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Degradation of cyanidin-3-rutinoside and formation of protocatechuic acid methyl ester in methanol solution by gamma irradiation

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ABSTRACT

Anthocyanins are naturally occurring phenolic compounds having broad biological activities including anti-mutagenesis and anti-carcinogenesis. We studied the effects and the degradation mechanisms of the most common type of anthocyanins, cyanidin-3-rutinoside (cya-3-rut), by using gamma ray. Cya-3-rut in methanol (1 mg/ml) was exposed to gamma-rays from 1 to 10 kGy. We found that the reddish colour of cya-3-rut in methanol disappeared gradually in a dose-dependent manner and effectively disappeared (>97%) at 10 kGy of gamma ray. Concomitantly, a new phenolic compound was generated and identified as a protocatechuic acid methyl ester by liquid chromatography, ^{1}H, and ^{13}C NMR. The formation of protocatechuic acid methyl ester increased with increasing irradiation and the amount of protocatechuic acid methyl ester formed by decomposition of cya-3-rut (20 μg) at 10 kGy of gamma ray was 1.95 μg. In addition, the radical-scavenging activities were not affected by gamma irradiation.

1. Introduction

Anthocyanins, a group of natural phenolic compounds, are natural pigments widely distributed in nature and are responsible for the colouring of flowers, fruits, vegetables, and plants (Mazza & Miniati, 1993). They are the glycosylated form of anthocyanidins, which are polyhydroxyl and polymethoxy derivatives of 2-phenylbenzopyrylium or flavylium salts. Anthocyanins have a wide range of biological activities including antioxidant, anti-inflammatory, and chemoprotective properties (Casto et al., 2002; Chen, Hwang, Rose, Nines & Stoner, 2006; Middleton, Kandaswami, & Theoharides, 2000; Seeram, Momin, Nair, & Bourquin, 2001; Tulio et al., 2008).

Recent trends of using natural products in industry have tended toward producing multifunctional, high quality, and high value foods and cosmetics. To meet the needs of consumers, cosmetics, medicines, and foods should contain proper amounts of natural products. The dark colour of some natural products such as green tea and persimmon leaf makes it very difficult to apply the proper amount to food, cosmetic, and pharmaceutical products. Thus, colour removal without changing the biological activities in natural products can be important. Although colour removal processes such as filtration and absorption by clay are useful, these procedures are difficult, time-consuming, and costly (Jo, Son, Lee, & Byun, 2003; Lee et al., 2010).

Radiation technology, an advanced oxidation process, has emerged as a solution to overcome these problems. This has been applied to various areas such as the decomposition and decolouration of dyes, removal of undesirable colours in biomaterials, improvement and maintenance of biological activities, as well as inactivation of pathogens (Chung et al., 2012; Jo et al., 2003; Kim, Kim, Ahn, Park, & Byun, 2005; Lee et al., 2011; Ting & Jamaludin, 2008; Vahdat, Bahrami, Arami, & Motahari, 2010; Wang, Yang, Wang, Shen, Bian, & Zhu, 2006).

The radiation sensitivity of natural products that are extracts derived from *Lithospermum erythrorhizon*, green tea leaves, red beet, and *Schisandra chinensis* (Jo et al., 2003; Lee, Lee, Hong, Bai, Lee, & Chung, 2012; Lee et al., 2010, 2011) in terms of their colour characteristics, have been widely studied. Recently, we reported that the cyanidin-3-*O*-xylosylrutinoside (cya-3-*O*-xylrut), which is one of the most abundant anthocyanins in the fruit of *S. chinensis* Baillon, effectively degraded in a dose-dependent manner by gamma irradiation (Lee et al., 2011). Irradiation also generates flavonoids such as quercetin and unknown compounds by the destruction of cya-3-*O*-xylrut (Lee et al., 2011; Lee, Lee, Hong, Yoo et al., 2012). In addition, flavonols in methanol or ethanol solution are easily degraded while all other flavonoids (flavanones, flavones, dihydroflavonols, and catechins) are not degraded after irradiation (Marfak, Trouillas, Allais, Calliste, Cook-Moreau &

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Duroux, 2004). Radiolysis of the flavonol quercetin leads to the formation of depsides such as {2-[(3′,4′-dihydroxybenzoil)oxy]-4,6-dihydroxyphenyl}(oxy) methyl acetate and {2-[(3′,4′-dihydroxybenzoil)oxy]-4,6-dihydroxyphenyl}(oxy) acetic acid (Marfak, Trouillas, Allais, Calliste, & Duroux, 2003; Marfak, Trouillas, Allais, Champavier, Calliste & Duroux, 2002). Gamma-irradiated antioxidant kaempferol is also degraded into two major depsides, {2-[(4′-hydroxybenzoyl)oxy]-4,6-dihydroxyphenyl}(oxo) methyl acetate and {2-[(4′-hydroxybenzoyl)oxy]-4,6-dihydroxyphenyl}(oxo) ethyl acetate, in methanol and ethanol solutions, respectively. Other compounds formed in low concentrations were identified as [4-hydroxyphenyl](oxo) methyl acetate, [4-hydroxyphenyl](oxo) ethyl acetate, and depside {2-[(4′-hydroxybenzoyl)oxy]-4,6-dihydroxyphenyl}(oxo) acetic acid (Marfak, Trouillas, Allais, Calliste et al., 2003; Marfak, Trouillas, Allais, Champavier et al., 2003c). In addition, the well known isoflavonoid rotenone was converted to rotenoisin A and rotenoisin B by gamma irradiation in methanol (Park et al., 2013). However, the mechanisms of the decay of pigments or generation of new compounds via degradation of pigments by radiation treatment are still uncertain. Therefore, we focused on the mechanism of the degradation or generation of a new compound using a common anthocyanin, cyanidin-3-rutinoside (cya-3-rut), by gamma irradiation. Cya-3-rut is one of the most abundant anthocyanins, which are natural colourants found in black raspberry, litchi, black currant, capulin, and mulberry (Chen, Chu, Chiou, Kuo, Chiang & Hsieh, 2006; Liu, Cao, Xie, Sun, & Wu, 2007; Ordaz-Galindo, Wesche-Ebeling, Wrolstad, Rodriguez-Saona, & Argaiz-Jamet, 1999; Rubinskiene, Jasutiene, Venskutonis, & Viskelis, 2005; Tulio et al., 2008; Zikri, Riedl, Wang, Lechner, Schwartz & Stoner, 2009). In this study, we suggest the degradation mechanism and identification of a new compound from cya-3-rut in methanol solution by gamma irradiation.

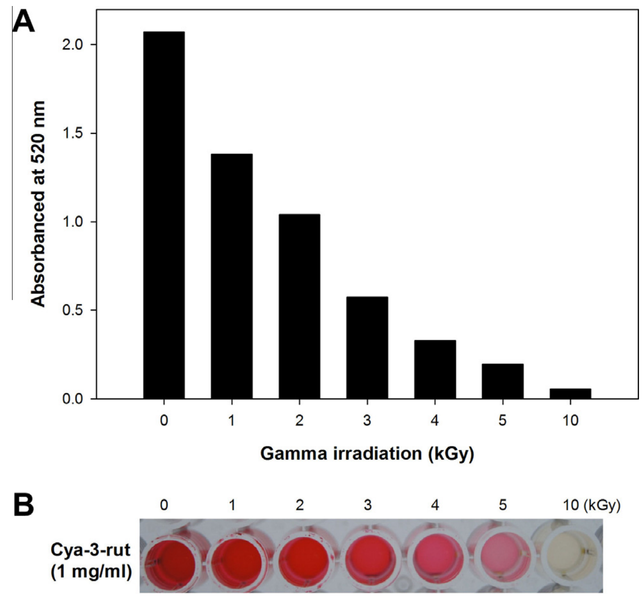

Fig. 1. The effect of gamma irradiation on the colour removal of cya-3-rut methanolic solution. The colour changes in cya-3-rut methanolic solution following gamma irradiation were monitored spectrophotometrically (A) or visually (B).

2. Materials and methods

2.1. Materials

Cya-3-rut was purchased from Polyphenols Laboratories (Sandnes, Norway). Methanol, acetonitrile, formic acid, and ethylacetate were purchased from Sigma–Aldrich (St. Louis, MO, USA) or Merck (Darmstadt, Germany). Protocatechuic acid methyl ester was purchased from Toronto Research Chemiclas Inc. (North York, Canada). All other chemicals used were of analytical grade.

2.2. Gamma irradiation

Gamma irradiation was carried out at ambient temperature using a high-level cobalt-60 irradiator (point source AECL, IR-79, MDS Nordion International Co., Ltd., Ottawa, ON, Canada) in the Advanced Radiation Technology Institute, Korea Atomic Energy Research Institute (Jeongeup, Korea). A cobalt-60-γ-source with an activity of approximately 215 kCi (7.96×10^{15} Bq) with a dose rate

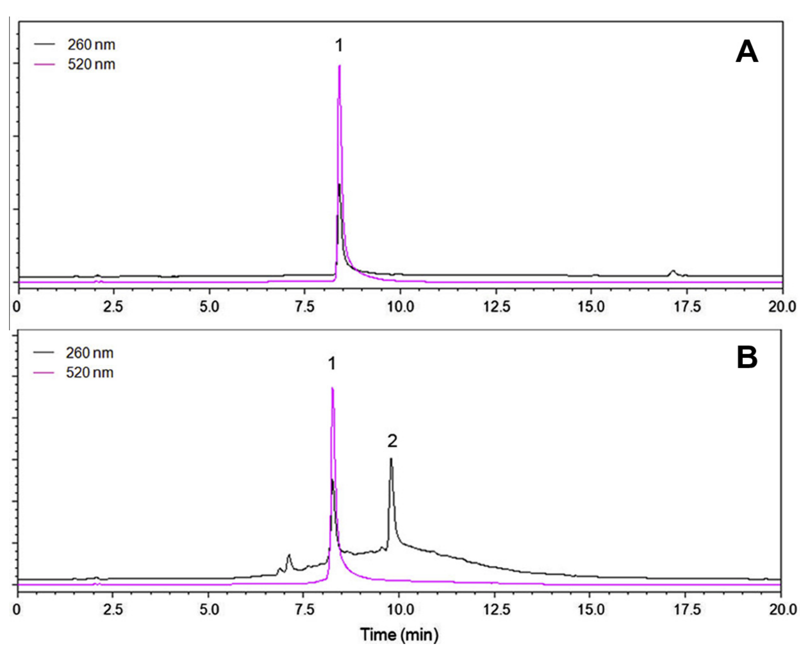

Fig. 2. The generation of a phenolic compound by degradation of cya-3-rut after gamma irradiation. Non-irradiated (A) or 10 kGy-irradiated (B) samples (1 mg/ml of cya-3-rut in 100% methanol) were monitored using an HPLC at 520 and 260 nm for detection of anthocyanin and phenolic compounds, respectively. (1) cya-3-rut; (2) protocatechic acid methyl ester.