ORIGINAL ARTICLE

HYGIENIC ASSESSMENT OF THE INFLUENCE OF PESTICIDES ON THE FATTY COMPOSITION OF SUNFLOWER SEED LIPIDS

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ABSTRACT

The aim: Evaluation of the influence of plant protection chemicals on the fatty acid composition of sunflower seeds.

Materials and methods: Study of the effects of pesticides, study of the effects of pesticides on the fatty acid composition (lipid) of sunflower seed by gas-liquid chromatography was studied.

Results: It was found that the content of oleic and linoleic unsaturated fatty acids did not differ significantly from the control. The content of linolenic and arachidonic acids was at the level of the control group. A similar pattern was observed in relation to the content of saturated fatty acids, in particular myristic, pentodecanoic, palmitic, margaric, stearic. The total content of fatty acids (unsaturated fatty acids and saturated fatty) selected under different seed protection schemes did not differ significantly from control.

Conclusions: It is proved that the application of the investigated pesticides in various schemes of chemical protection of sunflower crops does not affect the nutritional and biological value of the seeds.

KEY WORDS: biological value of sunflower seeds, pesticides, fatty acid composition, lipids, sunflower oil

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INTRODUCTION

Today, Ukraine is one of the dominant countries in the cultivation and processing of sunflower [1, 2]. Thus, according to the State Statistics Service, Ukraine maintains its leading position on sunflower oil exports and over the past years has been the leading exporter of sunflower oil, ahead of major oil-importing countries – India, China, European Union countries such as Spain, the Netherlands, Italy, etc. [3-5].

Vegetable fats play a very important role in the human body. They perform energy function, are structural elements of cell membranes, carriers and solvents of fat-soluble vitamins, form biological regulators (factor of activation of platelets, eicosanoids, lipo- and hydroperoxides, sex and steroid hormones), carry out receptors, regulate activity of transcription factors, lipid modification of proteins (attachment of fatty acids to proteins, which provides lipid – protein and protein – protein interactions (bonds), perform regulatory function (according to cholesterol levels increase, regulate hormonal balance), have a protective function, are a source for the formation of endogenous water, are involved in the transmission of intracellular signals, and also improve the taste of food [6, 7].

Therefore, sunflower oil is a useful food, first of all, as a source of polyunsaturated fatty acids (PUFA). Thus, in the fatty acid spectrum, it contains a significant amount of linoleic acid (about 80%), which belongs to the family ω6 and oleic acid (about 10-14%), which belongs to the family ω9 and is extremely useful for the human body. Unrefined oil is also a powerful source of phospholipids and vitamin E [7].

Thus, the issues of increasing yields, preserving the nutritional and biological value of crops, including sunflower, are very relevant

Sunflower yields depend to a large extent on the phytosanitary status of agricultural land. One of the main reasons for the decline in yield is damage to plants by diseases and pests such as phomopsis, lupus, white, gray and dry rot, malfunctioning powdery mildew, phomos, rust, larvae of pieces (drones), various types of bugs, including berry, field, alfalfa and violation of scientifically based alternation of crops in rotation, returning it to the same branches in 1-4 years [4-6].

An important component of intensive sunflower growing technology is a robust chemical protection system. Chemicals for crop protection for weed control, pest and disease control include herbicides, insecticides, fungicides and desiccants. However, the effect of pesticides on the lipid composition of sunflower seeds is still unknown.

Thus, studying the possible (both quantitative and qualitative) effects of pesticides on the fatty acid composition of sunflower seeds is an important part of assessing the effects of pesticides on the biological value of plants.

THE AIM

To study the evaluation of the influence of plant protection chemicals on the fatty acid composition of sunflower seeds.

Table I. Fatty acid spectrum of unsaturated sunflower seed fatty acids grown using different plant chemical protection schemes (in %)

№ of sample	Fatty acids			
	oleic	linoleum	linolenic	arachidonic
1.	17,9	67,8	0,3	0,3
2.	14,5	77,4	0,2	0,2
3.	9,5	81,6	0,2	0,2
4.	10,4	80,5	0,2	0,2
5.	9,3	81,3	0,2	0,2
6.	11,2	79,6	0,1	0,1
7.	12,0	78,7	0,2	0,2
8.	13,8	77,4	0,2	0,3
9.	11,1	80,4	0,2	0,2
10.	9,6	82,6	0,2	0,2
11.	10,7	81,9	0,1	0,2
12.	10,0	82,0	0,1	0,1
13.	12,0	81,3	0,2	0,2
13.	11,0	81,0	0,2	0,2
15	11,8	79,7	0,2	0,2
16	12,7	79,4	0,2	0,3
17	9,4	83,3	0,2	0,1
18. c'	11,1	80,0	0,2	0,2
19.c'	11,0	82,0	0,2	0,2
20.c'	10,6	82,2	0,2	0,2

c' - control (benchmarks)

MATERIALS AND METHODS

Based on the Department of Hygiene and Ecology #4 of Bogomolets National Medical University and the Institution of Hygiene and Ecology conducted a study of the effects of pesticides, namely (Agil KE (propaquizafop); Akris CE (dimethenamid-P); Basta 200 (glufosinate ammonium); Fusilade forte 150 к.е. EC (fluazifop-P-butyl); Square PK (diquat dibromide); Euro–Lightning PK (imazamox, imazetapir); Vidblok Plus ME (imazetapir, propakhizafop); Primextra TZ Gold 500 SC к.с. (S-Metolachlor, terbuthylazine); Pledge 50 s.p. (Flumioxazine); Racer KE (flurochloridone); Challenge 600 SC KC (aclonifen); Prometrex KC (Prometryn); Acetogan KE (Acetochlor); Proponit 720 к.е. (propisochlor); Pulsar BP (Imazamox)) on the fatty acid composition (lipid) of sunflower seed by gas-liquid chromatography was studied. Sample preparation and gas chromatographic analysis were performed by the method [8].

Samples for gas chromatographic analysis were prepared as follows: samples of 1-3 grams of seeds were placed in a homogenizer and the resulting homogenate of the seeds was transferred into a 10 ml centrifuged tube and filled with the extraction mixture. Lipid extraction was performed with 5 ml of chloroform-methanol mixture (2: 1 ratio) and kept in the refrigerator for 30 minutes. For better phase distribution, 1 ml of distilled water was added. Next, the lower chloroform phase was selected with a Pasteur pipette and concentrated the resulting liquid by evaporation to a volume of one drop.

Hydrolysis and methylation of higher fatty acids of sunflower seed lipid fatty acids were performed by adding 1% of H_2O_4 lipid to dry matter in methanol in an amount of 5 ml and transferring this solution into a 10 ml glass ampoule.

After sealing, the ampoule was carried out hydrolysis and methylation in a thermal bath at a temperature of 85°C for 20 minutes.

Extraction of ethylated fatty acids was performed twice with hexane-ether mixture (1: 1 ratio) in an amount of 5 ml. To distribute the phases, 1 ml of distilled water was added, then the upper phase was selected with a Pasteur pipette and the combined extracts evaporated to dryness in a stream of nitrogen at t- 45°C in a water bath. The dry precipitate was dissolved in 40-50 μl of pure hexane and introduced into the evaporator of the chromatograph in the amount of 5 μl.

In the spectrum of sunflower lipids, the 9 most informative fatty acids were identified: C14:0 – myristic, C15:0 – pentodecanoic, C16: 0 – palmitic, C17: 0 – margaric, C18:0 – stearic, accounting for the amount of saturated fatty acids (NLCs), and C18:1 is oleic, C18:2 is linoleic, C18:3 is linolenic, C20:4 is arachidonic, which make up the sum of unsaturated fatty acids (NLCs). Content C18:2, C18:3 and C20:4 are included in the amount of polyunsaturated fatty acids (PUFA) and are defined as irreplaceable.

Table II. The fatty acid spectrum of saturated fatty acids of sunflower seeds grown when applying various schemes of chemical protection of plants (in %)

№ of sample	Fatty acids				
	myristic	pentodecane	palmitic	margarine	stearic
1.	0,3	0,3	6,0	0,3	6,6
2.	0,2	0,2	4,0	0,1	3,2
3.	0,2	0,2	5,0	0,2	3,0
4.	0,2	0,2	5,0	0,2	3,1
5.	0,2	0,2	5,0	0,2	3,7
6.	0,1	0,1	5,0	0,1	4,0
7.	0,2	0,2	5,0	0,2	3,6
8.	0,2	0,3	4,4	0,2	3,2
9.	0,2	0,2	5,0	0,2	2,6
10.	0,2	0,2	4,5	0,2	2,4
11.	0,1	0,2	4,4	0,1	2,3
12.	0,1	0,1	4,3	0,1	2,8
13.	0,2	0,2	4,0	0,2	2,0
14.	0,2	0,2	4,4	0,2	2,6
15.	0,2	0,2	4,5	0,2	3,0
16.	0,2	0,3	4,2	0,2	2,5
17.	0,1	0,1	4,6	0,1	1,9
18. c'	0,2	0,2	4,7	0,2	3,2
19.c'	0,2	0,2	4,1	0,1	2,3
20.c'	0,2	0,2	4,3	0,2	3,1

c' - control (benchmarks)

RESULTS

The influence of plant protection chemicals on the fatty acid composition of sunflower seed lipids was evaluated (Table I).

Studies have found that the highest percentage of unsaturated fatty acids in sunflower seeds is oleic and linoleic acids. The result of the experiment revealed that the amount of oleic acid (C18:1) in the samples under numbers 9, 11, 14 does not differ from the control parameters; in samples 1, 2, 6, 7, 8, 13, 15, 16 there is a deviation toward the increase from the control data (6.8%, 3.4%, 0.1%, 0.9%, 2.7 %, 0.9%, 0.7%, 1.6% respectively), but they are not statistically significant; in samples 3, 4, 5, 10, 12, 17 there was a tendency to decrease values (1.1%, 0.2%, 3.1%, 1.0%, 0.2%, 1.4% respectively).

The content of linoleic acid (C18:2) in samples 3, 4, 5, 9, 11, 12, 13, 14 did not differ from the control data; in the samples under numbers 1, 2, 6, 7, 8, 15, 16 changes in the concentration of this acid is not statistically significantly lower than the control parameters (12.2%, 2.6%, 0.4%, 1.3%, 2.6%, 0.3%, 0.6% respectively). Studies in numbers 10 and 17 tend to increase the content of linoleic acid (1.0% and 1.7% respectively).

Analysis of the content of linolenic (C18:3) and arachidonic acids (C20:4) in sunflower seeds was not statistically significantly different from the control samples. The largest fluctuations were observed only in sample number 1 for oleic acid by 6.8% and for linoleic acid by 12.2%.

Analyzing the fatty acid spectrum of saturated fatty acids (Table II), namely myristic, pentodecanoic, palmitic, margarine, stearic, after application of plant protection chemicals, established a tendency to increase palmitic content (in samples № 1, 2-7), in samples № 1, 3, 16), margarine (in sample № 1) in relation to the control indicators. However, there was a tendency to decrease the content of myristic acid (in samples No. 6, 11, 12, 17), pentodecanoic (in samples № 6, 12, 17), stearic acids (in sample № 13). However, all these differences were not significant ($p > 0.05$).

Data provided in Table III, it was found that the total spectrum of fatty acids (saturated, unsaturated and polyunsaturated) in most samples did not differ from the control ($p > 0.05$).

Only in sample №1 was recorded an increase of 5% in the content of saturated fatty acids and a decrease of 5% and 12% of the amount of unsaturated and polyunsaturated fatty acids, accordingly.

DISCUSSION

Sunflower is the main oil crop in Ukraine and one of the most important oilseeds in the world. An important aspect of oilseeds is the ability to produce natural and quality oil. But sunflower is mostly grown using crop protection chemicals. Therefore, the requirements for the quality of oilseeds with the use of such means of protection have become a necessary factor today. [5, 9].

Table III. The sum of the fatty acid spectrum of solar seeds produced by applying different chemical schemes (in %)

№ of sample	The sum of saturated fatty acids	The sum of unsaturated fatty acids	The sum of polyunsaturated fatty acids
1.	13,5	86,5	68,4
2.	7,7	92,3	77,8
3.	8,6	91,8	82,0
4.	8,7	91,3	80,9
5.	9,4	91,0	81,7
6.	9,3	91,0	79,8
7.	9,3	91,1	79,0
8.	8,3	91,7	77,8
9.	8,1	91,9	80,8
10.	7,5	92,6	83,0
11.	7,1	92,9	82,2
12.	7,5	92,5	82,2
13.	6,4	93,7	81,7
14.	7,6	92,4	81,4
15.	8,1	91,9	80,1
16.	7,4	92,6	79,9
17.	6,8	93,2	83,6
18.c*	8,5	91,5	80,4
19.c*	6,9	93,4	82,4
20.c*	8,0	93,2	82,6

c' - control (benchmarks)

In accordance with these requirements, we have assessed the impact to crop protection chemicals, namely that Agil KE (propaquizafop); Akris CE (dimethenamid-P); Basta 200 (glufosinate ammonium) ; Fusilade forte 150 к.е. EC (fluazifop-P-butyl); Square PK (diquat dibromide); Euro–Lightning PK (imazamox, imazetapir); Vidblok Plus ME (imazetapir, propakhizafop); Primextra TZ Gold 500 SC к.с. (S-Metolachlor, terbuthylazine); Pledge 50 s.p. (Flumioxazine); Racer KE (flurochloridone); Challenge 600 SC KC (aclonifen); Prometrex KC (Prometryn); Acetogan KE (Acetochlor); Proponit 720 к.е. (propisochlor); Pulsar BP (Imazamox) on the spectrum of fatty acid composition of lipids in sunflower seeds.

A number of authors in determining the amount of macronutrients in sunflower oil did not note significant changes in lipid concentration after treatment of the crop with plant chemicals [9-11]. However, there aren't studies that have been performed on the presence or absence of changes in the fatty acid spectrum of the oil after chemical treatment. This was the purpose of our study.

We investigate the probability of changes in the spectrum of fatty acids (FA) 9 of the most informative acids:: C14:0 – myristic, C15:0 – pentodecanoic, C16: 0 – palmitic, C17: 0 – margaric, C18:0 – stearic and separately their sum (sum of saturated FA) as well C18:1 – oleic, C18:2 – linoleic, C18:3 – linolenic, C20:4 – arachidonic (and their amount is also sum of unsaturated FA). In all studied samples the content of saturated FA s: myristic, pentodecanoic,, margarine almost did not differ from the control data. Increased content of palmitic and stearic fatty acids is observed only in sample №1 (on 36% and 50% respectively), which is an exception and does not carry statistically significant data, in all other samples – the data are not significantly different from the control.

The results of the content of linolenic and arachidonic acids, the amount of unsaturated fatty acids studied did not differ from the control data. Slight changes in both increase and decrease in values were observed in oleic and linoleic fatty acids compared to control data, but they were not statistically significant (not reliable).

CONCLUSIONS

Thus our research results give reason to believe that the studied pesticides (Agil KE (propaquizafop); Akris CE (dimethenamid-P); Basta 200 (glufosinate ammonium); Fusi lade forte 150 к.е. EC (fluazifop-P-butyl); Square PK (diquat dibromide); Euro–Lightning PK (imazamox, imazetapir); Vidblok Plus ME (imazetapir, propakhizafop); Primextra TZ Gold 500 SC к.с. (S-Metolachlor, terbuthylazine); Pledge 50 s.p. (Flumioxazine); Racer KE (flurochloridone); Challenge 600 SC KC (aclonifen); Prometrex KC (Prometryn); Acetogan KE (Acetochlor); Proponit 720 к.е. (propisochlor); Pulsar BP (Imazamox)) in various schemes of chemical protection of sunflower crops does not affect the nutritional and biological value of the seeds (the fatty acid composition of sunflower seed).

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The Authors declare no conflict of interest.

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