Food Sci. Biotechnol. Vol. 14, No. 3, pp. 363 ~ 367 (2005)

Food Science and Biotechnology

Change in Ginsenosides and Maltol in Dried Raw Ginseng during Extrusion Process

Dae-Chul Ha, Jong-Won Lee[1] and Gi-Hyung Ryu*

Department of Food Science and Technology, Kongju National University, Yesan, Choongnam 340-805 Korea
Herbal Resource Research Center, Kongju National University, Yesan, Choongnam 340-805 Korea
[1]KT & G Central Research Institute, Taejon 305-805 Korea

Abstract Although widely applied in the food industry, extrusion cooking has not been applied to the traditional red ginseng process for steaming and drying ginseng. We therefore investigated the change in the effective components in red ginseng (total saponins, ginsenosides and maltol) from extruded raw ginseng. The variables were the drying temperature of the sliced raw ginseng (80 and 90°C) before the extrusion process and the moisture content (15 and 22%, w.b.) during the extrusion process. Ginsenosides Rg1 and Rg2 were detected in dried ginseng at 80°C, but ginsenoside Rg3, which was contained in red ginseng, was not detected. On the other hand, ginsenosides Rg1, Rg2 and Rg3 were detected in extruded ginseng at moisture contents of 15 and 22%. Total ginsenosides were highest at 90°C drying temperature and 22% moisture content for the extrusion process.

Key words: extrusion process, red ginseng, ginsenosides

Introduction

Scientific studies of ginseng started with Garriques who isolated an amorphous glycoside from Western ginseng and named it *Panaquilon* in 1854. However, full-scale studies using modern scientific techniques started with Brekhman, a Soviet pharmacologist who reported in 1957 that the effective component in ginseng was saponin. After this report, many scientists in Korea, Japan, European countries, Russia, and China began active research into saponin. Thus, various ginsenosides contained in ginseng, such as Ro, Ra, Rb1, Rb2, Rc, Rd, Re, Rg1, Rg2, and Rg3, were isolated and their chemical structures were examined, thereby facilitating further studies to determine the pharmacologic effectiveness of ginseng according to each component.

The traditional processing of red ginseng involves washing and steaming (90 to 100°C) of raw ginseng, followed by first drying (moisture content 35 to 40%), storage and aging, second drying (moisture content 16%), and molding to improve the storage characteristics. The saponins, amino acids, and color undergo chemical changes such as browning during the process. White ginseng is produced by peeling raw ginseng and sun or hot-air drying. Its color is either milky white or light yellow. On the other hand, red ginseng is processed by washing raw ginseng without peeling, streaming, or drying, so that the ginseng is light yellowish brown or light reddish brown (1).

When raw ginseng is steamed and heat treated during the processing of red ginseng, chemical changes occur in the ginseng compositions to produce active substances that do not exist in raw ginseng or white ginseng. The major components of these changes occurring during the processing of red ginseng are saponins, non-saponin polyacetylene, acidic polysaccharides, and amino acids. It was reported that 30 different saponins were isolated from red ginseng and 22 from white ginseng. Among these, 18 different saponins were present in both red and white ginseng, 12 only in red ginseng, and 4 only in white ginseng.

Both the traditional processing of red ginseng and the recent developed processing include heat treatment and drying processes. The application of the extrusion process to the processing of red ginseng could probably shorten the processing.

During the extrusion process, various steps such as mixing, grinding, heating, molding, and drying occur within a short time, and this process is therefore effective and economical compared with other thermal processes. Especially, the substance within the screw in the extruder experiences a shear force due to the screw rotation when the heat processing is applied, and the extrusion process is a continuous one with physical force accompanied at high temperatures, even while the pressure is controlled by the process variables (2). Although this extrusion process has been applied diversely in biologic and food industries (3-6), it has not in the processing of red ginseng, either in Korea or abroad.

Thus, we investigated changes in the effective components in red ginseng (total saponins, ginsenosides and maltol) following treatment from dried raw ginseng at different drying temperatures (80 and 90°C) before the extrusion process and at different moisture contents (15 and 22%) during the extrusion process.

*Corresponding author: Tel: 82-41-330-1484; Fax: 82-41-335-5944
E-mail: ghryu@kongju.ac.kr
Received April 12, 2005; accepted May 5, 2005

Materials and Methods

Materials Five-year-old raw ginseng cultivated in

Geumsan, Korea, was purchased at a ginseng market. Raw ginseng was removed of root hair, cut into rice grain size using a vegetable chopper (Hwajin Precision Co., Korea), and then dried at 80 and 90 to reduce the moisture content below 10%.

Extrusion process A corotating twin-screw extruder (THK 31, Incheon Machinery Co., Korea) was used in the study. Its L/D ratio was 20:1. Fig. 1 shows the screw configuration. The diameter of the die exit was 3 mm. Water was injected into the feed section of the barrel to control the moisture content of the dried ginseng. The barrel temperature was controlled using electric heating and circulating cooling water. The variable during the extrusion process was the amount of injected moisture: 15 and 22% (w.b.). The barrel temperature was controlled at 110/110/60/40°C at the barrel numbers of 1/2/3/4, respectively. The screw speed was fixed at 200 rpm and the feed rate of dried ginseng at 110 g/min.

Extruded ginseng was dried at 80°C, and ground to powder (aperture 500 μm) for analysis.

Saponin analysis The isolation and quantification of crude saponin were done according to the method of water-saturated butanol extraction by Ando et al. (7) and Namba et al. (8). Briefly, 50 mL of water-saturated butanol solution was added into 5 g of sample. The mixture was refluxed and extracted at 80°C for 1 hr and filtered. The mixture was refluxed and extracted twice by adding 50 mL of water-saturated butanol solution into the remaining solution. The filter paper was washed by pouring 10 mL of water-saturated butanol. The water-saturated butanol solution layer was extracted by adding 50 mL of distilled water. After vacuum concentration, ether was added into the sample, which was then refluxed and extracted. After ester was removed, the residue was dried at 105°C for 2 hr and weighed.

Ginsenoside analysis The isolation and quantification of ginsenosides were done after the addition of 50 mL of 80% ethanol into 1 g of sample. This mixture was refluxed twice in a water bath for 1 hr each time, extracted by cooling, filtered, and concentrated. The remaining solution was dissolved in distilled water and its volume was brought up to 5 mL. This resulting sample was used as the sample in a Sep-Pak C_{18} cartridge (300 mg, Waters Co., Milford, MA, USA). After 2 mL of methanol was loaded to activate the Sep-Pak C_{18} cartridge, the cartridge was washed with 4 mL of distilled water, 3 mL of sample was loaded, 12 mL of distilled water was loaded to remove the sugar content, and reflux was done using 12 mL of 30% methanol to remove the lipid content. After 5 mL of methanol for HPLC was loaded, the resulting solution was obtained and filtered through a 0.2 μm membrane filter to act as an HPLC sample. The HPLC system consisted of a separation module (Waters 510, Waters Co., Milford, MA, USA), ELSD detector (92°C, 2.0 L/min Nebulizing gas nitrogen), and NH_2 column (250 x 4.6 mm, Merck Co., USA). The mobile phase elution was set with a flow rate of 1 mL/min and composition of acetonitrile/water/isopropanol (solvent A: 80/5/15, solvent B: 80/20/25). The injection volume was 20 μL. Based on the HPLC chromatograms, the peak areas were compared with those of the standard curve. The contents of each ginsenoside, i.e., Rg1, Rg2, Rg3, Rb1, Rb2, Rc, Re, Rf and total saponin, were calculated.

Maltol analysis The maltol component was analyzed adding 5 g of extruded ginseng powder into a round flask with 100 mL of 80% methanol solution, and refluxed and extracted for 1 hr in a water bath at 70°C. After 100 mL of 80% methanol was added into the residue after filtering, the sample was again refluxed and extracted for 1 hr. The first and second filtrate were combined and extracted under vacuum, dissolved in 50 mL of distilled water, and extracted using 50 mL of ethylacetate by placing the mixture into a fraction funnel. The supernatant was then isolated, vacuum evaporated, dissolved in 1 mL of methanol, and used as the sample solution. The standard solution used was a mixture of 1 mg of maltol standard and 1 mL of methanol. After 10 μl of the sample solution and 10 μl of the standard solution were placed into the silica gel plate for TLC to wet the plate, the mixture of benzene and acetone (4:1, v/v) was used as the developing solvent and air dried on a thin layer plate by spreading over a circle of 10 cm diameter. One of several spots that appeared after $FeCl_3$ was sprayed was adjusted so that it would have the same spot as the red spot appearing with the standard solution and Rf. It was then heated at 110°C for 5 min.

Results and Discussion

Saponins and ginsenosides Table 1 shows the results of analyzing the various ginsenosides, including Rg1, Rg2,

Table 1. Contents of saponin components in dried and extruded ginseng

Ginseng sample[a]	Crude saponin (%)	Ginsenoside (mg/g)									
		Rg2	Rg3	Rg1	Rf	Re	Rd	Rc	Rb2	Rb1	Total
D80	3.90	-	0.074	1.383	0.626	1.294	0.197	0.309	0.214	0.691	4.787
D80E15	4.32	0.041	0.184	1.409	0.619	1.225	0.246	0.474	0.296	1.013	5.506
D80E22	4.33	0.049	0.113	1.540	0.708	1.347	0.243	0.452	0.292	0.929	5.673
D90	4.79	-	-	1.091	0.526	1.136	0.464	0.415	0.271	0.738	4.642
D90E15	5.08	0.040	0.089	1.296	0.673	1.375	0.596	0.506	0.296	0.838	5.708
D90E22	5.02	0.057	0.135	1.489	0.754	1.482	0.616	0.492	0.304	0.863	6.192

[a]D80: dried at 80°C (control); D80E15: extruded sample D80 at moisture content 15%, barrel temperature 110°C, and screw speed 200 rpm; D80E22: extruded sample D80 at moisture content 22%, barrel temperature 110°C, and screw speed 200 rpm; D90: dried at 90°C (control), D90E15: extruded sample D90 at moisture content 15%, barrel temperature 110°C, and screw speed 200 rpm; D90E22: extruded sample D90 at moisture content 22%, barrel temperature 110°C, and screw speed 200 rpm.

Rg3, Rf, Rd, Rc, Rb_1, Rb_2, and Re and total saponins, following drying at 80 or 90°C and ginseng extruded at 15 or 22% moisture content. The percentage of crude saponin was 3.90% in D80, which was a non-extruded sample of dried raw ginseng at 80°C. It was slightly increased by extrusion process to 4.32% in D80E15, which was an extruded sample of dried raw ginseng at 15% moisture content, and to 4.33% in D80E22, which was an extruded sample at 22% moisture content. It was 4.79% in D90, which was a non-extruded sample of dried raw ginseng at 90°C. It was 5.08% in extruded sample D90E15, and 5.02% in extruded sample D90E22.

The amount of crude saponin was higher in sample D90, dried at 90°C, than in sample D80, dried at 80. The amount was also increased through the extrusion process but was not significantly affected by the moisture content of ginseng during the extrusion process. Extruded ginseng at a moisture content of 15 and 22% contained higher crude saponin content than dried ginseng at 80 and 90°C. These results suggest that the molecular structure of saponin was changed by the drying and extrusion process so that the release of crude saponin became easier with increasing pre-drying temperature and through the extrusion process.

The amount of total saponin was 4.828 mg/g in the dried ginseng sample D80, 5.465 mg/g in D80E15 and 5.673 mg/g in D80E22, showing that the total saponin was slightly increased with increasing moisture content during the extrusion process, compared with dried ginseng. The amount of total saponin was 4.642 mg/g in the dried ginseng sample D90, 5.708 mg/g in extruded ginseng D90E15, and 6.129 mg/g in extruded ginseng, showing the amount of total saponin was increased with the increase in moisture content from15% to 22% during the extrusion process.

The amount of major ginsenosides (Rg group) in commercial red ginseng produced by traditional manufacturing was higher in the extruded ginseng groups than in the non-extruded groups. Especially, the specific ginsenosides Rg1 and Rg3 were contained at minute quantities in the dried ginseng samples, D80 and D90. However, there was no Rg2 in dried ginseng. On the other hand, there was no Rg2 or Rg3 in dried ginseng at 90°C, D90 but there were minute quantities in extruded ginseng D90E15 and D90E22. These results showed the differences in the components according to the extrusion process conditions but the total amount of the Rg group was higher at the moisture content of 22%. Thus, the extrusion condition at the moisture content of 22% for the extruded ginseng D90E22 was determined to be better, because it contained higher ginsenoside Rg group, which is the specific ginsenoside in red ginseng produced by the traditional process.

Given that among the components of white ginseng, it is malonyl-ginsenoside that changes to ginsenoside component due to heat and pressure treatment, the conversion efficiency of the ginsenosides was increased by the extrusion process, especially at the moisture content of 22% since the extrusion process is a continuous thermal process with relatively high pressure. The amount of total ginsenosides was increased by the extrusion process because the cells or tissues of ginseng underwent transformations which allowed easier extraction of these components through the extrusion process (9).

Furthermore, the degree of deformation applied to the plant cell tissue with shear stress by extrusion cooking is determined according to the screw dimension, and the shear stress affected by the changing shear rate (10-13). The results showed that more total saponin was contained in the extruded ginseng at higher moisture content with a flow property of low viscosity, compared with that at lower moisture.

During the extrusion process for transforming raw ginseng to red ginseng, the amount of total saponin increased, probably because more saponin was converted due to the shear stress and pressure arising from the thermal and mechanical energy dissipated as the raw ginseng passed through the screw inside the extruder barrel. The ginsenoside Rg group is contained in the red ginseng that is processed with steaming and drying in the traditional process. Ginsenosides Rg1, Rg2 and Rg3 were increased when dried raw ginseng was extruded at a moisture content of 15% and 22%.

Analysis of maltol using TLC In ginseng containing saponin, the saponin was not removed easily through pure purification process but usually remained present as phenol compounds. Among these compounds, the maltol component was not detected in raw ginseng and is known

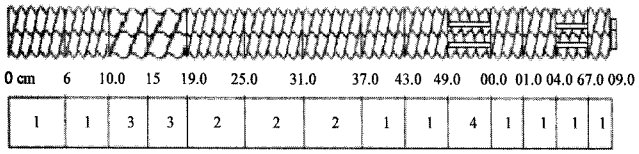

Fig. 1. Screw configuration for ginseng root extrusion.

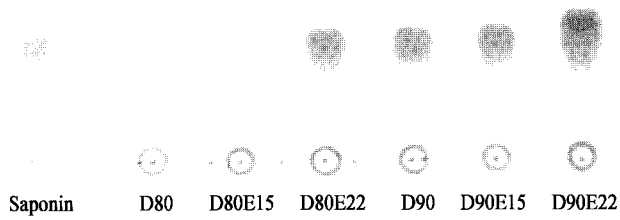

Fig. 2. Thin-layer chromatogram of maltol from ginseng samples prepared by various drying and extrusion conditions. Saponin: 1% maltol standard; D80: dried at 80°C (control); D80E15: extruded sample D80 at moisture content 15%, barrel temperature 110°C, and screw speed 200 rpm; D80E22: extruded sample D80 at moisture content 22%, barrel temperature 110°C, and screw speed 200 rpm; D90: dried at 90°C (control); D90E15: extruded sample D90 at moisture content 15%, barrel temperature 110, and screw speed 200 rpm; D90E22: extruded sample D90 at moisture content 22%, barrel temperature 110°C, and screw speed 200 rpm.

as a characteristic component of red ginseng produced secondarily due to heat treatment during the steaming process for red ginseng (13, 14). The maltol component exhibits an activity in protecting living tissues from oxidative damages (15). The phenol compound contained in ginseng, p-coumaric acid, prevents platelet clotting and has the physiological activation of preventing the production of prostaglandin by controlling the arachidonic acid metabolism (16).

The maltol component of each sample prepared by the drying and extrusion process was investigated using thin-layer chromatography and the results are shown in Fig. 2. Unlike in the dried ginseng D80, the maltol component was confirmed in extruded ginseng at a moisture content of 22%, D80E22. Unlike in the dried ginseng D90, the same maltol component was confirmed in extruded ginseng at moisture contents of 15% and 22%, D90E15 and D90E22, respectively. Especially, the maltol component was increased by the extrusion process. Thus, the maltol component was present in the highest extruded ginseng at a moisture content of 22%.

Analysis of maltol component using GC/MS Fig. 3 shows the results of the maltol component confirmed in dried ginseng at 90°C and in the extruded ginseng at a moisture content of 15% (D90E15) and 22% (D90E22) using GC/MS, respectively. The maltol component was confirmed in both D90E15 and D90E22. In the case of D80E15, the presence of maltol was not confirmed on TLC but was confirmed in minute quantity according to GC/MS. Furthermore, compared with D90, maltol underwent a change in quantity in D90E15 and D90E22 (data not shown). This result also agreed with the TLC analysis result of the maltol component. These results indicated that maltol production and content could be changed by controlling the extrusion process conditions. In the present study, we have therefore confirmed that it is possible to develop a process to increase selectively the amount of the main antioxidative component, maltol, during the extrusion process.

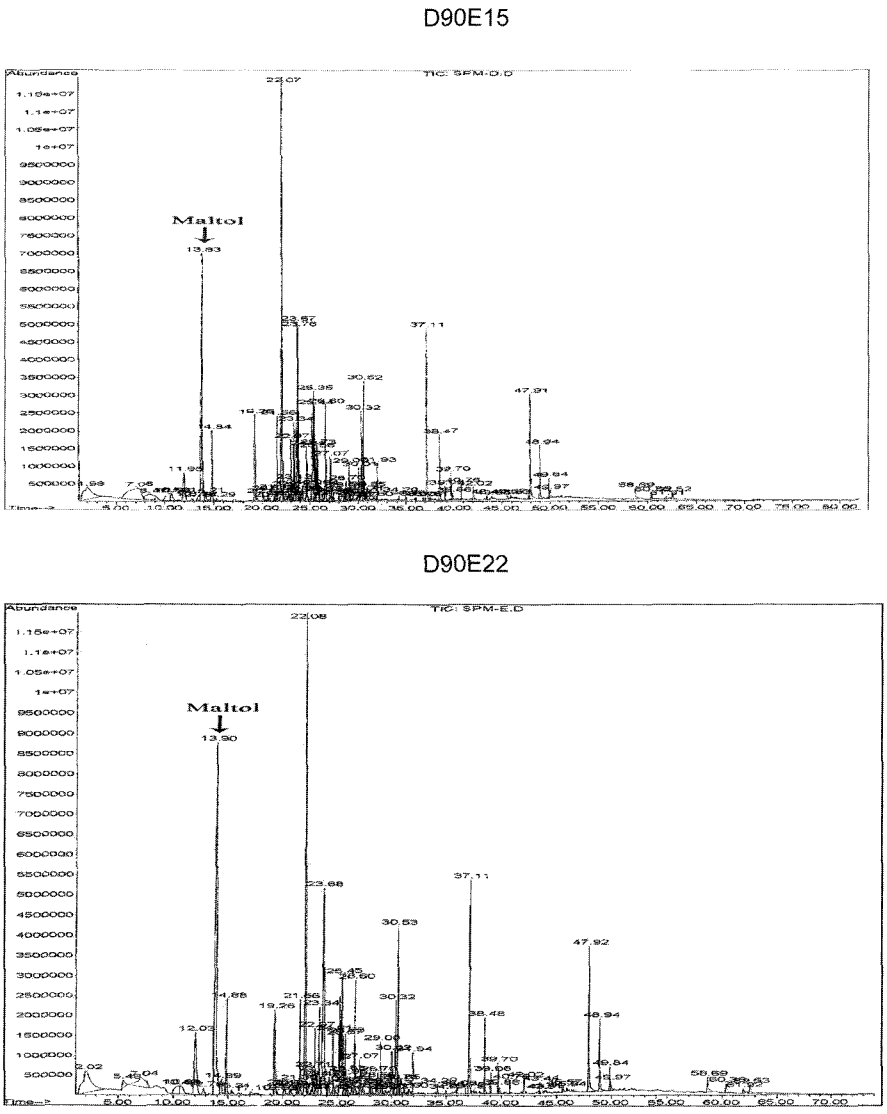

Fig. 3. Mass spectra of maltol in extruded ginseng at moisture contents of 15% (D90E15) and 22% (D90E22). Drying temperature 90°C, barrel temperature 110°C, and screw speed 200 rpm.

References

1. Cho JS, Han YN, Oh HI, Park, H, Sung HS, Rark, JH. Understanding of Korean Ginseng. The Society for Korean Ginseng, Seoul, Korea. pp. 35-46 (1995)
2. Harper JM. Food extruders and their application. pp 1-18. In: Extrusion Cooking. Mercier CP, Linko P, Harper JM (ed). AACC, St. Paul, MN (1989)
3. Harper JM. Extrusion of Foods. CRC Press, Boca Raton, FL (1981)
4. Hwang JK, Kim TK, Hong SI, Kim CJ. Solubilization of plant cell walls by extrusion. J Korean Soc. Food Nutr. 23: 358-370 (1994)
5. Ryu GH. Treatment of Biji by extrusion-cooking and its utilization. Korea Soybean Digest. 12: 43-48 (1995)
6. Ryu GH, Kim BS, Mulvaney SJ. Optimization of extrusion process for dairy ingredient fortification of cornmeal puffed via CO_2 gas injection. Food Sci. Biotechnol. 11: 552-556 (2002)
7. Ando T, Tanaka O, Sibata S. Chemical studies on the oriental plant drugs. Comparative studies on the saponins and sapogenins of ginseng and related crude drugs. Soyakugaku Zasshi. 25: 28-37 (1971)
8. Namba T, Yoshizaki M, Tomimori T, Kobashi K, Matsui K, Hase J. Fundamental studies on the evaluation of the crude drugs. III. Chemical and biochemical evaluation of ginseng and related crude drugs. Yakugaku Zasshi. 94: 52-260 (1974)
9. Ha DC. Development of red ginseng manufacturing by using extrusion process. MS thesis, Food Science Department, Kongju National University, Yesan, Korea (2003)
10. Dickinson E, Stainsby G. Colloid in Food. Elsevier Applied Science Publishers, New York, USA (1982)
11. Prentice JH. Measurements in the Rheology of Foodstuffs. Elsevier Applied Science Publishers, New York, USA (1984)
12. Bourne MC. Food Texture and Viscosity: Concept and Measurement. Academic Press, New York, USA (1982)
13. Sherman P. Food Texture and Rheology. Academic Press, New York, USA (1979)
14. Han BH. Studies on the anti-oxidant components of Korea ginseng. In: Proceedings of the 2nd International Ginseng Symposium. Korea Ginseng Research Institute, Seoul, Korea. pp 13-17 (1978)
15. Shim JG, Park JW, Pyo JK, Kim MS and Chung MH. Protective effects a ginseng component, maltol(2-methyl-3-hydroxy-γ-pyrone) against tissue damages induced by oxygen radicals. pp. 45-48. In: Proceedings of International Symposium on Korean Ginseng. The Society for Korean Ginseng, Seoul, Korea. pp. 45-48 (1990)
16. Park H, Cho BG and Lee MK. Nitrogen compounds of Korean ginseng and their physiological significance. pp. 175-189. In: In: Proc. Int'l Sym on Korean ginseng. The Society for Korean Ginseng, Seoul, Korea (1990)