STUDY OF THE KINETICS OF π-COMPLEXES FORMATION IN OIL-IODINE SYSTEM

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Abstract: The use of the iodinated sunflower oil represents a cheap accessible method for the iodine deficiency eradication along with other iodine sources. A small amount of iodinated oil (0.25 – 1%) incorporated in the product can represent a significant source of iodine for the human body.
The possibility and capacity of the molecular iodine incorporation in the sunflower oil was studied. It was established that during oil iodination the iodine is not simply added to the oil, but a process of fixation of molecular iodine to the double bond with π complexes formation takes place without double bond from the unsaturated fatty acids being broken.
Kinetic parameters of the π compounds iodine – triglycerides formation in the sunflower oil were investigated. It was established that the process is described by a first order kinetic reaction. The reaction constant values and the half-time values were established: $k = 2.12 \cdot 10^{-2}$ h^{-1} and $t_{1/2} = 32.69$ h (for T = 298 K).

Keywords: *iodinated sunflower oil, oil iodination, food lipids, π compounds iodine – triglycerides*

INTRODUCTION

Iodine is one of the microelements which overall amount in the body represents about 15 – 22 mg and it is essential for the synthesis of the thyroid hormones [thyroxin (T_4) – 65%, triiodothyronine (T_3) – 59%] which play an important role in the cell metabolism especially for the differentiation of the brain tissue and bone tissue [1, 2]. Iodine deficiency leads to important thyroid gland dysfunctions and can be manifested as physical and mental non development [3, 4]. For the Republic of Moldova a normal iodine deficiency is characteristic [5]. According to the previous drown studies, in the Republic of Moldova among 8-10 years old children about 37% have goitres of 1st and 2nd degree [6].

Among main preventive methods for the iodine deficiency eradication, salt and other products iodination plays the most important role [7, 8]. But the iodine intake from the salt is still insufficient [3, 9]. There are population categories (such as children, elderly, sick people) for which the amount of the consumed salt should be decreased. Therefore the iodine deficiency eradication methods should be suitable from multiple points of view.

In the regions with moderate and severe iodine deficiency, the iodine prophylaxis is made through the administration of the iodinated oil as injections or orally [10, 11]. The injection of the iodinated oil with 475 mg iodine/mL brings a high amount of iodine which will slowly adsorb depending on the body requirements. For the 0 – 6 years old children 0.2 – 0.4 mL is administered and for the persons from 6 – 45 years old up to 1 – 2 mL (475 – 950 mg iodine) which covers body requirements for a period of 3 – 5 years. However, an increased iodine intake realized through the injection of the iodinated oil increases accidentally the toxicities incidence [1].

Food fortification with micronutrients represents the method through which the nutrient is added in the products – vehicles aiming to improve the quality of the human alimentation [12].

The use of the iodinated sunflower oil represents a cheap accessible method for the iodine deficiency eradication along with other iodine sources [13]. A small amount of iodinated oil (0.25 – 1%) incorporated in the product can represent a significant source of iodine for the human body.

The aim of the present study is the evaluation of iodine incorporation methods in the vegetal lipids – sunflower oil.

MATERIALS AND METHODS

In this study, double refined and deodorized oil was used (purchased from local stores), STAS – 18848-73. To obtain the iodinated oil, in one litter of oil 1g of chemically pure, crystalline iodine (I_2) was administrated, STAS – 4159-79.

The oil with the total iodine content 1000 μg/mL, was diluted (1:100), obtaining a product with iodine content of 10 μg/mL. Diluting last product (1:10) the oil sample with 1μg/mL was obtained. After the establishment of the equilibrium, iodinated oils were used as samples for the present study.

The analysis of the fatty acids in the samples with iodinated oil was performed by gas chromatography with flame ionization detector, using gas chromatograph (helium)

HPCHEM 1 FID1 A, equipped with a database and an autosampler. Fatty acids were separated depending on the length of the chain and depending on the non saturation degree. Parameters: start temperature 55 ºC; temperature at the loop of the column and the transfer line 110ºC; ventilation 10 sec; injection 1.0 min, 1µL. The temperature of the injector - 180ºC and the components of the eluent were detected using a flame ionization detector at 250ºC. The concentrations were determined from the area of the peak using the standard curve of the authentic oil and the database.
Spectral analysis of the iodinated oil (compared to the analogous initial oil) and iodine (compared to the reference) was made using the spectrophotometer DR-5000 (HACH-LANGE).

RESULTS AND DISCUSSIONS

It is well known that halogens are able to saturate double bonds present in the fats. In the case of the active halogens such as fluoride and chloride addition in the double bond position it is made according to the mechanism which implies the formation of an ion type "halonium" as a result of the bimolecular nucleophyle substitution. Molecular iodine addition to the non saturated fats triglycerides doesn't take place because the iodine activity is very low and the increase of the carbon atoms number in the acid chain decreases the activity of the double bonds and reduces the saturation speed [15].
The saturated fatty acid, monounsaturated, and polyunsaturated acids analysis in the reference sample after the iodine administration in the oil showed that the amount of the main fatty acids in the sunflower oil (oleic and linoleic acid) basically doesn't vary (table 1).

Table 1. The amount (%) of the fatty acids in the iodinated sunflower oil

No.	Type of oil	µg I / mL oil	Temp, ºC	Concentration, %				
				$C_{16:0}$ Palmitic	$C_{18:0}$ Stearic	$C_{18:1}$ Oleic	$C_{18:2}$ Linoleic	$C_{20:0}$ Arahidic
1	Reference	0	18	6,46	3,37	22,37	66,40	0,46
2	1:1000	1	18	6,42	3,38	22,37	66,70	0,56
3	1:100	10	18	6,42	3,37	22,29	66,57	0,75
4	1:10	100	18	6,42	3,37	22,23	66,61	0,63
5	1:1	1000	18	6,41	3,33	22,29	66,77	0,67
1	Reference	0	140	6,56	3,49	22,70	66,53	0,70
2	1:1000	1	140	6,61	3,49	22,74	66,14	-
3	1:100	10	140	6,60	3,59	22,63	66,62	-
4	1:10	100	140	6,48	3,48	22,63	66,37	-
5	1:1	1000	140	6,62	3,51	22,79	66,67	-

The molecular iodine incorporation in the oil doesn't break the double bond and the addition of the iodine doesn't take place, this process being characteristic for other halogens as well. The verification of the instauration degree of the product (iodine index) confirms the invariability of the double binds number in the triglyceride molecule.

In the infrared region of the electromagnetic field the fatty mass adsorbs the radiant energy at 2 wave lengths specific in the middle infrared - $\lambda_{max} = 3,45$ µm and 5,73 µm and 2 wave lengths specific for the near infrared - 1724 cm^{-1} and 1230 cm^{-1}. It was established that the intensity of the light absorption bands for these wave lengths almost doesn't vary regardless the iodine concentration and corresponds to the literature data for the sunflower oil.
In the UV/visible field the displacement of the maximum adsorption was noticed which is characteristic for the triglycerides from the sunflower oil (fig. 1).

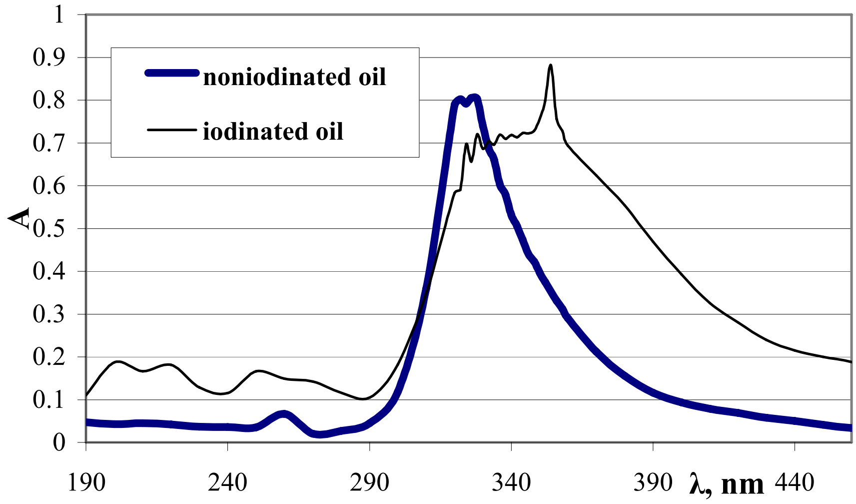

Figure 1. *Spectrum of the sunflower oil before and after iodination in the UV/VIS field*

This fact indicates the displacement of the double bonds in the fatty acids molecule. Administered iodine is fixed but not through covalent bonds but through the formation of certain molecular complexes due to the displacement of the electronic density and displacement of the double bonds. Molecular iodine fixation to the double bond of the unsaturated fatty acids takes place through the formation of the π complexes without double bond from the acid molecules being broken [16]. The bond between the electron acceptor (iodine) and donor is formed with the double bond π electrons participation from the fatty acids:

\ /
C
|| ⟶ $\mathbf{I}^{\delta+}$ — $\mathbf{I}^{\delta-}$
C
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Within the formed compounds, the displacement of the double bound takes place along with the displacement of the electronic density towards the iodine molecule this being more electronegative which ensures the stability of the formed complex. The maximal absorption registered at 354 nm proves the formation for the π complexes.
To be able to investigate the iodine fixation by the sunflower oil, the relationship between the absorbance and the administered iodine amount within the maximal absorption field (λ_{max} = 520 nm) was studied. It was established that in the

concentrations range 1 – 400 μg/mL the iodine concentration increase doesn't lead to an essential increase of the absorbance (fig. 2).

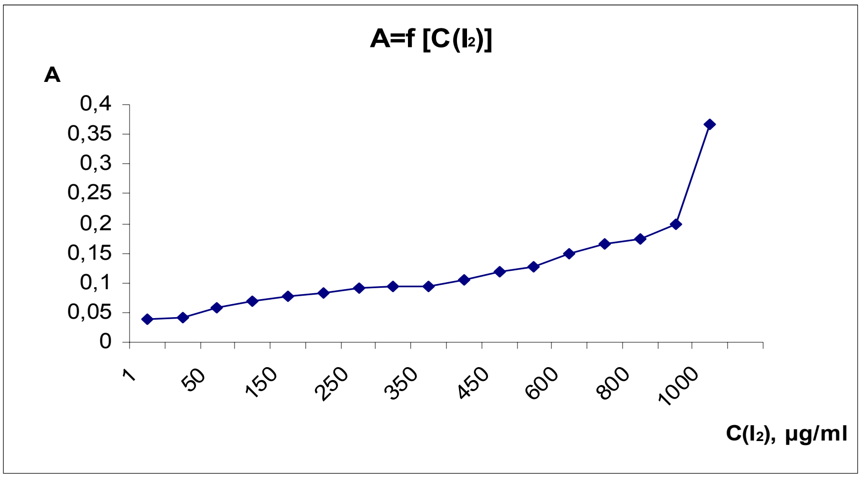

Figure 2. *The influence of the iodine concentration on the absorbance of the sunflower oil ($\lambda_{\max}$ = 520 nm)*

Subsequently, a non significant increase of the slope (450 – 900 μg/mL) was noticed. After 950 μg I_2 /mL a steep increase of the absorbance was noticed this being due to the free iodine present.

This sudden variation of the absorbance shows that the sunflower oil ability to fix molecular iodine is kept for a limited concentration range. Therefore, if the maximum concentration of the iodine fixed as π complexes is 950 μg/mL of sunflower oil, this amount corresponds to 3.74 μmol/mL or 3.74 mmol/L of sunflower oil. If this characteristic is compared with the iodine index of the sunflower oil (127 – 131 g I_2 /100g sunflower oil, thus 5 mol/kg of sunflower oil) it is obvious that only a tiny part of the double bonds present in the sunflower oil are able to fix molecular iodine without breaking these bonds.

This work was lead to investigate the evolution of the kinetic parameters during iodination process of the triglycerides in the sunflower oil.

We consider the reaction (1):

$$Triglyceride + \nu\, I_2 \leftrightarrow \pi\ \text{- } complex \tag{1}$$

or:

	A	$+\ \nu B \leftrightarrow$	C
initial:	a	b	-
equilibrium:	(a – b_x)	(b – b_x)	b_x

Because the reaction stoechiometry (1) is not known, for the kinetics examination of this reaction the notion of reaction promotion was used which can be determined from the equation [17]:

$$\frac{dn_i}{\nu_i} = d\xi \tag{2}$$

where ξ means the reaction promotion, which means its evolution towards the equilibrium state and ν_i - represents the stoechiometry coefficient of the i component which amount variation of which can be analyzed. By integration of the differential equation (2) we obtain:

$$\frac{1}{\nu_i}\int_{no}^{ni} dn_i = \int_0^{\xi} d\xi \qquad (3)$$

where:

$$\frac{n_i - n_0}{\nu_i} = \xi \text{, or } n_i = n_0 + \nu_i \xi \qquad (4)$$

Therefore, the issue regarding reaction rate description is defined through the unique reaction rate with variation speed of the reaction promotion:

$$v = \frac{1}{\nu_i}\cdot\frac{dn_i}{dt} = \frac{d\xi}{dt} \qquad (5)$$

The reaction rate can be defined according to the law of mass effect through the relation:

$$v = k\prod [R_i]^{\alpha_i} \qquad (6)$$

where k is the reaction constant; $[R_i]$ - reactants concentration, and α_i - partial order of the reaction compared to the respective reactant. It is obvious that the algebraic sum of the partial orders represent the global order of the reaction:

$$n = \alpha_1 + \alpha_2 + \ldots.$$

For the examined case (1), the expression for the reaction rate can be written as follows:

$$v = k[Triglyceride]^{\alpha_1}\cdot[I_2]^{\alpha_2} \qquad (7)$$

But the triglyceride concentration is not higher that iodine concentration and during reaction process till the equilibrium state is reached this varies no significantly. Due to this, in the kinetic equation of the reaction, reaction promotion compared to the triglyceride concentration can be neglected which means that the rate expression will be given by the following relation:

$$v = \frac{d\xi}{dt} = k([A]_0 - \xi)^{\alpha_1}\cdot[B]_0^{\alpha_2} \qquad (8)$$

or

$$\frac{d\xi}{dt} = k^1([A]_0 - \xi)^{\alpha_1} \text{, where } k^1 = k[B]_0^{\alpha_2} \qquad (9)$$

In this case, the reaction order is considered to be degenerated and the reaction constant k^1 also known as pseudo-constant will depend on the excess component concentration.
During this study the reaction order variation depending on the molecular iodine which is considered as the component, whose initial concentration is noted as $[A]_0$, and the reaction order is α_1.
In order to establish the reaction order during this work we studied the evolution of the iodine concentration in time. It was established that this relationship has an exponential form (fig. 3). A similar variation of the reactive concentration is characteristic for the first order reaction.
For the first order reaction the reaction speed can be expressed by the following relation:

$$v = -\frac{1}{1}\cdot\frac{d[A]}{dt} = \frac{d\xi}{dt} = k[A] \qquad (10)$$

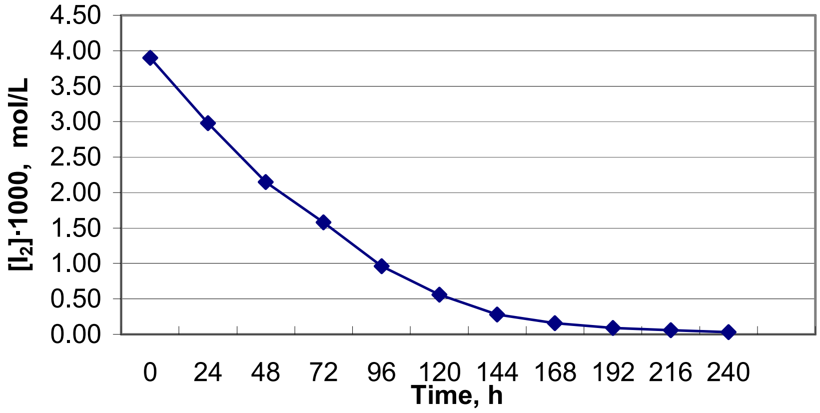

Figure 3. *Iodine concentration evolution during iodination of the sunflower oil ($[I_2]=3,9\cdot10^{-3}$ Mol.L^{-1}; t = 25 ºC)*

After integration we obtain:

$$\ln\frac{[A]_0}{[A]} = kt\,,\quad \text{or}\quad [A]=[A]_0 e^{-kt} \tag{11}$$

Based on the equation (9) we can calculate the value of the speed constant considering the reaction progression:

$$\ln\frac{[A]_0}{[A]_0-\xi} = kt \tag{12}$$

The results are presented in figure 4.

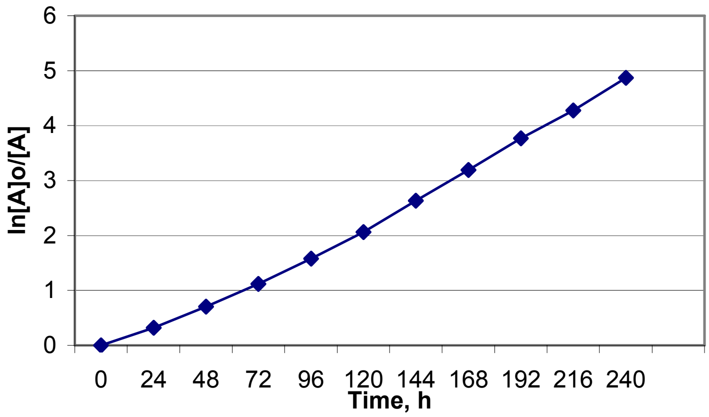

Figure 4. *Relation $\ln\{[I_2]_0/[I_2]\} = f(t)$ for the iodination reaction of the triglycerides from the sunflower oil ($[I_2]_0=3,9\cdot10^{-3}$ Mol.L^{-1}; t = 25 ºC)*

From the data plotted in fig. 4, it was established that $tg\ \alpha = 2.12\cdot10^{-2}$ h^{-1}. But $tg\ \alpha = k$, thus the rate constant of the reaction (1) has the value:

$$k = 2.12\cdot10^{-2}\ \text{h}^{-1}\qquad (\text{for T} = 298\ \text{K})$$

If the order and the rate constant of the reaction are known the half-time of the reaction can be established. For a first order reaction the following relation can be used:

$$\ln \frac{[A]_0}{[A]_0 / 2} = k \cdot t_{1/2} = \ln 2 \qquad (13)$$

which leads to the relation:

$$t_{1/2} = \frac{0.693}{k} \qquad (14)$$

Therefore, the half-time reaction of the triglycerides iodination process from the sunflower oil constitutes:

$$t_{1/2} = 32.69 \text{ h (for T = 298 K)}$$

Aiming the elucidation of the temperature influence on the reaction rate, the reaction rate was examined at different temperatures. For the temperature range 298 – 340 K it was established a reaction progressing and the reaction rate and the rate constant were calculated. The results are presented in table 2.

Table 2. *Kinetic parameters of the reaction iodine-triglycerides* from the sunflower oil depending on the temperature*

Temp. [K]	**Reaction evolution, ξ [mol.L^{-1}]**	**Reaction rate, v [mol.L^{-1}.h^{-1}]**	**Rate constant, k [s^{-1}]**	**Arrhenius parameters of the reaction**	
				activation energy, E_a [kJ.mol^{-1}]	**frequency factor, A [s^{-1}]**
298	$1,9 \cdot 10^{-4}$	$7,9 \cdot 10^{-6}$	$2,12 \cdot 10^{-2}$		94,7
310	$2,5 \cdot 10^{-4}$	$12,1 \cdot 10^{-6}$	$2,84 \cdot 10^{-2}$		89,6
320	$3,2 \cdot 10^{-4}$	$13,3 \cdot 10^{-6}$	$3,72 \cdot 10^{-2}$	20,735	91,4
330	$4,1 \cdot 10^{-4}$	$17,1 \cdot 10^{-6}$	$4,79 \cdot 10^{-2}$		91.5
340	$5,2 \cdot 10^{-4}$	$21,7 \cdot 10^{-6}$	$6,14 \cdot 10^{-2}$		95,3

* Initial concentration $[I_2]_0 = 3.9.10^{-3}$ mol.L^{-1}

It was established that although the reaction speed increases when temperature increases, the thermal coefficient is not too high:

$$\frac{k_{T+10}}{k_T} \approx 1.28$$

This proves that the reaction is limited not by the kinetic factors but by the diffusion factors. These are caused by the high viscosity of the system as well as by the steric factors which hinders the molecular iodine penetration in the sites assigned for the π compounds formation. It is obvious that the settlement of the electronic density requires energy and time outlay.

In order to establish the Arrhenius parameters of the iodine-triglyceride reaction from the sunflower oil the diagram ln *k* in terms of 1/T was drown (fig. 5).

It was established that the relationship $-\ln k =$ f(1/*T*) represent a straight line which proves that the examined process may be described using Arrhenius equation:

$$\ln k = \ln A - \frac{E_a}{RT} \qquad (15)$$

From the diagram the slope was established:

$$-\ln k = f(1/T) = \frac{E_a}{R} = 2.494$$

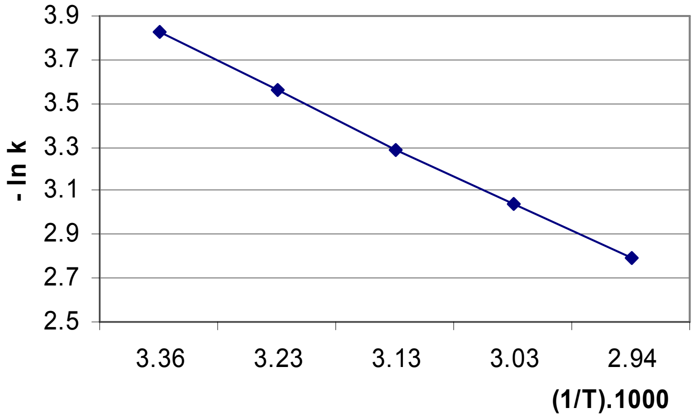

Figure 5. *Relationship between the rate constant of the reaction and the temperature*

The activation energy of the examined reaction is 20.735 $J.mol^{-1}$, or 20,735 $kJ.mol^{-1}$. The calculations made through analytical method based on the relation:

$$\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{16}$$

proved that the average of the obtained values for the activation energy of the triglyceride iodination process of the sunflower oil are:

$$E_a \approx 20{,}74 \cdot 10^3\,\mathrm{J.mol^{-1}}$$

Subsequently, the values of the frequency factor (A) were calculated based on the Arrhenius equation and the average value of the activation energy:

$$\ln A = \ln k + \frac{E_a}{RT}$$

Obtained values are indicated in the table 2. The average value of the frequency factor is:

$$A = 92.5\ \mathrm{s^{-1}}$$

The obtained results show that the reaction involved in the π compounds triglycerides-iodine formation are characterized by a relatively low activation energy - $E_a \approx 20{,}74 \cdot 10^3\,\mathrm{J.mol^{-1}}$, but the frequency factor is extremely low which explains the low speed of the π complex formation reaction iodine – triglyceride from the sunflower oil.

CONCLUSIONS

The possibility and capacity of the molecular iodine incorporation in the sunflower oil was studied. It was established that during oil iodination the iodine is not simply added to the oil, but a process of fixation of molecular iodine to the double bond with π complexes formation takes place without double bond from the unsaturated fatty acids being broken.

Kinetic parameters of the π compounds iodine – triglycerides formation in the sunflower oil were investigated. It was established that the process is described by a first order kinetic reaction. The reaction constant values and the half-time values were established: $k = 2.12 \cdot 10^{-2}$ h^{-1} and $t_{1/2} = 32.69$ h (for T = 298 K).

For the temperature range 298 – 340 K the reaction evolution was established and the reaction rate and rate constant value have been calculated for the process of formation of π compounds iodine – triglyceride in the sunflower oil. The thermal coefficient of the reaction was established to be 1.28. Also we observed that this process can be described by the Arrhenius equation which was proved by the straight line obtained in the diagram $-\ln k = f(1/T)$. The Arrhenius parameters of the reaction were calculated:

$$E_a \approx 20.74.10^3 \text{ J.mol}^{-1} \text{ and } A = 92.5 \text{ s}^{-1}$$

The relatively low value of the activation energy and the extremely low value of the frequency factor prove that the reaction is limited by the diffusion factors and not by the kinetic factors. These are caused by the high viscosity of the system as well as by the steric factors which hinder the molecular iodine penetration in the sites assigned for the π compounds formation. Therefore the thermal factor does not seam to have a decisive influence on the reaction speed.

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