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THE GRAPE MARC AS POTENTIAL SOURCE OF BIOLOGICALLY ACTIVE COMPOUNDS

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Abstract

Grape culture is one of the most widespread in the world, with about 77 million tonnes of grapes harvested only in 2016. After the winemaking process, the main waste is grape marc. Traditionally, grape marc was thrown into the field, thus losing an important source of valuable compounds. The main purpose of this paper is to present some aspects of the grape marc valorisation obtained from vinification of Romanian autochthonous grapes varieties (Fetească Neagră, Busuioacă de Bohotin, Băbească Neagră etc.). This information will be analysed in terms of the compounds present in widely used grape varieties. Regarding Romanian grape varieties, the bibliographic sources are limited and it is necessary to carry out some analyses and characterizations of the grape marc obtained from native grape varieties as a potential source of alternative products (use in cosmetics, animal feeds, composting etc.).

Key words: *grape marc, Romanian grapes.*

INTRODUCTION

Biomass is a residual material resulting from food production processes, from agriculture, horticulture or human waste. Its issued in various industrial processes, such as energy production, supplement in animal feed, or as raw materials for chemical products.

As the need for food is higher day by day, agriculture generate large amounts of biomass residues. Some of the residues are left in the field to improve the quality of the soil by return of the nutrients. Others, can provide different added-value products by various processing techniques with applications in cosmetics industry or as alternative sources of feed or as compost.

With around 63 million tons produced worldwide, grapes are one of the most cultivated crops around the world (FAOSTAT, 2013). From the total weight of the grapes, approx. 20% constitute the main winemaking by-product, the grape or wine marc (Laufenberg et al., 2003). Grape (or wine) marc is a residue of pressed grapes, pieces of stalks and yeast from the wine fermentation process.

The wine production process generates huge amounts of by-products consisting mainly in organic wastes (Musee et al., 2007; Rondeau et al., 2013). For a long time, due to the lack of knowledge, wine marc was an under-valued product. Traditionally, wine marc was subjected to distillation, producing alcohol (Silva et al., 2000) or used as fertilizer (Arvanitoyannis et al., 2006). Around the world, grape marc is processed in different manners: recovery of grape seed for oil extraction (Vera, 2016), in the soap manufacture, as animal feed, fertilizer or as part of varnish and paints. Usually, grape marc consists in seeds, skins, stalks and residual moisture, residual sugars, organic acids and some quantities of alcohol. Residual alcohol and sugars concentration in marc varies according to the processes and practices used in winemaking (Devesa-Rey et al., 2011; Hixson et al., 2014; Zheng et al., 2012).

One of the operations that can influence the quality and content of the marc is pressing. Depending on the type of press used (traditional presses, vertical presses, horizontal presses, pneumatic horizontal presses, horizontal presses with membrane or presses with continuous action), the yield of the marc is inversely proportional to the must. The higher the yield of the presses, the resulting marc is less rich in nutrients (Baltes, 2016).

Sustainable aspects of winemaking

Wine making is a process that produce a large amount of organic and inorganic waste. Bibliographic sources specify that during cultivation and harvesting about 5 tons of solid waste is generated per hectare per year (Zacharof, 2017). In this respect, the adoption of sustainable cultivation practices for grape and wine crops has been encouraged. (Rugani et al., 2013; Cuccia, 2015; Da Ros et al., 2016).

A sustainable winemaking process consists in maximizing resources and reducing emissions from the production process (Castillo-Vergara et al., 2015; Cuccia, 2015). At global level, the wine sector produces about 0.3% of annual greenhouse gas emissions (Amienyo et al., 2014).

European legislation explicitly uses the term by-products only for grape marc and lees.

Based on the by-product definition given by the Waste Framework Directive (Directive 2008/98/EC on waste), grape marc are substances resulting from a production process, the primary aim of which was not the production of such residues and, furthermore, they are able to be used afterward (Spigno, 2017).

The added- value conversion of the bio-products from winemaking can help in reducing the negative costs and demonstrating sustainability in winemaking. It is important to maximize product recovery and minimize the secondary wastes. Is necessary to understanding the potential benefits of the reuse of winery wastes and by-products (Nerantzis, 2006).

In order to reduce the negative environmental impact, companies have to take into account technologies proposed in the industry to add value to the residues produced in the wine-making industry (Rosa et al., 2011).

Depending on the winemaking process, the marc characteristics may vary. For the red wine production process, the must and the marc are fermented together. This allows the release of pigments (such as anthocyanins) that give the specific colour to red wine. Also, this process is the only one that brings changes to the marc, because fermentation reduces its sugar content. In the case of white wine, the must is fermented separately (Dwyer et al., 2014) and the resulting marc has a higher content in pulp and sugars (Mendes et al., 2013). Figure 1 presents the process of white and red wine production and the marc resulting.

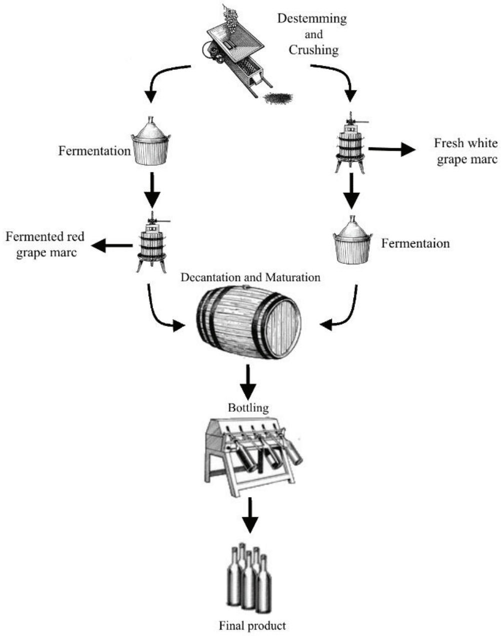

Figure 1. White and red grape marc resulted from the winemaking process (adapted after Muhlack et al., 2018)

GRAPE MARC APPLICATIONS

Grape marc is a rich source of high-value products such as ethanol, tartrate and maltase, citric acid, grape seed oil, hydrocolloids and dietary fibres. In addition, the grape marc is characterized by a high content of phenol, due to poor extraction during winemaking, which makes their use useful and supports sustainable agricultural production (Kammerer et al., 2004).

The products resulting from the wine making process are cheap raw materials with a high amount of antioxidant substances that can be used in human or animal nutrition or in the production of substances with phytochemical activity (Alonso et al., 2002; Negro et al., 2003; Gonzalez-Paramas et al., 2004).

In Romania, a few studies have been focused on the use of grape marc. An important study was carried out by Olteanu et al. (2014), in which the marc from South Eastern Romanian winery was studied for the feeding value and antioxidant capacity. In their study were used three marc varieties consisted of: (1) fresh grape peals, pulp and seeds of red grapes, with no stems; (2) dry, seed-less red grape peals and pulp, with no fermentation smell, and (3) the seed cakes, by-product of oil extraction, with no smell of fermentation or rancidity.

A close correlation between the antioxidant capacity and the polyphenols concentration shows a higher antioxidant character for the dry grape marc sample.

Usually, when studying the feed properties of winemaking by-products some standardized analysis methods are recommended:

- the dry matter (DM) to be determined by gravimetric method according to Regulation (CE) nr. 152/2009 and standard SR ISO 6496:2001;
- crude protein (CP) to be determined by the Kjeldahl method;
- the amino acids to be determined by High Pressure Liquid Chromatography (HPLC);
- the crude fat to be determined by extraction in organic solvents;
- the fatty acids to be determined by gas chromatography;
- the crude fibre to be determined by the method with intermediary filtration;
- the ash to be determined with the gravimetric method;
- the calcium, copper, iron, manganese and zinc to be determined by atomic absorption spectrometry;
- the phosphorus to be determined by spectrophotometry;
- the gross energy to be determined by calculation, using the dry matter, protein, fibre, fat, nitrogen-free extractives and ash, using the equations developed by Burlacu et al. (2002).
- the polyphenols concentration (mg equivalent gallic acid/g sample) to be determined according to the modified method described by Mihailovic et al. (2013);
- antioxidant capacity (mM equivalent Trolox/g sample) to be determined by the DPPH (2,2-diphenyl-1-picrylhydrazyl) method proposed by Marxen et al. (2007).

The use of marc as a component of compost is the most readily available. In his book, Madjar et al. (2007), concludes that compost with marc helps to improve soil with nutrients needed for plants. Also, due to the high-level content of organic matter in the composted marc, it helps to increase the level of life in the soil layers by increasing the level of respiration in the soil, supporting the catalase activity, the urease and the phosphatase activity.

Marc compost can also help sandy soils. When applying a rotation of appropriate crops, the application of marc compost can lead to the improvement of trophic and biological soil characteristics (Ion et al., 1996).

Another approach was taken by Bărbulescu et al. in 2017 with fermented Merlot grape marc, taken from the Oprișor area. The fermentation was carried out under natural light and in darkness; in the study were used in the fermentation yeast isolates also from the Oprișor area. The dried grape marc was grounded and added in the fermentation mix after 13 hours of fermentative process. The authors have noticed that in the presence of natural light, both unfermented and fermented grape residues, compared to similar samples processed at darkness, have lower values (content in polyphenols, protein and antioxidant activity). Also, the biomass obtained through fermentation shows higher antioxidant activity in both light and darkness in comparison with similar samples to the initial grape residue.

Baltes et al. (2016) have analysed quantitatively and qualitatively the polyphenols from the varieties of Cabernet Sauvignon, Merlot, Pinot Noir and Fetească Neagră harvested in 2014 and 2015. For the study, the marc was dried and crushed and then subjected to solvent extraction consisting of ethyl alcohol and water (1: 1 ratio) and then quantitative analysed using the modified Folin-Ciocâlteu method. Following the analyses, the studied samples showed values ranging from 558.6 mg to 608.2 mg/100 g grape marc.

Higher values showed the samples of Pinot Noir grape marc (approx. 600 mg/100 g), and the lowest were the marc of Cabernet Sauvignon (558.6 mg/100 g). Merlot and Fetească Neagră varieties showed similar values: from 566.3 mg to 587.5 mg/100g grape marc.

The values obtained for total phenolic content place grape marc on an equal footing with:
- black currant - 758 mg/100 g;
- capers - 654 mg/100 g;
- black olives - 569 mg/100 g;
- high bush - 560 mg/100 g (J Pérez-Jiménez et al., 2010).

Some Romanian studies have covered also health aspects related to the marc extracts. Studies conducted by Balea et al. (2018) on Fetească Neagră and Pinot Noir marc harvested in Romania in 2015 showed that the marc extracts (fresh and fermented) have improved cardiac parameters and oxidative stress when were administrated to rats. They assumed this result are due to the higher values of phenols and antioxidant activity in the fermented marc compared to fresh marc extracts. Regarding the cardio-protective effect, the fresh Fetească Neagră marc had a higher cardio-protective effect than fermented marc. Pinot Noir extract presented equal cardiovascular effects.

CONCLUSIONS

In the current global context, when the tendency is to use the most of the resources (even some by-products like grape marc), efficient valorisation is a win-win situation. Grape marc brings, besides a significant amount of protein, fats and fibres, a large amount of bio-compounds with a strong antioxidant effect.

The high concentration of polyphenols recommends grape marc utilization particularly in diets enriched in polyunsaturated fatty acids like diets used for the production of animal feed high in omega 3 fatty acids. The use of winery by-products, in animal feeding, in composting or in different extractions also solves the problems of their storage, transformation or disposal, thus maintaining the environmental balance.

The identification of beneficial compounds present in grape marc is important because the identified elements can be a natural source of beneficial compounds. As it is demonstrated, grape marc is an important source of polyphenols.

In Romania, the bibliographic sources are limited and it is necessary to carry out some analyses and characterizations of the grape marc obtained from native grape varieties as a potential source of alternative products.

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REFERENCES

Amienyo, D., Camilleri C., Azapagic, A. (2014). Environmental impacts of consumption of Australian red wine in the UK. *Journal of Cleaner Production* 72, 110–119.

Balea, S., Pârvu, E. A., Pop, N., Marin, Z. F., Cotoi, O., Pîrcu, M. (2018). Polyphenolic compounds, antioxidant and cardioprotective effects of pomace extracts from Fetească neagră and Pinot noir cultivars, *Pathophysiology*, Volume 25, Issue 3, 169. https://doi.org/10.1016/j.pathophys.2018.07.026.

Baltes, V. M. (2016). Valuation of winemaking byproducts with valuable products for industry and food, University “Lucian Blaga” of Sibiu, Faculty of *Agricultural Sciences, Food Industry and Environnemental protection*. E-ISSN 978-973-744-430-1.

Barbulescu, I. D., Teodorescu, I. D., Chedea, S. V., Grigorica, L., Roceanu, G., Marinescu, S. I., Frîncu M., Albu, K. G. M., Cîrîc, A., Matei, P. M., Tamaian, R., Dumitrache, C., Tudor, V., Begea, M. (2017). Obtaining of an active product based on yeast biomass by fermentation of a waste from winemaking process from Oprisor area. *Progress of Cryogenics and Isotopes Separation,* 20(2), 43-50.

Benedetto, G. (2013). The environmental impact of a Sardinian wine by partial life cycle assessment. *Wine Economics and Policy*, 2, 33–41. doi 10.1016/j.wep.2013.05.003.

Castillo-Vergara, M., Alvarez-Marin, A., Carvajal-Cortes, S. (2015). Implementation of a cleaner production agreement and impact analysis in the grape brandy (pisco) industry in Chile. *Journal of Cleaner Production* 96, 110–117. doi 10.1016/j. jclepro.2013.09.048.

Christ, K.L., Burrit, R.L. (2013). Critical environmental concerns in wine production: an integrative review. *Journal of Cleaner Production* 53, 232–242. doi /10.1016/j. jclepro.2013.04.007.

Cuccia, P. (2015). Ethics + economy + environment = sustainability: Gambero Rosso on the front lines with a new concept of sustainability. *Wine Economics*

Policy 4, 69–70. doi/10.1016/j.wep.2015.05.003.
Devesa-Rey, R., Vecino, X., Varela-Alende, J. L., Barral, M. T., Cruz J. M., Moldes A. B. (2011). Valorization of winery waste vs. the costs of not recycling, *Article in Waste Management* 31(11):2327-35, doi 10.1016/j.wasman.2011.06.001.
Directive 2008/98/EC on waste (Waste Framework Directive). http://ec.europa.eu/environment/waste/framework/.
Dwyer, K., Hosseinian, F., Rod, M. (2014). The market potential of grape waste alternatives. *J. Food Res*. 3, 91–106. http://dx.doi.org/10.5539/jfr.v3n2p91.
García Lomillo, J. and González SanJosé, M. L. (2017). Applications of Wine Pomace in the Food Industry: Approaches and Functions. *Comprehensive Reviews in Food Science and Food Safety*, 16, 3-22. doi:10.1111/1541-4337.12238.
https://en.wikipedia.org/wiki/Biomass.
Ion, P., Alexandrescu C., Gheorghe, D. (1996). Some aspects concerning orientation of sand and sandy soils fertility in the South of Oltenia county [Romania]. *Analele Institutului de Cercetari pentru Pedologie si Agrochimie*. ISSN 0365-0189.
Laufenberg, G., Kunz, B., Nystroem, M. (2003). Transformation of vegetable waste into value added products:(A) the upgrading concept; (B) practical implementations. *Fuel and Energy Abstracts* 44. doi 10.1016/S0960-8524(02)00167-0.
Lavelli, V., Torri, L., Zeppa, G., Fiori, L., Spigno, G. (2016). Recovery of winemaking by-products for innovative food applications – a review. Italian *Journal of Food Science*, [S.l.], 28(4), 542-564. doi10.14674/1120-1770/ijfsv507.
Lorenzen, L., Aldrich, C. (2007). Cellar waste minimization in the wine industry: A systems approach. *Journal of Cleaner Production* 15, 417-431. doi 10.1016/j.jclepro.2005.11.004.
Madjar, R., Gheorghiță, N., Davidescu, V., Mănescu, C. (2007). *Cercetari agrochimice privind valorificarea unor deseuri organice sub forma de substraturi*. Editura INVEL – Bucuresti. ISBN 978-973-7753-67-0.
Mendes, J. A. S., Xavier, A. M. R. B., Evtuguin, D. V., Lopes, L. P. C. (2013). Integrated utilization of grape skins from white grape pomaces. *Ind. Crop. Prod*. 49, 286 – 291. doi10.1016/j.indcrop.2013.05.003.
Muhlack, R., Potumarthi, R., Jeffery, D. (2018). Sustainable wineries through waste valorisation: A review of grape marc utilisation for value-added products. *Waste Management*, Volume 72, 2018, 99-118. Doi 10.1016/j.wasman.2017.11.011.
Nerantzis, E., Tataridis, P. (2006). Integrated Enology Utilization of winery by-products into high added value products, e-*Journal of Science & Technology* (e-JST), 1:12, ISSN: 1735-1472. URL: http://e-jst.teiath.gr/eng/trito_teuxos_eng.htm.
Notarnicola, B., Tassielli, G. (2003). *Life cycle assessment (LCA) of wine production. Environmentally-friendly Food Processing*, Woodhead Publishing Ltd., Cambridge, England, 306–326. doi 10.1533/9781855737174.2.306.
Olteanu, M. et al. (2014). Study of the feeding value and antioxidant capacity of winery by-products, potential natural antioxidants for farm animal diet formulations. *Archiva Zootechnica* 17(2), 55-69. ISSN: 2344-4592.
Perez-Jimenez, J., Neveu, V., Vos, f., Scalbert, A. (2010). Identification of the 100 richest dietary sources of polyphenols: An application of the Phenol-Explorer database. *European Journal of Clinical Nutrition*, 64, S112–S120. doi 10.1038/ejcn.2010.221.
Regulamentul (CE) nr. 152/2009 al Comisiei din 27 ianuarie 2009 de stabilire a metodelor de eșantionare și analiză pentru controlul oficial al furajelor. http://www.ansvsa.ro/download/legislatie/nutritie/reg-152-din-2009.pdf.
Rondeau, P., Gambier, F., Jolibert, F., Brosse, N. (2013). *Compositions and chemical variability of grape pomaces from French vineyard*. Ind. Crops Prod. doi 10.1016/j.indcrop.2012.06.053.
Rugani, B., Vázquez-Rowe, I., Benedetto, G., Benedetto, E. (2013). A comprehensive review of carbon footprint analysis as an extended environmental indicator in the wine sector. *Journal of Cleaner Production* 54, 61–77. Doi 10.1016/j.jclepro.2013.04.036.
Spigno, G. (2017). *Handbook of Grape Processing By-Products*. doi 10.1016/B978-0-12-809870-7.00001-6.
SR ISO 6496:2001 Nutreţuri. Determinarea conţinutului de umiditate şi de alte substanţe volatile. magazin.asro.ro/standarde/can/1/S45/113473268.
Teixeira, A., Baenas, N., Dominguez-Perles, R., Barros, A., Rosa, E., Moreno, D. A., Garcia-Viguera, C. (2014). Natural bioactive compounds from winery by-products as health promoters: a review. *International journal of molecular sciences,* 15(9), 15638-78. doi 10.3390/ijms150915638.
Ur-Rehman, S. Mushtaq. Z., Zahoor, T. Jamil, A. Murtaza, M. A. (2015). Xylitol: a review on bioproduction, application, health benefits, and related safety issues. *Critical Reviews in Food Science and Nutrition.* 55 (11): 1514–28. doi10.1080/10408398.2012.702288.
Villanueva-Rey, P., Vázquez-Rowe, I., Moreira, M. T., Feijoo, G. (2014). Comparative life cycle assessment in the wine sector: biodynamic vs. conventional viticulture activities in NW Spain. *Journal of Cleaner Production,* 65, 330–341. doi 10.1016/j.jclepro.2013.08.026.
Zacharof, M-P. (2017). Grape Winery Waste as Feedstock for Bioconversions: Applying the Biorefinery Concept, *Waste and Biomass Valorization*, 8(4), 1011–1025. doi 10.1007/s12649-016-9674-2.

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