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Analytical Methods

A triple-isotope approach for discriminating the geographic origin of Asian sesame oils

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ABSTRACT

The aim of this study was to investigate the effects of the geographic location and climatic characteristics of the sesame-producing sites on the carbon, hydrogen, and oxygen stable isotope ratios of Korean sesame oil. In addition, the study aimed to differentiate Korean sesame oil from Chinese and Indian sesame oils using isotopic data in combination with canonical discriminant analysis. The isotopic data were obtained from 84 roasted oil samples that were prepared from 51 Korean, 19 Chinese, and 14 Indian sesame seeds harvested during 2010–2011 and distributed in Korea during the same period. The $\delta^{13}C$, δD, and $\delta^{18}O$ values of Korean sesame oil were negatively correlated with latitude, distance from the sea, and precipitation (May–September), respectively. By applying two canonical discriminant functions, 89.3% of the sesame oil samples were correctly classified by their geographic origin, indicating that the triple-isotope approach is a useful tool for the traceability of the oils.

1. Introduction

Sesame (*Sesamum indicum* L.) is an oilseed crop that is primarily cultivated in Asian and African countries. Roasted sesame oil is unrefined edible oil obtained from sesame seeds roasted at 180–200 °C (Namiki, 1995). This oil is frequently used as a flavor enhancer in Eastern Asian cooking since Eastern Asians, including Koreans, prefer the characteristic flavor of the oil that develops during roasting (Kim & Akoh, 2006). Sesame seeds are available in three different colors, black, brown, and white. White sesame seeds are mostly used in the manufacturing of roasted sesame oil in Korea (Jeon et al., 2013).

False indications of the geographic origin of sesame products became an issue of public concern in Korea after the 1990s. In the 2000s, Koreans consumed approximately 100,000 tonnes of sesame seeds per year. Because the annual domestic production (approximately 13,000 tonnes) of sesame seeds could not sustain the national need, Korea imported approximately 140,000 tonnes of sesame seeds during 2009 and 2010 (FAO, 2012). Indian and Chinese sesame seeds occupy approximately 43% and 38% of Korea's sesame imports, respectively (KFDA, 2012). Chinese and Indian sesame seeds/oils that are deliberately labeled as domestic often appear in Korean local markets, because Korean sesame seeds/oils are 3–4 times higher in price than Chinese or Indian sesame products. This has created the need for analytical methods to distinguish Korean sesame oil from the oil obtained from imported sesame seeds.

The geographic location and climatic conditions of cultivation sites influence the stable isotopic signature of plants. The carbon stable isotope ratio ($^{13}C/^{12}C$) of plant materials is preferentially affected by the types of photosynthetic processes, i.e., the C_3 and C_4 pathways, which the plants employ for fixing atmospheric carbon dioxide (Smith & Epstein, 1971). Climatic factors, such as relative humidity, temperature, and the amount of precipitation, which affect the stomatal conductance of carbon dioxide, cause variations in the carbon stable isotope ratio of C_3 plants including sesame (Farquhar, Ehleringer, & Hubick, 1989; Farquhar, O'Leary, & Berry, 1982). The hydrogen ($D/^1H$) and oxygen ($^{18}O/^{16}O$) stable isotope ratios of plant material are strongly correlated with those ratios in the local precipitation water that is incorporated by the plant. The isotopic composition of precipitation is primarily affected by geographic and climatic conditions, such as latitude, distance from the sea, altitude, temperature, and the amount of precipitation (Gat, Mook, & Meijer, 2000). Some climatic factors (e.g., relative humidity and temperature) influence the stomatal transpiration of water, thereby inducing the fractionation of hydrogen and oxygen isotopes in plant materials (Perri, Benincasa, & Muzzalupo, 2012). Therefore, the combined analysis of carbon,

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hydrogen, and oxygen stable isotope ratios could be a useful tool for the traceability of oils derived from plant sources.

Several researchers have utilized the triple-isotope approach for identifying the geographic origin of plant oils produced in European regions, such as olive oil and rapeseed oil (Bontempo et al., 2008; Camin, Larcher, Nicolini, et al., 2010; Camin, Larcher, Perini, et al., 2010; Richter, Spangenberg, Kreuzer, & Leiber, 2010). In contrast, little is known about the stable isotopic signature (particularly, $D/^1H$ and $^{18}O/^{16}O$) of sesame oil. Furthermore, no published studies have characterized the geographic origin of the oil using the triple-isotope approach.

The aim of this study was to investigate the effects of the geographic location and climatic characteristics of the sesame-producing sites on the carbon, hydrogen, and oxygen stable isotope ratios of Korean sesame oil. In addition, the study was designed to differentiate Korean sesame oil from Chinese and Indian sesame oils that are distributed in Korea using isotopic data.

2. Materials and methods

2.1. Sample preparation

Samples of white sesame seeds ($n = 51$) were collected from 36 sites in Korea during the 2010 and 2011 harvests (Fig. 1). Samples of Chinese white sesame seeds ($n = 19$) and Indian white sesame seeds ($n = 14$), which were imported by the Korea Agro-Fisheries Trade Corporation between 2010 and 2011, were purchased from local grocery stores in Korea. The sesame seeds were roasted in a drum roaster (model THDR-01; Taehwan Automation Industry Co., Seoul, Korea) at 200 °C for 30 min. The oil was extracted from the roasted sesame seeds using an oil press (model Oil Love; National ENG Co., Goyang, Korea) and was centrifuged at 9600*g* for 10 min. The roasted sesame oils were completely dried under nitrogen flushing. The water content of the oils was monitored using a Karl-Fisher moisture analyzer (model 803 Ti Stand; Metrohm, Herisau, Switzerland) and was adjusted to <300 mg/kg. A sample of commercial Korean roasted sesame oil was obtained from an edible oil manufacturing company.

2.2. Geographic and climatic data analysis

Data of the geographic characteristics (latitude, distance from the sea, and altitude) of the production sites of Korean sesame seeds used in this study were collected from Google Earth (http://earth.google.com). Climatic data including precipitation, mean relative humidity, and mean temperature during the five months (May–September) corresponding to the growth period of the sesame were obtained from the Korea Meteorological Administration (http://www.kma.go.kr).

2.3. Stable isotope analysis

The carbon stable isotope ratio of the sesame oil samples was analyzed using an IsoPrime 100 (GV instruments, Manchester, UK) isotope ratio mass spectrometer (IRMS) coupled with a vario MICRO cube (Elementar Analysensysteme GmbH, Hanau, Germany) elemental analyzer (EA). An aliquot of the oil samples was placed into a 5 × 3.5 mm tin capsule (Elemental Microanalysis, Okehampton, UK) and injected into the EA. The combustion and reduction tubes were maintained at 1150 °C and 850 °C, respectively, in order to convert the carbon in the oil samples into CO_2 gas under a stream of helium and oxygen. The resultant CO_2 was separated in a gas chromatography (GC) column packed with 5 Å molecular sieves, and its isotopic composition was measured on the IRMS. Reference CO_2 gas was inserted into the helium carrier flow as pulses of pure standard gas. The analysis of the hydrogen and oxygen stable isotope ratios of the oil samples was performed using an HT-PyrOH (EuroVector, Milan, Italy) pyrolyzer connected to the IsoPrime 100 IRMS. An aliquot of the oil samples that was wrapped in a 5 × 3.5 mm silver capsule (Elemental Microanalysis) was pyrolyzed at 1350 °C under a helium flow and passed through a column packed with glassy carbon chips in order to convert the hydrogen and oxygen in the oil samples into H_2 and CO gases, respectively. The H_2 and CO were subsequently separated in a GC column packed with 5 Å molecular sieves, and their isotopic compositions were analyzed on the IRMS. Reference H_2 and CO gases were inserted into the helium carrier flow as pulses of pure standard gas. The stable isotope ratio was expressed as the delta (δ) value in per mille (‰) deviation from the respective international standard, i.e., VPDB (Vienna Pee Dee Belemnite) for carbon and VSMOW (Vienna Standard Mean Ocean Water) for hydrogen and oxygen, according to the following equation:

$$\delta(\text{‰}) = [(R_s - R_{std})/R_{std}] \times 1000, \quad (1)$$

where R represents the ratio of the heavy to light isotopes, and R_s and R_{std} are the isotope ratios of the sesame oil and the international standard, respectively. The isotope analyses were calibrated with the IRMS certified reference material EMA-P2 (Elemental Microanalysis), which had a $\delta^{13}C$ value of −28.19‰ on the PDB scale and a δD value of 26.88‰ and a $\delta^{18}O$ value of −87.80‰ on the VSMOW scale.

2.4. Statistical analysis

The isotopic values of the sesame oil samples represented the mean of triplicate measurements. All of the statistical analyses were conducted using PASW Statistics 18 software (SPSS Inc., Chicago, IL). Pearson's correlation test was used to determine whether there was a significant linear relationship between two variables ($p < 0.01$ or 0.05). A one-way analysis of variance (ANOVA) was performed to determine the differences in the oil samples. When the ANOVA F value was significant, the differences between the means were determined using Duncan's multiple-range test ($p < 0.05$). Canonical discriminant analysis was performed with stepwise selection of the variables that best distinguished the Korean, Chinese, and Indian sesame oils.

3. Results and discussion

3.1. Stable isotope ratio of Korean sesame oils

South Korea, officially the Republic of Korea, is located in the southern part of the Korean Peninsula, which extends approximately 1100 km southward from the Asian continent into the Pacific Ocean. It lies in the middle latitude zone (between 33.10°N and 38.45°N), is surrounded by seas, and has low mountainous terrain. Geographic and climatic information for the 36 harvesting sites for the Korean sesame seed samples used in this study are given in Table 1. The carbon, hydrogen, and oxygen stable isotope ratios of the oil samples obtained from the sesame seeds are also listed in the same table.

Pearson's correlation test was performed to determine whether there was a significant linear relationship between isotopic values or between the isotopic values and the environmental factors in Korean sesame oil (Table 2). The $\delta^{13}C$ value of Korean sesame oil showed a significant ($p < 0.01$) positive correlation with its δD or $\delta^{18}O$ value. This result was in accordance with the observation of Camin, Larcher, Nicolini, et al. (2010) that the hydrogen and oxygen stable isotope ratios were positively coupled with the carbon stable isotope ratio in European olive oil. The δD and $\delta^{18}O$ values