Dissipation, residues and evaluation of processing factor for spirotetramat and its formed metabolites during kiwifruit growing, storage and processing

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Research Article

Keywords: Kiwifruit, Spirotetramat, Metabolites, Dissipation dynamics, Storage stability, Processing factor

Posted Date: September 28th, 2023

DOI: https://doi.org/10.21203/rs.3.rs-3334098/v1

Version of Record: A version of this preprint was published at Environmental Science and Pollution Research on December 26th, 2023. See the published version at https://doi.org/10.1007/s11356-023-31639-6.

Abstract

Spirotetramat is widely used around the world to control sucking pests and may form in agricultural products. In the current study, the dissipation, residues and evaluation of processing factor (PF) for spirotetramat and its formed metabolites were investigated during kiwifruit growing, storage and processing. The residue analysis method was established based on high-performance liquid chromatography tandem mass spectrometry (HPLC-MS/MS) combined with a QuEChERS method to detect the residues of spirotetramat and its metabolites in kiwifruit and its processed products. The method provided recoveries of 74.7 – 108.7%, and the relative standard deviations (RSDs) were 0.6–13.1%. The residues dissipated following the first-order kinetics with a half-life of 9.90–10.34 days in the field and 24.75–30.13 days during storage. Residues of spirotetramat and its formed metabolites in kiwifruit would not pose dietary risk to consumers. Moreover, the peeling and fermentation was the highest removal efficiency for the spirotetramat and its formed metabolites residues during prosessing. The PF values calculated after each individual process were < 1, indicating significant reduction of residues in different processing processes of kiwifruit. The spirotetramat was degraded during kiwifruit wine-making process with half-lives of 3.36–4.91 days. B-enol and B-keto were the main metabolites detected in kiwifruit and its processed products. This study revealed the residues of spirotetramat and its formed metabolites in kiwifruit growing, storage and processing, which helps provide reasonable data for studying the dietary risk factors of kiwifruits and products.

Introduction

Kiwifruit has become a very popular product all over the world. It contains high level of sugars, dietary fiber, vitamin C and bioactive compounds, which helps prevent cancer, functional gastrointestinal disorders and cardiovascular-related diseases (Wang et al. 2023). Over the past few decades, the production of kiwifruit has increased greatly. Kiwifruit production was for more than 2.23 million tons in 2020 in China, which is the world's largest producers around the world. And Kiwifruit production accounted for 33.6% of the world. Nevertheless, with the enlargement of kiwifruit cultivation, serious pest problems had emerged. In order to reduce the economic losses, many insecticides were frequently used by growers in kiwifruit. The unreasonable application of pesticides leads to large amounts of residues in agricultural products and may be further transferred to processed products (Tian et al. 2022b). It may lead to increased health risks for consumers. As a result, more and more attention has been paid to the problem of pesticide residues in kiwifruit and its processing products.

Spirotetramat is a new type of quaternary ketonic acid insecticide. It is an inhibitor of lipid biosynthesis that inhibits Acetyl-CoA carboxylase. Spirotetramat penetrates into leaves and is defatted, which can conduct bidirectional conduction in xylem and phloem of the plants. It can be used to control sucking pests such as whitefly, aphids, psyllid on field crops, vegetables and fruit trees (Wang et al. 2022). At present, spirotetramat is widely used around the world. B-enol, B-mono, B-keto and B-glu are the major metabolites of spirotetramat. And some studies have confirmed that B-enol may cause reproductive toxicity in male rats (Li et al. 2016). More and more attention has been paid to pesticide metabolites with toxicological significance. However, the dissipation of spirotetramat and its four metabolites was not determined in kiwifruit and tis processing products. Thus, evaluating the dissipation of spirotetramat and its four metabolites has great significance during kiwifruit growth, storage and processing to ensure food safety.

At present, the research on spirotetramat in literature mainly includes detection and analysis methods, residual and dissipation dynamics tests, and the impact of processing or cooking methods on residue levels. Several methods for simultaneous determination of spirotetramat and its four metabolites by high-performance liquid chromatography tandem mass spectrometry (HPLC-MS/MS) combined with a modified QuEChERS procedure in vegetables, cereals, fruits or fruit products have been described in the literature (Chen et al. 2016, Faraji et al. 2018, Li et al. 2016, Zhu et al. 2013). For example, Li et al. conducted the analysis of spirotetramat and its four metabolites in vegetables and fruits using HPLC–MS/MS (Li et al. 2016). The studies on residual and dissipation dynamics tests mainly included the final residual and dissipation patterns of spirotetramat and its metabolites in tomato, citrus, soil, spinach, cotton, pepper, soybean and eggplant (Bhardwaj et al. 2016, Chen et al. 2016, Pandiselvi et al. 2010, Shukla et al. 2016, Vinothkumar et al. 2012, Zhang et al. 2018). The half-lives of spirotetramat and B-enol in eggplant were 1.71 and 1.36 days, respectively (Bhardwaj et al. 2016, Shukla et al. 2016). The half-lives of spirotetramat and its four metabolites in citrus was 1.74–5.83 days (Ye 2018). Spirotetramat was mainly metabolized to produce B-enol, B-keto and B-glu in citrus, and B-keto and and B-glu in soil (Ye 2018). A studied by Han et al. reported that the changes in residual amounts of spirotetramat and its metabolite (B-enol) in the apple processing into vinegar, including washing, peeling and coring, juicing, primary filtration, enzymatic hydrolysis, second filtration, sterilization and fermentation (Han et al. 2013). Jiang et al. reported the effects of five commonly used household processing methods, including cleaning, peeling, boiling and so on, on the degradation of spirotetramat and its metabolites in citrus, and found that the processing factors of spirotetramat, B-enol, B-keto and B-glu were < 0.041, 0.125, 0.294 and 0.313, respectively (Liu et al. 2016). With the widespread use of spirotetramat, the residues of spirotetramat and its metabolites may exist in agricultural products. Nevertheless, up to now, the residue analytical method has not been developed for the determination of spirotetramat and its metabolites in kiwifruit and its processing products. At the same time, there was no study on the dissipation of spirotetramat and its metabolites on kiwifruit and its processed products.

Therefore, the objective of this study was to develop a modified QuEChERS method coupled with HPLC-MS/MS for the determination of spirotetramat and its metabolites, and investigate the dissipation of spirotetramat and its metabolites in field kiwifruits, during its storage and different processing technology. Meanwhile, the processing factors (PFs) for each step among different processing technology was calculated to evaluate the dietary exposure of spirotetramat and its metabolites in different processed products. The results of this study will provide scientific guidance for the safe use and production supervision of spirotetramat in kiwifruit, and offer beneficial reference value for the efficient utilization of spirotetramat. This study also contributes to providing scientific advice for enterprises to reduce pesticide residues in different processing processes of kiwifruit.

Materials and methods

Chemicals and reagents

The spirotetramat and its four metabolites were purchased from Alta Scientific Co., Ltd. (Tianjin, China) and were of more than 98% purity. The commercial preservative products of spirotetramat (22.4%, SC) was purchased from Shandong Yijia Agrochemical Co., Ltd. (Shouguang, China). LC- grade acetonitrile and formic acid were procured from Sigma Aldrich (Steinheim, Germany). The analytical-grade reagents were purchased from Beijing Chemical Company (Beijing, China): sodium acetate (NaOAc) and anhydrous magnesium sulfate ($MgSO_4$). Primary secondary amine (PSA) (40 μM) was procured from Agela Technologies (Beijing, China).

For spirotetramat and its four metabolites, individual standard stock solutions of 1000 mg L^{-1} in acetonitrile were prepared. A standard intermediate mixture of 100 mg L^{-1} was diluted with acetonitrile. All solutions were stored at -20 °C in the dark. The matrix-matched standard solutions and standard working solutions were prepared by adding the appropriate amount of blank sample extracts and acetonitrile.

Field trials

The field trials were carried out at a commercial orchard, which were located in Zhengzhou, China. The size of trial plot were 50 m^2 and spirotetramat was not used in the past three years. Three replicates were performed in experimental plots for each treatment. The plot has never been used with spirotetramat and has been selected as a control. The spirotetramat commercial product (22.4%, SC) was applied at recommended dosage (RD = 88.5 g active ingredient/hectare) and double the recommended dosage (DD = 167 g active ingredient/hectare) on kiwifruit, respectively. The foliar spraying was performed under sunny and windless conditions. The kiwifruit samples (3 kg) were collected at 2 h, 1, 3, 5, 7, 10, 14, 21, 28 and 35 d (harvest). All the samples were placed in polyethylene bags and stored at -20 °C in a refrigerator in the laboratory.

For the storage experiment, the spirotetramat commercial product (22.4%, SC) was used with the foliar spraying mode at RD level and five times of the recommended dosage (FD = 442.5 g active ingredient/hectare), respectively. 80 kg kiwifruit samples were collected at three days after applying at the RD and FD levels. For the processing experiment, the spirotetramat (22.4%, SC) was applied at FD level. And the spirotetramat was applied three times with a 7 day interval using the above method. About 300 kg kiwifruit samples were harvested after three days. Subsequently, the kiwifruit samples were processed immediately.

Storage stability

To study the dissipation of spirotetramat and its metabolites under simulated storage conditions, kiwifruits (80 kg) treated with spirotetramat at RD and FD levels were stored at 2–4 °C in thermostats. And representative kiwifruit samples (3 kg) were randomly extracted at 0, 1, 3, 5, 7, 10, 14, 21, 28, 35, 42, 49, 56, 63 and 70 d. The samples were preserved in sterile polyethylene bags at -20 °C until analysis.

Sample collection

For the processing experimental, the kiwifruits were processed into six products: slices, juice, jam, canned, vinegar and wine. High-quality kiwifruit (10 kg) gathered were used for each product. Generally speaking, the processing steps for some products are the same, including cleaning, peeling, and slicing. First, for kiwifruit slices, the kiwifruit samples were washed with tap water for 10 min, and then sliced into 1 cm after peeling. Then, in order to protect the color, the sliced kiwifruit samples were soaked in 1% ascorbic acid (VC) solution for 30 min. Next, the samples were blanched for 30 s at 100 °C in boiling water. Afterwards, the samples were placed into oven at 70 °C for 2 h, and then they were placed in polyethylene bags and stored in a refrigerator at 1–2 °C for 12 h to ensure that the water content of kiwifruit slices were uniform. Ultimately, the kiwifruit slices were dried for 3 h in puffing dryer to acquire the kiwifruit slices. In the current study, kiwifruit juice was also treated in the same method. The kiwifruit slices were homogenized after hot water blanching. Next, the pectinase (5 g kg^{-1}) and cellulose (3 g kg^{-1}) were added for enzyme treatment and placed in water bath at 55 °C for 4 h. The samples were screened for 200 mesh to obtain the juice. Then, 0.4 g L^{-1} chitosan were added juice at 50 °C for 2 h for clarification. Finally, the supernatant was centrifuged at a low speed to obtain the kiwifruit juice.

For the canned kiwifruit and kiwifruit jam, the kiwifruit was cut into small pieces after peeling. Then, 500 g samples were placed into saucepan and added 2000 mL water. Next, the samples were boiled on the induction cooker for 10 min. 10 g of rock sugar were added and stirred constantly until it was completely melted to obtain canned kiwifruit. The kiwifruit samples were homogenized, and then put the kiwifruit puree into saucepan and simmered for 30–60 min to remove excess water. The chopsticks were put into the saucepan. The slow decline of kiwifruit puree from the chopsticks indicated completion of enrichment. The kiwifruit jam was obtained.

For the kiwifruit vinegar, 1500 g of kiwifruits samples were crushed and placed into a fermenter tank. Then, 3 L of pure water, 630 g of sucrose and 75 g of yeast powder were added into the tank with even stirring. The mixture was stirred three times a day. The tank was fermented at 20 ± 2°C for 20 days. Afterward, the fermentation supernatant was obtained by filtration and kept at 30 ± 2°C for 10 days to produce kiwifruit vinegar.

For the kiwifruit wine, the experiment was carried out into three groups (Group A, B and C). The groups were: removing the branches (Group A); washing with tap water for 10 min, and then removing the branches (Group B); washing with tap water for 10 min and removing the branches, and then then peeling artificially after the surface dried (Group C). Subsequently, the processing steps of the three groups are the same. Kiwifruits samples (5 kg) were crushed and placed into a 20 L fermenter tank. Then, 40 mg kg^{-1} of pectinase and 30 mg L^{-1} of SO_2 was added for Enzymatic and bactericidal treatment, respectively. After 2 h, 0.5 g kg^{-1} of *Saccharomyces cerevisiae* powder and 75 g kg^{-1} of sucrose was added into the tank for fermentation. The fermentation tanks were kept at 25 ± 1°C in a constant temperature incubator during the alcoholic fermentation process to obtain the kiwifruit wine. After 7 days, the fermentation process was completed. And the kiwifruit wine were separated by filtering. Subsequently, 1 g kg^{-1} of bentonite was added to the wine for clarification. Forty-eight hours later, the supernatant (clarified kiwifruit wine) were separated by siphoning. The representative samples were collected at each steps of different processed products to detect the level and variation of spirotetramat and its four metabolites in the course of processing.

Extraction, purification and analysis

Extraction and clean-up of kiwifruit, slices, juice, jam, canned, vinegar, wine and pomace samples was performed according to the method described by Tian et al. (Tian et al. 2023). Ten gram homogenized samples (kiwifruit, slices, juice, jam, canned, vinegar, wine and pomace) were placed into 50-mL polypropylene centrifuge tubes. Then, the tubes were treated with acetonitrile (10 mL) in 1% acetic acid. The samples were mixed thoroughly using a vortex mixer for 10 min. Afterwards, 4 g of anhydrous $MgSO_4$ and 1 g of anhydrous NaOAc were added, then mixed by shaking vigorously for 5 min on vortex and centrifuged at 2880 *g* for 5 min. The supernatant (1.5 mL) was transferred to a new clean centrifuge tube (2 mL) containing 50 mg PSA and 150 mg anhydrous $MgSO_4$. The tubes were mixed thoroughly using a vortex mixer for 1 min and centrifuged for 5 min at 2400 *g*. The supernatant (1 mL) was used for HPLC-MS/MS analysis after filtering through 0.22 μm nylon syringe filter.

Analysis by HPLC-MS/MS

The separation and analysis of spirotetramat and its metabolites were carried out with a HPLC-MS/MS system containing an Agilent 1290 Infinity LC coupled with 6460 triplequad mass spectrometer (Agilent technologies, Palo Alto, CA, USA). The separation of the target compounds was performed using an Agilent Poroshell 120 EC-C18 column (2.1 × 100 mm id, 2.7 μm particle size). The column was kept at a constant temperature of 35 °C to decrease viscosity. The mobile phase was water with 0.2% formic acid (A) and acetonitrile (B) and the flow rate was 0.3 mL min^{-1}. A gradient programme was as follows: 0 min 90% A phase; 1 min 60% A phase; 2–5 min 10% A phase; 5.1 min 90% A phase; 6 min 90% A phase. 5 μL (supernatant) was injected using an auto-sampler. The analytes were eluted within 3 min. The typical parameters were as follows: sheath gas flow 12 L min^{-1}; sheath gas temperature, 350 °C; drying gas flow 8 L min^{-1}; drying gas temperature 350 °C; nebulizer gas, 35 psi; capillary voltage, 4000 V. The determination of the spirotetramat and its metabolites was performed in multiple reactions monitoring (MRM). And the electrospray ionization (ESI) source in positive mode was chosen for the analysis of the target compounds. Ultimately, the mass parameters for each analyte were listed in Table S1.

Data analysis

The data were analyzed using the SPSS software (version 19.0 for Windows). All data were expressed as the means ± standard deviation. Dissipation kinetics of spirotetramat and its metabolites in kiwifruit was researched by using the best fit curve based on the data and the half-life was also calculated. The processing factors (PFs) are frequently used to evaluate data on pesticide residues in food processing. The calculation of PF was based on the following equation:

$$\mathrm{PFs} = \frac{\mathrm{Residuelevelinprocessedcommodity}}{\mathrm{Residuelevelinrawagriculturalcommodityorcommoditytobeprocessed}}$$

When the PFs values < 1, the pesticide was reduced during processing. It's worth noting that the pesticide was increased when the PFs values > 1.

Results and discussion

Method performance

The analysis method was validated and the satisfactory results were obtained, which accorded with the requirements of Chinese agricultural standards (NY/T788 2018). For the recoveries, the residues were estimated by comparing the peak area of the standard with that of spiked samples operating under the same conditions. The recoveries of spirotetramat and its four metabolites from kiwifruit, slices, juice, jam, canned, vinegar, wine and pomace were within the acceptable range of 74.7–108.7% at four fortified concentration levels (Table S2). The LOQ of the spirotetramat and its four metabolites was 1 μg kg^{-1} where they could be quantitatively detected at the minimum spiked concentration of each target analytes with acceptable recovery and precision. A good linearity was obtained at seven point range of 1-5000 μg L^{-1} and the correlation coefficient of determination (R^2) in matrix-matched standards and acetonitrile were always ≥ 0.9968. The accuracy of the developed method validated by spiking spirotetramat and its four metabolites at four concentrations (1, 100, 1000 and 5000 μg kg^{-1}) was satisfactory, as the recoveries of each target compounds were > 70% in all matrices. The intra-day precision expressed as RSD_r ranged from 0.6 to 9.4%. The inter-day precision expressed as RSD_R was calculated by analyzing the spiked samples on different three days and was within 1.3-13.1%. The matrix effect can suppress or enhance analyte signals, leading to quantification errors. Hence, in order to reduce the effect of matrix suppression or enhancement on the recoveries of target compounds, all quantifications in this study were performed using external matrix-matched calibration curves to obtain accurate results. These results indicated that the developed method was effective for the determination of the five analytes in kiwifruit and its products

Spirotetramat and its metabolites dissipation in the field

Figure 1(A, B) shows the residues of spirotetramat and its metabolites in kiwifruit throughout the entire experimental period at the RD and DD treatments. The average residues of spirotetramat were 158.4 ± 9.8 and 247.5 ± 19.6 μg kg^{-1} after 2 h of application of the RD and DD, respectively. The spirotetramat residues were decreased with the time. With 5 days about 62.4% spirotetramat residues dissipated from kiwifruit fruits at the RD, whereas 42.7% residue dissipation had occurred at the DD. After 10 days the residues dissipation of spirotetramat remained at 73.1% and 64.3% at the RD and DD, respectively. After 35 days, the residue dissipation of spirotetramat increased to 92.8% and 89.0% at the two dosages and the similar dissipation patterns of spirotetramat were observed at the two dosages. Meanwhile, spirotetramat dissipation occurring in the kiwifruit matrix followed the first-order kinetics (R^2 = 0.8964 at the RD and R^2 = 0.9551 at the DD) (Table 1). The half-lives for degradation of spirotetramat on kiwifruit was calculated to be 9.90 and 10.34 days, after application using the RD and DD, respectively (Table 1), a litter shorter than those of 30.1, 20.2, 12.4 and 12.0 days reported in persimmon, apricot, pear and hawthorn, respectively (Qian et al., 2019). Some studies also found that the half-lives of spirotetramat were 1.21 and 1.36 days in pepper and brinjal, respectively (Bhardwaj et al. 2016, Li et al. 2016). The half-lives were also longer than those of 1.6 and 6.2 days in citrus and peach, respectively (Ding et al. 2018, Tian et al. 2023). The results also indicated that the half-life values for degradation of spirotetramat were not significant different in kiwifruit at the RD and DD. The results were consistent with others. For instance, a study by Bhardwaj et al. proved that the half-lives of spirotetramat in brinjal were 1.09 and 1.36 days at dose of 625 and 1250 mL/ha, respectively (Bhardwaj et al. 2016), and the half-lives of isocycloseram in cabbage, cyflumetofen, tebuconazole, and triadimefon in cucumber were also similar from treatments at different dosages (Luo et al. 2022, Zhang et al. 2021). However, Mohapatra et al. found that the half-lives of spirotetramat were 3.3 and 5.2 days in mango from 90 and 180 g a.i./ha treatments, respectively (Mohapatra et al. 2012). The differeces of the half-lives of spirotetramat were observed in different crops. This is mainly due to different conditions, such as climate, amount of pesticide application, formulations, type of application, rainfall, temperature and crop types and so on (Kabir et al. 2017, Saber et al. 2016).

At present, the metabolites of pesticides have become one of the hot topics in the safety evaluation of pesticide residues. Some studies have reported that the main metabolites of spirotetramat in fruits and vegetables were B-enol, B-keto, B-mono and B-glu, also found that the types and content distribution of residual metabolites in different crops are different. For example, Chen et al. found that there were differences in the metabolic pathways of spirotetramat in the leaves, stems and roots of spinach. Spirotetramat was first metabolized to B-enol and B-keto on leaves, and then B-enol was further transformed into B-glu; in the stem, it was only degraded to B-enol, which then was transformed into B-glu; only B-enol was ultimately generated on the root. The total residue level was manifested as spinach leaves>stems>roots (Chen et al. 2016). Łozowicka et al. also found that spirotetramat could generate three metabolites in Dutch celery, dill, and radish tender leaves, with concentrations ranging from B-enol to B-keto > B-glu, while only the metabolite B-enol was generated in the roots. Moreover, the degradation pathways of spirotetramat in the tender leaves and roots of these three crops are the same as those in spinach leaves and roots, respectively (Lozowicka et al. 2017). B-mono is rarely detected in fruits and vegetables. In this study, spirotetramat was mainly degraded to B-enol and B-keto in kiwifruit, and B-mono and B-glu were not detected under field conditions. Figure 1(A, B) showed the residues of B-enol and B-keto in

kiwifruit over the time period of the experiment at the RD and DD. The concentrations of B-enol decreased gradually with time elapse at different dosages. The maximum residues of B-enol were 97.4 ± 8.6 μg kg^{-1} and 86.9 ± 6.1 μg kg^{-1} after two hours at the RD and DD, respectively. The concentrations of B-keto increased in the first 14 days and then decreased with time at different dosages. And the maximum residues of B-keto were 36.2 ± 2.7 μg kg^{-1} and 52.1 ± 4.1 μg kg^{-1} at the RD and DD at 14 days, respectively. In the 35 days after application, the residues of B-enol and B-keto were 13.8 ± 1.1 μg kg^{-1} and 20.0 ± 1.3 μg kg^{-1} at RD, and 19.5 ± 1.6 μg kg^{-1} and 39.0 ± 2.9 μg kg^{-1} at DD, respectively. The results also indicated that spirotetramat may be first degraded to B-enol, which then was transformed into B-keto. It was basically consistent with those of Li et al. and Ye (Li et al. 2016, Ye 2018). The maximum residue limit (MRL) established in kiwifruit by Japan for spirotetramat, which was “the sum of spirotetramat and B-enol”, was 3 mg kg^{-1}. The final spirotetramat and B-enol residues were less than the established MRL. Therefore, a pre-harvest interval (PHI) of spirotetramat was recommended 21 day for kiwifruit.

Spirotetramat and its metabolites dissipation during storage

In this study, the spirotetramat and the formation of four metabolites (B-enol, B-keto, B-mono and B-glu) were examined in a 70-day storage period at RD and FD. The results were presented in Figure 1C, D. The concentration of spirotetramat in kiwifruit was extensively degraded during storage. After 70 days, the residue dissipation of spirotetramat increased to 87.6% and 86.1% at RD and FD, respectively. The dissipation behaviors of spirotetramat exhibited the similar variation trends at RD and FD in kiwifruit. Notably, the spirotetramat at different dosages presented different degradation rates. It may be fitted using the first-order kinetic (Table 1). The half-lives of spirotetramat were 24.75 and 30.13 days at RD and FD, respectively. The results implied that the dosage had an obvious effect on the persistence of pesticide during storage. And the corresponding value of spirotetramat at FD was 1.22 times that at RD. Moreover, the spirotetramat half-lives during storage were higher than those in the field experiment. This may be due to the reduction of pesticide volatilization, enzymatic degradation and microbial activity at low temperatures during storage (Farha et al. 2016). Figure 1C, D revealed that only B-enol and B-keto metabolites were detected at different dosages in kiwifruit. The residues of B-enol were gradually decreased with the passage of time. After 70 dyas, the concentrations of B-enol 43.0 ± 1.9 μg kg^{-1} and 222.3 ± 13.1 μg kg^{-1} at RD and FD, respectively. And the residues was dissipated by 72.5% and 66.7% at RD and FD, respectively. The residues of B-keto remained relatively stable. B-keto reached maximum concentration at 63 and 0 days at RD and FD, with respective values at 32.9 ± 2.8 μg kg^{-1} and 308.5 ± 21.5 μg kg^{-1}, respectively. For this, it may be that the spirotetramat was first decreased to B-enol, and then B-enol was further transformed into B-keto. The results were consistent with others (Li et al. 2016). When spirotetramat was applied in the field, the residue of spirotetramat were efficiently transformed to B-enol and B-keto, leading to relative enrichment of the two metabolites.

Degradation of spirotetramat and its metabolites in kiwifruit during processing

The effects of different processing procedures on spirotetramat and its metabolites residues were investigated. The residues of spirotetramat and its metabolites during kiwifruit processing were presented in Table 2-4. The data indicated that spirotetramat and its metabolites had a similar downward trends under different process conditions.

Washing. Washing is the easiest method to remove pesticide residues from the kiwifruits during commercial processing. Many studies confirmed that the pesticide residues in fruits can be removed by washing (Kang et al. 2023, Li et al. 2021b, Quan et al. 2020b, Tian et al. 2022b). In the current study, the original concentrations of spirotetramat, B-enol and B-keto were 967.3 ± 85.1 μg kg^{-1}, 738.4 ± 48.6 μg kg^{-1} and 360.5 ± 23.5 μg kg^{-1} in kiwifruit, respectively. And the B-mono and B-glu were not detected in kiwifruit. After washing, the residues of spirotetramat, B-enol and B-keto decreased by 82.0%, 77.6% and 67.9%, respectively (Table 2). The removal effect of washing on spirotetramat, B-enol and B-keto were slightly stronger than that of other pesticides, with imazalil (13.9% loss) in apple and difenoconazole (16.0% loss) in tomato (Kong et al. 2012, Li et al. 2021b). This is mainly because spirotetramat (K_{ow} = 2.51) was lower than that of imazalil (K_{ow} = 4.10) and difenoconazole (K_{ow} = 4.36). The removal rates of B-enol and B-keto by washing were lower than that of spirotetramat. However, the K_{ow} of the B-enol and B-keto were unknown. Hence, the reason should be further studied. The results further suggested that the high $\log_{Kow}$ of pesticides were easy to penetrate the kiwifruit and difficult to remove by washing (Huan et al. 2015).

Peeling. Peeling is also a common step in fruit processing. Table 2 and 3 showed that the kiwifruit sample peeling resulted in spirotetramat, B-enol and B-keto residues with 97.0%, 93.8%, and 97.6% decrease, respectively. The kiwifruit skins contained the highest concentrations of spirotetramat, B-enol and B-keto. The concentrations of spirotetramat, B-enol and B-keto were 2990.3 ± 174.6 μg kg^{-1}, 1636.4 ± 109.7 μg kg^{-1} and 1396.9 ± 96.7 μg kg^{-1} in kiwifruit skins, respectively (Table 3). This is mainly because spirotetramat spray was in direct contact with the peel. Some studies have also reported that the removal rates of pesticide were between 50% and 100% by peeling in agricultural commodities (Chen et al. 2021, Han et al. 2013, Tian et al. 2022a). Han et al. found that the removal rates of spirotetramat by peeling was 76.4% in apple (Han et al. 2013). Besides, the results also suggested that peeling was stronger than washing to remove of spirotetramat, B-enol and B-keto. This is mainly because washing only removed the pesticides from the surface of the fruit skins (Quan et al. 2020a).

Color-protecting. From Table 2, we concluded that residual levels of spirotetramat, B-enol and B-keto were reduced by 7.8%, 15.7% and 20.7% after color-protecting, respectively. Compared with other pesticides, the color-protecting presented slightly worse elimination capability of spirotetramat B-enol and B-keto, with the 31.8% loss of cyflumetofen in apple (Quan et al. 2020a). It may be that the acidic environment was helpful to improve the stability of spirotetramat.

Blanching, boiling and simmering. Thermal treatments is another step used in the fruit processing. In the current study, from Table 2, residual levels of spirotetramat, B-enol and B-keto were reduced by 44.1%, 33.4% and 54.7% after blanching in the process of making kiwifruit slices, respectively. Whereas, during the process of canned kiwifruit, the effective elimination of spirotetramat, B-enol and B-keto with reductions of 45.2%, 3.8% and 6.9% after boiling, respectively. Meanwhile, the reductions of spirotetramat, B-enol and B-keto were 15.1%, 17.1% and 34.5% after simmering during the process of kiwifruit jam, respectively. The results indicated that partial chemical structures of spirotetramat, B-enol and B-keto may be destroyed under high temperature conditions, further leading to its concentration reduction. Our results proved that the residues of spirotetramat, B-enol and B-keto were decreased during blanching, boiling and simmering process. This is mainly due to the degradation or volatilization of spirotetramat, B-enol and B-keto caused by high temperature conditions (Han et al. 2016, Quan et al. 2020b). Some previous studies also support our results. A study by Jankowska et al. proved that thermal treatments resulted in decreasing the pesticide residues by 19-97% in broccoli and 43-93% in strawberries (Jankowska et al. 2019).

Puffing drying. As showed in Table 2, the results suggested that the residual levels of spirotetramat, B-enol and B-keto were obviously reduced by 36.3%, 31.5% and 27.6% after puffing drying, respectively. This may be mainly caused by changes in pressure and temperature. Some studies have also reported that high temperature enhanced the volatilization, degradation and hydrolysis of pesticides, resulting in the reduction of residue levels (Quan et al. 2020a). For example, a study by Quan et al. found that the reductions of (+)- and (−)-cyflumetofen were 31.2% and 42.1% after puffing drying, respectively (Quan et al. 2020a). Furthermore, the effectiveness of pesticide removal by pressure has also been studied. A study by Iizuka and Shimizu confirmed that 75% of hydrophobic pesticide were removed by the hydro-static pressure technology from cherry tomatoes (Iizuka &Shimizu 2014). Hence, the changes of temperature and pressure during the puffing drying was contribute to reduce pesticide residues in fruits.

Enzymolysis and clarification. In the process of making kiwifruit juice, the enzymolysis showed effective elimination of spirotetramat, B-enol and B-keto by 19.9%, 19.5% and 10.3%, respectively (Table 2). This finding was in accordance with some previous studies that found that the concentrations of spirotetramat and its metabolite were reduced by approximately 24% and cyflumetofen by approximately 19% in apples after enzyme treatment (Han et al. 2013, Quan et al. 2020b). The clarification slightly affected on the degradation of spirotetramat, B-enol and B-keto, decreasing residues by 13.7%, 9.2% and 11.5%, respectively. This also meant that the addition of chitosan reduced the residual amount of spirotetramat and its metabolites.

Fermentation. Many studies have shown that the pesticide residues in fermented foods can be significantly reduced by the action of microorganisms such as yeast (Li et al. 2021a, Regueiro et al. 2015). After the application of pesticides in the field, the pesticides remaining on the surface of kiwifruits will gradually transfer to the fermentation system, and gradually transferred and changed with the processing process. Ultimately, the residues in processed products posed a potential threat to consumer health. In the current study, the residue of spirotetramat, B-enol and B-keto could be reduced by fermentation to varying degrees in kiwifruit vinegar. Specifically, reductions in the spirotetramat, B-enol and B-keto were 85.6%, 57.2% and 31.0%, respectively (Table 2). As previously mentioned, Quan et al. found that concentrations of cyflumetofen in apple vinegar was reduced by approximately 79% during fermentation (Quan et al. 2020b). During the kiwifruit wine-making, the dissipation behavior of spirotetramat had similar trends in the three groups (Figure 2). The amounts of spirotetramat and its metabolites decreased significantly during the wine-making, including fermentation and clarification. At the same time, there is a significant difference in the distribution of target pesticides in the solid-liquid phase, and the pesticide residue level in the by-process products such as lees and wine mud was significantly higher than that in the liquid sake, indicating that the target pesticides were significantly enriched in the samples of lees and wine mud during processing (Table 3). Table 1 showed that the half-lives of spirotetramat were 4.15, 4.91 and 3.36 days in group A, B and C, respectively. Figure 2 indicated that the concentrations of spirotetramat in wine reduced quickly at the initial stage. The concentrations slowly decreased after 2 days and then tended to be stable during the fermentation. This may be due to spirotetramat in the solid phase entering the wine. In summary, Table 4 presented the final residue of spirotetramat, B-enol and B-keto in wine was reduced 23.5-99.8% in the three groups after the wine-making process. Nevertheless, Table 3 also showed that the residue of spirotetramat, B-enol and B-keto in pomace were higher than that in the wine. The potential risk of spirotetramat and its metabolites should be further researched in pomace, because pomace was often used to produce other products.

Processing factors

According to the definition of PFs, the influence of each process step on the spirotetramat and its metabolites residue levels were determined by calculating the PF of pesticide residue in its processed products. The PFs of spirotetramat, B-enol and B-keto were calculated and presented in Table 2 and 4 in each step. The processing factors of spirotetramat, B-enol and B-keto ranged from 0.0025 to 0.98 during each

step into six products, which indicated that each step can significantly reduce the residues of spirotetramat, B-enol and B-keto. Meanwhile, it can greatly reduce the amount of pesticide residues in human consumption. Some studies also confirmed that several processing steps could be effective removal of the pesticide residues to varying degrees in agricultural products (Li et al. 2021c, Tian et al. 2022b, 2023). In this work, the PF values of spirotetramat, B-enol and B-keto were 0.18, 0.22 and 0.32 during washing processing, respectively. Peeling could also be removed the spirotetramat, B-enol and B-keto, with PF values of 0.03, 0.06 and 0.02, respectively. The results were consistent with others. A study by Pan et al. proved that peeling was an effective method to remove the zoxamide, with a PF value of 0.059 (Pan et al. 2018). Such findings are not unique, Han et al. also found that the PF values of spirotetramat and B-enol were 0.14 and 0.22 after peeling in apple, respectively (Han et al. 2013). Therefore, peeling should be carried out at first time to reduce the pesticide residue in food for consumers.

In addition, the PF values of Color-protecting, blanching puffing drying, enzymolysis, clarification, boiling, simmering was less than one (Table 2 and 4). It indicated that these steps could also reduce pesticide residue levels to varying degrees. The PF values of spirotetramat, B-enol and B-keto acquired from fermentation were ranged from 0.13 to 0.98. The PF for kiwifruit wine was higher than that in kiwifruit vinegar, which was probably because the PH was different during the fermentation of kiwifruit vinegar and wine (Quan et al. 2020a). Zhao et al. confirmed that the PF values of triadimefon were 0.09 and 0.12 during the fermentation of jujube vinegar and wine, respectively (Zhao et al. 2017). In summary, the above results suggested that the kiwifruit after simple home preparation may be relatively safe for consumers. The peeling and fermentation steps were effective for the removal of spirotetramat and its metabolites residues. However, to ensure food safety, it is particularly necessary for detailed studies to optimize processing techniques to enhance the removal rate of pesticide residues.

Conclusions

This study was aimed to investigate the residues of spirotetramat and its four metabolites in field kiwifruits, during its storage and different processing technology. We developed a method to detect the residueal amounts of spirotetramat and its four metabolites in kiwifruits and its processed products (slices, juice, jam, canned, vinegar and wine) through an optimized QuEChERS method combined with HPLC-MS/MS. The developed method had the dvantages of simple operation, high sensitivity, accuracy and precision. In the field experiment, it was found that the half-lives of spirotetramat were 9.90 and 10.34 days at RD and DD, and there is no obvious difference. The final residues of spirotetramat and its four metabolites on kiwifruit was low than the MRL established by Japan. However, during storage, the half-life of spirotetramat was shorter at RD than FD. The results implied that the dosage the dosage had an obvious influence on the persistence of pesticide during storage. The processing procedures could affect the removal rate of spirotetramat and its metabolites to some extent. B-enol and B-keto were the main metabolites detected in kiwifruit and its processed products. The PFs of spirotetramat, B-enol and B-keto were less than 1 after each process step. Peeling and fermentation played the important role in eliminating spirotetramat and its metabolites residues. For consumers, it's important to peel fruits at home. In a word, this study clarified the changes and distribution patterns of spirotetramat and its four metabolites in different environment and processing steps, which can provide data reference and theoretical basis for food safety and actual production.

Declarations

Author Contributions All authors contributed to the study conception and design. Fajun Tian: Investigation, Writing - original draft, Formal analysis. Chengkui Qiao: Methodology. Caixia Wang: Methodology. Tao Pang: Formal analysis. Linlin Guo: Methodology. Jun Li: Validation. Rongli Pang: Investigation. Hanzhong Xie: Resources, Writing - review & editing.

Funding This work was supported by the National Natural Science Foundation of China (32202347), Henan Province science and technology research project (222102310542), the Agricultural Science and Technology Innovation Program (Grant CAAS-ASTIP-2022-ZFRI-09), and the Scientific Institution Basal Research Fund of ZFRI, CAAS (No. ZGS202204).

Availability of data and materials All data generated or analyzed during this study are included in this published article.

Ethical Approval and Consent to Participate No approval of research ethics committees was required to accomplish the goals of this study because experimental work was conducted with an unregulated invertebrate species.

Competing Interests The authors have no relevant financial or non-financial interests to disclose.

Consent to Publish Not applicable for this section.

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Tables

Table 1. Half-life ($T_{1/2}$) and correlation coefficient (R^2) of dissipation of spirotetramat at different conditions.

Dosage	Compounds	Conditions	Regression equation	R^2	$T_{1/2}$ (day)
Standard application dosage	Spirotetramat	Field	$C_t = 101.11e^{-0.070t}$	0.8964	9.90
2-fold standard application dosage	Spirotetramat	Field	$C_t = 211.69e^{-0.067t}$	0.9551	10.34
Standard application dosage	Spirotetramat	Storage	$C_t = 145.58e^{-0.028t}$	0.8039	24.75
5-fold standard application dosage	Spirotetramat	Storage	$C_t = 1351.98e^{-0.023t}$	0.9654	30.13
5-fold standard application dosage	Spirotetramat	Fermentation (Group A)	$C_t = 685.12e^{-0.167t}$	0.8781	4.15
5-fold standard application dosage	Spirotetramat	Fermentation (Group B)	$C_t = 114.84e^{-0.141t}$	0.7986	4.91
5-fold standard application dosage	Spirotetramat	Fermentation (Group C)	$C_t = 15.56e^{-0.206t}$	0.8108	3.36

Table 2. Reduction and PFs of spirotetramat and its metabolites in kiwifruit products except for the kiwifruit wine following different processing procedures.

Treatments	Spirotetramat		B-enol		B-keto	
	Reduction (%)	PFs	Reduction (%)	PFs	Reduction (%)	PFs
Washing	82.0	0.18	77.6	0.22	67.9	0.32
Peeling	97.0	0.03	93.8	0.06	97.6	0.02
Color-protecting	7.8	0.92	15.7	0.84	20.7	0.79
Blanching	44.1	0.56	33.4	0.67	54.7	0.45
Puffing drying (Slices)	36.3	0.64	31.5	0.69	27.6	0.72
Enzymolysis	19.9	0.80	19.5	0.81	10.3	0.90
Clarification (Juice)	13.7	0.86	9.2	0.91	11.5	0.88
Boiling (Canned)	45.2	0.55	3.8	0.96	6.9	0.93
Simmering (Jam)	15.1	0.85	17.1	0.83	34.5	0.66
Fermentation (Vinegar)	85.6	0.14	57.2	0.43	31.0	0.69

Table 3. Residues of spirotetramat and its metabolites in kiwifruit wine following different processing procedures (n = 3).

Treatments	Compounds	Concentration (μg kg^{-1})						
		Raw kiwifruits	Washed kiwifruits	Peeled kiwifruits	kiwifruits skin	Fermentation wine	Byproduct (pomace)	Clarification wine
Group A	Spirotetramat	967.3 ± 85.1	–	–	2990.3 ± 174.6	227.4 ± 16.4	800.5 ± 56.7	149.7 ± 7.6
	B-enol	738.4 ± 48.6	–	–	1636.4 ± 109.7	343.8 ± 24.5	516.5 ± 42.4	283.3 ± 14.8
	B-keto	360.5 ± 23.5	–	–	1396.9 ± 96.7	287.9 ± 23.6	336.6 ± 18.7	237.1 ± 18.7
Group B	Spirotetramat	967.3 ± 85.1	173.9 ± 13.6	–	–	43.6 ± 3.4	148.7 ± 8.5	35.0 ± 1.6
	B-enol	738.4 ± 48.6	165.7 ± 12.9	–	–	101.7 ± 5.5	104.0 ± 17.6	93.9 ± 7.8
	B-keto	360.5 ± 23.5	115.6 ± 10.2	–	–	96.5 ± 6.4	96.3 ± 6.8	88.4 ± 3.7
Group C	Spirotetramat	967.3 ± 85.1	–	28.3 ± 2.3	1646.5 ± 103.6	3.7 ± 0.1	5.37 ± 0.2	2.4 ± 0.1
	B-enol	738.4 ± 48.6	–	45.8 ± 2.1	774.0 ± 52.7	35.4 ± 1.7	41.7 ± 3.1	33.2 ± 3.1
	B-keto	360.5 ± 23.5	–	8.2 ± 0.4	607.8 ± 41.2	8.0 ± 0.5	11.2 ± 0.7	7.6 ± 0.6

Table 4. PFs of spirotetramat and its metabolites in kiwifruit wine following different processing procedures (n=3).

Treatments	Compounds	Reduction and PFs of processing types									
		Washing		Peeling		Fermentation		Clarification		Overall process	
		Reduction (%)	PFs	Reduction (%)	PFs	Reduction (%)	PFs	Reduction (%)	PFs	Reduction (%)	PFs
Group A	Spirotetramat	–	–	–	–	76.5	0.24	34.2	0.66	84.5	0.15
	B-enol	–	–	–	–	53.4	0.47	17.6	0.82	61.6	0.38
	B-keto	–	–	–	–	20.1	0.80	17.6	0.82	34.2	0.66
Group B	Spirotetramat	82.0	0.18	–	–	74.9	0.25	19.7	0.80	79.9	0.20
	B-enol	77.6	0.22	–	–	38.6	0.61	7.7	0.92	43.3	0.57
	B-keto	67.9	0.32	–	–	16.5	0.83	8.4	0.92	23.5	0.76
Group C	Spirotetramat	–	–	97.0	0.03	86.9	0.13	35.1	0.65	99.8	0.0025
	B-enol	–	–	93.8	0.06	22.7	0.77	6.2	0.94	95.5	0.045
	B-keto	–	–	97.7	0.02	2.4	0.98	5.0	0.95	97.9	0.021

Figures

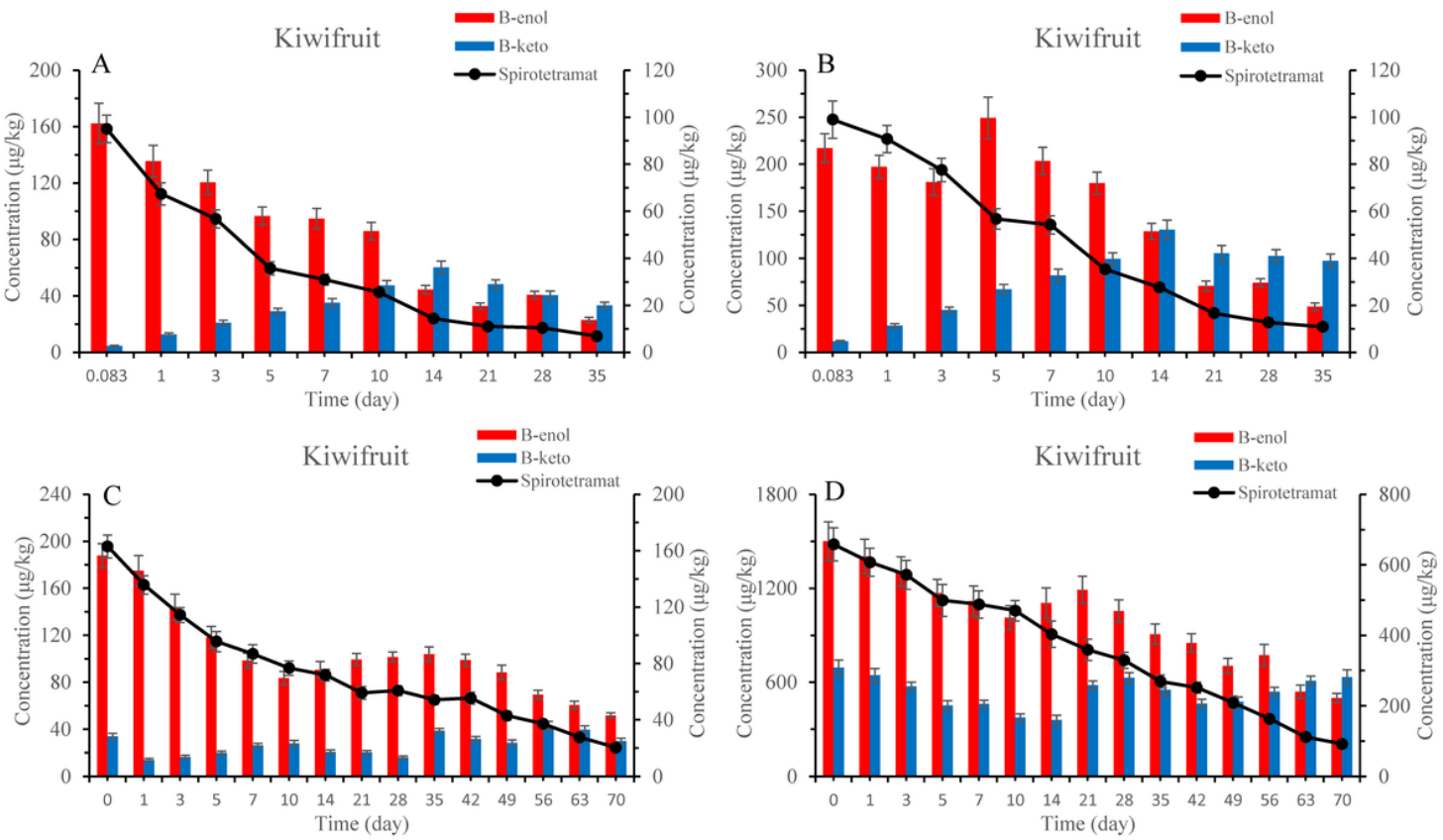

Figure 1

Degradation trend of spirotetramat and its metabolites in field kiwifruit (A: The standard dosage treatment; B: Double the standard dosage treatment) and storage (C: The standard dosage treatment; D: Five-fold the standard dosage treatment).

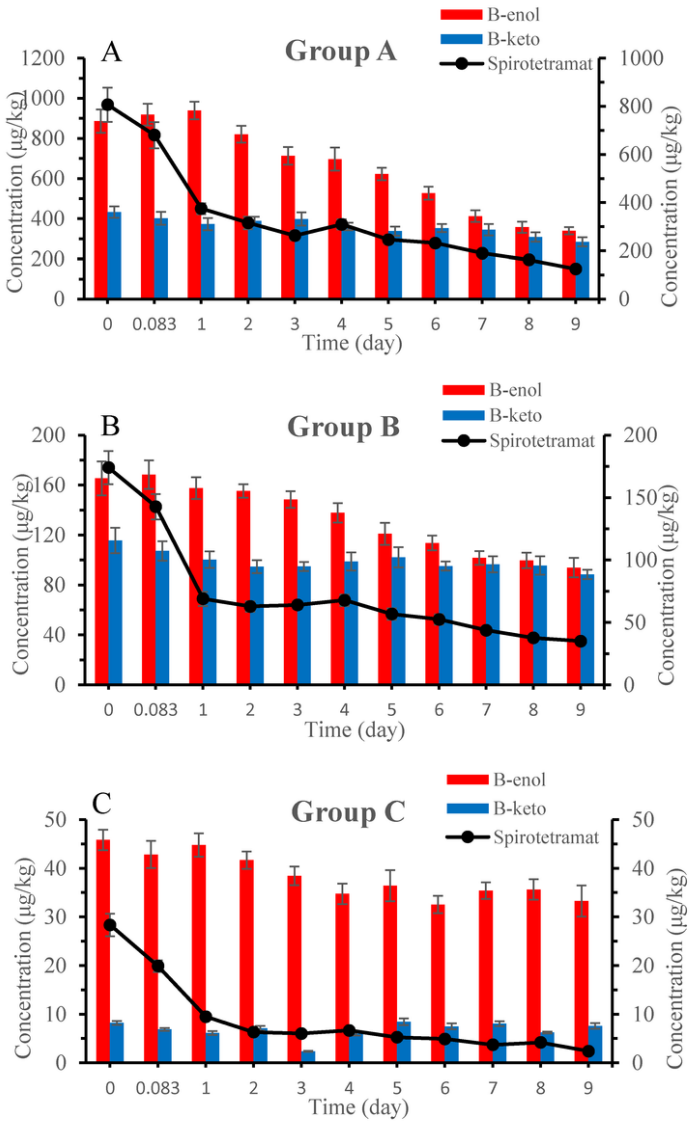

Figure 2

Degradation trend of spirotetramat and its metabolites in the process of rice fermentation into wine. ((A) kiwifruit wine in group A; (B) kiwifruit wine in group B; (C) kiwifruit wine in group C).

Supplementary Files

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