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Lidiya Mazaletskaya, Nataliya Sheludchenko and Lyudmila Shishkina

INHIBITORY EFFICIENCY OF ANTIOXIDANT AND PHOSPHOLIPID MIXTURES UNDER THE DIFFERENT OXIDATION EXTENT OF METHYL OLEATE

Emanuel Institute of Biochemical Physics of Russian Academy of Sciences,
4 Kosygin str., 119334 Moscow, Russia; lim@sky.chph.ras.ru

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Abstract. Results of investigations of the phospholipids (PL) and hydroperoxide influence on the antioxidant action efficiency of the synthetic phenolic antioxidants (InH) –2,6-di-*tert*-butyl-4-methylphenol (BHT), 4-methoxyphenol (MOP), 4-*tert*-butylphenol; natural InH – α-tocopherol (TP), quercetin (Q) and dihydroquercetin (QH_2) and hydrated quinoline – 2,2,4-trimethyl-6-ethoxy-1,2-dihydroquinoline (ethoxyquin, EQ), performed by the model of the initiated oxidation of methyl oleate are generalized. It is established that the PL additives lead to both an increase of the oxidation rate within the induction period (W_τ) and an alteration of the induction period duration (τ). According to the increase in W_τ for mixtures with PL studied InH is graded by the following sequence: QH_2 > Q > EQ > TP > MOP > BHT, that is conformed by the differential UV spectroscopy data. The value of τ increases in the presence of PL for TP, MOP and EQ, it is unchangeable for BHT and substantially decreases for QH_2 and Q. Reasons leading to an alteration of the InH efficiency in the PL presence are discussed.

Keywords: inhibition, synthetic antioxidant, α-tocopherol, quercetin, dihydroquercetin, phospholipids

1. Introduction

Biological activity of compounds is mostly due to their ability to take part in the regulation of oxidative processes in the organism. The intensity of oxidative processes is particularly reduced, if the system contains a special group of substances – antioxidants (InH), the reactivity of which depends on the conditions of oxidation, the nature of oxidation substrates, physicochemical properties of InH [1-6] are distinguished from the systems of varying degrees of complexity. In this work we consider the influence of natural components of cells – phospholipids (PL) and the primary molecular products of oxidation – hydroperoxides on the inhibiting efficiency of a number of InH by the initiated oxidation of methyl oleate.

2. Experimental

Following InH were used: synthetic phenols – 2,6-di-*tert*-butyl-4-methylphenol (BHT), 4-methoxyphenol (MOP), 4-*tert*-butylphenol (TBP), natural InH – α-tocopherol (TP), quercetin (Q), dihydroquercetin (QH_2) and hydrated quinoline – 2,2,4-trimethyl-6-ethoxy-1,2-dihydroquinoline (ethoxyquin, EQ), a molecule of which contains an active aminogroup. Studied PL were phosphatidylcholine from the egg yolk (PC, «Sigma»), dipalmitoylphosphatidylcholine (DPPC, «Sigma») and lecithin («Serva»). According to the TLC, the lecithin is a mixture of natural lipids, containing 56.6 % PL, among which 96.6 % were PC. Methyl oleate oxidation (333 K), initiated by azobisizobutironitrile (AIBN), was controlled by the kinetic of oxygen uptake. Methyl oleate in the mixture with inert dissolvent chlorobenzene (1:1) and the dissolved initiator were termostated. Then InH and PL were added. The initial rates of oxidation, as well as the duration of the induction period (τ), were determined from the kinetic curves of oxygen uptake by the method described in [7]. The induction period in the presence of InH was the equal interval from the beginning of the experience until projection the point of intersection of two straight lines for which tg α_1 = 2 tg α_2. The first line is corresponded to an extension of a straight of the oxygen uptake, when the reaction rate is constant after the complete consumption of InH. The second line is tangent to the kinetic curve of the oxygen uptake in the point, in which the reaction rate is twice less than that in the absence of the inhibitor.

3. Results and Discussion

The simplest kinetic scheme, describing the initiated oxidation process in the presence of InH includes the following reactions:

(i) AIBN → 2 r· (RH) → $2R^{\bullet}$
(1) $R^{\bullet} + O_2 \rightarrow RO_2^{\bullet}$
(2) $RO_2^{\bullet} + RH \rightarrow ROOH + R^{\bullet}$
(3) $ROOH \rightarrow RO^{\bullet} + OH^{\bullet}$
(6) $RO_2^{\bullet} + RO_2^{\bullet} \rightarrow ROOR + O_2$
(7) $InH + RO_2^{\bullet} \rightarrow In^{\bullet} + ROOH$
(8) $In^{\bullet} + RO_2^{\bullet} \rightarrow$ molecular products
(9) $In^{\bullet} + In^{\bullet} \rightarrow$ molecular products
(10) $In^{\bullet} + RH + O_2 \rightarrow RO_2^{\bullet} + InH$
(10') $In^{\bullet} + ROOH \rightarrow RO_2^{\bullet} + InH$
(11) $InH + ROOH \rightarrow$ molecular products
(12) $InH + O_2 \rightarrow In^{\bullet} + HO_2^{\bullet}$

As seen, along with the reactions which lead to break of the oxidation chain (Eqs. (7) and (8)), InH and their radicals may be involved in side reactions of the propagation chain (Eqs. (10), (10'), (12)). Reactions (11) and (12) lead to the "unproductive" consumption of InH and in such a way the InH concentration, involved in the process of the oxidation inhibition, is decreased. The efficiency of InH depends on a complex of reactions with their participation, the contribution of which changes a dependence on the oxidation conditions. The mathematical analysis of kinetic curves of the oxygen uptake in the presence of the InH additives, which was conducted by the software package KINS [8] testifies to the contribution of side reactions in the mechanism of the InH inhibition. Calculations show that kinetic curves of oxygen uptake in the presence of BHT or Q (methyl oleate, 333 K) correspond to the mechanism, when there is the interaction of these InH with peroxyl radicals mainly [9]. Hence, the role of side reactions in the inhibition mechanism for these InH is very small. On the contrary, the character of kinetic curves in the presence of TP, MOP and EQ suggests the InH involvement in the side reactions.

Experimental data, which evidence about the interaction of TP and EQ with hydroperoxide (ROOH) and the lack of interaction between Q and ROOH, are consistent with the results of the mathematical analysis. The reaction between Q and ROOH was studied by means of the consumption of Q under anaerobic conditions at 333 K. It is established, that the consumption rate of Q (W_Q) at $[ROOH]_0 = const$ is independent on $[Q]_0$ in the range of Q concentrations, provided the linear chain termination. However, W_Q increases with the growth in the $[ROOH]_0$ concentration at the fixed initial concentration of Q. The results obtained indicate that Q does not practically interact with ROOH under experimental conditions. The consumption of Q is due to its interaction with free radicals forming during the thermal decay of ROOH.

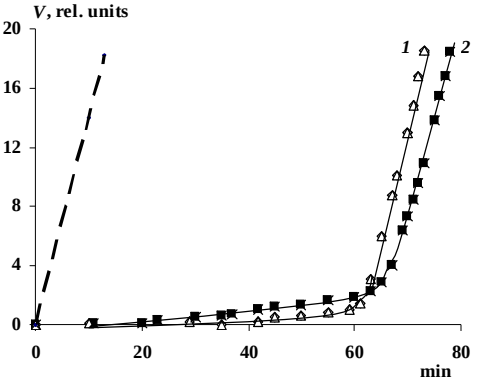

Fig. 1. Kinetic curves of oxygen uptake during the methyl oleate oxidation (333 K) without additives (the dotted line) and in the presence of 1.25 mg/ml lecithin (the dotted line): $2.5 \cdot 10^{-4}$ mol/l TP (1); $2.5 \cdot 10^{-4}$ mol/l TP and 1.25 mg/ml lecithin (2). Methyl oleate: chlorobenzene = 1:1, $W_i = 1 \cdot 10^{-7}$ mol/l s

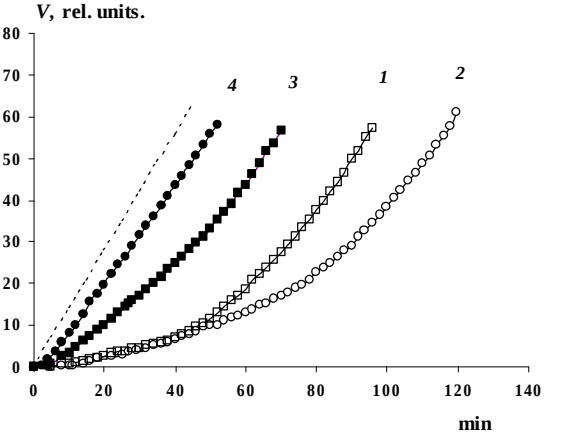

Fig. 2. Kinetic curves of oxygen uptake during the methyl oleate oxidation (333 K) without additives (the dotted line) and in the presence of 1.25 mg/ml lecithin (the dotted line): $2 \cdot 10^{-4}$ mol/l Q (1); $2 \cdot 10^{-4}$ mol/l QH_2 (2); $2 \cdot 10^{-4}$ mol/l Q and 1.25 mg / ml lecithin (3); $2 \cdot 10^{-4}$ mol/l QH_2 and 1.25 mg/ml lecithin (4). Methyl oleate: chlorobenzene = 1:1, $W_i = 1 \cdot 10^{-7}$ mol/l s

The ability of TP to decompose methyl oleate ROOH was confirmed, when TP at the concentration of $4.8 \cdot 10^{-2}$ mol/l was added to oxidized methyl oleate at room temperature: the concentration of ROOH decreased with $4.5 \cdot 10^{-2}$ to $3.7 \cdot 10^{-2}$ mol/l [10]. The result of the interaction of TP with ROOH, apparently, is reduction of the duration of the induction period with increasing initial concentration of ROOH. So, under $[ROOH]_0 = 2 \cdot 10^{-4}$ mol/l $\tau_{TP} = 61$ min, while under $[ROOH]_0 =$

= $1.2 \cdot 10^{-2}$ mol/l τ_{TP} = 48 min. Thus, the presence of the primary oxidation product – ROOH – in the system, may reduce the InH effectiveness even under conditions of moderate temperature (333 K) and high rate of generation of free radicals, that is due to the reaction between InH and ROOH. Individual PL almost had no influence on the reaction rate of initiated oxidation methyl oleate: kinetic curves in the presence and absence of PL coincided in all cases (Fig. 1, the dotted line). However, adding PL to InH alters the effectiveness of their action. Comparison of the kinetic curves of oxygen uptake during the oxidation of methyl oleate in the presence of TP (Fig. 1, curve 1) and the mixture of TP and lecithin (Fig. 1, curve 2) shows that the addition of lecithin alters the kinetic curves of the oxygen uptake, leading to an increased rate of oxidation during the induction period ($W\tau$). At the same time the duration of the induction period is increased. The different effect of the PL additives on the values $W\tau$ and τ can lead to indefinitive conclusions under the evaluation of the inhibiting action effectiveness for such mixtures. So, if the inhibition effectiveness is evaluated by oxygen uptake within the induction period or $W\tau$, then the action of the mixture can be described as antagonistic. When the comparative analysis is performed by the induction period duration, the mixture can be regarded as synergistic. Point of intersection of curves 1 and 2 (Fig. 1) formally corresponds to the additive action of the components in the mixture and isolates the antagonistic field from the synergistic action. Two other studied PL – PC and DPPC exert a similar influence on the efficiency action of TP. The increase of $W\tau$ in the presence of PL was also observed for BHT, MOP, TBP, Q, QH_2, EQ. The most powerful influence of PL on the $W\tau$ change was detected for the flavonoids.

To estimate changes in the efficiency of InH within the induction period the ratio of the efficiencies of inhibition in the presence of InH and its mixture with PL was calculated: (W_0/W_{InH}): $(W_0/W_{mix}) = W_{mix}/W_{InH}$, where W_0 is the rate of initiated oxidation, W_{InH} and W_{mix} are the rates of oxidation within the induction period in the presence of InH and the mixtures of InH with PL, respectively. The higher ratio of W_{mix}/W_{InH} is due to the greater reduction in the effectiveness of InH in the presence of PL within the induction period. As seen from Table 1, where the corresponding ratio for the mixtures of different InH and PL is presented the ratio magnitude depends on the InH structure and the PL concentration.

On the basis of these data antioxidants may be arranged according to their efficiency in the presence of PL as the following series:

$$QH_2 > Q > EQ > TP > MOP > BHT$$

Besides, the value of W_{mix}/W_{InH} depends on the initial concentration of the components in the mixture and increases with increasing concentrations of InH and PL (see Table 2).

Table 1

The values of W_{mix}/W_{InH} for antioxidants with different structures

Antioxidant	$[InH]_0 \cdot 10^4$, mol/l	$[PL]_0$, mg/ml	W_{mix}/W_{InH}
Dihydroquercetin (QH_2)	2	1.25*	10.2
Quercetin (Q)	2	1.25*	2.4
Ethoxyquin (EQ)	2.7	1.25**	1.1
Ethoxyquin	2.7	2.5**	3.0
α-Tocopherol (TP)	2.7	2.5**	2.1
4-Methoxyphenol (MOP)	2.7	2.5**	1.8
BHT	2.7	2.5**	1.4

Note: * Lethitin, ** PC

Table 2

The values of W_{mix}/W_{InH} in the oxidation of methyl oleate (333 K) at different initial concentrations of the components in the mixture. Methyl oleate: chlorobenzene = 1:1, $W_i = 1 \cdot 10^{-7}$ mol/l s

Antioxidant	$[InH]_0 \cdot 10^4$, mol/l	$[PC]_0$, mg/ml	W_{mix}/W_{InH}
Ethoxyquin	0.9	2.5	1.4
Ethoxyquin	2.7	2.5	3.0
Ethoxyquin	2.7	1.0	1.5
Ethoxyquin	2.7	1.25	1.1
α-Tocopherol	0.9	2.5	1.2
α-Tocopherol	2.7	2.5	2.4
α-Tocopherol	2.7	1.25	1.2

Dependence of W_{mix}/W_{InH} on $[PL]_0$ at a fixed concentration of InH, is a straight line, which cut off the segment on the ordinate axis, equal to 1. This is illustrated by data obtained during the oxidation of methyl oleate in the presence of mixtures of PC and EQ (Fig. 3).

Proceeding from the ability of several antioxidants to interact with the hydroperoxides, it can be assumed that the degree of the substrate oxidation may also change the effectiveness of a mixture of InH with PL. Effect of initial concentration of hydroperoxide ($[ROOH]_0$) in methyl oleate was examined by the example of mixtures of TP and MOP (Table 3).

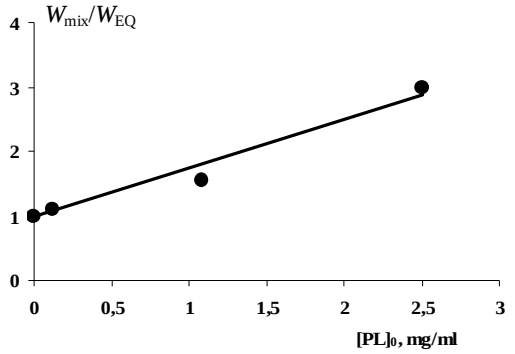

Fig.3. Dependence of W_{mix}/W_{EQ} on $[PC]_0$ during methyl oleate oxidation. Methyl oleate: chlorobenzene = 1:1, $W_i = 1 \cdot 10^{-7}$ mol/l, $[EQ]_0 = 2.7 \cdot 10^{-4}$, mol/l·s; 333 K

Table 3

The values of W_{mix}/W_{InH} in the oxidation of methyl oleate (333 K). Methyl oleate: chlorobenzene = 1:1, $W_i = 1 \times 10^{-7}$ mol/l s; $[InH]_0 = 2.7 \times 10^{-4}$ mol/l; $[PC]_0 = 2.5$ mg/ml

Antioxidant	$[ROOH]_0 \cdot 10^2$, mol/l	W_{mix}/W_{InH}
α-Tocopherol	0.02	1.2
α-Tocopherol	0.13	1.3
α-Tocopherol	0.61	1.8
α-Tocopherol	1.2	2.3
4-Methoxyphenol	0.13	1.3
4-Methoxyphenol	1.1	1.8

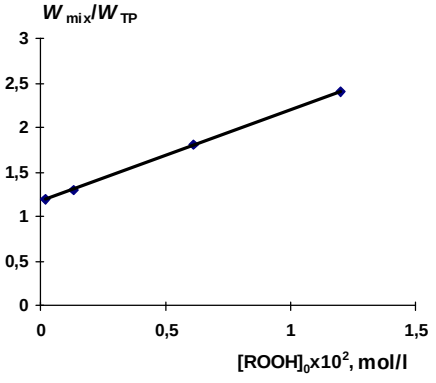

Fig.4. Dependence of W_{mix}/W_{TP} on $[ROOH]_0$ during methyl oleate oxidation. The temperature is 333 K, $[TP]_0 = 2.7 \cdot 10^{-4}$ mol/l, $[PC]_0 = 2.5$ mg/ml, methyl oleate : chlorobenzene = 1:1, $W_i = 1 \cdot 10^{-7}$ mol/l s

Indeed, the increase in $[ROOH]_0$ leads to an increase in W_{mix}/W_{InH} (Table 3), while the dependence of W_{mix}/W_{InH} on $[ROOH]_0$ is a straight line, the segment of which $W_{mix}/W_{InH} > 1$ at $[ROOH]_0 = 0$ (Fig. 4). The magnitude of this ratio indicates how many times W_{mix} increases compared with W_{InH}.

Change of $W\tau$ in the PL presence may be due to the interaction of components in the mixture. The reaction of the interaction of PL with InH was studied by means of the spectrophotometrical method at room temperature. The electron absorption spectra of lecithin with TP are presented in Fig. 5. The changes, observed in the differential absorption spectra of mixtures, indicate the interaction between components in the mixture. Similar results were obtained for other PL–PC in mixture with monophenols [11]. It was found that the scale of the changes of the absorption spectra of mixtures is determined by the degree of the steric hindrance for OH-group in molecules of monophenols, which are arranged in series TP > MOP > BHT. This series is coincided with the sequence of changes for W_{mix}/W_{InH} values, obtained for phenols containing one OH-group during methyl oleate oxidation. Authors [12] also established, that the interaction of Q with PL leads to the formation of complexes and is accompanied by a change in the electronic and the conformational structure of the Q molecule.

Reduction of the inhibiting action effectiveness of InH in the presence of PL allows us to suggest, that the interaction between them results in the formation of complexes, which are less active or inactive in the inhibition and are in equilibrium with the initial components of the mixture. In this case the concentration of InH, that is not bound into the complex, is determined by the Eq (I):

$$[InH] = [InH]_0/(1 + Kp\,[PL]_0) \quad (1)$$

where Kp is an equilibrium constant of the complex formation.

The assumption, that the formation of the complex inactive in the inhibition leading to a decrease in the effective concentration of InH, can satisfactorily describe the experimentally revealed increase of oxidation initial rate for the mixtures of PL and antioxidants. For this calculation we used data obtained during oxidation of model hydrocarbon – ethylbenzene in the presence of TBP and its mixtures with PC, by means of a chemiluminescence technique (Table 4).

The choice of TBP was determined by the moderate value of the rate constant of its interaction with peroxyl radicals, where $k_7 = 2.9 \cdot 10^4$ l/mol·s (333 K) [13]. Besides, the registration of the chemiluminescence intensity for mixtures of InH and PL is easily carried out by means of chemiluminescence for InH itself. As found, I/I_0 (where I_0 and I are the intensities of chemiluminescence without additives and in the presence of InH and PL) as well as W_{mix}/W_{InH}, gain with the increase of the PL concentration in the mixture (Table 4).

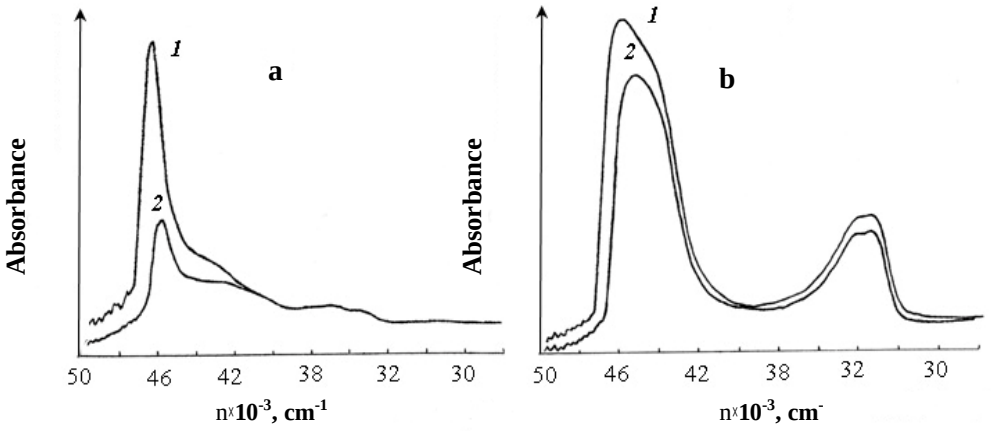

Fig. 5. Electronic absorption spectra of lecithin (1a) and TP (1b) and their mixture (2a and 2b), recorded against TP (2a) and lecithin (2b). Solvent – hexane, optical path length – 1 cm, $[\text{lecithin}]_0 = 0.625$ mg/ml, $[\text{TP}]_0 = 1 \cdot 10^{-4}$ mol/l

Table 4

The values of the relative residual chemiluminescence $(I/I_0)_0$ during initiated oxidation of ethylbenzene in the presence of 4-*tert*-butylphenol and its mixtures with PC

Temperature, K	$W_i \cdot 10^7$, mol/l s	$[\text{TBP}]_0 \cdot 10^4$ mol/l	$[\text{PC}]_0$, mg/ml	$(I/I_0)_0$
333	0.5	2.9	–	0.266
333	0.5	2.9	3.1	0.436
353	1.0	0.63	–	0.17
353	1.0	0.63	0.06	0.19
353	1.0	063	0.15	0.256
353	1.0	0.63	0.28	0.308
353	1.0	0.63	0.34	0.339
353	1.0	0.63	0.4	0.31
353	1.0	0.63	1.25	0.448
353	1.0	0.63	1.7	0.526
353	1.0	0.63	2.5	0.545
353	1.0	0.63	4.25	0.717

The values I/I_0 change were calculated taking into account the formation of the complex in dependence on $[\text{PL}]_0$. The rate of the inhibited oxidation under a mixed-chain breakage condition, in which it is realized for mixtures of TBP with PC and included the reactions $RO_2^{\bullet} + \text{InH}$ and $RO_2^{\bullet} + RO_2^{\bullet}$, is described by Eq. (2):

$$W_0/W_{\text{mix}} - W_{\text{mix}}/W_0 = f k_7 [\text{InH}]_0/(k_6 W_i)^{0,5} \qquad (2)$$

where W_0 is the rate of initiated oxidation of ethylbenzene in the absence of additives InH, k_6 is the reaction rate constant of square termination. As it was shown in [14], $W_0/W = (I_0/I)^{0.5}$. In the calculation it was assumed that [PC] = *const*, because in the reaction mixture [PC] >> [InH]. The final eguation obtained by taking into account Eq. (1) has the form:

$$[(I_0/I)^{0.5} - (I/I_0)^{0/5}]^{-1} = (k_6 Wi)^{0.5} (1 + \\ + K\text{p}[\text{PL}]_0)/fk_7[\text{InH}]_0 \qquad (III)$$

As can be seen from Fig. 6, the experimentally obtained values I/I_0 (Table 4) is linearized satisfactorily in coordinates of Eq. (3). Thus, the assumption about the formation of the complex inactive in inhibition allows us to describe satisfactorily the experimentally observed regularities, corresponding to the initial stages of the reaction. Analysis of the chemiluminescence curves showed that by the PC additive to the antioxidants there is some reduction for the tangent of the maximal slope (β) along with the increase of the chemiluminescence intensity. So, for $2.9 \cdot 10^{-4}$ mol/l TBP in the presence of 3.1 mg/ml PC, β is decreased from $1.84 \cdot 10^{-4}$ s^{-1} to $1.4 \cdot 10^{-4}$ s^{-1}. Similar results were obtained for MOP. Reduction of β, along with an increase of I/I_0 indicates that the complex formation, apparently, leads to a decrease in antiradical activity of InH in the mixture with PL. This conclusion is

consistent with the data of [15-17], where the observed decrease in the antiradical activity (k_7) of InH in the reaction with peroxyl radicals of tertiary amines as compared to k_7 for the same InH with peroxyl radicals of hydrocarbons is found. This result is associated with the formation of hydrogen bond between the H-atom of the hydroxyl group of InH and nitrogen-containing oxidation substrate.

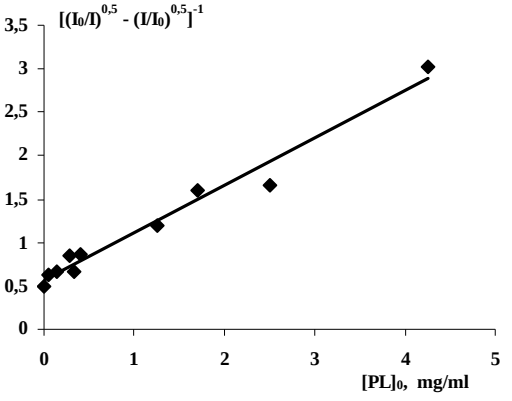

Fig. 6. Anamorphous of dependence of chemiluminescence intensity on the concentration of PC in coordinates of Eq. (III)

Thus, the decrease of inhibiting efficiency of InH by addition of PL at the initial stages of oxidation can be caused by reduction of the effective concentration of InH due to the complex formation and/or a decrease in antiradical activity of the product of the component interaction.

As already noted, in addition to increasing W_τ PL additive to InH can change the duration of τ. According to the influence of PL on the duration of τ for different InH, the latter can be divided into three groups.

The first group includes EQ, TP and MOP, for which the induction period in the presence of PL is increased. At the same time the scale of the effect depends on the nature of PL: for a mixture of TP + PC the value $(\tau_{mix} - \tau_{InH})/\tau_{InH}$ = 4 %, whereas for a mixture of TP and lecithin, this value is 15 %. The influence of PL on τ was established for another class of natural antioxidants – polihydroxynaphtoquinons [18]. It could be assumed that the increase in τ for this group of InH takes place due to the fact that formation of the complex leads to a decrease not only the rate of inhibition reactions, but also the rate of side reactions with the participation of InH. Another reason for the prolongation of inhibitory action of mixtures compared with InH may be the regeneration of InH mediated by the amino group of the tertiary amines. This conclusion is based on data [15, 17], according to which the retardation of tertiary amines oxidation leads to an increase of the stoichiometric inhibition coefficient, which is caused by repeated break of the oxidation chains.

Representatives of the second group are hindered phenols, for which the rate of side reactions is negligible. So, the PL additive to BHT has almost no impact on the value of τ.

For the third group, which includes flavonoids – Q and QH_2, a sharp decrease in the induction period is observed. So, the value of τ for Q, calculated from the kinetic curves (Fig. 2, curve 1), is τ = 67 min, while the mixture Q with lecithin (1.25 mg/ml) leads to reduction of τ to 37 min (Fig. 2, curve 3). QH_2 is very effective (Fig. 2, curve 2) in the absence of lecithin (τ = 82 min), but its mixture with lecithin almost completely loses the activity and only slightly retards the oxidation process (Fig. 2, curve 4). For this reason, the determination of the induction period from the kinetic curve of oxygen uptake in the presence of the mixture of QH_2 with lecithin is not possible. For mixtures of Q with PL the change of τ depends on the amount of added PL (lecithin). The most dramatic decrease in τ is observed within the concentration range of 0.1–0.3 mg/ml, a further increase in the amount of lecithin in the mixture practically does not change τ (Table 5). Thus, flavonoids differ from monophenols by the results of PL influence. For the mixture of flavonoids and PL there is not only the most significant increase in the rate of oxidation within the induction period, but a substantial decrease in τ, *i.e.* the mixture of flavonoids with PL can be classified as antagonistic at all criteria.

Table 5

The duration of the induction period (τ) during the oxidation of methyl oleate (333 K), inhibited by the mixtures of quercetin and lecithin, $[Q]_0 = 2\times10^{-4}$ mol/l, methyl oleate: chlorobenzene = 1:1, $W_i = 1\times10^{-7}$ mol/l s

[Lecithin]$_0$, mg/ml	–	0.1	0.3	0.63	1.25
τ, min	67	58	41	40	38

The differences, observed for the effecteveness of mixtures of flavonoids and monophenols with PL, may be related to the fact that flavonoids, in contrast to monophenols, are more hydrophilic, and may be localized whithin the polar region of the lecithin bilayer (or micelles) [19] under their interaction with PL, while TP is localized into the hydrophobic region. Since PL form directs micelles in organic solvents [20], the flavonoids are located inside micelles or bilayer, formed by the PL molecules. Perhaps, the hindered access of radicals to InH is due to the flavonoid location inside micelles or bilayer form of the PL molecules that leads to the reduction of the inhibition interval and to the increase of the initial oxidation rate, as well as the decrease of the antiradical

activity. It should be noted that among the studied flavonoids, QH_2 is more hydrophilic than Q, and, apparently, the reduction of the QH_2 effectiveness in the PL presence is more considerable for this reason. This assumption is consistent with the results given in [21], that Q had a higher efficiency compared with the more hydrophilic QH_2 under their effects on the free radical induced hemolysis of erythrocytes and the platelet aggregation because of their different ability to interact with the cell membranes.

4. Conclusions

The effectiveness of the inhibiting action of antioxidants, depending on their involvement in side reactions may decrease with an increasing content of hydroperoxides during the initiated oxidation at moderate temperatures. The PL additives to antioxidants lead to an increase in the rate of oxidation within the induction period. The scale of this effect increases with the increasing initial concentration of the components in the mixture and the hydroperoxides content in the oxidation substrate. According to the PL influence on the duration of the induction period InH can be divided into three groups:

– antioxidants, for which there are an increase of the induction period, – α-tocopherol, 4-metoxyphenol, etoxyquin;

– antioxidants, for which the induction period is not changed – BHT;

– antioxidants, for which the induction period is decreased – quercetin and dihydroquercetin.

Dependence of InH efficiency on the nature of phenol and PL is necessary to take into account while their use as biologically active additives.

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ІНГІБУЮЧА ЕФЕКТИВНІСТЬ СУМІШЕЙ АНТИОКСИДАНТІВ І ФОСФОЛІПІДІВ ПРИ РІЗНОМУ СТУПЕНІ ОКИСНЕННЯ МЕТИЛОЛЕАТУ

Анотація. *Приведено результати досліджень стосовно впливу фосфоліпідів (ФЛ) на ефективність антиокиснювальної дії синетитчних фенольних антиоксидантів (InH) – йонолу, 4-метоксифенолу (МОФ), 4-трет-бутилфенолу; природних InH – α-токоферолу (ТФ), кверцетину (Q), дигідрокверцетину (QH_2) і гідрованого хіноліну – 2,2,4-триметил-6-етокси-1,2-дигідрохі-ноліну (ЕХ) на моделі ініційованого окиснення метилолеату. Встановлено, що додавання ФЛ призводить як до збільшення швидкості окиснення всередині періоду індукції (W_τ), так і до зміни величини періоду індукції (τ). У відповідності до збільшення W_τ для сумішей з ФЛ вивчені InH розташовано в наступній послідовності: $QH_2 > Q > EX > TФ > МОФ >$ йонол, яка підтверджена даними диференційної УФ-спектроскопії. Величина τ збільшується в присутності ФЛ для ТФ, МОФ і ЕХ, не змінюється для йонолу і суттєво зменшується для QH_2 і Q. Розглянуто причини, які призводять до зміни ефективності InH в присутності ФЛ.*

Ключові слова: *інгібітування, синтетичний антиокси-дант, α-токоферол, кверцетин, дигідрокверцетин, фосфоліпіди.*