is confirmed by a much lower increase in the PV at the end of the 5-week experiment in sunflower oil compared to flaxseed oil (growing by 2.92 and 5.95 units, respectively) and lower (approximately by 1.8 times) average rates of peroxide accumulation.

Conclusion

It has been experimentally established that the influence of the lighting conditions of storing the studied oils on their organoleptic, physical, and chemical parameters of quality depended on both their degree of unsaturation and the conditions of their storage.

Analysis of the oxidation kinetics of oils by the parameters of the PV has revealed that the average rates of peroxide compounds accumulation was proportional to their degree of unsaturation.

A feature of the dynamics of flaxseed oil oxidation, in comparison with the sunflower oil, has been identified. It is the relative instability of the hydroperoxides formed, which, as a result of degradation, are converted into more stable secondary compounds. The detected mechanism most effectively manifests itself in the conditions of shortwave radiation.

It has been experimentally proved that the optimum storage condition for oxidative stability of vegetable oils at room temperature is the absence of light.

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ВПЛИВ СВІТЛА НА КІНЕТИКУ ОКИСЛЮВАЛЬНИХ РЕАКЦІЙ РОСЛИННИХ ОЛІЙ

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Анотація. Вивчено вплив світлового режиму зберігання на окислювальну стабільність рослинних олій різного ступеню ненасиченості та технології виготовлення (соняшникової – сиродавленої та нерафінованої, льняної) за основними показниками окислення: пероксидним (ПЧ), кислотним (КЧ) та колірним числами. Експериментально встановлено, що при природному освітленні, в кінці терміну зберігання, найбільш відчутно зросло ПЧ льняної олії з $0{,}55*10^{-3}$ до $11{,}2*10^{-3}$ ммольO_2/кг (у 20 разів). ПЧ соняшникових олій змінювались менше, так у нерафінованої олії – з $0{,}48*10^{-3}$ до $4{,}5*10^{-3}$ ммольO_2/кг (у 9 разів), у сиродавленій – з $0{,}3*10^{-3}$ до $4{,}4*10^{-3}$ ммольO_2/кг (14,7 разу). При штучному УФ випромінюванні у соняшникових олій ПЧ зросло в середньому від 0. 3 до 0.55 ммоль O_2/кг за 2 години експерименту і далі залишалось практично незмінним. У випадку олії льняної, після незначного зростання від 0,55 до 0,7 ммоль O_2/кг за той же час, далі відбувалось зниження значення ПЧ до 0,45 ммоль O_2/кг, що може свідчити про відносну нестійкість гідропероксидів, які в результаті деструкції перетворюються у більш стійкі вторинні сполуки. Аналіз кінетики окиснення олій за показниками ПЧ, показав, що співвідношення середніх швидкостей накопичення пероксидних сполук у нерафінованій, сиродавленій та льняній оліях відповідно склало $47*10^{-4}$; $48*10^{-4}$; $127*10^{-4}$ ммоль

½О/кг *год**.** При природному освітленні істинна швидкість зміни КЧ у досліджуваних оліях була нерівномірною в часі. На початку експерименту вона зростала (особливо відчутно у випадку льняної олії), в кінці терміну зберігання (п'ятий тиждень) – значно гальмувалась, знижуючись до від'ємних значень, а у льняній олії вона мала нульове значення, що свідчить про незмінну величину КЧ в умовах експерименту.

Ключові слова: рослинна олія, соняшникова нерафінована олія, соняшникова сиро давлена олія, лляна олія, кінетика окиснення.

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