Food Research International 95 (2017) 1–8

Contents lists available at ScienceDirect

Food Research International

journal homepage: www.elsevier.com/locate/foodres

Regeneration of *tert*-butylhydroquinone by tea polyphenols

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ARTICLE INFO

Article history:
Received 17 November 2016
Received in revised form 9 February 2017
Accepted 17 February 2017
Available online 20 February 2017

Keywords:
Antioxidant capacity
Regenerative properties
tert-Butylhydroquinone
Tea polyphenols

ABSTRACT

To study the antioxidant capacity (AC) regeneration of *tert*-butylhydroquinone (TBHQ) by tea polyphenols (TPs), a separable system has been designed for its evaluation. The AC values of three natural food matrices (liquorice, oat, and ginger) and TBHQ regenerated by TPs were all higher than their controls, and similar to the initial values ($p < 0.05$). The average regeneration efficiency (RE) value was 1.49 for these three natural food matrices, and 0.82 for TBHQ. Electron paramagnetic resonance spectroscopy analysis has revealed the synergistic effect of TBHQ and TPs, which arose from the regeneration of TBHQ by TPs. The RE value of TBHQ regeneration by TPs embedded in a gelatine membrane was 0.51. The results demonstrated that TPs showed a capacity for regenerating TBHQ, indicating a potential application in regenerative packaging, whereby one antioxidant would be added to the food matrix, with another one as the regenerator incorporated into the packaging material.

1. Introduction

Since the time interval between harvest and consumption of food increases with continuing urbanization, issues concerning the storage life of food products become more critical (Erickson, 1997). The main factors affecting the shelf life of food are lipid oxidation (Fattah et al., 2014), enzymatic browning (Remorini et al., 2016), microbial growth or reproduction (López-Malo, Palou, Barbosa-Cánovas, Tapia, & Cano, 2004) etc. during production, transport, processing, and storage. As a result, some treatments such as adding antioxidant (Elisabeth et al., 2006), sterilization (Sevenich et al., 2014), low temperature (Bárcenas & Rosell, 2006) and vacuum packaging (Santos & Regenstein, 2006) are most important to extend the shelf life of products. As the oxidation of lipids leads to quality deterioration of foods, it continues to be a major concern for scientists and processors (Shahidi & Ying, 2010). Among the approaches employed for preventing lipid oxidation, adding antioxidants is the most convenient, economical and effective strategy (Shahidi & Ying, 2010; Wanasundara & Shahidi, 2005). The most widely used antioxidants in food commodities are from synthetic agents, such as butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), *tert*-butylhydroquinone (TBHQ) (Frankel, 1993) or natural alternatives, for example tocopherols (Kamal-Eldin & Appelqvist, 1996).

Some early research concerned the cooperative effects of multiple antioxidants when mixed in a food matrix, which could extend the shelf life more effectively than adding a sole antioxidant (Guzman, Tang, Salley, & Ng, 2009). The requirement of consumers for food additive safety has also led to a demand for antioxidant-active packaging (AAP) (Kerry, O'Grady, & Hogan, 2006). Compared with the direct addition of antioxidants to the food matrix, AAP is much safer in that the antioxidants are incorporated into the packaging material. However, the efficacy of AAP in extending shelf life is somewhat spatially confined (Sanches-Silva et al., 2014; Vermeiren, Devlieghere, Mvan, Nde, & Debevere, 1999).

It has been proposed that the mechanism for the synergistic action of antioxidants is based on regeneration (R Amorati, Ferroni, Pedulli, & Valgimigli, 2003), namely, added antioxidants can regenerate pre-existing ones by donating hydrogen to their radical forms (Medina, Iuga, & Álvarez-Idaboy, 2014). The regeneration of vitamin E by co-existing natural antioxidants in food matrices, such as vitamin C (Packer, Slater, & Willson, 1979), flavonoids (Manuel, Mogens, Isabel, & Skibsted, 2007), tea polyphenols (TPs) (Zhou, Wu, Yang, & Liu, 2005), has been well documented. Reports have also provided evidence for the regeneration of TBHQ by BHA, BHT (Cini et al., 2014; Domingos, Saad, Vechiatto, Wilhelm, & Ramos, 2007), propyl gallate (Rhet, Tang, Steven, & Kysimon, 2009). It should be noted that all of the aforementioned experiments were conducted in single-phase hybrid systems, whereby the substrate to be oxidized was thoroughly mixed with the multiple antioxidants.

On account of AAP and the potential regeneration action between different antioxidants, a novel package system was designed in this paper — one kind antioxidant was added into the packaging material and the other one was mixed with the food matrix, and two antioxidants were selected as having shown regeneration action. It was expected that during the storage process, the regeneration action happened between the package and food matrix, and

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http://dx.doi.org/10.1016/j.foodres.2017.02.009
0963-9969/

resulted to extend food shelf life. In order to substantiate the claims, the regeneration of TBHQ by TPs was selected. To realize the novel package system, a two-phase system has been designed: the liquid phase was ethanolic solution of TBHQ and the solid phases were the powdered tea and TPs-modified β-cyclodextrin (β-CD) or TPs-modified polyglucose (PG). The antioxidant capacity of TBHQ was traced by 2,2′-diphenyl-1-picrylhydrazyl (DPPH) test during regeneration process, and the regeneration efficiency (RE) was evaluated.

To integrate the knowledge on this subject, the synergy between TBHQ and TPs, thoroughly mixed with corn germ oil (the oxidation substrate), was also evaluated by electron paramagnetic resonance (EPR) spectroscopy. Changes in the radicals generated in the oil were expected to further prove the regeneration of TBHQ by TPs. Consequently, the generation of TBHQ by TPs embedded in gelatine (the main material of capsule shells) has also been assessed in this study. If the regeneration of antioxidants in the two-phase system could be realized, this might be applied in a packaging system to extend the shelf life and ensure the safety of food products.

2. Materials and methods

2.1. Chemicals and reagents

DPPH and dimethyl pyridine *N*-oxide (DMPO) were purchased from J&K Scientific, Ltd. (Beijing, China). TPs were obtained from Siyuan Biological Technology Co., Ltd. (Zhengzhou, China), with TP contents up to 98%. β-CD was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China); PG was obtained from Longsheng Chemical Products Co., Ltd. (Zhengzhou, China). All reagents were of analytical grade. Standard stock solutions of TBHQ and DPPH were prepared by dissolving suitable amounts in ethanol. TBHQ and DPPH standard working solutions were prepared by diluting suitable amounts of the stock standard solutions in ethanol.

2.2. Preparation of the insoluble fraction of samples as regeneration objects

Three food samples, namely liquorice, oats, and ginger, were purchased from a local market. To remove water- and alcohol-soluble substances, ground samples were consecutively washed with large excesses of water and ethanol according to the procedure described elsewhere (Çelik & Gökmen, 2014). The washing procedure was repeated six times with alternating cycles of ethanol and water. The final insoluble powder samples were tested and found to be free of soluble antioxidant compounds. They were dried at room temperature and kept sealed prior to analysis.

The antioxidant capacity (AC) of each insoluble fraction was measured by applying the direct QUENCHER procedure with some modifications (Serpen, Gokmen, & Fogliano, 2012). A portion of the insoluble fraction (2 g) was weighed into a test tube, and the reaction was initiated by adding an aliquot (10 mL) of a 12 mmol/L DPPH working solution. The tube was vigorously shaken in a constant-temperature shaker (SHA-B, Guohua, China) in the dark, at 300 rpm for 30 min, and then centrifuged at 4000 rpm for 10 min. The optically clear supernatant (3 mL) was transferred to a cuvette, and the absorbance at 525 nm was measured on a UV/Vis spectrophotometer (UNICO 2000, Shanghai, China). The residue after the AC measurement contained radical forms of the bound antioxidants and excess DPPH radicals. Prior to regeneration, the remaining DPPH radicals were removed by washing with water (6 × 10 mL). The mixture of the residue and water was shaken for 10 min using the constant-temperature shaker, and the supernatant was removed after centrifugation at 4000 rpm for 5 min. The residue was dried at room temperature and kept sealed prior to analysis.

2.3. Regeneration of the AC of insoluble regeneration objects with an aqueous solution of TPs

To regenerate the radical forms of bound antioxidants of the residue, the residue was mixed with an aliquot (10 mL) of an aqueous 10 g/L pure TPs solution as regeneration agent. A control sample was mixed with an equivalent volume of pure water. The regeneration procedure was carried out as described by Gokmen with some modification (Celik, Gokmen, & Fogliano, 2013). The mixture was shaken in the dark using a constant-temperature shaker at 300 rpm for 2 h. The mixture was then centrifuged at 4000 rpm for 10 min and the supernatant was removed. To remove remaining traces of the regeneration agent, the residue after the regeneration procedure was washed with water (6 × 10 mL). The final aqueous washing was tested and found to be free from TPs. The insoluble residue was then measured for its AC against DPPH once more to calculate the RE.

2.4. Preparation of the TPs in the solid phase as regeneration agent

2.4.1. Preparation of the TPs–β-CD inclusion complex

A TPs–β-CD inclusion complex was prepared by co-precipitation (Wu et al., 2011a). A solution of β-CD (30 g) in distilled water (420 g) was heated at 60 °C in a water bath with magnetic stirring. After 2 h, a solution of TPs (1.5 g) in water (150 g) was slowly added to the β-CD solution. The vessel was sealed and the contents were continuously stirred for 6 h. Thereafter, the final mixed solution was refrigerated overnight at 4 °C. The precipitated TPs–β-CD complex was recovered by filtration and dried under vacuum at room temperature for 48 h after rinsing off the unencapsulated TPs. The finally obtained TPs–β-CD powder was collected and stored at 4 °C in an airtight bottle before the subsequent experiments. A fully homogeneous mixture of β-CD and TPs in the same molar ratio as TPs–β-CD was prepared using a mortar and pestle.

2.4.2. Preparation of the TPs–PG combination complex

TPs–PG combination complex was prepared by a spray-drying technique (Ying, Sun, Sanguansri, Weerakkody, & Augustin, 2011). PG (70 g) and TPs (5 g) were dissolved in distilled water (200 g) at 60 °C in a water bath with magnetic stirring. The vessel was sealed and the contents were continuously stirred for 10 h. The final solution was then diluted with a suitable volume of distilled water. The solution was then spray-dried using a spray drier (Mobile Minor™ 2000, Shanghai, China) with an inlet air temperature of 75–80 °C, an outlet temperature of 58–62 °C, and an airflow rate of 600 L/h. The obtained TPs–PG complex was washed with ethanol to remove uncombined TPs, and then dried under vacuum at room temperature for 8 h. A physical mixture of PG and TPs was prepared in the same way as the mechanical mixture of β-CD and TPs. Physicochemical characterization of the TPs–β-CD and TPs–PG was accomplished by UV/Vis spectrophotometry (UV-1800, Shimadzu, Japan) and scanning electron microscopy (SEM) (H-7650, Hitachi, Japan).

2.5. Regeneration of TBHQ in solution by TPs in the solid phase

A solution of TBHQ and DPPH in the requisite molar ratio was vigorously shaken in the dark at 300 rpm for 30 min to generate TBHQ radicals and then incubated in the dark at 4 °C overnight. Thereafter, incremental amounts of insoluble powdered tea that had previously been purged of soluble antioxidants were added to the reaction solution to regenerate TBHQ radicals. All samples were gently shaken in the dark at 300 rpm for 2 h, and the supernatants (6 mL) were collected after centrifugation at 4000 rpm for 10 min and their AC values were determined. The experiment was repeated, but with TPs–β-CD and TPs–PG in place of powdered tea respectively. The regeneration effect of a membrane made from gelatine, glycerine, water, and TPs–β-CD inclusion complex was determined by a similar method.