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# DETERMINATION OF CARBONIC ACID CONTENT IN CEDAR AND WALNUT MEALS BY CHROMATOGRAPHY

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#### **Abstract**

The method of chromatography determined the quantitative and qualitative composition of carboxylic acids in meal of cedar (CNM) and walnuts (WNM). It was found that CNM and WNM contain a total of 36 carboxylic acids. WNM also contains more dicarboxylic and polybasic carboxylic acids, and CNM is 2.4 times higher than WNM in terms of aromatic acids and their derivatives. The nutritional value of nut meal fats was assessed. It was found that WNM fats have a higher degree of unsaturation compared to CNM - the total content of MUFA and PUFA in walnut meal is 95.79 % of the total fat, and in pine nut meal - 80.19 %. According to the number of PUFAs, the fats of CNM and WNM almost do not differ - their content is 53.16 and 54.82 %, respectively. It is noted that PUFAs of pine nut meal are represented mainly by linolenic acid (94.6% of all PUFAs), and PUFAs of walnut meal - linoleic (57.3 % of all PUFAs). Studies of the ratio of SFA: MUFA: PUFA and omega-6: omega-3 have identified the feasibility of using nut meal in food technology to balance their fatty acid composition. Nut meal contains some organic acids, mainly citric, succinic, fumaric and malic. It is noted that SHVG significantly exceeds CNM in the content of malic and fumaric acids - 5.3 and 100 times, respectively. Pine nut meal has a higher content of citric and succinic acids (2.9 and 2.2 times, respectively). Despite the fact that the total nuber of organic acids does not meet the recommended consumption standards, the use of CNM and WNM in food technology will provide opportunities to slightly increase the content of these nutrients in the finished product. It was found that the composition of CNM includes 11.27 mg/ 100 g of aromatic acids and their derivatives, and the composition of WNM - 4.75 mg / 100 g, respectively. However, compared to other phenolic compounds, aromatic acids have less biological activity. In view of the above, further studies on the establishment of the content of polyphenols and polymeric phenolic compounds in CNM and WNM are promising.

*Keywords:* pine nut meal; walnut meal; carboxylic acids; fatty acids; gas-liquid chromatography.

## ВИЗНАЧЕННЯ ВМІСТУ КАРБОНОВИХ КИСЛОТ В ШРОТАХ КЕДРОВОГО ТА ВОЛОСЬКОГО ГОРІХІВ МЕТОДОМ ХРОМАТОГРАФІЇ

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#### Анотація

Методом хроматографії визначено кількісний та якісний склад карбонових кислот у шротах кедрового (ШКГ) і волоського горіхів (ШВГ). Встановлено, що до ШКГ та ШВГ входить сумарно 36 карбонових кислот. Також до складу ШВГ входить більша кількість дикарбонових та багатоосновних карбонових кислот, а ШКГ в 2.4 рази перевершує ШВГ за вмістом ароматичних кислот та їх похідних. Проведено оцінку харчової цінності жирів горіхових шротів. Встановлено, що жирам ШВГ притаманна більша ступінь ненасиченості порівняно з ШКГ - сумарний вміст МНЖК та ПНЖК у шроті волоського горіху становить 95.79 % загальної кількості жирів, а у шроті кедрового горіху - 80.19 %. За кількістю ПНЖК жири ШКГ та ШВГ майже не відрізняються - їх вміст складає 53.16 та 54.82 % відповідно. Відмічається, що ПНЖК шроту кедрового горіха представлені переважно ліноленовою кислотою (94.6% від всіх ПНЖК), а ПНЖК шроту волоського горіху лінолевою (57.3 % від всіх ПНЖК). Дослідження співвідношення НЖК : МНЖК : ПНЖК та омега-6 : омега-3 виявили доцільність використання горіхових шротів в технологіях харчових продуктів для збалансування їх жирнокислотного складу. В горіхових шротах встановлено наявність деяких органічних кислот, переважно лимонної, бурштинової, фумарової та яблучної. Відмічається, що ШВГ суттєво перевершує ШКГ за вмістом яблучної та фумарової кислот - у 5.3 та 100 рази відповідно. Для шроту кедрового горіху притаманний вищій вміст лимонної та бурштинової кислот (у 2.9 та 2.2 рази відповідно). Незважаючи на те, що сумарна кількість органічних кислот не відповідає рекомендованим нормам споживання, застосування ШКГ та ШВГ в харчових технологіях надасть можливості дещо підвищити вміст цих аліментарних речовин у готовій продукції.

Встановлено, що до складу ШКГ входить 11.27 мг/100 г ароматичних кислот та їх похідних, а до складу ШВГ – 4.75 мг/100 г відповідно. Однак, порівняно з іншими фенольними сполуками, ароматичним кислотами притаманна менша біологічна активність. Зважаючи на зазначене перспективними є подальші дослідження, щодо встановлення вмісту у ШКГ та ШВГ поліфенолів та полімерних фенольних сполук.

*Ключові слова:* шрот кедрового горіха; шрот волоського горіха; карбонові кислоти; жирні кислоти; газорідинна хроматографія.

### ОПРЕДЕЛЕНИЕ СОДЕРЖАНИЯ КАРБОНОВЫХ КИСЛОТ В ШРОТАХ КЕДРОВОГО И ВОЛОССКОГО ОРЕХОВ МЕТОДОМ ХРОМАТОГРАФИИ

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#### Аннотация

Методом хроматографии определен количественный и качественный состав карбоновых кислот в шротах кедрового (ШКО) и грецкого орехов (ШГО). Установлено, что в ШКГ и ШВГ входит суммарно 36 карбоновых кислот. Также в состав ШВГ входит большее количество дикарбоновых и многоосновных карбоновых кислот, а ШКГ в 2.4 раза превосходит ШВГ по содержанию ароматических кислот и их производных. Проведена оценка пищевой ценности жиров ореховых шротов. Установлено, что жирам ШВГ присуща большая степень ненасыщенности по сравнению с ШКГ - суммарное содержание МНЖК и ПНЖК в шроте грецкого ореха составляет 95.79 % от общего количества жиров, а в шроте кедрового ореха - 80,19%. По количеству ПНЖК жиры ШКГ и ШВГ почти не отличаются - их содержание составляет 53,16 и 54,82% соответственно. Отмечается, что ПНЖК шрота кедрового ореха представлены преимущественно линоленовой кислотой (94.6 % от всех ПНЖК), а ПНЖК шрота грецкого ореха - линолевой (57,3% от всех ПНЖК). Исследование соотношения НЖК: МНЖК: ПНЖК и омега-6: омега-3 выявили целесообразность использования ореховых шротов в технологиях пищевых продуктов для сбалансирования их жирнокислотного состава. В ореховых шротах установлено наличие некоторых органических кислот, преимущественно лимонной, янтарной, фумаровой и яблочной. Отмечается, что ШВГ существенно превосходит ШКГ по содержанию яблочной и фумаровой кислот - в 5.3 и 100 раз соответственно. Для шрота кедрового ореха присуще высшее содержание лимонной и янтарной кислот (в 2.9 и 2.2 раза соответственно). Несмотря на то, что суммарное количество органических кислот не соответствует рекомендованным нормам потребления, применение ШКГ и ШВГ в пищевых технологиях позволит несколько повысить содержание этих алиментарных веществ в готовой продукции. Установлено, что в состав ШКГ входит 11.27 мг/100 г ароматических кислот и их производных, а в состав ШВГ - 4.75 мг/100 г соответственно. Однако по сравнению с другими фенольными соединениями ароматическим кислотам присуща меньшая биологическая активность. Учитывая указанное, перспективными являются дальнейшие исследования относительно установления содержания в ШКГ и ШВГ полифенолов и полимерных фенольных соединений.

*Ключевые слова:* шрот кедрового ореха; шрот грецкого ореха; карбоновые кислоты; жирные кислоты; газожидкостная хроматография.

#### Introduction

Today, global nutrition trends are largely focused on creating safe and healthy products. The problem of nutrition became especially acute during the COVID-19 pandemic. The pandemicrelated food disruption, increased stress and hypodynamia due to quarantine restrictions have led to significant distortions in the structure of nutrition and negatively affected the absorption of essential nutrients. As a result, there is a dynamic increase in the body mass index, increased risk of cardiovascular and neurological diseases, decreased immunity, etc. [1]. A promising direction in eliminating deficiencies in diets is the modification of food products in the direction of their enrichment with vital substances for the human body. This indicates the urgency of finding new types of raw materials that can be used as enrichment additives.

Nuts and products of their processing deserve special attention from this point of view. Clinical studies have proven the positive effect of nuts on brain activity, the level of reduction of oxidative stress in the body, their preventive effect against cardiovascular disease and obesity, etc. [2–7].

Useful properties of nut raw materials are largely due to the peculiarities of their chemical composition. All types of nuts have a significant content of fats (up to 74 %), proteins with high biological value (up to 25 %), vitamins, minerals and other components important for human metabolism [8–10].

The peculiarity of nut lipids is the unique composition of fatty acids, which are considered one of the most useful nutrients to support the internal organs and hormonal system, the presence of fat-soluble vitamins (A, E) and other lipid compounds essential for the human body (choline, inositol, lecithin, etc.) [11–13]. Due to this, today nuts are widely used in the oil industry to obtain oils. The increase in demand for nut oils is largely due to the consumer's desire to exclude from the diet of unhealthy solid and

modified fats that contain significant amounts of saturated fatty acids or are characterized by the presence of their trans isomers. Harmfulness of such fat products is currently proven in the framework of domestic and European legislation [14].

Tendencies to increase the production of nut oils lead to a new problem related to the disposal of by-products of such production (meal and cake), the amount of which is about 40% [15]. It is known that meal and cake are a kind of concentrate of useful nutrients (proteins, nonstarch polysaccharides, polyphenols, minerals, vitamins, etc.), which have a positive effect on human metabolism [16]. Despite its high biological value, by-products of vegetable oil production are mainly used for animal feed, and only 15% goes to food production [15]. Meanwhile, due to the imbalance in the diets of modern man, it is promising to use such raw materials as a fortifier for foods. The advantage of such supplements is the absence of cholesterol, unique chemical composition, good digestibility by the human body, ease of transportation, storage and dosing.

In view of this, the study of by-products of the raw nut processing: their chemical composition, technological properties and biological and physiological value, is an urgent task today.

Formulation of the problem. The following types of nuts are most widely represented on the Ukrainian market: peanuts, walnuts, hazelnuts, almonds, cashews, pistachios and pine nuts. However, to date, hazelnuts, cashews, pistachios, peanuts and almonds are not used as raw materials for edible oils. From the list provided, only cedar and walnuts are processed into oils, which are traditional for the countries of the middle climate zone, which includes most countries in Europe, Central Asia and North America. The meal and flour differ in the mode of production. Cake is a product that remains after pressing of oil. The meal is obtained by extraction vegetable oils. The meal is usually characterized by a lower residual fat content. However, today many manufacturers position floure as meal. This causes some difficulties in analyzing the results of studies of the chemical composition of such products, which have been studied by various scientists. In view of this, one of the problems with the recommendation of byproducts of cedar and walnut processing for use as fortification additives for various types of food products is to determine the characteristics of their chemical composition. This will not only determine the effectiveness of such additives to improve the nutritional composition of products, but also cause them to show certain functional and technological properties [17].

Analysis of recent research and publications. In previous studies. It was found that walnut and cedar nut meal is characterized by a significant content of protein (33.6 and 38.1%, respectively) with high biological value, which makes them a promising source of protein replenishment in diets [18,19,20]. The content of carbohydrates in these supplements is almost the same (about 45%), they are mainly dietary fiber (25 and 42%), which are very important for normal bowel function and have good radioprotective properties. Carbohydrate of nut meal also contains a significant amount of mono and oligosaccharides (more than 25 and 40%, respectively), which give them a sweet taste. This may be the reason for reducing the prescription sugar content in products using such additives. Also due to the fact that these nut meals obtained by cold pressing they remain a significant amount of useful fats (12.2 and 7.1 % for walnut meal and cedar nut, respectively). In addition, according to research.

The studied products of nut processing include polyphenolic compounds, minerals (iron, potassium, calcium, manganese, copper, zinc, etc.) and vitamins (mainly vitamin E and B vitamins) in significant amounts for the human body [18–20].

As we can see, cedar and walnut meal can be a useful fortifier for a number of consumer products. In particular, pine nut meal is recommended for use in pate technologies [21], spreads [22], cream or cheese [23], sour milk drinks [24; 25], gingerbread [26] etc. Walnut meal is used in the manufacture of sugar and shortbread cookies [27; 28], gingerbread [29], bakery products [30], halva [31] and fillings for candies [32].

It is noted that the products using walnut meal and cedar nuts had a more harmonious taste, the introduction of these additives made their organoleptic characteristics more interesting for the consumer. Also, such products are characterized by improved nutrient composition - enriched with biologically valuable protein, dietary fiber, minerals and vitamins.

However, it is promising to evaluate cedar and walnut meal as a source of other biologically valuable compounds - including carboxylic acids, whose role in ensuring the normal functioning of the human body is very important. Among carboxylic acids, aliphatic acids (especially unsaturated), organic acids (citric, malic), as well

as aromatic acids and their derivatives (vanillic, lilac, ferulic), which belong to the group of phenolic compounds. have the greatest known nutritional value. It is that polyunsaturated fatty acids the prevent development of atherosclerosis by normalizing cholesterol metabolism, participate in the formation of immunity, are largely responsible for ensuring metabolic processes in the human body [33]. It is important not only the quantitative content of polyunsaturated fatty acids, but also their qualitative composition - the ratio of omega 3 and omega-6 fatty acids should be 1: (5... 8) [34; 35].

Dicarboxylic and polybasic carboxylic acids (malic, citric, succinic, etc.), which belong to organic acids, also have a positive effect on metabolism. They have anti-inflammatory and properties, improve antioxidant digestion, pathogenic prevent the development of microflora. Some of them (for example, succinic acid) have antiviral and antihypoxic effects and normalizing effects on brain function Phenolic compounds have antimicrobial, antioxidant, adaptogenic and immunostimulatory effects [36]. In view of the above, the following studies considered it appropriate to determine the content of these physiologically useful substances in nut meal.

The purpose of the study. The aim of the research was to determine the content of carboxylic acids in cedar and walnut meal.

The object of the study was cedar nut meal (CNM) and walnut meal (WNM) produced by Elitfito LLC (Ivano-Frankivsk, Ukraine). These products are obtained after extraction of oil by cold pressing with subsequent grinding and by definition they are cakes, but LLC "Elitfito" positions their product form as "meal", which was the basis for the use of this terminology in these studies.

**Experimental methodology.** The carboxylic acid content of nut meal was determined by gasliquid chromatography using an AgilentTechnologies 6890 chromatograph with detector 5973. The NIST05 and WILEY 2007 mass spectrum libraries with a total number of spectra of more than 470000 were used to identify the components in combination with NIST. The method of internal standard is used for quantitative calculations.

Analysis of fatty acid content was performed under standard conditions commonly used for the separation of carbonaceous hydrolysates. Peak areas of identified fatty acids were determined (automatically) for quantification. The amount of each identified acid was determined in nanomoles and nanograms in the aliquot used for analysis. Then the total acid content in mg / 100 ml was calculated.

To determine the bound fatty acids, a portion of the dry raw material was extracted with 80% ethyl alcohol, and then the sample was filled with purified water and concentrated hydrochloric acid, hydrolyzed and then determined the content of carboxylic acids. The concentration of free fatty acids was calculated as the difference between the concentration of total carboxylic acids and the concentration of bound carboxylic acids [37; 38].

To find out the total composition of carbon cedar and walnut meal acids to 50 mg of dried materials in a vial was added 2 ml of internal standard (50 mcg of tridecane in hexane) and poured 1.0 ml of methylating agent (14 % BCI $_3$  in methanol, Supelco 3-3033). The mixture was kept in a hermetically sealed vial for 8 hours. for temperatures of 65 °C. During this time, fatty oil is completely extracted from the plant material, it is hydrolyzed into fatty acid components and their methylation. Simultaneously, free organic and aromatic carboxylic acids are methylated [39, 40].

The reaction mixture was drained from the precipitate of plant material, diluted with 1 ml of distilled water. To remove the fatty acid methyl esters, 0.2 ml of methylene chloride was poured in, shaking gently several times over time, and then the resulting extract was chromatographed with methyl ether.

The introduction of the sample (2  $\mu$ l) into the chromatographic column was performed in splitless mode, occurs without flow separation, which allows to conduct the sample without loss on division and significantly (10–20 times) increase the sensitivity of the chromatographic method. The rate of addition of the sample 1.2 ml / min for 0.2 minutes

The method of internal standard was used for quantitative calculation [40]. The calculation of the components was performed according to the formulas

$$C = K_1 \cdot K_2 \cdot 1000, (M\Gamma/K\Gamma);$$

$$K_1 = \frac{\pi_1}{\pi_2};$$

$$K_2 = \frac{50}{M};$$

where P1 is the peak area of the test substance;

P2 - peak area of the standard;

50 – weight of the internal standard (m / kg) entered in the sample;

M - sample weight (mg).

To simplify the perception of the obtained results, the carboxylic acid content was recalculated per 100 g of the corresponding meal.

#### **Results and discussion**

The results of chromatographic studies of cedar and walnut meal are presented in Fig. 1 and 2.

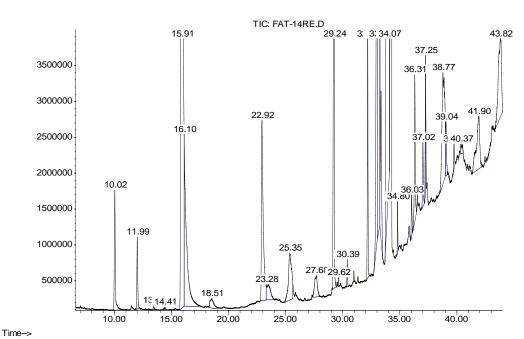


Fig. 1. Chromatogram of carboxylic acids of pine nut meal

Abundance

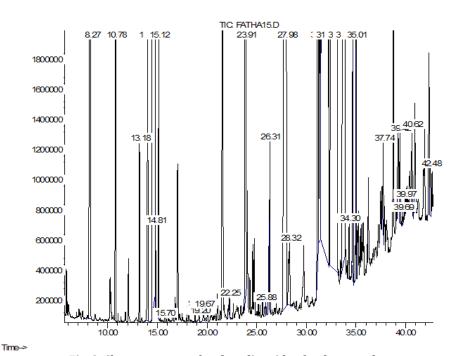


Fig. 2. Chromatogram of carboxylic acids of walnut meal

As a result of the analysis of the results of chromatographic studies in the studied samples of nut meal, 36 carboxylic acids were identified (Table 1). Significant amounts of these

compounds are present in both test samples, but some of them are specific to a particular meal. In particular, pentadecanoic, heptadecane, pcoumaric, m-coumaric, hexadecanedicarboxylic tricosanoic and ferulic acids, which are absent in CNM, were found in the WNM. At the same time, walnut meal contains carboxylic acids that are not included in cedar nut meal -  $\alpha$ -furan, benzoic,

phenylacetic, salicylic, lauric, 11-eicosan and poxybenzene.

Table 1

#### Carbon content in meal of cedar and walnuts

The name of the acid	Results of chromatogram analysis				
	for CN		for W	NM	
	P <sub>1</sub> - is the area of the test substance	Content of the substance, mg / 100 g of meal	P <sub>1</sub> - is the area of the test substance	Content of the substance, mg / 100 g of mea	
Oxalic	95.44	1.36	555.21	7.9	
Malonic	5.27	0.07	173.00	2.4	
Fumaric	4.92	0.07	494.07	7.0	
Levulinic	3213.83	45.6	8023.75	114.6	
α-furanic	-	-	47.36	0.5	
Amber	592.05	8.0	249.89	3.6	
Benzoin	-	-	4.03	0.05	
Phenylacetic	-	-	8.87	0.1	
Salicylic	-	-	8.00	0.1	
Lauric	-	-	16.67	0.2	
3-hydroxy-2-methylglutaric	55.84	0.7	17.96	2.0	
Apple	517.36	7.3	2766.60	39.0	
Myristic	92.91	1.3	24.55	0.3	
Pentadecanoic	235.84	3.3	-	-	
Azelaic	98.22	1.4	210.75	3.0	
Palmitic	1018.53	14.5	7472.83	2.5	
Palmitoleic	7.66	0.1	175.30	106.0	
Heptadecanoic	23.70	0.3	-	-	
Lemon	573.84	8.1	1989.24	28.0	
Stearic	620.90	8.1	645.04	9.2	
Oleic	3198.44	45.6	7298.58	104.0	
Linoleic	344.64	4.9	11300.62	161.0	
Linolenic	5980.73	85.0	8429.12	120.0	
Vanillic	38.91	0.5	84.73	1.2	
Arachidic	47.84	0.6	376.33	5.7	
r-cumaric	205.01	2.9	-	-	
m-cumaric	80.24	1.1	-	-	
11- eicosanoic	-	-	183.71	2.6	
Begenic	97.55	1.3	105.84	1.5	
Hexadecandicarboxylic	478.40	6.7	-	-	
p-hydroxybenzene	-	-	138.89	1.9	
Purple	40.36	0.57	13.78	0.1	
Tricosanoic	36.19	0.5	-	-	
Gentisic	41.11	0.5	17.69	0.2	
Tetracosanoic	275.95	3.9	154.13	2.2	
Ferulic	400.08	5.7	-	-	
In all		265.10		726.85	

As it can be seen in the table. 1, behind the gallbladder of carboxylic acids, the meal of the hairy peat significantly overturns the cedar - 2.8 times. The main number of identified half-fatty acids is fatty (aliphatic) acids, so that the pre-

juvenile stage of the WNM is, according to the CNM, a significantly larger surplus instead of fat (Table 2).

Table 2

Uzagalnye danny shodo vmistu carboxylic acids in cedar meal hairy mountains

Carboxylic acid groups	Acid content n	Acid content, mg / 100 g of mealm	
car boxyne acia groups	CNM	WNM	
Saturated fatty acids (SFA)	33.5	21.6	
Monounsaturated fatty acids (MUFA)	45.7	210.0	
Polyunsaturated fatty acids (PUFA)	89.9	281.0	
Dicarboxylic and polybasic saturated acids	79.53	201.0	
Unsaturated polybasic acids	0.07	7.0	
Aromatic acid compounds	11.207	4.75	

It was found that 100~g of SHKG contains 169.1~mg of fat, and 100~g of WNM - 3 times more (512.6 mg), which is 65.0~and 70.5% of the content of all carboxylic acids. In view of the

above, at the next stage it was considered expedient to evaluate the peculiarities of the fatty acid composition of the fats of the studied nut meal (Table 3).

Table 3

P1		c 1 1		c .
Fatty acid	composition	of cedar and	l walnut meal	iats

Fatty acids	Symbolic image	Content,%	of total fat
		in CNM	in WNM
Saturated (SFA), including:			4.21
Laurinic	C <sub>12:0</sub>	-	0.04
myristic	C <sub>14:0</sub>	0.77	0.06
Pentadecanoic	C <sub>15:0</sub>	1.95	-
palmitic	C <sub>16:0</sub>	8.58	0.49
stearicц	C <sub>18:0</sub>	4.77	1.79
Arachidic	C <sub>20:0</sub>	0.36	1.11
Begenic	C <sub>22:0</sub>	0.77	0.29
Tricosanoic	C <sub>23:0</sub>	0.30	-
Tetracosanoic	C <sub>24:0</sub>	2.31	0.43
Monounsaturated (MUFA), including:		27.03	40.97
palmitoleic (Omega-7)	C <sub>16:1n9</sub>	0.06	20.68
oleic (Omega-9)	C <sub>18:1n9</sub>	26.97	20.29
Polyunsaturated (PUFA), including:		53.16	54.82
linoleic (Omega-6)	C <sub>18:2n9,12</sub>	2.89	31.41
linolenic (Omega-3)	C <sub>18:3n9,12,15</sub>	50.27	23.41

The results of studies indicate a high content of unsaturated fatty acids in nut meal, and the degree of unsaturation of WNM fats characterized by a higher value compared to CNM fats: the total content of MUFA and PUFA in walnut meal is 95.79 % of total fat - 80.19%. According to the number of PUFAs, the fats of CNM and WNM almost do not differ - their content is 53.16 and 54.82 %, respectively. On the one hand, PUFAs have a high physiological value they are structural elements of phospholipids, lipoproteins and participate in the formation of myelin membranes of tissues, affect cholesterol levels and more. On the other hand, such fatty acids are easily oxidized, which will require some control over the state of the lipid complex of food products using these nut meals.

From a physiological point of view, it is important not only the quantitative content of PUFA, but also their qualitative composition. It is noted that PUFAs of pine nut meal are represented mainly by linolenic acid (94.6 % of all PUFAs), which belongs to the omega-3 family. PUFAs of walnut meal by 57.3 % consist of linoleic acid, which belongs to the omega-6 family. Omega-6 and omega-3 fatty acids have different effects on the human body. They compete for one enzyme - delta-6 desaturase, through which these PUFAs are converted into longer-chain acids, so the ratio of these fatty acids will significantly affect metabolic processes in the body. According to the requirements of nutrition, omega-6 and omega-3 fatty acids must enter the body in a ratio of (8-9): 1 for healthy people and in a ratio of 5: 1 for therapeutic and prophylactic nutrition [41]. The desired ratio of omega-6: omega-3 should be <5. It was found that for CNM fats this ratio is 1:17.4 = 0.06, and for WNM fats -

1:0.75 = 1.33 (Table 4), which allows us to recommend the use of these nut meals to improve the fatty acid composition foods that are dominated by PUFAs of the omega-6 family.

Table 4

Fats	•	Fatty acid ratios		
	omega-6 : omega-3 (18:2:	omega-6 : omega-9	SFA : MUFA : PUFA	
	18:3)	(18:2:18:1)		
Perfect fat	<5	>0.25	1:1:1	
fats CNM	0.06	0.11	1:1.4:2,7	
fats WNM	1.33	1.55	1:9.7:13	

Important from the point of view of determining the nutritional value of fats is the ratio of SFA: MUFA: PUFA, which should be 1: 1: 1.: 13. Given the congestion of modern diets with saturated fatty acids, the data indicate the feasibility of using CNM and WNM to balance foods with fatty acid composition.

Another indicator of the nutritional value of fats is the ratio of linoleic and oleic acids (18: 2: 18: 1). It is established that for CNM this ratio is

equal to 0,11, and for WNM – 1.55. The optimal ratio of linoleic to oleic acid in the diet should be> 0.25, therefore, for walnut meal it is optimal, and for cedar meal - no.

Biologically active substances that are part of nut meal also include some organic acids: citric, succinic, fumaric and malic.

It was found (Fig. 3) that WNM significantly exceeds CNM in the content of malic and fumaric acids - 5.3 and 100 times, respectively.

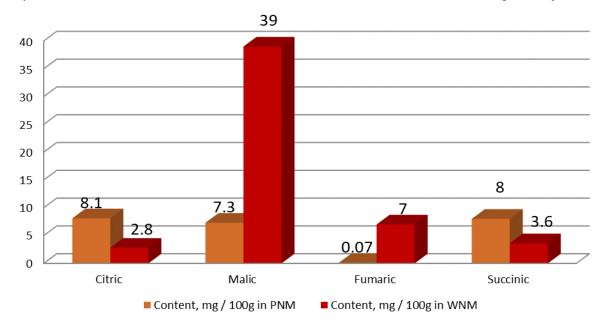


Fig. 3. Content organic acids in nut meal according to the data chromatographic study

Pine nut meal has a higher content of citric and succinic acids (2.9 and 2.2 times, respectively). The recommended intake of organic acids is about 500 mg / day, so the studied nut meal can not be considered as a source of such compounds. But their application in food technology will provide opportunities to slightly increase the content of these alimentary substances in products.

Also important is the presence of aromatic carboxylic acids in CNM and WNM, also called

phenolic acids. Their feature is the ability to exhibit the properties of both carboxylic acids and phenols. It was found (Table 2) that the content of phenolic acids and their derivatives of pine nut meal is 2.4 times higher than that of walnut meal. However, compared to other phenolic compounds, aromatic acids have less biological activity. In view of the above, further studies on the content of polyphenols and polymeric phenolic compounds in CNM and WNM are promising.

#### **Conclusions**

It was established by gas-liquid chromatography that cedar and walnut meals contain a total of 36 carboxylic acids. Special physiological importance among these compounds are fatty acids, organic acids, and aromatic acids belonging to the group of phenols.

Walnut meal is 2.8 times higher than cedar in total carboxylic acid content and 3 times higher in fatty acid content. WNM also contains more dicarboxylic and polybasic carboxylic acids, and CNM is 2.4 times higher than WNM in terms of aromatic acids and their derivatives.

The nutritional value of nut meal fats was assessed. It was found that WNM fats have a higher degree of unsaturation compared to. It is noted that PUFAs of pine nut meal are mainly linolenic acid, and PUFAs of walnut meal - linoleic. Studies of the ratio of SFA: MUFA: PUFA and omega-6: omega-3 have identified the feasibility of using nut meal in food technology to balance its fatty acid composition.

The presence of some organic acids was found in nut meal, mainly citric, succinic, fumaric and malic. Despite the fact that their total number does not meet the recommended consumption standards, the use of WNM and CNM in food technology will provide opportunities to slightly increase the content of these alimentary substances in products.

It is also important to have aromatic carboxylic acids and their derivatives in GCG and LNG. However, compared to other phenolic compounds, aromatic acids have less biological activity. In view of the above, further studies on the establishment of the content of polyphenols and polymeric phenolic compounds in WNM and CNM are promising.

#### References

- [1] Tsentr hromadskoho zdorovia MOZ Ukrainy. (2021). Chas obyraty zdorovia. Retrieved from https://www.phc.org.ua/news/pravilne-kharchuvannya-pid-chas-pandemii.
- [2] Petrović-Oggiano, G., Debeljak-Martačić, J., Ranković, S., Pokimica B., Mirić, A., Glibetić, M., & Popović, T. (2020). The Effect of walnut consumption on n-3 fatty acid profile of healthy people living in a non-mediterranean west Balkan Country, a small scale randomized study. *Nutrients*, 12(1), 192, 1-11. doi: https://doi.org 10.3390/nu12010192
- [3] Feng, L., Peng, F., Wang, X., Hongjie, M., & Huaide, L. X. (2019). Identification and characterization of antioxidative peptides derived from simulated in vitro gastrointestinal digestion of walnut meal proteins. *Food* research international, 116, 518–526. Retrieved from

- https://www.sciencedirect.com/science/article/abs/pii/S0963996918306835
- [4] Rock, C. L., Flatt, S. W., Barkai, H.-S., Pakiz, B., & Heath D. D. A. (2018). Walnut-containing meal had similar effects on early satiety, CCK, and PYY, but attenuated the postprandial GLP-1 and insulin response compared to a nut-free control meal. *Appetite*. 117, 51–57. doi: https://doi.org 10.1016/j.appet.2017.06.008.
- [5] Neale, E. P., Tran, G., & Brown, R. C. (2020). Barriers and Facilitators to Nut Consumption: A Narrative Review. International Journal of Environmental Research and Public Health.; 17(23):9127. Published online. doi: https://doi.org 10.3390/ijerph17239127.
- 6] Brown, R., Gray, R. A., Chua, M. G., Ware, L., Chisholm, A, & Tey, S. L. (2021). Is a handful an effective way to guide nut recommendations? Randomized controlled trial *International Journal of Environmental Research and Public Health.* 23;18(15):7812. doi: https://doi.org 10.3390/ijerph18157812.
- [7] Holscher, H. D., Guetterman, H. M., Swanson, K. S., Ruopeng, A., Matthan, N. R., Lichtenstein A. H., Novotny, J. A., & Baer D. J. (2018). Walnut consumption alters the gastrointestinal microbiota, microbially derived secondary bile acids and health markers in healthy adults: a randomized controlled trial. *The Journal of Nutrition*, 148(6), 861–867. doi: https://doi.org 10.1093/jn/nxy004
- [8] Tomaino, A., Martorana, M., Arcoraci, T., Monteleone, D., Giovinazzo, C., & Saija, A. (2010). Antioxidant activity and phenolic profile of pistachio (Pistacia vera L., variety Bronte) seeds and skins. *Biochimie*, 92(9), 1115–1122. doi: https://doi.org 10.1016/j.biochi.2010.03.027
- [9] Jackson, C. L., & Frank, B. H. (2014). Long-term associations of nut consumption with body weight and obesity. American journal of clinical nutrition, 100, 1(1):408-411. doi: https://doi.org 10.3945/ajcn.113.071332
- [10] Zheng, Y., Wu S., Wang R., Wu Y., Zhang, W., Han, Y., Tang, F., Shen D., & Liu, Y. (2020) Analysis and correlationship of chemical components of various walnut (Juglans regia L.) cultivars. *Journal of Food Measurement and Characterization*, 14(6), 3605-3614. doi: https://doi.org/10.1007/s11694-020-00603-0
- [11] Moodley, R., Kindness, A., & Sreekanth, B. (2007). Elemental composition and chemical characteristics of five edible nuts (almond, Brazil, pecan, macadamia and walnut) consumed in Southern Africa. *Journal of Environmental Science and Health. Part B, 42(5),* 585– 591. https://doi.org/10.1080/03601230701391591
- [12] Pan Z., Zhang R., Zicari, S. (2019). Integrated processing technologies for food and agricultural By-Products/Walnuts, 391–411. Retrieved from https://www.sciencedirect.com/science/book/9780128141380.pdf
- [13] Cittadini, M. C., Martín, D., Gallo, S., Fuente, G., Bodoira, R, Martínez, M., Maestri, D. (2020). Evaluation of hazelnut and walnut oil chemical traits from conventional cultivars and native genetic resources in a non-traditional crop environment from Argentina. *European Food Research and Technology*, 113. doi: https://doi.org/10.1007/s00217-020-03453-8

- [14] Chynni obmezhennia na palmovu oliiu v krainakh YeS. (2021). Retrieved from http://euinfocenter.rada.gov.ua/uploads/documents/29 481.pdf
- [15] Lyshaeva, L., Domoroshchenkova, M., & Kyryllova, O. (2010). Razvytye myrovoho runka shrotov y zhmukhov. Kombykorma, *6*, 15–17.
- [16] Wang, G., Zhong, D., Liu, H., Yang, T., Liang, Q., Wang, J., Zhang, R., & Zhang, Y. (2021). Water soluble dietary fiber from walnut meal as a prebiotic in preventing metabolic syndrome. *Journal of Functional Foods*, 78, 104358. doi: https://doi.org/10.1016/j.jff.2021. 104358.
- [17] Osendarp, S.J.M., Martinez, H., Garrett, G. S., Neufeld, L. M., De-Regil M. L., Vossenaar, M., & Darnton-Hill, I. (2018). Large-scale food fortification and biofortification in low- and middle-income countries: a review of programs, trends, challenges, and evidence gaps. Food Nutr Bull, 39(2), 315–331. doi: https://doi.org. 10.1177/0379572118774229.
- [18] Shydakova-Kameniuka, O. H., Novik, H. V., Chernushenko, O. O., Matsuk, Yu.A. (2018). Doslidzhennia osoblyvostei skladu shrotiv kedrovoho i voloskoho horikhiv ta zdobnoho pechyva z yikh vykorystanniam metodom ICh-spektroskopii. *Naukovyi visnyk LNUVMB im. S.Z. Hzhytskoho*. LNUVMB Lviv, 20(85), 56–61. doi: https://doi.org
- [19] Shydakova-Kameniuka, O. H., Novik, H.V., Kasabova, K.R., & Kravchenko, O. I. (2015). [Perspektyvy vykorystannia shrotiv kedrovoho ta hretskoho horikhiv dlia zbahachennia boroshnianykh kondyterskykh vyrobiv]. Prohresyvni tekhnika ta tekhnolohii kharchovykh vyrobnytstv restorannoho hospodarstva i torhivli: zb. nauk. prats, 2(13), 77–84. (In Russian).
- [20] Shydakova-Kameniuka, E., Novyk, A., & Bolkhovytyna, E. (2017). [Analyz soderzhanyia osnovnukh pyshchevukh veshchestv v produktakh pererabotky hretskoho y kedrovoho orekha]. Scientifik Letters of Academic of Michal Baludansky, 5(4), 121–124. (In Russian).
- [21] Naumova, N. L., Buchel, A. V., Lukyn, A. A., & Myhulia, Y. Yu. (2018). [Rezultatu yssledovanyi prymenenyia zhmrkha yader kedrovoho orekha v retsepture pechenochnoho pashteta]. *Vestnyk KamchatHTU*, 45, 50–57. https://doi.org/10.17217/2079-0333-2018-45-50-57. (In Russian).
- [22] Nahovskaia, V.O. Slyvka, N. B. Khachak, Yu. R., Mykhailytskaia, O.R, & Byluk O.E. (2020). [Tekhnolohyia spreda s razrabotkoi shrota kedrovoho orekha[. *Nauchnui vestnyk LNU veterynarnoi medytsynu y byotekhnolohyi. 22 (93)*: 9-14 doi: https://doi.org/10.32718/nvlvet-f9302 (In Russian).
- [23] Treviño, M. G. M., Galvão Do Vale D. O., Treviño A. P. E., Ruíz N. L. T., Moreno, F. R. (2021). Development and Analysis of a Product Made from Pink Pine Nuts in the South of Nuevo León. *International Journal of Food Engineering*, 7(2), 29-34. doi: https://doi.org: 10.18178/ijfe.7.2.29-34
- [24] Dyshluk, L. S., Sukhikh, S. A., Ivanova, S. A., Smirnova, I. A., Subbotina, M. A., Pozdnyakova, A. V., Neverov, E. N., & Garmashov, S. Yu. (2018). Prospects for using pine nut products in the dairy industry. *Foods and Raw Materials*.

- 6(2), 264–280. doi: https://doi.org: 10.21603/2308-4057-2018-2-264-280.
- [25] Zhao, M.-Y., Ling Show, T., Ju, X.-X., Dai, Y., Zhao, Y.-H. (2017). Component analysis of pine nut skin and its application in yogurt. *Modern food science and technology*, *33*(7), 133–140 doi: 10.13982/j.mfst.1673-9078.2017.7.020
- [26] Honchar, V. V., Shulvynskaia, Y. V., & Zaichenko, E. Yu. (2008). Yspolzovanye kedrovukh orekhov pry proyzvodstve zavarnukh prianychnukh yzdelyi. *Yzvestyia vuzov. Pyshchevaia tekhnolohyia*, *2*(3), 52–54.
- [27] Shydakova-Kameniuka, O. H., Rohova, A. L., & Misiulia, I. (2013, October). Vplyv diietychnoi dobavky «Klitkovyna yader voloskoho horikha» na yakist tsukrovoho pechyva. Prohresyvni tekhnika ta tekhnolohii kharchovykh vyrobnytstv : zb. nauk. prats, 1(17), 128–134.
- [28] Kravchenko M., Tkachenko L., & Mykhailyk V. (2016). Tekhnolohiia pisochnoho pechyva zi shrotamy oliinykh kultur. *Tovary i rynky*, *2*, 138–147.
- [29] Lysiuk, H. M., & Shydakova-Kameniuka, O. H. (2011, September). Doslidzhennia yakosti zavarnykh prianykiv z vykorystanniam diietychnoi dobavky «Klitkovyna yader voloskoho horikhu». *Prohresyvni tekhnika ta tekhnolohii kharchovykh vyrobnytstv : zb. nauk. prats, 2* (14), 233–238.
- [30] Pashova, N. V., Voloshchuk, H. I., Hrehirchak, N. M., & Karpyk, H. V. (2018). [Vplyv boroshna znezhyrenoho nasinnia oliinykh kultur ta poroshku topinambura na yakist ta bezpechnist zhytnoho khliba]. *Prodovolchi resursy*, 11, 139–147. (In Ukrainian).
- [31] [Sposob proyzvodstva khalvy]. (2008). 2335135 Rossyia: MPK A 23 G3/48. № 2007112442/13. (In Russian).
- [32] [Sposob proyzvodstva nachynky dlia konfet, karamely]. (2011). 2450529 Rossyia: MPK A 23 G3/34. № 2011110566/10. (In Russian).
- [33] Patel, M. R., Martin-Gonzalez, & M. F. San. (2012). Characterization of ergocalciferol loaded solid lipid nanoparticles. *Journal of Food Science*, 77, 8–13. doi: 10.1111/j.1750-3841.2011.02517.x
- [34] Candela, G. C, López B., L. M, & Kohen, L. V. (2011). Importance of a balanced omega 6/omega 3 ratio for the maintenance of health: nutritional recommendations. *Nutrición Hospitalaria*, *26*(2), 323–329 doi: https://doi.org: 10.3305/nh.2011.26.2.5117.
- [35] Kondratiuk, N., Harkusha, I. (2016). [Doslidzhennia ta skladu shokoladno-horikhovoi analiz pasty vlastyvostiamy]. polifunktsionalnymy Vostochno-Evropeiskyi zhurnal peredovykh tekhnolohyi, DOI: 1(10(79)), 36-41. https://doi.org: 10.15587/1729-4061.2016.59693 (In Ukrainian).
- [36] Rockenbach, I. I., Rodrigues, E., Gonzaga, L. V., Caliari, V., Genovese, M. I., Gonçalves, A. E., & Fett, R. (2011). Phenolic compounds content and antioxidant activity in pomace from selected red grapes (Vitis vinifera L. and Vitis labrusca L.) widely produced in Brazil Food Chemistry, 127(1), 174–179. https://doi.org. 10.1016/j.foodchem. 2010.12.137.
- [37] Amaral, J. S., Casal S., Pereira, J. A., Seabra R. M., & Oliveira B. P. P. (2003, February). Determination of sterol and fatty acid compositions, oxidative stability, and nutritional value of six walnut (Juglans regia L.)

- cultivars grown in Portugal. *Journal agric food chem,* 51(26), 7698 7702.
- [38] Cittadini, M. C., Martín, D., Gallo, S., Fuente, G., Bodoira, R., Martínez, M., & Maestri, D. (2020). Evaluation of hazelnut and walnut oil chemical traits from conventional cultivars and native genetic resources in a non-traditional crop environment from Argentina. *European Food Research and Technology*, 246, 833–843. doi: https://doi.org/10.1007/s00217-020-03453-8
- [39] Yilmaz, M. A. (2019). Quantitation of Fat Soluble Vitamins in Different Walnut Genotypes and Commercial Cultivars; a Comprehensive and Robust LC-MS/MS Method Validation. Journal of the Institute of

- *Science and Technology* 9(1), 562–571. doi: https://doi.org/10.21597/jist.505945
- [40] Afanaseva, V.A., & Alferov, S.V. (2018, June). Opredelenie sootnosheniya polinenasyshennyh zhirnyh kislot v pishevyh maslah. *Izvestiya TulGUyu Estestvennye nauki*, 4, 76–83.
- [41] Voskanian, O.S., Nykytyn, Y.A., Klokonos, M.V., & Huseva, D.A. (2020). [Optymyzatsyia sostavlenyia kupazhei rastytelnykh masel po soderzhanyiu nenasyshchennykh zhyrnukh kyslot metodom polnoho perebora (brute force)] *Pyshchevaia promushlennost, 1,* 8–13. doi: https://doi.org 10.24411/0235-2486-2020-10003 (In Russian).