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Phenolic composition, physicochemical properties and antioxidant activity of interspecific hybrids of grapes growing in Poland

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ABSTRACT

The study evaluated fruit quality parameters and chemical properties (soluble solids, pH, total acidity and total sugars content, phenolic compounds and antioxidant activity (ABTS, FRAP and ORAC methods)) of 30 grape cultivars of white, red and pink grape, as 28 interspecific hybrids and 2 *Vitis vinifera* L. popularly grown in Poland. Some of them were analyzed for the first time. A total of 49 polyphenolic compounds were identified by LC-PDA-QTOF/MS and quantified by UPLC-PDA-FL, as 26 anthocyanins, 9 flavonols and flavons, 7 phenolic acids, 6 flavan-3-ols, and 1 stilbene. The content of total polyphenols ranged from 1037.0 (Cascade cv.) to 5759.1 mg/100 g dm (Roesler cv.). However, the content of stilbene represented by trans resveratrol-3-glucoside was only 18.5–70.5 mg/100 g dm. Red grape cultivars like Roesler, Rothay and Swenson Red were characterized by the highest content of bioactive compounds and antioxidant activity (significantly more than 24, 12 and 53 mmol TE/100 g dm, by ABTS, FRAP and ORAC, respectively). Average total acidity and soluble solids for white (0.95 g of tartaric acid in 100 g fm and 17.1°Bx, respectively) and for red and pink (0.93 g of tartaric acid in 100 g fm and 17.4°Bx, respectively) cultivars were not significantly different ($p > 0.05$).

1. Introduction

Grape (*Vitis vinifera* L.) is one of the fruits most widely cultivated around the world. In 2013 its production exceeded 75 million tons. Nowadays, the top producers are China, Italy, the USA, Spain, and France. Over 80% of all grapes grown in the world are used for the manufacture of juice and wine (FAO, 2014; Iora et al., 2015).

In top grape producing countries (such as France, Italy, and Spain), wine industry is chiefly based on only a few dozen local cultivars, despite the existence of thousands of other cultivars. These local cultivars are diversified, particularly with respect to their biochemical traits. Determination of variability of local grape cultivars may help farmers to select an appropriate one for their local conditions (Eyduran, Akin, Ercisli, Eyduran, & Maghradze, 2015). Changes in the fruit quality result in obtaining different types of wine. However, *V. vinifera* L., despite yielding high quality wine, is also poorly resistant to fungal infections and winter frost. Multispecies hybrid grapes are obtained from crossing of two or more species of *Vitis*. The interspecific hybrids are characterized by different chemical composition, and are known to have high anthocyanin content and specific anthocyanin profile (Slegers, Angers, Ouellet, Truchon, & Pedneault, 2015; Socha, Gałkowska, Robak, Fortuna, & Buksa, 2015).

In recent years, consumer awareness and interest in healthy eating has been on the rise. Consumption of raw grape or products made from them (juices or wine) provides health-related benefits, mainly due to the presence of strong antioxidants and polyphenolic compounds. Phenolic compounds can be found in any part of the fruit (skin, pulp and seeds) and they include flavonoids (anthocyanins, flavanols and flavonols), phenolic acids, and stilbenes. These compounds protect the fruit, and after ingestion they help to fight free radicals in human cells and tissues (Granato, Katayama, & de Castro, 2011; Macedo et al., 2013). Thanks to their other properties, such as the protection of vessels and platelets, regulation of blood pressure and plasma lipid profile, improving the resistance to oxidative stress, inflammation, and endothelial dysfunction, the consumption of grapes is associated with a reduced risk of developing chronic diseases such as heart disease, atherosclerosis, diabetes, and cancer (Rolle, Torchio, Giacosa, & Rio Segade, 2015; Toaldo et al., 2015).

Poland is not a typically wine country but nowadays grapes are grown successfully in many regions. Polish wine-making tradition dates back to the Middle Ages, and the founders of the first vineyards were Cistercians and Benedictines, later joined by other

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monastic orders. For several decades now, the climate has been changing into milder and the growing season with an average temperature of 25 °C has been considerably extended. In the regions of Lubuskie and Lower Silesia, winemaking is experiencing intensive development initiated by German settlers (Tarko, Duda-Chodak, & Dojniczek, 2010). In the south-western part of Poland, i.e. in Lower Silesia winters with temperatures below −20 °C are rare.

The analyzed cultivars included some of the most popular one used in wine production, i.e. Cabernet Sauvignon, Riesling, Solaris, or Seyval Blanc. Grape quality is crucial to wine quality. Other important features determining the quality of the grapes and their products are acidity and the content of sugars, organic acids, and phenolic compounds (Eyduran et al., 2015).

Therefore, the aim of this work was to analyze physical and chemical properties (soluble solids, total sugar content, pH, and total acidity), phenolic compounds (LC–MS QTOF, UPLC-PDA-FL) and antioxidant activity (ABTS, FRAP and ORAC assays) of 30 different cultivars, beside them 28 interspecific hybrids of grape cultivated in Poland. These cultivars are grown in different parts of the world, some of them are well known and grown on a large scale, some are grown only locally. Many of them (e.g. Jutrzenka, Helios, Bolero, Rondo, Regent), have not yet been evaluated in this regard. The study results were analyzed in terms of health-promoting and expected sensory properties. The physicochemical characteristics of investigated grapes can be helpful in selecting cultivars most suitable for cultivation in specific vine regions.

2. Materials and methods

2.1. Chemicals

2,2′-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS), 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox), 2,4,6-tri(2-pyridyl)striazine (TPTZ), 2,2′-azobis (2-amidinopropane) dihydrochloride (AAPH), fluorescein disodium (FL), potassium persulfate, acetic acid, phloroglucinol, and methanol were purchased from Sigma-Aldrich (Steinheim, Germany). (−)-Epicatechin, (+)-catechin, procyanidins B1, *p*-coumaric acid, quercetin and kaempferol-3-*O*-glucoside, cyanidin-3-*O*-sophoroside, cyanidin-3-*O*-glucoside, cyanidin-3-*O*-rutinoside, peonidin-3-*O*-rutinoside, and pelargonidin-3-*O*-glucoside were purchased from Extrasynthese (Lyon, France). Acetonitrile for ultra-phase liquid chromatography (UPLC; Gradien grade) and ascorbic acid were from Merck (Darmstadt, Germany). UPLC grade water, prepared by HLP SMART 1000s system (Hydrolab, Gdańsk, Poland), was additionally filtrated through a 0.22 μm membrane filter immediately before use.

2.2. Plant materials

Twenty-eight grapes interspecific hybrids (Jutrzenka, Seyval Blanc, Solaris, Serena, Hibernal, Muscat Odesski, Biona, Merzling, Bianca, Sibera, Helios, Bolero, Rondo, Cascade, Medina, Monarch, Roesler, Kristaly, Rothay, Cabernet Sauvignon, Rosler, Swenson Red, Gołubok, Freiminer, Leon Millot, Regent, Sevar, Marechal Foch, Wiszniewyj; Table 1) and two *Vitis vinifera* (Riesling, Zweigelt) were used in this research; all of them were collected from Research Institute of Horticulture in Skierniewice, Poland, in year 2013. Titratable acidity (TA), pH, soluble solids and sugars were measured on whole fresh berries soon after harvest. For polyphenolic compounds and antioxidant activity analyses, the whole berries were cut directly to liquid nitrogen and crushed by laboratory mill for homogeneous powder in liquid nitrogen (IKA 11A; Staufen, Germany) and freeze-dried (24 h; Alpha 14 LSC; Martin Christ GmbH, Osterode am Harz, Germany). The samples were stored in a freezer (−80 °C; Frilabo; Lyon, France) until analysis, no longer than 2 weeks.

2.3. Physicochemical analyses

Titratable acidity (TA) was determined by titration aliquots, as described previously by Topalovic and Mikulic-Petkovsek (2010) (Schott Titroline 7500 KF Volumetric KFTitrator; Mainz, Germany) of homogenate of whole fresh grapes by 0.1 N NaOH to an end point of pH 8.1 using an automatic pH titration system and expressed as g of tartaric acid in 100 g. The extract was measured using a refractometer PAL-88S (AtagoCo., Tokyo, Japan) in triplicates, and results are represented in °Bx.

2.4. Determination of sugar content by HPLC

Sugar content was measure by HPLC in water extracts, prepared from freeze-drying powder. Analysis of sugars was described previously by Topalovic and Mikulic-Petkovsek (2010), and performed using a Thermo Separation Products HPLC with refractive index (RI) detector. Separation of sugars was carried out using a Rezex RC Mmonosaccharide column (300 mm × 7.8 mm; Phenomenex, Torrance, CA) with the column temperature maintained at 65 °C and flow rate of 0.6 ml min^{-1}. The samples were eluted according to the isocratic method, for the mobile phase, twice distilled water was used and also a refractive index detector for identification. Results are expressed in grams per 100 g dm.

2.5. Identification of phenolic compounds by the LC-PDA-MS method and analysis of procyanidins fractions

The extraction of grape berries for their polyphenols analysis was performed as described previously by Wojdyło, Nuncio Jáuregui, Carbonell-Barrachina, Oszmiański, and Golis (2013) The samples were analyzed by using an Acquity UPLC system (Waters, Milford, MA) with a Q-Tof mass spectrometer (Waters, Manchester, U.K.). Quantification was achieved by injection of solutions of known concentrations ranging from 0.05 to 5 mg/mL ($R^2 \leqslant 0.9998$) of phenolic compounds as standards. The results were expressed as mg per 100 g dry matter (dm).

Direct phloroglucinolysis of freeze-dried grapes was performed as protocol described previously by Wojdyło et al. (2013).

Polymeric procyanidins were analyzed by UPLC-FL using a diode array detector (ACQUITY UPLC™; Waters Corporation; Milford, USA). The mean degree of polymerization (DP) was obtained by calculating the molar ratio of both extension and terminal flavan-3-ol units to terminal units as previously described Wojdyło et al. (2013). All determinations were performed in triplicate and expressed as milligrams per 100 g dm.

2.6. Analysis of antioxidant activity

The solvent for analysis of antioxidant activity was prepared as described previously by Wojdyło et al. (2013). The free radical scavenging capacities were determined using the ABTS method described by Re et al. (1999), FRAP (ferric reducing antioxidant power) method described by Benzie and Strain (1996) and ORAC method described by Ou, Huang, Hampsh-Woodill, Flanagan, and Deemer (2002). Determinations of ABTS and FRAP methods were performed using a UV-2401 PC spectrophotometer (Shimadzu, Kyoto, Japan) but ORAC method performed using a RF5301 PC spectrofluorometer (Shimadzu, Kioto, Japan). All antioxidant activity analyses were done in triplicate, and results were expressed as millimoles of Trolox per 100 g dm.