

## ANTIOXIDANT ACTIVITY OF POMEGRANATE SEED OIL AND SOWING CORIANDER FRUIT

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*The purpose of our work is to study the antioxidant properties of pomegranate seed oil (PSO) and coriander fruit oil one(CFO). Used oils were received by the means of extraction from seeds of the mature pomegranate and coriander fruits growing in the areas of Shushi, Arsakh Republic. On the example of the model reaction of the cumene-initiated oxidation, the antioxidant (AO) effect of pomegranate seed oil and sowing coriander is investigated. . Experiments on oxidation were carried out on a manometric unit with automatic pressure regulation. It is shown that both types of oil demonstrate antioxidant features. The efficient antioxidant contents ( $f \cdot [InH]$ ) and their antioxidant activities are determined. The response rate constant is  $RO_2 + InH \xrightarrow{k_7} ROOH + In$ . It is demonstrated that 1 mg of pomegranate seed oil contains  $0,91 \cdot 10^{-4}$  moles / l of antioxidants which exceeds antioxidant content in the oil of coriander fruit 10 times.*

**Key words:** oils, antioxidant content, antioxidant activity, pomegranate seed, coriander fruit

### Introduction

In recent years the use of natural bio-antioxidants in folk and conventional medicine, food and beverage, cosmetic industry has greatly increased due to the growing consumer interest in the ingredients of natural origin, because synthetic additives are potentially harmful [1,2]. Thereby, it is noted that the alternative synthetic antioxidants (AO) can be the ether oils of vegetative raw materials. Recently, as a result of numerous studies, the biological activity of ether oils of spicy aromatic plants has been established, including their AO activity(AOA) [4-6]. Natural balance violation of radical peroxidation rate and AO activity of body resistance occurring under unfavorable external factors (environmental contamination, ultraviolet radiation, emotional stress, high content of easily digestible carbohydrates and fats in the diet, with synchronous decline of bio antioxidants in content) plays an important role in the emergence of many diseases such as oncologic, cardiovascular, gastrointestinal, etc. [7-9]. In this connection, the search and investigation of promising non-toxic substances with antiradical and high AO activity is an urgent task. Official herbs are rich in similar substances, which are the main intake sources of bioactive substances for human and other living organisms [10,11]. Among the main active ingredients in the essential oils of plant raw materials are flavonoids, polyphenols, x c c xphenolic carboxylic acids, tannins, vitamins, selenium, etc. In folk medicine pomegranate seed oil and coriander fruit oil have been used long ago. The healing properties of these oils are explained by nutrients of bioactive substances in their makeup. In particular, pomegranate seed oil contains *Punica Granatum* acid (62-85%), fatty acids (linoleic-9.8%, palmitic-3.2%, stearic-2.1%, oleic-7.7%), vitamins E (0, 33%), C, B, P, tocopherols (0.66%), flavonoids, copper, manganese, chromium, magnesium, phosphorus, calcium and other elements [20]. The main components of coriander oil are fatty oil (up to 28%), consisting of oleic, isooleic, linoleic, palmitic, stearic and myristic acids, proteins (up to 17%), vitamin C (0.14%), carotene (0.01 %), rutin (up to 0.145%), polyphenols [21]. The chemical constitution of these oils should be widely used in perfumery, cosmetics manufacturing and in medicine. In particular, pomegranate seed oil acts as an anti-inflammatory cure [11,14]. In folk medicine coriander oil is used in gastrointestinal diseases as an antihelminthic cure, pain reliever and cold remedy and is the originated material for the synthesis of aldehyde citral applied in ocular practice at the treatment of cataracts [14].

### Conflict settings

The purpose of our work is to study the antioxidant properties of pomegranate seed oil (PSO) and coriander fruit oil one(CFO). Used oils were received by the means of extraction [16] from seeds of the mature pomegranate and coriander fruits growing in the areas of Shushi, Arsakh Republic. The yield of PSO amounts 10,6%, CFO one is 8,4%. PSO is a viscous liquid of pale yellow color with density  $d = 0,942$  g/ml having a refractive index  $n_D^{20} = 1,5207$ , CFO is a viscous liquid of pale green color with  $d = 0,871$ g/ml and  $n_D^{20} = 1,4707$ . AO properties of PSO and CFO were studied by the kinetic method on the example of the model response initiated by azo-di-iso-butyronitrile (AIBN) cumene oxidation. Experiments on oxidation were carried out on a manometric unit with automatic pressure regulation. In all experiments the reaction mixture volume was 5 ml, cumene concentration 2.87 mol / l, the ether oil content varied between 0 ÷ 25 mg. Used reagents such as cumene, chlorobenzene, AIBN, ethyl acetate wererefined according to the above-described procedure. The AO content of the oils investigated is determined by the periods of induction ( $\tau$ ) found out on kinetic curves oxygen absorption via an equation (1) [16]

$$\tau = \frac{f \cdot [InH]_0}{V_i}$$

(1)

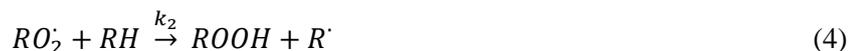
where  $[InH]_0$  is the AO content in the given sample of ether oil,  $V_i$ - the initiation rate,  $f$  – stoichiometric inhibition factor (the number of radicals terminating on one inhibitor molecule InH). Since the studied ether oils contain two or more AO in their chemical makeup, the parameters  $f$  have remained unmeasured hence, for this reason, not absolute, but effective contents of the AO are given in our calculations. The calculation results of AO activity (AOA) are also presented in the work. AOA inhibitors in oxidation reactions are characterized by a constant rate response of linear chain break.



In AOA calculations ( $k_7$ ), we have used the equation (2) [18],

$$[O_2] = -\frac{k_2}{k_7} [RH] \ln \left( 1 - \frac{t}{\tau} \right) \quad (3)$$

where  $k_2$ - is the rate constant reaction of chain continuation



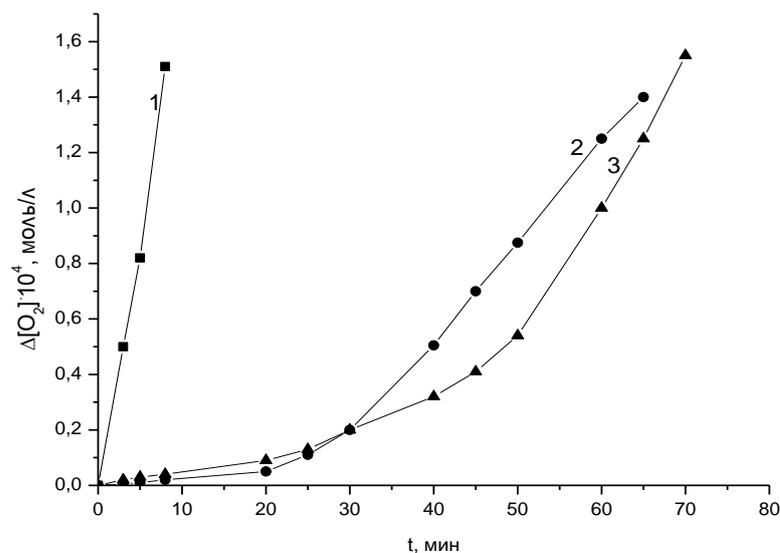
$[RH]$  is the concentration of the oxidizing hydrocarbon i.e. cumene

$[O_2]$  – the amount of absorbed oxygen during  $t < \tau$ , the induction period which is determined graphically on the kinetic curves of oxygen absorption along the coordinate of two lines intersection for which  $\text{tg} \alpha_1 = 2 \text{tg} \alpha_2$  or  $V_{O_2}^0 = 2V_{O_2}$  where  $V_{O_2}^0$  - [oxygen uptake rate](#) after the induction period yield,  $V_{O_2}$ -with inhibitor present ( fig. 1).

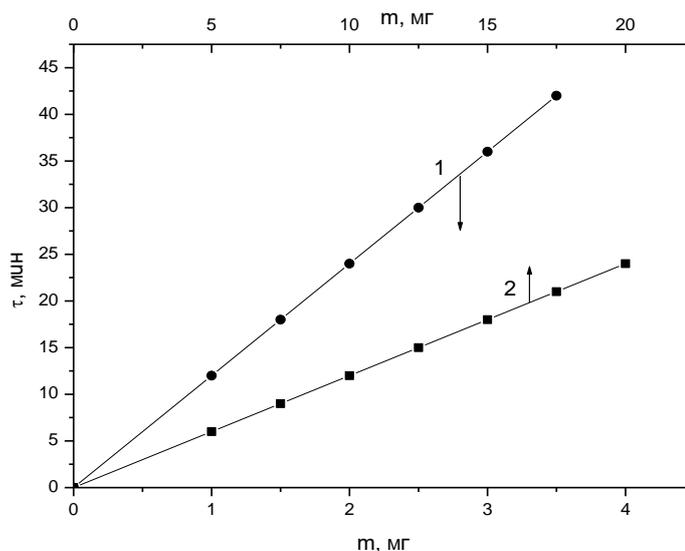
### Research results

Experiments have shown that during the cumene oxidation on the kinetic curves of oxygen uptake in the presence of studied extracts well-defined induction periods come out. (fig.1). The induction period occurrence indicates that AO substances exist in oils. The detected induction periods are being described (fig. 2) by the equation (1) that allowed determining the effective AO makeup in the investigated oils.

The results are shown in the featured line graphs:



**Fig.1. The kinetic curves of oxygen uptake during the process on cumene oxidation without (1) and with 3.9 mg PSO (2) and 22, 64 mg CFO (3).  $V_i = 1,25 \cdot 10^{-7}$  Mole/l · s, T=348K**



**Fig.2. Relation of oxygen uptake induction periods on cumene oxidation from PSO content (1) and CFO (2).  $V_i = 1,25 \cdot 10^{-7}$  Mole/l · s, T=348K.**

From the results shown in the graphs it is obvious that from PSO investigated oils with 348K contain 10 times more AO than CFO ones. The high content of AO in PSO ensures more than 1-year length of warranty. The graph also illustrates that the measured effectiveness of AO contents increase with the cumene oxidation temperature drop. When the temperature drops to 30 degrees (from 348K up to 328K) the change is 1.4 times in the case of PSO, and 3.3 times in the case of CFO ones. The growth of AO effective concentration can be explained by the fact that the experimented oils contain unsaturated fatty acids in sufficient supply, being subjected to auto oxidation, additionally initiate the

chain process of AO consumption. To determine the AO content at room temperature, we extrapolated the results given at coordinates  $\lg(f[\text{InH}])$  from the reverse value of temperatures (Fig.3).

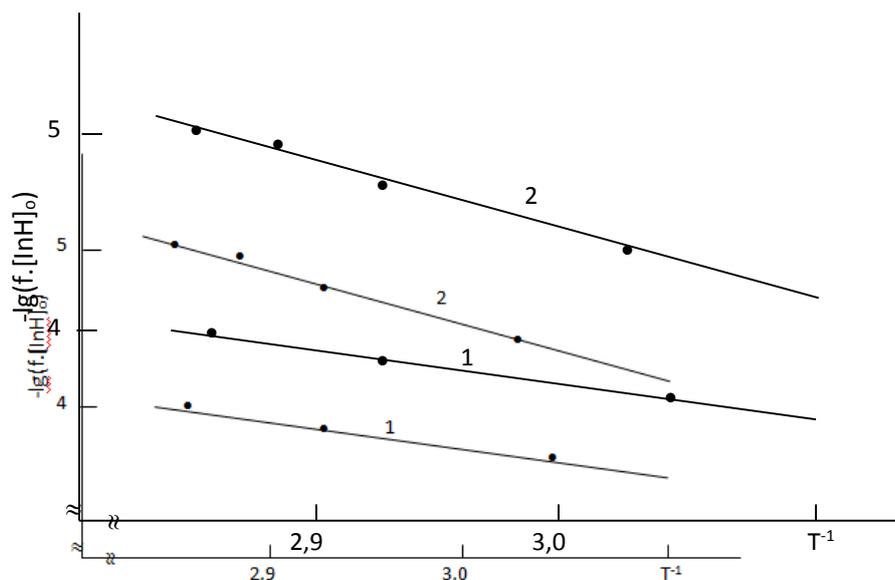


Fig.3. Temperature relation of antioxidants effective content in PSO (1) and CFO (2).

The graph indicates that the effective content of AO in the experimented ether oils per 1 mg depends on the temperature according to these equations:

$$(f[\text{InH}])_{\text{PSO}} = 6,16 \cdot 10^{-8} \exp(5042/RT), \text{ Mole/l}$$

$$(f[\text{InH}])_{\text{CFO}} = 1,99 \cdot 10^{-8} \exp(13721/RT), \text{ Mole/l}$$

The graph also shows the values of the parameters  $k_7$ , characterizing AOA oils. The values of  $k_7$  are determined by straightening out (Fig. 4) the oxygen uptake experimental data during the induction period at the coordinates of equation (2). It was taken into account that for cumene  $k_2 = 4,677 \cdot 10^6 \exp(-9800/RT) \text{ l/mole}\cdot\text{s}$  [19].

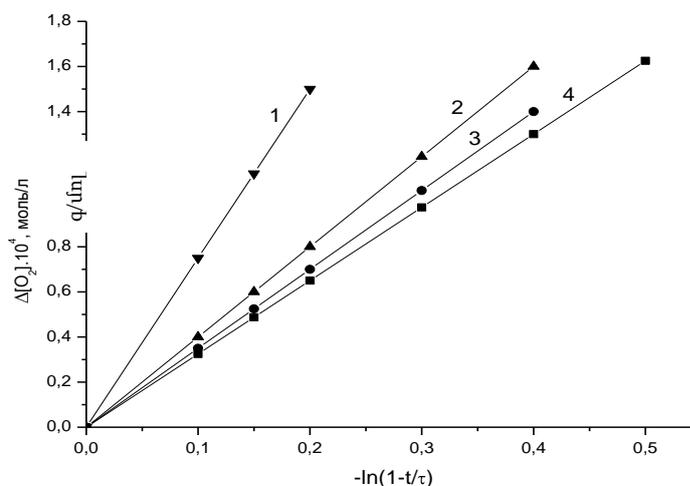


Fig.4. The concentration relation of oxygen uptake from the parameter  $-\ln(1-t/\tau)$  during the oxidation of cumene in the presence of 0,714mg (1), 3,90 mg (2) PSO, 3,06 mg (3) & 22,64 mg CFO. mole/l·s, T=328K (1,3) and 348K (2,4).

Experiments have revealed that in the presence of the studied oils, the cumene oxidation rate remains significantly underestimated after the withdrawal from the induction period in comparison with benzene-inhibited oxidation (see column 7 in table). This fact is explained by the AO properties of oxidation products (QH) of the original AO existing in oil [20, 21]. It is shown that the correlation is observed between the rates of uninhibited ( $V_0$ ) and inhibited cumene oxidation after the withdrawal from the induction period ( $V$ ),

$$\Phi = \frac{V_0}{V} - \frac{V}{V_0} = \frac{k_{71}[QH]}{\sqrt{k_6 V_i}} \quad (5)$$

Where  $k_{71}$  is the rate constant of the chain break on the oxidation products of the original AO, present in the examined oils.



$k_6$ -rate constant of quadratic chain break  $RO_2 + RO_2 \xrightarrow{k_6}$  molecular products.

During the calculations  $k_{71}$ , it was taken into account that for cumene  $k_6=4,74 \cdot 10^5 \exp(-1800/RT)$  [19] and that  $f \cdot [InH]_o = f \cdot [QH]$ . The collected data suggest that from the oxidation products the large number of AOA is AO, contained in CFO.

**Table 1**  
**AO and AOA content of ether oils in pomegranate seeds and coriander fruits**

Ether oils	T°K	$V_i \cdot 10^7$ , mole/l.s	Content,mg	$\tau$ , min	$f[InH]^a \cdot 10^4$ mole/l	$V^6 \cdot 10^6$ mole/l.s	$k_{71} \cdot 10^4$ l/mole.s	$k_{71} \cdot 10^2$ l/mole.s
Pomegranate seeds	348	1,25	0	0	-	3,00	-	-
	348	1,25	1,46	18	0,92	1,73	2,71	3,80
	348	1,25	2,675	32	0,90	1,57	2,71	3,81
	348	1,25	3,90	46	0,88	1,26	2,72	3,82
	348	2,50	0	0	-	4,25	-	-
			3,90	25	0,96	1,49	2,70	3,83
	348	0,625	0	0	-	2,12	-	-
			3,90	92	0,86	0,97	2,73	3,82
	339	0,733	0	0	-	2,00	-	-
	339	0,733	1,46	40	1,28	1,16	1,19	3,13
	339	0,733	2,92	80	1,29	0,74	1,18	3,15
	339	0,733	0,73	20	1,28	1,48	1,20	3,11
	328	0,344	0	0	-	1,00	-	-
	328	0,344	0,55	35	0,44	0,77	0,53	2,35
	328	0,344	0,714	45	1,43	0,70	0,55	2,32
328	0,344	1,42	89	1,40	0,51	0,57	2,30	
Coriander fruits	348	1,25	8,25	10	0,084	1,39	3,83	16,30
	348	1,25	16,50	18	0,082	0,83	3,81	16,42
	348	1,25	22,64	25	0,083	0,62	3,85	16,29
	348	2,50	22,64	13	0,083	1,23	3,8	15,80
	348	0,625	22,64	50	0,082	0,33	3,75	15,92
	348	0,35	22,64	90	0,084	0,18	3,90	16,48
	339	0,733	12,25	38	0,137	0,55	2,55	10,06
	339	0,733	24,50	76	0,137	0,33	2,60	8,96
	339	0,733	30,75	100	0,143	0,23	2,45	10,05
	339	1,250	48,00	82	0,129	0,25	2,55	11,20
	328	0,344	6,12	82	0,276	0,28	1,52	6,31
	328	0,344	3,06	41	0,280	0,46	1,48	6,34
	328	0,344	1,53	21	0,275	0,67	1,56	6,29
	328	0,344	4,80	64	0,274	0,34	1,53	6,35

a-per 1 mg of extract, b-after the withdrawal from the induction period

Straightening out the experimental data at coordinates  $\lg k_i$  from T-1 for the studied oils, the temperature correlation of AOA at coordinates and products of their oxidation are obtained.

Consequently, the results are:

1. for pomegranate seed oil  
 $k_7 = 1,17 \cdot 10^{14} \exp(-15488/RT)$ , l/mole.s  
 $k_{71} = 1,30 \cdot 10^6 \exp(-5620/RT)$ , l/mole.s,
2. for pomegranate seed oil  
 $k_7 = 1,88 \cdot 10^9 \exp(-10647/RT)$ , l/mole.s  
 $k_{71} = 8,20 \cdot 10^9 \exp(-10665/RT)$ , l/mole.s.

Thus, the research has shown that the ether oils of PS and CF possess AOA. Moreover, the effective AO content depends on the temperature measurement and increases with decreasing temperature which is linked to the extra initiating at the expense of auto-oxidation of unsaturated fatty acids contained in the experimented ether oils and in CFO in particular.

### Conclusion

Using the modeling response of cumene oxidation it is shown that the content of AO in PSO is 10 times more than in CFO (measured at 348K). It has been revealed that with decreasing temperature the effective measured content of AO increases, therefore, to prolong their shelf life they must be stored at relatively low temperatures.

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**ՆՈՒԱՆ ԿՈՐԻՉԻ ԵՎ ՀԱՄԵՄԻ ՍԵՐՄԵՐԻ ՅՈՒՂԵՐԻ ՀԱԿԱՕՔՍԻԴԱՆՏ ԱԿՏԻՎՈՒԹՅՈՒՆԸ**

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Մեր աշխատանքի նպատակն է եղել ուսումնասիրել նույն կորիզայուղի և համեմի սերմերի յուղի հակաօքսիդանտ ակտիվությունը: Օգտագործված յուղերը ստացվել են էքստրակցիոն մեթոդով՝ ԱՀ Շուշիի մերձավակայքում աճող նույն հասուն պտուղների կորիզներից և մշակվող համեմի սերմերից: Ուսումնասիրվել է նույն կորիզի յուղի և համեմի սերմնայուղի հակաօքսիդանտ հատկությունը կոմոլի

օքսիդացման մոդելային ռեակցիայի օրինակով: Օքսիդացման փորձեր իրականացվել են ճնշման ավտոմատ կարգավորվող մոնոմետրիկ սարքով: Ցույց է տրվել, որ երկու յուղերը օժտված են հակաօքսիդանտ հատկություններով: Որոշվել է հակաօքսիդանտների արդյունավետ պարունակությունը՝ ( $f \cdot [InH]$ ) և դրանց հակաօքսիդանտ ակտիվությունը՝ ռեակցիայի արագության հաստատունը՝  $RO_2 + InH \xrightarrow{k_7} ROOH + In\cdot$ : Ցույց է տրվել, որ նոսան կորիզայուղի 1մգ պարունակում է  $0,91 \cdot 10^{-4}$  մոլ/լ հակաօքսիդանտ, ինչը 10 անգամ գերազանցում է համեմի սերմնայուղի հակաօքսիդանտների պարունակությանը:

**Բանալի բառեր.** յուղ, հակաօքսիդանտների պարունակություն, հակաօքսիդանտային ակտիվություն, նոսան կորիզ, համեմի սերմ

## АНТИОКСИДАНТНАЯ АКТИВНОСТЬ МАСЛА КОСТОЧЕК ГРАНАТА PUNICA GRANATUM L. И ПЛОДОВ КОРИАНДРА ПОСЕВНОГО CORIANDRUM SATIVUM L.

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Целью нашей работы было исследование антиоксидантных свойств масел гранатовых косточек (МКГ) и плодов кориандра (МПК). И использованные масла получали экстракционным методом из косточек зрелых плодов граната и плодов кориандра, произрастающих в окрестностях Шуши Арцахской республики. На примере модельной реакции инициированного окисления кумола исследованы антиоксидантное (АО) действие масел косточек граната и кориандра посевного. Опыты по окислению проводили на манометрической установке с автоматическим регулированием давления. Показано, что оба масла проявляют антиоксидантные свойства. Определены эффективные содержания антиоксидантов ( $f \cdot [InH]$ ) и их антиоксидантные активности – константы скорости реакции  $RO_2 + InH \xrightarrow{k_7} ROOH + In\cdot$ . Показано, что в 1 мг масла косточек граната содержится  $0,91 \cdot 10^{-4}$  моль/л антиоксидантов, что в 10 раз превосходит содержание антиоксидантов в масле плодов кориандра.

**Ключевые слова:** масло, содержание антиоксидантов, антиоксидантная активность, косточки граната, семена кориандра