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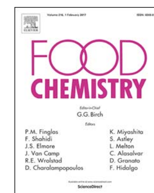

Structural identification of compounds for use in the detection of juice-to-juice debasing between apple and pear juices

Jamie L. Willems, Nicholas H. Low*

Department of Food and Bioproduct Sciences, University of Saskatchewan, Saskatoon, Saskatchewan S7N 5A8, Canada

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ABSTRACT

The ability to detect the undeclared addition of a juice of lesser economic value to one of higher value (juice-to-juice debasing) is a particular concern between apple and pear juices due to similarities in their major carbohydrate/polyol profiles. Fingerprint compounds for the detection of this type of adulteration were identified in both commercial apple and pear juices by HPLC-PDA, were isolated chromatographically, and structurally identified by LC-MS/MS. The apple juice fingerprint was identified as 4-*O*-*p*-coumarylquinic acid and two pear compounds as isorhamnetin-3-*O*-rutinoside and abscisic acid. Additionally, the HPLC-PDA profile of pear juices in combination with pear fingerprint compounds including arbutin could be used to identify samples originating from China versus those from other geographical locations.

1. Introduction

Food adulteration is a serious issue that can have negative impacts on both consumers and honest producers. In 2014, it was estimated that food fraud affected approximately 10% of all commercially sold food products costing the global food industry between $10 and $15 billion per year (Johnson, 2014). Fruit based products, such as juices and jams, are common targets for adulteration due to their high carbohydrate content and the availability of less expensive ingredients which can closely match the carbohydrate profile of the unadulterated product (Silva et al., 2000; Thavarajah & Low, 2006; Willems & Low, 2014). For example, one method of fruit juice adulteration is the undeclared addition of a less expensive juice, which is dependent upon its current market value, to one of higher value, and is referred to as juice-to-juice adulteration. This is a particular concern between apple and pear juices due to similarities in their organoleptic properties, such as colour, flavour and mouthfeel, coupled with their virtually indistinguishable major carbohydrate (glucose, fructose and sucrose) and polyol (sorbitol) profiles (Thavarajah & Low, 2006). The current (2017) market value of apple and pear juice concentrates in the United States are $8.20 and $9.00/US gallon, making the addition of apple-to-pear juice financially viable (personal communication). However, the value of these products can vary such that apple juice may have a higher market value than pear. Also, pear juice concentrate is valued at $5.10/gallon while apple juice concentrate is worth $5.40/gallon in China and the large price differences between geographical regions makes adulteration using concentrates from these regions financially incentivized.

One method to detect the undeclared addition of a fruit of lesser economic value to another fruit product is through phenolic profiling (Silva et al., 2000). Phenolics are secondary plant metabolites that are derived from phenylalanine and to a lesser extent tyrosine with more than 8000 different compounds reported in nature (Manach, Scalbert, Morand, Rémésy, & Jiménez, 2004; Terahara, 2015; Vermerris & Nicholson, 2008). Phenolics serve a variety of purposes in plants such as imparting colour, attracting or repelling insects, they exhibit both antimicrobial and antiviral activity, and they also provide UV protection (Manach et al., 2004). Many factors can affect the phenolic profile of a fruit including variety, maturity and ripeness, and growing, storage and processing conditions (Nayak, Liu, & Tang, 2015; Spanos & Wrolstad, 1992; Tanrıöven & Ekşi, 2005). Consistent differences in the phenolic profiles between fruits can be used to identify which fruit or fruits are present in a product. This can be accomplished via the identification of a unique phenolic/group of phenolics that can act as a fingerprint(s)/marker(s) for the presence or absence of that fruit in a product. For example, the glycosylated phenolic arbutin has been consistently reported to be present in pear and absent in apple making it a marker for pear to apple juice adulteration (Andrade, Carvalho, Seabra, & Ferreira, 1998; Thavarajah & Low, 2006; Willems & Low, 2014). However, there are many contradictory studies in literature where a phenolic has been identified as a specific apple or pear fruit marker. As examples, isorhamnetin-3-*O*-glucoside has been proposed as a potential pear marker, and phloridzin a potential marker for apple juice (Andrade et al., 1998; de Simón, Pérez-Ilzarbe, Hernández, Gómez-Cordovés, & Estrella, 1992; Schieber,

* Corresponding author.
E-mail address: nicholas.low@usask.ca (N.H. Low).

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Keller, & Carle, 2001; Versari, Biesenbruch, Barbanti, & Farnell, 1997). However, research has shown that phloridzin is not ubiquitous in apples/apple products nor isorhamnetin-3-*O*-glucoside in pear/pear products; in addition, isorhamnetin-3-*O*-glucoside has been reported in apple fruit (Alonso-Salces et al., 2004; Schieber, Keller, Streker, Klaiber, & Carle, 2002; Thavarajah & Low, 2006), thus eliminating their use as phenolic-based authenticity markers. Finally, it is possible to enzymatically hydrolyze a marker such as arbutin with the possibility of subsequent masking of the undeclared addition of pear juice addition to another fruit/food product (Thavarajah & Low, 2006).

Based on this literature information, the goal of this research was to identify unique compounds in commercial apple and pear juice samples for use in juice-to-juice authenticity analysis. For this purpose, a group of commercial apple (n = 27) and pear (n = 31) juices were obtained from major world producing regions. Fingerprint compounds for each fruit juice species were identified and structurally characterized.

2. Materials and methods

2.1. Materials

Thirty-one commercial pear juice and twenty-seven commercial apple juice concentrates (~70 °Brix) representing three production years (2012–14), and the major world producing regions for these fruits/juice concentrates were analyzed in this study. Pear juice concentrates were obtained from Argentina, Chile, China, New Zealand and the United States of America. Apple juice concentrates were obtained from Argentina, Brazil, Chile, China and the United States of America.

Abscisic acid, Amberlite XAD16 N resin, apigenin, arbutin, caffeic acid, 5-*O*-caffeoylquinic acid (chlorogenic acid), (+)-catechin, *p*-coumaric acid, (-)-epicatechin, ferulic acid, formic acid, gallic acid, 4-hydroxybenzoic acid, isorhamnetin-3-*O*-glucoside, isoquercetin, narigenin, phloridzin, quercetin, resveratrol and rutin were purchased from Sigma Aldrich Canada Ltd. (Oakville, ON, Canada). Isorhamnetin-3-*O*-rutinoside was purchased from Extrasynthese (Lyon, France). Acetonitrile (HPLC grade) and methanol (ACS grade) were purchased from Fisher Scientific (Ottawa, ON, Canada). The water used throughout this study was produced using a Milli-Q™ water system (Millipore Corp., Milford, MA, USA).

2.2. High performance liquid chromatography with photodiode array detection (HPLC-PDA)

Juice samples were prepared by dilution with water to 11.5 ± 0.1 and 12.0 ± 0.1 °Brix (Auto Abbe Refractometer; Lecia Inc., Buffalo, NY, USA) for apple and pear, respectively. Samples were syringe filtered (nylon, 0.2 µm pore size, 13 mm diameter, Chromatographic Specialties, Brockville, ON, Canada) into 2 mL amber HPLC vials (Chromatographic Specialties) prior to analysis. The sample injection volume was 60.0 µL.

Fingerprint compound identification was conducted using an Agilent 1100 series HPLC system with a photodiode array (PDA) detector controlled by ChemStation LC-3D software (Agilent Technologies Canada Inc., Mississauga, ON, Canada). Phenolic separation was accomplished on an ODS-3 (250 × 4.6 mm; 5 µm, C_{18}, 100 Å) column (Phenomenex, Torrance, CA, USA) in series with a guard column (4 × 3 mm) of the same stationary phase. A linear gradient mobile phase system employing 10.0 mM aqueous formic acid (mobile phase A; pH 3.5) and 70% acetonitrile:30% mobile phase A (v:v; mobile phase B) was used for phenolic separation as follows: initial 100% A for 3.0 min, followed by a gradient to 4.0% B at 16.0 min, followed by a gradient to 10.0% B at 25.0 min, followed by a gradient to 15.0% B at 40.0 min, followed by a gradient to 20.0% B at 45.0 min, followed by a gradient to 23.0% B at 50.0 min, followed by a gradient to 25.0% B at 55.0 min, followed by a gradient to 30.0% B at 61.0 min, followed by a gradient to 50.0% B at 75.0 min, followed by a gradient to 80.0% B at 80.0 min, hold at 80.0% B for 5.0 min. The column was then re-equilibrated with 100% A for 7.0 min prior to the next injection. The total run time was 95.0 min. Sample phenolic profiles were monitored at 254, 280 and 360 nm (Willems & Low, 2017).

2.3. Isolation of fingerprint compounds

Identified fingerprint compounds (one for apple and two for pear) were isolated from commercial apple and pear juice samples for structural identification as follows: (a) for each species, a selected (based on fingerprint compound concentration) juice concentrate was diluted to 24.0 ± 0.1 °Brix and 15 mL was added to a 8.0 cm × 3.0 cm glass column packed with approximately 55 mL of solvent treated Amberlite XAD-16 N resin. The resin was initially hydrated in 50% (v:v) aqueous methanol for 30 min before being transferred to the glass column followed by pre-conditioning with 110 mL of water then by 110 mL 90% (v:v) aqueous methanol and 110 mL of water. Once loaded on the resin, juice samples were fractionated with 110 mL water followed by 110 mL of 70% aqueous methanol (v:v). The 70% aqueous methanol fraction was collected and concentrated to approximately 5.0 mL using a Büchi rotary evaporator (Flawil, Switzerland) and the concentrated 70% aqueous methanol fraction was syringe filtered prior to HPLC-PDA fractionation to obtain purer fractions of the fingerprint compounds. The relative retention times of the fingerprint compounds were 57.7 min for apple and 70.6 and 77.1 min for pear. Chromatographically isolated fractions containing the identified fingerprint compounds were collected and combined prior to being concentrated employing rotary evaporation, followed by freeze drying (Hetro Lab Equipment, Allerod, Denmark) in 12 × 32 mm glass vials (Chromatographic Specialties, Brockville, ON, Canada). Isolated compounds were stored at −18 °C until structurally analyzed.

2.4. Mass spectrometric analysis

High resolution mass measurements of fingerprint compounds were obtained using an Agilent 1100 series HPLC as described above coupled with an API QSTAR XL MS/MS hybrid QqToF mass spectrometer equipped with an ESI source (Applied Biosystems Inc., CA, USA). Nitrogen was used as both the drying and ESI nebulizing gas. External calibration employing caesium iodide (*m/z* 132.9054) and sex pheromone inhibitor iPD1 (*m/z* 829.5398) were used to ensure high mass accuracies. Samples were analyzed in the negative mode and the injection volume was 20.0 µL. Mass spectra were analyzed using Analyst software (version 1.62).

Tandem MS was carried out for fingerprint compound structural identification using an Agilent 1200 series HPLC system with a photodiode array (PDA) detector coupled to a QTRAP 4000 LC/MS/MS system (Applied Biosystems, Foster City, CA, USA), which is a hybrid triple quadrupole linear ion trap mass spectrometer (QqQ-LIT) equipped with a Turbo V Ion Spray ESI source. Chromatography parameters were as described above; however, the injection volume was reduced to 7.5 µL and an analytical fixed flow post column splitter (split ratio of 3:1; ASI QuickSplit) was inserted after the PDA detector to reduce the amount of mobile phase entering the ESI source. All samples were analyzed in the negative ion mode.

2.5. Nuclear magnetic resonance spectroscopy (NMR)

^{1}H nuclear magnetic resonance spectroscopy of the fingerprint compounds was performed on a Brüker Avance 500 MHz spectrometer (Brüker, Rheinstetten, Germany) using D_2O as the solvent.

3. Results and discussion

The chromatographic profiles of the 27 commercial apple juices and 31 commercial pear juices were determined by HPLC-PDA. This

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