# Spectrophotometric and chromatographic study of radiolysis products of aerated aqueous solutions of alkylresorcinols

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Radiation-induced oxidation of alkylresorcinols in aerated aqueous solutions was studied by HPLC and spectrophotometry. Some of the products, the so-called "red forms", arise upon aggregation of oxidized intermediates. These red forms are more reactive than the starting compounds.

**Key words:** phenols, alkylresorcinols, orcinol, red forms, high performance liquid chromatography, UV-Vis spectrophometry, oxidation, radiolysis.

During the life, animals and plants experience the influence of numerous adverse factors; as a result, they pass to a stressed condition. This is accompanied by violation of redox processes and increase in concentrations of active forms of oxygen. Therefore, the search for biologically active compounds able to decrease the contents of active forms of oxygen and study of mechanisms of enhancement of the stability and metabolic adaptation of cells to stress impacts are highly topical tasks.

Biologically active compounds that exhibit antioxidant and antiradical activities are of considerable interest. Phenolic compounds belong to typical natural antioxidants;[1—6] their characteristic feature is the ability to interact with proteins and metal ions to form hydrogen bonds and complexes of various structure. Phenols themselves are readily oxidized by atmospheric oxygen to give reactive intermediates,[2] some of which possess antioxidant properties.

The problem of radiation-induced transformations of phenolic and polyphenolic compounds is the subject of numerous publications.[7—13] Solutions of phenols have been used as model systems to study the efficiency of radiation-chemical sewage treatment.[14—16] However, the mechanism of such transformation has not yet been elucidated.

It is known that hypometabolism and anabiosis represent natural protection mechanisms of many microorganisms from the impact of adverse factors, in particular, ionizing radiation. In this state, cells contain increased contents of alkylhydroxybenzenes[5,6] (AHB), which act as autoregulators of the growth and development of microorganisms and possess a pronounced antioxidant activity.[4,5] It was found that AHB control the growth of cell population in a microbial culture, inhibit the spore germination, and induce development of the anabiotic state of the cells. The metabolic activity of cells decreases due to the formation of complexes of AHB with cell membrane phospholipids and enzymes.[5,6] However, the chemical properties of the products formed on exposure of AHB to physicochemical factors such as light, radiation, or oxidants ($O_2$ and $H_2O_2$) have not yet been adequately studied.

Previously, the transformations of phenols and alkylresorcinols in aerated aqueous solutions upon chemical, photochemical, and radiation-induced chemical oxidation have been studied.[10,14—16] It was found that, under these conditions, both polymeric and low-molecular-weight products are formed. Elucidation of the mechanism of formation of these products requires studies of the initial steps of the reactions of AHB with free radicals (active forms of oxygen) responsible for oxidative processes in biological systems in normal and pathological states.

In the present study, oxidation of 5-methylresorcinol (orcinol, $C_7$) in aqueous solutions was initiated by stationary radiolysis ($\gamma$-irradiation using $^{60}Co$ as the source) and pulse radiolysis methods (the action of accelerated electrons), and the intermediate and final products responsible for these transformations were studied. The radiolysis products of $C_7$ in aqueous solutions taking place in the presence of atmospheric oxygen during the post-

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radiation period were analyzed by HPLC and spectrophotometry.

## Experimental

The action of ionizing radiation on aerated aqueous solutions of orcinol (5-methylresorcinol, recrystallized three times, Sigma) was studied. The aqueous solutions of $C_7$ with concentrations ranging from $1 \cdot 10^{-5}$ to $5.25 \cdot 10^{-3}$ mol $L^{-1}$ were prepared by dissolving an exact weighed amount in triply distilled water, pH 6.8.

Water (triply distilled, purified using Millipore, Milli-P QG, Waters), orthophosphoric acid (85%, for HPLC, Sigma), and acetonitrile ("chemically pure" grade, first-rate, Kriokhrom) were used.

The following setups designed at the Institute of Electrochemistry of the RAS were used as sources of ionizing radiation:

— GURKh 100 000 ($\gamma$-$^{60}$Co) for radiation doses of 5—50 kGy; the solutions were irradiated in the dark at room temperature;

— an ELU-12 electron accelerator with an energy of the electron beam of 4.5 MeV was used for pulse radiolysis with 2.2 μs pulses. The dose per pulse varied from $1.3 \cdot 10^{17}$ to $2.4 \cdot 10^{17}$ eV $g^{-1}$ (20—40 Gy) by varying the filament current of the injector. A DKSSh-500 lamp producing the analyzing light operated in the pulse mode synchronously with the electron pulse. Glass light filters were used to restrict the impact of light on the sample during irradiation with electrons. The dosimetry of the radiation sources was carried out by standard methods.[17]

The optical absorption spectra of the initial and irradiated solutions of $C_7$ were recorded on Specord M–40 and Beckmann spectrophotometers relative to water at specified time intervals at room temperature. Quartz cells with an optical path of 10 mm were used.

The oxidation products obtained from $C_7$ were analyzed on Milikhrom A-02 and Agilent 1100 liquid chromatographs. Reversed phase HPLC with UV-spectrophotometric and diode-array detection (DAD) was employed with steel chromatographic columns, 100×2.1 mm with Hypersil ODS (3 μm) (Agilent 1100) and 120×2 mm with Diasorb C16 (7 μm) (Milikhrom A-O2). Water and MeCN with phosphoric acid added to pH 3.5 were used as the mobile phase. The following gradient mode of elution was used: 0→3 min, 0→5% MeCN; 3→18 min, 5→100% MeCN; 18→20 min, 100% MeCN; 20→25 min, 100→5% MeCN; and 25→30 min, 5% MeCN. The flow rates of the mobile phase on Diasorb C16 and Hypersil ODS columns were 100 and 300 μL $min^{-1}$, respectively.

## Results and Discussion

The changes in the optical absorption spectra of aerated aqueous solutions of $C_7$ depending on the $\gamma$-radiation dose are presented in Fig. 1. It follows from comparison of the initial optical absorption spectrum (*1*), which is a doublet ($\lambda_{max}$ = 273 and 279 nm), and the spectra corresponding to different radiation doses (spectra *2*—*6*) that the irradiation changes the spectral pattern and the absorption intensity over the whole range of wavelengths. As the irradiation dose increases, the absorption intensity at ~250 nm grows and new poorly resolved absorption bands appear at $\lambda \approx 285$—290 and 400—600 nm. The change in

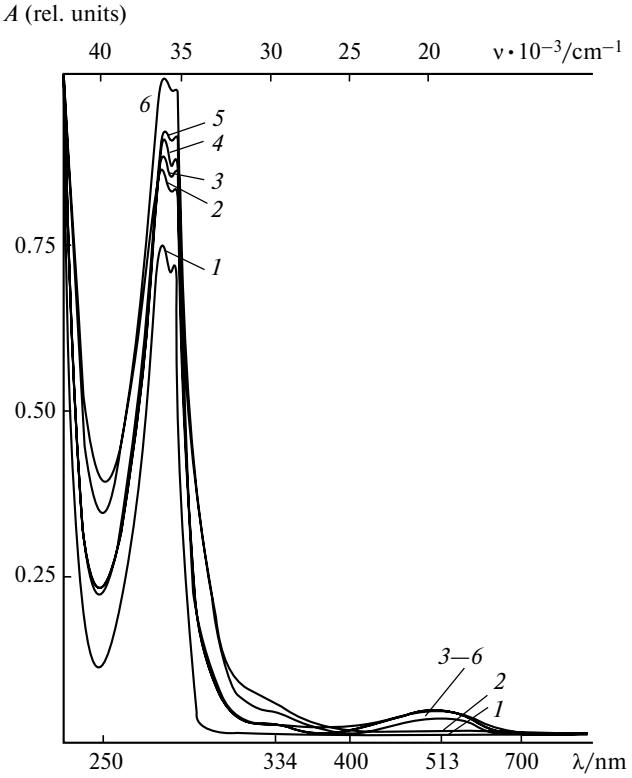


**Fig. 1.** Optical absorption spectra of aerated aqueous solutions of orcinol after irradiation with doses of 0 (*1*), 2 (*2*), 5 (*3*), 10 (*4*), 20 (*5*), and 30 kGy (*6*). The concentration of the starting solution of $C_7$ was $2.8 \cdot 10^{-3}$ mol $L^{-1}$.

the absorption intensity for each of these bands is nonlinear. This suggests that radiolysis of aerated aqueous solutions of the starting compound can give a number of products. Despite the low intensity of the spectrum in the region of λ 420—600 nm, the pink coloring of the irradiated samples can apparently be attributed to the formation of the so-called "red forms".[18—22] Previously,[23] labile "red form" compounds were detected upon radiolysis of alcoholic and aqueous solutions of flavonoids. The optical characteristics and the radiation stability of these products are similar to those of anthocyanin pigments. In radiation genetics, much emphasis is placed on the appearance of red forms, which are used as markers of the radiation damage of plants.[24] Moreover, biologists pay considerable attention to the detection of these compounds, which seem to act as protective factors against stress impacts in plant cells.[25—27]

The role of oxygen in the radiation-induced transformations of orcinol was elucidated by saturating its aqueous solutions ($5.3 \cdot 10^{-3}$ mol $L^{-1}$) with helium for 15—20 min and irradiation in the dark. It was shown that, irrespective of the radiation dose, only traces of red forms appear. However, after the contact of the irradiated aqueous solution of orcinol with atmospheric oxygen, these red forms were detected by spectrophotometry and HPLC. Hence,

these compounds are formed upon the radiation-induced oxidation of $C_7$ by atmospheric oxygen.

The composition of the products resulting from radiation-induced oxidation of orcinol was studied by HPLC. The chromatogram of the starting aqueous solution of $C_7$ and the chromatograms of solutions exposed to γ-radiation to doses of 5 and 30 kGy are shown in Fig. 2. It can be seen that radiolysis of the starting $C_7$ molecule gave fractions of radiolysis products with smaller and larger molecular masses. It is noteworthy that a peak D (see Fig. 2, *c*) detected at 290 nm appears, which confirms the formation of new products responsible for the poorly resolved optical absorption band at λ = 290 nm (see Fig 1).

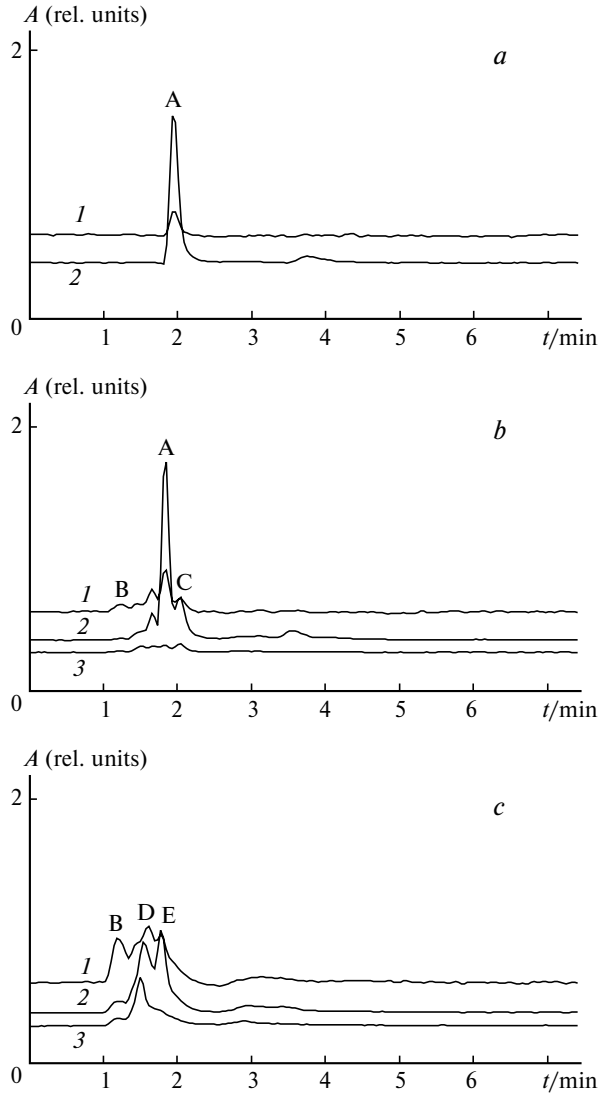


**Fig. 2.** Chromatograms of an aqueous solution of orcinol after irradiation with doses of 0 (*a*), 5 (*b*), and 30 kGy (*c*). Retention times of peaks (min): (*a*) 1.93 (A); (*b*) 1.85 (A), 1.22 (B), 2.05 (C); (*c*) 1.18 (B), 1.54 (D), 1.77 (E). Detection at λ = 240 (*1*), 272 (*2*), and 290 nm (*3*). Diasorb C16 column. The concentration of the initial solution of $C_7$ was $2.8 \cdot 10^{-3}$ mol $L^{-1}$.

The chromatograms of the radiation-induced oxidation products for radiation doses of 2—30 kGy with detection at 513 nm are shown in Fig. 3, *a*. This wavelength was chosen for detection on the basis of spectral data for new products in the region of 400—600 nm. Figure 3, *a* indicates that the changes in the processes of formation and stabilization of $C_7$ radiolysis products depend on the irradiation dose in a complex pattern. The products obtained upon irradiation of orcinol (doses 2—30 kGy) possess not only different retention times (see Fig. 3, *a*) but also different radiation stabilities. For example, no products were detected at 513 nm for the sample exposed to a dose of 20 kGy (see Fig. 3, *a*, chromatogram *4*), but some new products were again found (see Fig. 3, *a*, chromatogram *5*) for the sample exposed to a higher dose (30 kGy). The conclusion concerning the high lability of the oxidation products can also be drawn from analysis of the spectrophotometric (see Fig. 1) and chromatographic data (see Fig. 3, *b*), which indicate that the products formed in the radiation-induced oxidation of $C_7$ undergo transformations during the post-radiation period. During storage of an irradiated sample, peaks of new products can be detected (see Fig. 3, *b*), some of them having larger retention times than that of the starting compound. Thus we suggested that these peaks correspond to condensed orcinol oxidation products. Figure 4 shows the spectra of the products corresponding to the chromatographic peaks presented in Fig. 3, *b*. It can be seen that the structures of the absorption bands in the visible and UV regions in the spectra of products with different retention times are different. The spectra of orcinol oxidation products A and B recorded immediately after irradiation (see Fig. 4, A, B) exhibit the following absorption maxima: A, λ = 268 and 387.6 nm; B, λ = 247.6, 256.8, and 334.8 nm. Figure 4, I—K, shows the spectra of oxidation products 3 h after irradiation (I, J, K), responsible for the following maxima: I, λ = 210, 266.8, and 524 nm; J, λ = 207, 269.6, and 524 nm; K, λ = 200, 270, and 388 nm. The spectral characteristics of the oxidation products (L, M) 5 h after irradiation (see Fig. 4, L, M) are as follows: L, λ = 202, 232.8, and 272 nm; M, λ = 203, 230.8, and 277.2 nm. It can be seen that, apart from the shifts of individual absorption maxima, differences in the intensity ratios of these bands are observed. This supports our assumption that the oxidation of orcinol affords different products.

The complex pattern of accumulation of the products formed upon $C_7$ oxidation during both irradiation and post-radiation period hampers the detection and identification of these compounds. Therefore, to decrease the time and dose of the radiation treatment of aqueous solutions of $C_7$, we irradiated samples with 2.2 μs pulses of accelerated electrons. Using the potential of pulse radiolysis, we attempted to solve an additional problem, namely, to study the effect of photoradiation on the radiation-induced oxidation of aqueous solutions of orci-

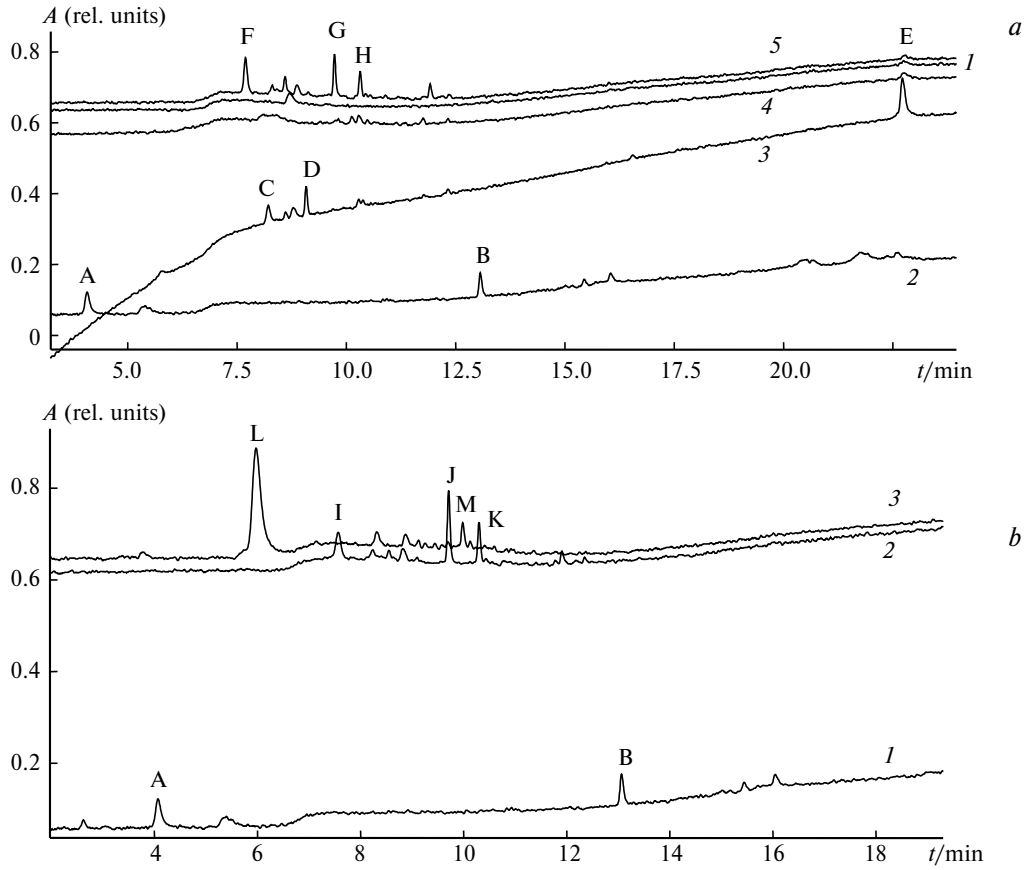


**Fig. 3.** Chromatograms of the products of radiation-induced oxidation of an aqueous solution of $C_7$ depending on the radiation dose (*a*): 0 (*1*), 2 (*2*), 5 (*3*), 20 (*4*), 30 kGy (*5*) and on time (*b*) for a radiation dose of 2 kGy during the post-radiation period: 0.3 (*1*), 3 (*2*), and 5 h (*3*). Retention time of peaks (min): (*a*) 4.070 (A), 13.063 (B), 8.216 (C), 9.082 (D), 22.723 (E), 7.694 (F), 9.731 (G), and 10.317 (H); (*b*) 4.070 (A), 13.063 (B), 7.566 (I), 9.709 (J), 10.298 (K), 5.971 (L), and 9.982 (M). Detection at λ 513 nm. Hypersil ODS column. The concentration of the initial solution of $C_7$ was $2.8 \cdot 10^{-3}$ mol $L^{-1}$.

nol. In order to solve this problem, we studied the post-radiation behavior of the orcinol oxidation products initiated by a single pulse of accelerated electrons or by an additional impact of the analyzing light from a DKSSh-500 lamp.

Figure 5 shows the chromatograms of aqueous solutions of $C_7$: initial solution (curve *1*), that exposed to one pulse of accelerated electrons (curve *2*), and a solution exposed simultaneously to electrons and to the full spectrum of a DKSSh-500 lamp (curve *3*). The dose per pulse of the accelerated electrons was ~20 Gy. The spectrum of a product (B), which is absent from the initial sample or the sample obtained upon photoradiation (see Fig. 5, inset), allows one to attribute this product to red forms, which are responsible for optical absorption bands in the region of 300—600 nm.

The optical absorption spectra of aqueous solutions of $C_7$ irradiated with accelerated electrons or electrons with simultaneous exposure to the light from a DKSSh-500 lamp (Fig. 6) show that both immediately after irradiation and after 1 week, more intense absorption bands are found in the spectra of samples irradiated with electrons without light. The ratios of the intensities of individual bands in the spectrum change in different ways. This implies that, apart from high radiation sensitivity, the oxidation products of alkylresorcinols possess also high photolytic activity, *i.e.*, upon simultaneous action of ionizing radiation and light, some of the quasi-stable oxidation products disappear (see Fig. 6, curves *1*, *2*). These differences in the formation of oxidation products caused by the photoradiation effect are also observed in the post-radiation period (see Fig. 6, curves *1′*, *2′*).

It is known[28,29] that oxidation of phenol derivatives gives compounds with carboxy and carbonyl groups, dimers, and polymers, whose optical absorption lies in the region of <400 nm. The physiological activities of these products did not exceed those of the initial compounds. The formation of colored red-brown oxidation products from quinone and pyrogallol under the action of light has been noted previously.[30] A study[29] of the oxidation of polyphenolic compounds showed the presence of short-lived (~20 s) colored forms responsible for absorp-

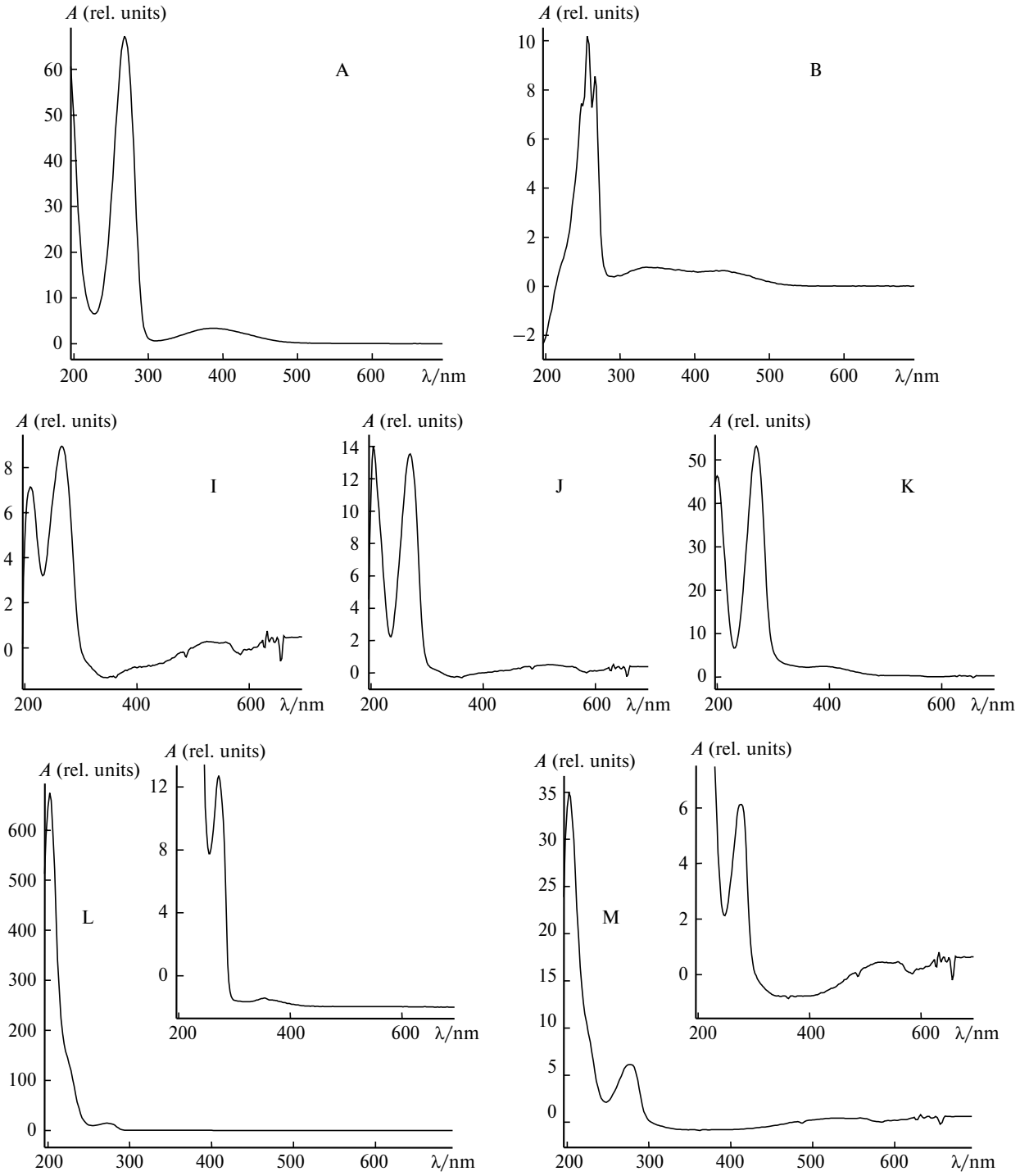


**Fig. 4.** Optical absorption spectra of the products of radiation-induced oxidation (see Fig. 3, *b*) of an aqueous solution of $C_7$ for a radiation dose of 2 kGy recorded during the post-radiation period for $t = 0$ (A, B), 3 (I—K), and 5 h (L, M). The concentration of the initial solution of $C_7$ was $2.8 \cdot 10^{-3}$ mol $L^{-1}$.

tion bands at about 550 nm. An ESR study did not confirm the radical nature of these products. In a study[26—28] of the oxidation of phenolic compounds with *meta*-OH groups, the formation of colored very labile substances responsible for absorption bands in the region of 400—560 nm was established and pathways of formation of the corresponding chromophores were proposed. However, neither detection of these compounds nor experimental determination of conditions for their formation were successful.[26,27,29]

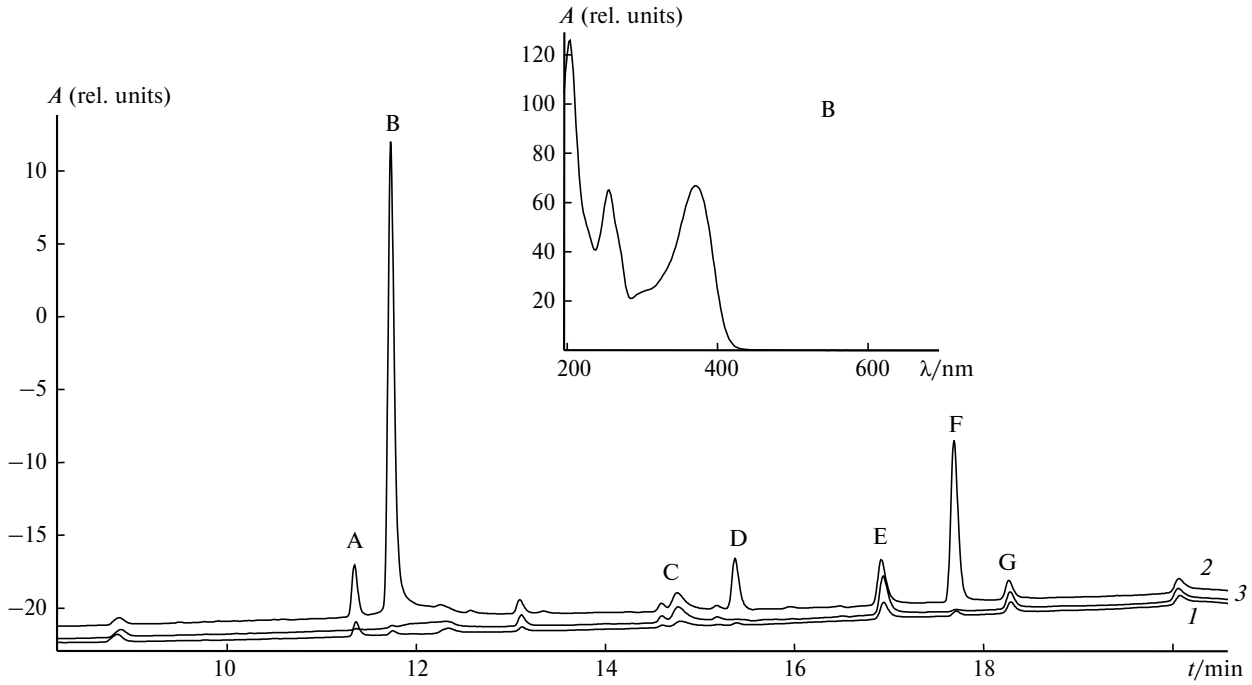


**Fig. 5.** Chromatograms of the initial aqueous solution of orcinol (*1*) and the products obtained on its exposure to a single pulse of accelerated electrons (*2*) and the same with simultaneous action of the full light from a DKSSh-500 lamp (*3*). Retention time of peaks (min): 11.347 (A), 11.729 (B), 14.760 (C), 15.371 (D), 16.918 (E), 17.687 (F), and 18.268 (G). Detection at λ 334 nm. Hypersil ODS column. The concentration of the initial solution of $C_7$ was $5.25 \cdot 10^{-3}$ mol $L^{-1}$. The inset shows the spectrum of product (B) resulting from exposure of an aqueous solution of $C_7$ to a single pulse of accelerated electrons (*2*).

Previously,[8,26] antioxidant properties of a number of phenolic compounds have been studied. The results obtained by pulse radiolysis indicate that anthocyanins (polyphenolic compounds containing a pyrylium ring) possess higher antiradical and radioprotective abilities than flavonoids, *i.e.*, polyphenolic compounds for which the principal band has $\lambda_{max}$ <400 nm.

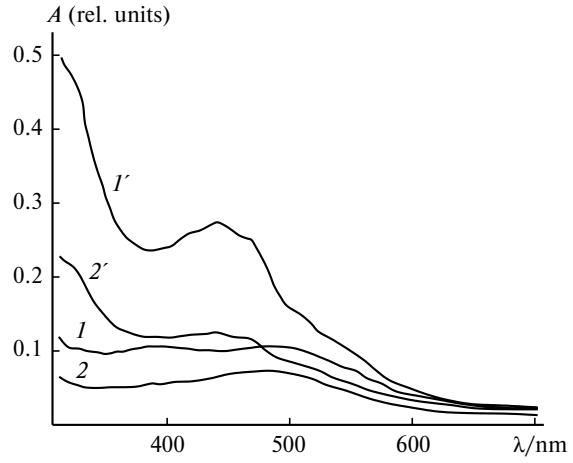


**Fig. 6.** Optical absorption spectra of the products formed on exposure of an aqueous solution of $C_7$ to a single pulse of accelerated electrons (*1*, *1′*) and the same with simultaneous action of the visible light from a DKSSh-500 lamp (*2*, *2′*). The spectra were recorded 15 min after the treatment (*1*, *2*) and after keeping the samples in the dark for a week (*1′*, *2′*). The radiation dose was 20 Gy. The concentration of the initial solution of $C_7$ was $5.25 \cdot 10^{-3}$ mol $L^{-1}$.

It is known[26] that natural phenolic compounds and their polymeric analogs with chromophore groups in the red spectral region possess high photophysical activities and, depending on the reaction conditions, they function as either traps or emitters of photons. Therefore, research into the properties and functional activities of these compounds has aroused increasing interest in recent years.

In this study, we used for the first time the radiation simulation of the oxidation of phenol derivatives using oxidation of orcinol in aqueous solutions as an example.

Using HPLC, we detected and analyzed for the first time the oxidation products of orcinol according to their retention times and spectroscopic characteristics. In our opinion, the most important point is the detection of new products with larger retention times, which cannot be interpreted in the context of destruction of the initial molecule.

We found that exposure of aqueous solutions of alkylresorcinols to ionizing radiation initiates complex redox processes, which endure during the post-radiation period and give rise to a set of diverse final products due to both destruction and aggregation of the intermediate oxidation products.

The radiation-induced oxidation was found to yield various condensation products of $C_7$, in particular, red forms, whose presence has been regarded[31,32] as the reason for higher physiological activity of the radiolysis products with respect to trypsin compared to the activity of the initial $C_7$.

The results obtained lead to important conclusions, namely, that parent alkylresorcinols are highly reactive and the transient species formed upon oxidation are even more reactive.

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