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EFFECT OF OXIDATION PRODUCTS AND OTHER PRECURSORS ON THE CONTENT OF 3-MCPD ESTERS AND GLYCIDOL ESTERS IN DEODORISED SUNFLOWER OIL

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Abstract. This paper investigates the effect of precursors on the formation of 3-MCPD esters (3-MCPD-E) and glycidol esters (GE) and discusses ways to reduce the concentration of these toxic esters in deodorised oils. As the content of oxidation products in sunflower oil increases, the amount of MCPD esters formed after deodorisation increases too: from 560 μg/kg (for oil with the peroxide value 1.06 mmol 1/2O/kg and the anisidine value 0.55) to 1290 μg/kg (for oil with PV=6.73 mmol 1/2O/kg and PAV=10.38). Thus, peroxides and aldehydes should be classified as the initiators of the formation of 3-MCPD-E. Accordingly, a way to reduce toxic 3-MCPD-E in deodorised oils is by preventing the formation of oxidation products during the extraction and processing of oils, or by reducing the content of oxidation products in oils before deodorisation. On the contrary, there is no correlation between the content of oxidation products and the amount of glycidol esters in deodorised oil. No relationship has been found between the content of natural antioxidants of oils, tocopherols, and the amount of 3-MCPD-E and GE. Increasing the pH of oils leads to a higher content of 3-MCPD-E resulting from deodorisation. As the number of acid groups increases, the amount of 3-MCPD-E increases too. Conversely, with bigger amounts of acid introduced into the oil, no additional quantities of glycidol esters are formed in the course of deodorisation.

Keywords: 3-MCPD esters, glycidol esters, peroxides, aldehydes, acids, antioxidants, oxidation.

Introduction. Formulation of the problem

Today, esters of 3-monochloropropane-1,2-diol (3-MCPD-E) and glycidol esters (GE) remain one of the most pressing problems of the food industry [1]. As a lot of data on their potential threat to human health have been accumulated, further research is necessary to determine why so large amounts of these esters are formed in deodorised vegetable oils – the main sources of 3-MCPD-E and GE. That is why special attention should be paid to studying the effect of oxidation on the formation of MCPD-E and GE.

Analysis of recent research and publications

Esters of 3-monochloropropane-1,2-diol (3-MCPD-E) and glycidol (GE) are a new group of toxic substances, which are fat-soluble and are formed as a result of exposing fats to high temperatures. They have the following toxic effects on the human body [1]:

– carcinogenic effect – glycidol is classified as a human carcinogen (Group 2A) [2];

– genotoxic effect – negatively affect cellular genetic material or DNA, with possible mutations;

– destructive effect on the fertile function in both males and females;

– nephrotoxicity – lead to kidney disease.

Glycidol esters in the human body break down into glycidol and fatty acids. They are also considered potential precursors of MCPD esters. That is why all these substances, though different in structure, belong to the same group of toxic pollutants. The LD_{50} value

for 3-MCPD varies, according to various studies, from 170 μg/kg to 290 μg/kg [3,4]. The introduction of a second fatty acid into the monoester 3-MCPD reduces its toxicity. Infants and young children are the most sensitive to all types of toxic effects of MCPD-E and GE (the most severe toxic effects accompanied by weight loss). This is the reason for the difference in the permissible content of these esters in products for adults and infants [5]. Recent data on the toxicity of MCPD and glycidol, as well as of their esters, have led to understanding that limiting their levels in food is an urgent issue. The European Commission in Regulation No. 1881/2006 [5] limited the content of GE in vegetable oils and fats to 1000 μg/kg and no more than 500 μg/kg when used for baby food production. For 3-MCPD esters, these values are, respectively, 1250 and 750 μg/kg. It is also allowed to produce fish oils and olive oil extracted from pomace containing up to 2500 μg/kg of 3-MCPD-E.

Esters of 3-monochloropropane-1,2-diol (3-MCPD) were isolated and identified in 1983 [6]. Esters of 3-monochloropropane-1,2-diol (3-MCPD-E) are present in food products together with esters of 2-monochloropropane-1,2-diol (2-MCPD-E) and esters of glycidol (GE) (Fig.1).

Crude oils, in particular, sunflower oil, contain almost no MCPD-E and GE [1]. The cycle of refining vegetable oils includes degumming, neutralisation (in case of chemical refining), bleaching, winterisation, and deodorisation [7]. MCPD-E and GE are formed mainly during the deodorisation process due to the high temperatures of this refining stage and as a result of other high-temperature processes where fats are involved (frying, grilling, and baking) [8]. The data accumulated by today on how conditions of deodorisation (or physical refining) affect the formation of MCPD-E and GE are summarised in Table 1.

Sunflower oil is one of the most important vegetable oils in human nutrition. In 2019–2020, 19.02 million metric tons of sunflower oil was produced [10]. Based on hundreds of results, the EFSA studies [2] established that refined sunflower oil contained, on average, 303 μg/kg of 3-MCPD esters and 218 μg/kg of 2-MCPD esters. Data from various studies on the content of 3-MCPD-E and GE in refined sunflower oil are collected in Table 2.

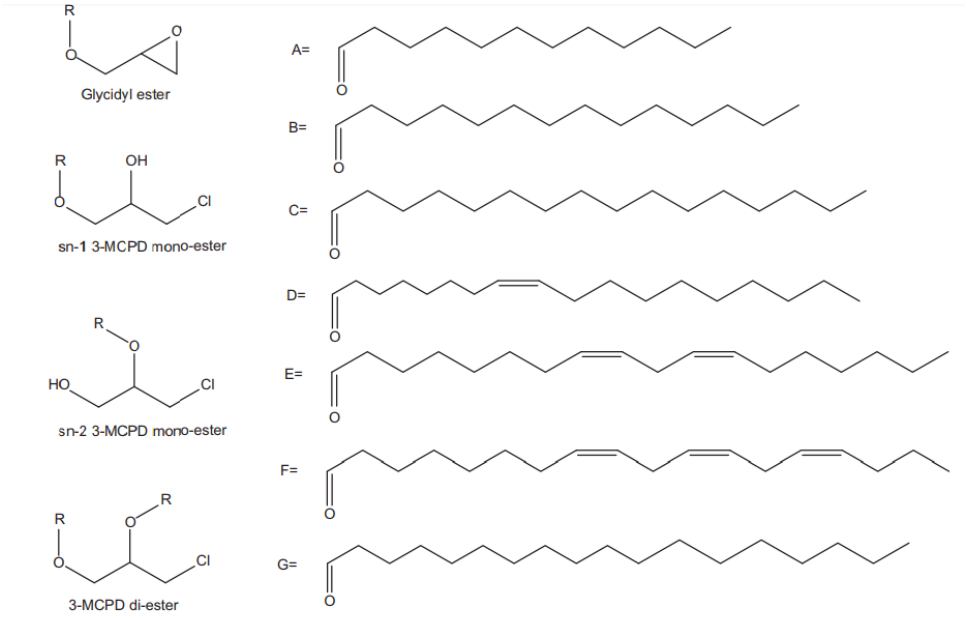

Fig. 1. Structure of esters of 2,3-MCPD and glycidol

Table 1 – Technological parameters affecting the formation of 3-MCPD-E and GE. Adapted from [9]

Factors of formation	3-MCPD	GE
Precursors	Triacylglycerols, esters of chlorohydrins	Mono- and diacylglycerols (at concentrations >7%)
Processing conditions that lead to an increased content	Acidic pH	Temperature
Mechanism of formation	Nucleophilic substitution (starting from 140°C)	Radical reaction (>230°C)
Critical stage of formation	Deodorisation	Deodorisation
Precursor formation stage	Degumming, bleaching	
Stability	Does not break down when deodorised	Volatile under deodorising conditions
Decrease in the content	Treatment with alkalis, using no acid-activated bleaching earths, using low levels of chlorine-containing pesticides, no chlorinated water	Treatment with alkalis, addition of antioxidants

Table 2 – Content of 2,3-MCPD-esters and esters of glycidol in refined sunflower oil

Number of samples tested	Content of 3-MCPD-esters, μg/kg	Content of 2-MCPD-esters, μg/kg	Content of glycidol esters, μg/kg	Ref.
6	730 (500–1044)	nd	nd	[11]
15	1000	nd	400	[12]
	760	nd	nd	[13]
4	Diesters – MCPD 470 (150–820) Monoethers – MCPD 550 (190–930)	nd	390 (120–900)	[14]
15	600 (100–2100)	200 (0–300)	100–400	[15]
11	230 (80–960)	110 (20–520)	360 (20–900)	[16]
596	303	218	nd	[2]
	100–2470	100–670	100–1190	[17]
12	260–1088	50	580	[18, 19]

Thus, refined sunflower oil in most cases meets the requirements of the standard content of GE (<1000 μg/kg) and 3-MCPD-esters (<12500 μg/kg). The data on the content of 2-MCPD-E are limited.

Refined sunflower oil used for frying accumulates significantly more esters: 3-MCPD-E – 260 to 2220 μg/kg, 2-MCPD-E – 50 to 690 μg/kg, GE – up to 580 μg/kg [20,21].

The **purpose** is to study how oxidation products, acids, and natural antioxidants affect the formation of 3-MCPD-esters and glycidol esters due to deodorisation of sunflower oil.

Objectives of the study.

1 Prevention of oxidation products formed during oil extraction and processing;

2 Reducing the content of oxidation products in oils before deodorisation.

Research materials and methods

The object of the study was deodorised sunflower oil produced by TM *Oleyna*, Ukraine. Activated carbon was from Chemviron Carbon (Calgon Carbon, USA), sulphuric acid, in the form of fixanal, of 0,1N from ALFARUS (Ukraine).

Laboratory deodorisation was performed as follows. Refined deodorised sunflower oil was placed in a 250 cm^3 flask, heated to 240°C, and kept, constantly stirred, for 2 hours at atmospheric pressure and a set temperature. The volume of the samples was 150 cm^3, the temperature was controlled with an error of ± 0.1°C. Stirring was performed using a magnetic stirrer (RIVA–04.4, Riva Stal, Ukraine) at 120 rpm. Heating was carried out using a heating ring, the temperature was monitored with an electric contact thermometer ТПК-7-П (measuring range 0–300°C). After deodorisation, the oil was cooled and stored at ±0.5°C in a closed dark glass flask for no more than 10 days.

Oxidation of sunflower oil was performed in a 200 cm^3 flask that was immersed in a water bath heated to 90°C (temperature fluctuations within ±0.1ºC). A bubbler was placed on the bottom of the flask and connected to the compressor (K25, Ukraine). The operating pressure of the compressor was ≤0.7 MPa. Stirring was carried out with a magnetic stirrer RIVA–04.4 (Riva Stal, Ukraine) at 60 rpm. The oxidation lasted 2 to 10 hours.

Tocopherols were removed from deodorised sunflower oil (TM *Oleyna*) by adsorption on activated carbon. The charcoal was ground and activated in a muffle furnace at 800°C for 3 hours. Filtration was performed through a layer of activated carbon using a Büchner funnel, a Bunsen flask, and a vacuum pump. After complete cooling, the carbon was distributed in a 10 cm thick layer on a folded filter, which was evenly placed in the Buchner funnel. The Bunsen flask was connected to the vacuum pump, and the oil was filtered by pressure differences. The oil sample was filtered through a layer of activated carbon 10–20 times (the oil was poured onto the surface of the charcoal), with the carbon periodically changed. The total activated carbon to oil ratio was 10:1.

The absence of tocopherols in the oil obtained was checked by determining the period of induction (Fig. 2). The kinetics of oil oxidation was determined on a volumetric installation [22]. The study was performed under conditions of initiated oxidation, i.e. a known amount of AIBN (azodiisobutyronitrile acid) was added to the oil sample. The nature of the dependence (direct, without the period of inhibition of the oxidation rate), which we see in Fig. 2, shows the absence of the induction period, i.e. the oil sample does not contain any antioxidants and does not inhibit the oxidation process.

Establishing the effect of oil acidity on the formation of 3-MCPD-E and GE. Weighed samples of sulphuric acid (fixanal 0.1 N) were added to the sunflower oil. The fixanal was opened before the start of the study, and its contents were transferred to a 100 cm^3 volumetric flask. A sample of acid solution (0.01 to 0.1 g) was weighed on analytical scales of class 5 accuracy, added to 100 g of sunflower oil, and laboratory deodorisation was performed according to the method described above. After deodorisation, the oil was cooled and stored at 5±0.5°C in a closed dark glass flask for not more than 10 days.

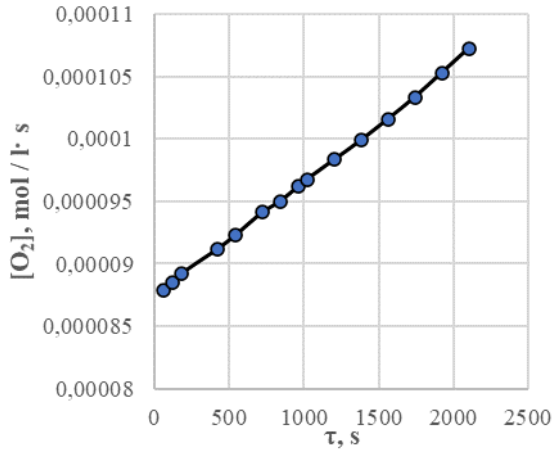

Fig. 2. Kinetics of oxidation of a sample of sunflower oil with tocopherols extracted (research temperature 70 °C, amount of AIBN 2%)

The acid value (AV), peroxide value (POV) and p-anisidine value (p-AnV) were determined according to the official AOCS methods 3d-63, Cd 8-53, and Cd18-90 respectively.

The content of 3-monochloropropanediol (3-MCPD) and glycidol was determined by gas-liquid chromatography on a gas-liquid chromatographic mass-spectrometer Agilent 7890V/5977V with an automated sample preparation system based on MPS Robotic (ISO 18363-1:2015, modified).

All measurements were performed in duplicate, and the data are presented as mean standard deviations (SD).

Results of the research and their discussion

The studies have revealed a correlation between the formation of MCPD esters and the oxidative state of fats [23], which indicates that changes in the number of MCPD esters may be related to the degree of oxidation of the oil. The studies also show that the presence of Fe^{3+} ions can promote the formation of esters of 3-MCPD and GE, while antioxidants inhibit their formation [24].

The first objective of our study was to examine the relationship between oxidation products in fats and the levels of MCPD esters and glycidol esters after deodorisation of these fats. To confirm or refute this statement, refined sunflower oil was oxidised at 90°C with oxygen so as to accumulate different amounts of oxidation products in one sample (to reduce research errors). We tried to obtain such values of peroxides and aldehydes that can be found in commercial samples of unrefined sunflower oil. The results of the accumulation of hydroperoxides and aldehydes are shown in Fig. 3.

Peroxides are the primary products of oxidation, and at the study temperature 90°C, they easily decompose and, in the first place, form aldehydes. That is why accumulation of large amounts of peroxides is not observed. The obtained values of peroxide numbers are found in commercial samples of sunflower oil. Next, laboratory deodorisation of the samples was performed. In the control sample (sunflower oil deodorised in the laboratory according to the standard method), the content of 3-MCPD-E was 560 μg/kg, and that of GE 440 μg/kg, which is consistent with the EFSA data on sunflower oil [2] and allows using the selected method of laboratory deodorisation. It is known that the content of hydroperoxides during deodorisation changes significantly (they are destroyed under the influence of high temperatures of deodorising, with the formation of secondary oxidation products). So, the content of hydroperoxides was determined in the deodorised samples separately. The acidity of the oils, too, significantly affects the formation of MCPD-E and GE, so to exclude the influence of this factor, the AV of the deodorised oils was determined. The results of studying the content of 3-MCPD-esters and glycidol esters in the samples are given in Table 3.

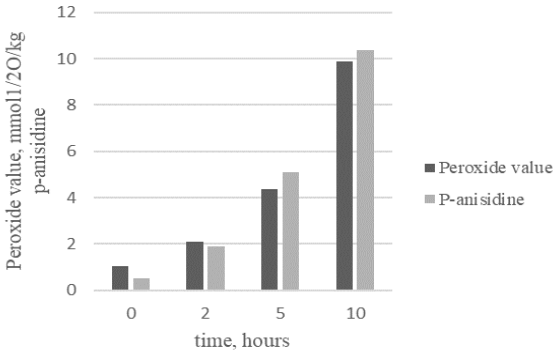

Fig. 3. Kinetics of sunflower oil oxidation by peroxide and anisidine values

The acid number of the oil samples was approximately the same, so it did not affect the results of the studies. The research results show that an increase in the content of oxidation products in sunflower oil leads to an increase in the amount of MCPD-esters formed after deodorisation: from 560 μg/kg (for oil with the peroxide value 1.06 mmol 1/2O/kg and the anisidine value 0.55) to 1290 μg/kg (for oil with PV=6.73 mmol 1/2O/kg and PAV=10.38). Thus, peroxides and aldehydes should be looked upon as initiators of the formation of 3-MCPD-E. Accordingly, a way to reduce the content of toxic 3-MCPD-E in deodorised oils is to prevent the formation of oxidation products during the extraction and processing of oils or to reduce the content of oxidation products in oils before deodorisation.

However, this correlation is not observed for glycidol esters. Some researchers obtained similar results: with the increase in the anisidine value during deep-frying, the number of glycidyl esters of palm oil did not increase correspondingly [23, 25].

The presence of antioxidants, too, reduces the formation of MCPD esters and esters of glycidol during deodorisation of oils. Thus, with palm oil used for deep-frying, the effect of various antioxidants on the formation of MCPD-E and GE was also evaluated in the research [26]. The effectiveness of the antioxidants studied increased in the following series: BHT (ionol) < BHA (butylhydroxyanisole) < sage extract < rosemary oleoresin < TBHQ. The authors attribute a decrease in the formation of MCPD-E and GE in the presence of antioxidants with a decrease in the formation of mono- and diacylglycerols during frying.

The relationship between antioxidants and the formation of MCPD-E and GE needs to be considered in more detail. In our study, it was decided to reduce the content of antioxidants already contained in sunflower oil tocopherols (the content of carotenoids in deodorised oil is already insignificant). For this purpose, two samples were compared – deodorised sunflower oil and the same oil from which tocopherols had been extracted (Table 4).

An increase in both 3-MCPD-E and GE was observed in the sunflower oil sample with tocopherols extracted. However, the growth is small, about 10% for both esters. The data obtained do not allow drawing conclusions about the effect of the amount of natural antioxidants on the formation of 3-MCPD-E and GE during deodorisation.

The paper [27] reports that with an increase in the concentration of tocopherols by 200 ppm when obtaining bakery products based on palm oil fractions, 3-MCPD-E, 2-MCPD-E, and GE in this oil did not decrease. When the concentration of tocopherols increased to 800 and 1200 mg/kg, a decrease in the GE content from 0.696 mg/kg to 0.533 and 0.494 mg/kg was observed. The data obtained in our study and the data [27] require additional research.

It is known that the levels of formation of MCPD-esters and esters of glycidol are influenced by the acidity of the medium, i.e. the number of acid groups in the composition of oils [28, 29]. To test this hypothesis, sulphuric acid was added to refined sunflower oil in certain concentrations (Table 4).

In order to exclude the influence of other factors of MCPD-E and GE formation, the content of peroxides and aldehydes was established before laboratory deodorisation (Table 5). This content was approximately the same in all samples, so it did not affect the comparative experimental data.

Table 3 – Effect of the amount of oxidation products in sunflower oil on the content of 3-MCPD-E and GE in the oil after deodorisation

No.	Sunflower oil sample	Peroxide value of the oil before deodorisation (and after deodorisation), mmol 1/2O/kg	Anisidine value of the oil before deodorisation	Acid value, mg/g	Content of 3-MCPD-E*, µg/kg	Content of GE**, µg/kg
1	Deodorised (0 hours of oxidation)	1.06±0.07 (4.75)	0.55±0.21	0.32±0.007	560±17	440±20
2	Oxidised (2 hours) and deodorised	2.11±0.09 (3.27)	1.89±0.30	0.33±0.007	750±17	270±20
3	Oxidised (5 hours) and deodorised	4.35±0.12 (4.76)	5.10±0.15	0.36±0.009	1230±17	270±20
4	Oxidised (10 hours) and deodorised	9.88±0.11 (3.21)	10.38±0.19	0.39±0.008	1290±17	390±20

*Mass fraction of the total amount of 3-monochloropropanediol (3-MCPD) and fatty acid esters of 3-MCPD in terms of 3-MCPD, µg/kg

**Mass fraction of esters of glycidyl fatty acids in terms of glycidol, µg/kg

Table 4 – Amounts of 3-MCPD-E and GE in sunflower oil with and without natural tocopherols

No.	Sunflower oil sample	Peroxide value of the oil before deodorisation (and after deodorisation), mmol 1/2O/kg	Anisidine value of the oil before deodorisation	Acid value, mg/g	Content of 3-MCPD-E*, µg/kg	Content of GE**, µg/kg
1	Deodorised	1.06±0.07 (4.75)	0.55±0.21	0.32±0.007	560±17	440±20
5	Tocopherol-free, deodorised	3.29±0.11 (4.08)	1.77±0.29	0.28±0.013	620±17	490±20

*Mass fraction of the total amount of 3-monochloropropanediol (3-MCPD) and fatty acid esters of 3-MCPD in terms of 3-MCPD, µg/kg

**Mass fraction of esters of glycidyl fatty acids in terms of glycidol, µg/kg

Table 5 – Effect of the amount of acid on the formation of 3-MCPD-E and GE in sunflower oil as a result of deodorisation

No.	Sunflower oil sample	Peroxide value, mmol 1/2O/kg	Anisidine value	Content of 3-MCPD-E*, µg/kg	Content of GE**, µg/kg
1	Deodorised	1.06±0.07	0.55±0.21	560±17	440±20
6	Deodorised with 0.01 mg H_2SO_4 /kg oil***	1.28±0.12	0.50±0.28	255±89	540±110
7	Deodorised with 0.025 mg H_2SO_4/kg oil	1.45±0.15	0.61±0.31	690±117	180±36
8	Deodorised with 0.059 mg H_2SO_4/kg oil	1.08±0.08	0.65±0.22	980±17	220±20
9	Deodorised with 0.1 mg H_2SO_4/kg oil	1.35±0.11	0.60±0.18	1450±246	890±117

*Mass fraction of the total amount of 3-monochloropropanediol (3-MCPD) and fatty acid esters of 3-MCPD in terms of 3-MCPD, µg/kg

**Mass fraction of esters of glycidyl fatty acids in terms of glycidol, µg/kg

***sulphuric acid 0.1 N was used

According to Table 5, the content of 3-MCPD-esters in deodorised sunflower oil increases with an increase in acid groups added before deodorisation. The data obtained confirm the need to reduce the acid treatment of oils during their processing (acid hydration, the use of acid-activated bleaching earths during adsorption purification, etc.). However, no correlation was observed between the acid content and the amount of glycidol esters. Presumably, it is the removal of metals (precursors of GE) that accounts for the positive effect of neutral pH on the reduction of not only 3-MCPD-E, but also GE after adsorption purification with bleaching earths [30].

Thus, H^+ ions of strong acid can be considered precursors of 3-MCPD-esters, but not esters of glycidol.

To reduce the formation of MCPD-E in oils, it is advisable to do the following:

– water degumming or other types of degumming with minimal use of acids. Performing the stage of neutralisation, which itself promotes reducing the levels of 3-MCPD-esters and glycidol esters. For example, in the study [31], neutralisation with NaHCO3 or KOH reduced the concentration of 3-MCPD-E to 81% and that of GE to 84%;

– avoiding acid activation of adsorption materials. Before the deodorisation stage, it is advisable to introduce an additional stage of treating oil with solutions of carbonates or other alkalis to reduce the pH of the oils

Conclusion

It has been shown that increasing the content of hydroperoxides (PV), aldehydes (PAV), and acids (AV) leads to a higher content of 3-MCPD-E in deodorised oil. In contrast, no correlation has been found between the amount of oxidation products and the acidity of sunflower oil and the amount of GE. A way to reduce the content of toxic 3-MCPD-E in deodorised oils is to prevent the formation of oxidation products during the extraction and processing of oils or to reduce the content of oxidation products in oils before deodorisation.

The data obtained allow formulating recommendations to prevent high values of MCPD-E and GE in deodorised oils:

– deodorisation of only oils with low content of oxidation products;

– minimising the contact of oils with strong acids during extraction and processing.

The results obtained can help better understand the mechanism of formation of MCPD and GE esters in vegetable oils and find ways to control their formation.

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ВПЛИВ ПРОДУКТІВ ОКИСНЕННЯ ТА ІНШИХ ПРЕКУРСОРІВ НА ВМІСТ 3-MCPD ТА ЕФІРІВ ГЛІЦИДОЛУ В ДЕЗОДОРОВАНІЙ СОНЯШНИКОВІЙ ОЛІЇ

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Анотація. У статті досліджується вплив прекурсорів на утворення 3-MCPD-ефірів та ефірів гліцидолу, а також способи зменшення концентрації цих токсичних ефірів у дезодорованих оліях. Встановлено, що зі збільшенням вмісту в зразках соняшникової олії продуктів окиснення зростає і кількість MCPD-ефірів, які утворюються після проведення дезодорування: від 560 мкг/кг для олії з пероксидним числом 1,06 ммоль1/2O/кг та анізидиновим числом 0,55 до 1290 мкг/кг для олії з PV=6,73 ммоль1/2O/кг та PAV=10,38. Таким чином пероксиди і альдегіди слід віднести до ініціаторів утворення 3-MCPD-E. Відповідно одним з шляхів зниження вмісту токсичних 3-MCPD-E в дезодорованих оліях є попередження утворення продуктів окиснення в ході добування та перероблянння олій або зниження вмісту продуктів окиснення в оліях перед проведенням дезодорування. Навпаки, не спостерігається кореляції між вмістом продуктів окиснення та кількістю ефірів гліцидолу в дезодорованій олії. Не виявлено зв'язку між вмістом природних антиоксидантів олій – токоферолів і кількістю 3-MCPD- ефірів та ефірів гліцидолу. Підвищення pH олій приводить до збільшення вмісту 3-MCPD-ефірів в результаті дезодорування. Зі збільшенням кількості кислотних груп збільшується кількість 3-MCPD-ефірів. І навпаки, ефіри гліцидолу при підвищенні кількості введеної в олію кислоти не утворюються в процесі дезодорування в додаткових кількостях.

Ключові слова: 3-MCPD-ефіри, ефіри гліцидолу, пероксиди, альдегіди, кислоти, антиоксиданти, окиснення.