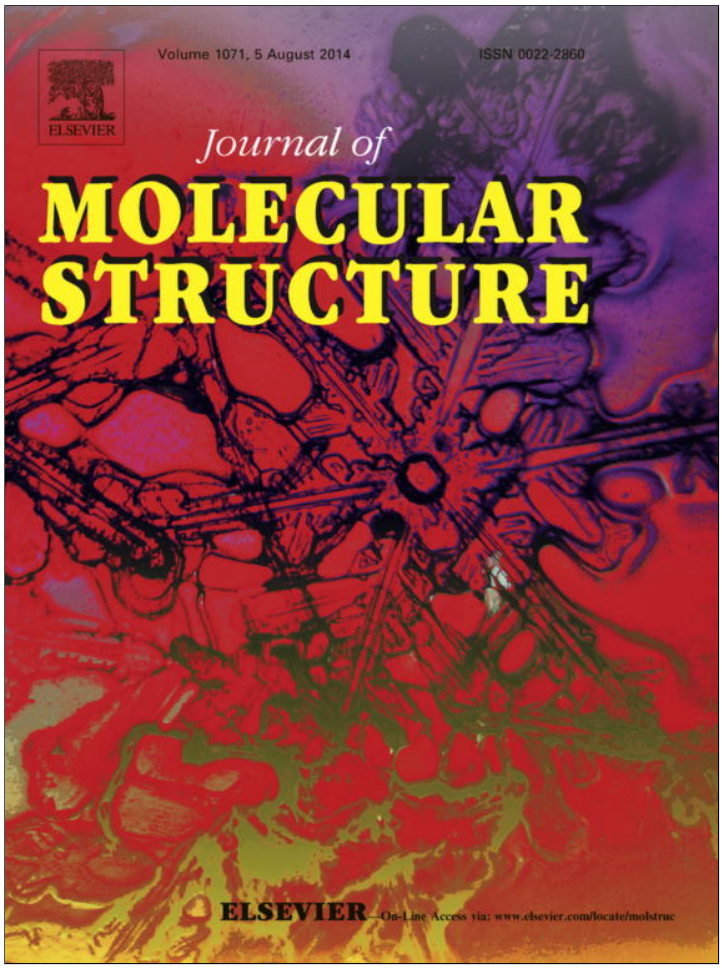

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ESR dosimetry and radical kinetics of gamma-irradiated propyl gallate

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HIGHLIGHTS

- Polycrystalline propyl gallate was γ-irradiated at room temperature and studied using ESR spectroscopy.
- Irradiated PG were present almost a singlet ESR spectra.
- Two different radical species were identified from the ESR spectra and simulation calculation.
- Kinetic features of the radicals were investigated at high and room temperatures, and the activation energies were calculated.

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ABSTRACT

Propyl gallate (PG) is one of the most effective synthetic antioxidant. In the present work, the effects of gamma radiation on powder PG were investigated by Electron Spin Resonance (ESR) spectroscopy. The experimental spectra of irradiated PG were found to be consisted of two different overlapped spectra that originated for different radical species. Structural and kinetic features of the radicals which are responsible for experimental ESR spectrum were explored through the variations of the signal intensity with applied microwave power, variable sample temperature, and high-temperature annealing studies. Activation energies of the radical species were determined using the data derived from annealing studies. The dosimetric potential was also investigated in the range of 0.5–25.0 kGy. It was found that the *G* value of PG is about 0.35.

Introduction

Propyl gallate (PG), or chemically n-propyl ester of 3,4,5-trihydroxybenzoic acid, is an ester of gallic acid, and it is freely soluble in ethanol and slightly soluble in water. PG is widely used as an antioxidant in food (E310), cosmetic, pharmaceutical and lubricants industry to prevent the oxidation of unsaturated fatty acids [1–8]. However, some early researchers emphasize that PG have some toxicological effects [9–16], the Cosmetic Ingredient Review Expert Panel reported that PG is safe to use at concentrations less or equal to 0.1% (6).

Ionizing radiation has been used for sterilization of foods, food additives and pharmaceuticals and established as a safe and effective method [17–19]. Using radiation to sterilize substances generally generates free radicals that have unpaired electron. Electron Spin Resonance (ESR) or Electron Paramagnetic Resonance (EPR) spectroscopy is successfully used in detection of radiation-induced radicals which have unpaired electron [20–35]. Moreover, kinetic features of the radiation-induced radicals and dosimetric potential of the material could be determined using ESR spectroscopy [25–31]. However, effects of ionizing radiation on PG have not been reported in the literature. The radiolytic degradation and oxidation effect of gallic acid in aqueous solution have been studied using different spectroscopic methods in the literature [36–38].

It is important to determine the radiation effect and the radiosensitivity of PG from the effectiveness of point of view in the case of radiation sterilization of materials containing it as additive. Thus, the aim of the present work is to determine radio-sensitivity of PG through a detailed ESR investigation carried out on the kinetic and spectroscopic parameters of the radicals produced upon gamma irradiation PG, and to determine the dosimetric potential of PG in the intermediate dose range (0.5–25 kGy).

Materials and methods

The PG samples (Fig. 1) were provided from Aldrich, and no further purification was performed. All irradiations were performed at room temperature (~290 K) on powder samples open to air using a ^{60}Co gamma source supplying by a dose rate of 0.80 kGy/h as an ionizing radiation source at the Sarayköy Establishment of Turkish Atomic Energy Agency in Ankara. The dose rate at the sample sites

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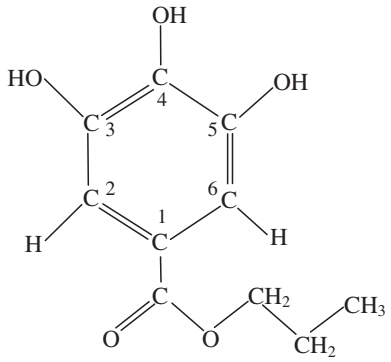

Fig. 1. Molecular structure of propyl gallate.

was measured by a Fricke dosimeter. A set of samples irradiated to doses of 0.5, 1.0, 2.0, 5.0, 7.0, 10.0, 15.0, 20.0, and 25.0 kGy were used to determine the radio-sensitivity of PG and to construct the dose–response curve. Samples irradiated with a dose of 10 kGy were used both to investigate spectral, and kinetic features of the radical species.

ESR measurements were carried out using a Bruker EMX-131 X-band ESR spectrometer equipped with a high sensitive cylindrical cavity. The magnetic field was measured with an NMR teslameter which provided the opportunity of measuring the actual magnetic field at the site of the sample. Thus, the g value could be determined directly from the experimental spectra. This was controlled by taking 2,2-diphenyl-1-picrylhydrazyl (DPPH) spectrum before and after each measurement (g = 2.0036). The operation conditions were used as follow; central field, 351 mT; microwave power, 0.4 mW; microwave frequency, ~9.86 GHz; (central field, 333.5 mT; microwave power, 0.04 mW; microwave frequency, ~9.37 GHz at low temperatures) scan range, 5 mT; modulation amplitude, 0.1 mT; receiver gain, 2.52×10^4; modulation frequency, 100 kHz; sweep time, 83.89 s. A digital temperature control unit (Bruker ER 411-VT) was used to monitor the sample temperature inside the microwave cavity. Cooling, heating and subsequent cooling cycles were adapted to monitor the free radical evaluation in a wide range of temperatures. The temperature of the samples was initially decreased to 130 K, starting from room temperature with a decrement of 20 K, then increased to 400 K, and finally decreased again to room temperature. Kinetic behaviors of the contributing radical species were evaluated through annealing studies at 370, 380, 390 and 400 K. The cavity was heated to a predetermined temperature then the samples were located inside the microwave cavity and kept at this temperature for a predetermined time for thermal equilibrium, and the ESR spectra were recorded at intervals of two minutes without cooling the samples back to room temperature.

Experimental results and discussion

Room temperature studies

While the unirradiated PG do not exhibit any ESR signal, the irradiated samples were found to present almost a singlet ESR spectra (Fig. 2b). Room temperature spectra was measured to spread over a magnetic field range of approximately 2.4 mT with 0.55 mT linewidth and centered at about g = 2.0045. Variations of the signal intensity (denoted as I, Fig. 2b) were investigated at different experimental conditions.

The microwave (MW) power dependence of the experimental ESR line was investigated using a sample irradiated with a dose of 10 kGy. Variations of the assigned line intensity with MW power

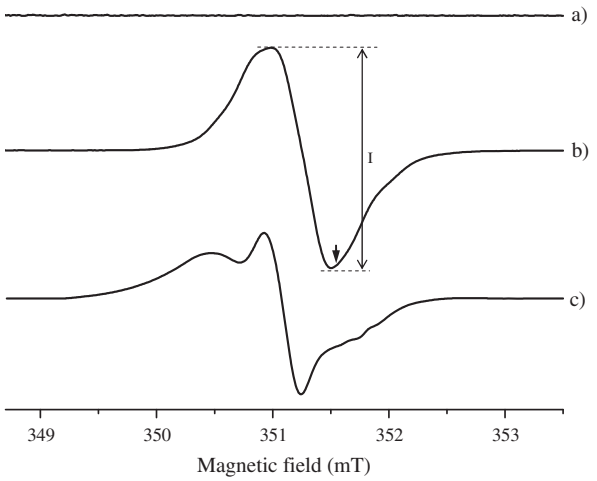

Fig. 2. ESR spectra of gamma irradiated PG at two different spectrometer conditions. (a) Unirradiated, (b) room temperature (MW power of 0.4 mW), and (c) 130 K (MW power of 1.6 mW). (The down-arrow indicate the g value of DPPH (g = 2.0036), and the two headed arrow indicate the signal intensity, I.)

were investigated both at room temperature (290 K) and at 130 K. The MW power was investigated in the ranges of 1.00×10^{-3}–5.05 mW and 1.00×10^{-3}–2.53 mW for room temperature and 130 K, respectively. The measured line exhibited the characteristic behavior of a homogeneously broadened resonance line at room temperature, which the signal intensity increases at low MW powers, and then starts to decrease at high MW powers (Fig. 3). As it is seen from the inset figure of Fig. 3 the same homogeneously broadened behavior is presented at low temperature (130 K), except it started to saturate at lower MW power values. In this figure (inset of Fig. 3) the MW power saturation of room temperature and 130 K are given together to make comparison in the range of 1.00×10^{-3}–1.00 mW. The MW powers of 0.4 mW and 0.04 mW were adapted to avoid the saturation effects at room and below room temperature experiments, respectively.

The pattern of the low temperature spectrum is started to change at MW power values higher than 0.63 mW (Fig. 2c). Almost the same pattern changes were determined at room temperature above 1.60 mW. The MW power saturation values are given in the MW power range of which the spectrum pattern is not changed

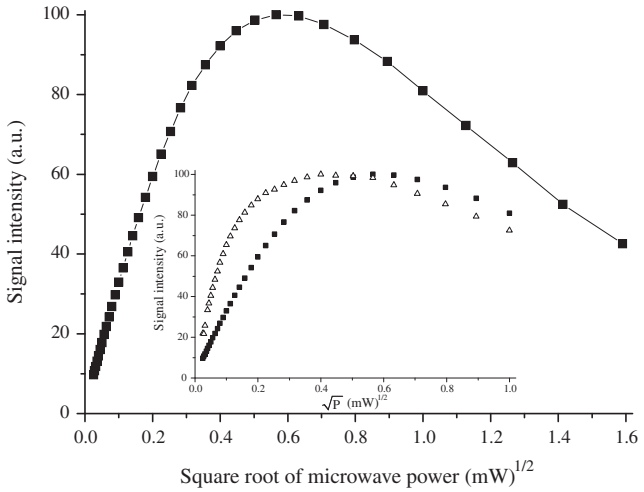

Fig. 3. Room temperature microwave saturation behaviors of the measured signal intensity at a dose of 10 kGy. Inset: the room and low temperature MW saturation behavior in the range of 1.0×10^{-3}–1.0 mW (■ room temperature, and Δ 130 K).

to ignore the dramatic change in the interested signal intensity. This pattern change has provided useful information about the radical formations of the irradiated PG. Namely, the experimental ESR spectra (Fig. 2b) was constituted by overlapping of more than one component that have different spectroscopic features.

The radical stability at room temperature of the sample irradiated to 10 kGy is monitored about 2 months, and the ESR spectra were recorded at regular time intervals. The measured experimental signal intensity variations on storage time are given in Fig. 4. The same decay function that used to describe the annealing study is used to determine the kinetic features at room temperature, and it is found to be a good agreement with the experimental data. Here, the relative weights findings from the simulation calculation are used for the initial ratio of each radical.

High temperature effect on the signal intensity

Changes in the signal intensities with temperature and time can give important information about the stabilities and the number of radical created upon irradiation. Variations of the signal intensity with temperature investigated in the temperature range of 130–400 K using a sample irradiated with a dose of 10 kGy. The unirradiated sample was also controlled for radical formation due to temperature up to 400 K, and no ESR signal was observed. The findings from the MW power saturation carried out at 130 K were adopted and it was set to 0.04 mW to avoid saturation effects. The measurements were taken 60 s after the temperature reached to the desired value. The measured intensities were normalized to the intensity at starting temperature (290 K) to make comparisons. Cooling the sample to 130 K and heating again to room temperature were presented reversible changes and the measured intensity reached to their initial values before cooling. Heating the sample above room temperature produced irreversible decreases in the investigated intensity (Fig. 5). As it is seen from the figure, the decay rate above 370 K is higher than below this temperature. This increase in decay rate was due to the softening in the solid matrix. The softening increases the mobility of the radicals, and as a consequence the radical decay rate was increased.

To get more information about the kinetic properties of the radicals produced after irradiation of PG, annealing studies carried out at high temperatures were performed. In this respect samples irradiated at 10 kGy were annealed at four different temperatures (370, 380, 390 and 400 K) for predetermined times up to 60 min. Experimental decay data obtained for the line intensity were fitted to a function consisting of the sum of two exponentially decaying

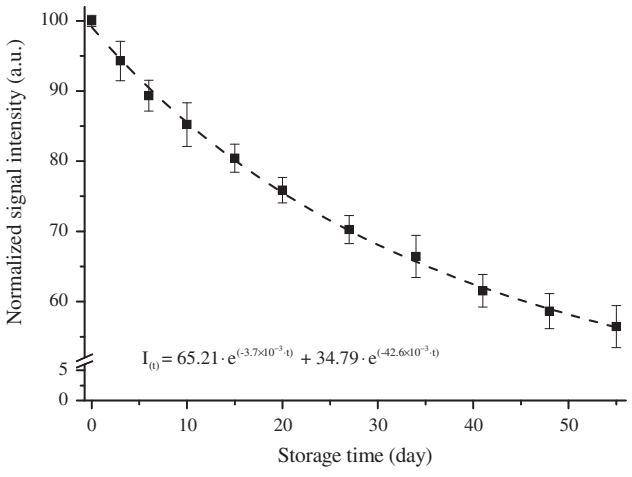

Fig. 4. Stability of the experimental ESR signal intensity at room temperature.

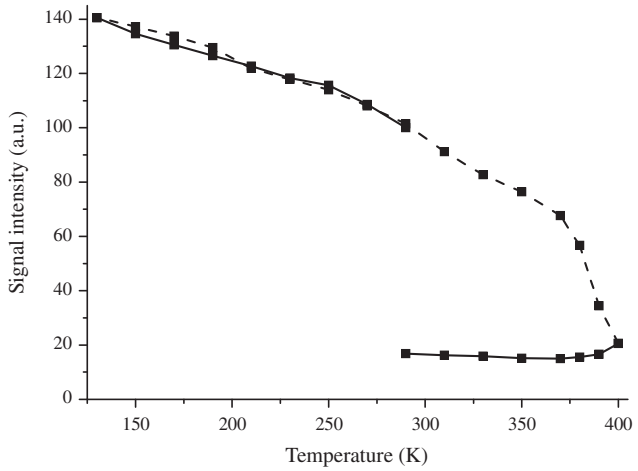

Fig. 5. Variation of the signal intensity with temperature for a sample irradiated at dose of 10 kGy. (Cooling from 290 to 130 K and from 400 to 290 K (dashed lines); heating from 130 to 400 K (solid lines)).

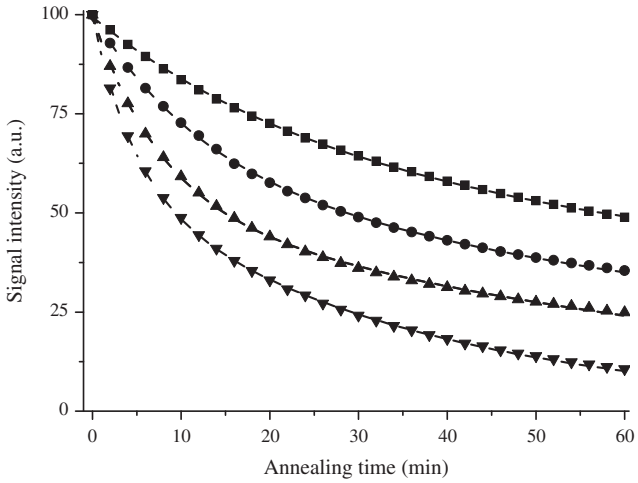

Fig. 6. Variation of the signal intensity for a sample irradiated at dose of 10 kGy with annealing time at different temperatures. Symbols represent experimental data (■ (370 K), ● (380 K), ▲ (390 K), ▼ (400 K)); dashed lines represent the calculated data.

functions ($I = I_{10} \cdot \exp(-k_1 \cdot t) + I_{20} \cdot \exp(-k_2 \cdot t)$) assuming that the radical species undergo first order kinetics (Fig. 6), and the decay constants of each radical (k_1 and k_2) were calculated at four different temperatures. The relative weights findings from the simulation calculation were used for the initial radical concentrations I_{10} and I_{20}. Activation energies of the involved species were also calculated from $ln(k)$–$\frac{1}{T}$ graphs and 79.08 kJ/mol and 71.03 kJ/mol were obtained for PG1 and PG2, respectively (Table 1).

Simulation calculation of experimental room spectrum

According to the MW power findings at high MW power values, and literature [36–38]; spectrum simulation calculations based on a model predicting the presence of two radical species with different spectroscopic features were tried to determine the experimental spectroscopic parameters of the gamma irradiated PG. Signal intensity data derived from the room temperature ESR spectrum of a sample irradiated with a dose of 10 kGy were used. The results of the simulation calculations are presented in Table 2. The theoretical spectrum of each species and their sum are given in Fig. 7 with their experimental counterpart for comparison. The similar

Table 1
Decay constants and activation energies calculated for responsible radical species at four different annealing temperatures.

Species	Decay constants ($\times 10^{-3}$) (min^{-1})				Activation energy (kJ/mol)
	370 K	380 K	390 K	400 K	
PG1	38.76	77.83	131.52	216.43	69.98 ± 5.41
PG2	4.40	8.79	13.06	29.28	74.67 ± 5.41

Table 2
Spectroscopic parameters calculated for contributing radical species.

Radical	Relative weight	Spectroscopic parameters
$\dot{O}(OH)_2C_6H_2COO(CH_2)_2CH_3$ (PG1)	35.0 (± 2.7)	ΔH_{pp} = 0.46 (±0.03) mT g_{iso} = 2.0044 (±0.0003)
$O(OH)_2\dot{C}_6H_2COO(CH_2)_2CH_3$ (PG2)	65.0 (± 2.3)	ΔH_{pp} = 0.63 (±0.06) mT g_{iso} = 2.0046 (±0.0002) A_{iso} = 0.50 (±0.07) mT

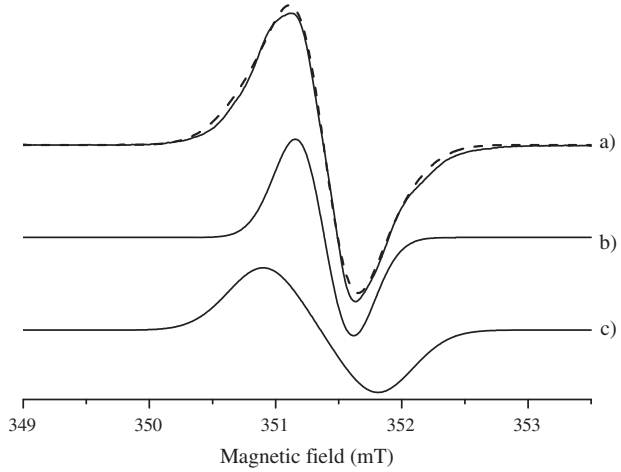

Fig. 7. (a) Experimental (black line) and simulated (dashed line) ESR spectra calculated using parameter values given in Table 2. (b) Spectra of radical PG1, and (c) spectra of radical PG2.

radicals proposed in the literature [36–38] were adopted to describe the experimental spectra of PG. The first radical denoted as PG1 is supposed to be produced by the loss of the hydroxyl H atom. The ESR spectrum of PG1 expected to be a singlet, and does not show any hyperfine splitting. The unpaired electron of the other radical (PG2) interacts with one proton and is present a doublet ESR spectra. Although the radical chemistry in aqueous solutions has expected to be different for solid state, the agreement between the experimental and model spectra have confirmed the correctness of the proposed radical (Fig. 7).

Dosimetric features of PG

The dosimetric features of PG were investigated in the range of 0.5–25.0 kGy using ESR spectroscopy. ESR is commonly used for dose measurement, and is successfully used in the discrimination of irradiated samples from unirradiated ones. Samples irradiated at dose range of 0.5–25.0 kGy were used to construct dose–response curves. The measured signal intensities, which normalized to mass of samples and spectrometer gain, were divided to the highest intensity at 25.0 kGy to make comparisons. It was concluded that the sum of two exponential function of applied dose, that has the type of $I_{(D)} = a_1 \cdot (1 - e^{-D/b_1}) + a_2 \cdot (1 - e^{-D/b_2})$ describes best experimental data (Fig. 8), where I and D stand for

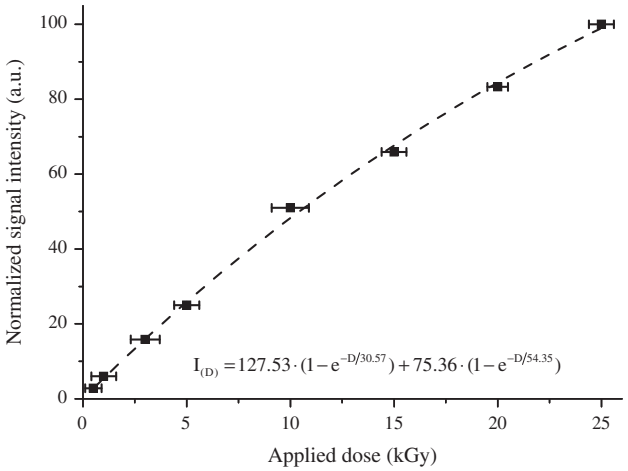

Fig. 8. Variation of the normalized signal intensity (I) with applied radiation dose. Dashed line: calculated using the exponential function (see Table 2).

the intensity and applied dose in kGy, respectively, and the constants in the equation are the parameters to determine.

Alanine was used as a reference standard to determine the radiation yield (G) of the interested material, which is described as number of radicals formed per 100 eV. Ikeya [39] was accepted $G = 1$ for alanine. The ESR spectrums of irradiated alanine and PG at 10 kGy are recorded in the same spectrometer condition (given in section 'Materials and methods'), and the spectrum area of the absorption curves, which found by double integration of the recorded experimental ESR spectra [40], are calculated and normalized to the mass and to the spectrometer gain. It is found that the G value of PG is about ~0.35.

Conclusion

Gamma irradiated PG exhibits an ESR spectrum originated for two different radicals, that their ESR spectra are overlapped and looks like as a singlet (Fig. 2b). These two spectra were separately distinguished at high MW power values at 130 K. Thus, a model based on the presence of two radical species denoted as PG1 and PG2 of different spectroscopic and kinetic features was found to describe well the experimental ESR spectra of the irradiation of PG. The radical PG1 supposed to be a singlet, and the unpaired electron located on the O atom bonded to the C3 or C5. The other radical (PG2) show a doublet due to the interaction of the unpaired electron with one proton (H) and has the form as shown in Table 2.

The decay of the assigned line is relatively fast above 370 K. While, the pattern of experimental ESR spectra at the end of the annealing at 400 K is not changed, it is concluded that the activation energies of each radical should not be very different, and the 69.98 and 74.67 kJ/mol values are found. The radicals are decayed even at room temperature and after two months of storage almost 45 percent of the radicals were decayed.

Instability of the radicals produced upon irradiation PG at the room and at high temperature, non-linear dose–response behavior, and low G value (~0.35) makes PG is not suitable to be a good dosi-

metric material. It is concluded that, due to low radiosensitivity there are no disadvantages in using PG as an antioxidant in radio-sterilized food, cosmetics, pharmaceutical drugs, etc.

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References

[1] J.W. Daniel, Xenobiotica 16 (1986) 1073.
[2] A. Gaathon, Z. Gross, M. Rozhanski, Enzyme. Microb. Tech. 11 (1989) 604.
[3] S. Gunckel, P. Santander, G. Cordano, J. Ferreira, S. Munoz, L.J. Nunez-Vergara, J.A. Squella, Chem. Biol. Interact. 114 (1998) 45.
[4] T.A. Hadi, R. Banerjee, B.C. Bhattacharya, Bioprocess Eng. 11 (1994) 239.
[5] S. Raghavan, H.O. Hultin, J. Agric. Food Chem. 53 (2005) 4572.
[6] L. Becker, Int. J. Toxicol. 26 (2007) 89.
[7] V. Kristinova, R. Mozuraityte, I. Storrø, T. Rustad, J. Agric. Food Chem. 57 (2009) 10377.
[8] S. Eymard, C. Jacobsen, C.P. Baron, J. Agric. Food Chem. 58 (2010) 6182.
[9] M.P. Rosin, H.F. Stich, J. Environ. Pathol. Toxicol. 4 (1980) 159.
[10] NTP, Carcinogenesis bioassay for propyl gallate in F344 rats and B63CF1 mice, National Toxicology Program (NTP-81–42), Maryland, NIH Publication No. 83–1796, 1982.
[11] C.A. Van der Heijden, P.J. Janssen, J.J. Strip, Food Chem. Toxicol. 24 (1986) 1067.
[12] M. Hirose, H. Yada, K. Hako, S. Takahashi, N. Ito, Carcinogenesis 14 (1993) 2359.
[13] JEFCA, Toxicological evaluation of certain food additives and contaminants in food, Joint FAO/WHO Expert Committee on Food Additives, Geneva, WHO Food Additives Series, No. 35, 1996, pp. 3–86.
[14] Y. Nakagawa, P. Moldéus, G.A. Moore, Toxicology 114 (1996) 135.
[15] S. Tayama, Y. Nakagawa, Mutat Res. Genet. Toxicol. Environ. Mutagen. 498 (2001) 117.
[16] H. Kobayashi, S. Oikawa, K. Hirakawa, S. Kawanishi, Mutat. Res. 558 (2004) 111.
[17] IAEA, Food Preservation by Irradiation, vols. I and II, Vienna, Austria, International Atomic Energy Agency, 1978.
[18] K.W. Bögl, Appl. Radiat. Isot. 40 (1989) 1203.
[19] G.P. Jacobs, J. Biomed. Appl. 10 (1995) 59.
[20] N.J.F. Dood, A.J. Swallow, F.J. Lea, Radiat. Phys. Chem. 26 (1985) 451.
[21] N.J.F. Dodd, J.S. Lea, A.J. Swallow, Nature 334 (1988) 387.
[22] M.F. Desrosiers, Appl. Radiat. Isot. 42 (1991) 617.
[23] M.F. Desrosiers, G.L. Wilson, C.R. Hunter, D.R. Hutton, Appl. Radiat. Isot. 42 (1991) 613.
[24] J. Raffi, M.H. Stevenson, M. Kent, J.M. Thiery, J.J. Belliardo, Int. J. Food Sci. Tech. 27 (1992) 111.
[25] H. Tuner, M. Korkmaz, Nucl. Instrum. Meth. Phys. Res. B 258 (2007) 388.
[26] H. Tuner, M. Korkmaz, Radiat. Res. 172 (2009) 120.
[27] H. Tuner, Radiat. Phys. Chem. 80 (2011) 731.
[28] H. Tuner, M.A. Kayikci, Radiat. Environ. Biophys. 51 (2012) 61.
[29] H. Tuner, Radiat. Eff. Defect. S. 168 (2013) 61–71.
[30] S.T. Cam, C. Aydas, B. Engin, U.R. Yüce, T. Aydın, M. Polat, Radiat. Eff. Defect. S. 167 (2012) 410.
[31] G. Korkmaz, M. Polat, M. Korkmaz, Radiat. Eff. Defect. S. 165 (2010) 252.
[32] U. Sayin, Ö. Dereli, E. Türkkan, J. Mol. Struct. 1007 (2012) 179.
[33] M. Walo, G. Przybytniak, J. Sadło, J. Mol. Struct. 1036 (2013) 488.
[34] Y. Ceylan, A. Usta, K. Usta, F. Durmaz, A. Coşkun, J. Mol. Struct. 1050 (2013) 69.
[35] A.M. Abdelghany, H.A. ElBatal, J. Mol. Struct. 1067 (2014) 138.
[36] A.C. Eslami, W. Pasanphan, B.A. Wagner, G.R. Buettner, Chem. Cent. J. 4 (2010) 15.
[37] R.P. Melo, J.P. Leal, M.L. Botelho, Rapid Commun. Mass Sp. 25 (2011) 218.
[38] R. Melo, J.P. Leal, E. Takács, L. Wojnárovits, J. Hazard. Mater. 172 (2009) 1185.
[39] M. Ikeya, New Applications of ESR Dating, Dosimetry and Microscopy, Word Scientific Publishing Co. Pte. Ltd., 1993 (Chapter 13).
[40] D. Barr, J.J. Jiang, R. Weber, Performing Double Integrations using WIN-EPR, Bruker biospin report 6, 1998.