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Consumption of quercetin and rutin in reactions with free radicals

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The consumption of flavonols quercetin and rutin in reactions with various free radicals has been studied in homogeneous solutions and in micellar systems of cetyl trimethylammonium chloride by UV spectrophotometry. Free radicals were produced by azoinitiators AAPH and AIBN decomposition in water and in organic medium, respectively. Both quercetin and rutin were used as free radical acceptors to determine the rates of free radical formation in the decomposition of cumene hydroperoxide (ROOH) and hydroperoxides derived from sunflower oil oxidation (LOOH) catalyzed by cetyl trimethylammonium chloride in organic and water media. It was found that apparent rutin consumption rates are 4 -10 times lower than quercetin consumption rates under the same conditions. The ratio of free radical initiation rate to that of flavonol consumption and the stoichiometric factors for quercetin and rutin are discussed.

Key words: quercetin, rutin, free radicals, lipid hydroperoxides, micelles of cetyl trimethylammonium chloride.

INTRODUCTION

Quercetin (Qu) and rutin (Ru) are naturally occurring polyphenolic compounds and they possess a wide range of biological activities [1–4], of which antioxidant and free radical scavenging activities have been extensively explored [5–13]. Quercetin was used as a free radical acceptor to measure the rates of free radical formation during initiator decay in micelle solution by inhibitor method [14].

Lipid hydroperoxides (LOOH) are important factors for oxidation stability of food, cosmetics and other products, containing lipids, due to their ability to decompose into free radicals [1, 2]. Surfactants are commonly used in food, perfume and pharmaceutical industries to stabilize products from stratification. Lipid hydroperoxides are found to be surface-active [15, 16], so hydroperoxides can form mixed aggregates with micelle-forming surfactants. It was shown that oxidation rate of fish oil emulsion (O/W) decreased when oil droplets in water were stabilized by cationic surfactants [15]. Contrary to that, cationic surfactants (S^+) were found to accelerate the oxidation of hydrocarbons and plant oils in organic medium [17–21]. The key stage of lipid oxidation, which is affected by cationic surfactant, is hydroperoxide decomposition, resulting in free radical generation. The rate of free radical generation in mixed micelles LOOH-S^+ was found to depend on a counterion of cationic surfactant, and the most pronounced effect was established in the case of chloride of cetyl trimethylammonium [16, 21]. In the study [16] quercetin was used as a free radical acceptor to measure the initiation rate by the inhibitor method.

It is known that surfactant micelles can alter the partitioning and reactivity of phenolic antioxidants in reverse and direct micelles and emulsions [2–7]. Rutin, considered to be quercetin glycoside (Fig. 1), is more hydrophilic than its aglycon, so rutin localization and partitioning in micelle solution can differ from that of quercetin. Here we report a quantitative kinetic study of the consumption of both quercetin (Qu) and rutin (Ru) in reactions with free radicals formed by micellar systems cetyltrimethylammonium chloride (CTAC) – lipid hydroperoxide or CTAC-cumene hydroperoxide and by azoinitiators AAPH in water and AIBN in organic medium, respectively. It is of interest to compare the consumption kinetics of Qu and Ru, which differ only by the hydrophilic 3-O-sugar substituent.

MATERIALS AND METHODS

Quercetin (Qu), rutin (Ru) and 2,2'-azodiisobutyramidine dihydrochloride (AAPH) (from Fluka, Switzerland) were purchased with highest purity available and used as it was received. Azobis(isobutyronitrile) (AIBN) was purified by recrystallization from ethanol. Cetyl trimethylammonium chloride (CTAC) (Fluka) was used as received. Chlorobenzene and water were purified by double distillation.

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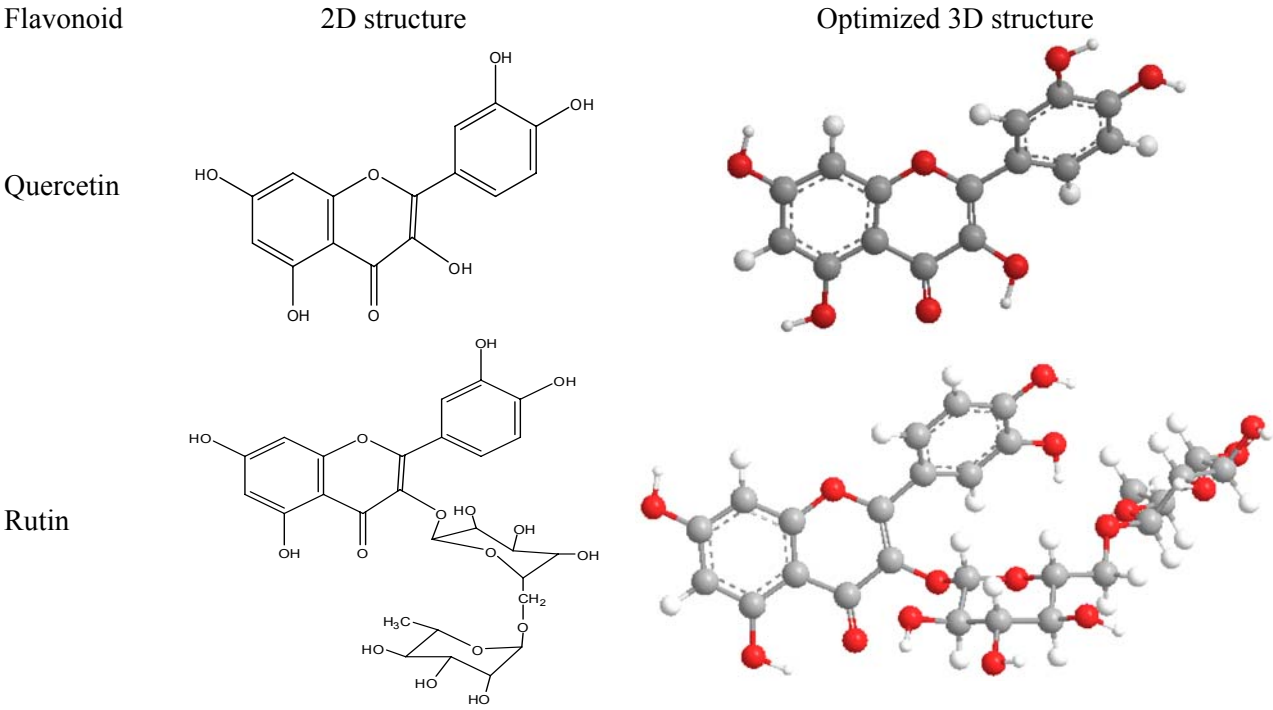


Fig. 1.

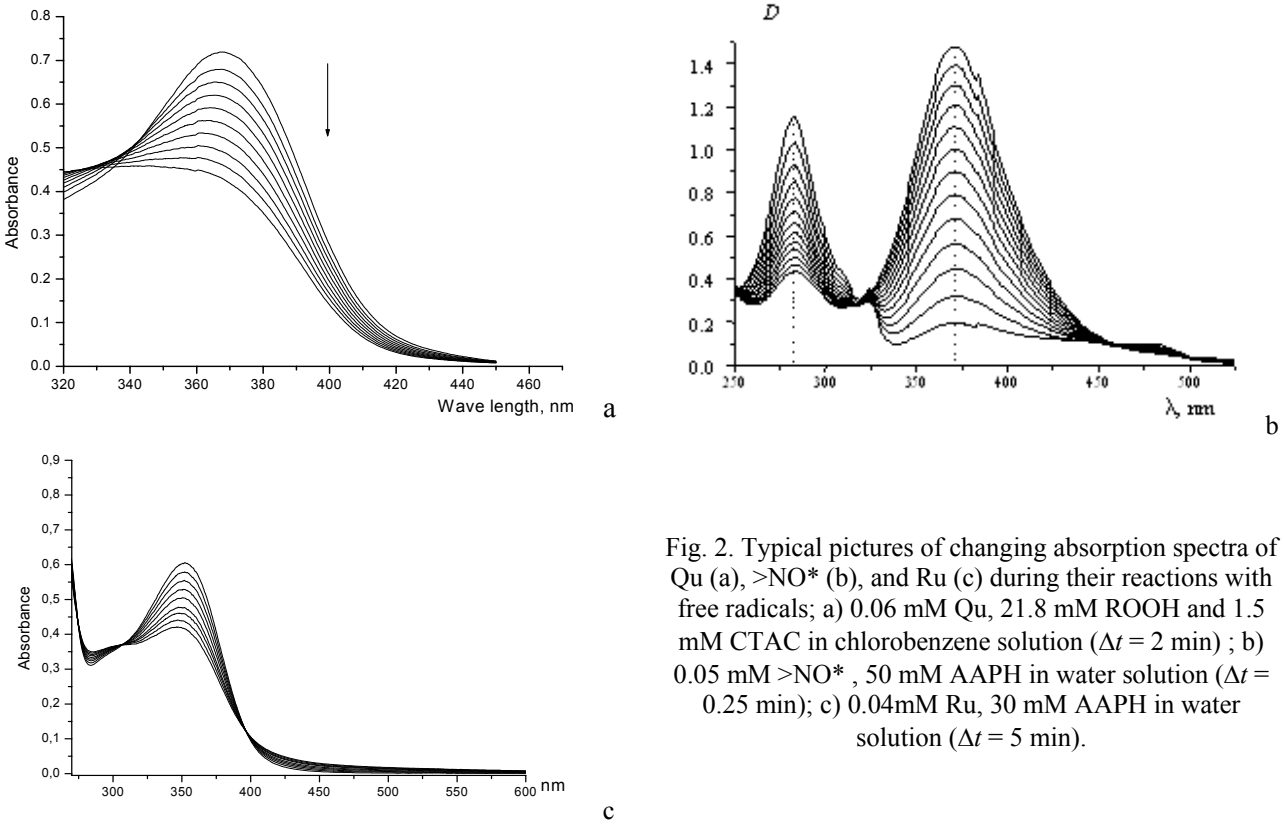


Fig. 2. Typical pictures of changing absorption spectra of Qu (a), >NO* (b), and Ru (c) during their reactions with free radicals; a) 0.06 mM Qu, 21.8 mM ROOH and 1.5 mM CTAC in chlorobenzene solution (Δt = 2 min) ; b) 0.05 mM >NO* , 50 mM AAPH in water solution (Δt = 0.25 min); c) 0.04mM Ru, 30 mM AAPH in water solution (Δt = 5 min).

As lipid hydroperoxides we used the hydroperoxides (LOOH) derived from the autooxidation of sunflower oil. Besides, kinetically pure triacylglycerols of sunflower oil (TGSO) were obtained by cleaning sunflower oil from pro- and antioxidants and trace metals by adsorption chromatography [22]. The lipid oxidation was carried out in a glass vessel by blowing air through the samples at a rate of 1.6 l/h at 80ºC. Cumene hydroperoxide (ROOH, Aldrich) was purified according the method described in [19]. Hydroperoxide concentration was determined by the iodometric method.

The rates of quercetin and rutin consumption were determined by UV spectrophotometry and compared with the consumption rate of the stable nitroxyl radical 4-(spirotetrahydrofuran-2′-yl)-2-spirocyclohexyl-1,2,3,4-tetrahydroquinolin-1-oxyl (>NO*), synthesized according to a known procedure [23]. This nitroxyl radical is a specific trap for peroxyl radicals since their spin adduct (quinone-nitrone) shows a characteristic absorption band in the visible spectrum [24]. The reactions producing free radicals were carried out in quartz cuvette of an Ultrospec 1100 pro spectrophotometer at 37ºC as follows: 2.5 ml of an initiator (AAPH or AIBN or mixture of hydroperoxide with CTAC) solution was placed in a cuvette and held at 37°C for 15 min; thereafter 5–25 μl of stock solution of acceptor (Qu, Ru or >NO*) were added and electronic absorption spectra of reaction mixture were recorded at intervals. Typical pictures of changing absorption spectra of Qu, >NO*, and Ru during their reactions with free radicals are represented in Fig. 2. All kinetic data are the mean arithmetic result of three independent experiments and were processed using the computer program Origin 7.

RESULTS

Both quercetin (Qu) and rutin (Ru) have rather intensive characteristic absorption bands that decrease during their consumption in reactions with free radicals (Fig. 2). Optical characteristics of Qu and Ru are represented in Table 1.

There is a hypsochromic shift of λ_{max} and a slight decrease of ε in water media, compared with those for Qu and Ru in chlorobenzene solution. Noteworthy, CTAC doesn't affect optical characteristics of flavonols in organic media, whereas in water solutions marked bathochromic shifts are observed in the presence of CTAC, which point to an interaction of Qu and Ru with CTAC micelles.

Figs. 3 and 4 show the consumption of Qu and Ru in the system of reverse mixed micelles of CTAC and lipid hydroperoxides in chlorobenzene solution. It must be noted that no flavonol consumption was observed when the same amounts of CTAC or hydroperoxides were taken separately (lines 1 and 2 in Figs. 3 and 4). The rates of Qu and Ru consumption under the experimental conditions do not depend on the initial concentration of flavonols. This is known to be typical for inhibitor consumption in reactions with free radicals when an inhibitor traps all the radicals produced with a constant initiation rate (R_i) [1–3, 9, 25].

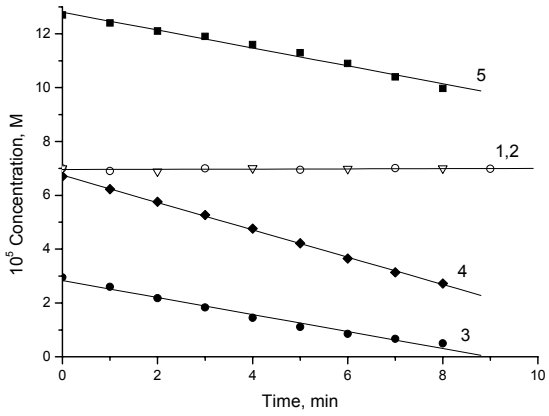


Fig. 3. Kinetic curves of Qu consumption in the presence of 1.65 mM CTAC (1), 20 mM LOOH (2), and in mixture 1.65 mM CTAC and 20 mM LOOH (3–5) in chlorobenzene solution at 37°C; $-d[Qu]/dt = 6.4\times10^{-8}$ M/s (3–5).

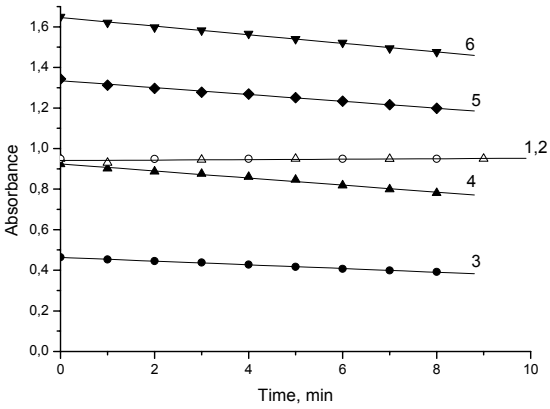


Fig. 4. Kinetic curves of Ru absorption decay in the resence of 1.65 mM CTAC (1), 20 mM LOOH (2), and in the mixture 1.65 mM CTAC and 20 mM LOOH (3–6) in chlorobenzene solution at 37ºC; apparent $-d[Ru]/dt = 1.8\times10^{-8}$ M/s (3–6).

Table 1. Optical characteristics Qu and Ru in organic and water media.

Media	Quercetin		Rutin	
	λ_{max}, nm	ε, $M^{-1}\cdot s^{-1}$	λ_{max}, nm	ε, $M^{-1}\cdot s^{-1}$
Chlorobenzene	373 ± 1	$(2.00 \pm 0.05)\times10^4$	360 ± 1	$(1.50 \pm 0.05)\times10^4$
Chlorobenzene + 1.65 mM CTAC	373 ± 1	$(2.00 \pm 0.05)\times10^4$	360 ± 1	$(1.50 \pm 0.05)\times10^4$
Water	367 ± 1	$(1.80 \pm 0.05)\times10^4$	351 ± 1	$(1.40 \pm 0.05)\times10^4$
Water + 1.65 mM CTAC	382 ± 1	$(1.70 \pm 0.05)\times10^4$	382 ± 1	$(1.20 \pm 0.05)\times10^4$
Water + ABAP	368 ± 1	$(1.80 \pm 0.05)\times10^4$	355 ± 1	$(1.45 \pm 0.05)\times10^4$
Buffer + ABAP	368 ± 1	$(1.70 \pm 0.05)\times10^4$		

ε – the molar extinction coefficient determined from the dependence of absorbance at λ_{max} on molar concentration of Qu or Ru accordingly.

$$-d[Qu]/dt = R_i/n_{Qu}; \quad (1)$$

$$-d[Ru]/dt = R_i/n_{Ru}; \quad (2)$$

Here, n_{Qu} and n_{Ru} are the stoichiometric factors for Qu and Ru, which denote the number of free radicals trapped by each flavonol molecule. It follows from Eqns. (1) and (2) that the ratio of Qu and Ru consumption rates is equal to the reverse ratio of their stoichiometric factors:

$$\{d[Qu]/dt\}/\{d[Ru]/dt\} = n_{Ru}/n_{Qu} \quad (3)$$

According to the data in Fig. 3 and 4, this ratio is equal $n_{Ru}/n_{Qu} = 3.6$. In other words, Qu traps smaller amounts of radicals than Ru. This result is unexpected because Qu is known to be a more efficient antioxidant than Ru [6–13]. Fig. 5 shows the antioxidant effects of Qu and Ru in TGSO autooxidation at 80ºC. It is seen that the induction periods (τ) in the presence of Qu are longer and the rates during the induction period are lower than those for oxidation in the presence of Ru. As a rule, the longer the induction period, the higher the stoichiometric factor is. When R_i remains constant, the induction period is proportional to n:

$$\tau = n\,[\text{Inhibitor}]/R_i \quad (4)$$

Under autooxidation conditions R_i increases in the course of reaction and antioxidants can undergo side reactions, which affect the duration of the induction period. The data of Table 2 show that the higher the initial concentration of flavonols is, the lower is the ratio τ_{Ru}/τ_{Qu}. So, Ru undergoes side reactions in a greater extent than Qu.

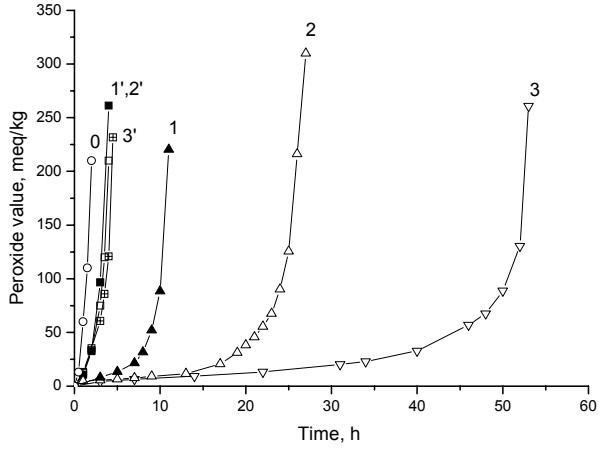


Fig. 5. Kinetic curves of TGSO autooxidation at 80ºC in the absence (0) and in the presence of 0.1 mM Qu (1) and Ru (1'), 0.5 mM Qu (2) and Ru (2'), and 1.0 mM Qu (3) and Ru (3').

To compare stoichiometric factors for Qu and Ru and their ratio in organic and water media we have studied the rates of Qu and Ru consumption in reactions with radicals produced in micellar system CTAC – cumene hydroperoxide (ROOH) in both organic and water media, and with radicals produced by azoinitiators AAPH and AIBN decomposition in water and organic media as well.

Table 2. The ratio of induction periods in the sunflower oil autoxidation in the presence of Qu and Ru at 80ºC.

Initial concentration of flavonols, mM	0.1	0.5	1.0
The ratio of induction periods, τ_{Ru}/τ_{Qu}	0.27	0.11	0.07

Fig. 6 shows that Qu is consumed faster than Ru (Table 3) in the system of reverse mixed micelles of CTAC and ROOH in chlorobenzene solution. The ratio of their consumption rates is equal to: $\{d[Qu]/dt\}/\{d[Ru]/dt\} = n_{Ru}/n_{Qu} = 10.4$. At the same initial concentration of all the components however in the system of normal mixed micelles CTAC-ROOH in water, the ratio of Qu and Ru consumption rates was found to be equal to: $\{d[Qu]/dt\}/\{d[Ru]/dt\} = n_{Ru}/n_{Qu} = 4.0$. Thus, the rate of Ru consumption is evidently lower than that of Qu both in organic and water media.

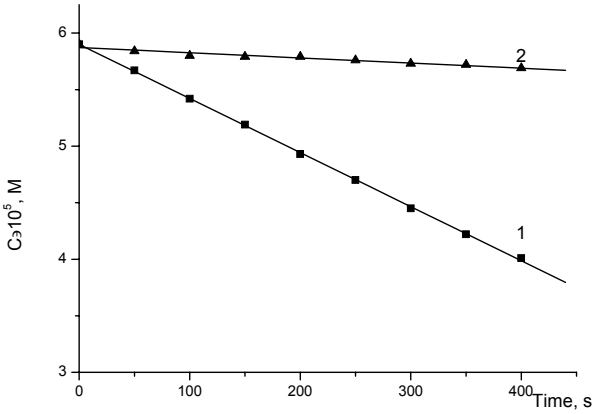


Fig. 6. Kinetic curves of Qu (1) and Ru (2) consumption in the system: 1.65 mM CTAC, 20 mM ROOH in chlorobenzene media at 37°C; $[Qu]_0 = [Ru]_0 = 5.9\times10^{-5}$ M

Table 3. The Qu and Ru consumption in reaction with free radicals produced by ROOH decomposition in micellar system ROOH-CTAC at 37ºC.

System under study	$-d[Qu]/dt, \times10^8$, M/s	$-d[Ru]/dt, \times10^8$, M/s
1.65 mM CTAC, 20 mM ROOH in chlorobenzene	4.78	0.457
1.65 mM CTAC, 20 mM ROOH in water	0.475	0.117

Fig. 7 shows that the rates of consumption of Qu (curve 1) and Ru (curve 2) in water solution of AAPH are proportional to the AAPH concentration.

The initiation rate, when azoinitiators are used, is equal to $R_i = k_i$ [AAPH] [1, 2, 25]. So, the slopes of the lines in Fig. 7 are equal to k_i/n, as follows from Eq. (1) and (2). There are some discrepancies in published values of k_i for AAPH at 37ºC (in s^{-1}): 0.4×10^{-6} [28]; 1.6×10^{-6} [7, 29]; 0.8×10^{-6} [6]. We have measured the free radical formation rate during AAPH decomposition by inhibitor method using stable nitroxyl radical 4-(spirotetrahydrofuran-2′-yl)-2-spirocyclohexyl-1,2,3,4-tetrahydroquinolin-1-oxyl (>NO*) as an acceptor. The chemical reaction of >NO* with peroxyl radicals is known [24] to result in quinone-nitron formation, i.e. the stoichiometric factor for >NO* is equal to 1:

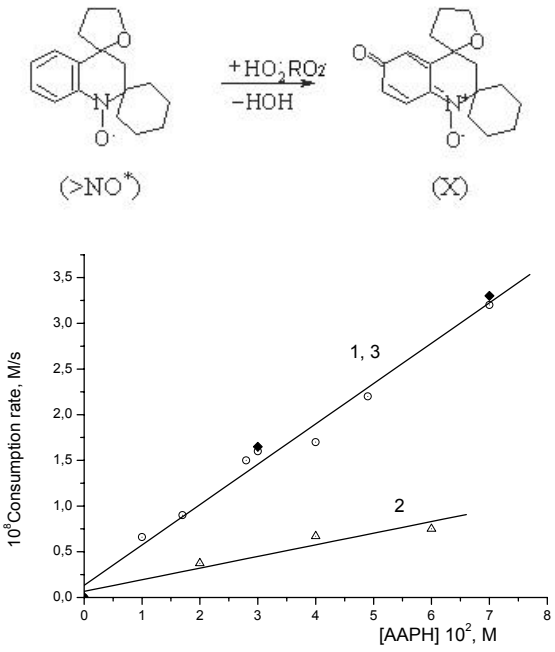


Fig.7. Dependencies of Qu (1) and Ru (2) consumption rates on AAPH concentration in water (o) and buffer (Δ) (pH = 7.2) solutions at 37°C; (3) - the rates of >NO* consumption (♦).

Fig. 7 shows that the values of the rates of quinone-nitron accumulation and Qu consumption practically coincide. It follows that the stoichiometric factor for Qu in the reaction with peroxyl radicals resulted from AAPH decomposition in water solution is equal to 1 and the apparent value for the rate constant of AAPH decomposition into free radicals in water (pH = 6.8) and in phosphate buffer (pH = 7.2) solutions is equal to $k_i = 0.44\times10^{-6}$ s^{-1}. On the basis of these results, the stoichiometric factor for Ru in the reaction with peroxyl radicals resulted from AAPH decomposition in water solution is equal to 4.

The rates of Qu and Ru consumption in chlorobenzene solution in reaction with peroxyl radicals produced by organic soluble azoinitiator AIBN are presented in Table 4. In this case the Qu consumption rate is nearly twice lower than that of >NO*, and the stoichiometric factor for Qu is equal to 2, which coincides with the value reported earlier [6, 14, 30]. The stoichiometric factor for Ru in the reaction with peroxyl radicals resulted from AIBN decomposition in chlorobenzene is equal to 10.

Table 4. Qu, Ru, and >NO* consumption rates in reaction with free radicals produced by 50 mM AIBN decomposition in chlorobenzene solution at 37ºC.

Free radical acceptor	Consumption rate $\times10^8$, M/s	n
Qu	0.8 ± 0.1	1.9 ± 0.2
Ru	0.15 ± 0.02	10 ± 1
>NO*	1.5 ± 0.1	1 ± 0.1

DISCUSSION

It must be noted that in all cases the rates of Qu and Ru consumption are concentration independent when [Qu], [Ru] ≥ 2×10^{-5} M (see, for example, Fig. 3 and 4). According to the theory [2, 6, 13, 25, 30] it means that the chain termination by flavonols (FlOH)

$$LO_2^{\bullet} + FlOH \rightarrow \text{products} \qquad R = k_F [LO_2^{\bullet}][FlOH]$$

is faster than the recombination/dispropotionation of peroxyl radicals:

$$LO_2^{\bullet} + LO_2^{\bullet} \rightarrow \text{products} \qquad R = 2k_t[LO_2^{\bullet}]^2$$

When the relationship (5) is valid:

$$k_F[FlOH][LO_2^{\bullet}] > 2k_t[LO_2^{\bullet}]^2, \qquad (5)$$

the rate of the inhibitor consumption is determined by the free radical initiation rate, R_i, as it is described by Eqns. (1) and (2): $-d[FlOH]/dt = R_i/n$.

To discuss the strange differences between the stoichiometric factors for Qu and Ru, we consider their consumption in reactions with free radicals initiated by the decomposition of known initiators (I). When all the radicals produced are scavenged by the antioxidant (FlOH), i.e. the relationship (5) is valid, the main reactions describing free radical initiation and termination may be represented as follows [6–13, 25]:

$$I \rightarrow rO_2^{\bullet} \qquad R_i = k_i [I] \qquad (i)$$

$$rO_2^{\bullet} + FlOH \rightarrow rO_2H + FlO^{\bullet} \qquad (i1)$$

$$rO_2^{\bullet} + FlO^{\bullet} \rightarrow \text{product-1} \qquad (i2)$$

$$FlO^{\bullet} + FlO^{\bullet} \rightarrow \text{product-2} \qquad (i3)$$

$$FlO^{\bullet} + FlO^{\bullet} \rightarrow FlOH + \text{product (quinone)} \qquad (i4)$$

The stoichiometric factor, determined as $n = R_i/(-d[FlOH]/dt)$, is equal to 1, when the radical termination occurs via the reactions i1 and i3. When the $rO_2^{\bullet}$ and $FlO^{\bullet}$ terminations occur *via* (i1), (i2) and/or (i4), the stoichiometric factor is equal to $n = 2$. This simplest consideration shows that the participation of antioxidant intermediate radicals ($FlO^{\bullet}$) in $rO_2^{\bullet}$ termination and the regeneration of FlOH in some reactions (here it is i4) lead to increase in n.

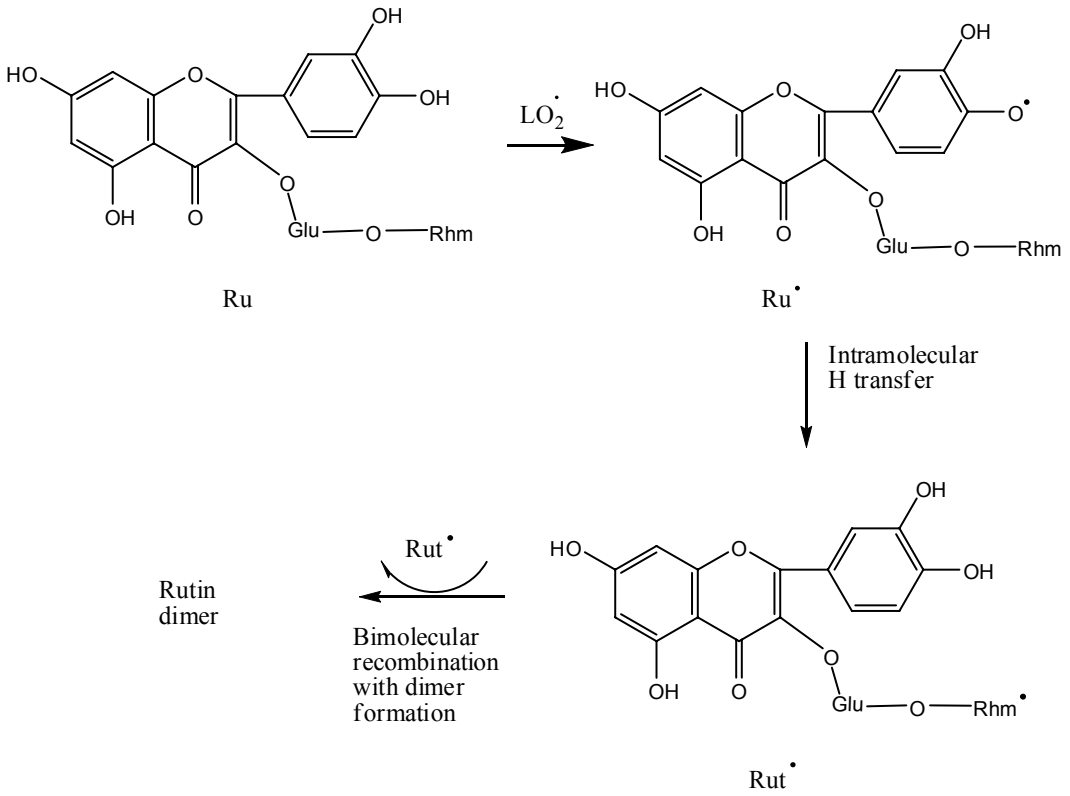
The data obtained (Fig. 6 and Table 4) show that quercetin is characterized by $n_{Qu} = 1$ in water solution and $n_{Qu} = 2$ in organic medium. The latter value coincides with that obtained for Qu in organic solutions by other authors [6, 25, 29]. A lower value n_{Qu}, obtained in water solutions, points to a change of quercetin intermediate radical ($Qu^{\bullet}$) reactivity in reactions i2 and i4, which are responsible for $n > 1$. In some studies stoichiometric factors are determined by the inhibition period (τ) according to the dependence (6):

$$n = R_i \cdot \tau/[FlOH]_0 \qquad (6)$$

This approach can result in higher values of n, because induction periods sum up antioxidant effects over all intermediate products. In the case of Qu (pentahydoxyflavon), the molecules of product-1 and product-2, containing phenolic hydroxyl groups, can interact with free radicals and elongate the induction period. So, stoichiometric factors deter-mined as the ratio between R_i and the initial consumption rates can be lower than n estimated on the basis of the induction periods.

In the case of Ru, the apparent stoichiometric factors are $n_{Ru} = 4$ in water and $n_{Ru} = 10$ in chlorobenzene solution (Fig. 6 and Table 4). Fig.5 and all the data available [6–13, 26] indicate that Ru is a less effective antioxidant than Qu. A lower consumption rate of Ru compared with Qu decay points to a regeneration of Ru-chromophore system in some reactions: In water solution, the assumed regeneration occurs to a lower extent than in chlorobenzene solution. To explain the low Ru consumption rates, we hypothesize about an intramolecular H-abstraction in rutin phenoxyl radical, which resulted in regeneration of all the hydroxyl groups and transfers the radical center to glycoside tail (Scheme 1).

The new transformed radical ($Rut^{\bullet}$) interacts with other radicals and/or substrates to form the products, which possess the same chromophore group as Ru. This makes the Ru transformation reactions invisible by spectrophotometry and decreases the apparent Ru consumption rate.



Scheme 1.

The intramolecular radical transformation changes the relatively stable initial phenoxyl radical inactive in oxidation chain propagation ($FlO^{\bullet}$) into alkoxyl radical $Rut^{\bullet}$, which is more active in H- abstraction than phenoxyl radical is. So, this reaction can be considered as an intramolecular chain transfer of an inhibitor radical, which causes a decrease in the antioxidant efficiency of Ru. Naturally, in water solution due to hydration of glycoside tail, the rate of intra-molecular transformation would be lower than that in organic medium. So, the difference between antioxidant effects of Ru and Qu would be greater in organic nonpolar medium than in water solutions. For example, the ratio between the induction periods τ_{Ru}/τ_{Qu} in oil medium, which are presented in Table 2, is less than 0.27. This ratio in AAPH-initiated oxidation of linoleic acid in SDS micelles at 37ºC inhibited by Qu and Ru in water solution is equal to 0.53 [7] and in CTAB solution $\tau_{Ru}/\tau_{Qu} = 0.6$ [7].

CONCLUSION

The results of the present kinetic study demonstrate that stoichiometric factors for flavonols depend greatly on the medium. Using quercetin and rutin as free radical acceptors it has also been shown that cetyltrimethylammonium chloride (CTAC) catalyzes the decomposition of hydroperoxides derived from sunflower oil oxidation (LOOH) into free radicals at physiological temperature. Noteworthy, the rate of free radical initiation by the mixture of CTAC and LOOH is ~1.5 times higher than that caused by the mixture of CTAC with cumene hydroperoxide at the same concentrations.

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ИЗРАЗХОДВАНЕ НА КВЕРЦЕТИН И РУТИН В РЕАКЦИИ СЪС СВОБОДНИ РАДИКАЛИ

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(Резюме)

Изучено е изразходването на флавонолите кверцетин и рутин по реакция със свободни радикали в хомогенни разтвори и мицеларни системи, съдържащи цетилтриметиламониев хлорид чрез прилагане на УВ-спектроскопия. Свободните радикали се зараждат при разпадането на азоинициаторите 2,2`-азобисизобутил-амидиндихидро-хлорид, ААРН и азобис(изобутилонитрил), АИБН съответно във водна и органична среда. И двата антиоксиданта кверцетин и рутин са използвани като акцептори на свободни радикали за определяне скоростите на образуване на свободни радикали при разпадането на кумиловите хидропероксиди (ROOH) и на хидропероксидите, получени при липидното автоокисление (LOOH), катализирано от цетилтриметиламониевия хлорид в органична и водна среда. Установено е, че скоростта на изразходване на рутина е 4–10 пъти по-бавна от скоростта на изразходване на кверцетина при същите експериментални условия. Дискутирано е съотношението на скоростта на зараждане на свободните радикали и на изразходването на флавонолите и стехиометричния фактор на кверцетина и рутина.