Study of quality indicators of processed cheese enriched with caviar and milt of Baltic herring (Clupea harengus membras) during storage

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Abstract. To study the hydrolytic and oxidative processes occurring in the lipids of the gonads (caviar and milt) of herring when stored in the freezer at a temperature of -18 ° C, the dynamics of changes in acid, peroxide and thiobarbitur numbers were determined. The shelf life of frozen caviar and milt is 3 months. The technology of processed cheese with the addition of herring gonads (Baltic herring) is proposed. In order to make processed cheese with the addition of caviar and milt ideal, mathematical planning of the experiment was used, namely, an orthogonal central compositional plan of the second order for two factors: the content of caviar and the content of milt. The optimization parameters of the mathematical model are an aggregate dimensionless characteristic consisting of five particular responses: organoleptic evaluation, dynamic viscosity, yield strength and mass fraction of moisture. The technology of processed cheese enriched with caviar and herring milt is proposed. To analyze the main quality indicators, as well as to establish the shelf life of the developed processed cheese, the dynamics of changes in organoleptic, hydrolytic and oxidative processes occurring in the lipids of the salaki gonads, as well as in enriched processed cheese, were studied. The assessment was carried out by acid (KCH), peroxide (IF) and thiobarbitur (TBH) numbers.

1 Introduction

The results of these experiments can be very useful and interesting for producers of processed cheese, as their enrichment with gonads (caviar and milt) of Baltic herring (Clupea harengus membras) improves the nutritional properties of the cheese, which can have a positive impact on consumer demand

Given the unique protein-lipid, vitamin-mineral composition of fish gonads, they are considered to be biologically valuable raw materials [1]. Therefore, the development of technology of processed cheese enriched with herring caviar and milt is relevant. The study of oxidative processes in processed cheeses with the addition of herring caviar and milt will

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make it possible to evaluate the effectiveness of this approach to improve the nutritional value of processed cheeses.

Table 1 shows the total chemical composition of herring caviar and milt caught at the end of March 2023 in the Kaliningrad Bay.

Table 1. General chemical composition of herring caviar and milt

Name of raw material	Mass fraction, %			
	water	squirrel	fat	minerals
Herring caviar	65.00 ± 0.15	21.70 ± 0.2	9.40 ± 0.2	3.90 ± 0.1
Herring milt	74.00 ± 0.2	16.22 ± 0.1	4.60 ± 0.15	5.18 ± 0.1

According to Table 1, caviar and milt have a high water content of 65% and 74% respectively. In addition, caviar contains 21.7% protein and 9.4% fat, while milt contains 16.22% protein and 4.6% fat [2].

2 Materials and methods

Gonads (caviar and milt) of Baltic herring (Clupea harengus membras) caught in March 2023 in the Kaliningrad Bay were used as starting materials for the experiment. The experiments were carried out using generally accepted research methods, such as organoleptic, physico-chemical and biochemical methods. All experiments were repeated five times.

The data were processed using standard methods of variance, correlation and regression analysis using OfficePro software (Word, Excel) and Mathcad 2000 Professional. This approach allowed obtaining accurate and reliable results that can be used in further work.

2.1 Changes in the quality indicators of fish gonads

Fish gonad fats are susceptible to degradation and changes in their properties duringstorage. This is because they oxidise easily, resulting in the formation of free fatty acids, peroxides and aldehydes, leading to an unpleasant odour and rancidity [3].

To study the hydrolytic and oxidative processes occurring in the lipids of herring gonads during freezer storage at -18°C, the dynamics of changes in the acid, peroxide and thiobarbituric numbers were determined. The acid number refers to the amount of free fatty acids present in the sample, while the peroxide and thiobarbituric acid numbers are indicators of the degree of oxidation and rancidity, respectively [4].

The results of the study are presented in Figures 1-3.

Analysis of the data in figure 1 shows that there was a slight accumulation of free acids during the 18 weeks of storage of herring caviar and herring milts in the freezer at minus 18°C. This observation is particularly important as it helps to understand the shelf life of these products. It was found that the acid number, which is a measure of the amount of free acid present [5], increased only slightly during this time. For herring caviar, the acid number increased by 1.8 and for herring milt by 2.5 mg KOH per 1 g of fat.

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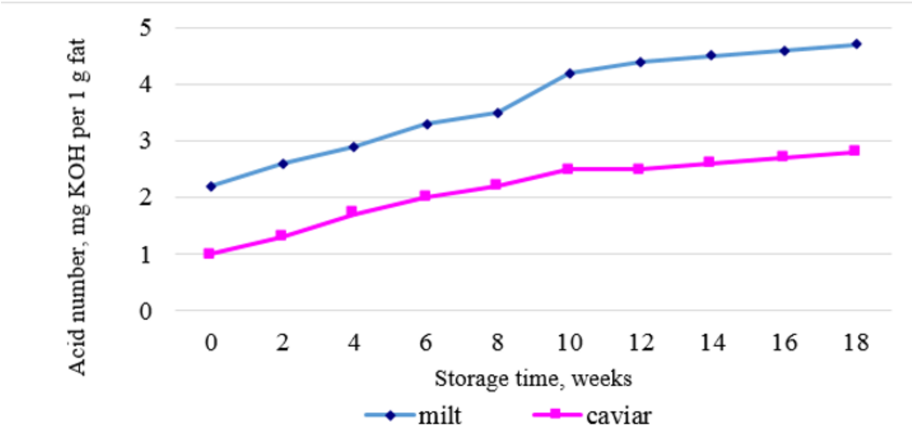

Fig. 1. Dynamics of changes in acid numbers of lipid gonads of herring.

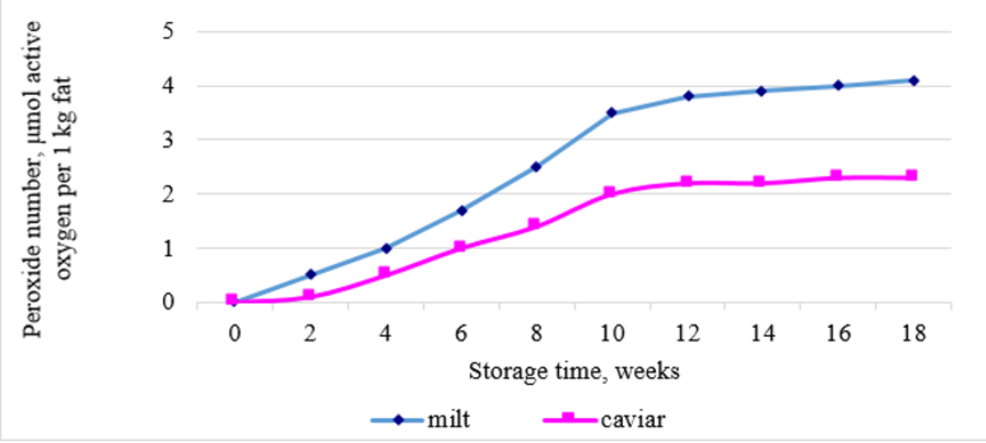

Fig. 2. Dynamics of changes in peroxide number in lipids of herring gonads

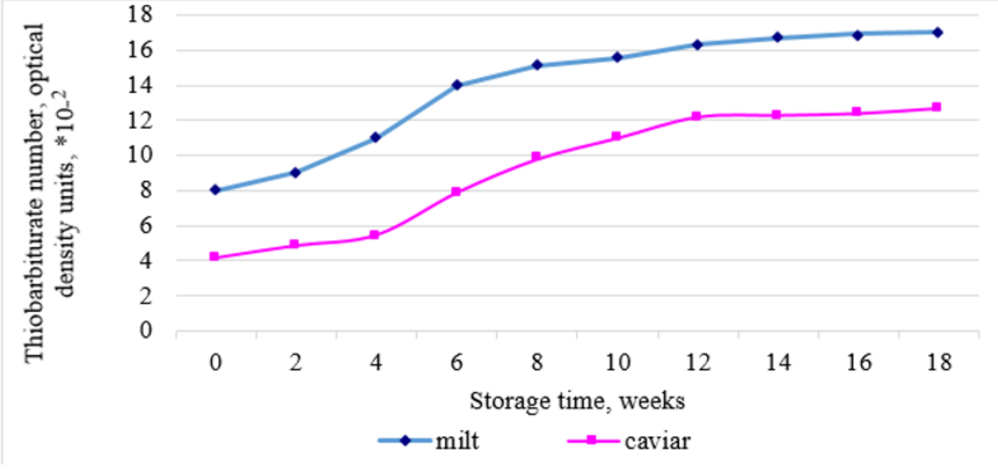

Fig. 3. Dynamics of thiobarbiturate number in lipids of herring gonads

Particularly interesting is the fact that, starting from the 10th week, there was a noticeable slowdown in the growth of acid number in herring caviar and milt. From week 10 to 18, the acid number increased by only 0.5 mg KOH per 1 g of fat in herring caviar and by 0.3 in milt. This finding is important because it suggests that the shelf life of these products can be extended beyond the guideline 10 weeks of storage.

Overall, these results provide valuable information on the stability and shelf life of herring caviar and herring spawn stored in the freezer at minus 18°C. The data indicate that the acid number is an important parameter for controlling the freshness of gonads during storage.

Studying the impact of long-term storage of herring caviar and herring spawn in the freezer on their quality and safety is a topical issue for many consumers and producers. A scientific study has shown that when these products are stored for 18 weeks (6 months), spoilage processes run smoothly and do not have a significant impact on the quality and safety of herring caviar and herring milts.

To assess the quality and safety of herring caviar and milt, a comparative study of hydrolytic and oxidative lipid deterioration rates was carried out. The results showed that the level of lipid spoilage in caviar and dairy products increases smoothly during a given storage period, but does not reach critical values [6]. Thus, it can be concluded that the products remain fit for consumption within the specified shelf life.

Active oxygen has also been measured in caviar and milt. Active oxygen is an oxygen molecule that can be formed as a result of oxidation of fats in food products and contribute to their spoilage [7]. The results of the study showed (fig. 2) that the content of active oxygen in herring milt samples is from 0 to 4.1 μmol per 1 kg of fat and in caviar - 2.3 μmol per 1 kg of fat, which does not exceed the established standards of research. Consequently, the products retain their safety within the prescribed shelf life and can be eaten.

Destruction of peroxides is accompanied by the appearance of oxidation products [7,8]. This can be seen from the increase in thiobarbiturate number in all samples (Fig. 3): from 0.042 to 0.130 OD for caviar and from 0.08 to 0.17 for milt. This indicates the safety of theproducts during the shelf life [8]. In studies, it was found that during the 18 weeks of storage the oxidative processes are slow. From the 10th week of storage, the accumulation of fat oxidation products in herring caviar and milt slows down. The findings show that caviar and milt can be used in the preparation of processed cheese.

Thus, studies have shown that keeping caviar and milt in the freezer for 18 weeks has no significant impact on the quality and safety of products, but it is recommended to set a shelf life of not more than 12 weeks (3 months) to avoid the risk of spoilage and preserve their flavour qualities. Based on this study, it can be recommended to use frozen raw materials for the preparation of combined processed cheeses.

2.2 Developing a recipe for processed cheese

Kaliningrad State Technical University has developed a technology for processed cheese using herring caviar and milt. The essence of the technology is to mix herring caviar and milt, 5% fat cottage cheese, 45% fat hard cheese, 2.5% fat cow's milt and Fanakon melting salt. Melt the cheese mass at 85±20°C, then add butter and Fito smoker, pour into moulds and cool.

In order to make processed cheese with the addition of caviar and milt ideal, mathematical planning of the experiment was used, namely an orthogonal central composition plan of the second order on two factors [9]. The study revealed two main factors that influence the properties of processed cheese: the mass fraction of milt and the mass fraction of herring caviar. Table 2 shows the range of variation of these factors and their intervals of variation in the studies.

Table 2. Values of the main factors, their levels, intervals of variation

Factor	**Levels**			**ΔX**
	-1	0	+1	
Caviar content in 100g of product, g, mi	5	10	15	5
Milt content in 100g product, g, mm	5	10	15	5

The optimisation parameters of the mathematical model are an aggregate dimensionless characteristic consisting of five partial responses. Their 'ideal' values used in the calculations are shown in Table 3.

The yield point and dynamic viscosity were measured with a Brookfield DV-II+ programmable digital viscometer. The device displayed the current viscosity value (cP) and the yield point (σt). The taste and quality of the processed cheese enriched with herring caviar and milt was assessed on a 5-point scale with a total score of 20. The significance ofeach quality indicator was taken into account.

Table 3. Partial responses and their "ideal" values

Name of the response	**Dimension**	**The ideal value**
Organoleptic evaluation (O)	Points	20
Yield strength (σt)	Pa	55
Dynamic viscosity (η)	cPs	1200
Mass fraction of moisture (ωv)	%	55

The experimental design for optimising the process under investigation is shown in Table 4.

Comparison of results from Table 4 showed that the best quality of processed cheese is achieved with caviar content - 15 g per 100 g of product and milt - 10 g per 100 gof product (sample No. 8). In this case, the finished product had low taste qualities (14.11 points), the fluidity exceeded the "ideal" value in 3.33 times, and the mass fraction of moisture was close to the "ideal" 58.68%. Viscosity was as close to the ideal value as possible and was 1003 cPs. Samples from experiment #3 and #4 had high quality scores: taste score of 17.00 and 16.88 respectively, fluidity of 59.9 and 77.7 Pa, viscosity of 234.9 and 979.4 cP and mass fraction of moisture of 60.16 and 59.76%. Implementation of the DCCP matrix plan and processing of experimental data with the help of given algorithms allowed to obtain a polynomial equation of the second order, which quantitatively relatesthe process of formation of quality of ready-made processed cheese with the parameters of its implementation:

$$y = 8.88-1.75Mi-0.059Mi-0.0136MiMm+0.09Mi^2+0.017Mm^2.$$

Regression analysis showed that the caviar content has a greater influence on the quality of the finished product than the quantity of milt.

As a result, the following optimum factors were determined: mass fraction of herring caviar - 9.3%, mass fraction of herring milt - 5.5%.

Table 4. Experimental plan for optimising the preparation of processed cheese using caviarand herring milt

N experience	**Experiment plan**		**Private feedback**				**Partial dimensionless responses**				**У**
	mi	mm	O	σt	η	ωv	SO^2, $*10^{-3}$	$S\sigma^2$, $*10^{-3}$	$S\eta^2$, $*10^{-3}$	$S\omega v^2$, $*10^{-3}$	
1	5	5	17.00	153.2	2055	58.52	22.5	3.18	507.6	4.098	2.837
2	5	10	18.33	96.6	946.0	58.81	6.97	5.72	44.8	4.799	2.830
3	5	15	17.00	59.9	234.9	60.16	22.5	7.94	646.8	8.802	0.161
4	10	5	16.88	77.7	979.4	59.76	24.3	170	33.79	7.49	0.166
5	10	10	18.44	71.3	607.8	60.81	6.08	87.8	243.5	11.16	1.012
6	10	15	16.44	70.5	398.6	61.64	31.7	79.4	446	14.57	1.011
7	15	5	16.76	155.0	775.4	59.95	26.2	3.30	125.2	8.10	2.787
8	15	10	14.11	183.2	1003	58.68	86.7	5.43	26.95	4.48	0.114
9	15	15	14.78	119.3	490.5	61.33	68.1	1.36	349.6	13.24	1.002

Based on the optimum parameters, a prototype of processed cheese with theaddition of herring caviar and milt was made. It has a homogeneous mass with evenly distributed individual eggs. The surface is smooth with no cut pattern or voids. The colour is light yellow to greyish. The taste and smell is cheesy and creamy with a hint of smokiness. The consistency is soft, pliable and spreadable. Organoleptic evaluation of processed cheese with the addition of caviar and milt was 19.22 points. The experimental sample is of high quality.

3 Results and discussion

Figure 4 shows the change in organoleptic evaluation scores of the experimental andcontrol samples of processed cheese. Organoleptic evaluation is a method of examining the properties of a product that can be detected by the senses, such as taste, texture and aroma [10]. The maximum score for organoleptic evaluation is 20 points.

As can be seen from the graph, the organoleptic values of the processed cheese samples remain high (above 15 points) throughout the expected shelf life. This means that the processed cheese will retain its desirable organoleptic properties for a considerable period of time.

However, the organoleptic properties gradually decrease during storage. This is due to biochemical processes occurring in the product which can lead to changes in the organoleptic properties of the product, such as taste, texture and aroma. By the end of 11 weeks of storage (77 smut) the organoleptic score was 13.9. This indicates that the organoleptic characteristics of processed cheese deteriorate significantly.

An organoleptic score of 13.9 classifies the product as "satisfactory quality". It is therefore recommended to set the shelf life of the tested product at 70 days. This ensures that the processed cheese retains its desired organoleptic properties and remains safe for consumption.

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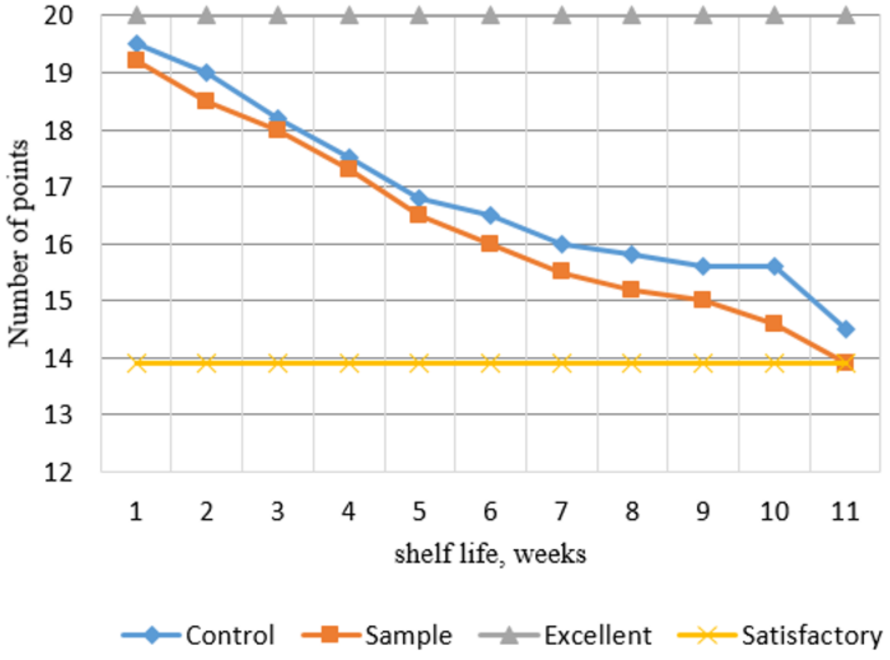

Fig. 4. Dynamics of organoleptic evaluation of processed cheese quality

The hydrolytic and oxidative processes occurring in the fats of processed cheese were further evaluated. These processes can be caused by the addition of sufficiently fatty fish raw materials such as caviar and milt to the recipe. Acid, peroxide and thiobarbiturate numbers were used to measure hydrolysis and oxidation levels.

The acid number is an indicator of the amount of acids formed during hydrolysis of fats [5]. The peroxide number indicates the level of oxidation of fats [7] and the thiobarbiturate number indicates the level of oxidation products [8]. The results of the measurements are shown in Figures 5-7.

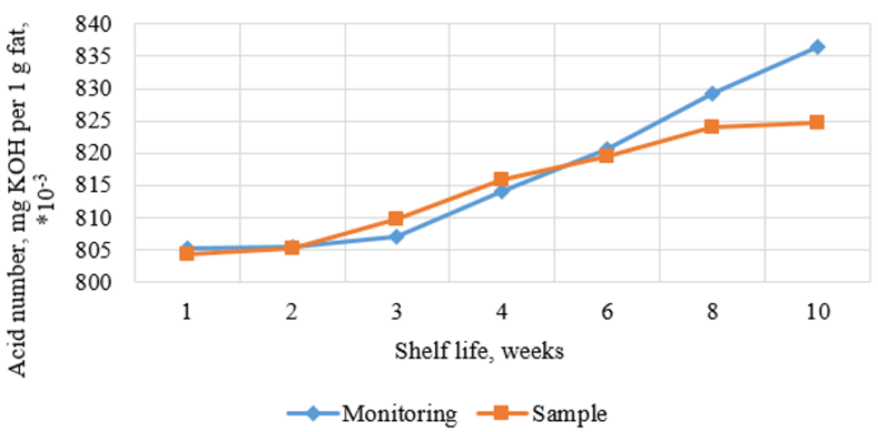

Fig. 5. Variation of the acid numbers of the lipids of processed cheese, mg KOH/1 g fat

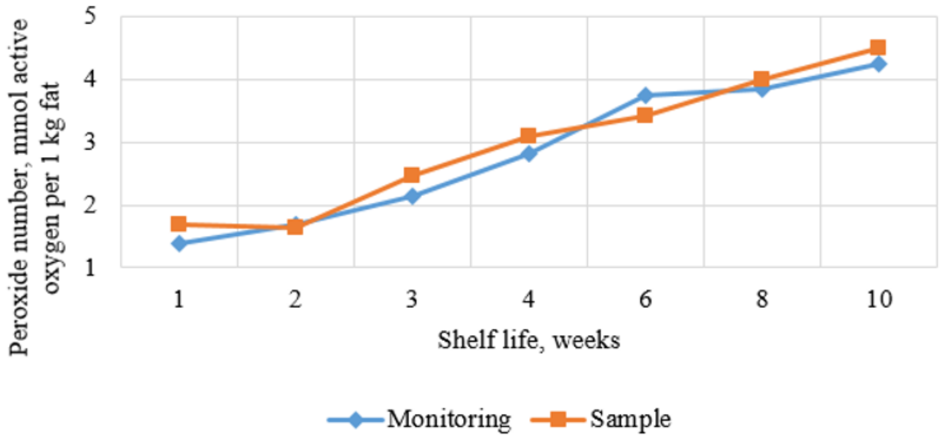

Fig. 6. Change in lipid peroxide number of processed cheese, % iodine

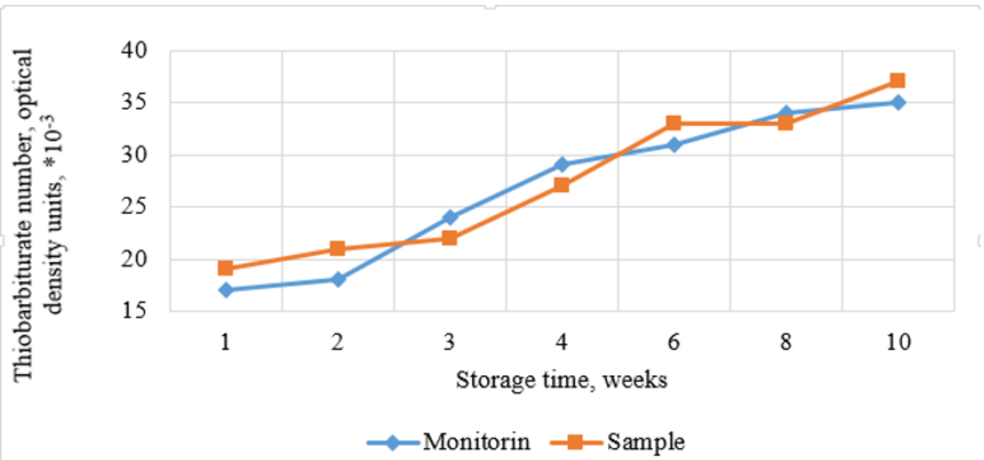

Fig. 7. Change in thiobarbiturate number, units optical density

4 Conclusions

Storage of the samples for 70 days showed the dynamics of oxidation processes. There was no rancid taste or odour in the experimental and control samples throughout the storage period. Comparison of the hydrolytic and oxidative deterioration of lipids in the control and experimental samples shows a similar pattern of changes: a smooth increase in the acid numbers in all samples. Peroxide degradation is then accompanied by the formation of secondary oxidation products, which can be traced by the growth of thiobarbiturate numbers also in all samples. The obtained processed cheese with the addition of caviar andherring milt is not inferior in all respects to the quality of the finished products of the control sample for the entire period of sample storage, although the high fat content of caviar and herring milt could significantly affect the organoleptic and physico-chemical parameters of the quality of processed cheese.

It is important to note that definitive conclusions can only be drawn after additional studies of changes in microbiological indicators during storage of processed combination cheeses. Microbiological indicators can be used to assess food safety and quality. Therefore, additional studies are needed to determine the effect of storage on the microbiological characteristics of processed cheese.

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