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Rare Earth Element Content in Fructus Sophorae from Different Areas

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Fructus sophorae is traditional Chinese medicinal herb. Fructus sophorae samples were collected from eleven areas of Dezhou and digested with various acids followed by ICP-MS analysis for 14 kinds of rare earth elements. The contents of total rare earth elements in Fructus sophorae samples from different areas ranged from 0.6826 μg/g to 1.0527 μg/g and the determined content of rare earth elements in Fructus sophorae varied from one area to another. The distribution tendency of rare earth elements was identical with Odd Harkin's rule. The plots of normalized element concentration *versus* atomic number showed some characteristic distribution tendencies. The geology condition and natural environment should be responsible for the difference, but the allocation mechanism of rare earth elements in Fructus sophorae should be further studied. Content and distribution of rare earth elements in Fructus sophorae were compared with that in Flos sophorae.

Key Words: Rare earth elements, ICP-MS, Fructus sophorae.

INTRODUCTION

Fructus sophorae, Chinese traditional medicinal herb, is the ripe fruit of leguminous plant *Sophora japonica* L.[1], which is mainly produced in many provinces of China, such as Hebei, Shandong, Henan and Jiangsu[2]. It has been used to cure the diseases including hemafecia, hemorrhoids blood, bloody flux, uterine bleeding, hematemesis, liver heat and red eyes, headache and dizziness and so on[3]. So they are well known to have pharmacological activities and health care functions in ancient period[4-6]. However, to our best of knowledge, there is no report about contents of rare earth elements from Fructus sophorae. In this study, 14 kinds of rare earth elements in Fructus sophorae samples derived from 11 different areas of Dezhou were measured by ICP-MS separately. The content and distribution tendency of rare earth elements were studied, providing basic data for curative mechanism and pharmacology characteristics of traditional Chinese medicinal herbs.

EXPERIMENTAL

ICP-MS (DRC-E, Perkin Elmer, USA) was operated under the following conditions: RF power of 1100W, nebulizer flow rate of 0.92 l/min, auxiliary flow rate of 1.20 l/min, plasma gas flow rate of 15.0 l/min, sample uptake of 1.0 mL/min, dwell time of 50 ms/AMU, scan times of 20/s,integral time of 1000 ms. The analysis was performed according to the Perkin Elmer manual. The following isotopes were measured: ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{151}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{172}Yb and ^{175}Lu.

HNO_3 (MOS, Beijing Chemical Reagent Research Institute); HCl (A.R., Shanghai Zhen Xing second chemical industry factory);HF(MOS,Beijing chemical reagent research institute); $HClO_4$ (G.R., Beijing Nan Shang Le Chemical Plant; 1.0 mg/mL standard solution of rare earth element (national research center of standards material). 18.2 MΩ high-purity water provided by Milli-Q. GBW 07605 tea leaves (State Bureau of Metrology, Beijing, China) was used to evaluate accuracy.

Preparation of samples: Fructus sophorae samples were collected from 11 different areas in Dezhou, including Xiajin, Ningjin, Linyi, Lingxian, Dechengqv, Wucheng, Qingyun, Yucheng, Pingyuan, Laoling and Qihe. The samples were ground in mill and sieved to obtain particles 0.25 mm in diameter. They were dried for 6 h at 60 ºC before use.

0.1 g dried samples were weighed accurately and were digested with 3 mL HNO_3 and 0.4 mL $HClO_4$ and 0.1 mL HF at 170 ºC for 6 h and placed on a hot plate (at about 120 ºC) and the solutions evaporated to dryness, then 0.4 mL $HClO_4$ was added in and acid was removed and the samples were adjusted to 10 mL with 0.32 mol/L HNO_3, ready for measurement.

RESULTS AND DISCUSSION

Content and distribution of rare earth elements: The analytical results of 14 kinds of rare earth elements in Fructus

TABLE-1
CONTENTS OF RARE EARTH ELEMENTS IN FRUCTUS SOPHORAE FROM DIFFERENT AREAS (μg/g)

Element	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Xiajin	0.1216	0.2118	0.0518	0.1191	0.0442	0.0381	0.0344	0.005	0.0289	0.0283	0.0386	0.0006	0.0321	0.0135
Ningjin	0.1471	0.291	0.0569	0.1412	0.0463	0.0433	0.0378	0.005	0.029	0.0284	0.0409	0.0007	0.0325	0.0149
Linyi	0.1393	0.2322	0.0549	0.1312	0.043	0.0383	0.0357	0.0053	0.0323	0.0288	0.0623	0.0008	0.0327	0.0136
Lingxian	0.1842	0.3526	0.0643	0.1651	0.0501	0.0399	0.0411	0.0056	0.0312	0.0288	0.0428	0.0007	0.0327	0.0136
Dechengqv	0.0747	0.2761	0.0612	0.1807	0.0476	0.0438	0.0483	0.0053	0.0293	0.0284	0.139	0.0009	0.0319	0.0136
Wucheng	0.1165	0.2123	0.0496	0.1145	0.0401	0.0369	0.0305	0.0045	0.0254	0.0275	0.04	0.00038	0.0308	0.0139
Qingyun	0.1504	0.2621	0.0575	0.1393	0.0466	0.0392	0.0362	0.005	0.0285	0.0283	0.0394	0.0006	0.032	0.0134
Yucheng	0.1335	0.3096	0.0541	0.1276	0.0424	0.0374	0.0337	0.0045	0.0255	0.0278	0.0444	0.0004	0.031	0.0132
Pingyuan	0.0961	0.1869	0.0457	0.0928	0.0363	0.0426	0.0292	0.0045	0.0255	0.0278	0.0494	0.0007	0.0307	0.0144
Laoling	0.0936	0.2241	0.0545	0.1248	0.0419	0.0391	0.0356	0.0056	0.0315	0.0336	0.0509	0.0005	0.0399	0.0128
Qihe	0.1624	0.2861	0.0599	0.1492	0.0463	0.0402	0.0372	0.0049	0.0294	0.0279	0.0462	0.0006	0.0313	0.0135

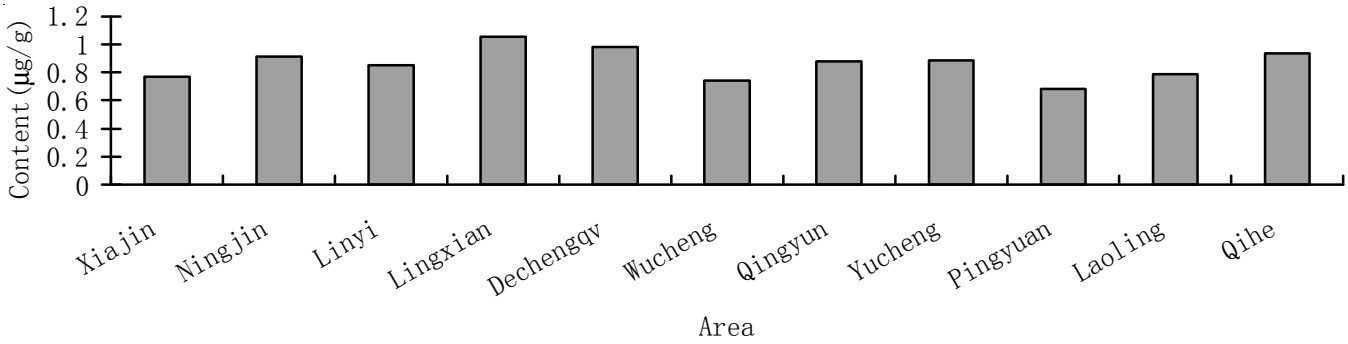

Fig. 1. Contents of total rare earth elements in Fructus sophorae samples from different areas

sophorae samples collected from 11 different areas in Dezhou were listed in Table-1. The contents of total rare earth elements in Fructus sophorae samples from different areas were summarized in Fig. 1. The contents of total rare earth elements in Fructus sophorae samples from different areas ranged from 0.6826 μg/g (Pingyuan, as dry weight, the same below) to 1.0527 μg/g (Lingxian). As can be seen from Table-1, different rare earth elements had big differences in content and the content of Ce was maximal and the content of Tm was lowest. The contents of La, Ce and Nd were higher than 0.09 μg/g except La in Fructus sophorae from Dechengqv, which was the same with the results before and could be the mechanism of curative effect[7-9]. In contrast, the contents of Tb, Tm and Lu were lower and content was 0.0045-0.0056, 0.00038-0.0009 and 0.0128-0.0149 μg/g. By comparing the contents of 14 rare earth elements in Fructus sophorae samples, we found that there were highly significant differences in the contents of an element between Fructus sophorae samples from one area to another. For example, the content of Ce in Fructus sophorae from Pingyuan was 0.1869 μg/g, while that from Lingxian was 0.3526 μg/g. However, the difference for some elements was not so significant. Furthermore, some elements had the same content, which could be seen from the contents of Tm in the samples from Ningjin and Lingxian. The results showed that the character and the contents of rare earth elements in Fructus sophorae samples from different areas were related to its geology condition and natural environment. This conclusion was confirmed by other studies on traditional Chinese medicinal herbs[7-9], but the allocation mechanism of rare earth elements in Fructus sophorae should be further studied.

Distribution tendency of rare earth elements: As can be seen from Table-1, the distribution tendency of rare earth elements was identical with Odd Harkin's rule, which coincided with other results[10-12]. In order to illuminate more clearly the distribution tendency of the rare earth elements in Fructus sophorae samples from different areas, we normalized the element concentrations. The normalized element concentration (NEC) *versus* atomic number is plotted for clarity (Fig. 2). The plots of normalized element concentration *versus* atomic number showed some characteristic distribution tendencies. The distribution tendency of light rare earth elements (La-Gd) was relatively flat except a positive Eu anomaly, however, the distribution tendency was steep and discrepant for heavy rare earth elements (Tb-Lu). The phenomenon suggests that rare earth elements in plant have an interdependent relationship. On the other hand, discrepancy of heavy rare earth elements may be related to existing state of element. Furthermore, the results provide a reference for study on relationship between the contents of rare earth elements and curative mechanism, the pharmacologic characteristics and its geology condition.

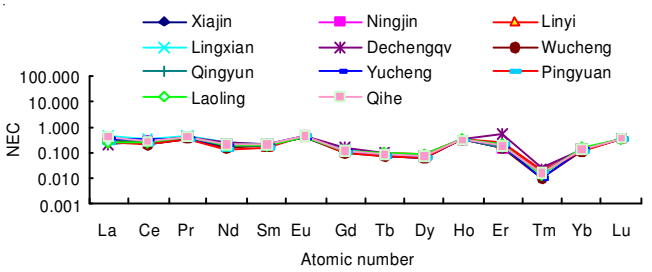

Fig. 2. Distribution tendency of concentrations of rare earth elements in Fructus sophorae after normalization

Comparison with Flos sophorae in content and distribution: The contents of total rare earth elements in Fructus

sophorae samples from different areas ranged from 0.6826 μg/g to 1.0527 μg/g, while that were from 1.2077 μg/g to 2.4742 μg/g in Flos sophorae samples from different areas[12]. Distribution tendency of concentrations of rare earth elements in Fructus sophorae after normalization was very similar with that in Flos sophorae. It could be also noticed that the contents of total rare earth elements in Fructus sophorae samples from different areas were obviously lower than that in the same area in Flos sophorae samples. However, the specific reasons for the phenomenon still needs further study.

Conclusion

The contents of total rare earth elements in Fructus sophorae samples from different areas ranged from 0.6826 μg/g to 1.0527 μg/g by ICP-MS analysis. The content of rare earth elements in Fructus sophorae varies largely with the samples collected from one area to another and the content of different rare earth elements had big differences in the same sample. The results showed that the character and the contents of rare earth elements in Fructus sophorae samples from different areas were related to its geology condition and natural environment, but the allocation mechanism of rare earth elements in Fructus sophorae should be further studied. The distribution tendency of rare earth elements was identical with Odd Harkin's rule. The plots of normalized element concentration *versus* atomic number showed some characteristic distribution tendencies. The phenomenon suggests that rare earth elements in plant have an interdependent relationship. Content and distribution of rare earth elements in Fructus sophorae were compared with that in Flos sophorae and distribution tendency of concentrations of rare earth elements in Fructus sophorae after normalization was similar with that in Flos sophorae.

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