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Fungicide and insecticide residues in rice grains

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ABSTRACT. The objective of this study was to analyse residues of fungicides and insecticides in rice grains that were subjected to different forms of processing. Field work was conducted during three crop seasons, and fungicides and insecticides were applied at different crop growth stages on the aerial portion of the rice plants. Azoxystrobin, difenoconazole, propiconazole, tebuconazole, and trifloxystrobin fungicides were sprayed only once at the R2 growth stage or twice at the R2 and R4 growth stages; cypermethrin, lambda-cyhalothrin, permethrin, and thiamethoxam insecticides were sprayed at the R2 growth stage; and permethrin was sprayed at 5-day intervals from the R4 growth stage up to one day prior to harvest. Pesticide residues were analysed in uncooked, cooked, parboiled, polished and brown rice grains as well as rice hulls during the three crop seasons, for a total of 1,458 samples. The samples were analysed by gas chromatography with electron capture detection (GC-ECD) using modified QuEChERS as the extraction method. No fungicide or insecticide residues were detected in rice grain samples; however, azoxystrobin and cypermethrin residues were detected in rice hull samples.

Keywords: *Oryza sativa* L., food, gas chromatography, pesticides, grains quality.

Resíduos de fungicidas e inseticidas em grãos de arroz

RESUMO. O estudo objetivou analisar resíduos de fungicidas e inseticidas nos grãos de arroz submetidos a diferentes formas de processamento. O trabalho foi realizado no campo durante três safras agrícolas com a aplicação de fungicidas e inseticidas sobre a parte aérea das plantas de arroz. Foi realizado um tratamento com a aplicação dos fungicidas azoxystrobin, difenoconazole, propiconazole, tebuconazole, trifloxystrobin no estádio de desenvolvimento R2, e outro tratamento com os mesmos fungicidas com duas aplicações nos estádios R2 e R4 em parcelas individuais. Um tratamento com inseticida consistiu na aplicação de cypermethrin, lambda-cyhalothrin, permethrin, thiamethoxam no estádio R2, e outro tratamento na aplicação de permethrin com intervalo de cinco dias entre as aplicações a partir do estádio de desenvolvimento R4 até um dia antes da colheita. Foram analisados resíduos de fungicida e inseticida nos grãos polidos e integral, cru, cozido e parboilizado, e na casca de arroz, totalizando 1.458 amostras. As amostras foram analisadas por cromatografia em fase gasosa com detecção por captura de elétrons (GC-ECD) usando QuEChERS modificados como método de extração. Resíduos de fungicidas e inseticidas não foram detectados nos grãos de arroz. No entanto, resíduos de azoxystrobin e cypermethrin foram detectados na casca de arroz.

Palavras-chave: *Oryza sativa* L., alimentos, cromatografia gasosa, agrotóxicos, qualidade de grãos.

Introduction

The use of pesticides in irrigated rice has intensified in recent years due to the higher incidence of foliar diseases and insect pests. In many cases, damage from these pests occurs close to harvest, causing economic loss. Thus, the use of pesticides has been determined to be an essential management practice to ensure optimal agricultural yield and food quality. However, the presence of pesticide residues in food is a major public health concern, and identifying the presence of such residues in all types of food (both fresh and industrialized) is important to guarantee food safety (Wang, Wu, & Zhang, 2012; Hou, Han, Dai, Yang, & Yi, 2013).

Several studies have analysed the presence of pesticide residues in rice grains. In India, a study involving the application of thiamethoxam and lambda-cyhalothrin insecticides at both the recommended rate and twice the recommended rate to the aerial parts of rice plants concluded that no residues were detected in the grains (Barik, Ganguly, Kunda, Kole, & Bhattacharyya, 2010). However, Zhang, Chai, and Wu (2012) detected residues in brown rice grains

(0.027 mg kg^{-1}) following the application of chlorantraniliprole insecticide both during and at the end of the rice crop cycle in China. The presence of insecticide residues in rice grain may vary depending on the part of the grain evaluated (hull, bran or polished grain) and its chemical group, as an insecticide from a certain group may be more likely to associate with a certain part of the grain (Teló et al., 2015a).

Studies of fungicide residues have also shown varying results. In China, some studies have found no residues of difenoconazole fungicide in rice grains, and such studies concluded that the 30-day period between the application of the fungicide and the harvest of rice, a period established by the country's legislation, is safe for grain consumption. Even when rates of 90 and 135 g ai ha^{-1} were applied, no residues were detected in rice grains (Wang et al., 2012). The temperature during rice grain processing may influence the persistence of pesticide residues because high temperatures may reduce up to 38% of the concentration of difeconazole found in the rice hull (Teló et al., 2015b). Furthermore, due to the distinct characteristics of the rice grain, the grain's external structures may present higher residue concentrations because they serve as physical barriers. Pareja et al. (2012) assessed the concentrations of azoxystrobin, epoxiconazole, difenoconazole, lambda-cyhalothrin, tebuconazole, thiamethoxam and tricyclazole residues in the rice bran and in both polished grains and whole grain rice. The results show that the highest detected concentrations are associated with rice bran and whole grain rice. Other rice processing techniques such as parboiling reduced up to 11% of the detected residue of tebuconazole in the hull, bran and polished rice grain compared to non-parboiled grains. The highest residue concentration was detected in the rice hull, with a value that was 71% higher than the value detected in the bran and 99% higher than the value found in the non-parboiled polished rice grain (Dors, Primel, Fagundes, Mariot, & Badiale-Furlong, 2011).

Notably, several other studies from different countries have reported both the presence and absence of pesticide residues in rice. Thus, the objective of this study was to analyse the presence or absence of azoxystrobin, difenoconazole, propiconazole, tebuconazole and trifloxystrobin fungicide residues and of cypermethrin, lambda-cyhalothrin, permethrin and thiamethoxam insecticide residues, which are commonly used in rice crops in Brazil, in rice grains and hulls when these pesticides are applied to the aerial parts of the plants.

Material and methods

This study was carried out in two stages: the first stage was performed in the field; the second stage, in the laboratory. The first stage was conducted during the 2007/08, 2008/09, and 2009/10 crop seasons in the lowland area belonging to the Department of Plant Science at the Universidade Federal de Santa Maria-UFSM (Federal University of Santa Maria) in southern Brazil. In all crop seasons, rice was planted in the second week of October, and levees were placed around the plots. Each plot consisted of nine 7-m long seed rows that were spaced 0.17 m from each other, where the IRGA 417 rice cultivar was planted at a rate of 95 kg ha^{-1} in three replications. Management practices were conducted according to technical recommendations (Sociedade Sul-brasileira de Arroz Irrigado [SOSBAI], 2010).

Fungicides and insecticides were applied at different crop growth stages to the aerial parts of the rice plants as described in Table 1. In one treatment, the selected fungicides were applied at the R_2 growth stage, and in the other treatment, they were applied at both the R_2 and R_4 growth stages (phenology based on Counce, Keisling, & Mitchell, 2000). The selected insecticides were applied at the R_2 stage in one treatment, and in another treatment, only the permethrin insecticide was applied to the different plots at 5-day intervals from the R_4 growth stage up to one day before harvest. The applications were performed according to the labelled rates for each pesticide using a CO_2 pressurized back sprayer (pressure of 276 kPa) attached to a boom spray with four hollow cone nozzles (JA-2).

Table 1. Active ingredient, chemical group, rates applied to the aerial part of the plants, safety interval from application to harvest set by the Brazilian National Agency for Sanitary Surveillance (ANVISA) and octanol-water partition coefficient (log K_{ow}).

	Active ingredients	Chemical group	Rate (g ai ha^{-1})	Safety interval (days) [1]	Log K_{ow} [2]
Fungicides	Azoxystrobin	Strobilurin	100.0	30	2.5
	Trifloxystrobin[3]	Strobilurin	75.0	15	4.5
	Trifloxystrobin[4]	Strobilurin	93.7	15	4.5
	Difenoconazole	Triazole	75.0	45	4.3
	Propiconazole[3]	Triazole	93.7	45	1.3
	Tebuconazole[4]	Triazole	150.0	35	3.7
Insecticides	Cypermethrin	Pyrethroid	25.0	10	5.3
	Lambda-cyhalothrin	Pyrethroid	21.2	21	6.9
	Permethrin	Pyrethroid	25.0	20	6.1
	Thiamethoxam	Neonicotinoid	28.2	21	-0.1

[1]Agência Nacional de Vigilância Sanitária (ANVISA, 2016). [2]International Union of Pure and Applied Chemistry (IUPAC, 2015). [3]Commercial product with two active ingredients applied in the same plot. [4]Commercial product with two active ingredients applied in the same plot.

In each crop season, 54 rice plots were planted (18 treatments with 3 replications). For the residue analyses, grains were harvested from a 4.76 m^2 (4.0×1.19 m) area in the centre of each plot when the average moisture content reached 22%. After the grain was threshed, a 3 kg sample of homogeneous rice was collected from the previously mentioned area in each plot, for a total of 162 plots for the entire study period. Afterwards, samples were cleaned and dried by forced air ventilation at 38±2°C until a rice grain moisture of 13% was reached. The samples were then stored at -20°C.

To analyse fungicide and insecticide residues, each of the 3 kg samples harvested was subdivided according to processing method into 486 subsamples per crop season and 1458 total subsamples for the entire study period. The different treatments used in the analyses were the rice hulls from rice processing on a testing rice mill (Zaccaria PAZ-1-DTA), polished rice grains obtained by a grain polishing process, brown rice grains (processed grains with no polishing process), cooked polished rice grains (polished and processed grains that were cooked in a 1:2.5 grain mass:water ratio with ultrapure water heated at 45°C until the sample was completely dried), cooked brown rice grains (unpolished processed grain, cooked as described above), parboiled polished rice grains (raw grains [with hull] that were soaked [1:1.5 grain mass:water ratio] in water heated up to 65±1°C for 300 min. and autoclaved at 110±1°C [pressure of 0.6±0.05 kPa] for 10 min.). After the subsamples were divided into treatment groups, each grain sample was dried with forced air ventilation until the moisture reached 13% and was then processed to obtain parboiled polished rice grains, parboiled brown rice grains, cooked parboiled polished rice grains and cooked parboiled brown rice grains as previously described.

In the second stage of the study, the analysis of pesticide residues in the rice grains was conducted at the Laboratory of Pesticide Residue Analysis (LARP) at UFSM. Analytical standards of the pesticides were obtained from Dr. Ehrenstorfer (Augsburg, Germany) with purities above 95%. A full-scan analysis revealed no contamination. In total, 9 pesticides were analysed; these pesticides are listed in Table 1.

Prior to chromatographic analysis, the samples were subjected to an extraction process using the modified QuEChERS method (Prestes, Friggi, Adaime, & Zanella, 2009), which involves an initial extraction step in a 50-mL tube with 10 g of slurry prepared as described by Kolberg, Prestes, Adaime, and Zanella (2010) with a mixture 1:1 (w/w) rice:water and 1:3 (w/w) hull:water, into which 10 mL of acetonitrile containing 1% (v/v) of acetic acid was added. The tube was shaken vigorously by hand for 1 min., followed by a partition step after 3 g of anhydrous magnesium sulphate and 1.7 g of sodium acetate were added. Afterwards, the tube was centrifuged at 3,300 rpm for 8 min. Cleaning was done by the addition of 500 mg of the sorbent C_{18} and 600 mg of anhydrous magnesium sulphate in a 15-mL tube containing 4 mL of extract. The tube was capped, shaken vigorously by hand for 1 min and centrifuged at 3,300 rpm for 8 min. The extract was then ready for analysis.

Analyses were done by gas chromatography with electron capture detection (GC-ECD) using a CP 3800 gas chromatograph from Varian (USA) with a CP 8410 autosampler and using a DB-5 fused silica capillary 30-meter column with an internal diameter of 0.25 mm and film thickness of 0.25 μm. Helium was used as carrier gas with a constant flow rate of 1.3 mL $min.^{-1}$. The injector used programmed temperature vaporization as follows: initial temperature of 80°C (0.1 min), increasing at a rate of 200°C $min.^{-1}$ until 250°C was reached. The injection volume was 2 μL in the splitless mode. The temperature of the column was 80°C (0.1 min.), increasing at a rate of 25°C $min.^{-1}$ until a temperature of 215°C was reached (6 min) and then at a rate of 5°C $min.^{-1}$ until 250°C was reached. The detector temperature was maintained at 330°C.

The method was validated by determining the limits of detection and the quantification (LOD and LOQ), linearity, precision and accuracy, in terms of recovery. The pesticides lindane and methyl parathion were used as the internal and surrogate standars, respectively.

Results and discussion

Method validation

The method validation confirmed that the sample preparation by the modified QuEChERS method and the analysis by GC-ECD were adequate for the determination of residues of the selected pesticides in different parts of the rice grains subjected to different processing procedures.

The calibration curves obtained from the matrix matched standards of rice grains and rice hulls extracts presented good linearity with coefficients of determination greater than 0.995 for all studied pesticides. The method presented recovery values between 80.7 and 119.7% with good precision in terms of relative standard deviation (RSD), with values ranging from 0.4 to 19.4% for the different processed grains. For the rice hull, recovery ranged from 80.1 to 111.8%, with RSD values from 1.2 to 18.7%. No interferences were observed.

Pesticide residue analysis in rice grains

Residues of azoxystrobin and cypermethrin were detected in the rice hulls from the 2007/08 crop season (Table 2), and cypermethrin was detected at a higher concentration than azoxystrobin. Residues of fungicides and insecticides in the rice grains were not detected by the method of analysis used in this study, regardless of the form of rice used during the analysis.

Table 2. Limit of detection (LOD) and concentration of pesticide residues detected in rice hull, uncooked grains, and cooked grains (brown and polished grains) and in uncooked and cooked parboiled grains (brown and polished grains).

Active ingredients	LOD (mg kg-1)		Pesticide concentration (mg kg-1)				
			Rice hull	Cooked and uncooked grains		Parboiled grains Cooked and uncooked	
	Grains	Hull		Brown	Polished	Brown	Polished
Azoxystrobin[1]	0.005	0.01	0.02±0.005*	n.d.	n.d.	n.d.	n.d.
Azoxystrobin[2]	0.005	0.01	0.03±0.008*	n.d.	n.d.	n.d.	n.d.
Difenoconazole[1,2]	0.02	0.04	n.d.	n.d.	n.d.	n.d.	n.d.
Propiconazole[1,2]	0.02	0.04	n.d.	n.d.	n.d.	n.d.	n.d.
Tebuconazole[1,2]	0.02	0.04	n.d.	n.d.	n.d.	n.d.	n.d.
Trifloxystrobin[1,2]	0.002	0.004	n.d.	n.d.	n.d.	n.d.	n.d.
Cypermethrin[1]	0.01	0.02	0.12±0.021*	n.d.	n.d.	n.d.	n.d.
Lambda-cyhalothrin[1]	0.002	0.004	n.d.	n.d.	n.d.	n.d.	n.d.
Permethrin[1]	0.01	0.02	n.d.	n.d.	n.d.	n.d.	n.d.
Thiamethoxam[1]	0.01	0.02	n.d.	n.d.	n.d.	n.d.	n.d.
Permethrin (30)[3]	0.01	0.02	n.d.	n.d.	n.d.	n.d.	n.d.
Permethrin (25)	0.01	0.02	n.d.	n.d.	n.d.	n.d.	n.d.
Permethrin (20)	0.01	0.02	n.d.	n.d.	n.d.	n.d.	n.d.
Permethrin (15)	0.01	0.02	n.d.	n.d.	n.d.	n.d.	n.d.
Permethrin (10)	0.01	0.02	n.d.	n.d.	n.d.	n.d.	n.d.
Permethrin (5)	0.01	0.02	n.d.	n.d.	n.d.	n.d.	n.d.
Permethrin (1)	0.01	0.02	n.d.	n.d.	n.d.	n.d.	n.d.

[1]Application at the R_2 growth stage. [2]Application at the R_2+R_4 growth stages. [3]Application before grain harvest (days). *Residues detected only in the 2007/08 crop season. n.d.=not detected.

The literature presents several hypotheses regarding what factors may influence the concentrations of pesticide residues in irrigated rice crops, and many of these hypotheses have not yet been fully tested because of the numerous variables involved. Some of the primary factors that can influence the persistence of pesticides are weather conditions, characteristics of the pesticide (Komárek, Cadková, Bollinger, Bordas, & Chrastný, 2010), level of plant development at the moment of application (Navarro, Vela, & Navarro, 2011), solar radiation, temperature (Peña, Rodríguez-Liébana, & Mingorance, 2011), and the persistence of the pesticides in the plant (Macedo, Araujo, & Castro, 2013).

The results found in this study regarding the non-detection of fungicide residues in rice grains may be related to the time of application, which occurred 40 days before grain harvest. During this period, degradation and/or metabolism of the fungicide molecules by the plant may have occurred. This hypothesis could explain such results. In a study conducted with the objective of evaluating the persistence of the fungicide tricyclazole in rice plants (Phong, Nhung, Yamazaki, Takagi, & Watanabe, 2009), residues were detected until the 13th day after application in the first year and until 14th day after application in the second year. In this case, the pesticide molecules were metabolized within a short period; thus, their translocation might not have occurred in the original structure of tricyclazole during grain filling. Similar results were observed for azoxystrobin applied at different rates (125, 250, and 500 g ai ha^{-1}) on the aerial part of rice plants in which residues were not detected in the rice grains from harvest, which supports the hypothesis of metabolization of the original molecule by plants (Sundravadana, Kutalam, & Samiyappan, 2007).

Metabolism of the original structure of the molecule of propiconazole was studied using a ^{14}C-labeled molecule to assess its behaviour in rice plants (Kim, Beaudette, Shim, & Trevors, 2002). The authors analysed the metabolites after harvest and detected only 0.0004% of the initial concentration of 1.7% of the radioactive molecule that had been applied to the plant; they attributed this result to the fragmentation of the original molecular structure. These results highlight the need for more studies to identify and detect metabolites in rice grains. Thus, triazole group fungicides such as propiconazole, difenoconazole, and tebuconazole are metabolized within the plant and may undergo oxidation, reduction, hydrolysis, or the formation of other compounds, or even total degradation into simpler compounds (Zambolin, Picanco, Silva, Ferreira, & Ferreira, 2008).

The hypothesis related to the degradation of fungicides in plants is also relevant for insecticides. Studies related to the dynamics and persistence of imidacloprid, from the neonicotinoid chemical group, did not detect insecticide residues in rice grains (Kanrar et al., 2006). The authors linked the results to the degradation of imidacloprid molecules in the plant. A reduction of 80% of the initial concentration was measured in plants 30 days after the application of the insecticide; it has a half-life of 11 days. Regarding the dissipation and degradation of thiamethoxam and lambda-cyhalothrin in rice plants, there was an 88% reduction of the initial concentration measured in the plants on the 15th day after the application of thiamethoxam and a reduction of more than 50% of the initial concentration measured after the first day for lambda-cyhalothrin; residues were not detected in rice grains (Barik et al., 2010).

It is a well-known fact that several factors may influence the persistence of pesticides in plants by interfering with the absorption and metabolization of pesticides by the plant (Santos, Areas, & Reyes, 2007; Macedo et al., 2013). Thus, residues of the fungicides azoxystrobin and difenoconazole and of the insecticide lambda-cyhalothrin were assessed in the irrigated rice plants after 40 days (the period from the moment of the pesticide application up to the rice harvest); however, according to a previous study by Teló et al. (2015b), no residues from the previously mentioned pesticides could be found in rice grains.

For the sequential applications of permethrin, which was applied up to 1 day before harvest, residue was also not detected in rice grains. Several processes, such as photodegradation, volatilization, chemical degradation, and biological degradation (Linders, Mensink, Stephenson, Wauchope, & Racke, 2000), may be associated with the non-detection of residues in rice grains. The pyrethroid chemical group has a high rate of degradation mainly due to solar radiation, which is characteristic of the molecules in this group (Laskowski, 2002), and the permethrin insecticides have a half-life of 1 day under aqueous photolysis (IUPAC, 2015). In this context, it is noteworthy that the insecticides were applied during the months of the highest solar radiation incidence. The results of this study could be explained by the hypothesis that molecules are degraded by solar radiation. It is also notable that insecticides of the pyrethroid chemical group have low absorption and translocation rates in plants (Garrido, Martínez, Martínez, & López-López, 2005).

Another important point refers to pesticide applications performed in the period close to harvest, which may be associated with low or almost zero mobility of photoassimilates in the plant due to natural senescence. The reduction of respiration in the caryopsis, which acts as a barrier to absorption of the insecticide by the plant and thereby contributes to the degradation of the molecules by exposure to solar radiation, must also be considered.

Additionally, analyses were carried out with limits set to 20 times lower than the Maximum Residue Limit (MRL) allowed and regulated for rice grains by the Brazilian National Agency for Sanitary Surveillance (ANVISA), as shown in Table 3.

The MRL of rice grains among different countries varies according to the legislation of each administrative organization, and some pesticides used in this study were not registered for rice in certain countries. The MRL in Brazil for the pesticides used in this study are below the limits set by the *Codex Alimentarius*, which is the United Nations' international reference from the Food and Agriculture Organization (FAO), an international authority for solving disputes over food safety and consumer protection. This may be a positive point for Brazilian rice exports because of the existing legislation being very stringent regarding the quality of rice produced. It should be noted that the limit of quantification for the method used is always set equal to or below the regulated MRLs presented by the different agencies responsible for food quality.

It is important that management practices respect the minimum time between pesticide application and grain harvest, which is regulated by ANVISA in Brazil. Overall, if the pesticides are applied according to Good Agricultural Practices (GAP), MRLs are not exceeded; however, the misuse of these compounds is worrying and may result in significant amounts of residues found in both food and the environment (Thurman, Ferrer, & Fernández-Alba, 2006; Jardim, Andrade, & Queiroz, 2009).

Table 3. Comparisons among the maximum residue limits (mg kg^{-1}) for rice grains set by the Codex Alimentarius, Brazil, the United States (U.S.), the European Union (E.U.), Canada, India, Japan, China and Korea.

Pesticide	Codex[1]	Brazil[2]	U.S.[1]	E.U.[1]	Canada[1]	India[1]	Japan[1]	China[1]	Korea[1]
Azoxystrobin	5.0	0.1	5.0	5.0	5.0	-*	0.2	-	1.0
Difenoconazole	-	1.0	-	0.05	0.01	-	-	-	0.2
Propiconazole	-	0.1	1.0	0.05	0.05	-	0.1	-	0.1
Tebuconazole	1.0	0.1	1.0	0.02	-	-	0.05	-	0.05
Trifloxystrobin	5.0	0.2	3.5	0.02	3.5	-	1.6	-	-
Cypermethrin	2.0	0.05	-	2.0	-	-	0.9	-	1.0
Lambda-cyhalothrin	1.0	1.0	1.0	0.02	0.01	-	-	-	-
Permethrin	-	0.1	-	0.05	-	-	2.0	-	-
Thiamethoxam	-	1.0	0.02	0.05	0.02	0.02	0.3	0.1	0.1

[1]United States Department of Agriculture (USDA, 2016). [2]ANVISA (2016). *no registration for rice crop.

Usually, fungicides and insecticides are applied to the aerial part of rice plants, so the determination of residues in rice grains is fundamental as a means of ensuring the quality of the grain. However, pesticides may also affect human life due to pesticide build-up throughout the food chain, which may lead the ecological phenomenon of biomagnification, or bioaccumulation, of a pesticide in an ecological food chain by residue transfer from the food into a person's body tissues. However, there are no consolidated studies on pesticide residue concentrations detected in food items, especially those which exceed the maximum limits for human consumption; the information regarding the effects of accumulation of these compounds in humans is still very restricted (Mostafalou & Abdollahi, 2013) but indicates that such effects may be associated with health problems linked to the nervous system (Costa, Giordano, Guizzetti, & Vitalone, 2008), reproductive system (Saadi, & Abdollahi, 2012) and diseases such as cancer (Alavanja & Bonner, 2012).

The results show that the method of analysis used in this study did not detect any pesticide residues in rice hulls. Thus, the identification of a method that allows the detection of residues at lower concentrations in grains is a goal that should be pursued to ensure optimal food quality.

Conclusion

Residues of azoxystrobin (0.02 and 0.03 mg kg^{-1}) and cypermethrin (0.12 mg kg^{-1}) were detected in rice hulls only in the 2007/08 crop season.

Residues of azoxystrobin, difenoconazole, propiconazole, tebuconazole, and trifloxystrobin fungicides and of cypermethrin, lambda-cyhalothrin, permethrin, and thiamethoxam insecticides were not found in rice grains, regardless of the processing method used.

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