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Grape Seed: physico-chemical, structural characteristics and oil content

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Abstract

Grape seeds from different grape varieties from different growing regions have been studied in terms of the physico-chemical and structural characteristics. Also the content obtained from the seed oil and the quality of the oil were analyzed. The chemical values obtained from the analyzed species, as a percentage of dry matter varies between 8,68 and 9,78 - for protein, between 6,26 and 9,01 - for oil, between 2,14 and 8,28 for Ash and the total of carbohydrates is between 64,72 and 73,01%.

Grape seed oil obtained by extraction with petroleum ether can be used for technical purposes only.

Keywords: Grape seed, oil, petroleum ether extraction, structural analysis, chemical composition analysis

1. Introduction

The sub products resulting from the wine industry are a rich source of raw materials, which can be used to manufacture new products with an important role in the economy. Grape seeds are about 15% of the solid waste produced in wine [16] and are increasingly recognized as products that require a more proper analysis of their value.

Depending on the grape variety, the seed is between 2% to 6% of the weight of the berries and 1% to 4% of the weight of the grape. The average yield of a seed is between 20-25% of the weight of the marc; marc dry seeds contain 40-65% and have an oil content of 12-22% [20]. Scientific studies conducted in Spain conclude that the humid marc of white grape varieties contains 23-26% seed and the marc of red varieties seeds contains 25-28% [13].

Grape seeds, used for oil production, belong to a category which typically contains 8% to 15% oil, with a recognized quality due to the high level of unsaturated fatty acids, namely oleic and linoleic [6] and they are also rich in antioxidant compounds.

The oil content varies depending on the grape variety, the degree of ripeness of the grapes, soil, climate, etc. Usually, this content is between 10-16% of dry matter [16]. From the comparative study conducted by Iancov A., in 1967 [21] it results that the volume of oil in red grape seeds is 16-19%, and that in the white grape, it varies from 15,5 to 18%. Research conducted in the U.S. on European varieties and American hybrids have shown that these American varieties contain 13,0-18,4, with an average of 14,72%.

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The same research indicates that in the oil content of the seeds, linolenic acid predominates, which represents over 71,5% of fatty acids [17].

In another study [21] it is stated that grape seed oil contains 88% unsaturated fatty acids of which 72% is linoleic acid.

The chemical composition of the grape seed contains: water (28-40% of its weight), cellulose (28%), nitrogenous (0,8-1,2%), tannins (4-6%), oil (10-25%), mineral substances (2-4%), fatty acids and other components [5]. Licev V. and collaborators [14] indicate that grape seeds contain: water 25-45% 34-36% oil, oil by 20%, tannin 4-6%, 2-4% phenolic substances, nitrogenous 4-6%, 2-4% mineral substances, fatty acids up to 10%, 10-11% cellulose, pentozane 8-10%, 25-28% lignin. The experimental data obtained by N. Razuvaev [22] shows that the composition of grape seeds before drying includes: water 30-40%, 3.7% tannin, mineral substances 1-2%, 8-10% oil, 44-57% cellulose.

In the chemical composition of grape oil the following fatty acids are found: linoleic 66%, 13,69-21,47% olein; palmitinic 5,78-7,64% 0,04-0,67% iristinic, stearic 2,50-3,49% [17]. The percentage of linoleic acid is higher than any other oil, including that of safflower, sunflower and maize [10]. Other studies and research carried out by Gattuso and staff indicates that grape seed oil has a linoleic acid content between 68,3% and 75,34% and the quantitative ratio between the linoleic acid and oleic acid is 3,52-5,61 [4, 8].This finding explains the stability of grape seeds oil in storage. The low oxidization of this oil determines its use as a stabilizer in easily oxidizing oil blends [13]. Due to the high resistance to oxidation of the grape seed oil, it can be used as a cosmetic ingredient. In this way it is used for the treatment of dry skin and protection against aging [12, 20]. Grape seed oil is widely used for culinary, pharmaceutical and medical purposes [20]. The high content of unsaturated fatty acids (about 85-90%) makes this oil, with high nutritional qualities, useful in the prevention of thrombosis, in reducing cholesterol, dilated blood vessels and regulates the autonomic nervous [15].

The industrial scale process to obtain grape seed oil contains several stages: seed conditioning (cleaning and drying), grinding and oil extraction. The following extraction methods are used: extraction by pressure, the yield is 4-5% and solvent extraction, the yield is 7-8% [5]. In recent years, alternative methods for oil extraction, without organic solvents, have been proposed: hot water extraction [23] and extraction using supercritical fluid extraction as an agent of carbon dioxide [2, 3, 11, 18, 19]. Extraction with supercritical carbon dioxide results in similar yields as the oil extraction through solvent and has a similar quality. Supercritical fluid extraction [10] removes the solvent removal process and subsequent stages of refinement. The method is rarely used because the cost of the equipment is high when compared to the extraction with organic solvents or by pressure. A viable alternative to conventional methods of extracting grape seed oil is a superheated hexane extraction [16].

The purpose of this work was to evaluate the chemical composition and structure of the seeds from different grape varieties and to determine their content in oil.

2. Materials and method

Seed - study material Grape seed were gathered in different parts of the country, during wine season. Seeds were separated from the wet grape pomace and dry grape pomace. The seeds were dried in the open air at 20-25oC. Separation was achieved by removing the seed impurities, sifting and aeration.

Analitycal methods. All analytical determinations were performed at least three times and the value of each determined parameter is the average of three values, at which is added with ± the standard deviation values.

Physico-chemical analysis of grape seed. Grape seeds: the content of impurities, size and volume density. The impurity content of the studied grape seeds was determined as recommended in SR EN ISO 658:2003.

The geometrical sizes of the seeds collected from five grape varieties were determined as an average of 10 measurements. For each seed sample, the length, width and thickness were measured using a micrometer. The hectoliter mass volume or volumetric density was determined according SR ISO 7971-2:2002, using the Granomat device version 1.0 (Pfeuffer) and a container with a capacity of 1 liter.

Moisture content and volatile matter. After the separation of impurities, the content of water from the seeds and the volatile matter were determined according to SR EN ISO 665:2003. The samples used

in the research were 2 g of pure seed that has been dried in an oven at 103°C at atmospheric pressure until constant weight was obtained.

The oil content. This has been determined according to SR EN 659-2003. The weight of the oil extracted from 10 g of powdered seed was used to calculate the oil content of the seeds separated from the impurities. The result is expressed as a percentage of dry mass of dust grains.

Protein content. The total proteins have been determined through the Kjeldhal method with accordance with the SR EN ISO 20483:2007. The proteins have been calculated using the general factor 6,25. The data was expressed in percentage of the dried substance.

Ash and mineral content. In order to remove carbon, every 2 g of powdered seeds of each variety were weighed and put in a crucible and then incinerated in an oven at 550°C closed for 6 hours. The total ash content, determined according to SR ISO 2171:2009, is the percentage of dry matter. The determination of mineral content was performed with an energy dispersive spectrometer using Röntgen radiation, Shimadzu EDX type 900HS, of high sensitivity and resolution, to highlight the chemical composition of seed.

Carbohydrate content. Carbohydrate content was estimated as the difference of mean values: 100 - (amount in percentage of moisture, ash, protein and fat) [1].

Microscopic study. The microscopic study of the seeds structure from the analyzed varieties has been conducted with the use of an electronic microscope (SEM)-Vega/LMU-Tescan (Czech Rep.) equipped with a micro sensor EDX - Bruker.

Oil extraction. The oil was extracted with the help of the Soxhlet equipped with 6 working hubs. For each hub of the equipment, 10g of grinded seeds, with the dimension of 1 mm have been used, which have been grinded with an electrical grinder and the extraction was done with petrol ether at 50-60°C. The extraction was repeated 5 times for each variety of seeds. The boiling was set in order to allow a number of 12 sprinklings per hour. The period of the extraction process was about 8-10 hours, and the end of the extraction was determined through the control of the presence/lack of fat on the watch glass after a drop was evaporated from the extract. The percentage of oil from the grinded seeds was determined through weighing, with the application of further calculus. For each sample, three determinations have been made and then an average was obtained.

3. Results and Discussion

Grape seeds: impurity content, dimensions and volumetric density

Table 1 shows the results obtained from the determination of the grape seeds size according to the variety, obtaining method and cultivation area.

The impurities content, volume density, moisture and volatile matter content, defined as the percentage of the sample of the studied grape seed varieties is given in Table 2. The oil, protein, the total content of ash and carbohydrates for the studied seeds is shown in the table 3.

The mineral content determined from the studied grape seeds are in Table 4. Large amounts of calcium, potassium and phosphorus content and essential elements such as iron, manganese, copper and zinc, allow grape seeds to be considered an excellent source of bio elements. The microstructure of the studied seeds is reproduced in Figure 1 a) for Aligoté seed in Figure 1 b) for Frăguță in Figure 1 c) for Nohan. The image analysis shows similar structures for the studied grape seed varieties.

4. Conclusion

The data analysis shows that the seed size, length, width and thickness depend on the variety, but it is not significantly different. These sizes can be used for the selection of sites required for optimal design of a seed separator. The structural analysis of grape seed structure shows that there are structures specific to every variety.The determination of the oil content in grape seeds shows that this index varies between large limits, from 6,26% to 9,01 % in dependence with the grape variety and the cultivation area.The comparative analysis of the oil content in the studied seeds shows that there are no essential differences between the studied varieties.

Higher oil concentrations have been obtained from grape seeds from an area with a warmer climate – the Vrancea area, in comparison with the northern Moldavia – Suceava area. The oil content of the Frăguță dry grape pomace is greater then the quantity of oil form Frăguță wet grape pomace.Aligoté variety seeds have higher protein content than the hybrid variety Nohan.

Table 1. Dimensions depending on the variety of grape seeds, obtaining method and areas of origin

The area of cultivation	Grape variety	Seeds from	Length, mm	Width, mm	Thickness, mm
Vrancea County Area Region growing Hills Moldova,	Mixtures of white varieties	Grape pomace dry	5,70	3,74	2,75
Vineyard Odobeşti: Vineyard Center Jariştea	Aligoté	Grape pomace dry	6,20	3,57	2,77
Vrancea County Area City Pufeşti, Vrancea county	Hybrid variety Nohan alb	Grape pomace wet	6,39	3,20	4,61
Hills Moldova - Northern Zone	Hybrid variety Frăguță *a*	Grape pomace wet	6,70	4,78	3,50
City Boroaia, Suceava county	Hybrid variety Frăguță *b*	Grape pomace dry	6,89	4.82	3.56

Table 2. The content of impurities, humidity and volumetric density

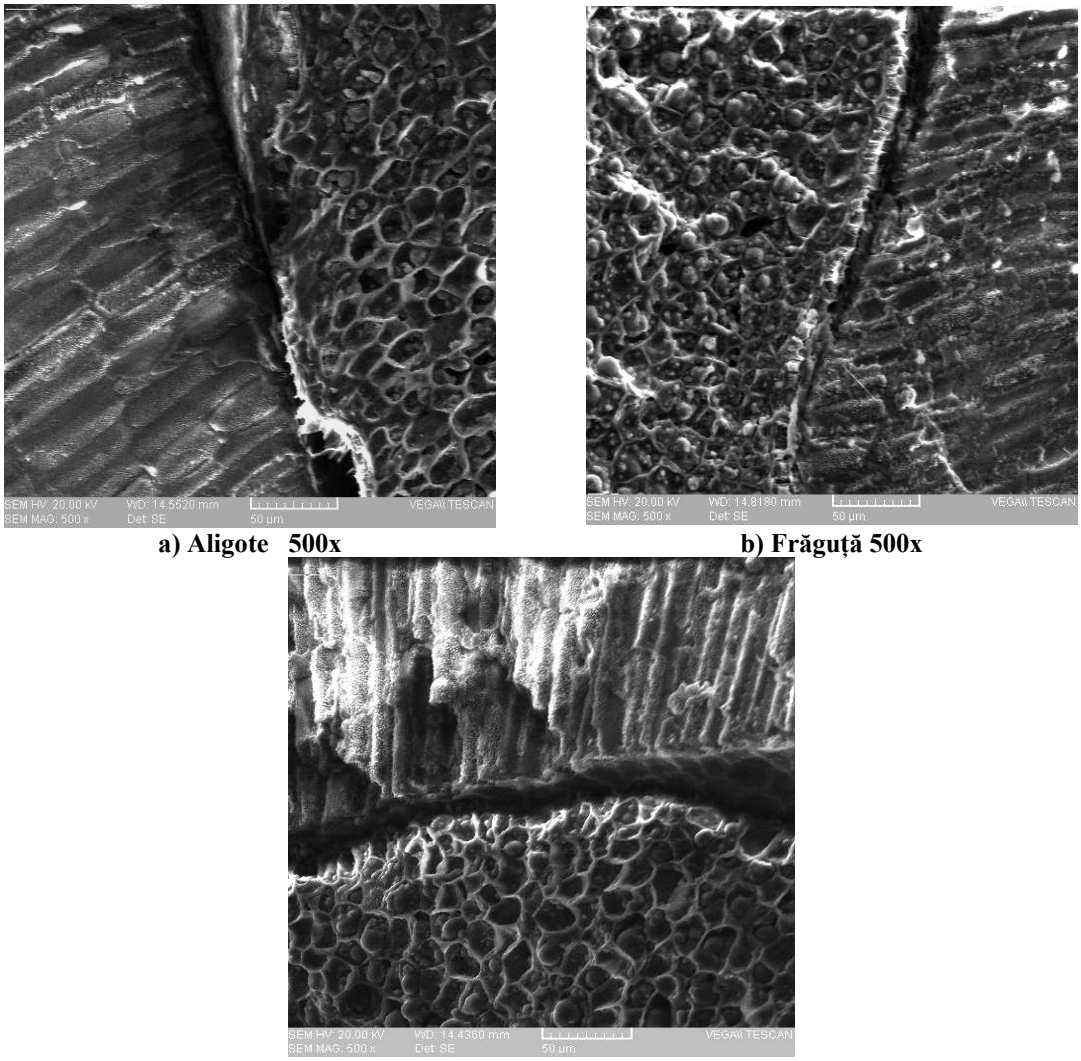
Grape Variety	Content of impurities, %	Moisture and volatile matter content, %	Volumetric density, kg/hl
Mixtures of white varieties	12,16	5,56	43,71
Aligoté	19,46	7,16	45,57
Hybrid variety Nohan alb	0,62	6,48	66,11
Hybrid variety Frăguță *a*	0,65	6,98	63,50
Hybrid variety Frăguță *b*	1,23	6,96	65,68

Table 3. The oil, protein, Ash and carbohydrate content

Grape Variety	Oil content, %	Protein content, %	Total Ash content, %	Content of carbohydrates, %
Mixtures of white varieties	6,26	9,0	3,18	73,01
Aligoté	7,21	9,78	3,35	72,12
Hybrid variety Nohan white	8,08	8,68	2,14	72,82
Hybrid variety Frăguță *a*	8,15	8,75	3,20	71,19
Hybrid variety Frăguță *b*	9,01	9,0	8,28	64,72

Table 4. Mineral content

Grape Variety	Mineral content, % ± Std.Dev.								
	Ca	K	P	S	Mn	Fe	Zn	Cu	Pt
Mixtures of white varieties	55,764 ±0,078	26,447 ±0,051	15,346 ±0,178	2,088 ±0,043	0,253 ±0,003	-	0,123 ±0,001	0,069 ±0,001	-
Aligoté	53,477 ±0,067	27,403 ±0,045	16,632 ±0,159	1,942 ±0,038	0,314 ±0,003	-	0,149 ±0,001	0,082 ±0,001	-
Hybrid variety Nohan white	55,058 ±0,078	23,655 ±0,050	18,853 ±0,198	1,759 ±0,045	-	0,246 ±0,003	0,070 ±0,001	0,054 ±0,001	0,010 ±0,002
Hybrid variety Frăguță *a*	52,153 ±0,097	23,918 ±0,065	21,263 ±0,257	2,247 ±0,061	0,236 ±0,004	-	0,082 ±0,001	0,100 ±0,002	-
Hybrid variety Frăguță *b*	52,697 ± ,080	23,051 ±0,053	21,676 ±0,215	2,238 ±0,052	0,173 ±0,003	-	0,097 ±0,001	0,068 ±0,001	-



a) Aligote 500x **b) Frăguță 500x**

c) Nohan 500x

Figure 1. SEM (scanning electron microscopy) observation of the studied grape seeds

5. References

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