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SELECTED QUALITY INDICATORS OF SUNFLOWER SEED AND OIL SOLD IN UKRAINE

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Abstract. *Due to the growing need for healthy food, the demand for high-oleic sunflower oil is increasing every year, both in the world and in Ukraine. Oil has valuable properties for both manufacturers and consumers. Therefore, setting standards for the fatty acid composition of sunflower seeds and sunflower oil is quite relevant and important. The purpose of this work is to carry out a comparative analysis of the Ukrainian and the international regulations on the content of fatty acids in sunflower oil; to study the sunflower oil and sunflower seeds available on the Ukrainian market by separate quality indicators and to determine the proportion of high-oleic oil.*

The article provides a comparative analysis of national and international regulations. The current DSTU 4492: 2017 does not have a distribution of sunflower oil according to the oleic acid content. This acid is normalized in the range of 14.0–39.4 %, which corresponds to ordinary oil. According to international requirements, sunflower oil is divided into ordinary, with an average content of oleic acid and high-oleic acid, and some more fatty acids regulated. We used gas chromatography to determine the fatty acid composition of sunflower seeds and sunflower oil samples received for research at ULQSAP during 2017–2019. It was found that the market of Ukraine had a significant

share of high-oleic oil, particularly in 2019 (57.14 %), compared to 2018 (18.8 %) and 2017 (40 %). This confirms the worldwide trend of growing varieties of high oleic acid sunflower breeds in Ukraine.

A comparative analysis of sunflower seeds by mass fraction of oil for 2017-2019 was carried out. We established that by mass fraction of oil, sunflower seeds used for the production of sunflower oil in Ukraine mainly belong to the second class.

Keywords: *fatty acids, high-oleic oil, sunflower seeds, oleic acid, the mass fraction of oil*

Introduction

The composition of sunflower oil is quite variable and depends on the type of sunflower and its place of cultivation, the method of obtaining the product and methods of its purification. The following vitamins are present in the crude oil: A, D, E, group B (B_1, B_2, B_3, B_5, B_6). It is known that systematic use of oil improves the cardiovascular system (lowers cholesterol, strengthens the vascular walls, protects against atherosclerosis, severe pathologies of blood vessels and heart); oil has a positive effect on brain function (improvement of cognitive function), endocrine and urinary system; it promotes the normalization of the gastrointestinal tract function; it prevents premature aging (due to its high tocopherol content, which is three times higher than in olive oil). Sunflower oil contains a significant amount of lipids (that are not synthesized in the body and need to be obtained from food), phytosterols, vitamins. In addition, it contains linoleic, oleic, palmitic, stearic, linolenic and arachidonic fatty acids, which take part in the nervous system operation, namely in the creation of nerve tissues membranes and cell membranes.

However, the results of studies on the benefits and harms of human polyunsaturated fatty acids are controversial. In particular, the differences concern the allowable levels of ω-3, ω-6, ω-9 in the diet. There is some evidence of the preventive effect of these acids on cardiovascular disease (Ushkalov et al., 2017; Uriho et al., 2019). At the same time, it is suggested that large amounts of ω-3 can cause prostate cancer (Sanders et al., 2014), and ω-6 increases the ratio of collagen I/III in the myocardium, which leads to stagnation in the heart and disrupts transmitral blood flow (Beam et al., 2015).

Discussions also address the issue of heat resistance of different types of edible oils. Studies on their compatibility and the possibility of combined use are being conducted. Thus, the combination of sunflower and sesame oil provides sufficient heat resistance and makes the industrial use of oils safe (Grosh et al., 2019). A mixture of rapeseed, corn, olive, peanut and high-oleic sunflower oils can prevent and control cardiovascular disease (Uriho et al., 2019).

Oleic acid ω-9 is a monounsaturated fatty acid substantially contained in olive oil. It is oleic acid that is a part of lipids – important components of cell membranes that ensure the normal course of many vital processes in the body. In the absence of oleic acid in the body, it is replaced by other fatty acids that results in dramatic change of cell membranes permeability, which in turn leads to metabolic disorders. In part, ω-9 is produced by the body itself, but a significant proportion comes from ω-9 containing products (Euralis, 2020).

Due to the growing popularity of healthy foods, the demand for high-oleic sunflower oil is increasing every year – both in Ukraine and in the world. Now the demand is being formed mainly by EU countries and is expected to increase in the nearest future due to the introduction of mandatory labeling of products with specification of oil source (Euralis, 2020). Due to the fact that the share of high-oleic sunflower is increasing every year – both in Ukraine and worldwide – the issue of establishing standards for fatty acid composition becomes quite relevant and important.

Analysis of recent researches and publications

The volume of of sunflower seeds production in Ukraine is 13.3 million tons, which is about 32 % of the world volume. The production of sunflower oil is over 4.66 million tons. This is the market with prevailing export operations. The level of domestic consumption is only is only 450–500 million tonnes (Landlord, 2020), though some upward trend has been observed recently. Currently, there are hybrid sunflower seeds with high oleic fat content in the Ukrainian market: ES Schedule SL (89 %), ES Romantic (86 %), ES Aromatic SU (89 %). According to the 2018 data, ES seeds Schedule SL with recommended areas of forest steppe and northern steppe are grown in seven regions of Ukraine. ES Romantic seeds are recommended for steppe, forest-steppe and woodland areas in fifteen regions of Ukraine. ES Aromatic SU is cultivated in steppe, forest-steppe and woodland areas in sixteen regions of Ukraine (2018) (Euralis, 2020).

Sunflower is considered high oleic if the content of monounsaturated oleic fatty acid (Omega 9) in the oil obtained from it is more than 82 % and if the content of polyunsaturated linoleic fatty acid (Omega 6) is low. This type of sunflower was derived by breeding methods and the genetic potential of its oleic acid content is up to 95 %, which is the highest rate among all oil crops. High-oleic sunflower oil has the highest content of natural antioxidant – vitamin E – 45 mg/100 g, which reduces the risk of cardiovascular system diseases (the main cause of premature human death nowadays), prevents the emergence of tumors and strengthens human immunity (Syngenta, 2020; Landl, 2020; Ukrolia, 2020).

Processing of traditional sunflower oil (high in linoleic fatty acid) for the production of margarine and during frying results in formation of active trans-isomers. These substances raise the blood cholesterol level, cause cardiovascular and tumor diseases («harmful» cholesterol). Trans fats raise low-density lipoprotein («bad cholesterol» or LDL-C) levels and lower high-density lipoprotein (HDL-C) levels, and thus double the risk of cardiovascular disease. During the heat treatment and hydrolysis of oils with high oleic acid content, carcinogens and cholesterol reducing cis-isomers are formed.Therefore, for more than 10 years high-oleic sunflower oil has been widely used in healthy foods production. This oil has a long cycle of use during frying at high temperatures (24-hours) and contains not more than 10 % of saturated fats. The shelf life of high-oleic oil and its derivatives (margarine) is four times longer than the shelf life of traditional oil (Manzo et al., 2019; Syngenta, 2020; Ukroliya, 2020).

Requirements for the quality of oils, and for sunflower oil in particular are presented in DSTU 4492: 2017 Sunflower oil. Specifications; GOST 30418-96

Vegetable oils. Method of determination of fatty acid composition (Vegetable oils. Methods of determination of fatty acid composition); Codex Stan 210–1999 Codex standard for named vegetable oils.

The purpose of this work was to carry out a comparative analysis of international regulations and regulations of Ukraine on the content of fatty acids in sunflower oil; to study the sunflower oil and sunflower seeds available on the Ukrainian market according to separate quality indicators and to determine the proportion of high-oleic oil.

Materials and methods of research

The research was conducted in 2017–2019 at the Ukrainian Laboratory for Quality and Safety of Products of AIC NULES of Ukraine in the context of the scientific theme: "Monitoring of quality of bioresources and production of agro-industrial complex for ensuring food and environmental safety of Ukraine". The research material was sunflower seeds and sunflower oil from various manufacturers. Oil sampling was performed in accordance with DSTU 4349: 2004 Oils. Methods of sampling (ISO 5555: 1991, NEQ), sampling of seeds – in accordance with DSTU 4601: 2001 Oilseeds. Sampling methods.

To determine the fatty acid composition of the oil according to GOST 30418-96, the samples were thoroughly mixed. 3–5 drops of oil were taken and dissolved in 1.9 cm^3 of hexane. 0.1 cm^3 sodium methylate solution in methanol (2 mol/dm^3) was added to the resulting solution and stirred thoroughly for 2 min. After settling (5 min), the sample was filtered through a paper filter (blue ribbon), leaving a precipitate at the bottom of the tube (GOST, 1998).

Fatty acid methyl esters (FAs) were analyzed on a Trace GC Ultra (USA) gas chromatograph with a flame ionization detector. Chromatographic conditions: column temperature 140–240 °C, detector temperature – 260 °C. The sample was introduced into the chromatograph with a 1 μl TriPlus autosampler. Duration of analysis – 65 min.

The identification of fatty acids was performed using a standard Supelco 37 Component FAME Mix sample containing 37 fatty acids. Quantitative assessment of the spectrum of fatty acids was carried out by the method of internal normalization, the content was determined in percentage. All samples were examined in 2 parallels.

Mass fraction of oil was determined according to DSTU 7577:2014. The method involves complete extraction of free lipids from the crushed seeds with solvents on a Soxhlet apparatus. The determination of the oil content was carried out on an extraction apparatus for the quantitative separation of substances from mixtures using organic solvents Solvent Extractor SER 148 (DSTU, 2014).

To calculate the oil content of the dry substance, the moisture was determined paralelly in in accordance with DSTU4811:2007. The studies were performed in 2 parallels.

Statistical processing of experimental data was carried out by conventional methods of variational statistics. Statistical significance of difference in indicators was evaluated by the Student's t-criteria.

Results of the research and their discussion

According to DSTU 4492: 2017 Sunflower oil. Specifications (Appendix E) for sunflower oil present stan-

dards for 11 fatty acids. Moreover, there is no division into groups, depending on the amount of oleic acid. In this document, the requirements are presented in numerical terms and are consistent with the Codex Alimentarius requirements for 10 oleic acids of conventional oil. However, in contrast to the Code, margaric, heptadecenic, erucic, docosadienic and lignoceric acids are not standardized by the national standard. Also, the digital values are different from those presented in GOST 30623-98 for six fatty acids (Table 1). According to this regulation, only 20 fatty acids are isolated in vegetable oils. Different amounts of these fatty acids are normalized for different oils. Sunflower oil is divided into two groups according to its fat content: high oleic oil and regular. 7 fatty acids are normalized in high-oleic oil, 13 – in normal oil.

In contrast to this, the Codex Stan 210–1999 divides sunflower seed oil into three groups, depending on the oleic acid content: high (75.0–90.7 %), medium (43–71.8 %) and low (14.0–39.4 %). This document provides standardization of 15 fatty acids for low oleic acid sunflower oil, 14 for medium oleic fatty acid sunflower oil and 15 for high oleic sunflower oil (Table 1).

In all three regulatory documents 11 fatty acids are normalized regardless the division into groups of: myristic, palmitic, palmitoleic, stearic, oleic, linoleic, α-linolenic, arachic, gondoic, begenic, lignocerinic. As for oils with a high content of oleic fatty acids, the Codex Alimentarius normalized myris-

1. Requirements for the fatty acid composition of sunflower oil in accordance with applicable regulatory documents

The name and code of the fatty acid	DSTU 4492: 20 17	GOST 30623-98		CODEX FLAT 210-1999		
	sunflower oil	sunflower oil	high-oleic sunflower oil	sunflower-seed oil	high oleic acid	mid-oleic acid
Myristic C14:0	to 0.2	to 0.2	no norms	to 0.2	to 0.1	to 1.0
Palmitic C16:0	5.0 – 7.6	5.6 – 7.6	4.2 – 4.6	5.0 – 7.6	2.6 – 5.0	4.0 – 5.5
Palmitoleic C16:1	to 0.3	to 0.3	no norms	to 0.3	to 0.1	to 0.05
Margarine C17:0	no norms	no norms	no norms	to 0.2	to 0.1	to 0.05
Heptadecene C17:1	no norms	no norms	not norms	to 0.1	to 0.1	to 0.06
Stearic C18:0	2.7 – 6.5	2.7 – 6.5	4.1 – 4.8	2.7 – 6.5	2.9 – 6.2	2.1 – 5.0
Oleic C18:1ω9	14.0 – 39.4	14.0 – 39.4	61.0 – 69.8	14.0 – 39.4	75 – 90.7	43.1 -71.8
Linoleic C18:2ω6	48.3 – 7 4.0	18.3 – 74.0	21.9 – 28.4	48.3 – 74.0	2.1 – 17	18.7 -45.3
α-linolenic C18:3ω3	to 0.3	to 0.2	no norms	to 0.3	to 0.3	up to 0.5
Arachic C20:0	0.1 – 0.5	0.2 – 0.4	to 0.7	0.1 – 0.5	0.2 – 0.5	0.2 – 0.4
Gondoic C20:1ω9	to 0.3	to 0.2	up to 0.5	to 0.3	0.1 – 0.5	0.2 – 0.3
Begenic C22:0	0.3 – 1.5	0.5 – 1.3	0.7 – 1.2	0.3 – 1.5	0.5 – 1.6	0.6 – 1.1
Erucic C22:1	no norms	to 0.2	not about rm.	to 0.3	to 0.3	no norms
Docosadiene C22:2	no norms	to 0.3	no norms	to 0.3	not norms	to 0.09
Lignocerin C24:0	up to 0.5	0,2 – 0,3	no norms	up to 0.5	not norms	0.3 – 0.4

Note: data are presented as mass fraction of fatty acid in % of total fatty acids.

tic, palmitoleic, margaric, heptadecenic, α-linolenic, erucic fatty acids, while in GOST they are not normalized. The numerical values also differ from those given in GOST for almost all fatty acids except gondoic acid.

Thus, all described normative documents differ both in quantitative and qualitative standards.

We also analyzed the data on the fatty acid composition of sunflower oil samples received for research at the UL-QSAP during 2017–2019. By high-sensitivity gas chromatography, 13 fatty acids were identified and quantified in sunflower oil: myristic (C14: 0), palmitic (C16: 0), palmitoleic (C16: 1), stearic (C18: 0), oleic (C18: 1), linoleic (C18: 2), arachin (C20: 0), α-linolenic (C18: 3ω3), gondoin (C20: 1ω9), begenic (C22: 0), erucic (C22: 1), docosadiene (C22: 2), lignocerin (C24: 0) (Table 2).

In the current DSTU 4492: 2017 no distribution of sunflower oil by oleic acid content is presented: this acid is normalized in the range of 14.0–39.4 %,

2. Results of studies of the fatty acid composition of sunflower oil (2017 –2019), *M* ± *m*

The name and code of the fatty acid	Sunflower oil, 2017		Sunflower oil, 2018		Sunflower oil, 2019	
	sunflower-seed oil n = 6	high oleic acid n = 4	sunflower-seed oil n = 18	high oleic acid n = 4	sunflower-seed oil n = 1 5	high oleic acid n = 20
Myristic C14:0	0.070 ± 0.002	0.080 ± 0.012	0.0600 ± 0.0016	0.0400 ± 0.0014	0.080 ± 0.002	0.130 ± 0.004
Palmitic C16:0	6.94 ± 0.42	2.80 ± 0.31	5.55 ± 0.72	4.42 ± 0.99	6.58 ± 0.62	4.330 ± 0.023
Palmitoleic C16:1	0.120 ± 0.051	0.090 ± 0.005	0.0800 ± 0.0021	0.070 ± 0.002	0.100 ± 0.002	0.080 ± 0.005
Stearic C18:0	3.440 ± 0.073	3.19 ± 0.02	3.57 ± 0.98	3.070 ± 0.065	3.79 ± 0.03	2.610 ± 0.021
Oleic C18:1ω9	20.40 ± 1.61	87.39 ± 1.86	26.11 ± 1.32	83.20 ± 2.11	26.39 ± 1.71	82.19 ± 1.99
Linoleic C18:2ω6	67.65 ± 0.92	4.13 ± 0.34	63.30 ± 2.35	7.24 ± 0.89	61.58 ± 1.53	9.10 ± 0.95
Arachic C20:0	0.250 ± 0.011	0.290 ± 0.031	0.2200 ± 0.0013	0.230 ± 0.016	0.230 ± 0.021	0.1400 ± 0.0054
α-linolenic C18:3ω3	0.080 ± 0.003	0.25 ± 0.05	0.050 ± 0.007	0.1100 ± 0.0003	0.080 ± 0.004	0.2000 ± 0.0015
Gondoin C20:1ω9	0.120 ± 0.002	0.260 ± 0.007	0.1300 ± 0.0003	0.170 ± 0.001	0.140 ± 0.002	0.12000 ± 0.00023
Begenic C22:0	0.64 ± 0.05	1.10 ± 0.02	0.66 ± 0.03	0.92 ± 0.03	0.72 ± 0.04	0.95 ± 0.08
Erucic C22:1	0.020 ± 0.005	0.050 ± 0.001	0.030 ± 0.003	0.060 ± 0.002	0.0200 ± 0.0001	0.080 ± 0.004
Docosadiene C22:2	0.020 ± 0.001	0.030 ± 0.001	0.050 ± 0.003	0.460 ± 0.007	0.040 ± 0.009	0.050 ± 0.006
Lignocerin C24:0	0.25 ± 0.07	0.34 ± 0.03	0.190 ± 0.002	0.040 ± 0.001	0.250 ± 0.004	0.200 ± 0.001

Note: the data is presented as a mass fraction of fatty acid in % of the sum of fatty acids.

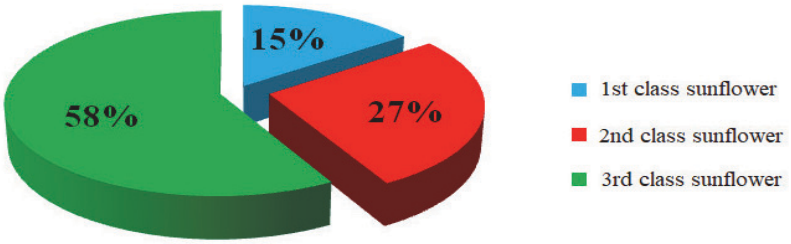

Fig. 1. Class of sunflower seeds, depending on the mass fraction of oil

which corresponds to ordinary oil. Therefore, a significant proportion of sunflower oil produced in Ukraine does not meet the requirements of the current DSTU, since the oleic acid content is higher than 39.4 %. Therefore, the tested oil refers to high oleic.

After analyzing the results of the study of the fatty acid composition of oil sold in Ukraine and received at the ULQSAP in 2017–2019, it can be noted that the highest share of high-oleic sunflower oil was in 2019 (57.14 %), slightly lower - in 2017 (40 %) and the lowest in 2018 (18.8 %).

The trend of high-oleic oil share growth in the Ukrainian market can be explained by the promotion of healthy food, the increased need of the oil industry for new types of oil having the necessary qualities.

Qualitative indicators of sunflower oil are directly dependent on raw materials (sunflower seeds). One of the important indicators of the quality of sunflower seeds is the mass fraction of oil (DSTU 7011: 2009).

According to DSTU 7011: 2009 the mass fraction of oil in terms of dry matter

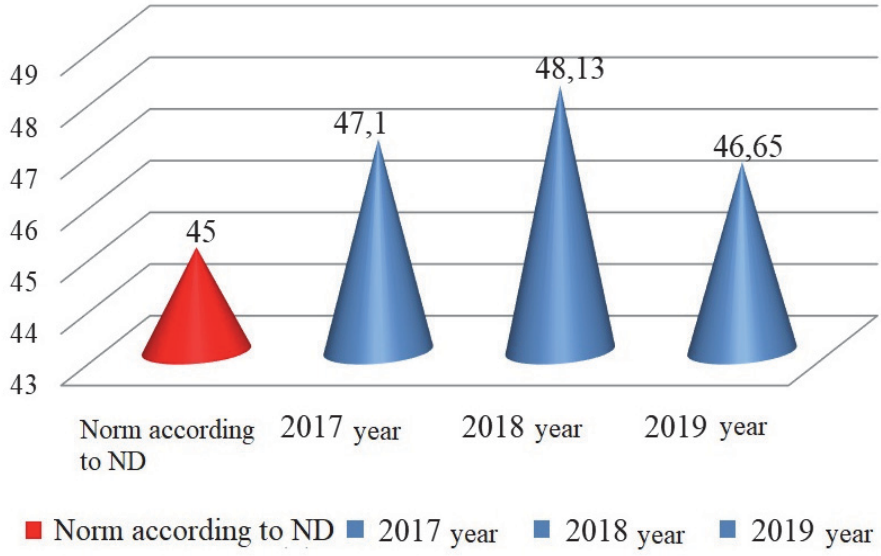

Fig. 2. Mass fraction of oil in seeds and sunflowers in terms of dry matter, %

for the first class of sunflower should be not less than 50,0 %, for the second - not less than 45, for the third class - not less than 40.

During 2019, 33 sunflower seed samples were analyzed for this indicator by the ULQSP AIC. Of these, 58 % were in class 2, 27 % were in class 3 and 15 % were in class 1. The average oil content is 46.65 (Fig. 1, 2). Studies of 78 samples of sunflower seeds in 2018 showed that a larger proportion of the seeds used for oil production are also 2nd class (65.52 %) with an average oil content of 48.13 % (Fig. 2). According to the research of 42 samples of sunflower seeds in 2017, it was found that the majority – 77.14 % of the samples – were classified as 2nd class, with an average oil content of 47.1 % (Fig. 2).

Therefore, in the Ukrainian market, raw materials for the production of oil, mainly belong to the 2nd clas. As to the sunflower oil itself, according to its oleic acid content and with average oil yield, the most part of the oil belongs to high oleic. The highest oil content of the second class was in 2018. This is 1 % higher than in 2017 and 1.48 % higher than in 2019. The decrease in sunflower seed oil output in 2019 can be explained by the influence of the soil and climatic conditions of cultivation, since this year there was not enough rainfall throughout the growing season.

Conclusions and further research prospects

An analysis of regulations such as DSTU 4492:2017, GOST 30623-98, CODEX STAN 210-1999 regarding the fatty acid composition of sunflower oil indicates that the current DSTU needs to be amended with respect to the requirements for high oleic oil as for the prevailing product in the Ukrainian market.

The proportion of high-oleic sunflower oil samples received for research at ULQSAP in 2019 has increased compared to 2018. This confirms the global trend towards increasing the cultivation of sunflower seeds with high oleic acid content.

In Ukraine, sunflower seeds of 2nd class are mainly used for the production of sunflower oil. This shows the need for improving the requirements for the first stage of oil production - growing and obtaining sunflower seeds.

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Анотація. *Попит на високоолеїнову соняшникову олію у зв'язку зі зростаючою потребою людства у корисних для здоров'я харчових продуктах як в Україні, так і в світі щороку зростає. Вона має цінні властивості як для виробників, так і споживачів. Отже, встановлення норм щодо жирнокислотного складу насіння соняшника і соняшникової олії стає досить актуальним і важливим. Мета роботи – провести порівняльний аналіз нормативно-правових актів України та міжнародних щодо вмісту жирних кислот у соняшниковій олії; дослідити олію соняшникову та насіння соняшника, що є на ринку України, за окремими показниками якості та встановити частку високоолеїнової олії.*

У статті проведено порівняльний аналіз вітчизняних та міжнародних нормативних документів. В чинному ДСТУ 4492:2017 відсутній розподіл соняшникової олії залежно від вмісту олеїнової кислоти. Ця кислота нормується в межах 14,0–39,4 %, що відповідає звичайній олії. За міжнародними вимогами олія соняшникова поділяється на звичайну, із середнім вмістом олеїнової кислоти і високоолеїнову та регламентується більша кількість жирних кислот. Нами проведено визначення жирнокислотного складу насіння соняшника та соняшникової олії, що надходила для досліджень в УЛЯБП АПК впродовж 2017–2019 рр., методом газової хроматографії. Встановлено, що на ринку України в реалізацію надходить значна частка високоолеїнової олії, зокрема, найбільше у 2019 р. (57,14 %), порівняно з 2018 роком (18,8 %) та 2017 (40 %). Це підтверджує світову тенденцію щодо збільшення вирощування сортів соняшнику з високим вмістом олеїнової кислоти в Україні.

Здійснено порівняльний аналіз насіння соняшника щодо масової частки олії за 2017–2019 рр. Встановлено, що за вмістом масової частки олії насіння соняшнику, що використовують для виготовлення олії соняшникової в Україні, відноситься переважно до другого класу.

Ключові слова: *жирні кислоти, високоолеїнова олія, насіння соняшнику, олеїнова кислота, масова частка олії*

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