CHARACTERIZATION OF WALNUT OIL EXTRACTED BY SUPERCRITICAL CO_2

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Abstract: Walnut (*Juglans regia* L.) oil was extracted with compressed carbon dioxide (CO_2) at the temperature 35 °C and the pressure 40MPa, for 30 min. It was studied the chemical composition of extracted oil: fatty acid profile, saponification and iodine index, acidity and peroxide values and compared to the cold pressed oil and oil obtained with hexane. The main FA was linoleic acid, followed by oleic acid and linolenic acid. Oxidative stability determined by PV revealed the modification of this value during storage for two months. Oil extracted by supercritical CO_2 was more stable that cold pressed oil and hexane oil.
Key words: Juglans regia L., CO_2 extract, walnut kernel, fatty acid

Moldova is one of Europe's largest producers and exporters of walnuts and kernels walnuts, reaching about 10 000 tonnes per year [1]. The main varieties of walnuts growing in Moldova are Calarasi, Chisinau, Corjeuti, Schinoasa, Kogylnichanu and Cazacu [2]. These varieties of walnuts provide high yields. They are mainly used for the production of biscuits, bread, cakes, ice cream, sauces, as well as for the production of cold pressed oil. Walnut oil is prized as specialty oil because of its characteristic flavor and aroma and its potential health benefits [2].

A particular importance for the national economy presents the walnut oil production, which in terms of walnut commercialization difficulties could be exported with the same success as raw material.

Supercritical dioxide extraction – new method to extract oil

Presently, a great attention is paid to the new technologies that permit to obtain natural biologically active compounds. One of these is the supercritical extraction with carbon dioxide. This extraction technique allow to extracting fatty acids of vegetable raw materials with supercritical carbon dioxide, which has an intermediate state between liquid and gas, and this provides an excellent power extraction, adjustable as desired by handling conditions of temperature and pressure, so the properties of carbon dioxide can be easily controlled [3].

Critical fluid extraction has been applied for sometime now in the extraction of speciality oils, such as borage, black currant, wheat germ, avocado, sorghum brand/germ oat, and amaranth. Partial deoiling has also been performed using SC-CO_2, to developing a functional food ingredient that has less fat (oil) or cholesterol content (low-calorie peanuts, walnuts) [4].

The advantages of this method of extraction with CO_2 as solvent: it is non-toxic, volatile, and easy to recover, with high diffusion rates, good mass transfer and low cost [3].

In this context, we have been studied the CO_2 extraction technology of walnut kernels. It was studied the parameters of extraction process (pressure, temperature and time). It was established the chemical composition of the walnut CO_2 extract and its stability during storage for two months. Characteristics of oil obtained under supercritical fluid extraction (SFE) conditions were compared to those of cold pressed oil and Soxhlet hexane-extracted oil.

Materials and methods

The experiments were conducted using as raw material crumbs of walnut kernel (from the varieties Chisinau, Corjeuti, Schinoasa, Kogylnichanu and Cazacu) from the walnut processing company “Prometeu-T”. The cold pressed oil was bought at the same company.

After mechanical breakage of the shell of walnuts get up to 30-40% of crumbs, those are used for industrial purposes. The crumbs of walnut kernels were packaged in bulk in vacuum foil (fig. 1.), with a mass of 7.5 kg packed as 2 packs in cardboard boxes and stored at 0-3 °C and relative humidity of air about 60-65%.

Fig. 1. Crumbs and cold pressed oil of walnut kernel from “Prometeu-T”

The research of the physico-chemical composition of raw material and oil simples has been carried out in accordance with the method of measuring, gravimetric and chemical method [5-12]. The following indicators have been established:

- moisture content;
- fiber content;
- lipid content;
- protein content;
- relative density;
- refractive index;
- free acidity in oleic acid;
- iodine index;
- saponification index;
- polyunsaturated fatty acids.

Physico-chemical composition of walnuts kernel is as follows: 65.5% lipids, who are constituted mostly of polyunsaturated fatty acids, carbohydrates – 5%, proteins – 12%, and a high fiber content – 5.5%, moisture content – 4%.

Results and discussions

Preparation of raw material for SFE

SFE process requires that the raw materials have a moisture content not exceeding 14%. So in the walnut crumbs purchased from enterprise "Prometeu-T" was determined moisture content, which was 4% and then walnut kernel was fragmented in particles up to 0.5-1mm diameter. Then the raw material was conditioned to extraction process.

Physic and chemical composition of obtained oils

The CO_2-extract is yellow, it is clear, transparent, without impurities, taste - delicate, pleasant, slightly bitter at end, fragrant, barely noticeable characteristic of walnut kernels without foreign taste or odor, homogeneous consistency.

Oil quality is determined by: peroxide and acid values, iodine index, iodine color, profile of fatty acids, etc. The results of investigations are presents in table 1.

Table 1. Quality indexes in studied oils

Quality indexes	**CO_2 extract**	**Cold pressed oil**	**Oil extracted by hexane**	**Cold pressed oil of walnut kernel as RT***
Moisture content,%	0,0002	0,0002	0,007	Max. 0,02
Relative density, mg/cm^3 at 20 °C	0,915	0,914	0,919	0,919-0,928
Refractive index at 20 °C	1,4773	1,4777	1,4773	_
Free acidity in oleic acid,%	1,15	0,52	0,85	Max. 0,4%
Iodine index, I_2 g/100g	155	156	151	140-165
Saponification index, mg KOH /g	196	195	196	187-198
Color of iodine, I_2 mg/100ml	10	10	10	Max. 30

RT* - Technical Regulation "Edible vegetable oils", approved by decision of the Government of RM №. 434 at 27.03.2010 [13].

According to data presented in Table 1 the quality indexes in samples of walnut kernel oil don’t differs essential one of other, and correspond to indexes stipulated in Technical Regulation "Edible vegetable oils".

Because the cold pressed oil of walnuts oxidizes very quickly, we have studied if the CO_2extract is oxidized under the same conditions of temperature as cold pressed oil and hexane oil. Samples were stored for two months at 8°C. We determined the change of acidity and peroxide values during two months. It was established that for two month the peroxide value increased considerably for hexane oil (fig. 2).

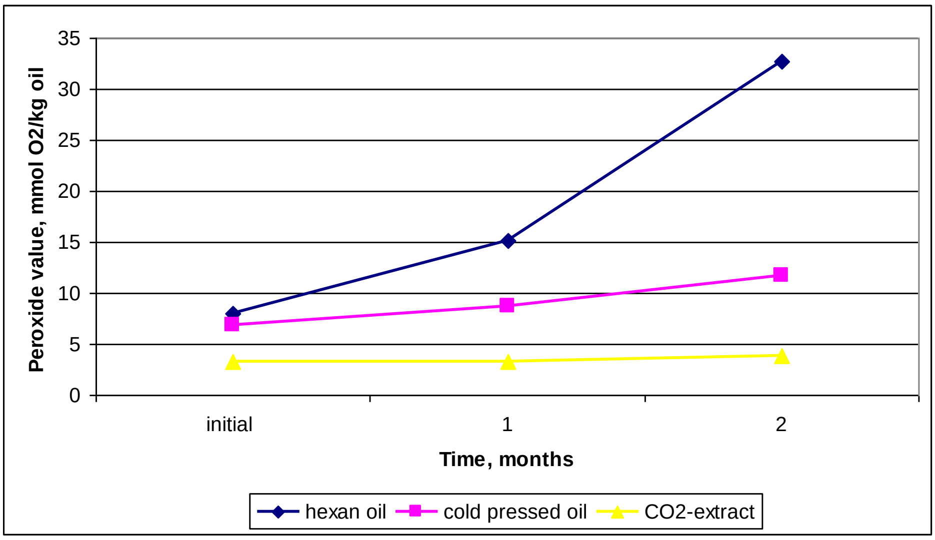

Fig.

Fig. 2. The modification of peroxide value for two months

It was found that for two months of storage the peroxide value increased from 3.3 to 3.9 ½ O mmol/kg for the walnut CO_2 extract, in the cold-pressed oil it increased from 6.8 to 11.7 ½ O mmol/kg and in hexane oil it increased from 8 to 32.7 ½ O mmol/kg. According to these results the walnut CO_2 extract is more stable during storage compared to the cold-pressed oil and n-hexane oil.

It was also established that the acid value has not changed at all for almost two months. In the walnut CO_2 extract this value decreased from 2.5 to 2.3 mg KOH/g, in the cold-pressed oil it rests 1.0 mg KOH/g and in hexane oil it is 1.6 mg KOH/g.

In Food Quality Control laboratory of Practical Scientific Institute of Horticulture and Food Technology it was determined the fatty acid composition in samples of CO_2-extract, hexane oil and cold pressed oil.

Samples were analyzed for free fatty acids by standardized methods that are approved in Moldova. Methyl esters were prepared from the oil and analyzed by gas liquid chromatography (GLC). The data obtained are presented in Table 2.

Table 2. Fatty acid composition in samples of extracted oils by different methods

№	Extraction parameters	Mass fraction of AG in relation to the total amount of triglycerides, %						Ratio ω-3/ ω-6
		C14:0 Miristic	C16:0 Palmitic	C18:0 Stearic	C18:1 Oleic	C18:2 Linoleic	C18:3 Linolenic	
1	Cold pressed oil	-	7,78	2,04	17,11	64,41	8,66	1:7,44
2	n-hexane oil	traces	8,12	1,79	16,35	64,55	9,33	1:6,92
3	CO_2-extract	-	7,52	2,14	17,08	63,94	9,32	1:6,86

The major unsaturated fatty acids of walnut CO_2 extract are: linoleic – 64.41% (ω-6), linolenic – 9.32% (ω-3) and oleic – 17.08%. According to nutritionists, for functional food the ratio of ω-3/ω-6 is very important to be about 1:5, and 1:10 for healthy food [15]. In walnut CO_2 extract this ratio is 1:6.34-1:7.70 that confirms that the content of PUFA is well-balanced in walnut extract.

According to data presented in Table 2, the ratio ω-3/ω-6 does not differ much from one sample to another, being close to 1:7, so walnut oil is recommended for healthy food.

Conclusions

It was established that the main polyunsaturated fatty acids of CO_2-extract of walnut kernel are: linoleic – 63.94% and linolenic – 9.32% acids. Walnuts oil contains in ideal proportion ω-3/ω-6 fatty acids.

After two months of storage of three simples of walnut oil obtained by different methods, the acidity values rests unchanged, but the peroxide value increased a lot for hexane oil. During the storage CO_2-extract of walnut kernel was stable at oxidative modifications.

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