Heavy-ion-induced sucrose radicals investigated using EPR and UV spectroscopy

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ABSTRACT

The potential use of a sucrose dosimeter for estimating both linear energy transfer (LET) and the absorbed dose of heavy ion and X-ray radiation was investigated. The stable free radicals were produced when sucrose was irradiated with heavy ions, such as helium, carbon, silicon and neon ions, and when the X-ray radiation was similar to the obtained electron paramagnetic resonance (EPR) spectra, which were ∼7 mT wide and composed of several hyperfine structures. In addition, the total spin concentration resulting from heavy-ion irradiation increased linearly as the absorbed dose increased, and decreased logarithmically as the LET increased. These empirical relations imply that the LET at a certain dose can be determined from the spin concentration. For sucrose and alanine, both cross-sections following C-ion irradiation with a 50 Gy dose were ∼1.3×10^{-12} [μm^2], taking into account the molecular size of the samples. The values of these cross-sections imply that multiple ionizing particles were involved in the production of stable radicals. Furthermore, UV absorbance at 267 nm of an aqueous solution of irradiated sucrose was found to linearly increase with increasing absorbed dose. Therefore, the EPR and UV results suggest that sucrose can be a useful dosimeter for heavy-ion irradiation.

KEYWORDS: EPR, UV spectrometry, sucrose, radical, heavy ion, irradiation, X-ray, alanine, cross-section, sugar

INTRODUCTION

Radiological techniques can be useful for advancing human life. In addition, knowledge of radiation–material interactions is essential for advancing basic science. Understanding the effects of radiation on various materials is very important for determining the durability of materials exposed to radiation and for providing information regarding decomposition due to radiation–material interactions. In particular, the effects caused by heavy-ion particles are of special interest. These particles exert considerably larger impulses on the orbital electrons of molecules in a target material, causing excitations and ionizations. The impulses lead to the production of secondary electrons, which can induce free radical formation. The free radicals thus formed exhibit a profound dependence on the particle type and energy. Therefore, radical production can be useful as an indicator of heavy ion exposure [1–7].

Different types of ionizing radiation have different track structures when passing through matter based on their linear energy transfer (LET) [3]. The track structure produced by positively charged particles also differs from that of electrons because the scattering of electrons is quite large. More specifically, the track structure strongly depends on the particle velocity and charge. Typically, the absorbed dose is very high within the small volume surrounding the traversing particle axis, which is referred to as the 'core' [8]. Moreover, because secondary electrons cause radical production in the target sites, the core appears to be related to free radical production. These radicals (produced as a result of particle–matter interactions) can be detected using EPR spectroscopy.

Differential ferric ion yields for a range of ionizing particles were measured by LaVerne *et al.* [3], who found that the yield for the oxidation of ferrous ions by heavy ions is not only dependent on the LET but also on the charge of the ionizing particle. This chemical dosimeter requires the use of a ferrous ion solution and a special irradiation cell. On the other hand, sucrose can be used without the need for any special chemical preparation.

Sucrose is a household sugar that has been known to form stable radicals upon irradiation at ambient temperature [1, 6]. Irradiated sucrose has been studied using various EPR techniques to determine

the radical sites [4, 5]. Recently, EPR spectroscopic analysis of sucrose exposed to very high radiation doses has been reported (0.01–4 kGy) [9, 10]. However, even though sucrose may be an ideal material for monitoring heavy-ion irradiation, there have been few reports on low-dose irradiation of sucrose at ambient temperature.

During the past decade, sucrose has been revealed to be a very promising material for dosimetric purposes using electronic spectroscopy (ES) combined with lyoluminescence, in which the light emitted upon the recombination of sucrose radicals during dissolution is recorded [9, 11, 12]. High-energy irradiation generates free radicals in organic matter, some of which are trapped in the solid matrix, while others combine to produce new species with different properties, such as color changes. These effects are used for dosimetric purposes in EPR dosimetry [13, 14] and ES, with several of the latter dosimetric systems having been approved [15]. Color changes are also used for the direct measurement of light absorption by irradiated sugar crystals [16–19].

Although stable sucrose radicals are well known, reports on radicals produced using heavy-ion irradiation are limited [4]. The details of sucrose radicals produced through interaction with heavy ions, as well as the effects of various particles and LET on radical production, were investigated. The EPR results were then confirmed by UV spectroscopy [10].

MATERIALS AND METHODS
Samples
Sucrose and L-alanine (hereafter, alanine) were purchased from Nacalai Tesque Inc., Japan. Glucose and fructose were obtained from Tokyo Chemical Industry Co. Ltd., Japan. Spin label 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) was obtained from Aldrich, USA. All the chemicals were of the highest grade and were used as received without further purifications. Polycrystalline sucrose (0.50 g) or alanine (0.50 g) was placed on an acrylic plate (4×4 cm^2) that was subsequently wrapped with plastic wrap. The wrapped samples were then mounted on the sample holder.

Irradiation
Irradiation using heavy-ion beams was performed in a biology experiment room at the Heavy Ion Medical Accelerator in Chiba (HIMAC) at the National Institute of Radiological Sciences (NIRS). The biology room was equipped with an irradiation system similar to that found in a treatment room, including dose monitors, a binary filter, and a wobbler system [20]. A target in the atmosphere was placed at a distance of 50 cm from a thin aluminum window that sealed the vacuum in the beam ducts. The wobbler system had a 10 cm diameter uniform field with a uniformity of 2% or less. Beam intensity was measured using dose monitors installed in the beam course. A binary filter composed of poly(methyl methacrylate) plates, with thicknesses ranging from 0.5 to 128 mm, was used to adjust the LET [20]. The radiation dose was maintained at 50 Gy at the sample, unless otherwise noted. A schematic illustration of the experimental setup for sample irradiation is presented in Fig. 1.

In addition to heavy-ion irradiation, X-rays (200 kV, 20 mA) were used. The dose rate was 1.23 Gy/min, and 0.5 mm copper and 0.5 mm aluminum were used to filter the low-energy radiation
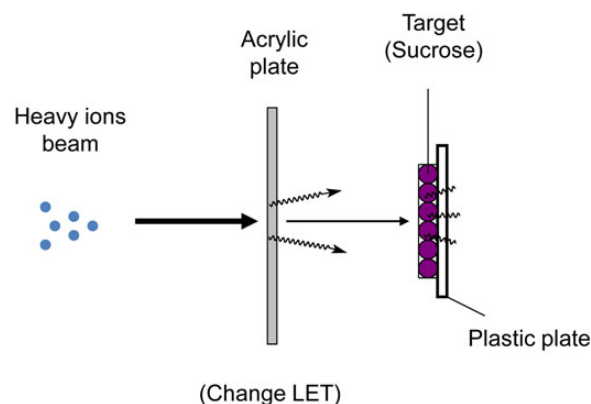

Fig. 1. Schematic illustration of the experimental setup for sample irradiation. The acrylic plate was used to adjust the LET.

[21–23]. All the irradiated samples were maintained at ambient temperature for a few days prior to EPR measurements.

EPR measurements
The various radicals generated following irradiation were measured using a JEOL RE 3X X-band EPR spectrometer. The resonance frequency was measured using an X-band microwave frequency counter EMC-14 (Echo Electronics Co. Ltd, Japan). The optimum EPR conditions were as follows: sweep width, 10 mT; time constant, 0.1 s; modulation, 0.03 mT; receiver gain, 1000; microwave power, 5 mW. Each spectrum was composed of a single scan.

Spin concentrations were estimated using a calibration curve for known concentrations of TEMPO in benzene [21]. All the irradiation processes and analytical measurements were performed at ambient temperature.

UV measurements
UV spectra of the aqueous solutions of irradiated solid samples were recorded on a Specord UV/Vis spectrophotometer (Carl Zeiss, Jena) at ambient temperature. Quartz cells with path lengths of 1 or 5 cm were used, depending on the absorbed dose and the concentration of the aqueous solutions. Irradiated and non-irradiated crystalline sucrose were dissolved in distilled water to prepare aqueous solutions with a concentration of 5%. The UV spectrum of non-irradiated sucrose in aqueous solution was obtained as a reference.

RESULTS
X-ray and particle irradiation
The EPR spectra of sucrose radicals induced by particle and X-ray irradiation were examined. Figure 2 shows the EPR spectra of sucrose radicals produced following C-ion (LET values of 13.1 and 78.3 keV/μm) and X-ray irradiation (dose of 50 Gy). The EPR spectral patterns were the same for both C-ion and X-ray irradiation, except for the intensity. Similar EPR results were obtained following Si-ion irradiation. The consistent spectral pattern suggested that the stable radical species generated following exposure to the various types of radiation were very similar. Moreover, these preliminary experimental results suggested that a 1 Gy dose provided recognizable signal intensities.
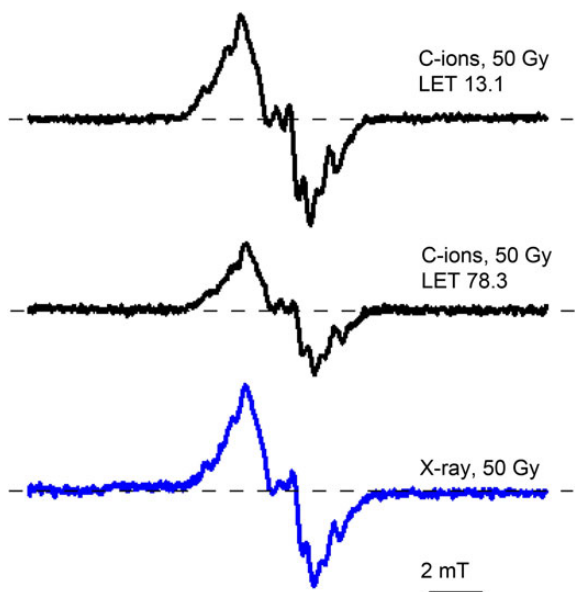
Fig. 2. EPR spectra of sucrose radicals produced because of C-ion and X-ray irradiation. The EPR conditions were the same. Sucrose (0.50 g) was irradiated with C ions with LET values of 13.1 and 78.3 keV/μm. The dose was 50 Gy for each.

Fig. 3. EPR response of sucrose irradiated with various heavy ions as a function of the absorbed dose.

Fig. 4. EPR spectra of sucrose and alanine radicals produced due to C-ion (290 MeV/u) irradiation at a LET of 67 keV/μm. The dose was 50 Gy for each.

Low dose X-ray irradiation of sucrose has also recently been reported [22].

The possibility that stable radicals were produced by secondary background radiation induced by heavy-ion irradiation, and not by the heavy-ion particles themselves, was also considered. Thus, a second sample of sucrose was placed near the irradiated target area. This sample showed no signals corresponding to the radicals observed following radiation with a 50 Gy dose. Therefore, the secondary radiation was concluded to be negligible under the conditions used in this study.

Figure 3 presents the EPR response as a function of dose for the different types of radiation. Notably, He ions produced more radicals than C ions, particularly at higher doses, while the EPR responses to Ne ions were slightly different to those of C ions.

Typical EPR spectra obtained under identical conditions for sucrose and alanine irradiation with C ions with a LET of 67 keV/μm and a dose of 50 Gy are shown in Fig. 4. As the same EPR conditions were used, comparing the EPR signal intensities for sucrose and alanine was possible. As can be seen in Fig. 4, the EPR spectral patterns are the same as those previously reported [24]. The signal intensity of the EPR spectrum for the irradiated alanine was greater than that for the irradiated sucrose as the molecular weights of sucrose and alanine are 342 and 89, respectively; thus, the number of alanine molecules per unit volume is 3.8 times greater than that of sucrose. When this difference was taken into consideration, the EPR intensities per molecule were similar for both the irradiated sucrose and alanine.

In addition, the EPR signal areas for both sucrose and alanine exhibited a linear relation to the absorbed dose [21]. As was observed with the signal intensity, the slope of the line for alanine was ~3.3
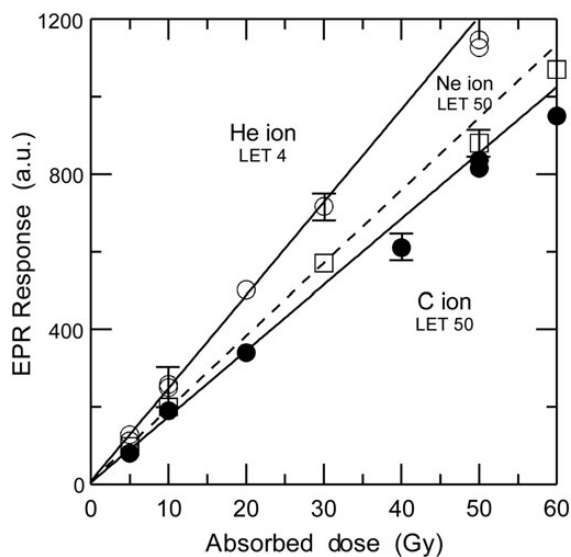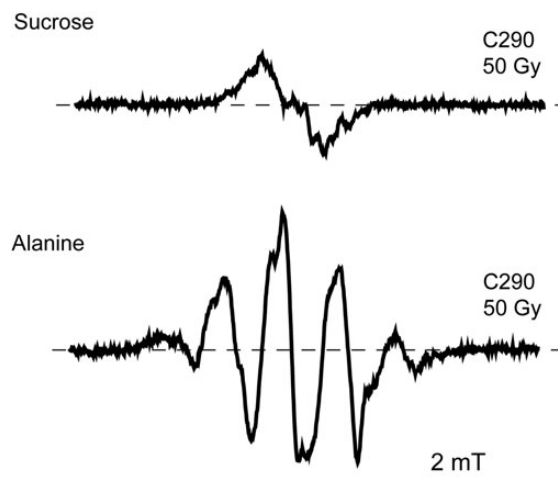
times greater than that of sucrose due to the difference in their molecular weights. The linear correlation between the EPR area and the dose implies that sucrose is a good candidate for use as an EPR dosimeter.

Figure 5 presents a plot of the number of unpaired spins (spin-yield) generated due to heavy-ion irradiation as a function of the LET. Both the samples were found to exhibit LET dependence as well as particle dependence [8, 9, 20]. For each heavy ion, the number of unpaired spins in the irradiated samples decreased with an increase in the LET for each heavy ion (LET dependence). In addition, the generation of sucrose radicals appeared to be more sensitive to particle species than that of alanine radicals.
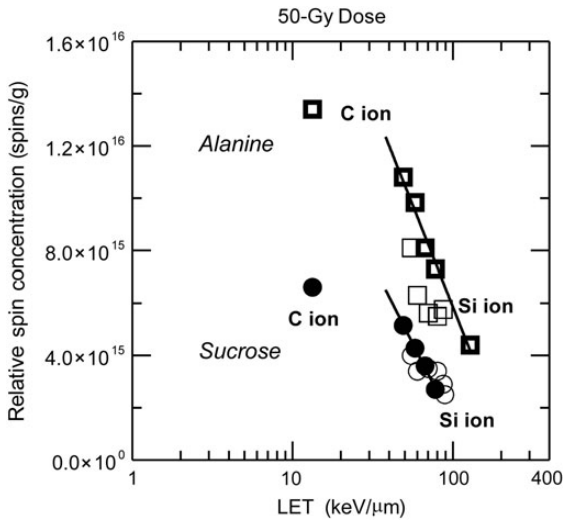
Fig. 5. Plot of the relative spin concentrations of sucrose and alanine after C-ion and Si-ion irradiation as a function of the LET. Each datapoint corresponds to a dose of 50 Gy. The straight lines are the datapoints for C-ion irradiation, except for when the LET = 13.1 keV/μm.
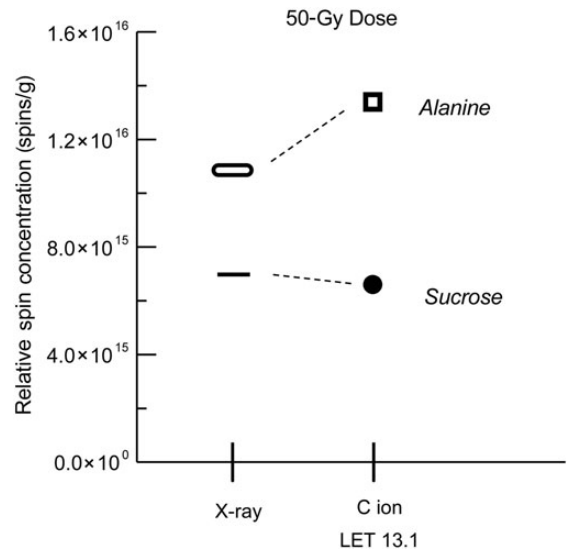

Fig. 6. Comparison of the relative spin concentrations (sucrose and alanine radicals) produced using X-rays and C-ions at a LET of 13.1 keV/μm. The dose was 50 Gy for each.

Furthermore, Si-ion irradiation resulted in the production of stable radicals similar to those generated following irradiation with C ions at the same LET and dose. This result is consistent with a previous observation [20]. The relationship between the EPR area and the dose implies that sucrose is a good candidate for use as an EPR dosimeter.

Then, alanine and sucrose samples (0.50 g) were irradiated with C ions with a LET value of 13.1 keV/μm, and X-rays at a dose of 50 Gy. The radicals produced in both the molecules are plotted (dotted lines) in Fig. 6. Notably, X-ray and heavy-ion radiation are different in terms of material and radiation interactions, and X-ray radiation is considered low-LET (1–2 keV/μm). Despite this difference, the sucrose radicals obtained following X-ray irradiation were similar to those following C-ion irradiation at a LET value of 13.1 keV/μm, while those for alanine were smaller.

UV study of aqueous solutions of sucrose previously irradiated with high doses of gamma and heavy-ion radiation

Typical UV spectra of aqueous solutions of solid sucrose previously irradiated with varying doses of heavy particles exhibited an absorption band at 267 nm (Fig. 7). The intensity of the absorption band increased linearly with an increase in the absorbed dose of high-energy radiation. In addition, although UV absorption increased for all the solutions with increase in storage period, the linear dependence of UV absorption on the radiation dose remained unchanged for each set of measurements [18, 19]. Unlike UV absorption spectroscopy, EPR analysis is a non-calibrated method. Thus, UV data may be used to confirm EPR results. Therefore, Fig. 8 presents the relationship between the EPR and UV responses for sucrose irradiated with heavy ions.
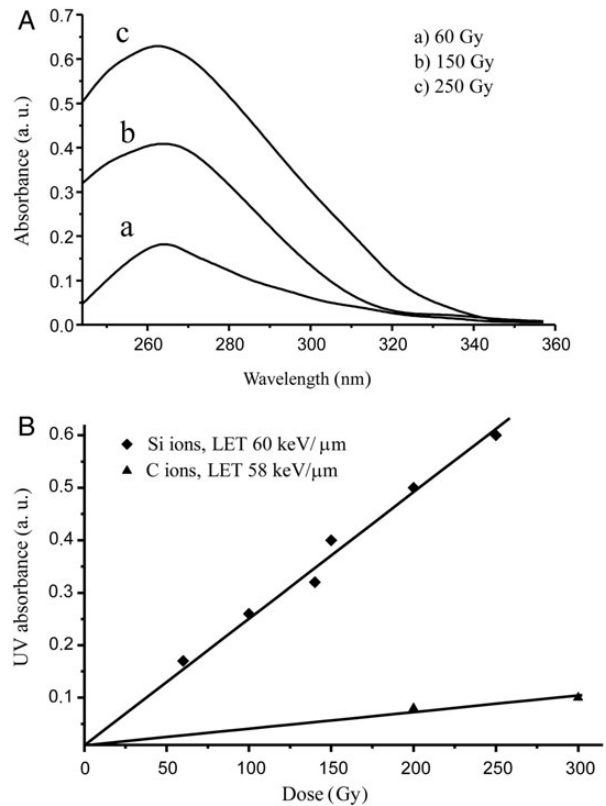

Fig. 7. (A) UV spectra of 5% aqueous solutions of sucrose samples irradiated with different doses of Si ions. (B) Dependence of the UV absorbance of an aqueous solution of irradiated solid sucrose as a function of the applied dose of high-energy radiation.
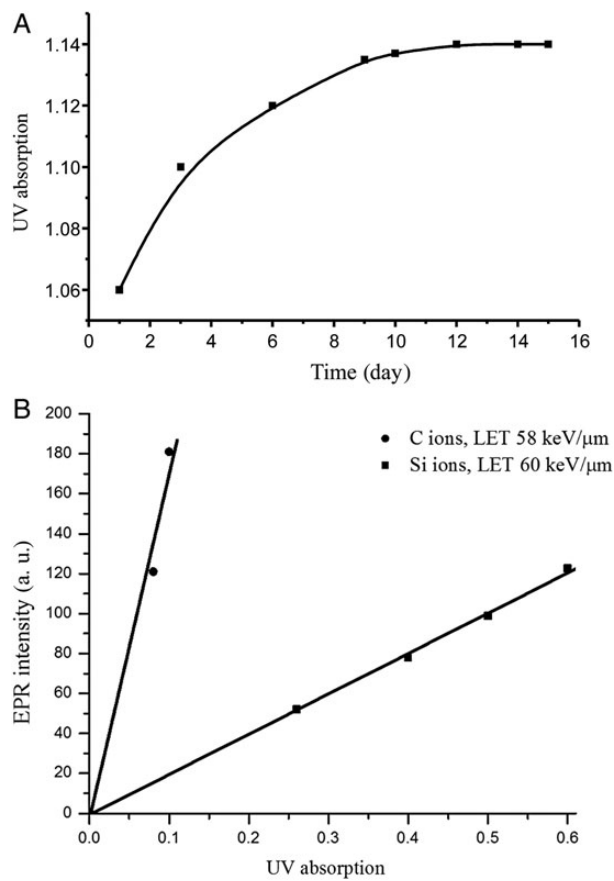
Fig. 8. (A) Time dependence of the UV absorption of an aqueous solution of γ-irradiated sucrose. (B) Correlation between the EPR responses and UV absorptions for sucrose irradiated with C and Si ions.

DISCUSSION

The radicals produced after the irradiation of sucrose with various heavy ions and X-rays were stable at ambient temperature. In addition, identical spectra were obtained for various irradiated samples stored in capped EPR tubes for one year; however, the intensities were slightly decreased. Furthermore, an identical EPR pattern was obtained for all the doses of X-ray and heavy-ion radiation. These results indicate that the stable radical species generated following the irradiation of sucrose can be used in an EPR dosimeter.

Ionizing radiation generally causes an impulsive perturbation of the orbital electrons of sucrose molecules, leading to their ejection from the molecules. The rate of energy loss per unit path length of charged particles in a medium, also known as stopping power (*S*, which is nearly equal to the LET), is roughly given as

$$S(\approx LET) \equiv -\frac{dE}{dx} \propto \frac{z^2}{v^2} \propto \frac{z^2}{E}, \tag{1}$$

where *z*, *v* and *E* are the charge, velocity and energy of the incident particle, respectively. The radical products formed (mainly through

secondary processes) are expected to exhibit a dependence on both *z* and *E*.

Notably, the measurement of the LET was achieved using certain beam ranges that were expected to simultaneously change the values with the beam energies. In other words, the trends in the LET results were accurate, even if the LET values were slightly different from the absolute values. The influence of fragmentation due to the binary filter on the estimated LET values was 10% or less, and the relative uncertainty in the LETs was ~10%. Hence, the LET values for the primary beams directly reflected the production of stable radicals. However, no spectral differences were observed with or without the filter.

The spin concentration decreased logarithmically as the LET increased (Fig. 5) [24], and the following empirical relationship was obtained:

$$Y = -A \ln(LET) + B, \tag{2}$$

where Y is the relative yield [spins/g], A is the slope, and B is the *y*-intercept. The slopes for the heavy ions were similar for sucrose and alanine: -5.2×10^{15} and -6.7×10^{15} spins/g, respectively. In addition, both the C and Si ions produced a similar number of radicals at the same LET. Thus, sucrose responded well to heavy-ion irradiation at various LETs in terms of the steady-state radical concentration. Therefore, the total number of unpaired spins in sucrose can be used to describe the LET for heavy-ion irradiation at a certain dose. This result is the first clear example of the effect of heavy-ion irradiation on a solid organic sample.

Although only a slight difference was observed in the radical production following C- and Si-ion irradiations, a significant difference in the spin concentration at a LET of 13.1 keV/μm was observed compared with those obtained at higher LETs. In general, the number of radicals along the particle tracks was very high, and the energy loss of the passing particles was greater at higher LETs (leading to complex processes, including radical formation and recombination, that reduce the number of stable radicals).

A slight difference in the sucrose radicals was observed following irradiation with X-rays and C ions, as shown in Fig. 6. This result suggests that radical recombination led to the formation of stable radicals. However, interaction of the particles with sucrose may have been more complex at higher LET values. On the other hand, alanine radicals may be less reactive than sucrose radicals.

Irradiation-induced radical sites

The EPR spectra of the irradiated sucrose samples were relatively broad (~7 mT wide), with asymmetry at the center. The asymmetric pattern suggests the presence of several different radical sites. To identify specific radical sites in the irradiated sucrose, X-ray irradiated glucose and fructose were analyzed. The chemical structures of sucrose, glucose and fructose are depicted in Fig. 9. Although the responses of glucose and fructose to irradiation cannot fully explain the chemical nature of sucrose, the behavior of both the compounds should provide information regarding the hyperfine structures obtained.

The addition spectrum for irradiated glucose and fructose is presented in Fig. 9A. The spectra for both irradiated glucose and fructose exhibited complex patterns, as presented in Fig. 9B, differing only in intensity in the central region. The conformational differences with
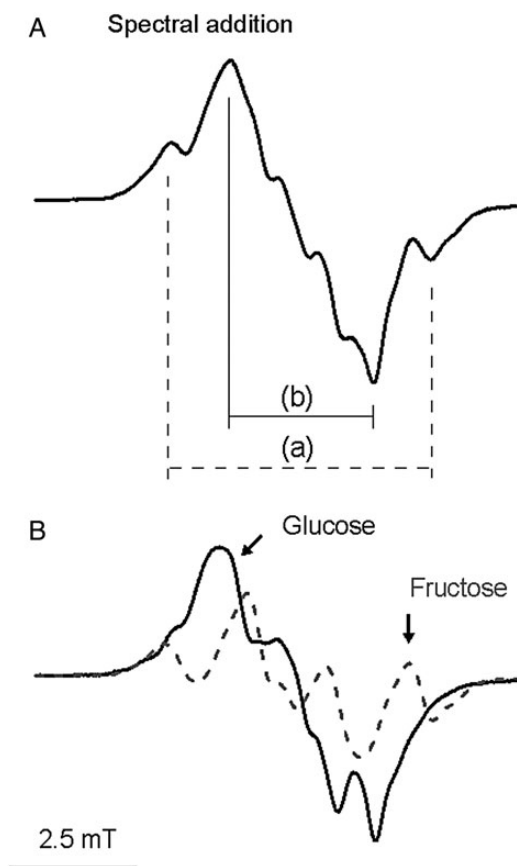
A   Spectral addition

B

Glucose

Fructose

2.5 mT

Fig. 9. (A) Spectrum resulting by the addition of γ-irradiated glucose and fructose. (B) Spectra measured for irradiated glucose (solid line) and fructose (dotted line).

respect to the plane of the C–C and C–H bonds are possibly affected by the hyperfine coupling. Of particular interest, the reproduction of the EPR spectra suggested that the sucrose radicals were composed of glucose and fructose radical sites. Given the complex, asymmetric spectra, each component potentially contained multiple radicals. Furthermore, the applied magnetic field in the central position for the addition spectrum did not match that for the sucrose spectrum in Fig. 9A because glucose and fructose have different particle sizes, and the different solid sizes caused a shift in the microwave frequency.

It is important to note that the EPR spectral patterns were very similar for the different radiation sources, LETs and samples. These results suggest that CH(OH)—CH—CH(OH) is a possible radical site. The α–hydrogen splits into a doublet, and two β–hydrogens further split into a 1:2:1 triplet. These hydrogens normally exhibit large hyperfine couplings in irradiated organic solids [6]. Two C-centered radicals were also suggested based on the results of the single crystal studies of irradiated sucrose [6, 8]. The broad peaks can be attributed to multiple radicals and the various orientations of the sites.

Radical-production cross-section

The stable radical-production cross-section (σ) was then investigated to gain insight into the particle–material interactions. Generally,

the yield (Y) due to ionizing particle irradiation can be empirically obtained using the radical-production cross-section. Thus, the radical production per particle was calculated using the radical-production cross-section:

$$Y = [1 - \exp(-\sigma Nt)] \bullet \Phi, \tag{3}$$

where Y is the yield due to the ionizing particle interaction, σ is the radical-production cross-section, N is the number of molecules per unit volume, t is the sample thickness, and Φ is the number of trajectories [21].

If the exponential in Eq. (3) is replaced with power series expansions, the cross-section can be simplified as

$$P = \sigma Nt, \tag{4}$$

where P is the number of radicals produced by a single traversing particle, σ is the radical-production cross-section, N is the number of molecules per unit volume, and t is the sample thickness. The obtained σ-values for sucrose and alanine using this equation were $\sim 1.3 \times 10^{-12}$ and $\sim 6.8 \times 10^{-13}$ μm^2, respectively. The cross-sectional area of sucrose was approximately three times larger than that of alanine. However, if the difference in the sizes of the molecules is taken into account, sensitivity with respect to the production of radicals was approximately the same for these two compounds. Moreover, both the σ values were less than the corresponding molecular areas (in the order of 10^{-19} m^2) by an order of magnitude, suggesting that stable radicals were produced via the ionization of a single molecule by several particles.

The radical-production cross-section of a target molecule and an ion track for heavy-ion irradiation can then be theoretically calculated as

$$\sigma = \pi(R + t)^2, \tag{5}$$

where R is the radius of the target molecule and t is the radius of the ion track. Figure 10 shows a schematic description of a target molecule and an ion track for particle irradiation. The σ-value for this model calculation can predict the possibility of stable radical production due to heavy-ion irradiation.

The behavior of the σ values with increasing LET was also evaluated. Figure 11 presents the σ values obtained following C- and Si-ion irradiation as a function of the LET. From the figure, the σ
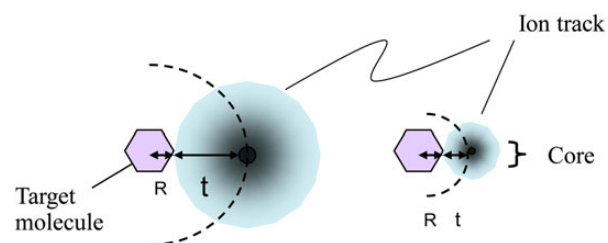

Fig. 10. Schematic of a target molecule and an ion track produced following particle irradiation of the molecule. The radical production cross-section (σ) can be calculated using π(R + t)², where R is the radius of the target molecule and t is the radius of the ion track.
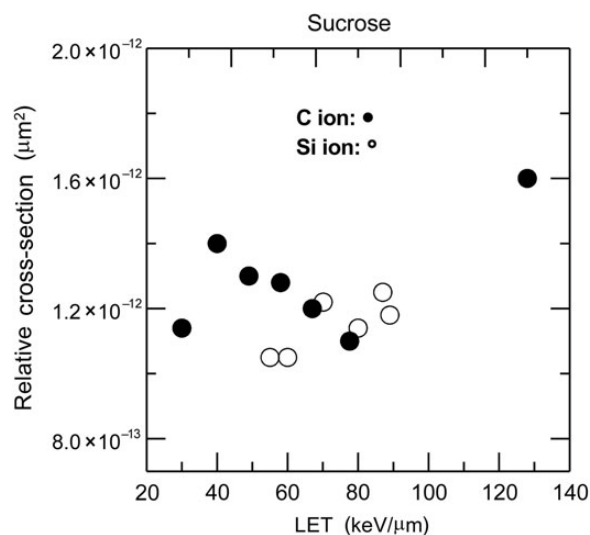
Fig. 11. Plot of the radical production cross-section (σ) as a function of the particle LET. C and Si ions were used for particle irradiation. Each datapoint corresponds to a dose of 50 Gy.

values clearly increased as the particle LET increased. This result indicates that the cross-section increased when energy deposition at the target site in the material increased. This implies that the radical-production reaction occurred in proportion to the energy deposition of the incoming particles at low LET values of ~100 keV/μm. However, the spin concentration deviated from the linear relationship at higher LET values with heavier ions because of the complexity of the processes, including radical recombination and the varying stabilities of the intermediate radicals [24–27]. It can be presumed that there is a high probability for recombination in the core.

The σ values of sucrose for C- and Si-ion irradiation were $1.29 \times 10^{-12} \pm 0.64 \times 10^{-12}$ μm^2 and $1.14 \times 10^{-12} \pm 0.34 \times 10^{-12}$ μm^2, respectively [21]. Considering the structural sizes of sucrose and alanine [28], the σ values for both of these molecules were approximately the same. These results imply that sucrose is suitable for use as a dosimeter for heavy-ion irradiation.

UV study of aqueous solutions of sucrose previously irradiated with high doses of gamma rays and heavy-ions

The application of UV spectroscopy in the field of dosimetry is based on the fact that sucrose turns brown upon irradiation, which intensifies with higher absorbed doses. This brown color is attributed to products formed from the recombination of radiation-induced free radicals [29]. UV spectroscopy has been used for the dosimetry of gamma rays [17–19, 30], which has been expanded to the dosimetry of heavy ion-irradiated samples. UV spectra for the aqueous solutions of sucrose samples previously irradiated with heavy ions exhibit an absorption band at 267 nm, which is also observed in the spectrum of sucrose irradiated with gamma radiation. Therefore, the UV spectrum of irradiated solid sucrose is concluded to be independent of the ionizing radiation, and is likely due to the formation of identical products following irradiation with gamma rays and heavy ions [30]. The detection

limit is comparable to and in some cases is lower than the dose limits associated with other methods [15].

During irradiation with heavy ions, the weight of the particles plays an important role. Heavier particles generate a greater number of radical recombination products compared with lighter ions because of their shorter penetration depth in a material, which results in the formation of more closely situated free radicals. As a consequence, during the UV analysis of aqueous solutions of sucrose samples that were previously irradiated with C- and Si-ions, higher sensitivity was observed for heavier particles (see Fig. 7).

In general, EPR analysis is a non-calibrated method. Thus, the EPR results should be compared with data obtained using different analytical techniques, such as UV absorption, which can serve as a reference method for confirmation of EPR results. Using this approach, the EPR results can be calibrated. The plots of the EPR and UV responses seen in Fig. 8 demonstrate that there is a linear correlation between the results obtained by these two techniques for heavy-ion irradiation, suggesting the possibility for confirmation of the EPR results [31].

CONCLUSION

The EPR results obtained for sucrose irradiated with a range of heavy ions confirmed the following: (i) sucrose radicals are very stable at ambient temperature; (ii) the steady state spin concentration has a logarithmic relation to the LET at a given dose; (iii) the production of sucrose radicals is dependent on the LET and the heavy-ion particles, and the radical yield for He-ion irradiation exhibited a strong LET dependence compared with that for C-ion irradiation, providing the first evidence of the effects of different heavy ions during sucrose irradiation; (iv) the total spin concentration increases linearly as the corresponding dose increases; and (v) the EPR results were consistent with the UV absorption data. Furthermore, the radical sites in sucrose were investigated by analyzing the products generated from the irradiation of the similar compounds glucose and fructose.

These results support the conclusion that sucrose, which is an inexpensive and easy to handle material, should be a useful EPR dosimeter.

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