Discriminating Red Grape Extracts

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Hydroalcoholic extracts obtained from the skin/seed/pulp of red grapes are good sources of polyphenols and flavonoids, compounds known for their antioxidant action and for their protection against diseases, such as cancer, diabetes, cardiovascular disease, and neurodegenerative diseases. The anthocyanin content of the extracts obtained from the skin of the four varieties of red grapes can be defined as moderate, as it is known that factors, such as maturity and climate, can change the presence of these compounds in grapes. Previous studies revealed that the hydroalcoholic extracts obtained from the skin of the organic system varieties (e.g., Feteasca Neagra, Merlot, and Pinot Noir), contain a high content of polyphenols, flavonoids and tannins.

vibrational spectroscopy | red grape extracts | organic/conventional vineyards | chemometrics

1. Overview

Food plants provide a regulated source of delivery of functional compounds, plant secondary metabolites production being also tissue specific. In grape berries, the phenolic compounds, flavonoids and non-flavonoids, are distributed in the different parts of the fruit. The aim of this study was to investigate the applicability of FTIR and Raman screening spectroscopic techniques combined with multivariate statistical tools to find patterns in red grape berry parts (skin, seeds and pulp) according to grape variety and vineyard type (organic and conventional). Spectral data were acquired and processed using the same pattern for each different berry part (skin, seeds and pulp). Multivariate analysis has allowed a separation between extracts obtained from organic and conventional vineyards for each grape variety for all grape berry parts. The innovative approach presented in this work is low-cost and feasible, being expected to have applications in studies referring to the authenticity and traceability of foods. The findings of this study are useful as well in solving a great challenge that producers are confronting, namely the consumers' distrust of the organic origin of food products. Further analyses of the chemical composition of red grapes may enhance the capability of the method of using both vibrational spectroscopy and chemometrics for discriminating the hydroalcoholic extracts according to grape varieties.

2. Grapes

The beneficial health effects of fruits have been attributed to the presence of fibers, minerals, vitamins (i.e., provitamin A, carotenoids, vitamins C and E) and phytochemicals, including phenolic acids, flavonoids, and anthocyanins. Food plants provide a regulated source of delivery of functional compounds. In addition, most of the bioactive substances have specific functions within the plant. Plant secondary metabolites production is generally under strict regulatory control and is tissue specific; any attempt to regulate their biosynthesis might result in adverse effects elsewhere in the plant and toxicity [1]. The synthesis of specific metabolites, which can be very plant specific, is controlled through highly branched pathways and carefully regulated. Given the wide diversity in the structure and function of these metabolites in the plant, differences in temporal and spatial distribution of the metabolite can occur, depending on the stage of the development of the plant and between different plant organs and cell types [1][2][3].

The constant interest in the biological activity of organically grown grapes and grape by-products contributes to their capitalization as a source of bioactive phytochemicals with potential applications in the cosmetics, pharmaceutical and food industries [4][5][6][7][8][9]. The full understanding of the phytochemical composition and antimicrobial activity of the different anatomical parts of fruits may contribute to developing new applications. The potential correlation of these properties with the culture management system, or with the grape variety, may add valuable practical data. Traditionally, morphological and agronomical characteristics have been the main criteria for differentiating grapevine cultivars, but it is well known that many of those properties are strongly influenced by environmental conditions [10]. Grapevine varieties are not generally homogenous and intravarietal diversity varies across cultivars [11][12]. Even vines multiplied by vegetative propagation display a broad range of characteristics, such as the grape phenolic profile that depends greatly on the grape variety [10]; Liang et al. A study by [13] showed that polyphenolic profiles revealed significant differences among 344 European grape varieties, which included both table and wine grapes.

In the grape berries, the phenolic compounds, flavonoids and non-flavonoids according to their chemical structure, are distributed in the different parts of the fruit. Flavonoids are found mainly in grape seeds and skins; proanthocyanidins are present mainly in the berry skin and seeds [14][15]. With regards to grape skins, each variety has its unique set of anthocyanins with their biosynthesis being influenced by several factors, such as climatic conditions, temperature, light and cultural practices [14][16].

In general, grapes produced under organic farming systems are increasing around the world. Since their agronomic system does not allow the use of chemical pesticides and fertilizers, these fruits are perceived by the public as safer and healthier when comparing to those produced by conventional agriculture. However, these grapes are more susceptible to the action of phytopathogens inducing the synthesis of higher amounts of phenolic compounds as protection and defense [14][17]. As a series of studies [18][19][20] have observed, the choice of agricultural practice (organic vs. conventional) resulted in different amounts of resveratrol, anthocyanins, and tannins in grape juices. This difference is due to the fact that no pesticides are used in organic vineyards and that they have a longer ripening period than conventional ones. As flavonoids are formed during this last-mentioned period, it is believed that organic vineyards yield grapes with higher phenolic content [14][21][22].

Hydroalcoholic extracts obtained from the skin/seed/pulp of red grapes are good sources of polyphenols and flavonoids [6], compounds known for their antioxidant action and for their protection against diseases, such as cancer, diabetes, cardiovascular disease, and neurodegenerative diseases. The anthocyanin content of the extracts obtained from the skin of the four varieties of red grapes can be defined as moderate, as it is known that factors, such as maturity and climate, can change the presence of these compounds in grapes. Previous studies [6]

[7][8][23] revealed that the hydroalcoholic extracts obtained from the skin of the organic system varieties (e.g., Feteasca Neagra, Merlot, and Pinot Noir), contain a high content of polyphenols, flavonoids and tannins.

The analytical information contained in complex FTIR and Raman spectra can be extracted using multivariate analysis techniques that relate analytical variables to chemical properties of the matrix constituents [24][25][26][27]. The application of chemometrics together with infrared (IR) spectroscopy has been reported in literature for the analysis of natural products [25][26][27][28], medicinal and aromatic plants and their essential oils, and phenolic compounds [29][30][31][32]. Principal components analysis (PCA) and partial least squares (PLS) regression are some of the most commonly used multivariate data analysis techniques applied to grape and wine analysis [33][34][35]. Compared to traditional methods, multivariate analysis combined with modern instrumental techniques often give new and better insight into complex problems [33].

3. Conclusions

The red grape varieties included in the present study (Merlot, Feteasca Neagra, Pinot Noir, and Muscat Hamburg) are used mainly in the fresh state and also for obtaining, on a smaller segment, aromatic wines, according to OIV standard 2018 [36]. The selection of the varieties has been made for the following reasons: (1) they are grown in both vineyard systems (i.e., in organic, and conventional culture) thus, being able to make a comparative evaluation of the phytochemical profile of red grape extracts; (2) the continental climate, with thermal amplitudes and long and sunny summers favors a good ripeness of the grapes; (3) the chosen vineyards are in a hilly area, of different altitudes, on a slope, with open valleys and ventilated due to the winds; (4) the approximately similar surface soil type (black-brown clay-limestone) with calcareous subsoil [37].

For the conventional vineyard, an effective phytosanitary protection is applied (synthetic systemic fungicides, but also the copper fungicide Bordeaux mixture), fertilizers, and synthetic pesticides, which ensure a good sanitary condition of the vine and soil. If the autumn is rainy and there is a high risk of mold attack, the technique of partial defoliation is applied to rich foliar stems.

The process of organic cultivation of the studied *Vitis vinifera* L. varieties has the advantage of using phytosanitary treatments and natural fertilization (Bordeaux juice) applied in well-established periods. The irrigation is dripping, and does not use synthetic chemicals, which, even if they are systemically applied within the limits allowed by the relevant legislation, alter the properties of grapes. Thus, natural grapes are obtained without chemical residues. The organic vineyard highlights the fact that the use of synthetic products for phytosanitary treatments is prohibited, and the health of the vine is ensured in a preventive manner, being allowed only products based on simple mineral salts (copper, sulfur, and sodium silicate), or plant extracts within the limits of the rules established by the relevant legislation (i.e., EC Regulations no. 834/2007 and no. 889/2008).

Excepting Pinot Noir, the rest of the red grape varieties show notable differences between organic and conventional vineyards (M-O vs. M-C, FN-O vs. FN-C and respectively MH-O vs. MH-C), the corresponding extracts for each variety, organic and conventional, being assigned in the two main clusters.

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