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A Multianalytical Approach for Determining the Geographical Origin of Ginseng Using Strontium Isotopes, Multielements, and ^{1}H NMR Analysis

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Supporting Information

ABSTRACT: Asian ginseng (*Panax ginseng* C.A. Meyer) is widely used as an Oriental medicine in the East Asian regions, particularly Korea and China. In the study, the strontium isotope ratios (^{87}Sr/^{86}Sr), multielements, and metabolite profiles of 35 ginseng samples collected from Korea and China were examined in an attempt to develop a method to distinguish the origin of ginsengs from the two countries. A multivariate statistical approach was performed to analyze the multielements and the ^{1}H nuclear magnetic resonance (NMR) data. Results of a *t*-test for Mg, Fe, Al, and Sc showed significant variation between Korean and Chinese ginsengs, indicating potential tracers for discriminating them. Discriminating between the ginsengs from the two countries was generally successful when both the ^{87}Sr/^{86}Sr ratios and rare earth element (REE) contents were used together. Moreover, principal component analysis (PCA) derived from the ^{1}H NMR data revealed a significant separation between the ginsengs originating from the two countries. The major metabolites responsible for differentiation were sugars such as glucose, xylose, and sucrose. The results suggest that this multiplatform approach offers a comprehensive method to distinguish the origin of ginsengs.

KEYWORDS: Asian ginseng (*Panax ginseng*), geographical origin, metabolite profile, multielements, strontium isotopes

INTRODUCTION

Herbal-based traditional medical practices, which rely on various plant materials for preventive and therapeutic uses, constitute an integral part of clinical therapy in the Asia and many other parts of the world. Among herbal medicines, ginseng (*Panax* sp.) is considered one of the best medicines. Ginseng is a slow growing perennial herb with fleshy roots predominantly existing in the cooler regions of the Northern Hemisphere. It is used by many cultures around the world, but particularly in Korea, Japan, and China, because of its potential to cure several diseases without considerable side effects. Thirteen *Panax* species (Araliaceae) have been recorded with detailed historical accounts from the central Himalayas, China, Korea, Japan, Vietnam, and North America.[1] All species in this genus are used as a source of medicine, but among all species, *Panax ginseng* C.A. Meyer, or Asian ginseng, is considered the most important.

By reason of its attractive medicinal and healing properties, which are well-documented in both ancient and modern literary medicine treatises,[1−9] demand for ginseng is increasing in Korea, and so its domestic-market price is high. This high price has led to its frequent adulteration with low-priced ginseng by some dishonest merchants to make appreciable profits. Currently, the selling price of Korean ginseng in Korean markets is much higher than that in Chinese ginseng markets. Because of considerable differences in prices, Chinese ginseng has been frequently substituted for Korean ginseng and/or adulterated with Korean ginseng with the intention of making considerable profits. This situation is worsened as distinguishing the geographic origin of these two ginsengs is difficult based on morphological and/or genetic factors. Thus, a need exists to develop effective tools to standardize the quality control, as well as to identify the two ginsengs and ensure safe unadulterated ginseng.

The strontium isotope ratio (^{87}Sr/^{86}Sr) is a tool that can be used to solve this problem. The ^{87}Sr/^{86}Sr does not change during its progression from geology to different trophic levels,[10] and this ratio reflects the geochemical characteristics of the soil in which the plant is grown. Consequently, plants display particularly strong isotopic signals because they construct their tissues from such small molecules. This natural phenomenon can be used to explain interlithological differences and effects of these interlithological variations on plant elemental composition. Based on the premise of significant heterogeneity in ^{87}Sr/^{86}Sr ratios in different rock systems and their age and the reflection of the same in plants parts,[10] ^{87}Sr/^{86}Sr ratios can provide a way to discriminate the geographical origin of ginseng. Young volcanic rocks

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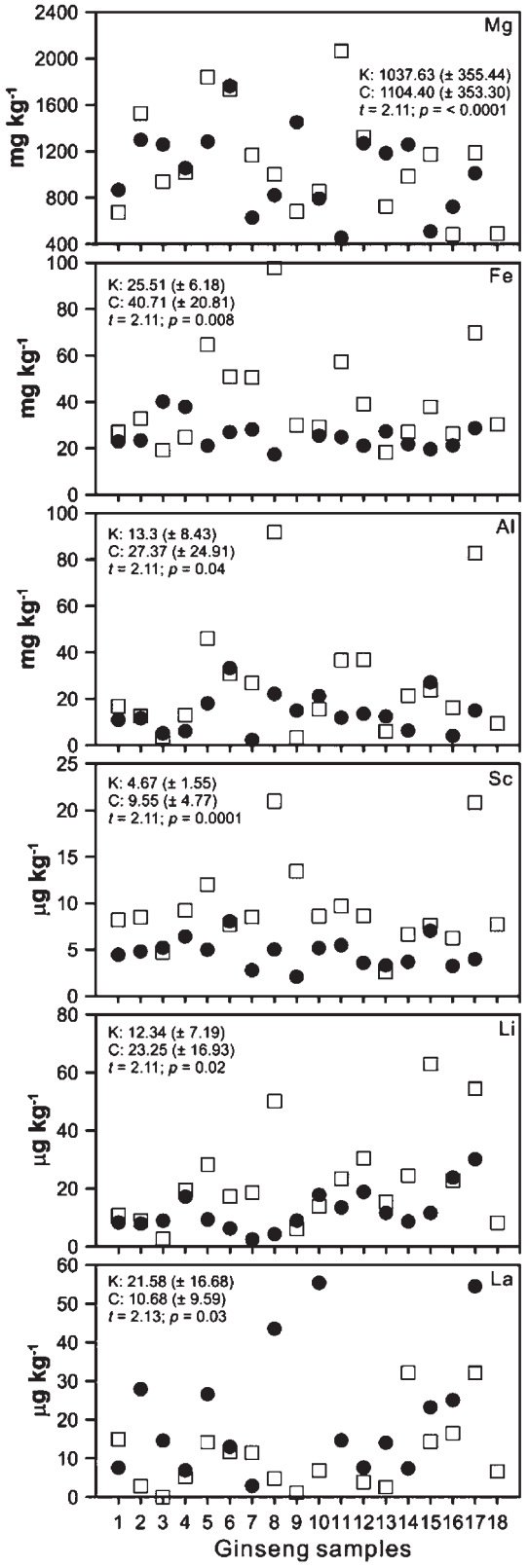

Figure 1. Multielement concentrations for the Korean and Chinese ginseng. The symbol ■ represents Korean ginseng samples (17 in number), and Δ represents Chinese samples (18 in number). Numerical values are averages for Korean (K) and Chinese (C) ginseng. Values in parentheses are standard deviations. Values of Student's *t* test are significant $p < 0.05$; ns, nonsignificant.

with low Rb/Sr ratios such as basalts generally have very low $^{87}Sr/^{86}Sr$ ratios, whereas old crystalline rocks such as gneisses or granites display high $^{87}Sr/^{86}Sr$ ratios.[10] For this reason, $^{87}Sr/^{86}Sr$ has been used as a tracer to identify the origins of foods such as wheat,[11] wines,[12,13] coffees,[14] and butter.[15]

This characteristic of $^{87}Sr/^{86}Sr$ can be extended to trace the origin of ginsengs and to ensure the efficacy and safe use of ginseng and ginseng-related products. A recent study was conducted by Choi et al.[16] to discriminate Korean from Chinese ginseng using the $^{87}Sr/^{86}Sr$ ratio. However, their results are questionable due to methodological deficiencies.[17]

Kang et al.[18] identified different types of ginseng roots from China and Korea using nuclear magnetic resonance (NMR)-based metabolomics, while Lee et al.[19] discriminated Asian ginseng (*Panax ginseng*) from American ginseng (*Panax quinquefolius*) grown in China by employing principal component analysis (PCA) of ^{1}H NMR spectra. More recently, Horacek et al.[20] applied stable isotopes of C, N, and H to identify ginsengs collected from Korea and China, but only the H isotope was partly successful in distinguishing them.

In this study, a comprehensive method to identify the geographic origins of Korean and Chinese ginsengs using a multianalytical platform approach was attempted: $^{87}Sr/^{86}Sr$, major, minor, trace, and rare earth elements (REEs), and ^{1}H NMR analyses. Multivariate statistical analyses were used to interpret the geographic origins of the ginsengs.

■ MATERIALS AND METHODS

Sample Collection and Treatment. Seventeen pieces of ginseng root were collected from 11 districts in Korea, where most Korean ginseng is cultivated encompassing Mesozoic granites and/or Precambrian metamorphic rocks such as gneiss and schist.[21] Eighteen pieces of ginseng root were acquired from an Oriental medical clinic in Beijing (Dongindang). According to the information attached to these Chinese ginseng products, they were cultivated in Beijing and Jilin belonging to Quaternary sedimentary rocks, and Cenozoic to Mesozoic sedimentary rocks, respectively.[22] However, information as to the origin of several Chinese ginseng samples could not be obtained.

Prior to chemical treatments, all the samples were washed properly with deionized water to remove adhered soil particles. The external surfaces of all the samples were removed using ceramic scissors to eliminate or minimize adhered soil particles as potential contaminants.[23] Subsequently, all samples were oven-dried at 90 °C for 12 h and finely pulverized in an agate mortar.

Multielement Analysis. About 0.5 g of each ginseng root sample was digested with 10 mL of 70% HNO_3 solution (reagent grade) using a microwave digestion system fitted with Teflon vessels and then dried on a hot plate at 180 °C. When the acid was sufficiently evaporated, the remaining solution (ca. 0.1 mL) was mixed with 5 mL of 1% HNO_3. Major (Ca, Mg, Fe, and Al), minor (P), and trace (Mn, Zn, Cu, Ni, and Sr) elements were determined with ICP-AES (Optima 4300DU; PerkinElmer, Waltham, MA, USA), and additionally some trace (Co, Li, and Sc) elements and REEs (La−Lu) were determined with ICP-MS (X7; Thermo Electron, Cambridge, U.K.) at the Korea Basic Science Institute (KBSI). Two standard reference materials (SRM 1573a and SRM 1570a) were used to verify analytical quality of the instruments.

Strontium Isotope Analysis. Approximately 0.5 g of each sample was placed in Teflon vessels. After addition of 5 mL of HNO_3, the vessels were heated on a hot plate to 150 °C. When the solution had evaporated, 3 mL of HNO_3 and 1 mL of $HClO_4$ were added to each vessel to entirely dissolve the samples, and then the vessels were again heated overnight on the hot plate. The remaining particles in the vessel after hot-plate wet

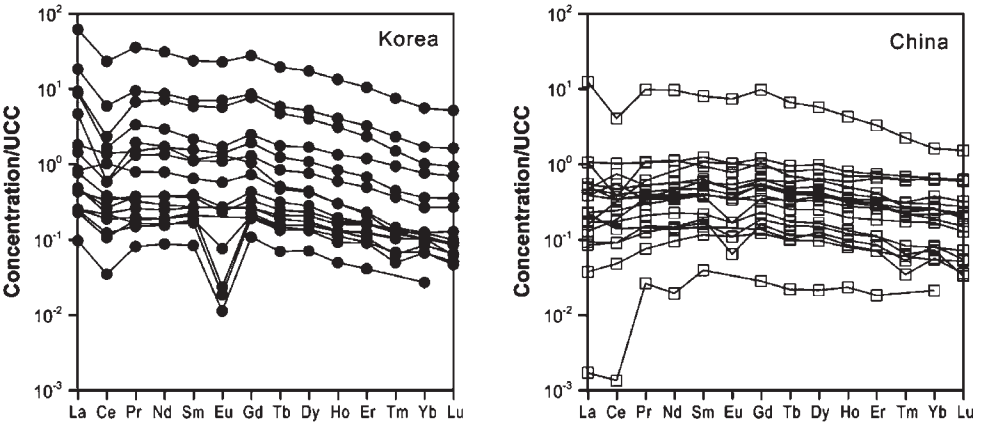

Figure 2. Upper continental crust (UCC)-normalized rare earth element (REE) patterns for the Korean and Chinese ginsengs.

digestion were removed using a centrifuge (10,000 rpm, 7 min). After checking that the samples were completely dissolved, 6 N HCl was added to each vessel, and heating was continued. When the acid was sufficiently evaporated, 2.5 N HCl was added to each vessel, and heating was again continued until the samples were completely dry. Finally, the dried samples were dissolved in 0.5 mL of 2.5 N HCl, and the resulting solutions were stored in clean conditions prior to strontium separation using a cation column using a cation exchange resin (Dowex AG 50W-X8, 200−400 mesh; Dow Chemical Company, Midland, MI, USA).[24]

The wet-digested sample solution, prepared as described above, was mixed with one to two drops of $HClO_4$ to prevent resin deterioration, and the solution was dried. Two or three drops of HNO_3 were added, and the sample was dried again at approximately 150 °C. Finally, the dried samples were loaded onto a tantalum filament using 1 M phosphoric acid.[24] The $^{87}Sr/^{86}Sr$ ratio was analyzed using a thermal ionization mass spectrometer (VG 54-30; VG Isotech, Middlewich, Cheshire, U.K.) at KBSI. The analytical reproducibility of $^{87}Sr/^{86}Sr$ obtained from the replicate measurement of NBS 987 (U.S. National Bureau of Standards) was 0.710243 ± 0.000004 (n = 30, ±2σ SE) with a background value of less than 0.1 ng.

Nuclear Magnetic Resonance (NMR) Analysis. About 50 mg of powdered root material was extracted in a 1.5 mL tube containing 500 μL of 99.8% methanol-d_4 (Sigma-Aldrich Co., Seoul, Korea), 400 μL of sodium phosphate buffer solution (0.2 M, pH 7.0) and 100 μL of DSS (sodium 4,4-dimethyl-4-silapentane-1-sulfonate) as an internal standard at a chemical shift (δ) of 0.0 ppm. The extracts were sonicated for 20 min, followed by a 10 min centrifugation (13,000 rpm) at room temperature. The upper layer (600 μL) was transferred to 5 mm NMR tubes and used for the NMR analysis.[19,25]

^{1}H NMR spectra were acquired on a VNMRS 600 MHz NMR spectrometer using a triple resonance HCN salt-tolerant cold probe (Aglient Technologies Inc., Santa Clara, CA, USA) at KBSI. A NOESY-PRESAT pulse sequence was applied to suppress the residual water signal. D_2O and DSS provided a field-frequency lock and the chemical shift reference (^{1}H, δ 0.00), respectively. For each sample, 64 transients were collected in 32K data points using a spectral width of 9615.4 Hz with a relaxation delay of 2.0 s, an acquisition time of 4.00 s, and a mixing time of 100 ms. A 0.5 Hz line-broadening function was applied to all the spectra prior to Fourier transformation. All the NMR spectra were phased and baseline-corrected using Chenomx NMR Suite version 6.0 (Chenomx Inc., Edmonton, Alberta, Canada). The regions corresponding to the solvent and DSS (4.75−5.12, 3.30−3.33, and 0.0−0.7 ppm) were excluded, and the remaining spectral regions were divided into 0.01 ppm bins. Spectra were then normalized to the total spectral area and converted to ASCII format. The ASCII format files were imported into MATLAB (R2006a; Mathworks, Inc., Natick, MA, USA), and all the spectra were aligned using the correlation optimized warping method.[26] Quantification was achieved using the 600 MHz library from Chenomx NMR Suite version 6.0, which uses the concentration of a known reference signal (in this case DSS) to determine the concentration of individual compounds. The library was predicated on a database of individual metabolite spectra acquired using the noesypresat sequence, and contained 260 metabolites.[27,28]

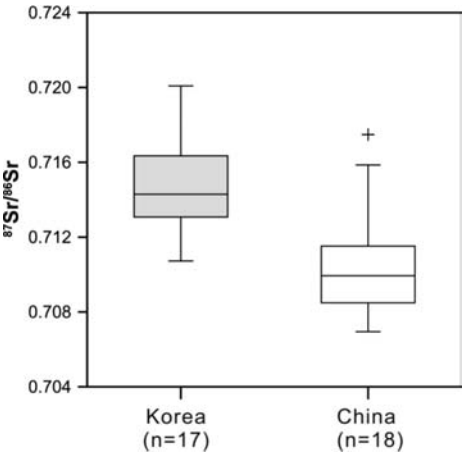

Figure 3. Box-and-whisker diagram showing $^{87}Sr/^{86}Sr$ ranges for ginsengs cultivated in Korea and China.

Statistical Analysis. Multielement concentration of the ginseng samples was compared between the two countries using a two-sample independent t-test (p < 0.05). All the analysis were done employing SPSS version 18 (SPSS, Inc., Chicago, IL, USA). NMR data sets were imported into the SIMCA-P version 12.0 (Umetrics, Umeå, Sweden) for the multivariate statistical analysis. All the imported data were Pareto-scaled for the multivariate analysis. PCA was performed to examine the intrinsic variation in the data set and to obtain an overview of the variations between the groups. The significance of the differences among group in metabolite levels were determined by analysis of a Mann−Whitney test. The differences were tested on a 95% probability level (p < 0.05).

RESULTS AND DISCUSSION

Multielement Contents. The concentration of 13 elements, four major (Ca, Mg, Fe, and Al), one minor (P), and the remaining trace elements (Mn, Zn, Cu, Ni, Co, Li, Sc, and Sr), from the ginseng samples obtained from Korea and China are compared. Only six selected elements (Mg, Fe, Al, Li, Sc, and La)

are presented in Figure 1 (refer to the Supporting Information for other elements). The Korean and Chinese ginseng samples showed a wide range of concentrations for the 13 trace elements. Most of the elements had overlapping values between the Korean and Chinese ginsengs.

There is a high coincidence in the Ca (2152.2 ± 943.2 mg kg^{-1}) and P (2473.3 ± 732.8 mg kg^{-1}) values for Korean ginseng with that of Chinese ginseng, Ca (2741.4 ± 1716.1 mg kg^{-1}) and P (2589.5 ± 495.1 mg kg^{-1}). Hence results of a *t*-test showed nonsignificant differences between the two ginsengs, for both Ca (t = 2.12, p = 0.22) and P (t = 2.04, p = 0.58). Concentrations of Mg were seen higher for Korean ginseng (1037.6 ± 355.4 mg kg^{-1}) than Chinese ginseng (1104.4 ± 453.3 mg kg^{-1}). Although the average Fe value of Chinese ginseng (40.7 ± 20.8 mg kg^{-1}) was seen higher than Korean ginseng (25.5 ± 6.2 mg kg^{-1}), it was more uniform for Korean ginseng (SD ± 6.2) than Chinese, which showed a wide range (SD ± 20.8). In Korean samples the majority of the Fe values were ≤30 mg kg^{-1} with only two values exceeding this range but within ≤40 mg kg^{-1}. Higher average Fe values for Chinese ginseng were attributed to one outlier (97.7 mg kg^{-1}); apart from this there was no consistent pattern noticed for the Chinese ginseng. Thus, there was a significant difference between the Korean and Chinese ginseng for these two elements, a high and significant difference for Mg (t = 2.11, p < 0.0001) but modest significance for Fe (t = 2.11, p < 0.008) (Figure 1). Although Al was showing a weak but significant variation (t = 2.12, p = 0.04) between the two, there was no apparent characteristic range for this element in the Korean (13.88 ± 8.43 mg kg^{-1}) and Chinese samples (27.4 ± 24.9 mg kg^{-1}).

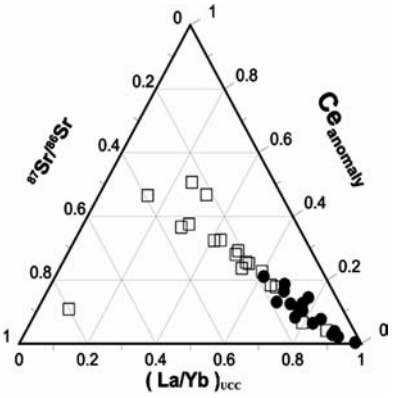

Figure 4. Ternary diagram of $(La/Yb)_{UCC}$ vs $^{87}Sr/^{86}Sr$ vs $Ce_{anomaly}$ for Korean (circles) and Chinese (rectangles) ginsengs.

Within the trace elements, Sc (t = 2.11, p = 0.0001) along with Li (t = 2.11, p = 0.02) showed significant difference between the two ginsengs. For Sc, Chinese ginseng samples (9.55 ± 4.77 mg kg^{-1}) were found to be more enriched compared to Korean ginseng samples (4.67 ± 1.55 mg kg^{-1}). Most values were <6.0 μg kg^{-1} for Chinese ginseng, with most of them between 7.5 and 9.0 μg kg^{-1}, while for Korean ginseng, all the values were found to be >7.0 μg kg^{-1}, with the majority of them between 3 and 5 μg kg^{-1}. Similarly, Li was also found comparatively higher in Chinese samples (23.25 ± 16.93 mg kg^{-1}) than Korean (12.34 ± 7.19 mg kg^{-1}). Most of the values for Chinese are found to be >10 μg kg^{-1} and more variable, and Korean samples <20 μg kg^{-1}. For other trace elements, viz., Mn (t = 2.06, p = 0.20), Zn (t = 2.04, p = 0.36), Cu (t = 2.06, p = 0.47), Ni (t = 2.03, p = 0.32), Co (t = 2.03, p = 0.92), and Sr (t = 2.04, p = 0.21), nonsignificant results were obtained from a *t*-test. Except for Cu, the mean concentrations of all these trace elements were seen

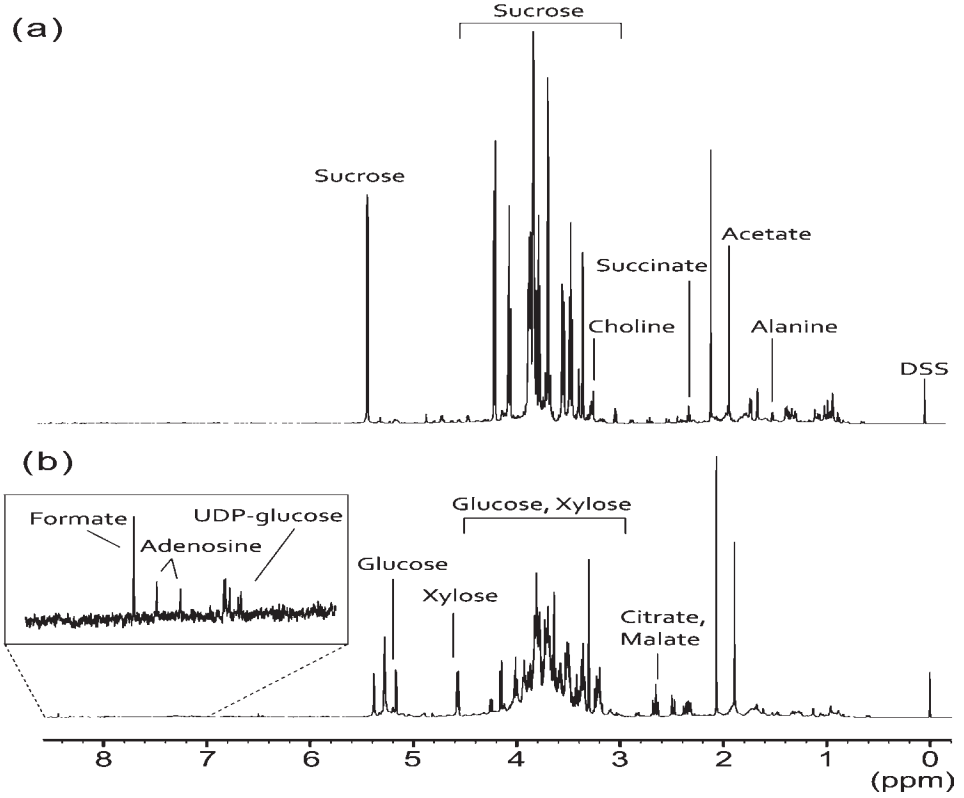

Figure 5. Representative 600 MHz ^{1}H nuclear magnetic resonance (NMR) spectra of ginsengs: China (a) and Korea (b).

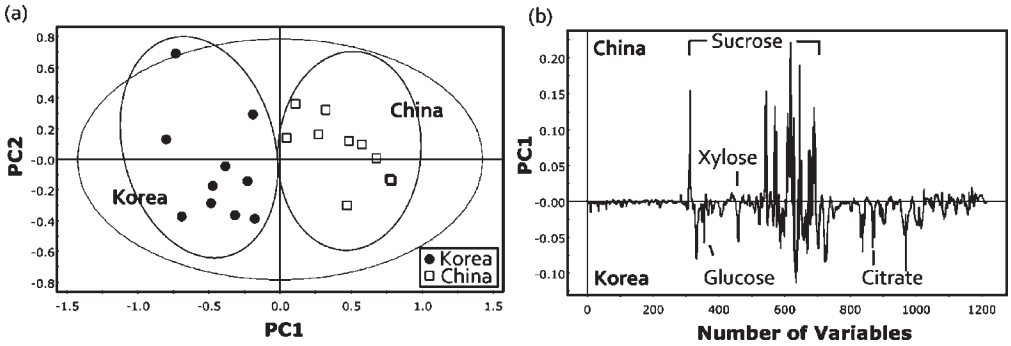

Figure 6. (a) Principal components analysis (PCA) ($R^2 = 0.793$, $Q^2 = 0.671$) and (b) loading line plot from the PCA derived from the ^{1}H NMR spectra of Korean and Chinese ginsengs.

higher in the Chinese samples than Korean samples, but comparatively more variable in the Chinese than Korean samples.

Ko et al.[29] discriminated Korean ginsengs by higher Mn, Fe, Cu, and Ni contents from Chinese ginsengs, which had high Zn concentrations. They attributed this difference to the geochemical characteristics of the soils in which ginseng is grown, and they reported that the difference in content of trace metals between Korean and Chinese ginsengs was small. However, our results were not compatible with their discrimination criteria. Although in our study Mg ($p < 0.0001$), Fe ($p = 0.008$), Al ($p = 0.04$), Li ($P = 0.02$), and Sc ($p = 0.0001$) showed a significant difference in the two ginsengs, except for Sc no other elements were seen showing any particular discriminatory pattern for the two. Apart from Sc, Fe shows a weak discriminating pattern (Figure 1). Hence, differences did exist between the samples collected from the respective countries, but they were not that conspicuous as to be used in provenance discrimination studies. Here, we failed to obtain any generalized pattern in the case of the major, minor, and trace element contents of the ginseng roots from the two countries. Thus, a simple comparison of the concentrations of these elements was not sufficient to distinguish Korean from Chinese ginsengs.

The REE concentrations of the Korean and Chinese ginsengs were also compared. Except for La ($t = 2.13$, $p = 0.03$), the result of a *t*-test for other REE elements showed no significant difference between the two ginsengs. It was expected that REEs in the soil would reflect the REE concentrations in ginseng because crops are intrinsically linked to the soil in which they are grown in terms of REE contents and distribution.[30,31] The average REE concentrations in Korean ginseng were higher than those in Chinese ginseng, except for Lu (same concentration); perusal of Figure 1 clearly shows that no identifiable pattern and difference exist for REEs in the two ginsengs. Whatever little difference exists in the two ginsengs' REEs in part may have been due to the lithological differences between Korea and China.

The normalized pattern of the mean REE concentrations for the Korean ginsengs relative to those of the upper continental crust (UCC) reported by Taylor and McLennan[32] showed a progressively decreasing tendency from LREEs to HREEs (Ho, Er, Tm, Yb, and Lu) (Figure 2). Overall, Korean ginseng showed a LREE-enriched pattern, whereas Chinese ginseng showed a MREE-enriched pattern. The UCC-normalized REE patterns for ginseng samples analyzed for this study were very compatible with those of the river-mouth sediments collected from Korea.[33] Such a pattern can be used as a way to discriminate the Korean and Chinese ginsengs. However, we could not clearly determine the geographical origin of ginsengs cultivated in Korea and China through REE concentrations or REE distribution patterns alone due to some overlap in the concentration ranges among samples. A relatively small variation in the REE concentration from LREEs to HREEs was found in the Chinese ginseng samples.

Strontium Isotope Ratios. The $^{87}Sr/^{86}Sr$ ranges for ginseng samples obtained from Korea and China are shown in given Figure 3, which clearly indicates the higher $^{87}Sr/^{86}Sr$ ratios in Korean ginsengs compared to those in Chinese ginsengs. The majority of the Korean ginseng $^{87}Sr/^{86}Sr$ ratios were <0.712 (mean 0.71450 ± 0.00229). Most of the values are found concentrated around 0.71274−0.71684, although values as high as 0.72008 and as low as 0.71072 was also noticed. $^{87}Sr/^{86}Sr$ ratios for all Chinese ginseng was >0.712 (mean 0.71046 ± 0.00279), with most of the values lying within 0.70694−0.71152. The lowest value noticed was 0.70694 and the highest 0.71748.

A high and very significant ($p < 0.0001$) variation along with clearly demarcated discerning pattern was observed in the $^{87}Sr/^{86}Sr$ ratios of Korean and Chinese ginsengs. This indicates that the two ginsengs from their respective countries can effectively be differentiated based only on their $^{87}Sr/^{86}Sr$ ratios. The $^{87}Sr/^{86}Sr$ ratios of Chinese ginseng samples undertaken in this study were found much higher than those previously reported by Choi et al.[16]

The $^{87}Sr/^{86}Sr$ ratios for ginsengs are primarily determined by the lithological characteristics of the Korean and Chinese cultivation areas. Most Korean ginsengs are cultivated in the regions with Precambrian to Mesozoic granitic clastic sedimentary rocks, whereas most Chinese ginsengs originate from the Jilin, Liaoning, and Heilongjiang areas which are characterized by Cenozoic to Mesozoic sedimentary rocks.[22,34,35]

Discrimination between Korean and Chinese ginsengs was generally successful when both the $^{87}Sr/^{86}Sr$ and REEs were used together (Figure 4). The Korean ginseng exhibited higher La/Yb and $^{87}Sr/^{86}Sr$ ratios, but lower $Ce_{anomaly}$ than those of Chinese ginseng. These results were probably due to the lithological differences between the cultivated regions of the two countries.[33] La/Yb represents a LREE/HREE ratio, and $Ce_{anomaly}$ is a phenomenon whereby the Ce concentration is either depleted or enriched in a rock relative to other REEs; i.e. Ce anomaly is defined by $Ce/(La + Pr)/2$.[31]

^{1}H NMR Analysis. Figure 5 shows the representative ^{1}H NMR spectra for the ginseng samples derived from Korea and China. The metabolites were identified using Chenomx profiler, a module of the Chenomx NMR Suite version 6.0. The ginseng sample spectra were dominated by several metabolites such as

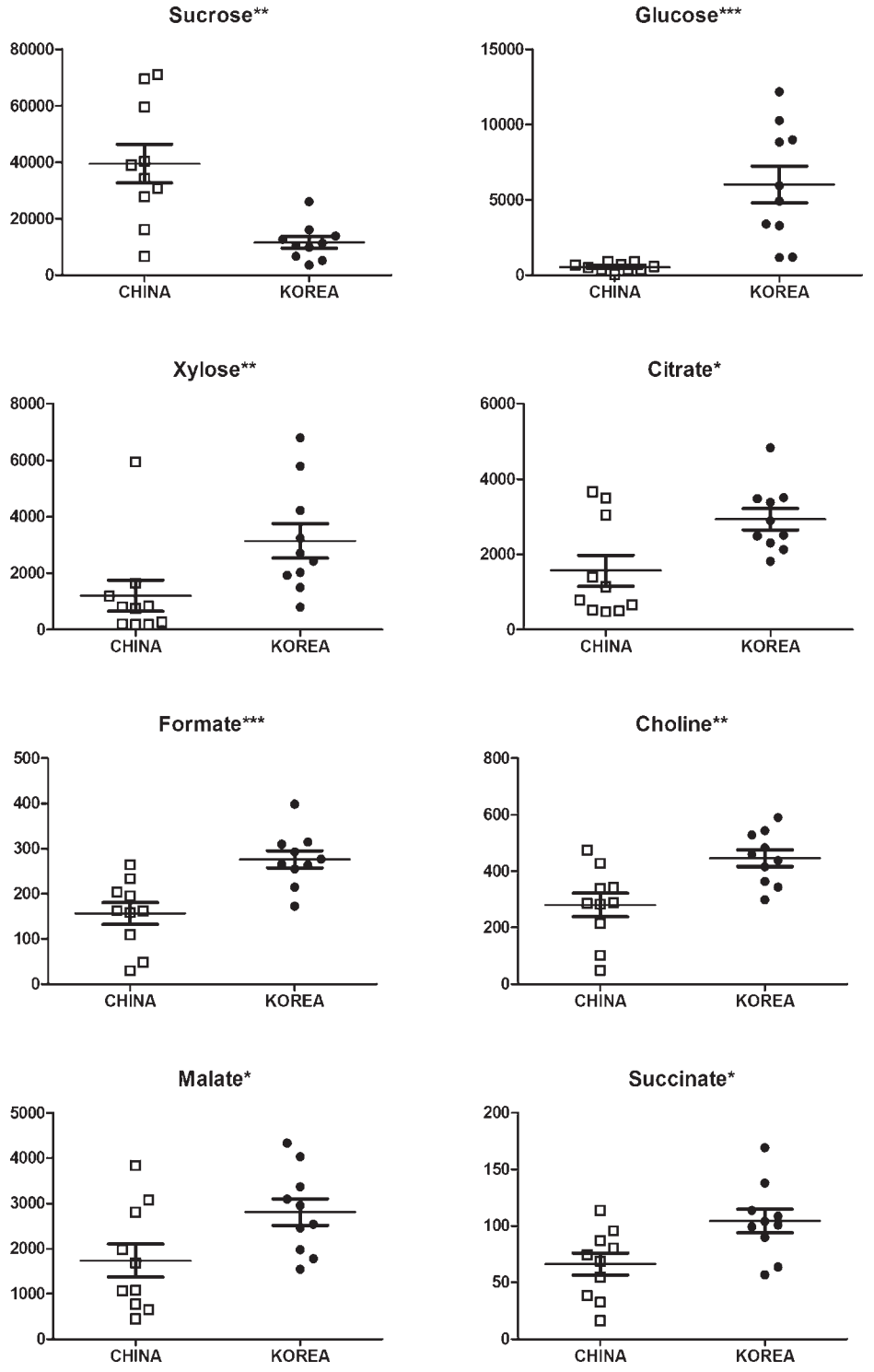

Figure 7. Concentration (μM) of significant metabolites in ginsengs cultivated in Korea and China. Statistical significance: * represents $p < 0.05$, ** represents $p < 0.01$, *** represents $p < 0.001$.

glucose, sucrose, xylose, formate, choline, malate, succinate, acetate, alanine, citrate, adenosine, 4-aminobutyrate, allantoin, arginine, and UDP-glucose. The differences among spectroscopic fingerprints were visible between the Korean and Chinese samples. The Korean ginseng included a large amount of glucose, xylose, formate, choline, malate, and succinate compared to the Chinese ginseng, whereas Chinese ginseng showed a predominantly higher sucrose concentration. Most of the ginseng samples from both countries showed higher intensities in the sugar region. Peaks in the aliphatic, aromatic, and methyl regions of the spectra were lower than the sugar peaks.

Discriminating between Korean and Chinese ginsengs using statistical analyses. We conducted a PCA based on the ^{1}H NMR spectra for the ginseng samples (Figure 6). PCA is an

unsupervised classification method requiring no a priori knowledge of the data set and acts to reduce the dimensionality of multivariate data while preserving most of the variance within it. PCA score plot was used to determine whether the metabolite fingerprints of ginseng samples were sufficiently unique to discriminate samples from the different geographical regions. Each point in the score plot represents an individual sample. The PCA score plot showed a fairly clear differentiation between the Korean and Chinese samples, indicating that the ginseng root metabolites were strongly influenced by the environmental conditions at each cultivation area. R^2 and Q^2 values were calculated for the models to assess any significant differences. R^2 represents the goodness of fit in the PCA model, and Q^2 reveals the predictability of the PCA model. These models exhibited fairly good reproducibility and predictability to explain the differences between the groups. PCA loading plots were generated to identify the contribution of metabolites to distinguish the PCA score plots between the two countries. The loading plots indicated which metabolites were quantitatively higher or lower when compared among groups (Figure 7). The plot shows increased levels of glucose, xylose, and citrate in the Korean ginseng samples, whereas increased levels of sucrose were found in the Chinese samples.

Accurate concentrations of the metabolites in ginseng were measured rapidly using a target-profiling procedure, and the differences in the metabolite levels were compared subsequently. Among them, sucrose in the Chinese ginsengs was almost double that in the Korean ginsengs. In contrast, glucose, xylose, and citrate were higher in the Korean ginsengs than in the Chinese ginsengs (refer to Table 1 in Supporting Information).

Results of a *t*-test for Mg, Fe, Al, and Sc showed significant variation between Korean and Chinese ginsengs, indicating potential tracers for discriminating them. $^{87}Sr/^{86}Sr$ ratios combined with REEs discriminated the Korean ginsengs from the Chinese ginsengs. Korean ginseng exhibited a LREE-enriched pattern, whereas Chinese ginseng showed a MREE-enriched pattern, indicating lithological differences between the two. Sugar metabolites—sucrose, glucose, and xylose—also provided meaningful information to distinguish the geographical origin of Asian ginsengs, since Korean ginseng has a large amount of glucose and xylose against that of Chinese ginseng, characterized predominantly by high sucrose concentration. Our study suggests that the combined use of multiple tracers is very useful for discriminating the geographical origins of ginsengs cultivated in Korea and China.

■ ASSOCIATED CONTENT

Supporting Information. Expanded version of Figure 1, map showing sample locations, and Table 1 providing chemical shift and quantification of metabolites identified from ginseng of Chian and Korea using ^1H NMR. This material is available free of charge via the Internet at http://pubs.acs.org.

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