Establishing the HPLC-MS/MS Method for Monitoring the Residue and Degradation of Butralin in Ginseng during Field and Risk Assessments

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Abstract: Butralin can effectively mitigate the spreading of weeds in ginseng fields, however, the dissipation and residues of butralin in ginseng have not been investigated. In this study, we established a high-performance liquid chromatography tandem mass spectrometry (HPLC-MS/MS) method to determine the butralin residue and its dissipation in ginseng and its dietary intake risk. The mean recoveries of butralin in ginseng (fresh, dried, plants, and soil) ranged from 93.1–107.5% with relative standard deviations of 0.7–6.4%. The half-lives of butralin in ginseng plant and soil were 10.81–18.91 days, and its final residues in ginseng, dried ginseng, ginseng plant, and soil were <0.01, <0.010–0.02, 0.011–0.19, and 0.162–0.410 mg/kg, respectively. The dietary risk quotient of butralin was $3.25 \times 10^{-4}$, which suggests that the consumption of butralin-treated ginseng during the harvest period does not affect human health.

Keywords: butralin; ginseng; degradation dynamics; final residues; dietary risk assessment

1. Introduction

Ginseng, a perennial herb that belongs to the Araliaceae family, has been used in traditional Chinese medicine as a dietary supplement for thousands of years [1,2]. Studies have shown that ginseng and its products can increase the metabolism, regulate the physiological functions, and support the treatment of cardiovascular, stomach, and liver diseases, as well as diabetes, and different types of neurasthenia [3,4]. Recently, ginseng was reported to inhibit tumour growth and improve the immunity of the organism [5].

In China, Ginseng cultivation has a long history. It has been cultivated for over 1700 years, and the large-scale production of ginseng started approximately 400 years ago. Most ginseng cultivation areas represent suitable natural forest lands after they have been logged, however, there is a limited amount of forest area in China due to its growing human population. Thus, China has gradually shifted from planting ginseng into forests to its cultivation in farms in order to protect the forest ecosystems and prevent soil erosion. However, these soil conditions do not meet the requirements for obtaining high-quality ginseng roots with a sufficient yield. Achieving high yields of ginseng roots is further complicated by its short lifespan as a perennial plant [6]. Compared to the forest cultivation of it, the damage of the weeds in the farmlands is more significant. The weeds can negatively affect the ventilation, lighting, and yield of the ginseng field and manual weeding is not only time-consuming, but it is also associated with high labour costs. To date, there are no approved herbicides for ginseng fields, and therefore, it is of great practical importance to select chemical herbicides with high efficiency and low residual content and toxicity for the mitigation of the weeds in ginseng fields.

In China, butralin (Figure S1) is commonly used as a herbicide in the cultivation of ginseng. It is a type of dinitroaniline herbicide that is used for soil treatment before
germination takes place [7]. Since the 1980s, butralin has been used as a sucker control agent to slow the growth of tobacco axillary buds [8]. Due to its contact-killing ability and local absorption, butralin can be absorbed by the roots and buds of plants to inhibit the division and differentiation of the meristem cells in plants, thereby effectively hindering the growth of the weeds [9]. Moreover, it has the ability to limit the growth of a wide range of weeds, as well as having a low toxicity level and low amounts of residue and a high safety factor. Therefore, in recent years, butralin has been increasingly used as a selective preemergence herbicide to control the annual gramineous and broadleaf weeds [10]. Based on the results of the field pesticide effect experiment, butralin has the highest efficacy for controlling the weeds in ginseng fields.

Butralin residue detection has been reported in tobacco [11–13], soil [14], soybean [15,16], fruit [17], and rice [18]. As ginseng contains saponins, volatile oils, phenols, amino acids, organic acids, vitamins, fats, sterols, and other components, its matrix is complicated. When the physical and chemical properties of pesticides are unstable or the concentration of the target analyte is too low, the detection of pesticide residues in ginseng is difficult to achieve [19]. However, few studies have investigated the dissipation behaviour, residual level, and risk assessment of butralin application on ginseng. In this study, we aimed to investigate the degradation behaviour and residue distribution of butralin in the field using established methods, as well as the associated dietary risks of it.

2. Materials and Methods

2.1. Field Experiment

In 2019, field experiments for identifying the dissipation and terminal residues were conducted in Baishan, Fusong County, and Yanji of the Jilin Province, as well as in Huanren County of the Liaoning Province, China. The experiments were performed according to NY/T788-2018 guidelines on pesticide residue trials, which were issued by the Ministry of Agriculture, China. The formulation that was used was 48% butralin emulsifiable concentrate (EC) (recommended dose is 1800 g a.i./ha), and the Damaya variety of ginseng was used.

The residue dissipation experiments were conducted on the soil where the ginseng was grown. The plot area was 50 m$^2$, and 48% butralin EC was applied to the soil once at a dosage of 1800 g a.i./ha. We used the soil spray method, which involved evenly spraying butralin on the soil surface. Soil samples were collected randomly from the sampling plots at 0 (2 h after spraying), 1, 3, 7, 14, 20, 30, 45, and 60 days after the application. The ginseng plant samples were collected at days 0, 1, 3, 7, 14, 20, 30, 45, and 60, and harvested after the ginseng plant reached a height of 15 cm after the butralin application.

In terminal residue experiments, the plot area was 50 m$^2$, and the formulation was applied before the emergence of ginseng at a dosage of 1800 g a.i./ha. Ginseng (underground fleshy root part), ginseng stems and leaves, and ginseng soil samples were collected during harvest. Additionally, a control was set up as a protective belt between the treatment areas.

2.2. Instruments and Chemicals

The Agilent 1260-6470 LC-MS/MS system (Agilent Technologies, Santa Clara, CA, USA) which comprised a high-performance liquid chromatograph that was connected to a triple quadrupole MS analyser with an electrospray ionisation (ESI) interface was used. A Zorba $\times$ RRHD Eclipse Plus C18 column (3.0 $\times$ 50 mm, 1.8 µm) was employed for the separation of the analyte at 30 °C.

The butralin standard (98.7% purity) was purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Methanol (HPLC grade) and acetonitrile (HPLC grade) were purchased from MREDA Technology Inc. (Beijing, China). Formic acid (99.9% purity, HPLC grade) was purchased from Fuchen Chemical Reagent Co., Ltd. (Tianjin, China). Ammonium acetate (HPLC grade) was purchased from Sigma-Aldrich Chemicals (Shanghai, China). Sodium chloride (NaCl) was purchased from Beijing Chemical Works (Beijing, China). HPLC grade water was provided by Wahaha Group Co., Ltd. (Hangzhou, Zhejiang,
China). A CleanertNH₂ cartridge (1 g/6 mL) was purchased from Agela Technologies Inc. (Newark, DE, USA).

2.3. Preparation of Standard Solutions

The butralin standard (0.0101 g) was accurately weighed and diluted to 10 mL with methanol to prepare a standard stock solution with a concentration of 1000 mg/L. The standard stock solution of butralin was diluted with acetonitrile to prepare a standard working solution with a concentration of 100 mg/L.

2.4. Extraction and Purification

According to GBT19506-2009 “Product of geographical indication-Jilin Chang Baishan ginseng”, the fresh ginseng was stored at −20 °C, sliced using a microtome, and dried in an oven at 80 °C for 24 h. The dried ginseng was crushed using a food processor, passed through a sieve with a diameter of 180 µm, packed, sealed, and stored at −20 °C.

Fresh ginseng roots or ginseng plant samples (20 g) were weighed accurately and placed in a 250 mL beaker. Subsequently, 100 mL of acetonitrile/water (8:2, v/v) solution was added to the beaker; the mixture was homogenised at high speed for about 2 min and filtered under vacuum into a stopper measuring cylinder containing 5–7 g sodium chloride. The cylinder was shaken 250 times before it was left on the table for more than 1 h. Sufficient time was allowed to pass before the phase separation of the acetonitrile and water was performed.

Five grams of dried ginseng sample or 20.0 g of ginseng soil sample were weighed accurately and placed into a 250 mL flask with a stopper, and 50 mL of acetonitrile/water (8:2, v/v) was added. The flask was shaken for 1 h and filtered under a vacuum into a stopper measuring cylinder containing 5–7 g sodium chloride. The cylinder was shaken 250 times before it was placed on the table for over 1 h.

The acetonitrile phase (20 mL) was placed in a 250 mL flat-bottomed flask and evaporated to near dryness in a 40 °C water bath. The extract in the flat-bottomed flask was redissolved in 2 mL acetonitrile/methylbenzene (3:1, v/v) solution and purified using an NH₂ cartridge. The NH₂ cartridge was pre-eluted with 4 mL acetonitrile/methylbenzene (3:1, v/v) solution, and the effluent was discarded. The redissolved solution was transferred to the cartridge when the liquid level dropped to the top of the column packing. It received a new flat-bottomed flask, which was washed three times with 2 mL of acetonitrile/methylbenzene (3:1, v/v) solution, and transferred to the cartridge. Finally, 20 mL of acetonitrile/methylbenzene (3:1, v/v) solution was used to elute the pesticides and chemicals in the cartridge. The eluate was collected and evaporated to near dryness at 40 °C. The remaining droplets in the flask were dried with nitrogen. Acetonitrile/methylbenzene (5 mL; 3:1, v/v) solution was added to the above flat-bottomed flask to rinse it, and the mixture was then mixed, filtered through a 0.22 µm filter membrane, and analysed using HPLC-MS/MS.

2.5. Chromatographic and Mass Spectrometric Parameters of LC-MS/MS

For the chromatography, the Agilent Zorba × RRHD Eclipse Plus C18 column (3.0 × 50 mm, 1.8 µm) was used at 30 °C. The mobile phase consisted of methanol and aqueous solution (with 0.1% formic acid and 5 mmol ammonium acetate) at a ratio of 8:2 (v/v), the flow rate was 0.3 mL/min, and the injection volume was 5 µL.

Mass spectrometry was conducted using ESI in positive ion mode. The scanning method was multiple reaction monitoring (MRM), capillary voltage was 4000 V, nebulising gas was nitrogen, the pressure of the nebulising gas was 0.207 Mpa, temperature of the drying gas was 300 °C, drying gas flow rate was 7 L/min, sheath gas temperature was 300 °C, and sheath gas flow rate was 8 L/min. The mass spectrometry parameters of butralin are listed in Tables S1 and S2.

For the recovery test, 20 g of fresh ginseng, 5 g of dried ginseng, 20 g of ginseng plant, and 20 g of ginseng soil without butralin were weighed. The fresh and dried ginseng samples
were treated with 0.01, 0.05, or 0.5 mg/kg of butralin, whereas the ginseng plant and soil were treated with 0.01, 0.05, 0.5, or 10.0 mg/kg of butralin, and each treatment was repeated five times. The samples were extracted and purified according to the pre-treatment process.

In LC-MS/MS analysis, the ESI is susceptible to the influence of the matrix components other than the target compound in the sample, which compete with each other during the ionisation process to produce a matrix effect [20,21]. Matrix effects can change the accuracy and reproducibility of LC-MS/MS in quantitative analyses [22]. In order to improve the accuracy of the analysis, a concentration gradient series of standard solutions were prepared with the solvent and blank matrix extraction solutions. The prepared concentration series were analysed under the same chromatographic conditions. According to the calibration curve slope of the standard solution, Equation (1) (He et al. [23]) was used to calculate the matrix effect of fresh and dried ginseng, ginseng plant, and soil.

\[ M_e = \frac{K_{\text{matrix}}}{K_{\text{solvent}}} \]  

where, \( K_{\text{matrix}} \) is the slope of the standard curve prepared using the matrix blank extract, and \( K_{\text{solvent}} \) is the slope of the standard curve prepared using acetonitrile. With an \( M_e \) value of 0.8–1.2, the matrix effect can be ignored, whereas an \( M_e \) value of >1.2 results in a matrix enhancement effect, and an \( M_e \) value of <0.8 results in a matrix weakening effect.

According to the national food safety standard GB 2763-2019, the ADI value of butralin is 0.2 mg/kg bw. As butralin is considered to be a low toxicity herbicide, a short-term dietary risk assessment of butralin in ginseng was not conducted, but the long-term dietary intake risk assessment was calculated using Equations (2) and (3):

\[ \text{NEDI} = \sum \left[ \text{STMRi} \times \text{Ei} \times \text{Pi} \times \text{Fi} \right] / \text{bw} \]  

\[ \text{RQ} = \frac{\text{NEDI}}{\text{ADI}} \]  

where NEDI is the estimated daily intake in mg/kg bw, STMRi is the median value of the standardised residue experiment in category i food, \((\text{STMRi} \times \text{Ei} \times \text{Pi}) \times \text{Fi}\) refers to the median value of the standard residue experiment which was corrected by the edible part coefficient \( E_i \) and the processing factor \( P_i \), \( F_i \) is the average daily dietary intake of the food, ADI is the allowable intake of pesticides per kilogram of body weight, and RQ is the risk entropy value. Generally, the risk entropy RQ, which is the percentage of the estimated daily intake to the ADI value, is used to express the risk. When RQ < 1, it is expressed as an acceptable risk; the smaller the value is, then the smaller the risk is. Conversely, if RQ ≥ 1, it is expressed as an unacceptable risk, and the greater the value is, then the greater the risk is. According to the Ministry of Health, the consumption of ginseng, which is artificially grown for 5 years or fewer, should not exceed 3 g/day, and the per capita weight in China is calculated to be 63 kg. Dietary risk assessment was carried out on the final field residue data of butralin-treated ginseng in 2019.

3. Results and Discussion

3.1. Optimisation of Mass Spectrometry Conditions

To achieve the highest detection sensitivity of butralin, a 1.0 mg/kg of butralin standard solution was directly injected at a flow rate of 0.3 mL/min to scan it in the positive and negative ionisation modes (ESI+ and ESI−). In ESI+, the precursor ion peaks with a higher abundance \([M+H]^+\) were obtained. In the negative ion mode (ESI−), the abundance and response of the precursor ion peaks were lower than those in the positive ion mode. This is due to the secondary amine group of butralin, which can easily be added to obtain positive ions, resulting in a remarkable ionisation effect of the \([M+H]^+\) ion peak of butralin in the positive ion mode. The characteristic ions of the products were obtained by further optimising the conditions of the secondary mass spectrometry, and the two ions with a strong abundance, higher response values, and less interference were selected as the quali-
tative and quantitative ion pairs. The ion transitions that were obtained were 296.2/240.2 and 296.2/222.2.

3.2. Optimisation of Chromatographic Conditions

The C18 chromatographic column has an adequate resolution and a strong retention for most compounds, and it is widely used in liquid chromatography. Thus, the Eclipse Plus C18 (3.0 × 50 mm 1.8 µm) chromatographic column was selected for this experiment. For the reversed-phase chromatography, acetonitrile and methanol are commonly used as the organic mobile phase solvents. The surface tensions of the acetonitrile and methanol were 0.030 and 0.024 N/m, respectively. When the surface tension of the solvent is small, then the atomisation efficiency is high [24], the generation rate of the pesticide-charged ions is relatively high, and the mass spectrum peak area response is strong. Therefore, the organic mobile phase in this study was a methanol solution with a smaller surface tension, and under the condition of the isocratic elution, the response value and peak shape of butralin under different mobile phase conditions were observed as shown in Figure 1. The response value of butralin was the highest and the peak type was sharper when the organic phase consisted of a pure methanol solution and the aqueous phase contained 0.1% formic acid and 5 mmol ammonium formate. The H+ in the formic acid promoted the ionisation of [M+ H+] the ion peaks and improved the response of them. In addition to stabilising the pH value of the buffer solution and increasing its capacity, the buffer salt in the aqueous phase has been shown to increase the ionic strength of the mobile phase, which reduces the tailing factor and the peak width, and notably improves the peak type [25]. Therefore, methanol and water (0.1% formic acid + 5 mmol ammonium acetate) were used as the mobile phase. The relative retention time of butralin on LC-MS/MS was approximately 5.4 min.

![Figure 1. The effects of different mobile phase combinations on the chromatographic peak of butralin. We compared (a) methanol and water (0.1% formic acid + 5 mmol ammonium formate), (b) methanol and water (0.1% formic acid), (c) methanol and water (5 mmol ammonium hydroxide), and (d) methanol and water.](image-url)
3.3. Linearity and Matrix Effect

A matrix standard curve was obtained by diluting the matrix standard solution to concentrations of 0.002, 0.005, 0.01, 0.02, 0.05, 0.1, 0.2, and 0.5 mg/L. A standard curve was plotted, and a linear regression equation was established with the concentration of butralin (x) as the abscissa and the peak area (y) as the ordinate. As shown in Table S3, the correlation coefficients (r) were between 0.9979 and 0.9997 and the p-Value is <0.0001 for all, which indicated that a good linearity was obtained for butralin.

As shown in Table S3, the Me values of butralin in the fresh and dried ginseng, and the ginseng plants and soil were all greater than 1.2, showing that it had a matrix enhancement effect. Therefore, to ensure the accuracy of the analysis method that is in this experiment, the matrix effect of the sample was eliminated by using the matrix matching standard solution to correct the sample, which meets the requirements of the residue analysis.

3.4. Recovery and RSD

The results showed that similar recoveries of butralin were obtained from the fresh and dried ginseng, the ginseng plant, and the soil samples (Table S4). The limit of quantitation (LOQ) of butralin was 0.01 mg/kg, and the limit of detection (LOD) was $1.1 \times 10^{-5}$ ng. The accuracy and precision met the requirements of the quantitative analysis of pesticide residues.

3.5. Dissipation Behaviour of Butralin in Ginseng Plant and Soil Samples

The field dissipation kinetic experiments were performed in Baishan, Jilin Province and Huanren County, Liaoning Province in 2019. The dissipation kinetics of butralin in different samples were analysed using a first-order kinetic model, which can be calculated using Equation (4).

$$C_t = C_0 e^{-kt}$$ (4)

where k is the degradation rate constant, $C_0$ is the initial concentration of the pesticide, which is also called the original deposition amount, and $C_t$ is the concentration of the pesticide at time t. As shown in Table 1, the residual amount of butralin in the ginseng soil gradually decreased with the extension of the harvest interval after the application of it. The original deposition amount of butralin in the ginseng soil sample from Baishan was 2.53 mg/kg. After 3 days, the residual amount of butralin in the soil sample had decreased notably, and a further decrease was observed after 60 days, where the residual amount of butralin in the ginseng soil sample was 0.322 mg/kg and the dissipation rate reached 87.3%. The original deposition amount of butralin in the ginseng soil sample from Huanren was 1.366 mg/kg. After 3 days, the residual amount of butralin in the sample had decreased notably, and after 60 days, the residual amount of butralin in the ginseng soil sample was 0.293 mg/kg, and the dissipation rate reached 78.6%. The half-lives of butralin in the ginseng soil samples of Baishan and Huanren were 12.63 and 18.91 days, respectively. This shows that butralin degrades quickly in the ginseng soil, and butralin can therefore be characterised as an easily degradable pesticide ($t < 30$ days).

The original deposition amount of butralin in the ginseng plant samples from Baishan was 3.139 mg/kg (Table 1). At day 60, after the application, the residual concentration of butralin in the ginseng plant samples was 0.356 mg/kg, and the dissipation rate reached 88.7%. The original deposit amount of butralin in the ginseng plant sample from Huanren was 2.511 mg/kg, and after 60 days, the residual concentration of butralin in the ginseng plant sample was 0.276 mg/kg, and the dissipation rate reached 89.0%. The half-lives of butralin in the ginseng plant samples of Baishan and Huanren were 11.80 and 10.81 days, respectively.
Table 1. Degradation dynamics of butralin.

| Sampling Days (d) | Ginseng Soil | Ginseng Plant |
|-------------------|--------------|---------------|
|                   | Baishan      | Huanren       | Baishan      | Huanren       |
|                   | Residue (mg/kg) | Dissipation Rate (%) | Residue (mg/kg) | Dissipation Rate (%) | Residue (mg/kg) | Dissipation Rate (%) | Residue (mg/kg) | Dissipation Rate (%) |
| 0                 | 2.530        | -             | 1.366        | -             | 3.139         | -             | 2.511         | -             |
| 1                 | 2.026        | 19.9          | 1.211        | 11.3          | 2.571         | 18.1          | 1.874         | 25.4          |
| 3                 | 1.584        | 37.4          | 0.848        | 37.9          | 2.430         | 22.6          | 1.646         | 34.4          |
| 7                 | 1.310        | 48.2          | 0.824        | 39.7          | 2.021         | 35.6          | 1.397         | 44.3          |
| 14                | 1.118        | 55.8          | 0.678        | 50.4          | 1.280         | 59.2          | 0.928         | 63.0          |
| 20                | 0.846        | 66.6          | 0.659        | 51.8          | 0.907         | 71.1          | 0.807         | 67.9          |
| 30                | 0.674        | 73.4          | 0.527        | 61.4          | 0.505         | 83.9          | 0.459         | 81.7          |
| 45                | 0.518        | 79.5          | 0.336        | 75.4          | 0.435         | 86.2          | 0.458         | 81.7          |
| 60                | 0.322        | 87.3          | 0.293        | 78.6          | 0.356         | 88.7          | 0.276         | 89.0          |

The half-life of butralin in the ginseng plants was found to be lower than it was in the ginseng soil. The reason for this may be that the growth and development status and the physical and chemical characteristics of ginseng plants have a certain influence on the degradation of butralin. The reported half-life of butralin in the soil is 9.04–11.17 days [26], and the half-life of butralin in tobacco leaves was reported to be 5.2–12.2 days [15,16]. The half-life of butralin in the ginseng plant was found to be similar in this experiment, whereas the half-life of butralin in the ginseng soil was relatively longer. As ginseng is cultivated in a shed, after spraying it with butralin, the ginseng soil was less affected by light, rainfall, and other environmental factors, and photolysis and hydrolysis are important for the degradation of the pesticides [27]. This may result in a relatively slow degradation of butralin in the ginseng soil. The differences in the climate, soil microbiome, organic matter content, and uniformity of the field test sample collection are also factors that affect the degradation of the pesticides in the soil [28].

3.6. Terminal Residues of Butralin in Ginseng

The results of the final residue experiment in Yanji, Baishan, Fusong County of the Jilin province, and Huanren County of the Liaoning Province are shown in Table 2. Before the emergence of ginseng, 48% of the butralin EC was applied once at a dosage of 3750 g/ha (1800 g a.i./ha). The final residues of butralin were <0.010–0.010 mg/kg in fresh ginseng, <0.010–0.024 mg/kg in dried ginseng, 0.011–0.190 mg/kg in ginseng plant, and 0.162–0.410 mg/kg in ginseng soil. The results of the final butralin residue analysis in different geographical positions were similar, and there were no notable differences between the butralin residue levels that were detected in the same matrices. The final residues of butralin in the ginseng soil that were collected during the harvest period were also consistent with the digestion trend of butralin residue which was determined in the degradation dynamics experiment.

Table 2. Final residue of butralin in fresh ginseng, dried ginseng, ginseng plant, and ginseng soil.

| Sample Type    | Dosage (g a.i. ha\(^{-1}\)) | Numbers of Times Sprayed | Terminal Residue |
|----------------|-----------------------------|--------------------------|-----------------|
|                |                             |                          | Yanji | Baishan | Fusong | Huanren |
| Fresh ginseng  | 1800                        | 1                        | 0.010 | 0.01   | <0.01  | <0.01  |
| Dried ginseng  | 1800                        | 1                        | 0.015 | 0.01   | <0.01  | 0.024  |
| Ginseng plant  | 1800                        | 1                        | 0.011 | 0.018  | 0.020  | 0.190  |
| Ginseng soil   | 1800                        | 1                        | 0.256 | 0.272  | 0.162  | 0.410  |
3.7. Dietary Risk Assessment

The total NEDI of butralin was calculated using the STMRs and MRLs (Table S5). The STMRs were obtained from terminal residues experiments in this paper, and the selection of reference MRLs (of the relevant registered crops in China) adhered to the following priority order: China, Codex Alimentarius Commission (CAC), US, Australia, Korea, EU, and Japan [29]. The average body weight of Chinese adults was calculated to be 63 kg [30].

The median butralin residue in dried ginseng was 0.013 mg/kg. The total NEDI was 0.0251 mg, and the RQ value was $2.0 \times 10^{-3}$, showing that the dietary risk of butralin in dried ginseng is low and acceptable.

Therefore, butralin can be safely used as an effective herbicide in the cultivation of ginseng. In this study, we demonstrated that use of butralin at the recommended dosage and application times does not pose an unacceptable risk to human health after the ginseng is harvested.

4. Conclusions

This study aimed to detect the butralin residues in ginseng ecosystems under open-field conditions by establishing a detection method based on HPLC-MS/MS. The risk quotient of butralin was calculated to be $3.25 \times 10^{-4}$, showing that the intake of residual butralin that is contained in ginseng presents an acceptable risk. Moreover, the potential dietary risk of residual butralin in ginseng was found to be not significant for consumers.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/agronomy12112675/s1, Figure S1: Chemical structure of Butralin; Table S1: The MRM for analysis of Butralin; Table S2: The parameters for the ESI source in HPLC-MS/MS; Table S3: Linear equation and matrix effect of butralin in different ginseng matrices; Table S4: Recovery and RSD ($n = 5$) of butralin in ginseng; Table S5: The long-term dietary intake risk assessment of butralin based on the Chinese dietary pattern.

Author Contributions: The contributions of the authors were as follows: Conceptualisation, X.W. and Z.H.; methodology, X.W. and Q.Y.; validation, Q.Y. and X.Y.; formal analysis, H.G., Y.G., L.W. (Liran Wang) and L.W. (Liping Wei); resources, Z.L. and Z.H.; original draft preparation, X.W.; manuscript review and editing, Z.H.; funding acquisition, Z.L. and Z.H. All authors have read and agreed to the published version of the manuscript.

Funding: Partial funding was received from the Agricultural Industry Standard of the Chinese Ministry of Agriculture (2018) (grant no. 181721301092371097) and Jilin Agricultural University Undergraduate Science and Technology Innovation Fund (2021) (grant no. S202110193073).

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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