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Kinetics of oxidation of adenosine by *tert*-butoxyl radicals – protection and repair by rosmarinic acid

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The rates of oxidation of adenosine and rosmarinic acid by tert-butoxyl radicals have been studied by measuring the absorbance of adenosine at 260 nm and rosmarinic acid at 324 nm spectrophotometrically. Tert-butoxyl radicals are generated by photolysis of tert-butyl hydroperoxide in presence of tert-butyl alcohol to scavenge OH• radicals. The rates and the quantum yields (φ) of oxidation of rosmarinic acid by *t*-BuO• radicals have been determined in the absence and presence of varying concentrations of adenosine. An increase in the concentration of adenosine has been found to decrease the rate of oxidation of rosmarinic acid suggesting that adenosine and rosmarinic acid compete for *t*-BuO• radicals. From competition kinetics, the rate constant of rosmarinic acid reaction with *t*-BuO• radicals has been calculated to be 2.51×10^{9}dm^3 mol^{-1} s^{-1}. The quantum yields (φ_{expt}) have been calculated from the experimentally determined initial rates of oxidation of rosmarinic acid under different experimental conditions. Assuming that rosmarinic acid acts as a scavenger of *t*-butoxyl radicals only, quantum yields (φ_{cal}) have been theoretically calculated. The values of φ_{expt} and φ_{cal} suggest that rosmarinic acid not only protects adenosine from *t*-BuO• radicals but also repairs adenosine radicals formed by the reaction of adenosine with *t*-BuO• radicals.

Keywords: Rosmarinic acid, adenosine, oxidation, protection, repair, *tert*-butoxyl radicals.

INTRODUCTION

Reactive oxygen species (ROS) are generated in biological systems as by-product of normal cellular processes [1], exposure to UV radiation, and in the presence of transition metal ions [2]. In the presence of oxygen, these species react rapidly with biological targets such as lipids, carbohydrates, proteins, nucleic acids, etc. to form alkyl hydroperoxides [3, 4]. Metabolic degradation of endogenous and exogenous peroxides is thought to play a role in the etiology of several diseases including cancer [5, 6]. DNA is one of the main molecular targets of toxic effects of free radicals formed in mammalian cells during respiration, metabolism and phagocytosis. The lethal effects of the hydroxyl radicals on DNA and its constituents have been extensively studied but relatively little is known about the biological effects of alkoxyl radicals and the key cellular targets for these species. Recent studies have demonstrated that the exposure of cultured cells to alkoxyl radicals resulted in the generation of DNA strand breaks [7-9], though the mechanism of damage has not been elucidated. Previous studies on the reactivity of tertiary butoxyl radicals suggest that these species might be expected to attack both the sugar and the base moieties of DNA [10]. The experimental evidence indicates that base radicals also contribute to strand breaks by transfer of their radical sites from base moiety to sugar moiety. Strand breaks are considered to be a very serious kind of damage to DNA [11, 12].

Antioxidants are substances, when present in small quantities prevent the oxidation of cellular organelles by minimizing the damaging effects of oxidative stress [13, 14]. Antioxidants such as phenolics are widely distributed in the plant kingdom and are therefore an integral part of the diet, with significant amounts being reported in fruits, vegetables and beverages [15]. Chemical, biochemical, clinical and epidemiological evidence has supported the role that dietary antioxidants play an important role in the prevention of several chronic diseases including cardiovascular diseases, cancer, ageing and diabetes [16,17]. The pharmacological actions of phenolic antioxidants stem mainly from their free radical scavenging and metal chelating properties as well as their effects on cell signaling pathway and on gene expression [18]. From our laboratory, caffeic acid has been reported [19, 20] to repair adenosine radicals in addition to

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efficiently scavenging of SO_4• and tert-butoxyl radicals. In this context, studies involving rosmarinic acid assume importance due to its presence in many dietary phytochemicals in higher concentrations.

The t-BuO• radicals have been generated by steady state photolysis of tert-butyl hydroperoxide in the presence of t-BuOH to scavenge the hydroxyl radicals in aqueous solution [21]. The reactions of t-BuO. radicals with adenosine have been studied in the presence of rosmarinic acid with a view to assess the protection by rosmarinic acid towards oxidation of adenosine by t-BuO• radicals and also repair, if any, offered by rosmarinic acid towards adenosine radicals.

MATERIALS AND METHODS

Adenosine and rosmarinic acid were purchased from Sigma and used as received. All solutions were prepared afresh using double distilled water. tert-Butyl hydroperoxide (t-BuOOH) was used as received from Merck-Schuchardt of Germany. There was no contamination of other peroxides in the assay of the sample. t-BuOOH was estimated by the iodometric method [22]. The irradiations were carried out at room temperature in a quantum yield reactor model QYR-20, supplied by Photophysics, England, and attached with 400 W medium pressure mercury lamp. The quartz cuvette, containing the sample, was irradiated and the irradiations were interrupted at definite intervals of time and the absorbance was noted. The light intensity corresponding to the irradiating wavelength (254 nm) was measured using peroxy-disulphate chemical actinometry [23]. On photolysis, t-BuOOH is activated at 254 nm to generate •OH and t-BuO• radicals by homolytic cleavage of –O-O-bond [24]. The •OH radicals produced have been scavenged using sufficient concentration of t-BuOH [21]. In a typical kinetic run the aqueous reaction mixture of adenosine, t-BuOOH and t-BuOH was taken in a specially designed one-centimeter path length quartz cuvette, suitable for both irradiations and absorbance measurements. The absorbance measurements were made at the λ_{max} of adenosine (260 nm) on a Chemito UV-Visible spectrophotometer (model 2100).

The photochemical reaction of rosmarinic acid in the presence of t-BuOOH and other additives, viz., t-BuOH and adenosine, has been followed by measuring the absorbance of rosmarinic acid at 324 nm at which adenosine is totally transparent. It is known that t-BuOOH is activated to radical reaction by the absorption of light at 254 nm [20]. However, the substrates used in the present work, viz., rosmarinic acid and adenosine have strong absorption in this region. But in the absence of t-BuOOH, rosmarinic acid, adenosine or rosmarinic acid-adenosine mixtures have not undergone any observable chemical change on shining the light. Even though a small fraction of the total light intensity is absorbed by t-BuOOH directly in the presence of adenosine and/or rosmarinic acid, a considerable chemical change has been observed with adenosine as well as with rosmarinic acid. If adenosine and rosmarinic acid act as only inner filters, the rates of the reaction of adenosine or rosmarinic acid with t-BuO. would have been decreased with increase in concentration of adenosine or rosmarinic acid. But the results in Table 1 and Table 2 are contrary to this. Another fact against the inner filter concept is that the rate of oxidation of rosmarinic acid in the presence of adenosine would have been much less than the

Table 1. Effect of *t*-BuOOH and adenosine on the rate and quantum yield of photooxidation of adenosine by *t*-BuOOH in the presence of light in aqueous neutral medium.

$10^5 \times$ [adenosine] (mol dm^{-3})	$10^3 \times$ [*t*-BuOOH] (mol dm^{-3})	$10^{10} \times$ Rate (mol $dm^{-3}s^{-1}$)	φ_{expt}
1.0	5.0	2.2183	0.000147
2.0	5.0	2.5866	0.000172
4.0	5.0	3.4362	0.000228
5.0	5.0	4.1222	0.000274
5.0	8.0	5.3467	0.000356
5.0	10.0	6.5324	0.000434

Light Intensity = 2.7168×10^{15} quanta s^{-1}, λmax = 260 nm, pH ~ 7.5; temperature = 298 K, [*t*-BuOH] = 1.0 mol dm^{-3}.

Table 2. Effect of t-BuOOH and rosmarinic acid on the rate and quantum yield of photooxidation of rosmarinic acid by t-BuOOH in the presence of light and t-BuOH in an aqueous solution.

10^5 x [rosmarinic acid] (mol dm^{-3})	$10^3 \times$ [*t*-BuOOH] (mol dm^{-3})	$10^9 \times$ Rate (mol $dm^{-3}s^{-1}$)	φ expt
2.0	1.0	1.6476	0.00109
2.0	2.0	2.3428	0.00155
2.0	5.0	3.4190	0.00227
0.5	5.0	0.7334	0.00049
0.8	5.0	1.1428	0.00076
1.0	5.0	1.3809	0.00092
3.0	5.0	4.8476	0.00346
4.0	5.0	7.4857	0.00695

Light Intensity = 2.7168×10^{15} quanta s^{-1} , λmax = 324 nm, pH ~ 7.5; temperature = 298 K, [*t*-BuOH] = 1.0 mol dm^{-3}.

experimentally observed values (Table 4). Hence, we propose that the excited states of rosmarinic acid and adenosine act as sensitizers to transfer energy to t-BuOOH to produce radical species. This type of sensitizing effect has been proposed in similar systems earlier [19, 25]. Therefore, the light intensity at 254 nm has been used to calculate the quantum yields of oxidation of adenosine as well as rosmarinic acid under different experimental conditions.

RESULTS AND DISCUSSION

The oxidation of adenosine by t-BuO• radicals has been carried out by irradiating the reaction mixture containing known concentrations of adenosine and t-BuOOH in the presence of sufficient amount of t-BuOH to scavenge OH radicals completely [20]. The reaction was followed by measuring the absorbance of adenosine at 260 nm (λ_{max} of adenosine) with time. The reported [20] initial rates and quantum yields of oxidation of adenosine by t-BuO• are presented in Table 1. UV-visible absorption spectra of rosmarinic acid in presence of t-BuOOH and t-BuOH at different irradiation times were recorded (Fig.1). The initial rates of photooxidation of rosmarinic acid by t-BuOOH in presence of t-BuOH have been calculated from the plots of absorbance of rosmarinic acid at 324 nm *vs*. time using microcal origin computer program on a personal computer (Table 2). In order to find the protection, offered to adenosine by rosmarinic acid towards oxidation by t-BuO•, the reaction mixture, containing known concentrations of adenosine, t-BuOOH and t-BuOH, was irradiated in presence of varying concentrations of rosmarinic acid. The reactions were followed by measuring the absorbance of rosmarinic acid at 324 nm (Fig.2) at which adenosine is transparent and the rate data are presented in Table 3.

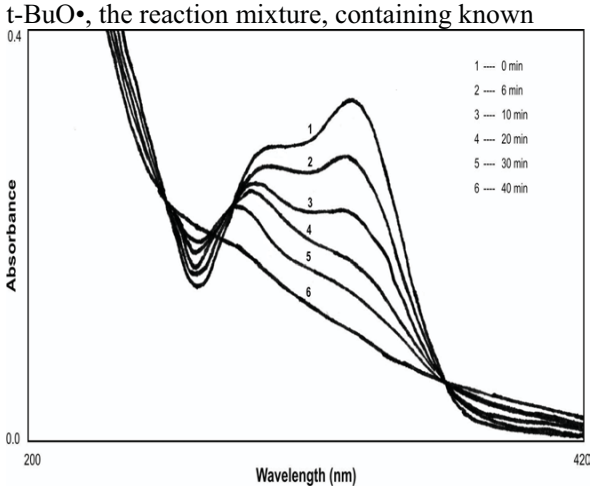


Fig. 1. Absorption spectra of photooxidation of rosmarinic acid in the presence of tert-butyl-hydroperoxide at different irradiation times; [rosmarinic acid] = 2 × 10-5 mol dm-3, [*t*-BuOOH] = 5 × 10-3 mol dm-3, Light Intensity = 2.7168 ×1015 quanta s-1, λmax = 324 nm, pH ~ 7.5, temperature = 298K, [*t*-BuOH] = 1.0 M

Table 3. Effect of varying [rosmarinic acid] on the rate and quantum yield of photooxidation of rosmarinic acid by *t*-BuOOH in the absence and presence of adenosine in aqueous solution

10^5 × [rosmarinic acid] (mol dm^{-3})	10^4 × [adenosine] (mol dm^{-3})	10^9 × Rate (mol $dm^{-3}s^{-1}$)	φ_{expt}
0.5	0.0	0.7334	0.00049
0.8	0.0	1.1428	0.00076
1.0	0.0	1.3809	0.00092
2.0	0.0	3.4190	0.00227
0.5	5.0	0.3162	0.00021
0.8	5.0	0.8384	0.00056
1.0	5.0	0.9714	0.00065
2.0	5.0	2.1619	0.00144

[*t*-BuOOH] = 5 × 10^{-3} mol dm^{-3}, Light Intensity = 2.7168 × 10^{15} quanta s^{-1}, λ_{max} = 324 nm, pH ~ 7.5, temperature = 298 K, [*t*-BuOH] = 1.0 M.

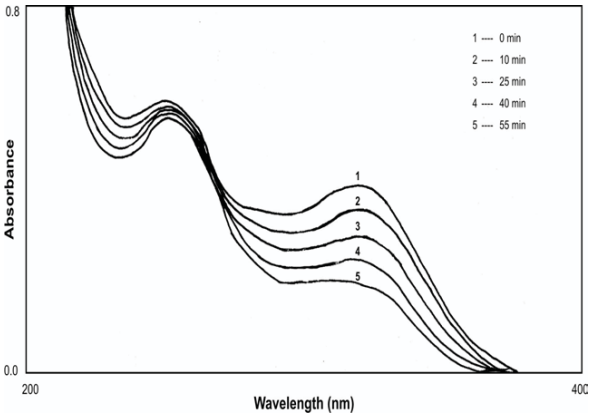


Fig. 2. Absorption spectra of photooxidation of rosmarinic acid in the presence of tertbutyl hydroperoxide and adenosine at different irradiation times; [rosmarinic acid] = 2 × 10-5 mol dm-3, [*t*-BuOOH] = 5 × 10-3 mol dm-3, [adenosine] = 2 × 10-5 mol dm-3, Light Intensity = 2.7168 × 1015 quanta s-1, λmax = 324 nm, pH ~ 7.5, temperature = 298K, [*t*-BuOH] = 1.0 M

The photooxidation of rosmarinic acid by *t*-BuO**.** at different concentrations of adenosine was also studied (Fig.3) and the data is presented in Table 4. The oxidation rate of adenosine in the presence of *t*-BuOH refers exclusively to the reaction of *t*-BuO**.** with adenosine [20]. These rates have been found to increase with increase in concentration of adenosine as well as *t*-BuOOH. The quantum yield values are also found to increase

Table 4. Effect of varying [adenosine] on the rate and quantum yield of photooxidation of rosmarinic acid in the presence of *t*-BuOOH, *t*-BuOH and light in aqueous solution.

$10^5 \times$ adenosine (mol dm^{-3})	$10^9 \times$ Rate (mol dm^{-3} s^{-1})	φ_{expt}	φ_{cal}	p	φ'	% scavenging	% repair
0.00	3.41	0.00227	0.00227	1.0000	0.00227	100.0	0.00
5.00	3.14	0.00209	0.00201	0.8876	0.00235	88.76	3.73
8.00	2.97	0.00198	0.00185	0.8178	0.00242	81.78	6.45
10.0	2.94	0.00196	0.00177	0.7819	0.00250	78.19	10.37
20.0	2.69	0.00179	0.00146	0.6419	0.00279	64.19	22.73
50.0	2.16	0.00144	0.00095	0.4176	0.00344	41.76	51.68
100.0	1.64	0.00109	0.00060	0.2639	0.00413	26.39	81.78

[rosmarinic acid] = 2.0×10^{-5} mol dm^{-3}, [*t*-BuOOH] = 5.0×10^{-3} mol dm^{-3}, [*t*-BuOH] = 1.0M, Light Intensity = 2.7168×10^{15} quanta s^{-1}, λ_{max} = 324 nm, pH~7.5, temperature = 298 K.

with increase in [adenosine] as well as [*t*-BuOOH] (Table 1).

The rate of oxidation of rosmarinic acid has been found to increase with increase in concentration of rosmarinic acid (Table 2). The quantum yields of oxidation of rosmarinic acid have been calculated from the initial rates and the light intensity at 324 nm. These values are also found to increase with increase in concentration of rosmarinic acid (Table 2). Having known the rates of t-BuO• radical reactions with adenosine as well as with rosmarinic acid under varying experimental conditions, both adenosine and rosmarinic acid are introduced for the competitive studies with t-BuO• radical. Aqueous solutions of reaction mixture containing rosmarinic acid t-BuOOH and t-BuOH were irradiated in the presence of varying concentrations of adenosine (Fig.3). The initial rates and quantum yields of oxidation of rosmarinic acid by t-BuO• radicals were found to decrease with the increase in concentration of adenosine (Table 4). Comparison of the initial rates and quantum yields of oxidation of rosmarinic acid in the presence and absence of adenosine clearly indicate that the initial rates and quantum yields of oxidation of rosmarinic acid are substantially decreased in the presence of adenosine (Table 4). These observations clearly demonstrate that adenosine and rosmarinic acid are in competition for t-BuO• radicals.

The rate constant of the reaction of *t*-BuO• with adenosine has been reported [12] to be 1.40×10^8 dm^3 mol^{-1}s^{-1} under similar experimental conditions of the present work. The rate constant for the reaction of *t*-BuO• with rosmarinic acid has been calculated by the adenosine competition method, which is very similar to the one chosen to determine the rate constant for the reaction of •OH radicals with polyhydric alcohols in competition with KSCN [26]. In the present study, solutions containing rosmarinic acid and varying amounts of adenosine in presence of *t*-BuOOH and *t*-BuOH were irradiated for two minutes and the decrease in absorbance of rosmarinic acid was measured. The decrease in absorbance of rosmarinic acid reflects the extent of *t*-BuO• radicals reacted with rosmarinic acid. From the known rate constant of the reaction of adenosine with *t*-BuO• radical under similar experimental conditions of the present work ($k_{adenosine}$=1.40×10^8 dm^3 mol^{-1} s^{-1}), the rate constant of *t*-BuO• radical reaction with rosmarinic acid ($k_{rosmarinic\ acid}$) is calculated using Eq. (1).

$$\frac{[\text{Absorbance of rosmarinic acid}]_o}{[\text{Absorbance of rosmarinic acid}]_{adenosine}} = 1 + \frac{k_{adenosine}\,[\text{adenosine}]}{k_{rosmarinic\ acid}\,[\text{rosmarinic acid}]} \quad (1)$$

$$p_{(t\text{-}BuO^{\bullet} + \text{rosmarinic acid})} = \frac{k_{\text{rosmarinic acid}}\,[\text{rosmarinic acid}]}{k_{\text{adenosine}}\,[\text{adenosine}] + k_{\text{rosmarinic acid}}\,[\text{rosmarinic acid}]} \quad (2)$$

In Eq.(1), [Absorbance of rosmarinic acid]$_o$ and [Absorbance of rosmarinic acid]$_{adenosine}$ are the absorbance values of rosmarinic acid in the absence

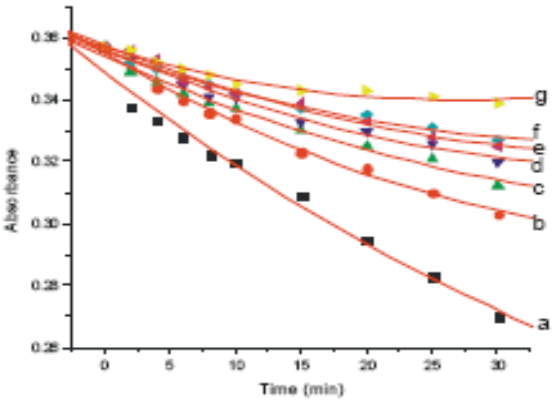


Fig. 3. Effect of varying concentrations of adenosine on the photooxidation of rosmarinic acid (2.0×10^{-5} moldm^{-3}) in the presence of *t*-BuOOH (5×10^{-3} mol dm^{-3}) at 298 K. [adenosine] = (a) 0.0, (b) 5×10^{-5} mol dm^{-3}, (c) 8×10^{-5} mol dm^{-3}, (d) 1×10^{-4} mol dm^{-3}, (e) 2×10^{-4} mol dm^{-3}, (f) 5×10^{-4} mol dm^{-3}, (g) 1×10^{-3} mol dm^{-3}, [*t*-BuOH] = 1.0 M.

and presence of adenosine respec-tively, at the same interval of time. Experiments of this kind can be carried out with great accuracy. Using Eq.(1) the rate constant for the reaction of *t*-BuO• radical with rosmarinic acid ($k_{\text{rosmarinic acid}}$) has been calculated at different concentrations of rosmarinic acid and adenosine and the average of these values is found to be 2.51×10^{9} dm^3 mol^{-1} s^{-1}. As rosmarinic acid has strong absorption at 260 nm, it is not possible for the direct determination of protection and repair offered to adenosine by rosmarinic acid at this wavelength. However, one can calculate indirectly the extent of protection offered to adenosine by rosmarinic acid from competition kinetic studies measured at 324 nm, λ_{max} of rosmarinic acid. When the system containing adenosine, rosmarinic acid and *t*-BuOOH in the presence of *t*-BuOH is irradiated, the probability of *t*-BuO• radicals reacting with rosmarinic acid {p(*t*-BuO• +rosmarinic acid)} is calculated using Eq. (2).

If rosmarinic acid scavenges only t-BuO• radicals and does not give rise to any other reaction (e.g. reaction with adenosine radicals), the quantum yield of oxidation of rosmarinic acid (φcal) at each concentration of adenosine may be given by Eq. (3):

$$\varphi_{cal} = \varphi^{0}_{expt} \cdot p \quad (3)$$

where φ^{o}_{expt} is the quantum yield of oxidation of rosmarinic acid in the absence of adenosine, and p is the probability given by Eqn. 2.

The calculated quantum yield (φ_{cal}) values at different adenosine concentrations are presented in Table 4. The data show that φcal values are lower than experimentally measured quantum yield (φ_{expt}) values. This indicates that more of rosmarinic acid is consumed in the system than theoretically expected. The most likely route for this is H atom donation by rosmarinic acid to adenosine radicals, generated during competition reactions. Table 4 presents the fraction of t-BuO• radicals scavenged by rosmarinic acid at different concentrations of adenosine. These values refer to the measure of protection, offered to adenosine due to scavenging of t-BuO• radicals by rosmarinic acid. Using the φexptl values, a set of values, viz.,′φvalues, have been calculated from Eq. (4) and are presented in Table 4:

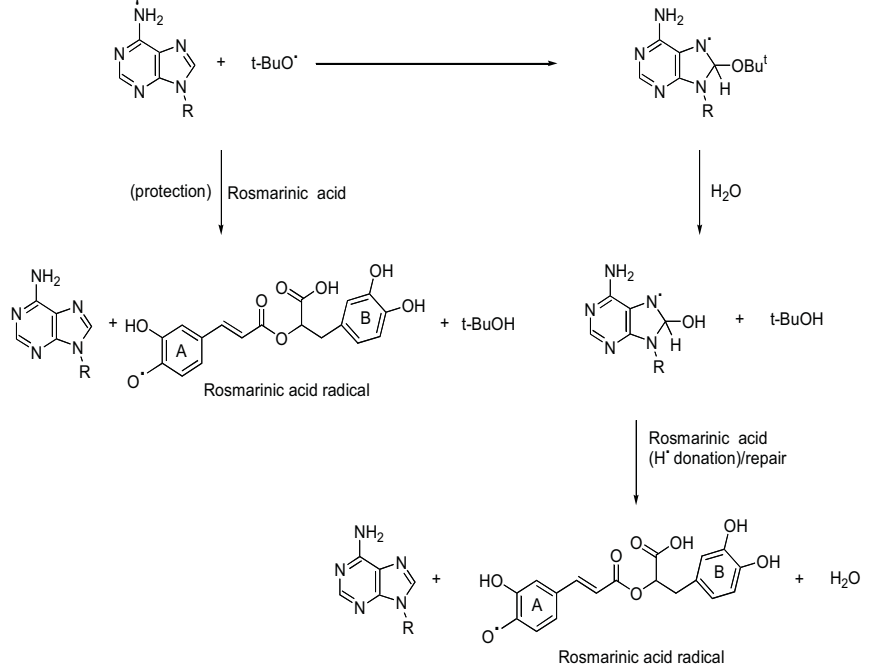
$$\varphi' = \frac{\varphi_{expt}}{p} \quad (4)$$

where φ′ represents experimentally found quantum yield values if no scavenging of adenosine radicals by rosmarinic acid occurs. In the absence of any "repair" of adenosine radicals by rosmarinic acid, φ′ values should all be equal to φ^{o}_{expt}. The observed increase φ′ with increasing adenosine concentration (Table 4) clearly indicates that repair of adenosine radicals does occur. The extent of repair may be quantified by the following equation:

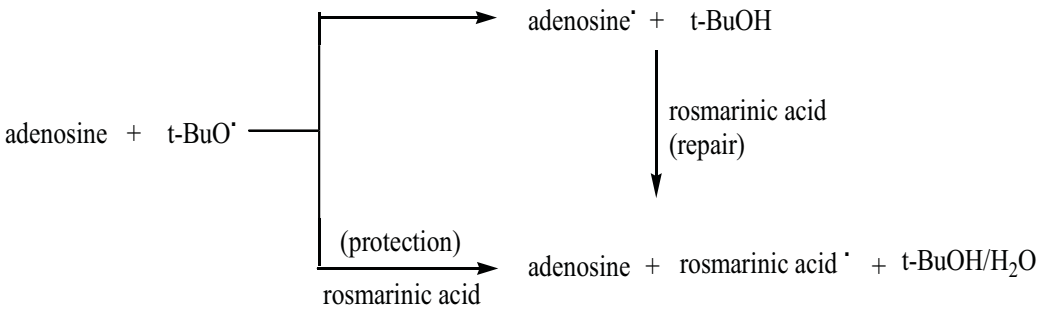
$$\%\,\text{Repair} = \frac{\varphi' - \varphi^{0}_{expt}}{\varphi^{0}_{expt}} .100 \quad (5)$$

The data on percentage repair is presented in Table 4. The experimentally determined quantum yield (φ_{expt}) values are higher than the quantum yield (φ_{cal}) values, calculated using Eq.(3) under the assumption that rosmarinic acid acts only as a t-BuO• radical scavenger. This shows that rosmarinic acid acts not only as an efficient scavenger of t-BuO• radicals but also as an agent for the repair of adenosine radicals. The repair reaction of rosmarinic acid is explained in terms of H donation as shown below in Scheme 1.

The results obtained in the present study (Table 4) indicate that adenosine radicals are efficiently repaired by rosmarinic acid to the extent of ~82 % at about 20 μM of rosmarinic acid concentration. The protection of adenosine and repair of adenosine radicals are summarized in Scheme 2.



Scheme 1



Scheme 2

The electron density calculations show that C8 in adenosine is more electron rich compared to C4 or C5 [27]. The bulkiness of the t-BuO• radical is another reason that it prefers C8 position where no steric hindrance is present. The attack of t-BuO• radical at C8 leads to the formation of N7-centered radical, the nature of which has been reported to be oxidizing. Caffeic acid is known to react with oxidizing transient radicals very efficiently. This has been realized in the competition studies of caffeic acid with adenosine radicals [20]. The rosmarinic acid, which is very similar in nature to caffeic acid, is expected to repair the transient oxidizing radicals of adenosine in a similar way.

The obtained percentage of repair, in this study by rosmarinic acid (~82%, cf. Table 4), supports our contention that rosmarinic acid repairs, oxidizing the adenosine transient radicals.

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КИНЕТИКА НА ОКИСЛЕНИЕТО НА АДЕНОЗИН ОТ *tert*-БУТОКСИЛОВИ РАДИКАЛИ - ЗАЩИТА И ВЪЗСТАНОВЯВАНЕ С РОЗМАРИНОВА КИСЕЛИНА

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(Резюме)

Изследвана е скоростта на окисление на аденозин и розмаринова киселина с tert-бутоксилови радикали. Спектрофотометрично е определяна абсорбцията на аденозина при 260 nm и на розмартиновата киселина при 324 nm. Третичните бутоксилови радикали се генерират чрез фотолиза на третичен бутилов хидропероксид в присъствие на третичен бутанол за улавянето на OH• - радикалите. Скоростите и квантовите добиви (φ) на окислението на розмариновата киселина от *t*-BuO• - радикалите са определяни в отсъствие и при различни концентрации на аденозин. Повишаването на концентрацията на аденозина води до понижаване скоростта на окисление на розмариновата киселина, което се обяснява с конкуренцията на двата реагента за *t*-BuO• - радикалите. Скоростната константа на реакцията на розмариновата киселина, отчитайки конкуренцията саденозина е определена на 2.51×10^{9} $dm^{3}mol^{-1}s^{-1}$. Пресметнати са квантовите добиви (φ_{expt}) от опитно определените начални скорости на окисление на розмариновата киселина при различни експериментални условия. Приемайки, че розмариновата киселина улавя само *t*-бутоксиловите радикали е изчислен "теоретичния" квантов добив (φ_{cal}). Сравняването на двата квантови добива показва, че розмариновата киселина не само защищава аденозина от *t*-BuO• -радикалите, но и възстановява аденозиновите радикали, образувани при реакцията на аденозина с *t*-BuO• - радикалите.