THE OBTAINMENT AND THE CHARACTERIZATION OF THE ANTHOCYANIDINS VEGETAL FROM THE GRAPE PEELS

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The anthocyanidins are the red, violet and blue colorants that are found in the vegetal materials together with the flavones, flavonoids, tannins, etc. The anthocyanidins, d\besides the fact that they represent a source of natural colorants, have also been a subject of research due to their oenological, antibacterial and anti-neoplastic properties. This paper demonstrates the testing of two extracting methods: the discontinuous method with the variants with and without stirring and the Soxhlet continuous method. The efficiency of the extracting methods was considered taking into account the time of extraction and the concentration of anthocyanidins of the vegetal extracts. As vegetal raw materials there were used the grape peels of Vitis vinifera belonging to the varieties of Cabernet Sauvignon, Merlot, Babeasca neagra and Feteasca neagra The extracting process in the discontinuous system without stirring was proven to be the best for the achievement of the anthocyanidins vegetal extracts because they are performed at a temperature of only 30C and do not favor the processes of oxidation of the active substances due to the lack of stirring of the extracting system. Among the tested vegetal materials it was noticed the richest in anthocyanidins are the peels of the varieties Cabernet and Merlot through the no stirring discontinuous method, that is 2520,61 mg/L and 1703,63 mg/L. In the case of the extracting processes in continuos method that used the peels of grapes of the varieties Babeasca neagra, Merlot and Feteasca neagra, the concentrations of anthocyanidins of the obtained extracts were 63% smaller than in the case of the anthocyanidins extract from the peels of Babeasca neagra, with 38% smaller than in the peels of Merlot and with 45% than in the case of the extract from the peels of Feteasca neagra.

***Keywords**: anthocyanidins, polyphenol, tannoid matters, Vitis Vinifera.*

The anthocyanidins in grapes are located in the vacuoles of the cells from the epidermis and hypodermis of the peels, as well as in the cells close to the pulp [5,8]. The anthocyanidins are characterized as flavonoids having the structure of flavones, made up of two benzene cycles A and B, reunited by a heterocycle comprising three atoms of carbon and one of oxygen. In the peel of the grapes, there were identified, out of the group of the flavonoidal compounds, a number of eight flavonol – mono glycosides and three di glycosides.

Using as a solvent the methanol that is added small quantities of chloride acid, in general, performs the extraction of the anthocyanidins from the vegetal materials. Still, the specialized literature contains information that states that the acidulation of the methanol occurs a degradation of the anthocyanidins from the red grapes [6, 7, 9]. Thus, in the extractive processes of the anthocyanidins performed in the present paper, the chosen solvent (ethanol) was not acidulated.

Also, the temperature represents another very important parameter in the unfolding of the extractive processes of the anthocyanidins. Taking into account this aspect, for the identification of the vegetal material with a high content of anthocyanidins, two extractive methods were tested, that is the Soxhlet continuous system method at the temperature that allows the reflux of the ethylic alcohol and the method with a discontinuous system at the temperature of 30 °C.

MATERIAL AND METHOD

The extractive processes of the anthocyanidins from the grape peels of *Vitis vinifera* were performed, in the case of the discontinuous method, in the variants without stirring and with stirring, in recipients with ground glass stopper where there were introduced the vegetal materials and the solvent (ethylic alcohol heated at 40 °C) with a ratio of 1/10 (solid material/solvent).The vegetal extracts obtained at 15,30,60 and 1440 minutes , starting with the moment of the adding of the solvent, were separated from the vegetal materials by centrifugation for 10 minutes at the speed of 6000 rpm.

The extractive materials produced by the Soxhlet continuous method were also performed with the abidance of the ratio of 1/10 (solid material/solvent), using the same vegetal materials as in the discontinuous extractive method. For the performance of the analysis, the poliphenolic extracts were maintained at 4 °C.

The consideration of the efficiency of the extractive processes was done through the determination of the content in anthocyanidins (mg/l) by the use of the R Gayon and Sonestreet method – 1965 [10], of the index of tannin materials (IMT) according to Bourzeix – 1986 [2] an of the total polyphenols (g GAE/L) through the Singleton and Rossi method. – 1965 [11].

RESULTS AND DISCUSSIONS

The extracting procedure in the continuous system, in the Soxhlet device, insures a maximum extraction of the active principles from the vegetal materials due to the modality of functioning that allows a refreshing of the solvent, as well as an adequate time of contact or extraction (approximately 20 minutes for the performance of the reflux). The length in time of the extraction was determined so that it insures an efficient valorization of the tested vegetal materials, leading the extraction until they are fully used, having an average length of 3 hours.

The extracting procedure in the discontinuous system, for both variants, was performed at a temperature of maximum 30 °C without changing the volume of the solvent for 1440 minutes.

The first part of the paper presents the results obtained in the extracting processes in the continuous method. The data exposed in *figure 1* led to the fact

that the biggest concentration of anthocyanidins was found in the extract obtained from the peels of the Cabernet Sauvignon variety, that is 1754,73 mg/l. In the case of the extracting processes that used the peels of grapes of the varieties Babeasca neagra, Merlot and Feteasca neagra, the concentrations of anthocyanidins of the obtained extracts were 63 % smaller than in the case of the anthocyanidins extract from the peels of Babeasca neagra, with 38 % smaller than in the peels of Merlot and with 45 % than in the case of the extract from the peels of Feteasca neagra.

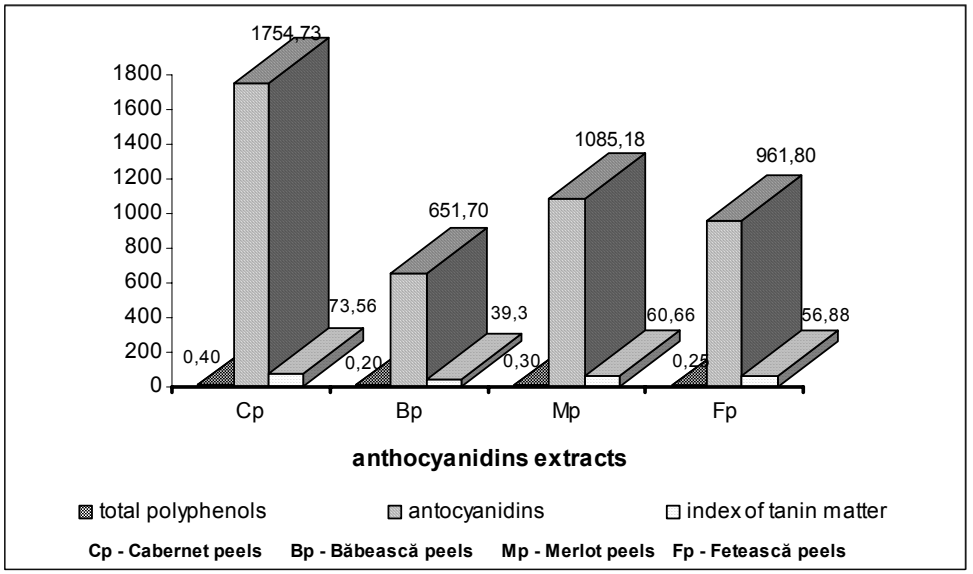

Figure 1. **The characterization of the anthocyanidins extracts obtained through the Soxhlet continuous extracting method**

The anthocyanidins extract obtained from the peels of the Cabernet variety was noticed, at the same time, due to its higher content in total polyphenols and tannin matter.

The extracting processes performed in the discontinuous system, in the variants with stirring and still, there were observed in dynamics, sample being taken for analyses, at intervals of 15, 30, 60 and 1440 minutes. Taking a birds' eye view in the data obtained, there was noticed a common aspect for all the anthocyanidins extracts, that is during 15 – 60 minutes the concentrations of anthocyanidins, total polyphenols and the value of the index of tannin matter increase progressively, the differences being only in the expression of the value of the studied parameters depending on the tested vegetal materials.

The efficiency of the extracting processes manifested obviously only after 1440 minutes, reason that supported the presented in detail of only these results, in the present paper.

The data obtained in the study of the extracting processes in the discontinuous system with stirring are presented in *figure 2*. The graphic expression of the data emphasizes that the anthocyanidins extract obtained from the

peels of grapes of the variety Cabernet present the highest levels of content of anthocyanidins (2382,36 mg/l), of total polyphenols (0,3 g GAE/L), as well as of the index of tannin matter (68,52). In comparison with this anthocyanidins extract, the other 3 extracts presented values smaller with 70% in the case of the extract from the peels of Babeasca neagra, with 40% in the case of the extract from the peels of Merlot and with 75% in the case of the anthocyanidins extract obtained from the peels of Feteasca neagra.

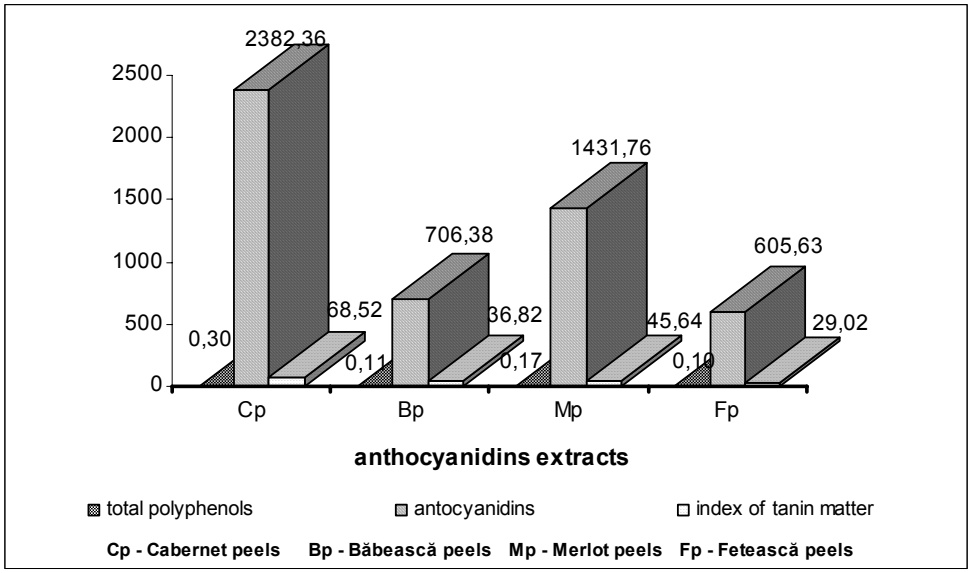

Figure 2. **The characterization of the vegetal extracts obtained through the discontinuous system method with stirring for 1440 minutes**

The data obtained from the extracting processes in the discontinuous system without stirring, are presented in the figure no. 3. The evolution of the extracting processes under the conditions of the non stirring discontinuous system was proven the best because all the vegetal extracts obtained presented higher concentrations of anthocyanidins and total polyphenols, as well the highest value of the index of tannin matter.

Just like the previous experiments the extract from the peels of grapes of the variety of Cabernet was noticed due to concentrations the highest for the studied parameters that is 2520,61 mg/L anthocyanidins, 0,31 g GAE/L total polyphenols and the value of 90,9 for the index of tannin matters.

Comparing the used extraction methods it was noticed that in the extracting processes performed still there appears an increase of the concentrations of anthocyanidins with 5,5 % opposed to the method of extraction with stirring and with 30,4 % opposed to the Soxhlet continuous extracting method.

Also, among the vegetal materials tested the peels of the varieties of Cabernet and Merlot were noticed as being richer in anthocyanidins.

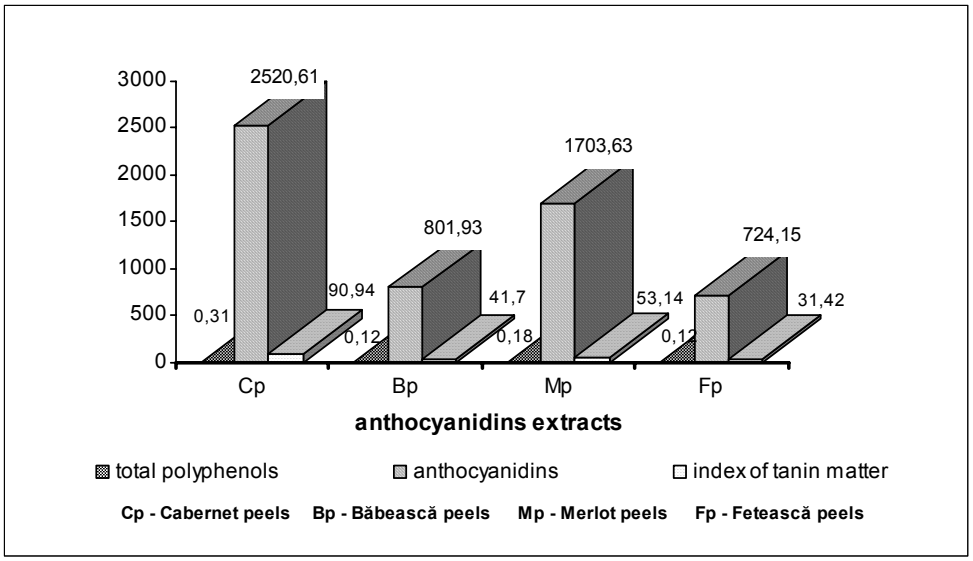

Figure 3. **The characterization of the vegetal extracts obtained through the discontinuous system method without stirring for 1440 minutes**

CONCLUSIONS

1. The extracting process in the discontinuous system without stirring was proven to be the best for the achievement of the anthocyanidins vegetal extracts because they are performed at a temperature of only 30C and do not favor the processes of oxidation of the active substances due to the lack of stirring of the extracting system.

2. Among the tested vegetal materials it was noticed the richest in anthocyanidins are the peels of the varieties Cabernet and Merlot through the no stirring discontinuous method.

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