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FEATURES OF PLANT EXTRACTS INFLUENCE ON THE KINETICS OF CUMENE OXIDATION

L. R. VARDANYAN *

Department of Biology and Chemistry Goris State University, Armenia

On the example of the model reaction of cumene oxidation herbal extracts are classified as antioxidants. It is established that according to the character of oxidation influence on the process, the extracts are divided into four major groups: 1) extracts, which function as conventional classic antioxidants, in the presence of these extracts on the kinetic curves of oxygen absorption, distinct induction periods appear; 2) extracts-moderators, in the presence of which kinetic curves of oxygen absorptions function without induction periods; 3) extracts, which operate as antioxidants at low concentrations and at relatively high concentrations, they undergo auto oxidation; 4) extracts, that inhibit the oxidation process to some extent. The mechanism of the effect of the extracts as antioxidants on the oxidation of cumene covering these groups is suggested.

***Keywords*:** herbal antioxidants, classification, auto oxidation mechanism of activity, induction periods.

Introduction. Interest in essential oils and plant extracts for the last decade has attracted more attention both in scientific medicine as well as in Chemistry and Biology. This is due to their rich content of biologically active substances, among which an important place is occupied by a compound with antioxidant properties. Herbal antioxidants are widely used in scientific medicine for treating various diseases, which was initiated by the excess concentration of free radicals accumulating in living organisms under the influence of environment, stresses, smoking, poor diet, etc. Consequently, the search for plants containing the most abundant antioxidant substances is of great practical and scientific interest.

In [1–4] more frequent information about the content of antioxidant substances in essential oils and extracts in a hundred or more herbs, berries, fruits and vegetables are measured by different physical-chemical methods [5]. However, these studies mainly provide total content of antioxidants not being studied at the specific oxidation reaction of an antioxidant effect. Actually extracts and, moreover, essential oils, contain more than 100 organic compounds besides antioxidants, which may differently affect their inhibitory activity, and on the overall oxidation process. In this regard, before recommending an active extract or essential oil as a source of an antioxidant, the study of their inhibitory effect on the

* E-mail: luisemari@rambler.ru

specific oxidation reaction is a prerequisite. Especially because these compounds can lead to the effect of synergies or antagonism [6].

Kinetic method, on the sample of model reaction of initiated oxidation of cumene, we determined the total content of antioxidant substances in the extracts of more than 160 plants [7–10]. It is established that all investigated extracts contain substances with antioxidant properties. However, not all the extracts have the same influence on the kinetics of cumene oxidation. In this study, we investigated extracts which are classified in 4 groups by their acting characters on the kinetics of initiated oxidation of cumene.

Group 1. From the investigated 150 extracts approximately 75% of them in the process of cumene oxidation function as conventional antioxidants. Distinct periods of induction appear at the initiated oxidation of cumene in the presence of these extracts on the kinetic curves of oxygen absorption (Fig. 1). Discovered induction periods (τ) are described by Eq. (1), Fig. 1, which allow to define the total content of antioxidant substances with great accuracy in the studied extracts:

$$\tau = f \cdot [\mathrm{InH}] / W_i , \qquad (1)$$

where W_i is initiation rate, f is number of radicals, terminating on one molecule of antioxidant. For illustrating Fig. 2, on the sample of an extract from the leaves of *Amarant paniculate* (AP), are demonstrated the dependence of τ on the extract content and initiation rate. The total content of antioxidant substances in the studied extract is within $(0.02 - 2.94) \cdot 10^{-4}$ *M/mg* [7–10].

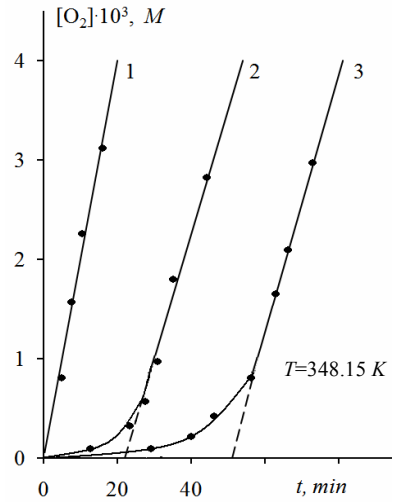

Fig. 1. Oxigen absorption kinetic curves in cumene oxidation with ethyl acetate extracts of the leaves of AP, $W_i = 1.25 \cdot 10^{-7}$ $M \cdot s^{-1}$: 1. [AP]=0; 2. [AP]=0.3 *g/L*; 3. [AP]=0.65 *g/L*.

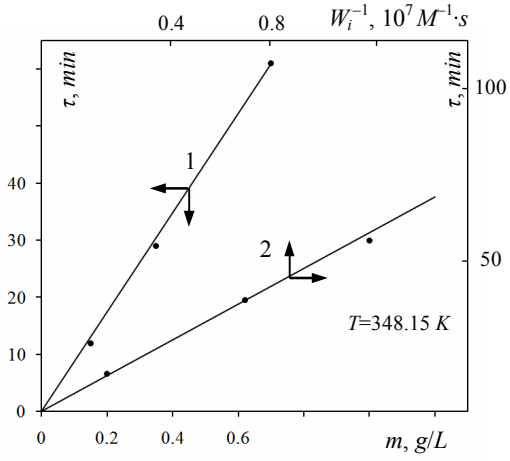

Fig. 2. Dependence of the induction period of cumene oxidation on the content of ethyl acetate extracts of the leaves of AP (1) and at the initiation rate $W_i = 1.25 \cdot 10^{-7}$ $M \cdot s^{-1}$, $m_{\text{extr.}}$=0.65 *g/L* (2).

Moreover, the most saturated antioxidants are found in extracts from *Crataegus Sanguinea* ($3.5 \cdot 10^{-4}$ *M*) and *Zhoster* ($2.94 \cdot 10^{-4}$ *M*). For extracts of this group their oxidants have also been identified as the reaction rate constants of inhibitors k_7 contained in extracts with peroxide radicals:

$$\mathrm{RO_2^{\bullet}} + \mathrm{InH} \xrightarrow{k_7} \mathrm{ROOH} + \mathrm{In^{\bullet}}.$$

In this case we used the equation

$$[O_2] = (k_2/k_7)\,[ROOH]\,\ln(1-t/\tau), \qquad (2)$$

where $k_2 = 4.68\cdot10^6 \exp(-9800/RT)$ is constant of reaction rate of chain, $[O_2]$ is the concentration of absorbed oxygen during $t < \tau$ ($RO_2^{\bullet} + RH \rightarrow ROOH + R$), [RH] is the concentration of oxidizing substance (here cumene). It was found that the antioxidant activity of extracts of medicinal plants do not give way to classic synthetic inhibitors. Thus, for example, for the extracts from the *Crataegus Sanguinea* fruits and elderberry leaves k_7 are respectively equal to $5.5\cdot10^5$ and $3.0\cdot10^5$ $M^{-1}\cdot s$ and for α-naphtol and ionol $k_7 = 1.14\cdot10^4$ and $2.2\cdot10^4$ $M^{-1}\cdot s$ respectively [11].

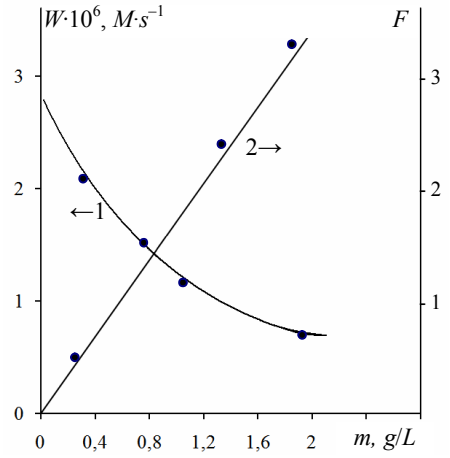

Fig. 3. Dependence of cumene oxidation rate after exiting the induction period (1) and the parameter F (2) from the content of the extract from the leaves of AP.

In the presence of oxidation products of initial antioxidants (Q) the rate of cumene oxidation (W) is significantly undervalued compared to the rate of oxidation (W_0) of individual cumene (compare, for example, the tangents of the angles of the O_2 absorption in Fig. 1). Here this fact is explained Q products exhibiting the antioxidant properties. Wherein the oxygen absorption rate after exiting the induction periods is described by equation (Fig. 3) [12]

$$F = W_0/W - W/W_0 = k_{71}\, f[Q]/\sqrt{k_6 W_i}\,, \qquad (3)$$

where k_6 is the rate constant of quadratic chain termination ($RO_2^{\bullet} + RO_2^{\bullet} \rightarrow$ molecular products (MP)), that characterizes the antioxidant activity of oxidation products of original antioxidants in the studied extracts, k_{71} is reaction rate constant $RO_2^{\bullet} + Q \rightarrow ROOH + Q^{\bullet}$, in the calculations of k_{71} it was taken into account that $k_6 = 4.74\cdot10^5 \exp(-1800/RT)$ for cumene [11].

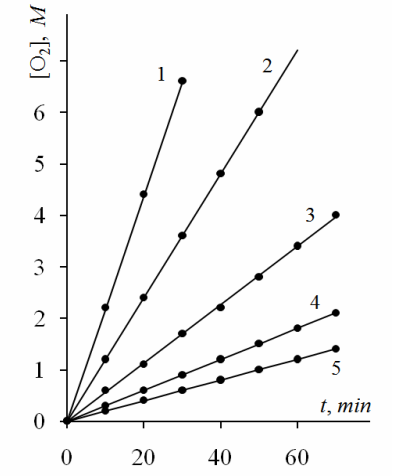

Fig. 4. Kinetic curves of oxygen absorption: in the absence of cumene oxidation (1), in the presence of extracts from the groose-grass seeds, 6.25 *g/L* (2); tomatoes, 1.5 (3); olives, 2.2 (4); mugwort, 4.8 *g/L* (5). $W_i = 1.64\cdot10^{-7}\, M\cdot s^{-1}$, $T = 348.15K$.

Group 2. *Extracts inhibitors*. The induction periods are not found in the presence of these extracts on the kinetic curves of oxygen absorption (Fig. 4). The studied extracts with such kind of properties have benzene extracts from the seeds of goosegrass, mugwort, yarrow, tomatoes, olives, pressed juice from the fruit Caper etc. In the presence of these extracts cumene oxidation rate significantly decreases over time and does not tend to no-inhibited oxidation. These extracts work as negative catalysts. Besides, the cumene oxidation rate in the presence of these extracts is described by Eq. (3) (Fig. 5, a). However, the parameters k_7 for these extracts are not determined, as the content of antioxidants (f·[InH]) has not been defined for them due to the lack of induction period on kinetic curves of oxygen absorption.

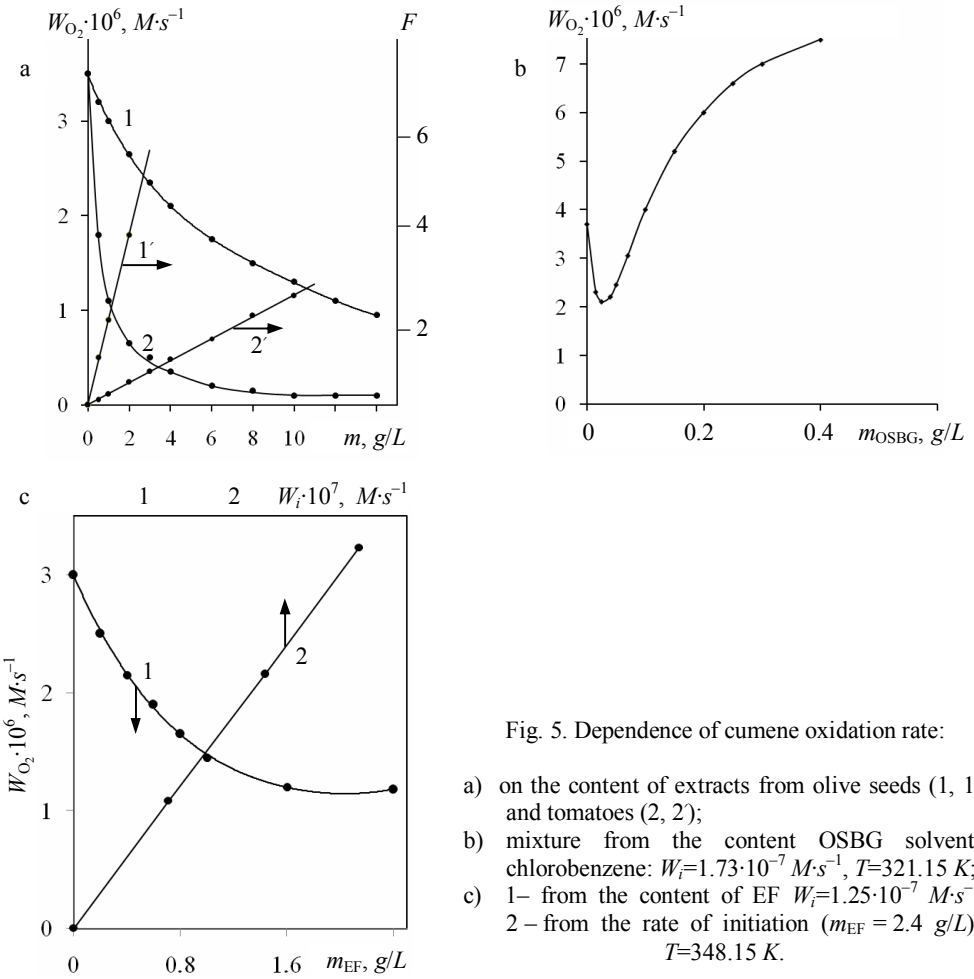

Fig. 5. Dependence of cumene oxidation rate:

a) on the content of extracts from olive seeds (1, 1′) and tomatoes (2, 2′);
b) mixture from the content OSBG solvent–chlorobenzene: W_i=1.73·10^{-7} $M\cdot s^{-1}$, T=321.15 K;
c) 1– from the content of EF W_i=1.25·10^{-7} $M\cdot s^{-1}$, 2 – from the rate of initiation (m_{EF} = 2.4 g/L), T=348.15 K.

Group 3. *The extracts at relatively low concentrations possess antioxidant properties, but at high concentrations they undergo auto oxidation.* These extracts are seeds of hemp, barbed nettle, oil of black grapes (OSBG) [13], vitamin C [14], isopropyl ether of vitamin A [15] and so on. For the illustration of Fig. 5, b there are demonstrated the dependence of cumene oxidation rate from the content of the seeds of OSBG. It is seen that with the increasing amounts of extracts the cumene

oxidation rate passes through a minimum. The increase in oxidation rate is confirmed by the fact that the extracts are subjected to auto-oxidation.

Group 4. *The extracts, in presence of which the rate of oxidation of hydrocarbons, particularly of cumene, is decreasing and tending to a constant value.* In the presence of these extracts on the kinetic curves no induction periods are found. The extracts of the seeds of flax (EF) have the following properties (Fig. 5, c).

The reason for such an action EF is explained with the complexation of cumene peroxide radicals with polar compounds having found in the extracts $(RO_2^{\bullet} + SH \rightarrow RO_2^{\bullet}...HS)$, which bring into disactivation of $RO_2^{\bullet}$ radicals [16].

The limit rate of cumene oxidation is described by the equation

$$W = k_2[RH]W_i / 2k_7, \quad (4)$$

where k_2 and k_7 are the rate reaction constants 8) and 9).

In the whole, cumene initiative oxidation in the presence of plant extracts can be demonstrated in the following Scheme:

1. $AIBN \rightarrow 2r^{\bullet} + N_2 \xrightarrow{O_2, RH(SH)} RO_2^{\bullet}(SO_2^{\bullet})$
2. $SH + O_2 \rightarrow S^{\bullet} + HO_2^{\bullet}$
3. $RO_2^{\bullet} + RH \rightarrow ROOH + R^{\bullet}$
4. $RO_2^{\bullet} + SH \rightarrow ROOH + S^{\bullet}$
5. $SO_2^{\bullet} + RH \rightarrow SOOH + R^{\bullet}$
6. $SO_2^{\bullet} + SH \rightarrow SOOH + S^{\bullet}$
7. $RO_2^{\bullet} + InH \leftrightarrow RO_2^{\bullet} \ldots InH$
8. $RO_2^{\bullet} \ldots InH + RH \rightarrow ROOH + InH + R^{\bullet}$
9. $RO_2^{\bullet} \ldots InH \rightarrow ROOH + In^{\bullet}$
10. $RO_2^{\bullet} + InH \rightarrow ROOH + In^{\bullet}$
11. $SO_2^{\bullet} + InH \rightarrow SOOH + In^{\bullet}$
12. $RO_2^{\bullet} + InH \rightarrow Q$
13. $SO_2^{\bullet} + InH \rightarrow MP$
14. $RO_2^{\bullet} + RO_2^{\bullet} \rightarrow MP$
15. $RO_2^{\bullet} + SO_2^{\bullet} \rightarrow MP$
16. $SO_2^{\bullet} + SO_2^{\bullet} \rightarrow MP$
17. $RO_2^{\bullet} \ldots InH + In^{\bullet} \rightarrow MP$
18. $RO_2^{\bullet} \ldots InH + RO_2^{\bullet} \ldots InH \rightarrow MP$
19. $RO_2^{\bullet} + RO_2^{\bullet} \ldots InH \rightarrow MP$
20. $RO_2^{\bullet} + Q \rightarrow ROOH + Q^{\bullet}$
21. $RO_2^{\bullet} + Q \rightarrow MP$

The scheme includes all elementary reactions for the considered types of extracts, according to the mechanism of antioxidant activity. Particularly, extracts

of Group 1 are characterized by reactions 1, 3, 10, 12, 20, 21; extracts of Group 2 by reactions 1, 3, 10, 12, 14, 20 and 21, extracts of Group 3 reactions by reactions 1–6, 10–16; extracts of Group 4 reactions by reactions 1, 7–9, 17–19.

Thus, despite the fact that all plants extracts contain sufficient amounts of antioxidant substances, they function differently on the oxidation process. Therefore, before using this extract as an antioxidant, it is recommended to test on a specific model of the oxidation reaction of any easily oxidized substance.

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