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Stable isotope ratio analysis of different European raspberries, blackberries, blueberries, currants and strawberries

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ABSTRACT

To date the stable isotope ratios of berries have never been extensively explored. In this work the H, C, N and O isotopic ratios of 190 samples of different soft fruits (strawberries, raspberries, blueberries, blackberries and currants) produced in a northern Italian region and at two sites in Romania and Poland collected over three harvest years are presented and discussed.

The different soft fruits showed a typical range for one or more isotopic parameters that can be used to verify the authenticity of the fruit composition declared on the label. The $\delta^{13}C$ and $\delta^{15}N$ of pulp and the $\delta^{18}O$ of juice can be considered effective tools for identifying the different geographical origin of fruit. A significant effect of crop cover on juice $\delta^{18}O$ and fertilisation practices on pulp $\delta^{15}N$ was demonstrated and must be considered with attention when evaluating data.

1. Introduction

In the last few years, consumers have showed an increasing desire for a healthy diet. In particular, consumers are increasingly monitoring food labels (list of ingredients and nutritional facts panel) and basing purchasing decisions on them (Frey & French, 2014). Thanks to the low content in terms of fat, carbohydrates and calories, and the high level of fibre, vitamins, minerals and antioxidants, berries are one of the best nutritional bargains around (Deighton et al., 2002).

For this reason, the European berry market has made remarkable progress in developing quality and quantity. While no growth is highlighted in official databases, several commercial sources state that from 2004 to 2015, production rose from around €620 million to approximately €1.3 billion. There were particularly strong rises in 2011 and 2015, with an increase of more than 18% in value (Escodo, 2016). In Europe, the main berry producers are represented by Serbia, Germany, Spain, Poland and others with lower production, such as the UK, Holland, Italy and Romania (European Commission., 2014). With regard to Italy, as internal production does not meet the continuously increasing demand from the domestic market, the country imports nearly 80% of its soft fruit and strawberries, in particular from Spain, South America and Eastern Europe (from countries such as Poland and Romania) (Oy, 2008).

The higher or lower price of soft fruit for fresh and processing purposes depending on origin, and the possibility of soft fruit juice adulteration (e.g. addition of sugar, pulp or water), have prompted a preliminary study of isotopic characterisation. The use of H, C, O and N stable isotope ratios analysis has been described as a powerful and effective method for controlling food provenance (Camin et al., 2015; Förstel, 2007) and detecting adulteration (Antolovich, Li, & Robards, 2001; Stocker, Rossmann, Kettrup, & Bengsch, 2006).

The ability to differentiate samples of different origin using $^{18}O/^{16}O$ and D/H is based on the variation in these isotopes in precipitation (Schmidt, Werner, & Rossmann, 2001), due mainly to factors, such as distance from the sea (Clark & Fritz, 1997) and temperature (Moser & Rauer, 1980).

The carbon isotope ratio ($^{13}C/^{12}C$) is related to climatic conditions, plant type (e.g. C3 or C4 plants) (O'Leary, 1988) and agricultural practice (Georgi, Voerkelius, Rossmann, Graßmann, & Schnitzler, 2005). The nitrogen isotope ratio ($^{15}N/^{14}N$) is influenced by the pedo-climatic characteristics of the geographical area (Choi, Ro, & Hobbie, 2003) and can be satisfactorily used to distinguish between crops that are grown with or without the application of synthetic nitrogen fertiliser (Bateman, Kelly, & Woolfe, 2007). Many different stress factors (such as low temperature or the

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dearth of water) can raise the isotopic value (Amundson et al., 2003).

In this study we considered around 190 samples of different types of soft fruit (strawberries, raspberries, blueberries, blackberries and currants) cultivated in Italy, Poland and Romania.

Each sample was subjected to analysis of the $^{18}O/^{16}O$ of fruit juice water and the $^{13}C/^{12}C$ and $^{15}N/^{14}N$ of pulp. In a selected number of samples, analysis of the $^{13}C/^{12}C$ of acid and sugar extract from the juice and $(D/H)_I$, $(D/H)_{II}$ $^{13}C/^{12}C$ in ethanol produced by fermentation and distillation was also performed.

Whereas in the literature there are several works regarding multi-element stable isotope ratio characterisation of different fruits, such as oranges (Bontempo et al., 2014), apples, cherries, Mirabelle plums, pears, (Bauer-Christoph, Wachter, Christoph, Rossmann, & Adam, 1997; Engel et al., 2007; Martin, Danho, & Vallet, 1991; Mimmo et al., 2015; Oganesyants, Panasyuk, Kuzmina, & Kharlamova, 2016) and grapes (Camin et al., 2015), the stable isotope ratios of soft fruits have never been extensively explored. Camin et al., 2011 investigated strawberries from different sites in Italy, reporting the stable isotope ratios of extracted pulp and juice, while Li, Chen, Ding, & Lin, 2013 applied the isotopic technique, trying to differentiate the origin of Chinese blackcurrants.

The aim of the study was to define and characterise the variability ranges of isotopic values for the various berries (strawberries, raspberries, blueberries, blackberries and currants) on the basis of different cultivation practices, in order to carry out preliminary evaluation of the effectiveness of isotopic analysis as a method for authenticating geographical origin and label declaration.

2. Materials and methods

Three strawberry cultivars and several soft fruits, in particular the red raspberry (*Rubus idaeus* L.), blackberry (*Rubus fruticosus* L.), highbush blueberry (*Vaccinium corymbosum* L.), and currants (*Ribes* spp.) (Table 1) produced in the northern Italian region of Trentino and at two sites in Romania and Poland were investigated, with a total of 190 samples.

The samples were mainly collected in 2005 and 2006 in the framework of the Interberry project funded by the Autonomous Province of Trento (ITALY) through the Research Fund.

Moreover, a limited number of samples produced in 1999 in Trentino were considered.

2.1. Site description and cultivation

Italy: Fruit from Italy was sampled from two different experimental fields, located at 700 m a.s.l. in Vigolo Vattaro and at 520 m a.s.l. in Vigalzano (Trentino, Italy), named here Trentino VV, and from different private fields located in other 2 small locations of Trentino region: Piné and the Valsugana, named Trentino PV. Berry plants (5 per genotype) were grown either in single plots in fields or in pots, and covered with hail nets (protected cultivation). The raspberry plants were grown in 22 cm diameter pots, and the plants were renewed annually, by selecting the two healthiest and most vigorous canes in late autumn and keeping under straw during winter in order to prevent damage from cold. The canes of primocane fruiting raspberries were completely cut off in late autumn and kept similarly under straw in winter. Three to four-year-old blackberries were grown in 35 l pots, as were the currant plants. Blueberries were grown on peat moss mixed with pine bark in raised beds. All the plants of Trentino VV were trained and drip irrigated with constantly controlled nutrient solution, while the plants of Trentino PV were fertilised with organic products.

For strawberries, the observations were conducted in a field trial in Vigolo Vattaro. Plants were grown using a container system, in $45 \times 25 \times 10$ cm buckets, with six plants in each bucket. The resulting planting density was 18 plants m^2. Water and nutrients were supplied by drip irrigation, with one emitter per plant.

As regards the protection systems used in different Italian plots, in Vigolo Vattaro only strawberries were under high tunnels, along with strawberries, raspberries and blackberries at all the other sites in Trentino. Blueberries were covered in the plot at highest altitude, while all the remaining crops were uncovered.

Berries for sampling were harvested manually every 2–3 days, from plants deemed to be mature and transported to the laboratory on the same day for storage in a deep freezer (−20 °C).

As regards fertilisation of Trentino VV, raspberries and blackberries in the soil were fertilised in early spring on average with 25 kg N, 20 kg P_2O_5, 30–40 kg K_2O per 1 ha and during blooming with N 50 kg per 1 ha; primocane raspberries in early spring with

Table 1
Samples.

Type of fruit	Production site	YEAR			Variety
		1999	2005	2006	
Strawberry	Italy	4	2	4	Elsanta, Sonata
Strawberry	Poland	–	–	7	Darselect, Elsanta
Strawberry	Romania	–	–	–	
Raspberry	Italy	4	9	14	Anne, Autumn Bliss, Benefis, Caroline, Glen Ample, Heritage, Himbotop, Laszka, Octavia, Opal, Polana, Polka, Popiel, Pokusa, Tulameen
Raspberry	Poland	–	2	10	Autumn Bliss, Glen Ample, Heritage, Polka, Tulameen
Raspberry	Romania	–	1	5	Autumn Bliss, Heritage, Polka, Tulameen, VII
Blackberry	Italy	2	5	11	Apache, Chesapeake, Chester, Lochness, Thornfree, Triple Crow
Blackberry	Poland	–	–	3	Chester, Lochness
Blackberry	Romania	–	2	2	Arapaho, Chester, Lochness, Triple Crow
Blueberry	Italy	3	6	14	Bluecrop, Brigitta Blue, Chandler, Duke, Elliott, Jubilee, Legacy, Ozarkblue
Blueberry	Poland	–	1	6	Bluecrop, Brigitta Blue, Duke, Ozarkblue
Blueberry	Romania	–	1	8	Augusta, Azur, Bluecrop, Brigitta Blue, Delicia, Duke, Lax, Simultan
Whitecurrant	Italy	2	4	6	Blanka, Victoria, Werdavia, Zitavia
Whitecurrant	Poland	–	–	3	Victoria, Werdavia, Zitavia
Whitecurrant	Romania	–	2	3	Blanka, Victoria, Zitavia
Blackcurrant	Italy	4	6	6	Abanos, Ben Lomond, Deea, PC 166, PC 425, PC 1, Tsema
Blackcurrant	Poland	–	–	4	Ben Lomond, Deea, Geo
Blackcurrant	Romania	–	2	5	12414, Abanos, Deea, Geo, Tsema
Redcurrant	Italy	1	6	8	Cassa, Jonkeer VT, Junifer, Redpoll, Roodneus, Rovada
Redcurrant	Poland	–	–	–	
Redcurrant	Romania	–	–	2	Jonkeer VT, Redpoll