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Examination the Quality of Oil Obtained from Cornelian Cherry (*Cornus mas* L.) Seeds as an Additive in the Production of Cosmetic Preparations and Food Supplements

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ABSTRACT

From ancient times the natural plant Cornelian cherry is used for various purposes. The healing properties of Cornelian cherry suit the human body and give it the necessary vitamins, acids, and everything else it needs for the body to function normally and healthily. Due to its antioxidant, antiallergic, antimicrobial, and antihistamine properties, it is increasingly used as a dietary supplement, as well as for medical and pharmaceutical purposes. In addition to the fruit of the Cornelian cherry, in the past, the oil of Cornelian cherry seeds was used, the content of which can be up to 30%. However, the data available in the literature are scanty and do not show true values because the oil content depends on many factors, such as the geographical origin of the Cornelian cherry, the harvest period, varieties, etc., which also affects the oil content in the seeds.

Therefore, the aim of this study is to determine the average oil content of Cornelian cherry seeds, and to determine the obtained oil physico-chemical parameters that show the quality of the oil, namely oil viscosity, iodine value, peroxide value, acid value, and saponification value. Based on the obtained results, more information is clearly given about the quality of the obtained oil, as well as its use in the production of cosmetic preparations.

Based on the conducted analyzes, it was shown that the oil obtained from the Cornelian cherry seeds was high quality, and that it was analyzed in its fatty acid composition similar to other vegetable oils such as sunflower oil, pumpkin oil, corn oil. The low of the peroxide value showed that the oil used has good resistance to oxidative spoilage, which is attributed to the composition of fatty acids and the presence of oil components that have a pronounced antioxidant effect, while the iodine value indicates that it is oil rich in saturated fatty acids such as palmitic, stearic and arachid, etc. where genotype plays an important role. The saponification value showed that these are fatty acids present in the triacylglycerols of this oil, which are low molecular weight, ie there are fewer of those with a larger number of C atoms. All obtained values of the analyzed physical and chemical parameters are in accordance with the requirements imposed by the Regulations on edible vegetable oils (Official Gazette of the Federation Bosnia and Herzegovina No.21/11.), and as such can be used for cosmetic purposes.

Keywords- Cornelian cherry, seeds, oil, physico-chemical parameters, cosmetic preparations.

I. INTRODUCTION

Cornelian cherry (*Cornus mas* L.) is a shrub or small tree 3 m to 9 m high that belongs to the family Cornaceae. Due to the resilience of the tree itself, which can experience late age and the fantastic health and healing properties of the fruit - we know the saying we often hear: "Healthy as a Cornelian cherry" [1]. Herbal extracts and substances obtained from the Cornelian cherry show only strong antibacterial but antioxidant and tonic properties, which effectively develops the development of inflammation in living organisms [2]. The fruits of this plant are a source of active ingredients, such as phenolic compounds, vitamin C, iridoids, flavonoids and anthocyanins. [3] [4] The fruit of the Cornelian cherry is also rich in microelements such as copper, zinc and manganese, and their values in fresh fruit are estimated at 110–170, 260–350 and 2400–2900 µg/100 g, respectively. [5] The Cornelian cherry is powerful source of potassium - it contains over 3500 mg/100 g of fresh fruit, which means that 1 g of Cornelian cherry satisfies the full potassium intake recommended by the WHO [6]. Fresh Cornelian cherry juice contains twice as much ascorbic acid than orange; as well as compared to other voice juices like plum, pear and apple juice. [7]

Cornelian cherry fruits and their seeds are a source of fat used in the cosmetics industry [8]. Oil can be extracted from the Cornelian cherry seeds, and it is known that the seeds contain up to 30% oil of the total composition. Cornelian cherry seed oil shows the possibility of recovery and regeneration of external and

internal epidermal tissues and has a significant antimicrobial effect. Fatty acids obtained from the Cornelian cherry seeds have shown antimicrobial activity against Gram-positive and Gram-negative strains, respectively: Staphylococcus aureus and Escherichia coli [9]. Minerals such as calcium, potassium, phosphorus, magnesium and sodium have also been found in the Cornelian cherry seeds, with the genotype plays an important role in seed mineral composition. [10] The active substances contained in the Cornelian cherry seeds have a surprisingly beneficial effect on human skin and can successfully replace synthetic substances. [11] Studies have shown that antioxidant activity also inhibits the enzyme elastase, which is responsible for the breakdown of elastin and delaying the aging process.

Therefore, due to all ingredients that contain Cornelian cherry seeds or oil obtained from Cornelian cherry seeds by cold pressing, the use of the Cornelian cherry-based products is desirable for cosmetic purposes. As an important factor in testing the quality and stability of these products is oil viscosity, iodine value, peroxide value, acid value and saponification value, these parameters were examined in this paper.

II. EXPERIMENTAL PART

2.1. Material

As a material in this paper, cold-pressed oil obtained from the Cornelian cherry seeds was used, which determined the physico-chemical parameters: viscosity; iodine value, peroxide value, acid value, as well as saponification value, in order to examine the quality of oil intended for cosmetic purposes and as food supplement.

2.2. Methods

Viscosity as a property that represents the resistance with which a liquid resists flow. Viscosity was determined using an Ostwald viscometar. First, the flow time of the standard liquid was measured, i.e. water through the capillary from mark A to mark B, and then measuring the discharge time of the oil obtained from the Cornelian cherry seeds. The measurement was performed at room temperature 25°C, and the following relation calculated the altitude:

$$\eta = \eta_2 \frac{\rho_1 \cdot t_1}{\rho_2 \cdot t_2} \eta = \eta_2 \frac{\rho_1 \cdot t_1}{\rho_2 \cdot t_2} \qquad (1)$$

Where is:

η_2 –viscosity of standard liquid;

ρ_1- density of the oil obtained from the Cornelian cherry seeds;

ρ_2 –density of standard liquid;

t_1- the expiration time of the oil obtained from the Cornelian cherry seeds;

t_2 –the expiration time of standard liquid.

Density was determined as the ratio of mass to volume, and calculated by the following relation:

$$\rho = \frac{m}{v} \rho = \frac{m}{v} \qquad (2)$$

The iodine value was determined by the Hanuch method. By definition, an iodine value is expressed as a gram of iodine absorbed by 100 g of an oil sample and expresses the amount of iodine that that oil or fatty acid can connect by addition. In order to determine the iodine value, the weighed amount of oil obtained from the Cornelian cherry seeds was dissolved in 15 ml of chloroform, then 25 ml of iodine monobromide solution, 15 ml of 10% KI solution and 150 ml of freshly boiled cooled water were added and titrated with constant stirring 0.1 M $Na_2S_2O_3$ solution. Then a few drops of starch solution were added and titrated carefully until the blue color disappeared. Simultaneously with the cause of the oil obtained from the Cornelian cherry seeds, a blank was performed, and the iodine content was calculated by the following relation:

$$\textbf{Iodine Value} = \frac{\textbf{(A – B) x 0,0127 x 100}}{\textbf{m}} \qquad (3)$$

Where is:

A-ml of spent 0.1 M $Na_2S_2O_3$ solution for blank;

B-ml of spent 0.1 M $Na_2S_2O_3$ solution for oil obtained from the Cornelian cherry seeds.

M-mass of the oil sample.

The peroxide value was determined by the Wheeler method, which is based on the determination of iodine isolated by the action of peroxide on iodides in an acidic medium. It was determined by dissolving a sample of oil obtained from the Cornelian cherry seeds in a freshly made mixture of glacial acetic acid and chloroform in a ratio (3: 2), and with the addition of saturated KI solution, water and starch titrated with 0.01 M $Na_2S_2O_3$ solution. Along with the oil sample, a blank test is performed to check the purity of the reagents. The peroxide value is expressed as the number of millimoles of active oxygen derived from the resulting peroxide present in 1 kg of oil (mmol O_2 /kg) is calculated according to the formula:

$$\textbf{Peroxide Value} = \frac{\textbf{(A – B) x 5}}{\textbf{m}} \qquad (4)$$

Where is:

A-ml of spent 0.01 M $Na_2S_2O_3$ for oil obtained from the Cornelian cherry seeds;

B-ml of spent 0.01 M $Na_2S_2O_3$ for blank;

M-mass of the oil sample.

Determination of the saponification value of the oil was performed using an alcoholic solution of KOH of known molarity, whereby the excess of unused alkalis was re-titrated with a solution of hydrochloric acid. Fat saponification was performed in two stages. In the first phase, with alcoholism, fatty acids are converted into the

corresponding ethyl esters, which are soluble in an alkaline-alcoholic environment. In the second phase, the awarded esters are very easily saponified by giving soaps. In parallel with the sample, a blank test was performed, and both samples were titrated with 0.5 M HCl, where the difference in consumption of 0.5 M HCL between the sample and the blank shows how many ml of 0.5 M KOH solution used for saponification, where the saponification number is calculated by the relation:

$$\textbf{Saponification Value} = \frac{(A-B)\ x28,1}{m} \qquad (5)$$

Where is:
A-ml of spent 0.5 M HCl for sample titration;
B-ml of spent 0.5 M HCl for blank titration;
M-mass of oil sample;
28,1- number of milligrams of KOH contained in 1ml 0.5 HCl.

The acid value is expressed as the number of mg of KOH required to neutralize free fatty acids in 1g of fat. In the fat solution, the free fatty acids are determined by titration with sodium hydroxide solution and calculated by the relation:

$$\textbf{Acid Value} = \frac{(A\ x\ 5,61)}{m} \qquad (6)$$

Where is:
A-ml of spent 0.1M KOH for sample;
5,6104- number of miligrams of KOH contained in 1 ml 0,1 M KOH;
M-mass of oil sample.

Based on the data on the content of KOH base consumed and its concentration, the % of free fatty acids was calculated, expressed as oleic acid according to the following relation:

$$\textbf{SMK= (V×C×M) (10 × m)} \qquad (7)$$

Where is:
V-ml of spent 0.1 M KOH for sample;
C-concentration KOH;
M-molar mass of oleic acid (282, 47 g/mol);
M-mass of oil sample.

III. RESULTS AND DISCUSSION

Physico-chemical characteristics are very important parameters of each oil, considering that they indicate not only the properties of the tested oil, but also the quality and possibility of its application. Iodine and saponification value, density, viscosity are especially important characteristics of oil and serve for its identification. [12] In order to examine the quality of oil obtained from the Cornelian cherry seeds, the following parameters were analyzed: viscosity, oxidation value, acid value, iodine value and saponification value, and their values are presented in Table 1.

Table 1: Presentation of analyzed physicochemical parameters

Sample-oil obtained from Cornelian cherry (*Cornus mas* L.) seeds	
Parameters	**Value**
Density (kg/m^3)	947,27
Viscosity (mm^2/s)	0,419
Peroxide value (mmol O_2/kg)	2
Acid value (mg/g)	1,87
Iodine value (g/100g)	88,106
Saponification value (mg/g)	256,41
Free fatty acids (%)	0,94

Physical properties

Knowledge of the physico-chemical and rheological properties of fats and oils are of great importance for quality and use in the food and pharmaceutical industries. Density and viscosity were considered among the most important of these parameters. [13] The importance of these parameters in his study was also discussed by Gulla et al. [14] The density value for the sample of oil obtained from the Cornelian cherry seeds was 947.27 kg/m^3, while the viscosity value of the same sample was 0.419 mm^2/s, with a large role played by molecular structure, chain length and the degree of unsaturation of fatty acids, because the viscosity decreases with increasing unsaturation, and increases with saturation and polymerization. [15]

Chemical properties

1) Peroxide value is considered an indicator of the initial phase of oil oxidation because the resulting hydroperoxides are extremely unstable and decompose very quickly into secondary oxidation products (unsaturated ketones, aldehydes, acids, epoxies, etc.). Oils with a peroxide value ranging from 1 to 3 mmol O_2/kg are considered fresh and of good quality, while oils with a peroxide value not exceeding 10 mmol O_2/kg are considered suitable for human consumption. From the results shown in Table 1., we see that the peroxide value was 2 mmol O_2/ kg, which indicates that it is a quality and fresh oil obtained from the Cornelian cherry seeds, whose value is in accordance with the requirements imposed by the Regulations on edible vegetable oils (Official Gazette of the Federation Bosnia and Herzegovina No.21/11) Such a low of the peroxide value shows good resistance of this oil to oxidative spoilage, which is attributed to the composition of fatty acids and the presence of oil components that have a pronounced antioxidant effect.

2) Saponification value is a measure of the average molecular weight of fatty acids in a sample, and is inversely proportional to the average molecular weight of fatty acids or the length of their chain. Saponification value is an insight into the composition of lipids, and its value depends on the length of the fatty acid chain in the triacylglycerol molecule. Fats with low molecular weight fatty acids have a high saponification number in contrast to fats that contain long-chain fatty acids. Saponification value is a characteristic value for identifying the type of oil and ranges within the limits given in Table 2. [16]

Table 2: Saponification value of certain types of edible vegetable oils

Type of oil	Saponification value (mgKOH/g)
Olive oil	185-198
Sesame oil	187-195
Sunflower oil	188-194
Palm oil	190-209
Coconut oil	248-265

In the sample of oil obtained from the Cornelian cherry seeds, the saponification value was 256.41 mg/g, which indicates that these are fatty acids present in triacylglycerols of this oil, which are low molecular weight, i.e. less than those with a larger number of C atoms. Previous research has shown that with longer storage and storage of oil, the value of the saponification number increases. [17]

3) The iodine value expresses the content of iodine that can be bound by the addition of some fat (oil) or fatty acid and is considered an important characteristic of oils and fats because it indicates their unsaturation, i.e. the presence of unsaturated (usually double) bonds of fatty acids in the triacylglycerol molecule. It can serve as a criterion in assessing the purity of lipids or fatty acids, i.e. serves as an important indicator for identifying, i.e. proving the type and origin of oil. Oils rich in saturated fatty acids have a low number of iodine, while oils rich in unsaturated fatty acids have a high number of iodine. [18]

The iodine value of coconut oil usually ranges from 7.5-10.5, olive oil from 74-94, pumpkin oil 116-128 and sunflower oil from 125-136 g /100g. [19] By the way, oil obtained from the Cornelian cherry seeds is similar in its fatty acid composition to other vegetable oils such as sunflower oil, pumpkin oil, and corn oil. [20] In the sample of oil obtained from Cornelian cherry seeds, the iodine number was 88.106 gJ_2 /g, which indicates that it is an oil rich in unsaturated fatty acids such as palmitic, stearic and arachidonic acid, in which genotype plays an important role.

4) ***Acid number***- represents the number of mg of KOH required to neutralize free fatty acids in 1g of fat. The content of free fatty acids is determined as the acidity of oils and fats, but is expressed as the proportion of oleic acid or as an acid number. [21] In the sample of oil obtained from the Cornelian cherry seeds, the acid number was 1.87, which also corresponds to the requirements imposed by the Regulations on edible vegetable oils (Official Gazette of the Federation Bosnia and Herzegovina No.21/11)

5) ***Free fatty acids*** - Fats and oils, in addition to fatty acids that are connect in triglycerides; also contain a certain amount of free fatty acids. Free fatty acids are formed as products of hydrolytic degradation of triglycerides and their share depends on the method of obtaining the oil, the raw materials used and the storage conditions. Analysis of a sample of oil obtained from the Cornelian cherry seeds showed that the % of free fatty acids was 0.94.

IV. CONCLUSION

Analysis of the physical and chemical parameters of oil obtained by cold pressing from the Cornelian cherry seeds showed that it is a high quality oil, which also corresponds to the requirements imposed by the Regulations on edible vegetable oils (Official Gazette of the Federation Bosnia and Herzegovina No.21/11)

When it comes to the physical and rheological properties of oils, it has been proven that they depend on the molecular structure, chain length and the degree of unsaturation of fatty acids, because the height decreases with increasing unsaturation, and increases with saturation and polymerization. The low value of the peroxide value shows that the oil used has good resistance to oxidative spoilage, which is attributed to the composition of fatty acids and the presence of oil components that have a pronounced antioxidant effect, while the iodine value indicates that it is oil rich in saturated fatty acids such as palmitic, stearic and arachid, etc. where genotype plays an important role. The saponification value showed that these are fatty acids present in the triacylglycerols of this oil, which are low molecular weight, i.e. there are fewer of those with a larger number of C atoms. Based on the analyzed parameters, it was shown that the oil obtained from the Cornelian cherry seeds in its fatty acid composition is similar to other vegetable oils such as sunflower oil, pumpkin oil, corn oil.

As previously proven, such oils have a beneficial effect on the skin after direct application in several ways. Not only are they effective antioxidants, but they also inhibit enzymes that break down the skin's structural proteins, and inhibit the enzyme elastase, which is responsible for breaking down elastin and helping to delay the aging process. Multiple studies have also shown that extracts and plant substances obtained from the Cornelian cherry seeds show strong antioxidant, antibacterial, tonic and astringent effects and effectively prevent inflammation, with further use of the analyzed sample of oil obtained from the Cornelian cherry seeds suitable for use in cosmetics and as food supplement.

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