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Chemical composition, bioactive compounds, and volatiles of six table grape varieties (*Vitis vinifera* L.)

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ABSTRACT

Six table grape cultivars (Centennial Seedless, Chasselas, Italia, Italia Rubi, Alphonse Lavallée, and Muscat de Hambourg) were analyzed for their levels of soluble solids, titratable acidity, sugars, organic acids, vitamin C and E, carotenoids, polyphenolics and volatile compounds during two successive years. Descriptive sensory analyses of the six table grape varieties were also performed. Mainly due to anthocyanins, black cultivars had the highest total phenolic contents. Alphonse Lavallée had also both the highest levels of *trans*-resveratrol and piceid, and Muscat de Hambourg the highest levels of α-tocopherol, β-carotene and monoterpenols, well-known key aroma compounds in Muscat varieties having also interesting pharmacological properties. This study shows that the two traditional black French cultivars, Muscat de Hambourg and Alphonse Lavallée, are particularly rich in bioactive compounds and have a great potential for human health. Finally, Muscat de Hambourg was significantly rated sweeter, juicier and more aromatic than the others cultivars.

1. Introduction

Grapes are one of the world's largest fruit crops behind bananas, watermelons, and apples. In 2014, the worldwide production was about 75 million tons, of which about 21 million tons for table grapes (FAOSTAT, 2017). In Europe, production of table grapes (about 2.3 million tons) remains concentrated in Mediterranean-type areas, and the four main producers are Italy (62%), Spain (14%), Greece (13.5%) and France (2.2%). In France, the production is mainly located in Vaucluse and Tarn-et-Garonne, and three cultivars represent about 80% of the production: Muscat de Hambourg, Chasselas, and Alphonse Lavallée. French table grape production (~60,000 tons) accounts for ~37% of the national consumption. The remainder is mainly imported from Italy and Spain, of which ~70% of cultivar Italia.

A great number of studies have shown that a greater consumption of fruits and vegetables (F & V) lowers the risk of chronic diseases, such as cardiovascular diseases and cancer (Turati, Rossi, Pelucchi, Levi, & La Vecchia, 2015; Vieira et al., 2016). This beneficial effect of F & V has been attributed to the presence of fibers, minerals, vitamins (provitamin A carotenoids, vitamin C and E), and phytochemical compounds including phenolic acids, flavonoids, and anthocyanins (Perestrelo, Silva, Pereira, & Câmara, 2014; Rodriguez-Casado, 2016; Shahidi & Ambigaipalan, 2015). Grapes contain a wide range of vitamins, carotenoids and polyphenolic compounds (Perestrelo et al., 2014; Rodriguez-Casado, 2016; Xia, Deng, Guo, & Li, 2010) and because they are consumed as fruits, wine, juice, or raisins, they are important sources of health promoting compounds for many people. Polyphenols are secondary plant metabolites, generally divided into two groups: non-flavonoid (hydroxybenzoic acids, hydroxycinnamic acids, and stilbenes) and flavonoid compounds (anthocyanins, flavonols, and flavan-3-ols). In grape berries, hydroxybenzoic acids, stilbenes, flavonols and anthocyanins are mainly located in the skin whereas hydroxycinnamic acids are primarily located in the pulp, and flavan-3-ols in seeds (Cheynier & Rigaud, 1986). Besides their antioxidant activities (Shahidi & Ambigaipalan, 2015), polyphenols also play an important role in grape quality because of their contribution to the taste and color. Anthocyanins are directly responsible for the red color in grapes, whereas flavan-3-ols and flavonols contribute to astringency and bitterness (Drewnowski & Gomez-Carneros, 2000). Grapes also contain carotenoids, mainly β-carotene and lutein. Other xanthophylls such as neoxanthin, violaxanthin, or lutein-5,6-epoxide are also present but at lower concentrations (Mendes-Pinto, Ferreira, Oliveira, & Guedes de Pinho, 2004). Carotenoids are well-known natural pigments, responsible for the red, orange, and yellow hues in F & V, but they are also important to human health since they are precursors of vitamin A (β-carotene primarily). Vitamin A is essential for normal growth, reproduction, and resistance to infection. It also plays a role in vision, and a severe deficiency can lead to irreversible blindness (Tee & Lee, 1992). Different studies also report carotenoids as antioxidants (Stahl & Sies, 2003), and β-carotene was suggested to have preventive benefits

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against lung and colorectal cancer (Fraser & Bramley, 2004). Grapes are also sources of vitamin C and E. Vitamin C is generally considered as the most important vitamin in F & V for human nutrition (Lee & Kader, 2000), nevertheless vitamin E is also another important natural antioxidant (Traber & Atkinson, 2007). Vitamin E consists of four tocopherols (α-, β-, γ- and δ) and the corresponding tocotrienols. Alpha-tocopherol is generally recognized as the most highly active form of vitamin E in humans (Kamal-Eldin & Appelqvist, 1996). In grapes, tocopherols are rather homogeneously distributed in all tissues (pericarp, mesocarp, and seeds) and α-form is generally predominant. In *Vitis vinifera* L., tocotrienols are only present in the seeds (Horvath et al., 2006).

Although they are an important source of health promoting compounds, grapes are mainly appreciated by consumers for their sweetness, juiciness, and aroma. Aroma is effectively one of the essential factors contributing to grape quality, and generally the floral aroma typical of Muscat varieties is highly appreciated by consumers. In contrast to neutral varieties, which contain few volatiles other than C_6-compounds, numerous studies have shown that Muscat varieties contain generally high levels of free monoterpenes, and the importance of these compounds in the characteristic floral aroma of these varieties is widely accepted (Mateo & Jiménez, 2000). Besides their importance in the aroma of grapes, recent studies have shown that monoterpenes also have various pharmacological properties including antifungal, antibacterial, antioxidant, anticancer, and anti-spasmodic action (Karkabounas et al., 2006; Perestrelo et al., 2014). Some epidemiological studies also suggested that monoterpenes may be helpful in the prevention and therapy of several cancers including mammary, skin, lung, colon, and prostate carcinomas (Thoppil & Bishayee, 2011).

The aim of this study was to determinate the levels of sugars, organic acids, polyphenolics, carotenoids, vitamin C and E and volatile compounds of six table grape cultivars. The samples were also subjected to descriptive sensory analyses by a trained panel. Muscat de Hambourg, Chasselas and Alphonse Lavallée were chosen because they are the three main varieties produced in France. As the first imported variety on the French market, Italia was also selected. Two varieties recently marketed in France were chosen as well: Italia Rubi, a natural mutation of cv. Italia, and Centennial seedless, due to its seedlessness which is a commercial trait more and more appreciated by French consumers. Levels of vitamins, phytochemicals and volatile compounds in grapes are known to be influenced by genetic background, maturity, environmental factors, or cultural practices, but to our best knowledge, this work seems to be the first comparative study taking into account both descriptive sensory analysis, compounds of interest for health and compounds related with organoleptic quality in table grape.

2. Materials & methods

2.1. Chemicals and reagents

Ethanol (99.8%), 2-octanol (98%), formic acid (96%), KH_2PO_4 (99.5%), H_3PO_4 (33.5–36.5%), anhydrous Na_2SO_4 (99%), metaphosphoric acid (MPA, 99.9%), tris(2-carboxyethyl)phosphine (TCEP; 98%), $(NH_4)_2SO_4$ (≥99%), methyl 4-hydroxybenzoate (≥99%), and *n*-alkane standards (C_8-C_{40}) were obtained from Sigma-Aldrich (Saint-Quentin-Fallavier, France). Acetonitrile (99.99%), hexane (99.99%), acetone (99.98%), dichloromethane (99.9%), and methanol (99.99%) were all of HPLC gradient grade (Fisher Chemical, Leicestershire, UK). Reference compounds were obtained from Sigma-Aldrich (sucrose, glucose, fructose, tartaric acid, malic acid, ascorbic acid, (*Z*)-3-hexenal, hexanal, hexanol, (*E*)-2-hexenal, (*Z*)-3-hexenol, linalool, geraniol, (*E*)-furan linalool oxide, (*Z*)-furan linalool oxide, β-carotene, (+)-catechin, caftaric acid, (−)-epicatechin, procyanidin dimer B2, α-tocopherol, γ-tocopherol, *trans*-resveratrol, quercetin-3-O-glucoside, quercetin-3-O-rutinoside, *trans*-β-apo-8′-carotenal), Interchim (Montluçon, France) (hotrienol), and Extrasynthese (Lyon, France) (procyanidin dimer B1, lutein, quercetin-3-glucuronide, (−)-epigallocatechin, delphinidin-3-glucoside, cyanidin-3-glucoside, malvidin-3-glucoside, peonidin-3-glucoside, piceid). Deionized water (0.050 μS cm^{-1}) used in all experiments was obtained from a Purelab Flex system (ELGA Labwater, Antony, France).

2.2. Materials

In 2014 and 2015, three white table grape cultivars (Centennial Seedless, Chasselas, and Italia), two black table grape cultivars (Alphonse Lavallée and Muscat de Hambourg) and one pink table grape cultivar (Italia Rubi) were harvested at technological ripening from the collection vineyard of the experimental center La Tapy (Carpentras, France) (GPS location 44 °05′38.1″N 5 °03′05.4″E) or purchased from local fruit markets. For each cultivar, three healthy 100-berry samples were selected from about 5 kg of clusters. Berries were then immediately frozen under liquid nitrogen and reduced to powder using a mortar grinder (Pulverisette 2, Fritsch) with liquid nitrogen. The frozen powders were then stored at −80 °C until analysis. All analyses were performed in triplicate (100 berries per replicate).

2.3. Determination of soluble solids and titratable acidity

About 25 grams of frozen powder (−80 °C) was thawed for ~30 min at room temperature and then centrifuged (14,000*g*, 5 min, 4 °C) (Sigma 4K15, Sigma Laborzentrifugen GmbH, Osterode am Harz, Germany). Soluble solids content (SSC) was determined from the supernatant with an Atago PR-32 digital refractometer (Atago Co., Ltd., Tokyo, Japan). The results were expressed in °Brix. Titratable acidity (TA) was determined by diluting 5 mL of supernatant with 30 mL of deionized water and titrating to pH 8.1 with 0.1 N NaOH using an automatic titrator with autosampler (Titroline 7000, Schott SI Analytics, Mainz, Germany). The results were expressed in g/L of tartaric acid.

2.4. Determination of sugars and organic acids

The levels of individual sugars (glucose, fructose, and sucrose) and organic acids (tartaric and malic acid) were simultaneously determined by HPLC. One mL of supernatant, previously obtained (see § 2.3), diluted 20-fold with deionized water was filtered (RC 0.2 μm Phenex; Phenomenex, Le Pecq, France) and directly injected in HPLC. An Acquity UPLC® H-Class system (Waters, Milford, MA, USA) was used with a photodiode array detector (Acquity PDA eλ) and a refractive index (Acquity RI) detector connected in series. The PDA was set at 210 nm. The RI temperature was set at 34 °C. Ten μL of each sample was injected using a sample manager on a 300 mm × 7.8 mm i.d. ion-exclusion Rezex ROA-Organic H + column equipped with a Carbo-H guard column (Phenomenex). The column oven temperature was set at 27 °C. The flow of mobile phase (5.10^{-4} N H_2SO_4) was 0.4 mL/min. Identifications were performed by comparing retention times (t_R) with those of standards and by spiking samples with pure compounds. Quantifications were carried out using five-points calibration curves prepared for sucrose (1–10 g/L), glucose (40–120 g/L), fructose (40–120 g/L), malic acid (0.5– g/L), and tartaric acid (2–10 g/L) using the corresponding standards.

2.5. Determination of vitamin C

One gram of frozen powder added to 10 mL of MPA (2%) was homogenized for 60 s at 20,000 rpm with an Ultra-Turrax (IKA T25-Digital, Staufen, Germany). After centrifugation (Sigma 4K15, 14,000*g*, 5 min, 4 °C), the supernatant was filtered (RC 0.2 μm Phenex; Phenomenex). Ascorbic acid (AA) was determined by direct injection in HPLC (see conditions below) of 500 μL of extract added to 500 μL of MPA (2%). Total vitamin C was determined by HPLC after 3 h of