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Original Research Article

Elemental and stable isotopic study of sweeteners and edible oils: Constraints on food authentication

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ABSTRACT

Elemental concentrations and stable isotopic compositions of 41 sweeteners (syrups, honeys, and sugars) and 43 edible oils were determined to evaluate their potential as parameters for food authentication. The addition of as little as 10% of corn syrup to pure maple syrup can be detected using molar ratios of Na/(Na + K) and Na/(Na + Ca) for maple syrups. The detection of more than 15% adulterant in maple syrup and honey is also possible due to the 13‰ difference in carbon isotopic composition of C3 plants for authentic honeys and maple syrups (25.1 ± 1.1‰) relative to the carbon isotopic composition of C4 plants for corn syrups and cane sugars (−11.4 ± 0.8‰) as major adulterant agents. Nearly constant net oxygen (1.028 ± 0.002) as well as hydrogen (0.974 ± 0.005) isotope fractionation factors between honeys and average local meteoric waters from two areas, Kingston and Costa Rica, suggests that these isotope ratios of honeys are good candidates to authenticate their geographic locations. The net oxygen (1.03 ± 0.001) as well as hydrogen (0.894 ± 0.003) isotope fractionation factors between olive oils and local meteoric waters from different parts of Italy suggests that these isotope ratios are independent of the oil processing method and therefore can be used to trace geographic locations.

1. Introduction

Natural food products, whose commodity and economic values are high because of their high quality and purity, are major targets for adulteration. The quality of food depends primarily on two parameters, the purity of its ingredients and geographic location of its production (Drivelos and Georgiou, 2012; Kelly et al., 2005). Critical to the study of food authentication is the characterization of pure ingredients as well as common adulterant agents (Kelly et al., 2005). Various techniques have been developed to evaluate the quality of food products, including elemental concentrations and isotopic ratios.

Elemental concentrations of various food products, such as honeys (e.g., González-Miret et al., 2005; González Paramás et al., 2000; Rodriguez-Otero et al., 1994; Pisani et al., 2008; Nanda et al., 2003; Hernández et al., 2005), wines (e.g., Frías et al., 2001, 2003; Monaci et al., 2003; Martin et al., 1999), olive oils (e.g., Camin et al., 2010; Benincasa et al., 2007, 2012), and cheeses (e.g., Gambelli et al., 1999; Pillonel et al., 2003) can be used to discriminate their production from different geographic locations. However, their use in tracing the addition of adulterant agents has been limited.

Both adulterants and pure food products are mixtures of organic molecules consisting of carbon, oxygen and hydrogen and thus, isotope ratios of these elements can characterize both pure foods and adulterants. The carbon isotope ratios of food products, such as fruit juices (e.g., Magdas et al., 2012; Pupin et al., 1998; Simpkins et al., 2000), cheeses (e.g., Camin et al., 2004), beers (e.g., Brooks et al., 2002), wines (e.g., Martinelli et al., 2003), honeys (e.g., White and Doner, 1978; Padovan et al., 2003), and olive oils (e.g., Angerosa et al., 1999; Spangenberg et al., 1998; Camin et al., 2010) have been used to characterize their purity. Oxygen and hydrogen isotope ratios of food products such as milk (e.g., Crittenden et al., 2007; Renou et al., 2004), wines (e.g., Martin et al., 1999; Bréas et al., 1994), cheeses (e.g., Pillonel et al., 2003; Camin et al., 2004), beef (e.g., Boner and Förstel, 2004), butters (Rossmann et al., 2000) and coffee seeds (e.g., Weckerle et al., 2002) have generally been used to map out their harvest or production locations.

Previously, statistical approaches were used for elemental concentrations (e.g., Camin et al., 2010; Benincasa et al., 2007; González Paramás et al., 2000) and stable isotope data (Schellenberg et al., 2010; Pillonel et al., 2003; Camin et al., 2010; Rossmann et al., 2000) of food products to discriminate their geographic origin. However, the effects of food processing techniques on

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discrimination of different chemical parameters were not reported. Furthermore, the relationships of $\delta^{18}O$ and $\delta^{2}H$ values between natural food products and local meteoric waters were not documented, which is fundamental for endorsing the geographic locations of food products.

This contribution investigates the potential of trace element concentrations to determine the level of adulteration of honeys, maple syrups and edible oils, as well as to discriminate their geographic location of origin considering both processing techniques and bedrock geology. In addition, the detection limits of adulteration for natural sweeteners and edible oils using carbon isotope ratios of bulk samples have been assessed and the oxygen and hydrogen isotope fractionation factors between natural food products and local meteoric waters have been measured to validate their use as geographic locators of specific food products.

2. Materials and methods

2.1. Samples

A total of 41 samples of the 'sweetener' group, 43 samples of the 'edible oil' group, and 2 samples of bees wax were analyzed in this study. The 41 sweeteners include 17 maple syrups, 3 corn syrups, 14 honeys, 4 sugar samples, 2 artificial sweeteners, and 1 agave syrup. The 43 edible oils include 25 olive oils (21 extra virgin oils, 4 olive oils), 2 sesame oils, 2 sunflower oils, 2 palm oils, 2 walnut oils, 1 coconut oil, 1 pumpkin seed oil, 1 mustard oil, 1 soybean oil, 1 canola oil, 1 hemp seeds oil, and 4 vegetable butters. Authentic honeys and maple syrups were collected from different artisan operations and therefore, their actual hive and production locations are well known (Table 1). The specific harvest locations of canes and corns for cane sugars and corn syrups, respectively, are not known. The edible oils were purchased from local markets and in most cases, only the countries from which oils were produced are known from the product labels (Table 2).

2.2. Elemental analysis

Honeys (~0.4 g), maple syrups (~0.4 g) and edible oils (~0.6 g) were weighed into the Teflon microwave tubes and digested using microwave heating. The digestion of honeys and maple syrups were performed by adding 4 mL of distilled, concentrated (69–70%) reagent grade HNO_3 and 2 mL of ultrapure 30% H_2O_2 to the samples. The digestion of edible oils were performed by adding 5 mL of distilled, concentrated HNO_3, 3 mL of 30% H_2O_2, and 1 mL of ultrapure (32–38%) HCl. The HNO_3 and HCl stock solutions were obtained from Fisher Scientific (Fisher Scientific Company, Ottawa, ON, Canada) and the H_2O_2 were obtained from Seastar Chemicals (Seastar Chemicals Inc., Sidney, BC, Canada). The Teflon microwave tubes were capped and digested in an Anton Paar multiwave 3000 series microwave (Anton Paar USA Inc., Ashland, VA, USA) for 1 h. After digestion, the samples were transferred into clean, Savillex Teflon containers (Savillex Corporation, Eden Prairie, MN, USA) and evaporated to dryness in a clean laboratory on a hot plate at 70 °C. Once dry, samples were diluted to 8 mL with 2% HNO_3 spiked with 1 ppb Indium. The diluted samples were analyzed using a Thermo iCAP 6000 Series ICP-OES (Thermo Fisher Scientific Inc., Waltham, MA, USA) for major element concentrations (Ca, K, Mg, and Mn) and Thermo Element 2 XR high resolution ICP-MS (Thermo Fisher Scientific Inc.) for trace element concentrations. One procedure blank and one reference material (NIST 1547) were included for each 14 samples. The international standard NIST 1547, peach leaves, was obtained from the National Institute of Standards and Technology (Gaithersburg, MD, USA).

2.3. Stable isotope ratios analysis

The samples were weighed into tin capsules (~0.4 μg) for carbon isotope analyses and into silver capsules (~0.1 μg) for oxygen and hydrogen isotope analyses. The crushed silver capsules were heated in an oven at 100 °C for 15 min to remove any moisture outside the capsules. The crushed tin capsules were not preheated for carbon isotope ratio analysis. The tin and silver capsules were purchased from Elemental Microanalysis Ltd. (Okehampton, UK).

The carbon isotope ratios of samples were analyzed by combustion to CO_2 in a Costech Analytical elemental analyzer (EA) (Costech Analytical Technologies Inc., Valencia, CA, USA) in-line with a Thermo-Finnigan Delta plus XP isotope ratio mass spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA). The oxygen and hydrogen isotope ratios of samples were analyzed by a Thermo-Finnigan high temperature conversion elemental analyzer (TC/EA) in-line with a Thermo Scientific MAT 253 isotope ratio mass spectrometer (Thermo Fisher Scientific Inc.). Samples were introduced into the TC/EA via a Costech Analytical zero-blank auto sampler. The TC/EA is equipped with one pyrolysis column at 1450 °C, which converted to sample to CO and H_2 that were separated using a 1-meter molecular sieve 5A gas chromatography column (Costech Analytical Technologies Inc.) at 85 °C.

Stable isotope ratios of samples are reported in delta (δ) notation in units of per mil (‰). Both oxygen and hydrogen isotope ratios are reported relative to Vienna Standard Mean Ocean Water (VSMOW) and carbon isotope ratios are reported with respect to Vienna Pee Dee Belemnite (VPDB). Samples were analyzed with duplicates and reference materials. The NBS 22 ($\delta^{13}C = -30.03 \pm 0.1$‰, $\delta^{2}H = -117 \pm 0.3$‰), NBS 21 ($\delta^{13}C = -28.1 \pm 0.1$‰), NBS 127 ($\delta^{18}O = 9.3 \pm 0.4$‰) were used as international isotopic standards and obtained from National Institute of Standards and Technology. The NBS 22, NBS 21, and NBS 127 are oil, graphite, and barium sulfate, respectively. The analytical precision of $\delta^{2}H$, $\delta^{13}C$, and $\delta^{18}O$ data are better than 2, 0.2 and 0.3‰, respectively.

3. Results

3.1. Elemental compositions of sweeteners

Maple syrups have K concentrations of 902–2220 mg/kg, Ca of 165–2190 mg/kg, Mg of 45–258 mg/kg, low Na of 2–48 mg/kg, and Al of 0.2–19 mg/kg (Table 1). The Zn concentrations are high, ranging from 2 to 19 mg/kg and Mn concentrations range from 1 to 30 mg/kg. The Fe concentrations of maple syrups are below 1 mg/kg, except in four samples (3–21 mg/kg). The Rb/Sr ratios of maple syrups range from 0.06 to 5.9.

Corn syrups have the highest concentrations of Na (1390–1690 mg/kg), but low K (4–439 mg/kg), Ca (13–128 mg/kg), Mg (2–42 mg/kg), and Al (1.2–2.3 mg/kg; Table 1). The concentrations of Zn (0.2–0.5 mg/kg) and Mn (0.1–0.2 mg/kg) in corn syrups are less than 1 mg/kg. The Fe concentrations in corn syrups are also less than 1 mg/kg except for one sample (3.3 mg/kg). The Rb/Sr ratios of corn syrups range from 0.07 to 2.1.

Honey samples have moderate K contents of 90–1880 mg/kg and Ca of 32–79 mg/kg (Table 1). The Na concentrations range from 13 to 62 mg/kg and Mg concentrations range from 9 to 26 mg/kg. The concentrations of Zn are also moderate at 0.5–1.8 mg/kg, with Mn of 0.13–1.3 mg/kg, and high Fe of 0.6–3.2 mg/kg. The Rb/Sr ratios of honeys range from 1.6 to 24.9.

3.2. Elemental compositions of edible oils

The elemental concentrations of all edible oils are lower than those of the sweeteners (Table 2). The Ca concentrations of most of the edible oils are below detection limit (0.7 mg/kg) except 1 extra